Regioselective Addition of $PRPh_2$ to the C_α Atom of the Diphenylallenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i{}_3)]BF_4$

Miguel A. Esteruelas,* Angel V. Gómez, Ana M. López, Javier Modrego, and Enrique Oñate

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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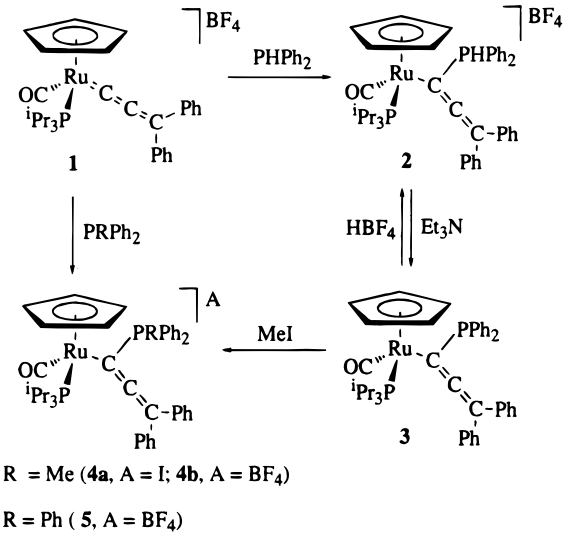
Summary: *The allenylidene ligand of* $[Ru(\eta^5\text{-}C_5H_5)\{C{=}C{=}CPh_2\}(CO)(PPr^i{}_3)]BF_4$ *adds* $PHPh_2$, $PMePh_2$, *and* PPh_3 *selectively at the* C_α *atom, whereas* OH^- *and* $[OMe]^-$ *are added at the* C_γ *atom.*

EHT-MO calculations on transition-metal allenylidene complexes indicate that the C_α and C_γ atoms of the allenylidene ligands are electrophilic centers and that the C_β atom is nucleophilic.[1] There are marked differences in reactivity depending upon the particular metallic fragment which stabilizes the allenylidene unit. This is nicely illustrated by the behavior of diphenylallenylidene in iron triad complexes. For example, $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CPh_2)(PPr^i{}_3)$ is nucleophilic and reacts with HBF_4 and dimethyl acetylendicarboxylato to afford $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CPh_2)(PPr^i{}_3)]BF_4$ and $Os(\eta^5\text{-}C_5H_5)Cl\{C{=}C(CO_2Me)C(CO_2Me){=}C{=}CPh_2\}(PPr^i{}_3)$.[2] In contrast, the cationic compounds $[Os\{C[C(O)OMe{=}CH_2\}(C{=}C{=}CPh_2)(CO)(PPr^i{}_3)_2]BF_4$,[3] $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)L_2]PF_6$ (L_2 = 2 PPh_3, dppe, dppm),[1c,4] $[RuCl(C{=}C{=}CPh_2)(dppm)_2]PF_6$,[5] $[Ru(\eta^5\text{-}C_nH_m)(C{=}C{=}CPh_2)(PPh_3)\text{-}\{\kappa^1\text{-}Ph_2PCH_2C(O)Bu^t\}]PF_6$ (C_nH_m = C_5H_5, C_9H_7),[6] and $[RuCl(C{=}C{=}CPh_2)\{N(CH_2CH_2PPh_2)_3\}]PF_6$[7] are electrophilic and react with RLi and $Na[OCH_3]$ to give alkynyl derivatives resulting from regioselective additions at the C_γ atom of the allenylidene.

Diphenylallenylidene groups stabilized by less basic metallic fragments, such as $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i{}_3)]^+$,[8] $[Ru(\eta^5\text{-}C_9H_4Me_3)(CO)(PPh_3)]^+$,[9] and $[RuCl(\eta^6\text{-}C_6H_4X_2)(PMe_3)]^+$ (X = H, Me),[10] show stronger electrophilic character and add alcohols at the $C_\alpha{-}C_\beta$ double bond of the allenylidene to afford α,β-unsaturated alkoxycarbene derivatives.

Scheme 1



The reactivity of these allenylidene complexes toward phosphines[4] seems to be controlled not only by the metallic fragment but also by the cone angle of the phosphine. This may be the reason that reactions with phosphines bulkier than PMe_2Ph have not been previously observed.

We report herein that $PHPh_2$ adds regioselectively to the C_α atom of the allenylidene ligand in $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i{}_3)]BF_4$ (**1**) to afford adduct **2** according to Scheme 1. Characteristic spectroscopic features of **2** are the C=C=C stretching frequency in the IR spectrum at 1884 cm^{-1} and the three resonances in the $^{13}C\{^1H\}$ NMR spectrum at 215.7, 104.5, and 71.8 ppm for the C_β, C_γ, and C_α allenyl carbon atoms. Complex **2** reacts with Et_3N in toluene to afford the neutral allenyl−phosphine derivative $Ru(\eta^5\text{-}C_5H_5)\{C(PPh_2){=}C{=}CPh_2\}(CO)(PPr^i{}_3)$ (**3**), which regenerates **2** by protonation with $HBF_4{\cdot}OEt_2$. A view of the molecular geometry of **3** is shown in Figure 1.

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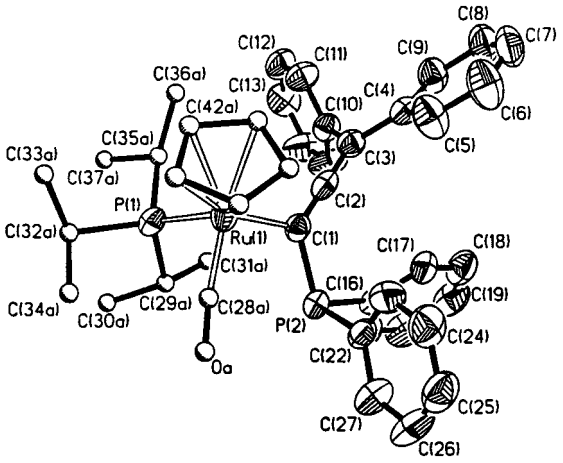


Figure 1. Molecular diagram of complex **3**. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) 2.325(2), Ru(1)−C(1) 2.139(5), C(1)−C(2) 1.292(7), C(2)−C(3) 1.333(7), C(3)−C(4) 1.478(7), C(3)−C(10) 1.518(7), P(2)−C(1) 1.827(5), P(2)−C(16) 1.841(5), P(2)−C(22) 1.840(5); Ru(1)−C(1)−C(2) 122.6(4), Ru(1)−C(1)−P(2) 117.0(2), C(1)−C(2)−C(3) 178.7(5), C(2)−C(3)−C(4) 123.4(4), C(2)−C(3)−C(10) 119.1(4), C(1)−P(2)−C(16) 106.6(2), C(1)−P(2)−C(22) 103.4(2).

The geometry around the ruthenium center in **3** is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The Ru−C(1) distance [2.139(5) Å] is that expected for a Ru−Csp^2 single bond and comparable to the related distance in alkenyl−ruthenium complexes.[11] The C(1)−C(2) [1.292(7) Å] and C(2)−C(3) [1.333(7) Å] bond lengths, as well as the C(1)−C(2)−C(3) angle [178.7(5)°], which are in agreement with those reported for other transition-metal compounds of this type,[12] strongly support the allenyl formulation.[13] In accordance with the structure shown in Figure 1, the IR spectrum of **3** shows the characteristic C=C=C stretching frequency at 1867 cm^{-1}, and the ^{13}C{^{1}H} NMR spectrum contains the three resonances corresponding to the C_β, C_γ, and C_α atoms at 200.0, 99.1, and 84.3 ppm.

Complex **3** reacts with MeI to give the I$^-$ salt of the allenyl−phosphonio cation [Ru(η^5-C_5H_5){C(PMePh$_2$)=C=CPh$_2$}(CO)(PPr$^i_3$)]$^+$ (**4**). The [BF$_4$]$^-$ salt is obtained by direct reaction of **1** with PMePh$_2$ in CH$_2$Cl$_2$ as solvent. Similarly, treatment of **1** with PPh$_3$ affords [Ru(η^5-C_5H_5){C(PPh$_3$)=C=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (**5**). The identity of **4** and **5** are confirmed by a comparison of spectroscopic data with that for **2** and **3** (see Experimental Section).

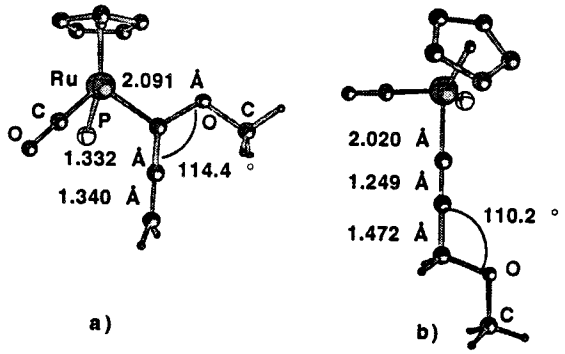
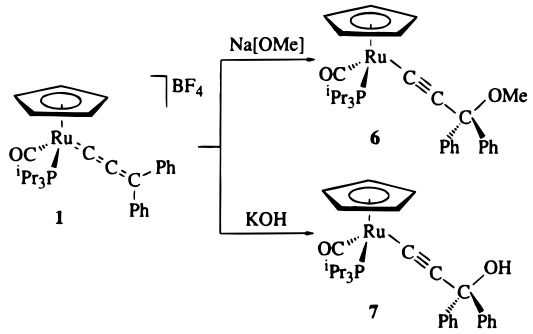


Figure 2. Partially optimized structures of Ru(η^5-C_5H_5)-{C(OMe)=C=CH$_2$}(CO)(PH$_3$) (**a**) and Ru(η^5-C_5H_5)(C≡CC-(OMe)H$_2$}(CO)(PH$_3$) (**b**) obtained by ab initio calculations at the MP2 level using the LANL2DZ basis for Ru and P, and 6-31G for the rest of atoms.

Scheme 2



The exclusive formation of **4** starting from **3** and **1** suggests that the addition of bulky phosphines to the C_α atom is kinetic and thermodynamically favored over addition at the C_γ atom. The origin of this preference may be the steric congestion due to the phenyl groups on the C_γ atom.[4] In fact, theoretical calculations at the MP2 level on the model compounds [Ru(η^5-C_5H_5)-{C(PH$_3$)=C=CH$_2$}(CO)(PH$_3$)]$^+$ and [Ru(η^5-C_5H_5){C≡CC-(PH$_3$)H$_2$}(CO)(PH$_3$)]$^+$ indicate that both isomers are minima on the potential energy surface and that the difference of energy between them is not more than 3 kcal·mol^{-1}.

In contrast to PRPh$_2$ (R = H, Me, Ph), the nucleophiles [OMe]$^-$ and OH$^-$ add at the C_γ atom of **1**, leading to the alkynyl complexes Ru(η^5-C_5H_5)(C≡CC(OR)Ph$_2$}-(CO)(PPr$^i_3$) [**6** (R = Me), **7** (R = H)] in Scheme 2. Their formation is mainly supported by the IR and ^{13}C{^{1}H} NMR spectra. The IR spectra show the ν(C≡C) bands at 2108 (**6**) and 2119 (**7**) cm^{-1}, while the ^{13}C{^{1}H} NMR spectra contain resonances at 107.6 and 96.5 (**6**) and 112.1 and 95.3 (**7**) ppm, corresponding to the C_β and C_α atoms of the alkynyl ligands.

Although the alkoxyallenyl complex Ru(η^5-C_5H_5)-{C(OMe)=C=CPh$_2$}(CO)(PPr$^i_3$) has been previously reported,[8a] isomerization of **6** into this derivative is not observed. This is in agreement with theoretical calculations on the complexes Ru(η^5-C_5H_5){C(OMe)=C=CH$_2$}-(CO)(PH$_3$) and Ru(η^5-C_5H_5)(C≡CC(OMe)H$_2$}(CO)(PH$_3$) (**a** and **b** in Figure 2), which indicate that the second model compound is 9.29 kcal·mol^{-1} more stable than the first one.[14] Furthermore, according to EHT-MO calculations,[1d] the net charge on the C_α atom of [Ru(η^5-C_5H_5)-(C=C=CH$_2$)(CO)(PH$_3$)]$^+$ (−0.36) is significantly higher

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than that on C_γ (−0.05). So, the addition of hard nucleophiles at the C_γ atom of **1** appears to be favored from an electronic point of view.

In conclusion, the allenylidene ligand of **1** adds bulky phosphines at the C_α atom, whereas hard nucleophiles such as OMe^- and OH^- add at the C_γ atom. The preference of the phosphine nucleophiles has its origin in the steric congestion due to the phenyl groups on the C_γ atom. However, the preference of the hard nucleophiles seems to be electronic and related to the smaller net charge on the C_γ atom.

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 starting material [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF_4 (**1**) was prepared by the published method.[8a]

NMR spectra (^{1}H at 300 MHz, ^{31}P at 121.4 MHz, and ^{13}C at 75.4 MHz) were recorded at 293 K, and chemical shifts are expressed in ppm downfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of [Ru(η^5-C_5H_5){C(PRPh$_2$)=C=CPh$_2$}(CO)(PPr$^i_3$)]BF_4 [R = H (2), Me (4), Ph (5)]. A solution of **1** (150 mg, 0.24 mmol) in 5 mL of CH_2Cl_2 was treated with PRPh$_2$ (0.24 mmol). Immediately, the color changed from dark red to yellow, and solvent was concentrated to ca. 1 mL. By addition of diethyl ether, a yellow solid precipitated. **2:** Yield: 180 mg (93%). Anal. Calcd for $C_{42}H_{47}BF_4OP_2Ru$: C, 61.70; H, 5.79. Found: C, 61.56; H, 6.05. IR (cm^{-1}): ν(PH) 2435 (w), ν(CO) 1941 (vs), ν(C=C=C) 1884 (m), ν(BF_4) 1078 (vs, br). NMR [(CD_3)$_2$CO]: ^{1}H δ 9.20−6.50 (21H, 4 Ph + PH), 5.14 (s, 5H, Cp), 2.20 (m, 3H, PC*H*CH$_3$), 1.13 (dd, 9H, *J*(HH) = 7.0, *J*(PH) = 14.4, PCHC*H*$_3$), 0.99 (dd, 9H, *J*(HH) = 7.0, *J*(PH) = 12.9, PCHC*H*$_3$); ^{31}P{^{1}H} δ 73.7 (s, PPr$^i_3$), 22.4 (s, PHPh$_2$); ^{13}C{^{1}H} δ 215.7 (br, C_β), 206 (hidden by signal of solvent, CO), 137.2−121.7 (Ph), 104.5 (d, *J*(PC) = 24.1, C_γ), 86.5 (s, Cp), 71.8 (dd, *J*(PC) = 17.3, *J*(PC) = 11.4, C_α), 27.3 (d, *J*(PC) = 23.3, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 18.9 (d, *J*(PC) = 1.8, PCH*C*H$_3$). **4**: Yield: 180 mg (90%). Anal. Calcd for $C_{43}H_{49}BF_4OP_2Ru$: C, 62.10; H, 5.94. Found: C, 61.70; H, 5.51. IR (cm^{-1}): ν(CO) 1910 (vs), ν(C=C=C) 1858 (m), ν(BF_4) 1066 (vs, br). NMR ($CDCl_3$): ^{1}H δ 7.68−7.06 (18H, Ph), 6.34 (2H, Ph), 4.95 (s, 5H, Cp), 2.88 (d, *J*(PH) = 12.3, Me), 2.07 (m, 3H, PC*H*CH$_3$), 1.05 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 15.0, PCHC*H*$_3$), 0.87 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.9, PCHC*H*$_3$); ^{31}P{^{1}H} δ 66.2 (s, PPr$^i_3$), 24.2 (s, PMePh$_2$); ^{13}C{^{1}H} (plus dept) δ 214.3 (dd, *J*(PC) = 1.9, C_β), 206.6 (dd, *J*(PC) = 6.4, *J*(PC) = 20.2, CO), 137.4−121.7 (Ph), 101.8 (d, *J*(PC) = 23.0, C_γ), 84.8 (s, Cp), 74.6 (dd, *J*(PC) = 9.2, *J*(PC) = 18.9, C_α), 25.7 (d, *J*(PC) = 23.0, P*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$), 17.8 (d, *J*(PC) = 2.8, PCH*C*H$_3$), 11.6 (d, *J*(PC) = 61.6, Me). **5**: Yield: 200 mg (93%). Anal. Calcd for $C_{48}H_{51}BF_4OP_2Ru$: C, 64.51; H, 5.75. Found: C, 64.17; H, 5.28. IR (cm^{-1}): ν(CO) 1929 (vs), ν(C=C=C) 1868 (s), ν(BF_4) 1067 (vs, br). NMR ($CDCl_3$): ^{1}H δ 7.71−6.73 (25H, Ph), 4.74 (s, 5H, Cp), 2.22 (m, 3H, PC*H*CH$_3$), 1.11 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCHC*H*$_3$), 0.96 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 13.2, PCHC*H*$_3$); ^{31}P{^{1}H} δ 62.8 (s, PPr$^i_3$), 29.8 (s, PPh$_3$); ^{13}C{^{1}H} (plus dept) δ 217.3 (d, *J*(PC) = 2.3, C_β), 206.4 (dd, *J*(PC) = 6.0, *J*(PC) = 19.3, CO), 135.8−121.5 (Ph), 101.6 (d, *J*(PC) = 23.4, C_γ), 85.1 (s, Cp), 74.1 (dd, *J*(PC) = 7.8, *J*(PC) = 14.7, C_α), 27.4 (d, *J*(PC) = 22.5, P*C*HCH$_3$), 20.0, 18.7 (both s, PCH*C*H$_3$).

Preparation of Ru(η^5-C_5H_5){C(PPh$_2$)=C=CPh$_2$}(CO)(PPr$^i_3$) (3). A suspension of **2** (219 mg, 0.27 mmol) in 5 mL of toluene was treated with Et_3N (38 μL, 0.28 mmol). The mixture was stirred for 1 h, and the yellow suspension was filtered. Solvent was removed in vacuo, and the residue was washed with methanol to afford a yellow solid. Yield: 156 mg (80%). Anal. Calcd for $C_{42}H_{46}OP_2Ru$: C, 69.12; H, 6.35. Found: C, 68.89; H, 5.96. IR (cm^{-1}): ν(CO) 1925 (vs), ν(C=C=C) 1867 (s). NMR (C_6D_6): ^{1}H δ 7.95−6.85 (20H, Ph), 4.72 (s, 5H, Cp), 1.98 (m, 3H, PC*H*CH$_3$), 1.01 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCHC*H*$_3$), 0.76 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 12.9, PCHC*H*$_3$); ^{31}P{^{1}H} δ 70.0 (d, *J*(PP) = 5.3, PPr$^i_3$), 12.4 (d, *J*(PP) = 5.3, PPh$_2$); ^{13}C{^{1}H} δ 207.1 (dd, *J*(PC) = 20.4, *J*(PC) = 16.6, CO), 200.0 (dd, *J*(PC) = 6.8, *J*(PC) = 3.0, C_β), 142.3, 140.9 (both s, $C_{ipso,Ph}$), 141.6 (d, *J*(PC) = 25.6, $C_{ipso,Ph}$), 140.6 (d, *J*(PC) = 18.9, $C_{ipso,Ph}$), 136.0−125.4 (Ph), 99.1 (d, *J*(PC) = 5.6, C_γ), 85.5 (s, Cp), 84.3 (dd, *J*(PC) = 71.1, *J*(PC) = 10.9, C_α), 27.1 (d, *J*(PC) = 22.4, P*C*HCH$_3$), 20.11 (d, *J*(PC) = 2.3, PCH*C*H$_3$), 19.21 (s, PCH*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){C≡CC(OR)Ph$_2$}(CO)(PPr$^i_3$)] [R = Me (6), H (7)]. A solution of **1** (130 mg, 0.20 mmol) in 5 mL of THF was treated with Na[OMe] (19 mg, 0.35 mmol) or KOH (50 mg, 85%, 0.76 mmol). The resulting suspension was stirred for 10 min or 4 h, respectively. Solvent was removed in vacuo, and the residue was extracted in 10 mL of toluene or 30 mL of hexane. The suspension was filtered, and solvent was removed in vacuo. The residue was washed with cold methanol to afford **6** or **7** as white solids. **6:** Yield: 89 mg (75.1%). Anal. Calcd for $C_{31}H_{39}O_2PRu$: C, 64.46; H, 6.83. Found: C, 64.78; H, 6.10. IR (cm^{-1}): ν(C≡C) 2108 (m), ν(CO) 1938 (vs). NMR (C_6D_6): ^{1}H δ 7.96 (m, 4H, o-Ph), 7.21 (m, 4H, m-Ph), 7.07 (m, 2H, p-Ph), 4.79 (s, 5H, Cp), 3.57 (s, 3H, OMe), 1.90 (m, 3H, PC*H*CH$_3$), 1.02 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.5, PCHC*H*$_3$), 0.78 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.1, PCHC*H*$_3$); ^{31}P{^{1}H} δ 74.8 (s); ^{13}C{^{1}H} δ 206.3 (d, *J*(PC) = 18.1, CO), 147.7, 147.4 (both s, C_{ipso}), 128−126.6 (Ph), 107.6 (s, C_β), 96.5 (d, *J*(PC) = 21.6, C_α), 85.5 (d, *J*(PC) = 1.8, Cp), 82.4 (s, C_γ), 51.6 (s, OMe), 27.2 (d, *J*(PC) = 23.4, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$), 19.4 (d, *J*(PC) = 1.9, PCH*C*H$_3$). **7:** Yield: 92 mg (79%). Anal. Calcd for $C_{30}H_{37}O_2PRu$: C, 64.15; H, 6.63. Found: C, 64.32; H, 6.99. IR (cm^{-1}): ν(OH) 3560 (m), ν(C≡C) 2119 (m), ν(CO) 1941 (vs). NMR (C_6D_6): ^{1}H δ 7.97 (m, 4H, o-Ph), 7.20 (m, 4H, m-Ph), 7.07 (m, 2H, p-Ph), 4.79 (s, 5H, Cp), 2.59 (s, 1H, OH), 1.91 (m, 3H, PC*H*CH$_3$), 1.02 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.5, PCHC*H*$_3$), 0.80 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.1, PCHC*H*$_3$); ^{31}P{^{1}H} δ 74.7 (s); ^{13}C{^{1}H} δ 206.2 (d, *J*(PC) = 17.4, CO), 149.2 (s, C_{ipso}), 128−126.5 (Ph), 112.1 (s, C_β), 95.3 (d, *J*(PC) = 21.1, C_α), 85.6 (d, *J*(PC) = 1.5, Cp), 75.8 (s, C_γ), 27.2 (d, *J*(PC) = 23.3, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$), 19.4 (d, *J*(PC) = 2.3, PCH*C*H$_3$).

X-ray Structure Determination of 3. Complex **3** is triclinic, space group $P\bar{1}$, a = 10.163(4) Å, b = 12.749(4) Å, c = 15.449(6) Å, α = 98.10(2)°, β = 100.62(2)°, γ = 108.76(2)°, Z = 2; 9507 reflections ($\pm h$, $+k$, $\pm l$) were collected at room temperature with a Siemens Stoe-AED2 diffractometer over a 2θ range of 3−50°. An empirical absorption correction from Ψ scans was applied to the data (μ = 0.55 mm^{-1}). Structural solutions by Patterson and least-squares refinement (based on F^2) were performed with SHELXTL v. 5.0. The refinement on 5720 ($F_o^2 > 0$) data converged at $wR_2(F^2)$ = 0.1594 for all data and $R_1(F)$ = 0.0528 for 4246 observed data ($I > 2\sigma(I)$). More details in the Supporting Information.

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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 (17 pages). Ordering information is given on any current masthead page.

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(14) Although complex **6** appears to be thermodynamically more stable than Ru(η^5-C_5H_5){C(OMe)=C=CPh$_2$}(CO)(PPr$^i_3$), isomerization of the latter into **6** is not observed. This could be due to the fortress of the C_α−OMe bond, which imposes a high activation barrier for the isomerization.