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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Received February 20, 1996[®]

The five-coordinate complex [RuHCl(CO)(PPri3)2] (1) reacts with cyclopentadiene in methanol under reflux to give $[RuH(\eta^5-C_5H_5)(CO)(PPr^i_3)]$ (2) and $[HPPr^i_3]Cl$. The protonation of **2** in dichloromethane- d_2 leads to the dihydrogen complex $[Ru(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(PPr_3)]$ -BF₄ (3) in equilibrium with traces of the dihydrido tautomer $[RuH_2(\eta^5-C_5H_5)(CO)(PPr^i_3)]$ BF₄ (4). The reaction of 2 with HBF₄·Et₂O in acetone affords the solvated complex $[Ru(\eta^5 C_5H_5$)(CO) $\{\eta^1$ -OC(CH₃)₂ $\}$ (PPrⁱ₃)]BF₄ (5), which reacts with CO, dimethyl acetylenedicarboxylate, and NaCl to give $[Ru(\eta^5-C_5H_5)(CO)_2(PPr^i_3)]BF_4$ (6), $[Ru(\eta^5-C_5H_5)\{\eta^2-C_2(CO_2CH_3)_2\}(CO)(PPr^i_3)]$ BF₄ (7), and $[Ru(\eta^5-C_5H_5)Cl(CO)(PPr_3)]$ (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=CPh₂)(CO)(PPr¹₃)]BF₄ (9), which affords [Ru(η^5 -C₅H₅){C(OH)CH=CPh₂}- $(CO)(PPr_3)]BF_4$ (10) by reaction with water. 10 is converted into the acyl derivative [Ru- $(\eta^5-C_5H_5)\{C(O)CH=CPh_2\}(CO)(PPr_3)\}$ (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- $(\eta^5-C_5H_5)\{C(OH)CH=CH_2\}(CO)(PPr_3)\}BF_4$ (12). Similarly to 10, 12 is converted into [Ru- $(\eta^5-C_5H_5)\{C(O)CH=CH_2\}(CO)(PPr_3)\}$ (13), when the solutions of 12 are passed through an Al₂O₃ column. Treatment of 5 with 1-ethynyl-1-cyclohexanol leads to a mixture of organometallic compounds including $[Ru(\eta^5-C_5H_5)\{C(OH)CH=C(CH_2)_4CH_2\}(CO)(PPr_3)]BF_4$ (14). Chromatography of the mixture affords $[Ru(\eta^5-C_5H_5)\{C(O)CH=\dot{C}(CH_2)_4\dot{C}H_2\}(CO)$ $(PPr^{i}_{3})]$ (15) and $[Ru(\eta^{5}-C_{5}H_{5})\{C \equiv C\dot{C} = CH(CH_{2})_{3}\dot{C}H_{2}\}(CO)(PPr^{i}_{3})]$ (16). 9 reacts with alcohols and thiols to give $[Ru(\eta^5-C_5H_5)\{C(ER)CH=CPh_2\}(CO)(PPr^i_3)]BF_4$ (ER = OMe (17), OEt (18), SPrⁿ (21)), which by treatment with NaOMe afford $[Ru(\eta^5-C_5H_5)\{C(ER)=C=CPh_2\}(CO)-C(ER)=CPh_2\}(CO)$ (PPr_3^i)] (ER = OMe (19), OEt (20), SPrⁿ (22)). Similarly, the reaction of 9 with benzophenone imine leads to $[Ru(\eta^5-C_5H_5)]\{C(CH=CPh_2)=N=CPh_2\}\{CO\}(PPr^i_3)\}$ BF₄ (23), which by reaction with NaOMe gives $[Ru(\eta^5-C_5H_5)\{C(N=CPh_2)=C=CPh_2\}(CO)(PPr^i_3)]$ (24). The structure of 23 was also determined by an X-ray investigation. The C=N bond lengths are 1.283(9) and

Introduction

1.252(9) Å, while the C-N-C angle is 149.9(6)°.

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 and homogeneous catalysis.

Bis(phosphine)—cyclopentadienyl³ and —indenyl⁴ and chloro—phosphine—arene⁵ 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

 $^{^{\}dagger}$ Dedicated to Professor Juan Bertrán on the occasion of his 65th birthday.

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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(η^5 -C₅H₅)Cl(CO)- (PR_3)]⁷ and $[Ru(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(PR_3)]^{+8}$ 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 RuCl₃·xH₂O with triisopropylphosphine in refluxing methanol leads to the five-coordinate hydrido-chloro complex [RuHCl(CO)(PPri3)2] in good yield.10 This complex, which is an active and highly selective catalyst for the reduction of unsaturated organic substrates¹¹ and for the addition of HSiEt₃ 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 monoand binuclear tetrahydridoborato derivatives. 19 We have now observed that the reaction of the complex [RuHCl(CO)(PPrⁱ₃)₂] with cyclopentadiene leads to the cyclopentadienyl complex [RuH(η^5 -C₅H₅)(CO)(PPrⁱ₃)], which affords the dihydrogen derivative $[Ru(\eta^5-C_5H_5) [\sqrt[4]{q^2}-H_2)(CO)(PPr^i_3)]BF_4$ by reaction with HBF₄. Interest **f** the change of properties of the unsaturated η^1 -carbon Egands on moving from the more basic ruthenium existents led us to recommend the more basic ruthenium systems led us to prepare carbonyl-triisopropylphosphine—cyclopentadienyl complexes of ruthenium con-Eaining unsaturated η^1 -carbon ligands.

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Here, we report the synthesis and characterization of new allenylidene and α,β-unsaturated-hydroxycarbene, -acyl, -alkoxycarbene, -(alkylthio)carbene, -2azaallenyl, alkoxyallenyl, (alkylthio)allenyl, and iminoallenyl derivatives containing the $Ru(\eta^5-C_5H_5)(CO)$ -(PPrⁱ₃) unit. In addition, the X-ray structures of the complexes $[Ru(\eta^5-C_5H_5)\{C(O)CH=CPh_2\}(CO)(PPr_3^i)]$ and $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=N=CPh_2\}(CO)(PPr_3^i)]BF_4$ are also reported.

Results and Discussion

1. Synthesis and Protonation of [RuH(η^5 -C₅H₅)- $(CO)(PPr^{i}_{3})$] (2). Treatment of a refluxing suspension of [RuHCl(CO)(PPri3)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 [HPPrⁱ₃]Cl affords a yellow solution, from which the hydrido-cyclopentadienyl complex [RuH- $(\eta^5-C_5H_5)(CO)(PPr_3)$] (2) was isolated as a white solid in 86% yield (eq 1). The related complexes [RuH(η^5 - C_5H_5 (CO)(PR₃)] (PR₃ = PCy₃, PPh₃, PMe₂Ph, PMe₃) have been previously prepared by phosphine substitution of $[RuH(\eta^5-C_5H_5)(CO)_2]$ in overall lower yield.^{8b}

The IR spectrum of 2 in Nujol shows absorptions due to $\nu(RuH)$ at 1985 cm⁻¹ and $\nu(CO)$ 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 $^{31}P\{^{1}H\}$ 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 HBF₄·OEt₂ to a solution of **2** in dichloromethane- d_2 leads, after a few seconds, to the dihydrogen complex $[Ru(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(PPr^i_3)]^+$ (3) in equilibrium with traces of the dihydrido tautomer $[RuH_2(\eta^5-C_5H_5)(CO)(PPr_3^i)]^+$ (4) (eq 2). 20 At room tem-

perature, the ¹H NMR spectrum of the equilibrium

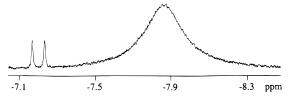


Figure 1. ¹H NMR spectrum (300 MHz, 293 K, CD₂Cl₂) in the hydride region for the mixture of $[Ru(\eta^5-C_5H_5)(\eta^2-\eta^2)]$ H_2 (CO)(PPr i_3)]BF₄ (3) and [RuH₂(η^5 -C₅H₅)(CO)(PPr i_3)] (4).

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 p K_a of **3** is lower than the p K_a of HNEt₃⁺.

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 chose previously reported for related compounds.8b The related iron complexes $[Fe(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(L)]^+$ have been recently reported. They react with silanes \mathbf{E} generate $[Fe(\eta^5-C_5H_5)(\eta^2-HSiR_3)(CO)(L)]^+$ (L = PEt₃, ું €o gener EPh₃).^{8f}

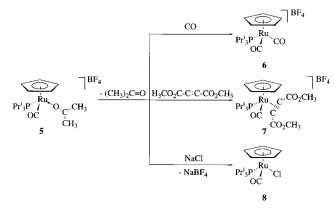
 $\frac{5}{2}$ There is a marked difference toward protonation We tween 2 and the related osmium complex $[OsH(\eta^5-Q_5H_5)(CO)(PPr^i_3)]$. We have previously observed that the reaction of the osmium compound with the stoichiometric amount of $HBF_4 \cdot OEt_2$ exclusively leads to the hydrido derivative $[OsH_2(\eta^5-C_5H_5)(CO)(PPr^i_3)]BF_4$.²¹ In this context, it should be noted that ruthenium is a \wp oorer π -back-bonder than osmium, because the osmium ads.²² Therefore, the dihydrido tautomers are more favored with osmium than with ruthenium.

The protonation of 2 with LPE OF

 $\frac{2}{5}$ The protonation of **2** with HBF₄·OEt₂ in acetone leads $\overset{6}{\circ} \overset{1}{t_0} \text{ the solvated complex } [\text{Ru}(\eta^5 - \text{C}_5\text{H}_5)\{\eta^1 - \text{OC}(\text{CH}_3)_2\} (CO)(PPr_3^i)]BF_4$ (5) (eq 3), which was isolated as an grange solid in 99% yield.

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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains a singlet at 230.4 ppm for the carbon atom of the carbonyl group

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 ¹³C{¹H} NMR spectra. The IR spectrum in Nujol shows a strong absorption at 1869 cm⁻¹, which is characteristic of the $\nu(C = C)$ vibration,²⁴ while in the ¹³C{¹H} NMR spectrum the acetylenic carbon atoms appear at 73.4 and 72.5 ppm as broad resonances.

2. Reactions of $[Ru(\eta^5-C_5H_5)(CO)\{\eta^1-OC(CH_3)_2\}$ -(PPrⁱ₃)]BF₄ (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 ligand²⁵ at 2002 cm⁻¹. In the ¹³C{¹H} 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 ¹H NMR spectrum. An alternative *cisoid* dihydrido structure should give rise to two hydrido resonances.

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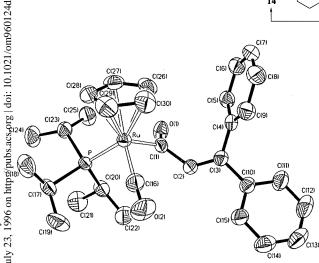
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Eigure 2. Molecular diagram of complex $[Ru(\eta^5-C_5H_5)-C(O)CH=CPh_2](CO)(PPr^i_3)]$ (11). Thermal ellipsoids are shown at 50% probability.

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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The ^1H NMR spectrum shows a singlet at 7.09 ppm due to the CH= proton and a broad resonance at 12.8 ppm corresponding to the -OH proton. In the $^{13}\text{C}\{^1\text{H}\}$ 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 CH= and CPh_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 , $^3P\{^1H\}$, and $^1C\{^1H\}$ 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

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Ru(\eta^5-C_5H_5)\{C(O)CH=CPh_2\}(CO)(PPr^i_3)]$ (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) P-Ru-C(16) P-Ru-G(1) ^a C(1)-Ru-C(16) C(1)-Ru-G(1) ^a C(16)-Ru-G(1) ^a	91.82(8) 93.8(1) 126.5(1) 92.6(1) 117.1(1) 125.8(1)	Ru-C(1)-C(2) O(1)-C(1)-C(2) C(1)-C(2)-C(3) C(2)-C(3)-C(4) C(2)-C(3)-C(10) C(4)-C(3)-C(10)	116.1(2) 119.6(2) 129.2(2) 123.2(2) 120.0(2) 116.8(2)
Ru-C(1)-O(1)	123.9(1)	C(4)-C(3)-C(10)	110.0(2)

^a G(1) is the midpoint of the C(26)-C(30) Cp ligand.

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- $\{C(O)Me\}I(CO)_2(Pr^i\text{-}DAB)]\ (2.078(8)\ \mbox{\normalfont\AA})^{27}$ and about 0.1A longer than that found in the five-coordinate derivative $[Ru\{C(O)Me\}Cl(CO)(PPr_3)_2]$ (1.957(6) Å). 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- $(\eta^5 - C_5 H_5) \{ (E) - C(O)C(CH_2 OMe) = C(Me)Ph \} (CO) \{ P - C(O) + C(O) + C(O) \}$ $(OPh)_3$] (1.329(4) Å),²⁸ $[Fe(\eta^5-C_5H_5)\{(E)-C(O)CH=CH-CH_5\}\}$

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Me $\}(CO)(PPh_3)]$ (1.316(6) Å),²⁹ [Fe(η^5 -C₅H₅) $\}(Z)$ -C(O)C-(Me)=C(Ph)Me $\{(CO)\{P(OPh)_3\}\}\ (1.332(4) \text{ Å}), \text{ and } [Fe (\eta^5-C_5H_5)\{(E)-C(O)C(Me)=C(Me)SPh\}(CO)\{P(OPh)_3\}$ $(1.327(6) \text{ and } 1.314(6) \text{ Å})^{30} \text{ and does not seem to be}$ lengthened by any appreciable conjugation with the acyl

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=0, CH=, and =CPh₂ 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 $\nu(OH)$ and $\nu(C=C)$ 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 [BF₄]⁻ at 1091 and 1002 cm⁻¹ are also observed. The splitting of the expected T_d symmetry of the [BF₄] group suggests that, in this case, the anion also interacts with the -OH group of the $\frac{6}{8}$ Earbene ligand. In the 1 H NMR spectrum of 12 the most g Boticeable resonances include a double doublet at 7.24 gpm with H–H coupling constants of 17.0 and 10.7 Hz, which was assigned to the CH= proton, two doublets at 5.94 and 5.45 ppm with H-H coupling constants of End 5.94 and 5.45 ppm with H—H coupling constants of £7.0 and 10.7 Hz, respectively, which were assigned to \mathfrak{E}_{n} the $=CH_{2}$ protons, and a broad resonance at 13.1 ppm \mathfrak{E}_{n} corresponding to the -OH proton. In the $^{13}C\{^{1}H\}$ NMR \mathfrak{E}_{n} spectrum, the Ru=C(OH) carbon atom of the unsaturated η^{1} -carbon ligand gives rise to a doublet at 296.3 $\stackrel{\text{at}}{\text{et}}$ ed η^1 -carbon ligand gives rise to a doublet at 296.3 Ξ great η --carbon figantic gives rise to a doublet at 296.5 Ξ gapm with a P-C coupling constant of 9.9 Hz, while the Ξ glefinic carbon atoms display singlets at 150.0 and 121.2 ≧ **p**pm.

When a dichloromethane solution of 12 was passed rough an Al_2O_3 (neutral, activity grade V) column, the \overline{a}_{β} -unsaturated-acyl compound 13 was also formed. This complex was isolated as a yellow microcrystalline **s**olid in 42% yield. The presence of the α,β -unsaturated- $\overline{2}$ cyl ligand is supported by the IR and ¹H and ¹³C{¹H} NMR spectra. The IR spectrum in Nujol contains two bands at 1606 and 1562 cm⁻¹, which were assigned to the $\nu(C=C)$ and $\nu(C=O)$ vibrations of the alkenylacyl ligand. In the ¹H 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 ${}^{13}C\{{}^{1}H\} \text{ NMR}$ spectrum, the Ru-C=0 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 ³¹P{¹H} 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 (Al₂O₃ 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 ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectroscopy. In the IR spectrum in Nujol, the most noticeable absorptions are those corresponding to the $\nu(C=O)$ and $\nu(C=C)$ vibrations of the alkenylacyl ligand, which appear at 1557 and 1612 cm⁻¹, respectively. In the ¹H NMR spectrum, the presence of the acyl ligand is mainly supported by a singlet at 6.85 ppm and in the ¹³C{¹H} 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 (CH=) and 137.7 (= CPh_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 ¹³C{¹H} NMR spectra. Thus, the IR spectrum contains bands at 2088 and 1618 cm⁻¹, characteristic of the $\nu(C = C)$ and $\nu(C = C)$ vibrations of an α,β -unsaturated-alkynyl group. In the ¹³C{¹H} NMR spectrum, the carbon atoms of the alkynyl fragment appear as doublets at 92.4 (Ru-C=) and 126.1 ($\equiv C-$) 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 HBF4·OEt2 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 $\nu(OH)$ and $\nu(C=C)$ 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 ¹H NMR spectrum of 14 shows the -OH resonance, at 13.2 ppm, and a singlet at 6.94 ppm, due to the CH= 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 CH= and = CPh_2 carbons give rise to singlets at 138.6 and 155.3 ppm, respectively. As has been previously mentioned, the ³¹P{¹H} 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

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Scheme 3

$$[Ru] + O = C \xrightarrow{CH_3} \xrightarrow{H - C \equiv C - CR_2} \xrightarrow{[Ru] = C = C} \xrightarrow{R} \xrightarrow{H_2O} \qquad [Ru] = C = C \xrightarrow{R}$$

 $[Ru] = [Ru(\eta^5 - C_5H_5)(CO)(PPr^i_3)]^+$

1-ethynyl-1-cyclohexanol. In addition, MO calculations on the model compound $[Mn(\eta^5-C_5H_5)(C=C=CH_2)(CO)_2]$ 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

Hydroxycarbene complexes have been previously pro-

Sosed as reaction intermediates in the transformation, in the presence of water, of cationic vinylidene compounds into alkyl-carbonyl derivatives.³³ The reactions $\frac{1}{2}$ gounds into alkyl-carbonyl derivatives. The reactions $\frac{1}{2}$ of alkyn-1-ols with metallic fragments to give α, β -5 thinsaturated hydroxycarbene compounds have no pre-Edisaturated hydroxycarbene compounds have no preedent. 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-eyclohexanol, 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 Ehe result of the deprotonation of a vinylvinylidene complex in the chromatography column. Dixneuf has closely studied related reactions of alkynols with $\mathbb{R}uCl_2(\eta^6-C_6H_6)(PMe_3)$] in MeOH/NH₄PF₆. In agreement with the results collected in Scheme 2, for 1,1diphenyl-2-propyn-1-ol, the allenylidene complex [RuCl- \mathcal{E}_{6}^{6} -C₆H₆){C=C=CPh₂}(PMe₃)]PF₆ was isolated, whereas For 1,1-dimethyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol, the α,β -unsaturated methoxycarbene compounds $[RuCl(\eta^6-C_6H_6)\{C(OMe)CH=CR_2\}(PMe_3)]PF_6$ (R = Me, $R_2 = C_5H_{10}$) were obtained exclusively, via allenylidene intermediates.⁵ On the other hand, the behavior of the $[Ru(\eta^5-C_5H_5)(CO)(PPr^i_3)]^+$ fragment contrasts with that previously observed for the related osmium fragment $[Os(\eta^5-C_5H_5)(CO)(PPr^i_3)]^+$, which reacts with 1-ethynyl-1-cyclohexanol to afford the vinylvinylidene $[Os(\eta^5-C_5H_5)\{C=C(H)C=CH(CH_2)_3CH_2\}(CO)$ -

(PPrⁱ₃)]⁺ in 78% yield.²¹ Vinylvinylidene products are also obtained exclusively from reactions of the richelectron fragment $[Ru(\eta^5-C_5H_5)(PMe_3)_2]^+$ with alkyn-1ols containing hydrogen atoms adjacent to the hydroxy group.3b

3. Reactions of $[Ru(\eta^5-C_5H_5)(C=C=CPh_2)(CO)$ - $(\mathbf{PPr^{i}_{3}})|\mathbf{BF_{4}}$ (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 ¹³C-{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 CH= and OCH_3 protons, respectively, while, in the ${}^{13}C\{{}^{1}H\}$ NMR spectrum, the most noticeable signals are two broad resonances at 305.0 and 136.7 ppm due to the Ru=Cand CH= 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 (CH=), a quartet at 4.73 ppm (OC H_2), and a triplet at 1.52 ppm (C H_3), while, in the ${}^{13}C\{{}^{1}H\}$ NMR spectrum, the Ru=C and CH= 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 (OCH₂) and 14.6 (CH₃) 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 $[RuCl(\eta^6-arene)\{C=C=CR_2\}(PR_3)]^+$ add alcohols at the C_{α} and C_{β} atoms to afford α,β -unsaturatedalkoxycarbene derivatives,5g whereas the cumulene ligands stabilized by the electron-rich fragments [Ru- $(\eta^5 - C_5H_5)(PMe_3)_2]^+,^{31a} [RuCl(dppm)_2]^+ (dppm = bis-$ (diphenylphosphino)methane), 34 [RuCl(NP₃)]⁺ (NP₃ = $N(CH_2CH_2PPh_2)$, 35 and $[Ru(\eta^5-C_9H_7)L_2]^+$ (L₂ = 2 PPh₃, dppm, dppe)4b are inert. This suggest that the electronic nature of unit $[Ru(\eta^5-C_5H_5)(CO)(PPr_3^i)]^+$ is similar to that of the fragments $[RuCl(\eta^6-arene)(PR_3)]^+$.

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 ${}^{13}C\{{}^{1}H\}$ 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) = 13.3Hz), and 106.6 (s) (20) ppm for the C_{β} , C_{α} , and C_{ν} 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-

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Stress [OsCl₂(CH=C=CPh₂)(NO)(PR₃)₂] (PR₃ = PPrⁱ₃, PPhPrⁱ₂).³⁷ Fischer has also reported that the alle- ϵ Eylidene complex [Cr(CO)₅{C=C=C(C₆H₄NMe₂-p)₂}] adds isylidene complex $[Cr(CO)_5\{C=C=C(C_6H_4NMe_2-p)_2\}]$ adds phosphines at the C_α carbon atom to give ylide complexes $[Cr(CO)_5\{\eta^1-C(PR_3)=C=C(C_6H_4NMe_2-p)_2\}]$ (PR₃ PMe₃, PHPh₂, PH₂Mes). At room temperature, the complex $[Cr(CO)_5\{\eta^1-C(PHPh_2)=C=C(C_6H_4NMe_2-p)_2\}]$ rearranges to $[Cr(CO)_5\{PPh_2[CH=C=C(C_6H_4NMe_2-p)_2\}]$ is 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 [Rudope). Ab In agreement with this, we have recently

ppe).4b In agreement with this, we have recently served that complex 9 reacts with CH₃O⁻ to afford $\mathbb{R}u(\eta^5-C_5H_5)\{C \equiv CC(OMe)Ph_2\}(CO)(PPr_3^i)\}$ 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 so-

Scheme 5

dium 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.

Complex 21 was isolated as an orange solid in 98% yield. In the ¹H 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 (SC H_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=Ccarbon atom and two singlets at 142.9 and 138.1 due to the CH= and = CPh_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 ¹³C{¹H} 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

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Figure 3. Molecular diagram of complex $[Ru(\eta^5-C_5H_5) \{C(CH=CPh_2)=N=CPh_2\}(CO)(PPr^i_3)]BF_4$ (23). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=N=CPh_2\}(CO)(PPr_3)]BF_4$ (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-P 6007 Ru-C(1) 6007 Ru-C(29) Ru-C(39)	1.834(7)	C(3)-C(10)	1.485(10)		
$\approx R_{11} - C(30)$	2.244(7)	N-C(1)	1.283(9)		
	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)		
ਵ ਉ Ru−C(43)	2.210(7)	O(1)-C(29)	1.136(9)		
$\frac{1}{2} \frac{1}{20} C(1) - C(2)$	1.486(9)				
5 to 5					
□ g 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)		
$\Sigma = \mathbb{R} - \mathbb{R} u - \mathbb{G}(1)^a$	124.2(2)	C(1)-C(2)-C(3)	129.9(6)		
5 €C(1)−Ru−C(29)	89.2(3)	C(2)-C(3)-C(4)	119.0(6)		
$\subseteq \mathfrak{X}(1) - \mathrm{Ru} - \mathrm{G}(1)^a$		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)		
\mathcal{C} \mathcal{C} Ru-C(1)-C(2)	120.8(4)	N-C(16)-C(23)	120.7(6)		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
Ö ∰ Efti 3lD(lth, and l3C(lth, NMD anastrossess, and V no					
$\mathbb{F}_{H}^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectroscopy, and X-ray					
A view of the molecular geometry is shown					
Figure 3. Selected bond distances and angles are					
45 . 1. m 11 0 A C 44 .1					

Figure 3. Selected bond distances and angles are Ested in Table 2. As for 11, the geometry around the Futhenium 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 $[Ru\{C(=CHPh)OC(O)CH_3\}(CO) {\eta^{1}\text{-OC}(CH_{3})_{2}}(PPr^{i}_{3})_{2}^{+} (1.967(8) \text{ Å}),^{6} [\dot{R}u(\eta^{5}\text{-}C_{5}H_{5})\{C^{-}u^{5}, C^{-}u^{5}\}]$ (=CHCO₂CH₃)OC(O)CH₃}(PPh₃)] (2.002(2) Å),⁴⁰ [ku{C- $(=C(CO_2CH_3)CH=CHC(CH_3)_3)C(O)OCH_3\}CI(CO)$ $(PPh_3)_2$] (2.03(1) Å),⁴¹ [Ru{(E)-CH=CHC₃H₇}Cl(CO)(Me₂-Hpz)(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 $[Ru\{(E)-(E)-(E)\}_2$ $CH=CHCMe_3$ {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 $[Ru(\eta^5-C_5H_5)\{C(=CHPh)OPr^i\}$ - $(CO)(PPh_3)$] (2.103(6) Å)⁹ and Ru{C(=CHCO₂CH₃)CO₂-CH₃}(CO)(NCCH₃)₂(PPh₃)₂|ClO₄ (2.12(5) Å), 45 where a Ru-C(sp2) 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 $1.264(5) \text{ Å})^{46}$ 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 $149.9(6)^{\circ}$, 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 $[Cr\{C(Ph)=N=C-P^{t_2}\}]$ HPh $\{(CO)_5\}$ 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 $v_{as}(C=N=C)$ 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 ¹³C{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;

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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=CR₂}(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=CR₂}(CO)₅] were obtained from aminocarbene compounds by condensation of the NH₂ group with organic carbonyl compounds in the presence of NEt₃ and POCl₃/ 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 $[Et_3O]BF_4$.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 $[M(\eta^5-C_5H_5) (=C=CHR)(CO)_2$] (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 stretching frequency in the IR spectrum, which $\stackrel{\circ}{\rm g}$ be observed at 1888 cm $^{-1}$, and the three resonances in the $^{13}{\rm C}\{^{1}{\rm H}\}$ NMR spectrum at 194.7 (s), 114.9 (d, $J({\rm PC})$ $\mathfrak{S} \stackrel{\cong}{=} 12.9$), and 102.3 (s) ppm for the C_{β} , C_{α} , and C_{γ} allenyl

Earbon atoms, respectively. Complex **24** is also significant because, as far as we know, iminoallenyl complexes have not been previously reported.

Concluding Remarks

Concluding Remarks

This study has revealed that the five-coordinate management [RuHCl(CO)(PPrⁱ₃)₂] is a useful starting matesial for the preparation of new cyclopentadienyl theorem compounds containing unsaturated η^1 -carbon for the preparation of new cyclopentadienyl theorem compounds containing unsaturated η^1 -carbon for the preparation of new cyclopentadienyl theorem compounds containing unsaturated η^1 -carbon for the preparation of new cyclopentadienyl theorem cyclopentadienyl the À figands, 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(n⁵-C₅H₅)(CO)(PPrⁱ₃)]. Acecyclopentadiene to give [RuH(η^5 -C₅H₅)(CO)(PPrⁱ₃)]. Acetone solutions of this complex react with HBF₄·Et₂O to afford the solvated compound $[Ru(\eta^5-C_5H_5)(CO)\{\eta^1-OC-\eta^2-C_5H_5\}]$ (CH₃)₂}(PPrⁱ₃)]BF₄, which is a novel precursor for the preparation of the unsaturated η^1 -carbon complexes.

The chemical behavior of the fragment [Ru(η^5 -C₅H₅)-(CO)(PPrⁱ₃)]⁺ has some characteristics in common with the arene systems $[RuCl(\eta^6-arene)(PR_3)]^+$ but marked differences with the chemical behavior of the related osmium fragment $[Os(\eta^5-C_5H_5) (CO)(PPr^i_3)]^+$ and the more electron-rich half-sandwich ruthenium units [Ru- $(\eta^5-C_5H_5)(PMe_3)_2]^+$ and $[Ru(\eta^5-C_9H_7)(PR_3)_2]^+$. Thus, the acetone complex $[Ru(\eta^5-C_5H_5)\{\eta^1-OC(CH_3)_2\}(CO)(PPr_3^i)]$ BF₄ reacts with alkyn-1-ols to afford α,β -unsaturatedhydroxycarbene compounds via allenylidene intermediates, whereas, under similar experimental conditions, the fragments $[Os(\eta^5-C_5H_5)(CO)(PPr_3)]^+$ and $[Ru(\eta^5-C_5H_5)(CO)(PPr_3)]^+$ C₅H₅)(PMe₃)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 -C₅H₅)-(C=C=CPh₂)(CO)(PPrⁱ₃)]BF₄ also shows a markedly different reactivity with that observed for the allenylidene ligands stabilized by the fragments [Ru(η^5 - $C_5H_5)(PMe_3)_2]^+$ and $[Ru(\eta^5-C_9H_7)L_2]^+$ ($L_2=2$ PPh_3 , dppm, dppe). While the complex $[Ru(\eta^5-C_5H_5)(C=$ C=CPh₂)(CO)(PPrⁱ₃)]BF₄ reacts with alcohols to give α,β -unsaturated alkoxycarbene derivatives, the latter are inert. 4b,31a The allenylidene complex [Ru(η^5 -C₅H₅)-(C=C=CPh₂)(CO)(PPrⁱ₃)]BF₄ 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-1cyclohexanol (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)(PPri3)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 Me₄Si (¹H and ¹³C) and 85% H_3PO_4 (31P). Coupling constants, J, are given in Hz. The T_1 experiments were performed on a Varian UNITY 300 spectrophotometer with a standard $180^{\circ}-\tau-90^{\circ}$ 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 $[RuH(\eta^5-C_5H_5)(CO)(PPr^i_3)]$ (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 [HPPri3]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 C15-H₂₇OPRu: 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. ¹H NMR (300 MHz, 293 K, C_6D_6) δ 4.87 (s, 5H, Cp), 1.73 (m, 3H, $PCHCH_3$), 1.01 (dd, 9H, J(HH) = 7.1, J(PH) = 10.1, $PCHCH_3$), $0.96 \text{ (dd, 9H, } J(\text{HH}) = 7.1, J(\text{PH}) = 9.8, \text{ PCHC} H_3), -12.05 \text{ (d, } H_3)$ 1H, J(PH) = 30.7, RuH). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 91.6 s.

Preparation of $[Ru(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(PPr^i_3)]BF_4$ (3) and $[RuH_2(\eta^5-C_5H_5)(CO)(PPr_3)]BF_4$ (4). A solution of 2 (15) mg, 0.042 mmol) in 0.5 mL of CD2Cl2 in an NMR tube was treated with a stoichiometric amount of tetrafluoroboric acid $(5.7 \mu L, 0.042 \text{ mmol}, 54\% \text{ in diethyl ether})$. The NMR tube was sealed under argon and measurements initiated im-

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mediately. Spectroscopic data for 3: $^1\mbox{H}$ NMR (300 MHz, 293 K, CD_2Cl_2) δ 5.67 (s, 5H, Cp), 2.40 (m, 3H, $PCHCH_3$), 1.35 (dd, 9H, J(HH) = 4.4, J(PH) = 7.1, PCHCH₃), 1.30 (dd, 9H, J(HH) = 4.7, J(PH) = 7.1, $PCHCH_3$), -7.95 (br. 2H, $Ru(\eta^2-H_2)$); T_1 $(Ru(\eta^2-H_2), 300 \text{ MHz}, CD_2Cl_2) = 34 \text{ ms} (253 \text{ K}), 22 \text{ ms} (233 \text{ K})$ K), 13 ms (213 K), 6 ms (193 K); ³¹P{¹H} NMR (121.4 MHz, 293 K, CD_2Cl_2) δ 81.4 (br). Spectroscopic data for 4: ¹H NMR (300 MHz, 293 K, CD_2Cl_2) δ 5.80 (s, 5H, Cp), -7.17 (d, 2H, J(PH) = 19.8, RuH₂); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, CD₂-Cl₂) δ 86.7 (s).

Preparation of [RuD(η^5 -C₅H₅)(CO)(PPrⁱ₃)] (2d) and $[\mathbf{Ru}(\eta^5-\mathbf{C}_5\mathbf{H}_5)(\eta^2-\mathbf{HD})(\mathbf{CO})(\mathbf{PPr}_3)]\mathbf{BF}_4$ (3d). A solution of 2 (11 mg, 0.031 mmol) in 0.5 mL of CD₃OD 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, CD₃OD) δ 4.95 (s, Cp), 1.95 (m, 3H, PCHCH₃), 1.06 (dd, 18H, J(HH) = 7.2, J(PH) = 13.9, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, CD₃OD) 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 CDCl₃, followed by treatment with the stoichiometric amount of tetrafluoroboric acid (4.2 μ L, 0.031 mmol, 54% in diethyl ether). The NMR tube was sealed under argon, and measurements were made immediately. Spectroscopic data for 3d: ¹H NMR (300 MHz, 213 K, CDCl₃) δ 5.63 (s, Cp), 2.32 (m, 3H, PC*H*CH₃), 1.34 (dd, 9H, J(HH) = 4.9, J(PH) = 7.1, PCHC H_3), 1.29 (dd, $\mathfrak{Q}H$, J(HH) = 4.9, J(PH) = 7.1, $PCHCH_3$), -7.87 (1:1:1 t, 1H, $\mathfrak{D}(HD) = 28.5$, Ru(η^2 -HD); $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $\mathfrak{C}DCl_3$) δ 78.6 (br s).

Reaction of [Ru(η"-U₅II₅)(η -11₂)(U₇-11₂)(U₇-11₂) NEt₃. Addition of a stoichiometric amount of NEt₃ to a NMR tube afforded 2 Exaction of $[Ru(\eta^5-C_5H_5)(\eta^2-H_2)(CO)(PPr^i_3)]BF_4$ (3) with \mathfrak{S} thloroform- d_1 solution of **3** in an NMR tube afforded **2** Emmediately, as shown by 'H and 3!P{1H} NMR spectroscopy. $\ddot{\circ}$ Preparation of [Ru(η_5 -C₅H₅)(CO){ η^1 -OC(CH₃)₂}(PPrⁱ₃)]- $\mathbf{\overline{B}F_4}$ (5). A solution of 2 (600 mg, 1.69 mmol) in 5 mL of acetone $\sqrt{2}$ as treated with tetrafluoroboric acid (253.7 μ L, 1.86 mmol, 54% in diethyl ether). Immediately the color turned from pale yellow to orange, and the solution was concentrated almost to tryness. By addition of diethyl ether an orange solid precipitated. The solid was washed with diethyl ether and dried in \mathbf{z} acuo. Yield: 838 mg (99%). Anal. Calcd for $C_{18}H_{32}BF_4O_2$ -🛱 ĒRu: C, 43.30; H, 6.46. Found: C, 43.29; H, 6.59. IR (Nujol, \mathcal{E} m⁻¹): ν (CO) 1958 vs. ν (C=O) 1652 s. ν (BF₄) 1053 vs. br. ¹H \gtrsim NMR (300 MHz, 293 K, CD₂Cl₂) δ 5.28 (s, 5H, Cp), 2.44 (s, \S_{η}^{1-} OC(CH₃)₂}), 2.42 (m, 3H, PC*H*CH₃), 1.26 (dd, 9H, \mathcal{J} (HH) \cong \S_{η}^{2} 7.1, \mathcal{J} (PH) = 14.7, PCHC*H*₃), 1.24 (dd, 9H, \mathcal{J} (HH) = 7.1, \mathcal{J} (PH) = 13.9, PCHC*H*₃); 31 P{ 1 H} NMR (121.4 MHz, 293 K, $\overline{Z}(PH) = 13.9$, PCHC H_3); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, $\stackrel{\circ}{\Box}$ $\stackrel{\circ}{\mathbb{C}}$ D₂Cl₂) δ 64.6 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃) δ 230.4 (s, $\{\eta^1 - OC(CH_3)_2\}$), 203.8 (d, J(PC) = 18.4, CO), 83.7 (s, $\stackrel{\text{\tiny CE}}{=}$ p), 32.7 (s, { η^1 -OC(CH₃)₂}), 26.5 (d, J(PC) = 22.6, PCHCH₃), 49.6, (s, PCHCH₃), 19.4 (d, J(PC) = 1.0, PCHCH₃).

Preparation of $[Ru(\eta^5-C_5H_5)(CO)_2(PPr^i_3)]BF_4$ (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 C₁₆H₂₆BF₄O₂PRu: C, 40.95; H, 5.58. Found: C, 40.92; H, 5.50. IR (Nujol, cm⁻¹): ν (CO) 2050, 1993 both vs, ν (BF₄) 1050 vs, br. 1 H NMR (300 MHz, 293 K, CDCl₃) δ 5.82 (s, 5H, Cp), 2.43 (m, 3H, PCHCH₃), 1.27 (dd, 18H, J(HH) = 7.2, J(PH) = 15.9, PCHC H_3); ³¹P{¹H} NMR (121.4 MHz, 293 K, CDCl₃) δ 73.8 s. MS (FAB⁺): m/z = 383 (M⁺).

Preparation of $[Ru(\eta^5-C_5H_5)\{\eta^2-C_2(CO_2CH_3)_2\}(CO) (PPr_{3}^{i})BF_{4}$ (7). A solution of 5 (80 mg, 0.16 mmol) in 5 mL of dichloromethane was treated with dimethyl acetylenedicarboxylate (60 μ L, 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 C₂₁H₃₂BF₄O₅PRu: 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 (BF₄) 1056 vs, br. ¹H NMR (300 MHz, 293 K, CDCl₃) δ 5.91 (s, 5H, Cp), 3.96, 3.89 (both br s, 6H, CO₂CH₃), 2.52 (m, 3H, PCHCH₃), 1.26 (dd, 9H, J(HH) = 6.9, J(PH) = 15.4, $PCHCH_3$), 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, CDCl₃) δ 65.2 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃, plus APT) δ 199.0 (-, d, J(PC) = 17.5, CO), 161.9, 158.2 (-, both br s, CO_2CH_3), 92.3 (+, s, Cp), 73.4, 72.5 (-, both br s, C=C), 54.4, 54.3 (+, both s, CO_2CH_3), 28.0 (+, d, J(PC) = 24.4, $PCHCH_3$), 19.7 (+, s, $PCHCH_3$), 19.4 (+, d, J(PC) = 1.9, PCH CH₃). MS (FAB⁺): m/z = 497 (M⁺).

Preparation of [Ru(η^5 -C₅H₅)Cl(CO)(PPrⁱ₃)] (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 NaBF₄ 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 C₁₅H₂₆ClOPRu: 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. ¹H NMR (300 MHz, 293 K, CDCl₃) δ 5.08 (s, 5H, Cp), 2.47 (m, 3H, PCHCH₃), 1.27 (dd, 9H, J(HH) = 7.1, J(PH) = 14.5, $PCHCH_3$), 1.20 (dd, 9H, J(HH) = 7.1, J(PH) =13.2, PCHC H_3); ³¹P{¹H} NMR (121.4 MHz, 293 K, CDCl₃) δ 66.4 s. MS (FAB⁺): m/z = 390 (M⁺).

Preparation of $[Ru(\eta^5-C_5H_5)(C=C=CPh_2)(CO)(PPr^{i_3})]$ BF₄ (9). A solution of 5 (100 mg, 0.20 mmol) in 5 mL of dichloromethane was treated with 1,1-diphenyl-2-propyn-1ol (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 C₃₀-H₃₆BF₄OPRu: 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, $\nu(BF_4)$ 1076 vs, br. ¹H NMR (300 MHz, 293 K, CDCl₃) 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, PCHCH₃), 1.22 (dd, 9H, J(HH) = 7.1, J(PH) = 10.4, $PCHCH_3$), 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, CDCl₃) δ 79.8 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃) δ 288.3 (d, J(PC) = 13.8, C_{α}), 199.9 (d, J(PC) = 15.2, CO), 188.5 (d, J(PC) = 2.3, C_{β}), 164.4 (s, C_{γ}), 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, PCHCH₃), 19.9 (s, PCHCH₃), 19.5 (d, J(PC) = 0.9, PCH CH₃). MS (FAB⁺): m/z = 545 (M⁺).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OH)CH=CPh_2\}(CO)-$ (PPri₃)]BF₄ (10). Route a. A solution of 9 (150 mg, 0.24 mmol) in 5 mL of tetrahydrofuran was treated with water (120 μ L, 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 μ L. 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 C30H38-BF₄O₂PRu: 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 (BF₄) 1093, 1032, 976 all vs. 1 H NMR (300 MHz, 293 K, CDCl₃) 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, PCHCH₃), 1.28 (dd, 9H, J(HH) = 7.1, J(PH) = 15.4, $PCHCH_3$), 1.23 (dd, 9H, J(HH) = 7.1, J(PH) = 15.1, $PCHCH_3$); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, 293 K, CDCl₃) δ 66.5 s; $^{13}C\{^{1}H\}$ NMR (75.4 MHz, 293 K, CDCl₃, plus APT) δ 298.7 (-, d, *J*(PC) = 9.8, Ru=C), 202.9 (-, d, J(PC) = 15.1, CO), 145.3 (-, s,

=CPh₂), 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, $PCHCH_3$), 19.9, 19.8 (+, both s, $PCHCH_3$).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(O)CH=CPh_2\}(CO) (PPr_{3}^{i})$ (11). A solution of 9 (190 mg, 0.30 mmol) in 6 mL of tetrahydrofuran was treated with water (120 μ L, 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 C₃₀H₃₇O₂PRu: 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, PCHCH₃), 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, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4) MHz, 293 K, C_6D_6) δ 71.3 s; $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_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, PCHCH₃), 19.9, 19.5 (+, both s, PCHCH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OH)CH=CH_2\}(CO)-CH=CH_2\}$ **PPr**ⁱ₃)**BF**₄ (12). **Route a.** A solution of 5 (110 mg, 0.22) ramol) in 2 mL of dichloromethane at 263 K was treated with Epropyn-1-ol (15.4 μ L, 0.26 mmol). The solution was stirred for 2 min, and the color turned from orange to yellow. The g gr 2 min, and the color turned from orange to yellow. The mixture was rapidly cooled to 195 K, and slow addition of $\boldsymbol{\xi}$ ðyl ether precipitated a yellow solid. The solid was washed

Several times with cold diethyl ether and dried in vacuo. Field: 99 mg (90%).

Route b. A solution of 13 (80 mg, 0.20 mmol) in 5 mL of Ethyl ether was treated with tetrafluoroboric acid (28 μ L, 6.20 mmol, 54% in diethyl ether), and immediately a yellow solid precipitated. The solid was washed with diethyl ether splid precipitated. The solid was washed with diethyl ether and dried in vacuo. Yield: 74 mg (76%). Anal. Calcd for $\S_{18}H_{30}BF_4O_2PRu$: C. 43.47: H 6.08 Found: C. 43.41 M 6.66 $\stackrel{>}{\simeq}$ PR (Nujol, cm⁻¹): ν (OH) 3400–3050 br, ν (CO) 1975 vs, ν (C=C) 233 (m, 3H, PCHCH₃), 1.28 (dd, 9H, J(HH) = 7.1, J(PH) = 4.9, PCHC H_3), 1.20 (dd, 9H, J(HH) = 7.1, J(PH) = 14.9, **E**CHC H_3); ³¹P{¹H} NMR (121.4 MHz, 293 K, CD₂Cl₂) δ 68.2 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CD₂Cl₂) 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=CH₂), 90.2 (s, Cp), 29.4 (d, J(PC) = 24.7, PCHCH₃), 19.7, 19.6 (both s, PCHCH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(O)CH=CH_2\}(CO)(PPr^i_3)]$ (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 C₁₈H₂₉O₂PRu: 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. ¹H NMR (300 MHz, 293 K, C₆D₆) δ 6.94 (dd, 1H, $J_{\text{trans}} =$ 16.9, $J_{cis} = 9.7$, CH=CHH), 5.63 (dd, 1H, $J_{trans} = 16.9$, $J_{gem} = 16.9$ 2.3, CH=C*H*H), 4.86 (s, 5H, Cp), 4.73 (dd, 1H, $J_{cis} = 9.7$, J_{gem} = 2.3, CH=CHH), 1.99 (m, 3H, PCHCH₃), 1.02 (dd, 9H, J(HH) = 7.2, J(PH) = 13.9, $PCHCH_3$), 0.89 (dd, 9H, J(HH) = 7.2, J(PH) = 13.6, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, C_6D_6) δ 72.4 s; ${}^{13}C\{{}^{1}H\}$ NMR (75.4 MHz, 293 K, C_6D_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=CH₂), 87.4 (s, Cp), 27.2 (d, J(PC) = 22.6, PCHCH₃), 19.9, 19.6 (both s, PCHCH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OH)CH=C(CH_2)_4CH_2\}$ $(CO)(PPr_3)BF_4$ (14). A solution of 15 (290 mg, 0.61 mmol) in 5 mL of diethyl ether was treated with tetrafluoroboric acid (83 μ L, 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 C₂₃H₃₈BF₄O₂PRu: 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 (BF₄) 1094, 968 vs, br. ¹H NMR (300 MHz, 293 K, CDCl₃) 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, PCHCH₃), 2.37 (m, 2H, Cy), 1.88-1.42 (m, 6H, Cy), 1.30 (dd, 9H, J(HH) = 7.1, J(PH) = 11.2, $PCHCH_3$), 1.26 (dd, 9H, J(HH) = 7.1, J(PH) =11.3, PCHC H_3); ³¹P{¹H} NMR (121.4 MHz, 293 K, CDCl₃) δ 66.7 s; ${}^{13}C\{{}^{1}H\}$ NMR (75.4 MHz, 293 K, CDCl₃, 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, PCHCH₃), 19.3, 19.2 (+, both s, PCHCH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(O)CH=C(CH_2)_4CH_2\}$ (CO)(PPr $^{i}_{3}$)] (15) and [Ru(η^{5} -C $_{5}$ H $_{5}$){C=C-C=CH(CH $_{2}$) $_{3}$ CH $_{2}$ }-(CO)(PP \mathbf{r}^{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 C23H37-O₂PRu: 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. ¹H NMR (300 MHz, 293 K, C_6D_6) δ 6.85 (s, 1H, CH=), 4.94 (s, 5H, Cp), 2.71 (m, 2H, Cy), 2.07 (m, 3H, PCHCH₃), 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, $PCHCH_3$), 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_6D_6) δ 72.7 s; ${}^{13}C\{{}^{1}H\}$ NMR (75.4 MHz, 293 K, C_6D_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, PCHCH₃), 19.9, 19.7 (+, both s, PCHCH₃). **16** was obtained as a white solid from the pale yellow fraction. Yield: 25 mg (5%). Anal. Calcd for C23H35OPRu: 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. ¹H NMR (300 MHz, 293 K, C_6D_6) δ 5.99 (m, 1H, CH=), 4.77 (s, 5H, Cp), 2.37 (m, 2H, Cy), 2.05 (m, 5H, PCHCH₃ + Cy), 1.53 (m, 4H, Cy), 1.17 $(dd, 9H, J(HH) = 7.1, J(PH) = 14.4, PCHCH_3), 0.90 (dd, 9H,$ J(HH) = 7.1, J(PH) = 12.9, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4) MHz, 293 K, C_6D_6) δ 74.7 s; $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6 , plus APT) δ 206.4 (-, d, J(PC) = 17.9, CO), 126.1 (-, d, J(PC) = 0.9, $\equiv C-$), 125.2 (+, s, CH=), 113.3 (-, s, $\equiv C$), 92.4 $(-, d, J(PC) = 23.0, Ru-C \equiv)$, 87.6 (+, s, Cp), 31.9, 25.6, 23.5, 22.7 (-, all s, Cy), 27.5 (+, d, J(PC) = 23.9, PCHCH₃), 20.3 $(+, s, PCHCH_3), 19.6 (+, d, J(PC) = 1.4, PCHCH_3).$

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OMe)CH=CPh_2\}(CO) (PPr_{3}^{i})$] **BF₄** (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 C₃₁H₄₀BF₄O₂PRu: 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 (BF₄) 1050 vs, br. 1 H NMR (300 MHz, 293 K, CDCl₃) δ 7.4—7.0 (m, 10H, Ph), 6.47 (s, 1H, CH=), 4.94 (s, 5H, Cp), 4.26 (s, 3H, OCH₃), 2.20 (m, 3H, PC*H*CH₃), 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, CDCl₃) δ 65.9 s; 13 C{ 1 H} NMR (75.4 MHz, 293 K, CDCl₃) δ 305.0 (br, Ru=C), 202.8 (d, J(PC) = 16.0, CO), 139.6, 137.8 (both s, C_{ipso} + =CPh₂), 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, OCH₃), 29.3 (d, J(PC) = 24.2, P*C*HCH₃), 19.6, 19.3 (both s, PCH*C*H₃). MS (FAB⁺): m/z = 577 (M⁺).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OEt)CH=CPh_2\}(CO) (PPr_{3}^{i})BF_{4}$ (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 C₃₂H₄₂BF₄O₂PRu: 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, $\nu(C-O)$ 1261 s, $\nu(BF_4)$ 1057 vs, br. 1H NMR (300 MHz, 293 K, CDCl₃) 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 CH₃), 2.31 (m, 3H, $PCHCH_3$), 1.52 (t, 3H, J(HH) = 7.0, OCH_2CH_3), 1.30 (dd, 9H, J(HH) = 7.1, J(PH) = 15.1, $PCHCH_3$), 1.24 (dd, 9H, J(HH) = ${\mathbb Z}_1$ 1, J(PH) = 14.4, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293) \mathbb{K} , CDCl₃) δ 65.9 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃) δ $\mathfrak{F}03.8$ (br, Ru=C), 203.0 (d, J(PC) = 15.8, CO), 139.8, 137.9 8 (both s, C_{ipso} + = CPh_2), 137.0 (br s, CH=), 131.2, 129.7,129.6, 2428.7, 128.7, 128.5 (all s, Ph), 89.5 (s, Cp), 77.2 (s, OCH_2CH_3), $\mathcal{L}_{2} = 0.5 \text{ (d, } J(PC) = 24.3, PCHCH_3), 19.8 \text{ (s, PCH}CH_3), 19.5 \text{ (d, } 19.8 \text{ (s, PCH}CH_3), 19.5 \text{ (d, } 19.8 \text{ (s, PCH}CH_3), 19.8 \text{ (s, PCH}CH_3), 19.8 \text{ (d, } 19.8 \text{ (s, PCH}CH_3), 19.8 \text{ (d, } 19$ $\frac{2}{3} \mathcal{L}(PC) = 1.4, PCH CH_3), 14.6 (s, OCH_2 CH_3).$

 $\ddot{5}$ Preparation of $[Ru(\eta^5-C_5H_5)\{C(OMe)=C=CPh_2\}(CO)-CO\}$ (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, C(41 mmol), and the mixture was stirred for 2 h. The color tirned from yellow to pale yellow, and the solvent was removed ia vacuo. A 12 mL volume of toluene was added and the mixture filtered to eliminate NaBF₄. The solvent was removed 🛱 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 C₃₁H₃₉O₂PRu: C, 64.68; H, 6.83. Found: C, 64.37; H, 6.56. **ÉR** (Nujol, cm⁻¹): ν (CO) 1913 vs, ν (C=C=C) 1871 m, ν (Ph) 1595 南, ν (C-O) 1049 s. ¹H NMR (300 MHz, 293 K, C₆D₆) δ 7.75 (m, 4H, Ph), 7.31 (m, 4H, Ph), 7.17 (m, 2H, Ph), 4.99 (s, 5H, $\stackrel{\circ}{\Box}$ $\stackrel{\circ}{\Box}$ p), 3.55 (s, 3H, OCH₃), 1.99 (m, 3H, PC*H*CH₃), 1.03 (dd, 9H, $\mathcal{A}(HH) = 7.2$, J(PH) = 13.7, $PCHCH_3$), 0.91 (dd, 9H, J(HH) = 13.7) Ξ_{2} , J(PH) = 13.7, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293) $\vec{\mathbf{K}}$, C₆D₆) δ 70.4 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆) 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_v), 86.0 (s, Cp), 58.2 (s, OCH₃), 27.8 (d, J(PC) = 22.6, PCHCH₃), 20.0, 19.6 (both s, $PCHCH_3$).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(OEt)=C=CPh_2\}(CO)-$ (PPrⁱ₃)] (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 NaBF₄. 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. ¹H 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, OCH₂- CH_3), 1.89 (m, 3H, $PCHCH_3$), 1.05 (t, 3H, J(HH) = 7.1, OCH_2CH_3), 0.91 (dd, 9H, J(HH) = 7.2, J(PH) = 13.7, $PCHCH_3$), 0.80 (dd, 9H, J(HH) = 6.9, J(PH) = 12.6, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$

Preparation of $[Ru(\eta^5-C_5H_5)\{C(SPr^n)CH=CPh_2\}(CO)-$ (PPrⁱ₃)|BF₄ (21). A solution of 9 (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with 1-propanethiol (23 μ L, 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 C₃₃H₄₄BF₄OPRuS: 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 (BF₄) 1074, 1051, 1030, all s. ¹H NMR (300 MHz, 293 K, CDCl₃) δ 7.46-7.08 (m, 10H, Ph), 6.91 (s, 1H, CH=), 5.10 (s, 5H, Cp), 3.34 (m, 2H, SC*H*₂CH₂CH₃), 2.42 (m, 3H, PCHCH₃), 1.76 (m, 2H, SCH₂CH₂CH₃), 1.32 (dd, 9H, J(HH) = 6.9, J(PH) = 12.0, $PCHCH_3$), 1.27 (dd, 9H, J(HH) =6.9, J(PH) = 11.4, $PCHCH_3$), 1.01 (t, 3H, J(HH) = 7.2, SCH_2 -CH₂CH₃); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, CDCl₃) δ 60.6 s; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 293 K, CDCl3, 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, =CPh₂), 131.1, 129.3, 129.0, 128.7, 128.6, 128.3 (+, all s, Ph), 90.4 (+, s, Cp), 48.4 (-, s, SCH₂CH₂CH₃), 29.3 $(+, d, J(PC) = 24.1, PCHCH_3), 20.5 (-, s, SCH_2CH_2CH_3), 20.1$ $(+, s, PCHCH_3), 19.6 (+, d, J(PC) = 1.5, PCHCH_3), 13.3 (+, s, J(PC) = 1.5, PCHCH_3)$ SCH₂CH₂CH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(SPr^n)=C=CPh_2\}(CO)-$ (PPrⁱ₃)] (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 NaBF4. 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 C₃₃H₄₃OPRuS: 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. ¹H 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, SCH₂CH₂CH₃), 2.00 (m, 3H, PCHCH₃), 1.57 (m, 2H, SCH₂CH₂CH₃), 1.05 (dd, 9H, J(HH) = 7.2, J(PH) = 14.3, $PCHCH_3$, 0.81 (dd, 9H, J(HH) =7.2, J(PH) = 12.6, $PCHCH_3$), 0.81 (t, 3H, J(HH) = 7.2, SCH_2 -CH₂CH₃); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293 K, C₆D₆) δ 71.1 s; 13 C{ 1 H} NMR (75.4 MHz, 293 K, C₆D₆) 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_v), 90.1 (d, J(PC) = 11.3, C_u), 85.7 (s, Cp), 39.0 (s, $SCH_2CH_2CH_3$), 26.8 (d, J(PC) = 22.6, $PCHCH_3$), 22.7 (s, SCH₂CH₂CH₃), 19.9, 18.8 (both s, PCHCH₃), 13.4 (s, SCH₂CH₂CH₃).

Preparation of $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=N=CPh_2\}$ -(CO)(PPrⁱ₃)]BF₄ (23). A solution of 9 (125 mg, 0.20 mmol) in 5 mL of tetrahydrofuran was treated with benzophenone imine (37 μ L, 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 C₄₃H₄₇BF₄NOPRu: 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, v(BF₄) 1055 vs, br. ¹H NMR (300 MHz, 293 K, CDCl₃) δ 7.66-6.60 (m, 21H, Ph + CH=), 5.29 (s, 5H, Cp), 2.26 (m, 3H, $PCHCH_3$), 1.20 (dd, 9H, J(HH) = 7.2, J(PH) = 14.5, $PCHCH_3$), 1.18 (dd, 9H, J(HH) = 7.2, J(PH) = 14.3, $PCHCH_3$); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, 293 K, C₆D₆, plus DEPT) δ 67.0 s;

Table 3. Crystal Data and Data Collection and Refinement Parameters for [Ru(η^5 -C₅H₅){C(O)CH=CPh₂}(CO)(PPr₃ⁱ)] (11) and $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=N=CPh_2\}(CO)(PPr^{i_3})]BF_4$ (23)

	11	23
	Crystal Data	
formula	$C_{30}H_{37}O_2PRu$	C ₄₃ H ₄₇ BNOF ₄ PRu
mol wt	561.665	812.698
color and habit	yellow, irregular prism	orange, irregular prism
cryst size, mm	$0.29\times0.17\times0.35$	$0.40 \times 0.38 \times 0.20$
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 K α) radiation, 0.710 73; bisecting geometry Å: techniaue

11, 00011111440		
monochomator		graphite oriented
₽ mm ^{−1}	0.66	0.50
蒙an type 都 range, deg 聽. of data collect	$\omega/2\theta$	$\theta/2\theta$
🐲 range, deg	$3 \le 2\theta \le 50$	$2 \leq 2\theta \leq 50$
ந். of data collect	7354	8650
др. of unique data	4756	6822
no. of params refined	308	470
$\Re R2(\bar{F}^2, \text{ all data})$	0.0724	0.1452
$R1(F, F_0 > 4.0\sigma F)$	0.0256	0.0592

color turned from orange to yellow, and the solvent was memoved in vacuo. A 12 mL volume of toluene was added, and The mixture was filtered to eliminate NaBF₄. 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 C₄₃H₄₆NOPRu: 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. 1 H NMR (300 MHz, 293 K, $C_{6}D_{6}$) δ 8.05–6.92 (m, 20H, Ph), 4.57 (s, 5H, Cp), 2.03 (m, 3H, PCHCH₃), 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, $PCHCH_3$); ${}^{31}P\{{}^{1}H\}$ NMR (121.4 MHz, 293) K, CDCl₃) δ 71.8 s; ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃, plus APT) δ 207.5 (-, d, J(PC) = 19.8, CO), 194.7 (-, s, C_{β}), 155.0 (-, s, N=CPh₂), 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 $(-, s, C_{\gamma})$, 85.6 (+, s, Cp), 27.5 $(+, d, J(PC) = 22.6, PCHCH_3)$, 20.0, 19.5 (+, both s, PCHCH₃).

X-ray Structure Analysis of $[Ru(\eta^5-C_5H_5)\{C(O)CHCPh_2\}$ (CO)(PPr $^{i}_{3}$)] (11) and [Ru(η^{5} -C₅H₅){C(CH=CPh₂)=N= CPh₂}(CO)(PPrⁱ₃)|BF₄ (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 Et₂O into a concentrated solution of 23 in CH2Cl2. 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 $20 \le 2\theta \le 42^{\circ}$ (11) (60 reflections in the range 20 $\leq 2\theta \leq 30^{\circ}$ 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 leastsquares 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-PLUS⁵³ and SHELXL93.⁵⁴

Acknowledgment. We thank the DGICYT (Project PB-95-0806, Programa de Promoción General del Conocimiento) and the EU (European Union) (Project: Selective Processes and Catalysis Involving Small Molecules) for financial support.

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.

OM960124D

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