Chapter 3

Synthesis and Activity of New Ruthenium Alkylidene Complexes Coordinated with Phosphine and N-Heterocyclic Carbene Ligands

Introduction

As described in Chapter 1, changes in the ligand sphere of ruthenium alkylidene complexes can have profound effects on their catalytic activity, stability, and selectivity. Although often unpredictable, these effects are valuable because they guide the development of improved olefin metathesis catalysts and provide information about the reactivity patterns of ruthenium alkylidenes. The most successful modifications to date have involved tricyclohexylphosphine (PCy_3) ligands, as in $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**), and N-heterocyclic carbene (NHC) ligands, as in $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.2**) (H_2IMes = 1,3-dimesityl-imidazolidine-2-ylidene). These complexes provide a starting point for further modifications, and the aim of the work in this chapter was to examine the effects of various X- and L-type ancillary ligands and carbene substituents. The results include several new ruthenium complexes coordinated with NHC, phosphine, pyridine, imidazole, and cyclic carbene ligands.

Results and Discussion

I. Ruthenium alkylidene complexes with N-heterocyclic carbene (NHC) ligands

The emphasis of recent studies has been on ruthenium alkylidene complexes coordinated with NHC ligands, which parallels the use of NHCs in other catalytic systems,[1] such as Heck and

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[1] Reviews: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290-1309. (b) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181-222. (c) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. *Adv. Organomet. Chem.* **2001**, *48*, 1-69. (d) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1998**, *36*, 2163-2187.

Suzuki couplings, aryl amination, hydrogenation, and hydroformylation.[2] NHC derivatives can have widely varied steric and electronic properties,[3] and the selection used in this study includes the aryl-substituted ligands Ph_3Tri (1,3,4-triphenyl-4,5-dihydro-1*H*-triazol-5-ylidene), IMes (1,3-dimesityl-imidazoline-2-ylidene), and H_2IMes, and the alkyl-substituted ligands IAda (1,3-diadamantyl-imidazoline-2-ylidene), and ImIPC [1,3-(+)-diisopinocamphenyl-imidazolidine-2-ylidene].

Preparation of (Ph_3Tri)(PCy_3)$(Cl)_2$Ru=CHR (R = Ph and CH=CMe_2).[4] The triazole-based methanol adduct Ph_3Tri(H)(OMe) has been isolated by Enders and coworkers from the reaction of the triazolium salt [Ph_3Tri(H)][ClO_4] with sodium methoxide.[5] This adduct reacts cleanly with the ruthenium benzylidene precursor $(PCy_3)_2(Cl)_2$Ru=CHPh (**3.1**) to provide (Ph_3Tri)(PCy_3)$(Cl)_2$Ru=CHPh (**3.3**) (Scheme 3.1). Complete conversion is achieved quickly by heating the reaction mixture briefly, and then **3.3** is separated from the tricyclohexylphosphine and methanol byproducts by precipitation from pentane. Complex **3.3** is a mixture of two conformational isomers, in which only the orientations of the triazolylidene ligand and/or the alkylidene moiety are different. By ^{1}H NMR, two doublet resonances for the alkylidene α-protons occur at δ 19.56 [$^3J_{HP}$ = 8 Hz] and 19.37 [$^3J_{HP}$ = 6.5 Hz] in a 60:40 ratio. Likewise, ^{31}P NMR shows one singlet resonance for each of the isomers, at δ 24.14 and 23.04. The identity of the product is further supported by high resolution mass spectrometry data, which reveal only one product molecular ion peak.

Complex **3.3** also can be obtained by *in situ* deprotonation of the triazolium salt with NaH followed by addition of $(PCy_3)_2(Cl)_2$Ru=CHPh (**3.1**), or by direct reaction of **3.1** with the

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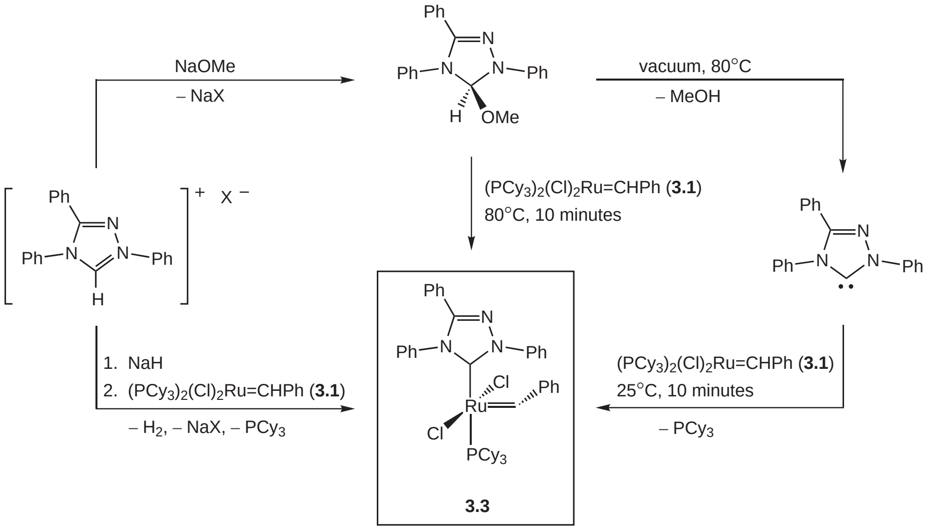
[2] Representative examples: (a) Jackstell, R.; Andreau, M. G.; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 986-989. (b) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 3202-3203. (c) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* **2002**, 32-33. (d) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002**, *4*, 1411-1414. (e) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201-202. (f) Mathews, C. J.; Smith, P. J.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **2001**, *20*, 3848-3850. (g) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878-8879. (h) Tulloch, A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247-1248. (i) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741-748. (j) Chen, J. C. C.; Lin, I. J. B. *Organometallics* **2000**, *19*, 5113-5121. (k) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239-247. (l) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348-352. (m) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165-178. (n) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217-228. (o) Hill, J. E.; Nile, T. A. *Trans. Met. Chem.* **1978**, *3*, 315-316.

[3] Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-91.

[4] These results have been published. (a) 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.* **2003**, in press. (b) Grubbs, R. H.; Trnka, T. M. *U.S. Patent* 6,426,419 B1, 2002.

[5] (a) Teles, J. H.; Melder, J.-P.; Ebel, K.; Schneider, R.; Gehrer, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helvetica Chim. Acta.* **1996**, *79*, 61-83. (b) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem. Int. Ed. Eng.* **1995**, *34*, 1021-1023.

isolated free carbene (Scheme 3.1).[6] However, the air-stable $Ph_3Tri(H)(OMe)$ adduct is more convenient to isolate and handle, and this route provides **3.3** in 59% yield on a half-gram scale with minimal purification.



Scheme 3.1

The dimethylvinyl alkylidene derivative $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHCH{=}CMe_2$ (**3.5**) can be synthesized by the analogous reaction between $Ph_3Tri(H)(OMe)$ and the bis(phosphine) precursor $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ (**3.4**). Like **3.3**, this product is a mixture of conformational isomers characterized by two doublets of doublets by ^1H NMR at δ 19.56 ($^3J_{HP}$ = 5.5 Hz, $^3J_{HH}$ = 11 Hz) and 19.37 ($^3J_{HP}$ = 2.5 Hz, $^3J_{HH}$ = 11 Hz) for the alkylidene α-protons, two doublets with $^3J_{HH}$ = 11 Hz at δ 7.85 and 7.71 for the vinyl protons, and two ^{31}P NMR singlet resonances at δ 28.11 and 26.43.

Unfortunately, both **3.3** and **3.5** are unstable in solution. After several hours in C_6D_6 or CD_2Cl_2 at room temperature under an N_2 atmosphere, significant decomposition is visible by NMR. Included among the decomposition products are the $[Ph_3Tri(H)]^+$ salt and $(PCy_3)_2(Cl)_2Ru{=}CHR$, which suggests that the Ph_3Tri ligand dissociates from the metal center and phosphine reassociates to yield the more stable bis(phosphine) complex.[7] Because this decomposition pathway is accelerated at elevated temperatures and under catalytic turnover

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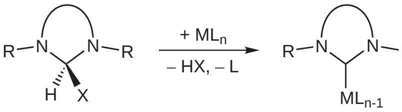
[6] The synthesis of $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHPh$ from the free Ph_3Tri carbene also has been reported by Fürstner and coworkers. Fürstner, A.; Guth, O.; Düffels, Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811-4820.

[7] Although *ortho*-metallation of the Ph_3Tri ligand occurs in some metal complexes (Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1997**, *130*, 1253-1260), we have not observed this reaction in the $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHR$ system.

conditions, **3.3** and **3.5** are not ideal olefin metathesis catalysts. Nevertheless, the synthesis of **3.3** and **3.5** from the methanol adduct $Ph_3Tri(H)(OMe)$ established that NHC adducts provide a new route to NHC-coordinated ruthenium alkylidene complexes.

Significance of Scheme 3.1. The synthesis of NHC-coordinated complexes can be achieved in several ways.[3,8,9] One of the most widely used methods, pioneered by Lappert and coworkers in the 1970s and 80s, is the thermal cleavage of enetetramines in the presence of metal species.[10] Unfortunately, this route is not compatible with the synthesis of ruthenium alkylidene complexes because the high temperatures required for enetetramine cleavage (≥100°C) lead to decomposition of alkylidene-containing precursors. Another popular approach is the reaction of free NHCs with a variety of metal species, which became possible after Arduengo and co-workers successfully isolated the first free NHC in the early 1990s.[11] This route has been the method of choice for the synthesis of NHC-containing ruthenium alkylidene complexes because the substitution of a free NHC for a phosphine ligand in bis(phosphine) precursors like $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) is generally a clean and straightforward reaction.[12]

The use of NHC adducts as "protected" forms of the free carbenes is a new route for the synthesis of ruthenium alkylidene complexes. These adducts may contain alkoxide or trichloromethyl groups, and as illustrated in Scheme 3.2, can eliminate alcohol or chloroform to unmask the carbene, which then coordinates to the metal center.[13]



Scheme 3.2

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[8] Reviews: (a) Raubenheimer, H. G.; Cronje, S. *J. Organomet. Chem.* **2001**, *617-618*, 170-181. (b) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12-22. (c) Liu, S.-T.; Reddy, K. R. *Chem. Soc. Rev.* **1999**, *28*, 315-322.

[9] Other methods include the reduction of thiones, nucleophilic addition to coordinated isocyanide ligands, and carbene transfer from one metal center to another. See references 3 and 8.

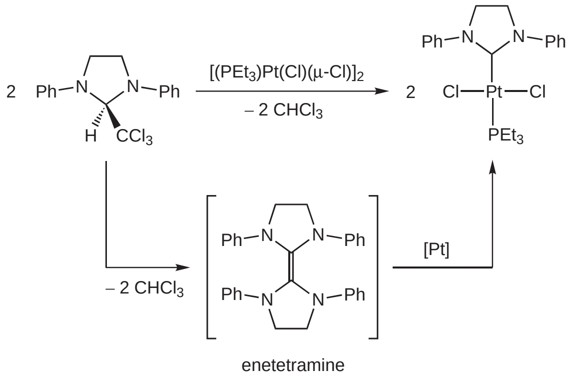
[10] (a) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185-214. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826-836. (c) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 837-844. (d) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172-2180. (e) Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139-159. (f) Çetinkaya, B.; Dixneuf, P.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1827-1833.

[11] (a) Arduengo, A. J.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742-12749. (b) Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027-11028. (c) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.

[12] Examples: (a) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247-2250. (b) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187-5190. (c) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490-2493.

[13] The mechanism of this process has not been studied, but is reasonable to propose that some free carbene is released from the adduct in solution. Coordination of the free NHC to the metal center would then drive the adduct–carbene equilibrium toward more free carbene. This mechanism is supported by the observation that free carbenes are obtained when the adducts are heated under vacuum to remove the alcohol or chloroform byproduct (reference 5). However, a metal-facilitated adduct deprotection or ligand substitution mechanism cannot be discounted at this time.

The direct use of an isolated NHC–alcohol adduct in the synthesis of a metal complex was unprecedented at the time this study was initiated, although Lappert and coworkers had used NHC–chloroform and –amine adducts to make (NHC)(PEt_3)$(Cl)_2$Pt and $(NHC)_2(Cl)_2$Pt complexes.[14] However, in the case of this particular chloroform adduct, 1,3-diphenyl-2-(trichloromethyl)imidazolidine, it is not clear whether the released NHC reacts directly with the platinum precursor, or whether two equivalents first dimerize to form the enetetramine *in situ* (Scheme 3.3).[15] This ambiguity exists because the free carbene has a strong tendency to dimerize[16] and the enetetramine is known to react with $[(PEt_3)Pt(Cl)(\mu\text{-}Cl)]_2$ to provide (NHC)(PEt_3)$Pt(Cl)_2$.[14a] In related carbene adduct chemistry, diazirines and oxadiazolines have been used to generate free alkoxy-, amino-, and thiocarbenes by thermal elimination of dinitrogen and/or ketones,[17] and various carbene adducts have been proposed as reaction intermediates.[15,18]



Scheme 3.3

As first demonstrated by the transformations in Scheme 3.1, the application of NHC adducts to the synthesis of metal complexes is a facile and reliable way to synthesize ruthenium alkylidene complexes. In addition, this route is general and has been extended to other NHC

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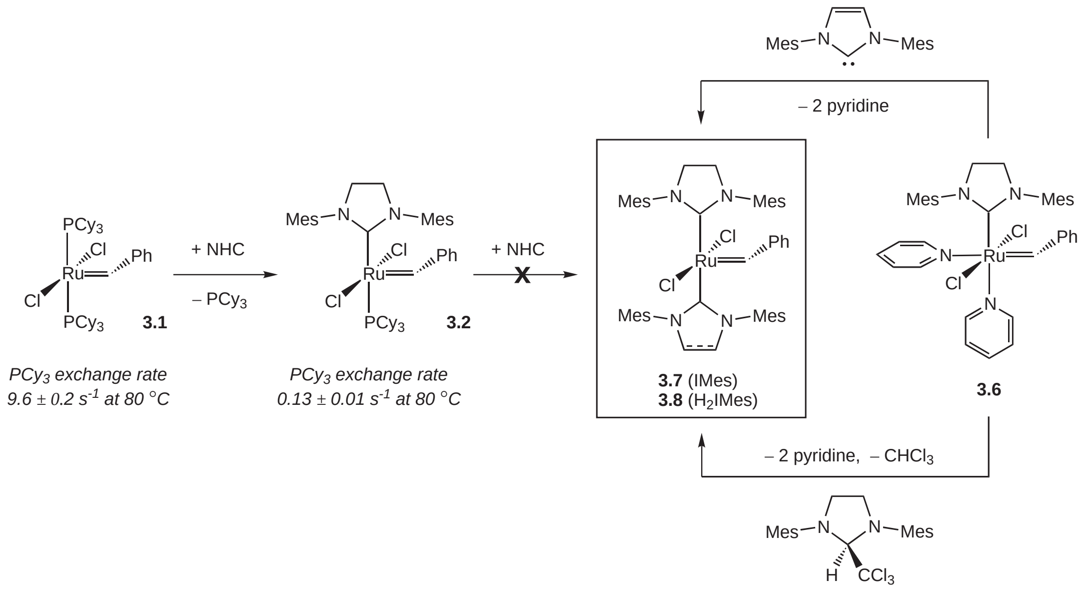
14. (a) Cardin, D. J.; Çetinkaya, B.; Çetinkaya, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 514-522. (b) Chamizo, J. A.; Lappert, M. F. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Norwell, MA, 1989; pp. 47-58.
15. (a) Çetinkaya, B.; Çetinkaya, E.; Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Küçükbay, H.; Lappert, M. F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2047-2054. (b) Çetinkaya, E.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Kostas, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 561-567. (c) Wanzlick, H. W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75-80.
16. Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1314-1317.
17. (a) Moss, R. A. *Acc. Chem. Res.* **1999**, 32, 969-974. (b) Ross, J. P.; Couture, P.; Warkentin, J. *Can. J. Chem.* **1997**, *75*, 1331-1335. (c) Couture, P.; Warkentin, J. *Can. J. Chem.* **1997**, *75*, 1281-1294. (d) Couture, P.; Terlouw, J. K.; Warkentin, J. *J. Am. Chem. Soc.* **1996**, *118*, 4214-4215. (e) Rigby, J. H.; Cavezza, A.; Ahmed, G. *J. Am. Chem. Soc.* **1996**, *118*, 12848-12849.
18. (a) Lappert, M. F.; Pye, P. L. *J. Less-Common Met.* **1997**, *54*, 191-207. (b) Hocker, J.; Merten, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 964-973. (c) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 754-765. (d) Wiberg, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 766-779.

ligands, such as H_2IMes.[4a,19,20] This methodology has been used recently by Herrmann and coworkers in the synthesis of (COD)M(Cl)(L) (L = NHC; M = Rh, Ir) complexes,[21] by Blechert and coworkers to prepare polymer-supported **3.2**,[22] and by Fürstner and coworkers to prepare various ruthenium alkylidene complexes.[6] In addition, the reactions of Ph_3Tri(H)(OMe) or other NHC adducts with molybdenum hexacarbonyl afford the pentacarbonyl derivatives $(CO)_5$Mo(L) (L = NHC).[23]

Several properties of NHC adducts make them highly desirable reagents: (i) they are easy to synthesize and use, (ii) they are air-stable and easier to handle than their free carbene counterparts, and (iii) the latent carbene is readily released in solution. Unlike the example in Scheme 3.3, there is no evidence for dimer formation with the Ph_3Tri ligand, and therefore the Ph_3Tri(H)(OMe) adduct provides direct access to metal–NHC complexes.

Preparation of (H_2IMes)(L)$(Cl)_2$Ru=CHPh (L = IMes or H_2IMes).[4a] In the synthesis of NHC-coordinated complexes **3.2**, **3.3**, and **3.5**, the mono(substituted) product (NHC)$(PCy_3)(Cl)_2$Ru=CHR is observed exclusively, even in the presence of a large excess of NHC. In theory, the bis(substituted) product also could form, and $(NHC)_2(Cl)_2$Ru=CHR has been



Scheme 3.4

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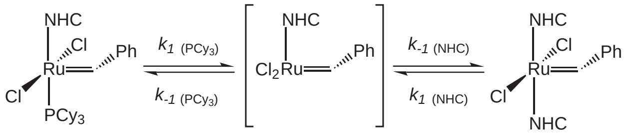
[19] Morgan, J. P. Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 2002.
[20] Scholl, M. Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 2000.
[21] Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219-224.
[22] Schürer, S. C.; Gessler, S.; Buschmann, N.; Blechert, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3898-3901.
[23] See chapter 5.

observed when NHC = 1,3-dicyclohexyl-imidazoline-2-ylidene.[12c] However, the origin of this effect is not entirely steric congestion, as originally believed, and examples of bis(IMes) metal complexes have been synthesized.[24] As shown in Scheme 3.4, the phosphine exchange rate decreases dramatically when one of the PCy_3 ligands in **3.1** is replaced by H_2IMes.[25] This slow phosphine exchange rate in **3.2** may effectively prevent further PCy_3 substitution by the accepted dissociative ligand substitution pathway. According to Scheme 3.5, this corresponds to a situation where $k_{1\ (\mathrm{NHC})}$ is less than $k_{1\ (\mathrm{PCy_3})}$, which is already slow. In addition, there may be a contribution from the reverse rates if $k_{-1\ (\mathrm{NHC})}$ is less than $k_{-1\ (\mathrm{PCy_3})}$, although this relationship cannot be confirmed because values of $k_{-1\ (\mathrm{PCy_3})}$ have been experimentally inaccessible.[25]



Scheme 3.5

However, bis-substitution can be achieved by using derivatives of **3.2** with more labile ligands in place of the tricyclohexylphosphine, such as the pyridine complex $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ (**3.6**).[26] For example, addition of the free IMes: carbene to **3.6** cleanly provides the mixed H_2IMes–IMes complex $(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$ (**3.7**) (Scheme 3.4). Similarly, the reaction of **3.6** with the chloroform adduct $H_2IMes(H)(CCl_3)$ provides the bis(H_2IMes) complex $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**3.8**) (Scheme 3.4). These products are highly stable and can be purified by column chromatography on silica gel.[27] At room temperature, the ^{1}H NMR spectra of **3.7** and **3.8** each contain a sharp alkylidene α-proton resonance at low field, but the rest of the resonances appear broadened due to hindered rotation of the H_2IMes, IMes, and/or benzylidene ligands. At lower temperature (−15°C), these resonances sharpen into distinct peaks for each set of inequivalent protons.

The crystal structure of **3.7** is shown in Figure 3.1, and the metrical data are presented in

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24. Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944-4945.
25. (a) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749-750. (b) Sanford, M. S., Love, J. A., Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554.
26. Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314-5318.
27. Other ruthenium alkylidene complexes (including **3.2**) also can be purified in this way. (a) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791-799. (b) Tallarico, J. A.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157-7158.

Table 3.1 along with comparisons to the mixed phosphine-NHC derivatives **3.2** and (IMes)(PCy_3)$(Cl)_2$Ru=CHPh. Both of the Ru–NHC distances in **3.7** are longer than in either of the corresponding mono(NHC) complexes, which surely reflects the greater steric congestion in **3.7** and possibly also a more electron-rich ruthenium center. Unfortunately, further comparisons of the internal NHC bond lengths and angles have little meaning because of disorder between the H_2IMes and IMes ligands in this structure.

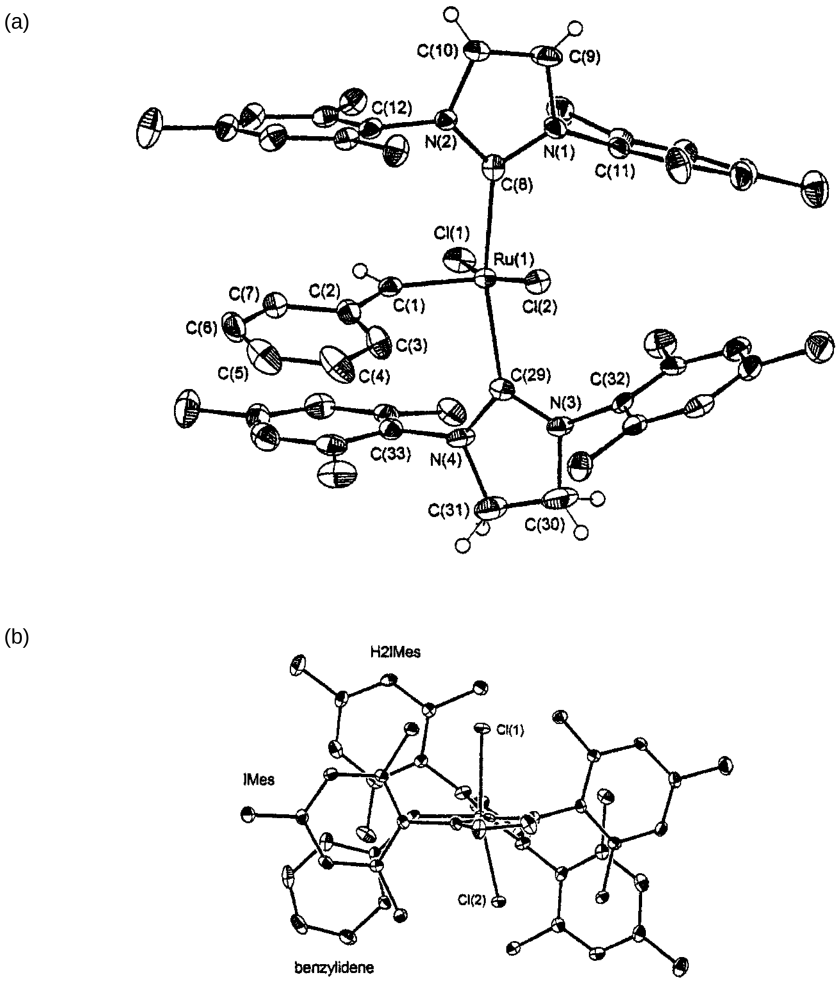

Figure 3.1: Structure of (H_2IMes)(IMes)$(Cl)_2$Ru=CHPh (**3.7**) (CCDC #167135). Side (a) and top (b) views. For clarity, only one molecule in the asymmetric unit is shown, and most of the hydrogen atoms have been omitted. Displacement ellipsoids are drawn at 50% probability; hydrogens atoms are drawn at arbitrary scale.

Table 3.1: Structural comparisons. In cases where there is more than one chemically equivalent bond length or angle, the values have been averaged.

distances (Å) and angles (deg)	**$(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$** (**3.7**)	**$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$** (**3.2**, reference 28)	**$(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$** (reference 29)
Ru–CN_2 (IMes)	2.093(3)*	—	2.07(1)
Ru–CN_2 (H_2IMes)	2.125(3)*	2.085(2)	—
Ru–Cl	2.381(1)	2.395(1)	2.388(3)
Ru=C	1.819(3)	1.835(2)	1.84(1)
RuC–Ph	1.472(4)	1.470(3)	1.40(2)
CH_2–CH_2 backbone	1.421(5)*	1.515(3)	—
CH=CH backbone	1.382(5)*	—	1.30(1)
C–N (IMes)	1.364(3)*	—	1.36(1)
C–N (H_2IMes)	1.359(3)*	1.348(2)	—
N–Mes (IMes)	1.435(3)*	—	1.46(1)
N–Mes (H_2IMes)	1.434(3)*	1.436(2)	—
Cl–Ru–Cl	166.11(3)	167.71(2)	168.6(1)
N_2C–Ru–L	164.9(1)	163.73(6)	163.2(3)
Ru=C–Ph	136.1(2)	140.0(2)	141(1)
N–C–N (IMes)	104.7(2)*	—	101.0(8)
N–C–N (H_2IMes)	104.3(2)*	107.3(2)	—

* These bond lengths and angles are compromised because of disorder between the H_2IMes and IMes ligands.

Olefin metathesis activity of 3.3 and 3.8. The activities of these two complexes were evaluated in representative RCM and ROMP reactions. As shown in Table 3.2, complex **3.3** is superior to **3.1** in the cyclization of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene derivatives, and the differences are more pronounced for sterically encumbered substrates. This activity profile is comparable to that of complex **3.2**.[30]

Although the Ph_3Tri-coordinated catalysts **3.3** and **3.5** are unstable in solution, the NHC adduct Ph_3Tri(H)(OMe) provides easy access to *in situ*-generated $(Ph_3Tri)(PPh_3)(Cl)_2Ru{=}CHPh$ (**3.9**).[31] Upon mixing at room temperature, $(PPh_3)_2(Cl)_2Ru{=}CHPh$ and one equivalent of Ph_3Tri(H)(OMe) form **3.9**, which then catalyzes the ROMP of COD at a fast rate (Table 3.3). This protocol is also effective for the ROMP of bulk dicyclopentadiene. In comparison, the

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[28] Sanford, M. S. Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 2002.

[29] Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678.

[30] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953-956.

[31] A related *in situ* preparation of catalyst **3.2** consisting of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ + $[H_2IMes(H)][BF_4]$ + $KOBu^t$ + phosphine scavenger has been described. Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153-3155.

bis(triphenylphosphine) starting material $(PPh_3)_2(Cl)_2Ru{=}CHPh$ is completely inactive toward this substrate.

Table 3.2: Ring-closing metathesis activity of **3.3** compared to **3.1** (E = CO_2Et). Conditions: 5 mol % catalyst, 0.05 M CD_2Cl_2, 40°C.

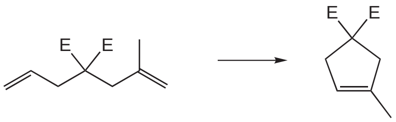
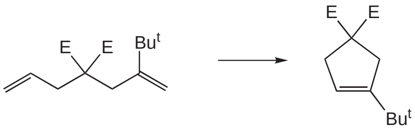
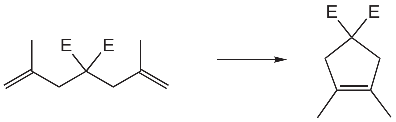
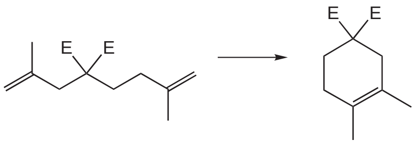
	3.1	**3.3**
	30 minutes 82% conversion	30 minutes 98% conversion
	no reaction	30 minutes 85% conversion
	no reaction	30 minutes 53% conversion
	no reaction	30 minutes 82% conversion

Table 3.3: k_{rel} values for various ruthenium catalysts for the ROMP of 1,5-cyclooctadiene; kinetics measured by ^1H NMR spectroscopy. Conditions: 5 mM catalyst and 1500 mM cyclooctadiene in CD_2Cl_2 at 25ºC.

Catalyst	**k_{rel} for ROMP**[b]
$(PPh_3)_2(Cl)_2Ru{=}CHPh$	0
$(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**)	1
$(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**3.8**)	0
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.2**)	27
$(PPh_3)_2(Cl)_2Ru{=}CHPh$ + 1 equiv. $Ph_3Tri(H)(OMe)$	66

We were particularly interested in the olefin metathesis activity of the bis(NHC) complexes **3.7** and **3.8** because, according to our mechanistic model, one NHC ligand would have to dissociate from the ruthenium center for the catalyst to initiate.[25] $(H_2IMes)_2(Cl)_2Ru{=}CHPh$

(**3.8**) shows slight activity for the RCM of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene at 40°C and no ROMP activity at 25°C, but respectable turnover for both reactions can be achieved at 80°C (100% after 12 hrs). However, **3.8** does not react with ethylene to form the corresponding methylidene derivative [Ru]=CH_2 at any temperature. Although the latter result is consistent with no observable catalyst initiation, the fact that **3.8** displays any RCM or ROMP activity at all suggests that some initiation can occur, at least at elevated temperatures.

To test for NHC dissociation, $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**3.8**) was heated in the presence of excess PCy_3 to trap any of the 14-electron intermediate $[(H_2IMes)(Cl)_2Ru{=}CHR]$ as the 16-electron phosphine complex $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.2**). As illustrated in Figure 3.2, significant quantities of **3.2** form during the course of the reaction: after 36 hours, **3.2** is present in a 6.3 : 1.0 ratio compared to **3.8**. The reaction of **3.8** with one equivalent of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) also generates **3.2**, but this reaction is not as clean. This evidence strongly suggests that **3.8** is metathesis active because some H_2IMes dissociation occurs at elevated temperatures and provides the necessary initiation pathway. The resulting 14-electron species $[(H_2IMes)(Cl)_2Ru{=}CHR]$ is extraordinarily active, and a very small amount is capable of producing the observed catalysis.[25]

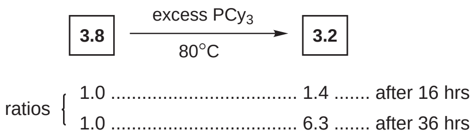


Figure 3.2

It is reasonable to expect that NHC dissociation occurs in other $(NHC)_2(Cl)_2Ru{=}CHPh$ complexes, such as those reported by Herrmann and coworkers in 1998.[12c] The $(IPr^i)_2(Cl)_2Ru{=}CHPh$ derivative (IPr^i = 1,3-diisopropyl-imidazoline-2-ylidene), for example, exhibits ROMP activity that is comparable to **3.1**. This activity may be attributed to dissociation of one IPr^i ligand from $(IPr^i)_2(Cl)_2Ru{=}CHPh$, which provides a small amount of the 14-electron species $[(IPr^i)(Cl)_2Ru{=}CHPh]$ that carries out catalysis. Interestingly, Herrmann and coworkers also have reported that the reaction of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) and $(ICy)_2(Cl)_2Ru{=}CHPh$ (ICy = 1,3-dicyclohexyl-imidazoline-2-ylidene) provides $(ICy)(PCy_3)(Cl)_2Ru{=}CHPh$ in 15% yield after 12 hrs, which they attribute to a bimolecular NHC transfer mechanism.[32] Thus, although one of the most widely cited features of NHC ligands is their strong bonding to metal centers,[1] there is a growing list of examples that exhibit facile NHC dissociation and NHC transfer.[8c,33] For this reason, predictions about the lability of NHC ligands in new organometallic complexes should be made with care.

Ruthenium complexes with alkyl-substituted N-heterocyclic carbene ligands. Alkyl- and aryl-substituted NHCs differ substantially with respect to their steric and electronic properties. For example, the adamantyl-substituted free carbene IAda: (1,3-diadamantyl-imidazoline-2-ylidene)[11c] does not react with $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**), but it does react with $(PPh_3)_2(Cl)_2Ru{=}CHPh$ at room temperature to provide $(IAda)(PPh_3)(Cl)_2Ru{=}CHPh$ (**3.10**). Unfortunately, this product could not be isolated because the reaction does not go to completion even in the presence of excess IAda:, and because **3.10** is unstable in solution. Presumably, the complete substitution of a phosphine ligand by IAda: is difficult because of the steric bulk of the adamantyl substituents.[34]

The ImIPC ligand [1,3-(+)-diisopinocamphenyl-imidazolidine-2-ylidene] is more compact than IAda, and preliminary studies have shown that $(ImIPC)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.11**) is an isolable product.[20] As illustrated in Scheme 3.6, the $[ImIPC(H)][BF_4]$ salt[35] was first treated with $KOBu^t$ to generate the alkoxy adduct $ImIPC(H)(OBu^t)$ *in situ*, which was then added to a solution of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**). This reaction mixture must be kept at room temperature because complex **3.11** is thermally unstable; it slowly decomposes at room temperature, both in solution and the solid state.[36] By NMR, the reaction in Scheme 3.6 provides ~95% of **3.11** and ~5% of the bis(substituted) derivative $(ImIPC)_2(Cl)_2Ru{=}CHPh$. However, **3.11** is isolated cleanly in only 19% yield after column chromatography, which is probably due to the instability of this complex. The ^1H NMR spectrum of **3.11** reveals two singlet resonances for the $Ru{=}CH_\alpha$ proton at δ 20.583 and 20.577 corresponding with two isomers, as also exhibited by complex **3.3**.

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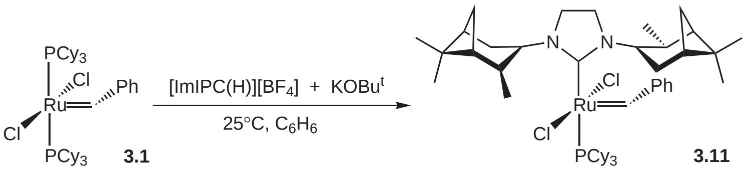
[32] Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362-365.

[33] (a) Simms, R. W.; Drewitt, M. J.; Baird, M. C. *Organometallics* **2002**, *21*, 2958-2963. (b) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun.* **2001**, 1388-1389.

[34] Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375.

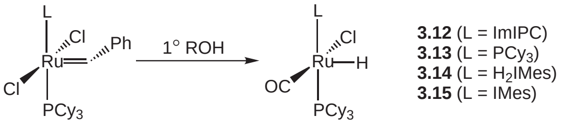
[35] This salt has also been used for the enantioselective formation of oxindoles. Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402-3416.

[36] One of the decomposition products is complex **3.1**.



Scheme 3.6

Attempts to grow crystals of **3.11** from methanol unexpectedly provided crystals of the hydrido-carbonyl-chloride complex (ImIPC)(PCy$_3$)(Cl)(CO)(H)Ru instead.[37] This yellow species was identified by distinctive upfield ^{1}H NMR resonances at δ –24.63 and –24.70, which are each split into doublets with $^2J_{HP}$ = 23 and 25 Hz. These resonances are characteristic of a hydride situated trans to an empty coordination site and cis to a phosphine, and they also indicate that there are again two isomers present in solution. Reaction of this monocarbonyl complex with carbon monoxide provides (ImIPC)(PCy$_3$)(Cl)(CO)$_2$(H)Ru, which also has distinctive hydride chemical shifts at δ –4.39 [d, $^2J_{HP}$ = 22 Hz] and –4.52 [d, $^2J_{HP}$ = 23 Hz], due to the new CO ligand trans to the hydride.



Scheme 3.7

The use of methanol as a wash solvent with **3.1**, **3.2**, and other ruthenium alkylidene complexes also leads to similar metal-hydride impurities. In the case of (H$_2$IMes)(PCy$_3$)(CO)(H)(Cl)Ru (**3.14**), the presence of the hydride is indicated by its ^{1}H NMR resonances at δ –24.90 [d, $^2J_{HP}$ = 21 Hz], similar to this resonance in the closely related (IMes)(PCy$_3$)(CO)(H)(Cl)Ru derivative (**3.15**) (δ –24.83, d, $^2J_{HP}$ = 21 Hz).[38] The transformation of ruthenium alkylidene complexes to hydrido-carbonyl-chloride derivatives was confirmed by direct reaction with methanol to provide (ImIPC)(PCy$_3$)(Cl)(CO)(H)Ru (**3.12**), (PCy$_3$)$_2$(CO)(H)(Cl)Ru (**3b**), (H$_2$IMes)(PCy$_3$)(CO)(H)(Cl)Ru (**3.14**), and (IMes)(PCy$_3$)(CO)(H)(Cl)Ru (**3.15**) (Scheme 3.7). Although the decarbonylation of primary

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37. Trnka, T. M.; Henling, L. M.; Grubbs, R. H. **2001**, unpublished results.
38. Lee, H. M.; Smith, D. C.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794-797.

alcohols by group 8 metal precursors is a general route to hydrido-carbonyl complexes,[39] the mechanism of this process is unknown, and it is not clear what happens to the benzylidene fragment in Scheme 3.7.

Although **3.11** ultimately could not be crystallized, the crystal structure of the related complex $(CO)_5Mo(ImIPC)$ was determined instead.[40] As shown in Figure 3.3, the orientation of the isopinocamphenyl substituents positions the NC–H protons toward the ML_n fragment. The same ligand orientation occurs in the structures of Cp*Ru(Cl)(ImIPC)[41] and $(ImIPC)(PCy_3)(Cl)(CO)(H)Ru$.

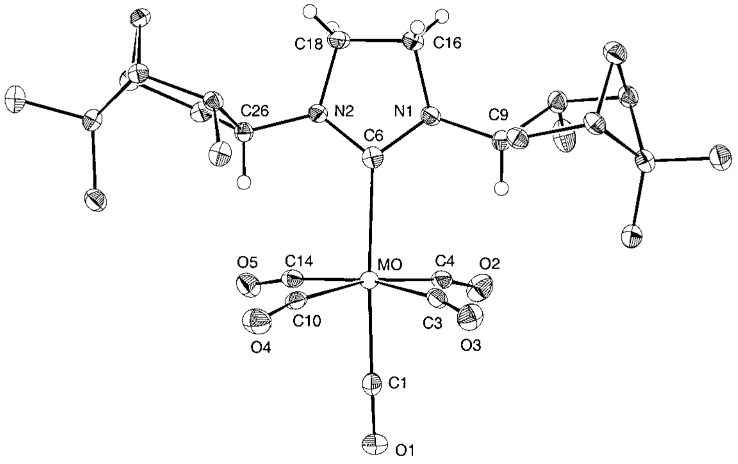

Figure 3.3: Structure of $(CO)_5Mo(ImIPC)$ (CCDC #178188).

Initial studies revealed that **3.11** is a poor catalyst for enantioselective olefin metathesis reactions.[20,42] However, several cross metathesis results indicated that **3.11** had potential for olefin cis/trans selectivity. For example, the yields and *E*:*Z* ratios in the cross metathesis of allyl benzene and *cis*-2-butene-1,4-diacetate with **3.1**, **3.2**, and **3.11** are compared in Table 3.4.[43] In the reactions with catalysts **3.1** and **3.2**, the favored product is the more thermodynamically stable *E* olefin geometry. The *E* olefin is formed selectively in the vast majority of cross metathesis

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[39] (a) Gill, D. F.; Shaw, B. L. *Inorg. Chim. Acta* **1979**, *32*, 19-23. (b) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221-231. (c) Moers, F. G.; Langhout, J., P. *Recueil* **1972**, *91*, 591-600. (d) James, B. R.; Preece, M.; Robinson, S. D. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, D.C., 1982; pp. 145-161.

[40] $(CO)_5Mo(ImIPC)$ was synthesized by the reaction of $(CO)_6Mo$ with $[ImIPC(H)][BF_4]/KOBu^t$; see chapter 5 for more examples.

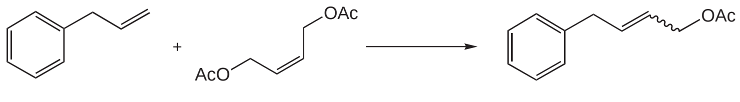
[41] Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878-2882.

[42] Ward, D. W.; Grubbs, R. H. **2000**, unpublished results.

[43] Chatterjee, A. K.; Grubbs, R. H. **2000**, unpublished results.

reactions, as well as in ring-closing metathesis reactions that form macrocycles.[44] For this reason, it would be highly desirable to develop a "cis-selective catalyst" that could overcome thermodynamic factors and provide *Z* olefins in higher yields.

Table 3.4: Cross metathesis with catalysts **3.1**, **3.2**, and **3.11**. Conditions: 5 mol % catalyst, 0.5 M CH_2Cl_2, reflux for 12 hours.



Catalyst	**Isolated yield**	***E : Z***
$(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**)	77%	3 : 1
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.2**)	82%	7 : 1
$(ImIPC)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.11**)	69%	1 : 1

The activity of **3.11** was investigated in greater detail because of this interesting lead. The "inherent" selectivities of catalysts **3.1**, **3.2**, and **3.11** were determined using the stoichiometric and irreversible reaction with 2,3-dihydrofuran.[45,46] As illustrated in Scheme 3.8, this reaction provides the alkoxy-substituted carbene products $[Ru]{=}CH(OCH_2CH_2CH{=}CHPh)$. The crystal structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH(OCH_2CH_2CH{=}CHPh)$, which crystallized as the *E* isomer, is shown in Figure 3.4 for illustrative purposes.

The *E:Z* ratio of the pendant olefin reflects the "inherent" selectivity of various catalysts and can be measured by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy.[45] With $(ImIPC)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.11**), this ratio is ~2:1, which is enriched in *E* olefin compared to **3.1** (~ 3:1 ratio) and **3.2** (~ 4:1 ratio). The differences in these ratios are consistent with the results in Table 3.4. Furthermore, the rate of the reaction with dihydrofuran provides a measure of the initiation properties of these catalysts. This reaction with **3.11** is complete within 30 minutes at room temperature, whereas it takes **3.1** three hours and **3.2** eight hours to reach 100% conversion. The differences in these reaction times indicates that **3.11** initiates qualitatively much faster than either **3.1** (already considered a fast initiator) or **3.2**.

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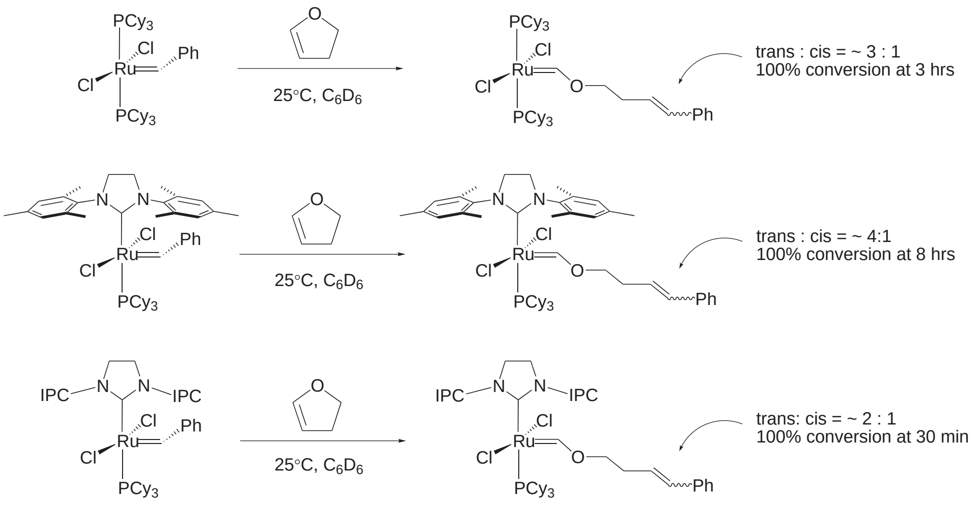
[44] Examples: (a) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58-71. (b) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783-3784.

[45] Wu, Z.; Nguyen, S. T. Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[46] Sanford, M. S.; Grubbs, R. H. **2000**, unpublished results.



trans : cis = ~ 3 : 1
100% conversion at 3 hrs

trans : cis = ~ 4:1
100% conversion at 8 hrs

trans: cis = ~ 2 : 1
100% conversion at 30 min

Scheme 3.8

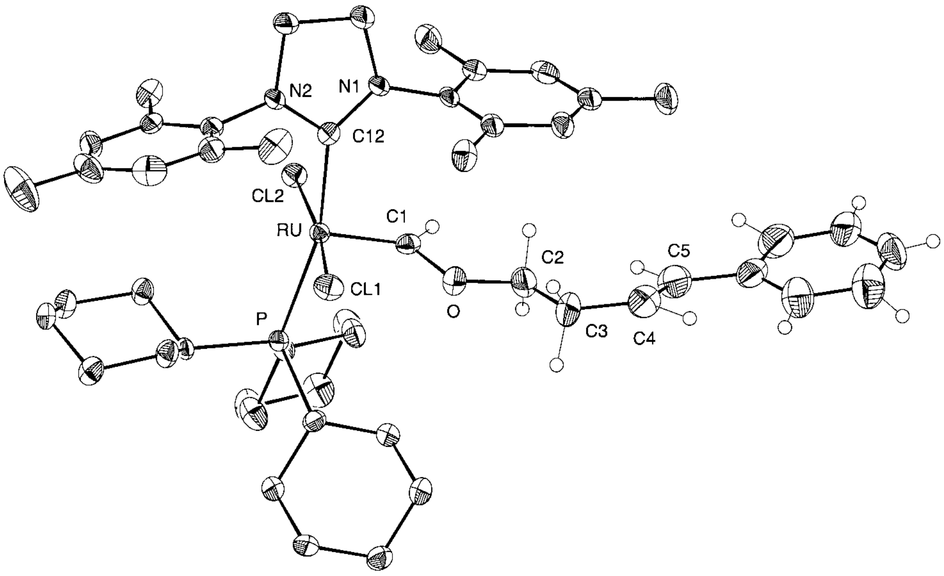


Figure 3.4: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH(OCH_2CH_2CH{=}CHPh)$ (CCDC #157844).

However, further studies revealed that **3.11** has a short lifetime under turnover conditions. The reactivity profiles of catalysts **3.1**, **3.2**, and **3.11** in the ring-closing metathesis of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene are shown in Figure **3.5**. With **3.11**, the conversion to ring-closed product levels off after ~1000 seconds due to catalyst decomposition. In addition, the reaction of **3.11** with ethylene leads to complete disappearance of the alkylidene within two hours at room temperature. This reaction is not clean, and a variety of resonances in the –13 to –25 ppm range are present. Thus, despite the fast initiation of **3.11**, its overall activity is only moderate, *i.e.*, intermediate between **3.1** and **3.2**. The instability of both **3.11** and the putative propagating species [(ImIPC)(Cl)$_2$Ru=CHR] may be caused by the electronics of the N-alkyl substituents and/or by steric influence of the NC–H isopinocamphenyl protons that are directed toward the [Cl$_2$Ru=C] plane.

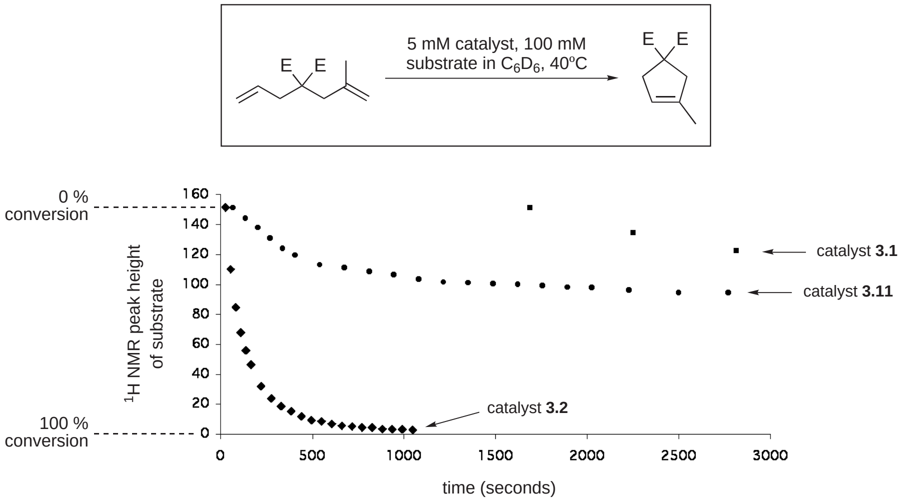
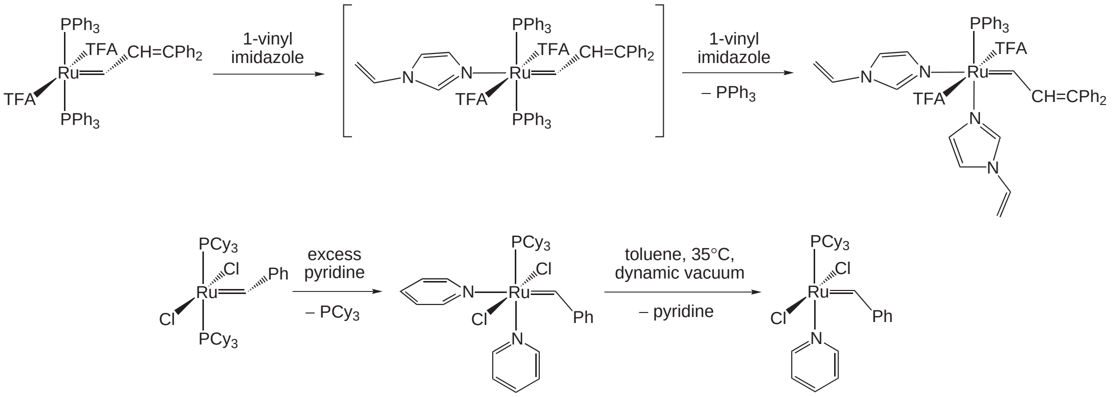


Figure 3.5

Catalyst **3.11** does indeed provide a higher ratio of *E* olefin compared to other ruthenium alkylidenes, but it is likely that this selectivity is due to a fortuitous combination of fast initiation and fast decomposition properties. In this situation, all of the catalyst decomposes after a number of turnovers and so becomes unavailable for the re-metathesis of product. As a result, a kinetic rather than thermodynamic product distribution is isolated.

II. Ruthenium alkylidene complexes with heterocyclic N-donor ligands

Previous work has shown that the reaction of $(PPh_3)_2(TFA)_2Ru{=}CHCH{=}CPh_2$ (TFA = trifluoroacetate) with 1-vinylimidazole initially produces a mono(imidazole) species in which the imidazole is coordinated trans to the vinylcarbene ligand (Scheme 3.9).[45] However, the ultimate product is the bis(imidazole) complex $(PPh_3)(1\text{-vinylimidazole})_2(TFA)_2Ru{=}CHCH{=}CPh_2$. This result provided the first evidence that heterocyclic N-donor ligands could be used to stabilize ruthenium alkylidene complexes. Further studies showed that the reaction of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) with an excess of pyridine (py) cleanly furnishes an 18-electron bis(pyridine) complex $(PCy_3)(py)_2(Cl)_2Ru{=}CHPh$ (Scheme 3.9).[47]



Scheme 3.9

$(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ can be synthesized in a similar fashion from **3.2** and pyridine, and this complex is a precursor for a variety of $(H_2IMes)(L)(Cl)_2Ru{=}CHPh$ compounds.[48,49] The purpose of this study was to extend the range of ruthenium alkylidene complexes coordinated with pyridine and other N-donor ligands.

Pyridine-coordinated ruthenium vinylcarbene complexes. As illustrated in Scheme

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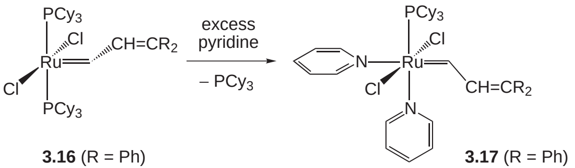
[47] Dias, E. L. Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 1998.

[48] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314-5318.

[49] In addition, a bis(pyridine) derivative with a chiral N-heterocyclic carbene ligand has been reported, as well as two ruthenium alkylidene complexes with tethered pyridine ligands. (a) Denk, K.; Fridgen, J.; Herrmann, W. A. *Adv. Synth. Catal.* **2002**, *344*, 666-670. (b) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225-3228. (c) van der Schaaf, P. A.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. *J. Organomet. Chem.* **2000**, *606*, 65-74.

3.10, reaction of the diphenylvinylcarbene complex $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ (**3.16**)[50] with excess pyridine furnishes the bis(pyridine) product $(PCy_3)(py)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ (**3.17**). Like the benzylidene analog $(PCy_3)(py)_2(Cl)_2Ru{=}CHPh$, complex **3.17** is characterized by a ^{1}H NMR doublet at δ 20.2 ($^3J_{HP}$ = 12 Hz) for the Ru=CH$_\alpha$ proton, a ^{13}C{^{1}H} NMR resonance at δ 312.7 for the carbene carbon, and a ^{31}P{^{1}H} NMR resonance at δ 30.2 for the tricyclohexylphosphine ligand. The vinyl proton appears as a doublet at δ 8.8 ($^3J_{HH}$ = 12 Hz).



3.16 (R = Ph)
3.18 (R = Me)

3.17 (R = Ph)
3.19 (R = Me)

Scheme 3.10

The crystal structure of **3.17** is shown in Figure 3.6. The diphenylvinylcarbene ligand [C(1)–C(2)–C(3)] is tilted ~30° out of the Cl(1)–Ru–Cl(2)–C(1) plane, with the diphenyl substituent directed away from the tricyclohexylphosphine. In comparison, the vinylcarbene moiety in the structure of $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ (**3.16**) is oriented fully in the Cl–Ru–Cl–C$_\alpha$ plane,[50] whereas in the structures of $(PPh_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ and $(PPh_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$,[51,52] it is oriented fully in the P–Ru–P–C$_\alpha$ plane. These changes are likely due to the different steric requirements of the pyridine and phosphine ligands. Another notable feature is that the Ru–N bond located trans to the vinylcarbene is significantly longer [by 0.136(2) Å] than that located trans to the tricyclohexylphosphine. A similar effect occurs in $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ and can be ascribed to the strong structural trans influence of the alkylidene ligand.[48]

Reaction of $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ (**3.18**)[53] with pyridine provides the dimethylvinylcarbene derivative $(PCy_3)(py)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ (**3.19**) (Scheme 3.10), but this isolated material decomposes within one hour at room temperature when redissolved in C_6D_6. As a result, **3.19** has been characterized only by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR of **3.19** is similar to **3.17** except for the absence of the phenyl resonances and the presence of two methyl

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[50] Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.
[51] Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114,* 3974-3975.
[52] Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *J. Organomet. Chem.* **2002**, *641*, 220-226.
[53] Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867-3869.

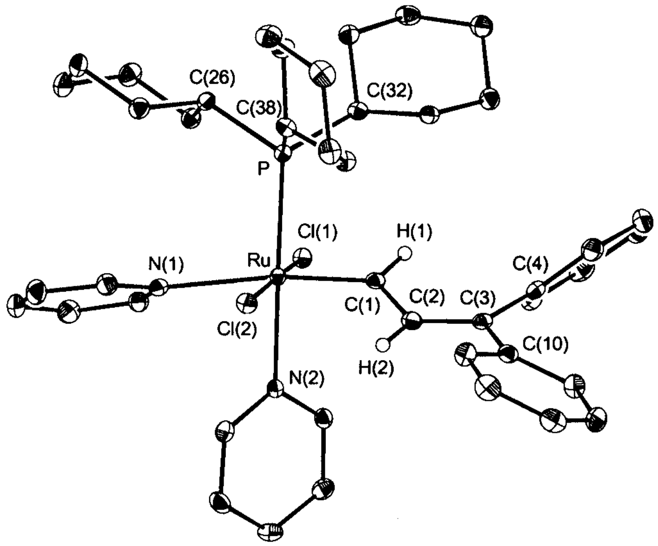
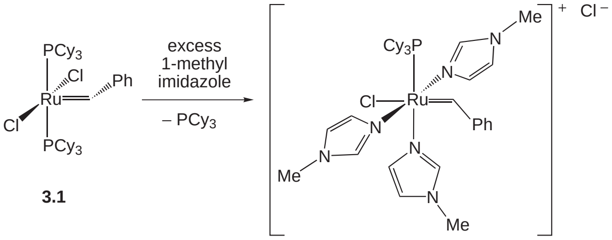


Figure 3.6: Structure of $(PCy_3)(py)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ (**3.17**) · py (CCDC #178708). Displacement ellipsoids are drawn at 50% probability; hydrogen atoms are drawn at arbitrary scale. Selected bond distances [Å] and angles [deg]: Ru–C(1) 1.877(2), Ru–N(1) 2.319(1), Ru–N(2) 2.183(1), Ru–P 2.3743(4), Ru–Cl(1) 2.4128(4), Ru–Cl(2) 2.3939(4), C(1)–C(2) 1.426(2), C(2)–C(3) 1.366(2), C(3)–C(4) 1.482(2), C(3)–C(10) 1.486(2), P–C(26) 1.865(2), P–C(32) 1.872(2), P–C(38) 1.859(2), C(1)–Ru–N(1) 171.76(6), Cl(1)–Ru–Cl(2) 174.92(1), N(2)–Ru–P 177.89(4), Ru–C(1)–C(2) 126.7(1), C(1)–C(2)–C(3) 127.6(2), C(4)–C(3)–C(10) 118.0(1).

signals at δ 1.26 and 0.75. Although previous work has shown that the dimethylvinylcarbene ligand can be deprotonated to yield vinylvinyl species,[4a,28] this product is not present in the decomposition of **3.19**. The only identifiable byproduct is free pyridine.

Presumably, these substitution reactions of one phosphine ligand with two pyridine ligands occur through an associative mechanism, by analogy to the conversions of $(PPh_3)_2(TFA)_2Ru{=}CHCH{=}CPh_2$ to $(PPh_3)(1\text{-vinylimidazole})_2(TFA)_2Ru{=}CHCH{=}CPh_2$ (Scheme 1)[45] and $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ to $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$.[48] In this mechanism, one pyridine first binds trans to the alkylidene, followed by phosphine dissociation and coordination of the second pyridine.

Imidazole-coordinated ruthenium benzylidene complexes. Surprisingly, reaction of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) with 1-methyl imidazole (1-MeIm) does not provide $(PCy_3)(1\text{-MeIm})_2(Cl)_2Ru{=}CHPh$ by analogy to the transformations in Scheme 3.9, but instead yields the cationic tris(imidazole) complex $[(PCy_3)(1\text{-MeIm})_3(Cl)Ru{=}CHPh][Cl]$ (**3.20**) (Scheme 3.11). By ^1H NMR, this unexpected product features a $Ru{=}CH_\alpha$ resonance at δ 20.42 (d, $^3J_{HP}$ = 11 Hz), as well as two methyl resonances at δ 3.70 and 3.53 in a 2:1 ratio which are consistent with two equivalent and one inequivalent 1-MeIm ligands. Complex **3.20** also exhibits a distinctive $^{13}C\{^1H\}$ NMR resonance at δ 324.97 for the carbene carbon and a $^{31}P\{^1H\}$ NMR resonance at δ 22.77 for the tricyclohexylphosphine ligand. This product is insoluble in aromatic solvents, but it is soluble in chlorinated solvents and methanol.



3.1

3.20

Scheme 3.11

In the formation of **3.20**, halide abstraction or displacement is achieved by the neutral 1-methylimidazole ligand. The mild conditions for this transformation are uncommon but not unprecedented for other substitutionally labile ruthenium precursors; for example, reaction of $(binap)(PPh_3)(Cl)_2Ru$ with acetonitrile at room temperature provides the cationic tris(acetonitrile) complex $[(binap)(MeCN)_3(Cl)Ru][Cl]$.[54] In comparison, other cationic ruthenium carbene complexes, such as $[(Tp)(PCy_3)(H_2O)Ru{=}CHPh][BF_4]$ and [(*p*-cymene)$(PPh_3)(Cl)$-$Ru{=}C{=}C{=}CPh_2][PF_6]$, are typically synthesized by the abstraction of a halide ligand with Ag^+.[55,56]

The identity of **3.20** was confirmed by x-ray diffraction (Figure 3.7). Unfortunately, the quality of this structure is poor because the crystal is twinned and contains multiple disordered dichloromethane solvent molecules. The Ru=C distance in **3.20** [1.874(6) Å (average values for molecules A and B)] is somewhat longer than is usually found in neutral, five-coordinate ruthenium benzylidene complexes [*e.g.*, 1.838(2) Å in **3.1**]. This has also been observed in the related complex $[(Tp)(PCy_3)(H_2O)Ru{=}CHPh][BF_4]$ [1.878(4) Å].[55] The Ru–Cl distance [2.570(2) Å (avg A and B)] is substantially elongated compared to those in **3.1** [2.390(1) Å (avg)], presumably because of electronic effects from the trans benzylidene ligand. The Cl–Ru–C(1) angle is distorted by ~10° from linearity away from the bulky tricyclohexylphosphine ligand.

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54. Fogg, D. E.; James, B. R. *Inorg. Chem.* **1997**, *36*, 1961-1966.
55. Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384-5389.
56. Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, R. H. *Chem. Commun.* **1998**, 1315-1316.

The Ru–N(1) and Ru–N(3) distances [2.114(5) and 2.110(5) Å, respectively (avg A and B)] are within the range of Ru–N distances in the homoleptic 1-methylimidazole dication $[(1\text{-MeIm})_6\text{Ru}]^{2+}$ [2.098(4)–2.113(4) Å].[57] However, the Ru–N(5) bond located trans to the tricyclohexylphosphine ligand is elongated by ~0.02 Å. This distance [2.140(6) (avg A and B)] is comparable to that for a similar Ru–N bond [2.131(7) Å] situated trans to the triphenylphosphine ligand in $(\text{PPh}_3)(1\text{-MeIm})_2(\text{Cl})_3\text{Ru}$.[58]

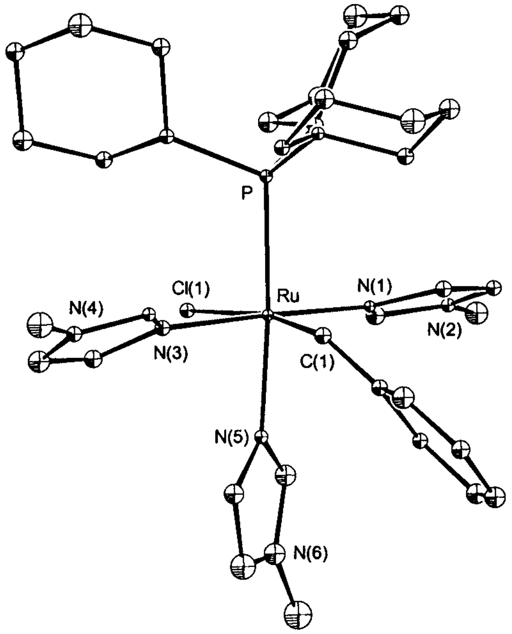

Figure 3.7: Structure of the cationic portion of $[(\text{PCy}_3)(1\text{-MeIm})_3(\text{Cl})\text{Ru=CHPh}][\text{Cl}]$ (**3.20**) · 2.33 CH_2Cl_2 (molecule A) (CCDC #180988). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg]: Ru–C(1) 1.887(6), Ru–N(1) 2.109(5), Ru–N(3) 2.113(5), Ru–N(5) 2.138(6), Ru–Cl(1) 2.582(2), Ru–P 2.408(2), P–C(20) 1.853(6), P–C(26) 1.859(7), P–C(32) 1.870(7), N(1)–Ru–N(3) 176.4(2), P–Ru–N(5) 175.8(2), C(1)–Ru–Cl(1) 170.7(2).

A similar transformation using 1,5-dicyclohexylimidazole provides $[(\text{PCy}_3)(1,5\text{-dicyclohexylimidazole})_3(\text{Cl})\text{Ru=CHPh}][\text{Cl}]$, but no reaction occurs with more sterically hindered derivatives, such as 1,3,4-triphenyl-2-methylimidazole. In the case of 1,2-dimethylimidazole,

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[57] (a) Baird, I. R.; Rettig, S. J.; James, B. R.; Skov, K. A. *Can. J. Chem.* **1998**, *76*, 1379-1388. (b) Clarke, M. J.; Bailey, V. M.; Doan, P. E.; Hiller, C. D.; LaChance-Galang, K. J.; Daghlian, H.; Mandal, S.; Bastos, C. M.; Lang, D. *Inorg. Chem.* **1996**, *35*, 4896-4903.

[58] Batista, A. A.; Polato, E. A.; Queiroz, S. L.; Nascimento, O. R.; James, B. R.; Rettig, S. J. *Inorg. Chim. Acta.* **1995**, *230*, 111-117.

several new species appear as small doublets in the Ru=CH$_\alpha$ region of the ^{1}H NMR spectrum, but these decompose in solution within a day at room temperature.

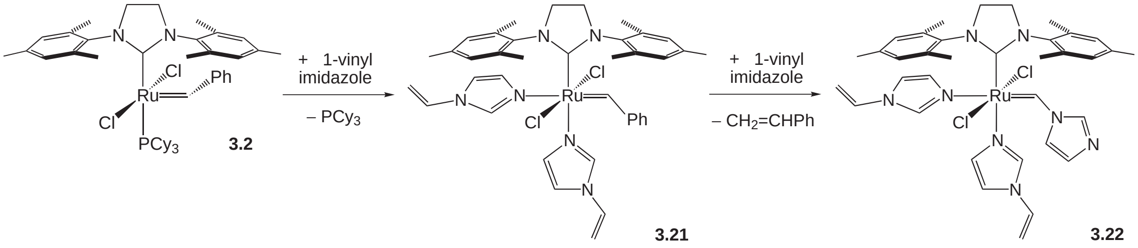
[(PCy$_3$)(1-MeIm)$_3$(Cl)Ru=CHPh][Cl] (**3.20**) is slightly active in the ring-closing metathesis of diethyl diallylmalonate. With a catalyst loading of 5 mol% in 0.05 M CD$_2$Cl$_2$, the reaction went to 52% conversion after 2.5 hours at 40°C. At this time, no carbene H$_\alpha$ signals were present and the reaction did not continue, consistent with catalyst decomposition. Although **3.20** does not react with ethylene at room temperature, when heated at 70°C for 30 minutes, the benzylidene Ru=CH$_\alpha$ resonance disappears and several resonances from δ –4 to –5 appear, which indicate the presence of ruthenium hydride decomposition products.

In contrast to (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh (**3.1**), the reaction of (H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh (**3.2**) with excess 1-methylimidazole provides simply the imidazole-coordinated complex (H$_2$IMes)(1-MeIm)$_2$(Cl)$_2$Ru=CHPh, not a cationic tris(imidazole) product. (H$_2$IMes)(1-MeIm)$_2$(Cl)$_2$Ru=CHPh is characterized by a ^{1}H NMR alkylidene resonance at δ 20.00 (s). This reactivity difference is consistent with the decreased substitutional lability of the chloride ligands of **3.2** compared to **3.1**, and it causes halide abstraction to be less favored for **3.2** than **3.1**.[26]

The reaction of **3.1** with excess 1-vinylimidazole at room temperature affords a green material that is insoluble in benzene and hexanes but soluble in dichloromethane. Both ^{1}H and ^{31}P NMR show the presence of three products, each containing a carbene and a tricyclohexylphosphine ligand: ^{1}H δ 20.44 (d, $^3J_{HP}$ = 11 Hz) and ^{31}P{^{1}H} δ 23.21 (s) (major product); ^{1}H δ 20.47 (d, $^3J_{HP}$ = 12 Hz) and ^{31}P{^{1}H} δ 29.99 (s) (minor product); ^{1}H δ 20.37 (d, $^3J_{HP}$ = 12 Hz) and ^{31}P{^{1}H} δ 32.11 (s) (minor product). In addition, the ^{1}H NMR contains multiple resonances for the cyclohexyl groups on PCy$_3$ and coordinated 1-vinylimidazole. Based on the solubility properties of this material and by analogy to the reaction of (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh with 1-methylimidazole, the most likely product is a cationic tris(imidazole) complex [(PCy$_3$)(1-vinylimidazole)$_3$(Cl)Ru=CHPh][Cl]. The sets of minor NMR resonances may be due to different conformations of the 1-vinylimidazole and benzylidene ligands.

The reaction of **3.2** with excess 1-vinylimidazole initially provides a bright green solution that contains (H$_2$IMes)(1-vinylimidazole)$_2$(Cl)$_2$Ru=CHPh (**3.21**), which displays a ^{1}H NMR alkylidene resonance at δ 20.12 (s) (Scheme 3.12). After approximately one hour at room temperature, another species begins to form, with a ^{1}H NMR alkylidene resonance at δ 16.00 (s).

This upfield chemical shift is typical of alkoxy- and amino-substituted carbenes,[45,59] and it is consistent with $(H_2IMes)(1\text{-vinylimidazole})_2(Cl)_2Ru{=}CH(N_2C_3H_3)$ (**3.22**) (Scheme 3.12). This product is the result of one cross metathesis turnover of **3.21** with 1-vinylimidazole. Heating this reaction at 65°C for twelve hours provides a murky green solution, and ^1H NMR confirms complete conversion to **3.22**. Unfortunately, this product decomposes during isolation attempts.



Scheme 3.12

III. Ruthenium complexes with cyclic carbene ligands

Ruthenium olefin metathesis catalysts with cyclic carbene ligands have received little attention. The first examples were the cyclopropane and cyclobutane derivatives $(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_x$ (x = 2, 3), which were synthesized by reaction of the vinylcarbene $(PPh_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ with methylene cyclopropane or methylene cyclobutane.[45] Unfortunately, the resulting triphenylphosphine-coordinated alkylidenes were inactive for subsequent metathesis. The aim of this study was to synthesize cyclic carbene complexes coordinated with N-heterocyclic carbenes and determine whether these more σ-donating ligands activate the cyclic carbene moiety for olefin metathesis. Cyclic carbene complexes of this type would be formed during the dimerization of methylene cyclopropane or methylene cyclobutane to the tetrasubstituted olefins dicyclopropylidene and dicyclobutylidene, respectively. These transformations are challenging due to steric effects, and the successful dimerization of methylene cyclobutane has been reported only with the $Re_2O_7/Al_2O_3/PbEt_4$ catalyst system.[60]

Cyclic carbene complexes with NHC ligands can be synthesized by the cross metathesis of **3.2** with 1,1-disubstituted olefin. As shown in Scheme 3.13, **3.2** reacts with an excess of

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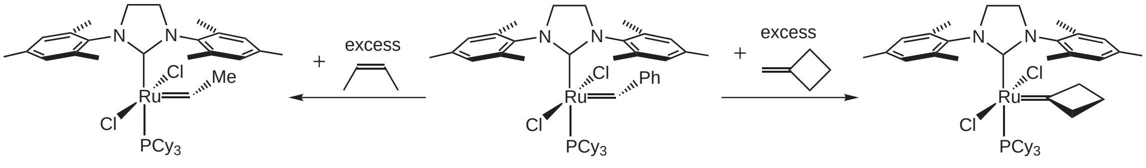
[59] (a) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153-2164. (b) Katayama, H.; Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4513-4515.

[60] Finkel'shtein, E. S.; Bykov, V. I.; Portnykh, E. B. *J. Mol. Cat.* **1992**, *76*, 33-52.

methylene cyclobutane at room temperature to provide the cyclobutane-substituted alkylidene complex **3.23** in 65% isolated yield. An unusual feature of this complex is the ^{13}C NMR resonance of the alkylidene carbon at δ 340.9, which is positioned further downfield than the typical ruthenium alkylidene (δ 310–280). However, a similar chemical shift is displayed by $(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_3$ (δ 344.5).[45] In addition, the fact that the cyclobutane moiety is characterized by four distinct multiplets in the ^{1}H NMR spectrum is consistent with hindered rotation about the ruthenium–carbene bond.



3.24 **3.2** **3.23**

Scheme 3.13

The ethylidene complex **3.24** can be synthesized in a similar fashion from **3.2** and *cis*-2-butene.[61] However, the related dimethyl-substituted derivative $(H_2IMes)(PCy_3)(Cl)_2Ru{=}C(CH_3)_2$, which has been observed in the reaction of **3.2** with isobutylene, is unstable to isolation.[61]

The initiation rate of **3.23** was determined to be 7.2×10^{-5} s^{-1} at 35°C by using the stoichiometric reaction with ethyl vinyl ether. This rate is several times slower than that of **3.2** at the same temperature (4.6×10^{-4} s^{-1}).[25] Although it is difficult to identify the electronic impact of a cyclobutane alkylidene versus a benzylidene ligand, it is likely that the compact cyclobutane ring contributes to the reduced phosphine lability in **3.23**.[62] Nevertheless, this complex is active for subsequent olefin metathesis, in contrast to the bis(triphenylphosphine) derivative $(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_3$. When **3.23** (or **3.2**) and neat methylenecyclobutane are heated at 70°C in a sealed ampoule, a small amount of the bicyclobutylidene dimer is produced. Unfortunately, it was not possible to get an accurate product yield because of volatility problems.

Another cyclic carbene complex, **3.25**, can be synthesized by the cross metathesis of **3.2** with 2-methylene-1,3-dioxepane (Scheme 3.14). In contrast, the reaction of **3.2** with 1,1-diethoxyethylene is unsuccessful, presumably due to the slightly greater steric bulk of this acyclic

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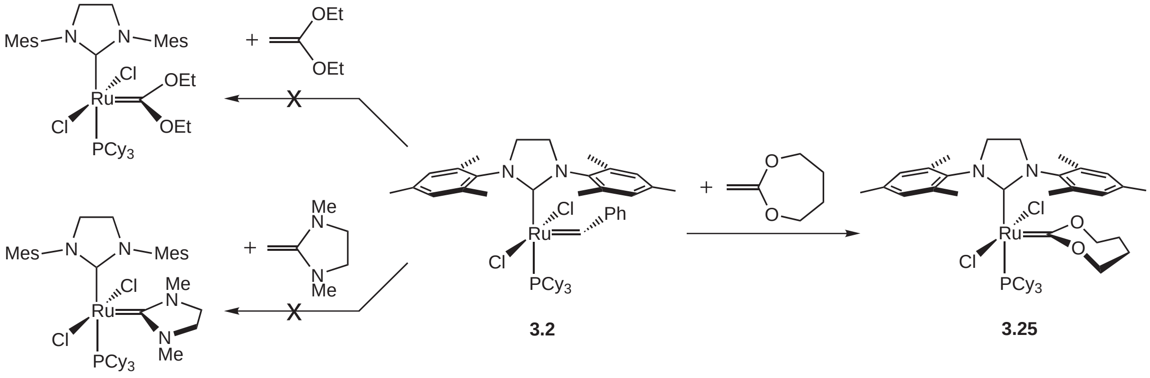
[61] **3.24** also has been observed in the reaction of **3.2** with 2-methyl-2-butene. Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Organic Lett.* **2002**, *4*, 1939-1942.

[62] Importantly, there is excellent agreement between k_{init} values determined by ^{1}H NMR with the ethyl vinyl ether reaction and phosphine dissociation rates determined by $^{31}P\{^1H\}$ NMR magnetization transfer. See reference 25b.

olefin compared to 2-methylene-1,3-dioxepane. Attempts to make a cyclic amino carbene derivative, effectively a bis(NHC) complex with an NHC ligand in the apical site, by reaction of **3.2** with 2-methylene-1,3-dimethyl-imidazolidine[63] were also unsuccessful. In this case, the product mixture contained two ruthenium hydride species with characteristic ^{1}H NMR resonances at δ –24.88 (d, J = 21 Hz) and –27.65 (d, J = 21 Hz). The ^{31}P{^{1}H} NMR spectrum contained three new resonances at δ 33.3 (s), 43.9 (d, J = 13), and 47.3 (d, J = 11), and the ^{13}C{^{1}H} NMR spectrum indicated the presence of four NHC carbon centers. It is possible that one of these products is the bis(NHC) complex $(H_2IMes)(H_2IMe)(PCy_3)(Cl)(H)Ru$ (where H_2IMe = 1,3-dimethyl-imidazolidine-2-ylidene), but this assignment has not yet been confirmed.



Scheme 3.14

The crystal structures of **3.23**, **3.24**, and **3.25** are shown in Figures 3.8, 3.9, and 3.10, and the structures of $(PCy_3)_2(Cl)_2Ru{=}CHMe$ and $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) are included for comparison (Figures 3.11 and 3.12). A compilation of selected bond lengths and angles is provided in Table 3.5. The orientation of the alkylidene ligand in $(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_3$ is dramatically different from that in all the other complexes. The cyclobutane ring of $(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_3$ is tilted out of the $[Cl_2Ru{=}C]$ plane, such that the Cl–Ru–C_α–C_β dihedral angle equals 59°. In contrast, the alkylidene ligands in **3.1**, **3.2**, **3.23**, **3.24**, and **3.25** are oriented approximately in the $[Cl_2Ru{=}C]$ plane. The [Ru=C] distances lie within the range of 1.812 to 1.839 Å, but there is no clear trend in these or other values as the ligands are systematically varied.

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[63] Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2053-2064.

Table 3.5: Comparison of selected bond distances (Å) and angles (deg).

Complex	**Ref.**	**Ru=C**	**Ru–Cl$_{avg}$**	**Ru–P**	**Ru–CN$_2$**	**Cl–Ru–Cl**	**L–Ru–P**
$(PPh_3)_2(Cl)_2Ru{=}C(CH_2)_3$	[a]	1.830(4)	2.361(1)	2.381(1)$_{avg}$	—	150.4(1)	170.9(1)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}C(CH_2)_3$ (**3.23**)	[b]	1.812(2)	2.406(1)	2.481(1)	2.070(2)	178.79(6)	157.79(6)
$(PCy_3)_2(Cl)_2Ru{=}CHMe$	[b]	1.816(2)	2.406(1)	2.415(1)$_{avg}$	—	173.65(2)	161.74(2)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHMe$ (**3.24**)	[b]	1.812(2)	2.406(1)	2.481(1)	2.070(2)	178.14(2)	157.79(6)
$(PCy_3)_2(Cl)_2Ru{=}CH(OEt)$	[c]	1.812(5)	2.382(1)	2.379(1)$_{avg}$	—	173.50(4)	164.67(4)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}C[O_2(CH_2)_4]$ (**3.25**)	[b]	1.825(2)	2.389(1)	2.433(1)	2.097(2)	168.18(2)	168.17(7)
$(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**)	[b]	1.838(2)	2.390(1)	2.416(1)$_{avg}$	—	168.21(2)	161.90(2)
$(PCy_3)_2(Cl)_2Ru{=}CH(p\text{-}ClC_6H_4)$	[d]	1.839(1)	2.398(1)	2.416(1)$_{avg}$	—	167.6(1)	161.1(1)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**3.2**)	[e]	1.835(2)	2.395(1)	2.425(1)	2.085(2)	167.71(2)	163.73(6)

[a] Reference 45; [b] this work; [c] reference 59a; [d] reference 64; [e] reference 28.

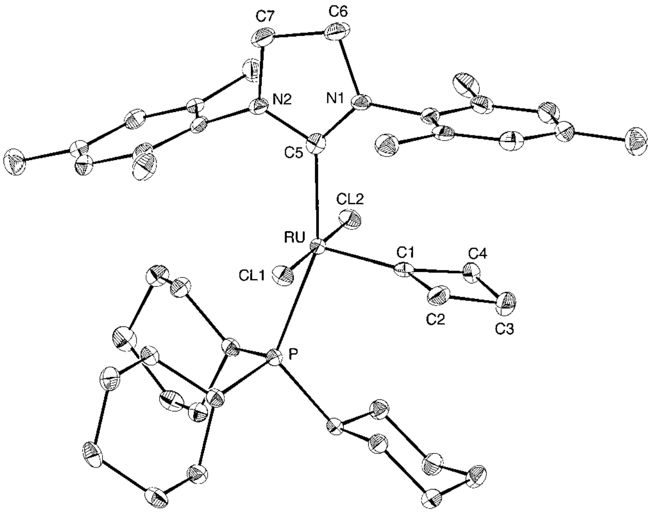

Figure 3.8: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}C(CH_2)_3$ (**3.23**) (CCDC #183905). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg] in addition to those in Table 3.5: C(1)–C(4) 1.529(3), C(1)–C(2) 1.532(3), C(2)–C(3) 1.541(3), C(3)–C(4) 1.539(3), C(4)–C(1)–Ru 134.2(2), C(2)–C(1)–Ru 134.9(2).

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64. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

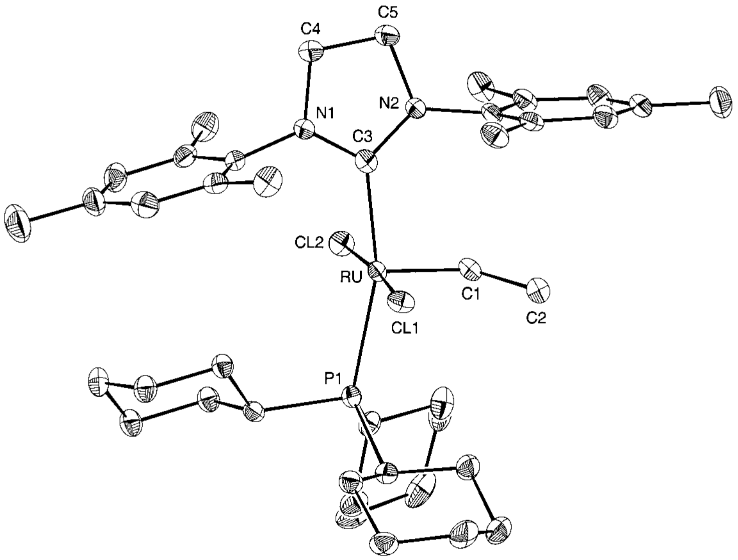

Figure 3.9: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHMe$ (**3.24**) (CCDC #190914). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg] in addition to those in Table 3.5: N(1)–C(3) 1.344(2), N(1)–C(4) 1.475(2), N(2)–C(3) 1.348(2), N(2)–C(5) 1.476(2), C(1)–C(2) 1.485(2), C(4)–C(5) 1.506(3), C(2)–C(1)–Ru 133.4(1), N(1)–C(3)–N(2) 106.8(1).

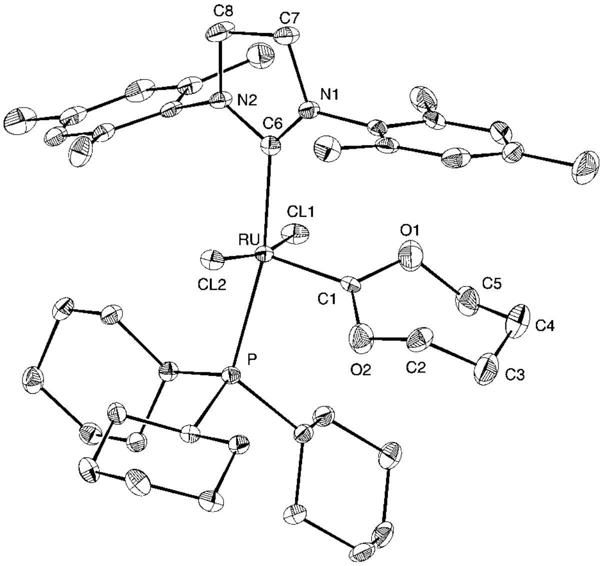

Figure 3.10: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}C[O_2(CH_2)_4]$ (**3.25**) (CCDC #178954). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg] in addition to those in Table 3.5: O(1)–C(1) 1.352(3), O(1)–C(5) 1.460(3), O(2)–C(1) 1.336(3), O(2)–C(2) 1.440(3), N(1)–C(6) 1.350(3), N(2)–C(6) 1.357(3), C(2)–C(3) 1.521(4), C(3)–C(4) 1.477(4), O(2)–C(1)–Ru 123.6(2), O(1)–C(1)–Ru 122.6(2), N(1)–C(6)–N(2) 106.7(2).

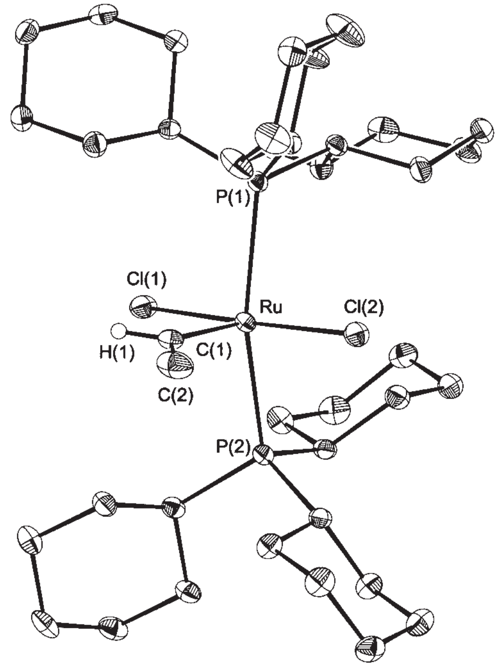

Figure 3.11: Structure of $(PCy_3)_2(Cl)_2Ru{=}CHMe$ (CCDC #167134). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg] in addition to those in Table 3.5: C(1)–C(2) 1.482(3), C(2)–C(1)–Ru 132.7(2).

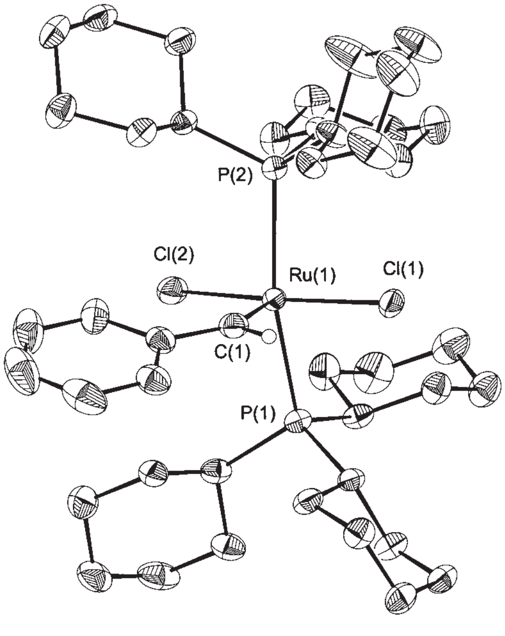

Figure 3.12: Structure of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**) (CCDC #150275).

Conclusions

The results in this chapter highlight the diversity of ruthenium carbene complexes that can be synthesized within the L_2X_2Ru=CHR framework. The examples include derivatives coordinated with a variety of NHC, phosphine, pyridine, imidazole, and cyclic carbene ligands. It is clear that small changes in ligand architecture have a large impact on the catalytic stability and activity of these complexes, and kinetic studies reveal important information about these effects.

The synthesis of (Ph_3Tri)(PCy_3)$(Cl)_2$Ru=CHR (R = Ph, CH=CMe_2) from $(PCy_3)_2(Cl)_2$Ru=CHR and Ph_3Tri(H)(OMe) provided the first example of NHC adducts in organometallic synthesis, and it paved the way for the application of this useful methodology in other cases. The synthesis of bis(NHC) complexes (H_2IMes)(IMes)$(Cl)_2$Ru=CHPh and $(H_2IMes)_2(Cl)_2$Ru=CHPh was achieved by using the substitutionally labile pyridine derivative (H_2IMes)$(py)_2(Cl)_2$Ru=CHPh. Their reactivity with free phosphine provides evidence for how bis(NHC) olefin metathesis catalysts enter the catalytic cycle, *i.e.*, by NHC dissociation. The ruthenium benzylidene coordinated with an isopinocamphenyl-substituted NHC ligand, (ImIPC)(PCy_3)$(Cl)_2$Ru=CHPh, provides greater *Z* olefin selectivity in cross-metathesis reactions. However, the origin of this selectivity appears to be the instability of the catalyst itself, which leads to kinetic product distributions.

A variety of new pyridine- and imidazole-coordinated ruthenium alkylidene complexes have been prepared, but this ligand substitution leads to mediocre activity in the ring-closing metathesis of diethyl diallylmalonate. In addition, the properties of cyclic carbene derivatives have been studied and preliminary results indicate that ruthenium catalysts are capable of dimerizing terminal olefins to tetrasubstituted olefin products.

Experimental

General considerations: All manipulations involving organometallic complexes 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 obtained on Varian Inova 500 and 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. ^{31}P NMR spectra were referenced using H_3PO_4 ($\delta = 0$) as an external standard. Coupling constants are in hertz. IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer; the data are reported in reciprocal centimeters. Elemental analyses were measured by Midwest Microlab, Indianapolis, IN. Mass spectral analysis was performed at the Southern California Mass Spectrometry Facility (University of California at Riverside). Silica gel for the purification of organometallic complexes was obtained from TSI Scientific, Cambridge, MA (60 Å, pH 6.5-7.0).

$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$,[4] $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$,[48] $H_2IMes(H)(CCl_3)$,[4a,19] IMes,[65] IAda,[11c] $(PCy_3)_2(Cl)_2Ru{=}CHMe$,[64] and 4,4-dicarboethoxy-2-methyl-1,6-heptadiene[66] were prepared by literature procedures. *N*-phenylbenzamide phenylhydrazone, $[Ph_3Tri(H)][ClO_4]$, and $Ph_3Tri(H)(OMe)$ were prepared by the methods of Enders and coworkers.[5] Although no problems were encountered during the preparation and use of the perchlorate salt, suitable care and precautions should be taken when handling this potentially hazardous material.[67] $(PCy_3)_2(Cl)_2Ru{=}CHPh$, $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$, $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$, and other chemicals were obtained from commercial sources.

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).

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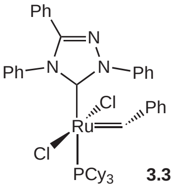
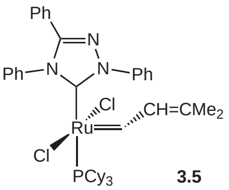
[67] (a) Wolsey, W. C. *J. Chem. Ed.* **1973**, *50*, A335-A337. (b) Muse, L. A. *J. Chem. Ed.* **1972**, *49*, A463-A466. (c) Everett, K.; Graf, F. A. In *CRC Handbook of Laboratory Safety*, 2nd Edition; N. V. Steere, Ed.; CRC Press: Boca Raton, FL, 1971; pp. 265-276.

Synthesis and characterization of (Ph$_3$Tri)(PCy$_3$)(Cl)$_2$Ru=CHPh (3.3): A Schlenk flask was charged with 0.500 g (0.608 mmol) of (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh (**3.1**), 0.195 g (0.592 mmol) of Ph$_3$Tri(H)(OMe), and 17 mL toluene. The reaction was stirred first at room temperature for 20 min and then at 80°C for 10-20 min. The resulting brown solution was pumped down under vacuum. 100 mL pentane was added to the residue and gently warmed to dissolve most of the material. Upon cooling to −78°C, a tan-colored precipitate formed. The supernatant was filtered off by cannula and the solid dried under vacuum to yield 0.293 g of **3.3** as a brown solid (59%). ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz): δ 19.56 [d, $^3J_{HP}$ = 8, Ru=CH, major isomer (~60%)], 19.37 [d, $^3J_{HP}$ = 6.5, Ru=CH, minor isomer (~40%)], 8.21 [d, *J* = 7.5, CH$_{aryl}$], 7.85 [br d, *J* = 6.5, CH$_{aryl}$], 7.71 [t, *J* = 7.5, CH$_{aryl}$], 7.58 [m, CH$_{aryl}$], 7.44 [t, *J* = 7.5, CH$_{aryl}$], 7.40 [m, CH$_{aryl}$], 7.31 [m, CH$_{aryl}$], 7.21 [t, *J* = 8, CH$_{aryl}$], 7.11-6.99 [m, CH$_{aryl}$], 6.88 [br, CH$_{aryl}$], 2.11 [q, *J* = 11.5, PCy$_3$], 1.59 [br m, PCy$_3$], 1.31-1.01 [m, PCy$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz): δ 308.24 [m, Ru=C], 304.91 [m, Ru=C], 192.79 [d, $^2J_{CP}$ = 89, Ru–CN$_2$], 191.22 [d, $^2J_{CP}$ = 92, Ru–CN$_2$], 154.88 [d, $^3J_{CP}$ = 3, *ipso*-CHPh], 154.02 [d, $^3J_{CP}$ = 4, *ipso*-CHPh], 151,23 [s, Ph$_3$Tri], 151.09 [s, Ph$_3$Tri], 141.84 [s, Ph$_3$Tri], 140.31 [s, Ph$_3$Tri], 136.83 [s, Ph$_3$Tri], 135.95 [s, Ph$_3$Tri], 131.18 [br], 130.88 [s], 130.77 [br], 130.70 [s], 130.59 [s], 130.56 [s], 130.36 [br], 130.16 [br], 130.13 [s], 130.11 [s], 129.75 [s], 129.68 [s], 129.61 [s], 129.49 [s], 129.02 [s], 128.99 [s], 128.97 [s], 128.77 [s], 128.65 [s], 128.62 [s], 128.57 [s], 128.51 [s], 126.81 [s], 126.78 [s], 125.14 [s], 125.77 [s], 33.17 [d, J_{CP} = 16, PCy$_3$], 33.08 [d, J_{CP} = 16, PCy$_3$], 28.23 [d, J_{CP} = 10, PCy$_3$], 28.18 [d, J_{CP} = 10, PCy$_3$], 26.81 [s, PCy$_3$], 26.78 [s, PCy$_3$]. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.9 MHz): δ 24.14 [s, minor isomer], 23.04 [s, major isomer]. HRMS analysis (FAB) *m/z*: calcd [M$^+$] 839.2476, found 839.2450. Anal. Calcd. for C$_{45}$H$_{54}$N$_3$Cl$_2$PRu: C, 64.35%; H, 6.48%; N, 5.00%. Found: C, 64.64%; H, 6.31%; N, 5.04%.



3.3

(Ph$_3$Tri)(PCy$_3$)(Cl)$_2$Ru=CHCH=CMe$_2$ (3.5): Synthesized analogously to **3.3** but starting with (PCy$_3$)$_2$(Cl)$_2$Ru=CHCH=CMe$_2$. ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz): δ 19.56 [dd, $^3J_{HP}$ = 5.5, $^3J_{HH}$ = 11, Ru=CH, major isomer (~60%)], 19.37 [dd, $^3J_{HP}$ = 2.5, $^3J_{HH}$ = 11, Ru=CH, minor isomer (~40%)], 8.63 [d, *J* = 8, CH$_{aryl}$], 8.00 [d, *J* = 8, CH$_{aryl}$], 7.97 [d, *J* = 8, CH$_{aryl}$], 7.85 [d, $^3J_{HH}$ = 11, RuCH–C*H*, (major isomer)], 7.71 [d, $^3J_{HH}$ = 11, RuCH–C*H*, minor isomer], 7.35 [t, *J* = 7.5, CH$_{aryl}$], 7.29 [br d, *J* = 7.5, CH$_{aryl}$], 7.13 [m, CH$_{aryl}$], 7.00 [m, CH$_{aryl}$], 6.85-6.66 [m, CH$_{aryl}$], 2.44 [q, *J* = 11.5, PCy$_3$], 1.89 [m, PCy$_3$], 1.70 [m, PCy$_3$], 1.63 [m, PCy$_3$], 1.42 [m,

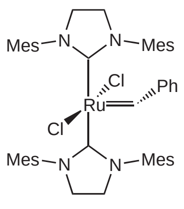


3.5

PCy_3], 1.23 [m, PCy_3], 1.01 [s, Me_2vinyl, major isomer], 0.98 [s, Me_2vinyl, minor isomer], 0.80 [s, Me_2vinyl, major isomer], 0.78 [s, Me_2vinyl, minor isomer]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): δ 297.72 [m, Ru=C], 294.33 [m, Ru=C], 194.90 [d, $^2J_{CP}$ = 81, Ru–CN_2, minor isomer], 193.51 [d, $^2J_{CP}$ = 85, Ru–CN_2, major isomer], 155.09 [d, $^3J_{CP}$ = 2, RuCH*C*H, minor isomer], 153.83 [d, $^3J_{CP}$ = 3, RuCH*C*H, major isomer], 146.89, 146.80, 141.09, 140.91, 136.98, 136.28, 135.69, 134.71, 133.11, 132.17, 132.03, 131.39, 130.90, 130.85, 130.78, 130.74, 130.70, 130.37, 130.23, 130.07, 130.01, 129.89, 129.84, 129.71, 129.64, 129.58, 129.39, 128.98, 128.85, 127.46, 126.70, 126.58 [br s], 126.14, 125.66, 122.72, 121.35 [br s], 32.92 [d, J_{CP} = 17, PCy_3], 32.81 [d, J_{CP} = 16, PCy_3], 29.29 [s, PCy_3], 29.27 [s, PCy_3], 28.25 [d, J_{CP} = 10.5, PCy_3], 27.82 [s, CH_3, major isomer], 27.80 [s, CH_3, minor isomer], 26.88 [s, PCy_3], 20.96 [s, CH_3, minor isomer], 20.90 [s, CH_3, major isomer]. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): δ 28.11 [s, minor isomer], 26.43 [s, major isomer]. HRMS analysis (FAB) *m/z*: calcd [M^+] 817.2632, found 817.2645.

Formation of (Ph_3Tri)(PPh_3)$(Cl)_2$Ru=CHPh (3.9): A screw cap NMR tube was charged with 0.010 g (0.013 mmol) of $(PPh_3)_2(Cl)_2$Ru=CHPh, 0.004 g (0.012 mmol) of Ph_3Tri(H)(OMe), and 0.6 mL of C_6D_6. The solution remained green in color throughout the reaction. ^1H and ^{31}P NMR spectra were recorded after 7 hrs at 40°C. ^1H NMR (299.9 MHz): δ 19.37 [d, $^3J_{HP}$ = 16, Ru=CH, major isomer], 19.28 [d, $^3J_{HP}$ = 12, Ru=CH, minor isomer], 8.68 [d, J = 7.5], 8.05 [m], 7.88 [d, J = 7.5], 7.76-7.58 [several m], 7.39 [m], 7.20-6.68 [several m], 6.43 [m]. $^{31}P\{^1H\}$ NMR (161.9 MHz): δ 31.26 [s], 30.90 [s].

Synthesis and characterization of $(H_2IMes)_2(Cl)_2$Ru=CHPh (3.8): A small ampoule was charged with 0.175 g (0.270 mmol) of $(H_2IMes)(py)_2(Cl)_2$Ru=CHPh, 0.173 g (0.406 mmol) of H_2IMes(H)(CCl_3), and 8 mL of benzene. The reaction mixture was heated at 80°C for 20 hrs. The solution was then concentrated to ~1.5 mL and purified by column chromatography in air (silica gel, 5:1 pentane/THF). The brown fraction was stripped of solvent, and the resulting material was redissolved in a minimum amount of benzene and lyophilized to yield 0.125 g (0.143 mmol) of **3.8** as a fluffy, pale brown solid (53%). Crystals for x-ray analysis were obtained by slow evaporation of a dichloromethane solution. ^1H NMR (CD_2Cl_2, 25ºC, 499.9 MHz): δ 18.95 [s, 1H, Ru=CH], 8.81 [d, *J* = 8, 1H, Ph], 7.18 [tt, *J* = 1 and 7, 1H, Ph], 6.94 [dt, *J* = 1 and 7, 1H, Ph], 6.81 [br s, 4H, *m*-CH_{Mes}], 6.74 [dt, *J* = 1 and 7, 1H, Ph], 6.55 [br s, 2H, *m*-CH_{Mes}], 5.97 [d, *J* = 7.5, 1H, Ph], 5.58 [br s, 2H, *m*-CH_{Mes}], 3.56 [br s, 6H, CH_2CH_2], 3.42 [br s,



3.8

2H, CH_2CH_2], 2.48 [br s, 6H, Me], 2.21 [br m, 18H, Me], 1.90 [br s, 6H, Me], 1.82 [br s, 6H, Me]. ^{1}H NMR (CD_2Cl_2, −15ºC, 499.9 MHz): δ 18.81 [s, 1H, Ru=CH], 8.74 [d, *J* = 8, 1H, Ph], 7.16 [tt, *J* = 1 and 7, 1H, Ph], 6.93 [dt, *J* = 1 and 7, 1H, Ph], 6.80 [s, 4H, *m*-CH_{Mes}], 6.73 [dt, *J* = 1 and 7, 1H, Ph], 6.52 [s, 2H, *m*-CH_{Mes}], 5.91 [d, J = 8, 1H, Ph], 5.52 [s, 2H, *m*-CH_{Mes}], 3.55 [m, 6H, CH_2CH_2], 3.39 [m, 2H, CH_2CH_2], 2.46 [s, 6H, Me], 2.21 [s, 6H, Me], 2.17 [s, 6H, Me], 2.11 [s, 6H, Me], 1.87 [s, 6H, Me], 1.78 [s, 6H, Me]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): δ 296.32 and 296.04 [Ru=C], 221.19 [$RuCN_2$], 150.79 and 150.77 [*ipso*-C_{Ph}], 138.26 [br], 137.60 [br], 137.19 [br], 136.41 [br], 136.40, 131.61 and 131.59, 130.49 [br], 129.77 and 129.75 [CH_{Mes}], 129.16 [br], 127.12 [CH_{Mes}], 126.79 [CH_{Mes}], 126.55 [CH_{Mes}], 53.56 [br, NCH_2CH_2N], 52.34 [br, NCH_2CH_2N], 21.50 [br m, CH_3], 19.29 [br m, CH_3]. IR (KBr pellet): 2937 [w], 2914 [m], 2954 [w], 1609 [w], 1478 [m, ν_{CN}], 1441 [w], 1417 [m], 1379 [w], 1266 [s], 1239 [m], 1176 [w], 1035 [w], 896 [w], 849 [w], 738 [w], 686 [w], 642 [w], 577 [w]. Anal. Calcd. for $C_{49}H_{58}N_4Cl_2Ru$: C, 67.26%; H, 6.68%; N, 6.40%. Found: C, 67.24%; H, 6.71%; N, 6.21%.

Reaction of $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ with PCy_3: A screw cap NMR tube was charged with 0.015 g of **3.8**, 0.015 g of PCy_3, and 0.8 mL C_6D_6. This solution was heated in a 80ºC oil bath and periodically monitored by ^{1}H and $^{31}P\{^1H\}$ NMR.

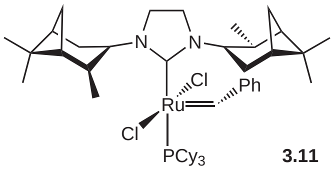
Reaction of 3.8 with $(PCy_3)_2(Cl)_2Ru{=}CHPh$: A screw cap NMR tube was charged with 0.008 g of **3.8**, 0.008 g of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**3.1**), and 0.8 mL of C_6D_6. This solution was heated in a 70ºC oil bath and periodically monitored by ^{1}H and ^{31}P NMR. After 23 hrs, the $(PCy_3)_2(Cl)_2Ru{=}CHPh$: **3.8** : **3.2** ratio was 0.5 : 1.0 : 0.2; after 47 hrs, the ratio was 0.0 : 1.0 : 0.8.

Reaction of $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ with ethylene: A J. Young NMR tube was charged with ~0.015 g of **3.8** and 0.8 mL of C_6D_6. The headspace in the tube was replaced with 1 atm ethylene. This solution was heated in a 60ºC oil bath for 24 hrs. No reaction was observed by ^{1}H or ^{31}P NMR.

ROMP reactions: An NMR tube with septum cap was charged with 0.60 mL of a catalyst stock solution (5 mM in CD_2Cl_2, 0.003 mmol catalyst per run) in the glovebox. The tube was equilibrated at 25°C in the NMR probe. Then 110 μL of COD (0.90 mmol, 1500 mM) was injected into the tube. The reaction was monitored by measuring the increasing ^{1}H NMR signals of the product over at least three half lives. The data were fit to a first-order exponential with Varian kinetics software.[68]

Generation of (IAda)(PPh_3)$(Cl)_2$Ru=CHPh (3.10): A J. Young NMR tube was charged with 0.010 g (0.013 mmol) of $(PPh_3)_2(Cl)_2$Ru=CHPh, 0.005 g (0.015 mmol) of IAda:, and 1 mL of C_6D_6. After 1.5 hr at room temperature, NMR spectra showed 79% conversion to **3.10**. Characteristic resonances: ^{1}H NMR (C_6D_6, 299.9 MHz): δ 21.48 [s, Ru=CH_α]. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 35.8 [s].

Synthesis and characterization of (ImIPC)(PCy_3)$(Cl)_2$Ru=CHPh (3.11): In a nitrogen-filled glovebox, a large Schlenk flask was charged with 0.475 g [IPCimid(H)][BF_4] (1.120 mmol), 0.131 g KOBu^t (1.120 mmol), and 30 mL anhydrous, degassed benzene. This mixture was stirred at room temperature for 6 hrs. Then a solution of 0.400 g of **3.1** (0.486 mmol) in 15 mL benzene was added, and the reaction was stirred for 30 min at room temperature, during which time the mixture changed from purple to brown. The reaction was concentrated to a third of its original volume under vacuum and transferred to a silica gel column (1.5×16″). The product was quickly eluted with 5:1 heptane:ether. The second, brown band was collected and stripped of solvent. The oily residue that remained was redissolved in a minimum amount of benzene and lyophylized to yield 0.080 g of **3.11** as a brown powder (19%). ^{1}H NMR (299.817 MHz, 20°C, CD_2Cl_2): δ 20.583 and 20.577 [two s, two orientations of Ru=CH_α], 8.54 [br s], 7.60 [t, J = 7], 7.34 (t, *J* = 8], 5.16 (qt, *J* = 5], 3.46–3.96 [m], 2.86 (t, *J* = 12], 2.34–2.50 [m], 1.44–2.20 [m], 1.43 (s), 1.41 (s), 0.82–1.31 [m], 1.26 [s], 1.12 [s], 1.01 [s], 0.57 [d, *J* = 7], 0.25 [s]. ^{1}H NMR (299.817 MHz, –70°C, CD_2Cl_2): δ 20.32 [s, Ru=CH_α], 9.07 [d, *J* = 8], 7.87 [t, *J* = 7], 7.59 [t, *J* = 7], 7.35 [m], 4.92 [br], 3.30–3.90 [m], 2.69 [m], 2.44–0.78 [m], 1.33 [s], 1.16 [s], 1.02 [s], 0.90 [s], 0.88 [s], 0.86 [s], 0.80 [s], 0.78 [s], 0.43 [s], 0.11 [br d, *J* = 6]. $^{31}P\{^1H\}$ NMR (121.39 MHz, 25°C, CD_2Cl_2): δ 21.72 [s]. $^{31}P\{^1H\}$ NMR (121.39 MHz, –65°C, CD_2Cl_2): δ 21.95 [s], 21.16 [s].



3.11

Formation of (PCy_3)(L)(CO)(Cl)(H)Ru: In a glovebox, a vial was charged with 0.020 g of (L)(PCy_3)$(Cl)_2$Ru=CHPh, ~2 mL of MeOH, and 5 drops of CH_2Cl_2. This mixture was stirred

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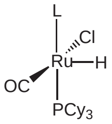
[68] VNMR 6.1B Software; Varian Associates, Inc.

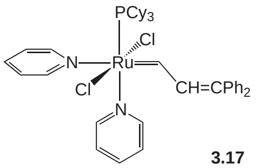
at room temperature for 12 hrs. Then the yellow-orange supernatant was decanted into a Schlenk flask and pumped down under vacuum. In all cases, ^{1}H and ^{31}P NMR showed partial conversion to the (PCy_3)(L)(CO)(Cl)(H)Ru product, unreacted ruthenium benzylidene starting material, and other unidentified side products. Characteristic resonances for (ImIPC)(PCy_3)(CO)(Cl)(H)Ru (**3.12**): ^{1}H NMR (C_6D_6, 299.9 MHz): δ –24.63 [d, $^{2}J_{HP}$ = 23, Ru–H, one isomer], –24.70 [d, $^{2}J_{HP}$ = 25, Ru–H, another isomer]. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ 214.8 [d, $^{2}J_{CP}$ = 89, NCN], 202.6 [m, CO, one isomer], 202.2 [m, CO, another isomer], 59.8 [d, J = 7, NCH2CH2N], 58.0 [d, J = 15, NCH2CH2N]. IR (KBr pellet): 1903.4 cm^{-1} (ν_{CO}). Characteristic resonances for (H_2IMes)(PCy_3)(CO)(Cl)(H)Ru (**3.14**): ^{1}H NMR (C_6D_6, 299.9 MHz): δ –24.90 [d, $^{2}J_{HP}$ = 21, Ru–H], 6.86 [s, *m*-H on Mes], 6.81 [s, *m*-H on Mes], 2.67 [s, Me], 2.13 [s, Me]. ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz): δ 47.12 [s]. ^{1}H and ^{31}P{^{1}H} NMR data for **3.13** and **3.15** match those reported in references 38 and 69.



3.12 (L = ImIPC)
3.13 (L = PCy_3)
3.14 (L = H_2IMes)
3.15 (L = IMes)

Formation of (ImIPC)(PCy_3)$(CO)_2$(Cl)(H)Ru: A J. Young NMR tube was charged with ~0.005 g of (ImIPC)(PCy_3)(CO)(Cl)(H)Ru (**3.12**) and 0.7 mL of C_6D_6. The headspace in the tube was replaced with 1 atm of carbon monoxide. The solution changed instantly from yellow to almost colorless. Characteristic resonances for (ImIPC)(PCy_3)$(CO)_2$(Cl)(H)Ru: ^{1}H NMR (C_6D_6, 299.9 MHz): δ –4.39 [d, $^{2}J_{HP}$ = 22, Ru–H, one isomer], –4.52 [d, $^{2}J_{HP}$ = 23, Ru–H, another isomer].

Characterization of (PCy_3)$(py)_2$$(Cl)_2$Ru=CHCH=$CPh_2$ (3.17): ^{1}H NMR (299.9 MHz, C_6D_6): δ 20.18 [app t, Ru=CH, $^{3}J_{HP}$ = 12], 9.17 [br, py], 9.09 [br, py], 8.81 [d, CH, J_{HH} = 12], 7.70 [d, Ph, J_{HH} = 7], 7.47 [d, Ph, J_{HH} = 7], 7.46 [d, Ph, J_{HH} = 8], 7.22 [m, Ph], 7.10 [m, Ph], 6.97 [br, py], 6.86 [t, Ph, J_{HH} = 8], 6.69 [br, py], 6.56 [br, py], 6.32 [br, py], 2.38 [br q, PCy_3, J_{HP} = 10], 2.14 [br d, PCy_3, J_{HP} = 11], 1.70 [br, PCy_3], 1.59 [br, PCy_3], 1.13 [br m, PCy_3]. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 30.21 [s]. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ 312.73 [m, Ru=C], 159.81 [s, py or CH=CPh_2], 158.79 [s, py or CH=CPh_2], 155.64 [s, py or CH=CPh_2], 153.79 [br, py or CH=CPh_2], 151.66 [br, py or CH=CPh_2], 147.80 [s, py or CH=CPh_2], 144.86 [s, py or CH=CPh_2], 142.92 [s, py or CH=CPh_2], 137.68 [s, py or CH=CPh_2], 136.15 [s, py or CH=CPh_2],



3.17

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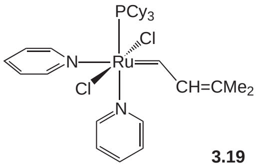
69. Moers, F. G.; Ten Hoedt, R. W. M.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2279-2282.

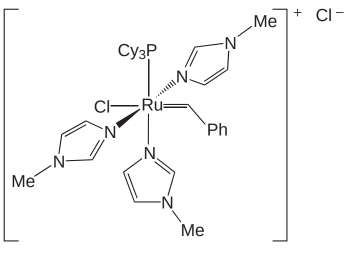
130.15 [s, py or CH=CPh_2], 129.63 [s, py or CH=CPh_2], 128.98 [s, py or CH=CPh_2], 128.84 [s, py or CH=CPh_2], 128.74 [s, py or CH=CPh_2], 128.69 [s, py or CH=CPh_2], 123.88 [br, py or CH=CPh_2], 123.30 [br, py or CH=CPh_2], 123.27 [s, py or CH=CPh_2], 122.87 [s, py or CH=CPh_2], 37.00 [d, PCy_3, J_{CP} = 16], 36.10 [d, PCy_3, J_{CP} = 19], 29.99 [s, PCy_3], 28.66 [d, PCy_3, J_{CP} = 10]. Anal. Calcd. for $C_{43}H_{55}N_2Cl_2PRu$: C, 64.33%; H, 6.90%; N, 3.49%. Found: C, 64.38%; H, 6.95%; N, 3.63%.

Characterization of (PCy_3)(py)$_2$(Cl)$_2$Ru=CHCH=CMe_2 (3.19): As soon as the isolated product is dissolved in C_6D_6, the solution begins to change from green to orange-red in color. The NMR data for **3.19** was obtained within 10 minutes of preparing the sample. As decomposition progressed, free pyridine was observed by ^{1}H NMR. ^{1}H NMR (499.9 MHz, C_6D_6): δ 20.18 [app t, 1H, $^3J_{HP}$ = 10, Ru=CH], 9.14 [br s, 4H, py], 8.07 [d, 1H, $^3J_{HH}$ = 12, CH], 6.68 [br s, 3H, py], 6.43 [br m, 3H, py], 2.54 [qt, 3H, J_{HP} = 12, PCy_3], 2.27 [d, 6H, J_{HP} = 12, PCy_3], 1.91 [qt, 6H, J_{HP} = 12, PCy_3], 1.78 [d, 6H, J_{HP} = 11, PCy_3], 1.62 [m, 4H, PCy_3], 1.26 [s, 3H, Me], 1.23 [m, 8H, PCy_3], 0.75 [s, 3H, Me]. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 37.17 [s].



3.19

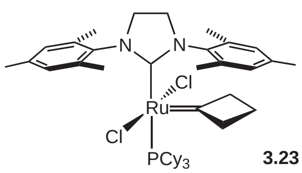
Synthesis and characterization of [(PCy_3)(1-MeIm)$_3$(Cl)Ru=CHPh][Cl] (3.20): A Schlenk flask was charged with 0.500 g (0.608 mmol) of (PCy_3)$_2$(Cl)$_2$Ru=CHPh (**3.1**) and 15 mL of toluene. 0.250 g (3.045 mmol) of 1-methylimidazole was added with stirring. After 1 hr, the reaction mixture was allowed to settle, and the yellow supernatant was decanted from the green precipitate. This material was washed with 30 mL of toluene and dried under vacuum to provide 0.437 g of **3.20** as a bright green powder (~96%). The isolated material always included solvent that was not removed by vacuum; thus, a satisfactory elemental analysis could not be obtained. ^{1}H NMR (499.9 MHz, CD_2Cl_2): δ 20.42 [d, 1H, $^3J_{HP}$ = 11, Ru=CH], 8.55 [s, 2H, Im], 7.65 [d, 3H, J_{HH} = 9, Ph], 7.47 [s, 1H, Im], 7.21 [t, 2H, J_{HH} = 8, Ph], 6.99 [s, 2H, Im], 6.85 [s, 2H, Im], 6.53 [s, 1H, Im], 5.66 [s, 1H, Im], 3.70 [s, 6H, Me], 3.53 [s, 3H, Me], 1.89 [br, 6H, PCy_3], 1.69 [d, J_{HP} = 11, 6H, PCy_3], 1.59 [m, 6H, PCy_3], 1.34 [q, J_{HP} = 13, 6H, PCy_3], 1.16 [m, 3H, PCy_3], 0.88 [m, 6H, PCy_3]. ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ 324.97 [m, Ru=C], 152.35 [s, Ph], 141.92 [d, J_{CP} = 35, trans Im], 139.93 [d, J_{CP} = 9], 138.21 [m], 132.38 [s], 132.19 [s], 132.06 [br], 130.15 [m], 129.60 [d, J = 9], 128.57 [m], 121.45 [d, J_{CP} = 18, trans Im], 120.28 [d, J_{CP} = 33, trans Im], 36.00



3.20

[d, J_{CP} = 15, PCy_3], 35.13 [s, Me], 34.91 [s, Me], 29.55 [m, PCy_3], 28.46 [m, PCy_3], 27.12 [s, PCy_3], 26.78 [s, PCy_3]. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 22.77 [s]. HRMS analysis (FAB) *m/z*: calcd [M^+] 753.3114, found 753.3147.

Synthesis and characterization of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}C(CH_2)_3$ (3.23): In the glovebox, a 20 mL vial was charged with 0.120 g of 3.2, 1 mL of methylene cyclobutane (excess), and 15 mL of hexanes. This pink-brown solution was stirred at room temperature overnight, then cooled at −10°C for 24 hours. The solution was decanted from the brown, microcrystalline solid at the bottom of the vial. This solid was dried under vacuum to provide 0.075 g of 3.23 (65%). ^1H NMR (CD_2Cl_2, 499.85 MHz): δ 6.96 [d, 2H, *J* = 0.5, *m*-H], 6.95 [d, 2H, *J* = 0.5, *m*-H], 3.86 [m, 4H, NCH_2CH_2N], 2.66 [m, 2H, CH_2], 2.57 [s, 6H, Me of Mes], 2.49 [s, 6H, Me of Mes], 2.39 [m, 1H, CH_2], 2.34 [s, 3H, Me of Mes], 2.29 [s, 3H, Me of Mes], 2.12 [m, 3H, PCy_3], 1.98 [m, 2H, CH_2], 1.83 [m, 1H, CH_2], 1.63 [br, PCy_3], 1.56 [br, 12H, PCy_3], 1.20-1.06 [br m, 15H, PCy_3]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.71 MHz): δ 340.89 [d, $^2J_{CP}$ = 6, $Ru{=}C_\alpha$], 219.23 [d, $^2J_{CP}$ = 72, NCN], 139.53 [s, Mes], 138.98 [s, Mes], 138.81 [s, Mes], 138.72 [s, Mes], 138.10 [s, Mes], 135.05 [s, Mes], 130.34 [s, Mes], 130.01 [s, Mes], 64.54 [s, $CH_2(\beta)$], 52.79 [d, $^4J_{PC}$ = 3, NCH_2CH_2N], 52.76 [d, $^4J_{PC}$ = 4, NCH_2CH_2N], 33.71 [d, J_{PC} = 16, PCy_3], 29.42 [s, $CH_2(\gamma)$], 28.18 [d, J_{PC} = 10, PCy_3], 27.03 [s, PCy_3], 23.28 [s, Me], 23.21 [s, Me], 21.43 [s, Me], 21.35 [s, Me], 20.09 [s, Me], 19.16 [s, Me]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.39 MHz): δ 21.68 [s]. Anal. Calcd. for $C_{43}H_{65}N_2Cl_2PRu$: C, 63.53%; H, 8.06%; N, 3.45%. Found: C, 63.64%; H, 8.21%; N, 3.37%.

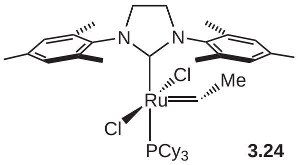


3.23

NMR initiation kinetics for 3.23: A screw-cap NMR tube fitted with a rubber septum was charged with **3.23** (0.0106 mmol) in 0.6 mL of toluene-d_8. This solution was allowed to equilibrate in the NMR probe at 35°C. Then 30 equivalents of ethyl vinyl ether were injected into the NMR tube by micro-syringe. The reaction was monitored by measuring the peak heights of the starting alkylidene as a function of time over greater than three half lives, and this data was fitted to a first order exponential using Varian kinetics software.[68]

Synthesis and characterization of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHMe$ (3.24): A thick-walled glass ampoule was charged with 0.585 g (0.691 mmol) of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$

(**3.2**) in 15 mL benzene. The atmosphere in the ampoule was replaced with 1 atm *cis*-2-butene, and the reaction was heated at 60°C for 4 hrs with vigorous stirring. The resulting brown solution was concentrated to ~3 mL and purified by column chromatography in air (silica gel, 5:1 pentane/THF). The first pink band was discarded (unreacted **3.2**). The second orange-brown band was collected, stripped of solvent, and dried under vacuum to provide 0.440 g of 3.24 as a brown solid (81%). ^{1}H NMR (CD_2Cl_2, 499.85 MHz): δ 18.47 [q, $^3J_{PH}$ = 5.5, 1H, Ru=CH_α], 6.97 [s, 2H, *m*-H], 6.93 [s, 2H, *m*-H], 3.88 [m, 4H, CH_2CH_2], 2.59 [s, 6H, *o*-Me], 2.41 [s, 6H, *o*-Me], 2.29 [s, 3H, *p*-Me], 2.28 [s, 3H, *p*-Me], 2.15 [m, 3H, PCy_3], 1.60 [m, 12H, PCy_3], 1.49 [dd, $^3J_{HH}$ = 5.5, $^4J_{PH}$ = 1.5, 3H, Ru=CHCH_3], 1.47–0.88 [multiple peaks, 15H, PCy_3]. ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz): δ 315.34 [m, Ru=C], 220.46 [d, $^2J_{PC}$ = 75, CN_2], 139.38 [s, Mes], 139.07 [s, Mes], 138.68 [s, Mes], 138.56 [s, Mes], 138.14 [s, Mes], 135.33 [s, Mes], 130.37 [s, *m*-CH on Mes], 52.58 [d, $^4J_{PC}$ = 3.5, CH_2CH_2], 51.89 [d, $^4J_{PC}$ = 2.5, CH_2CH_2], 46.61 [s, Ru=CHCH_3], 32.15 [d, J_{PC} = 18, PCy_3], 29.41 [s, PCy_3], 28.29 [d, J_{PC} = 10, PCy_3], 26.83 [s, PCy_3], 21.43 [s, *p*-Me on Mes], 21.34 [s, *p*-Me on Mes], 20.08 [s, *o*-Me on Mes], 18.93 [s, *o*-Me on Mes]. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.39 MHz): δ 30.82 [s].



3.24