Chapter 2

Ruthenium Carbene Complexes with Electron-Withdrawing Substituents: [Ru]=CF_2 and [Ru]=CH(CN)

Introduction

The development of ruthenium olefin metathesis catalysts coordinated with N-heterocyclic carbene ligands is a highly significant advance because it has extended the scope of the reaction to more challenging substrates, *i.e.*, those that are sterically demanding or electronically deactivated, as well as monomers with low ring strain.[1] However, there are many cases that remain problematic. A number of these involve directly functionalized olefins, which are particularly interesting from an organometallic perspective because the mechanism of olefin metathesis requires α-substituted carbene intermediates. This situation is illustrated in Scheme 2.1 for $(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh$ (**2.1**) (H_2IMes = 1,3-dimesityl-imidazolidine-2-ylidene). Once this catalyst undergoes the initial turnover with functionalized olefin $H_2C=CH(X)$, the propagating species becomes an α-substituted carbene derivative $[(H_2IMes)(Cl)_2Ru=CH(X)]$. With terminal olefin substrates, this species alternates with the methylidene intermediate $[(H_2IMes)(Cl)_2Ru=CH_2]$.

Previous studies have revealed that α-carbene substituents can have a large impact on the olefin metathesis reactivity and stability of the resulting catalyst species. These effects are

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[1] Examples: (a) A. K. Chatterjee, D. P. Sanders, R. H. Grubbs, *Org. Lett.* **2002**, *4*, 1939-1942. (b) S. J. Spessard, B. M. Stoltz, *Org. Lett.* **2002**, *4*, 1943-1946. (c) J. Sun, S. C. Sinha, *Angew. Chem. Int. Ed.* **2002**, *41*, 1381-1383. (d) J. P. Morgan, C. Morrill, R. H. Grubbs, *Org. Lett.* **2002**, *4*, 67-70. (e) T.-L. Choi, A. K. Chatterjee, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 1277-1279. (f) H. D. Maynard, S. Y. Okada, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 1275-1279. (g) S. W. Craig, J. A. Manzer, E. B. Coughlin, *Macromolecules* **2001**, *34*, 7929-7931. (h) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783-3784. (i) C. W. Bielawski, R. H. Grubbs *Angew. Chem. Int. Ed.* **2000**, *39*, 2903-2906. (j) R. Stragies, U. Voigtmann, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 5465-5468. (k) J. A. Smulik, S. T. Diver, *Org. Lett.* **2000**, *2*, 2271-2274. (l) A. K. Chatterjee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 1751-1753. (m) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787-4790. (n) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953-956. (o) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247-2250.

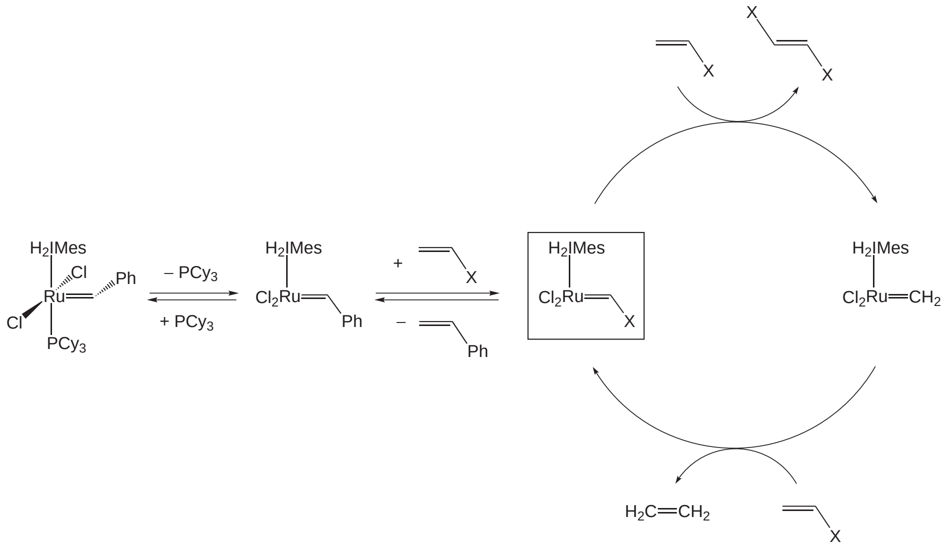

Figure 2.1

reflected in the overall catalytic activity of ruthenium alkylidene catalysts, which vary in the order [Ru]=CH(COOR) > [Ru]=CH(R) > [Ru]=CH(Ph) > [Ru]=CH_2 > [Ru]=CH(OR) (where R = alkyl), from the most active ester carbenes to the least active alkoxy-substituted derivatives.[2]

One set of α-functionalized substrates that has received relatively little attention is the halogenated olefins.[3] These reactions would involve a monohalo [M]=CXR or dihalo [M]=CX_2 carbene complex instead of the usual alkylidene [M]=CHR. This possibility has been previously considered by Beauchamp and coworkers, who speculated about the possible metathesis of directly fluorinated olefins with nickel or manganese complexes.[4] In addition, the active species in the $W(CO)_6/CCl_4/h\nu$ catalyst system has been proposed to be a tungsten dichlorocarbene complex [W]=CCl_2.[5] However, there has been only one report of metathesis involving directly halogenated olefins, namely the cross metathesis of 1-chloro- and 1-bromoethylene with propylene using a heterogeneous catalyst, $Re_2O_7/Al_2O_3/Me_4Sn$.[6]

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[2] Examples: (a) Louie, J.; Grubbs, R. H. *Organometallics*, **2002,** *21*, 2153-2164. (b) Sanford, M. S., Love, J. A., Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554. (c) Ulman, M.; Belderrain, T. R.; Grubbs, R. H. *Tetrahedron Lett.* **2000**, *41*, 4689-4693. (d) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887-3897. (e) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (f) Wu, Z.; Nguyen, S. T. Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[3] (a) K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press: San Diego, CA, 1997. (b) Mol, J. C. In *Olefin Metathesis and Polymerization Catalysts*, Imamoglu, Y., Ed.; Kluwer Academic: The Netherlands, 1990, pp 115-140.

[4] (a) L. F. Halle, P. B. Armentrout, J. L. Beauchamp, *Organometallics* **1983**, *2*, 1829-1833. (b) A. E. Stevens, Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 1981, pp 73-120.

[5] (a) D. Borowczak, T. Szymanska-Buzar, J. J. Ziólkowski, *J. Mol. Cat.* **1984**, *27*, 355-365. (b) F. Garnier, P. Krausz, H. Rudler, *J. Organomet. Chem.* **1980**, *186*, 77-83.

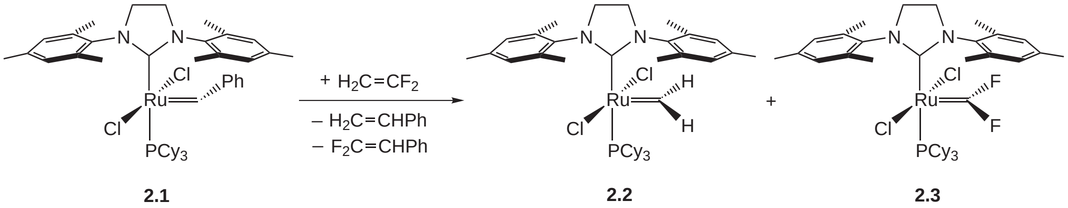
[6] R. A. Fridman, A. N. Bashkirov, L. G. Liberov, S. M. Nosakova, R. M. Smirnova, S. B. Verbovetskaya, *Doklady Akad. nauk S.S.S.R.*, **1977**, *234*, 1354-1357.

Another challenging substrate is acrylonitrile, which has been used in cross metathesis only with Schrock's arylimido molybdenum alkylidene catalyst[7] and the ether-tethered ruthenium alkylidene derivative $(H_2IMes)(Cl)_2Ru{=}CH(C_6H_4OPr^i)$.[8] All attempts with the bis(phosphine) complex $(PCy_3)_2(Cl)_2Ru{=}CHPh$ and **2.1** have inexplicably failed.[1h,7c,8a,9] These reactions would involve a cyano-carbene intermediate [M]=CH(CN).

The purpose of this study was to investigate the metathesis of directly functionalized olefins with catalyst **2.1**, in order to determine the effects of α-carbene substitution on catalyst activity and other properties. Two specific olefins were examined in detail, 1,1-difluoroethylene and acrylonitrile, based on a preliminary screen for olefins that react cleanly with **2.1** to provide new carbene species.

Results and Discussion

Olefin metathesis with 1,1-difluoroethylene.[10] Under an atmosphere of 1,1-difluoroethylene, **2.1** reacts to form the corresponding methylidene and difluorocarbene complexes, $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2$ (**2.2**)[11] and $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2$ (**2.3**) (Scheme 2.1).[12] When the reaction is performed at room temperature, the product mixture contains approximately 40% **2.2** and 60% **2.3**, as well as styrene and β,β-difluorostyrene. However, the proportion of **2.3**



Scheme 2.1

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[7] (a) W. E. Crowe, D. R. Goldberg, *J. Am. Chem. Soc.* **1995**, *117*, 5162-5163. (b) W. E. Crowe, D. R. Goldberg, Z. J. Zhang, *Tetrahedron Lett.* **1996**, *37*, 2117-2120. (c) O. Brümmer, A. Rückert, S. Blechert, *Chem. Eur. J.* **1997**, *3*, 441-446.

[8] (a) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973-9976. (b) S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, *Synlett* **2001**, 430-432. (c) J. Cossy, S. BouzBouz, A. H. Hoveyda, *J. Organomet. Chem.* **2001**, *634*, 215-221.

[9] D. L. Wright, L. C. Usher, M. Estrella-Jimenez, *Org. Lett.* **2001**, *3*, 4275-4277.

[10] Some of these results have been published. T. M. Trnka, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 3441-3444.

[11] The methylidene complex **2.2** has been synthesized by the reaction of **2.1** with ethylene. See reference 2b.

[12] In a similar fashion, $(PCy_3)_2(Cl)_2Ru{=}CHPh$ reacts with 1,1-difluoroethylene to afford $(PCy_3)_2(Cl)_2Ru{=}CF_2$. Unfortunately, this reaction is very slow (~2 weeks at 80°C).

increases to greater than 98% when the reaction is carried out at 60°C instead, and these conditions can be used to synthesize this complex in 86% isolated yield.

These differences with reaction temperature suggest that pathway A is preferred over pathway B (Figure 2.2) at elevated temperatures. It is perhaps not surprising that the initial metathesis of 1,1-difluoroethylene is facile, considering that the C=C double bond in this molecule is weaker than that in ethylene (130 vs. 172 kcal mol^{-1}). However, the organic products of a second turnover of olefin metathesis—ethylene and tetrafluoroethylene—are not present in the product mixture, which indicates that the reaction of **2.1** with 1,1-difluoroethylene is stoichiometric.

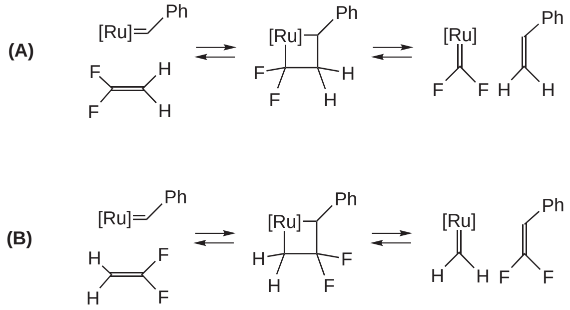
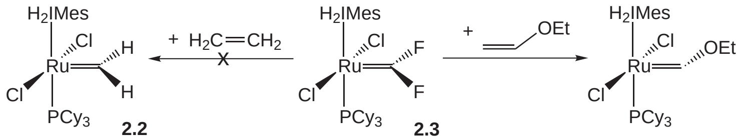


Figure 2.2

Furthermore, the [2+2] cycloadditions in Figure 2.2 are theoretically reversible transformations, but in fact, the back reactions have not been observed. For example, **2.3** does not react with ethylene to form the methylidene (**2.2)** and 1,1-difluoroethylene (Scheme 2.2), and **2.2** decomposes when heated in the presence of 1,1-difluoroethylene. However, **2.3** reacts with an excess of ethyl vinyl ether at 60°C to provide the thermodynamically more stable alkoxy-carbene derivative ($(H_2IMes)(PCy_3)(Cl)_2Ru=CH(OEt)$) (Scheme 2.2).



Scheme 2.2

The reaction in Scheme 2.1 is the first example of olefin metathesis involving a directly fluorinated olefin, and it provides access to a 16-electron ruthenium difluorocarbene complex, which has not been previously accessible.[13] Complex **2.3** is unambiguously identified as the difluorocarbene by NMR spectroscopy. It is characterized by a $^{31}P\{^1H\}$ NMR resonance at δ 32.1 and a ^{19}F NMR resonance at δ 133.7, both doublets with $J = 4.5$ Hz from $^{31}P–^{19}F$ coupling. This low field ^{19}F chemical shift is also diagnostic for metal–fluorocarbenes, which resonate between 80 and 200 ppm.[13,14] The $^{13}C\{^1H\}$ resonance for the carbene carbon appears as a triplet of doublets at δ 218.1 ($^2J_{CP} = 12$ Hz, $^1J_{CF} = 430$ Hz) (Figure 2.3). This resonance is shifted significantly upfield compared to alkyl-substituted ruthenium carbenes; for example, the benzylidene carbon of **2.1** and the methylidene carbon of **2.2** appear at δ 295.1 and 294.8, respectively.[11] The N-heterocyclic carbene carbon appears in the same region at δ 217.2 ($^2J_{CP} =$ 87 Hz) (Figure 2.3).

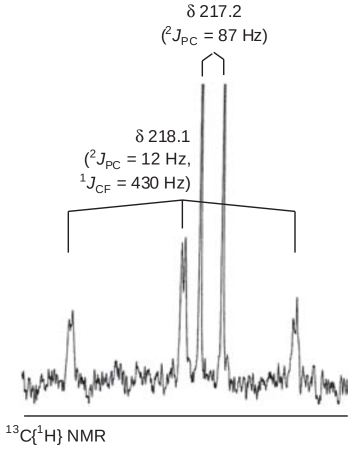


Figure 2.3

The molecular structures of **2.2** and **2.3** were determined by x-ray diffraction (Figures 2.4 and 2.5). Notably, **2.2** is the first structurally characterized ruthenium methylidene complex.[15] In

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[13] For an excellent review of halocarbene complexes, see: P. J. Brothers, W. R. Roper, *Chem. Rev.* **1988**, *88*, 1293-1326.

[14] D. Huang, P. R. Koren, K. Folting, E. R. Davidson, K. G. Caulton, *J. Am. Chem. Soc.* **2000**, *122*, 8916-8931.

[15] A small number of Ta, W, Os, Ir, and Re methylidene complexes have been structurally characterized. See references 16b, 21, and (a) Takusagawa, F.; Koetzle, T. F.; Sharp, P. R.; Schrock, R. R. *Acta Cryst.* **1988**, *C44*, 439-443. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411-447. (c) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708-6710. (d) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Holmes, S. J. *Acta Cryst.* **1984**, *C40*, 590-592. (e) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804-5811.

both cases, the carbene is oriented in the [Cl–Ru–Cl] plane.[16] The *d*(Ru=C) of 1.800(2) Å in **2.2** is shorter than typical for ruthenium benzylidenes [Ru]=CHPh but similar to values observed for phenyl-substituted vinylidenes [Ru]=C=CHPh.[17] Complex **2.3** (Figure 2.5), which is isostructural with **2.2**, exhibits an even shorter [Ru=C] bond length of 1.775(3) Å. This value also is short compared to the *d*(Ru=C) of 1.83(1) Å for $(PPh_3)_2(CO)_2Ru=CF_2$, a trigonal bipyramidal, 18-electron complex reported by Roper and coworkers.[16a,18] This difference between $(PPh_3)_2(CO)_2Ru=CF_2$ and **2.3** may be rationalized by enhanced ruthenium→carbene π-back-bonding from the more electron-rich metal center of **2.3**.

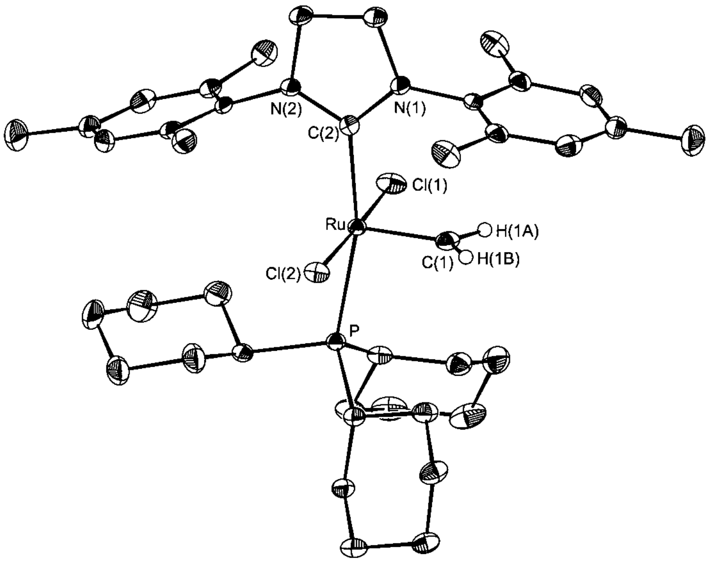

Figure 2.4: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru=CH_2$ (**2.2**) (CCDC #162849). Displacement ellipsoids are drawn at 50% probability; H(1A) and H(1B) are drawn at arbitrary scale. Selected bond distances [Å] and angles [deg]: Ru–C(1) 1.800(2), Ru–C(2) 2.065(2), Ru–Cl(1) 2.379(1), Ru–Cl(2) 2.393(1), Ru–P 2.427(1), C(1)–H(1A) 0.93(2), C(1)–H(1B) 0.92(2), C(1)–Ru-C(2) 97.29(7), C(1)–Ru–Cl(1) 89.77(7), C(2)–Ru–Cl(1) 90.01(5), C(1)–Ru–Cl(2) 92.90(7), C(2)–Ru–Cl(2) 90.91(5), Cl(1)–Ru–Cl(2) 177.05(2), C(1)–Ru–P 96.90(6), C(2)–Ru–P 165.81(5), Cl(1)–Ru–P 90.28(2), Cl(2)–Ru–P 88.14(2), Ru–C(1)–H(1A) 123(1), Ru–C(1)–H(1B) 128(1), H(1A)–C(1)–H(1B) 108(2).

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[16] In contrast, the carbenes in $(PPh_3)_2(CO)_2Ru=CF_2$ and $(PPh_3)_2(NO)(Cl)Os=CH_2$ are oriented in the [P–Ru–P] plane. (a) G. R. Clark, S. V. Hoskins, T. C. Jones, W. R. Roper, *J. Chem. Soc. Chem. Commun.* **1983**, 719-721. (b) A. F. Hill, W. R. Roper, J. M. Waters, A. H. Wright, *J. Am. Chem. Soc.* **1983**, 5939-5940.

[17] The average *d*(Ru=C) for the 7 ruthenium benzylidene complexes [Ru]=CHPh in the Cambridge Structural Database is 1.85 Å. The average *d*(Ru=C) for the 20 phenyl-substituted ruthenium vinylidene complexes [Ru]=C=CHPh is 1.80 Å. CSD Version 5.20. *3D Search and Research Using the Cambridge Structural Database*, F. H. Allen, O. Kennard, *Chemical Design and Automation News* **1993**, *8*, 1 and 31-37.

[18] Another structurally characterized ruthenium difluorocarbene complex is $(PPr^i_3)_2(CO)(F)(H)Ru=CF_2$, which contains an even longer *d*(Ru=C) of 1.952(3) Å. In this case, however, the hydride ligand is located trans to the difluorocarbene. See reference 14.

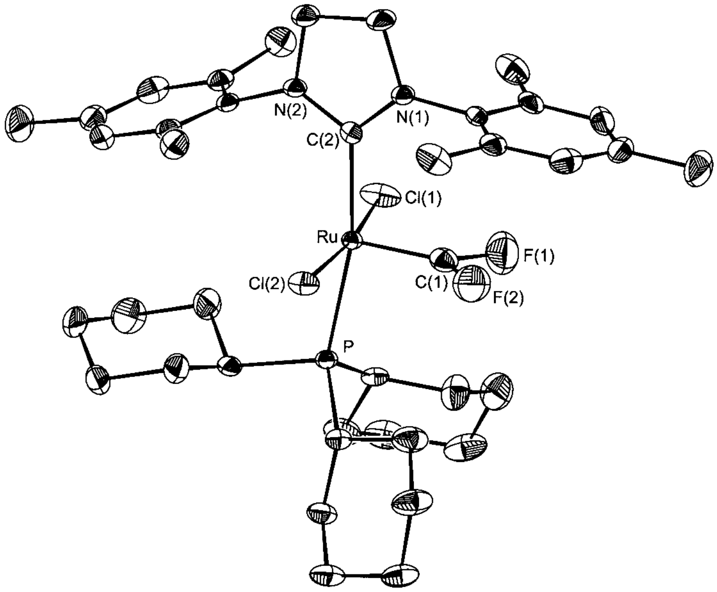

Figure 2.5: Structure of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2$ (**2.3**) (CCDC #162850). Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg]: Ru–C(1) 1.775(3), Ru–C(2) 2.076(2), Ru–Cl(1) 2.365(1), Ru–Cl(2) 2.385(1), Ru–P 2.433(1), F(1)–C(1) 1.335(3), F(2)–C(1) 1.305(3), C(1)–Ru–C(2) 96.9(1), C(1)–Ru–Cl(1) 94.37(9), C(2)–Ru–Cl(1) 88.65(6), C(1)–Ru–Cl(2) 94.66(9), C(2)–Ru–Cl(2) 91.39(6), Cl(1)–Ru–Cl(2) 170.90(3), C(1)–Ru–P 95.38(8), C(2)–Ru–P 167.69(6), Cl(1)–Ru–P 89.57(2), Cl(2)–Ru–P 88.45(2), F(2)–C(1)–F(1) 103.4(2), F(2)–C(1)–Ru 130.0(2), F(1)–C(1)–Ru 126.6(2).

A comparison of selected bond lengths along the series **2.1-2.3** and with $(PCy_3)_2(Cl)_2Ru{=}CHPh$ is provided in Table 2.1. There is little change in any of the ruthenium-ligand bond lengths when going from the bis(phosphine) benzylidene to the mixed phosphine–N-heterocyclic carbene analog (**2.1**). However, there are substantial changes when the carbene substituents are altered. The fact that *d*(Ru=C) in **2.3** is shorter than in **2.1** or **2.2** may be explained by the stronger acceptor properties of the difluorocarbene.[19] In addition, the fact that *d*(Ru=C) in **2.2** is shorter than in **2.3** may be explained, at least in part, by the smaller size of the methylidene compared to the benzylidene.

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[19] Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428-1438.

Table 2.1: Comparison of selected bond distances (Å) in a series of (L)$(PCy_3)(Cl)_2Ru{=}CR_2$ complexes.

Complex	d(Ru=C)	$d(\text{Ru–Cl})_{\text{avg}}$	d(Ru–P)	$d(\text{Ru–CN}_2)$
$(PCy_3)_2(Cl)_2Ru{=}CHPh$	1.838(2)	2.390(1)	$2.416(1)_{\text{avg}}$	—
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**)[20]	1.835(2)	2.395(1)	2.425(1)	2.085(2)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2$ (**2.2**)	1.800(2)	2.386(1)	2.427(1)	2.065(2)
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2$ (**2.3**)	1.775(3)	2.375(1)	2.433(1)	2.076(2)

The other structurally characterized, matched pair of methylidene and dihalocarbene complexes consists of $(PPh_3)_2(NO)(Cl)Os{=}CH_2$ and $(PPh_3)_2(NO)(Cl)Os{=}CF_2$.[21] In contrast to **2.2** and **2.3**, the [Os=C] bond length *increases* in going from the osmium methylidene [1.92(1) Å] to the osmium difluorocarbene [1.976(6) Å]. Carter and Goddard have rationalized this trend with a bonding model that predicts longer metal–carbon bonds for covalent (Schrock-type carbene) compared to donor/acceptor (Fischer-type carbene) bonding.[22,23] Complexes **2.2** and **2.3** clearly differ from these osmium examples in that they contain more electron-donating tricyclohexyl phosphine and N-heterocyclic carbene ligands, and because they are electronically unsaturated.

Complexes **2.1-2.3** also differ in their rates of NHC ligand rotation, measured by ^1H NMR magnetization transfer experiments.[20] As shown in Table 2.2, the barrier to NHC rotation decreases as the carbene is varied from benzylidene to methylidene to difluorocarbene. The higher barrier in **2.1** is probably due to the larger size of the phenyl substituent, but the difference

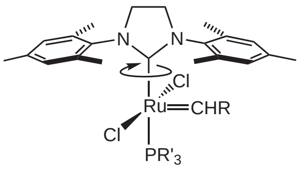

Table 2.2: Activation parameters for NHC rotation and rates of methyl group exchange (k_E).

Complex	$\Delta G^{\ddagger}$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	k_E (358 K) (s^{-1})
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**)[20]	21.8 ± 0.3	23.0 ± 1	6.0 ± 4	0.58 ± 0.03
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2$ (**2.2**)	20.1 ± 0.3	19.8 ± 1	–0.9 ± 4	4.2 ± 0.4
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2$ (**2.3**)	19.6 ± 0.4	18.5 ± 1	3.7 ± 4	50.4 ± 2

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[20] Sanford, M. S. Ph.D. Dissertation; California Institute of Technology: Pasadena, CA, 2001.

[21] See reference 16b and M. A. Gallop, W. R. Roper, *Adv. Organomet. Chem.* **1986**, *25*, 121.

[22] However, Benson and Cundari have calculated [Ru=C] bond lengths of 1.886 and 1.990 Å for $(PH_3)_2Cl_2Ru{=}CH_2$ and $(PH_3)_2Cl_2Ru{=}CF_2$, respectively. M. T. Benson, T. R. Cundari, *Int. J. Quantum Chem.* **1997**, *65*, 987-996.

[23] E. A. Carter, W. A. Goddard III, *J. Am. Chem. Soc.* **1986**, *108*, 2180-2191.

between **2.2** and **2.3** most likely has electronic origins, *i.e.*, the electron withdrawing properties of the difluorocarbene moiety has the effect of reducing the Ru–H_2IMes bond strength.

The results in Table 2.3 provide a measure of the olefin metathesis activities of **2.1-2.3** for the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene.[1i,2b] Complex **2.3** is clearly a poor catalyst, especially with respect to **2.1**. It seemed likely that the problem was poor catalyst initiation, based on the absence of NMR signals for CF_2 end groups in the polymer product. Recent studies have shown that the initiation of $(L)(PR_3)(X)_2Ru{=}CHR'$ catalysts requires phosphine dissociation, which can be monitored by $^{31}P\{^1H\}$ NMR magnetization transfer.[2b,24] These experiments on complex **2.3** revealed no observable phosphine dissociation up to 100°C, translating into a phosphine dissociation rate of < 0.01 s^{-1}. In comparison, the phosphine dissociation rate for **2.1** is 1.64 s^{-1} at the same temperature.[24a] Notably, complex **2.3** is stable at 100°C, whereas **2.2** decomposes at elevated temperatures, even in the presence of free PCy_3. As a result, it has not been possible to measure the phosphine dissociation rate for **2.2**.[2b]

Table 2.3: ROMP of 1,5-cyclooctadiene with **2.1**, **2.2**, and **2.3**.[a]

Catalyst	*T* [°C]	Additive[b]	*t* [hr]	Product [%][c]
2.1[d]	20	—	0.03	100
2.2[d]	20	—	1.25	62
2.3	25	—	1.25	9
2.3	50	—	5	72
2.3	50	CuCl	5	81
2.3	50	HCl	5	92
2.3	50	$AlCl_3$	5	21

[a] Reaction conditions: 0.005 M [Ru] + 300 equivalents COD in CD_2Cl_2; [b] five equivalents of additive; HCl used as a 1M solution in Et_2O; [c] Percent conversion determined by ^1H NMR integration; [d] Reference 2b.

Higher temperatures and additives that promote phosphine dissociation helped improve the activity of **2.3** (Table 2.3).[25] The best results were obtained with HCl, which is capable of reversible phosphine protonation. In contrast, addition of $AlCl_3$ resulted in immediate and irreversible decomposition.

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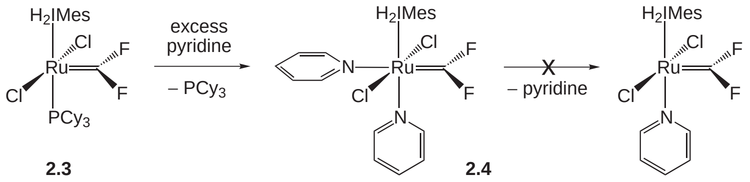
[24] (a) M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749-750. (b) Love, J. A.; Sanford, M. S.; Grubbs, R. H. *J. Am. Chem. Soc.* **2002**, in press.

[25] (a) J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153-3155. (b) M. S. Sanford, L. M. Henling, R. H. Grubbs, *Organometallics* **1998**, *17*, 5384-5389. (c) E. L. Dias, R. H. Grubbs, *Organometallics* **1998**, *17*, 2758-2767. (d) D. M. Lynn, B. Mohr, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 1627-1628.

Another attempt to activate **2.3** for olefin metathesis consisted of making the bis-(pyridine) derivative $(H_2IMes)(py)_2(Cl)_2Ru{=}CF_2$ (**2.4**), by reaction of **2.3** with an excess of pyridine (Scheme 2.3).[26] However, the pyridine ligands in this molecule are not labile, and all attempts to remove one equivalent of bound pyridine by heating **2.4** in toluene under vacuum were unsuccessful.[27] Complex **2.4** is similar to **2.3** in olefin metathesis activity.

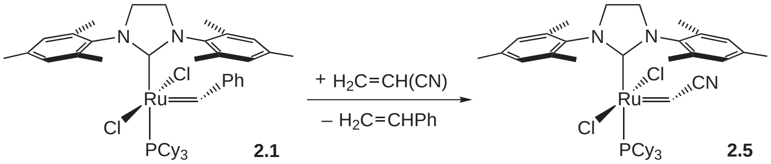


2.3

2.4

Scheme 2.3

Olefin metathesis with acrylonitrile.[28] As illustrated in Scheme 2.4, the reaction of **2.1** with acrylonitrile at room temperature cleanly provides the cyano-substituted carbene complex $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH(CN)$ (**2.5**). Even in the presence of a large excess of acrylonitrile, no metathesis beyond the initial turnover occurs, *i.e.*, no fumaronitrile H(CN)C=CH(CN) or ethylene forms. Although **2.5** decomposed during isolation attempts, it was characterized *in situ* by NMR and IR spectroscopy. The cyano-carbene moiety is distinguished by a ^1H NMR resonance at δ 18.44 for the carbene proton, a ^{13}C NMR resonance at δ 238.0 for the carbene carbon, a ^{13}C NMR resonance at δ 114.0 for the cyano group, and an IR stretching frequency at 2196 cm^{-1} for the C≡N bond.



2.1

2.5

Scheme 2.4

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[26] Likewise, $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ has been synthesized by reaction of **2.1** with an excess of pyridine. Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314-5318.

[27] This procedure has been used to convert $(PCy_3)(py)_2(Cl)_2Ru{=}CHPh$ to $(PCy_3)(py)(Cl)_2Ru{=}CHPh$. Dias, E. L. Ph.D. Thesis; California Institute of Technology: Pasadena, CA, 1998.

[28] Some of these results have been published. Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, 41, 4035-4037.

Cyano-carbene complexes are relatively rare, and the majority of examples contain bridging rather than terminal cyano substituents.[29,30] One example of a terminal cyano-amino carbene complex is $Fe_2[=C(CN)(NPr^i_2)](CO)(Cp)(\mu\text{-}CO)_2$.[29a] In the $^{13}C\{^1H\}$ NMR of this complex, the carbene carbon resonance appears at δ 232-234 and the resonance of the cyano substituent appears at δ 113-114. Both of these values are similar to those measured in this work for $(H_2IMes)(PCy_3)(Cl)_2Ru=CH(CN)$ (**2.5**). In contrast, bridging cyano groups typically resonate between 140 to 160 ppm.[31]

The $\nu_{C\equiv N}$ value also can be used to distinguish between terminal and bridging cyano bonding modes. The value of 2196 cm^{-1} for **2.5** is in the range of other terminal cyano-carbene groups; for example, 2177 cm^{-1} for $Fe_2[=C(CN)(NPr^i_2)](CO)(Cp)(\mu\text{-}CO)_2$,[29a] 2192 cm^{-1} for $(CO)_5Cr=C(CN)(NMe_2)$,[29b] and 2141 and 2159 cm^{-1} for $(Cp)(CO)_2M=C(CN)(Ph)$ (M = Mn and Re).[29c] These values are lower for bridging cyano groups, such as 2072 cm^{-1} for $(Cp)(CO)_2Mn=C(Ph)(\mu\text{-}CN)[W(CO)_5])$.[30] Thus, comparison of the ^{13}C NMR and IR data for **2.5** with these examples suggests that the cyano-carbene is terminal rather than bridging.

Like $(H_2IMes)(PCy_3)(Cl)_2Ru=CF_2$ (**2.3**), complex **2.5** initiates poorly for subsequent olefin metathesis. The initiation rate for **2.5** was determined to be 0.47 ± 0.05 at 35°C by monitoring the stoichiometric reaction with ethyl vinyl ether. In comparison, the initiation rate of $(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh$ (**2.1**) under the same conditions is an order of magnitude greater (4.6 ± 0.4 s^{-1} at 35°C).[2b] For this reason, complexes **2.3** and **2.5** share the same problem: the electron-withdrawing carbene substituents cause phosphine dissociation to come to a standstill. This effect explains the low activity of catalyst **2.1** in acrylonitrile cross metathesis, as described in the introduction of this chapter. After the first turnover of these reactions, the 14-electron species $[(H_2IMes)(Cl)_2Ru=CH(CN)]$ is trapped by re-binding of PCy_3 as complex **2.5**, which cannot re-enter the catalytic cycle. In contrast, the isopropoxy-tethered and 3-bromopyridine derivatives $(H_2IMes)(Cl)_2Ru=CH(C_6H_4OPr^i)$ and $(H_2IMes)(3\text{-}BrPy)(Cl)_2Ru=CHPh$ (Figure 2.6) do not have this problem because the cyano-carbene species is less likely to remain trapped by the more weakly σ-donating ether and pyridine ligands.[28]

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29. Examples of terminal cyano-carbene complexes: (a) $Fe_2[=C(CN)(NPr^i_2)](CO)(Cp)(\mu\text{-}CO)_2$ V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V. G. Albano, M. Monari, F. Prestopino, F. Laschi, P. Zanello, *Organometallics* **1995**, *14*, 5232-5241. (b) $(CO)_5Cr=C(CN)(NMe_2)$ A. J. Hartshorn, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1976**, 761-762. (c) $(Cp)(CO)_2M=C(CN)(Ph)$ E. O. Fischer, P. Stückler, F. R. Kreissl, *J. Organomet. Chem.* **1977**, *129*, 197-202.
30. Examples of bridging cyano-carbene complexes: (a) $(Cp)(CO)_2Mn=C(Ph)(\mu\text{-}CN)[W(CO)_5]$ T. Tang, J. Sun, J. Chen, *Organometallics* **1999**, *18*, 2459-2465. (b) $\{[OCMe(CF_3)_2]_2(NAr)W=CH(CN)\}_4$ T. M. Cameron, A. S. Gamble, K. A. Abboud, J. M. Boncella, *Chem. Commun.* **2002**, 1148-1149.
31. L. Zhang, M. P. Gamasa, J. Gimeno, R. J. Carbajo, F. López-Ortiz, M. F. Guedes da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2000**, 341-350.

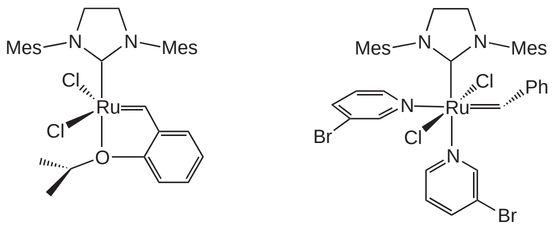

Figure 2.6

Conclusions

The reactions of 1,1-difluoroethylene and acrylonitrile with ruthenium catalyst **2.1** are significant for several reasons. Most importantly, they demonstrate that olefin metathesis with these α-functionalized substrates is possible. In particular, the reaction with 1,1-difluoroethylene is the first example of olefin metathesis involving a directly fluorinated olefin. Although these reactions are not catalytic with **2.1**, detailed studies reveal the impact of ruthenium difluoro-carbene and cyano-carbene species on the catalytic cycle. As summarized in Figure 2.7, the 14-electron species [$(H_2IMes)(Cl)_2Ru{=}CH(X)$] is trapped out of the catalytic cycle by reassociation of the strongly σ-donating PCy_3 ligand, and olefin metathesis halts after the first turnover. At the beginning of this study, it was not obvious that the cyano-carbene and difluorocarbene complexes would have similar reactivity profiles, especially because cyano substituents are considered to have strong π-acceptor properties, whereas fluoro substituents have weak π-donor properties.

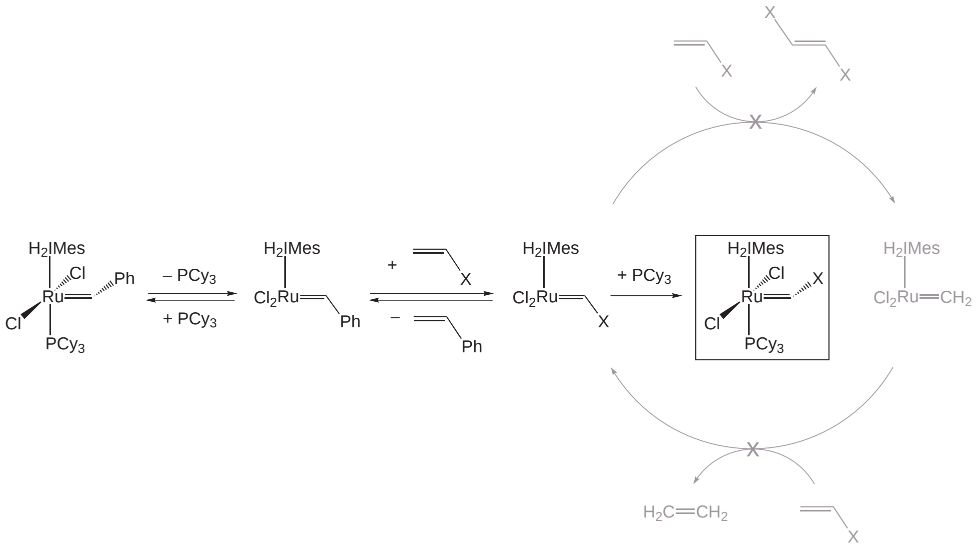

Figure 2.7

Of greater interest to the organometallic chemist, the reactions to form **2.3** and **2.5** provide a new route to α-functionalized carbene complexes. The success of these reactions testifies to the remarkable ability of the $[L_2X_2Ru]$ fragment to stabilize unsaturated ligands in the apical site; additional examples are provided by a series of ester-substituted ruthenium carbenes $(PCy_3)_2(Cl)_2Ru{=}CH(CO_2R)$ and the recently synthesized terminal carbido complexes $(L)(PCy_3)(Cl)_2Ru{\equiv}C$ (L = PCy_3 or H_2IMes).[2c,32] Perhaps in the future, the $[L_2X_2Ru]$ fragment can be used to stabilize other unsaturated species, such as silyl-, ketone-, or hydroxy-substituted carbenes, or even the silylene ligand $[Ru]{=}SiR_2$.

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[32] (a) Hejl, A.; Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Chem. Commun.* **2002**, 2524-2525. (b) Carlson, R. G.; Gile, M. A.; Heppert, J. A.; Mason, M. H.; Powell, D. R.; Velde, D. V.; Vilain, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 1580-1581.

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. ^{19}F NMR spectra were referenced using CCl_3F ($\delta = 0$) 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).

$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**)[33] and $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2$ (**2.2**)[11] were prepared by literature procedures. $(PCy_3)_2(Cl)_2Ru{=}CHPh$, 1,1-difluoroethylene, and other chemicals were obtained from commercial sources. Acrylonitrile, pyridine, and 1,5-cyclooctadiene were degassed before use.

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).

Synthesis and characterization of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2$ (2.3): A solution of 0.32 g (0.37 mmol) $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**) in dry, degassed benzene (15 mL) in a thick-walled glass ampoule was put under ~1.5 atm of 1,1-difluoroethylene. The reaction was heated at 60°C for 12 hrs, during which time it changed from reddish to brown in color. The solution was then concentrated to 5 mL and purified by column chromatography in air (silica gel,

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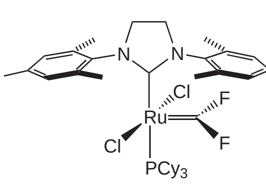
[33] Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, in press.

5:1 pentane/THF). The orange fraction was stripped of solvent and dried under vacuum to provide 0.26 g of **2.3** (86%). ^{1}H NMR (499.852 MHz, 25°C, CD_2Cl_2): δ 1.118 [br, 15H, PCy_3], 1.626 [br, 15H, PCy_3], 2.248 [s, 3H, *p*-CH_3 of Mes], 2.285 [s, 3H, *p*-CH_3 of Mes], 2.385 [m, 3H, PCy_3], 2.480 [s, 6H, *o*-CH_3 of Mes], 2.551 [s, 6H, *o*-CH_3 of Mes], 4.003 [s, 4H, NCH_2CH_2N], 6.921 [s, 4H, *m*-H of Mes]. $^{13}C\{^{1}H\}$ NMR (125.705 MHz, 30°C, C_6D_6): δ 19.44 [s, CH_3 of Mes], 20.65 [s, CH_3 of Mes], 21.49 [s, CH_3 of Mes], 21.50 [s, CH_3 of Mes], 26.92 [d, J = 1.3, PCy_3], 28.50 [d, J = 10, PCy_3], 30.14 [s, PCy_3], 33.34 [d, J = 18, PCy_3], 51.86 [d, $^{4}J_{PC}$ = 2.6, NCH_2CH_2N], 52.61 [d, $^{4}J_{PC}$ = 3.5, NCH_2CH_2N], 127.30 [s, Mes], 128.17 [s, Mes], 129.26 [s, Mes], 129.51 [s, Mes], 130.11 [s, Mes], 130.52 [s, Mes], 134.68 [d, $^{4}J_{PC}$ = 0.7, *ipso*-C of Mes], 136.85 [s, *ipso*-C of Mes], 138.91 [s, Mes], 138.93 [s, Mes], 139.03 [s, Mes], 139.67 [s, Mes], 217.23 [d, $^{2}J_{CP}$ = 87, NCN], 218.09 [td, $^{2}J_{CP}$ = 12, $^{1}J_{CF}$ = 430, Ru=CF_2]. ^{19}F NMR (282.192 MHz, 25°C, CD_2Cl_2): δ 133.74 [d, $^{3}J_{FP}$ = 4.5]. $^{31}P\{^{1}H\}$ NMR (121.392 MHz, 25°C, CD_2Cl_2): δ 32.15 (t, $^{3}J_{PF}$ = 4.4]. IR (KBr pellet): 1167 and 1172 ($\nu_{C\text{-}F}$).



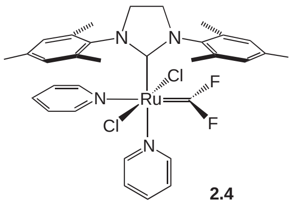
2.3

Reaction of 2.1 with 1,1-difluoroethylene: A J. Young NMR tube was charged with 0.020 g (0.024 mmol) of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**) and 0.7 mL of C_6D_6. The headspace of the NMR tube was replaced with 1 atm of 1,1-difluoroethylene. This solution was kept at room temperature and monitored by NMR until no further changes were observed. The final ratio of **2.2** to **2.3** was determined by $^{31}P\{^{1}H\}$ NMR integration (~4:6). The identity of the products was confirmed by mass spectrometry (FAB): Calculated for $(H_2IMes)(PCy_3)Cl_2Ru{=}CH_2$ (**2.2**): 772.299; found: 772.303 (–5.2 ppm). Calculated for $(H_2IMes)(PCy_3)Cl_2Ru{=}CF_2$ (**2.3**): 808.280; found: 808.280 (+1.0 ppm).

Generation of $(PCy_3)_2(Cl)_2Ru{=}CF_2$: A J. Young NMR tube was charged with 0.020 g (0.024 mmol) of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ and 0.07 mL of C_6D_6. The headspace of the NMR tube was replaced with 1 atm of 1,1-difluoroethylene. This solution was heated at 80°C for two weeks. During this time, NMR spectra showed the formation of $(PCy_3)_2(Cl)_2Ru{=}CF_2$, but the reaction was not clean. Characteristic data for $(PCy_3)_2(Cl)_2Ru{=}CF_2$: ^{19}F NMR (282.192 MHz, C_6D_6): δ 140.41 [t, $^{3}J_{FP}$ = 6]. $^{31}P\{^{1}H\}$ NMR (121.392 MHz, C_6D_6): δ 34.47 [t, $^{3}J_{PF}$ = 7].

Synthesis and characterization of $(H_2IMes)(py)_2(Cl)_2Ru{=}CF_2$ (2.4): A Schlenk flask was charged with 0.102 g (0.126 mmol) of $(H_2IMes)(PCy_3)Cl_2Ru{=}CF_2$ (**2.3**) and 1.5 mL of

CH_2Cl_2. Upon addition of 1 mL pyridine, the solution changed from orange to yellow in color. The reaction was stirred overnight at room temperature. Then ~20 mL hexanes were added and the solution cooled at –10°C for several hours. The resulting yellow precipitate was isolated by filtration. ^1H NMR (299.9 MHz, CD_2Cl_2): δ 2.160 [s, 6H, *p*-CH_3 of Mes], 2.485 [s, 12H, *o*-CH_3 of Mes], 3.934 [s, 4H, NCH_2CH_2N], 6.665 [s, 2H, pyridine or *m*-H of Mes], 6.758 [br s, 3H, pyridine or *m*-H of Mes], 6.913 [t, *J* = 7, 2H, pyridine], 7.350 [s, 1H, *m*-H of Mes], 7.422 [t, *J* = 8, 1H, pyridine], 8.637 [d, *J* = 5, 2H, pyridine], 8.910 [br s, 3H, pyridine]. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 19.31 [Me of Mes], 21.18 [Me of Mes], 52.55 [br, NCH_2CH_2N], 123.37 [br, pyridine or Mes], 129.68 [pyridine or Mes], 135.19 [br, pyridine or Mes], 136.90 [pyridine or Mes], 138.39 [pyridine or Mes], 138.48 [pyridine or Mes], 138.77 [br, pyridine or Mes], 151.10 [pyridine or Mes], 151.54 [pyridine or Mes], 215.96 [CNC], 224.04 [t, $^1J_{CF}$ = 404, Ru=CF_2]. ^{19}F NMR (282.2 MHz, CD_2Cl_2): δ 129.52 [s]. Anal. Calcd. for $C_{32}H_{34}N_4Cl_2F_2Ru$: C, 56.14%; H, 5.01%; N, 8.18%. Found: C, 55.91%; H, 5.30%; N, 7.99%.



2.4

$^{31}P\{^1H\}$ magnetization transfer experiments for 2.3: A J. Young NMR tube was charged with 0.024 mmol of **2.3**, 1.5 equivalents of PCy_3, and 0.6 mL of toluene-d_8. This solution was allowed to thermally equilibrate in the NMR probe. Then the free phosphine resonance was selectively inverted using a DANTE[34] pulse sequence, and after variable mixing times (0.00003–50 s), a non-selective 90° pulse was applied and an FID recorded. ^1H decoupling was applied during the 90° pulse. Spectra were collected as 4 transients with relaxation delays of 30 s. The peak heights of the free and bound phosphine resonances at variable mixing times did not change between 25 and 100°C.

^1H magnetization transfer experiments for 2.2 and 2.3: A J. Young NMR tube was charged with 0.012 mmol of **2.2** or **2.3** and 0.6 mL of toluene-d_8. The resulting solution was allowed to thermally equilibrate in the NMR probe. A methyl or *m*-H resonance of the H_2IMes ligand was selectively inverted using a DANTE[34] pulse sequence, and after variable mixing times (0.00003–50 s), a non-selective 90° pulse was applied and an FID recorded. Spectra were collected as 4 transients with relaxation delays of 30 s. The peak heights at variable mixing times

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[34] Morris, G. A.; Freeman, R. *J. Magn. Res.* **1978**, *29*, 433-462.

were analyzed using the computer program CIFIT[35] to obtain the exchange rate constants (k_E) at different temperatures. Activation parameters were calculated from Eyring plots (Figure 2.6).

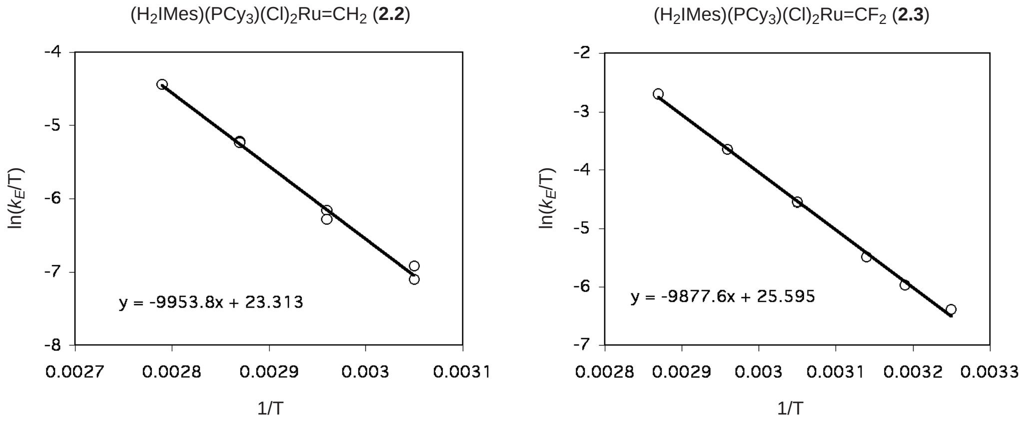
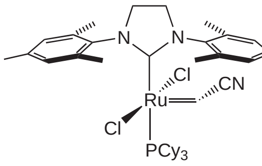


Figure 2.6

Generation and characterization of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH(CN)$ (2.5): 1.2 equivalents of acrylonitrile were added to a screw-cap NMR tube containing a solution of 15 mg $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2.1**) in 0.7 mL of C_6D_6. The reaction was ~98% complete after 6 hours at room temperature, during which time the solution changed from pink-red to dark brown. The sole products were the cyano-carbene complex and styrene. ^1H NMR (C_6D_6, 499.89 MHz): δ 18.44 (s, Ru=CH_α), 6.88 (s, *m*-H on Mes), 6.84 (s, *m*-H on Mes), 3.44 (s), 3.29 (s), 2.66 (s, 6H, *o*-CH_3 on Mes), 2.52 (s, 6H, *o*-CH_3 on Mes), 2.17 (s, 3H, *p*-CH_3 on Mes), 2.12 (s, 3H, *p*-CH_3 on Mes), 1.59 (br s, PCy_3), 1.11 (m, PCy_3). ^{13}C NMR (C_6D_6, 125.39 MHz): δ 238.0 (m, Ru=C_α), 217.3 (d, $^2J_{CP}$ = 68 Hz, $RuCN_2$), 139.6 (s, Mes), 139.4 (s, Mes), 138.3 (s, Mes), 137.8 (s, Mes), 137.7 (s, Mes), 137.6 (s, Mes), 134.3 (s, Mes), 132.2 (s, Mes), 131.1 (s, Mes), 130.6 (s, Mes), 129.1 (s, Mes), 126.9 (s, Mes), 114.0 (s, C≡N), 52.6 (s, NCH_2CH_2N), 51.4 (s, NCH_2CH_2N), 32.2 (d, J_{CP} = 16 Hz, PCy_3), 29.6 (s, PCy_3), 28.1 (d, J_{CP} = 10 Hz, PCy_3), 26.9 (s, PCy_3), 21.6 (s, *p*-CH_3 on Mes), 21.5 (s, *p*-CH_3 on Mes), 20.3 (s, *o*-CH_3 on Mes), 19.3 (s, *o*-CH_3 on Mes). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.39 MHz): δ 30.5 (s). IR (C_6D_6 thin film): 2196 (w, $\nu_{C\equiv N}$), 1482 (m, ν_{CN} of H_2IMes).



2.5

NMR initiation kinetics for 2.5: A screw-cap NMR tube fitted with a rubber septum

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[35] Bain, A. D.; Cramer, J. A. *J. Magn. Res.* **1996**, *118A*, 21-27.

was charged with **2.1** (0.0106 mmol) plus 1.5 equivalents of acrylonitrile in 0.6 mL of toluene-d_8. After conversion to **2.3** was complete, the 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.[36]

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[36] VNMR 6.1B Software, Varian Associates, Inc.