Reactions of Ruthenium Benzylidene Complexes with Cyclic and Acyclic Imines: Oligomerization of 1-Pyrroline and Metathesis via Tautomerism

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At room temperature, NMR spectroscopy indicates that the ruthenium benzylidene complex $(Cl)_2(PCy_3)_2Ru{=}CHPh$ reacts with 1-pyrroline to yield $(Cl)_2(PCy_3)$(1-pyrroline)$Ru{=}CHPh$. Heating a solution of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ with excess 1-pyrroline to 90 °C results in ring-opening oligomerization of the cyclic imine. The combination of ruthenium carbene complexes $(Cl)_2(PCy_3)_2Ru{=}CHPh$ and $(Cl)_2(PCy_3)(H_2IMes)Ru{=}CHPh$ (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) with acyclic imines of the type (R)N=CH(R′) results in metathesis reactions when the imine possesses a C−H bond α to the imine carbon. Imines that lack C−H bonds α to the imine carbon do not react with $(Cl)_2(PCy_3)_2Ru{=}CHPh$. The primary products from the reactions of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ and $(Cl)_2(PCy_3)(H_2IMes)Ru{=}CHPh$ with acyclic imines are olefins and new Fischer carbene complexes of the type $(Cl)_2(L)(L')Ru{=}CH\{N(H)R\}$ ($L = L' = PCy_3$; $L = PCy_3$, $L' = H_2IMes$). The ruthenium complex $(Cl)_2(PCy_3)_2Ru{=}CH\{N(H)Pr\}$ has been isolated from the reaction of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ with (Pr)N=CH(*i*-Pr) and has been fully characterized. A possible pathway for the reactions of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ and $(Cl)_2(PCy_3)(H_2IMes)Ru{=}CHPh$ with acyclic imines that involves imine to enamine tautomerism followed by C=C bond metathesis reactions is discussed. The failure of the ruthenium benzylidene complexes $(Cl)_2(PCy_3)_2Ru{=}CHPh$ and $(Cl)_2(PCy_3)(H_2IMes)Ru{=}CHPh$ to react with the C=N bonds of acyclic imines in combination with observed reactivity between $Ru(Cl)_2(PPh_3)_3$ and 1-pyrroline indicates that the oligomerization of 1-pyrroline with $(Cl)_2(PCy_3)_2Ru{=}CHPh$ likely proceeds via a Lewis acid catalyzed mechanism.

Introduction

Transition-metal carbene complexes that mediate bond-breaking and bond-forming reactions of carbon−carbon multiple bonds have become valuable synthetic tools and have been applied toward a variety of reactions, including olefin isomerization, metathesis polymerization, and the synthesis of small organic molecules via ring-closing metathesis sequences.[1−9] Synthetic applications of group VI alkylidene complexes have been driven primarily by high catalyst activities, while the tolerance of diverse functionality by ruthenium complexes has increased the scope of accessible reactions.[4−6,10−12]

There is significant interest in the ability to introduce heteroatomic functionalities into polymers,[13] and the extension of transition-metal-catalyzed metathesis polymerization reactions to carbon−heteroatom multiple bonds would allow the direct incorporation of functionality into polymer backbones. Catalysts for the cross-metathesis of acyclic imines that utilize zirconium, molybdenum, tantalum, titanium, and niobium systems have been reported.[14−21] However, with a few exceptions, the mechanisms of these reactions are not well defined, and only a single family of transition-metal imido systems that catalyze imine metathesis has been

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(1) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997.
(2) Imamoglu, Y. *Metathesis Polymerization of Olefins and Polymerization of Alkynes*; Kluwer Academic: Dordrecht, The Netherlands, 1998.
(3) Pariya, C.; Jayaprakash, K. N.; Sarkar, A. *Coord. Chem. Rev.* **1998**, *168*, 1−48.
(4) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158−165.
(5) Schrock, R. R. *Tetrahedron* **1999**, *55*, 8141−8153.
(6) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.
(7) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043.
(8) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037−2056.
(9) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565−1604.
(10) Schrock, R. R. *Pure Appl. Chem.* **1994**, *66*, 1447−1454.
(11) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450.
(12) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452.
(13) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479−1493.
(14) Lin-Tao, L. I.; Hua, G.; Sheng-Ming, M. A. *Chin. J. Org. Chem.* **2001**, *21*, 398−402.
(15) Cantrell, G. K.; Meyer, T. Y. *J. Am. Chem. Soc.* **1998**, *120*, 8035−8042.
(16) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61−68.
(17) Bruno, J. W.; Li, X. J. *Organometallics* **2000**, *19*, 4672−4674.
(18) McInnes, J. M.; Mountford, P. *Chem. Commun.* **1998**, 1669−1670.
(19) McInnes, J. M.; Blake, A. J.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3623−3628.
(20) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−985.
(21) Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 751−761.

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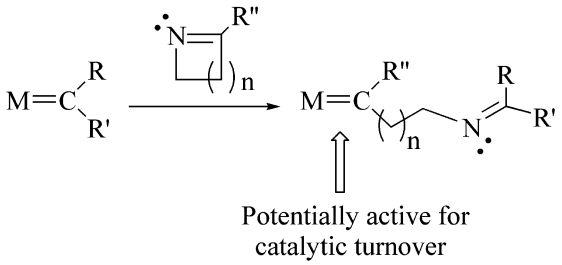
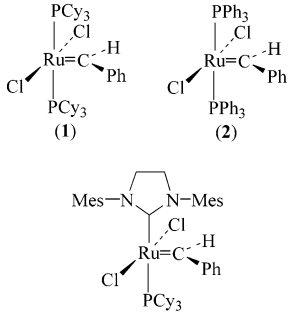
Scheme 1. Regioselective Metathesis of Carbon−Nitrogen Multiple Bonds Based on Metal Carbene Ligands Possibly Leading to Catalytic Turnover



demonstrated to proceed via diazametallacycle intermediates that are analogous to olefin metathesis intermediates.[20−23] In contrast, mechanistic studies of other imine metathesis catalysts have revealed the possibility of multiple reaction pathways.[18,24,25] In addition to imine metathesis, reactions of imido complexes with isocyanates or carbodiimides, stoichiometric metal insertion into pyridine, metal-catalyzed metathesis of P=P bonds, and intermolecular metal imido exchange reactions have been observed.[26−31]

Although imido ligands are often inert toward metathesis and other reactivity, carbene ligands are frequently active for metathesis transformations.[1,3−7,9,10,32−35] Thus, it might be anticipated that *catalytic* metathesis of C−N multiple bonds based on transition-metal carbene ligands would be more viable than reactions that incorporate imido ligands (Scheme 1). However, reactions of transition-metal carbene systems with imines, nitriles, or carbonyl compounds typically yield C=C and M=NR or M=O bond formation with catalytic turnover disrupted by the formation of reaction-inert imido or oxo complexes.[15,36−41] The group VI complex $(CO)_5W{=}CHPh$ reacts with carbodiimides with atypical regioselectivity

Chart 1. Ruthenium Benzylidene Complexes



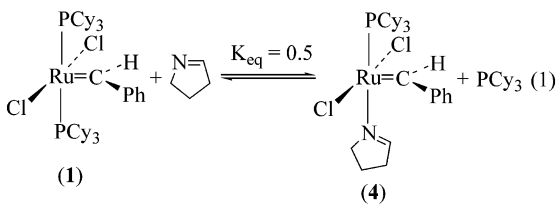
Mes = mesityl

to yield imines and $(CO)_5W{=}C{=}NR$ complexes.[42] We report herein the ring-opening oligomerization of 1-pyrroline with $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**) as catalyst as well as reactions of the series of metathesis catalysts $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**), $(Cl)_2(PPh_3)_2Ru{=}CHPh$ (**2**), and $(Cl)_2(PCy_3)(H_2IMes)Ru{=}CHPh$ (**3**) (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) with acyclic imines (Chart 1). Complexes **1** and **3** do not react with the C=N bonds of acyclic imines but rather with the C=C bonds of enamine tautomers.[6,43]

Results and Discussion

Reactions with 1-Pyrroline. Ligands that engage in multiple bonding with transition-metal complexes are known to exhibit variable reactivity (i.e., electrophilic vs nucleophilic character) as a function of metal identity, metal oxidation state, and the identity of ancillary ligands. Increased ligand-based electrophilic character has been observed as a progression from left to right in the transition series is made. An explanation for this phenomenon is the localization of the HOMO and LUMO that results from metal−ligand π-bonding,[44,45] and it might be anticipated that transition-metal−carbene bonds of later and more electronegative transition metals would serve to reverse the reaction regioselectivity of metathesis reactions with imines. Thus, we supposed that the regioselectivity of metathesis reactions of ruthenium carbene complexes might differ from that observed with earlier transition-metal systems (i.e., C=N bond formation might be accessible).

The combination of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**) with 1-pyrroline in C_6D_6 results in an immediate ligand exchange at room temperature to yield $(Cl)_2(PCy_3)$(1-pyrroline)$Ru{=}CHPh$ (**4**), as indicated by the decrease in intensity for the carbene CH singlet of complex **1** and the appearance of a new carbene CH resonance (doublet, $^3J_{PH}$ = 12 Hz) at 20.50 ppm in the ^1H NMR spectrum (eq 1). Coupling between the carbene proton and the

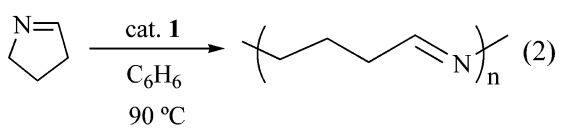


PCy_3 ligands of complex **1** is not observed. The lack of significant coupling is a result of the trans arrangement

(22) Krska, S. W.; Zuckerman, R. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11828−11829.
(23) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669−2670.
(24) Burland, M. C.; Pontz, T. W.; Meyer, T. Y. *Organometallics* **2002**, *21*, 1933−1941.
(25) Bühl, M. *J. Mol. Model.* **2000**, *6*, 112−118.
(26) Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023−1025.
(27) Birdwhistell, K. R.; Lanza, J.; Pasos, J. *J. Organomet. Chem.* **1999**, *584*, 200−205.
(28) Dillon, K. B.; Gibson, V. C.; Sequeira, L. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2429−2430.
(29) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1331−1332.
(30) Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322−329.
(31) Bell, S. A.; Meyer, T. Y.; Geib, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 10698−10705.
(32) Schrock, R. R. In *Metathesis Polymerization of Olefins and Polymerization of Alkynes*; Imamoglu, Y., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1998; pp 357−380.
(33) Yet, L. *Chem. Rev.* **2000**, *100*, 2963−3007.
(34) Randall, M. L.; Snapper, M. L. *J. Mol. Catal. A* **1998**, *133*, 29−40.
(35) Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1833−1836.
(36) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077−3081.
(37) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808−7809.
(38) Cantrell, G. K.; Geib, S. J.; Meyer, T. J. *Organometallics* **2000**, *19*, 3562−3568.
(39) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210−3222.
(40) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062−1067.

of the phosphine ligands, large P−Ru−P bond angle, and perpendicular carbene orientation.[46] In addition, a resonance consistent with a metal-bound imine CH appears at 7.82 ppm as well as a new resonance assigned as the metal-bound N−CH_2 moiety (3.5 ppm, triplet) and a new doublet due to the carbene phenyl ortho protons (8.48 ppm). Other resonances appear in the upfield region of the ^{1}H NMR spectrum, but definitive assignment is complicated by the multiple resonances for the reaction mixture (i.e., the mixture of complexes **1** and **4** and the presence of free 1-pyrroline monomer and trimer and tricyclohexylphosphine result in a complex spectrum). In addition to resonances due to the formation of free PCy_3 (10.9 ppm) and the Grubbs carbene complex **1**, a new resonance is observed at 30.1 ppm in the ^{31}P NMR spectrum of the reaction mixture. An equilibrium between the pyrroline complex **4** and PCy_3 with complex **1** and 1-pyrroline is observed ($K_{eq} \approx 0.5$ at room temperature, as determined by ^{1}H NMR spectroscopy), and the addition of excess 1-pyrroline pushes the equilibrium toward bound pyrroline (as determined by ^{1}H NMR spectroscopy). However, all attempts to isolate complex **4** have failed (possibly due to rapid imine dissociation in the absence of excess 1-pyrroline leading to decomposition). Two minor doublets (ratio of the carbene CH of **4** to minor doublets is ~2:1) observed at 20.15 and 19.15 ppm could be due to isomers of η^2-bound 1-pyrroline (a minor resonance at 25.6 ppm is observed in the ^{31}P NMR spectrum). To our knowledge, no precedent for η^2 coordination of a cyclic imine to a transition metal exists; however, η^2-bound acyclic imines and η^1-cyclic imines have been reported.[47−50] A second ligand substitution of PCy_3 with 1-pyrroline to yield *trans*-$(Cl)_2$(1-pyrroline)$_2$Ru=CHPh is possible; however, the carbene CH would resonate as a singlet (not observed). At room temperature, the mixture of complex **1** and 1-pyrroline does not undergo significant change for at least 24 h.

Heating complex **1** with excess 1-pyrroline to 90 °C results in a decrease in intensity for resonances due to the free 1-pyrroline monomer. A similar reaction also occurs at 60 °C, albeit at a reduced rate. After 1 h at 90 °C, use of an internal standard indicates that approximately 20% of the 1-pyrroline has been consumed with concomitant formation of a new triplet at 8.18 ppm as well as multiplets at 4.22, 2.15, and 1.55 ppm in the ^{1}H NMR spectrum. These results are consistent with ring-opening oligomerization of 1-pyrroline (eq 2). Sol-



(2)

vent removal followed by washing with pentane results in isolation of the oligomerized product. A COSY experiment reveals data that are consistent with the assignments of resonances due to polypyrroline (Figure 1). The ^{13}C NMR spectrum of the isolated product displays resonances at 170.7, 63.2, 37.1, and 21.9 ppm (see the Supporting Information). The cyclic imine 1-pyrroline exists as a cyclic trimer (Scheme 2) but can be reverted to the monomer upon heating,[38,51] and the total amount of monomer, trimer, and polypyrroline remains constant throughout the reaction. Use of an internal standard indicates that approximately 3.6 equiv of 1-pyrroline/equiv of catalyst is oligomerized. GPC analysis of the polymeric product reveals no high-molecular-weight polymer, and MALDI mass spectroscopy is consistent with low-molecular-weight polypyrroline (i.e., no compounds with molecular weight >830 are observed). TGA analysis results in 50% weight loss at 200 °C. Thus, the isolated poly(pyrroline) contains a significant amount of ruthenium impurities (consistent with elemental analysis). Results from reactions of complex **3** with 1-pyrroline are similar to those observed with complex **1**.

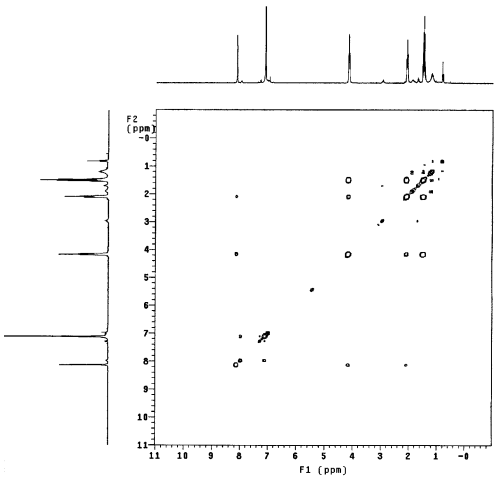
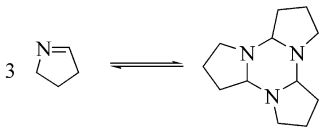


Figure 1. COSY spectrum of poly(pyrroline).

Scheme 2. Monomeric 1-Pyrroline in Equilibrium with Cyclic Trimer

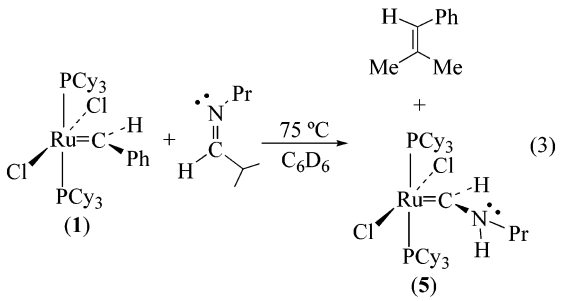


Heating the reaction solution for 24 h results in only minor amounts of additional polymerization. The discontinuation of polymerization could be due to catalyst decomposition; however, it is also possible that the lack of significant ring strain for 1-pyrroline could result in a thermodynamic inhibition to further polymerization. For example, the ROMP of cyclopentene to cis polymer is only slightly exergonic with $\Delta G° = -0.3$ kJ/mol.[1]

(41) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270−3272.
(42) Weiss, K.; Kindl, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 629−630.
(43) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.
(44) Nugent, W. A.; McKinney, R. J.; Kasowski, R. V.; Van-Catledge, F. A. *Inorg. Chim. Acta* **1982**, *65*, L91−L93.
(45) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.
(46) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.
(47) Cantrell, J. W. R.; Richter-Addo, G. B.; Gladysz, J. A. *J. Organomet. Chem.* **1994**, *472*, 195−204.
(48) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651−2660.
(49) Coles, N.; Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Organometallics* **1994**, *13*, 190−199.
(50) Galakhov, M. V.; Gómez, M.; Jiménez, G.; Royo, P. *Organometallics* **1995**, *14*, 1901−1910.
(51) Wiberg, K. B.; Nakaji, D. Y.; Morgan, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 3527−3532.

Fresh catalyst precursor **1** (approximately the same amount as the initial reaction) was added to the NMR solution, and after heating to 90 °C polymerization activity resumed. After an additional 1 h of heating, approximately 37% of the original 1-pyrroline monomer/trimer had been polymerized (compared with 20% after the initial catalyst consumption; see above). These results demonstrate that the observed loss of catalyst activity after approximately 1 h at 90 °C is not due to thermodynamic inhibition of polymerization.

Reactions with Acyclic Imines. Simple Lewis and protic acids are known to catalyze imine metathesis reactions.[52] To study the feasibility of metathesis reactions of ruthenium carbene complexes with C=N bonds, a series of reactions of acyclic imines with complexes **1**−**3** was explored. The reaction of complex **1** and the *N*-alkylimine (Pr)N=CH(*i*-Pr) (Pr = propyl) was monitored at 75 °C in an NMR tube (C_6D_6). After the mixture was heated for approximately 10 h, the formation of 2-methyl-1-phenyl-1-propene and the new Fischer carbene complex $(Cl)_2(PCy_3)_2Ru{=}CH\{N(H)Pr\}$ (**5**) was observed by ^{1}H NMR spectroscopy (eq 3). Small amounts



of other organic products are observed (possibly due to metathesis of the resulting olefins). After approximately 24 h, the conversion of **1** to complex **5** is complete. The carbene complex **5** can be isolated pure after workup and has been characterized by multinuclear NMR spectroscopy and elemental analysis. Salient features of the ^{1}H NMR spectrum include a downfield doublet due to the carbene proton at 13.60 ppm (J = 14 Hz) and a doublet of triplets (J = 14, 7 Hz) due to the amine proton that resonates at 9.15 ppm. COSY and proton-decoupling experiments are consistent with the assigned structure (see Supporting Information). The ^{13}C NMR spectrum reveals the carbene resonance at 240.1 ppm, and a resonance due to the new Ru complex is observed at 32.5 ppm in the ^{31}P NMR spectrum. The syntheses of other ruthenium carbene complexes that possess heteroatomic functionality (Fischer carbene complexes) have been previously reported.[53−58]

The reactions of complex **1** with the acyclic and alkyl imines (*i*-Pr)N=CH(Pr), (Pr)N=CH(Et), and (Pr)N=CH(Pr) (all reactions at approximately 70 °C) result in transformations closely related to that observed with (Pr)N=CH(*i*-Pr). In all reactions the formation of a new olefin as the primary organic product is observed by ^{1}H NMR spectroscopy (Table 1). In addition, the appearance of olefin is accompanied by the formation of new Ru carbene complexes, as indicated by doublets between 13 and 14 ppm (due to the carbene proton) and multiplets between 8 and 12 ppm (due to the amine proton) in the ^{1}H NMR spectra. In contrast, heating a solution of complex **1** with (*i*-Pr)N=CH(*t*-Bu) at 70 °C results in no observable reaction after 24 h. To determine if the failure of complex **1** to react with (*i*-Pr)N=CH(*t*-Bu) is due to steric inhibition by the bulky *tert*-butyl substituent, (*t*-Bu)N=CH(Pr) was reacted with **1**. After 10 h at 70 °C, the formation of *trans*-*β*-ethylstyrene and a new Ru carbene complex was observed (Scheme 3; Table 1). Thus, the incorporation of a *tert*-butyl group at the imine nitrogen does not inhibit metathesis reactivity, and the failure of (*i*-Pr)N=CH(*t*-Bu) to undergo reaction is not likely attributable to steric factors.

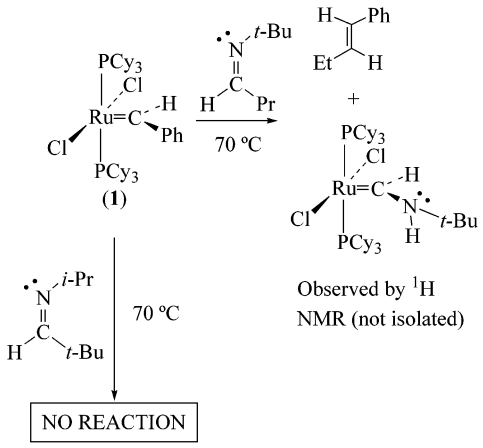
Metathesis reactions are also observed with *N*-arylimines. For example, the formation of *trans*-*β*-methylstyrene and a new Ru carbene complex is observed when complex **1** is reacted with (Ph)N=CH(Et) (Scheme 4). Although the presence of an *N*-aryl substituent does not disrupt the observed metathesis reactions, the incorporation of a phenyl substituent at the

Table 1. Metathesis Reactions of Acyclic Imines with Complexes 1−3[a]

imine	complex	reacn product[b]	^{1}H NMR[c]
(Pr)N=CH(*i*-Pr)	**1**	Me_2C=CH(Ph)	13.60,[d] 9.15 (dt)
(*i*-Pr)N=CH(Pr)	**1**	*trans*-(Et)HC=CH(Ph)	13.68, 8.96 (dd)
(Pr)N=CH(Et)	**1**	*trans*-(Me)HC=CH(Ph)	13.60, 9.15 (dt)
(Pr)N=CH(Pr)	**1**	*trans*-(Et)HC=CH(Ph)	13.60, 9.15 (dt)
(*i*-Pr)N=CH(*t*-Bu)	**1**	no reacn	N/A
(*t*-Bu)N=CH(Pr)	**1**	*trans*-(Et)HC=CH(Ph)	13.88, 9.25 (d)
(Ph)N=CHPh	**1**	no reacn	N/A
(*i*-Pr)N=CH(Ph)	**1**	no reacn	N/A
(Ph)N=CH(Et)	**1**	*trans*-(Me)HC=CH(Ph)	15.03, 11.26 (d)
(Pr)N=CH(Pr)	**2**	decomposition	N/A
(Pr)N=CH(Pr)	**3**	*trans*-(Et)HC=CH(Ph)	12.98, 8.80 (dt)

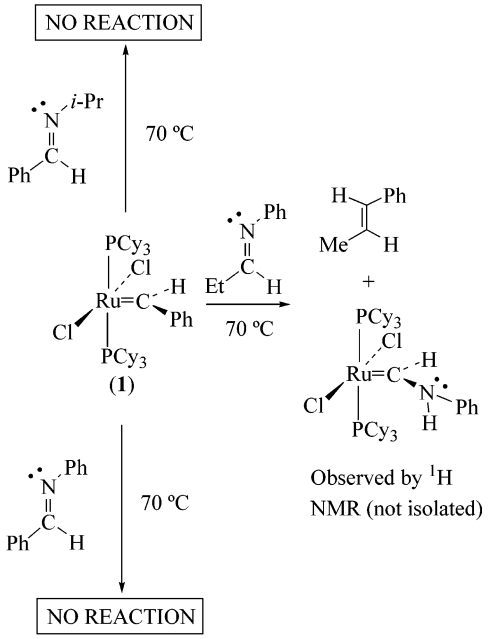
[a] All reactions performed in C_6D_6 between 70 and 75 °C. [b] In addition to olefin, the formation of new Ru carbene complexes is observed. [c] Chemical shifts of the resonances due to carbene proton and amine proton for the new ruthenium carbene complexes are listed consecutively. [d] Each carbene proton resonates as a doublet.

Scheme 3. Complex 1 Reacts with *N*-*t*-Bu Imine but Does Not React with Imines That Possess a *t*-Bu Group at the Imine Carbon

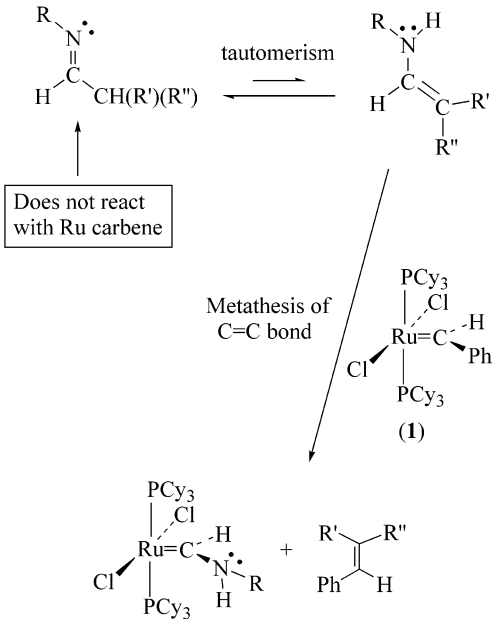


(52) Tóth, G.; Pintér, I.; Messmer, A. *Tetrahedron Lett.* **1974**, 735−738.
(53) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153−2164.
(54) Coalter, J. N., III; Caulton, K. G. *New J. Chem.* **2001**, *25*, 679−684.
(55) Katayama, H.; Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4513−4515.
(56) Schaaf, P. A. v. d.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. *J. Organomet. Chem.* **2000**, *606*, 65−74.
(57) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511.
(58) Coalter, J. N., III; Bollinger, J. C.; Huffman, J. C.; Werner-Zwanziger, U.; Caulton, K. G.; Davidson, E. R.; Gérard, H.; Clot, E.; Eisenstein, O. *New J. Chem.* **2000**, *24*, 9−26.

Scheme 4. Complex 1 Reacts with *N*-Aryl Imines but Does Not React with Imines That Possess Aryl Groups at the Imine Carbon



Scheme 5. Proposed Reaction Pathway for the Conversion of Ru Benzylidene Complexes and Acyclic Imines to New Olefin and Fischer Carbene Systems



imine carbon results in no reaction. For example, neither *N*-benzylideneaniline nor (*i*-Pr)N=CH(Ph) reacts with complex **1** after 24 h at 70 °C (Scheme 4).

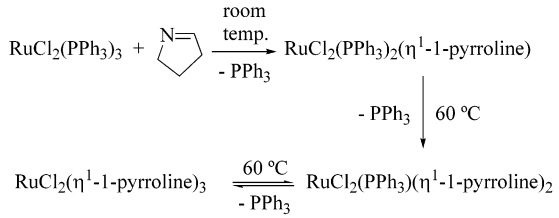
To compare the abilities of the ruthenium complexes to impact the reaction, complexes **2** and **3** were reacted with (Pr)N=CH(Pr). Complex **2** decomposes before reaction with the imine is observed, and similar results were obtained upon reacting complex **2** with (Ph)N=CH(Ph) or (*i*-Pr)N=CH(Ph). In contrast, complex **3** reacts with (Pr)N=CH(Pr) to yield identical organic products and a new Fischer carbene complex, as observed with the reaction of complex **1** (Table 1).

Reaction Pathway. No evidence for the formation of Ru imido complexes is observed upon reaction of complexes **1**−**3** with acyclic imines. The preparation of Ru imido complexes is relatively rare.[59−63] Although complex **1** does not appear to react directly with the C=N bond of acyclic imines, reactions with acyclic imines that possess C−H bonds α to the imine carbon to form new C=C bonds and new Fischer carbene complexes are observed. In contrast, imines that lack C−H bonds α to the imine carbon fail to react with the ruthenium carbene complexes. This reactivity trend along with the identities of the olefin products are consistent with a reaction pathway that involves imine tautomerism prior to C=C metathesis reactivity (Scheme 5). Tautomerism to enamine results in the formation of a carbon−carbon double bond with an amine functionality,[64,65] and the metathesis reaction of the ruthenium carbene moiety with the new C=C bond accounts for the formation of the new olefins (R′)(R″)C=CH(Ph) (Scheme 5). Metathesis reactions between ruthenium carbene complexes and olefins that possess electron-donating heteroatomic functionalities have been reported.[53,57,66,67] The incorporation of a phenyl group or a *tert*-butyl group at the imine carbon disrupts the formation of the enamine tautomer, and the presence of these substituents at the imine carbon results in no observed reaction between the ruthenium benzylidene complexes and acyclic imines. Thus, in contrast to Ta and Mo carbene complexes (see above), the ruthenium carbene complexes **1** and **3** do not react with the carbon−nitrogen bonds of acyclic imines under the observed reaction conditions.

The observation of acyclic imines reacting with complexes **1** and **3** as enamines suggests that the polymerization of 1-pyrroline catalyzed by complex **1** might proceed via a mechanism in which ruthenium catalyzes ring-opening polymerization by acting as a Lewis acid. However, $RuCl_3$ hydrate does not polymerize 1-pyrroline at 90 °C. The combination of $RuCl_2(PPh_3)_3$ with 1-pyrroline in C_6D_6 at room temperature results in PPh_3/1-pyrroline ligand exchange, as determined by ^{1}H and ^{31}P NMR spectroscopy (Scheme 6). The observation of a broad singlet at 8.31 ppm and a multiplet at 3.78 ppm (^{1}H NMR) are consistent with an η^1-bound 1-pyrroline ligand (free 1-pyrroline monomer resonates at 7.27 and 3.68 ppm), and the ^{31}P NMR spectrum reveals new resonances at −4.4 ppm for free PPh_3 and 38.3 ppm, consistent with the formation of $RuCl_2(PPh_3)_2(\eta^1$-1-pyrroline). Heating this solution to 60 °C for approximately 30 min results in the observation of new resonances at 8.47 ppm (broad singlet) and 4.25 ppm

(59) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−482.
(60) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 3771−3778.
(61) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203−1208.
(62) Che, C.-M.; Yam, V. W.-W. *Adv. Inorg. Chem.* **1992**, *39*, 233−325.
(63) Danopoulos, A. A.; Hay-Motherwell, R. S.; Wilkinson, G.; Cafferkey, S. M.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3177−3184.
(64) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975−2050.
(65) Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev. (Engl. Transl.)* **1979**, *48*, 107−117.
(66) Katayama, H.; Urushima, H.; Ozawa, F. *Chem. Lett.* **1999**, 369−370.
(67) Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem.* **2000**, *606*, 16−25.

Scheme 6. Ligand Substitution Reactions upon Combination of $RuCl_2(PPh_3)_3$ with Excess 1-Pyrroline



(multiplet) in the ^{1}H NMR spectrum as well an increase in the intensity of the resonance for free PPh_3 and a new resonance at 51.3 ppm in the ^{31}P NMR spectrum. These observations are consistent with the formation of $RuCl_2(PPh_3)(\eta^1$-1-pyrroline$)_2$ and 2 equiv of free PPh_3 (Scheme 6). Continuous heating (60 °C) for 2 h leads to the disappearance of the resonances corresponding to $RuCl_2(PPh_3)_2(\eta^1$-1-pyrroline) and a decrease in the intensity of resonances due to $RuCl_2(PPh_3)(\eta^1$-1-pyrroline$)_2$. At this point, two resonances are observed in the ^{31}P NMR due to free PPh_3 and $RuCl_2(PPh_3)(\eta^1$-1-pyrroline$)_2$. In addition, new resonances in the ^{1}H NMR are observed at 8.13 ppm (broad singlet) and 3.95 ppm (multiplet). These results are consistent with PPh_3/1-pyrroline ligand substitution to yield an equilibrium between $RuCl_2(\eta^1$-1-pyrroline$)_3$ and PPh_3 with $RuCl_2(PPh_3)(\eta^1$-1-pyrroline$)_2$ and 1-pyrroline (Scheme 6). Continued heating at 60 °C does not result in any observable changes to the reaction solution after 24 h. However, heating to 90 °C for 12 h yields resonances consistent with minor amounts of poly(1-pyrroline) after 12 h (<10% of the original 1-pyrroline is polymerized at this time). Clean isolation of the ruthenium complexes with bound pyrroline was not possible.

During the reactions of complex **1** with *acyclic* imines, no evidence of imine coordination to ruthenium is observed. In contrast, the cyclic imine 1-pyrroline undergoes a rapid ligand exchange reaction (at room temperature) with PCy_3 when combined with complex **1** in benzene. The different predilection toward imine coordination between 1-pyrroline and the acyclic imines is likely due to steric factors. Significant electronic contributions are unlikely, as indicated by the failure of the *N*-alkylimines (Pr)N=CH(Et) and (Pr)N=CH(Pr) to coordinate to the ruthenium complex **1**. The inability of complex **1** to react with the C=N bonds of acyclic imines suggests that the ring-opening oligomerization of 1-pyrroline may not occur via a metathesis reaction mechanism, and the ability of $RuCl_2(PPh_3)_3$ to catalyze a similar polymerization reaction at 90 °C supports this conclusion. However, it should be noted that the catalytic polymerization reaction with $RuCl_2(PPh_3)_3$ does not occur at 60 °C and is slow at 90 °C compared to reactions with complex **1**, and the ability of complex **1** to coordinate 1-pyrroline (in contrast to the acyclic imines) could lead to alternative reaction pathways for cyclic versus acyclic imines. In addition, it is perhaps noteworthy that simple ruthenium complexes that do not bear carbene ligands serve as catalyst precursors for C=C bond metathesis reactions.[68,69] Thus, while the tentative conclusion is that the polymerization proceeds via a Lewis acid ring-opening polymerization, the results do not conclusively rule out a metathesis reaction.

Summary and Conclusions

The ruthenium complexes **1** and **3** undergo metathesis reactions with acyclic imines that proceed via an imine/enamine tautomerism mechanism. The observed reaction pathways are in contrast with reactions of carbene ligands bound to earlier transition metals (i.e., Ta and Mo) and further illustrate the potential mechanistic complications of metathesis reactions involving C−N multiple bonds. The failure to observe reactions with the C=N bonds could be due to the inability of the ruthenium complexes to coordinate the acyclic imines. In contrast, the cyclic imine 1-pyrroline rapidly coordinates to complex **1** via a ligand exchange reaction in which PCy_3 dissociates, and heating a solution of excess 1-pyrroline with **1** results in ring-opening oligomerization. The mechanism of the 1-pyrroline oligomerization has not been definitively determined; however, a Lewis acid catalyzed mechanism seems likely, since $RuCl_2(PPh_3)_3$ catalyzes a similar reaction.

Experimental Section

General Methods. All procedures were performed under an inert atmosphere (nitrogen) in an Innovative Technologies glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer (O_2(g) <15 ppm for all reactions). Benzene and toluene were purified by distillation from sodium/benzophenone. Pentane was refluxed over P_2O_5 for a few hours followed by distillation. All solvents were purged with nitrogen for at least 10 min prior to use. Benzene-d_6 was degassed via three freeze−pump−thaw cycles prior to use and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric 300 or Varian Mercury 400 MHz spectrometer. All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and are referenced to tetramethylsilane using residual proton signals or the ^{13}C signals of the deuterated solvents. ^{31}P NMR spectra were recorded on a Varian Mercury 400 MHz instrument and referenced against external 85% phosphoric acid. MALDI-TOF mass spectroscopy was performed with a Bruker Perflex system using the matrix POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene). TGA was performed with a Hi-Res TGA 2950 thermogravimetric analyzer. GPC analyses of polymer molecular weights were performed on a Jasco system comprised of a PU-1580 intelligent HPLC pump, a RI-1530 intelligent refractive index detector, and a Borwin-GPC control system. The molecular weight was calibrated with polystyrene standards. Two PL-Gel mixed columns were used for analysis with chloroform at a flow rate of 1.0 mL/min. The Grubbs catalysts $(Cl)_2(PCy_3)_2Ru$=CHPh (**1**), $(Cl)_2(PPh_3)_2Ru$=CHPh (**2**), and $(Cl)_2(PCy_3)(H_2IMes)Ru$=CHPh (**3**) were prepared according to published procedures.[70,71] The procedure for the preparation of 1-pyrroline was reported by Meyer et al.[38] Ruthenocene was purchased from Aldrich Chemical Co. and used as the internal standard for NMR tube reactions without further purification. Imines were prepared by condensation of the appropriate aldehyde and amine as reported.[72] Aldehydes and amines were obtained from Aldrich

(68) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960−961.

(69) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542−7543.

(70) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(71) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

Chemical Co. and used without further purification. Elemental analysis was performed by Atlantic Microlab, Inc.

NMR Tube Reaction of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (1) with 1-Pyrroline. The ruthenium complex $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**; 0.0200 mg) was combined with 10−20 equiv of 1-pyrroline (as a mixture of monomer and trimer) in C_6D_6. Upon addition of 1-pyrroline the solution color changed from purple to green. To this solution was added 1−2 mg of Cp_2Ru as internal standard. A ^1H NMR spectrum was acquired using a 90° pulse and long pulse delay (10 s). The appropriate pulse delay was determined by incrementally increasing the delay until integration remained constant. The NMR spectrum showed a singlet corresponding to the carbene C*H* of the Grubbs complex **1** (20.58 ppm) and three new carbene resonances (major resonance at 20.50 (d) ppm and two minor resonances at 20.15 (d) and 19.15 (d) ppm; all P−H coupling constants are 12 Hz). A new doublet at 8.48 ppm (carbene phenyl ortho resonance), a singlet at 7.82 ppm (bound imine CH), and a multiplet at 3.5 ppm were also observed. Complete assignment of resonances due to the proposed 1-pyrroline complex **4** is impossible due to the presence of multiple resonances as a result of the complex equilibria between the Grubbs catalyst **1**, the 1-pyrroline adduct, free PCy_3, and isomers of bound 1-pyrroline. The ^{31}P NMR spectrum showed a resonance corresponding to the Grubbs catalyst **1** at 37.2 ppm, free PCy_3 at 10.9 ppm, and a new resonance at 30.1 ppm designated as the 1-pyrroline adduct. In addition, a minor resonance is observed at 25.6 ppm in the ^{31}P NMR spectrum. Heating the reaction solution to 90 °C in an oil bath for 1 h resulted in a color change to brown. The ^1H NMR spectrum of the resulting mixture showed that the Grubbs complex **1** had been consumed in addition to a new triplet at 8.18 ppm (imine CH of oligomer, t, $J_{HH} = 2$ Hz) and multiplets at 4.22, 2.15, and 1.55 ppm. Downfield resonances due to ruthenium carbene protons were not observed. Exact changes in the region between 1 and 3 ppm were difficult to discern to see due to the presence of free PCy_3; however, isolation of the oligomer (see below) allowed confirmation of the new upfield multiplets. Use of ruthenocene as internal standard in several different experiments confirmed that 3−4 equiv of 1-pyrroline/equiv of catalyst was consistently converted to oligomer, while the total amount of 1-pyrroline monomer, trimer, and oligomer remains the same.

Isolation of Polypyrroline. The ruthenium complex $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**; 0.2000 mg) and 10−20 equiv of 1-pyrroline were dissolved in benzene. The resulting solution was heated to reflux overnight, and volatiles were removed in vacuo. The residue was washed with pentane, and the resulting powder was dried in vacuo. Note: ^1H and ^{31}P NMR spectra reveal a small amount of PCy_3 impurity. ^1H NMR (C_6D_6; δ, ppm): 8.18 (1H, t, $^3J_{HH} = 2$ Hz, N=C*H* of oligomer), 4.22 (2H, m, CH_2 of oligomer), 2.15 (2H, m, CH_2 of oligomer), 1.55 (2H, m, CH_2 of oligomer). Minor resonances are also observed in the aromatic region and could be due to the phenyl group from the original carbene complex **1**. ^{13}C NMR (C_6D_6, δ, ppm): 170.7 (N=*C*H of oligomer), 63.2 ppm (*C*H_2 of oligomer), 37.1 (*C*H_2 of oligomer), 21.9 (*C*H_2 of oligomer). For the ^{13}C NMR spectrum see the Supporting Information. Anal. Calcd for C_4H_7N: C, 69.52; H, 10.21; N, 20.27 (C:N:H ratio is 6.81:1.98:1.00). Found: C, 33.36; H, 4.84; N, 9.12 (C:N:H ratio is 6.89:1.88:1.00). Analysis of the oligomeric product is consistent with the C:N:H ratio of pyrroline contaminated with ruthenium species.

NMR Tube Reactions of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ with Acyclic Imines. In a representative reaction, the ruthenium complex $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**; 0.0500 g) was combined with 0.0100 g of (*i*-Pr)N=CH(Pr) in approximately 0.5 mL of C_6D_6. The resulting solution was transferred to a screw-cap NMR tube, and a ^1H NMR spectrum was acquired of the homogeneous solution. Next, the reaction solution was heated to 75 °C in an oil bath for 12 h with periodic monitoring by ^1H NMR spectroscopy. Another ^1H NMR spectrum was acquired and compared with the spectrum that preceded heating. The ^1H NMR spectrum revealed that the Grubbs carbene complex **1** had been consumed and that the olefin *trans*-(Et)HC=CH-(Ph) was produced as the primary organic product, as indicated by a characteristic doublet at 6.25 ppm and a doublet of triplets at 6.05 ppm. In addition, new resonances appeared at 13.68 ppm (d, $^3J_{PH} = 14$ Hz) and 8.96 ppm (dd, $J = 14$ and 7 Hz) due to the formation of $(Cl)_2(PCy_3)_2Ru{=}CH\{N(H)i\text{-}Pr\}$.

Reaction of $RuCl_2(PPh_3)_3$ with 1-Pyrroline. In a screw-cap NMR tube, 0.0200 g of $RuCl_2(PPh_3)_3$ was combined with an excess of 1-pyrroline in C_6D_6. A broad singlet at 8.31 ppm and a multiplet at 3.78 ppm (^1H NMR) are observed and are consistent with an η^1-bound 1-pyrroline ligand, and the ^{31}P NMR reveals new resonances at −4.4 ppm for free PPh_3 and 38.3 ppm consistent with the formation of $(Cl)_2(PPh_3)_2Ru(\eta^1$-1-pyrroline). Heating this solution to 60 °C for 30 min results in the observation of new resonances at 8.47 ppm (broad singlet) and 4.25 ppm (multiplet) in the ^1H NMR spectrum as well as an increase in the resonance for free PPh_3 and a new resonance at 51.3 ppm in the ^{31}P NMR spectrum. Continuous heating for 2 h leads to disappearance of the resonances corresponding to $(Cl)_2(PPh_3)_2Ru(\eta^1$-1-pyrroline) and $(Cl)_2(PPh_3)$-$Ru(\eta^1$-1-pyrroline)$_2$ with only a single resonance in the ^{31}P NMR due to free PPh_3. In addition, new resonances in the ^1H NMR are observed at 8.13 ppm (broad singlet) and 3.95 ppm (multiplet). These results are consistent with complete PPh_3/1-pyrroline ligand substitution to yield $(Cl)_2Ru(\eta^1$-1-pyrroline)$_3$. Continued heating at 60 °C does not result in any observable changes to the reaction solution. However, heating to 90 °C for 12 h yields resonances consistent with minor amounts of poly(1-pyrroline) after 12 h (<10% of the original 1-pyrroline is polymerized at this time).

$(Cl)_2(PCy_3)_2Ru{=}CH\{N(H)(Pr)\}$ (5). A benzene solution (20 mL) of $(Cl)_2(PCy_3)_2Ru{=}CHPh$ (**1**; 0.2000 mg, 0.240 mmol) and (Pr)N=CH(*i*-Pr) (0.2000 mg, 1.77 mmol) was refluxed for approximately 12 h. After the resulting solution was cooled to room temperature, volatiles were removed under reduced pressure. The dry residue was washed with methanol (3 × 5 mL), and the purple powder was dried in vacuo overnight. A purple solid was collected in 57% yield (0.1100 mg). ^1H NMR (C_6D_6; δ, ppm): 13.60 (1H, d, $^3J_{HH} = 14$ Hz, Ru=C*H*), 9.15 (1H, dt, $J_{HH} = 14$, 7 Hz, N*H*), 2.76 (2H, m, NHCH_2), 2.1−1.2 (overlapping multiplets due to PCy_3 ligands), 1.08 (2H, m, N(H)CH_2CH_2), 0.56 (3H, t, $^3J_{HH} = 7$ Hz, N(H)(CH_2)$_2$CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6; δ, ppm): 32.5. $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 240.1 (s, Ru=*C*H), 55.8 (s, NH*C*H_2), 32.7 (t, $J = 9$ Hz, PCy_3), 30.2 (s, PCy_3), 28.3 (t, $J = 7$ Hz, PCy_3), 27.2 (s, PCy_3), 23.2 (s, NHCH$_2$*C*H$_2$), 11.3 (s, *C*H$_3$). Anal. Calcd for $C_{40}H_{75}NCl_2P_2Ru$: C, 59.75; H, 9.42; N, 1.74. Found: C, 59.42; H, 9.16; N, 1.77.

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Supporting Information Available: ^{13}C NMR spectrum of polypyrroline and COSY spectrum of complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0301029

(72) Cantrell, G. K.; Meyer, T. Y. *Organometallics* **1997**, *16*, 5381−5383.