Articles

Metathesis of Electron-Rich Olefins: Structure and Reactivity of Electron-Rich Carbene Complexes

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The addition of excess $H_2C=C(H)ER$ to $(PCy_3)_2Cl_2Ru=C(H)R$ (**1a,b**) afforded a series of well-defined ruthenium carbene complexes, $(PCy_3)_2Cl_2Ru=C(H)ER$ (ER = OEt (**5**), SEt (**6**), SPh (**7**), N(carbazole) (**8**), N(pyrrolidinone) (**9**)) in yields ranging from 66 to 90%. Such complexes containing an electron-donating group on the carbene carbon are often referred to as Fischer-type carbenes. Replacement of one phosphine ligand with 1,3-dimesitylimidazolylidene (IMes) afforded the respective mixed-ligand complexes (IMes)(PCy_3)Cl_2Ru= C(H)ER (**11**−**14**) in 48−89% yield. Alternatively, addition of $H_2C=C(H)OEt$ to (H_2IMes)-$(PCy_3)Cl_2Ru=C(H)Ph$ (**3a**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) afforded $(H_2IMes)(PCy_3)Cl_2Ru=C(H)OEt$ (**15**) in 93% yield. The crystal structures of complexes **5**, **7**−**9**, and **11** were determined and found to be structurally similar to the parent ruthenium alkylidene ([Ru]=C(H)R) complexes. In solution, the chemical shift of the [Ru]=C(*H*)ER resonance in ^1H NMR spectra was found to be inversely related to the electronegativity of the α-heteroatom; however, no trends were evident in the ^{31}P or ^{13}C NMR spectra. Intramolecular coordination of the pendant amide carbonyl group to the Ru center established a temperature-dependent equilibrium between complexes **9** and **14** and their cyclometalated forms. All Ru electron-rich complexes initiated the ring-opening metathesis polymerization (ROMP) of strained cyclic olefins and the ring-closing metathesis (RCM) of diethyl diallylmalonate. A general trend in the relative reactivities and thermal stabilities of the $(PCy_3)_2Cl_2Ru=C(H)ER$ complexes followed the order C > N > S > O. In addition, complexes coordinated with an N-heterocyclic carbene ligand (e.g., (IMes)(PCy_3)Cl_2Ru=C(H)ER) displayed enhanced activities in olefin metathesis and were thermally more stable than their bis(phosphine) analogues. Finally, the thermal decomposition product of $(PCy_3)_2Cl_2Ru=C(H)$-OEt was isolated and determined by X-ray analysis to be $(PCy_3)_2ClRu(H)CO$ (**10**).

Introduction

Over the past decade, the development of Ru-based olefin metathesis catalysts has led to their use in a variety of organic and polymer synthesis applications.[1] The catalysts with the general structure LL′X_2Ru=CHR have received the bulk of the attention because they are generally robust and functional group tolerant and because a variety of synthetic pathways exist. In addi-

tion, extensive synthetic,[2] mechanistic,[3] and theoretical[4] investigations have continually improved the performance of the catalysts and expanded their overall applicability. For example, early systems such as (PPh_3)_2-Cl_2Ru=C(H)C(H)=CPh_2 were only effective in the ring-opening metathesis polymerization (ROMP) of highly strained olefins (e.g. norbornene) and displayed rather limited thermal stability.[5] The incorporation of more bulky and electron-donating phosphines (e.g. PCy_3) afforded catalysts, (PCy_3)_2Cl_2Ru=CHR (**1a**−**c**; Figure 1), that are active in a wide variety of ring-closing metath-
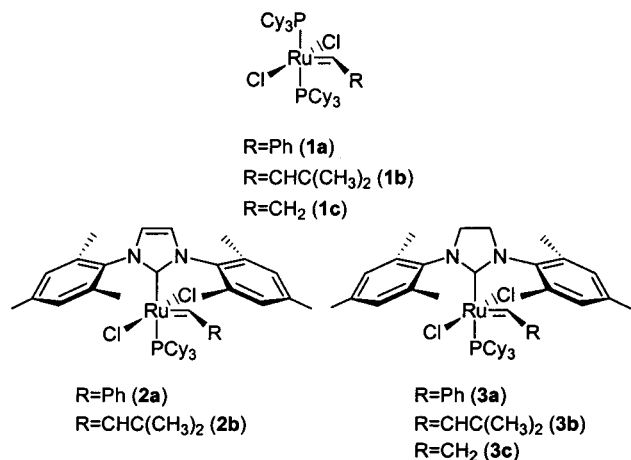
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R=Ph (**1a**)
R=CHC(CH₃)₂ (**1b**)
R=CH₂ (**1c**)

R=Ph (**2a**)
R=CHC(CH₃)₂ (**2b**)

R=Ph (**3a**)
R=CHC(CH₃)₂ (**3b**)
R=CH₂ (**3c**)

Figure 1. First- and second-generation ruthenium alkylidenes.

esis (RCM), cross-metathesis (CM), and ROMP applications.[6] However, they are limited to olefinic substrates that are not sterically hindered or that do not possess functionality in the α-position (such as unsaturated esters and amides). This limitation was recently overcome through incorporation of large, electron-donating imidazoylidene ligands.[7] The new catalysts (IMes)-(PCy₃)Cl₂Ru=CHR (**2a,b**) and (H₂IMes)(PCy₃)Cl₂Ru=CHR (**3a,b**) (IMes = 1,3-dimesitylimidazolylidene; H₂-IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene) have enabled the preparation of not only α-functionalized olefins but also di-, tri-, and tetrasubstitued olefins.[8] In addition, the increased activity of these catalysts has not resulted in the loss of functional group tolerance and inertness toward air and moisture.

The recent results with acrylates and related systems suggested that Ru electron-rich carbene complexes derived from functionalized olefins such as enols,[9] enamines,[10] and vinyl sulfides[9] were relatively unreactive in metathetical [2 + 2] reactions with olefins[11,12]

X = TFA   R = CHCHCPh₂   (**4a**)
X = TFA   R = OCH₂CH₃   (**4b**)
X = TFA   R = SPh   (**4c**)
X = TFA   R = N(carbazole)   (**4d**)

Figure 2. Triphenylphosphine-ligated ruthenium alkylidenes.

For example, an early report demonstrated that the ruthenium alkylidenes (PPh₃)₂(TFA)₂Ru=C(H)R (**4a**) reacted with vinyl ethers, amines, and sulfides to afford the Ru Fischer-type complexes (PPh₃)₂(TFA)₂Ru=C(H)-ER (**4b–d**, ER = OEt, SPh, N(carbazole); Figure 2), which were subsequently found to be inert toward olefins.[13] In fact, ethyl vinyl ether is commonly used to quench Ru-based ring-opening metathesis polymerizations, affording a methylene-terminated polymer and the Ru Fischer-type carbene (PCy₃)₂Cl₂Ru=C(H)OEt.[14]

However, a number of recent reports have indicated that [Ru]=C(H)OR type complexes may indeed be active olefin metathesis catalysts.[15] Although a few Ru Fischer-type carbenes have been synthesized and characterized, a detailed study of their fundamental structures and reactivity is required.[13,15b–d,16] In addition to reactivity, the thermal stability of Ru Fischer-type complexes has not been examined, even though they are believed to be more thermally stable than their alkylidene counterparts.[15c] To address the effect of directly modifying the electronic nature of the carbene carbon, we have prepared and characterized a series of well-defined carbenes (PCy₃)₂Cl₂Ru=C(H)ER and (L)(PCy₃)Cl₂-Ru=C(H)ER (L = IMes, H₂IMes; ER = OR, SR, NR). As will be discussed below, the complexes contain structural (solution and solid-state) and thermal characteristics similar to those of Ru alkylidenes. More importantly, these catalysts were found to be active in a variety of olefin metathesis reactions. These results define the requirements for the efficient metathesis of functionalized olefins such as enols, enamines, and vinyl sulfides.

Results and Discussion

Synthesis and Characterization of Bis(phosphine) Ru Electron-Rich Carbene Complexes. The reaction between various vinyl ethers and (PCy₃)₂Cl₂-

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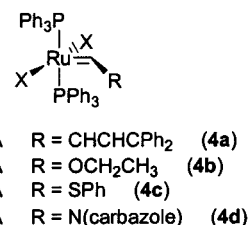
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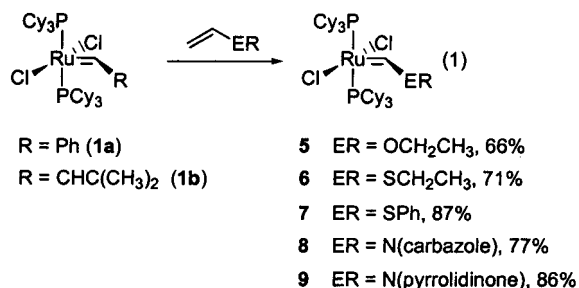
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Table 1. Selected ^{1}H, ^{31}P, and ^{13}C NMR Data^a

entry	complex	^{1}H NMR Ru=C(*H*)	^{31}P NMR	^{13}C NMR Ru=*C*
1	(PCy$_3$)$_2$Cl$_2$Ru=C(H)Ph (**1a**)[2b]	20.02	36.6	294.72
2[b]	(PCy$_3$)$_2$Cl$_2$Ru=C(H)Et (**1d**)[2b]	19.12[b]	36.4[b]	322.59[b]
3	(PCy$_3$)$_2$Cl$_2$Ru=C(H)OEt (**5**)	14.49	37.4	276.86
4	(PCy$_3$)$_2$Cl$_2$Ru=C(H)SEt (**6**)	17.67	32.9	281.60
5	(PCy$_3$)$_2$Cl$_2$Ru=C(H)SPh (**7**)	17.79	33.3	280.44
6	(PCy$_3$)$_2$Cl$_2$Ru=C(H)NR (**8**)[d]	17.59	41.3	227.99
7	(PCy$_3$)$_2$Cl$_2$Ru=C(H)NR (**9**)[e]	16.64[b]	38.5[b]	c
8[b]	(IMes)(PCy$_3$)Cl$_2$Ru=C(H)Ph (**2a**)[7a]	19.91	34.9	295.26
9	(IMes)(PCy$_3$)Cl$_2$Ru=C(H)OEt (**11**)	13.81	35.0	277.50
10	(IMes)(PCy$_3$)Cl$_2$Ru=C(H)SEt (**12**)	17.07	27.8	281.24
11	(IMes)(PCy$_3$)Cl$_2$Ru=C(H)NR (**13**)[d]	16.94	36.9	230.02
12[b]	(IMes)(PCy$_3$)Cl$_2$Ru=C(H)NR (**14**)[e]	16.12[b]	34.4[b]	246.79[b]
13	(H$_2$IMes)(PCy$_3$)Cl$_2$Ru=C(H)Ph (**3a**)[7b]	19.16	31.4	294.24
14	(H$_2$IMes)(PCy$_3$)Cl$_2$Ru=C(H)OEt (**15**)	13.63	32.6	276.75

^{a} Unless otherwise noted, CD$_2$Cl$_2$ was used as solvent. ^{b} Solvent C$_6$D$_6$. ^{c} Complex was only slightly soluble in C$_6$D$_6$. ^{d} NR = carbazole. ^{e} NR = pyrrolidinone.

Ru=C(H)Ph (**1a**) has been previously shown to afford complexes with the structure (PCy$_3$)$_2$Cl$_2$Ru=C(H)OR.[15] The reaction between **1a** and 10 equiv of ethyl vinyl ether was monitored in benzene-d_6 using a combination of ^{1}H and ^{31}P NMR spectroscopy. The reaction was found to be extremely rapid ($k_{obsd} \approx 10^2$ min^{-1}) and quantitatively afforded (PCy$_3$)$_2$Cl$_2$Ru=C(H)OEt (**5**).[3a] In addition, no methylidene was observed, which suggested that the reaction was regiospecific. Similar results were obtained when other Ru alkylidenes such as (PCy$_3$)$_2$-Cl$_2$Ru=C(H)C(H)C(Me)$_2$ (**1b**) were employed as the starting material and in other solvents including CD$_2$-Cl$_2$ and THF-d_8. In addition, the reaction appeared general; other functionalized olefins H$_2$C=C(H)ER (e.g., ER = N(carbazole), N(pyrrolidinone), SEt) gave similar results. In general, dichloromethane solutions (0.1 M) of **1a,b** were treated with excess H$_2$C=C(H)ER (ER = OEt, N(pyrrolidinone), N(carbazole), SEt, SPh), which produced red to purple powders after removal of solvent and residual H$_2$C=C(H)ER (eq 1). Recrystallization by

R = Ph (**1a**)
R = CHC(CH$_3$)$_2$ (**1b**)

5   ER = OCH$_2$CH$_3$, 66%
6   ER = SCH$_2$CH$_3$, 71%
7   ER = SPh, 87%
8   ER = N(carbazole), 77%
9   ER = N(pyrrolidinone), 86%

slow diffusion of pentane into saturated toluene solutions at −30 °C afforded pure (PCy$_3$)$_2$Cl$_2$Ru=C(H)ER (**5**−**9**) in 66−87% isolated yields.

Ruthenium alkylidenes (PCy$_3$)$_2$Cl$_2$Ru=C(H)R display characteristic chemical shifts in their ^{1}H, ^{13}C, and ^{31}P NMR spectra that provide valuble information for elucidating solution-state geometries of the complexes.[2a] When the phosphines are bulky (e.g., PCy$_3$), effectively no coupling is observed between the two phosphine ligands (^{31}P−^{31}P) or between the α-proton on the alkylidene moiety and the phosphines (^{31}P−^{1}H). These observations indicate that the phosphine ligands are orientated trans to each other and that the alkylidene moiety bisects the P−Ru−P plane.[2a] Relevant chemical shifts in the ^{1}H, ^{13}C, and ^{31}P NMR spectra for complexes **5**−**9** are shown in Table 1 and qualitatively suggested

that their solution structures were similar to Ru alkylidenes. (As discussed below, the structural similarities were later confirmed using X-ray crystallography). Relative to their alkylidene analogues, the respective ^{1}H resonances ([Ru]=C(*H*)ER) of complexes **5**−**9** were strongly shifted upfield (14.5−18 ppm) and appeared to be *inversely* proportional to the electronegativity of the α-heteroatom on the carbene moiety (Table 1). An additional signal (doublet, J = 4.0 Hz) was observed in the ^{1}H NMR spectrum of complex **9**, which was the result of chelation of the carbonyl group (**16**; vide infra). Similarly, ^{13}C NMR spectroscopy indicated that the chemical shifts for the carbene carbons ([Ru]=*C*(H)R) (228−282 ppm) were also upfield relative to those of typical Ru alkylidenes (**1a**, 294.72 ppm; **1d**, 322.59 ppm), although no direct correlation with electronegativity was evident (Table 1). The ^{31}P NMR resonances of complexes **5**−**9** were found to be singlets (i.e., no effective ^{1}H−^{31}P or ^{31}P−^{31}P coupling was observed), which suggested that the phosphines were disposed in a trans geometry perpendicular to the carbene ligands. Relative to Ru alkylidenes **1a** (36.6 ppm) and **1d** (36.4 ppm), downfield ^{31}P NMR signals were observed for complexes **5** (E = O), **8**, and **9** (E = N), whereas upfield signals were observed for complexes **6** and **7** (E = S).

Although solution-state NMR characteristics of complexes **5**−**9** provided some insight as to how the carbene moiety affects complex geometry and electronics, attention was shifted toward examining their respective solid-state structures. In general, crystals suitable for X-ray analysis were obtained by slowly diffusing pentane into a saturated solution of complexes **5**, **8**, and **9** in toluene at −30 °C. Notably, two slightly different geometries for complex **5** exist in the unit cell, which differ by only in a slight twist in the ethyl group. While the high solubility of complex **6** ([Ru]=C(H)SEt) thwarted efforts at inducing crystallization, cooling saturated toluene solutions of complex **7** ([Ru]=C(H)SPh) afforded maroon crystals that were suitable for X-ray analysis. Data collection parameters are given in Table 2, and representative bond lengths and angles are given in Table 3. Further details are provided in the Experimental Section and Supporting Information. The X-ray crystal structures of complexes **5** and **7**−**9** (Figures 3−6) were similar to those of the parent alkylidene complexes (PCy$_3$)$_2$Cl$_2$Ru=C(H)R (**1**).[2a,17] The phosphines were found to be mutually orientated in a trans disposition perpen-

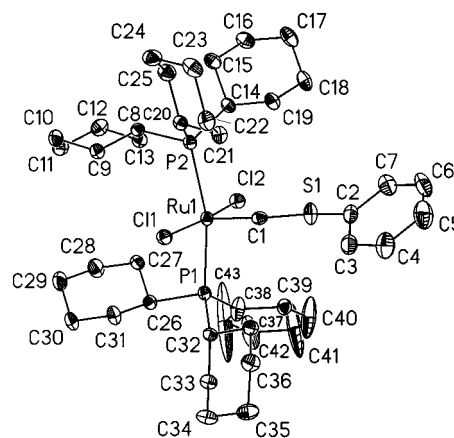**Table 2. Crystallographic Data for Complexes 5, 7, 8, and 9**

	5	**7**	**8**	**9**
formula	$C_{39}H_{72}Cl_2RuOP_2$	$C_{43}H_{72}Cl_2RuSP_2$	$C_{49}H_{75}Cl_2RuNP_2$	$C_{41}H_{73}Cl_2RuNOP_2$
fw	790.92	855.03	912.06	829.96
cryst syst	nonoclinic	triclinic	triclinic	nonoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.576(2)	9.8211(5)	12.6111(1)	9.4246(8)
b (Å)	36.738(7)	13.6315(7)	14.3083(1)	13.6142(1)
c (Å)	23.418(4)	18.7911(1)	17.0253(2)	37.570(3)
α (deg)	90	83.441(1)	83.518(1)	90
β (deg)	97.887(4)	78.732(1)	74.720(1)	92.123(2)
γ (deg)	90	78.190(1)	77.799(1)	90
V (Å^3)	9013(3)	2407.7(2)	2891.2(4)	4817.2(7)
Z	8	2	2	4
radiation (Kα, Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	98(2)	98(2)	98(2)	98(2)
D_{calcd} (mg m^{-3})	1.301	1.306	1.048	1.306
μ_{calcd} (mm^{-1})	0.57	0.58	0.45	0.54
F_{000}	3776	1008	968	2020
R1	0.053	0. 048	0. 064	0.058
wR2	0. 082	0. 089	0. 232	0.089
GOF	1.13	1.93	1.03	1.12

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (PCy$_3$)$_2$Cl$_2$Ru=C(H)ER Complexes (1d,[2b] 5, 7, 8, and 9)

	1d[2b]	**5**	**7**	**8**	**9**
ER	C$_6$H$_4$-*p*-Cl	OEt	SPh	N(carb)	N(pyr)
			Bond Distances (Å)		
Ru−C(1)	1.8393(3)	1.812(5)	1.829(3)	1.863(6)	1.828(4)
Ru−P(1)	2.397(1)	2.3683(13)	2.4041(9)	2.3994(1)	2.3979(12)
Ru−P(2)	2.435(1)	2.3904(13)	2.4167(9)	2.4082(1)	2.4036(12)
Ru−Cl(1)	2.401(1)	2.3886(12)	2.3952(7)	2.3742(1)	2.4041(10)
Ru−Cl(2)	2.395(1)	2.3749(12)	2.3968(8)	2.4088(1)	2.3881(10)
C(1)-E		1.275(5)		1.366(7)	1.365(5)
			Bond Angles (deg)		
C(1)−Ru−Cl(1)	103.7(1)	97.33(16)	92.56(9)	112.95(2)	102.70(13)
C(1)−Ru−Cl(2)	88.7(1)	89.17(16)	94.61(9)	85.09(2)	89.46(13)
C(1)−Ru−P(1)	101.2(1)	98.07(14)	98.43(9)	99.32(2)	99.17(13)
C(1)−Ru−P(2)	97.5(1)	97.26(14)	95.95(9)	96.04(2)	96.47(13)
Cl(1)−Ru−Cl(2)	167.6(1)	173.50(4)	172.81(3)	161.94(6)	167.80(4)
P(1)−Ru−P(2)	161.1(1)	164.67(4)	165.34(3)	164.28(5)	164.27(4)
Cl(1)−Ru−P(1)	90.8(1)	91.66(5)	87.55(3)	90.05(5)	89.98(4)
Cl(1)−Ru−P(2)	87.2(1)	88.16(4)	88.96(3)	87.06(5)	88.53(4)
Cl(2)−Ru−P(1)	86.5(1)	87.58(4)	91.87(3)	87.55(5)	87.77(4)
Cl(2)−Ru−P(2)	91.5(1)	90.87(4)	89.83(3)	90.43(5)	90.39(4)
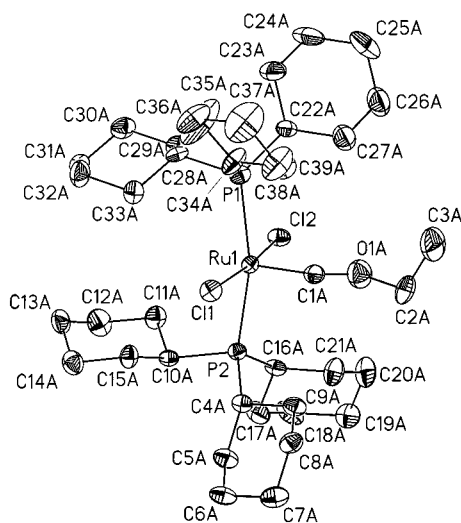
Figure 3. Molecular structure of (PCy$_3$)$_2$Cl$_2$Ru=C(H)OEt (**5**).
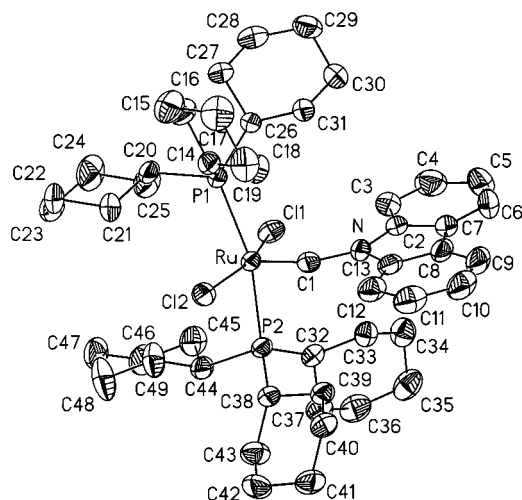

Figure 4. Molecular structure of (PCy$_3$)$_2$Cl$_2$Ru=C(H)SPh (**7**).

dicular to the carbene moiety, as expected from NMR analyses. The average Ru−P, Ru−Cl, and Ru=C bond distances of complexes **5** and **7**−**9** were slightly shorter (≤0.04 Å, ≤0.02 Å, and ≤0.03 Å, respectively) than their

parent alkylidene complex (PCy$_3$)$_2$Cl$_2$Ru=C(H)CH$_2$R. Slightly wider Cl−Ru−Cl angles (≤6°) and P−Ru−P angles (≤4°) were also observed, which are believed to stem from alleviation of the increased steric congestion around the Ru center. Finally, it is important to note

(17) (a) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872−12873. (b) Bielawski, C. W.; Louie, J.; Grubbs, R. H. Manuscript in preparation.

Figure 5. Molecular structure of $(PCy_3)_2Cl_2Ru=C(H)N$-(carbazole) (**8**).
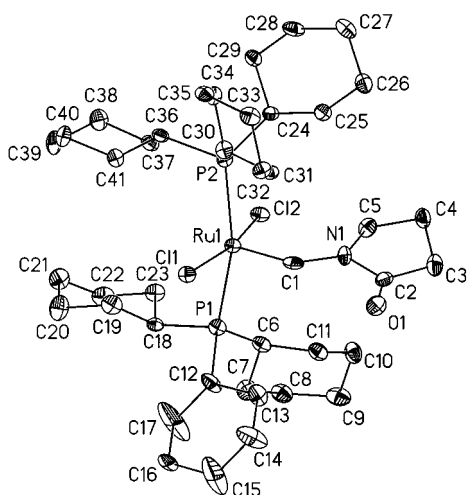
Figure 6. Molecular structure of $(PCy_3)_2Cl_2Ru=C(H)N$-(pyrrolidinone) (**9**).

that the Ru–C–H plane remained perpendicular to the P–Ru–C–P plane in complex **9** and the carbonyl oxygen was not twisted, as might be expected from its solution behavior (vide infra).

Measurement of the Thermal Stability of Ru Fischer-Type Carbene Complexes. Benzene-d_6 solutions (23 mM) of complexes **5**−**9** with 1,3,5-trimethoxybenzene (12 mM) as an internal standard were heated to 55 °C and monitored by ^1H and ^{31}P NMR spectroscopy.[18] Decomposition rates were determined by measuring the time required for half of the material to decompose ($\tau_{1/2}$), and the results are summarized in Table 4. Except for the oxygen-substituted complex **5** (vide infra), multiple decomposition pathways were evident, as mixtures of products were observed. For comparison, the $\tau_{1/2}$ value of complex **1a** (under identical conditions) has been included.[18] A general trend in the thermal stability of $(PCy_3)_2Cl_2Ru=C(H)ER$ complexes followed the order E = N > C > S > O. The high stability of **9** may be a result of the chelation of the amide carbonyl.

Isolation of the Thermal Decomposition Product of $(PCy_3)_2Cl_2Ru=C(H)OEt$. Prolonged heating of

(18) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207.

Table 4. Half-Lives for the Decomposition of Complexes 5−9

entry	complex	$\tau_{1/2}$
1	$(PCy_3)_2Cl_2Ru=C(H)OEt$ (**5**)	3 h
2	$(PCy_3)_2Cl_2Ru=C(H)SEt$ (**6**)	1 day
3	$(PCy_3)_2Cl_2Ru=C(H)SPh$ (**7**)	3 days
4	$(PCy_3)_2Cl_2Ru=C(H)Ph$ (**1a**)	8 days[a]
5	$(PCy_3)_2Cl_2Ru=C(H)N(carb)$ (**8**)	9 days
6	$(PCy_3)_2Cl_2Ru=C(H)N(pyr)$ (**9**)	20 days

[a] Data from ref 18.

Table 5. Crystallographic Data for $(PCy_3)_2ClRu(H)(CO)$ (10)

formula	$C_{37}H_{67}ClRuOP_2$
fw	726.37
cryst syst	triclinic
space group	$P2_12_12_1$
a (Å)	9.8521(12)
b (Å)	10.2242(12)
c (Å)	10.8316(13)
α (deg)	114.072(2)
β (deg)	108.518(2)
γ (deg)	91.270(2)
V (Å^3)	929.98(19)
Z	1
radiation (Kα, Å)	0.710 73
T (K)	98(2)
D_{calcd} (mg m^{-3})	1.297
μ_{calcd} (mm^{-1})	0.61
F_{000}	388
R1	0.026
wR2	0.058
GOF	1.90

solutions of $(PCy_3)_2Cl_2Ru=C(H)OEt$ (**5**) resulted in a distinctive color change from red to bright yellow (eq 2). This was concurrent with the disappearance of the
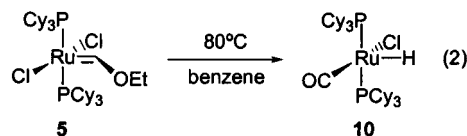
carbene resonance (singlet at 14.5 ppm) concomitant with the appearance of a hydride (triplet at −22 ppm) resonance in the ^1H NMR spectrum. In addition, a new signal at 47.1 ppm (singlet) in the ^{31}P NMR spectrum grew steadily as the signal at 35.6 ppm (resonance of $(PCy_3)_2Cl_2Ru=C(H)OEt$) was attenuated. Thus, the thermal decomposition process appeared to proceed with clean conversion to a single product. Analysis of the product using infrared spectroscopy revealed strong bands at 1906 and 1444 cm^{-1}, which are characteristic of Ru–H and Ru–CO complexes, respectively.[19] The decomposition product was isolated in 69% yield, and a crystal suitable for X-ray analysis was grown by cooling a saturated benzene solution of **10** from 60 °C to room temperature over 6 h. Crystal and data collection parameters are given in Table 5, and representative bond lengths and angles are given in Table 6. Additional details of the structure determination can be found in the Experimental Section and Supporting Information. Figure 7 shows an ORTEP diagram of $(PCy_3)_2ClRu(CO)$-(H) (**10**), clearly indicating the loss of the carbene functionality.[20] This complex has been previously re-

(19) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 2605−2611.
(20) This structure has recently been reported; see: Lee, H. M.; Smith, D. C.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794−797.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for (PCy₃)₂ClRu(H)(CO) (10)

Bond Distances (Å)			
Ru–P	2.3798(4)	Ru–H	1.36(4)
Ru–Cl	2.4022(18)	C(1)–O	1.162(6)
Ru–C(1)	1.777(6)		

Bond Angles (deg)			
P–Ru–P′	180.0	Cl–Ru–H	97.4(18)
P–Ru–Cl	88.18(4)	Cl′–Ru–H	82.6(18)
P′–Ru–Cl	91.82(4)	Cl–Ru–C(1)	178.4(2)
P–Ru–H	82.9(19)	C(1)–Ru–H	82.9(18)
P′–Ru–H	97.1(19)	C(1)′–Ru–H	97.1(18)
P(1)–Ru–C(1)	104.3(5)	O–C–Ru	179.1(9)
P(2)–Ru–C(1)	104.3(5)		
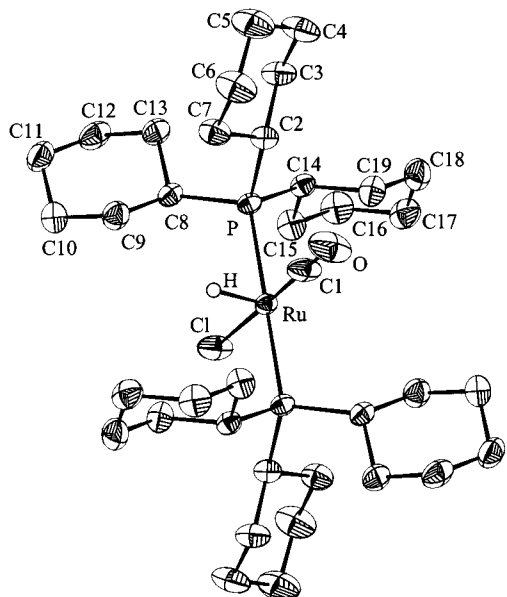
**Figure 7.** Molecular structure of (PCy₃)₂ClRu(H)(CO) (**10**).

ported by Yi and co-workers and can be prepared using other synthetic routes.[21] Possible mechanistic pathways of decomposition that lead to **10** have also been previously reported.[13]

Synthesis and Characterization of Ru Complexes Possessing an Imidazolylidene Ligand and a Phosphine Ligand. Treatment of the bis(phosphine) complexes **5**, **6**, **8**, and **9** with 2 equiv of the free carbene IMes in benzene afforded (IMes)(PCy₃)Cl₂Ru=C(H)ER (**11–14**) in 48–89% yield (eq 3). Alternatively, substitu-
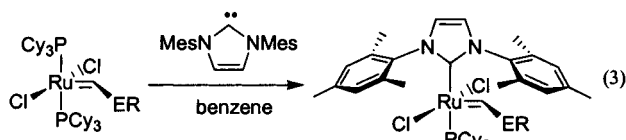
5 ER = OCH₂CH₃		**11** ER = OCH₂CH₃, 85%	
6 ER = SCH₂CH₃		**12** ER = SCH₂CH₃, 66%	
8 ER = N(carbazole)		**13** ER = N(carbazole), 48%	
9 ER = N(pyrrolidinone)		**14** ER = N(pyrrolidinone), 89%	

tion of one phosphine could be achieved by treatment with 1.2 equiv of IMes⁺Cl⁻ and KO-*t*-Bu in benzene to generate the free imidazolylidene carbene in situ, although with lower isolated yields (30–50%). In general, substitution of a phosphine ligand with an imidazolylidene ligand resulted in approximately equal up-

(21) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043–2045.
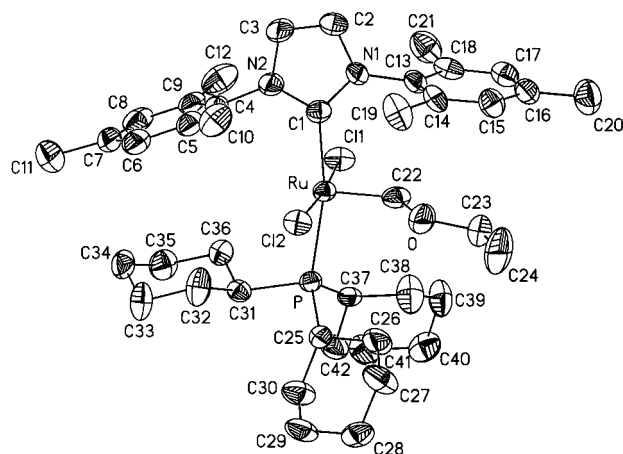
Figure 8. Molecular structure of (IMes)(PCy₃)Cl₂Ru=C(H)OEt (**11**).

Table 7. Crystallographic Data for (IMes)(PCy₃)Cl₂Ru=C(H)OCH₂CH₃ (11)

formula	C₄₂H₆₃Cl₂RuN₂OP
fw	814.93
cryst syst	orthorhombic
space group	P2₁2₁2₁
a (Å)	12.1718(1)
b (Å)	17.7113(2)
c (Å)	21.483(2)
V (Å³)	4631.4(9)
Z	4
radiation (Kα, Å)	0.710 73
T (K)	98(2)
D_calcd (mg m⁻³)	1.281
μ_calcd (mm⁻¹)	0.52
F₀₀₀	1888
R1	0.035
wR2	0.047
GOF	1.05

field shifts of the [Ru]=C(H)ER complexes in relevant ¹H (~0.6 ppm) and ³¹P (2–5 ppm) NMR spectra (Table 1). Minimal changes were observed in the ¹³C NMR spectra (0–2 ppm). Analogous shifts were observed in Ru alkylidene complexes and were found to reflect the increased electron-donating ability of the IMes ligand.[22] Interestingly, the ¹H NMR spectrum of complexes **13** and **14** at room temperature displayed six distinct methyl groups and four arene protons, in contrast to the case for other Ru Fischer-type carbene complexes, which display four methyl groups and two arene protons. The increased number of observed resonances may be related to slow rotation about the IMes–Ru bond or the [Ru]=C bond.[23]

To determine whether the IMes ligand induced structural changes, the X-ray structure of complex **11** was determined. A single crystal suitable for X-ray analysis was obtained by slow diffusion of methanol into a saturated solution of **11** in benzene at −30 °C, and an ORTEP diagram is shown in Figure 8. Crystal and data collection parameters are given in Table 7, and representative bond lengths and angles are given in Table 8. Details of the structure determination are provided in the Experimental Section and as Supporting Information. The Ru=C bond in (IMes)(PCy₃)Cl₂Ru=C(H)OEt

(22) (a) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370–2375. (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375–5380.
(23) Sanford, M. S.; Grubbs, R. H. Unpublished results.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for (TFA)₂(PPh₃)₂Ru=C(H)SPh (4a) and (IMes)(PCy₃)Cl₂Ru=C(H)OEt (11)

	4a[7c]	11
Bond Distances (Å)		
Ru−C(22)	1.841(11)	1.790(3)
Ru−C(1)	2.069(11)	2.080(2)
Ru−P	2.419(3)	2.4166(7)
Ru−Cl(1)	2.393(3)	2.4071(7)
Ru−Cl(2)	2.383(3)	2.3910(8)
Bond Angles (deg)		
C(22)−Ru−C(1)	99.2(5)	96.26(1)
C(22)−Ru−Cl(1)	104.3(5)	90.05(1)
C(22)−Ru−Cl(2)	87.1(5)	96.98(1)
C(22)−Ru−P	97.1(4)	95.92(9)
C(1)−Ru−Cl(1)		89.81(7)
C(1)−Ru−Cl(2)	86.9(3)	89.91(7)
C(1)−Ru−P	163.2(3)	167.79(7)
Cl(1)−Ru−Cl(2)	168.62(12)	172.95(3)
Cl(1)−Ru−P	89.86(9)	89.30(3)
Cl(2)−Ru−P		89.49(3)

(**11**) (1.79 Å) was shorter than the Ru−C bond of (IMes)-(PCy₃)Cl₂Ru=C(H)Ph (**2a**) (1.84 Å),[7c] as observed in the respective bis(phosphine) complexes (compare **1d** at 1.84 Å vs **5** at 1.81 Å; see above). Interestingly, the Ru=C bond was also shorter than in its bis(phosphine) analogue (PCy₃)₂Cl₂Ru=C(H)OEt (**5**) (1.81 Å). While all other lengths (Ru−Cl, Ru−P, Ru−C(1)ᵢₘₑₛ) were similar to those of the analalgous Ru alkylidene **2a**, the Cl−Ru−Cl and P−Ru−C(1)ᵢₘₑₛ angles were slightly wider (4 and 5°, respectively), as observed in the bis(phosphine) complexes. Nevertheless, the effects of the IMes ligand were minimal and apparently did not exert a significant structural influence on the structure of the complexes.

Synthesis and Characterization of a Ru Complex Possessing a Saturated Imidazolylidene Ligand and a Phosphine Ligand, (H₂IMes)(PCy₃)-Cl₂Ru=C(H)OEt (15). The synthetic method used to prepare complex **11** was unsuccessful for the preparation of (H₂IMes)(PCy₃)Cl₂Ru=C(H)OEt (**15**), and only decomposition of **5** was observed. However, as shown in eq 4, **15** could be prepared in 93% yield by adding
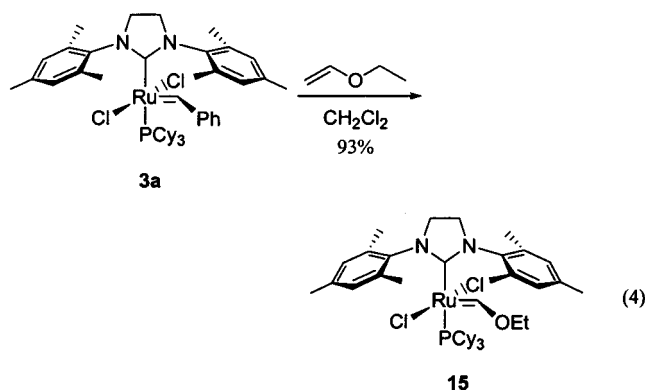
excess ethyl vinyl ether to a dichloromethane solution (0.1 M) of (H₂IMes)(PCy₃)Cl₂Ru=C(H)Ph (**3a**). Monitoring the reaction by ¹H NMR revealed that addition was regiospecific and no methylidene (**3c**) was observed over the course of the reaction. In comparison to (IMes)-(PCy₃)Cl₂Ru=C(H)OEt (**11**), slight upfield shifts were observed in the ¹H, ¹³C, and ³¹P NMR spectra. The shifts stem from the increased electron-donating ability of the saturated H₂IMes ligand as compared to IMes.[24] Similar

effects are observed in Ru alkylidene complexes (e.g., compare **2a** to **3a**).[7]

Synthesis and Characterization of Chelated Ruthenium Carbene Complexes. The behavior of **9** in solution is particularly interesting, as another carbene resonance was observed as a doublet at 13.99 ppm ($J = 4.0$ Hz) in the ¹H NMR spectrum. This doublet corresponded to the chelate complex **16** formed from dissociation of one PCy₃ ligand and intramolecular coordination of the amide carbonyl group (to the open coordination site trans to the ligated PCy₃ ligand).[25] In solution, complex **9** existed in a temperature-dependent equilibrium with the chelate complex **16** and free PCy₃ (eq 5).[26] The $\Delta H°$, $\Delta S°$, and $\Delta G°$ values (298 K) for the
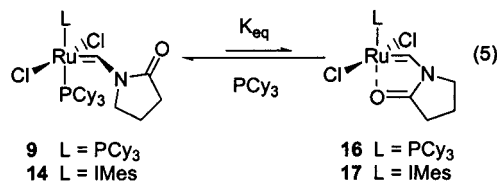

equilibrium in benzene-d_6 were determined to be 7.6 kcal/mol, 22.5 cal/mol K, and 0.9 kcal/mol, respectively. Complex **16** was isolated by the addition of 2 equiv of CuCl to a CH₂Cl₂ solution of complex **9**. After the reaction mixture was stirred at room temperature for 2 h, precipitated solids (which presumably were PCy₃−CuCl complexes) were filtered away and the resulting mother liquor was concentrated to afford a dark brown solid. Unfortunately, efforts to prepare a crystal suitable for X-ray analysis were thwarted, as **16** was extremely unstable and rapidly decomposed in the solid state over time. Nevertheless, NMR analysis demonstrated that only complex **16** was successfully isolated, as a singlet at 13.99 ppm was observed in the ¹H NMR spectrum and only a singlet at 57 ppm was observed in the ³¹P NMR spectrum.

Similarly complex **14** (doublet at 12.39 ppm) is in equilibrium with the chelate complex **17** (eq 5). The $\Delta H°$, $\Delta S°$, and $\Delta G°$ values (298 K) for this equilibrium in toluene-d_8 were measured to be 14.5 kcal/mol, 35.4 cal/mol K, and 4.0 kcal/mol, respectively. Formation of the chelated complex **17** from **14** is about 3 kcal/mol more favored than for formation of complex **16** from **9**, resulting from more favored enthalpic (6.9 kcal/mol) and entropic (12.9 cal/mol K) contributions. The enhanced enthalpic contribution was somewhat surprising, considering the IMes ligand places more electron density at the Ru center, as supported by NMR and crystal structure data. Regardless, the result was in agreement with recent mechanistic analyses, which suggested that the enhanced activity of second-generation Ru catalysts

(24) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163−2187. (b) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913−921.

(25) (a) Fürstner, A.; Thiel, O. R.; Lehmann, C. W. *Organometallics* **2002**, *21*, 331−335. (b) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799. (c) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168−8179. (d) Coalter, J. N., III; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **2000**, *39*, 3749−3756.

(26) The equilibrium exhibits an interesting thermochromic behavior which can be qualitatively assessed by visual inspection. Benzene solutions of **9** were purple at room temperature and gradually turned brown upon heating. Cooling the solutions back to room temperature returned the solution to a purple color, as expected.
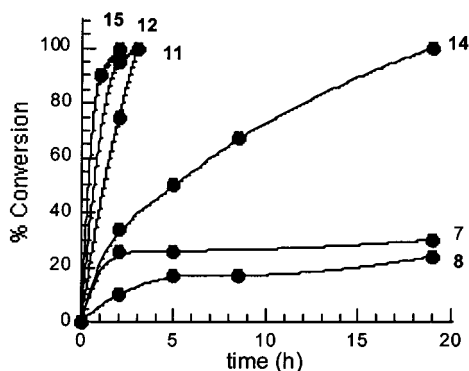
**Figure 9.** ROMP of COD (150 mM) at 60 °C using Ru Fischer-type carbenes (3 mM).

such as $(IMes)(PCy_3)Cl_2Ru=C(H)Ph$ (**2a**) or its saturated imidazolidene analogue $(H_2IMes)(PCy_3)Cl_2Ru=C(H)Ph$ (**3a**) may be related to the catalyst's preference to bind olefins over phosphines.[3a] After the isolation and characterization of Fischer-type complexes $(L)(PCy_3)Cl_2Ru=C(H)ER$ (L = PCy_3, **5−9**; L = IMes, **11−14**; L = H_2IMes, **15**), efforts were shifted toward examining their activities in a variety of olefin metathesis reactions.

Measurement of the Activity of Ru Fischer-Type Carbene Complexes in Ring-Opening Metathesis Polymerization (ROMP). All Ru Fischer-type carbene complexes initiated the ROMP of norbornene and norbornene derivatives at room temperature and afforded quantitative yields of polymer. Although the polymerizations were rapid ($\tau_{1/2} \approx$ minutes), they were significantly slower than those initiated with alkylidenes **1−3** ($\tau_{1/2} \approx$ seconds).[2a,5,27] To better define the relative activities, the polymerizations of monomers with less ring strain were studied.

A 150 mM benzene solution of 1,5-cyclooctadiene (COD) was added to 3 mM solutions of Ru Fischer-type complexes $L(PCy_3)Cl_2Ru=C(H)ER$ (**5−9**, **11−15**) with 50 mM 1,3,5-trimethoxybenzene (internal standard), and the reaction mixtures were heated to 65 °C. The reactions were monitored by ^{1}H NMR spectroscopy, and the results are summarized in Figure 9. In contrast to the polymerization of highly strained cyclic olefins (see above), a range of reactivity was observed that depended on the carbene substituent (ER). Complexes **5** (ER = OEt), **6** (ER = SEt), and **9** (ER = pyrrolidinone) were ineffective for initiating ROMP, even after prolonged periods at elevated temperature (60 °C, 11 h). However, minor perturbations of the ER group had a pronounced influence on activity: complexes **7** (ER = SPh) and **8** (ER = carbazole) gave moderate conversions of COD (26%, 5 h, 60 °C).[28] Unfortunately, this range of activities could not be correlated to NMR or crystal structure data and thus suggested that there was a complex relationship between catalyst electronic structure, catalyst activity, and complex stability. As expected from earlier work, all complexes containing an imidazolylidene ligand (**11−15**) were much more active and they all effectively initiated the ROMP of COD at 60 °C and afforded high yields of polymer. Complex **13** appeared to have the highest activity, as a quantitative
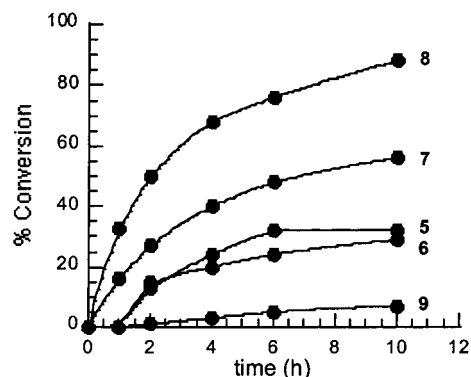
Figure 10. RCM of diethyl diallylmalonate (100 mM) at 60 °C using Ru Fischer-type carbenes **5−9** (3 mM).
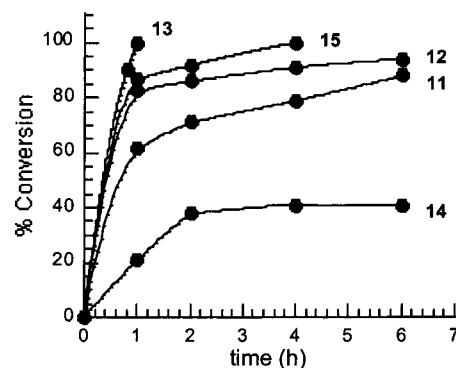
Figure 11. RCM of diethyl diallylmalonate (100 mM) at 60 °C using Ru Fischer-type carbenes **11−15** (3 mM).

yield of PBD was obtained in less than 4 h at room temperature.[29]

Measurement of the Activity of Ru Electron Rich Carbene Complexes in Ring-Closing Metathesis (RCM). A 100 mM solution of diethyl diallylmalonate was added to 3 mM solutions of Ru complexes **5−9** and **11−15** and 50 mM 1,3,5-trimethoxybenzene (internal standard), and then these mixtures were heated to 60 °C. Reaction progress was monitored by ^{1}H NMR spectroscopy and summarized in Figure 10 (complexes **5−9**) and Figure 11 (complexes **11−15**). Interestingly, all Ru Fischer-type complexes afforded the ring-closed product. However, the rates of the reaction were highly dependent on the α-heteroatom. Collectively, the rates of ROMP and RCM suggest that relative activities of $L(PCy_3)Cl_2Ru=C(H)ER$ complexes follow the general trend E = C > N > S > O. As expected, complexes ligated with IMes or H_2IMes display higher activities than their bis(phosphine) analogues.

Reaction of Ru-Functionalized Carbene Complexes with Functionalized Olefins. As discussed above, the activity of Ru Fischer-type carbene complexes appeared to heavily depend on the α-heteroatom of the carbene moiety. To help elucidate the source of the activity difference and possibly establish relative stabilities of the various complexes, the reactivities of the Ru carbenes described above with various functionalized olefins (Scheme 1) was examined.

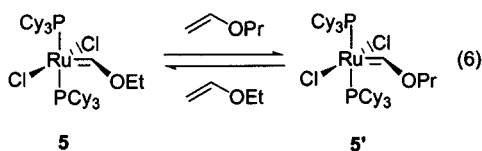(27) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.

(28) More concentrated conditions, addition of 0.01 M complex **8** to 0.22 M COD, led to 80% conversion at 65 °C in 10 h.

(29) Furthermore, More concentrated conditions, addition of 0.01 M complex **13** to 0.22 M COD, also led to complete conversion at room temperature in less than 1 h.

Scheme 1

Scheme 2
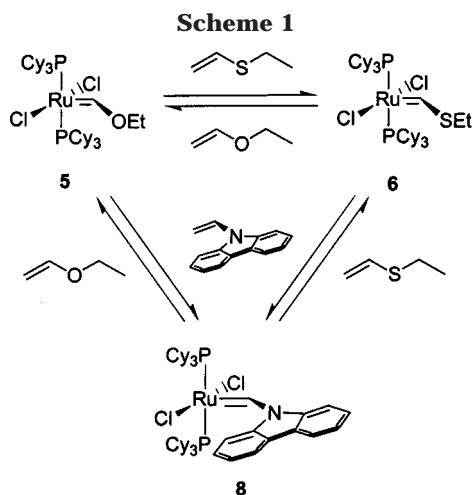
Complex **5** ([Ru]=C(H)OEt) reacted with a stoichiometric amount of ethyl vinyl sulfide. After 6 h at 60 °C, a 1:1.2 mixture of **5** and **6** ([Ru]=C(H)SEt) was observed. Similarly, the addition of an equivalent amount of ethyl vinyl ether to **6** afforded the identical 1:1.2 mixture of **5** and **6**. While no reaction was observed between complexes **5** and **6** and vinylcarbazole, the addition of a stoichiometric amount of ethyl vinyl ether to complex **8** ([Ru]=C(H)carbazole) quantitatively afforded complex **5** (and vinylcarbazole) after 6 h at 60 °C. A similar experiment with ethyl vinyl sulfide afforded **6** and vinyl carbazole over the same time period and temperature. Finally, complex **5** ([Ru]=C(H)OEt) was allowed to reacted with a stoichiometric amount of propyl vinyl ether (eq 6). In this reaction, the resulting metallocy-

clobutane intermediate would possess no (significant) electronic preference to revert to either complex **5** (ER = OEt) or **5′** (ER = OPr). Between 20 and 50 °C, complex **5′** was undetectable by ^{1}H NMR spectroscopy. However, ~10% was generated when the reaction mixture was warmed to 60 °C. Heating the reaction mixture to 80 °C led to a 1:1 mixture of **5** and **5′**, the expected ratio for a thermoneutral reaction. Collectively, these results demonstrate that the reaction of Ru-functionalized carbene complexes with functionalized olefins was an equilibrium-controlled process and that the oxygen- and sulfur-substituted complexes **5** and **6** were favored relative to the nitrogen-substituted complex **8**. In addition, the reaction between electron-rich carbene complexes and electron-rich olefins appeared to proceed with high regiospecificity, as no Ru methylidene ([Ru]=CH$_2$) was observed over the course of any of the above experiments. Likewise, the formation of difunctionalized olefins (e.g., 1,2-diethoxyethene) was also not observed.

For comparison, stoichiometric amounts of functionalized olefins were reacted with the Ru alkylidene complex [Ru]=C(H)Ph (**1a**). As shown in Scheme 2, the reaction of ethyl vinyl ether and ethyl vinyl sulfide led to complete conversion to complexes **5** and **6**, respectively, at room temperature. As expected, the addition
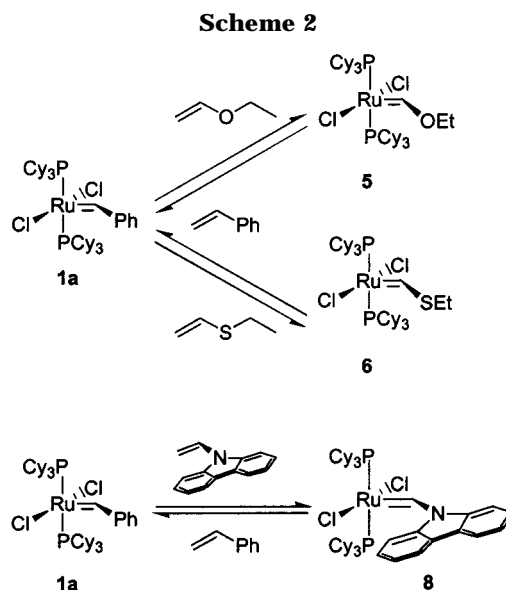
of styrene (stoichiometric or excess amounts) to **5** or **6** did not afford any Ru alkylidene species ([Ru]=CH$_2$ and [Ru]=C(H)Ph). However, the addition of styrene to complex **8** led to a 16:1 mixture of **8** and **1a** after 6 h at 60 °C and the same ratio was observed from the addition of vinylcarbazole to [Ru]=C(H)Ph (**1a**). In addition, the reactions appeared to be regiospecific, since formation of methylidene ([Ru]=CH$_2$) was not observed.

Conclusions

Ruthenium carbene complexes of the general structure (PCy$_3$)$_2$Cl$_2$Ru=C(H)ER were conveniently prepared in good yields by the addition of excess functionalized olefin H$_2$C=C(H)ER (ER = OEt, SEt, SPh, N(carbazole), N(pyrrolidinone)) to (PCy$_3$)$_2$Cl$_2$Ru=C(H)R. No methylidene byproducts ([Ru]=CH$_2$) were observed in any of these reactions. The respective mixed-ligand complexes (IMes)(PCy$_3$)Cl$_2$Ru=C(H)ER were also prepared, either through phosphine replacement with 1,3-dimesitylimidazolylidene (IMes) or 1,3-dimesityl-4,5-dihydroimidazolylidene (H$_2$IMes) or by the addition of a functionalized olefin to (L)(PCy$_3$)Cl$_2$Ru=C(H)R (L = IMes, H$_2$IMes). Although X-ray structure analyses suggested that Ru Fischer-type carbene complexes are structurally similar to typical Ru alkylidenes, the heteroatomic carbene moiety (ER) has strong effects on the chemical shifts of relevant NMR resonances. However, the effects of the moiety varied among all the complexes, and the only trend observed was an inverse relationship between the chemical shift of the α-^{1}H [Ru]=C(H)ER and the electronegativity of the heteroatom on the carbene moiety [Ru]=C(H)ER.

At equilibrium, all the Fischer-type complexes were inherently more stable than the alkylidene analogues. However, the order of thermal stability of complexes with the structure (PCy$_3$)$_2$Cl$_2$Ru=C(H)ER followed the general trend ER = NR > CR > SR > OR. In addition, complexes coordinated with an N-heterocyclic carbene ligand (e.g., (IMes)(PCy$_3$)Cl$_2$Ru=C(H)ER) were thermally more robust than their bis(phosphine) analogues. Although (PCy$_3$)$_2$Cl$_2$Ru=C(H)OEt was found to cleanly decompose to (PCy$_3$)$_2$ClRu(H)CO, multiple decomposition products (and thus pathways) were observed for the S- and N-substituted complexes.

The functionalized Ru carbene complexes ([Ru]=C(H)-ER) are active in a variety of olefin metathesis reactions, although with significantly lower rates than the corresponding carbon analogues. All the complexes initiated the ring-opening metathesis polymerization (ROMP) of strained cyclic olefins (e.g., norbornene) and the ring-closing metathesis (RCM) of diethyl diallylmalonate. In addition, $(PCy_3)_2Cl_2Ru=C(H)SPh$ and $(PCy_3)_2Cl_2Ru=C(H)NR$ type complexes initiated the ROMP of 1,5-cyclooctadiene, a monomer with low ring strain. Enhanced activities were observed when complexes coordinated with an N-heterocyclic carbene ligand (e.g., $(IMes)(PCy_3)Cl_2Ru=C(H)ER$) were employed. We also found that the carbene complexes were reactive toward a variety of functionalized olefins $CH_2=C(H)ER$ and regiospecifically (i.e., no [Ru]=CH_2 is observed) interconvert the functionalized Ru carbene complexes. The reaction appeared to be equilibrium-controlled, with the relative stability of the various complexes [Ru]=C(H)-ER being in the order ER = OR > SR > NR > CR. The lower reactivity of the Fischer carbene complexes may be related to their greater ground-state stability, since the order of metathesis activity (E = C > N > S > O) is the reverse of the equilibrium stabilities.

These results define the fundamental features that must be considered in the metathesis of electron-rich olefins. Traditionally, ROMP and other metathesis reactions have been quenched through the addition of functionalized olefins such as ethyl vinyl ether. As demonstrated, the resulting complex, [Ru]=C(H)OEt, is still metathesis active under some conditions. Low temperatures, rapid workup, and an excess of the vinyl ether minimizes the formation of byproducts. However, more importantly, the addition of sulfur- or nitrogen-functionalized olefins ($CH_2=C(H)SR$ and $CH_2=C(H)NR$) may not be effective quenching agents, as the resulting Ru complexes exhibit considerable activity. Similarly, Fischer-type carbene complexes with N-heterocyclic carbenes require additional care, as they also displayed relatively high activities.

Although the Ru complexes are reactive in the metathesis of electron-rich olefins, the degenerate nature of these reactions, i.e., no methylidenes are formed as intermediates, currently prevents the synthesis of difunctional olefins by a metathesis mechanism. Circumventing this pathway will provide an efficient method for preparing functionalized, electron-rich olefins, especially since a wide range of potential substrates, with O, N, and S atoms at the α-position, is available. It has recently been demonstrated that the electron-deficient olefins can take part in productive metathesis reactions when the catalysts contain the appropriate ligands.[8g] Thus, it is anticipated that appropriate ligand arrays will open reactions of olefins with electron-rich functionalities to metathesis as well.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere in a nitrogen-filled drybox or by using standard Schlenk techniques. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Solvents were dried over aluminum columns. NMR spectra were obtained on a GE QE 300 Plus (300.1 MHz, ^{1}H; 75.49 MHz, ^{13}C; 121.16 MHz, ^{31}P) spectrometer. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were determined by Midwest Microlab, Inc., Indianapolis, IN. HR-MS analyses were conducted by the University of California—Riverside Mass-Spectroscopy Facility.

$(PCy_3)_2Cl_2Ru=C(H)OEt$ (5). Ethyl vinyl ether (5 mL, 50 mmol) was added to a methylene chloride (10 mL) solution of Ru alkylidene **1b** (1 g, 1.2 mmol). After the reaction mixture was stirred at room temperature for 2 h, the solution turned from purple to red. The solvent was evaporated in vacuo, affording a red powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded $(PCy_3)_2Cl_2Ru=C(H)OEt$ (**5**) as bright red crystals in 66% yield (626 mg). ^{1}H NMR (CD_2Cl_2): δ 14.49 (s, 1H), 4.30 (dd, $J_1 = 14.3$ Hz, $J_2 = 6.9$ Hz, 2H), 2.66−2.58 (m, 6H), 1.94−1.90 (m, 12H), 1.79−1.70 (m, 19H), 1.58−1.47 (m, 13H), 1.34 (t, $J = 7.3$ Hz, 3H), 1.28−1.23 (m, 16H). ^{13}C NMR (CD_2Cl_2): δ 276.9, 77.6, 32.3, 30.1, 28.5, 27.2, 15.3. ^{31}P NMR (CD_2Cl_2): δ 37.4 (s). IR (KBr, cm^{-1}): 2933 (vs), 2847 (s), 1444 (s), 1391 (w), 1368 (w), 1306 (m), 1266 (w), 1194 (s), 1174 (m), 1128 (w), 1104 (m), 1013 (m), 916 (w), 889 (w), 853 (m), 816 (w), 732 (m), 518 (w), 488 (w). Anal. Calcd for $C_{39}H_{72}Cl_2RuOP_2$: C, 59.23; H, 9.18. Found: C, 59.27; H, 9.32. HR-MS calcd: 790.3472; found: [M$^+$]=790.3479.

$(PCy_3)_2Cl_2Ru=C(H)SEt$ (6). Ethyl vinyl sulfide (5 mL, 49 mmol) was added to a methylene chloride (10 mL) solution of Ru alkylidene **1b** (1.3 g, 1.6 mmol). The reaction was stirred at room temperature for 5 h during which the solution turned from purple to red-violet. The solvent was evaporated under dynamic vacuum and afforded a red-violet powder. Recrystallization by slowly diffusing of pentane into a saturated toluene solution at −30 °C afforded $(PCy_3)_2Cl_2Ru=C(H)SEt$ (**6**) as bright red crystals in 71% yield (917 mg). ^{1}H NMR (CD_2Cl_2): δ 17.67 (s, 1H), 3.17 (dd, $J_1 = 15.0$ Hz, $J_2 = 7.7$ Hz, 2H), 2.65−2.56 (m, 6H), 1.94−1.89 (m, 10H), 1.78−1.70 (m, 18H), 1.58−1.46 (m, 12H), 1.34 (t, $J = 7.7$ Hz, 3H), 1.31−1.25 (m, 20H). ^{13}C NMR (CD_2Cl_2): δ 281.6, 37.5, 32.6 (psuedo t, $J = 8.3$ Hz), 30.0, 28.15 (pseudo t, $J = 5.2$ Hz), 26.9, 15.0. ^{31}P NMR (CD_2Cl_2): δ 32.9 (s). IR (KBr, cm^{-1}): 2925 (vs), 2848 (s), 1445 (s), 1373 (w), 1343 (w), 1326 (w), 1298 (w), 1264 (m), 1232 (w), 1194 (m), 1172 (m), 1150 (m), 1130 (w), 1112 (w), 1072 (w), 1050 (w), 1004 (s), 970 (w), 914 (w), 895 (w), 846 (s), 816 (w), 731 (s), 516 (m), 506 (m), 488 (w), 472 (w), 461 (w). Anal. Calcd for $C_{39}H_{72}Cl_2RuSP_2$: C, 58.05; H, 8.99. Found: C, 58.32; H, 8.69.

$(PCy_3)_2Cl_2Ru=C(H)SPh$ (7). Phenyl vinyl sulfide (1 mL, 7.6 mmol) was added to a methylene chloride solution (10 mL) of Ru alkylidene **1b** (1.0 g, 1.3 mmol). The reaction mixture was stirred at room temperature for 5 h, during which time the solution turned from purple to red-violet. The solvent was evaporated under dynamic vacuum, affording a red-violet powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded $(PCy_3)_2Cl_2Ru=C(H)SPh$ (**7**) as dark maroon crystals in 87% yield (967 mg). ^{1}H NMR (CD_2Cl_2): δ 17.79 (s, 1H), 7.45−7.36 (m, 5H), 2.68−2.59 (m, 6H), 1.96−1.92 (m, 10H), 1.78−1.71 (m, 18H), 1.57−1.49 (m, 12H), 1.33−1.24 (m, 20H). ^{13}C NMR (CD_2Cl_2): δ 280.4 (t, $J = 76.6$ Hz), 141.6, 129.8, 129.6, 128.8, 32.9 (psuedo t, $J = 9.3$ Hz), 30.3, 28.4 (pseudo t, $J = 5.2$ Hz), 27.1. ^{31}P NMR (CD_2Cl_2): δ 33.3 (s). IR (KBr, cm^{-1}): 2926 (vs), 2849 (s), 1578 (w), 1478 (w), 1445 (s), 1327 (w), 1298 (w), 1266 (m), 1231 (w), 1197 (m), 1174 (m), 1129 (m), 1081 (w), 1024 (w), 1005 (s), 916 (w), 888 (m), 844 (s), 747 (s), 702 (m), 691 (m), 508 (s).

$(PCy_3)_2Cl_2Ru=C(H)N(carbazole)$ (8). N-Vinylcarbazole (2.4 g, 12 mmol) was added to a methylene chloride (10 mL) solution of Ru alkylidene **1b** (1 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 2 h, during which time the solution turned from purple to deep violet. The solvent was evaporated under dynamic vacuum, affording a violet powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded $(PCy_3)_2Cl_2Ru=C(H)N(carbazole)$ (**8**) as violet crystals in 77% yield (843 mg).

¹H NMR (C₆D₆): δ 17.59 (s, 1H), 8.94 (d, $J = 8.4$ Hz, 2H), 7.65 (dd, $J_1 = 7.7$ Hz, $J_2 = 0.7$ Hz, 2H), 7.93 (dt, $J_1 = 7.3$ Hz, $J_2 = 1.1$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 2H), 2.98–2.90 (m, 6H), 2.01–1.96 (m, 10H), 1.59–1.45 (m, 30H), 1.30–1.07 (m, 20H). ¹³C NMR (CD₂Cl₂): δ 228.0, 140.0, 127.4, 126.539, 124.6, 119.9, 116.4, 33.0 (d, $J = 9.3$ Hz), 30.5, 28.5 (d, $J = 5.2$ Hz), 27.2. ³¹P NMR (CD₂Cl₂): δ 41.3 (s). IR (KBr, cm⁻¹): 3060 (m), 2927 (vs), 2849 (s), 2605 (m), 2498 (w), 1482 (m), 1480 (m), 1444 (s), 1363 (m), 1322 (s), 1293 (vs), 1235 (m), 1197 (m), 1164 (s), 1128 (w), 1108 (w), 1089 (m), 1032 (w), 1005 (m), 887 (m), 847 (m), 828 (m), 757 (s), 724 (m), 698 (m), 630 (m), 579 (w), 510 (m), 489 (m). Anal. Calcd for C₄₉H₇₅Cl₂RuNP₂: C, 64.53; H, 8.29; N, 1.54. Found: C, 64.64; H, 8.10; N, 1.44.

(PCy₃)₂Cl₂Ru=C(H)N(pyrrolidinone) (9). 1-Vinyl-2-pyrrolidinone (3 mL, 28 mmol) was added to a methylene chloride (10 mL) solution of Ru alkylidene **1b** (1 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated under dynamic vacuum and afforded a lavender powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded (PCy₃)₂Cl₂Ru=C(H)N(pyrrolidinone) (**9**) as lavender crystals in 86% yield (857 mg). ¹H NMR (C₆D₆): δ 16.64 (s, 1H), 4.20 (t, $J = 7.0$ Hz, 2H), 2.93–2.86 (bm, 6H), 2.14–1.90 (m, 10H), 1.91 (t, $J = 8.1$ Hz, 2H), 1.74–1.22 (m, 52H). ³¹P NMR (C₆D₆): δ 38.5 (s). IR (KBr, cm⁻¹): 2926 (vs), 2851 (s), 2606 (w), 2498 (w), 1743 (m), 1686 (m), 1446 (m), 1360 (w), 1301 (vs), 1231 (w), 1198 (w), 1160 (s), 1130 (w), 1040 (w), 1005 (m), 934 (w), 917 (w), 888 (w), 874 (w), 848 (m), 798 (m), 732 (m), 638 (w), 526 (m), 492 (w). Anal. Calcd for C₄₁H₇₃Cl₂RuNOP₂: C, 59.33; H, 8.87; N, 1.69. Found: C, 59.43; H, 8.87; N, 1.48.

(PCy₃)₂Ru(H)(Cl)(CO) (10). A benzene (5 mL) solution of complex **5** (100 mg, 0.13 mmol) was heated to 65 °C for 12 h, upon which the solution changed color from red to orange. Slowly cooling the solution to room temperature afforded yellow crystals of **10** in 69% yield (65 mg). The spectroscopic analysis of **10** was identical with that previously reported for (PCy₃)₂Ru(H)(Cl)(CO).²¹ ¹H NMR (CD₂Cl₂): δ −27.74 (t, $J = 18.3$ Hz, 1H, Ru−H). ³¹P NMR (CD₂Cl₂): δ 48.5 (d, $J = 6.9$ Hz). IR (KBr, cm⁻¹): 1906 (vs, Ru−H), 1444 (s, Ru−CO).

(IMes)(PCy₃)Cl₂Ru=C(H)OEt (11). A 25 mL Schlenk flask was charged with IMes (91 mg, 0.299 mmol), complex **5** (196 mg, 0.250 mmol), and 10 mL of benzene. The red solution was stirred at room temperature for 12 h. Evaporation of the solvent under dynamic vacuum afforded a red powder. Recrystallization by slowly diffusing methanol into a saturated benzene solution at −30 °C afforded (IMes)(PCy₃)Cl₂Ru=C(H)-OEt (**11**) as red-orange crystals in 85% yield (173 mg). ¹H NMR (CD₂Cl₂): δ 13.81 (d, $J = 0.7$ Hz, 1H), 7.00 (s, 2H), 6.98 (s, 2H), 6.95 (dd, $J_1 = 7.7$ Hz, $J_2 = 1.8$ Hz, 2H), 3.36 (dd, $J_1 = 14.3$ Hz, $J_2 = 7.3$ Hz, 2H), 2.38 (s, 6H), 2.310 (s, 6H), 2.27 (s, 6H), 1.69–1.58 (m, 16H), 1.16 (t, $J = 7.3$ Hz, 3H), 1.13–1.04 (m, 17H). ¹³C NMR (CD₂Cl₂): δ 277.5, 191.4 (d, $J = 89.1$ Hz), 139.4, 138.8, 138.1, 137.6, 137.5, 135.6, 129.6, 129.3, 129.2, 128.5, 125.6, 125.0, 124.9, 124.2, 75.5, 31.8 (d, $J = 17.6$ Hz), 29.7, 28.5 (d, $J = 9.3$ Hz), 26.9, 21.5, 21.4, 19.8 (2C), 19.0 (2C), 15.1. ³¹P NMR (CD₂Cl₂): δ 35.0 (s). IR (KBr, cm⁻¹): 2924 (vs), 2850 (s), 1893 (m), 1673 (w), 1638 (w), 1606 (w), 1542 (w), 1480 (s), 1446 (s), 1396 (m), 1370 (w), 1318 (m), 1306 (m), 1264 (m), 1190 (w), 1131 (w), 1106 (w), 1090 (w), 1076 (w), 1017 (m), 924 (w), 889 (w), 855 (m), 735 (w), 696 (w), 685 (m), 582 (w), 580 (w), 512 (w), 492 (w). HR-MS: calcd, 814.3092; found [M⁺], 814.3099.

(IMes)(PCy₃)Cl₂Ru=C(H)SEt (12). A 25 mL Schlenk flask was charged with IMes (130 mg, 0.427 mmol), complex **6** (200 mg, 0.250 mmol), and 10 mL of benzene. The resulting red-purple solution was stirred at room temperature for 3 h. Evaporation of the solvent under dynamic vacuum afforded a maroon powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded (IMes)-(PCy₃)Cl₂Ru=C(H)SEt (**12**) as maroon crystals in 66% yield (137 mg). ¹H NMR (CD₂Cl₂): δ 17.07 (s, 1H), 6.99 (s, 2H), 6.94

(s, 3H), 6.92 (s, 1H), 2.50 (q, $J_1 = 7.7$ Hz, 2H), 2.38 (s, 6H), 2.31 (s, 6H), 2.25 (s, 6H), 1.63–1.57 (m, 16H), 1.19–1.08 (m, 17H), 1.08 (t, $J = 7.7$ Hz, 3H). ¹³C NMR (CD₂Cl₂): δ 281.2, 188.2 (d, $J = 86.0$ Hz), 141.8, 139.6, 138.7, 138.1, 137.8, 137.1, 135.1, 134.7, 130.1, 129.7, 129.1, 125.0, 124.9, 124.3, 37.9, 32.3 (d, $J = 16.6$ Hz), 29.8, 28.3 (d, $J = 10.4$ Hz), 26.9, 21.5, 21.5, 19.7 (2C), 19.0 (2C), 13.9. ³¹P NMR (CD₂Cl₂): δ 27.8 (s). IR (KBr, cm⁻¹): 2919 (vs), 2843 (s), 1607 (w), 1482 (m), 1446 (s), 1386 (m), 1353 (w), 1311 (s), 1260 (s), 1228 (w), 1208 (w), 1175 (w), 1152 (m), 1124 (w), 1073 (m), 1036 (m), 1005 (m), 923 (w), 891 (w), 854 (vs), 782 (w), 734 (m), 703 (m), 595 (w), 575 (w), 512 (w), 486 (w). Anal. Calcd for C₄₂H₆₃Cl₂RuN₂SP: C, 60.71; H, 7.64; N, 3.37. Found: C, 60.54; H, 7.66; N, 3.15.

(IMes)(PCy₃)Cl₂Ru=C(H)N(carbazole) (13). Potassium *tert*-butoxide (50 mg, 0.45 mmol) and [IMes]⁺Cl⁻ (150 mg, 0.44 mmol) were added to a solution of complex **8** (200 mg, 0.23 mmol) in 10 mL of benzene. The reaction mixture was stirred at 65 °C for 3 h, during which time the solution changed color from purple to a reddish brown. The reaction mixture was then filtered through Celite and concentrated under dynamic vacuum to afford a reddish purple powder. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded (IMes)(PCy₃)Cl₂Ru=C(H)N(carbazole) (**13**) as purple crystals in 48% yield (103 mg). ¹H NMR (CD₂Cl₂): δ 16.9 (s, 1H), 7.87–7.84 (m, 2H), 7.37–7.32 (m, 4H), 7.07 (d, $J = 1.8$ Hz, 1H), 7.03 (s, 2H), 6.95 (d, $J = 1.8$ Hz, 1H), 5.74 (bs, 2H), 2.48 (s, 6H), 2.34 (s, 6H), 2.27–2.21 (m, 3H), 2.20 (bs, 6H), 1.46–1.26 (m, 12H), 0.94–0.86 (m, 18H). ¹³C NMR (CD₂Cl₂): δ 230.0, 190.4 (d, $J = 91.1$ Hz), 139.3, 138.4, 138.2, 136.9, 136.0, 135.5, 130.2, 129.7, 129.5, 129.3, 128.8, 126.5, 125.3, 125.3, 124.1, 124.1, 123.7, 119.3, 32.5 (d, $J = 16.6$ Hz), 30.0, 28.5 (d, $J = 9.8$ Hz), 26.8, 21.5, 20.8, 20.3 (2C), 18.9 (2C). ³¹P NMR (CD₂Cl₂): δ 36.9 (s). IR (KBr, cm⁻¹): 3071 (m), 2924 (vs), 2848 (s), 1606 (m), 1594 (w), 1486 (m), 1444 (s), 1395 (m), 1379 (w), 1359 (w), 1319 (s), 1287 (vs), 1259 (m), 1236 (m), 1187 (w), 1163 (m), 1088 (w), 1076 (m), 1032 (w), 1004 (w), 924 (w), 909 (w), 848 (m), 828 (m), 756 (s), 760 (m), 744 (w), 733 (m), 721 (w), 697 (m), 629 (m), 593 (w), 577 (w), 509 (w), 489 (w). Anal. Calcd for C₅₂H₆₆Cl₂RuN₃P: C, 66.72; H, 7.11; N, 4.49. Found: C, 67.01; H, 7.02; N, 4.40.

(IMes)(PCy₃)Cl₂Ru=C(H)N(pyrrolidinone) (14). A 25 mL Schlenk flask was charged with IMes (130 mg, 0.427 mmol), complex **9** (215 mg, 0.260 mmol), and 10 mL of toluene. The red-purple solution was stirred at room temperature for 3 h. Evaporation of the solvent under dynamic vacuum afforded a maroon powder. Recrystallization from a mixture of toluene and pentane afforded (IMes)(PCy₃)Cl₂Ru=C(H)N-(pyrrolidinone) (**14**) as maroon crystals in 89% yield (198 mg). ¹H NMR (C₆D₆): δ 16.12 (s, 1H), 6.91 (s, 1H), 6.84 (s, 1H), 6.80 (s, 1H), 6.52 (s, 1H), 6.20–6.19 (m, 1H), 6.13 (d, $J = 1.8$ Hz, 1H), 4.20 (q, $J = 6.6$ Hz, 1H), 3.51 (q, $J = 7.3$ Hz, 1H), 2.72 (s, 3H), 2.67–2.56 (m, 2H), 2.56 (s, 3H), 2.45 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 2.06 (s, 3H), 1.92–1.82 (m, 5H), 1.70–1.50 (bm, 12H), 1.44–1.10 (m, 18H). ¹³C NMR (C₆D₆): δ 246.8, 193.5 (d, $J = 88.5$ Hz), 167.0, 139.3, 138.9, 138.7, 138.2, 138.0, 136.4, 136.3, 131.1, 130.2, 129.9, 128.9, 125.0, 124.9, 123.7, 54.0, 32.7 (d, $J = 16.6$ Hz), 31.5, 30.8, 30.3, 29.1 (d, $J = 9.3$ Hz), 28.9 (d, $J = 10.4$ Hz), 27.3, 21.8, 21.7, 21.0, 20.7, 19.5, 19.4, 17.5. ³¹P NMR (C₆D₆): δ 34.4 (s). IR (KBr, cm⁻¹): 2925 (vs), 2851 (s), 1735 (s), 1686 (m), 1560 (w), 1542 (w), 1490 (m), 1448 (m), 1396 (w), 1365 (w), 1290 (s), 1264 (m), 1173 (s), 1076 (w), 1050 (m), 925 (w), 850 (m), 798 (w), 731 (w), 678 (w), 583 (w), 526 (w). Anal. Calcd for C₄₄H₆₄Cl₂RuN₃OP: C, 61.89; H, 7.55; N, 4.92. Found: C, 61.87; H, 7.27; N, 4.75.

(H₂IMes)(PCy₃)Cl₂Ru=C(H)OEt (15). Ethyl vinyl ether (1 mL, 10 mmol) was added to a methylene chloride (3 mL) solution of Ru alkylidene **3a** (100 mg, 0.12 mmol). The reaction mixture was then stirred at room temperature for 2 h. Evaporation of the solvent under dynamic vacuum followed by washing the residual red powder with cold pentane and cold methanol afforded (PCy₃)(IMesH₂)Cl₂Ru=C(H)OEt (**15**)

in 93% yield (91 mg). ^{1}H NMR (CD$_2$Cl$_2$): δ 13.63 (d, J = 1.1 Hz, 1H), 6.96 (s, 2H), 6.94 (s, 2H), 3.89 (m, 4H), 3.24 (dd, J_1 = 14.3 Hz, J_2 = 7.3 Hz, 2H), 2.59 (s, 6H), 2.48 (s, 6H), 2.26 (s, 6H), 1.61 (bm, 16H), 1.12 (t, J = 7.3 Hz, 3H), 1.14−1.00 (bm, 17H). ^{13}C NMR (CD$_2$Cl$_2$): δ 276.7, 220.7 (d, J = 83.9 Hz), 138.9, 138.4, 138.2, 137.7, 137.6, 135.0, 129.8, 129.4, 128.4, 75.0, 52.2, 51.9, 31.4 (d, J = 15.5 Hz), 29.4, 28.3 (d, J = 10.4 Hz), 26.7, 21.2, 21.1, 20.0 (2C), 19.0 (2C), 14.8. ^{31}P NMR (CD$_2$Cl$_2$): δ 32.6 (s). IR (KBr, cm^{-1}): 2923 (vs), 2850 (s), 1604 (w), 1479 (s), 1444 (m), 1420 (m), 1370 (w), 1309 (m), 1266 (s), 1188 (vs), 1105 (m), 1019 (s), 888 (w), 855 (m), 814 (w), 734 (w), 688 (s), 627 (w), 579 (w), 511 (w), 490 (w).

(PCy$_3$)Cl$_2$Ru=C(H)N(pyrrolidinone) (16). A Schlenk flask equipped with a stirbar was charged with complex **9** (200 mg, 0.24 mmol), CuCl (52 mg, 0.53 mmol), and 12 mL of CH$_2$Cl$_2$. The heterogeneous mixture was stirred at room temperature for 3 h. After the residual solids were filtered away, the mother liquor was concentrated to dryness and afforded a red-brown solid. Recrystallization by slowly diffusing pentane into a saturated toluene solution at −30 °C afforded 110 mg (83%

yield) of (PCy$_3$)Cl$_2$Ru=C(H)N(pyrrolidinone) (**16**). ^{1}H NMR (C$_6$D$_6$): δ 16.64 (s, 1H), 4.20 (t, J = 7.0 Hz, 2H), 2.93−2.86 (bm, 6H), 2.14−1.90 (m, 10H), 1.91 (t, J = 8.1 Hz, 2H), 1.74−1.22 (m, 52H). ^{31}P NMR (C$_6$D$_6$): δ 38.5.

Supporting Information Available: Tables of experimental data, anisotropic displacement coefficients, atomic coordinates, interatomic distances and angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.