Development of Late Transition Metal Catalysts for the Transformation of Olefins

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Abstract

Chapter 1 describes the syntheses and reactivities of a series of $IrCl(CO)(PR_3)_2(\eta^2$-3,3-diphenylcyclopropene) complexes ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PEt_3). In addition, it describes a subsequent reaction of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene) in the presence of excess $IrCl(CO)(PMe_3)_2$. Spectroscopic data support the formation of an iridacyclobutene as part of a bimetallic complex where the iridacyclobutene moiety is stabilized by η^2-coordination to $IrCl(CO)(PMe_3)_2$. The mechanism of this reaction was studied by kinetic measurements and isotopic labeling studies where these studies support formation of this bimetallic complex by direct insertion of $IrCl(CO)(PMe_3)_2$ into the C-C σ-bond of the cyclopropene moiety.

Chapter 2 describes the reactions of the iridium dimer, $[Ir(COD)Cl]_2$, with 3,3-diphenylcyclopropene to form the bimetallic vinylcarbene complex $[Ir(COD)Cl]_2(=C-C=CPh_2)$, and examines the activity of this complex in ring-opening metathesis polymerization (ROMP). This chapter also describes the subsequent reaction of $[Ir(COD)Cl]_2(=C-C=CPh_2)$ with AgO_2CCX_3 (X = F and H) to form $[Ir_2(COD)_2Cl(O_2CX_3)](=C-C=CPh_2)$ and describes their reactivity in ROMP.

Chapter 3 describes the synthesis of Ir and Rh vinylcarbene complexes and examines their activities in olefin metathesis and olefin cyclopropanation. The Ir vinylcarbene appears to be active solely in olefin metathesis and the Rh vinylcarbene appears to be active solely in olefin cyclopropanation. In addition, this chapter investigates the oxidation state effects in the Rh-mediated cyclopropanation reaction by examining the affinities of the Rh complexes toward olefins as the oxidation state of the Rh metal is increased.

Chapter 4 describes the synthesis of salicylaldimine complexes of Ni(II)-aryls and their reactivity in ethylene polymerization. The effects of varying sterics and electronics of the salicyclaldimine ligand is discussed. Bulky ligands which block the axial faces of the Ni(II) square planar complexes, and provide steric bulk in the plane of the Ni(II)

square planar complex, are particularly effective in providing active ethylene polymerization catalysts that produce linear polymers with high molecular weight.

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Chapter 1

Reactions of 3,3-Diphenylcyclopropene with Iridium(I) Complexes: Probing the Mechanism of Cyclopropene Rearrangements at Transition Metal Centers

Introduction

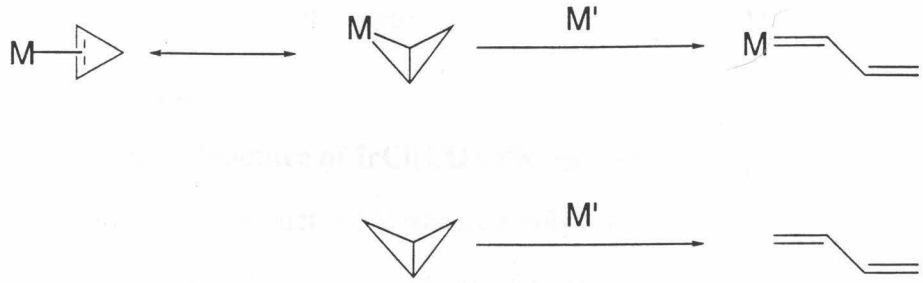
Transition metal-mediated reactions of cyclopropenes are of considerable interest and synthetic utility.[1] In recent years, the rearrangement of cyclopropenes in the presence of transition metal complexes has shown great promise as a method for generating transition metal vinylcarbene complexes. The first syntheses of transition-metal vinylcarbene complexes from the rearrangement of cyclopropenes were reported in 1989 by Binger for titanocene(II) and zirconocene(II) precursors.[2] More recently, vinylcarbene complexes of later transition metals such as tungsten,[3] rhenium,[4] and ruthenium[5] have been generated from the reactions of 3,3-diphenylcyclopropene with the appropriate precursors.

Despite the synthetic utility of using cyclopropenes as a carbene source, a complete understanding of the mechanism of the rearrangement of cyclopropenes to vinylcarbenes at metal centers remains obscure. Assuming that the transition metal center plays an important role in this arrangement, the ring-opening of cyclopropenes may be envisioned as proceeding through a stepwise sequence of cyclopropene —> metal η^2-cyclopropene —> metallacyclobutene/metal vinylcarbene. Although the intermediate metal η^2-cyclopropene,[2,3,6] metal vinylcarbene,[2,3,6a,7] and metallacyclobutene[8,9] complexes have been independently synthesized, and the direct conversion of the metal η^2-cyclopropene —> metal vinylcarbene has been observed,[3,6a] there has been to our knowledge no report of a metal η^2-cyclopropene —> metallacyclobutene conversion.

It has been observed by Johnson and Grubbs that $HgCl_2$ catalyzes the rearrangement of a tungsten(IV) η^2-cyclopropene complex to a tungsten(IV) vinylcarbene complex.[3] This observation bears a striking resemblance to the metal-catalyzed rearrangement of bicyclo[1.1.0]butane to butadiene.[10] Indeed, when the metal

η^2-cyclopropene complex is viewed as a metallabicyclo[1.1.0]butane, the similarity is unmistakable (Scheme 1). Given the extensive literature available on the metal-catalyzed rearrangement of bicyclo[1.1.0]butane, this analogy has prompted us to take a closer look

Scheme 1



at the possibility of a bimolecular mechanism in the formation of metal-vinylcarbenes from metal η^2-cyclopropene complexes.

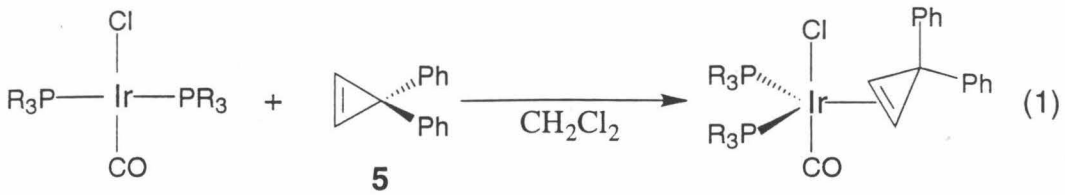
This chapter presents the results of studies of the reaction of 3,3-diphenylcyclopropene with $IrCl(CO)(PR_3)_2$ complexes. Syntheses of the Vaska's complexes, $IrCl(CO)(PR_3)_2$, were first reported in 1961;[11] their selection as precursors for this study was based on their coordinative unsaturation, which is in part responsible for their rich chemistry in such transformations as oxidative additions,[12] olefin hydrogenation,[13] and olefin isomerization.[14] The immediate goal was to study the coordination of 3,3-diphenylcyclopropene by these complexes and the subsequent rearrangement of the coordinated cyclopropene moiety to give an iridium vinylcarbene. In addition, the recent mechanistic studies by Hughes and coworkers on the reaction between tetrafluorocyclopropene and Vaska's complex[8a] have lead us to anticipate that the use of this metal system could provide some insight into the mechanism of 3,3-diphenylcyclopropene rearrangement to the corresponding vinylcarbene.

Here we report that 3,3-diphenylcyclopropene reacts with $IrCl(CO)(PR_3)_2$ precursors to afford stable η^2-olefin complexes. Among the PR_3 derivatives investigated, the equilibrium between free and bound 3,3-diphenylcyclopropene depends on the steric bulk of the tertiary phosphine: the smaller the cone angle of the tertiary phosphine, the more the equilibrium favors bound 3,3-diphenylcyclopropene. Furthermore, the $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene) complex rearranges to a bimetallic iridacyclobutene in the presence of excess $IrCl(CO)(PMe_3)_2$.

Results and Discussion

Synthesis and Structure of $IrCl(CO)(PR_3)_2(\eta^2$-3,3-Diphenylcyclopropene) Complexes. Stable olefin adducts of Vaska's complex, $IrCl(CO)(PR_3)_2$, are fairly rare. Although ethylene[15] and cyclohexene[16] adducts of Vaska's complex have been prepared, they are unstable and easily lose olefin to revert back to the parent complex. To date, the only stable olefin adducts of Vaska's complexes have been derived from electron-poor olefins such as tetracyanoethylene,[16,17] fumaronitrile,[17] maleic anhydride,[16] and tetrafluoroethylene.[18] There are also examples of stable adducts of Vaska's complex with electron-poor alkynes.[16] The fact that Vaska's complexes form stable π-complexes with relatively electron-poor olefins might best be understood when the Ir-olefin complex is viewed as a donor-acceptor complex (i.e., Vaska's complex is a better donor to electron-poor olefins than more electron rich π-substrates.)[19] In this section, we report the synthesis, characterization, and molecular structure of stable Vaska-type olefin complexes and comment on the ability of Vaska's complex to coordinate olefins as a function of the steric bulk of the phosphine ligands.

The reaction of 3,3-diphenylcyclopropene with $IrCl(CO)(PMe_3)_2$ in a minimum amount of CH_2Cl_2 produced the olefin complex $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene), **1**, in high yield (eq 1). The product was readily recrystallized



PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PEt_3
1 **2** **3** **4**

from a mixture of CH_2Cl_2/hexane to afford white crystals in high yield. Analogs of **1**, where PR_3 = PMe_2Ph (**2**), $PMePh_2$ (**3**), and PEt_3 (**4**) were synthesized similarly.

Spectroscopic data for the $IrCl(CO)(PR_3)_2(\eta^2$-3,3-diphenylcyclopropene) complexes are consistent with a trigonal bipyramidal arrangement of the ligands around the metal center. Notable features in the ^1H NMR spectrum of **1** (PR_3 = PMe_3) are a distorted doublet at 1.25 ppm due to the methyl protons of the cis tertiary phosphine ligands and a triplet at 3.32 ppm (J_{HP} = 9.4 Hz) due to coupling of the olefinic protons to the two phosphines. Key resonances in the ^{13}C NMR spectrum of **1** are a triplet at 17.7 ppm (J_{CP} = 15.5 Hz) due to overlapping doublets of the PMe_3 carbons and a pseudo-quintet at 37.1 ppm (J_{CP} = 29.7 Hz, J_{CH} = 220.9 Hz) due to overlapping triplets of the olefinic carbons. This J_{CH} coupling constant is similar to that observed for the bridgehead carbon of bicyclo[1.1.0]butane (205 Hz)[20] and for the η^2 olefinic carbons in [W](η^2-3,3-diphenylcyclopropene) complexes (194-195 Hz),[3] suggesting a significant amount of s character in the C-H bond forming hybrid orbital that is on the coordinated cyclopropene olefinic carbon of **1** (42%).[21] The ^{31}P NMR spectrum of **1** exhibits only a singlet at -51.2 ppm, and its IR spectrum shows a characteristic υ_{CO} stretching frequency at 1985.9 $cm,^{-1}$ significantly lower than that observed for $IrCl(CO)(PPh_3)_2(\eta^2$-cyclohexene) (ν_{CO} = 2040 cm^{-1}).[16] Table I summarizes selected NMR and IR data for complexes **1-4.**

Table 1. Selected NMR and IR Spectral Data for η^2-Cyclopropene Complexes.

η^2-Cyclopropene complex	^{1}H (t, HC=CH)		^{13}C (q, HC=CH)		^{31}P (δ)	υ_{CO} (cm^{-1})
	δ(ppm)	J_{HP}(Hz)	δ(ppm)	J_{HP}(Hz)		
$IrCl(CO)(PMe_3)_2(HC{=}CHCPh_2)$	3.32	6.4	37.07	29.7	-51.2	1985.9
$IrCl(CO)(PMe_2Ph)_2(HC{=}CHCPh_2)$	3.40	6.5	38.36	29.3	-38.5	1992.6
$IrCl(CO)(PMePh_2)_2(HC{=}CHCPh_2)$	3.47	6.7	38.66	26.7	-21.3	2000.7
$IrCl(CO)(PEt_3)_2(HC{=}CHCPh_2)$	3.25	6.3	35.67	33.8	-18.4	1979.3

^{1}H NMR and ^{31}P NMR spectra were acquired in C_6D_6, and ^{13}C NMR spectra were acquired in CD_2Cl_2.

The structure of **1** was confirmed with an X-ray crystallographic study. An ORTEP of this complex is shown in Figure 1 and selected bond distances and angles are given in Table II. The Ir-C bonds (2.116(6) and 2.118(6) Å) are within normal

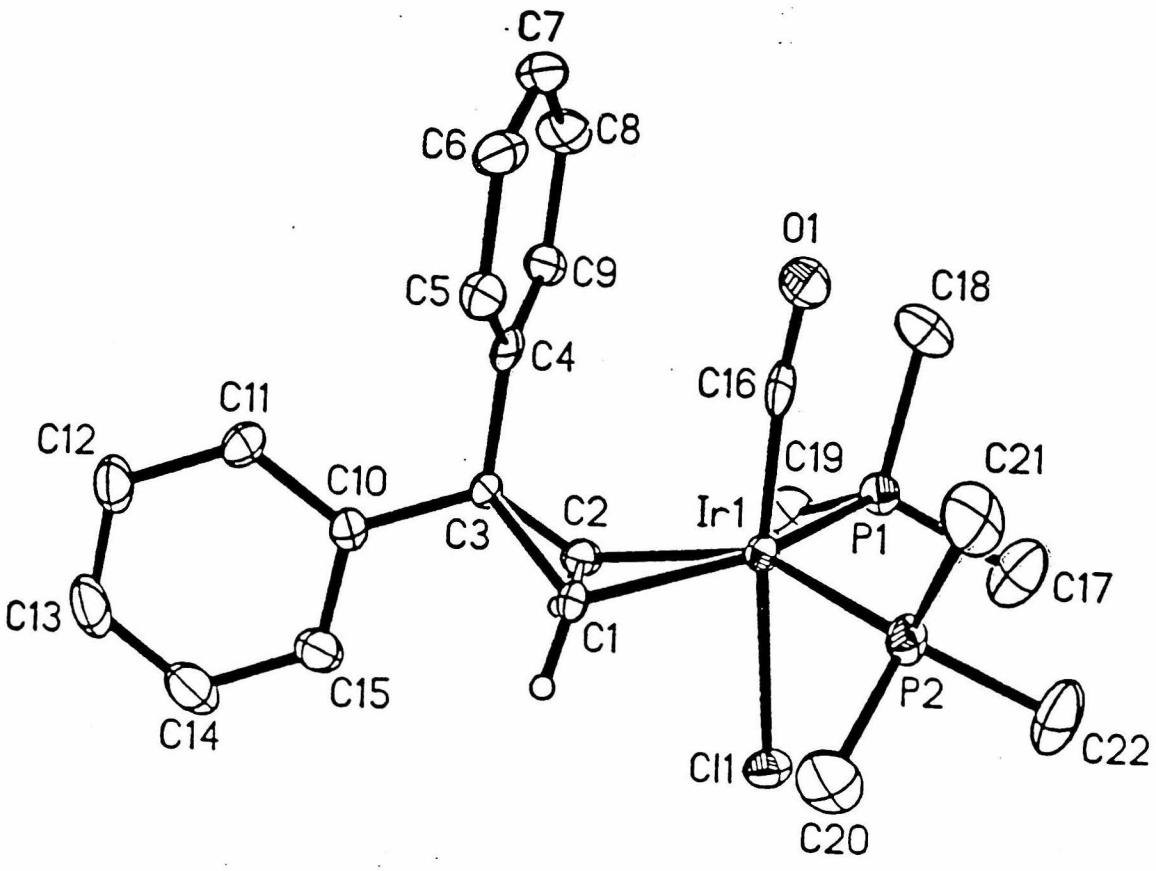


Figure 1. An ORTEP drawing of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclpropene). Thermal ellipsoids are shown at the 50 % probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**.

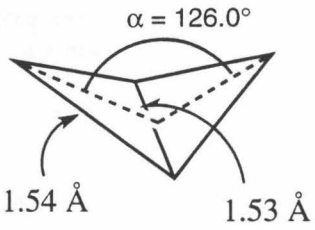
Bond Distances

Ir(1) - Cl(1)	2.442(2)	Ir(1) - P(1)	2.345(2)
Ir(1) - P(2)	2.340(2)	Ir(1) - C(1)	2.116(6)
Ir(1) - C(2)	2.118(6)	Ir(1) - C(16)	1.824(6)
O(1) - C(16)	1.156(8)	C(1) - C(2)	1.445(9)
C(1) - C(3)	1.528(8)	C(2) - C(3)	1.514(8)
C(3) - C(4)	1.497(8)	C(3) - C(10)	1.508(8)

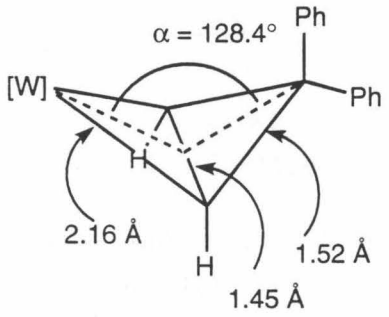
Bond Angles

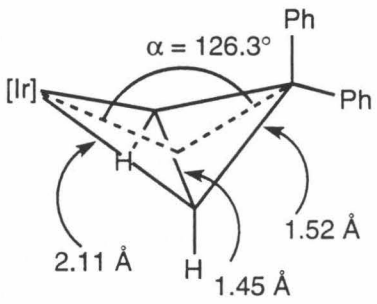
Cl(1) - Ir(1) - P(1)	86.5(1)	Cl(1) - Ir(1) - P(2)	85.2(1)
P(1) - Ir(1) - P(2)	108.6(1)	Cl(1) - Ir(1) - C(1)	85.6(2)
P(1) - Ir(1) - C(1)	142.0(2)	P(2) - Ir(1) - C(1)	107.6(2)
Cl(1) - Ir(1) - C(2)	82.5(2)	P(1) - Ir(1) - C(2)	102.2(2)
P(2) - Ir(1) - C(2)	145.9(2)	C(1) - Ir(1) - C(2)	39.9(2)
Cl(1) - Ir(1) - C(16)	172.5(2)	P(1) - Ir(1) - C(16)	91.1(2)
P(2) - Ir(1) - C(16)	88.9(2)	C(1) - Ir(1) - C(16)	100.6(2)
C(2) - Ir(1) - C(16)	104.9(2)	Ir(1) - C(1) - C(3)	108.9(4)
Ir(1) - C(1) - C(2)	70.1(3)	Ir(1) - C(2) - C(1)	70.0(3)
C(2) - C(1) - C(3)	61.1(4)	C(1) - C(2) - C(3)	62.2(4)
Ir(1) - C(2) - C(3)	109.4(4)	C(1) - C(3) - C(4)	123.1(5)
C(1) - C(3) - C(2)	56.7(4)	C(1) - C(3) - C(10)	113.4(5)
C(2) - C(3) - C(4)	119.9(5)	C(4) - C(3) - C(10)	115.4(4)
C(2) - C(3) - C(10)	115.7(5)	C(3) - C(4) - C(9)	120.0(5)
C(3) - C(4) - C(5)	121.4(5)		

distances,[17] and the cyclopropene C-C bond (1.445(9) Å) is similar to those reported for [W](η2-3,3-diphenylcyclopropene) complexes,[3] but slightly smaller than the value obtained from vibrational spectroscopy for bicyclo[1.1.0]butane (1.54 Å) (Figure 2).[22] The arrangement of ligands about the metal center exhibits two distortions from a perfect trigonal bipyramidal geometry. First, the equatorial olefin ligand is puckered out of the plane in a butterfly configuration, where the torsion angle between Ir(1), C(1), C(2), and C(3) is 126.3(4)°, which is remarkably similar to that observed for bicyclo[1.1.0]butane (126.0°)[22] (Figure 2). Second, the two apical ligands, Cl and CO, are bent slightly from



(a) Bicyclo[1.1.0]butane





(b) [W]-η2-3,3-diphenylcyclopropene **(c) [Ir]-η2-3,3-diphenylcyclopropene**

[W] = $W(NAr)Cl_2[P(OMe)_3]_2$ [Ir] = $IrCl(CO)(PMe_3)_2$

Figure 2. Comparison of the bond lengths and torsion angles of (a) bicyclo-[1.1.0]butane,[10] (b) $W(NAr)Cl_2[P(OMe)_3]_2(\eta^2$-3,3-diphenylcyclopropene),[3] and (c) $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene).[21]

perpendicular, away from the olefin ligand. To a first approximation, the metal-η2-cyclopropene moiety resembles a strained bicyclo[1.1.0]butane, a fact which might have

important consequences in the ability of **1** to undergo rearrangement (*vide infra*). Similar to that observed in $IrBr(CO)(PPh_3)_2(\eta^2$-tetracyanoethylene),[17] the phosphine ligands in **1** are cis rather than trans. The trans configuration was proposed for adducts of electron-poor olefins with Vaska's complex.[16]

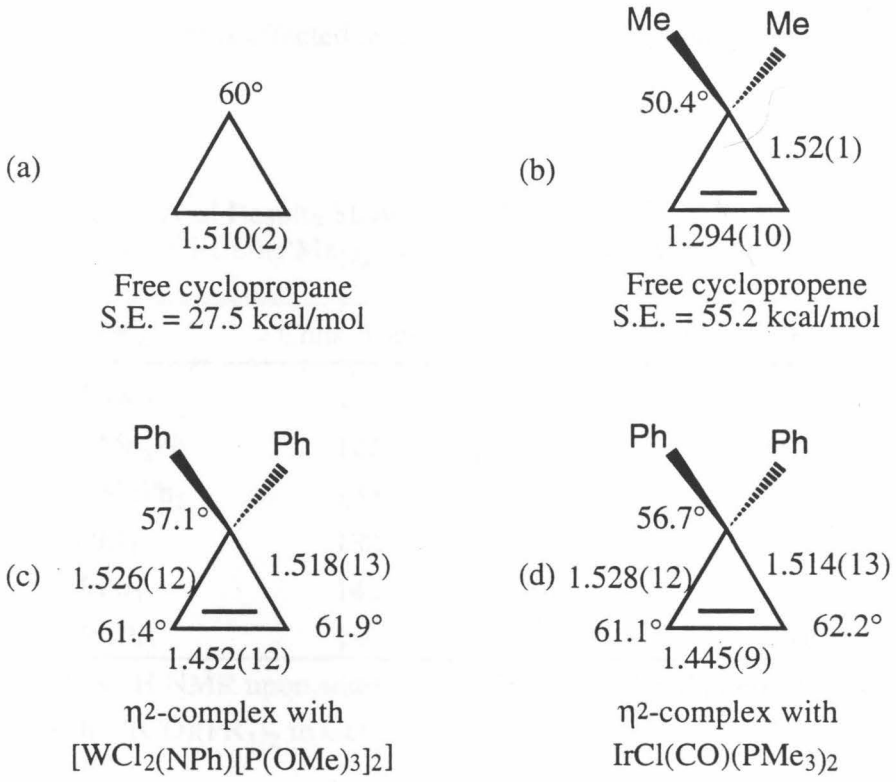


Figure 3. Comparison of the bond lengths and angles of (a) free cyclopropane,[1c] (b) free 3,3-dimethylcyclopropene,[1c] (c) η^2-complex with $[WCl_2(NPh)[P(OMe)_3]_2]$,[3] (c) η^2-complex with $IrCl(CO)(PMe_3)_2$.

Complexes **1-4** are the first stable olefin adducts of Vaska' s complex known to date where the olefin is not substituted with electron-withdrawing substituents (*vide infra*). The driving force for formation of the olefin complex is probably derived from the relief of the cyclopropene ring strain (estimated at 57.2 kcal/mole)[23] by coordination to the metal center. The relaxation of cyclopropene ring strain upon coordination to the metal center can be inferred from the crystal structural parameters (Figure 3d). The C-C double

bond is lengthened to 1.445(9) Å and the apical angle of the cyclopropene ring is increased to 56.7° compared to that of the uncomplexed cyclopropene (50.4°) (Figure 3b). These observations are consistent with those previously observed by Johnson and Grubbs[3] (Figure 3c).

Also particularly interesting is the observation that olefin complexation to the iridium (I) metal center is affected dramatically by the cone angles of the tertiary

Table 3. Summary of Results Showing the Degree of Complexation of 3,3-Diphenylcyclopropene to $IrCl(CO)(PMe_3)_2$ Complexes and the Cone Angles of the Tertiary Phosphines.

Entry	PR_3	Cone Angle (°)[23]	Olefin Complex/Starting Material[a]
1	PMe_3	118	>99/1
2	PMe_2Ph	122	>99/1
3	$PMePh_2$	136	70/30
4	PEt_3	132	40/60
5	PPh_3	145	0
6	P-*i*Pr_3	160	0

[a] Observed by ^1H NMR upon addition of 1.5 equiv of 3,3-diphenylcyclopropene to a solution of $IrCl(CO)(PR_3)_2$ in CD_2Cl_2 at rt.

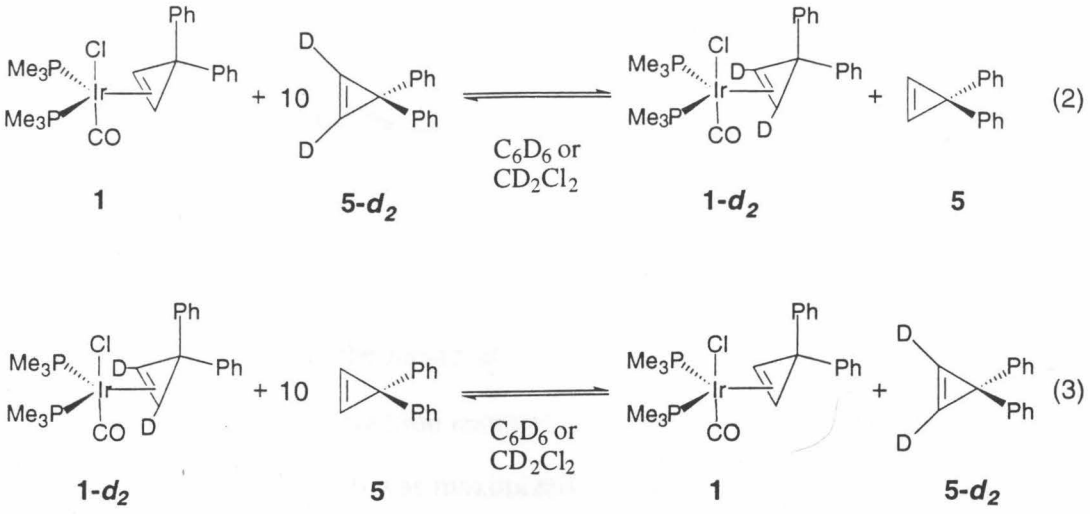
phosphines.[24] For example, while the PMe_3 and PMe_2Ph Vaska's complexes (in all cases, [Vaska's Complex] = $3.3x10^{-2}$ M) react with 1.5 equiv 3,3-diphenylcyclopropene to afford complete conversion to the olefin adducts **1** and **2**, respectively (Table 3, entries 1 and 2); under the same conditions, the $PMePh_2$ Vaska's complex affords only 70% conversion to the olefin complex **3**, and the PPh_3 Vaska's complex does not coordinate 3,3-diphenylcyclopropene at all (Table 3, entries 3 and 5). Thus, as the tertiary phosphines become more sterically demanding, coordination of the olefin is inhibited. This effect appears to be determined predominantly by steric rather than electronic factors.[25] When the PEt_3 and P(*i*-Pr)$_3$ Vaska's complexes were subjected to the same

reaction conditions (PEt_3 and P(*i*-Pr)$_3$ have similar electronic properties, but differ in their steric properties),[24] the PEt_3 Vaska's complex reacts with 1.5 equiv 3,3-diphenylcyclopropene to afford 40% conversion to the olefin complex **4**, while the P(*i*-Pr)$_3$ Vaska's complex does not coordinate 3,3-diphenylcyclopropene (Table 3, entries 4 and 6).

Stability of the η^2-Olefin Complexes and Reversibility of Binding of 3,3-Diphenylcyclopropene. The η^2-3,3-diphenylcyclopropene complexes are stable in solution under inert atmosphere for days without noticeable decomposition, and stable indefinitely in the solid phase under inert atmosphere. These complexes also exhibit moderate stability in air. For example, in solution, these olefin complexes can withstand short-term exposure to air (10-12 h) before oxidation to insoluble products is observed. In the solid phase, they are stable in air for several days before oxidation/decomposition is observed (detected as a discoloration of the solid).

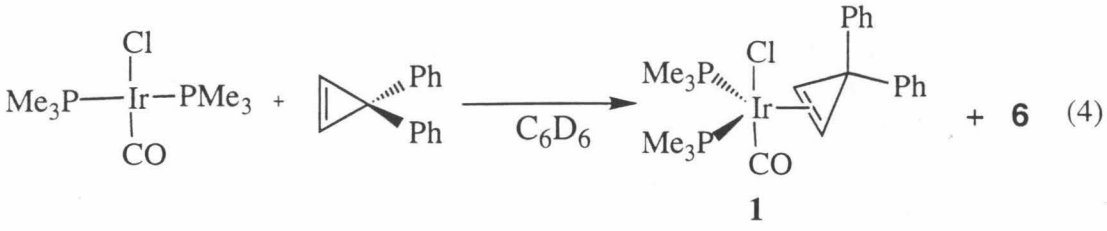
Although it has been observed by Johnson and Grubbs[3] that the use of a catalytic amount of $HgCl_2$ or irradiation of the η^2-cyclopropene complexes facilitates the ring opening of metal-η^2-cyclopropenes to metal vinylcarbenes in the case of tungsten, an iridium vinylcarbene complex could not be synthesized using these methods. Addition of a catalytic amount of $HgCl_2$ completely decomposed the olefin complex **1** over several days, while irradiation alone at 0 °C caused slow decomposition.

The coordination of 3,3-diphenylcyclopropene to the iridium(I) center was found to be reversible in the sense that the coordinated olefin will exchange with excess 3,3-diphenylcyclopropene. Reaction of **1** with 10 equiv of 3,3-diphenylcyclopropene-1,2-d_2, **5-*d*$_2$** , resulted in complete exchange of the olefin ligand in **1** with **5-*d*$_2$** (eq 2).

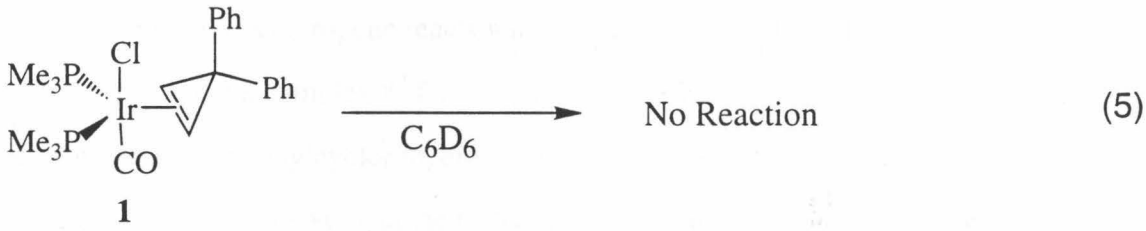


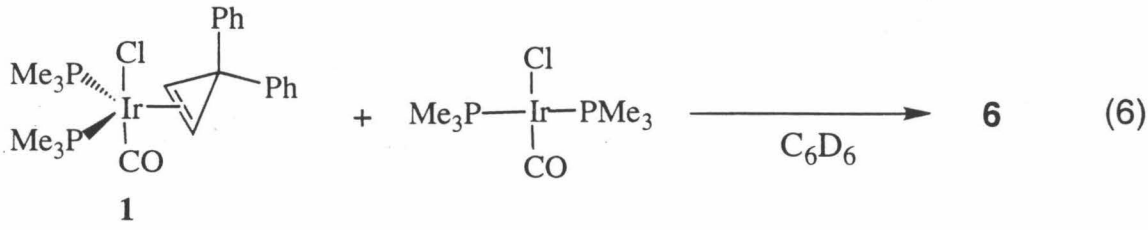
Conversely, the reaction of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene-1,2-d_2 (**1-d_2**,) with 10 equiv of 3,3-diphenylcyclopropene resulted in exclusive formation of **1** (eq 3). The exchange of olefin was found to be ~2.5 times faster in C_6D_6 than in CH_2Cl_2 (as described in the Experimental Section). Reaction of **1** with 1 equiv of various electron-deficient olefins such as tetracyanoethylene and dimethylmaleate also results in complete substitution of the olefin moiety.[26] These electron-deficient olefins are bound to the iridium metal center preferrentially over 3,3-diphenylcyclopropene in the sense that the reaction of $IrCl(CO)(PMe_3)_2(\eta^2$-Y), where Y is either tetracyanoethylene or dimethylmaleate, with up to 20 equiv of 3,3-diphenylcyclopropene does not form **1**. However, reaction of **1** with other cyclic olefins such as norbornene, cyclooctene, cyclopentene, and cyclohexene does not result in any exchange of the olefin moiety.[27]

Further Reaction of the η^2-3,3-Diphenylcyclopropene Complex 1. When $IrCl(CO)(PMe_3)_2$ reacts with less than 1 equiv of 3,3-diphenylcyclopropene in C_6D_6, two products were observed, one of which was the η^2-olefin complex **1**, the other was a new

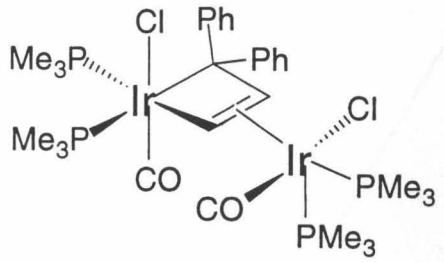


product **6** (eq 4). Increasing the molar ratio of $IrCl(CO)(PMe_3)_2$ to 3,3-diphenylcyclopropene in the reaction resulted in a decrease of **1** and an increase in the formation of **6**. Formation of **6** was maximized (i.e., complete disappearance of **1**) when this molar ratio was at least 4/1. We hypothesized that the generation of **6** proceeded through the intermediacy of the η^2-olefin complex **1,** which then reacted further with another molecule of $IrCl(CO)(PMe_3)_2$. To examine this hypothesis, two simultaneous reactions were carried out: in one case, the olefin complex **1** was dissolved in C_6D_6 and allowed it to stand on its own (eq 5); in the second case, one equivalent of $IrCl(CO)(PMe_3)_2$ was added to a C_6D_6 solution of **1** (eq 6). Only in the second case was **6** formed. The formation of **6** directly correlated with the disappearance of **1** and thus, appeared to involve the intermediacy of **1**. The available spectroscopic data (*vide infra*)





suggests that **6** is an iridacyclobutene that is stabilized by coordination in an η^2 fashion to another molecule of $IrCl(CO)(PMe_3)_2$. The proposed structure of **6** is shown in Figure 4.

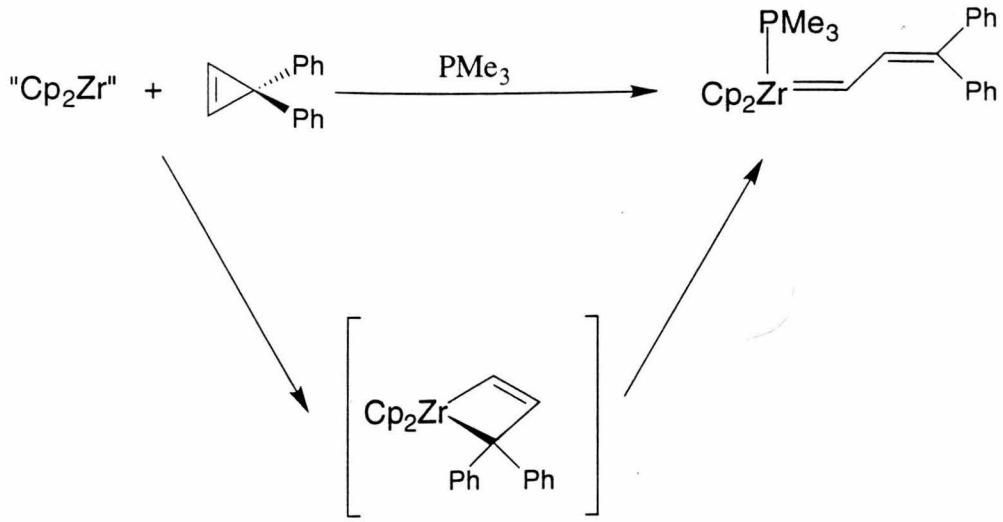


6

Figure 4. Proposed structure of **6**.

The formation of a metallacyclobutene from the metal-mediated rearrangement of cyclopropenes has precedence in the literature. Hughes and coworkers[8] reported that tetrafluorocyclopropenes react with $IrCl(CO)(PR_3)_2$ and Pt (II) complexes to afford metallacyclobutene complexes. However, these workers apparently did not observe the formation of an η^2-olefin complex as an intermediate. Binger and coworkers observed that 1,2-diphenylcyclopropene reacts with a zirconocene (II) precursor to form a metallacyclobutene complex.[9] This observation led Binger to propose that the ring-opening of 3,3-diphenylcyclopropenes to vinylcarbenes at transition metal centers proceeded to a metallacyclobutene through direct σ bond insertion (Scheme 2), although

Scheme 2



this type of intermediate has not been observed during the formation of metal-vinylcarbene complexes from 3,3-diphenylcyclopropene.

Spectroscopic Data for 6. Analysis by NMR spectroscopy supports a bimetallic structure for compound **6**. The ^{1}H NMR spectrum of **6** shows, for example, that the olefinic protons are inequivalent and highly coupled. One olefinic proton appears as an imperfect sextet at 2.62 ppm; the other olefinic proton appears as an imperfect septet at 4.23 ppm (Figure 5a). Homonuclear decoupling showed that these protons were coupled only to each other and to no other protons. Irradiation of the multiplet at 2.62 ppm collapsed the septet at 4.23 ppm into a sextet, while irradiation of the multiplet at 4.23 ppm collapsed the sextet at 2.62 ppm into a quintet (Figure 5b). The remainder of the complex coupling pattern probably results from ^{31}P coupling. These results are suggestive of a bimetallic structure since a single bis-phosphine metal center cannot produce such a highly coupled spectrum.[28] Other key features of the ^{1}H NMR spectrum

Figure 5. (a) 500 MHz ^{1}H NMR spectra of the olefinic protons at δ 2.62 and 4.23. (b) 500 MHz ^{1}H NMR spectra of the proton decoupled olefinic proton at δ 2.62 after irradiation at δ 4.23 and the proton decoupled olefinic proton at δ 4.23 after irradiation at δ 2.62. Chemical shift data are provided in Hz at the top of each peak.

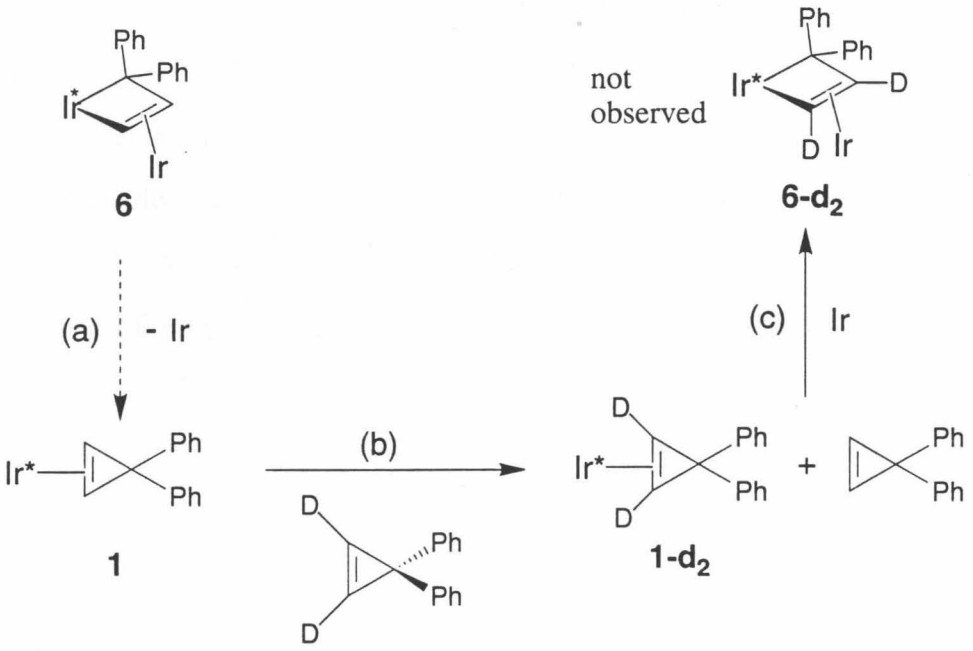
are doublets at 1.01 (J_{HP} = 9.0 Hz) and 1.16 ppm (J_{HP} = 10.5 Hz). These resonances probably correspond to the protons of inequivalent PMe_3 ligands of the metal bearing the metallacycle. The PMe_3 protons of the second metal appear as a doublet at 1.3 ppm, which suggests a cis arrangement of the tertiary phosphines on the second metal center. The ^{31}P NMR spectrum in C_6D_6 shows four resonances corresponding to the four inequivalent phosphines ligands. These include two doublets at -56.1 and -46.2 ppm (J_{PP} = 17.5 Hz), probably corresponding to the tertiary phosphine ligands on the metal bearing the metallacycle, and two broad singlets at -14.5 and -38.3 ppm, probably corresponding to the tertiary phosphines on the other metal center. Key features of the $\{^1H\}^{13}C$ NMR spectrum of **6** are assigned as follows: doublet of quartets at 14.1 ppm (J_{CP} = 95.5 Hz, $J_{CP'}$ = 6.7 Hz, J_{CH} = 391.8 Hz), corresponding to the olefinic carbon closest to the metal center which is coupled to four phosphines; a doublet of triplets at 66.0 ppm (J_{CP} = 37.6 Hz, $J_{CP'}$ = 4.2 Hz, J_{CH} = 168.9 Hz), corresponding to the olefinic β-carbon which is coupled to three phosphines; two doublets at 14.9 ppm (J_{CP} = 15.1 Hz) and 15.2 ppm (J_{CP} = 18.4 Hz), corresponding to the PMe_3 carbons at the metal center bearing the metallacycle; two doublets at 17.6 and 17.8 ppm (J_{CP} = 15.5 Hz), corresponding to the PMe_3 carbons of the other metal center; one doublet at 146.6 ppm (J_{CP} = 4.1 Hz) corresponding to the C_{ipso} of one phenyl ring and another doublet at 147.7 ppm (J_{CP} = 2.4 Hz) corresponding to the $C_{ipso'}$ of the other phenyl ring. Noteworthy is the fact that the ipso carbons of the phenyl rings are coupled to the phosphines, which suggests their proximity to the metal center and further supports the metallacyclobutene structure **6**. The IR spectrum of this compound exhibits two CO stretches: υ_{CO} = 2004.2 and 1944.8 cm^{-1} consistent with the presence of two inequivalent carbonyl groups and, perhaps, two iridium centers in different oxidation states.

Stability and Irreversible Formation of 6. Compound **6** is unstable in both C_6D_6 and CD_2Cl_2 and attempts to isolate it have not been successful. At low concentrations (ca 10^{-3} M) in either C_6D_6 or CD_2Cl_2, **6** is stable for 12 -20 h. At higher

concentrations (ca 10^{-1} M in the same solvents), however, **6** decomposes within several hours. It is quite stable in the solid phase, but attempts to purify it by recrystallization have so far been unsuccessful.

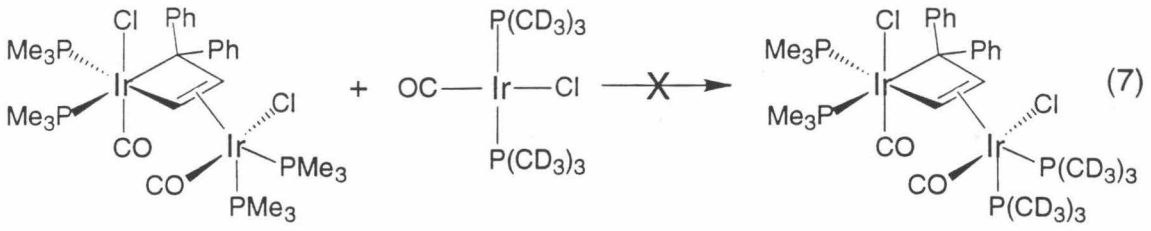
Furthermore, the addition of 1,2-*dideuterio*-3,3-diphenylcyclopropene, **5-*d*$_2$**, to a solution of **6** does not lead to exchange of the hydrocarbon moiety. Given the fact that olefin complexation in **1** is reversible, this suggests that **6** does not revert back to **1**, thus, the formation of **6** from **1** is apparently irreversible (Scheme 3). Also, it appears that

Scheme 3[a]



[a] Given that steps b and c are known to occur, step a does not occur since there is no observable deuterium incorporation into complex **6** upon treatment of **6** with 3,3-diphenylcyclopropene.

complexation of the iridacyclobutene to the second metal center is irreversible. Addition of labelled Vaska's complex, $IrCl(CO)[P(CD_3)_3]_2$, to a solution of **6** does not lead to exchange of the metal centers (eq 7).



(7)

6 not observed **6-d_{18}**

Kinetics of the Rearrangement of 1 to 6. The progress of the reaction between **1** and $IrCl(CO)(PMe_3)_2$ to yield **6** was monitored by ^1H NMR spectroscopy in both C_6D_6 and CD_2Cl_2 (as described in the Experimental Section). This rearrangement was examined by varying the initial concentration of $IrCl(CO)(PMe_3)_2$. The reaction exhibited clean second-order kinetics at room temperature (Tables IV and V).[29] This rearrangement does not appear to exhibit any solvent effect in the two solvents examined. Analysis of the data suggest that the second order rate constant (k_2) is approximately the same in both CD_2Cl_2 and C_6D_6.

Table 4. Kinetic Parameters for the Reaction of **1** with $IrCl(CO)(PMe_3)_2$ in C_6D_6 Including [**1**], $[IrCl(CO)(PMe_3)_2]$, and Second-Order Rate Constant (k_2).

$[IrCl(CO)(PMe_3)_2]$ (M) x 10^2	[**1**] (M) x 10^2	$k_2(M^{-1}s^{-1})$ x 10^3 [a]
1.17	1.67	8.29 ± 1.32
1.67	1.67	8.54 ± 1.36
3.33	1.67	10.6 ± 1.46
6.67	1.67	10.1 ± 1.54
9.72	1.67	7.07 ±1.60
3.33	3.33	6.90 ± 1.52
6.67	3.33	7.82 ± 7.82
10.0	3.33	8.53 ± 1.68
13.3	3.33	7.26 ± 1.72

[a] $k_2t = 1/\{B_o - A_o\}\ln\{A_o(B_o - X)/(A_o - X)B_o\}$,[29] where A_o is the starting concentration of **1**, B_o is the starting concentration of $IrCl(CO)(PMe_3)_2$, and X is the concentration of **6** at time *t*.

Table 5. Kinetic Parameters for the Reaction of **1** with $IrCl(CO)(PMe_3)_2$ in CD_2Cl_2 Including [**1**], $[IrCl(CO)(PMe_3)_2]$, and Second-Order Rate Constant (k_2).

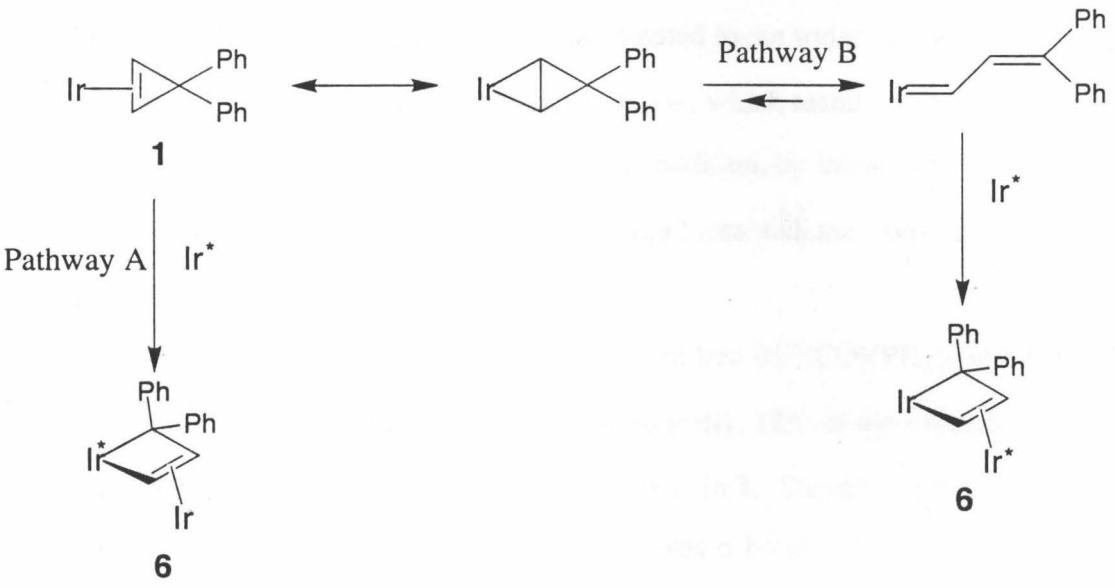
$[IrCl(CO)(PMe_3)_2]$ (M) x 10^2	[**1**] (M) x 10^2	$k_2(M^{-1}s^{-1})$ x 10^3 [a]
1.67	1.67	6.73 ± 1.32
3.33	1.67	7.07 ± 1.40
6.67	1.67	7.83 ± 1.47
9.72	1.67	7.52 ± 1.53

[a] $k_2t = 1/\{B_o - A_o\}\ln\{A_o(B_o - X)/(A_o - X)B_o\}$,[29] where A_o is the starting concentration of **1**, B_o is the starting concentration of $IrCl(CO)(PMe_3)_2$, and X is the concentration of **6** at time *t*.

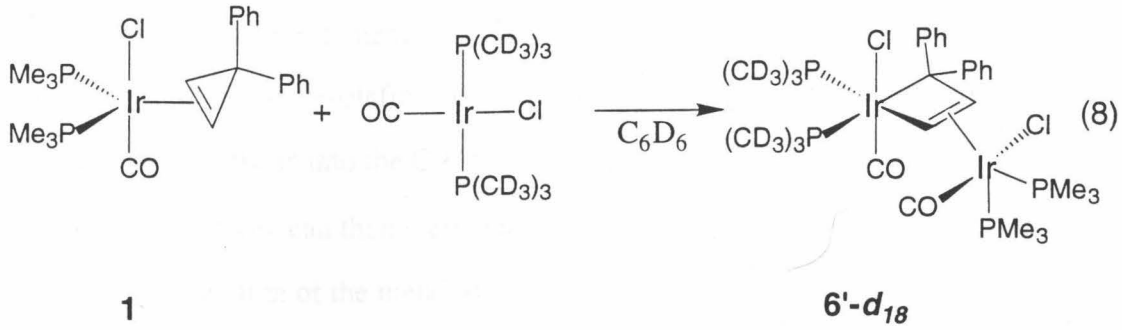
Mechanism of the Rearrangement and Isotopic Labeling Studies. There are at least two possible pathways for the formation of **6** from the reaction of **1** with $IrCl(CO)(PMe_3)_2$ as illustrated in Scheme 4. It should be possible to distinguish between these two pathways by labeling one of the two metal centers involved. If the reaction proceeds through a vinylcarbene intermediate (pathway B), then the metallacycle should contain the metal originally found in **1**. If, however, the reaction occurs by direct insertion of $IrCl(CO)(PMe_3)_2$ into the C-C bond of the cyclopropene ring in **1** (pathway A), then the metallacycle should contain the metal that participates in the σ-bond insertion.

We chose to distinguish the metal centers by using *perdeuterio*-trimethylphosphine on one metal center and unlabelled trimethylphosphine on the other. Thus, in one experiment $IrCl(CO)(PMe_3)_2$(3,3-diphenylcyclopropene) was reacted with

Scheme 4

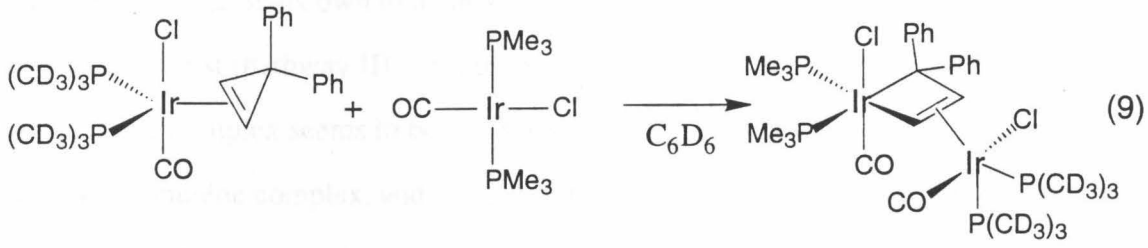


$IrCl(CO)(P[CD_3]_3)_2$ (eq 8), and in the other, $IrCl(CO)(P[CD_3]_3)_2$(3,3-diphenylcyclopropene) was reacted with $IrCl(CO)(PMe_3)_2$ (eq 9).



(8)

1 **6'-d_{18}**



(9)

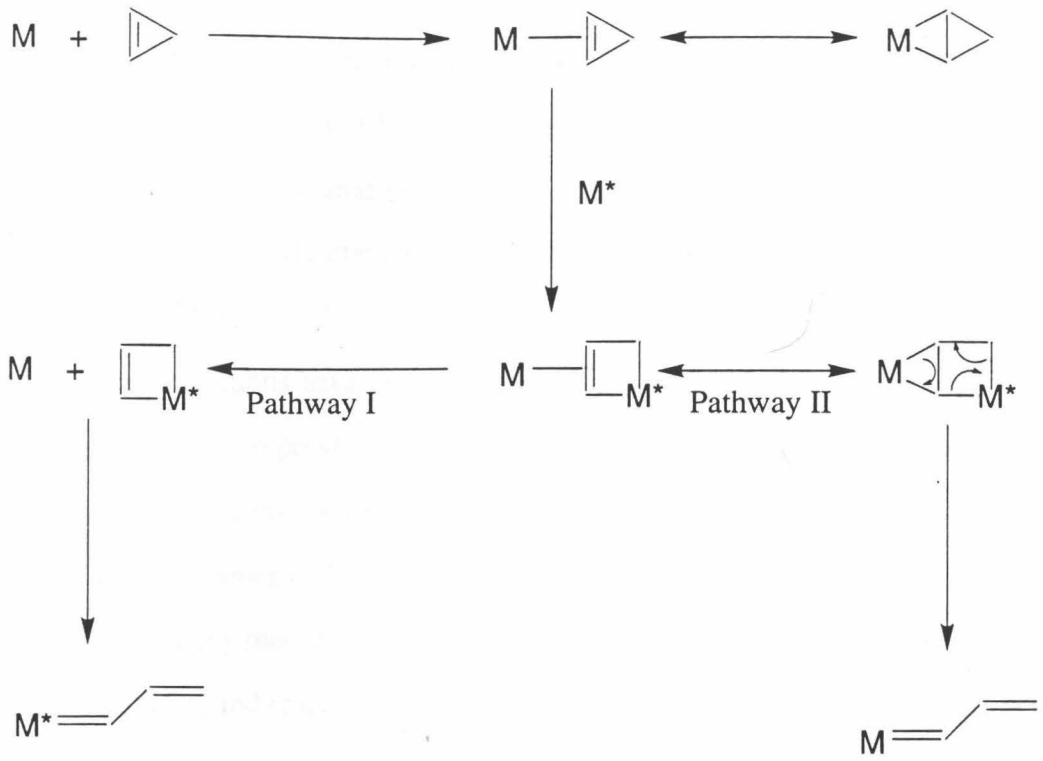
1-d_{18} **6-d_{18}**

Previous analysis of the ^1H NMR spectrum of **6** established that the resonances for the PMe_3 protons of the metal bearing the metallacycle were shifted approximately 0.2 ppm from the PMe_3 protons of the metal coordinated to the iridacyclobutene. Thus, we could establish the origin of the two metals in **6** (i.e., which metal comes from **1** and which metal comes from free $IrCl(CO)(PMe_3)_2$). In addition, by integrating both PMe_3 resonances relative to the olefinic resonances, we could establish the isotopic "cleanliness" of the reactions.

For both reactions (eqs 8 and 9), the metal from free $IrCl(CO)(PR_3)_2$ was found to be in 88% of the metallacycle metal centers. Consequently, 12% of the metallacycle metal centers were found to contain the metal originally in **1**. These results establish that the predominant pathway for the formation of **6** involves σ-bond activation of the cyclopropene moiety in **1** by $IrCl(CO)(PR_3)_2$ (i.e., pathway A in Scheme 4).

A Proposed Bimetallic Pathway for The Ring Opening of Cyclopropenes to Vinylcarbenes. On the basis of the preceding observations, a scheme for the bimetallic metal-mediated ring opening of metal η^2-cyclopropenes to metallacyclobutenes/metal vinylcarbenes is proposed (Scheme 5). First, the metal and cyclopropene react to form an η^2-olefin complex. This η^2-olefin complex undergoes subsequent reaction with another metal (M^*), which inserts into the C-C σ-bond to form a bimetallic metallacyclobutene complex. This complex can then rearrange further by several pathways. One pathway involves the dissociation of the metal M to form an isolated metallacyclobutene complex, which can rearrange on its own to a vinylcarbene (pathway I). The bimetallic complex can also rearrange on its own to a vinylcarbene —a pathway that uses the second metal (M^*) as a catalyst (pathway II). In the case presented here, however, the iridium vinylcarbene complex seems to be less stable than the bimetallic iridium metallacyclobutene complex, and thus rearrangement of the metallacyclobutene to the metal vinylcarbene is not observed. This observation can be rationalized if we consider the carbene moiety to be a neutral ligand. Assuming a constant ancillary ligand

Scheme 5



environment, rearrangement of the metallacyclobutene moiety would result in a 5-coordinate, 18-electron iridium(I) carbene complex, an inherently unstable species.[19] On the other hand, the metallacyclobutene configuration is preferred because it is formally an 18-electron complex of iridium (III), which can coordinate six ligands and adopt an octahedral geometry.

Group VIII metal complexes have long been known to catalyze the rearrangement of bicyclo[1.1.0]butane to butadiene.[30] In these reactions, it has been proposed that the first step involves the activation of a side $C_{methylene}$-$C_{methine}$ σ bond.[31] This proposal is analogous to our proposed mechanistic scheme where one metal center is part of the bicyclobutane and the other metal center functions as a catalyst for the rearrangement. The similarity between the rearrangement of metal-η^2-cyclopropene complexes and that

of bicyclo[1.1.0]butane is striking where the metal center in the η^2-cyclopropene complex behaves much like one of the methylene carbons in bicyclo[1.1.0]butane.

An additional example of the bimetallic pathway depicted in Scheme 5 may be inferred from recent work in our laboratory. Using the metal-η^2-cyclopropene/bicyclobutane analogy, Johnson and Grubbs succesfully catalyzed the formation of tungsten vinylcarbenes from tungsten η^2-3,3-diphenylcyclopropene complexes with $HgCl_2$.[3,32] There, the Hg^{2+} can be viewed to function as M^*. In a related paper, Swager and Grubbs have used both Hg^{2+} and Ag^+ to catalyze the isomerization of the bicylobutane rings in polybenzvalene to 1,3-dienes.[33] Although we are certain that a bimetallic path such as that shown in Scheme 5 is possible in the metal-mediated ring opening of cyclopropenes to metallacyclobutenes/metal vinylcarbenes, it is only one route among the many mechanistic pathways that exist. Depending on the metal center, ligand environment, and reaction conditions, the mechanism for this transformation may vary from system to system.

Conclusions

To summarize, $IrCl(CO)(PR_3)_2$ complexes react with 3,3-diphenylcyclopropene to afford stable η^2-olefin complexes. The binding of the olefin is reversible and depends on the steric bulk of the tertiary phosphine: complexation of the olefin becomes less favorable as the size of the tertiary phosphine increases. Addition of another equivalent of $IrCl(CO)(PMe_3)_2$ to the olefin complex **1** produces a bimetallic iridacyclobutene, where the iridacyclobutene moiety is stabilized by coordination in an η^2 fashion to a second metal center. Kinetic measurements show this rearrangement to be a second order process. Isotopic labelling studies suggest that formation of the bimetallic iridacyclobutene proceeds by a mechanism involving C-C bond activation of the olefin moiety in **1** by free $IrCl(CO)(PMe_3)_2$. This study provides further evidences that a

bimetallic C-C activation pathway is one possible mechanism in the metal-catalyzed ring opening of cyclopropenes to metallacyclobutenes/metal vinylcarbenes.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. NMR experiments were also prepared inside a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz 1H; 22.53 MHz 13C; 34.82 MHz ^{31}P, ^{7}Li external lock, ^{31}P NMR data referenced to external H_3PO_4 where PPh_3 has a chemical shift at -5.4 ppm), and a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer.

Materials. Hexane was stirred over concentrated H_2SO_4, dried successively over $MgSO_4$ and CaH_2, and then transferred onto sodium benzophenone ketyl solubilized with tetraglyme. *n*-Butyl ether and benzene were distilled or vacuum transferred from sodium benzophenone ketyl. Methylene chloride was stirred over either CaH_2 or P_2O_5, distilled under argon, and degassed by three continuous freeze-pump-thaw cycles. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Benzene-d_6 was dried over sodium benzophenone ketyl and then vacuum transferred. $[Ir(COD)Cl]_2$[34] and $IrCl(CO)(PR_3)_2$[35] were prepared according to literature procedures. 3,3-Diphenylcyclopropene was prepared following a procedure by Moore.[36] The following chemicals were obtained from commercial sources and used as received: dimethylsulfoxide-d_6 (Cambridge Isotopes); t-BuOK, Mg turnings, and iodomethane-d_3 (Aldrich Chemical Co.); silica gel, diethyl ether, and hexane (EM Science).

$IrCl(CO)(PMe_3)_2(\eta^2$-3,3-Diphenylcyclopropene) (1)

In a typical reaction, a 50 mL Schlenk flask equipped with a magnetic stirbar was charged with $IrCl(CO)(PMe_3)_2$ (1.0 g, 2.4 mmol) inside a nitrogen-filled drybox.

Methylene chloride (10 mL) was added to dissolve the complex. 3,3-Diphenylcyclopropene (0.69 g, 1.5 equiv) in CH_2Cl_2 (2 mL) was then added to the solution via cannula. The reaction was allowed to stir under argon at rt for 2 h. Hexane (20 mL) was added to the solution which was then cooled to -30 °C for 24 h upon which white crystals of the product formed. The supernatant was cannula-filtered away while the mixture was kept cold. The remaining crystals were washed with ice-cold hexane (2 x 10 mL) and dried under vacuum overnight. Yield = 1.1-1.3 g (75-90%). ^{1}H NMR (C_6D_6): δ 1.25 (pseudo-doublet, Ir-P(CH_3)$_3$, J_{HP} = 6.6 Hz), 3.32 (t, *H*-C=C-*H*, J_{HP} = 6.4 Hz); ^{31}P NMR (C_6D_6): δ -51.2 (s); ^{13}C NMR (CD_2Cl_2): δ 17.7 (t, Ir-P(*C*H$_3$)$_3$, J_{CP} = 17.1 Hz), 37.1 (quintet (overlapping triplets)), H-*C*=*C*-H, J_{CP} = 29.7 Hz), 64.3 (s, M(C=C-*C*), 165.9 (t, M(*C*O), J_{CP} = 8.9 Hz). IR (C_6H_6): υ_{CO} = 1985.9 cm.$^{-1}$ Anal. Calcd for $C_{22}H_{30}ClIrOP_2$: C, 44.03; H, 5.04. Found: C, 43.94; H, 5.05.

X-Ray Diffraction Study of IrCl(CO)(PMe$_3$)$_2$(η^2-3,3-Diphenylcyclopropene) (1)

A concentrated solution of IrCl(CO)(PMe$_3$)$_2$(η^2-3,3-diphenylcyclopropene), **1**, in dichloromethane (1 mL) was loaded into a 5 mm NMR tube inside a nitrogen-filled drybox, sealed with a rubber septum, and slowly cooled to -20 °C over 24 h upon which a large, pale yellow crystal was obtained. The supernatant was then carefully removed from the tube via pipet. The resulting crystal was transferred quickly into an oil-filled crystallizing dish and cut to ca. 0.20 x 0.33 x 0.40 mm with a razor blade.[37] Next, this crystal was oil-mounted[37] on a glass fiber and transferred to the Syntex P2$_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low temperature system. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[38] Intensity data were collected at 163 K using a $\theta - 2\theta$ scan technique with Mo Kα radiation. All 6876 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The difraction

symmetry was 2/m with systematic absences 0k0 for k = 2n+1 and h0l for h+l = 2n+1. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ (C_{2h}^5 ; No. 14), is therefore uniquely defined.

All crystallographic calculations were carried out using either the UCLA Crystallographic Computing Package[39] or the SHELXTL PLUS program set.[40] The analytical scattering factors for neutral atoms were used throughout the analysis;[41a] both real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[41b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008|F_o|)^2$. The structure was solved via an automatic Patterson routine (SHELXTL PLUS) and refined by full-matrix least-squared techniques. Hydrogen atoms were included using a riding model with d(C-H) = 0.96Å and U(iso) = 0.06Å^2. There is one molecule of dichoromethane present in the assymetric unit. Refinement of positional and thermal paramenters led to convergence with RF = 4.5%; R_{wF} = 5.0% and GOF = 1.26 for 271 variables refined against those 5282 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference Fourier synthesis yielded ρ(max) = 2.63eÅ^{-3} at a distance of 0.96Å from Ir(1).

IrCl(CO)(PMe_2Ph)$_2$(η^2-3,3-Diphenylcyclopropene) (2)

This compound was synthesized using a procedure similar to that described for the synthesis of **1**. Yield was 70-80%. ^{1}H NMR (C_6D_6): δ 1.47 (pseudo-doublet, Ir-P(*C*H$_3$)(C'H$_3$)(Ph), J_{CP} = 9.6 Hz), 1.59 (pseudo-doublet, Ir-P(CH$_3$)(*C*'H$_3$)(Ph), J_{CP} = 9.0 Hz), 3.40 (t, *H*-C=C-*H*, J_{CP} = 6.5 Hz); ^{31}P NMR (C_6D_6): δ -38.5 (s); ^{13}C NMR (CD_2Cl_2): δ 17.7 (t, P(*C*H$_3$)$_2$(Ph), J_{CP} = 17.1 Hz), 38.4 (quintet (overlapping triplets), Ir-(*C*=*C*-C), J_{CP} = 29.3 Hz, J_{CH} = 220.9 Hz), 167.5 (t, Ir(*C*O), J_{CP} = 8.9 Hz). IR (C_6H_6): υ_{CO} = 1992.6 cm.$^{-1}$ Anal. Calcd for $C_{32}H_{34}ClOP_2Ir$: C, 53.07; H, 4.73. Found: C, 52.85; H, 4.39.

$IrCl(CO)(PMePh_2)_2(\eta^2$-3,3-Diphenylcyclopropene) (3)

This compound was synthesized using a procedure similar to that described for **1.** The product could not, however, be separated from the starting Vaska complex $IrCl(CO)(PMePh_2)_2$: $IrCl(CO)(PMePh_2)_2$(3,3-diphenylcyclopropene) was isolated in a 7:3 mixture with $IrCl(CO)(PMePh_2)_2$. ^1H NMR (C_6D_6): δ 1.92 (pseudo-doublet, Ir-P(CH_3)(Ph)$_2$, J_{CP} = 9.0 Hz), 3.47 (t, *H*-C=C-*H*, J_{CP} = 6.7 Hz); ^{31}P NMR (C_6D_6): δ -21.3 (s); ^{13}C NMR (CD_2Cl_2): δ 14.3 (t, Ir-P(*C*H$_3$)(Ph)$_2$, J_{CP} = 17.1 Hz), 38.7 (quintet (overlapping triplets), Ir(*C*=*C*-C), J_{CP} = 26.7 Hz), 165.4 (t, Ir(*C*O), J_{CP} = 8.9 Hz). IR (C_6H_6): υ_{CO} = 2000.7 cm.$^{-1}$

$IrCl(CO)(PEt_3)_2(\eta^2$-3,3-Diphenylcyclopropene) (4)

This compound was synthesized using a procudure similar to that described for **1.** The product could not, however, be separated from the starting Vaska complex $IrCl(CO)(PEt_3)_2$: $IrCl(CO)(PEt_3)_2$(3,3-diphenylcyclopropene) was isolated in a 2:5 mixture with $IrCl(CO)(PEt_3)_2$. ^1H NMR (C_6D_6): δ 0.89 (m, Ir-P(CH_2CH_3)$_3$, J_{HP} = 7.5 Hz), 1.67 (m, Ir-P(*C*H$_2$CH$_3$)$_3$, J_{CP} = 8.1 Hz), 3.25 (t, *H*-C=C-*H*, J_{CP} = 6.3 Hz). ^{31}P NMR (C_6D_6): δ -18.4 (s). ^{13}C NMR (CH_2Cl_2): δ 8.6 (d, Ir-P(CH_2CH_3)$_3$, J_{CP} = 19.5 Hz), 18.5 (t, Ir-P(*C*H$_2$CH$_3$)$_3$, J_{CP} = 14.7 Hz), 35.7 (q, H*C*=*C*H, J_{CP} = 33.8 Hz), 172.8 (t, Ir-*C*O, J_{CP} = 11.0 Hz). IR (C_6H_6): υ_{CO} = 1979.3 cm.$^{-1}$

3,3-Diphenylcyclopropene-1,2-d_2 (5-d_2)

3,3-Diphenylcyclopropene (1.0 g, 5.2 mmol) and potassium *t*-butoxide (0.058 g, 0.52 mmol) were dissolved in dimethylsulfoxide-d_6 (200 mL). The reaction was stirred for 1 h and then quenched with ice-cold D_2O (50 mL). The resulting aqueous slurry was extracted with 2:1 hexane:diethyl ether (5 x 100 mL). The combined extracts were then concentrated using a rotary-evaporator to give a viscous yellowish-green liquid which was purified by column chromatography on silica gel using hexane as the eluant. Yield

after chromatography was 0.98 g (98%). ^{13}C NMR (CD_2Cl_2): δ 31.7 (s, C=C-*C*), 113.2 (t, *C*=*C*-C, J_{CD} = 35.4 Hz), 126.0 (s, C_{ortho}), 128.4 (s, C_{meta} and C_{para}), 147.7 (s, C_{ipso}).

Trimethylphosphine-d_9.

The procedure described here represents a modification of a published, large-scale preparation of trimethylphosphine.[42] Fresh magnesium turnings (5.0 g, 0.21 mol) were slurried in anhydrous *n*-butyl ether (50 mL) in a 250 mL Schlenk flask under argon. With the Schlenk flask placed in a bath of room-temperature water, iodomethane-d_3 (20 g, 0.14 mol) was added dropwise over 1.0 h. The solution containing the Grignard reagent was cannula filtered away from the excess Mg turnings and cooled to 0 °C. Tri-*o*-tolyl phosphite (16 g, 0.047 mol) in *n*-butyl ether (25 mL) was then added dropwise to the Grignard solution over 1.5 h. When the addition was complete, a distillation head was attached to the top of a reflux condenser filled with water (the water was not circulated continuously). The reaction mixture was then heated until the *n*-butyl ether refluxed vigorously (ca. 178°C). The product phosphine was slowly liberated from the mixture and collected in a storage flask equipped with a Kontes valve. The crude product was then vacuum transferred into another storage flask to remove excess *n*-butyl ether (2.1 g, 79% overall yield). ^{31}P NMR (C_6D_6): δ -65.9 (br s).

IrCl(CO)(P[CD_3]$_3$)$_2$(η^2-3,3-Diphenylcyclopropene) (1-d_{18})

This compound was synthesized using the procedure described for **1**, but employing $P(CD_3)_3$ rather than $P(CH_3)_3$. ^1H NMR (C_6D_6): δ 3.32 (t, *H*C=C*H*, J_{HP} = 9.5 Hz). ^{31}P NMR (C_6D_6): δ 53.9 (br s).

Kinetics of Reaction of 1 with 3,3-Diphenylcyclopropene-1,2-d_2 in C_6D_6 and CD_2Cl_2

In the drybox, IrCl(CO)(PMe_3)$_2$(3,3-diphenylcylopropene) (10 mg, 1 equiv) was weighed in each of two NMR tubes. To one tube was added C_6D_6 (500 μL) and to the

other tube was added CD_2Cl_2 (500 μL). 3,3-Diphenylcyclopropene-1,2-d_2 (6.4 mg, 2 equiv) was then added to each NMR tube. The disappearance of **1** and formation of new olefin complex **1-*d*$_2$** was observed by ^{1}H NMR using ferrocene as an internal standard. The kinetic runs were carried out at 21.6°C and monitored until a dynamic equilibrium was obtained.

Observation of the Formation of 6

The η^2-cyclopropene complex **1** (5.0 mg) and $IrCl(CO)(PMe_3)_2$ (13 mg, 4 equiv) were dissolved in C_6D_6 (500 μL) in a 5 mm NMR tube. The mixture was allowed to rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudo-sextet), 4.22 (pseudo-septet); ^{31}P NMR (C_6D_6): δ −56.1 and -46.2 (d, J_{PP} = 17.5 Hz), 38.3 (br s), 14.5 (br s); ^{13}C NMR (C_6D_6): δ 14.1 (d of q, J_{CP} = 95.5 Hz, $J_{CP'}$ = 6.7 Hz, J_{CH} = 391.8 Hz), 14.9 (d, J_{CP} = 15.1 Hz), 15.2 (d, J_{CP} = 18.4 Hz), 17.6 (d, J_{CP} = 15.5 Hz), 17.8 (d, J_{CP} = 15.5 Hz), 66.0 (d of t, J_{CP} = 37.6 Hz, $J_{CP'}$ = 4.2 Hz, J_{CH} = 168.9 Hz), 146.6 (d, J_{CP} = 4.1 Hz), 147.7 (d, J_{CP} = 2.4 Hz), 166.3 (d of d, J_{CP} = 5.7 Hz, $J_{CP'}$ = 2.9 Hz), 174.3 (triplet, J_{CP} = 10.5 Hz).

Observation of the Formation of 6-*d*$_{18}$.

The η^2-cyclopropene complex **1** (5.0 mg) and $IrCl(CO)(P[CD_3]_3)_2$ (13 mg, 4 equiv) were dissolved in C_6D_6 (500 μL) in a 5 mm NMR tube. The mixture was allowed to rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudo-sextet), 4.22 (pseudo-septet).

Observation of the Formation of 6'-*d*$_{18}$.

The η^2-cyclopropene complex **1-*d*$_{18}$** (5 mg) and $IrCl(CO)(PMe_3)_2$ (13 mg, 4 equiv) were dissolved in C_6D_6 (0.5 ml) in a 5 mm NMR tube. The mixture was allowed to

rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudo-sextet), 4.22 (pseudo-septet).

Kinetics of the Reaction of 1 with $IrCl(CO)(PMe_3)_2$ in C_6D_6 and CD_2Cl_2.

In the drybox, a stock solution of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene) in C_6D_6 and CD_2Cl_2 was made by dissolving 25.0 mg of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene) in 1.25 mL of C_6D_6 or CD_2Cl_2. Approximately 250 μL of this stock solution was syringed into each of 5 different 5 mm NMR tubes. Next, a stock solution of $IrCl(CO)(PMe_3)_2$ was made by dissolving 36.4 mg of $IrCl(CO)(PMe_3)_2$ in 1.00 mL of C_6D_6 or CD_2Cl_2. Varying amounts of this second stock solution (65.9 μL, 0.7 mol equiv; 93.4 μL, 1.0 mol equiv; 187 μL, 2 mol equiv, 280 μL, 3 mol equiv, 374 μL, 4 mol equiv) were syringed into each of the 5 NMR tubes. Finally, additional C_6D_6 or CD_2Cl_2 was appropriately added to each of the NMR tubes to insure equal concentrations. The kinetic runs were carried out at 21.6°C and monitored by ^{1}H NMR for ca. 3 half-lives. Concentration of product **6** at time *t* was determined by NMR integration. Data manipulation was done using the KaleidaGraph curve-fitting module[43] to extract the second-order rate constants (k_2).

References

1 For reviews, please see: (a) Binger, P.; Buch, H. M. *Topics Curr. Chem.* **1987**, *135*, 77-151. (b) Baird, M. S. *Topics Curr. Chem.* **1988**, *144*, 137-209. (c) Halton, B.; Banwell, M. G. in *The Chemistry of the Cyclopropyl Group*; Rappoport, Z.; Patai, S., Eds.; John Wiley: New York, 1987, pp. 1223-1339.

2 Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610-611.

3 Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130-8145.

4 Flatt, B. T.; Grubbs, R. H.; Blanski, R. L.; Calabrese, J. C.; Feldman, J., *Organometallics*, **1994**, in press.

5 Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975. (b) Gagne, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics*, **1992**, *11*, 3933-3935.

6 (a) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998-999. (b) Visser, J. P.; Schipperjin, A. J.; Lukas, J.; Bright, D.; DeBoer, J. *J. Chem. Soc., Chem Commun.* **1971**, 1266-1267. (c) Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350-351. (d) Lehmkuhl, H.; Kruger, P. C.; Tsay, Y. H.; Benn, R.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 1147-1161.

7 (a) Binger, P.; Muller, R.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 647-648. (b) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (c) Klimes, J.; Weiss, E. *Chem.,Ber.* **1982**, *115*, 2606-2614. (c) Valeri, T.; Meier, F.; Weiss, E. *Chem. Ber.* **1988**, *121*, 1093-1100.

8 (a) Hughes, R. P.; Mackenzie, E. K.; Robinson, D. J.; Spotts, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8919-8920. (b) Hermond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239-2241.

9 Binger, P.; Muller, P.; Hermann, A. T.; Phillips, P.; Gabor, B.; Langhau, F. *Chem. Ber.* **1991**, *124*, 2165-2170.

10 For a general review, see: Hoz, S. In *The Chemistry of the Cyclopropyl Group*; Rappaport, Z; Patai, S., Eds.; John Wiley: New York, 1987, pp. 1121-1192.

11 (a) Vaska, L.; Diluzo, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 2784-2785. (b) Vaska, L. *Science* **1966**, *152*, 769-771. (c) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335-344.

12 For a review see Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, California, 1987.

13 Stohmeier, W.; Fleischman, R. *J. Organomet. Chem.* **1972**, *42*, 163-168.

14 Lyons, J. E. *J. Org. Chem.* **1971**, *36*, 2497-2505.

15 Vaska, L.; Rhodes, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 4970-4971.

16 Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 844-850.

17 Monojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Discuss. Faraday. Soc.* **1969**, *47*, 84-92.

18 Parshall, G. W.; Jones, F. N. *J. Am. Chem. Soc.* **1965**, *87*, 5356-5361.

19 (a) Gray, H. B., California Institute of Technology, personal communication, 1994. (b) Potterfield, W. W. *Inorganic Chemistry*, 2nd. ed.; Academic Press: San Diego, 1993; pp. 732-739. (c) The reluctance of Vaska's complex to coordinate olefin and become a 5-coordinate Ir^{I} center has been documented within d^8 complexes of group VIII metals, see: Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 56-94.

20 Wurthrich, K.; Meiboom, S.; Sneider, L. C. *J . Chem. Phys*. **1970**, *52*, 230-233.

21 The % s character is calculated from an equation developed by Figeys and coworkers, see: Van-Alsenoy, C.; Figeys, H. P.; Geerlings, P. *Theor. Chim. Acta* **1980**, *55*, 87-101.

22 Haller, I.; Srinivasan, R. *J. Chem. Phys.* **1964**, *41*, 2745-2752.

23 Calculations were carried out by Dr. S. Joshua Jacobs of the California Institute of Technology using the PM3 Hamiltonian basis set (part of the MOPAC package).

24 Cone angle data and electronic parameters are taken from Tolman, C.A. *Chem. Rev.* **1977**, *77*, 313-348.

25 $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$ in electron donating capability; see also reference 24.

26 Observed by ^1H and ^{31}P NMR upon addition of 1equiv of tetracyanoethylene or dimethylmaleate to a solution of **1** in C_6D_6.

27 Observed by ^1H and ^{31}P NMR upon addition of 20 equiv of either norbornene, cyclooctene, cyclopentene, or cyclohexene to a solution of **1** in C_6D_6.

28 Line-shape analysis using the LAOCOON simulation program developed by Professor John D. Roberts of the California Institute of Technology showed that the coupling patterns of the olefinic protons must involve more than two ^{31}P nuclei. The precise lineshape could not be simulated.

29 Atkins, P. W. *Physical Chemistry*; W. H. Freeman & Co.: New York, 1986, pp. 695-696.

30 (a) Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748-7756. (b) Gassman, P. G.; Meyer, G. R.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7741-7748.

31 (a) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7733-7740. (b) Gassman, P. G.; Atkins, T. J.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 1812-1813.

32 Johnson, L. K., Ph.D. Thesis, California Institute of Technology, 1992.

33 Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc*. **1988**, *110*, 2973-2974.

34 Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18-20.

35 Burk, M. J.; Crabtree, R. H. *Inorg. Chem.* **1986**, *25*, 931-932.

36 Moore, J. S.; Nguyen, S. T.; Grubbs, R. H., California Institute of Technology, unpublished results.

37 The crystal was immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting-pin. Further details were described by Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization, ACS Symposium Series No. 357*; Wayda, A. L.; Derensbourg, M. Y., Eds.; American Chemical Society: Washington, D. C., 1987.

38 Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem*. **1977**, *16*, 265-271.

39 (a) UCLA Crystallographic Computing Package, University of California at Los Angeles, 1981. (b) C. Strouse, University of California at Los Angeles, personal communication.

40 Siemens Analytical X-Ray Instruments, Inc.; Madison, WI 1990.

41 *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; (a) pp. 99-101; (b) pp. 149-150.

42 (a) Wolfberger, W.; Schmidbauer, H. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 149-156. (b) Sharp, P. R. *Organometallics* **1984**, *3*, 1217-1223. (c) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Brandy, B. A.; Grabenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025-2035.

43 Kaleida Graph version 2.1; Abelbeck Sofware, 1990. This program is published and distributed by Synergy Software: Reading, PA.

Chapter 2

Synthesis of Bimetallic Iridium(I) Vinylcarbene Complexes and their Catalytic Activities in Ring-Opening Metathesis Polymerization (ROMP)

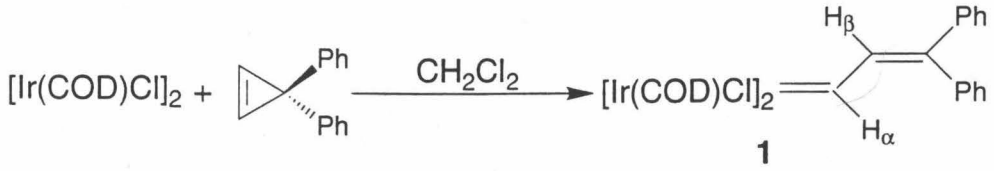
Introduction

Metal-carbene complexes catalyze a number of important reactions, including acyclic olefin metathesis,[1] ring-opening metathesis polymerization (ROMP),[1] acyclic diene metathesis polymerization (ADMET),[2] alkyne polymerization,[3] ring-closing metathesis,[4] and carbonyl olefinations.[4c,5] These complexes have traditionally been synthesized via α-hydride elimination routes.[6] Recently, our group has explored the use of cyclopropenes as a new route to catalytically active metal carbenes.[7,8] Metal-vinylcarbene complexes from the rearrangement of 3,3-diphenylcyclopropene were first reported for early transition metals such as zirconium and titanium.[9] We have extended this methodology to synthesize vinylcarbene complexes from the reaction of 3,3-diphenylcyclopropene with later transition metals: tungsten,[10] rhenium,[11] and ruthenium.[12,13] Although the overall activity of these carbene complexes decreases when moving from early to late-transition metals, functional group tolerance and stability are obtained with the later transition metal catalysts.[4d] With these considerations in mind, we wished to develop carbene complexes of the cobalt triad metals and explore their utility as highly active, functional-group tolerant metathesis catalysts. In addition, we hoped to utilize the convenience of the cyclopropene methodology to synthesize these metal-carbene complexes.

To date, there are few reports in the literature describing the use of iridium complexes as ring-opening metathesis polymerization (ROMP) catalysts.[1b] Of those reported, the catalysts are often ill-defined, and to the best of our knowledge, there has been no report of an iridium carbene complex that is active in ROMP. Here we report that 3,3-diphenylcyclopropene reacts with various types of Ir^{I} dimers to produce bimetallic, bridging vinylcarbene complexes that are active in ROMP.

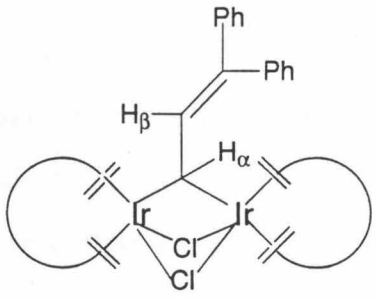
Results and Discussion

The reaction of $[Ir(COD)Cl]_2$ with one equiv of 3,3-diphenylcyclopropene in CH_2Cl_2 at room temperature yields the bimetallic vinylcarbene complex $[Ir(COD)Cl]_2(=CHCHCPh_2)$ (**1**) within minutes (eq 1)



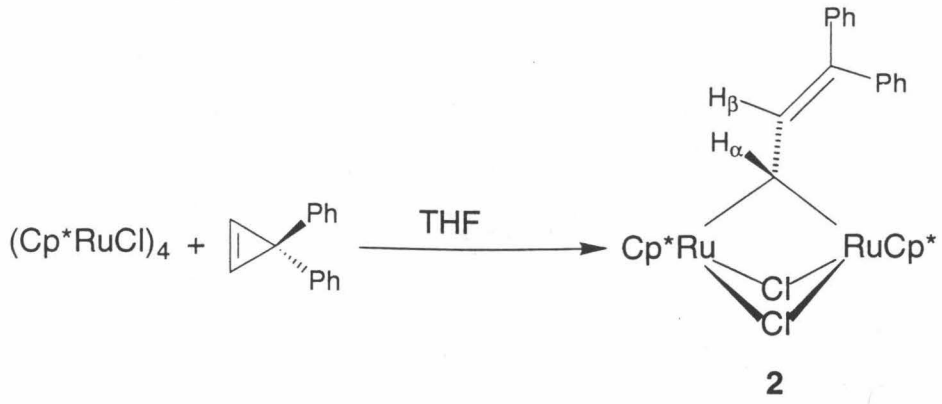
1 (1)

The ^1H NMR spectrum of this compound shows a doublet at 11.62 ppm assigned to H_α and a doublet at 8.19 ppm assigned to H_β (J_{HH} = 13.8 Hz). Careful observation of the vinylcarbene resonances by ^1H NMR shows the vinylcarbene to be visible for ca 30-40 minutes before complete decomposition takes place. The structure of the carbene complex is probably dimeric, where the carbene ligand is bridged between two metal centers (as shown below).



1

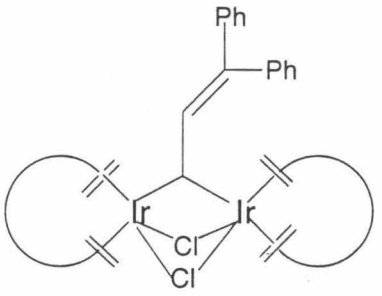
Precedence for this structure has been reported: previous work in our laboratory has shown that a binuclear, bridging vinylcarbene complex of ruthenium can be isolated from the reaction of a Ru^{II} precursor with 3,3-diphenylcyclopropene (eq 2).[13]



2 (2)

As observed for **1**, the ^{1}H NMR spectrum of **2** exhibits two doublets due to the H_α and H_β protons of the vinylcarbene moiety. Characteristics of the bridging vinylcarbene structure in **2** are the upfield chemical shift for H_α (13.32 ppm) and the larger H_α-H_β coupling constant (13.1 Hz),[13] which contrasts monomeric vinylcarbene complexes where the H_α resonance ranges between 17-20 ppm and the coupling constants are smaller (J_{HH} = 9-11 Hz).[12] A similar situation is observed for iridium when the ^{1}H NMR data of **1** (H_α = 11.62 ppm, J_{HH} = 13.8 Hz) is compared to that of monomeric iridium vinylcarbene complexes (H_α = 17-20 ppm, J_{HH} = 6-8 Hz).[14]

In order to stabilize **1,** which is formally an iridium(I) 16-electron carbene complex, we rationalized that substitution of the Cl anionic ligand by a chelating and more electron-withdrawing ligand might be beneficial. Indeed, by quickly reacting **1** with one equivalent of silver acetate or silver trifluoroacetate (AgTFA) in methylene chloride, we obtained new, stable vinylcarbene complexes $[Ir_2(COD)_2Cl(O_2CCX_3)]$ (=CHCHCPh$_2$) (X = F, **3**; X = H, **4**) (eq 3). The composition of complexes **3** and **4** is supported by elemental analysis (as reported in the Experimental), and the bimetallic structure of **3** and **4** is supported by molecular weight determination.[15]



1

$$+\ AgO_2CCX_3 \longrightarrow \qquad (3)$$

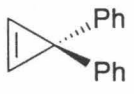
$[Ir_2(COD)_2Cl(O_2CCX_3)](=CHCHCPh_2)$

$CX_3 = CH_3$ or CF_3

3 **4**

Complexes **3** and **4** can also be generated by an independent method. In preparative scale reactions, we react $[Ir(COD)Cl]_2$ with 1 equiv of AgO_2CCX_3 in CH_2Cl_2 and filter the resulting solution through Celite to remove the AgCl salts. Subsequent addition of 1 equiv of 3,3-diphenylcyclopropene to the filtrate results in vinylcarbene complexes **3** or **4** in high yield (eq 4). Compounds **3** and **4** can be purified simply by washing the solid with cold pentane, or by recrystallization from a CH_2Cl_2/pentane (1/1:v/v) solution mixture. It should be noted that the use of two equiv of AgO_2CCX_3 in the first step does not lead to carbene formation.

$$[Ir(COD)Cl]_2 + AgO_2CCX_3 \xrightarrow[CH_2Cl_2]{} \left[[Ir_2(COD)Cl(O_2CCX_3)] \right] \qquad (4)$$



3, 4

The ^1H NMR spectra of **3** and **4** exhibit four different resonances for H_α, suggesting the presence of four distinct isomers. In addition, **3** and **4** give different stereoisomers thus, ruling out the possibility of a non-carbene impurity. These isomers do not

interconvert upon heating. However, upon treatment of **3** with a catalytic amount of HCl, isomerization to a single major isomer (corresponding to the major isomer originally observed in the mixture) is observed. Treatment of **4** with HCl does not lead to isomerization; however, the use of $HBF_4.Et_2O$ isomerizes all four isomers of **4** to a single species within minutes. Interestingly, this isomer is not the major isomer, but one of the minor isomers initially observed. Prolonged exposure (ca 2 h) of **4** to $HBF_4.Et_2O$ leads to complete decomposition of the metal-vinylcarbene complex.

The vinylcarbene isomers of **3** and **4** are stable under a variety of conditions. In solution, each of the four vinylcarbene isomers of **3** and **4** are stable indefinitely to prolonged exposure to oxygen and aqueous environments. In addition, they are also stable to certain acidic environments: little decomposition is observed after several days of exposure to 10 equiv of HCl or 10 equiv of glacial acetic acid. Also, these vinylcarbene species are thermally stable in refluxing benzene for 24 h.

Compounds **1**, **3**, and **4** are active ROMP catalysts and represent the first iridium-based carbene complexes that are active in olefin metathesis. Results are summarized in Table 1. Compound **1** will react with 100 equiv of norbornene at rt to afford complete conversion to the ROMP polymer within 1 h. The resulting polymer is high cis and has a high molecular weight (M_w = 380,000, and PDI = 1.9 as determined by Gel Permeation Chromatography).

Compound **3** will also effect the ROMP of norbornene. Reaction of **3** with 100 equiv of norbornene affords complete polymerization within 40 min. In contrast to that for **1**, this catalyst gives highly trans polynorbornene (M_w = 630,000 and PDI = 1.9). Interestingly, using **3** as a mixture of isomers or as a single isomer after treatment in acid does not affect the polydispersity of the polymer.

Compound **4** is the most active of these catalysts; it will effect the ROMP of both norbornene and cyclopentene. Reaction of **4** with 100 equiv of norbornene at rt affords complete polymerization within 30 min. Again, the polynorbornene obtained after work-

up is high trans and has a high molecular weight (M_w = 982,000 and PDI = 2.3). Complex **4** also catalyzes the ROMP of neat cyclopentene at rt to give polycyclopentene in 46% yield (M_w = 1,523,000 and PDI = 2.0).

Table 1. ROMP Activity of Complexes **1**, **3** , and **4**.

Catalyst	Monomer	Monomer/Catalyst	$\overline{M}w$	PDI
1	norbornene	100	3.8×10^5	1.9
3	norbornene	100	6.3×10^5	1.9
4	norbornene	100	9.8×10^5	2.3
4	cyclopentene	600	1.5×10^6	2.0

Norbornene ppolymerizations were carried out at 0.13 M in CH_2Cl_2. Cyclopentene polymerization was carried out in neat monomer.

The polymers obtained from the polymerizations catalyzed by **1**, **3**, and **4** are all very high molecular weight polymers which suggests that the rate of initiation is slow compared to the rate of propagation. This hypothesis is further supported by monitoring the polymerizations catalyzed by **3** and **4** against an internal standard using ^1H NMR spectroscopy; essentially all of the parent carbene are still present even when the polymerization is complete.

To summarize, the reaction of 3,3-diphenylcyclopropene with $[Ir(COD)Cl]_2$ produces what is believed to be the bimetallic, bridging iridium vinylcarbene **1**. This relatively unstable species can catalyze the ROMP of norbornene. Compound **1** can be stabilized by its reaction with silver acetate or silver trifuoroacetate to afford bridging vinylcarbene species **3** and **4,** which exist as mixtures of four isomers. These isomers will convert to a single isomer in the presence of an acid catalyst. Complexes **3** and **4** are stable to aqueous, oxygen, and acidic environments and can catalyze the ROMP of norbornene. In addition, compound **4** catalyzes the ROMP of cyclopentene.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. NMR experiments were also prepared inside a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) or a Bruker AM-500 (500.14 MHz ^{1}H; 125.77 ^{13}C; 470.56 ^{19}F) spectrometer. GPC molecular weight measurements were obtained in CH_2Cl_2 against polystyrene standards.

Materials. Hexane was stirred over concentrated H_2SO_4, dried successively over $MgSO_4$ and CaH_2, and then transferred onto sodium benzophenone ketyl solubilized with tetraglyme. Benzene was distilled or vacuum transferred from sodium benzophenone ketyl. Methylene chloride was stirred over either CaH_2 or P_2O_5, distilled under argon, and degassed by three continuous freeze-pump-thaw cycles. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Benzene-d_6 was dried over sodium benzophenone ketyl and then vacuum transferred. $[M(COD)Cl]_2$ dimers were prepared as described in the literature,[16] 3,3-Diphenylcyclopropene was prepared following a procedure by Moore.[17] All other materials were of the hieghest purity from commercially available sources.

Observation of $[Ir_2(COD)Cl]_2(=CHCHCPh_2)$ (1).

In a 5 mm NMR tube was dissolved $[Ir(COD)Cl]_2$ (30 mg, 0.045 mmol) in CD_2Cl_2 (600 μL) . An aliquot of 3,3-diphenylcyclopropene (8.6 mg, 1 equiv) was added to the solution. The tube was capped and shaken vigorously. The reaction mixture immediately turned from orange-red to dark red color. Formation of **1** was observed by ^{1}H NMR. - ^{1}H NMR (CD_2Cl_2): δ 11.62 (d, H_α, J_{HH} = 13.8 Hz), 8.19 (d, H_β, J_{HH} = 13.8 Hz).

$[Ir_2(COD)_2Cl(O_2CCX_3)](=CHCHCPh_2)$ where X = H (3), F (4).

Method A. In a Schlenk flask was dissolved $[Ir(COD)Cl]_2$ (0.50 g, 0.74 mmol) in CH_2Cl_2 (20 mL). In a seperate Schlenk flask was dissolved silver acetate or silver trifluoroacetate (0.74 mmol, 1.0 equiv) in THF (15 ml). The solution of the silver salt was added dropwise to the solution of $[Ir(COD)Cl]_2$ over 45 minutes. The orange-red solution turned fluorescent red. After the addition was complete, the solvent was removed under vacuum. The resulting red solid was then redissolved in CH_2Cl_2 (20 mL) and filtered through Celite to remove the AgCl salts. Finally, to the filtrate was added 3,3-diphenylcyclopropene (0.15 g, 0.80 mmol). The fluorescent red solution turned dark red. The reaction was allowed to stir for 1 h. The solvent was then removed under vacuum and the solid residue was washed with cold pentane (3 x 10 mL) to afford a red-purple solid. The yield of **3** was 0.59 g (89%); the yield of **4** was 0.06 g (84%).

Method B. In a Schlenk flask was dissolved $[Ir(COD)Cl]_2$ (0.50 g, 0.74 mmol) in CH_2Cl_2 (20 mL). To this solution was added 3,3-diphenylcyclopropene (0.16 g, 0.80 mmol). The orange-red solution turned bright red. After stirring at room temperature for 5 minutes, the solution was quickly cooled to -78°C. To this cooled solution was added dropwise a solution of silver acetate or silver trifuoroacetate (0.74 mmol, 1.0 equiv) in THF (10 mL) over 5 min. The solution was then allowed to warm to rt and the solvent was removed under vacuum. The resulting solid residue was redissolved in CH_2Cl_2 (20 ml) and filtered through Celite to remove the AgCl salts. The filtrate was evaporated to dryness affording a red-purple solid which was washed with cold pentane (3 x 10 mL). The yield of **3** was 0.52 g (78%); the yield of **4** was 0.54 g (77%).

Selected NMR data for **3**: ^1H and ^{13}C NMR (CD_2Cl_2): Major isomer has ^1H resonance for H_α at δ 11.10 and for H_β at δ 6.84 where J_{HH}= 14.0 Hz; ^{13}C resonance for C_α appears at δ 138.9 and for C_β at δ 123.9. For the other three isomers: ^1H resonace for H_α appears at δ 10.21 (J_{HH} = 13.8 Hz), 9.52 (J_{HH} = 11.6 Hz), 9.02 (J_{HH} = 13.4 Hz)

respectively. Relative abundances of the four isomers are 8:3:1:1 respectively. Anal. Calcd for $C_{33}H_{39}O_2Ir_2$: C, 44.67; H, 4.43. Found: C, 44.29; H, 4.39.

Selected NMR data for **4**. ^1H , ^{13}C, and ^{19}F NMR (CD_2Cl_2): Major isomer has ^1H resonance for H_α at δ 11.35 and for H_β at δ 6.87 where J_{HH}= 14.0 Hz; ^{13}C resonance for C_α appears at δ 141.3 and for C_β at δ 123.9; ^{19}F resonance for the CF_3 group appears at δ -72.97. For the other three isomers: ^1H resonance for H_α appears at δ 10.39 (J_{HH} = 14.0 Hz), ^{19}F resonance for the CF_3 group appears at δ -72.94; ^1H resonance for H_α appears at δ 9.63 (J_{HH} = 9.5 Hz), ^{19}F resonance for the CF_3 group appears at δ -72.74; ^1H resonance for H_α appears at 9.19 (J_{HH} = 11.6 Hz), ^{19}F resonance for the CF_3 group appears at δ -72.55. Relative abundances of the 4 isomers are 7:5:2:1 respectively. Anal. Calcd for $C_{33}H_{36}F_3O_2Ir_2$: C, 42.09; H, 3.85. Found: C, 42.43; H, 3.53.

Isomerization of 3.

Compound **3** (0.50 g, 0.56 mmol) was dissolved in C_6H_6 (30 mL). An aliquot of 1.0M HCl/Et_2O solution (400 μL) was then added and the mixture was stirred for 12 h. The solvent was removed under vacuum to yield 0.50 g (100%) of a single isomer of **3**. ^1H NMR (CD_2Cl_2): δ 11.10 (d, H_α, J_{HH} = 14.0 Hz), 6.84 (d, H_β, J_{HH} = 14.0 Hz).

Isomerization of 4.

Compound **4** (20 mg, 0.021 mmol) and ferrocene (2.0 mg, 0.011 mmol), used as an internal standard, was dissolved in C_6D_6 (600 μL). An aliquot of $HBF_4 \cdot Et_2O$ (0.5 mg, 3.1 x 10^{-3} mmol) was then added. The reaction was allowed to stand for 10 min and a ^1H NMR spectrum was taken. ^1H NMR (C_6D_6) shows a single vinylcarbene isomer at δ 9.63 (d, H_α, J_{HH} = 9.5 Hz). After 1 h, the reaction mixture turned from a dark red to a blue-green color. ^1H NMR of this mixture showed complete decomposition of the carbene complex.

Polymerization of Norbornene and Cyclopentene by 1, 3, and 4.

In a typical norbornene polymerization carried out in a drybox, 10 mg of **1**, **3**, or **4** was dissolved in CH_2Cl_2 (10 mL). A solution containing 100 equiv of norbornene in CH_2Cl_2 (5 mL) was then added to the catlalyst solution which was stirred until the solution became viscous. In a typical cyclopentene polymerization, 30 mg of **4** was dissolved in CH_2Cl_2 (100 μL). Neat cyclopentene (1.5 mL) was then added. The reaction was stirred unil the mixture became viscous (ca. 5 h).

Work-up: The reaction vials were taken out of the drybox and to them were added a solution consisting of CH_2Cl_2 (10 mL) and BHT (0.20 g). This mixture was then left at room temperature for 2 h during which time the gel dissolved, forming a viscous solution. The color changed from red to brownish yellow. The mixture was precipitated into a vigorously stirred solution of methanol (40 mL, containing 0.1% BHT). The resulting polymer was then washed with methanol (5 mL, containing 0.1% BHT) and dried under vacuum overnight.

For the polymerization catalyzed by **1:** Norbornene: Yield was 94 mg (87%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 380 K, PDI = 1.9. Ratio of cis/trans is 72/28.

For the polymerization catalyzed by **3**: Norbornene: Yield = 97 mg (91%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 630 K, PDI = 1.9. Ratio of cis/trans is 86/14.

For the polymerization catalyzed by **4**: (a) Norbornene: Yield = 91 mg (91%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 980 K, PDI = 2.3. Ratio of cis/trans is 74/26. (b) Cyclopentene: Yield = 0.53 g (46%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 1,500 K, PDI = 2.0.

References

1 For general references to the metathesis reaction, see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907-915. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed,; Pergamon Press, Ltd.: New York, 1982, Vol. 8, pp 499-551. (d) Leconte, M.; Basset, J. M.; Quignard, F.; Laroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986, Vol. 1, pp 371-420. (e) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S. Ed.; Plenum: New York, 1986, Vol. 1, pp 221-283. (f) Schrock, R. R. *Strem Chemiker* **1992**, *14*, 1-6. (g) Schrock, R. R. In *Ring-Opening Polymerization Mechanisms, Catalysis, Structure, Utility*; Brunelle, D. J., Ed.; Hansen Publisher: New York, 1993, pp 129-156. (h) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1-74.

2 (a) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649-2657. (b) Wagner, K. B.; Boncella, J. M.; Nel, J. G.; Dutweiler, R. P.; Hillmyer, M. A. *Makromol. Chem.* **1990**, *191*, 365-374.

3 (a) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004-8006. (b) Park, L. Y.; Schrock, R. R.; Stieglitz, S. G.; Crowe, W. E. *Macromolecules* **1991**, *24*, 3489-3495.

4 (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426-5427. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324-7325. (c) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800-3801. (d) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993,** *115*, 9856-9857.

5 (a) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Strauss, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733-1744. (b) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 531-533. (c) Heppert, J. A.; Dietz, S. D.; Morton, M. D. *Abstracts of Papers,*

199th National Meeting of The American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 1990; INOR 262. (d) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062-1067.

6 Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, **1988**; Chapter 3.

7 For examples of systems in which cyclopropenes are proposed as precursors to vinylcarbene intermediates, see: (a) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998-999. (b) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1991**, *56*, 6971-6972. (c) Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1991**, *32*, 3755-3758. (d) Muller, P.; Pautex, N.; Doyle, M. P.; Bagheri, V. *Helv. Chim. Acta.* **1990**, *73*, 1233-1241.

8 For general discussions regarding the physical properties, synthetic utility, and reactivity of cyclopropenes, see: (a) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77-151. (b) Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137-209. (c) Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group;* Rappaport, A., Ed.; John Wiley & Sons: New York, 1987; Part 2, Chapter 21, pp 1223-1339. (d) Salaun, J. In The *Chemistry of the Cyclopropyl Group*; Rappaport, A., Ed.; John Wiley & Sons: New York, 1987; Part 2, Chapter 13, pp 809-878.

9 Binger, P.; Muller, P; Benn., R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610-611.

10 Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130-8145.

11 Flatt, B. T.; Blanski, R. L.; Feldman, J.; Calabrese, J. C.; Grubbs, R. H., manuscript in preparation.

12 Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992,** *114*, 3974-3975.

13 Gagne, M. R.; Grubbs, R.H.; Feldman, J.; Ziller, J. W. *Organometallics*, **1992**, *11*, 3933-3935.

14 Li, R.T.; Zuercher, W.; Grubbs, R. H., unpublished results.

15 Molecular weight determination by vapor phase osmometry of **3** and **4** supports a bimetallic structure. Experimental apparatus is described in Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry: a Practicum in Synthesis and Characterization*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987, pp 94-95.

16 Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth*. **1973**, *14*, 92-95.

17 Moore, J. S.; Nguyen, S. T.; Grubbs, R. H., California Institute of Technology, unpublished results.

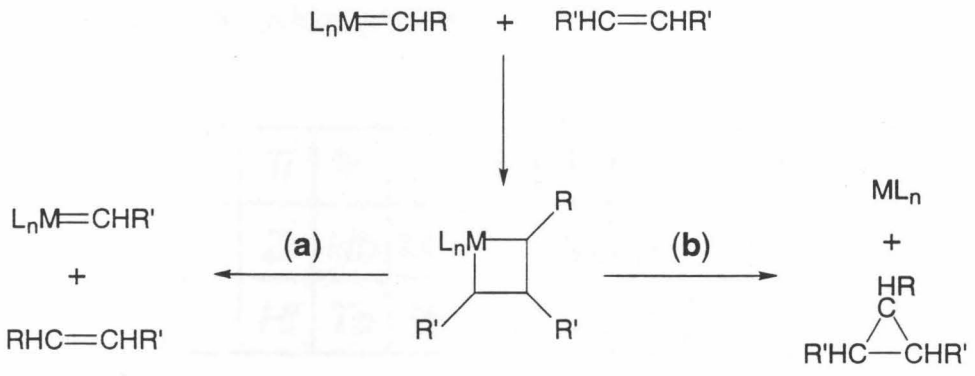
Chapter 3

Reactions of Iridium and Rhodium Vinylcarbene Complexes: A Look at Metal Effects and Oxidation State Effects

Introduction

Striving to understand how metal complexes mediate carbon-carbon bond formation is an important research goal in oganometallic chemistry.[1] A well-studied example is the reaction of metal-carbon double bonds, so-called carbenes or alkylidenes, with olefins.[2] Metal carbenes react productively with olefins by predominantly two pathways:[3] (a) olefin metathesis and (b) cyclopropanation, both of which may pass through a metallacyclobutane intermediate (Scheme 1).

Scheme 1



The boundary between olefin metathesis and cyclopropanation has been explained by the difference in reactivities of the two major forms of metal carbenes that exist in the literature to date. At one end of the spectrum is the nucleophilic carbene or "Schrock" type alkylidene which invariably metathesizes alkenes,[4a] and at the other end of the spectrum is the electrophilic or Fischer carbene which often cyclopropanates olefins.[2e, 4b,c] However, it is likely that the distinction between nucleophilic and electrophilic carbenes are only extreme cases of a continuum of metal carbene complexes. Roper and coworkers have published a large body of work supporting this idea.[3b] In the course of our work in the area of olefin metathesis, we became interested in the possibilities that there may be certain carbene complexes where both electrophilic and

nucleophilic properties may be observed. Such complexes may function as both olefin metathesis and cyclopropanation catalysts.

Further survey of the existing literature on olefin metathesis and cyclopropanation reveals additional interesting observations. With a few notable exceptions, of all the transition metals shown in Figure 1, the ones situated to the left side of the bold line participate mainly in olefin metathesis,[5] while the metals situated to the right of that line participate solely in olefin cyclopropanation. It is the metals at the border of this line that pose an interesting question of whether cross-over activities may exist for the complexes of the same type within a group. In our study, we look at this boundary by looking at the differences in the reactivities of Rh^I and Ir^I vinylcarbene complexes as they pertain to olefin metathesis and cyclopropanation.

	Ti	*V*	*Cr*	*Mn*	**Fe**	**Co**	Ni	**Cu**	
	Zr	*Nb*	*Mo*	Tc	***Ru***	**Rh**	**Pd**	**Ag**	
	Hf	*Ta*	***W***	*Re*	***Os***	*Ir*	**Pt**	Au	

Figure 1. A section of the periodic table. An italicized symbol denotes an element that is known to catalyze olefin metathesis. A bold-faced symbol denotes an element that is known to catalyze olefin cyclopropanation. An italicized, bold-faced symbol denotes an element that is known to catalyze both processes. The zig-zag, bold-faced line denotes an artificial separation between the two reactivity profiles.

During the course of our studies of the Rh^I vinylcarbene complexes we found that not only do these complexes cyclopropanate olefins, but they also exhibit a preference toward relatively electron-poor olefins. This is opposite of the trend observed for most carbene transfer reactions involving electrophilic metal carbenes where transfer reactions are successful for olefins possessing electron-donating substituents.[2e,f] Linear free energy studies with a series of para-substituted styrenes confirmed this observation. At this time, we became interested in using these linear free energy studies to investigate

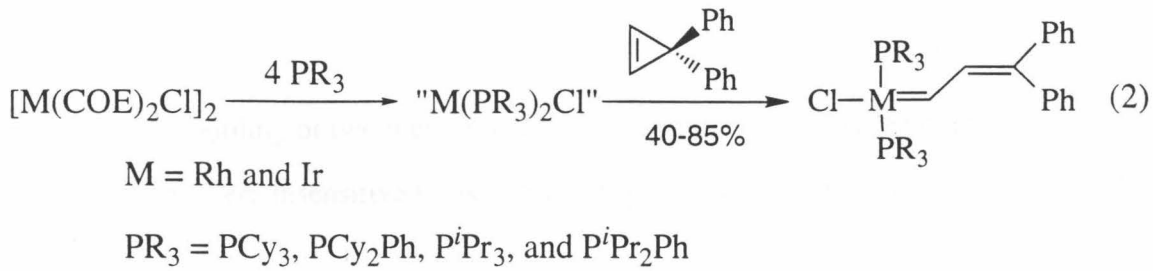
other well-known Rh carbenoid systems. Of these, the most well-documented are the Rh carboxylate dimers[6] and the Rh porphyrins.[7] The parent rhodium carboxylate dimer is dirhodium acetate, $Rh_2(OAc)_4$, which is a binuclear, D_{4h}-symmetric compound with four bridging acetates and one vacant coordination site per metal.[8] It is formally a Rh^{II} complex, which is active in a wide variety of metal-carbenoid transformations such as cyclopropanation, C-H insertion, ylide formation, and dipolar addition.[9] Halorhodium porphyrins are penta-coordinate Rh^{III} complexes whose activity in carbene transfer reactions was first exploited by Callot and coworkers[7a] and has received some attention of late.[7b] Both of these complexes are active in the cyclopropanation of olefins in the presence of diazo esters. In addition, it is not clear whether a single or multiple oxidation states of rhodium are active in this process for both Rh^{II} and Rh^{III} have been shown to be active in olefin cyclopropanation.[9,10] For these reasons, it has been difficult to modify these reactions in a rational manner and apply them to practical syntheses. Recent studies of regioselectivities,[11] enantioselectivities,[12] and chemoselectivities[13] in rhodium-mediated cyclopropanations demonstrate that some control can be exerted by varying the ligand environment, but no direct evidence for the molecular basis of selectivity has been provided.

In the present study, we examine the stoichiometric and catalytic cyclopropanation of olefins using $RhBr(PCy_2Ph)_2(=C\text{-}C=CPh_2)$, $Rh_2(OAc)_4$, and Rh(TPP)I as the metal reagents and 3,3-diphenylcyclopropene[14] (rather than a diazo compounds) as the carbene source. We chose 3,3-diphenylcyclopropene as the carbene source because we wished to examine trends in cyclopropanation where the carbene source is well-derived (eq 1).[15]

(1)

By comparing the observed trends using cyclopropene precursors to those obtained using diazo esters, we wished to further establish the nature of the metal-carbene participation in the diazo system. In addition, we explore the effect of varying electronics of the olefin substrate, and have quantified the ability of the Rh^{I}, Rh^{II}, and Rh^{III} complexes to cyclopropanate as a function of olefin electronics.

Synthesis and Reactivity of $MX(PR_3)_2(=C\text{-}C=CPh_2)$ Complexes. Reaction of $[M(COE)_2Cl]$ with 4 equiv of a bulky tertiary phosphine (PR_3 = PCy_3, P^iPr_3, PCy_2Ph, P^iPr_2Ph) in benzene at rt resulted in formation of the coordinatively unsaturated 14 electron complex, "$M(PR_3)_2Cl$".[16] Subsequent in situ reaction of this highly reactive complex with 3,3-diphenylcyclopropene[17] (1.5 equiv) formed the corresponding metal vinylcarbene complexes, $MCl(PR_3)_2(=C\text{-}C=CPh_2)$ (eq 2).



(2)

M = Rh and Ir

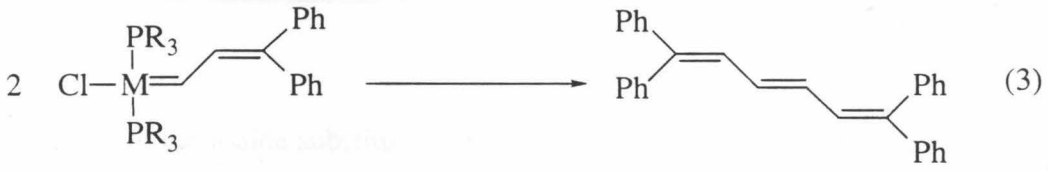
PR_3 = PCy_3, PCy_2Ph, P^iPr_3, and P^iPr_2Ph

The structural assignments for the various metal vinylcarbene complexes were made based on ^1H and ^{31}P NMR spectroscopy where characteristic resonances for the carbene's H_α and H_β protons and the phosphine ligands could be observed (Table 1). The ^1H chemical shifts and splitting patterns of each complex agrees with a bis phosphine formulation and the ^{31}P NMR spectra exhibit only singlet resonances[18] corresponding to equivalent trans, bis-phosphine geometry. However, these vinylcarbene complexes were very unstable and complete decomposition of the metal vinylcarbene complexes could be observed within 1 h to give 1,1',6,6'-tetraphenylhexatriene, the product resulting from the

Table 1. ^{1}H and ^{31}P NMR Data (C_6D_6) for $MCl(PR_3)_2(=C\text{-}C=CPh_2)$ Complexes

M	Complex	PR_3	δH_a	δH_β	J_{HH}(Hz)	J_{HP}(Hz)	$\delta^{31}P$
Ir	**1**	P^iPr_2Ph	17.17	5.36	12.8	12.6	25.10
Ir	**2**	PCy_2Ph	17.21	5.42	12.6	12.6	16.15
Ir	**3**	PCy_3	20.08	6.22	13.4	12.2	11.11
Ir	**4**	P^iPr_3	20.57	6.40	13.2	12.4	0.54
Rh	**5**	P^iPr_2Ph	13.19	6.24	13.2	12.3	31.33
Rh	**6**	PCy_2Ph	13.22	6.24	13.2	13.2	40.01
Rh	**7**	PCy_3	15.87	N.A	12.0	11.4	19.31
Rh	**8**	P^iPr_3	16.32	N.A	13.5	10.5	16.64

bimolecular coupling of two metal vinylcarbene complexes (eq 3). Stability of the metal vinylcarbenes were insensitive to the particular phosphine substituents.



(3)

However, enhanced stability of the metal vinylcarbene complexes could be achieved by substitution of the halide ligand. Reaction of $[M(COE)_2Br]_2$[19] dimers (M= Rh and Ir) with 4 equiv of a bulky tertiary phosphine (PR_3 = PCy_3, P^iPr_3, PCy_2Ph, P^iPr_2Ph) in benzene at room temperature resulted in formation of the coordinatively unsaturated 14 electron complex, "$M(PR_3)_2Br$". Subsequent in situ reaction of this intermediate complex with 3,3-diphenylcyclopropene (1.5 equiv) for 10 min followed by removal of the solvent and washing the residue with cold hexane (-78 °C) gave the corresponding

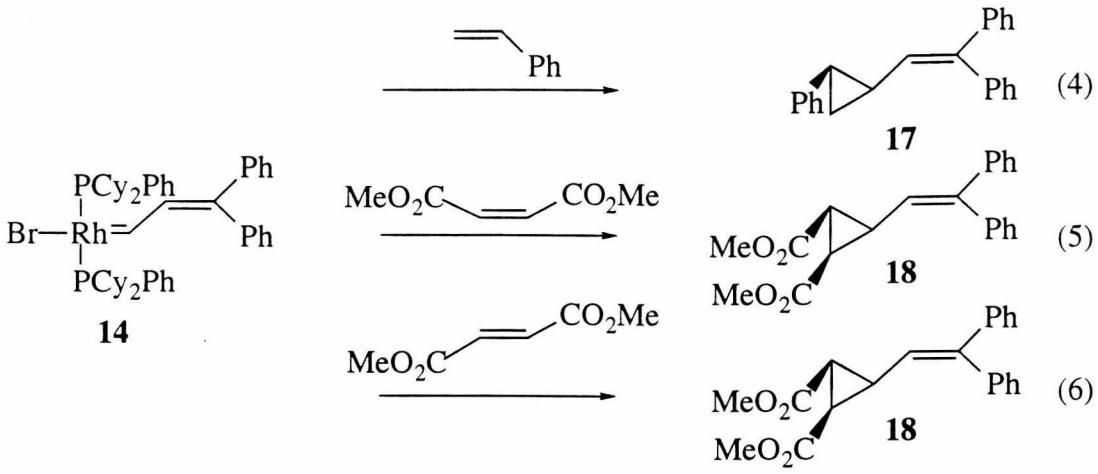
metal vinylcarbene in good yield. The vinylcarbene complexes can be isolated as green solids which are stable indefinitely at -30 °C in the drybox freezer. In solution, however, complete decomposition can also be observed after 24 h to give the bimolecular decomposition product, 1,1,6,6-tetraphenylhexatriene. The characteristic ^{1}H and ^{31}P NMR resonances for the carbene's H_{α} and H_{β} protons and the phosphine ligands could be observed and are listed below in Table 2.

Table 2. ^{1}H and ^{31}P NMR Data (C_6D_6) for $MBr(PR_3)_2(=C\text{-}C=CPh_2)$ Complexes

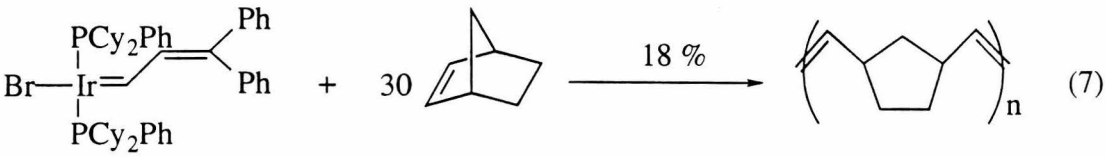
M	Complex	PR_3	δH_a	δH_β	J_{HH}(Hz)	J_{HP}(Hz)	$\delta^{31}P$
Ir	**9**	P^iPr_2Ph	16.90	5.24	13.2	12.9	24.63
Ir	**10**	PCy_2Ph	16.98	5.36	13.5	12.7	13.93
Ir	**11**	PCy_3	19.56	5.86	14.1	11.7	0.08
Ir	**12**	P^iPr_3	20.27	6.44	13.5	12.3	10.01
Rh	**13**	P^iPr_2Ph	13.20	6.12	13.8	13.5	39.95
Rh	**14**	PCy_2Ph	13.29	6.25	13.2	12.8	31.32
Rh	**15**	PCy_3	15.96	7.47	12.2	11.0	18.53
Rh	**16**	P^iPr_3	16.49	7.62	12.8	11.3	28.68

Synthesis of the iodide substituted derivatives were unsucessful due to the poor yields obtained from the halogen exchange reactions. Reaction of [M(COE)Cl] with LiI and NaI in a variety of solvent conditions yielded a mixture of products. We have examined the reactivities of these vinylcarbene complexes, specifically, the $Br(PCy_2Ph)_2M(=C\text{-}C=CPh_2)$ derivatives (M = Rh, **14** and M = Ir, **10**) toward a variety of olefins. Since these complexes have identical ligand environments, differences in reactivities would arise only as a consequence of the difference in metal centers. Reaction of **14** with styrene, dimethyl maleate, and dimethyl fumarate resulted in transfer of the diphenylvinylcarbene moiety to the olefin to form the corresponding vinylcyclopropane

(eq 4-6). Noteworthy is the fact that the same stereochemical outcome was achieved (i.e., cis arrangement of the methylester groups) when either dimethyl maleate or dimethyl fumarate was used (this issue is further discussed in a later section).[20] Complex **14** did not react with norbornene in a metathesis fashion nor were any cyclopropanation products observed. In contrast, reaction of **10** with norbornene (30 equiv) in C_6H_6 at rt

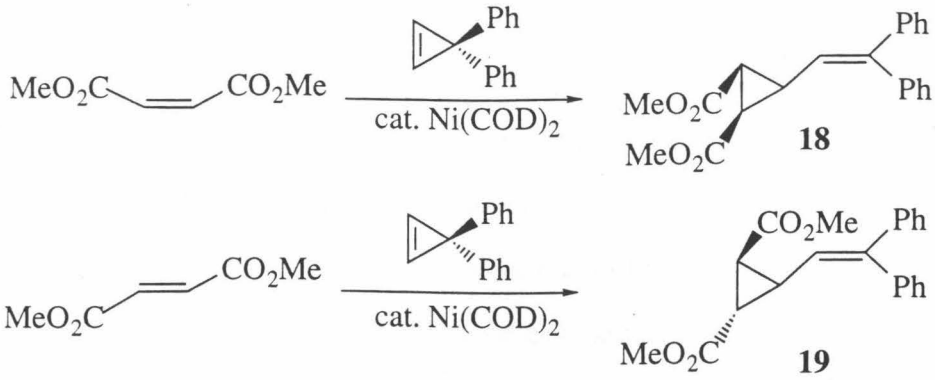


for 12 h resulted in the ring opening metathesis polymerization (ROMP) of norbornene in 18% yield where M_w was 7900 and the PDI was 1.69 (eq 7). However, vinylcyclopropane products were not observed in the reaction of **10** with styrene, dimethylfumarate, or dimethylmaleate. No reactions were observed for the reactions of the PCy_3 and P^iPr_3 derivatives (**11**, **12**, **15**, and **16**) with various olefins.



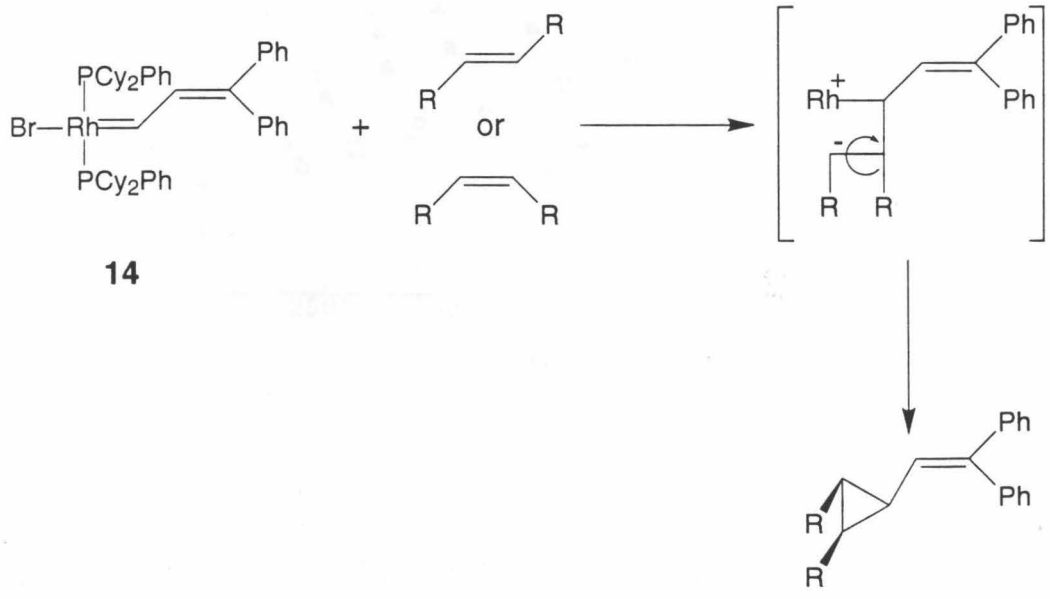
In summary, Rh^I and Ir^I vinylcarbene complexes of similar ligand environments were synthesized and found to have different reactivities toward olefins. The Ir^I vinylcarbene complexes only react with olefins via the olefin metathesis pathway, while Rh vinylcarbenes react with olefins via the cyclopropanation pathway. This reactivtiy difference may be attributed to the difference in metal centers, thus lending support to a possible metal-based boundary between olefin metathesis and cyclopropanation.

Reaction of Rh Vinylcarbene Complex 14 with Olefins: Reactions of Rh^I. As mentioned in the previous section, Rh vinylcarbene complex **14** cyclopropanates dimethyl maleate, dimethyl fumarate, and styrene — relatively electron-deficient olefins. No reaction was observed with 1-hexene, 2-hexene, vinyl ether, or cyclohexene which contrasts with that observed for other electrophilic metal carbene complexes where carbene transfer occurs preferentially with electron-rich olefins. Very interesting is the observation that the reaction of **14** with dimethyl maleate or dimethyl fumarate results in vinylcyclopropanes with the same stereochemical outcome where the ester groups are cis on the cyclopropane ring. Stereochemical assignments were confirmed by the direct synthesis of the cis and trans isomers using a method developed by Binger[21] and comparison of these authentic samples to our products by GC and ^1H NMR. Binger can catalytically cyclopropanate dimethyl maleate and dimethyl fumarate in the presence of 3,3-diphenylcyclopropene with a catalytic amount of $Ni(COD)_2$. In this case, retention of olefin geometry was observed, where cyclopropanation of cis olefin results in the cis isomer and cyclopropanation of the trans olefin results in the trans isomer (eqs 8 and 9).



To rationalize our results, we proposed the following reaction scheme depicted below in Scheme 2. In this model, Rh vinylcarbene complex **14** reacts with olefin to form a zwitterionic intermediate. The zwitterionic intermediate is stabilized by electron-withdrawing groups on the olefin. This intermediate is consistent with the observation that **14** reacts predominantly with electron-deficient olefins. In addition, the loss of double bond character in the olefin moiety allows for rotation in this intermediate to

Scheme 2



the observed stereochemical outcome. In order to test this model, we measured the relative rates of reaction of **14** with a series of para-substituted styrenes to examine the electronic effects in the absence of any steric influence. The rate of reaction of **14** with excess para-substituted styrenes was monitored by observing the rate of formation of product by ^{1}H NMR spectroscopy where the rate of formation of vinylcyclopropane product can be described by pseudo first-order kinetics, dP/dt = k[**14**]. The relative reactivity order of the para-substituted styrenes toward **14** was determined to be NO_2 > Cl > H > Me > OMe > NH_2 (Figure 2). Plotting log k/k_o against σ^- resulted in a good σ^- ρ

Figure 2. Rate of reaction of 14 with para-substituted styrenes.

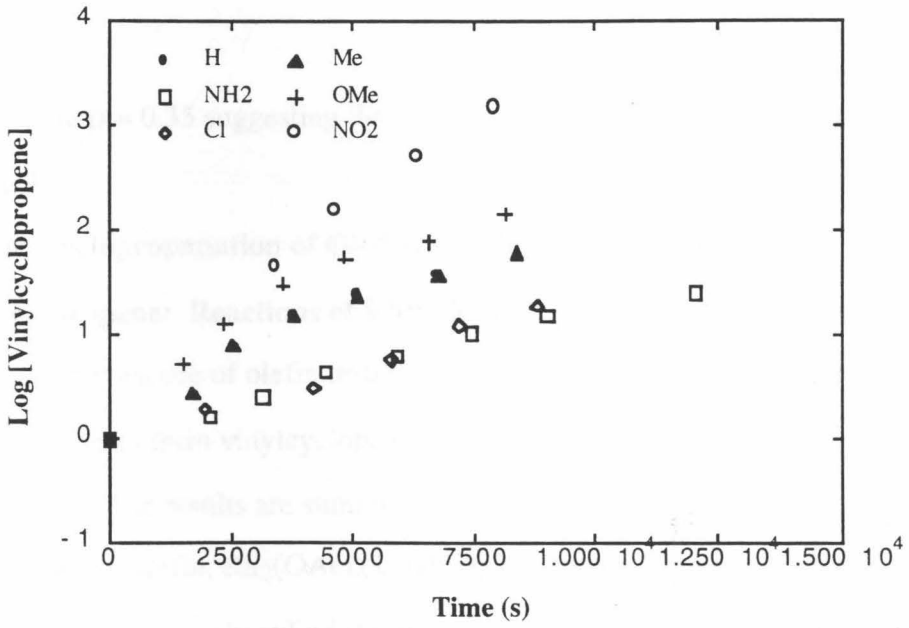
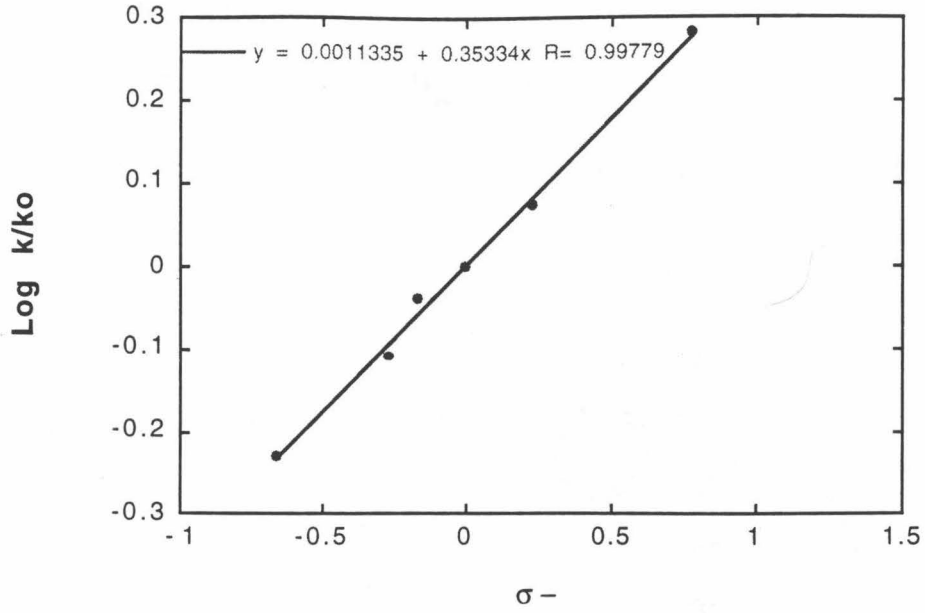


Figure 3. Plot of log k/k_o versus σ^- for the reaction of 14 with para-substituted styrenes.

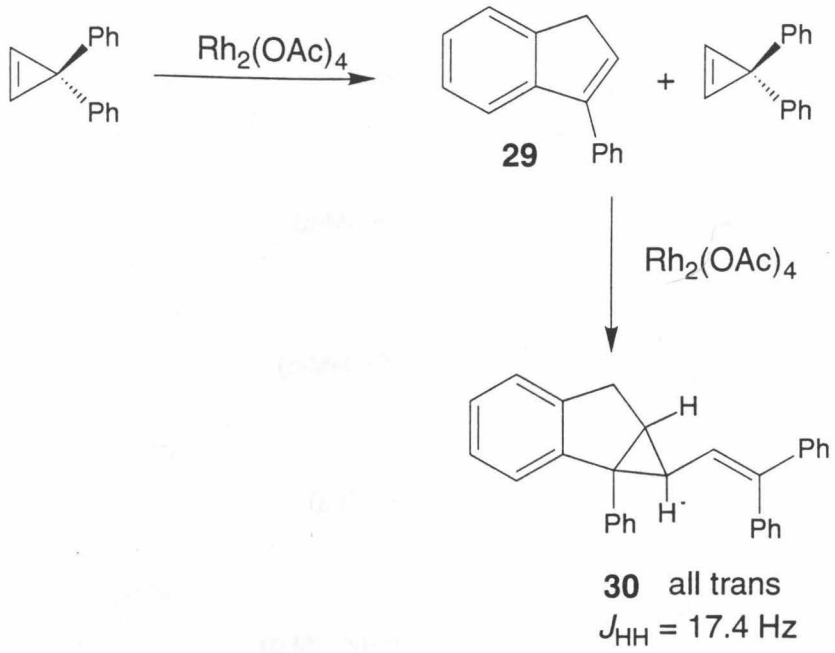


correlation where $\rho = 0.35$ suggesting that negative charge builds up in the transition state (Figure 3).

Catalytic Cyclopropanation of Olefins by $Rh_2(OAc)_4$ Using 3,3-Diphenylcyclopropene: Reactions of Rh^{II}. Reaction of 3,3-diphenylcyclopropene with $Rh_2(OAc)_4$ in the presence of olefin results in the net transfer of a diphinylvinylcarbene moiety to the olefin to form vinylcyclopropane adducts. We examined the reaction with a series of olefins. The results are summarized in Table 3.

In the absence of olefin, $Rh_2(OAc)_4$ catalyzes the rearrangement of 3,3-diphenylcyclopropene to 1-phenylindene, presumably through intramolecular carbon-hydrogen insertion of the vinylcarbene into the phenyl ortho-position, which then serves as a substrate for subsequent cyclopropanation by another molecule of 3,3-diphenylcyclopropene (Scheme 3). The thermal rearrangement of cyclopropenes to

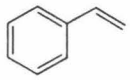
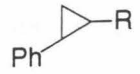
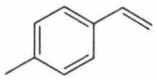
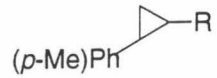
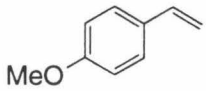
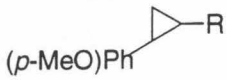
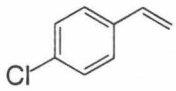
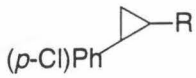
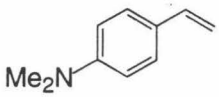
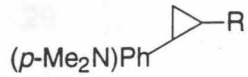
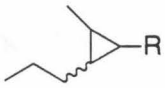
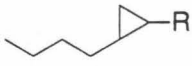
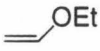
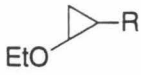
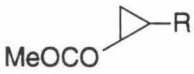
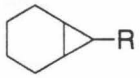
Scheme 3



phenylindenes is well-documented in the literature[22] as well as the intramolecular C-H insertion of electrophilic metal carbenes.[9] Traces of 1-phenylindene can be observed by ^1H NMR during the reaction. Furthermore, independent addition of 1-phenylindene results in its cyclopropanation to the vinylcyclopropane adduct. ^1H NMR and ^{13}C NMR spectrum of **30** was consistent with a single stereoisomer which wa assigned as the all trans product from the ^1H coupling constant.

The formation of vinylcyclopropanes in the presence of olefins, as well as the formation of 1-phenylindene and its cyclopropanated adduct, clearly supports the initial formation of a metal vinylcarbene intermediate. A plausible scenario for the mode of action of $Rh_2(OAc)_4$ in the presence of 3,3-diphenylcyclopropene and olefin is described in Scheme 4. In this reaction scheme, the Rh^{II} precursor reacts initially with 3,3-diphenylcyclopropene to form an intermediate Rh^{II} vinylcarbene complex. In the

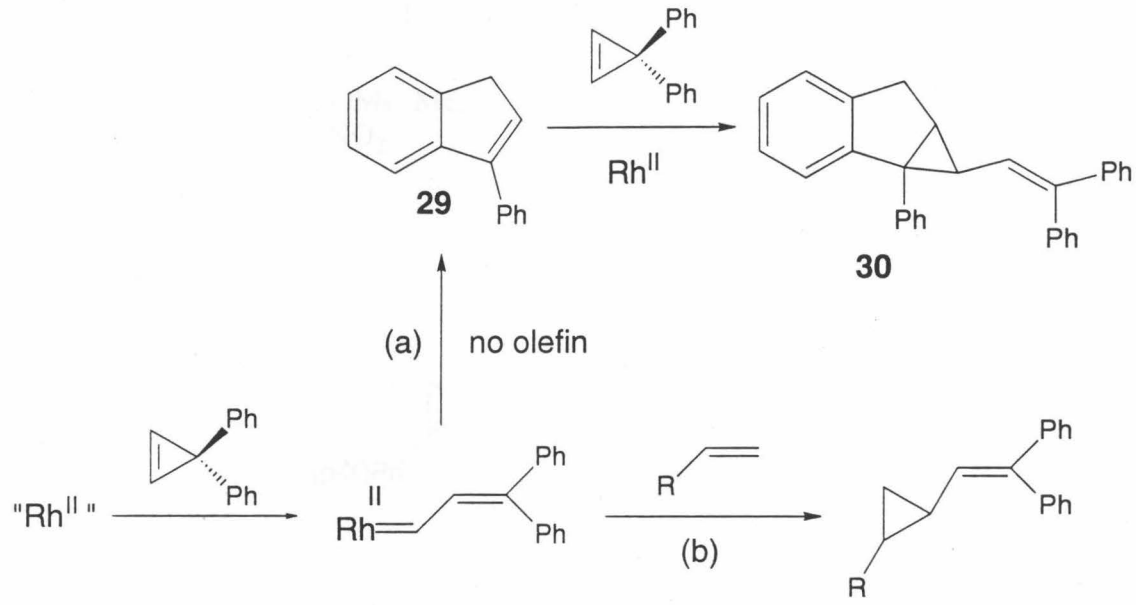
Table 3. Catalytic Cyclopropanation of Olefins by $Rh_2(OAc)_4$.[a]

Entry	Substrate	Product [b]		Yield	Cis/Trans
1			**17**	94.0	3.29
2			**20**	96.4	4.24
3			**21**	93.3	4.25
4			**22**	95.0	4.63
5			**23**	54.4	4.55
6			**24**	87.3	0.84 [c]
7			**25**	91.7	0.54
8			**26**	96.2	0.23
9			**27**	96.6	0.12
10			**28**	82.3	0.07 [c]

[a] Reactions were run using 1% mol $Rh_2(OAc)_4$ to 3,3-diphenylcyclopropene and 10 equiv of substrate to 3,3-diphenylcyclopropene. [b] R = diphenylvinyl. [c] Refers to the configuration of the olefin substituents in the cyclopropane product.

absence of olefin (pathway a), the Rh vinylcarbene reacts intramolecularly via C-H insertion reaction to form 1-phenylindene, **29**, which is subsequently cyclopropanated by another Rh vinylcarbene to form **30**. In the presence of olefin, the Rh vinylcarbene transfers its diphenylvinylcarbene moiety to form the corresponding vinylcyclopropanes.

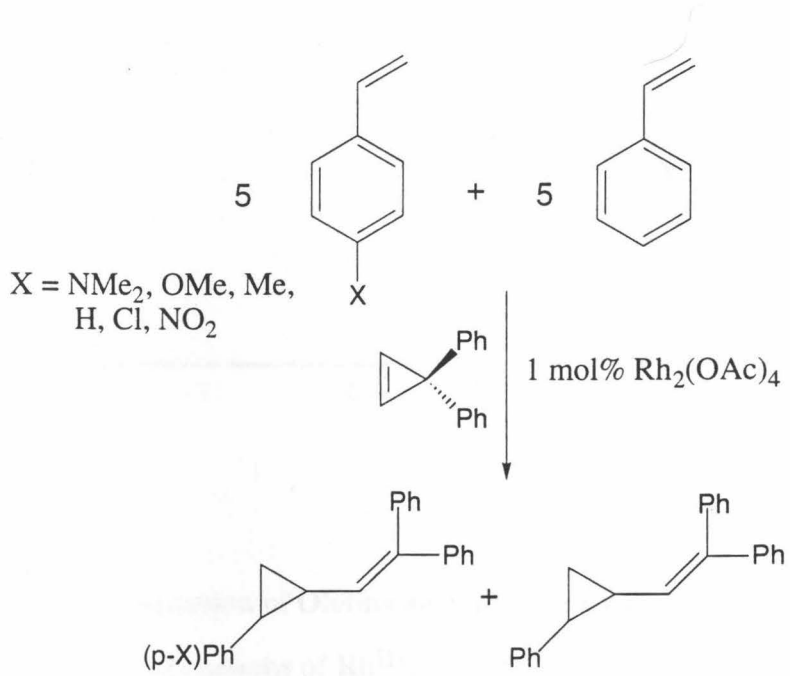
Scheme 4



In contrast to the Rh^I vinylcarbene system, the $Rh_2(OAc)_4$ catalyst reacts more efficiently with relatively electron-rich olefins since no vinylcyclopropane adducts were formed in the reactions with relatively electron-deficient olefins such as dimethyl maleate, dimethyl fumarate, and methyl methacrylate. To compare its mode of action in the cyclopropanation reaction with that of the Rh^I vinylcarbene, we carried out a comparative evaluation of the linear free energy relationship of $Rh_2(OAc)_4$ with a series of para-substituted styrenes. We employed competition experiments where equivalent

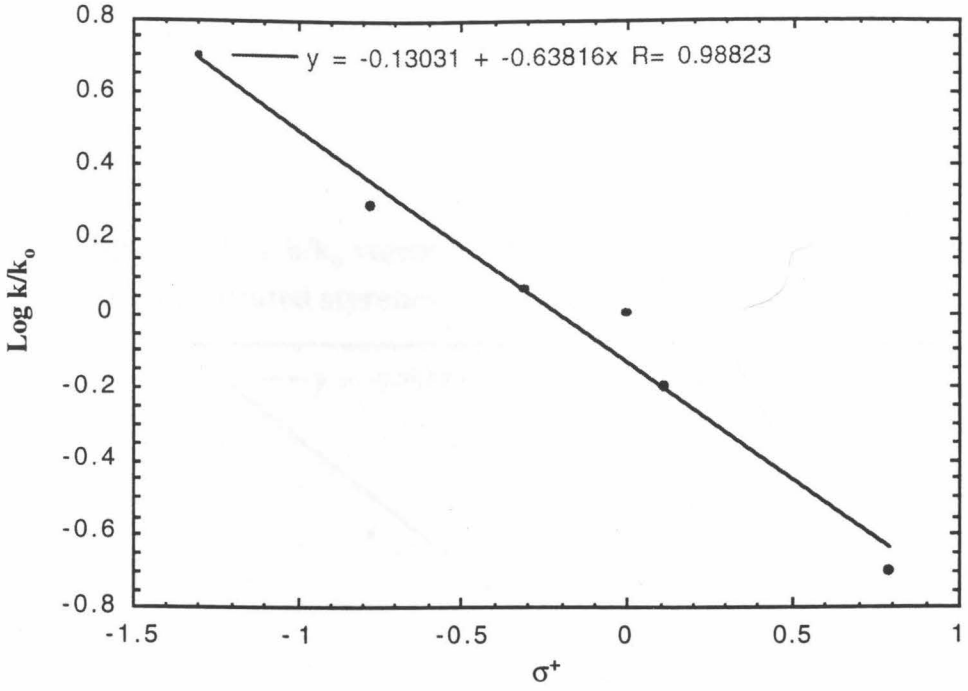
mixtures of 1-styrene and para-substituted styrene was reacted with 3,3-diphenylcyclopropene in the presence of a catalytic amount of $Rh_2(OAc)_4$. The ratio of products determined by GC would represent the relative reaction rates (k/k_o) (Scheme 5).

Scheme 5



By plotting log k/k_o against σ^+, a good $\sigma^+\rho$ correlation was obtained where the value of ρ was determined to be -0.64, indicating that positive charge builds up at the a carbon of the carbene moiety in the transition state, opposite of the result obtained in the Rh^I case. The corresponding Hamett plot is given in Figure 4.

Figure 4. Log k/k_0 versus σ^+ for the reaction of $Rh_2(OAc)_4$ with para-substituted styrenes.



Catalytic Cyclopropanation of Olefins and Alkynes by Rh(TPP)I and 3,3-Diphenylcyclopropene: Reactions of Rh^{III}. In 1982, Callot and coworkers reported that iodorhodium porphyrins were efficient catalysts for olefin cyclopropanation in the presence of diazo esters.[7a] Kodadek and coworkers subsequently identified what is believed to be the active catalytic species in this process.[7b]

The addition of 3,3-diphenylcyclopropene to various olefins in the presence of Rh(TPP)I resulted in net carbene transfer to form vinylcyclopropanes. Most interesting was the ability of this catalyst to transfer carbene to both mono- and disubstituted acetylenes to form vinylcyclopropenes. The results are summarized in Table 3. We also examined the linear free energy relationship of the reaction of Rh(TPP)I with olefins through competition experiments with a series of para-substituted styrenes. Plotting log k/k_0 against σ^+ resulted in a good $\sigma^+\rho$ correlation with a ρ value of -1.31 (Figure 5).

Figure 5. Log k/k_o versus σ^+ for the reaction of Rh(TPP)I with para-substituted styrenes.

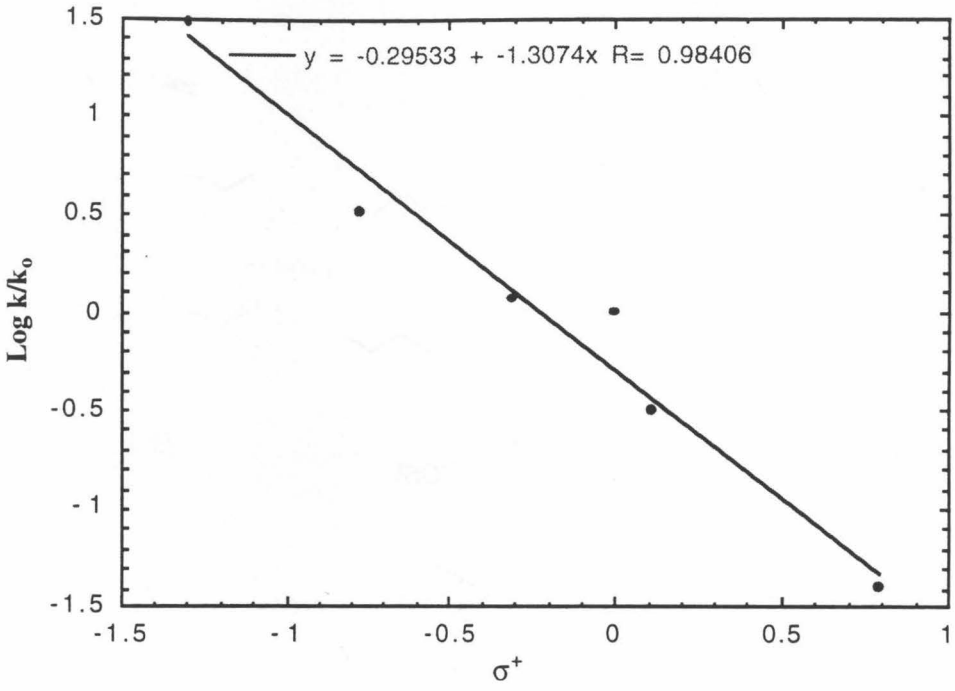
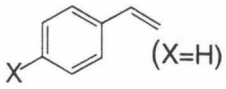
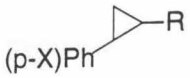
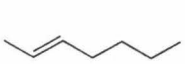
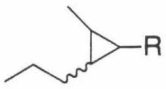
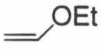
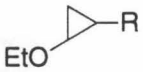
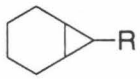
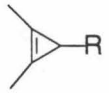
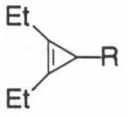
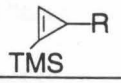


Table 4. Catalytic Cyclopropanation of Olefins by Rh(TPP)I.[a]

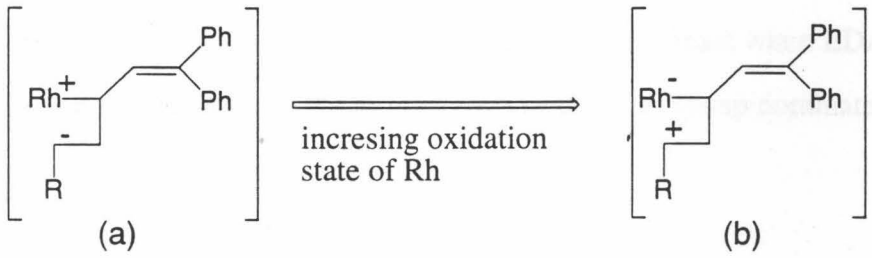
Entry	Substrate	Product[b]		Yield	Cis/Trans
15			**17**	97.8	2.31
16	X = Me		**20**	96.2	1.90
17	X = OMe		**21**	96.8	1.79
18	X = Cl		**22**	93.4	0.93
19	X = NMe_2		**23**	45.6	1.12
20			**24**	88.0	18.91 [c]
21			**25**	95.0	1.11
22			**26**	96.1	0.45
23			**28**	39.0	0.01 [c]
24			**31**	84.7	
25			**32**	77.8	
26			**33**	47.4	

[a] Reactions were run using 1% mol Rh(TPP)I to 3,3-diphenylcyclopropene and 10 equiv of substrate relative to 3,3-diphenylcyclopropene. [b] R = diphenylvinyl.

[c] Refers to the configuration of the olefin substituents in the cyclopropane product.

Comparison of the Cyclopropanation Reaction of Olefins with 3,3-Diphenylcyclopropene by Rh^{I}, Rh^{II}, and Rh^{III} Complexes. It appears that a common step in the cyclopropanation of olefins employing 3,3-diphenylcyclopropene by Rh^{I}, Rh^{II}, and Rh^{III} Complexes is the involvement of a Rh vinylcarbene complex. However, we can distinguish between the mode of action in the cyclopropanation of olefins by these complexes by their relative reactivities towards olefins, where higher oxidation states of Rh prefer more electron-rich olefins. In the case of Rh^{I}, a positive ρ value of 0.35 was obtained which indicated that negative charge builds up at the α carbon of the carbene moiety in the transition state which is stabilized by electron-donating groups on the olefin.

Figure 6. (a) Predicted transition state for the Rh^{I} mediated cyclopropanation. (b) Predicted transition state for the Rh^{II} and Rh^{III} catalyzed cyclopropanation.



When the oxidation state is increased to Rh^{II}, a negative ρ value of -0.64 was obtained which suggested that positive charge builds up at the α carbon of the carbene moiety in the transition state (see (b) in Figure 6) which is stabilized by electron-donating groups on the olefin. Finally, in the case of Rh^{III}, a negative ρ value of -1.31 was measured. This requires an even greater positive charge build up at the α carbon of the carbene moiety in the transition state. These results lend support toward an oxidation state effect in the Rh mediated cyclopropanation of olefin where higher oxidation state effects of Rh prefer more electron-rich olefins.

Cyclopropanation of Para-Substituted Styrenes by $Rh_2(OAc)_4$ and Rh(TPP)I Employing Ethyldiazoacetate (EDA) as the Carbene Source. The electronic effects of the olefin substrates were also explored in the $Rh_2(OAc)_4$ and Rh(TPP)I systems where ethyldiazoacetate (EDA) was used as the carbene source in order to compare this system to the system where 3,3-diphenylcyclopropene was employed. Olefin competition experiments with para-substituted styrenes were carried out analogous to the cases where 3,3-diphenylcyclopropene was used as the carbene source. For both catalysts, good $\sigma^+\rho$ correlations were obtained. The ρ value for the $Rh_2(OAc)_4$ catalyzed system was -0.36 and the ρ value for the Rh(TPP)I catalyzed system was -0.44 (Figures 7 and 8). These results show that when EDA is employed as the carbene source, the ρ values obtained are similar within experimental error. This observation contrasts the results obtained when 3,3-diphenylcyclopropene was used as the carbene source where there was a much greater change in ρ values going from Rh^{II} to Rh^{III}. These results may be interpreted in at least two ways: (1) oxidation state effects are not significant when EDA is employed as the carbene source and the electronic effect of the ester group dominates the reaction

Figure 7. Log k/k_o for the reaction of $Rh_2(OAc)_4$ with para-substituted styrenes using ethyldiazoacetate as the carbene source.

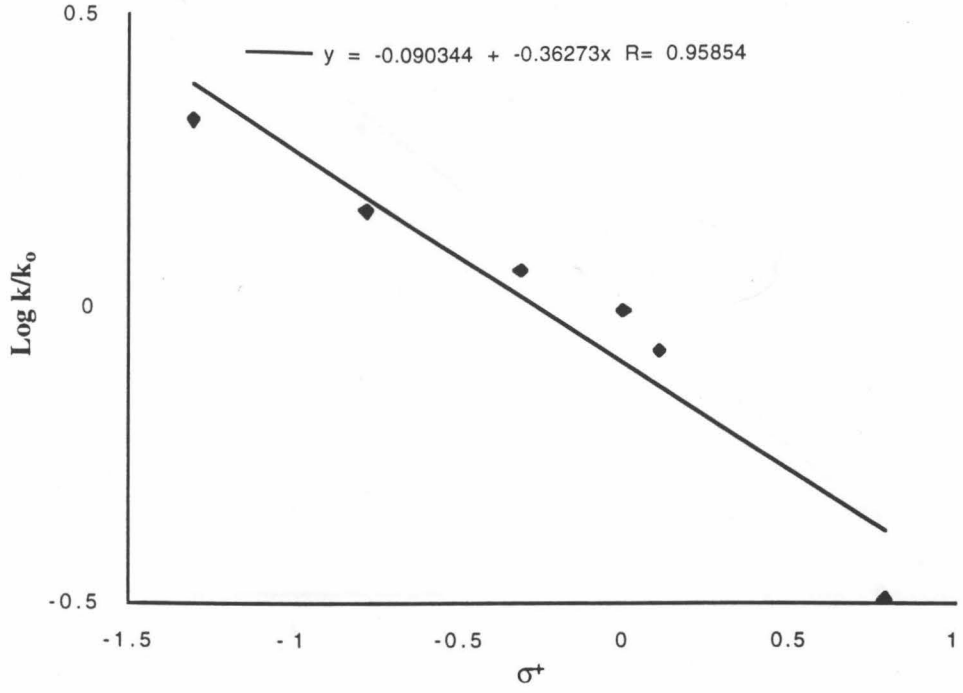
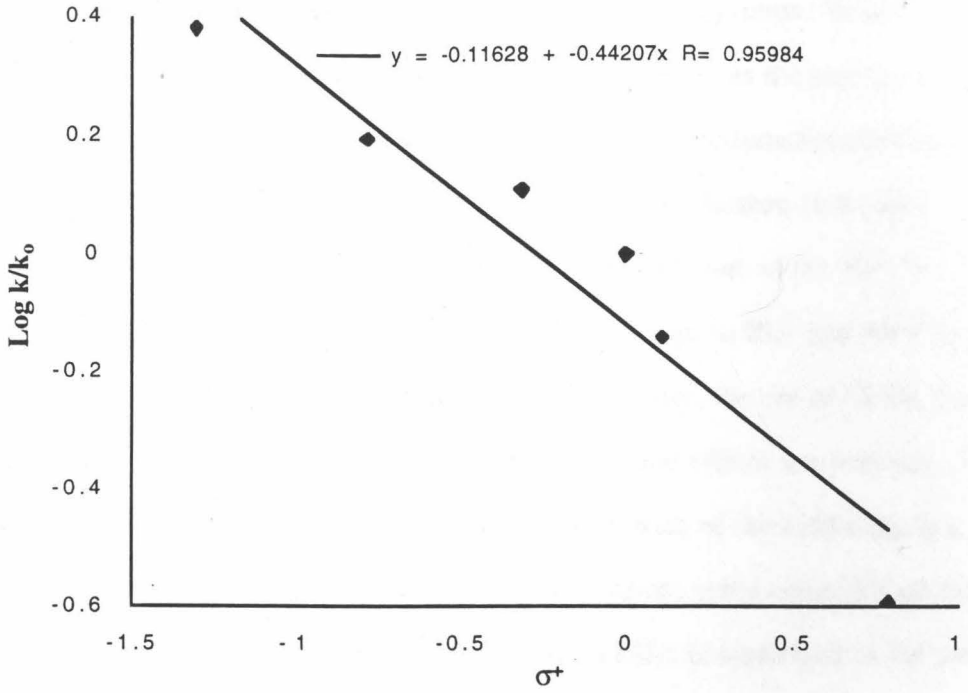


Figure 8. Log k/ko for the reaction of Rh(TPP)I with para-substituted styrenes using ethyldiazoacetate as the carbene source.



or (2) single oxidation states might be responsible for the observed reactivities in the EDA systems, regardless of the nature of the Rh precursor. There has been speculation that potential reduction of the Rh(TPP)I system may be occurring in the presence of EDA. In addition, there has been speculation that cleavage of the Rh-Rh bond in the $Rh_2(OAc)_4$ complex with the diazo compound may be taking place effectively producing a Rh^{I}-Rh^{III} redox couple. Both these suggestions could explain how a single oxidation state might be responsible for the catalysis by $Rh_2(OAc)_4$ and Rh(TPP)I in the cyclopropanation of olefins with EDA as the carbene source.

Conclusions

The ability of $Rh_2(OAc)_4$ and Rh(TPP)I to cyclopropanate olefins to form vinylcyclopropanes employing 3,3-diphenylcyclopropane as the carbene source, as well

as the ability of these complexes to rearrange 3,3-diphenylcyclopropene to 1-phenylindene and subsequently cyclopropanate this substrate, lends further support for the intermediacy of a metal carbenoid intermediate in these systems. In addition, the comparison of LFER studies using 3,3-diphenylcyclopropene as the carbene source, shows that there is indeed oxidation state effects in the Rh mediated cyclopropanation, where higher oxidation states of the Rh center prefer more electron-rich olefins. From the ρ values obtained in the Hammett relationships, we see that, in the Rh^{I} case, there is negative charge build-up in the transition state, but as we go to Rh^{II} and Rh^{III} there is more positive charge build-up in the transition state. Lastly, the use of LFER studies of these systems with EDA shows that similar oxidation state effects are not seen. This observation requires that either the effective oxidation state of the active catalyst is dissimilar in the above systems (3,3-diphenylcyclopropene versus ethyldiazoacetate), or that oxidation state effects are less pronounced when EDA is employed as the carbene source.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. NMR experiments were also prepared inside a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C; 34.82 MHz ^{31}P, ^{7}Li external lock, ^{31}P NMR data referenced to external H_3PO_4 where PPh_3 has a chemical shift at -5.4 ppm), or a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. GPC molecular weight measurements were obtained in CH_2Cl_2 against polystyrene standards.

Materials. Hexane was stirred over concentrated H_2SO_4, dried successively over $MgSO_4$ and CaH_2, and then transferred onto sodium benzophenone ketyl solubilized with tetraglyme. Benzene was distilled or vacuum transferred from sodium benzophenone ketyl. Methylene chloride was stirred over either CaH_2 or P_2O_5, distilled under argon, and degassed by three continuous freeze-pump-thaw cycles. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Benzene-d_6 was dried over sodium benzophenone ketyl and then vacuum transferred. $[M(COE)_2Cl]_2$ dimers were prepared as described in the literature,[23] 3,3-Diphenylcyclopropene was prepared following a procedure by Moore.[24] Rh(TPP)I was prepared following a procedure by Callot and coworkers.[7a] The following chemicals were obtained from commercial sources and used as received: $Rh_2(OAc)_4$ (Strem); dimethyl maleate, dimethyl fumarate, 1-hexene, 2-hexene, cyclohexene, vinyl ether, vinyl acetate, methyl methacrylate, 2-butyne, 3-hexyne, TMS-acetylene, styrene, 4-chlorostyrene, 4-methylstryene (Aldrich); 4-nitrostyrene, 4-methoxystryene (TCI); silica gel, dichloromethane and hexane (EM Science).

General Procedure for the NMR Observation of Metal Carbene Complexes of the type $MCl(PR_3)_2(=CC=CPh_2)$.

In an NMR tube was added $[M(COE)_2Cl]_2$ dimer (0.022 mmol) in C_6D_6 (500 μL), followed by addition of PR_3 (0.088 mmol). 3,3-Diphenylcylopropene was added and the reaction was observed by ^1H and ^{31}P NMR spectroscopy. Due to the instability of the resulting vinylcarbene complexes, they were not isolated.

$IrCl(P^iPr_2Ph)_2(=C\text{-}C=CPh_2)$ (1)

^1H NMR (C_6D_6): δ 17.17 (q, Ir=CH_α, J_{HH} = 12.8 Hz, J_{HP} = 12.6 Hz), 5.36 (d, Ir=C-CH_β, J_{HH} = 12.8 Hz). ^{31}P NMR(C_6D_6): δ 25.10 (s).

$IrCl(PCy_2Ph)_2(=C\text{-}C=CPh_2)$ (2)

^1H NMR (C_6D_6): δ 17.21 (q, Ir=CH_α, J_{HH} = 12.6 Hz, J_{HP} = 12.6 Hz), 5.42 (d, Ir=C-CH_β, J_{HH}=12.6 Hz). ^{31}P NMR (C_6D_6): δ 16.15 (s).

$IrCl(PCy_3)_2(=C\text{-}C=CPh_2)$ (3)

^1H NMR(C_6D_6): δ 20.08 (q, Ir=CH_α, J_{HH} = 13.4 Hz, J_{HP} = 12.2 Hz), 6.22 (d, Ir=C-CH_β, J_{HH} = 13.4 Hz). ^{31}P NMR (C_6D_6): δ 11.11 (s).

$IrCl(P^iPr_3)_2(=C\text{-}C=CPh_2)$ (4)

^1H NMR (C_6D_6): δ 20.57 (q, Ir=CH_α, J_{HH} = 13.2 Hz, J_{HP} = 12.4 Hz), 6.40 (d, Ir=C-CH_β, J_{HH} = 13.2 Hz. ^{31}P NMR (C_6D_6): δ 0.54 (s).

$RhCl(P^iPr_2Ph)_2(=C\text{-}C=CPh_2)$ (5)

^1H NMR (C_6D_6): δ 13.19 (q, Rh=CH_α, J_{HH} = 13.2 Hz, J_{HP} = 12.3 Hz), 6.24 (d, Rh=C-CH_β, J_{HH} = 13.2 Hz). ^{31}P NMR (C_6D_6): δ 31.33 (d, J_{RhP} = 153.0 Hz).

$RhCl(PCy_2Ph)_2(=C\text{-}C=CPh_2)$ (6)

^1H NMR (C_6D_6): δ 13.22 (q, Rh=CH_α, J_{HH} = 13.2 Hz, J_{HP} = 13.2 Hz), 6.24 (d, Rh=C-CH_β, J_{HH}= 13.2 Hz). ^{31}P NMR (C_6D_6): δ 40.01 (d, J_{RhP} = 153.0 Hz).

$RhCl(PCy_3)_2(=C\text{-}C=CPh_2)$ (7)

^1H NMR(C_6D_6): δ 15.87 (q, Rh=CH_α, J_{HH} = 12.0 Hz, J_{HP} = 11.4 Hz). ^{31}P NMR (C_6D_6): δ 19.31 (d, J_{RhP} = 149.0 Hz).

$RhCl(P^iPr_3)_2(=C\text{-}C=CPh_2)$ (8)

^1H NMR (C_6D_6): δ 16.32 (q, Rh=CH_α, J_{HH} = 13.5 Hz, J_{HP} = 10.5 Hz). ^{31}P NMR (C_6D_6): δ 16.64 (d, J_{RhP} = 149.0 Hz).

General Procedure for the Synthesis of Metal Vinylcarbene Complexes of the Type $MBr(PR_3)_2(=C\text{-}C=CPh_2)$.

In a Schlenk flask was dissolved $[M(COE)_2Br]_2$ dimer (0.62 mmol) in benzene (50 mL) followed by addition of the PR_3 (2.5 mmol). 3,3-Diphenylcyclopropene (1.2 mmol) was immediately added and the reaction was stirred for 15 min at rt. The reaction mixture was then frozen in a dry ice/acetone bath and the benzene was removed by sublimation in vacuo. The resulting residue was washed with cold hexane (-78 °C) and isolated as dark green solids.

$IrBr(P^iPr_2Ph)_2(=C\text{-}C=CPh_2)$ (9)

Yield was 0.88 g (83 %). ^1H NMR (C_6D_6): δ 16.90 (q, Ir=CH_α, J_{HH} = 13.2 Hz, J_{HP} = 12.9 Hz), 5.24 (d, Ir=C-CH_β, J_{HH} = 13.2 Hz). ^{31}P NMR(C_6D_6): δ 24.63 (s).

$IrBr(PCy_2Ph)_2(=C\text{-}C=CPh_2)$ (10)

Yield was 1.1 g (85 %). ^1H NMR (C_6D_6): δ 16.98 (q, Ir=CH_α, J_{HH} = 13.5 Hz, J_{HP} = 12.7 Hz), 5.36 (d, Ir=C-CH_β, J_{HH}=13.5 Hz). ^{13}C NMR (C_6D_6): δ 192.3 (Ir=C_α, J_{CH} = 154.2 Hz), 148.3 (Ir=C-C_β, J_{CH} = 121.8 Hz). ^{31}P NMR (C_6D_6): δ 16.93 (s). Anal. Calcd for $C_{51}H_{66}BrIrP_2$: C, 60.46; H, 6.57. Found: C, 60.96; H, 6.39.

$IrBr(PCy_3)_2(=C\text{-}C=CPh_2)$ (11)

Yield was 0.57 g (45 %). ^{1}H NMR(C_6D_6): δ 19.56 (q, Ir=CH_α, J_{HH} = 14.1 Hz, J_{HP} = 11.7 Hz), 7.47 (d, Ir=C-CH_β, J_{HH} = 14.1 Hz). ^{31}P NMR (C_6D_6): δ 0.08 (s).

IrBr(P^{i}Pr$_3$)$_2$(=CC=CPh$_2$) (12)

Yield was 0.56 g (58%). ^{1}H NMR (C_6D_6): δ 20.27 (q, Ir=CH_α, J_{HH} = 13.5 Hz, J_{HP} = 12.3 Hz), 7.62 (d, Ir=C-CH_β, J_{HH} = 13.5 Hz. ^{31}P NMR (C_6D_6): δ 10.91 (s).

RhBr(P^{i}Pr$_2$Ph)$_2$(=C-C=CPh$_2$) (13)

Yield was 0.77 g (79 %). ^{1}H NMR (C_6D_6): δ 13.20 (q, Rh=CH_α, J_{HH} = 13.8 Hz, J_{HP} = 13.5 Hz), 6.12 (d, Rh=C-CH_β, J_{HH} = 13.8 Hz). ^{31}P NMR (C_6D_6): δ 39.95 (d, J_{RhP} = 128.9 Hz).

RhBr(PCy$_2$Ph)$_2$(=C-C=CPh$_2$) (14)

Yield was 0.94 g (81 %). ^{1}H NMR (C_6D_6): δ 13.29 (q, Rh=CH_α, J_{HH} = 13.2 Hz, J_{HP} = 12.8 Hz), 6.25 (d, Rh=C-CH_β, J_{HH}= 13.2 Hz). ^{13}C NMR (C_6D_6): δ 296.2 (Rh=C_α, J_{CH} = 150.2 Hz), 155.6 (Rh=C-C_β, J_{CH} = 123.2 Hz). ^{31}P NMR (C_6D_6): δ 31.32 (d, J_{RhP} = 128.2 Hz). Anal. Calcd for $C_{51}H_{66}BrRhP_2$: C, 66.31; H, 7.20. Found: C, 66.84; H, 6.95.

RhBr(PCy$_3$)$_2$(=C-C=CPh$_2$) (15)

Yield was 0.48 g (40 %). ^{1}H NMR(C_6D_6): δ 15.96 (q, Rh=CH_α, J_{HH} = 12.2 Hz, J_{HP} = 11.0 Hz), 7.47 (d, Rh=C-CH_β, J_{HH} = 12.2 Hz). ^{31}P NMR (C_6D_6): δ 18.53 (d, J_{RhP} = 125.8 Hz).

RhBr(P^{i}Pr$_3$)$_2$(=C-C=CPh$_2$) (16)

Yield was 0.40 g (44 %). ^{1}H NMR (C_6D_6): δ 16.49 (q, Rh=CH_α, J_{HH} = 12.8 Hz, J_{HP} = 11.3 Hz), 7.62 (d, Rh=C-CH_β, J_{HH} = 12.8 Hz. ^{31}P NMR (C_6D_6): δ 28.68 (d, J_{RhP} = 128.1 Hz).

General Procedure for the Synthesis of Vinylcyclopropanes from RhBr(PCy$_2$Ph)$_2$(=C-C=CPh$_2$) (14)

In an NMR tube was added $RhBr(P^iPr_2Ph)_2(=C-C=CPh_2)$ (20 mgs) in CD_2Cl_2 (500 μL), followed by the olefin substrate (10 equiv). Reactions were monitored by ^1H NMR until the disappearance of the carbene resonances of the **14**. The reaction mixture was filtered through a plug of silica to remove the metal by-products. The yields were determined by GC by comparison to authentic vinylcyclopropane samples.

1-Diphenylvinyl, 2,3-(bis)Methylester Cyclopropane (18) from the reaction with dimethyl maleate

The yield was 67 % as determined by GC and ^1H NMR. Response factors were calculated using authentic samples synthesized by the route developed by Binger and co-workers.[25] The ratio of cis:trans ratio was 16.3:1 as determined by GC. ^1H NMR (CD_2Cl_2): δ 2.11 (d, J = 6.1 Hz, 2H), 2.67 (d of d, J = 9.6 Hz, J' = 6.1 Hz, 1H), 3.57 (s, 6H) 5.42 (d, J = 9.6 Hz, 1H), 7.0 - 7.5 (m, 10H).

1-Diphenylvinyl, 2,3-(bis)Methylester Cyclopropane (18) from the reaction with diemthyl fumarate

The yield was 65 % as determined by GC. Response factors were calculated using authentic samples synthesized by the route developed by Binger and coworkers. The ratio of cis:trans was 16.1:1 as determined by GC. ^1H NMR (CD_2Cl_2): δ 2.11 (d, J = 6.1 Hz, 2H), 2.67 (d of d, J = 9.6 Hz, J' = 6.1 Hz, 1H), 3.57 (s, 6H), 5.42 (d, J = 9.6 Hz, 1H), 7.0 - 7.5 (m, 10H).

1-Diphenylvinyl, 2-Phenylcyclopropane (17)

The yield was 18% as determined by GC. Response factors were calculated using authentic samples synthesized using the $Rh_2(OAc)_4$ catalyzed method (see below). Only the anti isomer was observed. ^1H NMR (CD_2Cl_2): δ 2.01 (m, 1H), 2.30 (m, 2H), 2.75, q, 1H), 5.81 (d, J = 9.8 Hz, 1H), 7.0-7.5 (m, 15H).

General Procedure for the ROMP of Norbornene by $IrBr(PCy_2Ph)_2(=C\text{-}C=CPh_2)$ (10)

In a Schlenk was dissolved the Ir vinylcarbene complexes (0.019 mmol) in benzene (2 mL), followed by addition of norbornene (30 equiv). Reaction was allowed to stir for 24 h.

Work-up: The reaction vials were taken out of the drybox and to them were added a solution consisting of CH_2Cl_2 (10 mL) and BHT (0.20 g). This mixture was then left at room temperature for 2 h during which time the gel dissolved. The mixture was precipitated into a vigorously stirred solution of methanol (40 mL, containing 0.1% BHT). The resulting polymer was then washed with methanol (5 mL, containing 0.1% BHT) and dried under vacuum overnight.

Kinetics of the Reaction of 14 with Para-Substituted Styrenes

In an NMR tube was added **14** (20 mgs, 0.022 mmol) in CD_2Cl_2 (400 μL), followed by 100 uL of a stock solution of para-substituted styrene (0.22 mM). The reaction was monitered by ^1H NMR until the carbene resonances of **14** disappeared.

General Procedure for the Synthesis of Vinylcyclopropanes via $Rh_2(OAc)_4$.

To a Schlenk flask was dissolved $Rh_2(OAc)_4$ (4.7 mg, 0.001 mol) in 10 mL of benzene. To this solution was added 3,3-diphenylcyclopropene (205 mg, 0.11 mol) and olefin substrate (1.1 mol). This solution was then refluxed for 8 h, after which the solvent was stripped in vacuo and the residue was loaded onto a silica gel column for purification.

1-Diphenylvinyl, 2-Phenylcyclpropane (17)

The product was eluted using hexane and as a viscous, clear yellow oil. Yield was 0.29 g (94%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 1.37 (m, 1H), 1.46 (m, 1H), 2.16 (m, 1H), 2.46 (q, 1H), 5.56 (d, *J* = 10.1 Hz, 1H), 7.0-7.5 (m, 15H); (anti isomer) δ 2.01 (m, 1H), 2.30 (m, 2H), 2.75 (q, 1H), 5.81 (d, *J* = 9.8 Hz, 1H), 7.0-7.5 (m, 15H). ^{13}C NMR (CD_2Cl_2): δ 13.97, 21.013, 25.197, 126.05, 126.16, 126.51, 127.11, 127.26, 127.44, 127.52, 127.69, 128.44, 128.59, 128.67, 128.75, 129.52, 130.14, 130.75, 133.05, 140.89, 142.09, 143.22. GC/MS for **17**: M/C = 296.

1-Diphenylvinyl, 2-(4-Methylphenyl)cyclopropane (20)

The product was eluted with hexane as a viscous, yellow-green oil. Yield was 0.32 g (96%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 1.31 (m, 1H), 1.39 (m, 1H), 2.05 (m, 1H), 2.46 (s, 3H), 5.51(d, *J* = 10.1 Hz, 1H), 7.0-7.5 (m, 14H); (anti isomer) δ 1.91 (m, 1H), 2.33 (m, 2H), 2.41 (s, 3H), 2.79 (q, 1H), 5.75 (d, *J* = 10.0 Hz, 1H), 7.0-7.5 (m, 14H). ^{13}C NMR (CD_2Cl_2): δ 13.98, 20.94, 21.28, 24.81, 126.05, 127.05, 127.38, 128.41, 128.55, 128.62, 129.33, 130.37, 133.23, 140.89, 141.87, 143.26. GC/MS for **20**: M/C = 310.

1-Diphenylvinyl, 2-(4-Methoxyphenyl)cyclopropane (21)

The product was eluted with 90:10 mixture of hexane: dichloromethane and was isolated as a viscous, yellow oil. Yield was 0.33 g (93%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 1.32 (m, 1H), 1.43 (m, 1H), 2.09 (m, 1H), 2.48 (q, 1H), 3.93 (s, 3H), 5.55 (d, *J* = 10.2 Hz, 1H), 7.0-7.5 (m, 14H); (anti isomer) δ 1.92 (m, 1H), 2.24 (m, 2H), 2.65 (q, 2H), 3.85 (s, 3H), 5.80 (d, *J* = 9.8 Hz, 1H), 7.0-7.5 (m, 14H). ^{13}C NMR (CD_2Cl_2): δ 14.09, 20.75, 24.37, 55.48, 113.99, 114.18, 126.13, 127.07, 127.66, 128.47, 128.66, 130.55, 130.78, 141.78, 143.27, 158.55. GC/MS for **21**: M/C = 326.

1-Diphenylvinyl, 2-(4-Chlorophenyl)cyclopropane (22)

The product was eluted with hexane and was isolated as a white crystalline solid. Yield was 0.34 g (95%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 1.24 (m, 1H), 1.42 (m, 1H), 2.06 (m, 1H), 2.40 (q, 1H), 5.43 (d, J = 10.1 Hz, 1H), 7.0-7.5 (m, 14H); (anti isomer) δ 1.95 (m, 1H), 2.19 (m, 2H), 2.61 (q, 1H), 5.73 (d, J = 9.7 Hz, 1H), 7.0-7.5 (m, 14H). ^{13}C NMR (CD_2Cl_2): δ 14.14, 21.02, 25.98, 127.20, 127.31, 127.48, 127.55, 127.65, 128.45, 128.57, 128.63, 128.73, 129.00, 130.67, 130.91, 132.09, 132.52, 138.03, 140.74, 142.54, 143.06. GC/MS for **22**: M/C = 330.

1-Diphenylvinyl, 2-(4-Dimethylaminophenyl)cyclopropane (23)

The product was eluted with 80:20 hexane: ethylacetate and was isolated as a yellow, orange viscous oil. Yield was 0.19 g (54%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 1.27 (m, 1H), 1.43 (m, 1H), 2.07 (m, 1H), 2.42 (q, 1H), 4.12 (s, 6H), 5.48 (d, J = 10.1 Hz, 1H), 7.0-7.5 (m, 14H); (anti isomer) δ 1.97 (m, 1H), 2.21 (m, 2H), 2.63 (q, 1H), 4.05 (s, 6H), 5.68 (d, J = 9.6 Hz, 1H), 7.0-7.5 (m, 14H). ^{13}C NMR (CD_2Cl_2): δ 14.15, 20.98, 25.32, 58.98, 114.43, 115.56, 126.56, 127.67, 127.78, 127.96, 128.45, 128.69, 130.87, 130.94, 131.23, 140.67, 141.55, 143.56. GC/MS for **23**: M/C = 340.

1-Diphenylvinyl, 2-propyl, 3-methylcyclopropane (24)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.26 mg (87%). ^{1}H NMR (CD_2Cl_2): (syn isomers) δ 5.80 (d, J = 5.0 Hz), 5.83 (d, J = 5.0 Hz), 7.0-7.5 (m, 10H); (anti isomer) δ 5.92 (d, J = 10.3 Hz), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 8.74, 14.12, 14.36, 17.53, 20.62, 26.39, 26.52, 120.52, 124.48, 125.21, 126.46, 126.84, 126.92, 127.12, 127.15, 127.20, 127.45, 127.55, 127.63, 127.94, 128.01, 128.39, 128.43, 128.94, 130.72, 130.81, 130.85, 131.03, 131.51, 142.90, 143.66, 143.93. GC/MS for **24**: M/C = 276.

1-Diphenylvinyl, 2-butylcyclopropane (25)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.27 g (92%). ^{1}H NMR (CD_2Cl_2): (syn isomer) δ 5.58 (d, J = 10.1 Hz, 1H), 7.0-7.5 (m, 10H); (anti isomer) δ 5.86 (d, J = 10.2 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 10.53, 14.38, 14.45, 15.76, 15.80, 17.93, 20.72, 20.78, 22.59, 22.89, 22.93, 23.06, 24.71, 26.30, 29.87, 32.04, 32.58, 33.72, 38.60, 120.58, 124.53, 125.27, 126.53, 126.87, 126.92, 126.97, 127.22, 127.38, 128.58, 127.99, 128.07, 128.47, 128.99, 130.76, 130.80, 131.12, 131.51, 134.78, 140.99, 141.04, 141.67, 145.30. GC/MS for **25**: M/C = 277.

1-Diphenylvinyl, 2-ethoxycyclopropane (26)

The product was eluted with 80:20 hexane: dichloromethane and was isolated as a clear, viscous oil. Yield was 0.27 g (96%). ^{1}H NMR (CD_2Cl_2): (anti isomer) δ 0.95 (m, 1H), 1.10 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.64 (m, 1H), 3.51 (m, 1H), 3.71 (q, J = 7.1 Hz, 2H), 5.55 (d, J = 10.2 Hz, 1H), 7.0-7.5 (m, 10H); (syn isomer) δ 1.20 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.81 (m, 1H), 1.92 (m, 1H), 3.61 (q, J = 7.1 Hz, 2H), 6.05 (d, J = 10.2 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 15.51, 19.90, 59.37, 61.37. 66.75, 127.05, 127.18, 127.33, 127.42, 127.52, 128.54, 128.65, 128.73, 128.77, 130.67, 141.07, 141.26, 143.39. GC/MS for **26**: M/C = 264.

1-Diphenylvinyl, 2-methylcarbonatecyclopropane (27)

The product was eluted with 50:50 hexane: dichloromethane and was isolated as a yellow, viscous oil. Yield was 0.28 g (97%). ^{1}H NMR (CD_2Cl_2): (anti isomer) δ 0.97 (m, 1H), 1.20 (m, 1H), 1.81 (m, 1H), 2.11 (s, 3H), 4.29 (m, 1H), 5.77 (d, J = 9.9 Hz, 1H), 7.0-7.5 (m, 10H); (syn isomer) δ 5.50 (d, J = 10.0 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 14.39, 18.87, 20.97, 54.72, 126.53, 127.29, 127.47, 127.56, 127.63, 128.44, 128.55, 129.06, 130.61, 140.47, 143.04, 143.22, 171.63. GC/MS for **27**: M/ C = 278.

1-Diphenylvinyl[1.4.0]bicycloheptane (28)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.24 g (82%). ^{1}H NMR (CD_2Cl_2): (anti isomer) δ 6.07 (d, J = 9.5 Hz, 1H) 7.0-7.5 (m, 10H); (syn isomer) δ 5.54 (d, J = 9.6 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 16.35, 19.89, 21.52, 23.03, 38.57, 120.53, 124.49, 125.22, 126.48, 127.01, 127.13, 127.20, 127.31, 127.57, 127.62, 127.96, 128.02, 128.42, 128.46, 128.96, 130.65, 130.88, 131.51, 143.83. GC/MS for **28**: M/C = 274.

Phenylindene Vinylcyclopropane (30):

In a Schlenk flask was added $Rh_2(OAc)_4$ (4.6 mgs, 0.001mol) in 10 mL of benzene. 3,3-Diphenylcyclopropene (0.21 g, 0.10 mmol) was added and the reaction was allowed to reflux for 8 h. The solvent was then removed in vacuo, the residue was then loaded onto a silica gel column where the product was eluted with dichloromethane. The product was isolated as a yellow crystalline solid. Yield was 0.20 g (97%). ^{1}H NMR (CD_2Cl_2): δ 1.97 (m, 1H), 2.74 (t, J = 8.7 Hz, 1H), 2.90 (d, J = 17.4 Hz, 1H), 3.11 (d, J = 6.7 Hz, 1H), 3.14 (d of d, J = 26.4 Hz, J' = 8.9 Hz, 1H), 5.58 (d, J = 8.9 Hz, 1H). ^{13}C NMR (CD_2Cl_2): δ 12.14, 12.49, 61.28, 84.04, 121.93, 122.32, 123.22, 124.46, 124.67, 124.87, 125.16, 125.23, 126.08, 126.40, 127.33, 128.33, 140.74, 141.46, 142.77, 149.90, 159.96. GC/MS for **30**: M/C = 384.

Olefin Competition Experiment with $Rh_2(OAc)_4$ and Para-Substitituted Styrenes in the Presence of 3-3-Diphenylcyclopropene.

In a Schlenk flask was added $Rh_2(OAc)_4$ (4.6 mg, 0.011 mmol) in benzene (10 mL). Unsubstituted styrene (0.56 g, 5.3 mmol) and para-substituted styrene (5.3 mmol) were then added to the solution. 3,3-Diphenylcyclopropene (0.21 g, 1.1 mmol) was then added and the reaction was refluxed. Aliquots were taken every 1 h to monitor the vinylcyclopropane formation by GC.

General Procedure for the Synthesis of Vinylcyclopropanes and Vinylcyclopropenes via Rh(TPP)I

In a round-bottomed flask was added Rh(TPP)I (9.0 mg, 0.011 mmol) in benzene (10 mL). The olefin substrate (11 mmol) and 3,3-diphenylcyclopropene (0.21 g, 1.1 mmol) were then added to the solution. The reaction was allowed to stir at rt for 24 h. After completion of reaction, the solvent was then removed in vacuo and the residue was loaded onto a silica gel column.

1-Diphenylvinyl, 2-phenylcyclpropane (17)

The product was eluted using hexane and was isolated as a viscous, clear yellow oil. Yield was 0.31 g (98%).

1-Diphenylvinyl, 2-(4-methylphenyl)cyclopropane (20)

The product was eluted with hexane and was isolated as a viscous, yellow-green oil. Yield was 0.32 g (96%).

1-Diphenylvinyl, 2-(4-methoxyphenyl)cyclopropane (21)

The product was eluted with 95:5 mixture of hexane:dichloromethane and was isolated as a viscous, yellow oil. Yield was 0.34 g (97%).

1-Diphenylvinyl, 2-(4-chlorophenyl)cyclopropane (22)

The product was eluted with hexane and was isolated as a white crystalline solid. Yield was 0.33 g (93%).

1-Diphenylvinyl, 2-(4-dimethylaminophenyl)cyclopropane (23)

The product was eluted with 80:20 hexane: ethyl acetate and was isolated as a yellow-orange, viscous oil. Yield was 0.19 g (54%).

1-Diphenylvinyl, 2-propyl, 3-methylcyclopropane (24)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.26 g (88%).

1-Diphenylvinyl, 2-butylcyclopropane (25)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.28 g (95%).

1-Diphenylvinyl, 2-Ethoxy Cyclopropane (26)

The product was eluted with 90:10 hexane: dichloromethane and was isolated as a clear, viscous oil. Yield was 0.27 mg (96%).

1-Diphenylvinylbicyclo[1.4.0]heptane (28)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.24 g (82%).

1-Diphenylvinyl, 2,3-dimetylcyclopropene (31)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.22 g (85%). ^{1}H NMR (CD_2Cl_2): δ 2.06 (d, J = 8.2 Hz, 1H), 2.10 (s, 6H), 5.64 (d, J = 8.2 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 10.31, 23.80, 110.73, 126.52, 127.16, 128.35, 128.37, 128.53, 130.92, 138.94, 143.79. GC/MS for **31**: M/C = 246.

1-Diphenylvinyl, 2,3-diethylcyclopropene (32)

The product was eluted with hexane and was isolated as a clear, viscous oil. Yield was 0.23 mg (78%). ^{1}H NMR (CD_2Cl_2): δ 1.24 (t, J = 7.5 Hz, 6H), 2.19 (d, J = 9.0 Hz, 1H), 2.53 (q, J = 7.5 Hz, 4H), 5.70 (d, J = 9.0 Hz, 1H), 7.0-7.5 (m, 10H). ^{13}C NMR (CD_2Cl_2): δ 12.30, 19.09, 23.37, 114.23, 125.76, 126.16, 126.55, 126.91, 128.06, 128.12, 130.65, 139.49, 143.56. GC/MS for **32**: M/C = 274.

1-Diphenylvinyl, 2-trimethylsilylcyclopropene (33)

The product was loaded onto a basic alumina column and eluted with hexane. Product was isolated as a yellow, viscous oil. Product was exceedingly unstable and decomposed within an hour in solution. Yield was 0.15 g (47%). ^{1}H NMR (CD_2Cl_2): -0.64 (d of d, J = 10.2 Hz, J' = 4.5 Hz, 1H), 0.20 (s, 9H), 5.50 (d, J = 10.2 Hz, 1H), 6.65 (d, J = 4.5 Hz, 1H).

Olefin Competition Experiment with Rh(TPP)I and Para-Substitituted Styrenes in the Presence of 3-3-Diphenylcyclopropene

In a Schlenk flask was added $Rh_2(OAc)_4$ (9.6 mg, 0.011 mmol) in benzene (10 mL). Unsubstituted styrene (0.56 g, 5.3 mmol) and para-substututed styrene (5.3 mmol) were then added. 3,3-Diphenylcyclopropene (0.21 g, 1.1 mmol) was finally added and the reaction was stirred at room temperature. Aliquots were taken every 1.5 h to monitor vinylcyclopropane formation by GC.

References

1 Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987, pp. 459-486.

2 For reviews see: (a) Grubbs, R.H.; Tumas, W. *Science* **1989**, *243*, 907-915. (b) Schrock, R. R. *Acc. Chem. Res*. **1990**, *23*, 158-165. (c) Ivin, J. J. *Olefin Metathesis*; Academic Press: New York, 1983. (d) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: New York, 1984, pp. 174-228. (e) Brookhart, M.; Studabaker, W. B. *Chem. Rev*. **1987**, *87*, 411-432.

3 The formation of allyl-hydride complexes is also known from the reaction of metal carbenes with olefins. See: (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197-204. (b) Roper, W. R. *Advances in Metal Carbene Chemistry*; U. Schubert, Ed.; Kluwer Academic: Dordrect, 1989; Vol. 269; p. 27. (c) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc*. **1976**, *99*, 3519-3520. (d) Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 510-512. (e) Fryzuk, M. D.; Gao, X.; Joshi, K.; MacNeil, P. A.; Massey, R. L. *J. Am. Chem. Soc*. **1993**, *115*, 10581-10590.

(a) Schrock, R. R. *Science* **1983**, *219*, 13-18. (b) Dotz, K. H.; Fischer, H.; Hoffman, P.; Kreissl, F.; Schubert, W.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beech, FL, 1983. (c) Grubbs, R. H. *Prog. Inorg. Chem*. **1978**, *24*, 1-48.

Casey, C.P.; Polichnowski, S. W. *J. Am. Chem. Soc*. **1977**, *99*, 6097-6099. (b) Casey, C. P.; Polichnowski, S. W.; Schusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc*. **1979**, *101*, 7292-7295. (c) Fischer, H.; Zeuner, S.; Ackermann, K. J. *J. Chem. Soc., Chem.*

Commun. **1984**, 684-686. (d) Nishiyama, H.; Park, S. B.; Itoh, K. *Chem. Lett.* **1995**, 599. (e) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511-2513.

6 (a) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348-356. (b) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263-309. (c) Adams, J.; Spero, D. M. Tetrahedron 1991, 47, 1765-1808. (d) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.

7 (a) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365-2369. (b) Maxwell, J. L.; Brown, K. C.; Bartley, D.; Kodadek, T. *Science* **1992**, *256*, 1544-1545.

8 For a review of the structure, bonding, and synthesis of dirhodium carboxylates, see: Jardine, F.H.; Sheridan, P. S. *Comprehensive Coordination Chemistry, IV*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; pp. 901-1096.

9 Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919-939 and references therein.

10 Taber, D. F.; Ruckle, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 7686-7693.

11 (a) Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958-964. (b) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436-441. (c) Taber, D. F.; Hoerner, R. S. *J. Org. Chem.* **1992**, *57*, 441-447. (d) Hashimoto, S.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1992**, *33*, 2709-2712. (e) Ceccherelli, P.; Curini, N.; Marcotullio, M. C.; Rosati, O. *Tetrahedron* **1991**, *47*, 7403-7405. (f) Doyle, M. P.; Pieters, R. J.; Taunton, J.; Pho, H. Q. Padwa, A.; Hertzog, D. L.; Precedo, L. *J. Org. Chem.* **1991**, *56*, 820-829. (g) Demonceau, A.; Noels, A. F.; Hubert, A. J. *Tetrahedron* **1990**, *46*, 3889-3896. (h) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. *J. Am. Chem. Soc.* **1990**, *112*, 1906-1912. (i) Doyle, M. P.; Bagheri, V.; Pearson, M. M.; Edward, J. D. *Tetrahedron Lett.* **1989**, *30*, 7001-7004.

12 (a) Doyle, M. P.; *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 305-316. (b) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1183-1185.

13 (a) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669-8680. (b) Padwa, A.; Austin, D. J.; Hornbuckle, S. F.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N. *J. Am. Chem. Soc.* **1992**, *114*, 1874-1876. (c) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem*. **1992**, *57*, 436-441. (d) Hashimoto, S.; Watanabe, N.; Ikegami, S. *J. Chem. Soc., Chem. Commun*. **1992**, 1508-1510. (e) Doyle, M. P.; Taunton, J.; Pho, H. Q. *Tetrahedron Lett.* **1989**, *30*, 5397-5400. (f) Cox, G. G.; Moody, C. J.; Austin, D. J.; Padwa, A. *Tetrahedron* **1993**, *49*, 5109-5126. (g) Doyle, M. P.; Pieters, R. J.; Taunton, J.; Pho, H. Q.; Padwa, A.; Hertzog, D. L.; Precedo, L. *J. Org. Chem.* **1991**, *56*, 820-829.

14 For reviews, see: (a) Binger, P.; Buch, H. M.; *Top. Curr. Chem.* **1987**, *135*, 77-151. (b) Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137-209. (c) Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappaport, Z., Patai, S., Eds.; John Wiley: New York, 1987; pp. 1223-1339.

15 (a) Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl*. **1989**, *28*, 610-611. (b) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc*. **1993**, *115*, 8130-8145. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc*. **1992**, *114*, 3974-3975. (c) Gagne, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3933-3935. (d) Flatt, B. T.; Grubbs, R. H.; Blanski, R. L.; Calabrese, J. C.; Feldman, J. *Organometallics* **1994**, *13*, 2728-2732.

16 Werner, H.; Daniel, T.; Knaupp, W.; Nurnberg, O. *J. Organomet. Chem*. **1993**, *460*, 163-175.

17 (a) Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl*. **1989**, *28*, 610-611. (b) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc*. **1993**,

115, 8130-8145. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.

18 Rh vinylcarbene complexes exhibit doublets in the ^{31}P NMR due to Rh-P coupling.

19 $[M(COE)_2Br]_2$ dimer is readily synthesized in quantitative yield from the reaction of the commercially available $[M(COE)_2Cl]_2$ dimer with 20 equiv of LiBr in THF.

20 Assignments of the cis and trans isomers made quantitatively by GC using authentic samples synthesized according to known literature procedure found in: Binger, P.; McMeeking, J.; Schafer, H. *Chem. Ber.* **1984**, *117*, 1551-1560.

21 Binger, P.; McMeeking, J.; Schafer, H. *Chem. Ber.* **1984**, *117*, 1551-1560.

22 Battiste, M. A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1966**, 907-909.

23 Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth*. **1973**, *14*, 92-95.

24 Moore, J. S.; Nguyen, S. T.; Grubbs, R. H., California Institute of Technology, unpublished results.

25 Binger, P.; MeMeeking, J.; Schafer, H. *Chem Ber.* **1984**, *117*, 1551-1560.

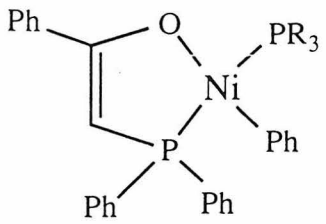
Chapter 4

Synthesis of Salicylaldimine Complexes of Ni(II)-Aryls and their Reactivity in Ziegler-Natta Polymerization

Introduction

The polyolefin industry relies upon Ziegler-Natta, chromium oxide, and other catalysts based upon early transition metals.[1] Although the array of catalysts available offers many different approaches to the manufacture of polyolefins having a variety of physical properties,[2] these catalysts are all extremely susceptible to deactivation by a range of poisons. Primary among these poisons are traces of oxygen, carbon monoxide, and water that can make their way into manufacturing facilities and laboratories in a variety of ways. Other oxygen donors such as ethers, alcohols, or ketones can also be poisons for these catalysts. As a result, the industry must carefully purify the olefin and solvents used for polyolefin manufacture. This sensitivity to oxygenated species also precludes copolymerization of, e.g., ethylene with polar monomers such as those containing ester or nitrile functionality. A catalyst that could accomplish the coordination polymerization of ethylene with polar comonomers under moderate pressures is clearly of interest.

The search for new catalyst systems resistant to deactivation by oxygenated species has focused on the late transition metals because they are less oxophilic than their early metal counterparts. Shell[3] has developed nickel-based oligomerization catalysts that yield higher-order olefins, but their patents and the patents[4] of others working in the area[5] do not disclose high molecular weight polyethylene or copolymerizations. Bayer AG reports the polymerization of ethylene with catalysts derived from nickel and phosphorous ylids.[6] Keim[7] and others[8] have continued to study the nickel systems in detail, and Keim[9] has reported an interesting catalyst system **a** that provides higher-order



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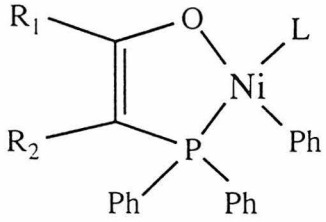
oligomers in toluene, but high molecular weight polymers in hexane. Ligands containing P-O chelates show an unusually high activity and selectivity in the nickel-catalyzed oligomerization and polymerization of ethylene. Ittel and coworkers have further investigated the use of P-O chelate ligands in nickel-based systems for ethylene homo- and copolymerization. Ittel has developed analogous nickel compounds based upon phosphorous-oxygen chelate ligands **b-e.**[10] These complexes are effective catalysts for

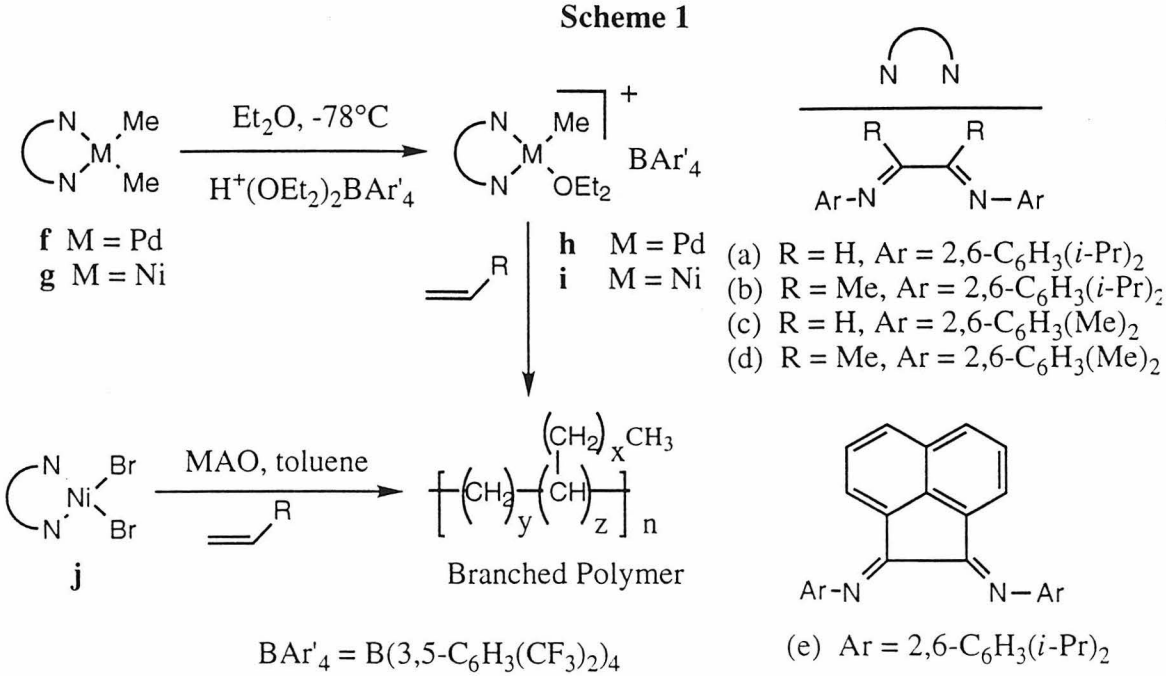


	R_1	R_2	L
b	Ph	OMe	PEt_3
c	SO_3Na	Ph	PPh_3
d	H	Ph	Pyridine
e	SO_3Na	Ph	Pyridine

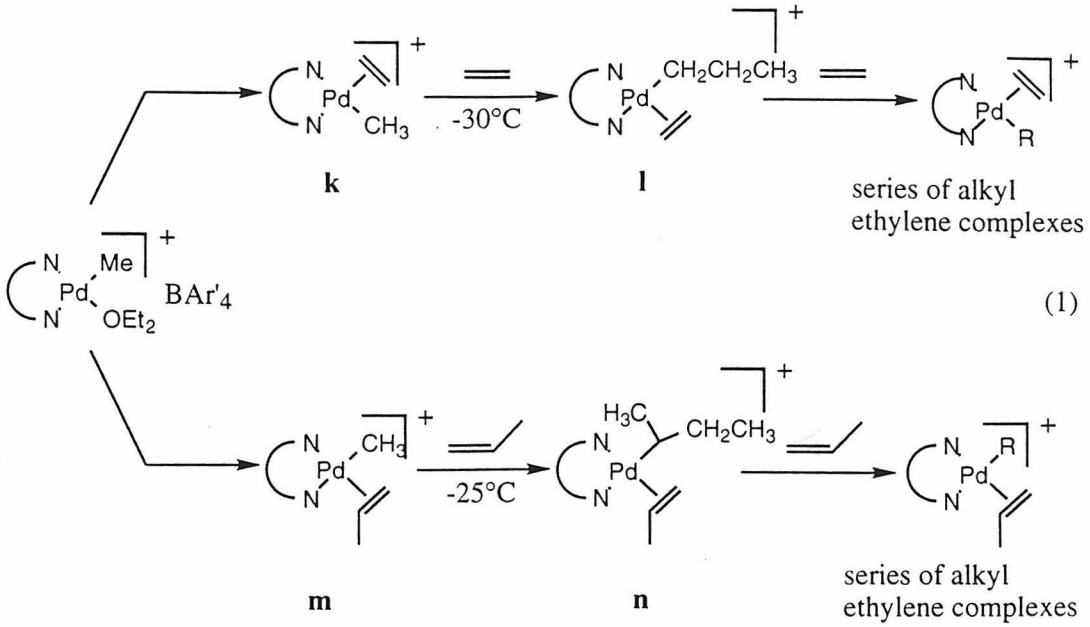
the homopolymerization of ethylene to high molecular weight polyethylene. They will also copolymerize ethylene with α-olefins, and more importantly, with polar monomers (e.g., vinyl acetate) and carbon monoxide. These catalysts have also been shown to be resistant to a variety of polar molecules such as nitriles, alcohols, and even water.

Recently, Brookhart has reported the use of novel Pd(II)- and Ni(II)-based catalysts for the polymerization of ethylene and α-olefins.[11] These Pd(II) and Ni(II) initiators are cationic methyl complexes $[ArN{=}C(R)C(R){=}NAr)M(CH_3)(OEt_2)]^+BAr'_4^-$ (M = Pd and Ni; Ar = 2,6-diisopropylaniline and 2,6-dimethylaniline; R = Me and H; Ar' = 3,5-$C_6H_3(CF_3)_2$) which incorporate bulky diimine ligands. Exposure of the Ni and Pd ether adducts **h** and **i** to ethylene, propylene, and 1-hexene results in formation of high molecular weight polymers (Scheme 1). The cationic Ni complexes can alternatively be

Scheme 1



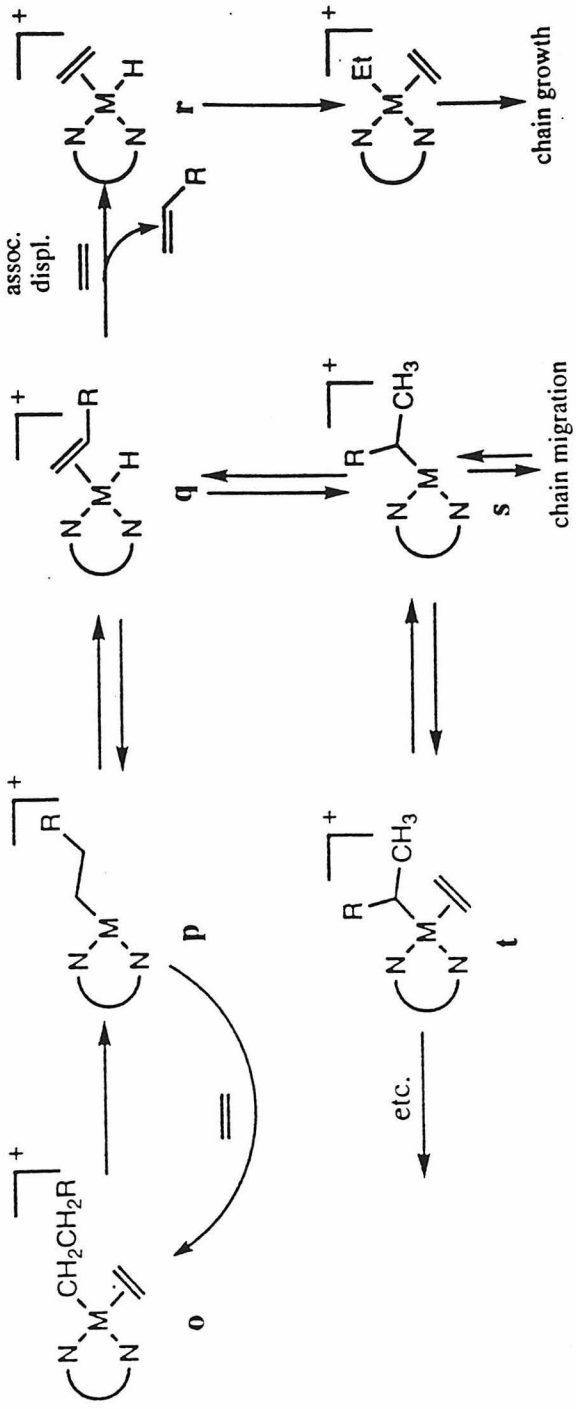
generated in situ by MAO activation of diimine nickel dibromide complexes, **l**, in the presence of olefins. Brookhart was able to gain insight into the polymerization mechanism by monitoring the reaction of the Pd ether adducts with ethylene at -80°C (eq 1).



Reaction of Pd ether adducts with ethylene at -80°C resulted in formation of ethylene adduct, **k**, and the rate of exchange of bound ethylene and free ethylene in **k** was dependent on ethylene concentration (which implies associative exchange). Upon warming, chain growth was monitored to be zero-order in ethylene concentration.

Scheme 2 provides a mechanistic rationale for the observed reaction kinetics. The catalyst resting states are alkyl-olefin complexes indicated by structure **o**. Migratory insertion results in **p**, which can be rapidly trapped by ethylene to regenerate an alkyl-ethylene species **o**. Alternatively, **p** can undergo β-hydride elimination to form an olefin-hydride complex **q.** Complex **q** can undergo reinsertion with opposite regiochemistry, which introduces a branched alkyl group in **s**. Trapping and insertion of **s** produces a methyl branch, while further chain migration via β-hydride elimination and readdition produces longer branches. In a chain transfer process, complex **q** can release olefin to yield **r**, which can initiate a new chain. However, in M(II) square planar complexes, conversion of **q** to **r** must be associative (as observed by the ethylene concentration dependence). The rates of associative displacement and chain transfer are greatly retarded by the steric bulk of the diimine ligands. The ortho substituents on the aryl

Scheme 2



rings of the diimine ligands serve to block the axial approach of the olefins. This feature results in rates of chain propagation that are much greater than chain transfer rates and thus permits formation of high molecular weight polymers.

The goal of the research reported in this chapter was to develop new late transition metal catalyst systems for the homopolymerization and copolymerization of ethylene and α-olefins based on the observations and results of the systems developed by Ittel[10] and Brookhart.[11] We wanted the catalysts to incorporate the following characteristics: (1) the catalysts will utilize late transition metals (Ni and Pd) since they are more resistant to deactivation by oxygenated species, in contrast to their early metal counterparts; (2) bidentate, chlelating ligands will be utilized since chelating ligands have been shown to have an unusual selectivity-controlling effect in the polymerization of ethylene and α-olefins; (3) the ligands will employ extreme steric bulk that can effectively shield the axial faces of the M(II) square planar complexes, thus enabling retardation of associative displacement processes and chain transfer; and (4) the ligands will employ steric bulk in the plane of the M(II) square planar complex, thus disfavoring chain migration processes that lead to highly-branched polymer chains.

Our first starategies were to synthesize phosphine-imine and ditertiary phosphine chelate complexes of Ni(II) (Figure 1) as analogs to the diimine system developed by Brookhart. CPK models of these complexes show that significant shielding of the axial faces is achieved with the bulky phosphine and aniline dervatives, as well as significant in-plane bulk. However, the lack of activity shown by these complexes for the

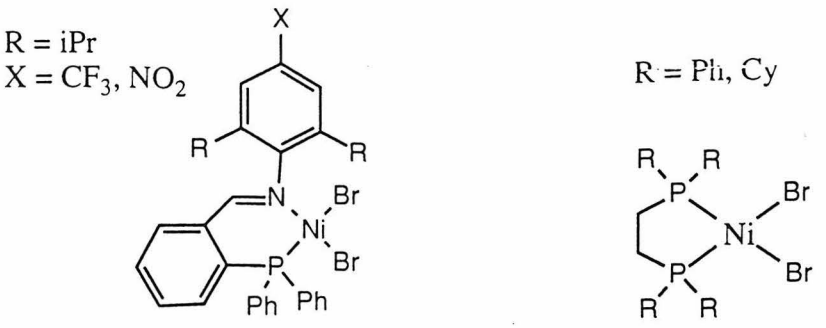
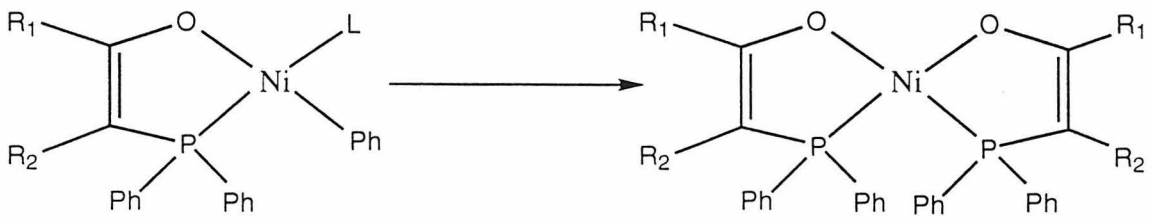


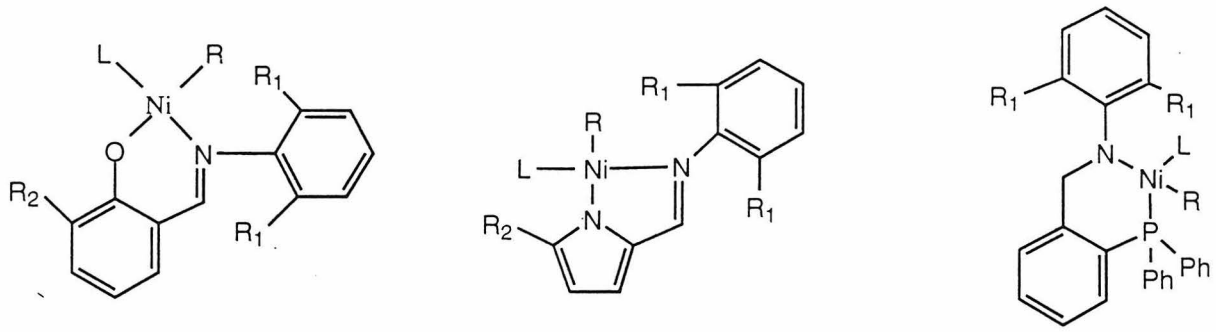
Figure 1. Proposed catalysts for olefin polymerization

polymerization of ethylene led us to investigate the synthesis of anionic, bidentate ligands for the synthesis of neutral nickel complexes, similar to those O-P chelate complexes investigated by Ittel. In our investigations, we tried to alleviate probems observed with the O-P chelate Ni complexes. Some of these problems include deactivation by ligand reorganization (eq 2).[12] In addition, the polymerization of olefins by these complexes



(2)

results in polymers that are highly branched and have low molecular weights which indicates that associative binding and chain migration rates are competitive with the rate of chain growth. To address these problems, we explored the design and synthesis of the following types of nickel complexes:

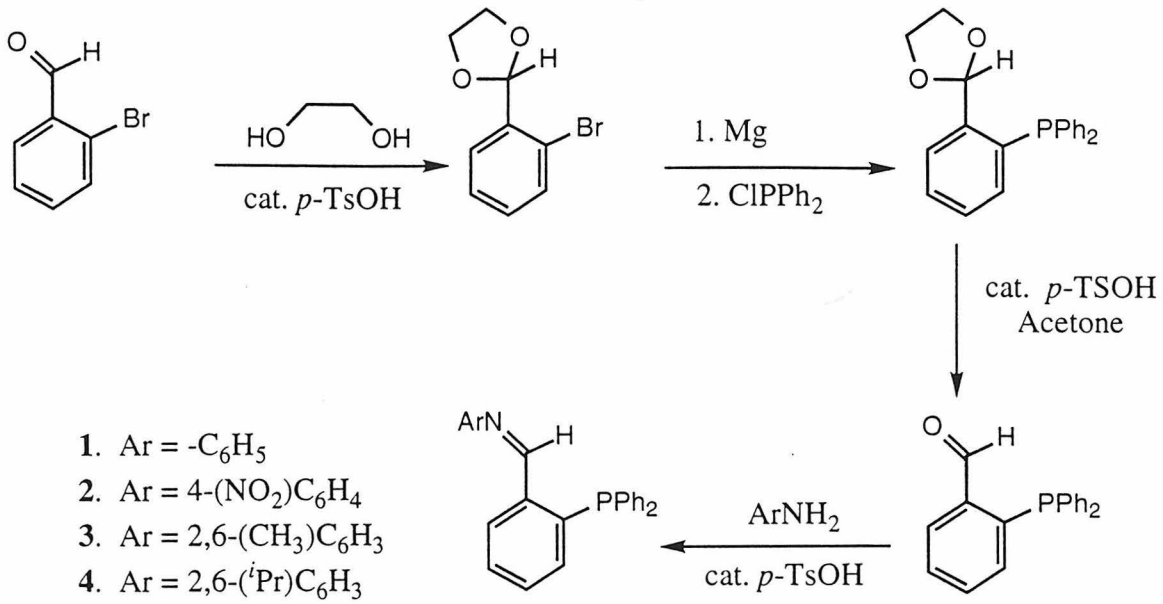


These ligand designs allow us to use bulky aromatic substituents on nitrogen (e.g., R_1 = ^{i}Pr) that can allow blockage of the M(II) axial faces, thus retarding the rates of associative displacement, which leads to chain termination. In addition, these designs allow us to place bulky substituents in the R_2 position, generating steric bulk in the plane of the M(II) square planar complexes, which can lead to retardation of chain migration processes, and thus limit branching. Finally, incorporation of these bulky ligands into the M(II) complexes should disfavor ligand reorganization which is believed to be the major deactivation pathway in the O-P chelate complexes developed by Keim[7] and Ittel.[12]

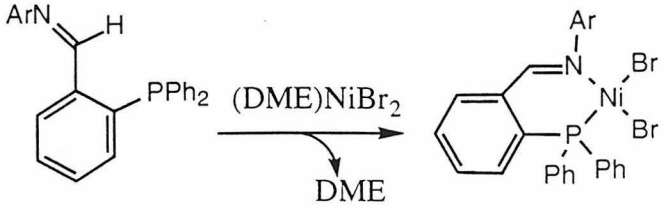
Results and Discussion

Synthesis of $NiBr_2(Ph_2P\text{-}C_6H_3\text{-}o\text{-}C{=}N\text{-}Ar')$, $NiBr_2(R_2P(CH_2)_2PR_2)$, $(Ph_2P\text{-}C_6H_3\text{-}C{=}N\text{-}Ar')Pd(Me)Cl$, and $(R_2P(CH_2)_2PR_2)Pd(Me)Cl$. Our initial efforts went into synthesizing the phosphine-imine ($Ph_2P\text{-}C_6H_3\text{-}C{=}N\text{-}Ar'$) bidentate ligands, which is outlined in Scheme 3. 2-Bromobenzaldehyde was protected as the 1,3-dioxolane by reaction with ethylene glycol and catalytic *p*-toluenesulfonic acid. Formation of the Grignard reagent followed by treatment with chlorodiphenylphosphine resulted in the formation of the 2-diphenylphosphinobenzaldehyde-dioxolane adduct. The dioxolane was deprotected by reaction in neat acetone and catalytic *p*-toluenesulfonic acid to form 2-diphenylphosphinobenzaldehyde.[13] The benzaldehyde was treated with several aniline derivatives to form the 2-diphenylphosphinobenzylimine derivatives **1-4**. Anilines of varying steric and electronic parameters were employed in order to examine these effects in olefin polymerization.

Scheme 3

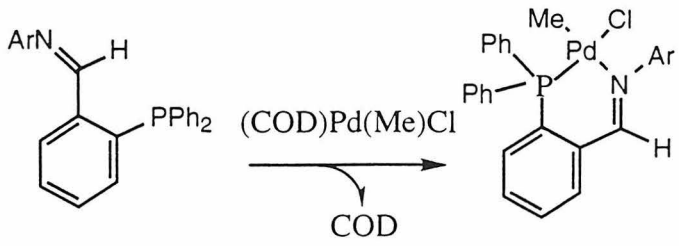


Synthesis of the corresponding $NiBr_2(Ph_2P\text{-}C_6H_3\text{-}C{=}N\text{-}Ar')$ complexes was accomplished by reacting 1.01 equiv of the P-N chelate ligand with $(DME)NiBr_2$ in CH_2Cl_2 for 24 hours (eq 3). Removal of the solvent in vacuo followed washing with



(3)

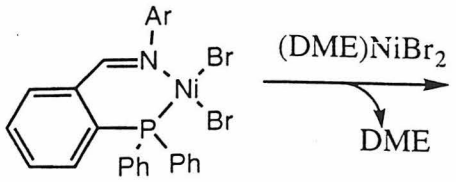
hexane yielded red-brown solids in 87-96% yield. The synthesis of the palladium analog`s was accomplished by reacting 1.01 equiv of the P-N chelate ligand with $(COD)Pd(Me)Cl$ in CH_2Cl_2 which results in instantaneous formation of $(Ph_2P\text{-}C_6H_3\text{-}o\text{-}C{=}N\text{-}Ar')Pd(Me)(Cl)$ adducts **9-12** in quantitative conversion (eq 4).



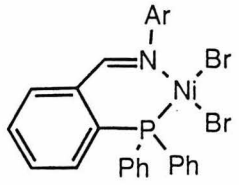
9. Ar = $-C_6H_5$
10. Ar = 4-$(NO_2)C_6H_4$
11. Ar = 2,6-$(CH_3)C_6H_3$
12. Ar = 2,6-(*i*-Pr)C_6H_3 (4)

$NiBr_2(R_2P(CH_2)_2PR_2)$ (R = Ph and Cy) and $(R_2P(CH_2)_2PR_2)Pd(Me)Cl$ (R = Ph and Cy) were synthesized by reported literature methods.[14]

Attempted Polymerization of Ethylene by Complexes 5-8. Polymerization of ethylene with Ni dibromide complexes **5-8** were carried out using protocols similar to those described by Brookhart[11] with the Pd(II)- and Ni(II)-diimine catalysts. A sample of 0.05 mmol of complexes **5-8** was dissolved in 100 mL of toluene and introduced to 1 atmosphere of ethylene. A solution of MAO (1000 equiv) in toluene was then injected at O°C (eq 5). In all cases, the red-brown solutions instantly became pale yellow upon exposure to MAO. Complexes **5-7** exhibited no ethylene uptake, while complex **8** exhibited rather slow ethylene uptake for only a few minutes. We speculated that exposure of the catalysts to MAO led to reduction of the Ni(II) species to Ni(O), which



5. Ar = -C_6H_5
6. Ar = 4-$(NO_2)C_6H_4$
7. Ar = 2,6-$(CH_3)C_6H_3$
8. Ar = 2,6-(*i*-Pr)C_6H_3 (3)

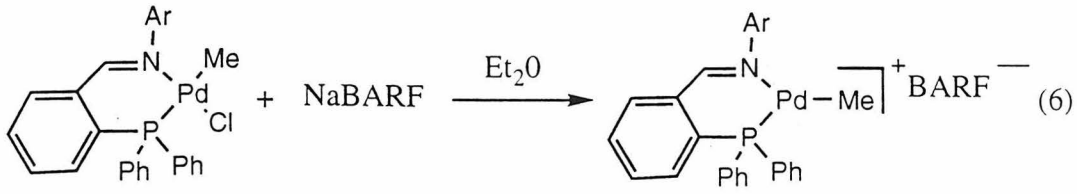


5-7 No Reaction
8 Oligomerization (5)

5. Ar = -C_6H_5
6. Ar = 4-$(NO_2)C_6H_4$
7. Ar = 2,6-$(CH_3)C_6H_3$
8. Ar = 2,6-(*i*-Pr)C_6H_3

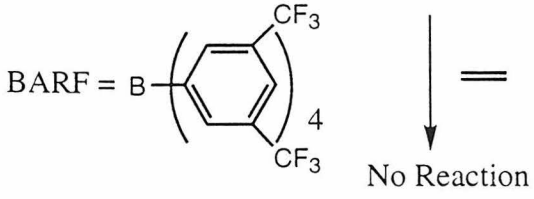
resulted in catalyst deactivation.

Polymerization of ethylene with complexes $NiBr_2(R_2P(CH_2)_2PR_2)$ (R = Ph and Cy) were carried out with little success. Exposure of these Ni dibromide complexes to MAO resulted in complete deactivation of the catalysts, and no ethylene uptake was evident. Efforts to polymerize ethylene with the corresponding Pd catalysts, (Ph_2P-C_6H_3-C=N-Ar')Pd(Me)(Cl) and ($R_2P(CH_2)_2PR_2$)Pd(Me)Cl (R = Ph and Cy), also met with little success (eq 6).

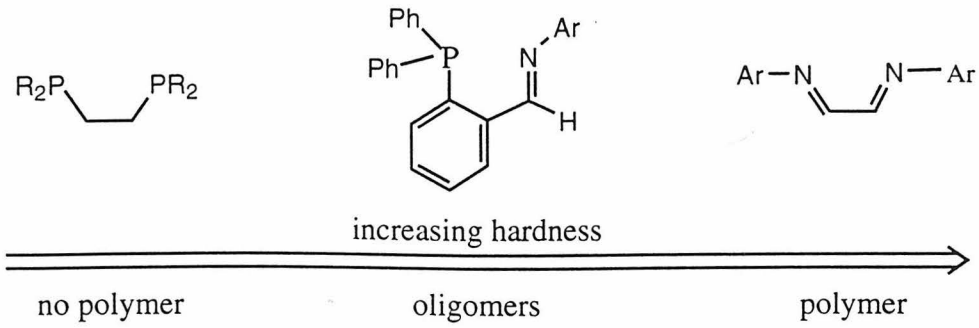


(6)

9. Ar = -C_6H_5
10. Ar = 4-$(NO_2)C_6H_4$
11. Ar = 2,6-$(CH_3)C_6H_3$
12. Ar = 2,6-(*i*-Pr)C_6H_3



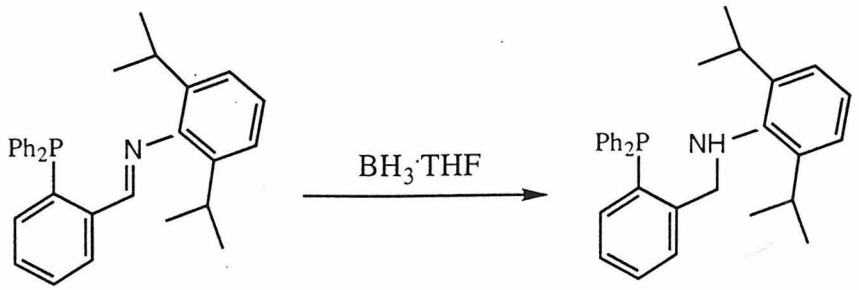
When we compare the two ligand systems above with the diimine system employed by Brookhart et al., an interesting trend can be noted. From the ditertiary phosphine ligands to the mixed phosphine-imine ligand and subsequently to the diimine system, there is an



increase in ligand "hardness." The harder ligand-nickel complexes are more active in ethylene polymerization, while the "softer" ligand nickel complexes deactivate immediately under polymerization conditions. This scenario is consistent with a deactivation pathway in which the Ni(II) complexes reduce to Ni(O) under the reaction conditions. The "harder" ligand systems are better able to stabilize the Ni(II) oxidation state than the "softer" more π-acidic ligand systems. Faced with the unlikely design of a cationic system superior to Brookhart's diimine system, we proceeded to investigate anionic, bidentate ligands for the synthesis of neutral Ni polymerization systems.

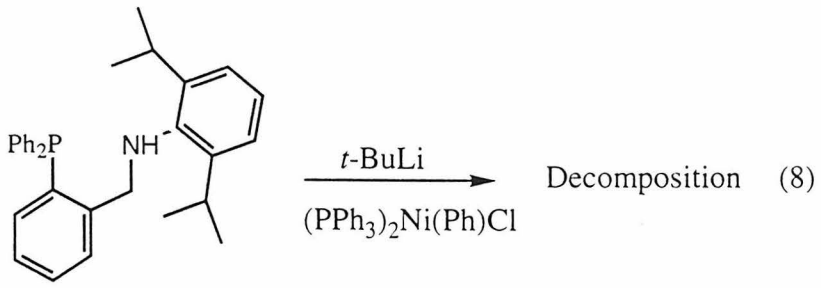
Synthesis [Ph_2P-C_6H_4-*o*-CH_2-N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(C_6H_5), [O-C_6H_4-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph), and [C_4H_3N-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph). We wished to improve upon the properties of the O-P chelating systems investigated by Keim and Ittel by incorporating more sterically demanding ligands for the reasons stated above. Also, we wished to incorporate harder ligands due to the observations in the previous section that harder ligands tend to better stablilize the Ni(II) oxidation state necessary for olefin polymerization.

The synthesis of Ph_2P-C_6H_4-*o*-CH_2-N-2,6-C_6H_3(*i*-Pr)$_2$ was easily accomplished by the reduction of imine complex **4** with BH_3·THF to form the arylamine complex **13**



4 **13** (7)

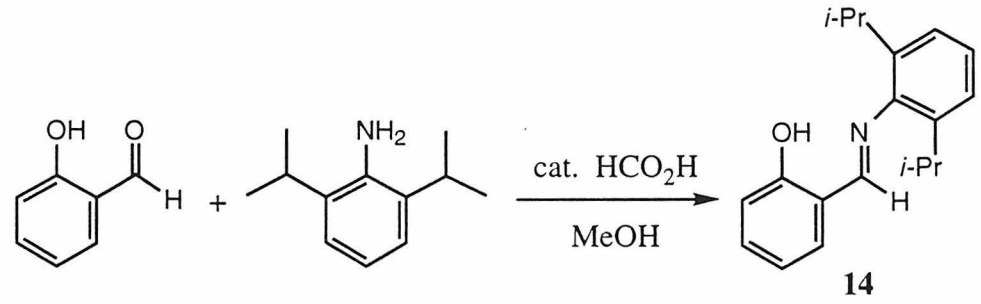
(eq 7). However, attempts to complex the ligand to various Ni(II) systems met with little success. Compound **13** reacts readily with *t*-BuLi to form the corresponding Li salt; however, subsequent reaction with $(PPh_3)_2Ni(Ph)Cl$[15] to form [Ph_2P-C_6H_4-*o*-CH_2-N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(C_6H_5) led to decomposition products as observed by ^1H and ^{31}P NMR (eq 8). Reaction with other Ni precursors such as $(PCy_3)_2Ni(H)Cl$[16] and [(η^3-



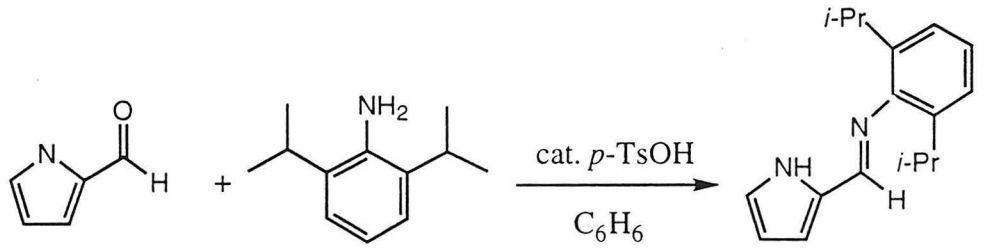
13 (8)

allyl)NiBr][17] also led to decomposition products. We speculated that the metalation reaction might have been ineffective due to the increased basicity of the arylamine ligand (compared to aryloxides) or to the presence of β-hydrogens. We then explored the

synthesis of ligands having decreased basicities and no β-hydrogens. Two such systems were available from the commercial materials salicylaldehyde and pyrole-2-carboxaldehyde. Reaction of salicylaldehyde with 2,6-diisopropylaniline in methanol using a catalytic amount of formic acid resulted in clean formation of the salicylaldimine ligand **14** (eq 9). Reaction of pyrole-2-carboxaldehyde with 2,6-diisopropylaniline in benzene with a catalytic amount of *p*-toluenesulfonic acid resulted in formation of the pyrole-2-carboxaldimine ligand **15** (eq 10).

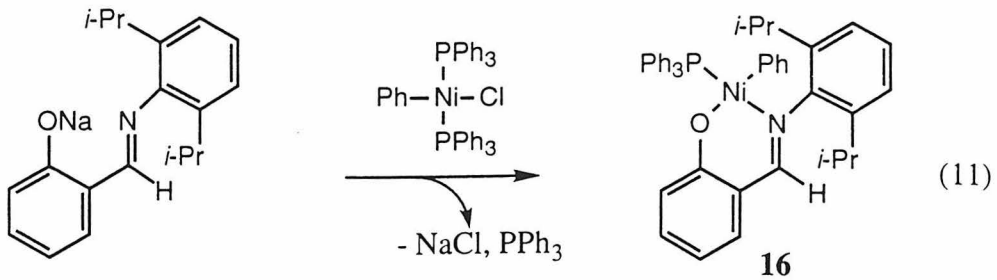


14 (9)



15 (10)

Deprotonation of **14** proceeds cleanly using excess NaH to form the corresponding Na salt. The Na salt of **14** reacted cleanly with $(PPh_3)_2Ni(Ph)Cl$ to form [O-C_6H_4-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph) (**16**) (eq 11). Deprotonation of **15** proceeds cleanly using 1.05 equiv of *t*-BuLi to form the Li salt. Reaction of the Li salt of **15** reacts cleanly with $(PPh_3)_2Ni(Ph)Cl$ and cleanly forms [C_4H_3N-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph) (**17**) (eq 12).



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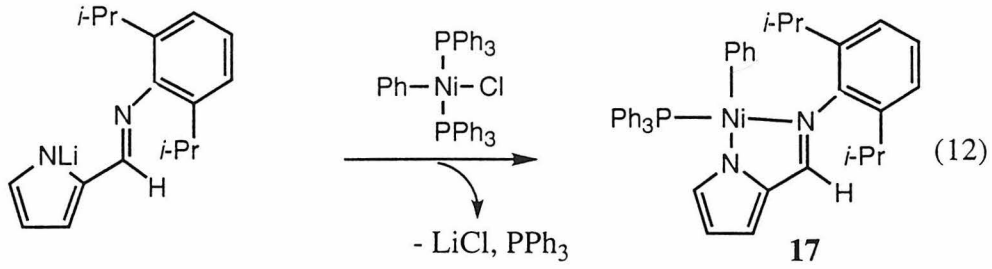
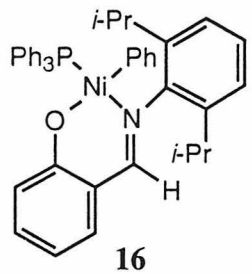


(12)

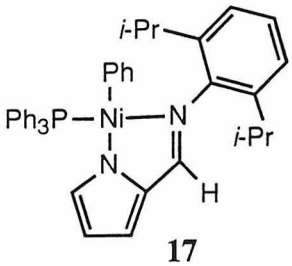
Some noteworthy characteristics of **16** and **17** in their ^{1}H NMR spectra are the inequivalency of the isopropyl methyl groups [-CH-($C\underline{H}_3$)$_2$] where the doublet of the free ligand splits into a doublet of doublets in the nickel complex. The methine proton of the isopropyl group [-$C\underline{H}$-(CH_3)$_2$] exhibits a characteristic downfield shift (~ 1 ppm) from the resonance in the free ligand. Also, the imine proton exhibits a characteristic ^{31}P coupling corresponding to bound PPh_3. ^{31}P NMR spectroscopy served as a valuable tool to observe the consumption of starting material and the purity of the resulting product; complexes **16** and **17** exhibit a single ^{31}P resonance.

Polymerization of Ethylene Catalyzed by Complexes 16 and 17. The polymerization of ethylene with complexes **16** and **17** was accomplished by first dissolving 0.15 mmol of catalyst in 80 mL of toluene under an atmosphere of ethylene, followed by subsequent injection of a toluene solution of 2 equiv of $Ni(COD)_2$, which has been employed by Ittel in the O-P chelate systems as a phosphine sponge.[12] The ethylene pressure was then raised to specified levels and the reactions were allowed to stir at room temperature (eq 13).

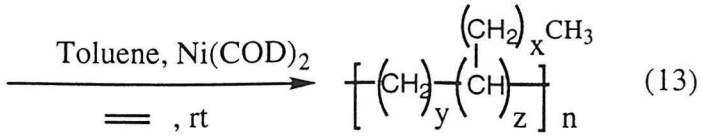


16

or



17



(13)

Table 1. Polymerization of Ethylene by **16**.[a]

Entry	Catalyst	Pressure	$\bar{M}w$	PDI	Yield (g PE)	# of Branches[b]
1	**16**	80 psi	4000	1.54	2.0	45
2	**16**	200 psi	10000	1.45	2.4	20

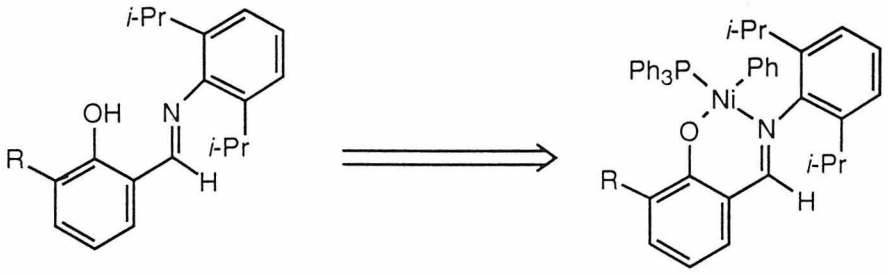
[a] Reactions were carried out using 1.8 mM [catalyst] and 2 equiv $Ni(COD)_2$ at rt for 40 min. [b] The number of $C_1 + C_2 + C_3 + C_4$ branches per 1000 carbons.

Exposure of **16** to ethylene under the conditions stated above resulted in the formation of polyethylene (results summarized in Table 1). Characteristic of the polymerization runs was a 5-10 minute induction period where ethylene uptake was relatively slow, followed by rapid uptake accompanied by a rapid rise in the reaction temperature. Ethylene uptake proceeded for approximately 30 min where uptake, at this point, stopped. Pressure dependence on the molecular weights (Mw) was observed, where Mw increased from 4000 to 10000 as the ethylene pressure was increased from 80

psi to 200 psi; however, the PDI's remain constant over the pressure range. The number of branches (determined by ^{13}C NMR) was shown to decrease with the increase in pressure, consistent with observations made by Brookhart et al.[11] The yield of polyethylene, however, exhibited no correlation with the pressure of ethylene: the yields were similar at the different pressures. Since any vacant coordination sites on the metal are more likely to be occupied by ethylene at higher pressures, this observation suggest a pathway for deactivation that does not involve a coordinatively unsaturated bimetallic decomposition of the type suggested by Ittel[12] (the ligand reorganization pathway; eq 2).

Exposure of **17** to ethylene at 80 psi resulted in rapid uptake of ethylene comparable to **16**. The products were identified, however, as C_{12}-C_{20} oligomers of ethylene.

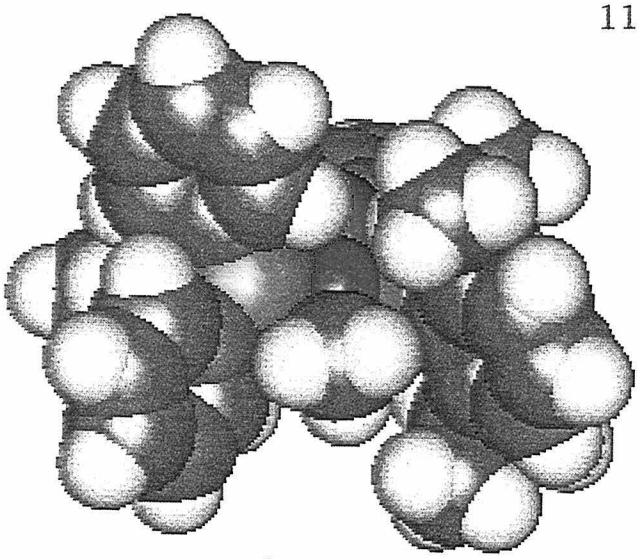
Synthesis of 3-Substituted Salicylaldimine Ligands and their Nickel Complexes. The results obtained from the polymerization reactions of **16** prompted us to focus on improving the design of the salicylaldimine ligand. Our initial plan was to introduce



bulky substituents in the 3-position of the salicylaldimine ring. This design was based on several factors: (1) the increased bulk should help to shield the axial faces and thus retard the chain termination steps so that higher Mw polymers can be obtained, (2) the substituent should be well-situated in the plane of the Ni(II) complex, and should thus retard chain migration processes that lead to branching, and (3) poor initiation by **16** was observed as evident by the 5-10 minute induction period for polymerization, presumably due to phosphine dissociation as the rate-determining step; we hoped that the increased

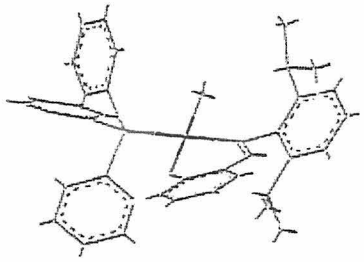
bulk on the salicylaldimine ring should enhance phosphine dissociation and, thus, improve initiation. BIOSYM simulations[18] of **16** (see Figure 2) show that one of the Ni(II) axial faces is shielded while the other face is partially shielded. In contrast, substitution at the 3-position of the salicylaldimine ligand would put steric bulk in the site occupied by bound PPh_3 (in-plane bulk) and would assist in the complete shielding of the partially open axial face.

Our initial effort involved placing either a phenyl or a*tert*-butyl group in the 3-position of the salicylaldimine ring. This was accomplished by formylation of 2-susbstituted phenols with paraformaldehyde and catalytic $SnCl_4$ (Scheme 4).[19] The resulting substituted salicylaldehydes were then treated with 2,6-diisopropylaniline with catalytic formic acid in MeOH to form the 3-substituted salicylaldimine complexes **18** (R = *t*-Bu) and **19** (R = Ph). Salicylaldimines **18** and **19** were subsequently deprotonated with NaH and then treated with $(PPh_3)_2Ni(Ph)Cl$ to form [O-(3-*t*-Bu)C_6H_3-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph) (**20**) and [O-(3-Ph)C_6H_3-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph) (**21**).



"top" view: blocked

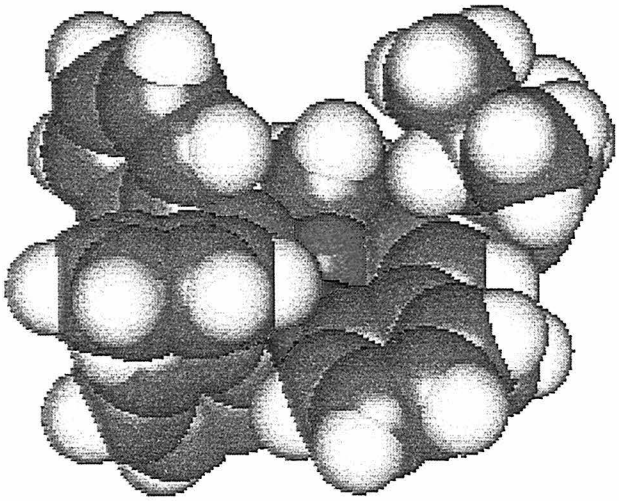
(a)



orange = phosphorus
green = nickel
red = oxygen

16

(c)

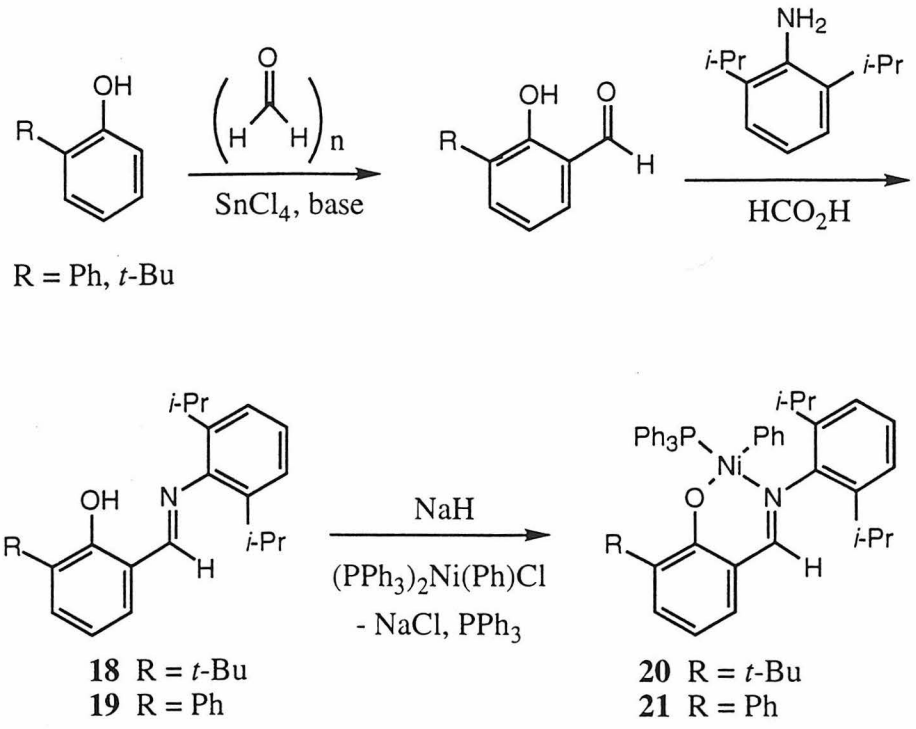


"bottom" view: open

(b)

Figure 2. BIOSYM Simulation of **16** showing (a) the "Top View," (b) the "Bottom View," and (c) a Stick Representation.

Scheme 4



Polymerization of Ethylene by 20 and 21. Polymerizations of ethylene by complexes **20** and **21** were carried out in a glass bomb where a specified amount of catalyst was introduced into the bomb and placed under full vacuum. The bomb was then backfilled with ethylene, and toluene was introduced at this time. A solution of 2 equiv of $Ni(COD)_2$ in toluene was injected and the ethylene pressure was raised to 80 psi. The results are summarized in Table 2.

Under similar conditions, complexes **20** and **21** were more active than the unsubstituted salicylaldimine Ni complex **16** for the polymerization of ethylene. Shorter induction periods for the uptake of ethylene for **20** and **21** were evident: rapid uptake was observed only 1-2 mintues after the introduction of ethylene. Presumably, the greater steric bulk in the Ni(II) plane of complexes **20** and **21** served to greater labilize

Table 2. Polymerization of Ethylene by **20** and **21**.[a]

Entry	Catalyst	[Cat] mM	Temp (°C)	Yield (g)	Mw	PDI	Total Branches[b]
1	**20**	1.8	r.t.	8.0	26000	2.25	55
2	**21**	1.8	r.t	20.0	23300	2.28	40
3	**20**	0.9	r.t	3.5	11400	1.84	55
4	**21**	0.9	r.t	8.9	11000	1.95	45
5	**20**	0.9	0°C	3.1	66000	3.10	25
6	**21**	0.9	0°C	3.9	108000	2.45	10

[a] All polymerizations reactions were carried out at rt, 80 psi of ethylene, and 2 equiv $Ni(COD)_2$ for 40 minutes. [b] Total number of $C_1 + C_2 + C_3 + C_4$ branches per 1000 carbons.

the bound PPh_3, thus leading to faster initiation of the polymerization and perhaps the initiation of more active catalyst sites.

Under similar conditions, complex **21** was more active than **20** for the polymerization of ethylene. Presumably, the more lengthy phenylgroup can reach further into the space occupied by the bound PPh_3 in the parent complex, thus more readily labilizing the bound PPh_3. Higher molecular weights were observed for catalysis by the sustituted complexes **20** and **21** versus the unsubstituted complex **16**. Substitution at the 3 position of the salicylaldimine ligand might serve to partially block the axial faces of the Ni(II) complex, disfavoring associative binding. As expected, the molecular weights increased and the total number of branches decreased as the polymerization temperature was reduced. This observation is consistent with the observations by Brookhart employing the diimine Ni systems where chain migration and associative displacement steps are retarded at lower temperatures. In addition, we examined the effects of the cocatalysts in the ethylene polymerizations. The results are summarized in Table 3. Higher concentrations of $Ni(COD)_2$ resulted in higher yields of polyethylene, which can be attributed to a greater number of catalyst sites initiated. Mw's and PDI's also increase with increasing $Ni(COD)_2$. To look at the generality of function of the cocatalyst, we surveyed another well-known phosphine sponge, $B(C_6F_5)_3$, known to form 1:1 adducts with PPh_3. Yields using $B(C_6F_5)_3$ are comparable to $Ni(COD)_2$ while the Mw's are significantly lower.

Table 3. Polymerization of Ethylene by **20** Varying the Cocatalyst.[a]

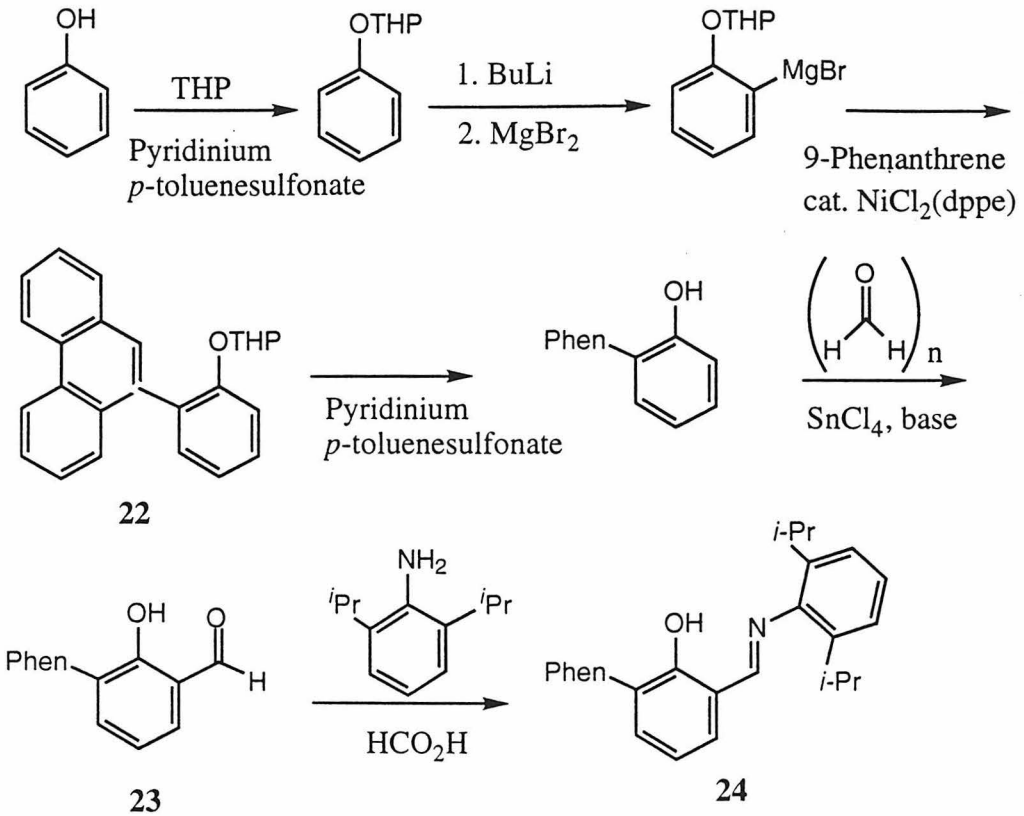
Entry	Catalyst	Cocatalyst (equiv)	Yield	$\bar{M}w$	PDI	Total Branches[b]
1	**20**	$Ni(COD)_2$ (2)	3.5 g	18400	1.84	55
2	**20**	$Ni(COD)_2$ (8)	4.8 g	43200	2.34	40
3	**20**	$B(C_6F_5)_3$ (1)	4.2 g	10400	1.69	55
4	**20**	$B(C_6F_5)_3$ (2)	3.3 g	11000	2.55	45

[a] All polymerizations reactions were carried out at 0.9 mM [catalyst], 80 psi of ethylene, rt for 40 minutes. [b] The number of $C_1 + C_2 + C_3 + C_4$ branches per 1000 carbons.

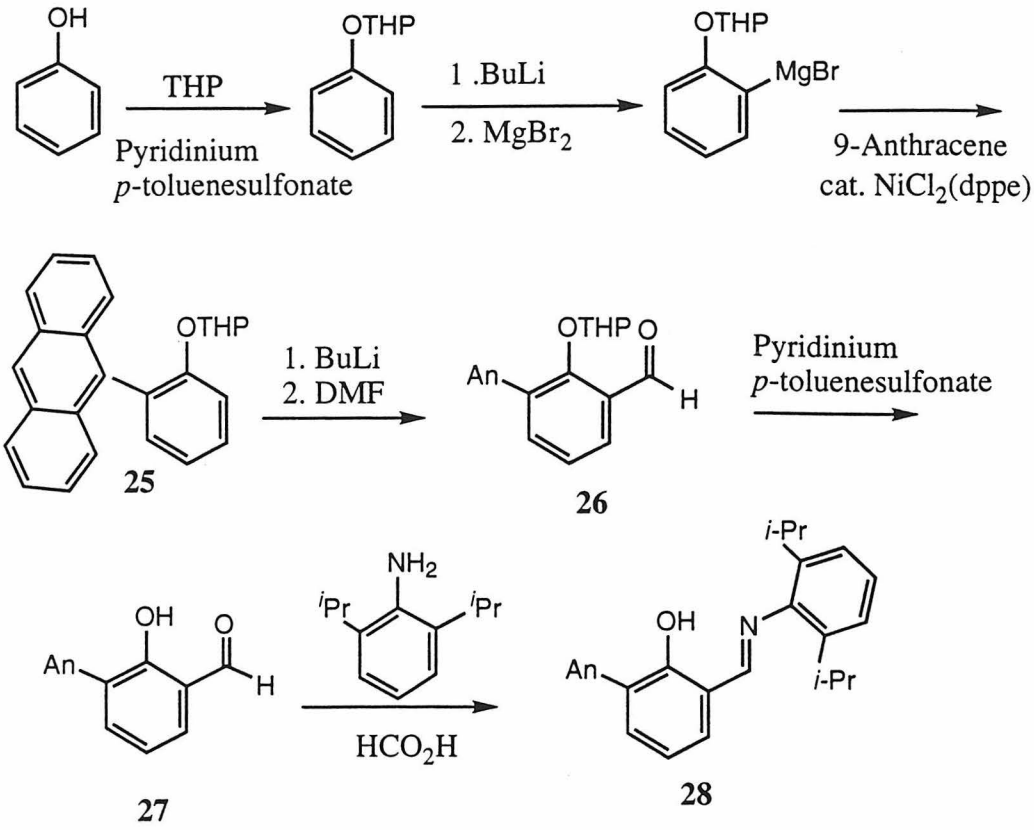
Synthesis of [O-3-(9-Phenanthrene)C_6H_3-*o*-C-N=C-2,6-C_6H_3(*i*-Pr)$_2$] Ni(PPh$_3$)(Ph) and [O-3-(9-Anthracene)C_6H_3-*o*-C-N=C-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh$_3$)(Ph). Due to the success of adding bulky substituents (Ph and *t*-Bu) to the 3-position of the salicylaldimine ring, we decided to design ligands with more sterically demanding substituents. We targeted the synthesis salicylaldimine ligands employing 9-phenanthrene and 9-anthracene substituents in the 3-position. The synthetic strategy is illustrated in Scheme 5. Phenol was first protected as the tetrahydropyran (THP) adduct using THP and catalytic pyridinium *p*-toluenesulfonate.[20] Treatment of the THP-protected phenol with BuLi and subsequently $MgBr_2$ formed the Grignard reagent, which was then coupled to 9-phenanthrene with catalytic $NiCl_2$(dppe) to form **22**.[21] Deprotection of **22** resulted in the free 9-phenanthrene substituted phenol. Formylation of the phenol with paraformaldehyde using a $SnCl_4$ catalyst resulted in the formation of the substituted salicylaldehyde **23.** This step proceeded in very low yields (25.9%) and was the bottleneck in this synthesis. Finally, reaction of **23** with 2,3-diisopropylaniline

using catalytic formic acid generated the 9-phenanthrene substituted salicylaldimine ligand **24**.

Scheme 5

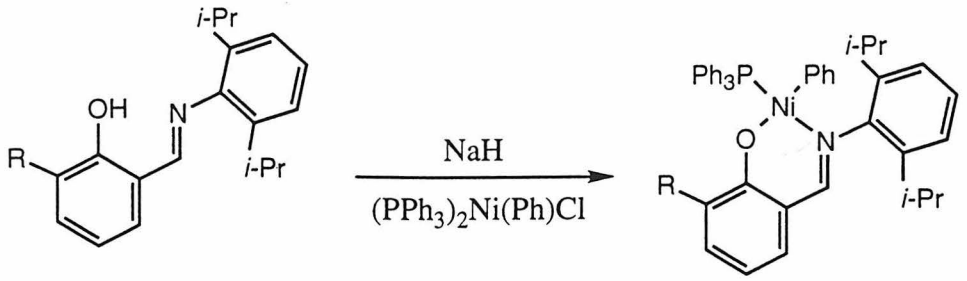


Scheme 6



The synthesis of the 9-anthracene substituted salicylaldimine ligand followed essentially the same strategy as the synthesis of **24** (Scheme 6). The procedure was analogous until the formylation step. Formylation of **25** proceeded by first treating with BuLi in which the THP oxygen directs the ortho-lithiation followed by quenching with DMF to form the THP-protected salicylaldehyde **26**.[22] The formylation of this derivative proceeded in much higher yields (97%) than the $SnCl_4$-catalyzed coupling of **22** to paraformaldehyde. However, we were unable to use this strategy for the phenanthrene derivative because non-selective lithiation. Deprotection of **26** with pyridinium *p*-toluenesulfonate followed by condensation with 2,6-diisopropylaniline formed the 9-anthracene substituted salicylaldimine **28**. Ligands **24** and **28** were deprotonated with

NaH and treated with $(PPh_3)_2Ni(Ph)Cl$ to form the corresponding Ni(II) complexes [O-3-(9-Phenanthrene)C_6H_3-*o*-C-N=C-2,6-C_6H_3(*i*-Pr)$_2$] (**29**) and [O-3-(9-Anthracene)C_6H_3-*o*-C-N=C-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph) (**30**) in high yields (eq 14).



(14)

R = 9-phenanthrene **24**
R = 9-anthracene **28**

R = 9-phenanthrene **29**
R = 9-anthracene **30**

Polymerization of Ethylene Catalyzed by Complexes 29 and 30. Exposure of the Ni(II) complexes to **29** and **30** to ethylene produced moderate molecular weight polyethylene. The polymerization reactions are summarized in Table 4.

The nickel catalysts, **29** and **30**, exhibited greater activities than the *t*-Bu (**20**) and phenyl derivatives (**21**). The yields for **29** and **30** were on the average 4-5 times greater than for **20** and **21** under similar reaction conditions. Polymerization activities are greatly decreased as the catalyst loads were decreased (Table 4, entries 1 and 2). Activities exhibited little variance with the different cocatalysts: $Ni(COD)_2$ and $B(C_6F_5)_3$ exhibited similar activities (Table 4 entries 1, 2, 6, and 7). As expected, the total number of branches was somewhat lower for catalysts **29** and **30** as these catalyst should possess greater in-plane bulk, which would limit chain migration processes. In addition, it appears that this greater in-plane bulk is able to labilize the bound PPh_3: the polymerization of ethylene occurs in the absence of a cocatalyst (Table 4, entry 5). A cocatalyst is required for all of the less bulky derivatives examined here.

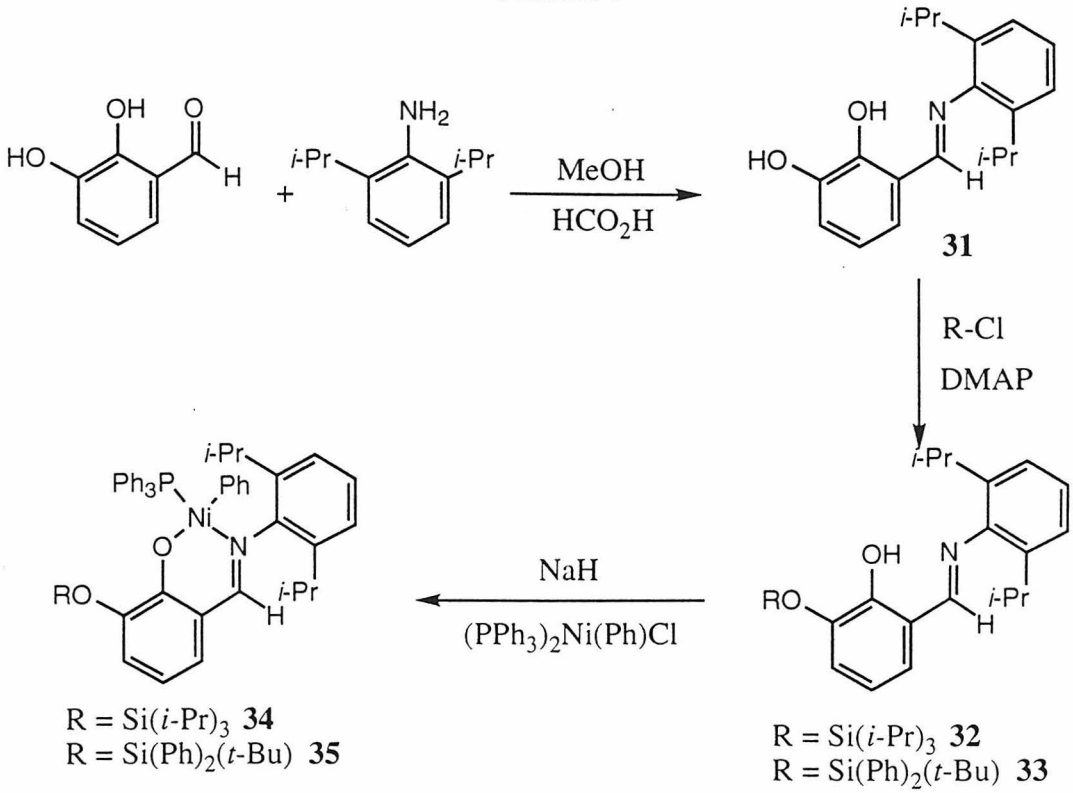
Table 4. Polymerization of Ethylene by **29** and **30**.[a]

Entry	Catalyst	[Cat] mM	Cocatalyst	Yield	$\overline{M}w$	PDI	Total Branches[c]
1	**29**	0.9	$Ni(COD)_2$	7.0	37700	3.85	30
2	**29**	0.5	$Ni(COD)_2$	0.8	56700	2.30	5
3	**29**	0.9	$B(C_6F_5)_3$	7.0	49500	6.84	35
4	**29**	0.9	$B(C_6F_5)_3$[b]	5.0	42500	3.63	20
5	**29**	0.9	none	0.4	14900	2.53	15
6	**30**	0.9	$Ni(COD)_2$	7.4	N.A.	N.A.	N.A
7	**30**	0.9	$B(C_6F_5)_3$	5.0	23800	7.19	50

[a] All polymerizations reactions were carried out at 80 psi of ethylene at rt for 15 min. Only 2 equiv of cocatalyst was used unless otherwise specified. [b] Only 0.5 equiv of $B(C_6F_5)_3$ used in the polymerization reaction. [c] Total number of $C_1 + C_2 + C_3 + C_4$ branches per 1000 carbons.

Synthesis of Other Ligand Systems. Due to the success we achieved utilizing bulky substituents at the 3-position of the salicylaldimine ligand, we explored the synthesis of ligands that incorporate bulky siloxane groups in this position (Scheme 7).

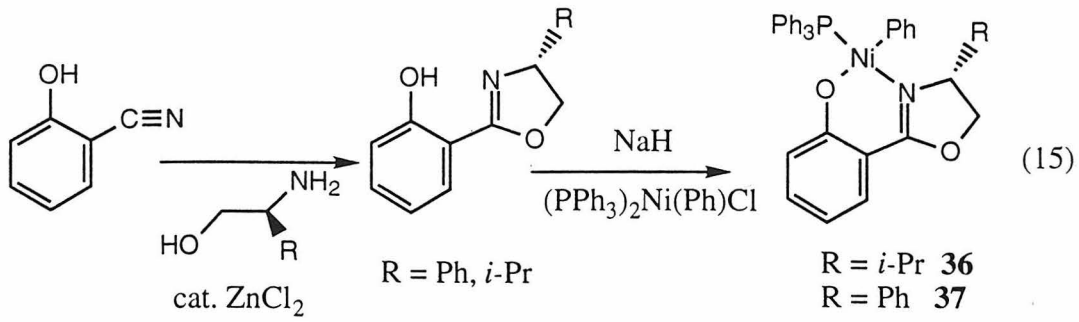
Scheme 7



The synthesis was carried out by first treating 2,3-dihydroxybenzaldehyde with diisopropylamine to form the Schiff's base complex **31**. Treatment of **31** with an appropriate silyl chloride generated the 3-siloxy-substituted salicylaldimines (R = Si(*i*-Pr)$_3$, **32** and R = Si(Ph)$_2$(*t*-Bu), **33**). Deprotonation of **32** and **33** with NaH followed by reaction with $(PPh_3)_2Ni(Ph)Cl$ produced the corresponding Ni(II) complexes **34** and **35**.

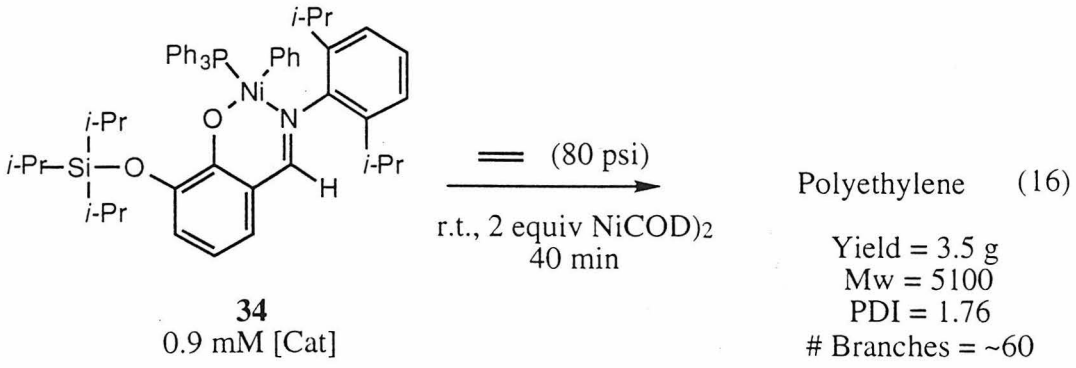
We also explored the synthesis of oxazole containing ligands due to their increased stability in Cu and Mn complexes as compared to their Schiff's base counterparts.[23] The sysntheses were carried out by treating 2-cyanophenol with an appropriate

enantiomerically pure aminoalcohols to form the 4,5-dihydro(2'-hydroxyphenyl)oxazoles. Deprotonation of the oxazoles with NaH followed by reaction with $(PPh_3)_2Ni(Ph)Cl$ yielded the corresponding Ni(II) complexes **36** and **37** (eq 15).



(15)

Polymerization of Ethylene Catalyzed by Complexes 34-37. Exposure of **34** to ethylene resulted in the formation of polyethylene (eq 16). Yields are similar to **20** (*t*-Bu derivative). The resulting polyethylene has a relatively low molecular weight and a higher number of branches as compared to catalysts derived from the substituted



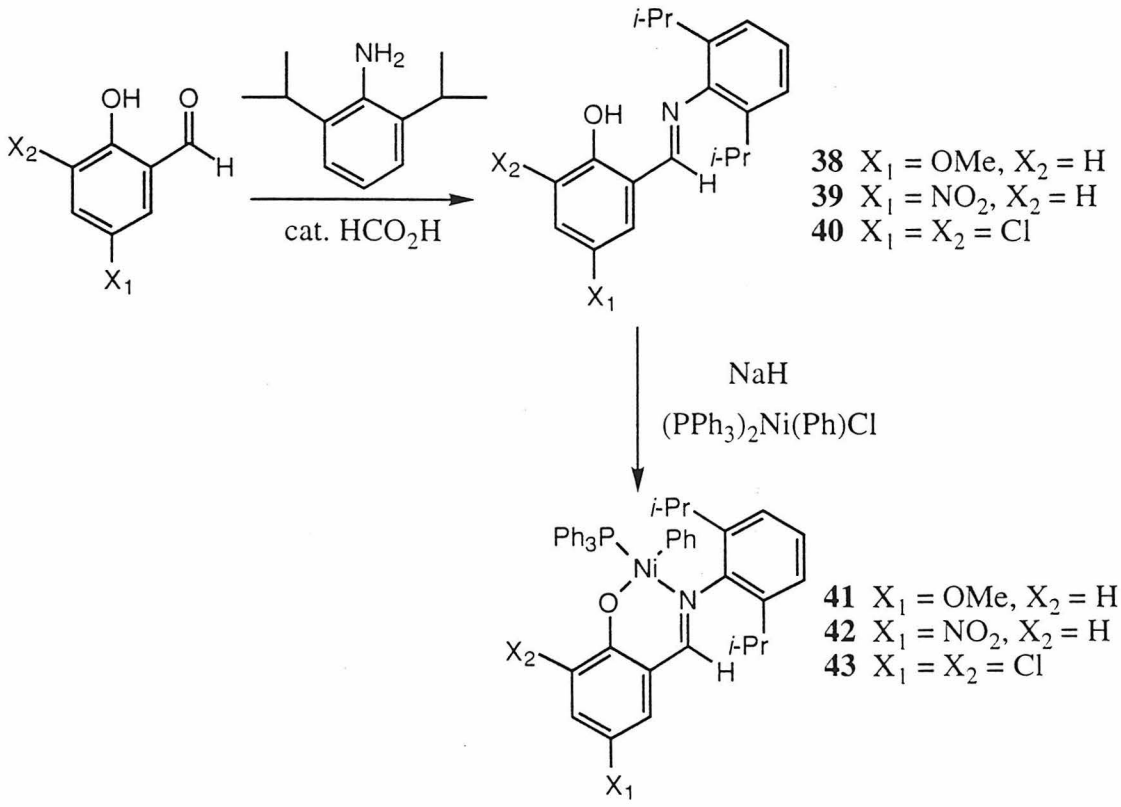
(16)

salicylaldimine ligands (*t*-Bu, Ph, phenanthrene, anthracene). Exposure of complexes **35-37** to ethylene resulted in little or no uptake of ethylene. Although this result was surprising, we surmised that the increased electron-donating abilities of the siloxane-

derived salicylaldimine ligands and the oxazoles could be detrimental to the catalytic activity of these complexes when compared to the other substituted salicylaldimine-derived Ni complexes. We then set out to test this hypothesis by synthesizing a series of aryl-substituted salicylaldimine ligands and their corresponding Ni(II) complexes.

Synthesis of [O-5-(NO_2)C_6H_4-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph), [0-5-(OMe)C_6H_4-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph), and [O-3,5-$Cl_2C_6H_4$-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Ni(PPh_3)(Ph). The synthesis of the aryl-substituted salicylaldimine ligands was accomplished in one step from readily available starting materials (**38-40**). The synthesis of the corresponding Ni complexes was also straightforward and proceeded in high yields (**41-43**) (Scheme 8).

Scheme 8



Polymerization of Ethylene Catalyzed by Complexes 41-43. Exposure of Ni complexes **41-43** to ethylene resulted in the formation of polyethylene. The results are summarized in Table 5.

Table 5. Polymerization of Ethylene by **16, 41-43.**[a]

Entry	Catalyst	[Cat] mM	Cocatalyst	Yield	$\overline{M}w$	PDI
1	**41**	0.9	$Ni(COD)_2$	1.0	7300	1.68
2	**16**	0.9	$Ni(COD)_2$	2.0	4000	1.54
3	**42**	0.9	$Ni(COD)_2$	8.0	366000	18.0
4	**43**	0.9	$Ni(COD)_2$[b]	1.5	22500	3.28

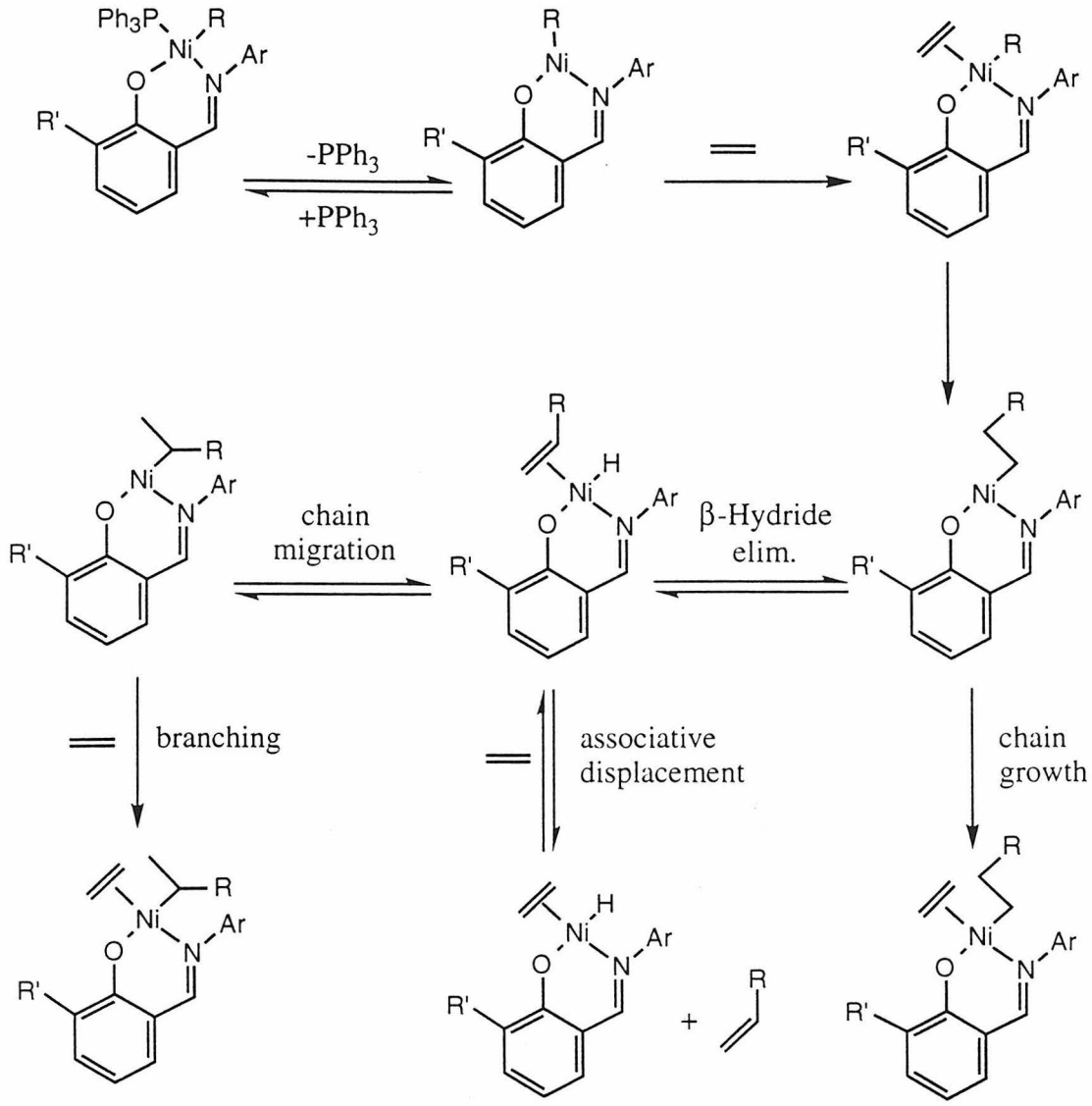
[a] All polymerizations reactions were carried out at 80 psi of ethylene at rt for 15 min. Only 2 equiv of cocatalyst was used unless otherwise specified. [b] Only 0.5 equiv of $B(C_6F_5)_3$ used in the polymerization reaction. [c] Total number of $C_1 + C_2 + C_3 + C_4$ branches per 1000 carbons.

The electron-deficient Ni complex **42** showed the greatest activity for the polymerization of ethylene and the relatively electron-rich Ni complex **41** showed the least activity. Polymerization with complex **42**, however, occurs with a relatively long induction period: ethylene uptake was neglible for 20 minutes. This observation is consistent with a mechanism in which phosphine dissociation is rate-determining. It appears that the electron-deficient salicylaldimine ligand strengthens the Ni-PPh_3 bond. Polymerization with complex **41** proceeded with a short induction period and slow ethylene uptake over a 40 minute period. Polymerization with **43** also proceeded with a relatively fast induction period; however, polymerization ceases after only 10 minutes of reaction.

Conclusions

In this investigation, several Ni-aryl complexes employing substituted salicylaldimine ligands were synthesized and their activities in ethylene polymerization were surveyed. Based on the activities of these various catalysts, we propose the following mechanistic scheme to explain the activities (Scheme 9). Catalyst must first lose PPh_3 to open up a coordination site, which is consistent with the observed induction period before ethylene

Scheme 9



uptake. The use of a cocatalyst [$Ni(COD)_2$ or BAr'_3] as a phosphine sponge facilitates phosphine dissociation equilibrium. However, if the R' group is sufficiently bulky enough (R = phenanthrene or anthracene), PPh_3 dissociation occurs without the use of a cocatalyst. Ethylene can then coordinate to the vacant coordination site. Insertion of the ethylene produces a Ni alkyl complex. The use of a bulky R' group favors the insertion process, which can rationalize why bulkier R' groups have greater activities. From this point, the new Ni alkyl can be rapidly trapped by ethylene to produce another alkyl-olefin complex as part of the chain growth process. Alternatively, the Ni alkyl can undergo β-hydride elimination to form the olefin-hydride complex. The olefin-hydride complex can either undergo primary insertion to reform the Ni-alkyl, or undergo secondary insertion to form a branched Ni-alkyl. Use of a bulky R' group disfavors the secondary insertion process, which is consistent with the observation that branching decreases with increasing size of R'.

Experimental Section

General Considerations. Manipulations of the Ni complexes were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. NMR experiments were also prepared inside a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with either a JEOL 400 (399.65 MHz ^{1}H; 100.40 MHz ^{13}C; 100.40 MHz ^{31}P; ^{31}P NMR data referenced to external H_3PO_4 where PPh_3 has a chemical shift at -5.4 ppm), or a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer.

Materials. Pentane, benzene, THF, diethyl ether, and toluene was dried and degassed by passage through solvent purification columns containing activated alumina and Cu.[24] Methylene chloride was dried by passage through solvent purification columns containing activated alumina and Cu. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Benzene-d_6 was dried over sodium benzophenone ketyl and then vacuum transferred. $NiCl(C_6H_5)(PPh_3)_2$,[15] (4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole,[21] and (4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole[21] were prepared according to known literature procedures. All other materials were of the highest purity from commercially available sources.

2-(Ph_2P)C_6H_4-C(H)=N-C_6H_5 (1)

To a benzene (20 mL) solution of 2-diphenylphosphinobenzaldehyde (1.0 g, 3.4 mmol) was added aniline (0.61 g, 6.5 mmol) and *p*-toluenesulfonic acid (50 mg, 0.3 mmol). The reaction was stirred at reflux for 4 h. After this time, the solvent was removed in vacuo and the remaining yellow oil was loaded onto a silica gel column and

eluted with 8:2 hexane:ethyl acetate. Removal of the solvent yielded 1.2 g (92%) of a crystalline, yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.05-8.37 (m, 19H), 9.24 (d, 1H, J_{HP} = 4.76 Hz); ^{13}C NMR (CD_2Cl_2): δ 121.2, 126.2, 128.5, 128.9 (d, J_{CP} = 6.7 Hz), 129.2, 129.5, 131.2, 133.8, 134.3 (d, J_{CP} = 20.1 Hz), 136.8 (d, J_{CP} = 9.8 Hz), 138.9 (d, J_{CP} = 20.7 Hz), 139.5 (d, J_{CP} = 17.1 Hz), 151.9, 158.9 (d, J_{CP} = 21.4 Hz); ^{31}P NMR (CD_2Cl_2): δ -12.05.

2-(Ph_2P)C_6H_4-C(H)=N-4-C_6H_4-NO_2 (2)

To a benzene (20 mL) solution of 2-diphenylphosphinobenzaldehyde (1.0 g, 3.4 mmol) was added 4-nitroaniline (0.95 g, 6.8 mmol) and *p*-toluenesulfonic acid (0.05 g, 0.30 mmol). The reaction was stirred at reflux for 8 h. After this time, the solvent was removed in vacuo and the remaining yellow oil was loaded onto a silica gel column and eluted with 7:3 hexane:ethyl acetate. Removal of the solvent yielded 0.84 g (59%) of a crystalline, yellow solid. ^{1}H NMR (CD_2Cl_2): δ 6.84-8.22 (m, 18H), 9.01 (d, 1H,J_{HP} = 5.12 Hz); ^{13}C NMR (CD_2Cl_2): δ 121.3, 124.9, 128.5, 128.9 (d, J_{CP} = 7.3 Hz), 129.1, 129.3, 131.9, 133.8, 134.2 (d, J_{CP} = 20.1 Hz), 136.8 (d, J_{CP} = 9.2 Hz), 138.3 (d, J_{CP} = 16.5 Hz), 139.7 (d, J_{CP} = 20.9 Hz), 145.5, 157.6, 161.3 (d, J_{CP} = 21.4 Hz); ^{31}P NMR (CD_2Cl_2): δ -11.27.

2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-$(Me)_2$ (3)

To a benzene (20 mL) solution of 2-diphenylphosphinobenzaldehyde (1.0 g, 3.4 mmol) was added 2,6-dimethylaniline (0.52 g, 4.3 mmol) and *p*-toluenesulfonic acid (0.05 g, 0.30 mmol). The reaction was stirred at reflux for 4 h. After this time, the solvent was removed in vacuo and the remaining yellow oil was loaded onto a silica gel column and eluted with 9:1 hexane:ethyl acetate. Removal of the solvent yielded 1.2 g (91%) of a crystalline, yellow solid. ^{1}H NMR (CD_2Cl_2): δ 2.01 (s, 3H), 6.99-8.44 (m, 17H), 9.06 (d, 1H,J_{HP} = 5.48 Hz); ^{13}C NMR (CD_2Cl_2): δ 18.2, 123.8, 127.3, 128.1,

128.9 (d, J_{CP} = 7.7 Hz), 129.2, 131.2, 133.6, 134.3 (d, J_{CP} = 26.8 Hz), 136.6 (d, J_{CP} = 9.2 Hz), 138.8 (d, J_{CP} = 20.1 Hz), 139.6 (d, J_{CP} = 17.7 Hz), 151.2, 161.3 (d, J_{CP} = 23.2 Hz); ^{31}P NMR (CD_2Cl_2): δ -13.36.

2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-(*i*-Pr)$_2$ (4)

To a benzene (20 mL) solution of 2-diphenylphosphinobenzaldehyde (1.6 g, 5.5 mmol) was added 2,6-diisopropylaniline (0.70 g, 6.2 mmol) and *p*-toluenesulfonic acid (0.10 g, 0.50 mmol). The reaction was stirred at reflux for 4 h. After this time, the solvent was removed in vacuo and the remaining yellow oil was loaded onto a silica gel column and eluted with 9:1 hexane:ethyl acetate. Removal of the solvent yielded 2.0 g (82%) of a crystalline, yellow solid. ^{1}H NMR (CD_2Cl_2): δ 1.16 (d, 6H, J_{HH} = 6.92 Hz), 2.94 (septet, 1H, J_{HH} = 6.92 Hz), 7.07-8.49 (m, 17H), 9.12 (d, 1H, J_{HP} = 8.40 Hz); ^{13}C NMR (CD_2Cl_2): δ 23.6, 28.1, 123.1, 124.3, 127.9, 128.9 (d, J_{CP} = 7.3 Hz), 129.1, 129.4, 131.3, 133.9, 134.2 (d, J_{CP} = 25.7 Hz), 136.6 (d, J_{CP} = 9.5 Hz), 137.8, 138.6 (d, J_{CP} = 20.8 Hz), 139.8 (d, J_{CP} = 18.3 Hz), 149.2, 160.8 (d, J_{CP} = 24.4 Hz); ^{31}P NMR (CD_2Cl_2): δ -14.37.

[2-(Ph_2P)C_6H_4-C(H)=N-C_6H_5]$NiBr_2$ (5)

In a Schlenk flask under an atmosphere of Ar was dissolved (DME)$NiBr_2$ (0.30 g, 0.97 mmol) and 2-(Ph_2P)C_6H_4-C(H)=N-C_6H_5 (0.36 mgs, 1.0 mmol) in CH_2Cl_2 (20 mL). The reaction was stirred at rt for 24 h. After this time, the solvent was removed in vacuo and the remaining red-brown solid was washed twice with hexane (10 mL) to yield 0.50 g (88%) of the title compound.

[2-(Ph_2P)C_6H_4-C(H)=N-4-C_6H_4-NO_2]$NiBr_2$ (6)

In a Schlenk flask under an atmosphere of Ar was dissolved (DME)$NiBr_2$ (0.30 g, 0.97 mmol) and 2-(Ph_2P)C_6H_4-C(H)=N-4-C_6H_4-NO_2 (0.42 g, 1.0 mmol) in CH_2Cl_2 (20

mL). The reaction was stirred at rt for 24 hours. After this time, the solvent was removed in vacuo, the remaining red-brown solid was washed twice with hexane (10 mL) to yield 0.57 g (93%).

[2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-$(Me)_2$]$NiBr_2$ (7)

In a Schlenk flask under an atmosphere of Ar was dissolved (DME)$NiBr_2$ (0.30 g, 0.97 mmol) and 2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-$(Me)_2$ (0.39 g, 1.0 mmol) in CH_2Cl_2 (20 mL). The reaction was stirred at rt for 24 hours. After this time, the solvent was removed in vacuo, the remaining red-brown solid was washed twice with hexane (10 mL) to yield 0.54 g (90%).

[2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-(*i*-Pr)$_2$]$NiBr_2$ (8)

In a Schlenk flask under an atmosphere of Ar was dissolved (DME)$NiBr_2$ (0.40 g, 1.3 mmol) and 2-(Ph_2P)C_6H_4-C(H)=N-2,6-C_6H_3-(*i*-Pr)$_2$ (0.60 g, 1.3 mmol) in CH_2Cl_2 (20 mL). The reaction was stirred at rt for 24 hours. After this time, the solvent was removed in vacuo, the remaining red-brown solid was washed twice with hexane (10 mL) to yield 0.83 g (96%).

NMR Observation of [2-(Ph_2P)C_6H_4-C(H)=N-C_6H_5]Pd(Me)Cl (9)

In an NMR tube under an atmosphere of N_2 was added 2-(Ph_2P)C_6H_4-C(H)=N-C_6H_5 (31 mg, 80 μmol) and (COD)Pd(Me)Cl (20 mg, 85 μmol) in CD_2Cl_2 (600 μL). Formation of product was observed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR (CD_2Cl_2): δ 0.47 (br s, 3H, Pd-C$\underline{H}_3$), 7.10-7.59 (m, 19 H), 8.15 (br s, 1H, ArN=C$\underline{H}$). ^{31}P NMR (CD_2Cl_2): δ 37.85.

NMR Observation of [2-(Ph_2P)C_6H_4-C(H)=N-4-$C_6H_4NO_2$]Pd(Me)Cl (10)

In an NMR tube under an atmosphere of N_2 was added 2-$(Ph_2P)C_6H_4$-C(H)=N-4-$C_6H_4NO_2$ (34 mg, 80 μmol) and (COD)Pd(Me)Cl (20 mg, 85 μmol) in CD_2Cl_2 (600 μL). Formation of product was observed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR (CD_2Cl_2): δ 0.50 (d, 3H, J_{HP} = 3.31 Hz, Pd-C*H*$_3$), 7.17-7.63 (m, 18 H), 8.13 (d, 1H, J_{HP} = 8.65 Hz, ArN=C*H*). ^{31}P NMR (CD_2Cl_2): δ 37.16.

NMR Observation of [2-$(Ph_2P)C_6H_4$-C(H)=N-2,6-C_6H_3-$(Me)_2$]Pd(Me)Cl (11)

In an NMR tube under an atmosphere of N_2 was added 2-$(Ph_2P)C_6H_4$-C(H)=N-2,6-C_6H_3-$(Me)_2$ (33 mg, 80 μmol) and (COD)Pd(Me)Cl (20 mg, 85 μmol) in CD_2Cl_2 (600 μL). Formation of product was observed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR (CD_2Cl_2): δ 0.49 (d, 3H, J_{HP} = 3.50 Hz, Pd-C*H*$_3$), 1.95 (s, 3H, Ar-C*H*$_3$), 7.33-7.68 (m, 17 H), 8.07 (br s, 1H, ArN=C*H*). ^{31}P NMR (CD_2Cl_2): δ 35.05.

[2-$(Ph_2P)C_6H_4$-C(H)=N-2,6-C_6H_3-(i-Pr)$_2$]Pd(Me)Cl (12)

In a Schlenk flask under an atmosphere of Ar was added 2-$(Ph_2P)C_6H_4$-C(H)=N-2,6-C_6H_3-(^{i}Pr)$_2$ (0.38 g, 0.84 μmol) and (COD)Pd(Me)Cl (0.20 g, 0.85 μmol) in CH_2Cl_2 (50 mL). The reaction was stirred at rt for 30 min. After this time, the solvent was removed in vacuo to leave a light green solid. The solid was washed twice with pentane (20 mL) and dried in vacuo to yield 0.41 g (82%) of the product. ^1H NMR (CD_2Cl_2): δ 0.51 (d, 3H, J_{HP} = 3.80 Hz, Pd-C*H*$_3$), 0.68 (d, 3H, J_{HH} = 6.83 Hz, -CH-(C*H*$_3$)$_2$), 1.18 (d, 3H, J_{HH} = 6.83 Hz, -CH-(C*H*$_3$)$_2$), 2.87 (septet, 1H, J_{HH} = 6.83 Hz, -C*H*-$(CH_3)_2$), 6.99-7.52 (m, 17 H), 8.09 (br s, 1H, ArN=C*H*). ^{31}P NMR (CD_2Cl_2): δ 34.95.

2-(Ph_2P)-C_6H_4-CH_2-N(H)-2,6-C_6H_3(i-Pr)$_2$ (13)

In a Schlenk flask under an atmosphere of Ar, compound **4** (1.5 g, 3.3 mmol) was dissolved in THF (10 mL). To the solution was added 1.0 M BH_3·THF (10 mL, 10 mmol) and the reaction was stirred at reflux for 6 h. After this time, H_2O was added to

quench the excess BH_3, and 80 mL of aqueous 6M HCl was added. The THF was removed by distillation and the remaining aqeuous solution was adjusted to pH 9 with 50% w/w KOH solution. The aqueous solution was then extracted with CH_2Cl_2 and the organic layer was dried over Na_2SO_4. The solvent was removed by rotary evaporation to yield a milky, white oil. Dropwise addition of methanol caused a white solid to be precipitated, which was collected by filtration through a glass frit and washed with additional methanol to yield 1.2 g (80%) of a white solid. ^1H NMR ($CDCl_3$): δ 1.12 (d, 6H, J_{HH} = 6.84 hz), 3.43 (septet, 1H, J_{HH} = 6.84 Hz), 3.49 (br s, 1H), 4.41 (s, 2H), 6.90-7.67 (m, 17H); ^{13}C NMR ($CDCl_3$): δ 24.2, 27.5, 54.2, 123.4, 123.8, 127.5, 128.6, 128.7, 128.8, 129.1, 133.4, 133.6, 133.9, 142.8, 142.9, 144.0, 144.3. ^{31}P ($CDCl_3$): δ -14.57.

HOC_6H_4-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (14)

To a methanol (25 mL) solution of salicylaldehyde (10 g, 82 mmol) was added formic acid (1 mL) and 2,6-diisopropylaniline (21 g, 120 mmol). The resulting mixture was stirred for 1 h. After this time, a yellow solid precipitated out of solution. The solid was collected by filtration through a glass frit and washed with methanol (2 X 10 mL) to yield 21 g (90%) of a yellow solid. ^1H NMR (C_6D_6): δ 1.24 (d, 12H, J_{HH} = 6.94 Hz), 3.07 (septet, 2H, J_{HH} = 6.94 Hz), 7.02-7.48 (m, 7H), 8.39 (s, 1H), 13.12 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.5, 28.2, 117.2, 119.1, 123.3, 125.6, 132.5, 133.3, 138.8, 146.4, 161.3, 167.0.

C_4H_3N(H)-2-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (15)

To a benzene (50 mL) solution of 2-pyrrolecarboxaldehyde (5.0 g, 54 mmol) was added 2,6-diisopropylaniline (12 g, 70 mmol) and *p*-toluenesulfonic acid (40 mgs). The reaction was stirred under reflux for 24 h. After this time, the solution was concentrated under vacuum to yield a red-brown oil. Methanol (30 mL) was added to the oil which resulted in precipitation of a white solid. The solid was isolated by filtration through a

glass frit and washed with additional methanol to yield 6.8 g (50%) of a white solid. ^{1}H NMR (C_6D_6): δ 1.10 (d, 12H, J_{HH} = 6.90 Hz), 3.06 (septet, 2H, J_{HH} = 6.90 Hz), 6.17 (br s, 1H), 6.40 (t, 1H, J_{HH} = 2.54 Hz), 6.61(d, 1H, J_{HH} = 2.54 Hz), 7.10-7.18 (m, 3H), 7.95 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.6, 27.9, 109.8, 116.7, 123.2, 124.2, 124.5, 129.8, 139.0, 148.4, 152.7.

[OC_6H_4-*o*-C=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (16)

In a Schlenk flask was dissolved Na salt of **14** (0.59 g, 1.5 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.44 mmol) of in benzene (20 mL). The reaction was stirred at rt for 1 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the reaction. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.74 g (76%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.03 (d, 6H, J_{HH} = 6.84 Hz), 1.29 (d, 6H, J_{HH} = 6.84 Hz), 4.05 (septet, 2H, J_{HH} = 6.84 Hz), 6.31-7.69 (m, 27H), 7.93 (d, 1H, J_{HP} = 8.80 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.5, 28.8, 117.4, 120.0, 122.8, 125.3, 126.2, 128.3, 128.6, 129.7, 130.5, 131.0, 131.5, 133.3, 133.8, 134.0, 134.4 (d, J_{CP} = 9.77 Hz), 137.4, 140.1, 149.4, 159.6, 165.2; ^{31}P NMR (C_6D_6): δ 25.94. Anal. Calcd for $C_{43}H_{42}NNiOP$: C, 76.35; H, 6.25; N, 2.07. Found: C, 76.20; H, 6.64; N, 1.89.

[C_4H_3N-2-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (17)

In a Schlenk flask was dissolved the Li salt of **15** (0.24 g, 0.72 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (0.50 g, 0.73 mmol) in Et_2O (20 mL). The reaction was stirred at rt for 1 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added and the reaction was cooled to -78 °C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.35 g (74%) of a yellow-orange

solid. ^{1}H NMR (C_6D_6): δ 1.11 (d, 6H, J_{HH} = 6.77 Hz), 1.30 (d, 6H, J_{HH} = 6.77 Hz), 3.96 (septet, 2H, J_{HH} = 6.77 Hz), 6.17 (br s, 1H), 6.40 (t, 1H, J_{HH} = 2.54 Hz), 6.61(d, 1H, J_{HH} = 2.54 Hz), 5.96-7.65 (m, 26H); ^{13}C NMR (C_6D_6): δ 22.6, 26.1, 28.9, 113.3, 117.9, 121.6, 122.6, 125.8, 125.9, 130.0, 130.1, 132.1, 132.7, 134.8 (d, J_{CP} = 10.8 Hz), 136.8, 140.3, 141.3, 142.4, 146.5, 162.3; ^{31}P NMR (C_6D_6): δ 33.10. Anal. Calcd for $C_{41}H_{41}N_2NiP$: C, 75.59; H, 6.34; N, 4.30. Found: C, 75.74; H, 6.41; N, 4.15.

HO-(3-*t*-Bu)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (18)

To a methanol (25 mL) solution of *t*-butylsalicylaldehyde (10 g, 82 mmol) was added formic acid (1 mL) and 2,6-diisopropylaniline (21 g, 120 mmol). The resulting mixture was refluxed for 10 h. After this time, the methanol was removed by rotary evaporation to yield a dark-brown oil. The oil was loaded onto a silica gel column and eluted with 90:10 hexane:ethyl acetate to yield 24 g (90%) of a viscous, orange oil. ^{1}H NMR (C_6D_6): δ 1.24 (d, 12H, J_{HH} = 6.85 Hz), 1.56 (s, 9H), 3.10 (septet, 2H, J_{HH} = 6.85 Hz), 6.94-7.49 (m, 6H), 8.39 (s, 1H), 13.71 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.5, 28.2, 34.9, 118.3, 118.6, 123.3, 125.4, 130.5, 130.8, 137.6, 139.0, 146.4, 160.7, 167.6.

HO-(3-Ph)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (19)

To a methanol (15 mL) solution of 6-phenyl salicylaldehyde (2.4 g, 12 mmol) was added formic acid (0.50 mL) and 2,6-diisopropylaniline (2.8 g, 16 mmol). The resulting mixture was refluxed for 10 h. After this time, the methanol was cooled to rt at which time yellow crystals precipitated from the solution. The crystals were collected by filtration and washed with methanol (2 X 10 mL) to yield 3.0 g (70%) of a yellow solid. ^{1}H NMR (C_6D_6): δ 1.01 (d, 12H, J_{HH} = 6.88 Hz), 2.96 (septet, 2H, J_{HH} = 6.88 Hz), 7.05-7.74 (m, 11H), 7.92 (s, 1H), 13.90 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.5, 28.5, 119.2, 119.3, 123.5, 125.9, 127.4, 127.7. 129.9, 130.8, 131.9, 134.7, 138.0, 138.9, 146.8, 159.4, 167.6.

[O-(3-*t*-Bu)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$] Nickel(phenyl)(PPh_3) (20)

In a Schlenk flask was dissolved the Na salt of **18** (2.1 g, 4.8 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (3.1 g, 4.4 mmol) in THF (50 mL). The reaction was stirred at rt for 1.5 h. After this time, the reaction was filtered by cannula filtration and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring and the reaction was cooled to -78 °C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 3.5 g (83%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.93 (s, 9H), 1.08 (d, 6H,J_{HH} = 5.88 Hz), 1.22 (d, 6H,J_{HH} = 5.88 Hz), 4.28 (septet, 2H, J_{HH} = 5.88 Hz), 6.21-7.83 (m, 26H), 7.97 (d, 1H, J_{HP} = 9.12 Hz); ^{13}C (C_6D_6): δ 22.7, 25.5, 28.9, 29.8, 34.6, 113.9, 120.2, 121.0, 122.8, 125.0, 125.9, 128.3, 128.5, 129.1, 129.7, 131.5, 131.8, 132.2, 133.3, 134.9 (d, J_{CP} = 10.4 Hz), 137.0, 140.8, 141.9, 150.2, 166.1, 166.8; ^{31}P NMR (C_6D_6): δ 23.35. Anal. Calcd for $C_{47}H_{50}NNiOP$: C, 77.06; H, 6.88; N, 1.91. Found: C, 76.93; H, 6.81; N, 1.63.

[O-(3-Ph)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (21)

In a Schlenk flask was dissolved the Na salt of **19** (0.56 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at reflux for 1 h. After this time, the reaction was filtered by cannula filtration and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the vigorously stirred solution. A light-green solid precipitated from solution, and was isolated by cannula filtration to yield 0.84 g (89%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.12 (d, 6H, J_{HH} = 6.56 Hz), 1.21 (d, 6H, J_{HH} = 6.56 Hz), 3.31 (s, 3H), 4.11 (septet, 2H, J_{HH} = 6.56 Hz), 3.29 (s, 3H), 6.18-7.80 (m, 31H), 7.99 (d, 1H, J_{HP} = 9.52 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.4, 119.8, 121.1, 122.7, 125.0, 126.0, 127.4, 128.6, 129.4, 129.6, 131.7, 132.1, 134.0, 134.3, 13.4.4 (d, J_{CP} = 9.76 Hz), 135.3,

136.8, 137.8, 140.1, 140.7, 150.0, 163.7, 166.5; ^{31}P NMR (C_6D_6): δ 21.87. Anal. Calcd for $C_{49}H_{46}NNiOP$: C, 78.20; H, 6.16; N, 1.86. Found: C, 77.69; H, 6.36; N, 1.42.

2-(9-Phenanthrene)phenol·tetrahydropyran adduct (22)

A solution of the THP-protected phenol (10 g, 56 mmol) in diethyl ether (100 mL) was treated at rt with BuLi (44 mL, 70 mmol) for 4.5 h. A solution of $MgBr_2$ was separately prepared by slowly adding 1,2-dibromoethane (5.3 mL, 62 mmol) to Mg turnings (1.6 g, 67 mmol) in diethyl ether (100 mL), and stirred for 4 h. The Li-salt was added via cannula to the $MgBr_2$ solution to form the Grignard reagent. This solution was added to a cooled solution (-78°C) of 9-bromophenanthrene (9.7 g, 38 mmol) and $NiCl_2$(diphenylphosphinoethylene) (0.62 g, 1.2 mmol). The mixture was slowly warmed to rt and heated at reflux overnight. After this time, the reaction mixture was poured through a short silica gel column with 1:1 dichloromethane:hexane. The solvent was removed under vacuum to leave an orange, viscous oil. The yield of crude product was 14 g (70%). ^{1}H NMR ($CDCl_3$): δ 1.02-1.48 (m, 6H,), 3.75 (m, 2H), 5.42 (d, 1H, J_{HH} = 8.40 Hz), 7.20-8.81 (m, 13H); ^{13}C NMR (C_6D_6): δ 17.7, 18.3, 25.2, 30.1, 61.6, 62.0, 96.3, 96.9, 115.1, 115.4, 121.8, 121.9, 122.7, 126.1, 126.2, 126.3, 126.5, 126.7, 128.7, 129.2, 129.3, 130.1, 130.2, 130.5, 130.6, 131.5, 131.6, 131.7, 131.9.

2-(Phenanthrene)salicylaldehyde (23)

To a solution of 2-(9-phenanthrene)phenol (6.8 g, 25 mmol) and 2,6-lutidine(4.6 g, 43 mmol) in toluene (50 mL) was slowly added $SnCl_4$ (0.75 mL, 6.4 mmol). The solution was stirred at rt for 20 min. Paraformaldehyde was added (4.3 g, 140 mmol) and the reaction was stirred at 110°C for 12 h. After cooling to rt, the reaction mixture was poured into water (30 mL) and adjusted to pH 1 with concentrated HCl. The mixture was extracted with diethyl ether (500 mL), and the organic layer was washed twice with sat. brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation to leave a

yellow oil. The oil was loaded onto a silica gel column and eluted with 9:1 hexane:ethyl acetate. The yield of product was 1.9 g (26%). ^{1}H NMR ($CDCl_3$): δ 7.21-8.78 (m, 12H), 10.02 (s, 1H), 11.32 (s, 1H); ^{13}C NMR (C_6D_6): δ 120.0, 120.6, 122.7, 123.0, 126.6, 126.9, 127.0, 128.5, 128.8, 130.5, 130.8, 131.5, 133.8, 139.1, 159.6, 196.9.

HO-3-(9-Phenanthrene)C_6H_3-*o*-C(H)-N=C-2,6-C_6H_3(*i*-Pr)$_2$ (24)

2-(9-Phenanthrene)salicylaldehyde (1.9 g, 6.4 mmol), 2,6-diisopropylaniline (1.4 g, 7.9 mmol), and *p*-toluenesulfonic acid (65 mg, 0.34 mmol) was dissolved in benzene (27 mL). The solution was stirred at reflux overnight. After this time, the benzene was removed under vacuum. To the resulting oil was added hexane (100 mL) under vigorous stirring at which time a white solid precipitated. The solid was collected by filtration through a glass frit. A second crop of product was obtained from the filtrate to yield 1.7 g (58%). ^{1}H NMR ($CDCl_3$): δ 1.22 (d, 12H, J_{HH} = 6.90 Hz), 3.07 (septet, 2H, J_{HH} = 6.90 Hz), 7.14-8.90 (m, 15H), 8.46 (s, 1H), 13.45 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.8, 28.2, 119.0, 122.7, 123.0, 123.4, 125.0, 126.6, 126.8, 127.2, 128.5, 128.9, 129.3, 130.4, 130.6, 131.2, 131.7, 132.2, 135.6, 138.9, 159.3, 166.9.

2-(Anthracene)phenol·tetrahydropyran adduct (25)

In a three-necked, 250 mL flask under an atmosphere of Ar was added Mg turnings (2.1 g, 87 mmol) in THF (20 mL). A few drops of 1,2-dibromoethane was added to activate the Mg. Then a solution of the THP-protected 2-bromophenol (22 g, 87 mmol) in THF (70 mL) was added dropwise, and the reaction was stirred at reflux overnight. After this time, the resulting slurry was added by cannula to a solution of 9-bromoanthracene (22 g, 88 mmol) and $NiCl_2$(dppe) (1.4 g, 2.6 mmol) in THF (175 mL). The resulting solution was heated at reflux for 4 days. After this time, the solvent was removed in vacuo, and the oily residue was chromatographed on a silica gel column with 90:10 hexane:ethyl acetate. Removal of solvent yielded 10 g (34%) of a white crystalline

solid. ^{1}H NMR ($CDCl_3$): δ 0.87-1.30 (m, 6H), 3.42 (m, 1H), 3.60 (m, 1H), 5.30 (s, 1H), 7.25-8.49 (m, 13H), ^{13}C NMR (C_6D_6): δ 17.7, 24.9, 30.0, 61.6, 61.9, 96.1, 96.4, 115.3, 115.8, 121.4, 121.7, 124.7, 125.2, 126.0, 126.6, 127.1, 127.5, 127.8, 128.2, 128.6, 129.0, 130.2, 130.3, 131.3, 132.5, 132.9, 133.9, 155.4.

2-(Anthracene)salicylaldehyde·tetrahydropyran adduct (26)

To a diethyl ether (250 mL) solution of theTHP-protected adduct of 2-(9-anthracene)phenol was added *n*-BuLi (28 mL, 43 mmol) dropwise. The resulting solution was stirred at rt for 4.5 h. After this time, the solution was cooled to -78°C and DMF (5.4 mL, 70 mmol) was added to the reaction, which was allowed to warm to rt. After this time, the reaction was quenched with H_20 and extracted with diethyl ether (200 mL). The organic layer was separated and dried with Na_2SO_4. The solvents were removed by rotary evaporation to yield a yellow solid. The solid was washed with hexane (50 mL) and dried in vacuo to yield 5.0 g (60%) product. ^{1}H NMR ($CDCl_3$): δ 0.56-1.97 (m, 6H), 2.89 (m, 1H), 3.48 (m, 1H), 4.27 (m, 1H), 7.46-8.10 (m, 13H), 8.57 (s,1H), 10.62 (s, 1H); ^{13}C NMR (C_6D_6): δ 19.5, 24.6, 29.9, 64.2, 102.4, 124.6, 125.5, 126.1, 126.2, 126.5, 127.6, 128.0, 128.4, 128.7, 130.0, 130.4, 130.8, 131.2, 131.3, 131.9, 132.9, 159.0, 191.8.

2-(Anthracene)salicylaldehyde (27)

The THP-protected 2-(9-anthracene)salicylaldehyde (8.4 g, 22 mmol) was dissolved in ethanol (75 mL) and THF (100 mL). To the solution was added pyridinium *p*-toluenesulfonate (0.28 g, 1.1 mmol), and the reaction was stirred at reflux overnight. The solvents were removed in vacuo to yield 6.7 g (99%) of crude product. ^{1}H NMR ($CDCl_3$): δ 7.25-8.55 (m, 13H,), 10.05 (s, 1H), 11.22 (s, 1H); ^{13}C NMR (C_6D_6): δ 120.0, 120.9, 125.3, 125.9, 126.1, 127.3, 127.6, 128.8, 130.3, 130.8, 131.5, 134.0, 140.4, 159.9, 196.9.

HO-3-(9-Anthracene)C_6H_3-*o*-C(H)-N=C-2,6-C_6H_3(*i*-Pr)$_2$ (28)

2-(Anthracene)salicylaldehyde (6.5 g, 22 mmol), 2,6-diisopropylaniline (4.6 g, 26 mmol), and *p*-toluenesulfonic acid (215 mg, 1.1 mmol) were dissolved in benzene (250 mL) and stirred under reflux for 3 h in a Dean-Stark apparatus. After this time, the solvent was removed in vacuo, and the resulting residue was washed with hexane (100 mL) and methanol (20 mL), and dried in vacuo. The yield of product was 8.8 g (88%). ^{1}H NMR ($CDCl_3$): δ 1.23 (d, 12H, J_{HH} = 6.90 Hz), 3.09 (septet, 2H, J_{HH} = 6.90 Hz), 7.23-8.52 (m, 15H), 8.59 (s, 1H), 13.33 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.8, 28.2, 119.0, 119.1, 123.4, 125.2, 125.6, 125.7, 126.7, 127.0, 127.3, 128.5, 128.8, 130.5, 131.6, 132.4, 132.5, 136.8, 138.9, 146.3, 159.6, 166.8.

[O-3-(9-Phenanthrene)C_6H_3-*o*-C(H)-N=C-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (29)

In a Schlenk flask was dissolved the Na salt of **24** (0.87 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.40 mmol) in benzene (20 mL). The reaction was stirred at rt for 1.5 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.92 g (75%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.08 (d, 6H, J_{HH} = 6.96 Hz), 1.19 (d, 6H, J_{HH} = 6.96 Hz), 1.21 (d, 6H, J_{HH} = 6.96 Hz), 1.32 (d, 6H, J_{HH} = 6.96 Hz), 4.16 (septet, 2H, J_{HH} = 6.96 Hz), 6.14-8.37 (m, 35H), 8.13 (d, 1H, J_{HP} = 11.36 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.2, 119.9, 121.2, 122.8, 124.5, 124.7, 124.9, 125.6, 126.1, 127.2, 127.4, 128.4, 128.9, 130.5, 130.8, 131.1, 131.5, 131.8, 133.5 (d, J_{CP} = 13.4 Hz), 134.7, 136.6, 137.4, 138.3, 140.7,

145.2, 146.4, 150.1, 165.2, 166.7; ^{31}P NMR (C_6D_6): δ 25.09. Anal. Calcd for $C_{57}H_{50}NNiOP$: C, 80.29; H, 5.91; N, 1.64. Found: C, 80.06; H, 6.14; N, 1.25.

[O-3-(9-Anthracene)C_6H_3-*o*-C(H)-N=C-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (30)

In a Schlenk flask was dissolved the Na salt of **28** (0.53 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (2.0 g, 2.9 mmol) in benzene (20 mL). The reaction was stirred at rt for 1.5 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring and the reaction was cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.71 mg (78%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.14 (d, 6H, J_{HH} = 6.56 Hz), 1.18 (d, 6H, J_{HH} = 6.56 Hz), 4.16 (septet, 2H, J_{HH} = 6.56 Hz), 6.17-7.83 (m, 40H), 8.15 (d, 1H, J_{HP} = 11.32 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.2, 119.9, 121.2, 122.8, 124.5, 124.7, 124.9, 125.6, 126.1, 127.2, 127.4, 128.4, 128.9, 130.5, 130.8, 131.1, 131.5, 131.8, 133.5 (d, J_{CP} = 13.4 Hz), 134.7, 136.6, 137.4, 138.3, 140.7, 145.2, 146.4, 150.1, 165.2, 166.7; ^{31}P NMR (C_6D_6): δ 22.99. Anal. Calcd for $C_{57}H_{50}NNiOP$: C, 80.29; H, 5.91; N, 1.64. Found: C, 79.77; H, 6.09; N, 1.49.

2,3-Dihydroxy, 1-(2,6)-diisopropyl)benzaldimine (31)

In a round-bottom flask was dissolved 10 g (72 mmol) of 1,2-dihydroxybenzaldehyde, 2,6-diisopropylaniline (16 g, 90 mmol), and formic acid (1 mL) in methanol (20 mL). The solution was stirred vigorously for 5 min at which time the light yellow-brown solution became dark red, and a light orange-red solid precipitated from solution. The solid was collected by filtration through a glass frit, washed twice with cold methanol (-20°C), and dried under vacuum to yield 22 g (98%). ^{1}H NMR (CD_2Cl_2): δ 1.27 (d, 12H, $_{HH}$ = 6.72 Hz), 3.11 (septet, 2H, J_{HH} = 6.72 Hz), 6.93 (t, 6H,

J_{HH} = 7.92 Hz), 7.04 (d, 1H, J_{HH} = 7.92 Hz), 7.15 (d, 1H, J_{HH} = 11.0 Hz) 7.29 (br s, 3H), 8.40 (s, 1H); ^{13}C NMR (CD_2Cl_2): δ 23.5, 28.4, 118.1, 118.3, 119.1, 123.2, 123.4, 126.0, 139.2, 145.4, 145.6, 149.7, 167.1.

HO-3-[O-Si(^{i}Pr)$_3$]C$_6$H$_3$-*o*-C(H)-N=C-2,6-C$_6$H$_3$(*i*-Pr)$_2$ (32)

In a Schlenk flask under an atmosphere of N_2 was dissolved **31** (3.0 g, 10 mmol), triisopropylsilylchloride (2.3 g, 12 mmol), and imidazole (0.96 g, 14 mmol) in DMF (40 mL). The reaction was stirred at rt for 4 h. After this time, Et_2O (250 mL) was added, and the solution was washed twice with water (2 X 100 mL). The Et_2O layer was dried with Na_2SO_4 and concentrated on a rotary evaporator to a yellow-orange oil. The oil was loaded onto a silica gel column and eluted with 95:5 hexane:ethyl acetate. Removal of solvent yielded 4.1 g (89%) of an orange oil. ^1H NMR (C_6D_6): δ 0.99 (d, 12H,J_{HH} = 6.86 Hz), 1.15 (d, 18H, J_{HH} = 6.83 Hz), 1.29 (septet, 3H, J_{HH} = 6.83 Hz), 2.93 (septet, 2H, J_{HH} = 6.86 Hz), 6.59-7.11 (m, 6H), 7.89 (s, 1H), 13.44 (s, 1H); ^{13}C NMR (C_6D_6): δ 20.4, 23.5, 26.7, 28.4, 118.5, 119.8, 123.5, 123.8, 124.9, 125.8, 130.1, 133.4, 135.9, 138.8, 144.8, 153.5, 167.4.

HO-3-[O-Si(Ph)$_2$(*t*-But)]C$_6$H$_3$-*o*-C(H)-N=C-2,6-C$_6$H$_3$(*i*-Pr)$_2$ (33)

In a Schlenk flask under N_2 atmosphere was dissolved **31** (3.0 g, 10 mmol), triisopropylsilylchloride (3.3g, 12 mmol), and imidazole (0.96 g, 14 mmol) in DMF (40 mL). The reaction was stirred at rt for 4 h. After this time, Et_2O (250 mL) was added and the solution was washed twice with water (2 X 100 mL). The Et_2O layer was dried with Na_2SO_4 and concentrated on a rotary evaporator to a yellow-orange oil. The oil was loaded onto a silica gel column and eluted with 90:10 hexane:ethyl acetate. Removal of solvent yielded 4.4 g (83%) of an orange oil. ^1H NMR (C_6D_6): δ 0.98 (d, 12H,J_{HH} = 6.84 Hz), 1.26 (s, 9H), 2.90 (septet, 2H, J_{HH} = 6.84 Hz), 6.28 (t, 1H, J_{HH} = 7.77 Hz), 6.47 (d, 1H, J_{HH} = 7.77 Hz), 6.82 (d, 1H, J_{HH} = 7.92 Hz), 7.10 (m, 3H), 7.87 (m, 1H),

13.49 (s, 1H); ^{13}C NMR (C_6D_6): δ 13.3, 18.2, 23.4, 28.5, 118.8, 119.8, 123.5, 124.1, 124.9, 125.8, 138.8, 145.4, 146.9, 153.7, 167.4.

[O-3-[O-Si(^{i}Pr)$_3$]C$_6$H$_3$-*o*-C(H)-N=C-2,6-C$_6$H$_3$(*i*-Pr)$_2$]Nickel(phenyl) (PPh$_3$) (34)

In a Schlenk flask was dissolved the Na salt of **32** (0.70 g, 1.3 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (30 mL). The reaction of was stirred at rt for 30 min. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added and the reaction was cooled to -78°C and stored at this temperature for 2 days. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.70 g (57%) of a waxy, yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.84 (br s, 18H), 1.09 (d, 6H, J_{HH} = 7.32Hz), 1.21 (d, 6H, J_{HH} = 7.32 Hz), 4.20 (septet, 2H, J_{HH} = 7.32 Hz), 6.15-7.80 (m, 30H), 7.97 (d, 1H, J_{HP} = 8.72 Hz); ^{13}C NMR (C_6D_6): δ 13.0, 18.0, 22.8, 25.5, 28.9, 113.1, 120.4, 120.7, 121.0, 122.7, 125.0, 125.9, 126.2, 129.5, 132.4, 132.8, 134.1, 134.8 (d, J_{CP} = 9.76 Hz), 136.7, 138.0, 140.7, 149.2, 150.0, 159.0, 166.0; ^{31}P NMR (C_6D_6): δ 23.13.

[O-3-[O-Si(Ph)$_2$(*t*-Bu)]C$_6$H$_3$-*o*-C(H)-N=C-2,6-C$_6$H$_3$(*i*-Pr)$_2$ Nickel(phenyl) (PPh$_3$) (35)

In a Schlenk flask was dissolved the Na salt of **33** (0.81 g, 1.3 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (30 mL). The reaction was stirred at rt for 1.5 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring, and the reaction was cooled to -25°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.92 g (68%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.52 (s, 9H), 1.05 (d, 6H,J_{HH} = 6.60 Hz), 1.21 (d, 6H, J_{HH} = 6.60 Hz), 4.12 (septet, 2H, J_{HH} = 6.60 Hz), 6.18-7.75 (m,

40H), 7.94 (d, 1H, J_{HP} = 9.16 Hz); ^{13}C NMR (C_6D_6): δ 18.8, 22.7, 25.5, 26.3, 28.8, 99.8, 113.1, 120.5, 121.1, 122.5, 122.9, 125.0, 126.2, 127.5, 129.6, 130.0, 132.5, 133.6, 134.9 (d, J_{CP} = 9.76 Hz), 135.7, 136.7, 140.8, 148.6, 150.0, 155.6, 158.8, 159.1, 166.2; ^{31}P NMR (C_6D_6): δ 22.78. Anal. Calcd for $C_{59}H_{60}NNiO_2PSi$: C, 75.96; H, 6.48; N, 1.50. Found: C, 75.57; H, 6.74; N, 1.03.

[(4S)-4,5-dihydro-2-(2'-oxidophenyl-χO)-4-isopropyloxazole-χN)]Nickel(phenyl)(PPh$_3$) (36)

In a Schlenk flask was dissolved the Na salt of (4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole (470 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at rt for 1.5 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~3 mL. Pentane (30 mL) was added with vigorous stirring and the reaction was cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.54 g (62%) of a yellow-orange solid. ^1H NMR (C_6D_6): δ 0.24 (d, 3H, J_{HH} = 8.80 Hz), 0.63 (d, 3H, J_{HH} = 8.80 Hz), 2.24 (septet, 1H, J_{HH} = 8.80 Hz), 2.92 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ = 2.92 Hz), 3.36 (t, 1H, J_{HH} = 8.80 Hz), 3.64 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ = 2.92 Hz), 6.09-7.73 (m, 29H); ^{13}C NMR(C_6D_6): δ 68.0, 74.2, 109.3, 113.1, 121.6, 122.5, 122.6, 126.3, 127.4, 127.8, 127.9, 128.3, 128.6, 129.6, 131.1, 131.5, 133.5, 133.7, 133.9, 134.5 (d, J_{CP} = 10.4 Hz), 143.4, 149.1, 149.5, 166.5, 168.8; ^{31}P NMR (C_6D_6): δ 28.88.

[(4S)-4,5-dihydro-2-(2'-oxidophenyl-χO)-4-isopropyloxazole-χN)]Nickel(phenyl)(PPh$_3$) (37)

In a Schlenk flask was dissolved the Na salt of (4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole (530 g, 1.6 mmol) and

bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction of was stirred at rt for 1.5 h. After this time, the reaction was filtered by canula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring, and the reaction was cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.71 g (78%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 4.13 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ = 8.32 Hz), 4.22 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ = 8.32 Hz), 4.43 (t, 1H, J_{HH} = 8.32 Hz), 6.09-7.73 (m, 29H); ^{13}C NMR (C_6D_6): δ 68.0, 74.2, 109.3, 113.1, 121.6, 122.5, 122.6, 126.3, 127.4, 127.8, 127.9, 128.3, 128.6, 129.6, 131.1, 131.5, 133.5, 133.7, 133.9, 134.5 (d, J_{CP} = 10.4 Hz), 143.4, 149.1, 149.5, 166.5, 168.8; ^{31}P NMR (C_6D_6): δ 28.01. Anal. Calcd for $C_{39}H_{32}NNiO_2P$: C, 73.61; H, 5.07; N, 2.20. Found: C, 73.77; H, 5.24; N, 2.23.

HO-5-(OMe)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (38)

To a methanol (25 mL) solution of 4-methoxysalicylaldehyde (10 g, 66 mmol) was added formic acid (1.0 mL) and 2,6-diisopropylaniline (15 g, 65 mmol). The resulting mixture was stirred at rt for 1 h. After this time, the solution was stored at -25°C for 24 h. Yellow crystals precipitated from solution. The crystals were filtered and washed with -25 °C methanol (2 X 20 mL) to yield 15 g (72%) of a yellow solid. ^{1}H NMR (C_6D_6): δ 1.07 (d, 12H, J_{HH} = 8.56 Hz), 2.98 (septet, 2H, J_{HH} = 8.56 Hz), 3.29 (s, 3H), 6.60-7.16 (m, 6H), 7.86 (s, 1H), 12.89 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.5, 28.5, 55.3, 115.8, 118.7, 120.7, 123.5, 125.8, 138.7, 147.1, 152.7, 156.2, 167.

HO-5-(NO_2)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (39)

To a methanol (15 mL) solution of 4-nitrosalicylaldehyde (10 g, 60 mmol) was added formic acid (1.0 mL) and 2,6-diisopropylaniline (13 g, 75 mmol). The resulting mixture was stirred at rt for 10 min. After this time, yellow crystals precipitated from the

solution. The crystals were filtered and washed with methanol (2 X 20 mL) to yield 15 g (96%) of a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 1.19 (d, 12H, J_{HH} = 6.85 Hz), 2.96 (septet, 2H, J_{HH} = 6.85 Hz), 7.14 (d, 1H, J_{HH} = 9.18 Hz), 7.23 (br s, 3H), 8.30 (d, 1H, J_{HH} = 9.18 Hz), 8.40 (s, 1H), 8.43 (s, 1H), 14.30 (s, 1H); ^{13}C NMR (CD_2Cl_2): δ 23.6, 28.6, 118.6, 123.8, 126.6, 128.7, 128.8, 133.1, 139.1, 140.9, 145.2, 166.0, 167.4.

H0-3,5-$Cl_2C_6H_2$-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$ (40)

To a methanol (15 mL) solution of 4,6-dichlorosalicylaldehyde (10 g, 52 mmol) was added formic acid (1.0 mL) and 2,6-diisopropylaniline (12 g, 65 mmol). The resulting mixture was stirred at rt for 10 min. After this time, yellow crystals precipitated from the solution. The crystals were filtered and washed with methanol (2 X 20 mL) to yield 17 g (95%) of a yellow solid. ^{1}H NMR (C_6D_6): δ 0.98 (d, 12H, J_{HH} = 6.88 Hz), 2.77 (septet, 2H, J_{HH}= 6.88 Hz), 6.60-7.11 (m, 5H), 7.47 (s, 1H), 14.02 (s, 1H); ^{13}C NMR (C_6D_6): δ 23.2, 28.2, 119.6, 123.1, 123.2, 123.3, 126.2, 129.7, 132.9, 138.3, 145.4, 156.3, 165.5.

[O-5-(OMe)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (41)

In a Schlenk flask was dissolved the Na salt of **38** (0.64 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at rt for 1 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the vigorously stirred solution, which was then cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.88 g (86%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.08 (d, 6H, J_{HH} = 6.84 Hz), 1.30 (d, 6H, J_{HH} = 6.84 Hz), 3.31 (s, 3H), 4.09 (septet, 2H, J_{HH} = 6.84 Hz), 3.29 (s, 3H), 6.32-7.69 (m, 40H), 7.88 (d, 1H, J_{HP} = 9.28 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.8, 55.4, 113.1, 117.6, 121.2, 122.6, 123.7, 125.0, 125.2, 126.0, 129.41, 131.6, 132.0, 134.5

(d, J_{CP} = 9.76 Hz), 138.2, 140.6, 149.4, 150.4, 161.9, 165.7; ^{31}P NMR (C_6D_6): δ 24.63. Anal. Calcd for $C_{44}H_{44}NNiO_2P$: C, 74.59; H, 6.26; N, 1.98. Found: C, 74.01; H, 6.20; N, 1.65.

[0-5-(NO_2)C_6H_3-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (42)

In a Schlenk flask was dissolved the Na salt of **39** (0.56 g, 1.6 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at reflux 1 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the vigorously stirred solution. A light-green solid precipitated from solution, and was isolated by cannula filtration to yield 0.84 g (89%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.96 (d, 6H, J_{HH} = 6.96 Hz), 1.22 (d, 6H, J_{HH} = 6.96 Hz), 3.89 (septet, 2H, J_{HH} = 6.96 Hz), 5.91-7.90 (m, 30H), 8.06 (d, 1H, J_{HP} = 2.92 Hz); ^{13}C NMR (C_6D_6) : δ 22.2, 25.5, 28.7, 118.4, 121.4, 122.4, 122.6, 123.3, 125.2, 126.1, 128.0, 128.3, 129.9, 130.4, 130.9, 131.7, 134.2 (d, J_{CP} = 9.91 Hz), 137.5, 140.1, 149.0, 165.8, 170.5; ^{31}P NMR (C_6D_6): δ 25.51.

[0-3,5-$Cl_2C_6H_2$-*o*-C(H)=N-2,6-C_6H_3(*i*-Pr)$_2$]Nickel(phenyl)(PPh_3) (43)

In a Schlenk flask was dissolved the Na salt of **40** (0.66 g, 1.5 mmol) and bis(triphenylphoshine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction of was stirred at rt for 1 h. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the reaction. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.91 g (74%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.98 (d, 6H, J_{HH} = 6.80 Hz), 1.22 (d, 6H, J_{HH} = 6.80 Hz), 3.92 (septet, 2H, J_{HH} = 6.80 Hz), 6.25-7.67 (m, 30H); ^{13}C NMR (C_6D_6): δ 22.6, 25.5, 28.8, 117.4, 120.0, 122.8, 125.3, 126.2, 128.3, 128.6, 129.7, 130.5, 131.0, 131.5, 133.3, 133.8, 134.0, 134.4 (d, J_{CP}

= 9.77 Hz), 137.4, 140.1, 149.4, 159.6, 165.2; ^{31}P NMR (C_6D_6): δ 25.93. Anal. Calcd for $C_{43}H_{40}ClNNiOP$: C, 69.29; H, 5.41; N, 1.88. Found: C, 69.87; H, 5.74; N, 1.63.

General Procedure for Polymerization of Ethylene by Ni Complexes

The appropriate amount of Ni catalyst was weighed into a pressure bottle under an atmosphere of N_2. The pressure bottle was evacuated and backfilled with ethylene. Toluene (80 mL) was then cannula transferred into the pressure bottle. Finally, a solution of cocatalyst, $Ni(COD)_2$ or $B(C_6F_5)_3$, in toluene (5 mL) was syringed into the pressure bottle. The ethylene pressure was raised to a specified value and the reaction was stirred for 40 min. Catalysts **24** and **28** were stirred for only 15 min since catalyst deactivation was faster for these catalysts. After completion of the polymerization reaction, methanol (500 mL) was added to the toluene solution to precipitate the polyethylene. The polyethylene was collected by filtration through a glass frit.

References

1 J. Boor, *Ziegler-Natta Catalysts and Polymerizations*, Academic Press: New York, 1979.

2 R. P. Quirk, Ed., *Transition Metal Catalyzed Polymerizations-Alkenes and Dienes*, M.M.I. Press: Harwood Academic Pub., New York, 1983.

3 (a) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, 73. (b) Keim, W. *Chem. Ing. Tech.* **1984**, *56*, 850.

4 (a) Bauer, R.; Chung, H.; Barnett, K.W.; Glockner, P. W.; Keim, W. U.S. Pat. 3,686,159 (1972). (b) Bauer, R.; Glockner, P. W.; Keim, W.; Mason, R. F. U.S. Pat. 3,647,915 (1972). (c) Bauer, R.; Chung, H.; Glockner, P. W.; Keim, W.; van Zwet, H. U.S. Pat. 3,644,563 (1972). (d) Bauer, R.; Chung, H.; Glockner, P. W.; Keim, W.; van Zwet, H. U.S. Pat. 3,635,937 (1972).

5 (a) Beach, D. L.; Harrison, J. J. U.S. Pat. 4,310,716 (1982). (b) Beach, D. L.; Harrison, J. J. U.S. Pat. 4,382,153 (1983). (c) Beach, D. L.; Harrison, J. J. U.S. Pat. 4,293,727 (1981). (d) Beach, D. L.; Harrison, J. J. U.S. Pat. 4,301,318 (1981). (e) Beach, D. L.; Harrison, J. J. U.S. Pat. 4,293,502 (1981).

6 Starewski, K-H. A. O.; Witte, J. U.S. Pat. 4,537,982, Ger. Pat. Appl. to Bayer AG (1985).

7 Keim, W.; Kowaldt, R.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

8 Qingchuan, Y.; Youqi, T.; Huali, L.; Minzhi, X.; Sen, L.; Weihua, X. *Acta Chem. Sinica* **1984**, *42*, 1128.

9 Keim, W. Ann, N. Y. *Acad. Sci.* **1983**, *415*, 191.

10 Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polymer Sci. Part A: Polymer Chemistry* **1987**, *25*, 1989-2003..

[11] Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

[12] Klabunde, U.; Ittel, S. D. *J. Molecular Catal.* **1987**, *41*, 123-134.

[13] The synthesis of 2-Diphenylphosphinobenzaldehyde is known: Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175-178.

[14] (a) Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3238-3241. (b) Van hecke, G. R.; Horrocks, W. D. *Inorganic Chem.* **1966**, *5*, 1968-1974.

[15] The synthesis of $(PPh_3)_2Ni(Ph)Cl$ is known: Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279-282,

[16] Saito, T.; Munakata, H.; Imoto, H. *Inorg. Synth.* **1975**, *17*, 83-94.

[17] Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 2013-2014.

[18] Nickel geometry is generated by Dmol calculation. Ligand geometry is refined by constrained MM2 calculation.

[19] Casirighi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans. I* **1980**, 1862-5.

[20] (a) Hoyer, S.; Laszlo, P. *Synthesis* **1986**, 655-7. (b) Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

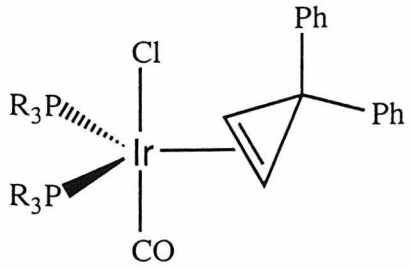
[21] Rice, J. E.; Lai, Z. W. *J. Org. Chem* **1993**, *58*, 1415-1426.

[22] Narasimhan, N. S.; Mali, R. S.; Barve, M. V. *Synthesis* **1979**, 906-9.

[23] Bolm, C.; Weickhardt, K.; Zehnder, M.; Glasmacher, D. *Helv. Chim. Acta* **1991**, *74*, 717-726.

[24] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

A. X-ray Diffraction Study of $Ir(Cl(CO)(PMe_3)_2(\eta^2$-3,3-Diphenylcyclopropene)



(See Chapter 1, Figure 1 for the ORTEP plot.)

Table A-1. Experimental Data for the X-ray Diffraction Study of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-Diphenylcyclopropene).

Formuala: $C_{22}H_{30}OP_2ClIr{\cdot}CH_2Cl_2$	Fw: 685.0
Temperature (K): 163	Crystal System: Monoclinic
Space Group: $P2_1/n$	Z = 4
a = 13.1195(14) Å	V = 2721.9(7) $Å^3$
b = 10.802(2) Å	b = 98.806(10)°
c = 19.435(3) Å	D_{calcd}, g/cm_3 = 1.672
Radiation: Mo Kα (γ = 0.710730 Å)	Diffractometer: Syntex $P2_1$ (Siemens R3m/V)
Data Collected: $+h, +k, \pm l$	Monochromator: Highly oriented graphite
Scan Range: 1.20° plus Kα-separation	Scan Type: θ-2θ
2θ Range: 4.0 to 55.0	Scan Speed: 3.0 deg min^{-1} (in ω)
Absorption Correction:	μ(MoKα), mm^{-1} = 5.31
Semi-empirical ψ-scan method)	Reflections Collected: 6876
No. of Variables: 271	Reflections with $\|F_o\| > 3.0\sigma(\|F_o\|)$: 5282
Goodness of Fit: 1.26	R_F = 4.5 %, R_{wF} = 5.0 %

Table A-2. Atomic Coordinates ($x10^5$) and Equivalent Isotropic Displacement Coefficients ($Å^2x10^4$).[a]

	x	y	z	U(eq)
Ir(1)	48769(2)	4133(2)	22386(1)	147(1)
Cl(1)	60125(11)	-10749(14)	30225(8)	237(4)
P(1)	63516(12)	16375(15)	23330(8)	198(4)
P(2)	42239(12)	7809(15)	33748(9)	211(5)
(1)	35585(39)	24983(45)	17249(26)	355(16)
C(1)	41069(43)	-11567(55)	18587(28)	167(16)
C(2)	49901(46)	-8635(55)	15271(31)	193(17)
C(3)	39519(42)	-9796(51)	10694(28)	139(16)
C(4)	34474(46)	1409(55)	7138(30)	181(17)
C(5)	23894(48)	3641(57)	6873(33)	228(18)
C(6)	19233(49)	13925(61)	3357(32)	255(19)
C(7)	25199(51)	22099(62)	144(34)	273(20)
C(8)	35613(55)	20029(62)	331(34)	287(21)
C(9)	40237(49)	9630(55)	3745(31)	210(18)
C(10)	37661(45)	-21743(55)	6687(29)	175(17)
C(11)	30615(51)	-22406(62)	485(30)	252(19)
C(12)	28596(58)	-33565(64)	-3048(36)	321(22)
C(13)	33604(68)	-44181(67)	-492(40)	395(26)
C(14)	40540(64)	-43791(64)	5569(40)	356(25)
C(15)	42621(50)	-32640(59)	9111(35)	255(19)
C(16)	40534(47)	16512(61)	19289(32)	240(19)
C(17)	71544(57)	20359(85)	31406(39)	446(27)
C(18)	61237(55)	31217(62)	18947(41)	352(24)
C(19)	72521(52)	8834(68)	18519(40)	326(22)
C(20)	36344(65)	-5971(67)	36784(42)	392(26)
C(21)	32232(60)	19386(73)	33481(41)	406(26)
C(22)	51208(62)	12369(84)	41353(37)	431(27)
C(23)	46632(68)	-39022(70)	32939(46)	452(29)
Cl(1)	41282(22)	-49247(23)	26285(13)	600(9)
Cl(2)	54309(19)	-46953(14)	39704(14)	632(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A-3. Interatomic Distances (Å) with Esd's.

Ir(1) - Cl(1)	2.442(2)	Ir(1) - P(1)	2.345(2)
Ir(1) - P(2)	2.340(2)	Ir(1) - C(1)	2.116(6)
Ir(1) - C(2)	2.118(6)	Ir(1) - C(16)	1.824(6)
Ir(1) - Cnt[a]	1.990		
P(1) - C(17)	1.803(7)	P(1) - C(18)	1.819(7)
P(1) - C(19)	1.809(8)	P(2) - C(20)	1.817(8)
P(2) - C(21)	1.808(8)	P(2) - C(22)	1.811(7)
O(1) - C(16)	1.156(8)	C(1) - C(2)	1.445(9)
C(1) - C(3)	1.528(8)	C(2) - C(3)	1.514(8)
C(3) - C(4)	1.497(8)	C(3) - C(10)	1.508(8)
C(4) - C(5)	1.402(9)	C(4) - C(9)	1.396(9)
C(5) - C(6)	1.396(9)	C(6) - C(7)	1.390(10)
C(7) - C(8)	1.379(10)	C(8) - C(9)	1.395(9)
C(10) - C(11)	1.404(8)	C(10) - C(15)	1.392(9)
C(11) - C(12)	1.392(9)	C(12) - C(13)	1.376(10)
C(13) - C(14)	1.375(11)	C(14) - C(15)	1.393(10)
C(23) - Cl(2)	1.763(8)	C(23) - Cl(3)	1.753(8)

[a] Cnt is the centroid of the C(1) - C(2) bond.

Table A-4. Interatomic Angles (deg.) with Esd's.

Cl(1) - Ir(1) - P(1)	86.5(1)	Cl(1) - Ir(1) - P(2)	85.2(1)
P(1) - Ir(1) - P(2)	108.6(1)	Cl(1) - Ir(1) - C(10	85.6(2)
P(1) - Ir(1) - C(1)	142.0(2)	P(2) - Ir(1) - C(1)	107.6(2)
Cl(1) - Ir(1) - C(2)	82.5(2)	P(1) - Ir(1) - C(2)	102.2(2)
P(2) - Ir(1) - C(2)	145.9(2)	C(1) - Ir(1) - C(2)	39.9(2)
Cl(1) - Ir(1) - C(16)	172.5(2)	P(1) - Ir(1) - C(16)	91.1(2)
P(2) - Ir(1) - C(16)	88.9(2)	C(1) - Ir(1) - C(16)	100.6(2)
C(2) - Ir(1) - C(16)	104.9(2)		
Ir(1) - P(1) - C(17)	120.2(3)	Ir(1) - P(1) - C(18)	115.0(2)
C(17) - P(1) - C(18)	103.3(4)	Ir(1) - P(1) - C(19)	110.7(2)
C(17) - P(1) - C(18)	102.5(3)	C(18) - P(1) - C(19)	103.2(4)
Ir(1) - P(2) - C(20)	111.7(3)	Ir(1) - P(2) - C(21)	116.9(3)
C(20) - P(2) - C(21)	103.5(4)	Ir(1) - P(2) - C(22)	118.1(3)
C(20) - P(2) - C(22)	102.3(4)	C(21) - P(2) - C(22)	102.3(4)
Ir(1) - C(1) - C(2)	70.1(3)	Ir(1) - C(1) - C(3)	108.9(4)
C(2) - C(1) - C(3)	61.1(4)	Ir(1) - C(2) - C(1)	70.0(3)
Ir(1) - C(2) - C(3)	109.4(4)	C(1) - C(2) - C(3)	62.2(4)
C(1) - C(3) - C(2)	56.7(4)	C(1) - C(3) - C(4)	123.1(5)
C(2) - C(3) - C(4)	119.9(5)	C(1) - C(3) - C(10)	113.4(5)
C(2) - C(3) - C(10)	115.7(5)	C(4) - C(3) - C(10)	115.4(4)
C(3) - C(4) - C(5)	121.4(5)	C(3) - C(4) - C(9)	120.0(5)
C(5) - C(4) - C(9)	118.6(5)	C(4) - C(5) - C(6)	120.8(6)
C(5) - C(6) - C(7)	119.4(6)	C(6) - C(7) - C(8)	120.6(6)
C(7) - C(8) - C(9)	120.0(6)	C(4) - C(9) - C(8)	120.6(6)
C(3) - C(10) - C(11)	121.3(5)	C(3) - C(10) - C(15)	121.3(5)
C(11) - C(10) - C(15)	117.4(6)	C(10) - C(11) - C(12)	121.2(6)
C(11) - C(12) - C(13)	120.0(6)	C(12) - C(13) - C(14)	120.0(7)
C(13) - C(14) - C(15)	120.3(6)	C(10) - C(15) - C(14)	121.2(6)
Ir(1) - C(16) - O(1)	173.7(6)	Cl(2) - C(23) - Cl(3)	111.3(4)

Table A-5. Anistropic Displacement Coefficients ($Å^2 \times 10^4$).[a]

	U_{11}	U_{22}	U_{33}	U_{21}	U_{13}	U_{23}
Ir(1)	167(1)	152(1)	125(1)	4(1)	37(1)	-10(1)
Cl(1)	150(7)	238(8)	215(7)	44(6)	14(6)	50(6)
P(1)	207(7)	199(8)	199(8)	-36(6)	66(6)	2(6)
P(2)	241(8)	229(8)	181(8)	-19(6)	93(6)	-41(6)
(1)	451(29)	257(26)	328(28)	175(23)	-30(23)	-60(22)
C(1)	225(27)	164(27)	113(27)	-2(23)	27(22)	-41(23)
C(2)	245(29)	169(28)	170(30)	36(24)	50(24)	14(24)
C(3)	205(26)	140(27)	82(25)	-8(22)	59(21)	-13(21)
C(4)	252(30)	209(30)	81(26)	14(23)	22(22)	-61(22)
C(5)	261(30)	223(32)	202(31)	-1(25)	37(24)	-8(26)
C(6)	276(31)	288(34)	191(31)	45(27)	5(25)	43(28)
C(7)	383(37)	228(32)	195(31)	60(28)	5(27)	33(26)
C(8)	419(38)	246(34)	220(33)	-21(29)	122(29)	82(28)
C(9)	307(32)	178(29)	157(29)	36(25)	75(25)	-9(24)
C(10)	251(29)	182(29)	110(27)	-66(23)	91(22)	-14(23)
C(11)	391(36)	262(34)	105(28)	-44(28)	45(26)	3(26)
C(12)	470(41)	277(35)	220(35)	-124(32)	59(30)	-77(29)
C(13)	675(54)	246(37)	286(39)	-156(37)	142(37)	-123(32)
C(14)	566(48)	202(35)	328(40)	-38(32)	154(35)	-12(30)
C(15)	315(33)	200(31)	255(34)	2(26)	58(27)	19(27)
C(16)	276(31)	276(34)	163(30)	-12(27)	22(24)	-135(27)
C(17)	340(39)	657(57)	332(42)	-241(39)	24(32)	7(40)
C(18)	390(39)	221(34)	476(47)	-9(30)	167(35)	44(32)
C(19)	307(35)	322(37)	386(41)	-24(29)	173(31)	10(32)
C(20)	517(47)	351(43)	372(44)	-82(34)	267(38)	32(33)
C(21)	476(44)	400(44)	398(45)	80(36)	246(36)	-83(36)
C(22)	503(46)	597(53)	212(36)	-161(41)	114(33)	-112(38)
C(23)	570(50)	281(41)	519(52)	-5(36)	132(42)	34(37)
Cl(1)	883(18)	451(12)	482(14)	44(12)	154(13)	-65(11)
Cl(2)	478(12)	902(20)	532(14)	50(12)	129(11)	238(14)

[a] The anistropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}$

Table A-6. H-Atom Coordinates ($x10^4$) and Isotropic Displacement Coeffiecients ($Å^2 \times 10^4$)

	x	y	z	U
H(1A)	4006	-1922	2090	600
H(2A)	5566	-1404	1507	600
H(5A)	1982	-204	910	600
H(6A)	1198	1539	320	600
H(7A)	2204	2923	-224	600
H(8A)	3968	2570	-192	600
H(9A)	4746	813	380	600
H(11A)	2714	-1502	-136	600
H(12A)	2368	-3384	-725	600
H(13A)	3216	-5187	-293	600
H(14A)	4412	-5117	730	600
H(15A)	4742	-3245	1337	600
H(17A)	7721	2538	3046	600
H(17B)	6757	2487	3433	600
H(17C)	7415	1291	3373	600
H(18A)	6765	3559	1918	600
H(18B)	5836	2983	1416	600
H(18C)	5651	3604	2116	600
H(19A)	7850	1397	1855	600
H(19B)	7455	102	2065	600
H(19C)	6929	751	1380	600
H(20A)	3375	-414	4103	600
H(20B)	3078	-869	3332	600
H(20C)	4144	-1239	3762	600
H(21A)	3018	2007	3800	600
H(21B)	3479	2723	3217	600
H(21C)	2640	1699	3014	600
H(22A)	4755	1357	4522	600
H(22B)	5630	600	4247	600
H(22C)	5454	1995	4040	600
H(23A)	4116	-3486	3477	600
H(23B)	5071	-3288	3105	600