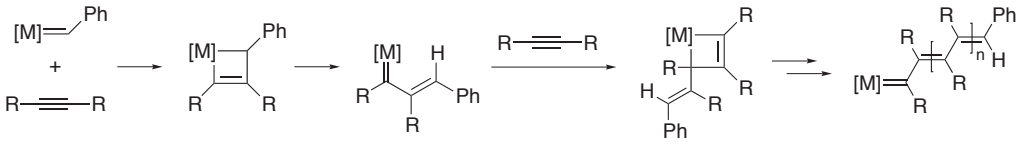
Chapter 4

Reactions of Ruthenium Carbene Complexes with Disubstituted Alkynes: Formation of η^3-Vinylcarbene and η^5-Cyclopentadienyl Derivatives versus Alkyne Polymerization

Introduction

The metathesis polymerization of alkynes is related mechanistically to the metathesis of olefins. As illustrated in Scheme 4.1, the interaction of a metal–carbene complex and an alkyne can lead to [2+2] cycloaddition and formation of a metallacyclobutene intermediate.[1] Subsequent rupture of the ring yields an η^1-vinylcarbene complex, and repetition of this cycle provides a growing polyacetylene chain. The analogous interaction between a metal–carbene complex and an olefin differs only in that [2+2] cycloaddition leads to a metallacyclobutane instead of a metallacyclobutene.[2]



Scheme 4.1

Alternatively, alkyne polymerization can be catalyzed by metal–vinyl species, and these

1. (a) Choi, S.-K.; Gal, Y.-S.; Jin, S.-H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645-1681. (b) Masuda, T. *Catalysis in Precision Polymerization*, Kobayashi, S., Ed.; Wiley: Chichester, 1997; Chapter 2.4. (c) Masuda, T. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996, pp. 32-40. (d) Masuda, T.; Tachimori, H. *J. M. S. Pure Appl. Chem.* **1994**, *A31*, 1675-1690. (e) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644-654. (f) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51-56.
2. (a) Katz, T. J. *Advances in Metal Carbene Chemistry*, Schubert, U., Ed.; Kluwer Academic, 1989. (b) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737-738. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422-424. (d) Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717-721.

reactions provide the same polyacetylene products as those catalyzed by metal–carbenes. However, these two cases are mechanistically distinct; propagation via a metal–vinyl intermediate occurs by insertion of the alkyne into the metal–carbon bond.[3] A similar situation exists for enyne metathesis, which can proceed through a metal–carbene catalyzed pathway via alternating metallacyclobutene and -cyclobutane intermediates,[2,4] or by an oxidative cyclization–reductive elimination–ring opening sequence.[5]

The conjugated materials produced by alkyne polymerization have unique electrical, optical, and gas permeability properties with many potential applications.[1,3] Therefore, an important goal is to develop synthetic routes to polyacetylenes that may provide access to new materials with desirable structures and characteristics. Although the ring-opening metathesis polymerization of cyclooctatetraene with ruthenium alkylidene catalysts is known to provide polyacetylene,[6] the polymerization of alkynes with these catalysts has been largely unexplored. There is a single report of 2-butyne polymerization with a bimetallic ruthenium alkylidene complex, but this reaction was not studied in detail.[7]

In fact, there are very few instances of alkyne polymerization mediated by well-defined metal–carbene complexes. The examples include the polymerization of 1-octyne with the arylimido molybdenum alkylidene complex $(NAr)(OR)_2Mo{=}CHR$,[8] and the polymerization of 2-butyne with the tantalum alkylidene complex $(DIPP)_3(py)Ta{=}CHR$ (DIPP = 2,6-diisopropylphenoxide).[1e] However, alkyne polymerization on a preparative scale is generally accomplished with ill-defined catalyst systems, such as $TaCl_5/Bu^n{}_4Sn$, which are more active than $(NAr)(OR)_2Mo{=}CHR$ or $(DIPP)_3(py)Ta{=}CHR$ in this reaction.[1c]

By analogy to olefin metathesis, the use of well-defined metal–carbene catalysts for alkyne polymerization should allow the properties of the initiator to be tuned in a systematic way, and thus provide better control over the course of the reaction and the polyacetylene products.

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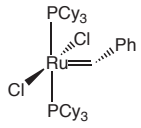
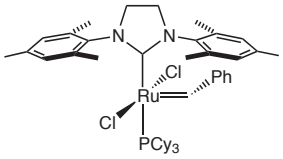
3. (a) Kanki, K.; Misumi, Y.; Masuda, T. *Inorg. Chim. Acta* **2002**, *336*, 101-104. (b) Miyake, M.; Misumi, Y.; Masuda, T. *Macromolecules* **2000**, *33*, 6636-6639. (c) Misumi, Y.; Kanki, K.; Miyake, M.; Masuda, T. *Macromol. Chem. Phys.* **2000**, *201*, 2239-2244. (d) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035-12044. (e) Misumi, Y.; Masuda, T. *Macromolecules* **1998**, *31*, 7572-7573.
4. Examples: (a) Kitamura, T.; Mori, M. *Org. Lett.* **2001**, *3*, 1161-1163. (b) Renaud, J.; Graf, C.-D.; Oberer, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3101-3104. (c) Mori, M. In *Alkene Metathesis in Organic Synthesis*, Fürstner, A., Ed.; Springer: Berlin, 1998; pp. 133-154. (d) Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388-12389. (e) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634-6640.
5. (a) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813-834. (b) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901-903. (c) Trost, B. M.; Kanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294-5295. (d) Trost, B. M.; Tonoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636-1638.
6. (a) Scherman, O. A.; Grubbs, R. H. *Synth. Met.* **2001**, *124*, 431-438. (b) Klavetter, F. L.; Grubbs, R. H. *Synth. Met.* **1989**, *28*, D99-D104.
7. Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758-2767.
8. Koltzenburg, S.; Eder, E.; Stelzer, F.; Nuyken, O. *Macromolecules* **1999**, *32*, 21-26.

For these reasons, the purpose of this study was to examine the alkyne polymerization activity of two ruthenium alkylidene complexes, namely $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**4.1**)[9] and $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**4.2**; H_2IMes = 1,3-dimesityl-imidazolidine-2-ylidene).[10]



4.1



4.2

Results and Discussion

Alkyne polymerization.[11] As shown in Table 4.1, the polymerization of a variety of terminal and disubstituted alkynes was tested with **4.1** and **4.2**. The results were disappointing. Very little or no polymer was obtained from 4-octyne, $(p\text{-}Bu^nC_6H_4)C{\equiv}C(p\text{-}Bu^nC_6H_4)$, $(p\text{-}Bu^nO_2CC_6H_4)C{\equiv}C(p\text{-}Bu^nO_2CC_6H_4)$, phenylacetylene, or 1-hexyne, and the small amount of

Table 4.1: Alkyne polymerization results.

monomer	catalyst	t (h)	T (°C)	% yield	M_n
diphenylacetylene	**4.1**	24	80	67	—
diphenylacetylene	**4.2**	24	80	50	—
4-octyne	**4.1**	24	80	0	—
4-octyne	**4.2**	24	80	0	—
$(p\text{-}Bu^nC_6H_4)C{\equiv}C(p\text{-}Bu^nC_6H_4)$	**4.1**	24	80	0	—
$(p\text{-}Bu^nC_6H_4)C{\equiv}C(p\text{-}Bu^nC_6H_4)$	**4.2**	24	80	0	—
$(p\text{-}Bu^nC_6H_4)C{\equiv}C(p\text{-}Bu^nC_6H_4)$	**4.1**	12	150	15	840
$(p\text{-}Bu^nC_6H_4)C{\equiv}C(p\text{-}Bu^nC_6H_4)$	**4.2**	12	150	16	890
$(p\text{-}Bu^nO_2CC_6H_4)C{\equiv}C(p\text{-}Bu^nO_2CC_6H_4)$	**4.1**	12	150	0	—
$(p\text{-}Bu^nO_2CC_6H_4)C{\equiv}C(p\text{-}Bu^nO_2CC_6H_4)$	**4.2**	12	150	5	2400
phenylacetylene	**4.1**	24	80	3	500
phenylacetylene	**4.2**	24	80	5	600
1-hexyne	**4.1**	24	80	0	—
1-hexyne	**4.2**	24	80	0	—

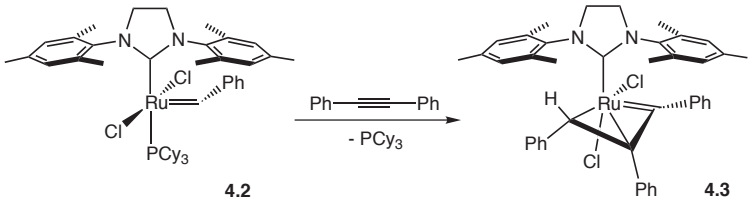
9. (a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039-2041.
10. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953-956.
11. The experiments involving alkyne polymerizations were performed in collaboration with Prof. Toshido Masuda and Toshikazu Sakaguchi at Kyoto University, Japan.

isolated material consisted of oligomers.

Curiously, the reactions of diphenylacetylene with **4.1** or **4.2** provided reasonable yields of polymer. This highly insoluble material appears to be poly(diphenylacetylene) by comparison of its IR spectrum with that reported in the literature.[12] It is not obvious why diphenylacetylene polymerizes and other *para*-substituted diphenylacetylenes do not, but the melt conditions of the reaction and insolubility of poly(diphenylacetylene) may contribute to its success.

These observations naturally lead to the question of why the polymerization of alkynes is not favored with complexes **4.1** and **4.2**. In the presence of terminal alkynes, it is likely that the ruthenium benzylidenes are transformed into vinylidene species [Ru]=C=CHPh, based on observations that $(PCy_3)_2(Cl)_2Ru{=}CH(CH_3)$ and $(PCy_3)_2(Cl)_2Ru{=}CH(CH_2Ph)$ react with phenylacetylene to yield $(PCy_3)_2(Cl)_2Ru{=}C{=}CHPh$.[13] Ruthenium vinylidenes are known to be less efficient olefin metathesis initiators than ruthenium benzylidenes, and this trend may be responsible for the low alkyne polymerization activity as well. However, at the beginning of this study there was no precedent for reactions of ruthenium alkylidenes with disubstituted alkynes, so these cases were examined in greater detail to provide some insight into the polymerization problem.

Formation of η^3-vinylcarbene complexes.[14] It quickly became apparent that **4.1** does not react with disubstituted alkynes, but that the more electron rich, N-heterocyclic carbene–coordinated derivative **4.2** does. For example, the reaction of **4.2** with an excess of diphenylacetylene cleanly affords the phosphine-free complex $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CPh)]$ (**4.3**) (Scheme 4.2).[15]



4.2 **4.3**

Scheme 4.2

12. Teraguchi, M.; Masuda, T. *Macromolecules* **2002**, *35*, 1149-1151.
13. Wolf, J.; Stüer, W.; Grünwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1827-1834.
14. These results have been published. Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Organometallics* **2001**, *20*, 3845-3847.
15. Alternatively, **4.3** can be synthesized by the addition of diphenylacetylene to the bis(pyridine) benzylidene derivative $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$.

By ^{1}H NMR, **4.3** displays a diagnostic signal at δ 4.78 for C*H*Ph, a higher field resonance than typically exhibited by unbound vinyl fragments.[16] The η^3-vinylcarbene moiety is characterized by a $^{13}C\{^{1}H\}$ NMR signal at δ 285 for the alkylidene carbon (Ru=*C*Ph), which is diagnostic for ruthenium alkylidenes of this type, and vinyl resonances at δ 67.87 (*C*HPhCPhCPh) and 91.67 (CHPh*C*PhCPh). These vinyl signals also appear at higher field than unbound vinyl fragments in either organic molecules or η^1-vinylcarbene complexes.[17] There is no NMR evidence for dissociation of the vinyl group from the metal center at up to 130°C.[18] The mesityl groups of the H_2IMes ligand are characterized by six methyl resonances in both the ^{1}H and $^{13}C\{^{1}H\}$ NMR, as well as four distinct meta protons, which is consistent with an asymmetric environment around the metal center and restricted rotation about the N-heterocyclic carbene–ruthenium bond. The aromatic region in the ^{1}H NMR spectrum of **4.3** contains several broad resonances at room temperature that decoalesce upon cooling to –45°C. This dynamic behavior is caused by rotation around one or more of the carbon–phenyl bonds.

The crystal structure of **4.3** (Figure 4.1) reveals several interesting features. Most surprisingly, the chlorides are in a cis configuration, with Cl(2) now situated trans to the N-heterocyclic carbene. This position is usually occupied by a phosphine or other donor ligand in L_2X_2Ru=CHR complexes. The other chloride, Cl(1), is located trans to the RuCHPh group, leaving the site trans to the Ru=C(3) bond vacant. In addition to the overall distorted square pyramidal geometry of the complex, the mesityl groups of the H_2IMes ligand are twisted with respect to each other by approximately 30°.

Selected bond lengths and angles for two x-ray structures of **4.3** (one with three molecules of co-crystallized methylene chloride) are presented in Table 4.2. The ruthenium–alkylidene [Ru=C(3)] bond length of 1.834(2) Å is comparable to *d*(Ru=C) values in related complexes, such as $(H_2IMes)(PCy_3)(Cl)_2$Ru=CHPh [1.837 Å][19] and $(IMes)(PCy_3)(Cl)_2$Ru=CHPh [1.841(11) Å].[20] Whereas the Ru–C(2) distance of 2.233(2) Å is typical for a ruthenium–carbon

16. In comparison, the signals for the terminal protons of the η^1-vinylcarbene complex $(PCy_3)_2Cl_2$Ru=CH–CH=CH_2 appear at δ 6.25 and 6.01. See reference 9a.
17. For instance, the $^{13}C\{^{1}H\}$ signals for $(PCy_3)_2Cl_2$Ru=CH–*C*H=*C*H_2 appear at δ 116 and 154. See reference 9a.
18. Dissociation of the vinyl group in $[W(CPhCHCMe_2)Br_2(CO)_2(4\text{-picoline})]$ has been observed. Mayr, A.; Asaro, M. F.; Van Engen, D. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; pp 167-169.
19. Sanford, M. S.; Henling, L. M.; Grubbs, R. H. **2000**, unpublished results.
20. Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678.

single bond,[21] the Ru–C(1) distance of 2.345(2) Å is slightly longer but not unprecedented. Within the vinyl fragment, the C(1)–C(2) distance of 1.410(3) Å is consistent with a C=C double bond (~1.35 Å), and the C(2)–C(3) distance of 1.443(3) Å is consistent with a C–C single bond (~1.55 Å).

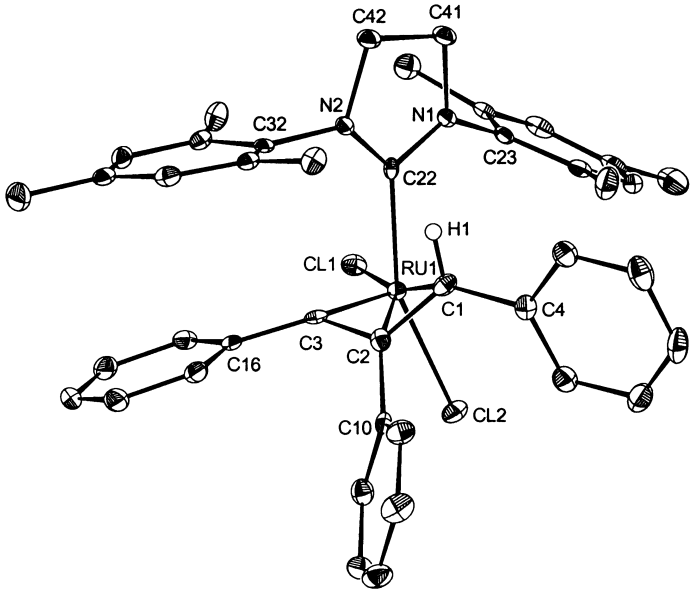


Figure 4.1: Structure of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CPh)]$ (**4.3**) (CCDC #177801). Displacement ellipsoids are drawn at 50% probability; H(1) is drawn at arbitrary scale.

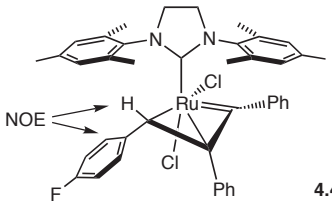
Table 4.2: Comparison of selected bond distances (Å) and angles (deg) for $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CPh)]$ (**4.3**) and $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CC{\equiv}CPh)(CPh)]$ (**4.5**).

	4.3 · 3 CH_2Cl_2	**4.3**	**4.5 · CH_2Cl_2**
Ru–C(1)	2.356(4)	2.345(2)	2.346(2)
Ru–C(2)	2.221(4)	2.233(2)	2.210(2)
Ru–C(3)	1.838(4)	1.834(2)	1.834(2)
Ru–C(22)	2.045(4)	2.043(2)	2.042(2)
Ru–Cl(1)	2.369(1)	2.348(1)	2.367(1)
Ru–Cl(2)	2.364(1)	2.369(1)	2.359(1)
C(1)–C(2)	1.409(6)	1.410(3)	1.399(3)
C(2)–C(3)	1.437(6)	1.443(3)	1.451(3)
C(1)–C(4)	1.478(5)	1.473(3)	1.468(3)

21. For example, *d*(Ru-C) for ruthenium-methyl complexes in the Cambridge Structural Database range from 2.09 to 2.24 Å. CSD Version 5.20. 3D Search and Research Using the Cambridge Structural Database, Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 1 and 31-37.

C(2)–C(10)	1.511(6)	1.492(3)	1.441(3)
C(3)–C(16)	1.453(5)	1.452(3)	1.447(3)
C(41)–C(42)	1.517(7)	1.516(3)	1.508(3)
N(1)–C(22)	1.347(5)	1.341(2)	1.346(3)
N(1)–C(41)	1.476(6)	1.482(3)	1.486(3)
N(1)–C(23)	1.436(6)	1.441(2)	1.438(3)
N(2)–C(22)	1.345(5)	1.358(2)	1.350(3)
N(2)–C(42)	1.501(5)	1.486(3)	1.485(3)
N(2)–C(32)	1.451(5)	1.438(2)	1.438(3)
Cl(1)–Ru–Cl(2)	86.77(4)	87.27(2)	87.99(2)
C(1)–Ru–Cl(1)	171.4(1)	167.19(6)	169.37(6)
C(1)–Ru–Cl(2)	101.6(1)	102.86(6)	101.95(6)
C(1)–C(2)–C(3)	116.0(3)	116.9(2)	116.8(2)
C(1)–Ru–C(3)	69.0(2)	69.91(8)	69.80(9)
C(2)–C(1)–Ru	66.9(2)	67.8(1)	66.9(1)
C(2)–C(3)–Ru	84.4(2)	85.0(1)	83.7(1)
C(3)–Ru–Cl(1)	110.0(1)	114.64(6)	111.25(7)
C(3)–Ru–Cl(2)	111.8(1)	108.48(6)	106.51(7)
Ru–C(22)–N(1)	118.6(3)	121.6(1)	120.3(2)
Ru–C(22)–N(2)	131.3(3)	129.2(1)	131.1(2)
N(1)–C(22)–N(2)	109.2(3)	108.3(2)	108.2(2)
C(22)–N(1)–C(23)	127.9(3)	127.3(2)	127.2(2)
C(22)–N(2)–C(32)	126.7(3)	127.0(2)	128.0(2)

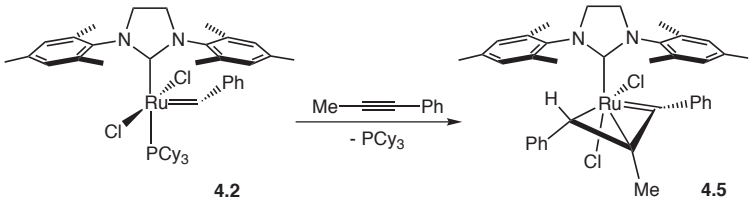
Reaction of diphenylacetylene with the *para*-fluoro(benzylidene) derivative of **4.2** provides $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CH(p\text{-}C_6H_4F))(CPh)(CPh)]$ (**4.4**). ^{19}F-coupling in the $p\text{-}C_6H_4F$ ring distinguishes these particular ortho and meta protons from the other aromatic resonances in the ^1H NMR spectrum of **4.4**, and it is possible to observe an NOE between these protons and the benzylic proton C*H*($p\text{-}C_6H_4F$). This experiment confirms that the benzylidene in the starting material (**4.2**) becomes the *CHPh*CPhCPh group in the product (**4.3**), as expected from the



4.4

mechanism of alkyne polymerization. The chemical shift difference of 0.06 ppm between the C*H*Ph proton in **4.3** and the C*H*(*p*-C_6H_4F) proton in **4.4** is also consistent with this assignment.

The reaction of **4.2** with 1-phenyl-1-propyne produces exclusively $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CMe)(CPh)] (**4.5**) (Scheme 4.3). The characterization data of **4.5** are similar to **4.3**, except for the additional methyl resonances at δ 1.79 and δ 11.49 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. In comparison, the methyl group of the ethylidene complex $(PCy_3)_2(Cl)_2Ru$=CHMe, appears at δ 2.59 and δ 49.15.[9a] These differences, especially of the ^{13}C chemical shifts, indicate that the methyl group in **4.5** is attached to the internal vinyl carbon (CHPh*CMe*CPh), rather than the alkylidene carbon (CHPhCPh*CMe*).

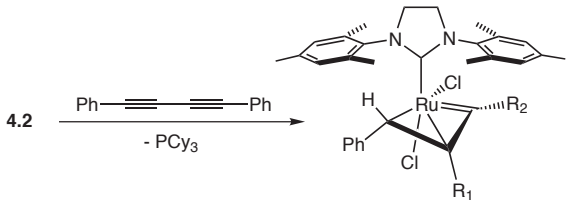


4.2 **4.5**

Scheme 4.3

In contrast to the selective formation of **4.5**, the reaction of **4.2** with 1,4-diphenyl-butadiyne yields a mixture of $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CC≡CPh)(CPh)] (**4.6**) and another isomer, most likely $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CPh)(CC≡CPh)] (**4.7**) (Scheme 4.4). Unfortunately, it was not possible to confirm the identities of **4.6** and **4.7** by $^{13}C\{^1H\}$ NMR because of the poor solubility of the products. The single crystal selected for x-ray diffraction corresponded to isomer **4.6**, and no other crystals were examined. The overall structure of **4.6** (Figure 4.2 and Table 4.2) and the geometrical data for the η^3-vinylcarbene fragment are similar to **4.3**. In addition, the C≡C bond distance of 1.196(3) Å and its IR $\nu_{C\equiv C}$ of 2195 cm^{-1} are comparable to values for related complexes.[22]

22. For example, *d*(C≡C) = 1.212(7) Å and $\nu_{C\equiv C}$ = 2123 cm^{-1} for $[Ru(\eta^5$-$C_5H_5)\{C(C\equiv CPh)CH=CPh_2\}(CO)(PPr^i_3)]BF_4$. Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Modrego, J.; Onate, E. *Organometallics* **1997**, *16*, 5826-5835.



4.6 R_1 = C≡CPh, R_2 = Ph
4.7 R_1 = Ph, R_2 = C≡CPh

Scheme 4.4

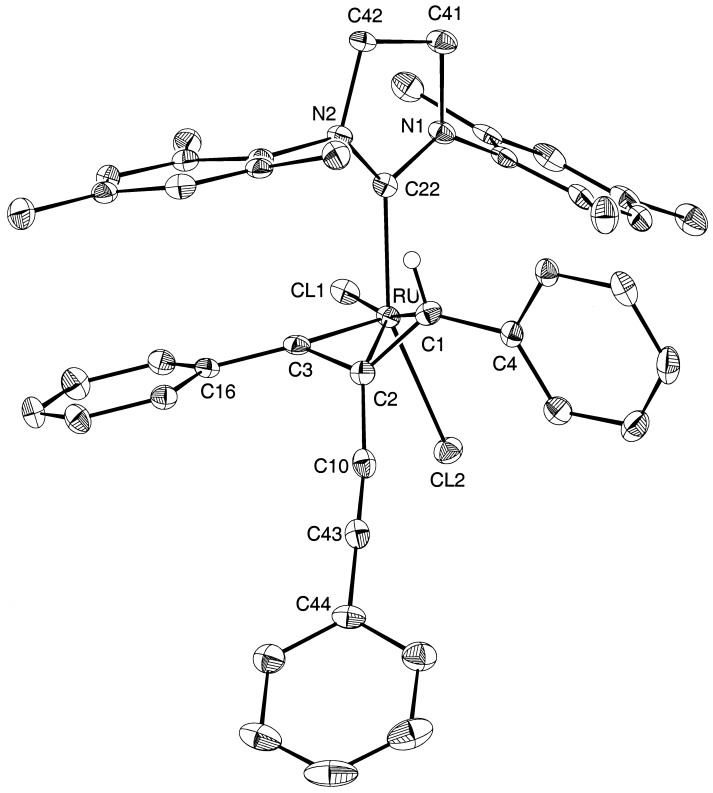


Figure 4.2: Structure of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CC{\equiv}CPh)(CPh)] \cdot CH_2Cl_2$ (**4.6**) (CCDC #156866). Displacement ellipsoids are drawn at 50% probability; H(1) is drawn at arbitrary scale. Additional bond distances [Å] and angles [deg]: C(10)–C(43) 1.196(3), C(43)–C(44) 1.432(3), RuC(2)C(10) 128.9(2), C(2)–C(10)–C(43) 170.0(3), C(10)–C(43)–C(44) 176.9(2).

The reaction of diphenylacetylene with $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (IMes = 1,3-dimesityl-imidazol-2-ylidene), where the N-heterocyclic carbene contains an unsaturated

backbone, yields the IMes analog to **4.3**. In contrast, η^3-vinylcarbene complexes are not formed from bis(phosphine) ruthenium alkylidenes, which suggests that the more electron-rich metal center in **4.2** is important to the success of these reactions.[23] Furthermore, the reaction was not observed with the methylidene [Ru]=CH_2 or dimethylvinyl carbene [Ru]=CH–CH=CMe_2 derivatives of **4.2**, or with alkynes containing electron-withdrawing substituents, such as dimethyl acetylenedicarboxylate and hexafluoro-2-butyne.

The reaction of **4.2** with cyclooctyne leads to polymerization rather than η^3-vinylcarbene formation. IR analysis and comparison with literature data indicates that the polymeric product is poly(cyclooctyne),[24] but it is not clear whether the structure contains exocyclic double bonds, as expected from a metal–carbene mechanism, or endocyclic double bonds, as expected from an insertion mechanism.

Several limiting structures for a [M(CHR)(CR)(CR)] moiety are illustrated in Figure 4.3: a metallacyclopropane–carbene species (A), an η^3-vinylcarbene species (B), an allyl-type species (C), and a metallacyclobutene species (D). The most common of these is D, which is seen in the structures of titanocene complexes like $Cp_2Ti[(CH_2)(CSiMe_3)_2]$.[25,26] Examples of C include $(Cp^*)(Cl)_2Re[(CH_2)(CCl)(CMe)]$, described as, "a substituted allyl system, with a carbene olefin resonance structure contributing to its metal-fixation."[27] However, based on the structural and spectroscopic data, the best bonding description for complexes **2.3**-**2.7** appears to be intermediate between A and B. It is neither C nor D because a double bond is clearly localized on Ru=C(3) instead of C(2)–C(3). D also is not consistent with the bent geometry of the RuC_3 subunit.

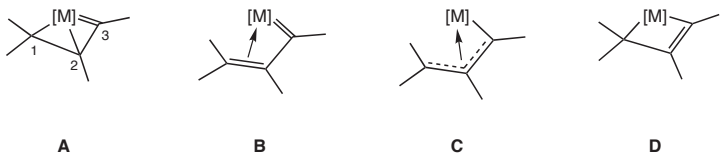


Figure 4.3

23. N-heterocyclic carbene ligands are generally stronger σ-donors than phosphine ligands. (a) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163-2187. (b) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717-774.
24. Yamada, K.; Nomura, R.; Masuda, T. *Macromolecules* **2000**, *33*, 9179-9181.
25. McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Collbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584-5586.
26. Another example: Cheng, Y.-C.; Chen, Y.-K.; Huang, T.-M.; Yu, C.-I.; Lee, G.-H.; Chen, J.-T. *Organometallics* **1998**, *17*, 2953-2957.
27. (a) Fischer, R. A.; Fischer, R. W.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2035-2040. (b) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1263-1265.

Although η^1-vinylcarbene complexes are common, **2.3**-**2.7** are the first examples of η^3-vinylcarbene complexes in ruthenium chemistry.[28] Previously, η^3-vinylcarbene complexes have been isolated in iron,[29] chromium,[30] and tungsten[31] carbonyl systems,[32] and they have been proposed as intermediates in the Dötz reaction (annulation of alkynes and Fischer carbene complexes).[33] In addition, Schrock and coworkers have reported a tantalum alkylidene that reacts with diphenylacetylene to yield an η^1-vinylcarbene complex.[34]

As illustrated in Scheme 4.1, the metal carbene–catalyzed polymerization of alkynes, occurs when an alkylidene reacts with an alkyne to form a metallacyclobutene intermediate, which then rearranges to a new alkylidene and a new alkyne. A growing polymer chain forms if this process continues. However, in complexes **2.3**-**2.7**, the vinylcarbene intermediate is trapped after the first turnover by coordination of the vinyl group to the metal center. This interaction, which stabilizes the otherwise 14-electron species, must be quite strong because the isolated η^3-vinylcarbene complexes are not active for subsequent olefin metathesis.

A possible mechanism for the formation of these complexes begins with tricyclohexylphosphine dissociation, followed by halide rearrangement and alkylidene rotation (Scheme 4.5). An alkyne can bind in the resulting open site and undergo metallacycle formation. Then this metallacyclobutene can open productively to afford a vinylcarbene, which is positioned to coordinate in an η^3-fashion. The orientation of coordinated 1-phenyl-1-propyne illustrated in Scheme 4.5 appears to be favored sterically.

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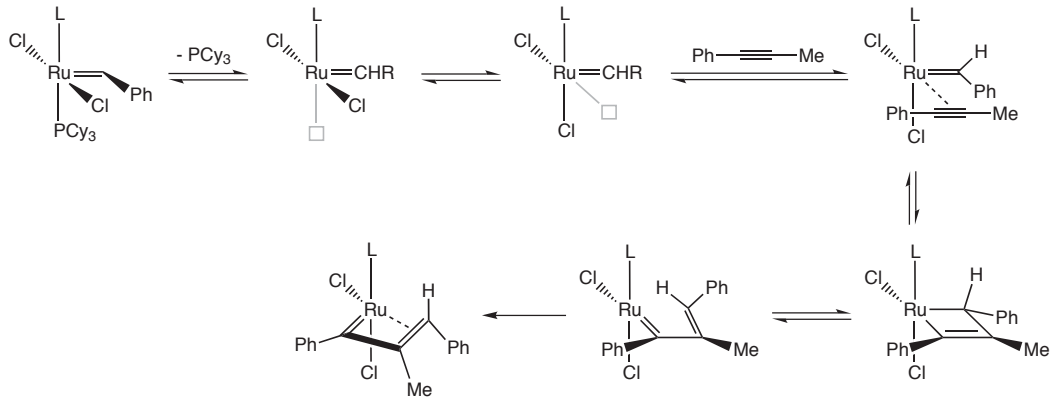
28. η^4-butadienyl (or allyl-carbene) complexes are also known in ruthenium chemistry. (a) Crocker, M.; Green, M.; Nagle, K. R.; Orpen, A. G.; Neumann, H.-P.; Morton, C. E.; Schaverien, C. J. *Organometallics* **1990**, *9*, 1422-1434. (b) Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H.-P.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351-1353.
29. (a) Mitsudo, T.; Fujita, K.; Nagano, S.; Suzuki, T.; Watanabe, Y.; Masuda, H. *Organometallics* **1995**, *14*, 4228-4235. (b) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413-3415. (c) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. d) Nakatsu, D.; Mitsudo, T.; Nakanishi, H.; Watanabe, Y.; Takegami, Y. *Chem. Lett.* **1977**, 1447-1448.
30. Barluenga, J.; Aznar, F.; Martín, A.; García-Granada, S.; Pérez-Carreño, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191-11192.
31. (a) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383-8391. (b) Mayr, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215-2216. (c) Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 6079-6080.
32. For a review of η^3-vinylcarbene complexes, see: Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525-1538.
33. (a) Barluenga, J.; Aznar, F.; Gutiérrez, I.; Martín, A.; García-Granada, Llorca-Barangaño, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 1314-1324. (b) Waters, M. L.; Bos, M. E.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6403-6413. (c) Gleichmann, M. M.; Dötz, K. H.; Hess, B. A. *J. Am. Chem. Soc.* **1996**, *118*, 10551-10560. (d) Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769-789. (e) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689-1706.
34. Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3211-3222.

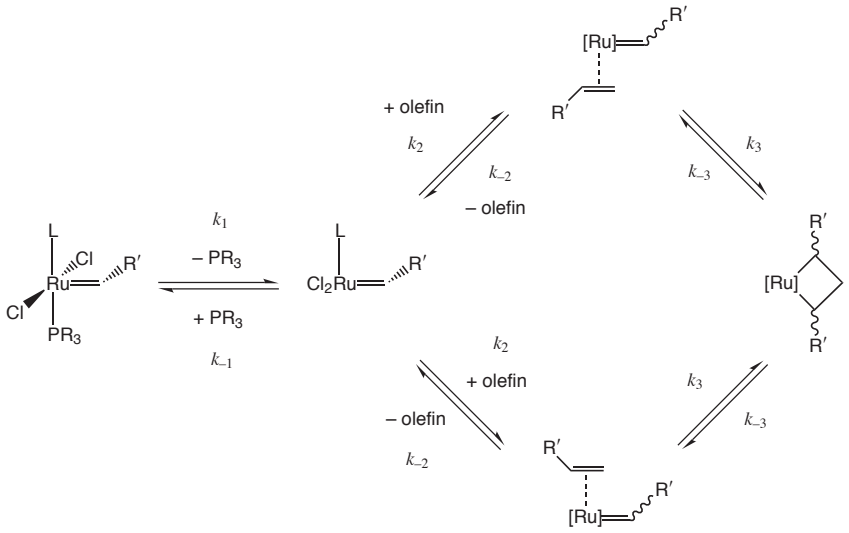


Scheme 4.5

To explain the observed equatorial orientation of the η^3-vinylcarbene moiety in **2.3**-**2.7**, it is likely that the trans to cis isomerization of the chlorides occurs before metallacyclobutene formation. The alternative, in which the alkyne binds immediately after phosphine dissociation, leads to an axial vinylcarbene moiety with the vinyl group trans to L. At that point, a non-trivial rearrangement of the ligands would be required to obtain the observed product.

Relevance of η^3-vinylcarbene complexes to olefin metathesis. Scheme 4.6 illustrates the olefin metathesis catalytic cycle mediated by **4.2** (L = H_2IMes), which proceeds through a phosphine-dissociated 14-electron species (L)$(Cl)_2$Ru=CHR, a 16-electron olefin adduct (L)(olefin)$(Cl)_2$Ru=CHR, and a metallacyclobutane complex.[35] The orientation of olefin co-ordination and geometry of the subsequent metallacyclobutane are particularly important to the stereoselectivity of the reaction. However, it is challenging to determine these structural features because to date none of the intermediates in Scheme 4.6 have been observed experimentally.

35. (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554. (b) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749-750.



Scheme 4.6

The η^3-vinylcarbene complexes **2.3**-**2.7** provide models for these olefin-coordinated and metallacyclobutane intermediates. For a similar purpose, Osborn and coworkers have studied metathesis-active tungsten alkylidene–olefin intermediates by low temperature ^{1}H and ^{13}C NMR,[36] and Mayr and coworkers have examined the structures of tungsten vinylcarbene and alkylidene–alkyne complexes.[18,31b-c]

Previously in the literature, two conformations have been proposed for the ruthenium–olefin adduct in Scheme 4.6: **E**, in which the olefin is bound trans to L in the site vacated by the phosphine ligand, and **F**, in which the chlorides adopt a cis arrangement in the alkylidene–halide–olefin plane (Figure 4.4).[37,38] Although geometry **E** was disfavored in early mechanistic studies,[37] recent computational results indicate that it is a low energy conformation.[38,39] An olefin complex of this type, shown in Figure 4.4, has been isolated from the reaction of $(PCy_3)_2(Cl)_2Ru$=CHPh (**2.1**) with a functionalized cyclobutene.[40] The x-ray crystal structure verifies that this complex contains an olefin coordinated trans to the phosphine and tethered to the alkylidene ligand. In comparison to the vinyl fragments in **4.3** and **4.6**, this coordinated olefin retains more "olefinic"

36. Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585-1587.
37. Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887-3897.
38. (a) Adlhart, C.; Chen, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4484-4487. (b) Adlhart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helvetica Chim. Acta.* **2000**, *83*, 3306-3311. (c) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204-8214. (d) Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2685-2689.
39. (a) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965-8973. (b) Vyboishchikov, S. F.; Bühl, M.; Thiel, W. *Chem. Eur. J.* **2002**, *8*, 3962-3975.
40. Tallarico, J. A.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157-7158.

character, which is reflected in the shorter C=C distance, the more planar geometry of the olefin, and the longer ruthenium–olefin distance. These differences may account for the fact that this adduct is active in subsequent metathesis reactions.

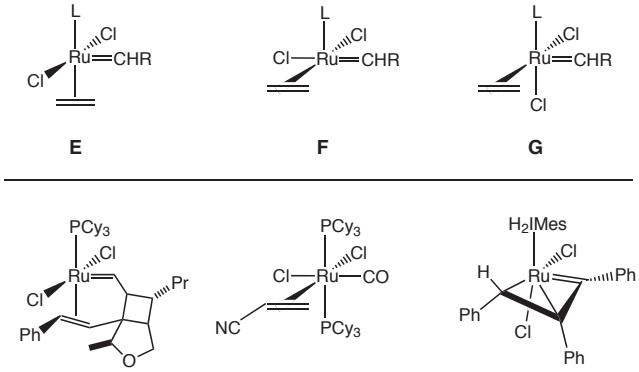


Figure 4.4

Geometry **F** was favored in early mechanistic investigations and has been substantiated by a quantum molecular dynamics study.[41] Structural models for **F** include $(PCy_3)_2(Cl)_2(CO)Ru[\eta^2\text{-}(CH_2{=}CHCN)$ (Figure 4.4) and related complexes.[42] Although these examples are six-coordinate and lack an alkylidene moiety, it has been suggested that the π-acid character of carbon monoxide makes it a reasonable alkylidene substitute.[37]

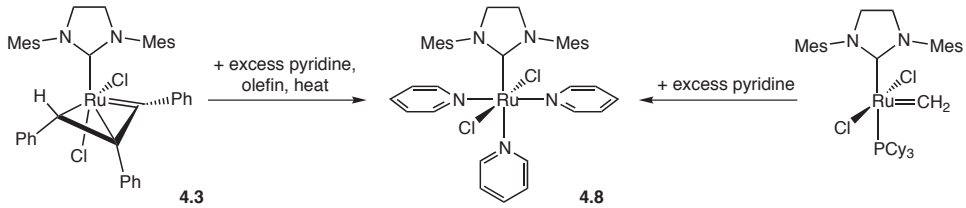
An alternative structure for the ruthenium–olefin intermediate, geometry **G**, involves a different trans/cis isomerization of the chloride ligands that ultimately positions one chloride trans to L (Figure 4.4). This conformation is supported by the structures of η^3-vinylcarbene complexes **4.3** and **4.6**, as well as by the recently determined structure of $(H_2IMes)(bipy)(Cl)_2Ru{=}C{=}CHBu^t$, which all contain cis chlorides similar to geometry **G**.[43] In addition, modeling studies suggest that such intermediates account for the observed stereoselectivities in asymmetric ring closing metathesis reactions.[44] However, the results of two computational studies are inconclusive. Thiel and coworkers find that olefin binding to $(L)(Cl)_2Ru{=}CHPh$ that involves this type of halide isomerization has a high-energy transition state, but they do not explore a scenario where halide

41. (a) Meier, R. J.; Aagaard, O. M.; Buda, F. *J. Mol. Cat. A.: Chem.* **2000**, *160*, 189-197. (b) Aagaard, O. M.; Meier, R. J.; Buda, F. *J. Am. Chem. Soc.* **1998**, *120*, 7174-7182.
42. (a) Brown, L. D.; Carnard, C. F. J.; Daniels, J. A.; Mawby, R. J.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2932-2935. (b) Moers, F. G.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 591-593.
43. Hajela, S.; Day, M. W. Unpublished results, 2002.
44. Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225-3228.

isomerization occurs before olefin binding.[39b] Likewise, calculations by Chen and coworkers indicate that the $(PH_3)(Cl)_2Ru(CH_2)_3$ metallacyclobutane intermediate with chlorides in a cis arrangement (as in **G**) is a lower energy conformation than when they are trans (as in **E**), but they do not explore halide isomerization prior to metallacycle formation.

An important point is that η^3-vinylcarbene complexes **4.3**-**4.7** are not actual intermediates in the olefin metathesis reaction. These complexes are inactive for ring-closing metathesis, and their *in situ* formation from **4.1** or **4.2** during enyne metathesis has not been reported.[45] Experiments in a related system indicate that the presence of five equivalents of diphenyl-acetylene during the RCM of 4,4-dicarbethoxy-2-methyl-1,6-heptadiene with **4.2** slows the rate of RCM by at least two orders of magnitude, but only a trace of **4.3** is formed. Nevertheless, the structures of these novel complexes demonstrate that the rearrangement of chloride ligands to provide geometry **G** is possible, and this conformation should be considered with respect to the olefin metathesis mechanism.[46]

Reactivity of η^3-vinylcarbene complexes. In an attempt to activate complex **4.3** for olefin metathesis, the ring-closing metathesis of diethyl diallylmalonate was performed in the presence of pyridine (Scheme 4.7). Although no ring-closed product was observed, even after heating at 80°C, the solution changed from green to red in color. A crystal structure analysis revealed that the organometallic product is the tris(pyridine) complex $(H_2IMes)(py)_3(Cl)_2Ru$ (**4.8**) (Figure 4.5). All bond distances and angles in this structure are typical, but the mesityl groups are twisted by ~25° with respect to each other, in contrast to their usual orientation perpendicular to the imidazolidine ring.



Scheme 4.7

45. (a) Stragies, R.; Voigtmann, U.; Blechert, S. *Tetrahedron Lett.* **2000**, *41*, 5465-5468. (b) Smulik, J. A.; Diver, S. T. *Org. Lett.* **2000**, *2*, 2271-2274.
46. (a) Nieczypor, P.; van Leeuwen, P. W. N. M.; Mol, J. C.; Lutz, M.; Spek, A. L. *J. Organomet. Chem.* **2001**, *625*, 58-66. (b) Hansen, S. M.; Rominger, F.; Metz, M.; Hofmann, P. *Chem. Eur. J.* **1999**, *5*, 557-566.

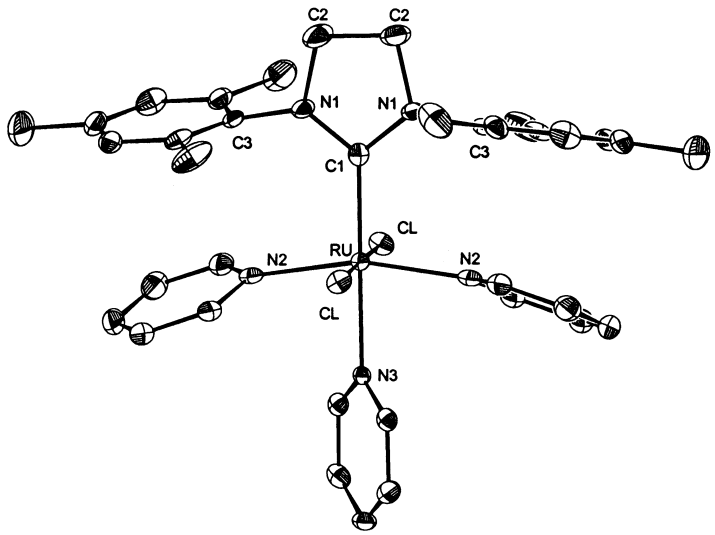


Figure 4.5: Structure of $(H_2IMes)(py)_3(Cl)_2Ru$ (**4.8**) (CCDC #185134). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg]: Ru–C(1) 2.052(3), Ru–N(2) 2.127(2), Ru–N(3) 2.176(2), Ru–Cl 2.442(1), N(1)–C(1) 1.371(2), N(1)–C(2) 1.475(3), C(2)–C(2)′ 1.479(5), N(1)–C(3) 1.427(2), C(1)–Ru–N(2) 97.92(4), C(1)–Ru–N(3) 180, C(1)–Ru–Cl 90.57(1), Cl–Ru–Cl′ 178.85(3), N(2)–Ru–Cl 90.88(5), N(3)–Ru–Cl 89.43(1), N(1)–C(1)–N(1)′ 103.9(2), C(1)–N(1)–C(3) 131.9(2), C(1)–N(1)–C(2) 113.8(2).

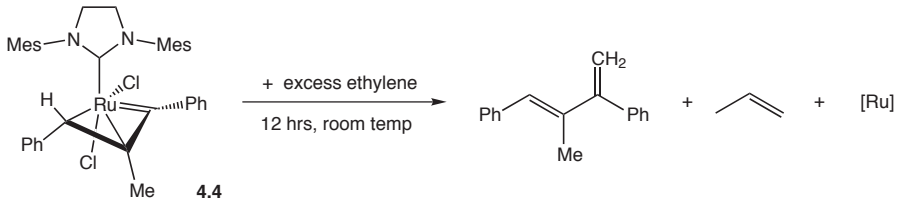
$(H_2IMes)(py)_3(Cl)_2Ru$ (**4.8**) is also the organometallic product from the reaction of the methylidene complex $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2$ with an excess of pyridine (Scheme 4.7). Werner and coworkers have reported that a similar reaction between the ruthenium methylidene complex $(PPr^i{}_2Ph)_2(CO)(Cl)(H)Ru{=}CH_2$ and pyridine yields $(PPr^i{}_2Ph)_2(py)(CO)(Cl)(H)Ru$.[47] In both these cases, the fate of the methylidene moiety is unclear.

Complex **4.3** undergoes halide exchange with sodium iodide to form $(H_2IMes)(I)_2Ru[\eta^3$-(CHPh)(CPh)(CPh)], which also can be prepared by reacting $(H_2IMes)(PCy_3)(I)_2Ru{=}CHPh$ with diphenylacetylene. Furthermore, **4.3** reacts with $HBAr^F{}_4$ to generate several alkylidenes with H_α NMR resonances between 16.0 and 19.5 ppm, but these species decomposed during isolation attempts.

Although complexes **4.3**-**4.7** do not react with typical olefin metathesis substrates, they do react cleanly with ethylene. This reaction is most facile with the least sterically encumbered

47. Werner, H.; Stüer, W.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 1707-1713.

derivative $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CMe)(CPh)]$ (**4.4**). As illustrated in Scheme 4.8, the products consist of one equivalent of diene CHPh=CMe−CPh=CH_2, one equivalent of propylene, and an unidentified ruthenium species (Scheme 4.8). Unfortunately, this species also decomposed during isolation attempts, but *in situ* ^1H and ^{13}C NMR indicates that the H_2IMes ligand remains bound to ruthenium.



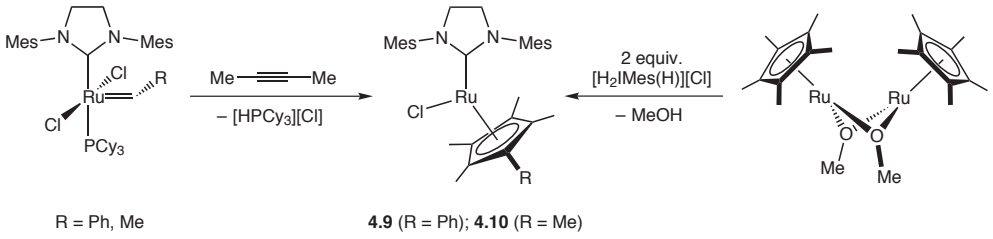
Scheme 4.8

The product mixture in Scheme 4.8 suggests a mechanism in which ethylene first coordinates to **4.4** and participates in one turnover of olefin metathesis, providing the free diene CHPh=CMe−CPh=CH_2 and a ruthenium methylidene intermediate. Then a second equivalent of ethylene coordinates to ruthenium and couples with the methylidene to provide an unsubstituted metallacyclobutane, which undergoes either α- or β-elimination and ultimately releases propylene. Examples of such a transformation have been reported for $(PPh_3)_2(Cl)(NO)Ru{=}CH_2$, which reacts with ethylene to form an ethylene complex and propylene,[48] for a variety of platinum metallacyclobutane complexes,[49] and more recently for a molybdenum metallacyclobutane complex.[50]

Formation of η^5-cyclopentadienyl complexes. In contrast to η^3-vinylcarbene formation, the reaction of **4.2** with 2-butyne follows a pathway that furnishes the η^5-cyclopentadienyl derivative $(H_2IMes)(Cp')(Cl)Ru$ (4.9; Cp′ = η^5-tetramethylphenylcyclopentadienyl) (Scheme 4.9). When the ethylidene derivative $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHMe$ is used instead of **4.2**, the product is the Cp* analog $(H_2IMes)(Cp^*)(Cl)Ru$ (**4.10**). This complex can be prepared independently by the reaction of $[Cp^*Ru(\mu\text{-}OMe)]_2$ with the H_2IMes chloride salt (Scheme 4.9).[51]

48. Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 609-614.
49. An example: Al-Essa, R. J.; Puddephatt, R. J.; Perkins, D. C. L.; Rendle, M. C.; Tipper, C. F. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1738-1745.
50. Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2002**, *20*, 5658-5669.
51. General route: Baratta, W.; Herrmann, W. A.; Rigo, P.; Schwartz, J. *J. Organomet. Chem.* **2000**, *593-594*, 489-493.

The crystal structures of **4.9** (Figure 4.6) and **4.10** (chapter 5) are quite similar and typical for "two-legged piano stool" complexes.



R = Ph, Me

4.9 (R = Ph); **4.10** (R = Me)

Scheme 4.9

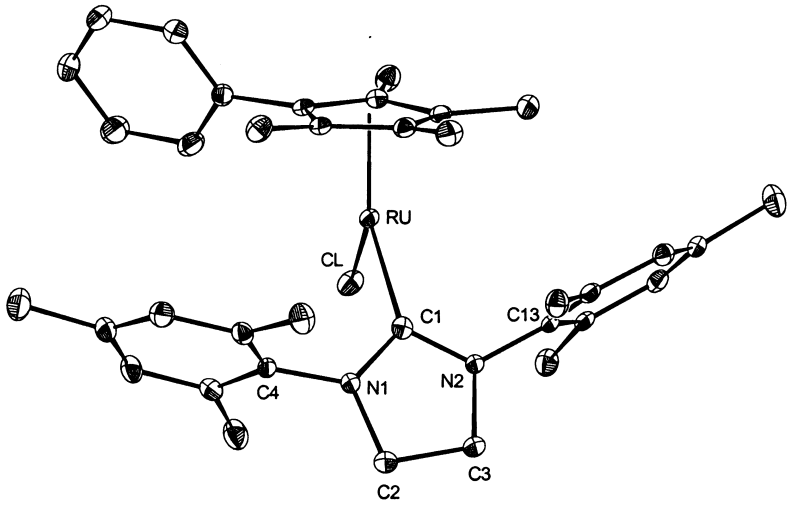
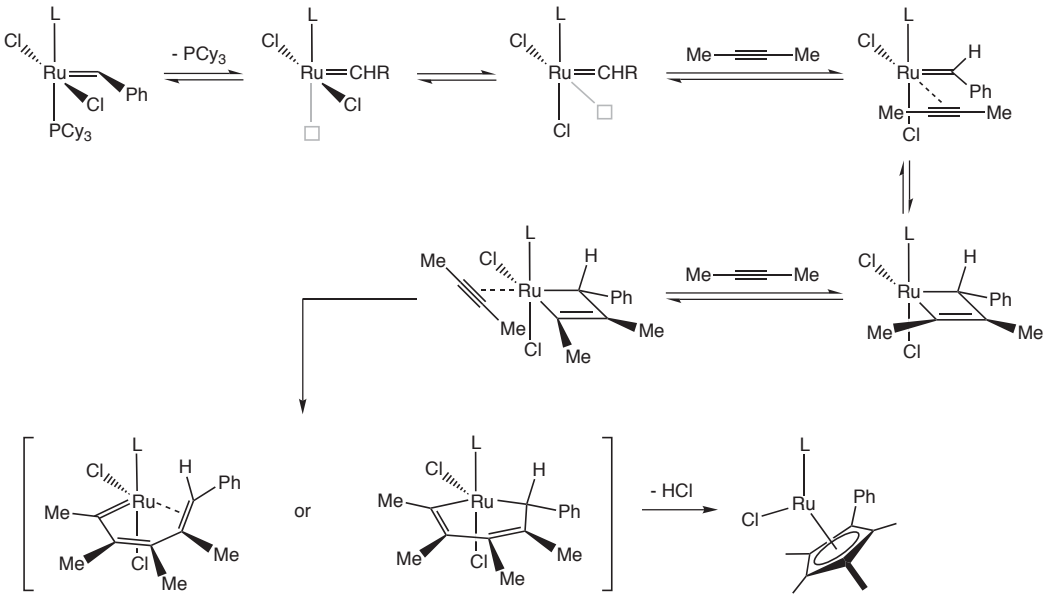


Figure 4.6: Structure of (H_2IMes)(Cp′)(Cl)Ru (**4.9**) (CCDC #177531). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg]: Ru–C(1) 2.093(2), Ru–Cl 2.384(1), Ru–Cp'_{cent} 1.77(1), N(1)–C(1) 1.349(2), N(2)–C(1) 1.354(2), N(1)–C(2) 1.471(2), N(2)–C(3) 1.473(2), C(2)–C(3) 1.524(3), N(1)–C(4) 1.439(2), N(2)–C(13) 1.440(2), C(1)–Ru–Cl 88.10(5), C(1)–Ru–Cp'_{cent} 141(1), Cl–Ru–Cp'_{cent} 129(1), C(1)–N(1)–C(4) 124.0(2), C(1)–N(2)–C(13) 125.4(2), C(1)–N(1)–C(2) 114.3(2), C(1)–N(2)–C(3) 113.8(1).

A mechanism for cyclopentadienyl ring formation starting from 4.2 is shown in Scheme 4.10. The first half of the process is analogous to η^3-vinylcarbene formation (Scheme 4.5).

However, after metallacyclobutene formation, a second equivalent of 2-butyne can coordinate to the metal center because of its smaller size. This coordination leads to a metallacyclohexadiene/ carbene–butadiene intermediate, which then eliminates HCl to provide the observed product.



Scheme 4.10

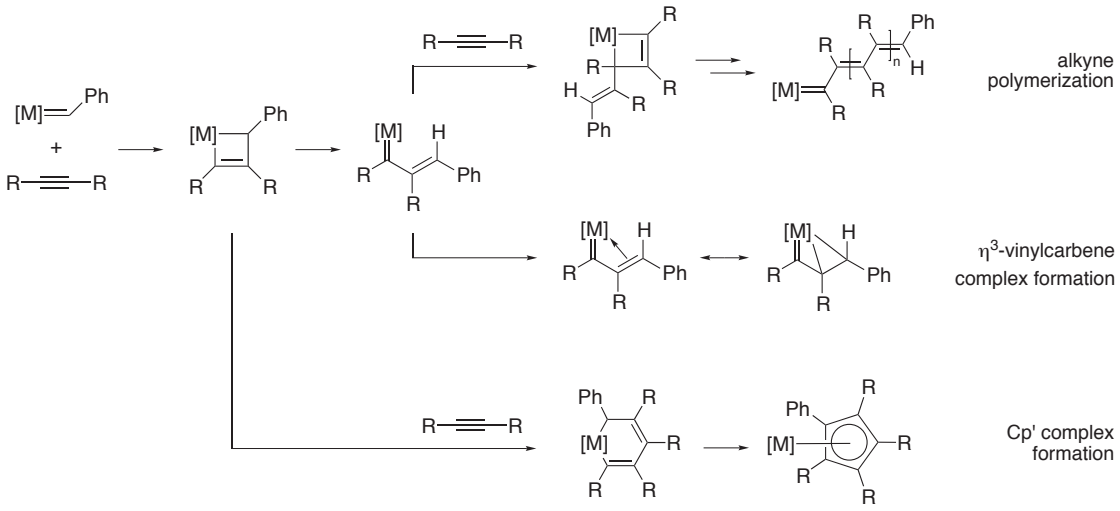
Similar transformations to multihapto-bound rings interfere with alkyne polymerization in molybdenum and tungsten systems.[52] For example, reaction of the tungsten alkylidyne $(dme)(Cl)_3W{\equiv}CBu^t$ with excess 2-butyne leads to an η^5-tetramethyl-*tert*-butylcyclopentadienyl complex.[52d] In a related case, Barluenga and coworkers have found that chromium η^3-vinyl-carbenes react with disubstituted, electron deficient alkynes to form carbene–butadiene complexes but with monosubstituted alkynes to form η^6-benzene derivatives.[33a]

Conclusions

The ruthenium alkylidene complexes $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**4.1**) and $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**4.2**) have been tested for alkyne polymerization and found to be

52. (a) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5999-6005. (b) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574-1583. (c) Churchill, M. R.; Wasserman, H. J. *Organometallics* **1983**, *2*, 755-759. (d) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808-6809.

ineffective in this transformation. More detailed studies with disubstituted alkynes reveal the reasons for this: reactions to form η^3-vinylcarbene complexes or η^5-cyclopentadienyl derivatives are more favorable than polymerization (Scheme 4.11).



Scheme 4.11

In addition, these η^3-vinylcarbene products are models for the important olefin-coordinated intermediate in the olefin metathesis catalytic cycle. The structures of these novel complexes provide experimental support for a trans/cis halide isomerization mechanism in ruthenium alkylidene chemistry. Preliminary results indicate that the organometallic chemistry of η^3-vinylcarbenes is interesting as well, and these complexes can be converted to alkylidene species under the appropriate conditions.

Experimental

General Considerations: All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen atmosphere, unless otherwise specified. Solvents were dried and degassed by standard procedures. NMR spectra were measured on Varian Inova 500 and Varian Mercury 300 spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and referenced internally with respect to the protio solvent impurity. ^{13}C NMR spectra were referenced internally with respect to the solvent resonance ($\delta = 54.00$ for CD_2Cl_2). ^{31}P NMR spectra were referenced using H_3PO_4 ($\delta = 0$) as an external standard. ^{19}F NMR spectra were referenced externally to a CCl_3F standard ($\delta = 0$). Coupling constants are in hertz. IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer as KBr pellets; the data are reported in reciprocal centimeters. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

All alkynes were obtained from commercial sources and degassed before use. $(PCy_3)_2(Cl)_2Ru$=CHPh (**4.1**) was obtained from Materia, Inc. $(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh (**4.2**) was prepared by the "hexanes" method.[53] $(H_2IMes)(PCy_3)(Cl)_2Ru$=CH(*p*-C_6H_4F) was prepared in an identical manner, starting from $(PCy_3)_2(Cl)_2Ru$=CH(*p*-C_6H_4F).[16] [Cp*Ru(μ-OMe)]$_2$,[54] [H_2IMes(H)][Cl],[53] $(H_2IMes)(py)_2(Cl)_2Ru$=CHPh,[55] $(H_2IMes)(PCy_3)(Cl)_2Ru=CH_2$,[35a] $(H_2IMes)(PCy_3)(Cl)_2Ru$=CHMe,[56] cyclooctyne,[57] and 4,4-dicarboethoxy-2-methyl-1,6-heptadiene[58] were synthesized according to literature procedures.

Crystallographic data (excluding structure factors) for the structures in this chapter have been deposited with the Cambridge Crystallographic Data Centre. Deposition numbers are included in the figure captions. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or by e-mail: deposit@ccdc.cam.ac.uk). Structure factors are also available by e-mail (xray@caltech.edu).

General procedure for alkyne polymerization:[11] A Schlenk flask was charged with 2.5 mmol of monomer and 0.025 mmol of **4.1** or **4.2**. This mixture was stirred and heated at 80°C or

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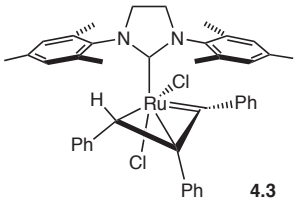
53. Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2002**, in press.
54. Koelle, U.; Kossakowski, J.; Grumbine, D.; Tilley, T. D. *Inorg. Synth.* **1992**, *29*, 225-228.
55. Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314-5318.
56. See Chapter 3.
57. Brandsma, L; Verkruijsse, H. D. *Synthesis* **1978**, 290.
58. Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310-7318.

150°C under a nitrogen atmosphere for 12 hrs or 24 hrs. Then the mixture was transferred into a large volume of methanol. The precipitate was isolated and dried under vacuum. The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ eluent, polystyrene calibration).

Additional polymerization of diphenylacetylene: In the glovebox, a glass ampoule was charged with 1.04 g diphenylacetylene and 1 mol % of catalyst **4.1** or **4.2**. The ampoule was sealed and immersed in an 80°C oil bath for 20 hrs. The product was washed with 50 mL methylene chloride and dried under high vacuum to yield a soft, pale yellow material (~0.7 g). It was not possible to obtain any other characterization data besides IR because of the insolubility of the polymer.

Synthesis and characterization of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CPh)]$ (4.3): A Schlenk flask was charged with 0.120 g (0.141 mmol) of $(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$ (**1**), 0.060 g (0.337 mmol, excess) of diphenylacetylene, and 4 mL of benzene. Under nitrogen, the reaction was heated at 60°C for 5 hours, during which time a dark green precipitate formed. The flask was then opened to air and the reaction mixture filtered through a coarse frit. The isolated green solid was washed with 15 mL hexanes and dried under vacuum. Yield: 0.070 g (66%). Crystals for x-ray analysis were obtained by slow evaporation of methylene chloride or acetone solutions of **4.3**. NMR assignments were aided with DEPT and COSY experiments.

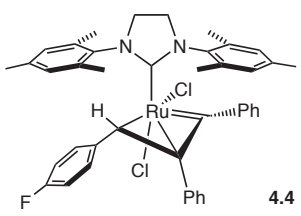


4.3

^{1}H NMR (499.852 MHz, **25°C**, CD_2Cl_2): δ 1.832 [s, 3H, CH_3], 2.089 [s, 3H, CH_3], 2.240 [s, 3H, CH_3], 2.269 [s, 3H, CH_3], 2.317 [s, 3H, CH_3], 2.552 [s, 3H, CH_3], 3.788 [dt, *J* = 10 and 12, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.032 [td, *J* = 9 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.257 [dd, *J* = 6 and 8, 2H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.777 [s, 1H, C$\underline{H}$Ph], 5.803 [s, 1H, *m*-CH_{Mes}], 6.35 [br s, 1H, Ph], 6.531 [s, 1H, *m*-CH_{Mes}], 6.667 [s, 1H, *m*-CH_{Mes}], 6.88-7.03 [multiple peaks, 6H, Ph], 6.978 [s, 1H, *m*-CH_{Mes}], 7.14 [br s, 2H, Ph], 7.262 [t, *J* = 7, 1H, *p*-H of CH$\underline{Ph}$], 7.46 [br s, 3H, Ph], 7.511 [t, *J* = 7, 1H, Ph], 9.22 [br s, 1H, *o*-H of Ru=CPh]. **^{1}H NMR** (499.852 MHz, **–45°C**, CD_2Cl_2): δ 1.772 [s, 3H, CH_3], 1.990 [s, 3H, CH_3], 2.173 [s, 3H, CH_3], 2.217 [s, 3H, CH_3], 2.333 [s, 3H, CH_3], 2.483 [s, 3H, CH_3], 3.740 [dt, *J* = 11 and 12, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.003 [td, *J* = 5 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.236 [m, 2H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.687 [s, 1H, C$\underline{H}$Ph], 5.635 [s, 1H, *m*-CH_{Mes}], 6.217 [d, *J* = 7.5, 1H, Ph], 6.547 [s, 1H, *m*-CH_{Mes}], 6.703 [s, 1H, *m*-CH_{Mes}], 6.822 [t, *J* = 7.5, 1H, Ph], 6.90-

6.93 [multiple peaks, 4H, Ph], 6.950 [s, 1H, *m*-CH_{Mes}], 7.00-7.04 [m, 2H, Ph], 7.164 [d, *J* = 7.5, 1H, Ph], 7.245 [t, *J* = 7.5, 1H, Ph], 7.331 [t, *J* = 7.5, 1H, Ph], 7.440 [t, *J* = 7.5, 1H, Ph], 7.517 [t, *J* = 7.5, 1H, Ph], 7.623 [d, *J* = 7.5, 1H, Ph], 9.169 [d, *J* = 9, 1H, *o*-H of Ru=CPh]. **^{1}H NMR** (499.852 MHz, **130°C**, C_6D_5Br): δ 1.93 [br s, 3H, CH_3], 2.11 [br s, 3H, CH_3], 2.32 [br s, 6H, 2 CH_3], 2.58 [br s, 3H, CH_3], 2.81 [br s, 3H, CH_3], 3.77 [br s, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 3.90 [br s, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.17 [br s, 2H, NC$\underline{H}_2$C$\underline{H}_2$N], 5.032 [s, 1H, C$\underline{H}$Ph], 6.08 [br s, 1H, *m*-CH_{Mes}], 6.54 [br s, 1H, *m*-CH_{Mes}], 6.56 [br s, 1H, *m*-CH_{Mes}], 6.84-6.87 [multiple peaks, 2H], 6.932 [br t, *J* = 7, 1H, Ph], 7.025 [br t, *J* = 7, 2H, Ph], 7.143 [s, 1H], 7.18-7.21 [multiple peaks, 2H, Ph], 7.29-7.38 [multiple peaks, 5H, Ph], 7.49 [s, 1H, Ph], 7.821 [d, *J* = 7, 1H, Ph], 8.16 [br s, 1H, *o*-H of Ru=CPh]. **^{13}C{^{1}H} NMR** (125.712 MHz, **25°C**, CD_2Cl_2): δ 19.10 [CH_3], 19.27 [CH_3], 19.47 [CH_3], 20.52 [CH_3], 20.02 [CH_3], 21.33 [CH_3], 53.02 [N$\underline{C}H_2\underline{C}H_2$N], 53.64 [N$\underline{C}H_2\underline{C}H_2$N], 67.87 [$\underline{C}$HPhCPhCPh], 91.67 [CHPh$\underline{C}$PhCPh], 127.37 [$CH_{aryl}$], 127.57 [$CH_{aryl}$], 128.26 [$CH_{aryl}$], 128.52 [$CH_{aryl}$], 129.33 [$CH_{aryl}$], 129.47 [$CH_{aryl}$], 130.29 [$CH_{aryl}$], 130.37 [$CH_{aryl}$], 130.90 [$CH_{aryl}$], 132.04 [$C_{aryl}$], 132.12 [br, CH_{aryl}), 134.16 [CH_{aryl}], 134.40 [C_{aryl}], 134.68 [C_{aryl}], 135.26 [C_{aryl}], 136.50 [C_{aryl}], 138.23 [C_{aryl}], 138.95 [C_{aryl}], 139.46 [C_{aryl}], 139.60 [C_{aryl}], 139.68 [C_{aryl}], 141.81 [C_{aryl}], 216.16 [Ru-$\underline{C}N_2(H_2IMes)$], 285.06 [Ru=$\underline{C}$Ph]. **IR:** 3055 (m), 3017 (m), 2953 (m), 2915 (m), 2857 (m), 2730 (w), 2363 (w), 2343 (w), 1609 (m), 1481 (s), 1444 (s), 1426 (s), 1375 (s), 1264 (s), 1181 (m), 1168 (m), 1090 (w), 1075 (m), 1028 (m), 990 (w), 950 (w), 918 (w), 849 (m), 820 (w), 780 (m), 764 (m), 748 (m), 694 (s), 652 (w), 637 (w), 625 (w), 606 (w), 576 (m), 537 (m), 517 (w), 473 (w). **Anal. Calcd. for $C_{42}H_{42}N_2Cl_2Ru$:** C, 67.55%; H, 5.67%; N, 3.75%. Found: C, 67.14%; H, 5.66%; N, 3.56%.

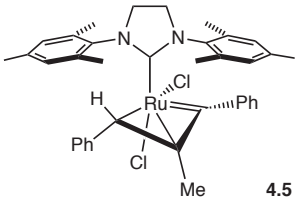
Synthesis and characterization of $(H_2IMes)(Cl)_2Ru[\eta^3$-(CH(*p*-C_6H_4F))(CPh)(CPh)] (4.4): Synthesis analogous to **4.3**, starting from $(H_2IMes)(PCy_3)Cl_2Ru$=CH(*p*-C_6H_4F). **^{1}H NMR** (499.852 MHz, **25°C**, CD_2Cl_2): δ 1.828 [s, 3H, CH_3], 2.138 [s, 3H, CH_3], 2.237 [s, 3H, CH_3], 2.254 [s, 3H, CH_3], 2.283 [s, 3H, CH_3], 2.558 [s, 3H, CH_3], 3.789 [dt, *J* = 11 and 12, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.019 [td, *J* = 7 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.252 [m, 2H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.719 [s, 1H, C$\underline{H}$(*p*-C_6H_4F)], 5.835 [s, 1H, *m*-CH_{Mes}], 6.30 [v br s, 1H, Ph], 6.493 [s, 1H, *m*-CH_{Mes}], 6.671 [s, 1H, *m*-CH_{Mes}], 6.850 [br s, 2H], 6.88-6.92 [m, 2H], 6.95-6.97 [m, 4H], 7.021 [tt, *J* = 1 and 7, 1H], 7.45 [br s, 3H], 7.510 [tt, *J* = 1 and 7, 1H], 9.20 [br s, 1H, *o*-H of Ru=CPh]. **^{1}H NMR** (499.852 MHz, **–50°C**, CD_2Cl_2): δ 1.780 [s, 3H, CH_3],



4.4

2.050 [s, 3H, CH_3], 2.190 [s, 3H, CH_3], 2.224 [s, 3H, CH_3], 2.295 [s, 3H, CH_3], 2.496 [s, 3H, CH_3], 3.745 [dt, *J* = 11 and 12, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.001 [td, *J* = 5 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.236 [m, 2H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.644 [s, 1H, C$\underline{H}$(*p*-C_6H_4F)], 5.664 [s, 1H, *m*-CH_{Mes}], 6.238 [d, *J* = 7, 1H, Ph], 6.533 [s, 1H, *m*-CH_{Mes}], 6.635 [td, *J* = 2 and 9, 1H, *p*-C_6H_4F], 6.719 [s, 1H, *m*-CH_{Mes}], 6.837 [t, *J* = 8, 1H, Ph], 6.91 [br s, 3H, Ph], 6.961 [s, 1H, *m*-CH_{Mes}], 7.052 [m, 3H, Ph], 7.201 [td, *J* = 2 and 7, 1H, *p*-C_6H_4F], 7.441 [t, *J* = 8, 1H, Ph], 7.529 [td, *J* = 1 and 7, 1H, *p*-C_6H_4F], 7.608 [td, *J* = 2 and 7, 1H, *p*-C_6H_4F], 9.160 [d, *J* = 8, 1H, *o*-H of Ru=CPh]. **^{19}F NMR** (282.148 MHz, **25°C**, CD_2Cl_2): δ –113.4 (m, *p*-C_6H_4F).

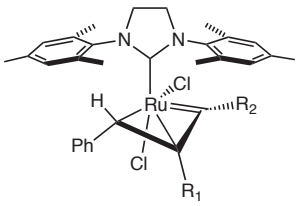
Synthesis and characterization of (H_2IMes)(Cl)$_2$Ru[η^3-(CHPh)(CMe)(CPh)] (4.5): A Schlenk flask was charged with 0.102 g (0.120 mmol) of (H_2IMes)(PCy_3)Cl_2Ru=CHPh, 0.080 g (0.689 mmol, excess) of 1-phenyl-1-propyne, and 4 mL of benzene. Under nitrogen, the reaction was heated at 60°C for 10 hours, during which time an emerald green precipitate formed. The flask was then opened to air and the reaction mixture filtered through a coarse frit. The isolated green solid was washed with 1 mL benzene, 2x10 mL methanol, and 15 mL hexanes, and dried under vacuum. Yield: 0.064 g (78%). **^{1}H NMR** (499.852 MHz, **25°C**, CD_2Cl_2): δ 1.794 [d, *J* = 0.5, 3H, C$\underline{Me}$], 1.872 [s, 3H, CH_3], 2.037 [s, 3H, CH_3], 2.061 [s, 3H, CH_3], 2.227 [s, 3H, CH_3], 2.295 [s, 3H, CH_3], 2.597 [s, 3H, CH_3], 3.782 [dt, *J* = 10 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 3.940 [td, *J* = 7 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.146 [dt, *J* = 10 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.259 [td, *J* = 7 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.557 [s, 1H, C$\underline{H}$Ph], 5.974 [s, 1H, *m*-CH_{Mes}], 6.401 [s, 1H, *m*-CH_{Mes}], 6.543 [s, 1H, *m*-CH_{Mes}], 6.975 [s, 1H, *m*-CH_{Mes}], 7.26-7.30 [multiple peaks, 5H, Ph], 7.344 [tt, *J* = 1 and 6, 1H, Ph], 7.53-7.55 [m, 2H, Ph], 7.640 [tt, *J* = 1 and 7, 1H, Ph], 7.90 [br s, 1H, Ph]. **^{1}H NMR** (499.852 MHz, **–70°C**, CD_2Cl_2): δ 1.795 [s, 3H, C$\underline{Me}$], 1.808 [s, 3H, CH_3], 1.959 [s, 3H, CH_3], 2.099 [s, 3H, CH_3], 2.158 [s, 3H, CH_3], 2.182 [s, 3H, CH_3], 2.488 [s, 3H, CH_3], 3.719 [dt, *J* = 11 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 3.916 [td, *J* = 6 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.137 [dt, *J* = 11 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.200 [td, *J* = 6 and 11, 1H, NC$\underline{H}_2$C$\underline{H}_2$N], 4.402 [s, 1H, C$\underline{H}$Ph], 5.739 [s, 1H, *m*-CH_{Mes}], 6.451 [s, 1H, *m*-CH_{Mes}], 6.604 [s, 1H, *m*-CH_{Mes}], 6.902 [d, *J* = 8, 1H, Ph], 6.959 [s, 1H, *m*-CH_{Mes}], 7.175 [t, *J* = 7, 1H, Ph], 7.27-7.35 [multiple peaks, 3H, Ph], 7.396 [t, *J* = 7, 1H, Ph], 7.535 [br d, 2H, Ph], 7.644 [td, *J* = 1 and 7, 1H, Ph], 7.498 [d, *J* = 7, 1H, Ph]. **^{13}C{^{1}H} NMR** (125.712 MHz, **22°C**, CD_2Cl_2): δ 11.49 [C$\underline{Me}$], 18.62 [CH_3], 19.17 [CH_3], 19.46 [CH_3], 20.69 [CH_3], 21.07 [CH_3], 21.32 [CH_3], 52.92



4.5

[N<u>C</u>H$_2$<u>C</u>H$_2$N], 52.98 [N<u>C</u>H$_2$<u>C</u>H$_2$N], 69.92 [<u>C</u>HPhCMeCPh], 91.67 [CHPh<u>C</u>MeCPh], 127.60, 128.43, 129.12, 129.54 (br), 129.60, 130.34, 130.36, 130.89, 131.13, 134.18, 134.66, 135.15, 136.54, 138.06, 138.74, 139.28, 139.33, 139.78, 141.67, 214.68 [Ru-<u>C</u>N$_2$(H$_2$IMes)], 288.142 [Ru=<u>C</u>Ph]. **IR:** 3051 (w), 3009 (w), 2947 (w), 2913 (m), 2854 (w), 1623 (m), 1600 (w), 1477 (s), 1459 (m), 1441 (m), 1425 (m), 1400 (m), 1374 (m), 1284 (m), 1265 (s), 1218 (w), 1176 (w), 1166 (w), 1073 (w), 1031 (m), 1012 (w), 984 (w), 849 (m), 803 (w), 756 (m), 692 (m), 632 (w), 575 (w), 559 (w), 497 (w). **Anal. Calcd. for $C_{37}H_{40}N_2Cl_2Ru$:** C, 64.90%; H, 5.89%; N, 4.09%. Found: C, 64.84%; H, 5.89%; N, 3.96%.

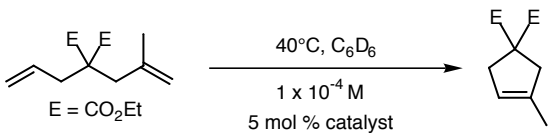
Synthesis and characterization of (H$_2$IMes)(Cl)$_2$Ru[η^3-(CPh)(CC≡CPh)(CHPh)] (4.6) + isomer (4.7): A Schlenk flask was charged with 0.115 g (0.135 mmol) of (H$_2$IMes)(PCy$_3$)Cl$_2$Ru=CHPh, 0.068 g (0.336 mmol, excess) of 1,4-diphenylbutadiyne, and 4 mL of benzene. Under nitrogen, the reaction was heated at 60°C for 12 hours, during which time a dark brown-green precipitate formed. The flask was then opened to air and the reaction mixture filtered through a coarse frit. The isolated green solid was washed with 15 mL hexanes and dried under vacuum. Yield: 0.057 g (54%). Crystals for x-ray analysis were obtained by slow evaporation of a methylene chloride solution. **^{1}H NMR** (499.852 MHz, **25°C**, CD_2Cl_2): δ 1.86 [br s], 2.04-2.40 [multiple peaks, some br], 2.53 [br s], 3.50 [br s], 3.828 [dt, *J* = 10, 11], 4.01 [br s], 4.24 [br s], 4.64 [br s], 5.85 [br s], 5.90 [br s] 6.54 [br s], 6.72-7.40 [multiple peaks, some br], 7.91 [br s], 8.19 [br s], 9.36 [br s]. **^{1}H NMR** (499.852 MHz, **–30°C**, CD_2Cl_2) diagnostic peaks of the major isomer (~60% of mixture): δ 1.819 [s, 3H, CH_3], 2.069 [s, 3H, CH_3], 2.202 [s, 3H, CH_3], 2.227 [s, 3H, CH_3], 2.259 [s, 3H, CH_3], 2.489 [s, 3H, CH_3], 3.793 [m, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 4.015 [m, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 4.246 [m, 2H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 4.575 [s, 1H, C<u>H</u>Ph], 5.727 [s, 1H, *m*-CH$_{Mes}$], 6.553 [s, 1H, *m*-CH$_{Mes}$], 6.736 [s, 1H, *m*-CH$_{Mes}$], 6.956 [s, 1H, *m*-CH$_{Mes}$]; other peaks δ 1.962 (s), 2.022 (s), 2.089 (s), 2.114 (s), 2.131 (s), 2.138 (s), 2.192 (s), 2.362 (s), 2.573 (s), 3.793 (m), 4.108 (m), 5.891 (s), 6.679 (s), 6.703 (s), 6.763 (s), 6.772 (s), 6.885 (s), 7.009 (s), 7.054 (s), 7.071 (s), 7.481-7.150 (multiple peaks), 7.718-7.652 (multiple peaks), 7.905 (br s), 8.024 (d), 8.90 (v br s). It was not possible to obtain a ^{13}C{^{1}H} NMR spectrum because of the poor solubilities of **4.6** and **4.7**. **IR:** 3051 (w), 2999 (w), 2958 (w), 2914 (m), 2854 (w), 2195 [w, ν(C≡C)], 1628 (w), 1608 (w), 1592 (w), 1479 (s), 1441 (s), 1427 (s), 1400 (m), 1375 (m),

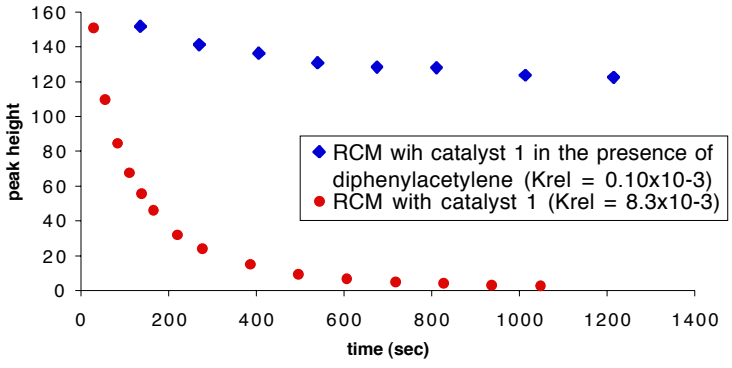


4.6 R_1 = C≡CPh, R_2 = Ph
4.7 R_1 = Ph, R_2 = C≡CPh

1280 (s), 1262 (s), 1181 (m), 1130 (w), 1099 (w), 1068 (w), 1028 (m), 989 (w), 912 (w), 883 (w), 850 (m), 812 (w), 759 (s), 725 (w), 688 (s), 652 (w), 637 (w), 576 (m), 530 (m), 512 (w), 474 (w). The product was recrystallized from methylene chloride/hexanes prior to elemental analysis. **Anal. Calcd. for $C_{45}H_{44}Cl_2N_2Ru$:** C, 68.56%; H, 5.49%; N, 3.63%. Found: C, 68.67%; H, 5.72%; N, 3.80%.

Comparison of the ring-closing metathesis activity of 4.2 in the presence and the absence of diphenylacetylene: For the RCM reaction without diphenylacetylene: In a glovebox, a Wilmad screw-cap NMR tube with septum was charged with 0.60 mL of a 1×10^{-4} M stock solution of catalyst **4.2** in C_6D_6. The temperature of the solution was equilibrated at 40°C in the NMR spectrometer probe, then 15 μL of 4,4-dicarbethoxy-2-methyl-1,6-heptadiene was injected and data collection started. For the RCM reaction with diphenylacetylene: A similar procedure was followed, except that 5 equivalents (based on **4.2**) of diphenylacetylene was added to the stock solution. The plot below shows the decrease of the diene substrate over time as it converts to ring-closed product, as measured by the decreasing peak heights (arbitrary scale) of the diene substrate. The k_{rel} values were obtained using the kinetics software on a 500 MHz Varian Unity Inova spectrometer., which fit the peak height data to a first order exponential (VNMR 6.1B Software, Varian Associates).





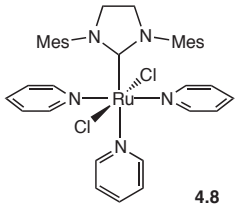
Reaction of (IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh with diphenylacetylene to generate (IMes)(Cl)$_2$Ru[η^3-(CPh)(CPh)(CHPh)]: A screw-cap Wilmad NMR tube was charged with 0.01 g (0.012 mmol) of (IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh, 0.01 g (0.056 mmol, excess) of diphenylacetylene, and 0.75 mL of CD_2Cl_2 under nitrogen. The reaction was heated at 60°C for 5 hours, during which time the solution color changed from dark red-brown to dark green. Characteristic **^{1}H NMR** data of the product (499.852 MHz, **25°C**, CD_2Cl_2): δ 1.899 [s, 3H, CH_3], 1.911 [s, 3H, CH_3], 1.987 [s, 3H, CH_3], 2.109 [s, 3H, CH_3], 2.390 [s, 3H, CH_3], 2.416 [s, 3H, CH_3], 5.421 [s, 1H, CPhCPhC<u>H</u>Ph], 6.087 [s, 1H, *m*-CH_{Mes}], 6.363 [s, 1H, *m*-CH_{Mes}], 6.546 [s, 1H, *m*-CH_{Mes}], 6.9-7.9 (multiple peaks, CH_{aryl} and NC<u>H</u>C<u>H</u>N).

Synthesis and characterization of (H$_2$IMes)(I)$_2$Ru[η^3-(CHPh)(CPh)(CPh)]: Method 1: Synthesis analogous to **4.3**, starting from (H$_2$IMes)(PCy$_3$)(I)$_2$Ru=CHPh. ^{1}H NMR (299.9 MHz, 25°C, CD_2Cl_2): δ 1.827 [s, 3H, CH_3], 2.048 [s, 3H, CH_3], 2.206 [s, 3H, CH_3], 2.357 [s, 3H, CH_3], 2.474 [s, 3H, CH_3], 2.493 [s, 3H, CH_3], 3.836 [dt, *J* = 11 and 14, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 3.997 [td, *J* = 4 and 11, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 4.143 [td, *J* = 4 and 11, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 4.285 [dt, *J* = 11 and 13, 1H, NC<u>H</u>$_2$C<u>H</u>$_2$N], 5.234 [s, 1H, C<u>H</u>Ph], 5.725 [s, 1H, *m*-CH_{Mes}], 6.606 [d, *J* = 7, 1H, Ph], 6.866 [t, *J* = 8, 1H, Ph], 7.059 [m, Ph], 7.185 [br t, 1H, Ph], 7.330 [t, *J* = 8, 1H, Ph], 7.347 [s, 1H, *m*-CH_{Mes}], 7.491 [t, *J* = 7, 1H, Ph], 7.668 [d, *J* = 7, 1H, Ph]. Method 2: A screw-cap NMR tube was charged with 0.020 g (0.027 mmol) of **4.3**, 0.020 g (0.133 mmol) of NaI, and 0.7 mL of CD_2Cl_2. After ~12 hrs at room temperature, the solution turned from green to brown in color and a ^{1}H NMR spectrum showed complete conversion to the diiodide product.

Reaction of (H$_2$IMes)(py)$_2$(Cl)$_2$Ru=CHPh with diphenylacetylene: A screw-cap NMR tube was charged with 0.020 g (0.028 mmol) of (H$_2$IMes)(py)$_2$(Cl)$_2$Ru=CHPh, 0.020 g (0.112 mmol) of diphenylacetylene, and 0.7 mL of CD_2Cl_2. After 6 hrs, a ^{1}H NMR spectrum showed complete conversion to **4.3**.

Synthesis and characterization of (H$_2$IMes)(py)$_3$(Cl)$_2$Ru (4.8): Method 1: A solution of 0.150 g (0.195 mmol) of (H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CH_2, 0.25 mL of pyridine (excess), and 1

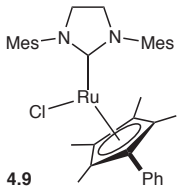
mL of toluene was stirred at room temperature for 30 min. 20 mL of hexanes were added, and the solution was allowed to sit without stirring for a few minutes. The red solution was decanted away from the pale yellow precipitate and then cooled to 0°C. The resulting red precipitate was collected and redissolved in a minimum amount of toluene. Again, 20 mL of hexanes were added, the solution cooled, and the red precipitate collected. This procedure was repeated three more times. Finally, the precipitate was dried under vacuum to provide 0.041 g of almost pure **4.8** as a red-orange solid (~29%). ^{1}H NMR of **4.8** (CD_2Cl_2, 499.85 MHz): δ 9.00 [d, *J* = 5.5, 4H, py], 8.70 [d, *J* = 5.5, 2H, py], 7.30 [t, J = 7.5, 1H, py], 6.98 [t, *J* = 7.5, 2H, py], 6.76 [t, *J* = 7.0, 2H, py], 6.76 [t, *J* = 7.0, 2H, py], 6.34 [s, 4H, *m*-H], 6.33 [t, *J* = 7.0, 4H, py], 3.98 [s, 4H, CH_2CH_2], 2.47 [s, 12H, *o*-Me], 2.02 [s, 6H, *p*-Me]. ^{13}C{^{1}H} NMR of **4.8** (CD_2Cl_2, 125.71 MHz): δ 198.2 [CN_2], 142.2 [Mes or py], 138.5 [Mes or py], 128.4 [Mes or py], 125.6 [Mes or py], 125.0 [Mes or py], 123.1 [Mes or py], 120.3 [Mes or py], 118.4 [Mes or py], 113.1 [Mes or py], 118.9 [Mes or py], 54.1 [CH_2CH_2], 25.7 [*p*-Me], 24.5 [*o*-Me]. Characterization data for the PCy_3 salt (?) impurity: ^{1}H NMR (CD_2Cl_2, 499.85 MHz): δ 0.880 [t, J = 6.5], 1.26-1.55 [m, 12H], 1.802 [br d, 2H], 1.937 [m, 4H], 1.983 [s, 6H], 2.007 [s, 6H], 2.529 [m, 3H]. ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz): δ 25.86 [d, *J* = 1], 26.86 [d, *J* = 12], 27.20 [d, *J* = 4], 30.60 [s], 30.94 [s]. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.9 MHz): δ 36.41 [s]. Complex **4.8** is air sensitive, both in solution and as a solid. The dark green decomposition product has characteristic ^{1}H NMR resonances at δ 4.097 [m] and 4.476 [m]. Method 2: A J. Young NMR tube was charged with 0.020 g (0.027 mmol) of $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CPh)(CPh)] (**4.3**), one drop of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene, one drop of pyridine, and 0.7 mL CD_2Cl_2. After heating at 80°C for ~12 hrs, the solution changed from green to red in color and a ^{1}H NMR spectrum showed the presence of **4.8**. Crystals for x-ray analysis were obtained by slow evaporation of this solution.



4.8

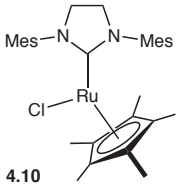
Synthesis and characterization of $(H_2IMes)(Cp')(Cl)Ru$ (4.9): A solution of 0.225 g (0.266 mmol) of $(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh (**4.2**), 1 mL of 2-butyne, and 10 mL of dichloromethane were stirred at room temperature for 30 min. The resulting royal blue solution was cooled to −10°C and the resulting dark blue microcrystals were collected. The supernatant was concentrated to half its volume and cooled to −10°C to furnish a second crop of microcrystals, for a total yield of 0.030 g (17%). Crystals for x-ray analysis were obtained

by slow diffusion of hexanes into a benzene solution of **4.9**. ^{1}H NMR (C_6D_6, 499.85 MHz): δ 7.37 [m, 2H, Ph], 7.11 [m, 3H, Ph], 6.75 [s, 2H, *m*-H], 6.74 [s, 2H, *m*-H], 3.18 [m, 4H, CH_2CH_2], 2.47 [s, 6H], 2.43 [s, 6H, Me], 2.12 [s, 6H, Me], 1.49 [s, 6H, Me], 1.01 [s, 6H, Me]. ^{13}C{^{1}H} NMR (C_6D_6, 125.71 MHz): δ 227.66 [CN_2], 139.11 [Mes or Ph], 137.93 [Mes or Ph], 137.79 [Mes or Ph], 137.78 [Mes or Ph], 137.47 [Mes or Ph], 136.16 [Mes or Ph], 132.10 [Mes or Ph], 131.84 [Mes or Ph], 130.62 [Mes or Ph], 130.17 [Mes or Ph], 129.51 [Mes or Ph], 129.07 [Mes or Ph], 128.48 [Mes or Ph], 128.30 [Mes or Ph], 127.77 [Mes or Ph], 126.93 [Mes or Ph], 126.45 [Mes or Ph], 82.76 [CPh on Cp′ ring], 76.05 [CMe on Cp′ ring], 72.07 [CMe on Cp′ ring], 51.58 [CH_2CH_2], 21.43 [Me on Mes], 21.27 [Me on Mes], 20.65 [Me on Mes], 20.54 [Me on Mes], 19.64 [Me on Mes], 19.57 [Me on Mes], 11.46 [Me on Cp′ ring], 11.43 [Me on Cp′ ring], 11.37 [Me on Cp′ ring], 11.33 [Me on Cp′ ring]. Anal. Calcd. for $C_{36}H_{43}N_2ClRu$: C, 67.53%; H, 6.77%; N, 4.38%. Found: C, 67.67%; H, 7.07%; N, 4.32%.



4.9

Synthesis and characterization of (H_2IMes)(Cp*)(Cl)Ru (4.10): Method 1: A mixture of 0.130 g (0.243 mmol) [Cp*Ru(μ-OMe)]$_2$ and 0.300 g (0.875 mmol) [H_2IMes(H)][Cl] in 8 mL benzene was stirred at 70°C for 14 hrs. The resulting purple mixture was filtered, and the supernatant was pumped down. The product was extracted into 30 mL hexanes, which was filtered and pumped down. The resulting solid was washed with 2 mL of cold hexanes and dried under vacuum to provide 0.065 g of **4.10** as a dark blue solid (23%). More product can be recovered by cooling the hexanes wash overnight at −10°C. ^{1}H NMR (THF-d_8, 499.85 MHz): δ 7.51 [s, 2H, *m*-H], 7.36 [s, 2H, *m*-H], 4.45 [m, 2H, CH_2CH_2], 4.29 [m, 2H, CH_2CH_2], 3.28 [s, 6H, Me], 2.81 [s, 6H, Me], 2.71 [s, 6H, Me], 1.59 [s, 15H, Cp*]. ^{13}C{^{1}H} NMR (THF-d_8, 125.71 MHz): δ 228.99 [CN_2], 139.36 [Mes], 138.60 [Mes], 137.98 [Mes], 136.82 [Mes], 130.27 [CH_{Mes}], 129.45 [CH_{Mes}], 74.03 [Cp ring], 52.07 [CH_2CH_2], 21.19 [Me on Mes], 20.27 [Me on Mes], 19.82 [Me on Mes], 10.81 [Me on Cp*]. Anal. Calcd. for $C_{31}H_{41}N_2ClRu$: C, 64.40%; H, 7.15%; N, 4.84%. Found: C, 64.49%, H, 7.12%; N, 4.95%. Method 2: A J. Young NMR tube was charged with 0.020 g (0.025 mmol) (H_2IMes)(PCy_3)(Cl)$_2$Ru=CHMe, one drop of 2-butyne (excess), and 0.7 mL C_6D_6. A ^{1}H NMR taken after 1 day at room temperature showed complete conversion to **4.10**.



4.10

Reaction of 4.4 with ethylene: A J. Young NMR tube was charged with 0.020 g (0.027 mmol) of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CMe)(CPh)]$ (**4.4**) and 0.7 mL CD_2Cl_2. The headspace of the tube was replaced with 1 atm of ethylene. Complete consumption of **4.4** occurred after ~12 hrs at room temperature. The volatiles were removed from the tube by vacuum line transfer, and propylene was identified by ^{1}H NMR. The non-volatile, orange-brown residue contains the diene product and a ruthenium species. Characterization data for CHPh=CMe–CPh=CH_2: ^{1}H NMR (CD_2Cl_2, 299.9 MHz): δ 2.083 [d, *J* = 1, 3H, Me], 5.212 [d. *J* = 1, 1H, CH_2], 5.411 [d, *J* = 1, 1H, CH_2], 6.468 [s, 1H, C<u>H</u>Ph], 7.19-7.37 [m, Ph]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.71 MHz): δ 153.78 [<u>C</u>CH_2], 142.09 [<u>C</u>Me], 138.67 [*ipso*-C of Ph], 138.40 [*ipso*-C of Ph], 131.27 [Ph], 129.68 [Ph], 129.13 [Ph], 128.60 [Ph], 127.84 [Ph], 127.08 [<u>C</u>Ph], 114.02 [CH_2], 16.88 [Me]. Characterization data for the unidentified ruthenium species: ^{1}H NMR (CD_2Cl_2, 299.9 MHz): δ 2.001 [s, 6H], 2.324 [s, 3H], 2.369 [s, 3H], 2.424 [s, 3H], 2.876 [s, 1H], 3.049 [m, 1H], 3.552 [s, 1H], 3.581 [m, 1H], 3.829 [m, 1H], 3.842 [m, 1H], 6.710 [s. 1H], 6.789 [s, 1H], 6.966 [s, 1H]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.71 MHz): δ 16.82, 19.15, 19.63, 19.80, 21.34, 53.33, 62.91, 64.34, 129.39, 129.43, 129.76, 136.22, 136.83, 137.97, 138.04, 138.56, 199.55, 200.27.