J|A|C|S
ARTICLES
Published on Web 02/12/2003

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

Tina M. Trnka, John P. Morgan, Melanie S. Sanford, Thomas E. Wilhelm, Matthias Scholl, Tae-Lim Choi, Sheng Ding, Michael W. Day, and Robert H. Grubbs*

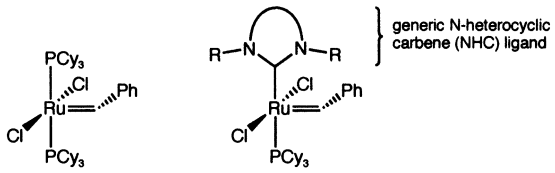
Contribution from the Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received September 4, 2002; E-mail: rhg@its.caltech.edu

Abstract: This paper reports the synthesis and characterization of a variety of ruthenium complexes coordinated with phosphine and N-heterocyclic carbene (NHC) ligands. These complexes include several alkylidene derivatives of the general formula $(NHC)(PR_3)(Cl)_2Ru{=}CHR'$, which are highly active olefin metathesis catalysts. Although these catalysts can be prepared adequately by the reaction of bis(phosphine) ruthenium alkylidene precursors with free NHCs, we have developed an alternative route that employs NHC-alcohol or -chloroform adducts as "protected" forms of the NHC ligands. This route is advantageous because NHC adducts are easier to handle than their free carbene counterparts. We also demonstrate that sterically bulky bis(NHC) complexes can be made by reaction of the pyridine-coordinated precursor $(NHC)(py)_2(Cl)_2Ru{=}CHPh$ with free NHCs or NHC adducts. Two crystal structures are presented, one of the mixed bis(NHC) derivative $(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$, and the other of $(PCy_3)(Cl)(CO)Ru[\eta^2\text{-}(CH_2\text{-}C_6H_2Me_2)(N_2C_3H_4)(C_6H_2Me_3)]$, the product of ortho methyl C−H bond activation. Other side reactions encountered during the synthesis of new ruthenium alkylidene complexes include the formation of hydrido-carbonyl-chloride derivatives in the presence of primary alcohols and the deprotonation of ruthenium vinylcarbene ligands by $KOBu^t$. We also evaluate the olefin metathesis activity of NHC-coordinated complexes in representative RCM and ROMP reactions.

Introduction

Since the discovery that well-defined ruthenium alkylidene complexes could catalyze the ring-opening metathesis polymerization reaction,[1] we[2] and others[3] have devoted considerable effort to developing derivatives with improved properties, especially enhanced activity, product selectivity, and stability. The most successful modifications to date have involved tricyclohexylphosphine (PCy_3) ligands, as in $(PCy_3)_2(Cl)_2Ru{=}CHPh$,[2l−o] and N-heterocyclic carbene (NHC) ligands, as in $(NHC)(PCy_3)(Cl)_2Ru{=}CHPh$.[4] These catalysts have enabled the widespread application of olefin metathesis in many areas of synthetic chemistry.[5]



The emphasis of recent studies has been on ruthenium

(1) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975.

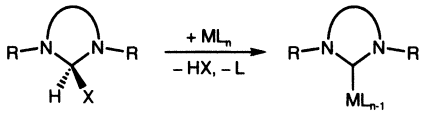
(2) (a) Rölle, T.; Grubbs, R. H. *Chem. Commun.* **2002**, 1070−1071. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (c) Sanford, M. S.; Henling, L. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3451−3453. (d) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872−12873. (e) Ulman, M.; Belderrain, T. R.; Grubbs, R. H. *Tetrahedron Lett.* **2000**, *41*, 4689−4693. (f) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601−6609. (g) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758−2767. (h) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384−5389. (i) Chang, S.; Jones, L.; Wang, C.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 3460−3465. (j) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897. (k) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867−3869. (l) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (m) Wu, Z.; Nguyen, S. T. Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511. (n) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (o) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859.

(3) Representative homogeneous examples: (a) Stüer, W.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **2002**, *641*, 203−207. (b) Buchowicz, W.; Ingold, F.; Mol, J. C.; Lutz, M.; Spek, A. L. *Chem.-Eur. J.* **2001**, *7*, 2842−2847. (c) Coalter, J. N.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 679−684. (d) Nieczypor, P.; van Leeuwen, P. W. N. M.; Mol, J. C.; Lutz, M.; Spek, A. L. *J. Organomet. Chem.* **2001**, *625*, 58−66. (e) Fürstner, A.; Guth, O.; Düffels, Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem.-Eur. J.* **2001**, *7*, 4811−4820. (f) Amoroso, D.; Fogg, D. E. *Macromolecules* **2000**, *33*, 2815−2818. (g) Werner, H.; Jung, S.; González-Herrero, P.; Ilg, K.; Wolf, J. *Eur. J. Inorg. Chem.* **2001**, 1957−1961. (h) Leung, W.-H.; Lau, K.-K.; Zhang, Q.-F.; Wong, W.-T.; Tang, B. *Organometallics* **2000**, *19*, 2084−2089. (i) Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem.* **2000**, *606*, 16−25. (j) Saoud, M.; Romerosa, A.; Peruzzini, M. *Organometallics* **2000**, *19*, 4005−4007. (k) van der Schaaf, P. A.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. *J. Organomet. Chem.* **2000**, *606*, 65−74. (l) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1273−1276. (m) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799. (n) Katayama, H.; Yoshida, T.; Ozawa, F. *J. Organomet. Chem.* **1998**, *562*, 203−206.

10.1021/ja021146w CCC: $25.00

alkylidene complexes coordinated with NHC ligands, which parallels the current use of NHCs in many other catalytic systems, such as Heck and Suzuki couplings, aryl amination, hydrogenation, and hydroformylation.[6,7] The synthesis of NHC-coordinated complexes for these applications can be achieved in several ways.[8] One of the most widely used methods, pioneered by Lappert and co-workers in the 1970s and 80s,[9] is the thermal cleavage of enetetramines in the presence of metal species. 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 the decomposition of alkylidene-containing precursors. Another popular approach is the reaction of free NHCs with a variety of metal species,[8] which became possible after Arduengo and co-workers successfully isolated the first free NHC in the early 1990s.[10] This route has been the method of choice for the synthesis of NHC-containing ruthenium alkylidene complexes because the substitution of a phosphine ligand with a free NHC in bis(phosphine) precursors such as $(PCy_3)_2(Cl)_2Ru{=}CHPh$ is a generally clean and straightforward reaction.[4] In our experience, however, the isolation of novel free carbenes is often not trivial due to difficulties with their synthesis or with decomposition, and we find the need to handle free NHCs under air-free conditions inconvenient for large-scale preparations.

For these reasons, one of our goals has been the development of improved ways to synthesize metal complexes with NHC ligands. In this report, we describe an approach that employs NHC adducts as "protected" forms of the free carbenes. These adducts contain alkoxide or trichloromethyl groups, for instance, and, as illustrated in eq 1, they can eliminate alcohol or chloroform to unmask the carbene, which then coordinates to the metal center.[11]



(1)

The direct use of an isolated NHC-alcohol adduct in the synthesis of a metal complex was unprecedented at the time we initiated our studies, although Lappert and co-workers had used NHC-chloroform and -amine adducts to make $(NHC)(PEt_3)(Cl)_2Pt$ and $(NHC)_2(Cl)_2Pt$ complexes.[12] 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 2 equiv first dimerize to form the enetetramine in situ (Scheme 1).[13] This ambiguity exists because the free carbene has a strong tendency to dimerize[14] and the enetetramine is

(4) (a) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035−4037. (b) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2403−2405. (c) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314−5318. (d) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225−3228. (e) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem.-Eur. J.* **2001**, *7*, 3236−3253. (f) Fürstner, A.; Krause, H.; Ackermann, L.; Lehmann, C. W. *Chem. Commun.* **2001**, 2240−2241. (g) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617*−*618*, 17−27. (h) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168−8179. (i) Katayama, H.; Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4513−4515. (j) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49−54. (k) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416−2419. (l) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (m) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362−365. (n) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956. (o) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (p) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187−5190. (q) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490−2493; *Angew. Chem., Int. Ed.* **1999**, *38*, 262.

(5) Recent reviews of olefin metathesis applications: (a) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−561. (b) Coates, G. W. *J. Chem. Soc., Dalton Trans.* **2002**, 467−475. (c) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3013−3043. (d) Tsuji, J. *Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: Chichester, 2000; Chapter 8. (e) Maier, M. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2073−2077. (f) Roy, R.; Das, S. K. *Chem. Commun.* **2000**, 519−529. (g) Jørgensen, M.; Hadwiger, P.; Madsen, R.; Stütz, A. E.; Wrodnigg, T. M. *Curr. Org. Chem.* **2000**, *4*, 565−588. (h) Yet, L. *Chem. Rev.* **2000**, *100*, 2963−3007. (i) Cook, G. R. *Curr. Org. Chem.* **2000**, *4*, 869−885. (j) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565−1604. (k) Grubbs, R. H.; Khosravi, E.; Davidson, T. A.; Wagener, K. B. In *Synthesis of Polymers: A Volume of the Materials Science and Technology Series*; Schlüter, A.-D., Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; Wiley-VCH: Weinheim, 1999; Chapter 3, pp 65−104 and Chapter 4, pp 105−122. (l) Zaragoza Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999. Phillips, A. J.; Abell, A. D. *Aldrichimica Acta* **1999**, *32*, 75−89. (m) Wright, D. L. *Curr. Org. Chem.* **1999**, *3*, 211−240. (n) Kingsbury, C. L.; Mehrman, S. J.; Takacs, J. M. *Curr. Org. Chem.* **1999**, *3*, 497−555.

(6) 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*, 22163−2187.

(7) 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. *Transition Met. Chem.* **1978**, *3*, 315−316.

(8) Other methods include the reduction of thiones, nucleophilic addition to coordinated isocyanide ligands, and carbene transfer from one metal center to another. 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) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91. (d) Liu, S.-T.; Reddy, K. R. *Chem. Soc. Rev.* **1999**, *28*, 315−322.

(9) (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.

(10) (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.

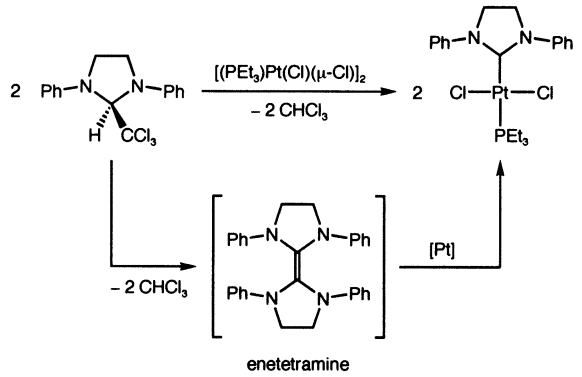
(11) The mechanism of this process has not been studied, but we believe that some free carbene is released from the adduct in solution. Coordination of the free NHC to the metal center would then drive the adduct−carbene equilibrium toward more free carbene. This mechanism is supported by the observation that free carbenes are obtained when the adducts are heated under vacuum to remove the alcohol or chloroform byproduct (ref 17). However, a metal-facilitated adduct deprotection or ligand substitution mechanism cannot be discounted at this time.

(12) (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.

(13) (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.

(14) Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1314−1317.

Scheme 1



known to react with $[(PEt_3)Pt(Cl)(\mu\text{-}Cl)]_2$ to provide (NHC)-$(PEt_3)Pt(Cl)_2$.[12a] In other 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,[15] and various carbene adducts have been proposed as reaction intermediates.[13,16]

As demonstrated in this work, the application of NHC adducts to the synthesis of metal complexes is a general, facile, and reliable approach, especially for the important class of ruthenium alkylidene complexes. We provide several examples of this methodology using two different NHC-alcohol adducts and one NHC-chloroform adduct, and we also describe a variety of unexpected ruthenium byproducts encountered during the development of this chemistry. In addition, the olefin metathesis activity of these new NHC-coordinated complexes is compared to that of previously reported catalysts in representative ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions.

Results and Discussion

Preparation of $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHR$ (Ph_3Tri = 1,3,4-Triphenyl-4,5-dihydro-1*H*-triazol-5-ylidene, R = Ph and $CH{=}CMe_2$). We began our study with the triazole-based methanol adduct $Ph_3Tri(H)(OMe)$, previously isolated by Enders and co-workers from the reaction of the triazolium salt $[Ph_3Tri(H)][ClO_4]$ with sodium methoxide (Scheme 2).[17] To avoid the perchlorate salt, the tetrafluoroborate derivative can be made by refluxing *N*-phenylbenzamide phenylhydrazone with ammonium tetrafluoroborate in triethyl orthoformate, or the tosylate salt can be obtained in a similar reaction with *p*-toluenesulfonic acid monohydrate and triethylorthoformate under azeotropic distillation conditions. Alternatively, the methanol adduct can be synthesized directly from *N*-phenylbenzamide phenylhydrazone in a one-pot procedure.

The isolated $Ph_3Tri(H)(OMe)$ adduct reacts cleanly with the ruthenium benzylidene precursor $(PCy_3)_2(Cl)_2Ru{=}CHPh$ to provide $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHPh$ (**1a**).[18] Complete conversion is achieved quickly by briefly heating the reaction mixture, and then **1a** is separated from the tricyclohexylphosphine and methanol byproducts by precipitation from pentane. Complex **1a** is a mixture of two conformational isomers, in which only the orientations of the triazolylidene ligand and/or the alkylidene moiety are different. By ^1H 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.

As illustrated in Scheme 2, complex **1a** also can be obtained by in situ deprotonation of the triazolium salt with NaH followed by addition of $(PCy_3)_2(Cl)_2Ru{=}CHPh$, or by direct reaction of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ with the isolated free carbene.[19] However, we have found the air-stable $Ph_3Tri(H)(OMe)$ adduct most convenient to isolate and handle, and this route provides **1a** in 59% yield on a half-gram scale with minimal purification.

The dimethylvinyl alkylidene derivative $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHCH{=}CMe_2$ (**1b**) can be synthesized by the analogous reaction between $Ph_3Tri(H)(OMe)$ and the bis(phosphine) precursor $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$. Like **1a**, this product is a mixture of conformational isomers characterized by two doublets of doublets in the ^1H NMR spectrum 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 **1a** and **1b** 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 the bis(phosphine) ruthenium derivative $(PCy_3)_2(Cl)_2Ru{=}CHR$, which suggests that the Ph_3Tri ligand dissociates from the metal center and phosphine reassociates to yield the more stable $(PCy_3)_2(Cl)_2Ru{=}CHR$ complex.[20] Because this decomposition pathway is accelerated at elevated temperatures and under catalytic turnover conditions, **1a** and **1b** are not ideal olefin metathesis catalysts. Nevertheless, the synthesis of **1a** and **1b** from the methanol adduct $Ph_3Tri(H)(OMe)$ established that NHC adducts could provide a viable new route to the ruthenium alkylidene complexes of interest.

Preparation and Side Reactions of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (H_2IMes = 1,3-Dimesityl-imidazolidine-2-ylidene). We next extended this adduct methodology to NHCs with saturated C−C backbones.[21] For example, the reaction of $KOBu^t$ with $[H_2IMes(H)][X]$ yields the *tert*-butyl alcohol adduct $H_2IMes(H)(OBu^t)$ (eq 2). It is characterized by a ^1H NMR resonance at δ 5.61 for the C(2) proton, and a ^{13}C NMR resonance at δ 95.4 for the C(2) carbon. In comparison, the C(2) of the free H_2IMes carbene appears much further downfield

(15) (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.

(16) (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.

(17) (a) Teles, J. H.; Melder, J.-P.; Ebel, K.; Schneider, R.; Gehrer, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helv. 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. Engl.* **1995**, *34*, 1021−1023.

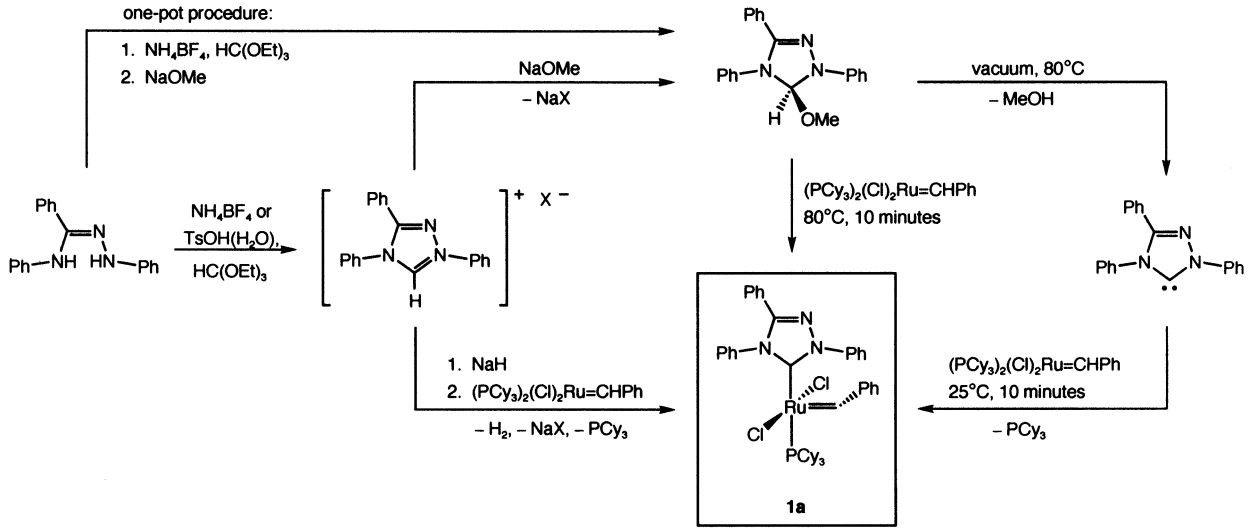
(18) For preliminary results, see: Grubbs, R. H.; Trnka, T. M. U.S. Patent 6,426,419 B1, 2002.

(19) The synthesis of $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHPh$ from the free Ph_3Tri carbene also has been reported by Fürstner and co-workers. See ref 4e.

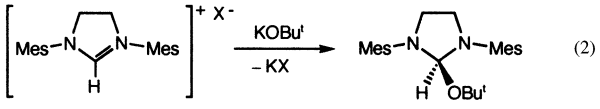
(20) Although ortho metallation of the Ph_3Tri ligand occurs in some metal complexes (Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1997**, *130*, 1253−1260), we have not observed this reaction in the $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHR$ system.

(21) For preliminary results, see ref 4n and Grubbs, R. H.; Scholl, M. PCT Int. Appl. WO 0071554, 2000.

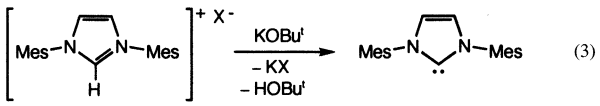
Scheme 2



at δ 244.[22] As in the H_2IMes-chloroform derivative,[40] the protons on the top and bottom faces of the CH_2CH_2 backbone and the ortho and meta mesityl ring positions are inequivalent. Notably, adduct formation does not occur with the imidazolium salt [IMes(H)][X] (IMes = 1,3-dimesityl-imidazoline-2-ylidene), which differs from [H_2IMes(H)][X] by an unsaturated C=C backbone. Reaction with KOBu^t instead results in direct and rapid deprotonation to the free NHC (eq 3).[23]



(2)



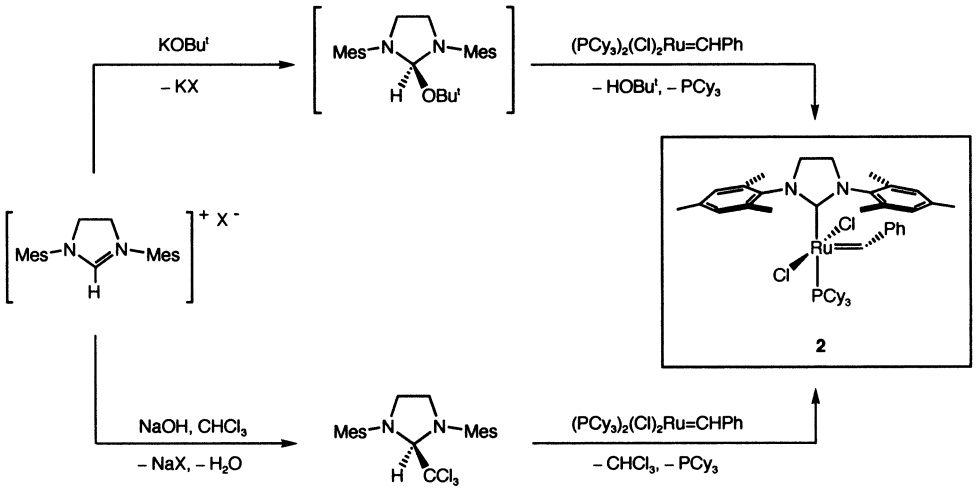
(3)

H_2IMes(H)(OBu^t) can be isolated as a semisolid, but because it decomposes by elimination of *tert*-butyl alcohol at room temperature, we find it most convenient to use when generated in situ. Our first reported preparation of (H_2IMes)(PCy_3)$(Cl)_2$-Ru=CHPh (**2**) involved this protocol followed by reaction with the ruthenium benzylidene precursor $(PCy_3)_2(Cl)_2Ru$=CHPh (Scheme 3, top pathway).[4n] However, we subsequently found that crude samples of **2** from this preparation often retained excess [H_2IMes(H)][BF_4] and the reaction byproducts KBF_4 and PCy_3, all of which decrease the catalytic activity of **2**.[24] To obtain cleaner product, the workup procedure can be modified to include filtration through Celite to remove residual salts, followed by multiple washings with methanol and pentane.

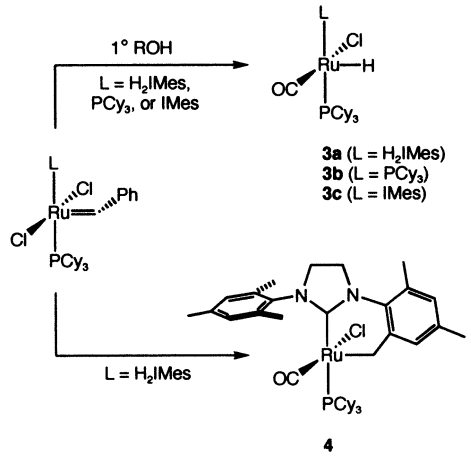
However, the use of methanol as a wash solvent leads to contamination with a small amount of metal-hydride impurity. This yellow species was isolated and identified as the hydrido-carbonyl-chloride complex (H_2IMes)(PCy_3)(CO)(H)-(Cl)Ru (**3a**). The presence of the hydride is indicated by the

(22) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534.
(23) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534.
(24) Morgan, J. P.; Goldberg, S. D.; Grubbs, R. H. 2001, unpublished results.
(25) (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, DC, 1982; pp 145−161.
(26) (a) In addition, **3b** has been obtained as a thermal decomposition product from $(PCy_3)_2(Cl)_2Ru$=CH(OEt). Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153−2164. (b) Formation of **3b** can be a problem in the preparation of Ru(H)(Cl)$(PCy_3)_2$(=COC_3H_6) as well. Coalter, J. N.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 679−684.
(27) Carbonyl/chloride disorder is common and occurs in many related molecules. For example: (a) $(PCy_3)_2$(Cl)(CO)(H)Os, Moers, F. G.; Noordik, J. H.; Beurskens, P. T. *Cryst. Struct. Commun.* **1981**, *10*, 1149−1152. (b) $(PPr^i_3)_2$(Cl)(CO)(H)Ru, Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087−8097. (c) $(PPh_3)_2$(Cl)(CO)Rh, Dunbar, K. R.; Haefner, S. C. *Inorg. Chem.* **1992**, *31*, 36776−3679. (d) $(PPh_3)_2$(Cl)(CO)Ir, Churchill, M. R.; Fettinger, J. C.; Buttrey, L. A.; Barkan, M. D.; Thompson, J. S. *J. Organomet. Chem.* **1988**, *340*, 257−266.
(28) This test is part of the International Union of Crystallography CIF checking program. Hirshfeld, F. L. *Acta Crystallogr.* **1976**, *A32*, 239−244.
(29) Jafarpour, L.; Nolan, S. P. *Organometallics* **2000**, *19*, 2055−2057.
(30) Jafarpour, L.; Hillier, A. C.; Nolan, S. P. *Organometallics* **2002**, *21*, 442−444.
(31) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194−1197.
(32) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944−4945.
(33) Representative ^{13}C NMR resonances for the NHC carbon in related compounds: (a) δ 219.6 for (H_2IMes)$(PPh_3)(Cl)_2Ru$=CHPh, δ 222.5 for (H_2IMes)$(PCy_3)(Cl)_2Ru$=CH_2, δ 219.1 for (H_2IMes)$(py)_2(Cl)_2Ru$=CHPh, Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554. (b) δ 217.2 for (H_2IMes)$(PCy_3)(Cl)_2Ru$=CF_2, Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3441−3444. (c) δ 216.2 for (H_2IMes)$(Cl)_2Ru[\eta^3$-(CHPh)(CPh)(CPh)], Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Organometallics* **2001**, *20*, 3845−3847. (d) δ 220.7 for (H_2IMes)$(PCy_3)(Cl)_2Ru$=CH(OEt), ref 26a.
(34) Representative ^{13}C NMR resonances for the carbonyl ligand in related compounds: (a) δ 201.9 for $(PCy_3)_2$(Cl)(CO)(H)Ru, Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045. (b) δ 202.4 for $[PBu^t_2(CH_2CH_2OPh)]_2$(Cl)(CO)(H)Ru, Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *J. Chem. Soc., Dalton Trans.* **2002**, 318−327. (c) δ 205.6 for $(PPr^i_3)_2$(Cl)(CO)(Ph)Ru, Coalter, J. N.; Huffmann, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569−3578. (d) δ 197.7 for $(PPr^i_2Ph)_2$(Cl)-(CO)(H)Ru, Werner, H.; Stüer, W.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 1707−1713.
(35) Representative ν_{CO} values: (a) 1896 cm^{-1} for (PCy_3)(IMes)(Cl)(CO)(H)-Ru, Lee, H. M.; Smith, D. C.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794−797. (b) 1902 (Nujol) or 1905 (C_6H_6) cm^{-1} for $(PCy_3)_2$(Cl)(CO)(H)Ru, ref 25c and d. (c) 1905 cm^{-1} for $(PPr^i_3)_2$-(Cl)(CO)(Ph)Ru, ref 34c. (d) 1906 cm^{-1} for $[PBu^t_2(CH_2CH_2OPh)]_2$(Cl)-(CO)(H)Ru, ref 34b. (e) 1910 cm^{-1} for $(PPr^i_3)_2$(Cl)(CO)(H)Ru, Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221−231.
(36) This geometry was confirmed in the crystal structure of **5**. Sanford, M. S. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 2001.
(37) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045.
(38) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258−4265.
(39) Harlow, K. J.; Hill, A. F.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1911−1912.
(40) Arduengo, A. J.; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348−2364.

Scheme 3



Scheme 4



distinctive upfield ^{1}H NMR resonance at δ −24.90 split into a doublet with $^2J_{HP}$ = 21 Hz, which is characteristic of a hydride situated trans to an empty coordination site and cis to a phosphine. This resonance in the closely related (IMes)(PCy$_3$)(CO)(H)(Cl)Ru derivative is similar (δ −24.83, d, $^2J_{HP}$ = 21 Hz).[35a] The transformation of ruthenium alkylidene complexes to hydrido-carbonyl-chloride derivatives was confirmed by direct reaction with methanol to provide (H$_2$IMes)(PCy$_3$)(CO)(H)(Cl)Ru (**3a**), (PCy$_3$)$_2$(CO)(H)(Cl)Ru (**3b**), and (IMes)(PCy$_3$)(CO)(H)(Cl)Ru (**3c**) (Scheme 4). Although the decarbonylation of primary alcohols by group 8 metal precursors is a general route to hydrido-carbonyl complexes,[25] the mechanism of this process is unknown, and it is not clear what happens to the benzylidene fragment in the case of (L)(PCy$_3$)(Cl)$_2$Ru=CHPh.

We have also observed **3a** or **3b** under conditions where (H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh (**2**) or (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh is heated for prolonged periods in the presence of oxygen-containing substrates, such as ethyl vinyl ether.[26] Because of this decomposition reaction, we have accidentally obtained crystals of (PCy$_3$)$_2$(CO)(H)(Cl)Ru (**3b**) and redetermined its structure (the crystal structures of **3b** and **3c** have been reported previously),[35a] and we refer the interested reader to the Supporting Information for these details. In this context, we also note that Fürstner and co-workers have reported a crystal structure of "(PCy$_3$)$_2$(Cl)$_2$(H)$_2$Ru", which they claim as, "the second known crystal structure of a dihydro-dichloro-bis-(phosphine)-ruthenium(IV) complex."[4e] However, it appears that this structure has been solved incorrectly and the compound is almost surely (PCy$_3$)$_2$(CO)(H)(Cl)Ru (**3b**) instead. We base this evaluation on (i) the distinctive ^{1}H NMR resonance (δ −24.4, t, $^2J_{HP}$ = 17 Hz) and IR ν_{CO} (1905 cm^{-1}) that match the data for **3b**,[25c] (ii) the fact that "(PCy$_3$)$_2$(Cl)$_2$(H)$_2$Ru" was obtained as a byproduct from a preparation of (L)(PCy$_3$)(Cl)$_2$Ru=CHPh [L = 1,3-di(2,6-diisopropylphenyl)-imidazolidine-2-ylidene] that included methanol, which accounts for the origin of **3b**, and (iii) the unit cell parameters that match those of **3b**. The crystallographic evidence suggests that carbonyl/chloride disorder is a significant problem in this structure.[27] For example, the Cl displacement ellipsoids of "(PCy$_3$)$_2$(Cl)$_2$(H)$_2$Ru" are anomalously large and elongated along the Cl−Ru−Cl bond axis, and the Hirshfeld rigid-bond test gives extremely poor results (a remarkably high 110 s.u.).[28]

To develop a synthesis of **2** that avoids salt contamination and hydride formation, we adapted the one-pot preparation reported by Nolan and co-workers for the synthesis of the related complex (IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh.[29] In our procedure for **2**, the ruthenium benzylidene precursor (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh, the imidazolinium salt [H$_2$IMes(H)][Cl], and KOBu^t are refluxed in hexanes for 1 day. Although it visually appears as though these sparingly soluble reactants remain suspended in the hexanes, the soluble H$_2$IMes(H)(OBu^t) adduct forms in situ and reacts with the bis(phosphine) precursor (Scheme 3). Once all the (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh is converted to **2**, a 2-propanol/water mixture is added to extract unreacted salts and phosphine oxide. Complex **2** remains largely insoluble in this solvent system and can be isolated as analytically pure material in good yield (∼75%) simply by filtration, even on multigram scales. It is unnecessary to use Nolan's substitution of potassium *tert*-amylate for KOBu^t,[30] particularly because KOBu^t is less expensive and more readily available.

In this preparation, the chloride salt [H$_2$IMes(H)][Cl] provides better results than the tetrafluoroborate salt [H$_2$IMes(H)][BF$_4$]. When the reaction is monitored by ^{1}H NMR spectroscopy, we observe that substantially more (Bu^{t}O)$_2$(PCy$_3$)Ru=CHPh forms with the tetrafluoroborate salt. (Bu^{t}O)$_2$(PCy$_3$)Ru=CHPh is the product from direct reaction of (PCy$_3$)$_2$(Cl)$_2$Ru=CHPh with KOBu^t, and it is identified by the downfield resonances of the alkylidene proton (δ 15.5, d, $^3J_{HP}$ = 4.4 Hz) and the phosphorus

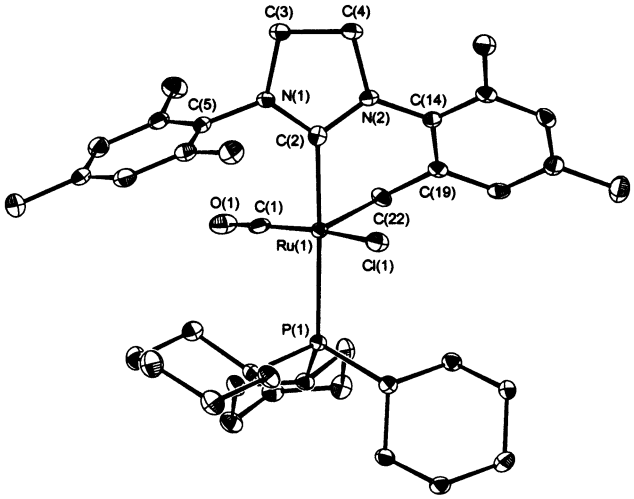


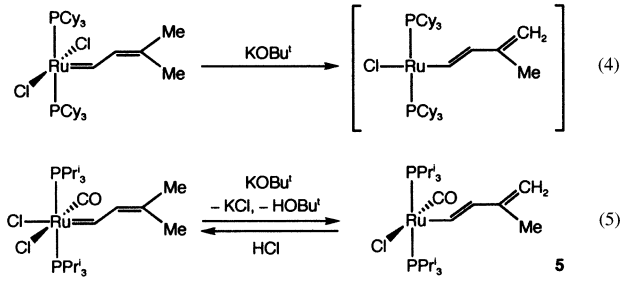
Figure 1. Structure of **4** · $^1/_2CH_2Cl_2$. For clarity, solvent and all hydrogen atoms have been omitted. Displacement ellipsoids are drawn at 50% probability. Selected bond distances [Å] and angles [deg]: Ru−C(1) 1.811(3), Ru−C(2) 2.037(3), Ru−C(22) 2.097(2), Ru−P 2.402(1), Ru−Cl 2.435(1), C(1)−O 1.126(3), C(2)−N(1) 1.343(3), C(2)−N(2) 1.350(3), C(3)−N(1) 1.468(3), C(4)−N(2) 1.481(3), C(5)−N(1) 1.445(3), C(3)−C(4) 1.523(4), C(14)−C(19) 1.408(3), C(14)−N(2) 1.436(3), C(19)−C(22) 1.487(3), C(1)−Ru−C(2) 93.7(1), C(2)−Ru−P 174.14(7), C(1)−Ru−Cl 165.73(8), O−C(1)−Ru 178.2(2), N(1)−C(2)−N(2) 108.2(2), C(19)−C(22)−Ru 108.1(2).

nucleus (δ 83.5).[2c] There are several possible explanations for this counterion effect, such as differences in salt solubility or the influence of chloride ion coordination to the C(2) proton in $[H_2IMes(H)][Cl]$, but these are speculative.

It is necessary to carry out this preparation of **2** under a moderately rigorous inert atmosphere. In instances when we used a round-bottom flask with condenser and a slow argon flow rather than a sealed Schlenk flask, we isolated a red-orange powder that proved to be the alkyl-carbonyl-chloride complex $(PCy_3)(Cl)(CO)Ru[\eta^2\text{-}(CH_2\text{-}C_6H_2Me_2)(N_2C_3H_4)(C_6H_2Me_3)]$ (**4**) instead of **2** (Scheme 4). This product is the result of C−H bond activation of one ortho methyl of the mesityl group, and both Nolan[31] and Whittlesey[32] have observed similar activation processes in rhodium- and ruthenium-NHC complexes. Compound **4** is characterized by ^{13}C NMR resonances at δ 220.3 ($^2J_{CP}$ = 90 Hz) for the NHC carbon[33] and at δ 203.0 ($^2J_{CP}$ = 15 Hz) for the carbonyl ligand,[34] as well as the IR carbonyl stretching frequency at 1899 cm^{-1}, which is within the range for similar compounds (1896−1910 cm^{-1}).[35] Not surprisingly, **4** is air-stable both in solution and in the solid state.

The crystal structure of **4** is shown in Figure 1. Compared to the structure of the closely related complex $(PPh_3)_2(CO)(H)Ru[\eta^2\text{-}(CH_2\text{-}C_6H_2Me_2)(N_2C_3H_2)(C_6H_2Me_3)]$,[32] there is a significant 0.14(1) Å contraction in the Ru−CH_2 bond length of **4**, presumably due to the absence of any ligand trans to the CH_2 linkage. There is also some shortening of the Ru−CN_2, Ru−CO, and C≡O bonds by 0.03(1)−0.06(1) Å, which can be attributed to differences between the 18-electron ruthenium center in $(PPh_3)_2(CO)(H)Ru[\eta^2\text{-}(CH_2\text{-}C_6H_2Me_2)(N_2C_3H_2)(C_6H_2Me_3)]$ and the 16-electron one in **4**.

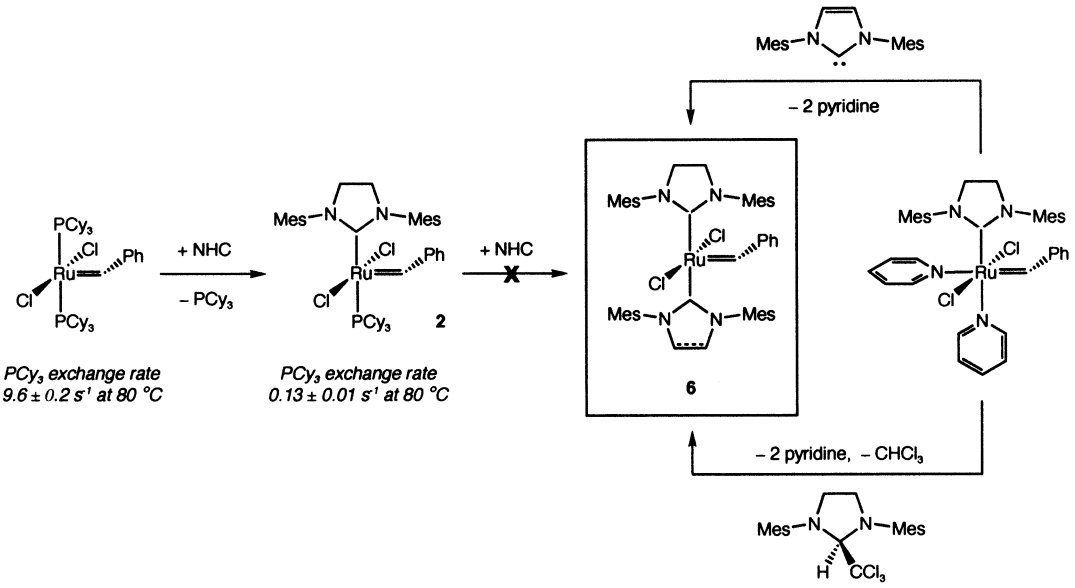
Because the bis(phosphine) dimethylvinyl alkylidene complex $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ is readily accessible,[2k] we hoped to use it to make the dimethylvinyl alkylidene derivative of **2**, $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHCH{=}CMe_2$. However, $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ is deprotonated by $KOBu^t$ and other bases to furnish a partially characterized ruthenium species with a vinylvinyl unit, that is, $[(PCy_3)_2(Cl)_2Ru{-}CH{=}CHCMe{=}CH_2]$ (eq 4). The ^1H NMR spectrum for this product contains two characteristic doublets at δ 8.93 and 6.27 (both $^3J_{HH}$ = 13 Hz) for the vinylic protons. Although this vinylvinyl species is unstable in solution and could not be isolated, the related vinylvinyl-carbonyl complex $(PPr^i_3)_2(Cl)(CO)Ru{-}CH{=}CHCMe{=}CH_2$ (**5**) was obtained cleanly by the analogous reaction of $(PPr^i_3)_2(Cl)_2(CO)Ru{=}CHCH{=}CMe_2$ with $KOBu^t$ (eq 5). The ^1H NMR spectrum of **5** likewise contains doublets at δ 7.96 and 5.80 (both $^3J_{HH}$ = 16 Hz) for the vinylic protons, and the coupling constant indicates a trans olefin geometry.[36] The PCy_3-substituted derivative of **5** has been synthesized by Yi and coworkers in a similar fashion by deprotonation of $[(PCy_3)_2(Cl)(CO)Ru{=}CH{-}CH{=}CMe_2][BF_4]$ with triethylamine.[37] The related cyclohexyl vinylvinyl compound $(PPr^i_3)_2(Cl)(CO)Ru{-}CH{=}CH[C{=}CH(CH_2)_4]$ has been reported as well,[38] and both of these examples exhibit ^1H NMR and IR data similar to those of **5**. As expected, addition of HCl to **5** regenerates the starting material $(PPr^i_3)_2(Cl)_2(CO)Ru{=}CHCH{=}CMe_2$ (eq 5). Similar transformations, such as from $(PPh_3)_2(Cl)(MeCN)_2Ru{-}CH{=}CHCPh_2OH$ to $(PPh_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ upon addition of HCl, have been observed by Hill and Welton.[39]



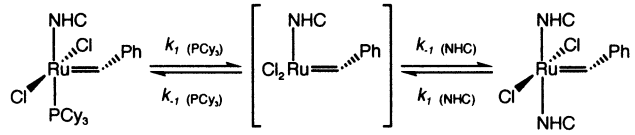
Access to catalyst **2** is also provided by the chloroform adduct $H_2IMes(H)(CCl_3)$, previously isolated by Arduengo and coworkers as the product of slow chloroform C−H activation by the H_2IMes free carbene.[40] As illustrated in Scheme 3, we have developed an improved synthesis of $H_2IMes(H)(CCl_3)$ directly from the imidazolinium salt $[H_2IMes(H)][Cl]$ plus sodium hydroxide and chloroform, which is advantageous because it avoids the free carbene and is amenable to large-scale preparations. Furthermore, the $H_2IMes(H)(CCl_3)$ adduct is significantly more thermally stable than the *tert*-butyl alcohol derivative $H_2IMes(H)(OBu^t)$, is easily isolated and purified by column chromatography, and is a free-flowing, solid material instead of the tacky $H_2IMes(H)(OBu^t)$ semisolid. As with other NHC adducts, the reaction of $H_2IMes(H)(CCl_3)$ with $(PCy_3)_2(Cl)_2Ru{=}CHPh$ is straightforward and provides **2** in good yield (84%) upon heating at 60 °C for 90 min (Scheme 3).

The spontaneous decomposition exhibited by the Ph_3Tricoordinated complexes **1a** and **1b** is not shared by **2** or its IMes derivative, both of which have excellent thermal stability. Even in the presence of excess PCy_3, neither **2** nor related mono(NHC) derivatives[4k] generate any detectable $(PCy_3)_2(Cl)_2Ru{=}CHPh$. This difference may be due to the ortho methyl groups on the mesityl substituents, which favor a perpendicular arrangement of the mesityl and imidazole rings by limiting N-Mes rotation, or other stabilizing effects.

Scheme 5



Scheme 6



Preparation of $(H_2IMes)(L)(Cl)_2Ru{=}CHPh$ (L = IMes or H_2IMes). In each synthesis of catalysts **1** and **2**, the mono-(substituted) $(NHC)(PCy_3)(Cl)_2Ru{=}CHR$ product is observed exclusively, even if a large excess of NHC is present. In theory, the bis(substituted) product could also form, that is, $(NHC)_2(Cl)_2Ru{=}CHR$, as observed when the NHC is 1,3-dicyclohexylimidazoline-2-ylidene.[4q] However, the origin of this effect is not entirely steric congestion, as originally believed, especially because examples of bis(IMes) metal complexes have been synthesized.[31] As illustrated in Scheme 5, the phosphine exchange rate decreases dramatically when one of the PCy_3 ligands in $(PCy_3)_2(Cl)_2Ru{=}CHPh$ is replaced by an H_2IMes ligand.[41] This slow phosphine exchange rate in **2** may effectively prevent further PCy_3 substitution by the accepted dissociative ligand substitution pathway. According to Scheme 6, this corresponds to a situation where $k_{1(NHC)}$ is less than $k_{1(PCy_3)}$, which is already slow. In addition, there may be a contribution from the reverse rates if $k_{-1(NHC)}$ is less than $k_{-1(PCy_3)}$, although we cannot confirm this relationship because values of $k_{-1(PCy_3)}$ have been experimentally inaccessible.[41]

Nevertheless, bis-substitution can be achieved by using derivatives of **2** with more labile ligands in place of the tricyclohexylphosphine, such as the pyridine complex $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$.[4c] For example, addition of the free IMes carbene to $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ cleanly provides the mixed H_2IMes-IMes complex $(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$ (**6a**) (Scheme 5). Similarly, the reaction of $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ with the chloroform adduct $H_2IMes(H)(CCl_3)$ provides the bis(H_2IMes) complex $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**6b**) (Scheme 5). These products are highly stable and can be purified by column chromatography on silica gel.[42] At room temperature, the ^1H NMR spectra of **6a** and **6b** 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 **6a** is shown in Figure 2, and the metrical data are presented in Table 2 along with comparisons to the mono(phosphine) derivatives $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ and $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$. Both of the Ru−NHC distances in **6a** are longer than those in either of the corresponding mono(NHC) complexes, which surely reflects the greater steric congestion in **6a** 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.

Olefin Metathesis Activity. With several new NHC-coordinated ruthenium alkylidene complexes in hand, we evaluated their catalytic activity in representative RCM and ROMP reactions. The cyclization of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene to the corresponding 4,4-dicarboethoxy-1-methylcyclopentene product and the polymerization of 1,5-cyclooctadiene were chosen as test cases because these transformations are moderately challenging and easily monitored by ^1H NMR spectroscopy. The k_{rel} values for various catalyst derivatives are collected in Table 3.

There is a great deal of variation in the overall activity of different catalyst derivatives. The general activity trend is $(PCy_3)_2(Cl)_2Ru{=}CH{-}CH{=}CMe_2 \approx (PCy_3)_2(Cl)_2Ru{=}CHPh < (Cl_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh < (IMes)(PCy_3)(Cl)_2Ru{=}CHPh < (H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**). This ordering is consistent with results determined by Fürstner and co-workers for a variety of substrates by IR-thermography $[(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHPh \approx (PCy_3)_2(Cl)_2Ru{=}CHPh < (Cl_2IMes)$-

(41) (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.

(42) Other ruthenium alkylidene complexes (including **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.

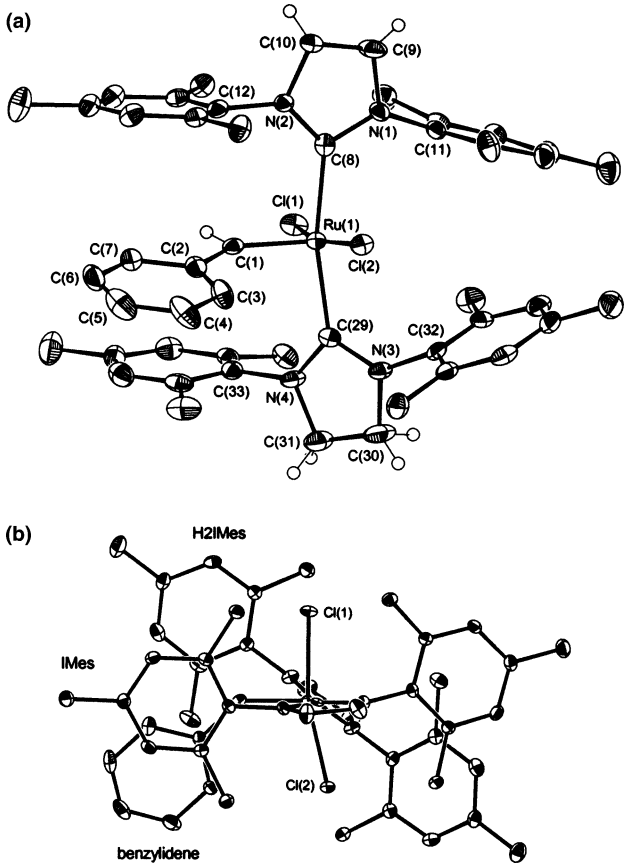


Figure 2. Structure of **6a**. Side (a) and top (b) views. For clarity, only one molecule in the asymmetric unit is shown, and most of the hydrogen atoms have been omitted. Displacement ellipsoids are drawn at 50% probability; hydrogens atoms are drawn at arbitrary scale.

Table 1. Crystal and Structure Refinement Data for $(PCy_3)(Cl)(CO)Ru[\eta^2\text{-}(CH_{2-C6}H_2Me_2)(N_2C_3H_4)(C_6H_2Me_3)]$ (**4**) and $(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$ (**6a**)

parameters	4	6a
empirical formula	$C_{40}H_{58}ClN_2OPRu\cdot {}^1/_2\ CH_2Cl_2$	$C_{49}H_{56}Cl_2N_4Ru$
formula weight	792.84	872.95
crystallization solvent	CH_2Cl_2	CH_2Cl_2
crystal habit	tabular	plate
crystal color	orange	brown
crystal size (mm^3)	0.26 × 0.19 × 0.07	0.25 × 0.16 × 0.04
a (Å)	10.276(1)	11.663(3)
b (Å)	13.039(1)	14.676(4)
c (Å)	14.723(1)	25.176(7)
α (deg)	92.336(2)	94.523(5)
β (deg)	103.428(1)	95.698(4)
γ (deg)	91.814(1)	90.666(5)
V ($Å^3$)	1915.5(3)	4274(2)
Z	2	4
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
θ range for data collection (deg)	2.0−28.4	1.4−28.6
absorption coefficient (Mo Kα) (mm^{-1})	0.624	0.531
reflections collected	28 236	101 139
independent reflections	8728 [R_{int} = 0.0917]	20 088 [R_{int} = 0.1006]
no. parameters	447	1457
final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0383, 0.0807	0.0421, 0.0629
R_1, wR_2 indices (all data)	0.0503, 0.0832	0.0857, 0.0696
GOF on F^2	1.187	1.026
largest diff. peak and hole (e $Å^{-3}$)	1.03 and −0.72	0.70 and −0.65

$(PCy_3)(Cl)_2Ru{=}CHPh \approx (IMes)(PCy_3)(Cl)_2Ru{=}CHPh \ll (H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**)],[4e] as well as with measurements by Mol and co-workers for the metathesis of methyl oleate $[(PCy_3)_2(Cl)_2Ru{=}CH{-}CH{=}CPh_2 < (PCy_3)_2(Cl)_2Ru{=}CHPh \ll (H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**)].[45] The larger variation in k_{rel} values for RCM as compared to those of ROMP is partly due to the higher temperature (40 °C for RCM vs 25 °C for ROMP)[46] because the NHC-coordinated catalysts initiate much more efficiently at elevated temperatures.[41] $(PCy_3)_2(Cl)_2Ru{=}CH{-}CH{=}CMe_2$ has a slightly lower k_{rel} than $(PCy_3)_2(Cl)_2Ru{=}CHPh$ because of its slightly lower initiation rate, but both catalysts provide the same propagating species once they initiate. We emphasize the remarkable differences in reaction rates when the backbone of the NHC is varied from saturated (H_2IMes) to unsaturated (IMes) to chloro-substituted (Cl_2IMes) (Table 3). The greater overall activity of $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ as compared to that of $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ has been noted previously.[4n,47]

Although the Ph_3Tri-coordinated catalysts **1a** and **1b** are unstable in solution, the NHC adduct $Ph_3Tri(H)(OMe)$ provides easy access to in situ-generated $(Ph_3Tri)(PPh_3)(Cl)_2Ru{=}CHPh$ (**1c**). Upon mixing at room temperature, $(PPh_3)_2(Cl)_2Ru{=}CHPh$ and 1 equiv of $Ph_3Tri(H)(OMe)$ form **1c**, which then catalyzes the ROMP of COD at a fast rate (Table 3). This protocol is also effective for the ROMP of bulk dicyclopentadiene. The RCM reaction is less successful and goes to only 15% conversion, probably because of catalyst decomposition. In comparison, the bis(triphenylphosphine) starting material $(PPh_3)_2(Cl)_2Ru{=}CHPh$ is completely inactive toward either of these substrates. A related in situ preparation of catalyst **2** consisting of $(PCy_3)_2(Cl)_2Ru{=}CHPh + [H_2IMes(H)][BF_4] + KOBu^t$ + phosphine scavenger has been described.[48]

We were particularly interested in the olefin metathesis activity of the bis(NHC) complexes **6a** and **6b** because, according to our mechanistic model, one NHC ligand would have to dissociate from the ruthenium center for the catalyst to initiate.[41] $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**6b**) shows slight activity for RCM 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 h). However, **6b** 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 **6b** displays any RCM or ROMP activity at all suggests that some initiation can occur, at least at elevated temperatures.

To test for NHC dissociation, $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**6b**) was heated in the presence of excess PCy_3 to trap any of the

(43) Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, in press.
(44) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678.
(45) Mol, J. C. *Green Chem.* **2002**, *4*, 5−13.
(46) The ROMP of COD was not carried out at 40 °C because the reaction is too fast to be monitored by ^{1}H NMR with some of these catalysts. Likewise, the RCM of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene was not carried out at 25 °C because the reaction is too slow to be conveniently monitored by ^{1}H NMR.
(47) (a) Schramm, M. P.; Reddy, D. S.; Kozmin, S. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4274−4277. (b) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.
(48) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153−3155.

Table 2. Structural Comparison of **6a**, $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$, and $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (in cases where there is more than one chemically equivalent bond length or angle, the values have been averaged)

bond distances (Å) and angles (deg)	$(H_2IMes)(IMes)(Cl)_2Ru{=}CHPh$ (**6a**, this work)	$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (ref 43)	$(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (ref 44)
$Ru-CN_2$ (IMes)	2.093(3)[a]		2.07(1)
$Ru-CN_2$ (H_2IMes)	2.125(3)[a]	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)[a]	1.515(3)	
CH=CH backbone	1.382(5)[a]		1.30(1)
C−N (IMes)	1.364(3)[a]		1.36(1)
C−N (H_2IMes)	1.359(3)[a]	1.348(2)	
N−Mes (IMes)	1.435(3)[a]		1.46(1)
N−Mes (H_2IMes)	1.434(3)[a]	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)[a]		101.0(8)
N−C−N (H_2IMes)	104.3(2)[a]	107.3(2)	

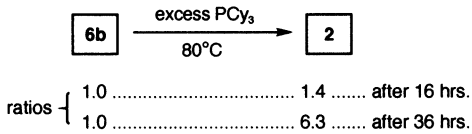
[a] These bond lengths and angles are compromised because of disorder between the H_2IMes and IMes ligands.

Table 3. k_{rel} Values for Various Ruthenium Catalysts in Representative RCM and ROMP Reactions; Kinetics Measured by ^1H NMR Spectroscopy

catalyst	k_{rel} for RCM[a]	k_{rel} for ROMP[b]
$(PPh_3)_2(Cl)_2Ru{=}CHPh$	0	0
$(PCy_3)_2(Cl)_2Ru{=}CH-CH{=}CMe_2$	0.8	0.8
$(PCy_3)_2(Cl)_2Ru{=}CHPh$	1	1
$(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (**6b**)	[c]	0
$(Cl_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$[d]	19	3
$(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$	53	8
$(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**)	138	27
$(PPh_3)_2(Cl)_2Ru{=}CHPh$ + 1 equiv of $Ph_3Tri(H)(OMe)$	[c]	66

[a] RCM conditions: 5 mM catalyst and 100 mM 4,4-dicarboethoxy-2-methyl-1,6-heptadiene in C_6D_6 at 40 °C. [b] ROMP conditions: 5 mM catalyst and 1500 mM 1,5-cyclooctadiene in CD_2Cl_2 at 25 °C. [c] The reaction did not reach completion under these conditions. [d] Cl_2IMes = 1,3-dimesityl-4,5-dichloro-imidazoline-2-ylidene; see ref 4e.

14-electron intermediate $[(H_2IMes)(Cl)_2Ru{=}CHR]$ as the 16-electron phosphine complex $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**). As illustrated in eq 6, significant quantities of **2** form during the course of the reaction: after 36 h, complex **2** is present in a 6.3:1.0 ratio as compared to **6b**. The reaction of **6b** with 1 equiv of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ also generates **2**, but this reaction is not as clean. This evidence strongly suggests that **6b** is metathesis active because H_2IMes dissociation at elevated temperatures 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.[41]



(6)

It is reasonable to expect that NHC dissociation occurs in other $(NHC)_2(Cl)_2Ru{=}CHPh$ complexes, such as those reported by Herrmann and co-workers in 1998.[4q] 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 that of $(PCy_3)_2(Cl)_2Ru{=}CHPh$. 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 co-workers also have reported that the reaction between $(PCy_3)_2(Cl)_2Ru{=}CHPh$ 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 h, which they attribute to a bimolecular NHC transfer mechanism.[4m] Thus, although one of the most widely cited features of NHC ligands is their strong bonding to metal centers,[6] there is a growing list of examples that exhibit facile NHC dissociation and NHC transfer.[8d,49] We caution that predictions about the lability of NHC ligands in new organometallic complexes should be made with care.

Conclusions

Our primary aim has been to demonstrate that NHC adducts can be used to prepare ruthenium alkylidene complexes with NHC ligands. We have presented several examples of this methodology, including three routes to the synthetically important olefin metathesis catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**). Several properties of NHC adducts make them highly desirable reagents: (i) they are easy to synthesize and use in either isolated form, such as $Ph_3Tri(H)(OMe)$ and $H_2IMes(H)(CCl_3)$, or when generated in situ, as in the case of $H_2IMes(H)(OBu^t)$, (ii) they are air-stable and thus easier to handle than their free carbene counterparts, and (iii) the latent carbene is readily released in solution. Unlike the introductory example in Scheme 1, there is no evidence for dimer formation with the Ph_3Tri or H_2IMes ligands, and therefore the adducts of these NHCs provide direct access to metal-NHC complexes.

For these reasons, NHC adducts have broad potential applications in the synthesis of countless other metal-NHC complexes. This methodology has been used recently by Herrmann and co-workers in the synthesis of (COD)M(Cl)(L) (L = NHC; M = Rh, Ir) complexes,[50] by Blechert and co-workers to prepare polymer-supported $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$,[51] and by Fürstner and co-workers to prepare various

(49) (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.
(50) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219−224.
(51) Schürer, S. C.; Gessler, S.; Buschmann, N.; Blechert, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3898−3901.

ruthenium alkylidene complexes.[4e] In addition, we have found that the reactions of $Ph_3Tri(H)(OMe)$ or $H_2IMes(H)(OBu^t)$ with molybdenum hexacarbonyl afford the pentacarbonyl derivatives $(CO)_5Mo(Ph_3Tri)$ and $(CO)_5Mo(H_2IMes)$, respectively.[52]

En route, we have described some interesting organometallic reactions encountered during the development of this chemistry. These results highlight the diverse reactivity patterns of ruthenium carbene complexes and, in the case of NHC dissociation, provide leading evidence for how bis(NHC) olefin metathesis catalysts enter the catalytic cycle. By testing a variety of catalyst derivatives in representative olefin metathesis reactions, we also have found that small changes in catalyst architecture have a large impact on the stability and activity of these complexes, and current studies are directed toward understanding the subtle steric and electronic factors that determine these properties.

Experimental Section

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 measured on Varian Inova 500, Varian Mercury 300, and JEOL JNM-GX400 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 used for the purification of organometallic complexes was obtained from TSI Scientific, Cambridge, MA (60 Å, pH 6.5−7.0). *N*-Phenylbenzamide phenylhydrazone, $[Ph_3Tri(H)][ClO_4]$, and $Ph_3Tri(H)(OMe)$ were prepared by the methods of Enders and co-workers.[17] 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.[53] $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$,[4c] IMes free carbene,[23] and 4,4-dicarboethoxy-2-methyl-1,6-heptadiene[54] were synthesized according to literature procedures. $(PCy_3)_2(Cl)_2Ru{=}CHPh$, $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$, and all other chemicals were obtained from commercial sources.

Synthesis of $[Ph_3Tri(H)][BF_4]$. A suspension of *N*-phenylbenzamide phenylhydrazone (0.38 g, 1.3 mmol) and ammonium tetrafluoroborate (0.14 g, 1.3 mmol) in triethylorthoformate (1.2 mL, excess) was refluxed for 4 h. The reaction mixture was cooled to room temperature, and the yellowish-brown product was isolated by filtration. This crude material was recrystallized from boiling ethanol to yield 0.35 g of the product as a dark brown solid (72%). The characterization data of this compound are similar to those of $[Ph_3Tri(H)][ClO_4]$.[17]

Synthesis of $[Ph_3Tri(H)][OTs]$. A suspension of *N*-phenylbenzamide phenylhydrazone (0.10 g, 0.35 mmol), *p*-toluenesulfonic acid monohydrate (0.08 g, 0.42 mmol), triethylorthoformate (0.3 mL, 2.0 mmol), and benzene (7 mL) was refluxed under azeotropic distillation conditions with a Dean−Stark apparatus. After 5 h, the reaction mixture was cooled to room temperature and concentrated under vacuum to a brown semisolid. This material was triturated in pentane to yield 0.18 g of the desired product as a white powder (100%). The characterization data of this compound are similar to those of $[Ph_3Tri(H)][ClO_4]$.[17]

One-Pot Synthesis of $Ph_3Tri(H)(OMe)$. A suspension of *N*-phenylbenzamide phenylhydrazone (0.20 g, 0.7 mmol) and ammonium tetrafluoroborate (0.073 g, 0.7 mmol) in triethylorthoformate (1.5 mL, excess) was refluxed for 4 h. The reaction mixture was cooled to room temperature and pumped down under vacuum to an orange solid. Methanol (4 mL) was added to the flask, followed by a solution of sodium methoxide (0.045 g, 0.84 mmol) in methanol (3 mL). This solution was stirred at room temperature for 15 min. The reaction mixture was pumped down under vacuum to a reddish-brown solid, which was extracted with pentane (3 × 10 mL). The combined extracts were stripped of solvent, and the resulting brown material was recrystallized from methanol to provide 0.095 g of the desired product as a yellowish solid (43%).

Synthesis and Characterization of $(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHR$ (1a, R = Ph). A Schlenk flask was charged with 0.500 g (0.608 mmol) of $(PCy_3)_2(Cl)_2Ru{=}CHPh$, 0.195 g (0.592 mmol) of $Ph_3Tri(H)(OMe)$, and 17 mL of 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. Next 100 mL pentane was added to the residue and gently warmed to dissolve most of the material. Upon being cooled to −78 °C, a tan-colored precipitate formed. The supernatant was filtered off by cannula, and the solid was dried under vacuum to yield 0.293 g of the desired product as a brown solid (59%). ^{1}H NMR (CD_2Cl_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_2Cl_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_3Tri], 151.09 [s, Ph_3Tri], 141.84 [s, Ph_3Tri], 140.31 [s, Ph_3Tri], 136.83 [s, Ph_3Tri], 135.95 [s, Ph_3Tri], 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_6D_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 $C_{45}H_{54}N_3Cl_2PRu$: C, 64.35; H, 6.48; N, 5.00. Found: C, 64.64; H, 6.31; N, 5.04.

$(Ph_3Tri)(PCy_3)(Cl)_2Ru{=}CHR$ (1b, R = CH=CMe_2). This was synthesized analogously to **1a** but starting with $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$. ^{1}H NMR ($CD_2Cl_2$, 499.9 MHz): δ 19.56 [dd, $^3J_{HP} = 5.5$, $^3J_{HH} = 11$, Ru=CH, major isomer (∼60%)], 19.37 [dd, $^3J_{HP} = 2.5$, $^2J_{HH} = 11$, 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, 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{^{1}H} 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,

(52) Trnka, T. M.; Grubbs, R. H. 1999, unpublished work.
(53) (a) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335−A337. (b) Muse, L. A. *J. Chem. Educ.* **1972**, *49*, A463−A466. (c) Everett, K.; Graf, F. A. In *CRC Handbook of Laboratory Safety*, 2nd ed.; Steere, N. V., Ed.; CRC Press: Boca Raton, FL, 1971; pp 265−276.
(54) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310−7318.

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 (1c). 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 h 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 of $H_2IMes(H)(CCl_3)$ from [$H_2IMes(H)$][Cl]. First 8.2 mL of dry, degassed toluene was added to a flame-dried, 50 mL round-bottomed flask equipped with stir bar and reflux condenser. A large excess of powdered potassium hydroxide (>10 mmol, ground in a mortar) was added to the flask, and the resulting suspension was stirred rapidly. Chloroform (77 μL, 0.96 mmol) was then added to the suspension by microsyringe. After 10 min at room temperature, 0.10 g (0.29 mmol) of [$H_2IMes(H)$][Cl] was added, and the reaction mixture was heated at 60 °C for 75 min. The mixture was allowed to cool to room temperature and filtered. The supernatant was concentrated under vacuum to a yellowish-white solid. This crude product was purified first through a silica gel plug (9:1 hexanes:ethyl acetate) and then by recrystallization from boiling hexanes to yield 0.110 g of $H_2IMes(H)$-(CCl_3) as a white solid (88%). ^1H and ^{13}C NMR match the data reported in ref 40.

Synthesis and Characterization of $H_2IMes(H)(OBu^t)$: Method 1. A flame-dried Schlenk flask was charged with a solution of [$H_2IMes(H)$][BF_4] (0.100 g, 0.30 mmol) in dry THF (3 mL). Next 0.028 g (0.25 mmol) of solid $KOBu^t$ was added to this solution. The initially colorless reaction mixture was stirred under a nitrogen atmosphere for 10 min, during which time a persistent yellowish color developed. The solution was pumped down under vacuum to a yellowish solid, which was washed with dry diethyl ether (5 mL) to yield 0.050 g of the desired product as a colorless semisolid (50%). This material decomposes by extrusion of $HOBu^t$ at room temperature.

Method 2. A J. Young NMR tube was charged with 0.040 g (0.101 mmol) of [$H_2IMes(H)$][BF_4], 0.011 g (0.101 mmol) of $KOBu^t$, and 1 mL of THF-d_8. ^1H and ^{13}C NMR were recorded after 6 h at room temperature. ^1H NMR (399.9 MHz): δ 6.82 [s, 2H, *m*-CH_{Mes}], 6.81 [s, 2H, *m*-CH_{Mes}], 5.61 [s, 1H, CH], 3.74 [m, 2H, CH_2CH_2], 3.27 [m, 2H, CH_2CH_2], 2.46 [s, 6H, CH_3 of Mes], 2.34 [s, 6H, CH_3 of Mes], 2.20 [s, 6H, CH_3 of Mes], 1.11 [s, 9H, OBu^t]. $^{13}C\{^1H\}$ NMR (100.5 MHz): δ 139.69, 138.76, 137.83, and 134.96 [*o*-C_{Mes}, *ipso*-C_{Mes}, and *p*-C_{Mes}], 129.19 [CH_{Mes}], 128.50 [CH_{Mes}], 95.40 [N_2C], 70.81 [$OCMe_3$], 48.58 [CH_2CH_2], 28.03 [CH_3 on OBu^t], 20.06 [CH_3 on Mes], 19.02 [CH_3 on Mes], 18.08 [CH_3 on Mes]. This solution was also subjected to HRMS analysis (EI) *m*/*z*: calcd for $C_{25}H_{36}N_2O$ [M^+] 380.2828, found 380.2831.

Synthesis of (H_2IMes)(PCy_3)($Cl)_2$Ru=CHPh (2): Revised Method 1. The workup procedure described in ref 4n can be modified to produce a cleaner product. Combine [$H_2IMes(H)$][BF_4] (0.90 g, 2.7 mmol), $KOBu^t$ (0.30 mg, 2.7 mmol), and THF (20 mL) in an oven-dried Schlenk flask. Stir the resulting yellow suspension for 1 h, and then add a solution of ($PCy_3)_2(Cl)_2$Ru=CHPh (1.1 g, 1.3 mmol) in benzene (20 mL). Heat the reaction mixture at 80 °C for 30 min. Remove the volatiles under vacuum, and dry the solid thoroughly to ensure that all of the THF is gone. Suspend the solid in benzene (25 mL), and filter through dry Celite. Concentrate the resulting solution to ~2 mL, and precipitate the product with methanol (50 mL). Wash the pink solid with methanol (4 × 50 mL) and pentane (3 × 25 mL), and then dry it under high vacuum to obtain (H_2IMes)(PCy_3)Cl_2Ru=CHPh in 45% yield (0.05 g).

Method 2. Charge a 750 mL Schlenk flask with dry [$H_2IMes(H)$]-[Cl] (6.60 g, 19.2 mmol), $KOBu^t$ (2.46 g, 21.9 mmol), ($PCy_3)_2(Cl)_2$-Ru=CHPh (9.06 g, 11.0 mmol), and anhydrous hexanes (100 mL, Aldrich SureSeal bottle). Attach the flask to a vacuum line, and degas the solution by pulling vacuum for a few minutes. Leave the flask under vacuum, wire down the septum, and heat the reaction at 60 °C for 24 h with very vigorous stirring. The suspension changes color from purple to orange-brown during the reaction time. Allow the reaction to cool to room temperature, open the flask to air, and add 1:1 2-propanol: water (250 mL). Stir this mixture rapidly in air for 30 min. Collect the peach-pink solid on a medium porosity frit, and wash it thoroughly with the 2-propanol:water (3 × 100 mL) and with hexane (3 × 100 mL). Dry the solid under vacuum overnight to obtain (H_2IMes)-(PCy_3)$(Cl)_2$Ru=CHPh in 75% yield (6.9 g). Anal. Calcd for $C_{46}H_{65}N_2Cl_2PRu$: C, 64.92; H, 7.94; N, 3.29. Found: C, 64.82; H, 7.74; N, 3.31.

Method 3. A flame-dried, 50 mL Schlenk flask was charged with 0.165 g of ($PCy_3)_2(Cl)_2$Ru=CHPh (0.20 mmol), 0.188 g of H_2IMes-($H)(CCl_3$) (0.44 mmol), and 5 mL of toluene. The reaction mixture was heated at 60 °C for 90 min under a nitrogen atmosphere. After the reaction cooled to room temperature, the solvent was removed under vacuum. The resulting brownish-pink semisolid was washed with methanol (2 × 5 mL) and pentane (3 × 10 mL), and was then dried under vacuum for 12 h to provide 0.140 g of **2** as a reddish solid (84%).

Alternative Purification. (H_2IMes)(PCy_3)$(Cl)_2$Ru=CHPh can be further purified by column chromatography on TSI-brand silica gel with gradient elution (7:1 hexanes:diethyl ether to 100% diethyl ether).

Formation of (PCy_3)(L)(CO)(Cl)(H)Ru (3). 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 at room temperature for 12 h. The yellow-orange supernatant was then decanted into a Schlenk flask and pumped down under vacuum. In all cases, ^1H 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. (H_2IMes)(PCy_3)(CO)(Cl)(H)Ru (**3a**), characteristic ^1H NMR (C_6D_6, 299.9 MHz): δ −24.90 [d, $^2J_{HP}$ = 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]. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 47.12 [s]. ($PCy_3)_2$-(CO)(Cl)(H)Ru (**3b**) and (IMes)(PCy_3)(CO)(Cl)(H)Ru (**3c**): ^1H and ^{31}P NMR data match those reported in refs 35a and 55.

Characterization of (PCy_3)(Cl)(CO)Ru[η^2-(CH_2-$C_6H_2Me_2$)-($N_2C_3H_4$)($C_6H_2Me_3$)] (4). ^1H NMR (C_6D_6, 299.9 MHz): δ 7.02 [s, 1H, *m*-CH_{Mes}], 6.94 [s, 1H, *m*-CH_{Mes}], 6.83 [s, 1H, *m*-CH_{Mes}], 6.80 [s, 1H, *m*-CH_{Mes}], 3.87 [dt, J = 5 and 9, 1H, NCH_2CH_2N], 3.44 [d, J = 9, $RuCH_2$], 3.30 [d, J = 11, $RuCH_2$], 3.28 [m, 1H, NCH_2CH_2N], 3.04 [q, J = 10, 1H, NCH_2CH_2N], 2.97 [dd, J = 7 and 9, 1H, NCH_2CH_2N], 2.49 [s, 3H, CH_3], 2.44 [s, 3H, CH_3], 2.40−2.28 [br m, 3H, PCy_3], 2.30 [s, 3H, CH_3], 2.18 [s, 3H, CH_3], 2.15 [s, 3H, CH_3], 2.10−2.02 [br m, 3H, PCy_3], 1.84−1.50 [br m, 15H, PCy_3], 1.40−1.16 [br m, 12H, PCy_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 74.5 MHz): δ 220.3 [d, $^2J_{CP}$ = 90, $RuCN_2$], 203.0 [d, $^2J_{CP}$ = 15, CO], 144.0 [C_{aryl}], 138.8 [C_{aryl}], 137.9 [C_{aryl}], 137.1 [C_{aryl}], 136.9 [C_{aryl}], 136.6 [C_{aryl}], 134.4 [C_{aryl}], 130.5 [C_{aryl}], 130.3 [CH_{aryl}], 129.5 [CH_{aryl}], 129.2 [CH_{aryl}], 125.9 [CH_{aryl}], 52.6 [d, $^4J_{CP}$ = 3, NCH_2CH_2N], 50.2 [d, $^4J_{CP}$ = 3, NCH_2CH_2N], 34.2 [d, $^1J_{CP}$ = 15, PCy_3], 31.0 [d, J_{CP} = 2, PCy_3], 29.9 [PCy_3], 28.0 [d, J_{CP} = 3, PCy_3], 27.9 [PCy_3], 26.7 [PCy_3], 21.3 [CH_3], 21.0 [CH_3], 20.5 [CH_3], 19.8 [CH_3], 18.9 [CH_3], 7.4 [d, $^2J_{CP}$ = 4, $RuCH_2$]. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 33.31 [s]. IR (KBr pellet): 2924 [s], 2849 [s], 2362 [w], 2346 [w], 2016 [w], 1899 [s, ν_{CO}], 1855 [w], 1617 [w], 1576 [w], 1472 [s], 1446 [s], 1424 [s], 1387 [m], 1380 [m], 1321 [m], 1298 [m],

(55) Moers, F. G.; Ten Hoedt, R. W. M.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2279−2282.

1264 [s], 1174 [m], 1106 [w]. Anal. Calcd for $C_{40}H_{58}N_2ClPORu$: C, 64.02; H, 7.79; N, 3.73. Found: C, 63.96; H, 7.87; N, 3.74. Crystals for X-ray analysis were obtained by slow evaporation of a dichloromethane solution.

Reaction of $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$ with $KOBu^t$. A screw cap NMR tube was charged with 0.010 g (0.012 mmol) of $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CMe_2$, 0.001 g (0.011 mmol) of $KOBu^t$, and 0.6 mL of C_6D_6. An immediate color change from purple to deep red occurred. ^1H and ^{31}P NMR spectra were recorded after 15 min at room temperature. ^1H NMR (299.9 MHz): δ 8.93 [d, $J_{HH} = 13$, Ru−CH], 6.27 [d, $J_{HH} = 13$, RuCH=C*H*], 4.75 [s, C=CH_2], 4.58 [s, C=CH_2], 2.58−1.17 [multiple peaks, CH_3 and PCy_3]. $^{31}P\{^1H\}$ NMR (121.4 MHz): δ 23.55 [s]. A second unidentified product, which contained a C=CH_2 group and a ruthenium-hydride ligand, was also present. Full conversion to this product occurred upon addition of more $KOBu^t$. ^1H NMR (299.9 MHz): δ 5.25 [s, C=CH_2], 5.00 [s, C=CH_2], 2.58−1.17 [multiple peaks], −27.52 [br t, $J = 14$, RuH]. $^{31}P\{^1H\}$ NMR (121.4 MHz): δ 48.64 [s].

Synthesis and Characterization of $(PPr^i_3)_2(Cl)(CO)Ru{-}CH{=}CHCMe{=}CH_2$ (5). A Schlenk flask was charged with 0.150 g (0.260 mmol) of $(PPr^i_3)_2(Cl)_2(CO)Ru{=}CHCH{=}CMe_2$, 0.057 g (0.510 mmol) of $KOBu^t$, and 15 mL of benzene. The reaction was stirred at room temperature for 30 min, during which time it changed color from orange to pink. The resulting suspension was filtered by cannula. The solvent was lyophilized to yield 0.11 g of the desired product as a pale pink powder (78%). ^1H NMR (CD_2Cl_2, 399.8 MHz): δ 7.96 [d, $J_{HH} = 16$, 1H, Ru−CH], 5.80 [d, $J_{HH} = 16$, 1H, RuCH=C*H*], 4.30 [s, 1H, C=CH_2], 4.16 [s, 1H, C=CH_2], 2.71 [m, 6H, CH of PPr^i_3], 1.70 [s, 3H, CH_3], 1.28 [m, 36H, CH_3 of PPr^i_3]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ 199.84 [t, $J_{CP} = 14$, Ru−CO], 146.78 [t, $J_{CP} = 9$, Ru−C], 138.64 [s, RuCH=*C*H], 134.92 [s, CH−*C*(Me)=CH_2], 101.02 [s, C=*C*H_2], 21.20 [vt, $J_{CP} = 9$, CH of PPr^i_3], 16.49 [s, Me of PPr^i_3], 16.21 [m, Me of PPr^i_3], 15.85 [s, CH_3]. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): δ 38.45 [s]. IR (CH_2Cl_2 thin film): 1549 [$\nu_{C=C}$], 1910 [ν_{CO}]. Anal. Calcd for $C_{24}H_{49}ClOP_2Ru$: C, 52.21; H, 8.95. Found: C, 52.17; H, 8.88.

Synthesis and Characterization of $(H_2IMes)_2(Cl)_2Ru{=}CHPh$ (6b). A small ampule was charged with 0.175 g (0.270 mmol) of $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$, 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 h. 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 the desired product 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, 25 °C, 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, 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]. ^1H NMR (CD_2Cl_2, −15 °C, 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 **6b**, 0.015 g of PCy_3, and 0.8 mL of C_6D_6. This solution was heated in an 80 °C oil bath and periodically monitored by ^1H and ^{31}P NMR. The results are shown in eq 6.

Reaction of 6b with $(PCy_3)_2(Cl)_2Ru{=}CHPh$. A screw cap NMR tube was charged with 0.008 g of **6b**, 0.008 g of $(PCy_3)_2(Cl)_2Ru{=}CHPh$, and 0.8 mL of C_6D_6. This solution was heated in a 70 °C oil bath and periodically monitored by ^1H and ^{31}P NMR. After 23 h, the $(PCy_3)_2(Cl)_2Ru{=}CHPh$:**6b**:**2** ratio was 0.5:1.0:0.2; after 47 h, 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 **6b** and 0.8 mL of C_6D_6. The headspace in the tube was replaced with 1 atm of ethylene. This solution was heated in a 60 °C oil bath for 24 h. No reaction was observed by ^1H or ^{31}P NMR.

RCM Reactions. An NMR tube with septum cap was charged with 0.60 mL of a catalyst stock solution (5 mM in C_6D_6, 0.003 mmol of catalyst per run) in the glovebox. The tube was equilibrated at 40 °C in the NMR probe. Next 15 μL of 4,4-dicarboethoxy-2-methyl-1,6-heptadiene (100 mM) was injected into the tube. The reaction was monitored by measuring the decreasing ^1H NMR signals of the starting material over at least three half-lives. The data were fit to a first-order exponential with Varian kinetics software.[56]

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. Next 110 μL of COD (0.90 mmol, 1500 mM) was injected into the tube. The reaction was monitored by measuring the increasing ^1H NMR signals of the product over at least three half-lives. The data were fit to a first-order exponential with Varian kinetics software.[56]

Crystal Structure Determination of 4 and 6a. Crystal, intensity collection, and refinement details are presented in Table 1. Data were collected on a Bruker SMART 1000 area detector running SMART.[57] The diffractometer was equipped with a Crystal Logic CL24 low-temperature device, and the data sets were collected at low temperature (98 K) using graphite-monochromated Mo Kα radiation with λ = 0.71073 Å. The crystals were mounted on glass fibers with Paratone-N oil. Data were collected as ω-scans with the detector 5 cm (nominal) distant at a θ of −28°. The data were processed with SAINT.[57] SHELXTL[57] was used to solve (Patterson method) and to refine both structures using full-matrix least-squares. No absorption or decay corrections were applied.

The asymmetric unit of compound **4** consists of one molecule of **4** and one-half of a dichloromethane molecule disordered about a center of symmetry. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with U_{iso} values based on the U_{eq} of the attached atom.

There are two crystallographically independent molecules in the asymmetric unit of **6a**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Unfortunately, the H_2IMes and IMes ligands are disordered with one another, in approximately a 60:40 ratio in each molecule. Consequently, the refined geometry is a mixture of the H_2IMes and IMes ligands.

The graphics were prepared with the Diamond and SHELXTL programs.[57]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic

(56) *VNMR 6.1B Software*; Varian Associates, Inc.
(57) (a) Bruker 1999 SMART, SAINT, and SHELXTL. Bruker AXS Inc., Madison, WI. (b) Diamond 2.1. 2000 Crystal Impact GbR, Bonn, Germany.

Data Centre as supplementary publication numbers 166803 (for **4**) and 167135 (for **6a**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Structure factors are available from the authors by e-mail: xray@caltech.edu.

Acknowledgment. This research was supported by the U.S. National Science Foundation and the National Institutes of Health. T.M.T. acknowledges the U.S. Department of Defense for a NDSEG graduate fellowship. We thank Lawrence M. Henling (Caltech) for contributions to the crystallography and Dr. Sharad P. Hajela (Materia) for helpful discussions.

Supporting Information Available: Crystal structure determination of $(PCy_3)_2(Cl)(CO)(H)Ru$ (**3b**) and comparison with other determinations, tables of crystallographic data for **4** and **6a**, and synthetic details for $(PPr^i_3)_2(Cl)_2(CO)Ru{=}CHCH{=}CMe_2$ and $[H_2IMes(H)][Cl]$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA021146W