Five-Coordinate Complex [RuHCl(CO)(PPr^i_3)$_2$] as a Precursor for the Preparation of New Cyclopentadienylruthenium Compounds Containing Unsaturated η^1-Carbon Ligands†

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The five-coordinate complex [RuHCl(CO)(PPr^i_3)$_2$] (**1**) reacts with cyclopentadiene in methanol under reflux to give [RuH(η^5-C_5H_5)(CO)(PPr^i_3)] (**2**) and [$HPPr^i_3$]Cl. The protonation of **2** in dichloromethane-d_2 leads to the dihydrogen complex [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(PPr^i_3)]-BF_4 (**3**) in equilibrium with traces of the dihydrido tautomer [RuH_2(η^5-C_5H_5)(CO)(PPr^i_3)]-BF_4 (**4**). The reaction of **2** with HBF_4·Et_2O in acetone affords the solvated complex [Ru(η^5-C_5H_5)(CO){η^1-$OC(CH_3)_2$}(PPr^i_3)]BF_4 (**5**), which reacts with CO, dimethyl acetylenedicarboxylate, and NaCl to give [Ru(η^5-C_5H_5)$(CO)_2$(PPr^i_3)]BF_4 (**6**), [Ru(η^5-C_5H_5){η^2-$C_2(CO_2CH_3)_2$}(CO)(PPr^i_3)]-BF_4 (**7**), and [Ru(η^5-C_5H_5)Cl(CO)(PPr^i_3)] (**8**), respectively. Complex **5** also reacts with alkyn-1-ols. The reaction with 1,1-diphenyl-2-propyn-1-ol leads to the allenylidene complex [Ru(η^5-C_5H_5)(C═C═CPh_2)(CO)(PPr^i_3)]BF_4 (**9**), which affords [Ru(η^5-C_5H_5){C(OH)CH═CPh_2}-(CO)(PPr^i_3)]BF_4 (**10**) by reaction with water. **10** is converted into the acyl derivative [Ru-(η^5-C_5H_5){C(O)CH═CPh_2}(CO)(PPr^i_3)] (**11**), when a CH_2Cl_2 solution of **10** is passed through an Al_2O_3 column. The structure of **11** was determined by an X-ray investigation. The reaction of **5** with 2-propyn-1-ol leads to the α,β-unsaturated hydroxycarbene complex [Ru-(η^5-C_5H_5){C(OH)CH═CH_2}(CO)(PPr^i_3)]BF_4 (**12**). Similarly to **10**, **12** is converted into [Ru-(η^5-C_5H_5){C(O)CH═CH_2}(CO)(PPr^i_3)] (**13**), when the solutions of **12** are passed through an Al_2O_3 column. Treatment of **5** with 1-ethynyl-1-cyclohexanol leads to a mixture of organometallic compounds including [Ru(η^5-C_5H_5){C(OH)CH═C$(CH_2)_4$$CH_2$}(CO)($PPr^i_3$)]$BF_4$ (**14**). Chromatography of the mixture affords [Ru(η^5-C_5H_5){C(O)CH═C$(CH_2)_4$$CH_2$}(CO)-($PPr^i_3$)] (**15**) and [Ru($\eta^5$-$C_5H_5$){C≡CC═$CH(CH_2)_3$$CH_2$}(CO)($PPr^i_3$)] (**16**). **9** reacts with alcohols and thiols to give [Ru(η^5-C_5H_5){C(ER)CH═CPh_2}(CO)(PPr^i_3)]BF_4 (ER = OMe (**17**), OEt (**18**), SPr^n (**21**)), which by treatment with NaOMe afford [Ru(η^5-C_5H_5){C(ER)═C═CPh_2}(CO)-(PPr^i_3)] (ER = OMe (**19**), OEt (**20**), SPr^n (**22**)). Similarly, the reaction of **9** with benzophenone imine leads to [Ru(η^5-C_5H_5){C(CH═CPh_2)═N═CPh_2}(CO)(PPr^i_3)]BF_4 (**23**), which by reaction with NaOMe gives [Ru(η^5-C_5H_5){C(N═CPh_2)═C═CPh_2}(CO)(PPr^i_3)] (**24**). The structure of **23** was also determined by an X-ray investigation. The C═N bond lengths are 1.283(9) and 1.252(9) Å, while the C−N−C angle is 149.9(6)°.

Introduction

The chemistry of transition metal complexes containing unsaturated η^1-carbon ligands has received increasing attention in recent years, owing to the possibilities offered by these compounds in organic synthesis[1] and homogeneous catalysis.[2]

Bis(phosphine)−cyclopentadienyl[3] and −indenyl[4] and chloro−phosphine−arene[5] half-sandwich ruthenium complexes containing unsaturated η^1-carbon ligands exhibit a particularly rich and interesting chemistry, which has formed one of the cornerstones in the development of organometallic chemistry. Although, it is known that

† Dedicated to Professor Juan Bertrán on the occasion of his 65th birthday.

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition-metal Chemistry*; University Science Books: Mill Valey, CA, 1987. (b) Brookhart, M.; Volpe, A. F., Jr.; Yoon, J. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: London, 1991; Vol 4.

(2) (a) Nguyen, S. B. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (c) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (d) Trost, B. M.; Martínez, J. A.; Kulawiec, R. J.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 10402. (e) Ruiz, N.; Péron, D.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 1095. (f) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(3) (a) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (b) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (c) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209. (d) Lomprey, J. R.; Selegue, J. P. *Organometallics* **1993**, *12*, 616. (e) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030. (f) de los Ríos, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1757.

(4) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1994**, *13*, 745. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2495.

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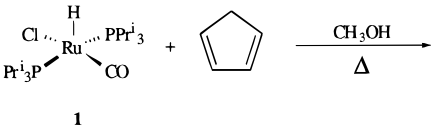
the electron density on the metallic center determines the reactivity of the unsaturated η^1-carbon ligands,[6] and starting complexes of the types $[Ru(\eta^5\text{-}C_5H_5)Cl(CO)(PR_3)]$[7] and $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(CO)(PR_3)]^+$ [8] can be easily prepared, surprisingly, the chemistry of the less basic carbonyl−phosphine−cyclopentadienyl−ruthenium systems has rarely been investigated.[9]

We have previously reported that the treatment of $RuCl_3 \cdot xH_2O$ with triisopropylphosphine in refluxing methanol leads to the five-coordinate hydrido−chloro complex $[RuHCl(CO)(PPr^i_3)_2]$ in good yield.[10] This complex, which is an active and highly selective catalyst for the reduction of unsaturated organic substrates[11] and for the addition of $HSiEt_3$ to phenylacetylene,[12] has been also the master key for the development of an extensive organometallic chemistry, including alkynyl,[13] vinyl,[14] acetatovinyl,[6] carbene, vinylcarbene,[15] acetatocarbene,[6] acyl,[16] π-butadiene,[17] dihydrogen,[18] and mono- and binuclear tetrahydridoborato derivatives.[19] We have now observed that the reaction of the complex $[RuHCl(CO)(PPr^i_3)_2]$ with cyclopentadiene leads to the cyclopentadienyl complex $[RuH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$, which affords the dihydrogen derivative $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(CO)(PPr^i_3)]BF_4$ by reaction with HBF_4. Interest in the change of properties of the unsaturated η^1-carbon ligands on moving from the more basic ruthenium systems led us to prepare carbonyl−triisopropylphosphine−cyclopentadienyl complexes of ruthenium containing unsaturated η^1-carbon ligands.

Here, we report the synthesis and characterization of new allenylidene and α,β-unsaturated-hydroxycarbene, -acyl, -alkoxycarbene, -(alkylthio)carbene, -2-azaallenyl, alkoxyallenyl, (alkylthio)allenyl, and iminoallenyl derivatives containing the $Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)$ unit. In addition, the X-ray structures of the complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(O)CH{=}CPh_2\}(CO)(PPr^i_3)]$ and $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ are also reported.

Results and Discussion

1. Synthesis and Protonation of $[RuH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$ (2). Treatment of a refluxing suspension of $[RuHCl(CO)(PPr^i_3)_2]$ (**1**) in methanol with freshly distilled cyclopentadiene in a 1:22 molar ratio for 4 h gives, after filtration and solvent removal, a sticky residue. Pentane extraction of the residue and filtration to remove the salt $[HPPr^i_3]Cl$ affords a yellow solution, from which the hydrido−cyclopentadienyl complex $[RuH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$ (**2**) was isolated as a white solid in 86% yield (eq 1). The related complexes $[RuH(\eta^5\text{-}C_5H_5)(CO)(PR_3)]$ (PR_3 = PCy_3, PPh_3, PMe_2Ph, PMe_3) have been previously prepared by phosphine substitution of $[RuH(\eta^5\text{-}C_5H_5)(CO)_2]$ in overall lower yield.[8b]



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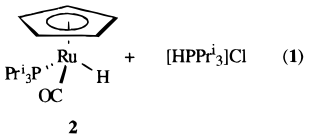

(1)

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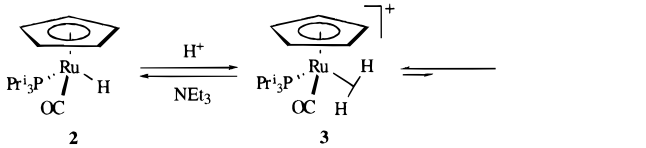
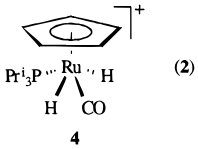
The IR spectrum of **2** in Nujol shows absorptions due to ν(RuH) at 1985 cm^{-1} and ν(CO) at 1920 cm^{-1}. The presence of the hydrido ligand is confirmed by the ^1H NMR spectrum in benzene-d_6, which contains a doublet at −12.05 ppm with a P−H coupling constant of 30.7 Hz together with the expected singlet at 4.87 ppm for the cyclopentadienyl ligand and the characteristic signals for the PPr^i_3 ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 91.6 ppm, which under off-resonance conditions is split into a doublet due to the P−H coupling.

The addition of 1 equiv of $HBF_4 \cdot OEt_2$ to a solution of **2** in dichloromethane-d_2 leads, after a few seconds, to the dihydrogen complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(CO)(PPr^i_3)]^+$ (**3**) in equilibrium with traces of the dihydrido tautomer $[RuH_2(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$ (**4**) (eq 2).[20] At room temperature, the ^1H NMR spectrum of the equilibrium



2 **3**



(2)

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(5) (a) Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163. (b) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1989**, 219. (c) Romero, A.; Vegas, A.; Dixneuf, P. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 215. (d) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (e) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (f) Lavastre, O.; Dixneuf, P. H.; Pacreau, A.; Vairon, J. P. *Organometallics* **1994**, *13*, 2500. (g) Pilette, D.; Moreau, S.; Le Bozec, H.; Dixneuf, P. H.; Corrigan, J. F.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 409. (h) Péron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319.

(6) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669.

(7) Davies, S. G.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1984**, 993.

(8) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (c) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (d) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554. (e) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* **1991**, *10*, 298. (f) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

(9) Bruce, M. I.; Duffy, D. N.; Humphrey, M. G.; Swincer, A. G. *J. Organomet. Chem.* **1985**, *282*, 383.

(10) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(11) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (b) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43.

(12) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377.

(13) (a) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187. (b) Bohanna, C.; Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1995**, *498*, 199.

(14) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(15) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258.

(16) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.

(17) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *Organometallics* **1995**, *14*, 4825.

(18) Buil, M. L.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *J. Am. Chem. Soc.* **1995**, *117*, 3619.

(19) (a) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (b) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* **1992**, *31*, 5580.

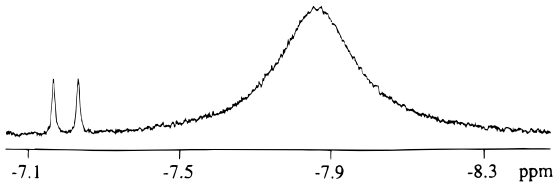


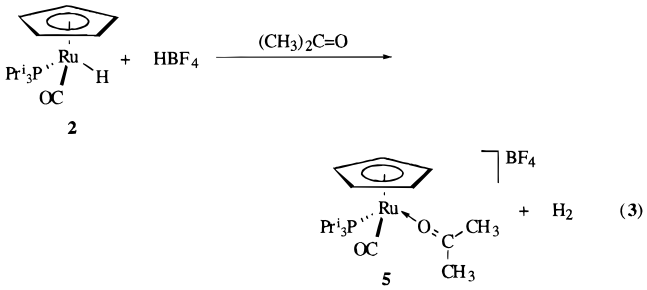
Figure 1. ^{1}H NMR spectrum (300 MHz, 293 K, CD_2Cl_2) in the hydride region for the mixture of [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(PPr$^i_3$)]BF_4 (**3**) and [RuH_2(η^5-C_5H_5)(CO)(PPr$^i_3$)] (**4**).

mixture shows, in the hydrido region (Figure 1), a very broad resonance centered at −7.95 ppm ($\omega_{1/2}$ = 75 Hz) for the dihydrogen ligand and a doublet at −7.17 ppm with a P−H coupling constant of 19.8 Hz for the dihydrido tautomer. T_1 measurements for the broad resonance at 300 MHz gave a value of 34 ms at 253 K which decreases to 6 ms at 193 K. The reaction is reversible, and **2** may be regenerated by addition of the stoichiometric amount of triethylamine, suggesting that the pK_a of **3** is lower than the pK_a of $HNEt_3^+$.

In methanol-d_4 as solvent, deuteration of the hydrido of **2** is observed. The protonation in chloroform-d_1 of the deuterated complex **2** yields the partial deuterated dihydrogen derivative **3**, which shows a H−D coupling constant of 28.5 Hz at 213 K in good agreement with those previously reported for related compounds.[8b] The related iron complexes [Fe(η^5-C_5H_5)(η^2-H_2)(CO)(L)]$^+$ have been recently reported. They react with silanes to generate [Fe(η^5-C_5H_5)(η^2-HSiR_3)(CO)(L)]$^+$ (L = PEt_3, PPh_3).[8f]

There is a marked difference toward protonation between **2** and the related osmium complex [OsH(η^5-C_5H_5)(CO)(PPr$^i_3$)]. We have previously observed that the reaction of the osmium compound with the stoichiometric amount of HBF_4·OEt_2 exclusively leads to the dihydrido derivative [OsH_2(η^5-C_5H_5)(CO)(PPr$^i_3$)]BF_4.[21] In this context, it should be noted that ruthenium is a poorer π-back-bonder than osmium, because the osmium valence orbitals have better overlap with ligand orbitals.[22] Therefore, the dihydrido tautomers are more favored with osmium than with ruthenium.

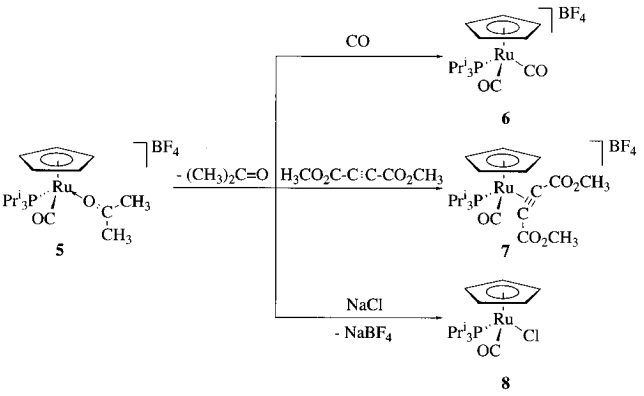
The protonation of **2** with HBF_4·OEt_2 in acetone leads to the solvated complex [Ru(η^5-C_5H_5){η^1-OC(CH_3)$_2$}(CO)(PPr$^i_3$)]BF_4 (**5**) (eq 3), which was isolated as an orange solid in 99% yield.



(3)

The IR spectrum of **5** in Nujol shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at

Scheme 1



1053 cm^{-1}, along with the ν(CO) band of the carbonyl group of the acetone ligand at 1652 cm^{-1}. This value suggests that the acetone molecule coordinates to the ruthenium atom by the oxygen atom.[23] In agreement with this, the ^{13}C{^{1}H} NMR spectrum contains a singlet at 230.4 ppm for the carbon atom of the carbonyl group of the acetone.

The acetone ligand of **5** is easily displaced by strong π-acceptor ligands such as carbon monoxide and dimethyl acetylenedicarboxylate and by chloride (Scheme 1). By passage of a slow stream of carbon monoxide through a dichloromethane solution of **5**, the dicarbonyl complex **6** is formed (Scheme 1). Similarly, treatment of **5** with dimethyl acetylenedicarboxylate affords **7**, and the addition of sodium chloride to a methanol solution of **5** leads to **8**.

The presence of the π-alkyne ligand in **7** is inferred by the IR and ^{13}C{^{1}H} NMR spectra. The IR spectrum in Nujol shows a strong absorption at 1869 cm^{-1}, which is characteristic of the ν(C≡C) vibration,[24] while in the ^{13}C{^{1}H} NMR spectrum the acetylenic carbon atoms appear at 73.4 and 72.5 ppm as broad resonances.

2. Reactions of [Ru(η^5-C_5H_5)(CO){η^1-OC(CH_3)$_2$}(PPr$^i_3$)]BF_4 (5) with Alkyn-1-ols. The investigation aimed at elucidating the reactivity of **5** toward alkyn-1-ols is summarized in Scheme 2.

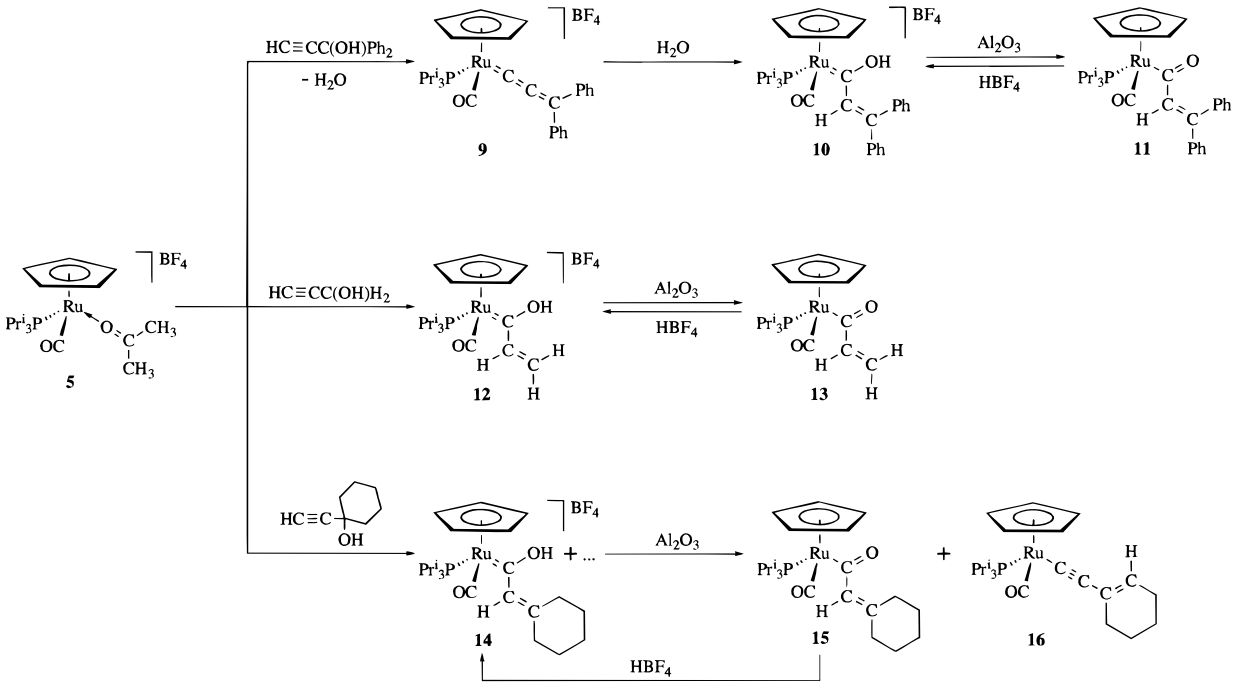
Treatment of a dichloromethane solution of **5** with a stoichiometric amount of 1,1-diphenyl-2-propyn-1-ol leads to a red solution, from which the allenylidene complex **9** can be isolated as a dark red solid in 87%. The IR spectrum of **9** in Nujol shows the characteristic ν(C=C=C) band of the allenylidene ligand[25] at 2002 cm^{-1}. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances of this ligand are two doublets at 288.3 and 188.5 ppm with P−C coupling constants of 13.8 and 2.3 Hz, which were assigned to the C_α and C_β carbon atoms, respectively, and a singlet at 164.4 ppm due to the C_γ carbon atom.

The allenylidene complex **9** reacts with an excess of water to give the α,β-unsaturated hydroxycarbene **10**, which was isolated as a yellow solid in 78% yield. The IR spectrum of **10** in Nujol contains a resonance at about 3050 cm^{-1}, characteristic of a ν(OH) absorption, along with a ν(C=C) band at 1560 cm^{-1} and absorptions due to $[BF_4]^-$ at 1093, 1032, and 976 cm^{-1}. The splitting of

(20) The *trans* disposition of the hydrido ligands of **4** is proposed on the basis of the single doublet observed in the ^{1}H NMR spectrum. An alternative *cisoid* dihydrido structure should give rise to two hydrido resonances.

(21) Esteruelas, M. A.; Gómez, A. V.; López A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878.
(22) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.
(23) Atencio, R.; Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1995**, 2171.
(24) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1995**, *14*, 263.
(25) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

Scheme 2



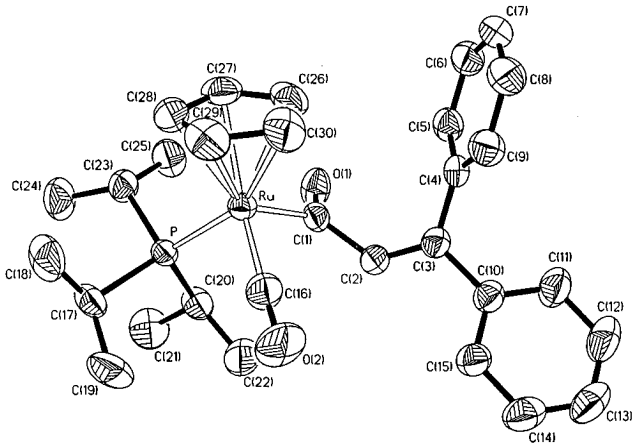


Figure 2. Molecular diagram of complex [Ru(η^5-C_5H_5)-{C(O)CH=CPh_2}(CO)(PPr^i_3)] (**11**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Ru(η^5-C_5H_5){C(O)CH=CPh_2}(CO)(PPr^i_3)] (11)

Ru−P	2.3288(9)	Ru−C(30)	2.258(5)
Ru−C(1)	2.060(2)	O(1)−C(1)	1.212(3)
Ru−C(16)	1.836(3)	C(1)−C(2)	1.502(3)
Ru−C(26)	2.266(4)	C(2)−C(3)	1.333(4)
Ru−C(27)	2.275(3)	C(3)−C(4)	1.487(4)
Ru−C(28)	2.298(3)	C(3)−C(10)	1.497(3)
Ru−C(29)	2.305(4)	O(2)−C(16)	1.152(3)
P−Ru−C(1)	91.82(8)	Ru−C(1)−C(2)	116.1(2)
P−Ru−C(16)	93.8(1)	O(1)−C(1)−C(2)	119.6(2)
P−Ru−G(1)[a]	126.5(1)	C(1)−C(2)−C(3)	129.2(2)
C(1)−Ru−C(16)	92.6(1)	C(2)−C(3)−C(4)	123.2(2)
C(1)−Ru−G(1)[a]	117.1(1)	C(2)−C(3)−C(10)	120.0(2)
C(16)−Ru−G(1)[a]	125.8(1)	C(4)−C(3)−C(10)	116.8(2)
Ru−C(1)−O(1)	123.9(2)		

[a] G(1) is the midpoint of the C(26)−C(30) Cp ligand.

the T_d symmetry of the anion suggests that it interacts with the OH group of the hydroxycarbene ligand. The presence of the hydroxycarbene is also supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum shows a singlet at 7.09 ppm due to the C*H*= proton and a broad resonance at 12.8 ppm corresponding to the −O*H* proton. In the $^{13}C\{^1H\}$ NMR spectrum, the Ru=*C*(OH) carbon atom of the unsaturated η^1-carbon ligand appears as a doublet at 298.7 ppm with a P−C coupling constant of 9.8 Hz, while the *C*H= and *C*Ph_2 carbon atoms of the alkenyl group were observed as singlets at 140.0 and 145.3 ppm, respectively.

When a dichloromethane solution of **10** was passed through an Al_2O_3 (neutral, activity grade V) column, the α,β-unsaturated acyl derivative **11** was formed. This complex was isolated as a white solid in 85% yield and characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction.

A view of the molecular geometry of **11** is shown in Figure 2. Selected bond distances and angles are listed in Table 1. The geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, carbonyl, and alkenylacyl ligands are all close to 90°. The most interesting features of the structure are those related to the α,β-unsaturated acyl ligand. The Ru−C(1) bond length of 2.060(2) Å is similar to those found in the complexes [PPN][$Ru_6C(CO)_{16}${C(O)Me}] (2.099(12) Å)[26] and [Ru-{C(O)Me}I$(CO)_2$(Pr^i-DAB)] (2.078(8) Å)[27] and about 0.1 Å longer than that found in the five-coordinate derivative [Ru{C(O)Me}Cl(CO)(PPr^i_3)$_2$] (1.957(6) Å).[16] The Ru−C(1)−O(1) and Ru−C(1)−C(2) angles are 123.9(2) and 116.1(2)°, and the C(1)−O(1) bond length is 1.212-(3) Å, as expected for a C=O double bond of an η^1-acyl ligand. The C(2)−C(3) (alkene) bond distance of 1.333-(4) Å is similar to those observed in the complexes [Fe-(η^5-C_5H_5){(*E*)-C(O)C(CH_2OMe)=C(Me)Ph}(CO){P-(OPh)$_3$}] (1.329(4) Å),[28] [Fe(η^5-C_5H_5){(*E*)-C(O)CH=CH-

(26) Chihara, T.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1990**, *383*, 367.

(27) Kraakman, M. J. A.; de Klerk-Engels, B.; de Lange, P. P. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 3774.

Me}(CO)(PPh$_3$)] (1.316(6) Å),[29] [Fe(η^5-C$_5$H$_5$){(*Z*)-C(O)C(Me)=C(Ph)Me}(CO){P(OPh)$_3$}] (1.332(4) Å), and [Fe(η^5-C$_5$H$_5$){(*E*)-C(O)C(Me)=C(Me)SPh}(CO){P(OPh)$_3$}] (1.327(6) and 1.314(6) Å)[30] and does not seem to be lengthened by any appreciable conjugation with the acyl group.

In agreement with the presence of an α,β-unsaturated acyl ligand in **11**, the IR spectrum in Nujol shows a ν(C=O) band at 1581 cm^{-1}, and the ^{13}C{^{1}H} NMR spectrum contains a doublet at 249.5 (J(PC) = 10.1 Hz) ppm and two singlets at 144.5 and 130.6 ppm, corresponding to Ru−*C*=O, *C*H=, and =*C*Ph$_2$ carbon atoms, respectively.

Treatment of a dichloromethane solution of **5** with the stoichiometric amount of 2-propyn-1-ol leads to a yellow solution from which the α,β-unsaturated-hydroxycarbene complex **12** was isolated as a yellow solid in 90% yield. Similarly to **10**, the IR spectrum of **12** in Nujol contains the ν(OH) and ν(C=C) absorptions of the α,β-unsaturated-hydroxycarbene ligand. The first one appears between 3400 and 3050 cm^{-1}, as a very broad band, and the second one at 1595 cm^{-1}. In addition two absorptions due to [BF$_4$]$^-$ at 1091 and 1002 cm^{-1} are also observed. The splitting of the expected T_d symmetry of the [BF$_4$]$^-$ group suggests that, in this case, the anion also interacts with the −OH group of the carbene ligand. In the ^{1}H NMR spectrum of **12** the most noticeable resonances include a double doublet at 7.24 ppm with H−H coupling constants of 17.0 and 10.7 Hz, which was assigned to the C*H*= proton, two doublets at 5.94 and 5.45 ppm with H−H coupling constants of 17.0 and 10.7 Hz, respectively, which were assigned to the =C*H*$_2$ protons, and a broad resonance at 13.1 ppm corresponding to the −O*H* proton. In the ^{13}C{^{1}H} NMR spectrum, the Ru=*C*(OH) carbon atom of the unsaturated η^1-carbon ligand gives rise to a doublet at 296.3 ppm with a P−C coupling constant of 9.9 Hz, while the olefinic carbon atoms display singlets at 150.0 and 121.2 ppm.

When a dichloromethane solution of **12** was passed through an Al$_2$O$_3$ (neutral, activity grade V) column, the α,β-unsaturated-acyl compound **13** was also formed. This complex was isolated as a yellow microcrystalline solid in 42% yield. The presence of the α,β-unsaturated-acyl ligand is supported by the IR and ^{1}H and ^{13}C{^{1}H} NMR spectra. The IR spectrum in Nujol contains two bands at 1606 and 1562 cm^{-1}, which were assigned to the ν(C=C) and ν(C=O) vibrations of the alkenylacyl ligand. In the ^{1}H NMR spectrum, the olefinic protons appear as double doublets at 6.94 (J(HH) = 16.9 and 9.7 Hz), 5.63 (J(HH) = 16.9 and 2.3 Hz), and 4.73 (J(HH) = 9.7 and 2.3 Hz) ppm. In the ^{13}C{^{1}H} NMR spectrum, the Ru−*C*=O carbon atom of the acyl ligand gives rise to a doublet at 247.2 ppm with a P−C coupling constant of 10.6 Hz, while the olefinic carbon atoms display singlets at 152.6 and 113.2 ppm.

The reaction of **5** with 1-ethynyl-1-cyclohexanol leads to a mixture of organometallic compounds. The most noticeable resonance of the ^{31}P{^{1}H} NMR spectrum of the mixture is a singlet at 66.7 ppm, corresponding to the α,β-unsaturated-hydroxycarbene complex **14** (vide infra). In agreement with the presence of **14** in the mixture, the acyl derivative **15** was separated as main product (60%) from this, by column chromatography (Al$_2$O$_3$ neutral, activity grade V). In addition, the α,β-unsaturated-alkynyl complex **16** was also obtained in a 5% yield.

Complex **15** was isolated as a yellow solid an characterized by elemental analysis and IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy. In the IR spectrum in Nujol, the most noticeable absorptions are those corresponding to the ν(C=O) and ν(C=C) vibrations of the alkenylacyl ligand, which appear at 1557 and 1612 cm^{-1}, respectively. In the ^{1}H NMR spectrum, the presence of the acyl ligand is mainly supported by a singlet at 6.85 ppm and in the ^{13}C{^{1}H} NMR spectrum by a doublet at 247.8 ppm with a P−C coupling constant of 9.6 Hz (Ru−*C*=O) and two singlets at 141.0 (*C*H=) and 137.7 (=*C*Ph$_2$) ppm.

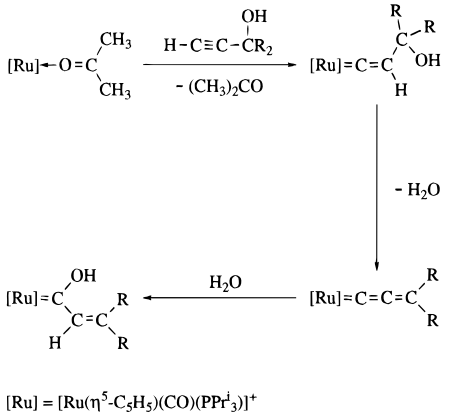
The alkynyl complex **16** was isolated as a white solid. The presence of an alkynyl ligand in this complex was inferred from its IR and ^{13}C{^{1}H} NMR spectra. Thus, the IR spectrum contains bands at 2088 and 1618 cm^{-1}, characteristic of the ν(C≡C) and ν(C=C) vibrations of an α,β-unsaturated-alkynyl group. In the ^{13}C{^{1}H} NMR spectrum, the carbon atoms of the alkynyl fragment appear as doublets at 92.4 (Ru−*C*≡) and 126.1 (≡*C*−) ppm, with P−C coupling constants of 23.0 and 0.9 Hz, respectively, while the olefinic carbon atoms display singlets at 113.3 (*C*=) and 125.2 (*C*H=) ppm.

The acyl complexes **11**, **13**, and **15** react with the stoichiometric amount of HBF$_4$·OEt$_2$ to afford the corresponding hydroxycarbene derivatives **10**, **12**, and **14**. By this procedure complex **14** was obtained as an analytically pure yellow solid in 84% yield. As for **10** and **12**, the IR spectrum of **14** shows ν(OH) and ν(C=C) vibrations, at 3331 and 1586 cm^{-1}, respectively, along with two bands due to [BF$_4$]$^-$ at 1094 and 968 cm^{-1}, suggesting that, also in this case, the anion interacts with the −OH group. The ^{1}H NMR spectrum of **14** shows the −O*H* resonance, at 13.2 ppm, and a singlet at 6.94 ppm, due to the C*H*= proton. In the ^{13}C{^{1}H} NMR spectrum, the Ru=*C*(OH) carbon atom appears at 295.6 ppm as a doublet, with a P−C coupling constant of 8.7 Hz. The olefinic *C*H= and =*C*Ph$_2$ carbons give rise to singlets at 138.6 and 155.3 ppm, respectively. As has been previously mentioned, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 66.7 ppm.

On the basis of the reaction of **5** with 1,1-diphenyl-2-propyn-1-ol to give **9**, and the reaction of the allenylidene complex **9** with water to afford **10**, the formation of **12** and **14** from **5** and the corresponding alkyn-1-ols can be rationalized according to Scheme 3. It is well-known that the addition of terminal alkynes to solvated complexes and coordinatively unsaturated metallic fragments leads to vinylidene derivatives through π-alkyne intermediates.[25] The dehydration of hydroxyvinylidenes, containing hydrogen atoms adjacent to the hydroxy group, can occur in two different directions to give either vinylvinylidene or allenylidene derivatives, depending on the electronic and steric properties of the metal.[31] In our case, the dehydration to the allenylidene seems to be favored, even for

(28) Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181.
(29) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C.; Jones, R. H.; Prout, K. *Tetrahedron* **1986**, *42*, 5123.
(30) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940.
(31) (a) Selegue, J. P. *Organometallics* **1982**, *1*, 217. (b) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921.

Scheme 3



1-ethynyl-1-cyclohexanol. In addition, MO calculations on the model compound $[Mn(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(CO)_2]$ have shown that the C_α and C_γ carbon atoms of allenylidene ligands are electrophilic centers, while the C_β carbon atom is nucleophilic.[32] According to this, the addition of water to allenylidene intermediates affords the α,β-unsaturated hydroxycarbene derivatives **12** and **14**.

Hydroxycarbene complexes have been previously proposed as reaction intermediates in the transformation, in the presence of water, of cationic vinylidene compounds into alkyl−carbonyl derivatives.[33] The reactions of alkyn-1-ols with metallic fragments to give α,β-unsaturated hydroxycarbene compounds have no precedent. As has been above mentioned, the formation of these complexes suggests that the dehydration of the hydroxyvinylidene intermediates leads to allenylidenes, although small amounts of a vinylvinylidene complex can be formed from the reaction of **5** with 1-ethynyl-1-cyclohexanol, as it is supported by the isolation of the alkynyl complex **16**. This compound is most probably the result of the deprotonation of a vinylvinylidene complex in the chromatography column. Dixneuf has closely studied related reactions of alkynols with $[RuCl_2(\eta^6\text{-}C_6H_6)(PMe_3)]$ in $MeOH/NH_4PF_6$. In agreement with the results collected in Scheme 2, for 1,1-diphenyl-2-propyn-1-ol, the allenylidene complex $[RuCl(\eta^6\text{-}C_6H_6)\{C{=}C{=}CPh_2\}(PMe_3)]PF_6$ was isolated, whereas for 1,1-dimethyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol, the α,β-unsaturated methoxycarbene compounds $[RuCl(\eta^6\text{-}C_6H_6)\{C(OMe)CH{=}CR_2\}(PMe_3)]PF_6$ (R = Me, $R_2 = C_5H_{10}$) were obtained exclusively, via allenylidene intermediates.[5] On the other hand, the behavior of the $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$ fragment contrasts with that previously observed for the related osmium fragment $[Os(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$, which reacts with 1-ethynyl-1-cyclohexanol to afford the vinylvinylidene $[Os(\eta^5\text{-}C_5H_5)\{C{=}C(H)\overline{C{=}CH(CH_2)_3CH_2}\}(CO)(PPr^i_3)]^+$ in 78% yield.[21] Vinylvinylidene products are also obtained exclusively from reactions of the rich-electron fragment $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$ with alkyn-1-ols containing hydrogen atoms adjacent to the hydroxy group.[3b]

3. Reactions of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (9). The allenylidene complex **9** reacts not only with water but also with alcohols, thiols, and benzophenone imine (Scheme 4). In methanol and ethanol as solvents, the allenylidene complex **9** evolves to the α,β-unsaturated-alkoxycarbene derivatives **17** and **18**, respectively, which were isolated as yellow solids in high yields (about 85%).

The presence of α,β-unsaturated-alkoxycarbene ligands in these compounds is inferred from their ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum of **17**, the unsaturated η^1-carbon ligand gives rise to two singlets at 6.47 and 4.26 ppm, which correspond to the C*H*═ and OCH_3 protons, respectively, while, in the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable signals are two broad resonances at 305.0 and 136.7 ppm due to the Ru═*C* and *C*H═ carbon atoms and a singlet at 66.8 ppm, which was assigned to the carbon atom of the methoxy group. In the ^1H NMR spectrum of **18**, the alkoxycarbene ligand displays a singlet at 6.56 ppm (C*H*═), a quartet at 4.73 ppm (OCH_2), and a triplet at 1.52 ppm (CH_3), while, in the $^{13}C\{^1H\}$ NMR spectrum, the Ru═*C* and *C*H═ carbon atoms appear at 303.8 and 137.0 ppm, as broad resonances, and the carbon atoms of the ethoxy group are observed at 77.2 (OCH_2) and 14.6 (CH_3) ppm, as singlets.

The reactivity previously reported toward methanol and ethanol of the allenylidene ligands bonded to ruthenium(II) fragments depends upon the remaining ligands of the complexes. Thus, in agreement with the behavior of **9**, the allenylidene ligands of compounds of the type $[RuCl(\eta^6\text{-arene})\{C{=}C{=}CR_2\}(PR_3)]^+$ add alcohols at the C_α and C_β atoms to afford α,β-unsaturated-alkoxycarbene derivatives,[5g] whereas the cumulene ligands stabilized by the electron-rich fragments $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$,[31a] $[RuCl(dppm)_2]^+$ (dppm = bis(diphenylphosphino)methane),[34] $[RuCl(NP_3)]^+$ (NP_3 = $N(CH_2CH_2PPh_2)$,[35] and $[Ru(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = 2 PPh_3, dppm, dppe)[4b] are inert. This suggest that the electronic nature of unit $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$ is similar to that of the fragments $[RuCl(\eta^6\text{-arene})(PR_3)]^+$.

Treatment of **17** and **18** with sodium methoxide in tetrahydrofuran produces the deprotonation of the olefinic groups of the alkoxycarbene ligands to give the allenyl derivatives **19** and **20** (Scheme 4). Complex **19** was isolated as a pale yellow solid in 80% yield, and complex **20** as a yellow oil in 93% yield. Characteristic spectroscopic features of **19** and **20** are the C═C═C stretching frequency in the IR spectra at 1871 (**19**) and 1890 (**20**) cm^{-1} and the three resonances in the $^{13}C\{^1H\}$ NMR spectra at 197.8 (s), 138.1 (d, $J(PC) = 13.6$ Hz), and 107.7 (s) (**19**) and 197.6 (s), 135.7 (d, $J(PC) = 13.3$ Hz), and 106.6 (s) (**20**) ppm for the C_β, C_α, and C_γ allenyl carbon atoms, respectively.

There are a variety of η^1-allenyl transition-metal compounds known, but most of them have been prepared by oxidative addition of propargyl or allenyl halides to electron-rich metal precursors.[36] Recently, Werner has observed that the alkynyl(hydrido)osmium complexes $[OsHCl\{C{=}CC(OH)Ph_2\}(NO)(PR_3)_2]$ react with acidic alumina to afford the allenylosmium(II) deriva-

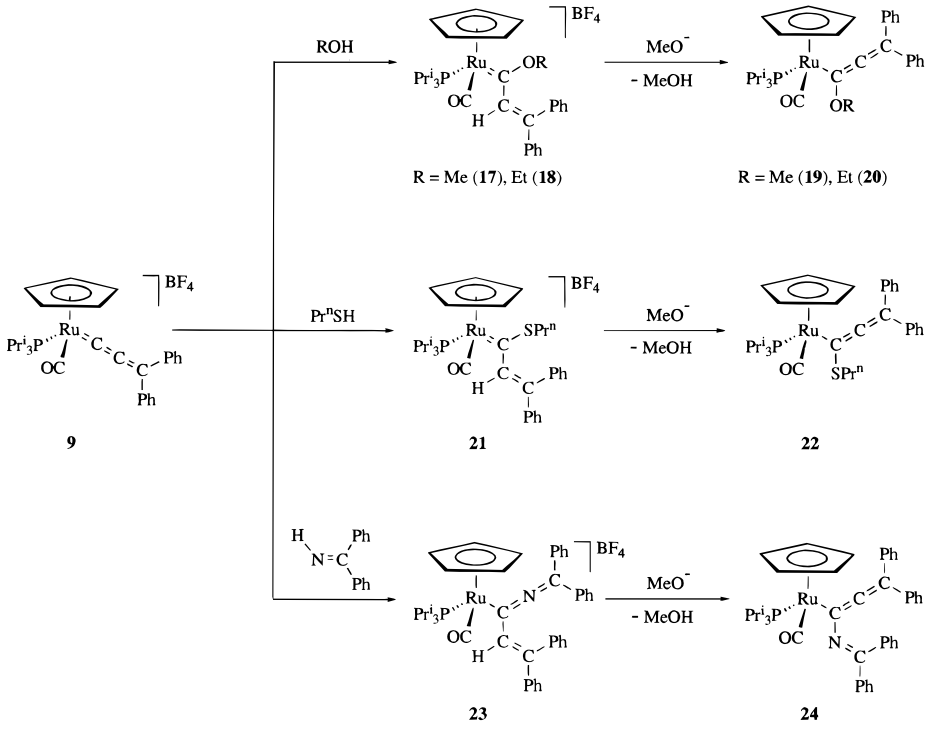
(32) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch., B* **1981**, *36*, 1277.

(33) (a) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. (b) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1992**, *430*, C39.

(34) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. J. *J. Chem. Soc., Chem. Commun.* **1991**, 980.

(35) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217.

Scheme 4

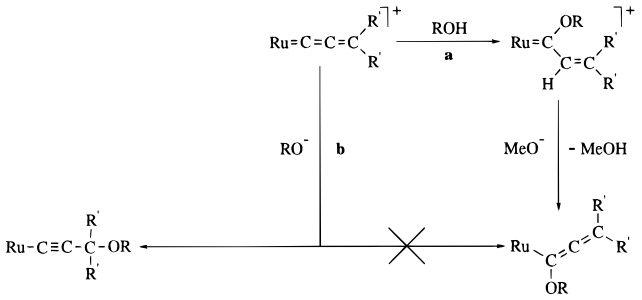


tives $[OsCl_2(CH{=}C{=}CPh_2\}(NO)(PR_3)_2]$ (PR_3 = PPr^i_3, $PPhPr^i_2$).[37] Fischer has also reported that the allenylidene complex $[Cr(CO)_5\{C{=}C{=}C(C_6H_4NMe_2\text{-}p)_2\}]$ adds phosphines at the C_α carbon atom to give ylide complexes $[Cr(CO)_5\{\eta^1\text{-}C(PR_3){=}C{=}C(C_6H_4NMe_2\text{-}p)_2\}]$ (PR_3 = PMe_3, $PHPh_2$, PH_2Mes). At room temperature, the complex $[Cr(CO)_5\{\eta^1\text{-}C(PHPh_2){=}C{=}C(C_6H_4NMe_2\text{-}p)_2\}]$ rearranges to $[Cr(CO)_5\{PPh_2[CH{=}C{=}C(C_6H_4NMe_2\text{-}p)_2]\}]$.[38]

Attempts to obtain (alkoxyallenyl)ruthenium(II) compounds by attack of alkoxy groups at the C_α carbon of an allenylidene ligand have been unsuccessful. Thus, Gimeno has found that CH_3O^- is added to the C_γ carbon atom of the allenylidene ligand of the complexes $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)L_2]PF_6$ (L_2 = 2 PPh_3, dppm, dppe).[4b] In agreement with this, we have recently observed that complex **9** reacts with CH_3O^- to afford $[Ru(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OMe)Ph_2\}(CO)(PPr^i_3)]$.[39] This seems to suggest that in order to obtain (alkoxyallenyl)-ruthenium(II) derivatives, route **a** of Scheme 5 is more useful than route **b**.

In a similar way to that shown in route **a** of Scheme 5, it is also possible to obtain (alkylthio)allenyl and iminoallenyl derivatives (Scheme 4). Treatment of a dichloromethane solution of **9** with the stoichiometric amount of 1-propanethiol leads to the α,*β*-unsaturated (alkylthio)carbene complex **21**, which reacts with sodium methoxide to afford the (alkylthio)allenyl **22**. Similarly, the reaction of **9** with benzophenone imine leads to **23**, which by reaction with sodium methoxide gives **24**.

Scheme 5



Complex **21** was isolated as an orange solid in 98% yield. In the ^{1}H NMR spectrum of **21**, the most noticeable resonances are a singlet at 6.91 ppm due to the C*H*= proton and the signals corresponding to the thiol group, which appear at 3.34 (SCH_2−), 1.76 (−CH_2−), and 1.01 (−CH_3) ppm. The ^{13}C{^{1}H} NMR spectrum shows a doublet at 311.6 ppm with a P−C coupling constant of 6.8 Hz assigned to the Ru=*C* carbon atom and two singlets at 142.9 and 138.1 due to the *C*H= and =*C*Ph$_2$ carbon atoms of the olefinic group of the α,*β*-unsaturated η^1-carbon ligand.

Complex **22** was isolated as a yellow solid in a 68% yield. Characteristic spectroscopic features of **22** are the C=C=C stretching frequency in the IR spectrum at 1887 cm^{-1} and the three resonances in the ^{13}C{^{1}H} NMR spectrum at 195.9, 103.4, and 90.1 ppm for the C_β, C_γ, and C_α allenyl carbon atoms. The first and the second resonances appear as singlets, whereas the third one appears as a doublet with a P−C coupling constant of 11.3 Hz.

Complex **23** was isolated as an orange solid in 91% yield and characterized by elemental analysis, IR and

(36) (a) Jacobs, T. L. *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 2, p 334. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Chemistry*; Wiley-Interscience: New York, 1984. (c) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35. (d) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289. (e) Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185. (f) Wouters, J. M. A.; Klein, R. E.; Elsevier, C. J.; Häming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586.

(37) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612.

(38) Fischer, H.; Reindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, *490*, 221.

(39) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. Manuscript in preparation.

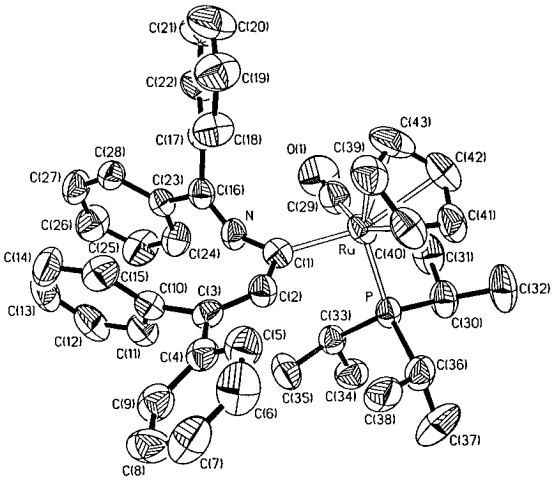


Figure 3. Molecular diagram of complex $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N{=}CPh_2\}(CO)(PPr^i{}_3)]BF_4$ (**23**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N{=}CPh_2\}(CO)(PPr^i{}_3)]BF_4$ (23)

Ru−P	2.353(2)	C(2)−C(3)	1.333(10)
Ru−C(1)	2.027(7)	C(3)−C(4)	1.485(9)
Ru−C(29)	1.834(7)	C(3)−C(10)	1.485(10)
Ru−C(39)	2.244(7)	N−C(1)	1.283(9)
Ru−C(40)	2.251(7)	N−C(16)	1.252(9)
Ru−C(41)	2.253(8)	C(16)−C(17)	1.486(8)
Ru−C(42)	2.253(7)	C(16)−C(23)	1.478(9)
Ru−C(43)	2.210(7)	O(1)−C(29)	1.136(9)
C(1)−C(2)	1.486(9)		
P−Ru−C(1)	98.1(2)	Ru−C(1)−N	123.3(5)
P−Ru−C(29)	90.8(2)	N−C(1)−C(2)	115.6(5)
P−Ru−G(1)[a]	124.2(2)	C(1)−C(2)−C(3)	129.9(6)
C(1)−Ru−C(29)	89.2(3)	C(2)−C(3)−C(4)	119.0(6)
C(1)−Ru−G(1)[a]	121.2(3)	C(2)−C(3)−C(10)	125.7(6)
C(29)−Ru−G(1)[a]	124.3(3)	C(1)−N−C(16)	149.9(6)
Ru−C(29)−O(1)	175.4(6)	N−C(16)−C(17)	118.9(6)
Ru−C(1)−C(2)	120.8(4)	N−C(16)−C(23)	120.7(6)

[a] G(1) is the midpoint of the C(39)−C(43) Cp ligand.

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction. A view of the molecular geometry is shown in Figure 3. Selected bond distances and angles are listed in Table 2. As for **11**, the geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face, and the angles formed by the triisopropylphosphine, the carbonyl group, and the unsaturated η^1-carbon ligand are close to 90°.

The unsaturated η^1-carbon ligand can be described as an α,β-unsaturated-2-azaallenyl unit. Thus, the Ru−C(1) distance (2.027(7) Å) is similar to those found in the alkenyl complexes $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PPr^i{}_3)_2]^+$ (1.967(8) Å),[6] $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHCO_2CH_3)OC(O)CH_3\}(PPh_3)]$ (2.002(2) Å),[40] $[Ru\{C(=C(CO_2CH_3)CH{=}CHC(CH_3)_3)C(O)OCH_3\}Cl(CO)(PPh_3)_2]$ (2.03(1) Å),[41] $[Ru\{(E)\text{-}CH{=}CHC_3H_7\}Cl(CO)(Me_2Hpz)(PPh_3)_2]$ (2.05(1) Å),[42] $[Ru\{(E)\text{-}CH{=}CHCMe_3\}Cl(CO)(Me_2Hpz)(PPh_3)_2]$ (2.063(7) Å),[43] and $[Ru\{(E)\text{-}CH{=}CHCMe_3\}(CO)\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]PF_6$ (2.067(8) Å)[44] and is slightly shorter than the Ru−C bond in the complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHPh)OPr^i\}(CO)(PPh_3)]$ (2.103(6) Å)[9] and $Ru\{C(=CHCO_2CH_3)CO_2CH_3\}(CO)(NCCH_3)_2(PPh_3)_2]ClO_4$ (2.12(5) Å),[45] where a Ru−C(sp^2) single bond has been also proposed. The C(1)−N distance (1.283(9) Å) is statistically identical with the N−C(16) bond length (1.252(9) Å), and they are consistent with those found in the 2-azaallenyl complexes $[Cr\{C(OEt){=}N{=}CBu^t{}_2\}(CO)_5]$ (1.272(5) and 1.264(5) Å)[46] and $[Cr\{C(Ph){=}N{=}CHPh\}(CO)_5]$ (1.260(4) and 1.265(4) Å)[47] and in organic azaallenium cations (between 1.23 and 1.33 Å).[48] The C(1)−C(2) (1.486(9) Å) and C(2)−C(3) (1.333(10) Å) distances also are in agreement with the sample mean of carbon−carbon bond lengths for single C(sp^2)−C(sp^2) (1.48(1) Å) and double C(sp^2)−C(sp^2) (1.32(1) Å) bonds.[49] In accordance with the sp^2 hybridization for C(1), the angles Ru−C(1)−C(2) and Ru−C(1)−N are 120.8(4) and 123.3(5)°, respectively. The angle C(1)−N−C(16) is 149.9(6)°, indicating that the fragment C=N=C is not strictly linear. Although the related angles in the complexes $[Cr\{C(OEt){=}N{=}C(CBu^t{}_2)_2\}(CO)_5]$ and $[Cr\{C(Ph){=}N{=}CHPh\}(CO)_5]$ are 171.7(4)[46] and 174.3(3)°,[47] close to the ideal value of 180°, angular distortions in this type of systems are not unusual. Thus, we note that for organic 2-azaallenium cations with C=N distances similar to those of **23**, the C−N−C angles are between 156 and 160°.[48d] Substituted 2-azaallenium cations are flexible, assuming conformations which are mainly determined by steric and electronic demands of substituents.[48] In addition, it should be mentioned that there seems to exist a rough linear proportionality between the C−N−C bond angle (α) and the wave number of the antisymmetric stretching vibration of this unit ($\alpha = 0.165\ \nu_{as} - 147$). Increasing the C−N−C bond angle decreases the C=N distance, enhancing the force constant for the stretching vibration.[48d] According to this, the IR spectrum of **23** in Nujol shows a ν_{as}(C=N=C) band at 1813 cm^{-1}, which gives rise to a value for the C−N−C angle of 152.0°, in good agreement with that determined by X-ray diffraction (149.9(6)°).

In solution, the presence of an α,β-unsaturated 2-azaallenyl ligand in **23** is mainly supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows a doublet due to C(1) at 207.1 (J(PC) = 9.0 Hz) ppm.

Transition metal 2-azaallenyl complexes are rare;

(40) Daniel, T.; Mahr, N.; Braun, T.; Werner, H. *Organometallics* **1993**, *12*, 1475.
(41) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413.
(42) Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 221.
(43) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988.
(44) López, J.; Santos, A.; Romero, A.; Echavarren, A. M. *J. Organomet. Chem.* **1993**, *443*, 221.
(45) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P. *J. Organomet. Chem.* **1989**, *373*, 249.
(46) Seitz, F.; Fischer, H.; Riede, J. *J. Organomet. Chem.* **1985**, *287*, 87.
(47) Aumann, R.; Althaus, S.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 357.
(48) (a) Al-Talib, M.; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365. (b) Jochims, J. C.; Abu-El-Halawa, R.; Jibril, I.; Huttner, G. *Chem. Ber.* **1984**, *117*, 1900. (c) Al-Talib, M.; Jochims, J. C. *Chem. Ber.* **1984**, *117*, 3222. (d) Al-Talib, M.; Jibril, I.; Huttner, G.; Jochims, J. C. *Chem. Ber.* **1985**, *118*, 1876. (e) Würthwein, E.-U.; Kupfer, R.; Allmann, R.; Nagel, M. *Chem. Ber.* **1985**, *118*, 3632. (f) Al-Talib, M.; Jochims, J. C.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1985**, *118*, 1887. (g) Kupfer, R.; Würthwein, E.-U.; Nagel, M.; Allmann, R. *Chem. Ber.* **1985**, *118*, 643. (h) Krestel, M.; Kupfer, R.; Allmann, R.; Würthwein, E.-U. *Chem. Ber.* **1987**, *120*, 1271.
(49) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

indeed, **23** is the only example for ruthenium. Apart from **23**, the only other 2-azaallenyl examples are the derivatives [Cr{C(Ph)=N=CR$_2$}(CO)$_5$], [Cr{C(CH$_3$)=N=CR$_2$}(CO)$_5$],[47] and [M{C(OEt)=N=CR$_2$}(CO)$_5$] (M = Cr, W).[46] Complex **23** is also significant because it is prepared from an allenylidene compound, while the complexes [Cr{C(Ph)=N=CR$_2$}(CO)$_5$] and [Cr{C(CH$_3$)=N=CR$_2$}(CO)$_5$] were obtained from aminocarbene compounds by condensation of the NH$_2$ group with organic carbonyl compounds in the presence of NEt$_3$ and POCl$_3$/NEt$_3$,[47] and the derivatives [M{C(OEt)=N=CR$_2$}(CO)$_5$] (M = Cr, W) by successive reaction of M(CO)$_6$ with Na[N=CR$_2$] and [Et$_3$O]BF$_4$.[46]

In addition, it should be pointed out that a difference in the reactivity exists between the allenylidene fragment of **9** and the vinylidene ligands of [M(η^5-C$_5$H$_5$)(=C=CHR)(CO)$_2$] (M = Mn, Re). While **9** reacts with benzophenone imine to give the 2-azaallenyl complex **23**, the reactions of the vinylidene derivatives afford iminocarbene complexes.[50]

The iminoallenyl complex **24** was isolated as a yellow solid in 92% yield. Similarly to the alkoxyallenyl (**19** and **20**) and the (alkylthio)allenyl (**22**) derivatives, the most characteristic spectroscopic features of **24** are the C=C=C stretching frequency in the IR spectrum, which is observed at 1888 cm^{-1}, and the three resonances in the ^{13}C{^{1}H} NMR spectrum at 194.7 (s), 114.9 (d, J(PC) = 12.9), and 102.3 (s) ppm for the C$_\beta$, C$_\alpha$, and C$_\gamma$ allenyl carbon atoms, respectively. Complex **24** is also significant because, as far as we know, iminoallenyl complexes have not been previously reported.

Concluding Remarks

This study has revealed that the five-coordinate complex [RuHCl(CO)(PPr$^i_3$)$_2$] is a useful starting material for the preparation of new cyclopentadienylruthenium compounds containing unsaturated η^1-carbon ligands, which includes allenylidene and α,β-unsaturated-hydroxycarbene, -acyl, -alkoxycarbene, -(alkylthio)-carbene, -2-azaallenyl, alkoxyallenyl, (alkylthio)allenyl, and iminoallenyl derivatives. Thus, it reacts with cyclopentadiene to give [RuH(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)]. Acetone solutions of this complex react with HBF$_4$·Et$_2$O to afford the solvated compound [Ru(η^5-C$_5$H$_5$)(CO){η^1-OC(CH$_3$)$_2$}(PPr$^i_3$)]BF$_4$, which is a novel precursor for the preparation of the unsaturated η^1-carbon complexes.

The chemical behavior of the fragment [Ru(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)]$^+$ has some characteristics in common with the arene systems [RuCl(η^6-arene)(PR$_3$)]$^+$ but marked differences with the chemical behavior of the related osmium fragment [Os(η^5-C$_5$H$_5$) (CO)(PPr$^i_3$)]$^+$ and the more electron-rich half-sandwich ruthenium units [Ru(η^5-C$_5$H$_5$)(PMe$_3$)$_2$]$^+$ and [Ru(η^5-C$_9$H$_7$)(PR$_3$)$_2$]$^+$. Thus, the acetone complex [Ru(η^5-C$_5$H$_5$){η^1-OC(CH$_3$)$_2$}(CO)(PPr$^i_3$)]BF$_4$ reacts with alkyn-1-ols to afford α,β-unsaturated-hydroxycarbene compounds via allenylidene intermediates, whereas, under similar experimental conditions, the fragments [Os(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)]$^+$ and [Ru(η^5-C$_5$H$_5$)(PMe$_3$)$_2$]$^+$ afford allenylidene derivatives or vinylvinylidene compounds when the alkyn-1-ols have hydrogen atoms adjacent to the hydroxy group.

The allenylidene ligand of the complex [Ru(η^5-C$_5$H$_5$)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ also shows a markedly different reactivity with that observed for the allenylidene ligands stabilized by the fragments [Ru(η^5-C$_5$H$_5$)(PMe$_3$)$_2$]$^+$ and [Ru(η^5-C$_9$H$_7$)L$_2$]$^+$ (L$_2$ = 2 PPh$_3$, dppm, dppe). While the complex [Ru(η^5-C$_5$H$_5$)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ reacts with alcohols to give α,β-unsaturated alkoxycarbene derivatives, the latter are inert.[4b,31a] The allenylidene complex [Ru(η^5-C$_5$H$_5$)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ also reacts with water, thiols, and benzophenone imine to afford α,β-unsaturated-hydroxycarbene, -alkoxycarbene, and -2-azaallenyl compounds, respectively. By deprotonation, the hydroxycarbene compounds give acyl derivatives, and the alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl complexes yield allenyl derivatives.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The reagents dimethyl acetylenedicarboxylate (Merk), 1,1-diphenyl-2-propyn-1-ol (ABCR), 2-propyn-1-ol (Aldrich), 1-ethynyl-1-cyclohexanol (Fluka), 1-propanethiol (Fluka), and benzophenone imine (Aldrich) were obtained from commercial sources, as indicated, and used without further purification. The starting material [RuHCl(CO)(PPr$^i_3$)$_2$] (**1**) was prepared by a published method.[10]

NMR spectra were recorded on either a Varian UNITY 300 or a Bruker 300 AXR spectrometer. Chemical shifts are expressed in ppm upfield from Me$_4$Si (^{1}H and ^{13}C) and 85% H$_3$PO$_4$ (^{31}P). Coupling constants, J, are given in Hz. The T_1 experiments were performed on a Varian UNITY 300 spectrophotometer with a standard 180°−τ−90° pulse sequence. IR spectra were run on a Perkin-Elmer 883 or a Nicolet 550 spectrophotometer (Nujol mulls on polyethylene sheets). Elemental analyses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Preparation of [RuH(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)] (2). An excess of freshly distilled cyclopentadiene (3 mL, 44.48 mmol) was added to a suspension of **1** (1.0 g, 2.06 mmol) in 20 mL of methanol. The mixture was stirred at reflux temperature for 4 h, undergoing a color change of orange to yellow. The solution was filtered and evaporated to dryness. The residue was treated with 20 mL of *n*-pentane, and the mixture was filtered to eliminate [HPPr$^i_3$]Cl. The yellow solution was concentrated to about 3 mL and cooled to 195 K. A cream colored solid precipitated, which was separated by decantation, washed with cold hexane, and dried in vacuo. The solid was recrystallized from methanol to give white crystals which were separated by decantation, washed with cold methanol, and dried in vacuo. Yield: 630 mg (86%). Anal. Calcd for C$_{15}$H$_{27}$OPRu: C, 50.69; H, 7.66. Found: C, 51.08; H, 7.94. IR (Nujol, cm^{-1}): ν(RuH) 1985 m, ν(CO) 1920 vs, br. ^{1}H NMR (300 MHz, 293 K, C$_6$D$_6$) δ 4.87 (s, 5H, Cp), 1.73 (m, 3H, PC*H*CH$_3$), 1.01 (dd, 9H, J(HH) = 7.1, J(PH) = 10.1, PCHC*H*$_3$), 0.96 (dd, 9H, J(HH) = 7.1, J(PH) = 9.8, PCHC*H*$_3$), −12.05 (d, 1H, J(PH) = 30.7, RuH). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C$_6$D$_6$): δ 91.6 s.

Preparation of [Ru(η^5-C$_5$H$_5$)(η^2-H$_2$)(CO)(PPr$^i_3$)]BF$_4$ (3) and [RuH$_2$(η^5-C$_5$H$_5$)(CO)(PPr$^i_3$)]BF$_4$ (4). A solution of **2** (15 mg, 0.042 mmol) in 0.5 mL of CD$_2$Cl$_2$ in an NMR tube was treated with a stoichiometric amount of tetrafluoroboric acid (5.7 μL, 0.042 mmol, 54% in diethyl ether). The NMR tube was sealed under argon and measurements initiated im-

(50) Terry, M. R.; Mercando, L. A.; Kelley, C.; Geoffroy, G. L.; Nombel, P.; Lugan, N.; Mathieu, R.; Ostrander, R. L.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.

mediately. Spectroscopic data for **3**: ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2) δ 5.67 (s, 5H, Cp), 2.40 (m, 3H, PC*H*CH_3), 1.35 (dd, 9H, J(HH) = 4.4, J(PH) = 7.1, PCHC*H*$_3$), 1.30 (dd, 9H, J(HH) = 4.7, J(PH) = 7.1, PCHC*H*$_3$), −7.95 (br, 2H, Ru(η^2-H$_2$)); T_1 (Ru(η^2-H$_2$), 300 MHz, CD_2Cl_2) = 34 ms (253 K), 22 ms (233 K), 13 ms (213 K), 6 ms (193 K); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD_2Cl_2) δ 81.4 (br). Spectroscopic data for **4**: ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2) δ 5.80 (s, 5H, Cp), −7.17 (d, 2H, J(PH) = 19.8, RuH_2); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD_2Cl_2) δ 86.7 (s).

Preparation of [RuD(η^5-C_5H_5)(CO)(PPr$^i_3$)] (2d) and [Ru(η^5-C_5H_5)(η^2-HD)(CO)(PPr$^i_3$)]BF$_4$ (3d). A solution of **2** (11 mg, 0.031 mmol) in 0.5 mL of CD_3OD in an NMR tube sealed under argon was heated at 338 K for 24 h. Spectroscopic data for **2d**: ^{1}H NMR (300 MHz, 293 K, CD_3OD) δ 4.95 (s, Cp), 1.95 (m, 3H, PC*H*CH_3), 1.06 (dd, 18H, J(HH) = 7.2, J(PH) = 13.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD_3OD) δ 91.9 (1:1:1 t, J(PD) = 4.4). The solvent was removed in vacuo, and the residue was dissolved in 0.5 mL of $CDCl_3$, followed by treatment with the stoichiometric amount of tetrafluoroboric acid (4.2 μL, 0.031 mmol, 54% in diethyl ether). The NMR tube was sealed under argon, and measurements were made immediately. Spectroscopic data for **3d**: ^{1}H NMR (300 MHz, 213 K, $CDCl_3$) δ 5.63 (s, Cp), 2.32 (m, 3H, PC*H*CH_3), 1.34 (dd, 9H, J(HH) = 4.9, J(PH) = 7.1, PCHC*H*$_3$), 1.29 (dd, 9H, J(HH) = 4.9, J(PH) = 7.1, PCHC*H*$_3$), −7.87 (1:1:1 t, 1H, ^1J(HD) = 28.5, Ru(η^2-HD); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 78.6 (br s).

Reaction of [Ru(η^5-C_5H_5)(η^2-H$_2$)(CO)(PPr$^i_3$)]BF$_4$ (3) with NEt$_3$. Addition of a stoichiometric amount of NEt_3 to a chloroform-d_1 solution of **3** in an NMR tube afforded **2** immediately, as shown by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Preparation of [Ru(η^5-C_5H_5)(CO){η^1-OC(CH$_3$)$_2$}(PPr$^i_3$)]BF$_4$ (5). A solution of **2** (600 mg, 1.69 mmol) in 5 mL of acetone was treated with tetrafluoroboric acid (253.7 μL, 1.86 mmol, 54% in diethyl ether). Immediately the color turned from pale yellow to orange, and the solution was concentrated almost to dryness. By addition of diethyl ether an orange solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 838 mg (99%). Anal. Calcd for $C_{18}H_{32}BF_4O_2PRu$: C, 43.30; H, 6.46. Found: C, 43.29; H, 6.59. IR (Nujol, cm^{-1}): ν(CO) 1958 vs, ν(C=O) 1652 s, ν(BF$_4$) 1053 vs, br. ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2) δ 5.28 (s, 5H, Cp), 2.44 (s, {η^1-OC(CH$_3$)$_2$}), 2.42 (m, 3H, PC*H*CH_3), 1.26 (dd, 9H, J(HH) = 7.1, J(PH) = 14.7, PCHC*H*$_3$), 1.24 (dd, 9H, J(HH) = 7.1, J(PH) = 13.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD_2Cl_2) δ 64.6 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$) δ 230.4 (s, {η^1-O*C*(CH$_3$)$_2$}), 203.8 (d, J(PC) = 18.4, CO), 83.7 (s, Cp), 32.7 (s, {η^1-OC(*C*H$_3$)$_2$}), 26.5 (d, J(PC) = 22.6, P*C*HCH$_3$), 19.6, (s, PCH*C*H$_3$), 19.4 (d, J(PC) = 1.0, PCH*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5)(CO)$_2$(PPr$^i_3$)]BF$_4$ (6). CO was bubbled through a stirred solution of **5** (100 mg, 0.2 mmol) in 10 mL of dichloromethane for 35 min. The color turned from orange to pale yellow, and the solution was concentrated almost to dryness. By slow addition of diethyl ether a white solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 60 mg (64%). Anal. Calcd for $C_{16}H_{26}BF_4O_2PRu$: C, 40.95; H, 5.58. Found: C, 40.92; H, 5.50. IR (Nujol, cm^{-1}): ν(CO) 2050, 1993 both vs, ν(BF$_4$) 1050 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 5.82 (s, 5H, Cp), 2.43 (m, 3H, PC*H*CH_3), 1.27 (dd, 18H, J(HH) = 7.2, J(PH) = 15.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 73.8 s. MS (FAB$^+$): m/z = 383 (M$^+$).

Preparation of [Ru(η^5-C_5H_5){η^2-C$_2$(CO$_2$CH$_3$)$_2$}(CO)(PPr$^i_3$)]BF$_4$ (7). A solution of **5** (80 mg, 0.16 mmol) in 5 mL of dichloromethane was treated with dimethyl acetylenedicarboxylate (60 μL, 0.49 mmol). Immediately the color turned from orange to yellow, and the solution was concentrated almost to dryness. By slow addition of diethyl ether a pale yellow solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 88 mg (94%). Anal. Calcd for $C_{21}H_{32}BF_4O_5PRu$: C, 43.23; H, 5.53. Found: C, 43.12; H, 5.57. IR (Nujol, cm^{-1}): ν(CO) 2025 vs, ν(C≡C) 1869 s, ν(C=O) 1717, 1705 both s, ν(C−O) 1248 s, ν(BF$_4$) 1056 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 5.91 (s, 5H, Cp), 3.96, 3.89 (both br s, 6H, CO_2CH_3), 2.52 (m, 3H, PC*H*CH_3), 1.26 (dd, 9H, J(HH) = 6.9, J(PH) = 15.4, PCHC*H*$_3$), 1.18 (dd, 9H, J(HH) = 6.9, J(PH) = 15.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 65.2 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus APT) δ 199.0 (−, d, J(PC) = 17.5, CO), 161.9, 158.2 (−, both br s, *C*O$_2$CH$_3$), 92.3 (+, s, Cp), 73.4, 72.5 (−, both br s, C≡C), 54.4, 54.3 (+, both s, CO$_2$*C*H$_3$), 28.0 (+, d, J(PC) = 24.4, P*C*HCH$_3$), 19.7 (+, s, PCH*C*H$_3$), 19.4 (+, d, J(PC) = 1.9, PCH*C*H$_3$). MS (FAB$^+$): m/z = 497 (M$^+$).

Preparation of [Ru(η^5-C_5H_5)Cl(CO)(PPr$^i_3$)] (8). A solution of **5** (300 mg, 0.60 mmol) in 5 mL of methanol was treated with NaCl (35 mg, 1.20 mmol). The solution was stirred at room temperature for 5 h, and the solvent was removed in vacuo. The residue was treated with 10 mL of dichloromethane, and the mixture was filtered to eliminate the $NaBF_4$ and excess of NaCl. The solvent was evaporated to dryness, and the residue was washed with *n*-pentane to afford a yellow solid which was dried under vacuum. Yield: 190 mg (81%). Anal. Calcd for $C_{15}H_{26}ClOPRu$: C, 46.21; H, 6.72. Found: C, 45.82; H, 6.38. IR (Nujol, cm^{-1}): ν(CO) 1927 vs, ν(RuCl) 295 s. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 5.08 (s, 5H, Cp), 2.47 (m, 3H, PC*H*CH_3), 1.27 (dd, 9H, J(HH) = 7.1, J(PH) = 14.5, PCHC*H*$_3$), 1.20 (dd, 9H, J(HH) = 7.1, J(PH) = 13.2, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 66.4 s. MS (FAB$^+$): m/z = 390 (M$^+$).

Preparation of [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ (9). A solution of **5** (100 mg, 0.20 mmol) in 5 mL of dichloromethane was treated with 1,1-diphenyl-2-propyn-1-ol (50.0 mg, 0.24 mmol). Immediately, the color turned from orange to dark red, and the solution was concentrated almost to dryness. By slow addition of diethyl ether a dark red solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 132 mg (87%). Anal. Calcd for $C_{30}H_{36}BF_4OPRu$: C, 57.06; H, 5.74. Found: C, 57.02; H, 5.65. IR (Nujol, cm^{-1}): ν(C=C=C) 2002 s, ν(CO) 1953 vs, ν(Ph) 1587 m, ν(BF$_4$) 1076 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.77 (m, 4H, *o*-Ph), 7.70 (m, 2H, *p*-Ph), 7.51 (m, 4H, *m*-Ph), 5.81 (s, 5H, Cp), 2.34 (m, 3H, PC*H*CH_3), 1.22 (dd, 9H, J(HH) = 7.1, J(PH) = 10.4, PCHC*H*$_3$), 1.17 (dd, 9H, J(HH) = 7.1, J(PH) = 9.6, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 79.8 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$) δ 288.3 (d, J(PC) = 13.8, C$_\alpha$), 199.9 (d, J(PC) = 15.2, CO), 188.5 (d, J(PC) = 2.3, C$_\beta$), 164.4 (s, C$_\gamma$), 141.7 (s, C$_{ipso}$), 133.8 (s, *p*-Ph), 132.1, 129.4 (both s, *o*-Ph, *m*-Ph), 91.4 (s, Cp), 28.8 (d, J(PC) = 25.3, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), 19.5 (d, J(PC) = 0.9, PCH*C*H$_3$). MS (FAB$^+$): m/z = 545 (M$^+$).

Preparation of [Ru(η^5-C_5H_5){C(OH)CH=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (10). Route a. A solution of **9** (150 mg, 0.24 mmol) in 5 mL of tetrahydrofuran was treated with water (120 μL, 6.67 mmol). After the solution was stirred for 2 h, the color turned from dark red to orange and the solvent was removed in vacuo. The residue was washed with diethyl ether to give a yellow solid, the solvent was decanted, and the product was dried in vacuo. Yield: 120 mg (78%).

Route b. A solution of **11** (100 mg, 0.18 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (25 μL, 0.18 mmol, 54% in diethyl ether). A yellow solid immediately precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 95 mg (82%). Anal. Calcd for $C_{30}H_{38}BF_4O_2PRu$: C, 55.47; H, 5.89. Found: C, 54.43; H, 5.63. IR (Nujol, cm^{-1}): ν(OH) 3050 br, ν(CO) 1969 vs, ν(Ph) 1580 w, ν(C=C) 1560 m, ν(C−O) 1296 s, ν(BF$_4$) 1093, 1032, 976 all vs. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 12.8 (br, 1H, OH), 7.42−7.19 (m, 10H, Ph), 7.09 (s, 1H, CH=), 5.31 (s, 5H, Cp), 2.32 (m, 3H, PC*H*CH_3), 1.28 (dd, 9H, J(HH) = 7.1, J(PH) = 15.4, PCHC*H*$_3$), 1.23 (dd, 9H, J(HH) = 7.1, J(PH) = 15.1, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 66.5 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus APT) δ 298.7 (−, d, J(PC) = 9.8, Ru=C), 202.9 (−, d, J(PC) = 15.1, CO), 145.3 (−, s,

=CPh$_2$), 140.5, 137.7 (−, both s, C$_{ipso}$), 140.0 (+, s, CH=), 130.8, 130.2, 129.8, 129.2, 129.0, 128.8 (+, all s, Ph), 90.1 (+, s, Cp), 29.3 (+, d, J(PC) = 24.5, P*C*HCH$_3$), 19.9, 19.8 (+, both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(O)CH=CPh$_2$}(CO)(PPr$^i_3$)] (11). A solution of **9** (190 mg, 0.30 mmol) in 6 mL of tetrahydrofuran was treated with water (120 μL, 6.67 mmol). After the solution was stirred for 2 h, the color turned from dark red to orange and the solvent was removed in vacuo. Chromatography of the products on a 10 cm alumina (neutral, activity grade V) column (eluent: dichloromethane/tetrahydrofuran, 15:1) afforded complex **11**. The solvent was removed in vacuo, and the white solid was washed with cold *n*-pentane and dried in vacuo. Yield: 144 mg (85%). Anal. Calcd for C$_{30}$H$_{37}$O$_2$PRu: C, 64.15; H, 5.38. Found: C, 64.42; H, 5.81. IR (Nujol, cm^{-1}): ν(CO) 1918 vs, ν(Ph) 1595 m, ν(C=O) 1581 s. ^{1}H NMR (300 MHz, 293 K, C$_6$D$_6$) δ 7.63 (m, 4H, Ph), 7.1 (m, 7H, Ph, CH=), 4.71 (s, 5H, Cp), 1.93 (m, 3H, PC*H*CH$_3$), 1.00 (dd, 9H, J(HH) = 7.1, J(PH) = 13.7, PCHC*H*$_3$), 0.87 (dd, 9H, J(HH) = 6.9, J(PH) = 12.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C$_6$D$_6$) δ 71.3 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C$_6$D$_6$, plus DEPT) δ 249.5 (C$_{quat}$, d, J(PC) = 10.1, Ru−C), 208.7 (C$_{quat}$, d, J(PC) = 18.4, CO), 144.5 (+, br s, CH=), 144.1, 140.2 (C$_{quat}$, both s, C$_{ipso}$), 131.8, 128.9, 128.5, 127.5, 127.4 (+, all s, Ph), 130.6 (C$_{quat}$, s, =CPh$_2$), 87.5 (+, s, Cp), 27.6 (+, d, J(PC) = 22.6, P*C*HCH$_3$), 19.9, 19.5 (+, both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(OH)CH=CH$_2$}(CO)(PPr$^i_3$)]BF$_4$ (12). Route a. A solution of **5** (110 mg, 0.22 mmol) in 2 mL of dichloromethane at 263 K was treated with 2-propyn-1-ol (15.4 μL, 0.26 mmol). The solution was stirred for 2 min, and the color turned from orange to yellow. The mixture was rapidly cooled to 195 K, and slow addition of diethyl ether precipitated a yellow solid. The solid was washed several times with cold diethyl ether and dried in vacuo. Yield: 99 mg (90%).

Route b. A solution of **13** (80 mg, 0.20 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (28 μL, 0.20 mmol, 54% in diethyl ether), and immediately a yellow solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 74 mg (76%). Anal. Calcd for C$_{18}$H$_{30}$BF$_4$O$_2$PRu: C, 43.47; H, 6.08. Found: C, 43.21; H, 6.23. IR (Nujol, cm^{-1}): ν(OH) 3400−3050 br, ν(CO) 1975 vs, ν(C=C) 1595 m, ν(C−O) 1297 m, ν(BF$_4$) 1091, 1002 vs, br. ^{1}H NMR (300 MHz, 293 K, CD$_2$Cl$_2$) δ 13.1 (br, 1H, OH), 7.24 (dd, 1H, J_{trans} = 17.0, J_{cis} = 10.7, C*H*=CHH), 5.94 (d, 1H, J_{trans} = 17.0, CH=C*H*H), 5.57 (s, 5H, Cp), 5.45 (d, 1H, J_{cis} = 10.7, CH=CH*H*), 2.33 (m, 3H, PC*H*CH$_3$), 1.28 (dd, 9H, J(HH) = 7.1, J(PH) = 14.9, PCHC*H*$_3$), 1.20 (dd, 9H, J(HH) = 7.1, J(PH) = 14.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD$_2$Cl$_2$) δ 68.2 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, CD$_2$Cl$_2$) δ 296.3 (d, J(PC) = 9.9, Ru=C), 202.9 (d, J(PC) = 15.6, CO), 150.0, 121.2 (both s, CH=CH$_2$), 90.2 (s, Cp), 29.4 (d, J(PC) = 24.7, P*C*HCH$_3$), 19.7, 19.6 (both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(O)CH=CH$_2$}(CO)(PPr$^i_3$)] (13). Complex **12** (277 mg, 0.56 mmol) was chromatographed on a 10 cm alumina (neutral, activity grade V) column (eluent: dichloromethane/tetrahydrofuran, 20:1), affording complex **13**. The solvent was removed in vacuo, and the solid was recrystallized from cold *n*-pentane to give a yellow microcrystalline solid. The solvent was decanted and the product dried in vacuo. Yield: 97 mg (42%). Anal. Calcd for C$_{18}$H$_{29}$O$_2$PRu: C, 52.80; H, 7.14. Found: C, 52.94; H, 7.63. IR (Nujol, cm^{-1}): ν(CO) 1922 vs, ν(C=C) 1606 m, ν(C=O) 1562 s. ^{1}H NMR (300 MHz, 293 K, C$_6$D$_6$) δ 6.94 (dd, 1H, J_{trans} = 16.9, J_{cis} = 9.7, C*H*=CHH), 5.63 (dd, 1H, J_{trans} = 16.9, J_{gem} = 2.3, CH=C*H*H), 4.86 (s, 5H, Cp), 4.73 (dd, 1H, J_{cis} = 9.7, J_{gem} = 2.3, CH=CH*H*), 1.99 (m, 3H, PC*H*CH$_3$), 1.02 (dd, 9H, J(HH) = 7.2, J(PH) = 13.9, PCHC*H*$_3$), 0.89 (dd, 9H, J(HH) = 7.2, J(PH) = 13.6, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C$_6$D$_6$) δ 72.4 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C$_6$D$_6$) δ 247.2 (d, J(PC) = 10.6, Ru−C), 208.7 (d, J(PC) = 18.1, CO), 152.6, 113.2 (both s, CH=CH$_2$), 87.4 (s, Cp), 27.2 (d, J(PC) = 22.6, P*C*HCH$_3$), 19.9, 19.6 (both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(OH)CH=C(CH$_2$)$_4$CH$_2$}(CO)(PPr$^i_3$)]BF$_4$ (14). A solution of **15** (290 mg, 0.61 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (83 μL, 0.61 mmol, 54% in diethyl ether). Immediately, a yellow solid precipitated, which was washed with diethyl ether and dried in vacuo. Yield: 288 mg (84%). Anal. Calcd for C$_{23}$H$_{38}$BF$_4$O$_2$PRu: C, 48.85; H, 6.77. Found: C, 48.43; H, 6.95. IR (Nujol, cm^{-1}): ν(OH) 3331 br, ν(CO) 1953 vs, ν(C=C) 1586 s, ν(C−O) 1244 s, ν(BF$_4$) 1094, 968 vs, br. ^{1}H NMR (300 MHz, 293 K, CDCl$_3$) δ 13.2 (br, 1H, OH), 6.94 (s, 1H, CH=), 5.56 (s, 5H, Cp), 2.56 (m, 2H, Cy), 2.35 (m, 3H, PC*H*CH$_3$), 2.37 (m, 2H, Cy), 1.88−1.42 (m, 6H, Cy), 1.30 (dd, 9H, J(HH) = 7.1, J(PH) = 11.2, PCHC*H*$_3$), 1.26 (dd, 9H, J(HH) = 7.1, J(PH) = 11.3, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CDCl$_3$) δ 66.7 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, CDCl$_3$, plus APT) δ 295.6 (−, d, J(PC) = 8.7, Ru=C), 203.2 (d, J(PC) = 16.1, CO), 155.3 (−, s, =C), 138.6 (+, s, CH=), 89.2 (+, s, Cp), 37.9, 31.6, 28.6, 27.7, 25.6 (−, all s, Cy), 28.6 (+, d, J(PC) = 24.4, P*C*HCH$_3$), 19.3, 19.2 (+, both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(O)CH=C(CH$_2$)$_4$CH$_2$}(CO)(PPr$^i_3$)] (15) and [Ru(η^5-C$_5$H$_5$){C≡C-C=CH(CH$_2$)$_3$CH$_2$}(CO)(PPr$^i_3$)] (16). A solution of **5** (538 mg, 1.08 mmol) in 5 mL of dichloromethane was treated with 1-ethynyl-1-cyclohexanol (136.54 mg, 1.08 mmol). The mixture was stirred for 6 h, and the color turned from orange to brown. The solution was concentrated to ca. 1 mL and chromatographed on alumina. Dichloromethane eluted a yellow fraction from which the solvent was removed in vacuo affording a yellow oil. The oil was chromatographed on a silica gel column. A diethyl ether/*n*-pentane mixture (1:5) first eluted a pale yellow fraction followed by a yellow fraction. Solvents were removed in vacuo from both fractions affording **15** as a yellow solid from the second fraction. Yield: 310 mg (60%). Anal. Calcd for C$_{23}$H$_{37}$O$_2$PRu: C, 57.84; H, 7.81. Found: C, 57.64; H, 7.82. IR (Nujol, cm^{-1}): ν(CO) 1912 vs, ν(C=C) 1612 m, ν(C=O) 1557 s. ^{1}H NMR (300 MHz, 293 K, C$_6$D$_6$) δ 6.85 (s, 1H, CH=), 4.94 (s, 5H, Cp), 2.71 (m, 2H, Cy), 2.07 (m, 3H, PC*H*CH$_3$), 2.00 (m, 2H, Cy), 1.52 (m, 4H, Cy), 1.38 (m, 2H, Cy), 1.09 (dd, 9H, J(HH) = 7.2, J(PH) = 13.8, PCHC*H*$_3$), 0.95 (dd, 9H, J(HH) = 7.2, J(PH) = 13.2, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C$_6$D$_6$) δ 72.7 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C$_6$D$_6$, plus APT) δ 247.8 (−, d, J(PC) = 9.6, Ru−C), 208.8 (−, d, J(PC) = 18.4, CO), 141.0 (+, s, CH=), 137.7 (−, s, =C), 87.6 (+, s, Cp), 36.9, 30.0, 29.3, 28.5, 27.0 (−, all s, Cy), 27.1 (+, d, J(PC) = 22.6, P*C*HCH$_3$), 19.9, 19.7 (+, both s, PCH*C*H$_3$). **16** was obtained as a white solid from the pale yellow fraction. Yield: 25 mg (5%). Anal. Calcd for C$_{23}$H$_{35}$OPRu: C, 60.11; H, 7.68. Found: C, 60.12; H, 8.04. IR (Nujol, cm^{-1}): ν(C≡C) 2088 m, ν(CO) 1930 vs, ν(C=C) 1618 w. ^{1}H NMR (300 MHz, 293 K, C$_6$D$_6$) δ 5.99 (m, 1H, CH=), 4.77 (s, 5H, Cp), 2.37 (m, 2H, Cy), 2.05 (m, 5H, PC*H*CH$_3$ + Cy), 1.53 (m, 4H, Cy), 1.17 (dd, 9H, J(HH) = 7.1, J(PH) = 14.4, PCHC*H*$_3$), 0.90 (dd, 9H, J(HH) = 7.1, J(PH) = 12.9, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C$_6$D$_6$) δ 74.7 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C$_6$D$_6$, plus APT) δ 206.4 (−, d, J(PC) = 17.9, CO), 126.1 (−, d, J(PC) = 0.9, ≡C−), 125.2 (+, s, CH=), 113.3 (−, s, =C), 92.4 (−, d, J(PC) = 23.0, Ru−C≡), 87.6 (+, s, Cp), 31.9, 25.6, 23.5, 22.7 (−, all s, Cy), 27.5 (+, d, J(PC) = 23.9, P*C*HCH$_3$), 20.3 (+, s, PCH*C*H$_3$), 19.6 (+, d, J(PC) = 1.4, PCH*C*H$_3$).

Preparation of [Ru(η^5-C$_5$H$_5$){C(OMe)CH=CPh$_2$}(CO)(PPr$^i_3$)] BF$_4$ (17). A solution of **9** (90 mg, 0.14 mmol) in 5 mL of methanol was stirred for 15 min, and the color turned from dark red to yellow. The solution was concentrated almost to dryness, and slow addition of diethyl ether precipitated a yellow solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 80 mg (85%). Anal. Calcd for C$_{31}$H$_{40}$BF$_4$O$_2$PRu: C, 56.11; H, 6.07. Found: C, 56.14; H, 6.45. IR (Nujol, cm^{-1}): ν(CO) 1953 vs, ν(C=C) 1593 m, ν(Ph) 1570

m, ν(C—O) 1275 s, ν(BF_4) 1050 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.4−7.0 (m, 10H, Ph), 6.47 (s, 1H, CH═), 4.94 (s, 5H, Cp), 4.26 (s, 3H, OCH_3), 2.20 (m, 3H, PC*H*CH_3), 1.20 (dd, 9H, J(HH) = 6.9, J(PH) = 15.4, PCHC*H*$_3$), 1.13 (dd, 9H, J(HH) = 6.6, J(PH) = 14.8, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 65.9 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$) δ 305.0 (br, Ru═C), 202.8 (d, J(PC) = 16.0, CO), 139.6, 137.8 (both s, C_{ipso} + ═CPh_2), 136.7 (br s, CH═), 131.0, 129.7, 129.5, 128.7, 128.6, 128.4 (all s, Ph), 89.5 (s, Cp), 66.8 (s, OCH_3), 29.3 (d, J(PC) = 24.2, P*C*HCH$_3$), 19.6, 19.3 (both s, PCH*C*H$_3$). MS (FAB$^+$): m/z = 577 (M^+).

Preparation of [Ru(η^5-C_5H_5){C(OEt)CH═CPh_2}(CO)(PPr^i_3)]BF_4 (18). A solution of **9** (100 mg, 0.16 mmol) in 5 mL of ethanol was stirred for 45 min, and the color turned from dark red to yellow. The solution was concentrated almost to dryness, and slow addition of diethyl ether precipitated a yellow solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 90 mg (84%). Anal. Calcd for $C_{32}H_{42}BF_4O_2PRu$: C, 56.72; H, 6.24. Found: C, 56.84; H, 5.91. IR (Nujol, cm^{-1}): ν(CO) 1952 vs, ν(Ph) 1585 w, ν(C═C) 1566 m, ν(C—O) 1261 s, ν(BF_4) 1057 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.5−7.1 (m, 10H, Ph), 6.56 (s, 1H, CH═), 4.99 (s, 5H, Cp), 4.73 (q, 2H, J(HH) = 7.0, OC*H*$_2$CH$_3$), 2.31 (m, 3H, PC*H*CH$_3$), 1.52 (t, 3H, J(HH) = 7.0, OCH$_2$C*H*$_3$), 1.30 (dd, 9H, J(HH) = 7.1, J(PH) = 15.1, PCHC*H*$_3$), 1.24 (dd, 9H, J(HH) = 7.1, J(PH) = 14.4, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 65.9 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$) δ 303.8 (br, Ru═C), 203.0 (d, J(PC) = 15.8, CO), 139.8, 137.9 (both s, C_{ipso} + ═CPh_2), 137.0 (br s, CH═), 131.2, 129.7,129.6, 128.7, 128.7, 128.5 (all s, Ph), 89.5 (s, Cp), 77.2 (s, O*C*H$_2$CH$_3$), 29.5 (d, J(PC) = 24.3, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 19.5 (d, J(PC) = 1.4, PCH*C*H$_3$), 14.6 (s, OCH$_2$*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C(OMe)═C═CPh_2}(CO)(PPr^i_3)] (19). A solution of **17** (250 mg, 0.38 mmol) in 5 mL of tetrahydrofuran was treated with sodium methoxide (22 mg, 0.41 mmol), and the mixture was stirred for 2 h. The color turned from yellow to pale yellow, and the solvent was removed in vacuo. A 12 mL volume of toluene was added and the mixture filtered to eliminate $NaBF_4$. The solvent was removed in vacuo, and the residue was washed with cold *n*-pentane to afford a pale yellow solid. The solvent was decanted and the product dried by vacuum. Yield: 173 mg (80%). Anal. Calcd for $C_{31}H_{39}O_2PRu$: C, 64.68; H, 6.83. Found: C, 64.37; H, 6.56. IR (Nujol, cm^{-1}): ν(CO) 1913 vs, ν(C═C═C) 1871 m, ν(Ph) 1595 m, ν(C—O) 1049 s. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ 7.75 (m, 4H, Ph), 7.31 (m, 4H, Ph), 7.17 (m, 2H, Ph), 4.99 (s, 5H, Cp), 3.55 (s, 3H, OCH_3), 1.99 (m, 3H, PC*H*CH$_3$), 1.03 (dd, 9H, J(HH) = 7.2, J(PH) = 13.7, PCHC*H*$_3$), 0.91 (dd, 9H, J(HH) = 7.2, J(PH) = 13.7, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δ 70.4 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6) δ 206.9 (d, J(PC) = 18.9, CO), 197.8 (s, C_β), 142.2, 141.9 (both s, C_{ipso}), 138.1 (d, J(PC) = 13.6, C_α), 129.1, 128.8, 128.2, 128.2, 125.9, 125.9 (all s, Ph), 107.7 (s, C_γ), 86.0 (s, Cp), 58.2 (s, OCH_3), 27.8 (d, J(PC) = 22.6, P*C*HCH$_3$), 20.0, 19.6 (both s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C(OEt)═C═CPh_2}(CO)(PPr^i_3)] (20). A solution of **18** (253 mg, 0.37 mmol) in 5 mL of tetrahydrofuran was treated with sodium methoxide (22 mg, 0.41 mmol), and the mixture was stirred for 2.5 h. The color turned from yellow to pale yellow, and the solvent was removed in vacuo. A 12 mL volume of toluene was added and the mixture filtered to eliminate $NaBF_4$. The solvent was removed in vacuo, and the residue was washed with cold *n*-pentane to afford an oily pale yellow solid, which was separated by decantation and dried by vacuum. At room temperature the product exists as a yellow oil. Yield: 205 mg (93%). IR (Nujol, cm^{-1}): ν(CO) 1932 vs, ν(C═C═C) 1890 m, ν(Ph) 1595 m, ν(C—O) 1047 s. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ 7.61 (m, 4H, Ph), 7.10 (m, 6H, Ph), 4.85 (s, 5H, Cp), 3.68 (m, 2H, OC*H*$_2$CH$_3$), 1.89 (m, 3H, PC*H*CH$_3$), 1.05 (t, 3H, J(HH) = 7.1, OCH$_2$C*H*$_3$), 0.91 (dd, 9H, J(HH) = 7.2, J(PH) = 13.7, PCHC*H*$_3$), 0.80 (dd, 9H, J(HH) = 6.9, J(PH) = 12.6, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δ 72.2 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus APT) δ 206.8 (−, d, J(PC) = 18.9, CO), 197.6 (−, s, C_β), 142.3, 142.0 (−, both s, C_{ipso}), 135.7 (−, d, J(PC) = 13.3, C_α), 129.2, 128.7, 128.2, 128.2, 125.8, 125.7 (+, all s, Ph), 106.6 (−, s, C_γ), 86.0 (+, s, Cp), 66.5 (−, s, O*C*H$_2$CH$_3$), 27.8 (+, d, J(PC) = 22.6, P*C*HCH$_3$), 20.1, 19.6 (+, both s, PCH*C*H$_3$), 15.5 (+, s, OCH$_2$*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C(SPr^n)CH═CPh_2}(CO)(PPr^i_3)]BF_4 (21). A solution of **9** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with 1-propanethiol (23 μL, 0.25 mmol). After the solution was stirred for 5 h, the color turned dark orange, and the solution was concentrated almost to dryness. Slow addition of diethyl ether precipitated an orange solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 165 mg (98%). Anal. Calcd for $C_{33}H_{44}BF_4OPRuS$: C, 56.01; H, 6.27; S, 4.53. Found: C, 55.94; H, 6.45; S, 3.34. IR (Nujol, cm^{-1}): ν(CO) 1964 vs, ν(Ph) 1585 w, ν(C═C) 1561 m, ν(BF_4) 1074, 1051, 1030, all s. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.46−7.08 (m, 10H, Ph), 6.91 (s, 1H, CH═), 5.10 (s, 5H, Cp), 3.34 (m, 2H, SC*H*$_2$CH$_2$CH$_3$), 2.42 (m, 3H, PC*H*CH$_3$), 1.76 (m, 2H, SCH$_2$C*H*$_2$CH$_3$), 1.32 (dd, 9H, J(HH) = 6.9, J(PH) = 12.0, PCHC*H*$_3$), 1.27 (dd, 9H, J(HH) = 6.9, J(PH) = 11.4, PCHC*H*$_3$), 1.01 (t, 3H, J(HH) = 7.2, SCH$_2$-CH$_2$C*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 60.6 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus DEPT) δ 311.6 (C_{quat}, d, J(PC) = 6.8, Ru═C), 202.6 (C_{quat}, d, J(PC) = 17.3, CO), 142.9 (+, br s, CH═), 140.9, 140.6 (C_{quat}, both s, C_{ipso}), 138.1 (C_{quat}, s, ═CPh_2), 131.1, 129.3, 129.0, 128.7, 128.6, 128.3 (+, all s, Ph), 90.4 (+, s, Cp), 48.4 (−, s, S*C*H$_2$CH$_2$CH$_3$), 29.3 (+, d, J(PC) = 24.1, P*C*HCH$_3$), 20.5 (−, s, SCH$_2$*C*H$_2$CH$_3$), 20.1 (+, s, PCH*C*H$_3$), 19.6 (+, d, J(PC) = 1.5, PCH*C*H$_3$), 13.3 (+, s, SCH$_2$CH$_2$*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C(SPr^n)═C═CPh_2}(CO)(PPr^i_3)] (22). A solution of **21** (159 mg, 0.22 mmol) in 5 mL of tetrahydrofuran was treated with sodium methoxide (13.5 mg, 0.24 mmol) and the mixture stirred for 1.5 h. The color turned from dark orange to pale yellow, and the solvent was removed in vacuo. A 12 mL volume of toluene was added, and the mixture was filtered to eliminate $NaBF_4$. The solvent was removed in vacuo and the residue washed with cold *n*-pentane to afford a yellow solid dried by vacuum. Yield: 94 mg (68%). Anal. Calcd for $C_{33}H_{43}OPRuS$: C, 63.95; H, 6.99; S, 5.17. Found: C, 63.72; H, 7.10; S, 5.20. IR (Nujol, cm^{-1}): ν(CO) 1930 vs, ν(C═C═C) 1887 m, ν(Ph) 1595 m. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ 7.63 (m, 4H, Ph), 7.27 (m, 4H, Ph), 7.14 (m, 2H, Ph), 5.04 (s, 5H, Cp), 2.85 (m, 2H, SC*H*$_2$CH$_2$CH$_3$), 2.00 (m, 3H, PC*H*CH$_3$), 1.57 (m, 2H, SCH$_2$C*H*$_2$CH$_3$), 1.05 (dd, 9H, J(HH) = 7.2, J(PH) = 14.3, PCHC*H*$_3$), 0.81 (dd, 9H, J(HH) = 7.2, J(PH) = 12.6, PCHC*H*$_3$), 0.81 (t, 3H, J(HH) = 7.2, SCH$_2$-CH$_2$C*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δ 71.1 s; ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6) δ 206.4 (d, J(PC) = 19.8, CO), 195.9 (s, C_β), 141.0, 140.6 (both s, C_{ipso}), 128.2−125.2, (all s, Ph), 103.4 (s, C_γ), 90.1 (d, J(PC) = 11.3, C_α), 85.7 (s, Cp), 39.0 (s, S*C*H$_2$CH$_2$CH$_3$), 26.8 (d, J(PC) = 22.6, P*C*HCH$_3$), 22.7 (s, SCH$_2$*C*H$_2$CH$_3$), 19.9, 18.8 (both s, PCH*C*H$_3$), 13.4 (s, SCH$_2$CH$_2$*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C(CH═CPh_2)═N═CPh_2}-(CO)(PPr^i_3)]BF_4 (23). A solution of **9** (125 mg, 0.20 mmol) in 5 mL of tetrahydrofuran was treated with benzophenone imine (37 μL, 0.21 mmol). After the solution was stirred for 6 h, the color turned to orange, and the solution was concentrated almost to dryness. By slow addition of diethyl ether an orange solid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 147 mg (91%). Anal. Calcd for $C_{43}H_{47}BF_4NOPRu$: C, 63.55; H, 5.83; N, 1.72. Found: C, 63.20; H, 5.97; N, 1.82. IR (Nujol, cm^{-1}): ν(CO) 1942 vs, ν(C═N═C) 1813 m, ν(Ph) 1593, 1577 both w, ν(C═C) 1550 s, ν(BF_4) 1055 vs, br. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.66−6.60 (m, 21H, Ph + CH═), 5.29 (s, 5H, Cp), 2.26 (m, 3H, PC*H*CH$_3$), 1.20 (dd, 9H, J(HH) = 7.2, J(PH) = 14.5, PCHC*H*$_3$), 1.18 (dd, 9H, J(HH) = 7.2, J(PH) = 14.3, PCHC*H*$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6, plus DEPT) δ 67.0 s;

Table 3. Crystal Data and Data Collection and Refinement Parameters for [Ru(η^5-C_5H_5){C(O)CH=CPh$_2$}(CO)(PPr$^i_3$)] (11) and [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (23)

	11	23
	Crystal Data	
formula	$C_{30}H_{37}O_2PRu$	$C_{43}H_{47}BNOF_4PRu$
mol wt	561.665	812.698
color and habit	yellow, irregular prism	orange, irregular prism
cryst size, mm	0.29 × 0.17 × 0.35	0.40 × 0.38 × 0.20
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	17.932(4)	15.039(3)
b, Å	9.442(2)	14.620(3)
c, Å	18.311(3)	18.825(4)
β, deg	118.68(1)	109.651(7)
V, Å^3	2720(1)	3898(1)
Z	4	4
D(calcd), g cm^{-3}	1.3716	1.3848
temp, K	293	293
	Data Collection and Refinement	
diffractometer	Siemens-STOE AED-2	Siemens-P4
λ(Mo Kα) radiation, Å; technique	0.710 73; bisecting geometry	
monochomator	graphite oriented	
μ, mm^{-1}	0.66	0.50
scan type	$\omega/2\theta$	$\theta/2\theta$
2θ range, deg	$3 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
no. of data collect	7354	8650
no. of unique data	4756	6822
no. of params refined	308	470
w$R2(F^2$, all data)	0.0724	0.1452
$R1(F, F_o > 4.0\sigma F)$	0.0256	0.0592

[a] w$R2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

$^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6) δ 207.1 (C_{quat}, d, J(PC) = 9.0, Ru−C=N), 203.2 (C_{quat}, d, J(PC) = 16.6, CO), 145.7, 139.6, 136.9, 134.1, 131.0, 130.0 (C_{quat}, all s, N=CPh_2 + C_{ipso} + CH=CPh_2), 131.9, 131.7, 130.3, 129.9, 129.8, 128.8, 128.7, 128.5, 128.3, 127.5, 127.5 (+, all s, Ph + CH=), 87.4 (+, s, Cp), 28.8 (+, d, J(PC) = 24.1, P$CHCH_3$), 19.7, 19.5 (+, both s, PCHCH_3).

Preparation of [Ru(η^5-C_5H_5){C(N=CPh$_2$)=C=CPh$_2$}(CO)(PPr$^i_3$)] (24). A solution of **23** (200 mg, 0.25 mmol) in 5 mL of tetrahydrofuran was treated with sodium methoxide (14.0 mg, 0.26 mmol) and the mixture stirred for 1.5 h. The color turned from orange to yellow, and the solvent was removed in vacuo. A 12 mL volume of toluene was added, and the mixture was filtered to eliminate $NaBF_4$. The solvent was removed in vacuo and the residue was washed with *n*-pentane to afford a yellow solid dried by vacuum. Yield: 164 mg (92%). Anal. Calcd for $C_{43}H_{46}NOPRu$: C, 71.24; H, 6.39; N, 1.93. Found: C, 70.81; H, 6.59; N, 1.78. IR (Nujol, cm^{-1}): ν(CO) 1935 vs, ν(C=C=C) 1888 m, ν(Ph) 1607 w, 1574 w, ν(C=N) 1594 m. ^1H NMR (300 MHz, 293 K, C_6D_6) δ 8.05−6.92 (m, 20H, Ph), 4.57 (s, 5H, Cp), 2.03 (m, 3H, P$CHCH_3$), 1.16 (dd, 9H, J(HH) = 7.1, J(PH) = 13.9, PCHCH_3), 0.84 (dd, 9H, J(HH) = 7.1, J(PH) = 13.2, PCHCH_3); $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$) δ 71.8 s; $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus APT) δ 207.5 (−, d, J(PC) = 19.8, CO), 194.7 (−, s, C_β), 155.0 (−, s, N=CPh_2), 142.8, 141.8, 141.6, 138.1 (−, all s, C_{ipso}), 130.2, 130.0, 129.1, 128.9, 128.8, 128.1, 128.0, 127.7, 127.6, 125.9, 125.3 (+, all s, Ph), 114.9 (−, d, J(PC) = 12.9, C_α), 102.3 (−, s, C_γ), 85.6 (+, s, Cp), 27.5 (+, d, J(PC) = 22.6, P$CHCH_3$), 20.0, 19.5 (+, both s, PCHCH_3).

X-ray Structure Analysis of [Ru(η^5-C_5H_5){C(O)CHCPh$_2$}(CO)(PPr$^i_3$)] (11) and [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (23). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **11** in toluene or by diffusion of Et_2O into a concentrated solution of **23** in CH_2Cl_2. A summary of crystal data, intensity collection procedure, and refinement is reported in Table 3 (**11** and **23**). The crystals were glued on a glass fiber and mounted on a Siemens-Stoe AED-4 (**11**) or a Siemens-P4 (**23**) diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 58 reflections in the range $20 \le 2\theta \le 42°$ (**11**) (60 reflections in the range $20 \le 2\theta \le 30°$ for **23**). The recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored, and no significant variation was observed. Reflections were also corrected for absorption by a semiempirical (Ψ-scan) method.[51] The structures were solved by Patterson (Ru atoms) and conventional Fourier techniques. Refinements were carried out by full-matrix least-squares methods with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were observed or calculated (C−H = 0.96 Å) and included in the refinement riding on carbon atoms with common isotropic thermal values. Atomic scattering factors, corrected for anomalous dispersion for Ru and P atoms, were taken from ref 52. All calculations were performed using SHELXTL-PLUS[53] and SHELXL93.[54]

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Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles (32 pages). Ordering information is given on any current masthead page.

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(51) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1969**, *24*, 351.
(52) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
(53) Sheldrick, G. M. SHELXTL PLUS; Siemens Analytical X-ray Instruments: Madison, WI, 1990.
(54) Sheldrick, G. M. SHELX93, Program for Crystal Structure, Univ. of Göttingen, 1993.