Synthesis and Reactivity of (η^6-Arene)(phosphino enolato)ruthenium(II) Complexes, Their Coupling Reaction with Phenylacetylene, and Thermal Rearrangement to a Phosphametallacyclopropane. X-ray Crystal Structures of {Ru[η^3-CH=C(Ph)CH(PPh$_2$)C(Bu^t)=O](*p*-cymene)}(PF$_6$), of {Ru[η^3-CH=C(Ph)C(Me)(PPh$_2$)C(Et)=O](mesitylene)}(BF$_4$), and of {Ru[η^3-CH(PPh$_2$)CPh=C(H)C(Bu^t)=O](mesitylene)}(BF$_4$)

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Received April 8, 1993®

The reaction of lithium enolates with chlorodiphenylphosphine provides a convenient large scale synthesis of β-keto phosphines. The coordination of β-keto phosphines **1** at an (η^6-arene)Cl$_2$-Ru fragment affords neutral complexes (η^6-arene)Cl$_2$Ru[η^1-*P*-Ph$_2$PCHR^{2}C(=O)R^1], **2**, cationic complexes {(η^6-arene)ClRu[η^2-*P*,*O*-Ph$_2$PCR^{3}R^{2}C(R^1)=O]}$^+$, **3**, and neutral enolato derivatives (η^6-arene)ClRu[η^2-*P*,*O*-OC(R^1)=C(R^2)PPh$_2$], **4**. Compounds **4** react under mild conditions with ligands L (L = Me$_2$S or RC≡N) to give cationic derivatives {(η^6-arene)(L)ClRu[OC(R^1)=C-(R^2)PPh$_2$]}$^+$, **5**. When L is PhC≡CH, carbon—carbon bond formation leads *via* regioselective coupling of the C≡C bond to both ruthenium and =C(PPh$_2$) carbon to complexes {(η^6-arene)-Ru[η^3-CH=C(Ph)C(R^2)(PPh$_2$)C(R^1)=O]}$^+$, **6**. The crystal structures of the compounds **6a** (arene = *p*-cymene, R^2 = H, R^1 = Bu^t), monoclinic, space group $P2_1/n$ (No. 14) with Z = 4, a = 14.870(4) Å, b = 20.087(6) Å, c = 12.454(5) Å, α = 90.0°, β = 92.67(3)°, γ = 90.0°, d(calcd) = 1.37 g/cm^3, and **6c** (arene = mesitylene, R^2 = Me, R^1 = Et), triclinic, space group $P\bar{1}$ (No. 2) with Z = 2, a = 10.962(1) Å, b = 15.473(2) Å, c = 10.910(1) Å, α = 100.10(1)°, β = 113.64(1)°, γ = 102.41(1)°, d(calcd) = 1.55 g/cm^3, have been determined. **6b** (arene = mesitylene, R^2 = H, R^1 = Bu^t) is cleanly thermally converted to the metallaphosphacyclopropane derivative {Ru-[η^3-CH(PPh$_2$)CPh=C(H)C(Bu^t)=O](mesitylene)}$^+$, **7**, as shown by the X-ray structure determination: triclinic, space group $P\bar{1}$ (No. 2) with Z = 2, a = 14.034(2) Å, b = 11.944(1) Å, c = 10.957(1) Å, α = 106.56°, β = 98.34(1)°, γ = 109.24(1)°, d(calcd) = 1.44 g/cm^3.

Introduction

The reactivity of ruthenium(II) complexes has especially attracted interest for the activation of terminal alkynes which provides a ready access to ruthenium(II) vinylidene intermediates under mild conditions. Such vinylidenes have been prepared starting from complexes containing cyclopentadienyl,[1] arene,[2] or chelating functional phosphine[3] ligands. The formation of the vinylidene ruthenium moiety is generally understood[1c,4] via η^2-coordination of the alkyne followed by proton migration with a first-order rearrangement. Poor electron donating ancillary ligands enhance the electrophilic character of the vinylidene carbon atom that adds methanol under mild conditions leading to methoxycarbene derivatives.[5] By contrast, reactions involving the first-step formed (η^2-HC≡CR)-Ru^{II} intermediates are uncommon but would be expected with reactive ligands in intramolecular processes. We have previously given evidence[6] for the reactivity of the phosphino thioenolato ligand in iron(II) complexes **I** in a sulfur—carbon coupling reaction with phenylacetylene leading to complexes **II**. However the structure of

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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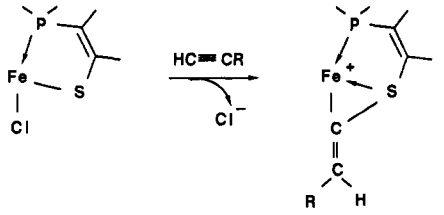
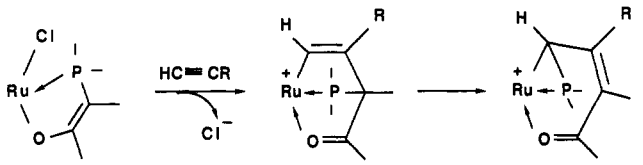


I II

complexes **II** shows that the coupling reaction occurred after the rearrangement into vinylidene has been effective.

These studies were limited by the specific access to the phosphino thioenolato ligand, from intramolecular coupling[7] of a phosphinoalkyne with iron coordinated carbon disulfide. Our aim to develop the chemistry of closely related but more easily accessible functional ligands, able to trap unstable or reactive transient species, led us to study the synthesis and reactivity of ruthenium(II) complexes of β-keto phosphines.[8] In the present paper we report (i) the synthesis of several new β-keto phosphines by reaction of lithium enolates with chlorodiphenylphosphine and their (η⁶-arene)ruthenium(II) complexes, (ii) the formation of complexes of type **III** that lead to intramo-



III IV V

lecular coupling between an η²-coordinated terminal alkyne and an η²-phosphino enolato ligand to give new tripodal ligand ruthenium complexes of type **IV**, and (iii) the evidence of a thermal rearrangement producing a novel phosphorus–carbon–ruthenium three-membered ring and a complex of type **V**. X-ray structure determinations of complexes of types **IV** and **V** are reported.

Experimental Section

All chemicals were reagent grade and were used as received or synthesized as described below. Reactions involving phosphines were performed under argon or nitrogen using Schlenk techniques. Chlorodiphenylphosphine was distilled prior to use and stored under argon. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were performed by the "Service de Microanalyse du CNRS", Vernaison, France. Solvents were dried and distilled under inert atmosphere before use by conventional methods, except ethanol for which anhydrous conditions are not required. Infrared spectra were recorded on a Nicolet 205 FT-infrared spectrometer as Nujol mulls. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on WP 80 FT (^1H, 80 MHz; ^{31}P, 32.38 MHz) and AC 300 FT (^1H, 300.13 MHz; ^{31}P, 121.50 MHz; ^{13}C, 75.47 MHz) Bruker instruments. The commercially available ketones were used without supplementary purification. *tert*-Butyl ethyl ketone and *tert*-Butyl isopropyl ketone were prepared according to published methods.[9] The complexes $[(p\text{-cymene})RuCl_2]_2$,[10] $[(\text{mesitylene})RuCl_2]_2$,[11] and $[(\text{hexamethylbenzene})RuCl_2]_2$[10] were prepared as literature described.

$Ph_2PCH_2C(=O)Bu^t$, 1a. To a cold solution (between −60 and −80 °C) of LDA obtained from 60 mL (96 mmol) of 1.6 M Bu^nLi hexane solution and 13.4 mL (102 mmol) of Pr^i_2NH in 100 mL of THF was added 11.0 mL (88.0 mmol) of pinacolone. The mixture was then stirred 2 h, allowing it to reach room temperature, and then evaporated to dryness. The crude white solid enolate was dissolved in 150 mL of hexane, and after cooling at −80 °C, 15.0 mL (83.6 mmol) of Ph_2PCl was added. The reaction mixture was stirred overnight at room temperature and then filtered through a short (10- × 4-cm) alumina column. The alumina was washed three times with 40 mL of hexane and the filtrate concentrated to 100 mL under vacuum. The solution was kept at −20 °C overnight, allowing the formation of white crystals. The crystals were separated, washed with 30 mL of cold pentane, and dried under vacuum. Yield: 17.8 g, 75%. Mp: 50 °C. IR, $\nu_{C=O}$: 1690 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: −20.2 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.35 (m, 10 H, Ph), 3.25 (s, 2 H, PCH_2), 1.11 (s, 9 H, Bu^t).

$Ph_2PCH_2C(=O)Ph$, 1b. The acetophenone enolate was prepared as for **1a** using 10.0 mL (86.0 mmol) of acetophenone and then reacted with Ph_2PCl using diethyl ether instead of hexane. The solution obtained after filtration over alumina was evaporated to dryness under vacuum, leaving a white solid that was used without further purification. Yield: 23.0 g, 90%. Mp: 71 °C.[8] IR, $\nu_{C=O}$: 1680 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: −17.1 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.10–7.20 (m, 15 H, Ph), 3.80 (s, 2 H, PCH_2).

$Ph_2PCH(Me)C(=O)Et$, 1c. The diethyl ketone enolate obtained from 15.0 mL (142 mmol) of diethyl ketone was dissolved in 200 mL of hexane and reacted with 21.5 mL (120 mmol) of Ph_2PCl as for **1a**. The resulting solution was evaporated to dryness, leaving a colorless oil that was used without further purification. Yield: 29.8 g, 92%. IR, $\nu_{C=O}$: 1700 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: −1.0 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.35 (m, 10 H, Ph), 3.50 (m, 1 H, $^2J_{PH}$ = 4.6 Hz, $^3J_{HH}$ = 7.1 Hz, PCH), 2.28 (m, 2 H, $^4J_{PH}$ = 2.0 Hz, CH_2Me), 1.23 (dd, 3 H, $^3J_{PH}$ = 13.4 Hz, PCMe), 0.88 (t, 3 H, CH_2Me).

$Ph_2PCH(Me)C(=O)Bu^t$, 1d. **1d** was prepared following the procedure described for **1c**, starting from 20.0 mL (140 mmol) of *tert*-butyl ethyl ketone. The hexane solution obtained after filtration was concentrated to 100 mL and then cooled to −20 °C to afford white crystals. Yield: 26.9 g, 75%. Mp: 60 °C. IR, $\nu_{C=O}$: 1700 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: −1.4 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.40 (m, 10 H, Ph), 3.95 (m, 1 H, $^2J_{PH}$ = 5.9 Hz, $^3J_{HH}$ = 6.8 Hz, PCH), 1.25 (dd, 3 H, $^3J_{PH}$ = 13.2 Hz, PCMe), 0.92 (s, 9 H, Bu^t).

$Ph_2PCH(Me)C(=O)Ph$, 1e. The enolate obtained from 6.0 mL (45.2 mmol) of propiophenone was dissolved in a hexane (100 mL)/diethyl ether (50 mL) mixture. After reacting with 7.50 mL (41.8 mmol) of chlorodiphenylphosphine as above, the solution was evaporated to dryness, leaving a colorless oil. On standing, crystallization of the oil occurs. Yield: 12.6 g, 94%. Mp: 35 °C. IR, $\nu_{C=O}$: 1670 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 1.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.90–7.21 (m, 15 H, Ph), 4.39 (m, 1 H, $^2J_{PH}$ = 5.1 Hz, $^3J_{HH}$ = 7.1 Hz, PCH), 1.39 (dd, 3 H, $^3J_{PH}$ = 12.5 Hz, PCMe).

$Ph_2PCMe_2C(=O)Pr^i$, 1f. **1f** was prepared as **1c**, starting from 20.0 mL (141 mmol) of diisopropyl ketone. The filtered hexane solution was concentrated to 100 mL and then cooled overnight to −20 °C, affording white crystals. Yield: 28.1 g, 78%. Mp: 100 °C. IR, $\nu_{C=O}$: 1700 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 14.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.34 (m, 10 H, Ph), 3.42 (m, 1 H, $^3J_{HH}$ = 6.6 Hz, $^4J_{PH}$ = 1.7 Hz, $CHMe_2$), 1.27 (d, 6 H, $^3J_{PH}$ = 10.7 Hz, $PCMe_2$), 1.01 (d, 6 H, $CHMe_2$). Phosphine **1f** was analyzed as its *oxide*. Anal. Found (Calcd) for $C_{19}H_{23}PO_2$: C, 72.81 (72.60); H, 7.00 (7.37); P, 9.96 (9.85).

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$Ph_2PCMe_2C(=O)Bu^t$, 1g. **1g** was prepared as **1f** from *tert*-butyl isopropyl ketone and was obtained as a colorless oil. Yield: 50%. Several recrystallizations from hexane afforded white crystals. Mp: 65 °C. IR, $\nu_{C=O}$: 1680 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 14.1 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.35 (m, 10 H, Ph), 1.34 (d, 6 H, $^3J_{PH}$ = 10.3 Hz, $PCMe_2$), 1.32 (s, 9 H, Bu^t).

(*p*-cymene)[$Ph_2PCH_2C(=O)Bu^t$]$RuCl_2$, 2a. A 4.65-g (7.60-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 4.33 g (15.2 mmol) of phosphine **1a** were stirred in 40 mL of dichloromethane for 1 h. The deep red solution was filtered and the filtrate covered with 180 mL of hexane. The dark red crystals resulting from the natural diffusion of the solvents were separated, washed with 30 mL of hexane, and dried. Yield: 7.90 g, 88%. Anal. Found (Calcd) for $C_{28}H_{35}PCl_2ORu$: C, 56.61 (56.95); H, 5.80 (5.97); P, 5.20 (5.25); Cl, 12.85 (12.01). IR, $\nu_{C=O}$: 1705 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 25.2 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.96–7.48 (m, 10 H, Ph), 5.22 (AB, 4 H, $^3J_{HH}$ = 5.9 Hz, C_6H_4), 4.02 (d, 2 H, $^2J_{PH}$ = 9.0 Hz, PCH_2), 2.51 (m, 1 H, C*H*Me_2), 1.87 (s, 3 H, *Me*Ar), 0.84 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 0.66 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 210.8 (d, $^2J_{PC}$ = 11.6 Hz, C=O), 133.6–85.7 (m, Ar), 45.7 (s, *C*Me_3), 30.6 (d, $^1J_{PC}$ = 25.8 Hz, PCH_2), 30.0 (s, *C*HMe_2), 25.4 (s, C*Me*$_3$), 21.4 (s, CH*Me*$_2$), 17.3 (s, *Me*Ar).

(mesitylene)[$Ph_2PCH_2C(=O)Bu^t$]$RuCl_2$, 2b. A 2.90-g (4.97-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 2.90 g (10.2 mmol) of phosphine **1a** were stirred overnight in 50 mL of dichloromethane. The reaction mixture was evaporated to dryness and the solid extracted with 40 mL of hot chloroform. The red solution was filtered and the filtrate covered with 150 mL of hexane. The resulting red crystals were separated and washed with 30 mL of diethyl ether. Yield: 4.60 g, 80%. Anal. Found (Calcd) for $C_{27}H_{33}PCl_2ORu$: C, 55.97 (56.25); H, 5.83 (5.77); P, 5.17 (5.37); Cl, 13.17 (12.30). IR, $\nu_{C=O}$: 1710 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 26.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.04–7.49 (m, 10 H, Ph), 4.71 (s, 3 H, C_6H_3), 4.08 (d, 2 H, $^2J_{PH}$ = 9.0 Hz, PCH_2), 1.85 (s, 9 H, Me_3Ar), 0.69 (s, 9 H, Bu^t).

(*p*-cymene)[$Ph_2PCH_2C(=O)Ph$]$RuCl_2$, 2c. A 1.87-g (3.06-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 1.85 g (6.09 mmol) of phosphine **1b** were stirred in 30 mL of chloroform for 1 h. The solution was filtered and the filtrate covered with 100 mL of hexane. Yield: 3.70 g, 99%. Anal. Found (Calcd) for $C_{30}H_{31}PCl_2ORu$: C, 58.67 (59.02); H, 5.22 (5.12); P, 4.95 (5.07); Cl, 11.25 (11.61). IR, $\nu_{C=O}$: 1670 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 27.7 (s). ^1H NMR $CDCl_3$, 80 MHz, δ: 7.93–7.43 (m, 15 H, Ph), 5.27 (AB, 4 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 4.42 (d, 2 H, $^2J_{PH}$ = 10.7 Hz, PCH_2), 2.52 (m, 1 H, C*H*Me_2), 1.90 (s, 3 H, *Me*Ar), 0.87 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, CH*Me*$_2$).

(mesitylene)[$Ph_2PCH_2C(=O)Ph$]$RuCl_2$, 2d. This complex was obtained in 95% yield as a red crystalline powder, starting from [(mesitylene)$RuCl_2]_2$ and phosphine **1b**, following the procedure detailed for complex **2b**. Anal. Found (Calcd) for $C_{29}H_{29}PCl_2ORu$: C, 58.46 (58.39); H, 4.82 (4.90); P, 5.10 (5.19); Cl, 12.08 (11.89). IR, $\nu_{C=O}$: 1670 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 29.0 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.00–7.37 (m, 15 H, Ph), 4.73 (s, 3 H, C_6H_3), 4.49 (d, 2 H, $^2J_{PH}$ = 18.7 Hz, PCH_2), 1.89 (s, 9 H, Me_3Ar).

(mesitylene)[$Ph_2PCH(Me)C(=O)Et$]$RuCl_2$, 2e. A 2.05-g (3.51-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 2.50 mL (excess) of the crude phosphine **1c** were stirred for 3 h in 30 mL of dichloromethane. The reaction mixture was evaporated to dryness and the residue extracted with a hot mixture of 15 mL of toluene and 20 mL of chloroform. The solution was filtered and the dark red filtrate covered with 150 mL of hexane. The deep red crystals were separated and washed twice with 30 mL of diethyl ether. Yield: 3.12 g, 79%. Anal. Found (Calcd) for $C_{28}H_{31}PCl_2ORu$: C, 55.30 (55.52); H, 5.36 (5.56); P, 5.30 (5.51); Cl, 13.42 (12.61). IR, $\nu_{C=O}$: 1710 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 29.0 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.11–7.46 (m, 10 H, Ph), 4.88 (m, 1 H, $^2J_{PH}$ = 5.9 Hz, $^3J_{HH}$ = 7.2 Hz, PCH), 4.54 (s, 3 H, C_6H_3), 2.62 (m, 2 H, CH_2Me), 1.88 (s, 9 H, Me_3Ar), 0.98 (dd, 3 H, $^3J_{PH}$ = 15.6 Hz, PCMe), 0.77 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_2Me). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 211.2 (d, $^2J_{PC}$ = 6.5 Hz, C=O), 135.9–85.8 (m, Ar), 40.7 (d, $^1J_{PC}$ = 17.4 Hz, PCH), 38.0 (d, $^3J_{PC}$ = 2.2 Hz, CH_2Me), 18.4 (s, *Me*$_3$Ar), 16.8 (d, $^2J_{PC}$ = 3.3 Hz, PC*Me*), 7.3 (s, CH_2*Me*).

(*p*-cymene)[$Ph_2PCH(Me)C(=O)Bu^t$]$RuCl_2$, 2f. A 1.00-g (1.63-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 0.97 g (3.26 mmol) of phosphine **1d** were stirred overnight in 20 mL of chloroform. Diethyl ether (100 mL) was added and the solution fastly filtered before cooling overnight to −20 °C. Yield: 1.12 g, 57%. Anal. Found (Calcd) for $C_{29}H_{37}PCl_2ORu$: C, 57.13 (57.61); H, 6.20 (6.17); P, 4.84 (5.12); Cl, 12.64 (11.73). IR, $\nu_{C=O}$: 1695 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 27.9 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.43–7.40 (m, 10 H, Ph), 5.20 (m, 1 H, $^2J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 7.1 Hz, PCH), 5.08 (m, 4 H, C_6H_4), 2.54 (m, 1 H, C*H*Me_2), 1.69 (s, 3 H, *Me*Ar), 1.18 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.14 (s, 9 H, Bu^t), 1.05 (dd, 3 H, $^3J_{PH}$ = 16.0 Hz, PCMe), 0.98 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$).

(mesitylene)[$Ph_2PCH(Me)C(=O)Bu^t$]$RuCl_2$, 2g. A 1.84-g (3.15-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 1.88 g (6.31 mmol) of phosphine **1d** were stirred overnight in 40 mL of dichloromethane. The reaction mixture was evaporated to dryness and the residue extracted with 30 mL of toluene. The solution was filtered and then covered with 130 mL of hexane to afford red crystals. Yield: 1.85 g, 50%. Anal. Found (Calcd) for $C_{28}H_{35}PCl_2ORu$: C, 56.70 (56.95); H, 5.90 (5.97); P, 5.14 (5.25); Cl, 12.33 (12.01). IR, $\nu_{C=O}$: 1695 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 31.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.55–7.39 (m, 10 H, Ph), 5.46 (m, 1 H, $^2J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.3 Hz, PCH), 4.50 (s, 3 H, C_6H_3), 1.89 (s, 9 H, Me_3Ar), 1.10 (s, 9 H, Bu^t), 1.03 (dd, 3 H, $^3J_{PH}$ = 16.8 Hz, PCMe).

(*p*-cymene)[$Ph_2PCH(Me)C(=O)Ph$]$RuCl_2$·$CHCl_3$, 2h. A 2.00-g (3.27-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 2.10 g (6.60 mmol) of phosphine **1e** were stirred in 40 mL of chloroform. The solution was filtered and the filtrate covered with 150 mL of hexane. The dark red crystals were separated and washed with 30 mL of ether. Yield: 3.80 g, 78%. Anal. Found (Calcd) for $C_{31}H_{33}PCl_2ORu$·$CHCl_3$: C, 51.42 (51.66); H, 4.59 (4.61); P, 4.11 (4.16); Cl, 23.86 (23.82). IR, $\nu_{C=O}$: 1675 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 28.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.42–7.25 (m, 15 H, Ph), 5.71 (m, 1 H, $^2J_{PH}$ = 4.8 Hz, $^3J_{HH}$ = 7.1 Hz, PCH), 5.30 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 4.94 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 2.49 (m, 1 H, C*H*Me_2), 1.72 (s, 3 H, *Me*Ar), 1.15 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.11 (dd, 3 H, $^3J_{PH}$ = 16.6 Hz, PCMe), 0.89 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$).

(mesitylene)[$Ph_2PCH(Me)C(=O)Ph$]$RuCl_2$, 2i. A 2.50-g (4.28-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 3.00 g (9.43 mmol) of phosphine **1e** were stirred overnight in 60 mL of dichloromethane. The reaction mixture was evaporated to dryness and the residue extracted with 40 mL of hot chloroform. The solution was filtered and 150 mL of hexane added to the filtrate. Yield: 2.91 g, 56%. Anal. Found (Calcd) for $C_{30}H_{31}PCl_2ORu$: C, 58.58 (59.02); H, 5.08 (5.12); P, 5.18 (5.07); Cl, 12.22 (11.61). IR, $\nu_{C=O}$: 1675 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 30.8 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.50–7.24 (m, 15 H, Ph), 6.00 (m, 1 H, $^2J_{PH}$ = 7.1 Hz, $^3J_{HH}$ = 6.8 Hz, PCH), 4.55 (s, 3 H, C_6H_3), 1.87 (s, 9 H, Me_3Ar), 1.11 (dd, 3 H, $^3J_{PH}$ = 16.5 Hz, PCMe).

{(η^6-mesitylene)$Ru(\mu$-Cl)$_3$Ru(Cl)[η^2-$Ph_2PC(Me)_2C(Pr^i)$=O]}. A 1.30-g (2.23-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 1.40 g (4.70 mmol) of phosphine **1f** were stirred overnight in 30 mL of dichloromethane. The solution was filtered and the filtrate covered with 15 mL of toluene and then 100 mL of hexane, affording dark red crystals. Yield: 0.65 g, 38%. Anal. Found (Calcd) for $C_{28}H_{35}PCl_4ORu_2$: C, 44.14 (44.11); H, 4.33 (4.63); P, 4.13 (4.06); Cl, 18.60 (18.60). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 32.38 MHz, δ: 104.1 (s). ^1H NMR, CD_2Cl_2, 80 MHz, δ: 8.00–7.38 (m, 10 H, Ph), 5.09 (s, 3 H, C_6H_3), 3.09 (m, 1 H, C*H*Me_2), 2.20 (s, 9 H, Me_3Ar), 1.56 (d, 3 H, $^3J_{PH}$ = 9.0 Hz, PCMe), 1.41 (d, 3 H, $^3J_{PH}$ = 14.9 Hz, PCMe′), 1.14 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*$_2$), 1.07 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 239.8 (d, $^2J_{PC}$ = 6.8 Hz, C=O), 136.8–127.9 (m, Ph), 99.0 (s, *C*Me, mesitylene), 74.5 (s, CH, mesitylene), 58.9 (d, $^1J_{PC}$ =

24.9 Hz, PCMe$_2$), 24.8 (s, CH*Me$_2$*), 20.9 (d, $^2J_{PC}$ = 10.2 Hz, PC*Me$_2$*), 19.0 (s, Me_3Ar).

[η^2-Ph$_2$PC(Me)$_2$C(Pr^i)=O]$_2$RuCl$_2$·CH$_2$Cl$_2$. A 1.62-g (2.77-mmol) sample of [(mesitylene)RuCl$_2$]$_2$ and 3.29 g (11.1 mmol) of phosphine **1f** were stirred for 2 days in 50 mL of dichloromethane. The mixture was evaporated to dryness and the residue washed with diethyl ether and then dissolved in 60 mL of a 1/1 toluene/dichloromethane mixture. The solution was filtered and the filtrate covered with 160 mL of hexane, affording a dark red crystalline solid. Yield: 2.58 g, 55%. Anal. Found (Calcd) for $C_{38}H_{46}P_2Cl_2O_2Ru$·CH_2Cl_2: C, 55.84 (54.87); H, 5.90 (5.67); P, 7.36 (7.26); Cl, 16.13 (16.61). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 32.38 MHz, δ: 64.0 (s). ^1H NMR, CD_2Cl_2, 80 MHz, δ: 8.43–7.37 (m, 20 H, Ph), 3.03 (m, 2 H, C*H*Me$_2$), 1.73 (t, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 7.8 Hz, PCMe + P′CMe), 1.31 (t, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 11.7 Hz, PCMe′ + P′CMe′), 0.94 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 0.21 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*).

{(*p*-cymene)(Cl)Ru[Ph$_2$PCH$_2$C(Bu^t)=O]}[BF$_4$], 3a, from 4a. A 0.50-g (0.90-mmol) sample of **4a** and 0.13 mL (0.91 mmol) of HBF$_4$–diethyl ether complex were dissolved in 30 mL of dichloromethane, and this solution was covered with 70 mL of diethyl ether. The orange crystals resulting from the diffusion of ether were washed with 20 mL of ether. Yield: 0.48 g, 83%. Anal. Found (Calcd) for $C_{28}H_{35}PClORuBF_4$: C, 52.50 (52.39); H, 5.36 (5.50); P, 4.62 (4.83); Cl, 5.36 (5.52). IR, $\nu_{C=O}$: 1610 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 55.9 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.86–7.16 (m, 10 H, Ph), 5.75 (AB, 2 H, $^3J_{HH}$ = 6.6 Hz, C_6H_4), 5.62 (AB, 2 H, $^3J_{HH}$ = 6.6 Hz, C_6H_4), 3.93 (ddd, 2 H, $^2J_{PH}$ = 10.7 Hz, $^2J_{HH}$ = 18.7 Hz, PCH$_2$), 2.81 (m, 1 H, C*H*Me$_2$), 1.96 (s, 3 H, *Me*Ar), 1.32 (dd, 6 H, CH*Me$_2$*), 1.31 (s, 9 H, Bu^t).

{(mesitylene)(Cl)Ru[Ph$_2$PCH$_2$C(Bu^t)=O]}[PF$_6$]·CH$_2$Cl$_2$, 3b, from 2b. A 0.55-g (0.95-mmol) sample of **2b** and 0.18 g (1.07 mmol) of NaPF$_6$ were stirred overnight in 25 mL of acetone. The reaction mixture was evaporated to dryness and the residue extracted with 20 mL of dichloromethane. The filtered solution was covered with 60 mL of diethyl ether, affording orange crystals. Yield: 0.45 g, 61%. Anal. Found (Calcd) for $C_{27}H_{33}P_2ClORuF_6$·CH_2Cl_2: C, 43.52 (43.52); H, 4.58 (4.58); P, 8.03 (8.04); Cl, 11.79 (13.80) (some loss of CH_2Cl_2 occurred). IR, $\nu_{C=O}$: 1610 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 61.8 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.60 (m, 10 H, Ph), 5.28 (s, 3 H, C_6H_3), 3.89 (ddd, 2 H, $^2J_{PH}$ = 11.0 and 10.5 Hz, $^2J_{HH}$ = 18.1 Hz, PCH$_2$), 2.07 (s, 9 H, Me_3Ar), 1.32 (s, 9 H, Bu^t).

{(*p*-cymene)(Cl)Ru[Ph$_2$PCH$_2$C(Ph)=O]}[BF$_4$], 3c, from 4d. A 0.50-g (0.87-mmol) sample of **4d** and 0.13 mL of HBF$_4$·Et$_2$O were dissolved in 30 mL of dichloromethane, and the resulting orange solution was covered with 70 mL of diethyl ether. Yield: 0.51 g, 89%. Anal. Found (Calcd) for $C_{30}H_{31}PClORuBF_4$: C, 54.23 (54.44); H, 4.59 (4.72); P, 4.73 (4.68); Cl, 5.89 (5.36). IR, $\nu_{C=O}$: 1550 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 58.1 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.22–7.34 (m, 15 H, Ph), 5.84 (AB, 2 H, $^3J_{HH}$ = 6.2 Hz, C_6H_4), 5.68 (AB, 2 H, $^3J_{HH}$ = 6.4 Hz, C_6H_4), 4.39 (ddd, 2 H, $^2J_{PH}$ = 11.2 Hz, $^2J_{HH}$ = 18.1 Hz, PCH$_2$), 2.70 (m, 1 H, C*H*Me$_2$), 2.00 (s, 3 H, *Me*Ar), 1.27 (dd, 6 H, $^3J_{HH}$ = 7.2 Hz, CH*Me$_2$*).

{(*p*-cymene)(Cl)Ru[Ph$_2$PCH(Me)C(Et)=O]}[PF$_6$], 3d. A 0.96-g (1.57-mmol) sample of [(*p*-cymene)RuCl$_2$]$_2$, 0.52 g (3.20 mmol) of NH$_4$PF$_6$, and 1.0 mL (3.7 mmol, excess) of phosphine **1c** were stirred for 2 h in 40 mL of methanol. The reaction mixture was evaporated to dryness and the residue extracted with 40 mL of dichloromethane. The filtered orange solution was covered with 100 mL of diethyl ether to afford orange crystals. Yield: 1.17 g, 54%. Anal. Found (Calcd) for $C_{27}H_{33}P_2ClORuF_6$: C, 47.56 (47.27); H, 4.87 (4.85); P, 9.21 (9.03); Cl, 5.20 (5.17). IR, $\nu_{C=O}$: 1625 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 73.8 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.63 (m, 10 H, Ph), 5.60 (m, 4 H, C_6H_4), 3.68 (m, 1 H, $^2J_{PH}$ = 7.1 Hz, PCH), 2.90 (m, 3 H, CH_2Me + C*H*Me$_2$), 1.98 (s, 3 H, *Me*Ar), 1.47 (dd, 3 H, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.6 Hz, PCMe), 1.29 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*), 1.29 (t, 3 H, $^3J_{HH}$ = 6.6 Hz, CH$_2$*Me*).

{(mesitylene)(Cl)Ru[Ph$_2$PCH(Me)C(Et)=O]}[PF$_6$], 3e. Following the procedure described for **3d**, **3e** was obtained as orange crystals starting from 1.50 g (2.57 mmol) of [(mesitylene)-RuCl$_2$]$_2$, 0.84 g (5.15 mmol) of NH$_4$PF$_6$, and 1.5 mL (5.6 mmol, excess) of phosphine **1c** that were stirred overnight in 40 mL of methanol. Yield: 1.17 g, 34%. Anal. Found (Calcd) for $C_{26}H_{31}P_2ClORuF_6$: C, 46.55 (46.47); H, 4.56 (4.65); P, 9.52 (9.22); Cl, 5.33 (5.28). IR, $\nu_{C=O}$: 1620 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 32.38 MHz, δ: 77.9 (s). ^1H NMR, CD_2Cl_2, 80 MHz, δ: 7.69–7.11 (m, 10 H, Ph), 5.11 (s, 3 H, C_6H_3), 3.85 (m, 1 H, $^2J_{PH}$ = 7.3 Hz, PCH), 2.91 (q, 2 H, CH_2Me), 2.07 (s, 9 H, Me_3Ar), 1.48 (dd, 3 H, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 7.1 Hz, PCMe), 1.26 (t, 3 H, CH$_2$*Me*).

{(mesitylene)(Cl)Ru[Ph$_2$PCH(Me)C(Bu^t)=O]}[PF$_6$], 3f, from 2g. A 1.00-g (1.69-mmol) sample of complex **2g** and 0.28 g (1.69 mmol) of NH$_4$PF$_6$ were stirred overnight in 50 mL of methanol. The reaction mixture was evaporated to dryness and the solid extracted with 20 mL of dichloromethane. The filtered solution was covered with diethyl ether (80 mL). Yield: 0.85 g, 72%. Anal. Found (Calcd) for $C_{28}H_{35}P_2ClORuF_6$: C, 47.93 (48.04); H, 4.97 (5.04); P, 9.08 (8.85); Cl, 5.32 (5.06). IR, $\nu_{C=O}$: 1590 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 78.5 (s, *major stereoisomer*), 65.6 (s, *minor stereoisomer*). ^1H NMR, CD_2Cl_2, 300.13 MHz, *major (2/3) stereoisomer*, δ: 7.67–7.00 (m, 10 H, Ph), 5.09 (s, 3 H, C_6H_3), 3.92 (m, 1 H, $^2J_{PH}$ = 11.9 Hz, PCH), 2.03 (s, 9 H, Me_3Ar), 1.56 (dd, 3 H, $^3J_{PH}$ = 11.6 Hz, $^3J_{HH}$ = 7.4 Hz, PCMe), 1.30 (s, 9 H, Bu^t). ^1H NMR, CD_2Cl_2, 300.13 MHz, *minor (1/3) stereoisomer*, δ: 7.67–7.00 (m, 10 H, Ph), 4.98 (s, 3 H, C_6H_3), 4.09 (m, 1 H, $^2J_{PH}$ = 11.5 Hz, PCH), 2.03 (s, 9 H, Me_3Ar), 1.39 (s, 9 H, Bu^t), 1.38 (dd, 3 H, $^3J_{PH}$ = 13.3 Hz, $^3J_{HH}$ = 7.7 Hz, PCMe).

{(*p*-cymene)(Cl)Ru[Ph$_2$PC(Me$_2$)C(Pr^i)=O]}[PF$_6$], 3g. A 3.06-g (5.00-mmol) sample of [(*p*-cymene)RuCl$_2$]$_2$, 1.63 g (10.0 mmol) of NH$_4$PF$_6$, and 3.0 g (10.0 mmol) of phosphine **1f** were stirred for 2 h at room temperature in 50 mL of methanol. The reaction mixture was evaporated to dryness and the remaining solid stirred with 50 mL of water. The yellow precipitate was separated by filtration and washed with water (50 mL), ethanol, and ether. Yield: 6.79 g, 95%. Recrystallization from dichloromethane/ether afforded dark orange crystals. Anal. Found (Calcd) for $C_{29}H_{37}P_2ClORuF_6$: C, 48.90 (48.78); H, 5.46 (5.22); P, 8.70 (8.68); Cl, 4.87 (4.96). IR, $\nu_{C=O}$: 1605 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 70.7 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.68 (m, 10 H, Ph), 5.84–5.40 (m, 4 H, C_6H_4), 3.06 (m, 2 H, C*H*Me$_2$), 1.93 (s, 3 H, *Me*Ar), 1.57 (d, 3 H, $^3J_{PH}$ = 10.0 Hz, PCMe), 1.39 (d, 3 H, $^3J_{PH}$ = 11.2 Hz, PCMe′), 1.42 (d, 9 H, $^3J_{HH}$ = 6.6 Hz, CH*Me$_2$*), 1.18 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CH*Me$_2$*).

{(mesitylene)(Cl)Ru[Ph$_2$PC(Me)$_2$C(Pr^i)=O]}[PF$_6$], 3h. A 0.60-g (1.02-mmol) sample of [(mesitylene)RuCl$_2$]$_2$, 0.62 g (2.08 mmol) of phosphine **1f**, and 0.35 g (2.15 mmol) of NH$_4$PF$_6$ were stirred for 24 h in 50 mL of methanol. The solvent was removed under reduced pressure and the residue extracted with 40 mL of dichloromethane. The filtered orange solution was covered with diethyl ether (120 mL). Yield: 1.04 g, 73%. Anal. Found (Calcd) for $C_{28}H_{35}P_2ClORuF_6$: C, 48.06 (48.04); H, 5.08 (5.04); P, 9.20 (8.85); Cl, 5.05 (5.06). IR, $\nu_{C=O}$: 1615 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 76.1 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.72–7.20 (m, 10 H, Ph), 5.01 (s, 3 H, C_6H_3), 3.24 (m, 1 H, PCH), 2.00 (s, 9 H, Me_3Ar), 1.52 (d, 3 H, $^3J_{PH}$ = 10.3 Hz, PCMe), 1.38 (d, 3 H, $^3J_{PH}$ = 12.2 Hz, PCMe′), 1.35 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me$_2$*), 1.18 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me$_2$*).

{(mesitylene)(Cl)Ru[Ph$_2$PC(Me)$_2$C(Bu^t)=O]}[PF$_6$], 3i. Starting from 0.87 g (1.49 mmol) of [(mesitylene)RuCl$_2$]$_2$, 0.95 g (3.04 mmol) of phosphine **1g**, and 0.50 g (3.07 mmol) of NH$_4$PF$_6$, complex **3i** was obtained as orange crystals, following the procedure described for **3h**. Yield: 1.73 g, 81%. Anal. Found (Calcd) for $C_{29}H_{37}P_2ClORuF_6$: C, 48.83 (48.78); H, 5.16 (5.22); P, 9.01 (8.68); Cl, 5.02 (4.96). IR, $\nu_{C=O}$: 1585 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 84.6 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.71 (m, 10 H, Ph), 4.99 (s, 3 H, C_6H_3), 2.03 (s, 9 H, Me_3Ar), 1.70 (d, 3 H, $^3J_{PH}$ = 11.2 Hz, PCMe), 1.48 (d, 3 H, $^3J_{PH}$ = 13.9 Hz, PCMe′), 1.44 (s, 9 H, Bu^t).

(*p*-cymene)(Cl)Ru[OC(Bu^t)=C(H)PPh$_2$], 4a. A 6.90-g (11.27-mmol) sample of [(*p*-cymene)RuCl$_2$]$_2$ and 6.44 g (22.67 mmol) of phosphine **1a** were stirred in 100 mL of ethanol for 2 h. Then 1.50 g (26.8 mmol) of KOH was added and the reaction

mixture stirred overnight. The resulting slurry was heated and filtered at the boiling temperature. Formation of orange crystals from the filtrate occurred upon cooling to −20 °C. Additional crystals were obtained after concentration of the mother solution. Overall yield: 10.95 g, 87%. Anal. Found (Calcd) for $C_{28}H_{34}PClORu$: C, 60.73 (60.70); H, 6.27 (6.19); P, 5.48 (5.60); Cl, 6.54 (6.40). IR, $\nu_{C=CO}$: 1505 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 52.6 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.54 (m, 10 H, Ph), 5.46 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 4.33 (AB, 2 H, $^3J_{HH}$ = 4.4 Hz, C_6H_4), 4.32 (d, 1 H, $^2J_{PH}$ = 3.2 Hz, PCH), 2.57 (m, 1 H, C*H*Me$_2$), 2.13 (s, 3 H, *Me*Ar), 1.20 (s, 9 H, Bu^t), 1.23 (d, 3 H, $^3J_{HH}$ = 5.1 Hz, CH*Me*$_2$), 1.02 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 199.6 (d, $^2J_{PC}$ = 15.5 Hz, =CO), 141.4–82.3 (m, Ar), 70.5 (d, $^1J_{PC}$ = 62.7 Hz, PCH), 38.1 (d, $^3J_{PC}$ = 11.9 Hz, *C*Me$_3$), 30.4 (s, *C*HMe$_2$), 29.6 (s, C*Me*$_3$), 22.7 (s, CH*Me*$_2$), 21.7 (s, CH*Me*$_2$), 18.3 (s, *Me*Ar).

(mesitylene)(Cl)Ru[OC(Bu^t)=C(H)PPh$_2$], 4b, from 2b. A 3.00-g (5.21-mmol) sample of complex **2b** and 0.50 g (8.93 mmol) of KOH were stirred in 40 mL of ethanol for 3 h at 40 °C. The mixture was filtered at the boiling temperature and the dark orange filtrate cooled to −20 °C, affording orange crystals. Yield: 2.15 g, 77%. Anal. Found (Calcd) for $C_{27}H_{32}PClORu$: C, 60.05 (60.05); H, 5.99 (5.97); P, 5.65 (5.74); Cl, 6.24 (6.56). IR, $\nu_{C=CO}$: 1525 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 56.7 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.73–7.46 (m, 10 H, Ph), 4.69 (s, 3 H, C_6H_3), 4.32 (d, 1 H, $^2J_{PH}$ = 3.4 Hz, PCH), 1.97 (s, 9 H, *Me*$_3$Ar), 1.20 (s, 9 H, Bu^t).

(hexamethylbenzene)(Cl)Ru[OC(Bu^t)=C(H)PPh$_2$], 4c. A 2.13-g (3.19-mmol) sample of [(hexamethylbenzene)$RuCl_2]_2$ and 1.81 g (6.37 mmol) of phosphine **1a** were stirred for 6 h in 50 mL of dichloromethane. The dark red solution was filtered to remove some insoluble material and evaporated to dryness. The remaining solid was dissolved in 60 mL of ethanol and 0.40 g (7.14 mmol) of KOH added. After stirring overnight, the solution was heated and filtered at the boiling temperature to afford orange crystals upon cooling to −20 °C. Yield: 2.76 g, 74%. Anal. Found (Calcd) for $C_{30}H_{38}PClORu$: C, 61.46 (61.90); H, 6.47 (6.58); P, 5.23 (5.32); Cl, 6.38 (6.09). IR, $\nu_{C=CO}$: 1505 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 53.4 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.61–7.19 (m, 10 H, Ph), 4.29 (d, 1 H, $^2J_{PH}$ = 3.1 Hz, PCH), 1.83 (s, 18 H, C_6Me_6), 1.19 (s, 9 H, Bu^t).

(*p*-cymene)(Cl)Ru[OC(Ph)=C(H)PPh$_2$], 4d, from 2c. A 3.00-g (4.92-mmol) sample of **2c** and 0.40 g (7.14 mmol) of KOH were stirred overnight in 70 mL of ethanol. The reaction mixture was heated and filtered and the light red filtrate cooled to −20 °C. Yield: 1.98 g, 70%. Anal. Found (Calcd) for $C_{30}H_{30}$-$PClORu$: C, 62.66 (62.77); H, 5.29 (5.27); P, 5.21 (5.40); Cl, 5.75 (6.18). IR, $\nu_{C=CO}$: 1515 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 51.5 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.72–7.33 (m, 15 H, Ph), 5.55 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 5.02 (d, 1 H, $^2J_{PH}$ = 2.0 Hz, PCH), 4.87 (AB, 2 H, $^3J_{HH}$ = 5.5 Hz, C_6H_4), 2.62 (m, 1 H, C*H*Me$_2$), 2.16 (s, 3 H, *Me*Ar), 1.05 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$).

(*p*-cymene)(Cl)Ru[OC(Et)=C(Me)PPh$_2$]·$^1/_2C_6H_{14}$, 4e. A 3.06-g (5.00-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 3.0 mL (excess) of phosphine **1c** were stirred for 1 h in 40 mL of ethanol. Then 0.60 g (10.7 mmol) of KOH was added, and the mixture was stirred overnight. Hexane (40 mL) was added before filtration and cooling. Yield: 5.08 g, 87%. Anal. Found (Calcd) for $C_{27}H_{32}PClORu\cdot{}^1/_2C_6H_{14}$: C, 61.68 (61.79); H, 6.71 (6.74); P, 5.31 (5.31); Cl, 6.01 (6.08). IR, $\nu_{C=CO}$: 1545 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 60.9 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.89–7.39 (m, 10 H, Ph), 5.61–4.39 (m, 4 H, C_6H_4), 2.37 (m, 3 H, C*H*$_2$Me + C*H*Me$_2$), 2.05 (s, 3 H, *Me*Ar), 1.72 (d, 3 H, $^3J_{PH}$ = 10.0 Hz, PCMe), 1.15 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH$_2$*Me*), 1.19 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.04 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 187.8 (d, $^2J_{PC}$ = 19.9 Hz, =CO), 138.6–85.5 (m, Ar), 78.2 (d, $^1J_{PC}$ = 55.8 Hz, PC=), 30.5 (s, *C*HMe$_2$), 27.8 (d, $^3J_{PC}$ = 11.8 Hz, *C*H$_2$Me), 22.6 (s, CH*Me*$_2$), 22.3 (s, CH*Me*$_2$), 22.2 (d, $^2J_{PC}$ = 8.3 Hz, PC*Me*), 17.9 (s, *Me*Ar), 12.3 (s, CH$_2$*Me*).

(mesitylene)(Cl)Ru[OC(Et)=C(Me)PPh$_2$], 4f, from 2e. A 3.80-g (6.76-mmol) sample of **2e** and 0.60 g (10.7 mmol) of KOH were stirred in 30 mL of ethanol for 3 h at 40 °C. The reaction mixture was filtered and the filtrate cooled to −20 °C. Yield: 2.85 g, 79%. Anal. Found (Calcd) for $C_{26}H_{30}PClORu$: C, 59.38 (59.37); H, 6.00 (5.75); P, 5.87 (5.89); Cl, 7.05 (6.74). IR, $\nu_{C=CO}$: 1555 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 66.8 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.38 (m, 10 H, Ph), 4.68 (s, 3 H, C_6H_3), 2.36 (m, 2 H, C*H*$_2$Me), 1.97 (s, 9 H, *Me*$_3$Ar), 1.66 (d, 3 H, $^3J_{PH}$ = 9.8 Hz, PCMe), 1.16 (t, 3 H, $^3J_{HH}$ = 7.6 Hz, CH$_2$*Me*).

(*p*-cymene)(Cl)Ru[OC(Bu^t)=C(Me)PPh$_2$], 4g. A 3.92-g (6.40-mmol) sample of [(*p*-cymene)$RuCl_2]_2$, 4.00 g (13.4 mmol) of phosphine **1d**, and 0.76 g (13.6 mmol) of KOH were stirred for 3 h in 70 mL of ethanol. The mixture was filtered at the boiling temperature and the filtrate cooled to −20 °C to give red crystals of **4g**. Yield: 5.52 g, 76%. IR, $\nu_{C=CO}$: 1529 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 121.50 MHz, δ: 68.1 (s). ^1H NMR, $CDCl_3$, 300.13 MHz, δ: 7.90–7.27 (m, 10 H, Ph), 5.54–4.38 (m, 4 H, C_6H_4), 2.57 (m, 1 H, C*H*Me$_2$), 2.04 (s, 3 H, *Me*Ar), 1.81 (d, 3 H, $^3J_{PH}$ = 11.2 Hz, PCMe), 1.26 (s, 9 H, Bu^t), 1.20 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.06 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$).

(mesitylene)(Cl)Ru[OC(Bu^t)=C(Me)PPh$_2$], 4h, from 2g. Following the same procedure, **4h** was obtained in 68% yield starting from **2g**. Anal. Found (Calcd) for $C_{28}H_{34}PClORu$: C, 60.86 (60.70); H, 6.35 (6.19); P, 5.15 (5.59); Cl, 6.64 (6.40). IR, $\nu_{C=CO}$: 1518 cm^{-1}. $^{31}P\{^1H\}$ NMR, C_6D_6, 121.50 MHz, δ: 72.4 (s). ^1H NMR, C_6D_6, 300.13 MHz, δ: 8.06–7.06 (m, 10 H, Ph), 4.23 (s, 3 H, C_6H_3), 1.88 (d, 3 H, PCMe, $^3J_{PH}$ = 11.3 Hz), 1.68 (s, 9 H, *Me*$_3$Ar), 1.46 (s, 9 H, Bu^t).

(*p*-cymene)(Cl)Ru[OC(Ph)=C(Me)PPh$_2$], 4i, from 2h. A 3.00-g (4.81-mmol) sample of **2h** and 0.34 g (6.07 mmol) of KOH were stirred in 50 mL of ethanol for 3 h at 50 °C (**2h** could be prepared *in situ* by stirring the corresponding stoichiometric amounts of [(*p*-cymene)$RuCl_2]_2$ and phosphine **1e** in ethanol for 2 h before the addition of KOH). Yield: 2.01 g, 71%. Anal. Found (Calcd) for $C_{31}H_{32}PClORu$: C, 63.21 (63.31); H, 5.43 (5.48); P, 5.13 (5.27); Cl, 5.93 (6.03). IR, $\nu_{C=CO}$: 1540 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 60.3 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.97–7.42 (m, 15 H, Ph), 5.32 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 4.91 (AB, 2 H, $^3J_{HH}$ = 5.9 Hz, C_6H_4), 2.62 (m, 1 H, C*H*Me$_2$), 2.10 (s, 3 H, *Me*Ar), 1.73 (d, 3 H, $^3J_{PH}$ = 10.0 Hz, PCMe), 1.21 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.09 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$).

{(hexamethylbenzene)(Bu^{t}CN)Ru[OC(Bu^t)=C(H)PPh$_2$]}(PF$_6$), 5a, from 4c. A 0.68-g (1.16-mmol) sample of **4c**, 0.20 g (1.23 mmol) of NH_4PF_6, and 0.50 mL (4.53 mmol, excess) of Bu^{t}CN were stirred for 20 h at room temperature in 40 mL of methanol. The resulting mixture was evaporated to dryness and the residue extracted with 20 mL of chloroform. The solution is filtered and the orange filtrate covered with 80 mL of diethyl ether, affording orange crystals. Yield: 0.71 g, 79%. Anal. Found (Calcd) for $C_{35}H_{47}P_2NORuF_6$: C, 54.48 (54.26); H, 6.12 (6.11); P, 7.98 (8.00); N, 1.77 (1.81). IR, $\nu_{C=CO}$: 1513 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 53.9 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.50–7.20 (m, 10 H, Ph), 4.43 (d, 1 H, $^2J_{PH}$ = 3.5 Hz, PCH), 1.89 (d, 18 H, J_{PH} = 0.7 Hz, C_6Me_6), 1.18 (s, 9 H, Bu^{t}CO), 0.88 (s, 9 H, Bu^{t}CN).

{(mesitylene)(Me$_2$S)Ru[OC(Bu^t)=C(H)PPh$_2$]}(PF$_6$), 5b, from 4b. Following the procedure detailed for **5a**, **5b** was obtained as orange crystals starting from 1.16 g (2.15 mmol) of **4b**, 0.41 g (2.52 mmol) of NH_4PF_6, and 1.0 mL (13.6 mmol, excess) of Me_2S. Yield: 0.84 g, 55%. Anal. Found (Calcd) for $C_{29}H_{38}P_2SORuF_6$: C, 49.18 (48.94); H, 5.56 (5.38); P, 8.58 (8.70); S, 5.45 (4.51); Cl, 0.07 (0.00). IR, $\nu_{C=CO}$: 1540 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 32.38 MHz, δ: 58.4 (s). ^1H NMR, CD_2Cl_2, 80 MHz, δ: 7.63 (m, 10 H, Ph), 5.10 (s, 3 H, C_6H_3), 4.55 (d, 1 H, $^2J_{PH}$ = 4.2 Hz, PCH), 2.02 (s, 9 H, *Me*$_3$Ar), 1.93 (s, 6 H, Me$_2$S), 1.23 (s, 9 H, Bu^t).

{(mesitylene)(MeCN)Ru[OC(Bu^t)=C(Me)PPh$_2$]}(PF$_6$), 5c, from 4h. Following the same procedure, **5c** was obtained as orange crystals starting from 0.75 g (1.35 mmol) of **4h**, 0.25 g (1.53 mmol) of NH_4PF_6, and 1.0 mL (excess) of MeCN. Yield: 0.25 g, 26%. Anal. Found (Calcd) for $C_{30}H_{37}P_2NORuF_6$: C, 50.89 (51.14); H, 5.30 (5.29); P, 9.60 (8.79); N, 2.00 (1.99). IR, $\nu_{C=CO}$: 1516 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 76.5 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.60–7.47 (m, 10 H, Ph), 4.96 (s,

3 H, C_6H_3), 1.89 (s, 9 H, Me_3Ar), 1.74 (d, 3 H, $^3J_{PH}$ = 11.8 Hz, PCMe), 1.73 (s, 3 H, MeCN), 1.23 (s, 9 H, Bu^t).

{(*p*-cymene)(Bu^{t}CN)Ru[OC(Bu^t)=C(Me)PPh$_2$]}(PF$_6$), 5d, from 4g. The same procedure was applied starting from 0.48 g (0.85 mmol) of **4g**, 0.20 g (1.23 mmol) of NH_4PF_6, and 0.50 mL (4.53 mmol, excess) of Bu^{t}CN. Yield: 0.43 g, 67%. Anal. Found (Calcd) for $C_{34}H_{45}P_2NORuF_6$: C, 54.38 (53.68); H, 6.05 (5.96); P, 8.05 (8.14); N, 1.30 (1.84). IR, $\nu_{C=CO}$: 1521 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 74.6 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.65–7.37 (m, 10 H, Ph), 5.73–4.99 (m, 4 H, C_6H_4), 2.52 (m, 1 H, C*H*Me$_2$), 1.99 (s, 3 H, *Me*Ar), 1.88 (d, 3 H, $^3J_{PH}$ = 11.8 Hz, PCMe), 1.24 (s, 9 H, Bu^{t}CO), 1.22 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.13 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 0.94 (s, 9 H, Bu^{t}CN).

{(mesitylene)(Me$_2$S)Ru[OC(Bu^t)=C(Me)PPh$_2$]}(PF$_6$), 5e, from 4h. Complex **5e** was prepared starting from 1.50 g (2.71 mmol) of **4h**, 0.50 g (3.07 mmol) of NH_4PF_6, and 1.0 mL (excess) of Me_2S. Yield: 1.27 g, 65%. Anal. Found (Calcd) for $C_{30}H_{40}P_2SORuF_6$: C, 49.80 (49.65); H, 5.61 (5.56); P, 8.21 (8.54); S, 5.26 (4.42). IR, $\nu_{C=CO}$: 1530 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 77.5 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.53–7.36 (m, 10 H, Ph), 5.00 (s, 3 H, C_6H_3), 1.96 (s, 9 H, Me_3Ar), 1.78 (s, 6 H, Me_2S), 1.71 (d, 3 H, $^3J_{PH}$ = 11.8 Hz, PCMe), 1.23 (s, 9 H, Bu^t).

{(*p*-cymene)(Me$_2$S)Ru[OC(Bu^t)=C(Me)PPh$_2$]}(PF$_6$), 5f, from 4g. Orange crystals of **5f** were obtained from 0.49 g (0.86 mmol) of **4g**, 0.20 g (1.23 mmol) of NH_4PF_6, and 0.50 mL (6.8 mmol, excess) of Me_2S. Yield: 0.51 g, 80%. Anal. Found (Calcd) for $C_{31}H_{42}P_2SORuF_6$: C, 50.67 (50.33); H, 5.75 (5.72); P, 8.42 (8.37); S, 5.63 (4.33). IR, $\nu_{C=CO}$: 1517 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 73.8 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.55–7.47 (m, 10 H, Ph), 5.78–4.89 (m, 4 H, C_6H_4), 2.56 (m, 1 H, C*H*Me$_2$), 2.01 (s, 3 H, *Me*Ar), 1.89 (br, 6 H, Me_2S), 1.76 (d, 3 H, $^3J_{PH}$ = 11.9 Hz, PCMe), 1.25 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.22 (s, 9 H, Bu^t), 1.18 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$).

Synthesis of 5f from 5d. A 0.18-g (0.24-mmol) sample of complex **5d** was dissolved in a mixture of 5.0 mL of dichloromethane and 0.50 mL of Me_2S and the resulting solution covered with 120 mL of diethyl ether to afford orange crystals identified to **5f** by NMR. Yield: 0.16 g, 92%.

{(*p*-cymene)(Me$_2$S)Ru[OC(Ph)=C(Me)PPh$_2$]}(PF$_6$), 5g, from 4i. Orange crystals of **5g** were prepared following the procedure detailed for **5a**, starting from 0.46 g (0.78 mmol) of **4i**, 0.18 g (1.08 mmol) of NH_4PF_6, and 0.50 mL (6.8 mmol, excess) of Me_2S. Yield: 0.42 g, 71%. Anal. Found (Calcd) for $C_{33}H_{38}P_2SORuF_6$: C, 52.18 (52.17); H, 4.92 (5.04); P, 8.56 (8.15); S, 4.77 (4.22). IR, $\nu_{C=CO}$: 1544 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 68.0 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.62–7.36 (m, 15 H, Ph), 5.79–4.95 (m, 4 H, C_6H_4), 2.65 (m, 1 H, C*H*Me$_2$), 2.10 (s, 3 H, *Me*Ar), 1.93 (br, 6 H, Me_2S), 1.74 (d, 3 H, $^3J_{PH}$ = 10.7 Hz, PCMe), 1.27 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.23 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$).

{(*p*-cymene)Ru[η^3-CH=C(Ph)CH(PPh$_2$)C(Bu^t)=O]}[PF$_6$], 6a, from 4a. A 0.70-g (2.77-mmol) sample of $AgPF_6$ and 0.30 mL of phenylacetylene were stirred in 50 mL of cold toluene (−60 °C), and then 1.50 g (2.71 mmol) of **4a** was added. The reaction mixture was slowly warmed to room temperature and stirred overnight after addition of 20 mL of dichloromethane. The solution was concentrated under reduced pressure and the yellow precipitate separated out and dried. Recrystallization from dichloromethane (40 mL) and diethyl ether (150 mL) afforded orange crystals. Yield: 1.40 g, 68%. Anal. Found (Calcd) for $C_{36}H_{40}P_2ORuF_6$: C, 56.50 (56.47); H, 5.38 (5.27); P, 8.05 (8.09). $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 126.8 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 9.87 (dd, 1 H, $^3J_{PH}$ = 1.7 Hz, $^4J_{HH}$ = 2.2 Hz, RuCH), 7.56–7.39 (m, 15 H, Ph), 6.29–5.93 (m, 4 H, C_6H_4), 5.68 (dd, 1 H, $^2J_{PH}$ = 10.3 Hz, PCH), 2.58 (m, 1 H, C*H*Me$_2$), 2.04 (s, 3 H, *Me*Ar), 1.10 (d, 3 H, $^3J_{HH}$ = 7.1 Hz, CH*Me*$_2$), 1.06 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 0.75 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 228.6 (d, $^2J_{PC}$ = 5.9 Hz, C=O), 166.2 (d, $^2J_{PC}$ = 14.4 Hz, RuC), 137.3 (d, $^2J_{PC}$ = 10.6 Hz, =*C*Ph), 132.9–89.0 (m, Ar), 66.4 (d, $^1J_{PC}$ = 32.0 Hz, PCH), 45.3 (d, $^3J_{PC}$ = 2.4 Hz, *C*Me$_3$), 31.7 (s, CHMe$_2$), 25.9 (s, C*Me*$_3$), 22.8 (s, CH*Me*$_2$), 22.3 (s, CH*Me*$_2$), 18.6 (s, *Me*Ar).

{(mesitylene)Ru[η^3-CH=C(Ph)CH(PPh$_2$)C(Bu^t)=O]}[BF$_4$], 6b, from 4b. A 0.76-g (3.90-mmol) sample of $AgBF_4$ was added under stirring to a cold (−60 °C) solution of 2.09 g (3.87 mmol) of **4b** and 0.35 mL (4.01 mmol) of phenylacetylene in 80 mL of dichloromethane. After overnight stirring, the reaction mixture was evaporated under reduced pressure and the residue washed with 50 mL of diethyl ether. The crude product was crystallized from dichloromethane/diethyl ether mixture. Yield: 2.30 g, 86%. Orange crystals of **6b·toluene** were obtained after dissolution in a 1/1 toluene/dichloromethane mixture and addition of hexane. Anal. Found (Calcd) for $C_{35}H_{38}PORuBF_4 \cdot C_7H_8$: C, 63.51 (64.20); H, 5.71 (5.90); P, 3.99 (3.94). $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 126.5 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 9.28 (dd, 1 H, $^3J_{PH}$ = 2.5 Hz, $^4J_{HH}$ = 1.5 Hz, RuCH), 7.53–7.20 (m, 20 H, Ph), 5.77 (dd, 1 H, $^2J_{PH}$ = 10.3 Hz, PCH), 5.57 (s, 3 H, C_6H_3), 2.34 (s, 3 H, Me–toluene), 2.23 (s, 9 H, Me_3Ar), 0.83 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 229.5 (d, $^2J_{PC}$ = 6.8 Hz, C=O), 171.8 (d, $^2J_{PC}$ = 13.8 Hz, RuC), 138.8 (d, $^2J_{PC}$ = 14.9 Hz, =*C*Ph), 138.2–85.7 (m, Ar), 67.5 (d, $^1J_{PC}$ = 30.5 Hz, PCH), 45.7 (d, $^3J_{PC}$ = 2.2 Hz, *C*Me$_3$), 26.2 (s, C*Me*$_3$), 19.6 (s, *Me*$_3$Ar).

{(mesitylene)Ru[η^3-CH=C(Ph)C(Me)(PPh$_2$)C(Et)=O]}[BF$_4$], 6c, from 4f. Following the same procedure, **6c** was prepared starting from 0.53 mL (4.83 mmol) of phenylacetylene, 0.85 g (4.37 mmol) of $AgBF_4$, and 2.30 g (4.37 mmol) of **4f** in 80 mL of dichloromethane. After overnight stirring at room temperature, the reaction mixture was filtered and the orange filtrate evaporated under reduced pressure. The residue was shaken with 50 mL of ether to obtain a yellow precipitate that was separated upon filtration and dried. The crude product (2.27 g, 76%) was dissolved in 35 mL of dichloromethane and the solution covered with 120 mL of ether to promote the formation of orange crystals. Yield: 1.45 g, 49%. Anal. Found (Calcd) for $C_{34}H_{36}PORuBF_4$: C, 60.16 (60.10); H, 5.07 (5.34); P, 4.81 (4.56). $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 144.9 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.91 (d, 1 H, $^3J_{PH}$ = 2.9 Hz, RuCH), 7.59–6.38 (m, 15 H, Ph), 5.35 (s, 3 H, C_6H_3), 2.89 (m, 2 H, C*H*$_2$Me), 2.15 (s, 9 H, Me_3Ar), 1.46 (d, 3 H, $^3J_{PH}$ = 11.7 Hz, PCMe), 1.31 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH$_2$*Me*). $^{13}C\{^1H\}$ NMR, $CDCl_3$, 75.47 MHz, δ: 225.8 (d, $^2J_{PC}$ = 7.6 Hz, C=O), 172.2 (d, $^2J_{PC}$ = 14.4 Hz, RuC=), 141.0 (d, $^2J_{PC}$ = 16.6 Hz, =*C*Ph), 139.4–85.5 (m, Ar), 75.0 (d, $^1J_{PC}$ = 26.8 Hz, P*C*Me), 34.8 (s, *C*H$_2$Me), 19.1 (s, *Me*$_3$Ar), 14.4 (d, $^2J_{PC}$ = 4.2 Hz, PC*Me*), 8.1 (s, CH$_2$*Me*).

{(*p*-cymene)Ru[η^3-CH=C(Ph)C(Me)(PPh$_2$)C(Ph)=O]}[BF$_4$], 6d, from 4i. Following the procedure described for **6c** and starting from 0.66 g (3.40 mmol) of $AgBF_4$, 2.00 g (3.40 mmol) of **4i** and 0.42 mL (3.82 mmol) of phenylacetylene, **6d** was obtained as an orange precipitate. Yield: 1.97 g, 78%. Red-orange crystals were obtained from dichloromethane/diethyl ether. Anal. Found (Calcd) for $C_{39}H_{38}PORuBF_4$: C, 62.83 (63.17); H, 5.12 (5.17); P, 4.25 (4.18). $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 150.5 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 9.41 (d, 1 H, $^3J_{PH}$ = 2.7 Hz, RuCH), 7.56–7.15 (m, 20 H, Ph), 5.98–5.47 (m, 4 H, C_6H_4), 2.47 (m, 1 H, C*H*Me$_2$), 2.17 (s, 3 H, *Me*Ar), 1.66 (d, 3 H, $^3J_{PH}$ = 12.0 Hz, PCMe), 1.00 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$).

{(mesitylene)Ru[η^3-CH(PPh$_2$)C(Ph)=C(H)C(Bu^t)=O]}[BF$_4$], 7, from 6b. A 1.40-g (2.02-mmol) sample of crude **6b** was refluxed in 30 mL of ethanol for 20 min, affording a dark red solution. On overnight standing at room temperature, red crystals were obtained from that solution. They were separated out and dried. Yield: 1.00 g, 71%. Anal. Found (Calcd) for $C_{35}H_{38}PORuBF_4$: P, 4.55 (4.47). $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 7.7 (s). ^1H NMR, $CDCl_3$, 80 MHz, δ: 7.72–7.36 (m, 15 H, Ph), 6.11 (dd, 1 H, $^4J_{PH}$ = 2.2 Hz, $^4J_{HH}$ = 1.2 Hz, =CH), 5.30 (s, 3 H, C_6H_3), 4.24 (dd, 1 H, $^2J_{PH}$ = 5.0 Hz, PCH), 2.09 (s, 9 H, Me_3Ar), 0.72 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 207.1 (s, C=O), 166.5 (s, =*C*Ph), 143.1–118.7 (m, Ar), 112.9 (s, =CH), 105.9 (s, *C*Me-mesitylene), 82.5 (s, CH–mesitylene), 43.9 (s, *C*Me$_3$), 27.7 (s, C*Me*$_3$), 22.8 (s, PCH), 19.6 (s, *Me*$_3$Ar).

Table I. Crystallographic Data for the Structural Analyses of Compounds {(*p*-cymene)Ru[η^3-CH=C(Ph)CH(PPh$_2$)C(Bu^t)=O]}[PF$_6$], 6a, {(mesitylene)Ru[η^3-CH=C(Ph)C(Me)(PPh$_2$)C(Et)=O]}[BF$_4$], 6c, and {(mesitylene)Ru[η^3-CH(PPh$_2$)C(Ph)=C(H)C(But)=O]}[BF$_4$], 7

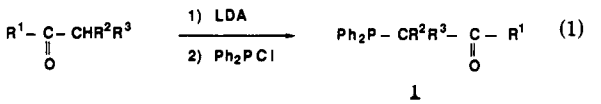
	6a	6c	7
	A. Crystal Data		
formula	$C_{36}H_{40}P_2O_1F_6Ru_1$	$C_{34}H_{36}P_1O_1F_4Ru_1$	$C_{35}H_{38}P_1O_1B_1F_4Ru_1$
mol wt	765.73	679.51	693.54
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	14.870(4)	10.962(1)	14.034(2)
b, Å	20.087(6)	15.473(2)	11.944(1)
c, Å	12.454(5)	10.910(1)	10.957(1)
α, deg	90.0	100.10(1)	106.56(1)
β, deg	92.67(3)	113.64(1)	98.34(1)
γ, deg	90.0	102.41(1)	109.24(1)
V, Å^3	3715.9	1451.0	1603.2
Z	4	2	2
d_{calc}, g cm^{-3}	1.37	1.55	1.44
μ(Mo Kα) cm^{-1}	5.52	6.34	
μ(Cu Kα) cm^{-1}			34.41
cryst size, mm	0.25 × 0.25 × 0.20	0.47 × 0.47 × 0.52	0.40 × 0.20 × 0.18
	B. Data Collection and Reduction		
diffractometer	Philips PW-1100	Enraf-Nonius CAD-4-1100	Philips PW-1100
scan type	ω–2θ	ω–2θ	ω–2θ
2θ range, deg	5–40	5–50	5–120
scan width, deg	0.9 + 0.35(tan θ)	0.8 + 0.35(tan θ)	0.7 + 0.15(tan θ)
scan speed, deg/min	0.04	0.07	0.05
	C. Solution and Refinement		
total no. of data	3780	5951	4446
no. of unique data, $I > 3(\sigma)$	2047	4626	4189
no. of parameters	180	354	278
R	0.079	0.045	0.055
R_w	0.075	0.047	0.062
abs corr min, max	1.199–0.854	1.156–0.875	0.630–0.442

X-ray Diffraction Studies. Crystal data, data collection parameters, and results of the calculations for structure solution and refinement are given in Table I, and the final positional parameters in Table II (complex **6a**), Table III (complex **6c**), and Table IV (complex **7**). All measurements were carried out at 23 °C. Unit cell dimensions were determined by least squares refinement of the positional parameters of 25 reflections. As a general procedure three standard reflections were collected every 2 h. Only in the case of compound **6a** was a decay as large as 15% observed. Moreover there were almost no measurable reflections for $2\theta > 40°$ and the low diffraction power of the crystal results in the final relatively high R factor (0.079). All the data were collected for Lorentz and polarization effects. A numerical absorption correction was applied in the case of compound **7** by using the appropriate algorithm of the SHELX76 program. In the other cases, an empirical correction for the absorption effect was performed at an advanced state of the structure's refinement by using the program DIFABS.[12] Atomic scattering factors are those tablulated by Cromer and Weber.[13] The structures were solved by Patterson methods. After the location of all the non-hydrogen atoms from F_o and ΔF maps, the least squares refinement was performed. Only for compound **6a** were the C_6 rings constrained to be rigid bodies with D_{6h} symmetry (C–C = 1.39 Å), with the exception of the η^6-coordinated arene ring. The atoms for which anisotropic thermal parameters were refined are distinguished by an asterisk (Tables II–IV). The hydrogen atoms were usually introduced at calculated positions except for compound **6c** for which all of these atoms have been located in ΔF maps. The final ΔF maps were almost featureless except for compound **6a** showing a few peaks slightly smaller than 1 e/Å^3. The largest one at position (0.468, 0.007, 0.468) makes a short vector of 1.2 Å with one of its symmetry images, but no chemical significance could be attributed to it. Selected bond distances and angles for the three complexes are listed in Table V.

(12) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *A39*, 158.
(13) Cromer, D. T.; Weber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

Results and Discussion

Synthesis of β-Keto Phosphines Ph$_2$PCR^{3}R^{2}C(=O)-R^1, 1. Some years ago[14] we described the reactivity of iron phosphino thioenolate complexes and their coupling reaction with phenylacetylene.[6] Such studies were limited by the specific access to the phosphino thioenolato ligand, from intramolecular coupling[7] of a phosphinoalkyne with coordinated carbon disulfide. The literature described[8] synthesis of the β-keto phosphine Ph$_2$PCH$_2$C(=O)Ph by reacting the lithium enolate derived from acetophenone with chlorodiphenylphosphine, and our aim to compare the reactivity of phosphino enolato ligands with those of their thio analogs led us to apply this convenient reaction to several ketones (eq 1).



(1)

1

1a, $Ph_2PCH_2C(=O)Bu^t$
1b, $Ph_2PCH_2C(=O)Ph$
1c, $Ph_2PCH(Me)C(=O)Et$
1d, $Ph_2PCH(Me)C(=O)Bu^t$
1e, $Ph_2PCH(Me)C(=O)Ph$
1f, $Ph_2PCMe_2C(=O)Pr^i$
1g, $Ph_2PCMe_2C(=O)Bu^t$

The β-keto phosphines were obtained in good yields as colorless crystals except in the case of **1c** isolated as a colorless oil. An important key of this synthesis requires the isolation of the (room temperature stable) lithium enolate before reacting it with chlorodiphenylphosphine, in hexane when R^1 is an alkyl group or diethyl ether when

(14) Samb, A.; Demerseman, B.; Dixneuf, P. H.; Mealli, C. *Organometallics* **1988**, *7*, 26.

Table II. Atomic Parameters for the Structure of Compound {(*p*-cymene)Ru[η^3-CH=C(Ph)CH(PPh$_2$)C(Bu^t)=O]}[PF$_6$], 6a[a]

atom	x	y	z	U or U_{eq},[b] Å^2
Ru1	286(1)	2061(1)	317(1)	48(1)*
P1	927(3)	2384(2)	8761(4)	46(3)*
O1	-232(7)	1349(5)	9194(9)	52(3)
C1	1398(11)	1473(9)	10296(14)	54(5)
C2	1690(11)	1244(8)	9344(13)	45(4)
C3	1107(10)	1525(8)	8352(13)	44(4)
C4	212(11)	1186(8)	8422(13)	49(5)
C5	-150(12)	677(9)	7669(14)	62(5)
C6	-951(17)	349(13)	8086(21)	111(8)
C7	607(17)	169(12)	7467(21)	110(8)
C8	-384(16)	1036(12)	6611(18)	96(7)
C9	-982(13)	1967(10)	11224(15)	67(5)
C10	-958(15)	2624(11)	10790(17)	77(6)
C11	-239(14)	3010(11)	10948(16)	79(6)
C12	549(13)	2832(9)	11553(15)	65(5)
C13	517(14)	2174(10)	12050(16)	71(6)
C14	-251(13)	1757(10)	11891(15)	64(5)
C15	-1746(15)	1510(12)	11041(20)	99(8)
C16	1341(16)	3300(12)	11706(19)	93(7)
C17	1188(27)	3710(19)	12706(31)	199(16)
C18	2220(18)	2956(15)	11833(25)	132(10)
C1,1	285(7)	2758(6)	7666(10)	49(5)
C2,1	658(7)	2779(6)	6660(10)	70(6)
C3,1	191(7)	3087(6)	5798(10)	88(7)
C4,1	-649(7)	3374(6)	5943(10)	91(7)
C5,1	-1022(7)	3353(6)	6950(10)	94(7)
C6,1	-555(7)	3045(6)	7811(10)	73(6)
C1,2	1977(7)	2857(6)	8811(10)	50(5)
C2,2	1877(7)	3548(6)	8844(10)	72(6)
C3,2	2634(7)	3954(6)	8988(10)	81(6)
C4,2	3489(7)	3671(6)	9099(10)	75(6)
C5,2	3589(7)	2981(6)	9066(10)	73(6)
C6,2	2832(7)	2574(6)	8922(10)	66(5)
C1,3	2436(9)	771(7)	9146(8)	52(5)
C2,3	2713(9)	350(7)	9989(8)	70(6)
C3,3	3430(9)	-87(7)	9868(8)	96(7)
C4,3	3870(9)	-103(7)	8904(8)	107(8)
C5,3	3594(9)	317(7)	8060(8)	111(8)
C6,3	2877(9)	755(7)	8181(8)	89(7)
P2	-3054(5)	3848(3)	-498(5)	91(2)
F1	-3053(12)	3967(10)	-1773(16)	164(7)
F2	-3083(12)	3624(9)	710(14)	156(6)
F3	-2885(13)	3073(10)	-752(17)	179(7)
F4	-4053(15)	3732(11)	-645(17)	192(8)
F5	-2047(15)	3909(11)	-374(17)	193(8)
F6	-3202(17)	4574(14)	-223(20)	231(10)

[a] Thermal parameters multiplied by 10^3, coordinates by 10^4. [b] U_{eq} defined as one-third of the trace of the orthogonalized thermal tensor.

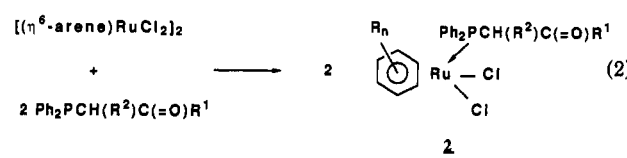
Table III. Atomic Parameters for the Structure of Compound {(mesitylene)Ru[η^3-CH=C(Ph)C(Me)-(PPh$_2$)C(Et)=O]}[BF$_4$], 6c[a]

atom	x	y	z	U or U_{eq},[b] Å^2
Ru1	4205(1)	1858(1)	291(1)	31(1)*
P1	5424(1)	3178(1)	2093(1)	33(1)*
O1	3936(3)	1411(2)	1921(3)	38(2)*
C1	6164(4)	1757(3)	1304(4)	33(1)*
C2	6863(4)	2056(3)	2697(4)	33(1)*
C3	6125(4)	2543(3)	3424(4)	35(1)*
C4	4841(5)	1789(3)	3143(5)	39(1)*
C5	7024(5)	3147(3)	4931(5)	50(2)*
C6	4655(6)	1477(4)	4304(6)	56(2)*
C7	3334(7)	668(5)	3806(7)	67(3)*
C9	3874(5)	1022(3)	-1785(4)	42(2)*
C10	4131(5)	1972(3)	-1703(5)	45(2)*
C11	3284(6)	2462(4)	-1416(5)	54(2)*
C12	2154(5)	2002(4)	-1206(6)	59(3)*
C13	1932(5)	1077(4)	-1207(5)	54(2)*
C14	2788(5)	591(3)	-1515(5)	49(2)*
C15	4771(6)	517(4)	-2096(5)	58(2)*
C16	3546(9)	3466(4)	-1383(8)	83(3)*
C17	810(7)	596(6)	-873(8)	86(3)*
C1,1	4371(5)	3833(3)	2510(5)	46(1)
C2,1	3348(10)	3437(7)	2847(10)	111(3)
C3,1	2361(13)	3891(8)	2903(12)	138(4)
C4,1	2439(9)	4700(6)	2616(9)	92(2)
C5,1	3459(8)	5114(5)	2362(8)	81(2)
C6,1	4421(7)	4683(4)	2298(7)	69(2)
C1,2	6947(4)	4043(3)	2289(5)	39(1)*
C2,2	7673(5)	4831(3)	3444(6)	49(2)*
C3,2	8815(6)	5498(4)	3548(7)	60(2)*
C4,2	9228(5)	5381(4)	2505(7)	61(2)*
C5,2	8544(5)	4600(4)	1384(7)	59(3)*
C6,2	7406(5)	3916(4)	1271(6)	48(2)*
C1,3	8225(5)	1923(3)	3522(4)	39(1)*
C2,3	9256(5)	2079(4)	3071(6)	52(2)*
C3,3	10479(6)	1866(6)	3731(7)	76(3)*
C4,3	10691(7)	1500(6)	4834(8)	86(3)*
C5,3	9692(7)	1359(5)	5295(6)	76(3)*
C6,3	8468(6)	1561(4)	4644(5)	55(3)*
B1	8225(8)	2416(5)	8453(8)	63(3)*
F1	8347(7)	2163(5)	9590(5)	139(3)*
F2	7808(10)	1687(4)	7361(7)	165(5)*
F3	7174(8)	2801(6)	8093(8)	156(4)*
F4	9352(8)	2976(7)	8557(10)	215(6)*

[a] Thermal parameters multiplied by 10^3, coordinates by 10^4. [b] U_{eq} defined as one-third of the trace of the orthogonalized thermal tensor.

R^1 is a phenyl group, and less soluble products obtained. The β-keto phosphines rapidly become oxidized in air, and the simple exposure of **1f** to air afforded without further treatment the corresponding phosphine oxide in an analytical state of purity (see Experimental Section). Therefore correct elemental analysis could not be obtained for the prepared β-keto phosphines, but **1a–1g** were found pure enough for the access to organometallic compounds and their ruthenium(II) complexes of types **2** and **3** analyze satisfactorily. Nevertheless the β-keto phosphines have been well characterized by IR and NMR (^{1}H, ^{31}P) spectroscopies. The IR spectra show the characteristic absorption of the carbonyl group, without significant change with respect to the corresponding primary ketone. The ^{31}P NMR chemical shift depends on the number of methyl substituents at the C_α position, with observed δ values of ~−20 ppm in the case of $Ph_2PCH_2C(=O)R^1$, ~0 ppm for the C_α monomethylated keto phosphines, and ~+14 ppm for the C_α dimethylated phosphines. The ^{1}H NMR spectra of the β-keto phosphines **1** show low $^2J_{PH}$ coupling constant values for the protons located at the C_α position, as precedently observed[8] for $Ph_2PCH_2C(=O)Ph$; this contrasts with $^3J_{PH}$ higher than 10 Hz observed for phosphines having a methyl group at the C_α position.

Synthesis of η^1-*P*-$Ph_2PCH(R^2)C(=O)R^1$ Ruthenium Complexes, 2. The β-keto phosphines $Ph_2PCH(R^2)C(=O)R^1$ **1a–1e** (R^3 = H) react readily with [(η^6-arene)$RuCl_2$]$_2$ ruthenium(II) derivatives by cleavage of the halogen bridges to afford the mononuclear neutral derivatives (η^6-arene)$Cl_2RuPPh_2CH(R^2)C(=O)R^1$, **2**, by η^1-(P) coordination of the keto phosphine (eq 2).



(2)

2

2a, (p-cymene)[$Ph_2PCH_2C(=O)Bu^t$]$RuCl_2$
2b, (mesitylene)[$Ph_2PCH_2C(=O)Bu^t$]$RuCl_2$
2c, (p-cymene)[$Ph_2PCH_2C(=O)Ph$]$RuCl_2$
2d, (mesitylene)[$Ph_2PCH_2C(=O)Ph$]$RuCl_2$
2e, (mesitylene)[$Ph_2PCH(Me)C(=O)Et$]$RuCl_2$
2f, (p-cymene)[$Ph_2PCH(Me)C(=O)Bu^t$]$RuCl_2$
2g, (mesitylene)[$Ph_2PCH(Me)C(=O)Bu^t$]$RuCl_2$
2h, (p-cymene)[$Ph_2PCH(Me)C(=O)Ph$]$RuCl_2$
2i, (mesitylene)[$Ph_2PCH(Me)C(=O)Ph$]$RuCl_2$

Table IV. Atomic Parameters for the Structure of Compound {(mesitylene)Ru[η^3-CH(PPh_2)C(Ph)=C(H)C(Bu^t)=O]}[BF_4], 7[a]

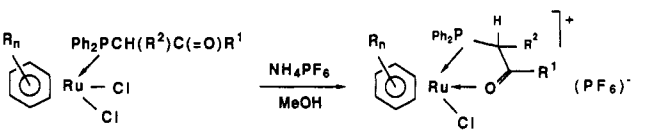
atom	x	y	z	U or U_{eq},[b] Å^2
Ru1	2330(1)	2498(1)	1055(1)	25(1)*
P1	3742(2)	2011(2)	1019(2)	30(1)*
O1	2326(4)	1684(5)	-754(5)	34(2)*
C1	2519(6)	692(7)	212(7)	32(3)*
C2	2208(6)	69(7)	-1206(7)	33(3)*
C3	2246(6)	685(7)	-2090(7)	34(3)*
C4	2316(6)	1948(7)	-1837(7)	33(3)*
C5	2307(6)	2427(8)	-3006(7)	39(4)*
C6	3250(8)	2319(12)	-3559(10)	72(6)*
C7	1286(7)	1564(10)	-4066(9)	64(5)*
C8	2358(10)	3776(10)	-2554(10)	78(6)*
C9	1128(6)	1797(7)	2076(7)	36(4)*
C10	2123(6)	2547(7)	2993(7)	35(4)*
C11	2702(6)	3806(7)	3082(7)	37(4)*
C12	2253(7)	4318(8)	2273(8)	43(4)*
C13	1280(7)	3595(9)	1333(8)	43(4)*
C14	717(7)	2315(8)	1235(8)	40(3)*
C15	549(8)	461(8)	2036(9)	56(4)*
C16	3742(7)	4572(9)	4056(8)	62(4)*
C17	877(9)	4141(42)	387(10)	69(6)*
C1,1	4518(6)	1863(7)	2381(8)	38(2)
C2,1	5609(7)	2373(9)	2661(9)	52(2)
C3,1	6224(9)	2289(10)	3732(11)	71(3)
C4,1	5742(9)	1749(10)	4539(11)	68(3)
C5,1	4665(8)	1227(9)	4274(9)	60(2)
C6,1	4039(7)	1259(8)	3196(8)	48(2)
C1,2	4581(6)	2266(7)	9930(7)	32(2)
C2,2	4775(7)	1281(8)	9149(8)	47(2)
C3,2	5523(7)	1526(9)	8435(9)	53(2)
C4,2	6015(7)	2748(9)	8497(9)	51(2)
C5,2	5823(7)	3725(8)	9249(8)	49(2)
C6,2	5083(6)	3483(8)	9971(8)	41(2)
C1,3	1808(6)	-1350(7)	-1735(8)	37(2)
C2,3	1147(7)	-2028(9)	-3001(9)	54(2)
C3,3	742(9)	-3369(11)	-3476(11)	72(3)
C4,3	1015(9)	-3989(11)	-2717(12)	78(3)
C5,3	1701(9)	-3308(10)	-1485(10)	71(3)
C6,3	2088(7)	-2001(8)	-1001(8)	47(2)
B1	1638(3)	8026(4)	3125(4)	66(3)
F1	2037(5)	7126(5)	3123(6)	128(2)
F2	2081(5)	9010(5)	4308(4)	150(2)
F3	580(3)	7507(6)	2937(7)	184(3)
F4	1855(5)	8462(6)	2131(5)	168(3)

[a] Thermal parameters multiplied by 10^3, coordinates by 10^4. [b] U_{eq} defined as one-third of the trace of the orthogonalized thermal tensor.

When the arene is mesitylene, the reactions were performed in dichloromethane. Starting from the soluble [(*p*-cymene)$RuCl_2$]$_2$, the reactions lead in ethanol to a red precipitate of **2**. Complexes **2** were isolated as red crystallized air stable solids and have been fully characterized by elemental analysis and spectroscopy. The ^{31}P NMR spectra show a single resonance in the range δ = 25–32 ppm. The carbonyl IR absorption is only slightly shifted to a higher frequency with respect to the uncoordinated keto phosphine.

Surprisingly, the keto phosphines **1f** and **1g** containing the bulky Ph_2PCMe_2 fragment exhibit a particular reactivity. After [(mesitylene)$RuCl_2$]$_2$ was stirred with 1 equiv of **1f** per Ru atom in dichloromethane, a dark red crystalline product was isolated in moderate yield and identified as (η^6-mesitylene)Ru(μ-Cl)$_3$Ru(Cl)[η^2-Ph_2PCMe_2-C(=O)Pr^i] on the basis of the elemental analysis and spectroscopic data. In the presence of 2 equiv of **1f** the same procedure allowed us to isolate a second but more soluble product corresponding to [η^2-Ph_2PCMe_2-C(=O)Pr^i]$_2RuCl_2$ with two *trans* phosphorus and two *cis* chlorine atoms.

Synthesis of η^2-(*P*,*O*)-$Ph_2PC(R^2R^3)C(R^1)$=O Ruthenium Complexes, 3. In a polar solvent such as methanol and in the presence of NH_4PF_6, the dissociation of one Ru—Cl bond in complexes **2** occurs, leading to cationic derivatives **3** (eq 3).

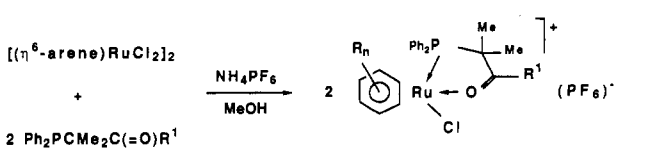


2 **3** (3a- 3f)

3a, {(p-cymene)(Cl)Ru[$Ph_2PCH_2C(Bu^t)$=O]}[BF_4]
3b, {(mesitylene)(Cl)Ru[$Ph_2PCH_2C(Bu^t)$=O]}[PF_6]
3c, {(p-cymene)(Cl)Ru[Ph_2PCH_2C(Ph)=O]}[BF_4]
3d, {(p-cymene)(Cl)Ru[Ph_2PCH(Me)C(Et)=O]}[PF_6]
3e, {(mesitylene)(Cl)Ru[Ph_2PCH(Me)C(Et)=O]}[PF_6]
3f, {(mesitylene)(Cl)Ru[Ph_2PCH(Me)C(Bu^t)=O]}[PF_6]

(3)

Alternatively, complexes **3** could be obtained under similar conditions (methanol and NH_4PF_6) starting from the stoichiometric amounts of [(arene)$RuCl_2$]$_2$ and phosphine. Specifically, complexes **3g–3i** were thus directly prepared from **1f** and **1g** having two substituents on the C_α carbon (eq 4).



3 (3g-3i)

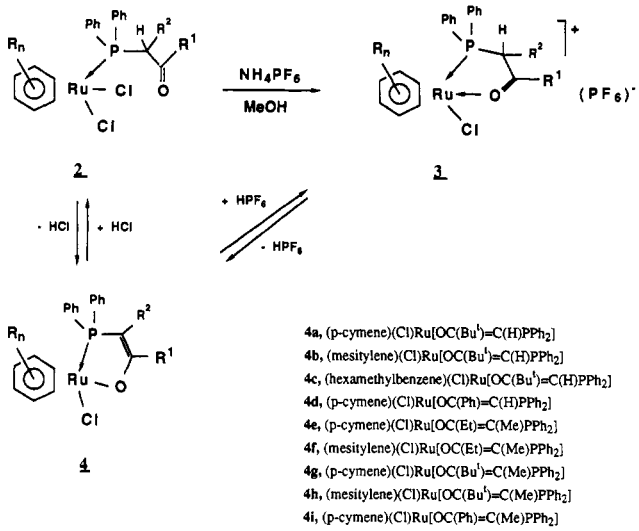
3g, {(p-cymene)(Cl)Ru[$Ph_2PC(Me)_2C(Pr^i)$=O]}[PF_6]
3h, {(mesitylene)(Cl)Ru[$Ph_2PC(Me)_2C(Pr^i)$=O]}[PF_6]
3i, {(mesitylene)(Cl)Ru[$Ph_2PC(Me)_2C(Bu^t)$=O]}[PF_6]

(4)

Table V. Selected Bond Distances (Å) and Angles (deg) for Compounds {(*p*-cymene)Ru[η^3-CH=C(Ph)CH(PPh_2)C(Bu^t)=O]}[PF_6], 6a, {(mesitylene)Ru[η^3-CH=C(Ph)C(Me)(PPh_2)C(Et)=O]}[BF_4], 6c, and {(mesitylene)Ru[η^3-CH(PPh_2)C(Ph)=C(H)C(But)=O]}[BF_4], 7

	6a	6c	7
Ru_1–P_1	2.293(5)	2.266(1)	2.243(2)
Ru_1–O_1	2.12(1)	2.119(4)	2.055(5)
Ru_1–C_1	2.03(1)	2.039(4)	2.211(8)
Ru_1–C_9	2.25(2)	2.246(5)	2.225(9)
Ru_1–C_{10}	2.27(2)	2.184(6)	2.172(8)
Ru_1–C_{11}	2.22(2)	2.207(6)	2.190(7)
Ru_1–C_{12}	2.21(2)	2.275(6)	2.251(9)
Ru_1–C_{13}	2.18(2)	2.256(4)	2.27(1)
Ru_1–C_{14}	2.23(2)	2.240(4)	2.246(9)
O_1–C_4	1.23(2)	1.233(4)	1.255(2)
P_1–C_1			1.787(6)
P_1–C_3	1.82(1)	1.893(5)	
C_1–C_2	1.36(2)	1.334(6)	1.44(1)
C_2–C_3	1.58(2)	1.557(8)	1.37(1)
C_3–C_4	1.50(2)	1.505(6)	1.42(1)
P_1–Ru_1–O_1	77.6(3)	79.21(9)	89.6(2)
P_1–Ru_1–C_1	77.5(5)	75.0(1)	47.3(2)
C_1–Ru_1–O_1	82.5(5)	79.21(9)	87.0(2)
Ru_1–P_1–C_3	92.3(5)	93.5(1)	
Ru_1–P_1–C_1			65.4(3)
P_1–C_1–C_2			120.86(6)
C_1–C_2–C_3	112(1)	114.9(4)	124.6(7)
C_2–C_3–C_4	104(1)	104.5(4)	126.7(7)
C_3–C_4–O_1	116(1)	118.4(4)	125.1(7)
C_4–O_1–Ru_1	120(1)	119.5(3)	132.1(5)
C_2–C_1–Ru_1	120(1)	120.2(4)	

Scheme I. Synthesis of Complexes (η^6-arene)(Cl)Ru[η^2-OC(R^1)=C(R^2)PPh_2], 4, and Coordinating Modes of β-Ketophosphines



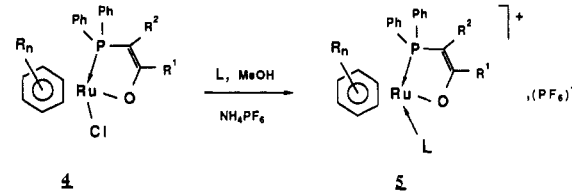
4a, (p-cymene)(Cl)Ru[OC(Bu^t)=C(H)PPh_2]
4b, (mesitylene)(Cl)Ru[OC(Bu^t)=C(H)PPh_2]
4c, (hexamethylbenzene)(Cl)Ru[OC(Bu^t)=C(H)PPh_2]
4d, (p-cymene)(Cl)Ru[OC(Ph)=C(H)PPh_2]
4e, (p-cymene)(Cl)Ru[OC(Et)=C(Me)PPh_2]
4f, (mesitylene)(Cl)Ru[OC(Et)=C(Me)PPh_2]
4g, (p-cymene)(Cl)Ru[OC(Bu^t)=C(Me)PPh_2]
4h, (mesitylene)(Cl)Ru[OC(Bu^t)=C(Me)PPh_2]
4i, (p-cymene)(Cl)Ru[OC(Ph)=C(Me)PPh_2]

Complexes **3a–3f** are also available by protonation of the corresponding phosphino enolato derivatives **4** with HPF_6 or HBF_4 (see later). Complexes **3** were isolated as air stable orange crystals and have been characterized by elemental analysis and spectroscopy (IR, NMR). The ^{31}P NMR spectra of the cation show a single resonance in the range δ = 55–85 ppm. As a consequence of the coordination of the keto function the carbonyl IR absorption is lowered by about 100 cm^{-1} relatively to the η^1-P coordinated keto phosphine. The ^1H NMR spectra of complexes **3a–3c** show the diastereotopy of the PCH_2 protons with a $^2J_{HH}$ constant value of ~18 Hz whereas the $^2J_{PH}$ value (~11 Hz) is not significantly changed relatively to the corresponding complexes **2** ($^2J_{PH}$ ~ 10 Hz). Evidence for two stereoisomers due to the asymmetric C_α carbon was shown by ^{31}P and ^1H NMR for complex **3f** in the approximative ratio 2/1. The ratio remains unchanged after deprotonation of **3f** under basic conditions to obtain the corresponding neutral phosphino enolato derivative of type **4** (see Scheme I) followed by protonation with HBF_4 of HPF_6, suggesting a kinetic equilibrium. The hemilabile character of keto phosphines[15] may account for this interconversion. The observation of only one isomer for complexes **3d** and **3e** obtained from the less bulky keto phosphine **1c** may be the result of a more sterically favored conformation rather than a stereoselective chloride–oxygen substitution process.

Synthesis of η^2-OC(R^1)=C(R^2)PPh_2 Enolato Ruthenium Complexes, 4. The η^2-P,O coordination mode is also achieved under basic conditions by abstraction of one molecule of HCl from complexes **2** or alternatively deprotonation of the cationic derivatives **3**, to afford the neutral phosphino enolato derivatives **4**, as shown on Scheme I.

These reactions, limited to derivatives of keto phosphines containing a hydrogen atom at the C_α position occur even with mild bases such as potassium acetate, but were more conveniently performed with KOH in ethanol from which complexes **4** could be obtained crystallized. Complexes **4** were obtained as orange crystalline products fairly soluble in common solvents to give solutions that slowly turn green on exposure to air. The starting materials **2** and **3** are readily recovered upon acidification by an acid ethanolic solution, HCl for complexes **2**, HPF_6 for complexes **3** (Scheme I). Complexes **4** have been characterized by elemental analysis and spectroscopy. The IR spectra show the disappearance of the carbonyl absorption band and a new strong absorption in the range 1505–1555 cm^{-1} attributable to the C=C(O) vibration.

Reactivity of the Neutral Derivatives 4. The neutral derivatives **4** retain a ruthenium–chlorine bond which is easily dissociated in the presence of NH_4PF_6 in methanol, allowing the coordination of soft ligands such as dimethyl sulfide at the ruthenium center to afford the stable orange cationic complexes **5b**, **5e**, **5f**, and **5g** (eq 5). Alternatively, nitriles (MeCN or Bu^tCN) react with complexes **4** to give complexes **5a**, **5c**, and **5d** (eq 5).



5a, {(hexamethylbenzene)(Bu^tCN)Ru[OC(Bu^t)=C(H)PPh_2]}(PF_6)
5b, {(mesitylene)(Me_2S)Ru[OC(Bu^t)=C(H)PPh_2]}(PF_6)
5c, {(mesitylene)(MeCN)Ru[OC(Bu^t)=C(Me)PPh_2]}(PF_6)
5d, {(p-cymene)(Bu^tCN)Ru[OC(Bu^t)=C(Me)PPh_2]}(PF_6)
5e, {(mesitylene)(Me_2S)Ru[OC(Bu^t)=C(Me)PPh_2]}(PF_6)
5f, {(p-cymene)(Me_2S)Ru[OC(Bu^t)=C(Me)PPh_2]}(PF_6)
5g, {(p-cymene)(Me_2S)Ru[OC(Ph)=C(Me)PPh_2]}(PF_6)

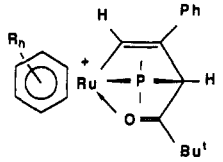
(5)

The structure of phosphino enolato complexes **5** was established on the basis of the elemental analysis and spectroscopic data. The isolation of the nitrile derivatives depends upon the nature of R^1, R^2, and the arene ligand. Noteworthy, the stability appeared to increase by the introduction of methyl groups at any position and could be obtained either with the permethylated arene ligand hexamethylbenzene or by substitution at the C_α position, as shown by complexes **5a** and **5d**, but attempts to isolate the analogous derivatives of **5a** containing mesitylene or *p*-cymene or those of **5d** with a phenyl group as R^1 remain unsuccessful. The weakness of the nitrile–ruthenium bond was evidenced as the easy substitution of the nitrile ligand by dimethyl sulfide occurs by simple recrystallization of the nitrile complex in the presence of a slight excess of dimethyl sulfide. This process was found irreversible.

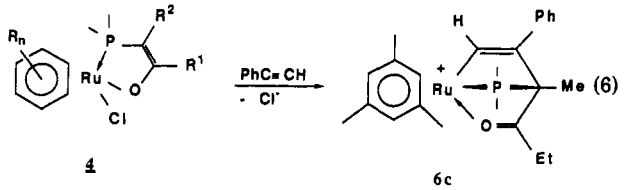
Activation of Phenylacetylene with Phosphino Enolato Complexes 4. The substitution of the same chloride ligand of complexes **4** by a terminal alkyne was then attempted. The coordination of phenylacetylene after the removal of the chloride ligand of derivatives **4** with $AgBF_4$ or $AgPF_6$ resulted in the formation of the novel complexes **6** in which the ruthenium center is linked to a new bifunctional phosphine arising from the regioselective intramolecular coupling reaction of the η^2-coordinated alkyne with the C_α carbon atom of the phosphino enolato ligand (eq 6).

Complexes **6** were isolated in good yields (49–86%) as orange air stable crystals and were characterized by elemental analysis and NMR spectroscopy. The IR spectra of **6** show a complex set of absorptions of medium or weak intensity in the range 1700–1500 cm^{-1}, and there was no direct evidence of the coordination of an acyl group. As spectroscopy could not allow the elucidation of the mode of coupling of the alkyne, the X-ray structure determi-

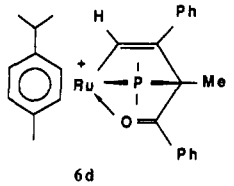
(15) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1978**, *18*, 2658.



6a, arene = p-cymene
6b, arene = mesitylene



4 **6c**



6d

nations of complexes **6a** and **6c** have been undertaken, the structure of **6a** has been previously reported in a preliminary communication.[16] The molecular structure of compounds **6a** and **6c** are shown on Figures 1 and 2, respectively. In both cases the ruthenium atom attains the 18 electron configuration by coordination of an arene ligand and of a newly formed tripodal ligand carrying three different donor functions, *i.e.* a phosphine, a σ-coordinated vinyl fragment, and an oxygen atom of a keto group. No significant change in bond distances and angles (Table V) observed for the metallabicyclic skeleton resulted from the substitution of the hydrogen atom located on the C_3 carbon atom in **6a** by a methyl group in **6c**. The Ru—O [2.12(1) Å for **6a** and 2.119(4) Å for **6c**] and Ru—C [2.03(1) Å for **6a** and 2.039(4) Å for **6c**] bond distances compare well with Ru—O [2.11(2) Å] in $Ru(CO)[C_6H_4MeC(O)C_6H_4Me]Cl(PMe_2Ph)_2$[17] and Ru—C [2.06(1) Å] in $Ru[CH{=}C(Me)C(O)OC_4H_9](H)(PPh_3)_3$.[18] The C_1—C_2 bond distance [1.36(2) Å for **6a** and 1.334(6) Å for **6c**] is typical of a C=C bond.

The formation of complexes **6** occurs but in lower yields under similar conditions ($MeOH/NH_4PF_6$) under which (η^6-arene)$(PR_3)RuCl_2$ led to methoxycarbene derivatives[5] as shown on Scheme II.

The reactivity of complexes **6** was then investigated, and this study showed that the thermal stability of complexes **6** depends on the nature of the R^2 substituent at the C_α position. When R^2 is a methyl group, the corresponding complexes **6c** and **6d** show no significant change after refluxing several hours in ethanol, but complex **6b**, R^2 = H, undergoes a fast rearrangement leading in refluxing ethanol to the red complex **7** (eq 7).

The ^{31}P NMR spectrum shows a dramatic shift of the phosphorus resonance from δ = 126.5 for **6b** to δ = 7.7 for complex **7**. The ^1H NMR spectrum of **7** shows that no incorporation of ethanol or loss of protons occurs and that

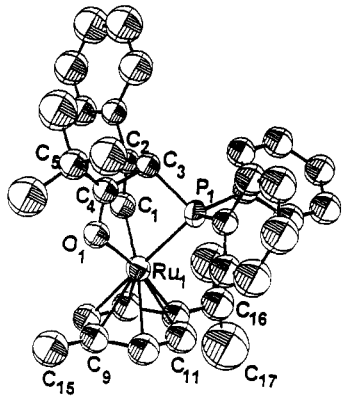


Figure 1. Molecular structure of compound {(*p*-cymene)-$Ru[\eta^3$-CH=C(Ph)CH(PPh_2)C(Bu^t)=O]}$[PF_6]$, **6a**.

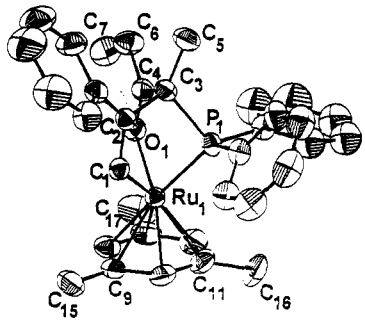
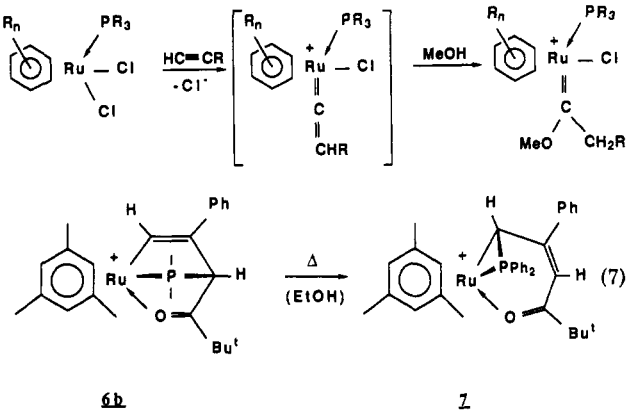


Figure 2. Molecular structure of compound {(mesitylene)-$Ru[\eta^3$-CH=C(Ph)C(Me)(PPh_2)C(Et)=O]}$[BF_4]$, **6c**.

Scheme II. Formation of Methoxycarbene Complexes



6b **7**

the transformation consisted of an isomerization process. The X-ray structure determination of **7** proved this transformation to be a 1,3-phosphorus–carbon bond shift (eq 7). The molecular structure of **7** (Figure 3) revealed a novel tripodal ligand araising from the conversion of the two five-membered metallacycles to a three-membered phosphametallacycle and a six-membered oxametallacycle. The Ru—P bond [2.243(2) Å] is slightly shorter than in complexes **6** but the Ru—C_1 bond [2.211(8) Å] is significantly longer than that in **6a** [2.03(1) Å] or **6b** [2.039 (4) Å]. The P—C(1) bond [1.787(6) Å] compares well with the P—C bond [1.761(4) Å] of the phosphazirconacyclopropane in $Cp_2Zr(Cl)[C(PMe_2)(SiMe_3)_2]$.[19] The C=O bond in **7** [1.255(2) Å] is equivalent to those observed for **6a** and **6c** [1.23(2) and 1.233(4) Å, respectively], but the Ru—O bond is somewhat shorter in **7** [2.055(5) Å] than

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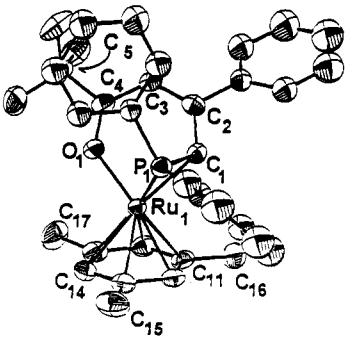
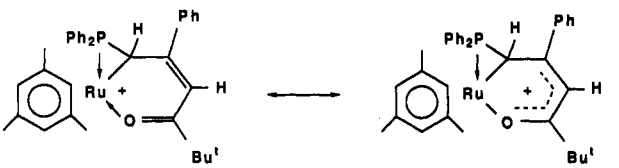


Figure 3. Molecular structure of compound {(mesitylene)-Ru[η^3-CH(PPh_2)C(Ph)=C(H)C(Bu^t)=O]}[BF_4], **7**.

Scheme III. Resonance Forms for Complex 7



in **6a** [2.12(1) Å] or **6c** [2.119(4) Å]. Noteworthy, the carbon—carbon bonds distances of the six-membered metallacycle [C_1–C_2, 1.44(1) Å; C_2=C_3, 1.37(1) Å; C_3–C_4, 1.42(1) Å] are indicative of a strong π-electron delocalization in this metallacycle, as described in Scheme III. For comparison the bonds distances in the Ru—O=C—C=C skeleton are similar to those [Ru—O, 2.09(1) Å; C=O, 1.30(2) Å; C—C, 1.38(2) Å; C=C, 1.36(3) Å] observed for the metallacycle Ru—O=C—C=C in the recently reported complex {(η^6-C_6Me_6)(PMe_3)Ru[η^2-C(OMe)=CH—C(CH=CPh_2)=O]}[PF_6].[20]

Moreover, the overall transformation **4** → **6** → **7** corresponds to the regioselective formal insertion of the alkyne into the P–C_α bond of the former phosphino enolato ligand of **4**.

Conclusion

The results presented here showed that a variety of β-keto phosphines are easily prepared from enolizable ketones. The study of their coordination on a [(η^6-arene)-Ru^{II}] fragment revealed that substitution at the C_α position enhanced the stability of the η^2-P,O coordination mode. The proton located at the C_α position exhibits an acidic character, allowing the access to the corresponding phosphino enolato ligand even under mild basic conditions. The phosphino enolato ligand retains a nucleophilic character that is involved in the observed coupling reaction with an η^2-coordinated alkyne intermediate, rather than the expected Ru(η^1-vinylidene), leading to novel polyfunctional coordinated phosphines. The latter gives an unprecedented example of a thermal induced 1,3-bond shift, achieving the formal insertion of the alkyne into the phosphorus-functional carbon bond.

Acknowledgment. This work was supported by the CNRS. The authors are grateful to J.-P. Guégan for NMR technical assistance and to the European ERASMUS programme for a grant to M.G., University of Oviedo.

Supplementary Material Available: Tables of positional parameters for hydrogen atoms and complete bond distances and angles (15 pages). Ordering information is given on any current masthead page.

OM9302251

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