Chelating and Hemilabile Properties of β- and γ-Keto Phosphines: (η^6-Arene)ruthenium(II) Derivatives from γ-Keto Phosphines and Synthesis and Reactivity of Bis(η^2-keto phosphine-*P,O*)ruthenium(II) Complexes

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The addition of the Ph_2P^- anion to α,β-enones followed by hydrolysis, provides a convenient synthesis of γ-keto phosphines. The coordination of the γ-keto phosphines, **1**, at an (η^6-arene)-$RuCl_2$ fragment affords neutral complexes (η^6-arene)(η^1-keto phosphine-*P*)$RuCl_2$, **2**. The formation of the cationic derivatives [(η^6-arene)(η^2-keto phosphine-*P,O*)RuCl]$^+$, **3**, is related to the structure of the functional ligand, as specified by the study of the competitive coordination of dimethyl sulfide *vs* the keto function. The replacement of the arene ligand in (η^6-arene)-(L)Ru(X)Cl [X = Cl; L = PMe_3, PPh_3, $P(OMe)_3$ or LX = phosphino enolato] complexes with β-keto phosphines occurs in methanol. The removal of both the arene and chloride ligands allows the coordination of two molecules of β-keto phosphine and results in the cationic derivatives [(η^2-keto phosphine-*P,O*)$_2$(L)RuCl]$^+$, **5**, and [(η^2-keto phosphine-*P,O*)$_2$(η^2-phosphino enolato-*P,O*)Ru]$^+$, **6**, isolated as their $(PF_6)^-$ salts. The substitution of the arene by carbon monoxide and one molecule of β- or γ-keto phosphine, results in the formation of the neutral (η^2-keto phosphine-*P,O*)(η^2-phosphino enolato-*P,O*)(CO)RuCl complexes, **7**. Starting from [(η^6-arene)-$RuCl_2$]$_2$ precursors, the removal of the arene by keto phosphines provides access to the neutral complexes (η^2-keto phosphine-*P,O*)$_2RuCl_2$, **9**, with *cis* phosphorus and *trans* chlorine atoms. The coordination of carbon monoxide on complexes **9** involves the hemilabile property of the keto phosphine ligands and leads to derivatives (η^2-keto phosphine-*P,O*)(η^1-keto phosphine-*P*)(CO)$RuCl_2$, **10**, with *trans* phosphorus atoms. The methanol induced cleavage of one ruthenium chlorine bond in complexes **9** and subsequent coordination of a nitrile or phenylacetylene afford the complexes [(η^2-keto phosphine-*P,O*)$_2$(RC≡N)RuCl](PF$_6$), **14**, and {[η^2-$Ph_2PC(Me)_2CH_2C$-(Me)=O-*P,O*]$_2$(PhCH=C=)RuCl}(PF$_6$), **15**, where the *cis* arrangement of the phosphorus atoms is retained. The phosphino enolato complexes [η^2-Ph_2PCH=C(Bu^t)O-*P,O*]$_2(CO)_2Ru$, **16**, with *trans* phosphorus and *trans* carbon monoxide, and [η^2-$Ph_2PC(R)$=C(Bu^t)O-*P,O*]$_2$(MeC≡N)$_2$-Ru, **17**, with *cis* phosphorus and *trans* acetonitrile, were obtained under mild basic conditions from complexes **9** incorporating enolizable β-keto phosphines.

Introduction

Organic compounds that contain oxygen provide an inexhaustible palette of valuable reagents for the synthesis of functional phosphines exhibiting chelating properties. A recent review[1] amply emphasized the dual interest of such compounds as both potentially hemilabile[2] ligands and phosphines carrying a reactive organic site interposing in organometallic processes. Functional phosphines have received applications in several important catalytic processes,[1] and their involvement as weakly chelating ligands both avoiding decomposition and preserving elevated reactivity of organometallic species continues to stimulate interest.[3,4]

The complexes incorporating keto phosphines or ester phosphines exhibit a specific reactivity related to their organic function. Since the pioneer work[5] showing the access to phosphino enolato complexes from β-keto phosphines, phosphino enolato derivatives have shown usefulness by the reversible carbon dioxide fixation into a palladium complex,[6] the activation of terminal alkynes to generate acetylides,[7] the access to C—C coupling products with activated alkynes[8] and aryl isocyanates,[9] or the access to O—P coupling products[10] with $PPhCl_2$ and PPh_2Cl. Most of these results and recent work[11] favor the

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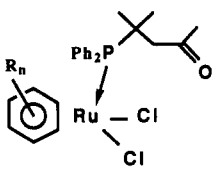
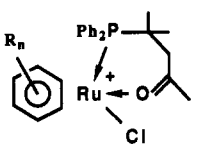
β-keto phosphine $Ph_2PCH_2C(=O)Ph$ and the β-ester phosphine $Ph_2PCH_2C(=O)OEt$. The alkali metal salts of the corresponding phosphino enolate anions were recently studied in order to rationalize their reactivity as a function of their electronic properties.[12] Emphasizing the lack of γ-keto phosphines, α-keto phosphines and related enolate derivatives are of current interest.[13]

We recently supplied access to new β-keto phosphines[14] and synthesized polyfunctional ligands which result from the coupling reaction of phenylacetylene with (η^6-arene)-(phosphino enolato)ruthenium(II) derivatives. Subsequent studies related to keto phosphines and phosphino enolato complexes allow us to now report (i) a simple access to γ-keto phosphines and, in order to specify their chelating ability, the study of their (η^6-arene)ruthenium-(II) complexes of types I and II, (ii) a straightforward



(I)



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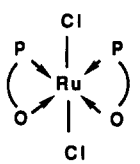

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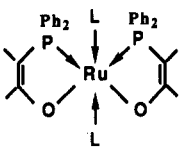

(IV)

synthesis of the novel (η^2-keto phosphine-*P,O*)$_2$RuCl$_2$ complexes of type III with *cis* phosphorus and *trans* chlorine atoms, from both β- and γ-keto phosphines, and (iii) the access under mild basic conditions to (η^2-phosphino enolato-*P,O*)$_2$(L)$_2$Ru(II) derivatives of type IV, from enolizable complexes of type III.

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 syringes and Schlenk type techniques. The melting points of the keto phosphines were determined in sealed capillaries and are uncorrected. Elemental analyses were performed by the "Service de Microanalyse du CNRS", Vernaison, France. Solvents were dried following conventional methods and distilled under an inert atmosphere before use. 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 AC 300 FT (^1H, 300.13 MHz; ^{31}P, 121.50 MHz; ^{13}C, 75.47 MHz) and WP 80 FT (^1H, 80 MHz; ^{31}P, 32.38 MHz) Bruker instruments. Both ^1H and ^{13}C spectra were referenced internally to the solvent peak. The abbrevations d_f, filled-in doublet (^1H), and m_5, five-line multiplet (^{13}C), are used, and NMR coupling constants are reported as absolute values. The syntheses from $RuCl_3 \cdot 3H_2O$ (Johnson Matthey) of the starting materials [(arene)RuCl$_2$]$_2$ (arene = benzene,[15] *p*-cymene,[16] mesitylene,[17] or hexamethylbenzene[16]) and (arene)(L)RuCl$_2$[18] [arene = *p*-cymene or mesitylene; L = PMe_3, PPh_3, $P(OMe)_3$, or SMe_2] were adapted from reported procedures. The commercially available ketones were used without supplementary purification and 1-propenyl *tert*-butyl ketone was prepared according to a published method.[19] The syntheses of β-keto phosphines and (arene)(phosphino enolato)RuCl derivatives were described elsewhere.[14] The IR and $^{31}P\{^1H\}$ NMR data for the γ-keto phosphines **1** and their complexes **2** and **3** are reported in Table 1.

Synthesis of the γ-Keto Phosphines, 1. An approximately 1 M THF solution of Ph_2PLi was obtained from lithium and freshly distilled chlorodiphenylphosphine. In a typical experiment 40 mL of a 1 M Ph_2PLi solution in THF was diluted in 50 mL of anhydrous diethyl ether. The solution was cooled to −50 °C and the enone (or a solution in diethyl ether) added slowly via a syringe until the characteristic orange color of the Ph_2P-anion disappeared. The mixture was stirred for 1 h at ambient temperature, and then 1 mL (an excess) of water was dropwise added into the flask. After being stirred for 1 h, the solution was filtered through a short (10- × 4-cm) alumina column that was then washed twice with 30 mL of diethyl ether. The collected solution was evaporated under reduced pressure to afford the crude product. In the case of the less soluble phosphines **1c** and **1d**, the reaction mixture was neutralized after hydrolysis by bubbling carbon dioxide and then evaporated to dryness. The residue was extracted with dichloromethane and the resulting solution filtered and then evaporated under vacuum to leave the crude keto phosphine.

$Ph_2PCH(Me)CH_2C(=O)Bu^t$, 1a. The phosphine **1a** was prepared from 5.50 mL (40.0 mmol) of 1-propenyl *tert*-butyl ketone and isolated as white needles after recrystallization from 50 mL of hot hexane. Yield: 6.90 g, 59%. Mp: 62 °C. ^1H NMR, $CDCl_3$, 300.13 MHz, δ: 7.50–7.32 (m, 10 H, Ph), 3.03 (m, 1 H, PCH), 2.56 (ddd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 10.4, $^3J_{PH}$ = 4.1 Hz, CH_2, H_a), 2.39 (ddd, 1 H, $^3J_{HH}$ = 2.7, $^3J_{PH}$ = 9.7 Hz, CH_2, H_b), 1.05 (s, 9 H, Bu^t), 0.96 (dd, 3 H, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 15.2 Hz, Me). Anal. Calcd for $C_{20}H_{25}OP$: C, 76.90; H, 8.07; P, 9.92. Found: C, 76.88; H, 8.07; P, 10.00.

$Ph_2PC(Me)_2CH_2C(=O)Me$, 1b. The crude phosphine **1b** was obtained as a colorless oil from 4.57 mL (40.0 mmol) of mesityl oxide. Yield: 9.5 g, 84%. ^1H NMR, $CDCl_3$, 300.13 MHz, δ: 7.60–7.35 (m, 10 H, Ph), 2.58 (d, 2 H, $^3J_{PH}$ = 6.7 Hz, CH_2), 2.06 (s, 3 H, MeCO), 1.32 (d, 6 H, $^3J_{PH}$ = 13.2 Hz, $PCMe_2$).

$Ph_2PCH(Ph)CH_2C(=O)Me$, 1c. The phosphine **1c** was obtained as white crystals from 5.83 g (40.0 mmol) of benzylidene acetone and after recrystallization from hot ethanol. Yield: 9.16 g, 69%. Mp: 130 °C. ^1H NMR, $CDCl_3$, 300.13 MHz, δ: 7.63–7.11 (m, 15 H, Ph), 4.10 (ddd, 1 H, $^2J_{PH}$ = 6.1 Hz, PCH), 3.06 (ddd, 1 H, $^2J_{HH}$ = 16.9, $^3J_{HH}$ = 10.9, $^3J_{PH}$ = 4.8 Hz, CH_2, H_a), 2.65 (ddd, 1 H, $^3J_{HH}$ = 3.2, $^3J_{PH}$ = 7.9 Hz, CH_2, H_b), 1.90 (s, 3 H, Me). Anal. Calcd for $C_{22}H_{21}OP$: C, 79.50; H, 6.37; P, 9.32. Found: C, 79.72; H, 6.32; P, 9.40.

$Ph_2PCH(Ph)CH_2C(=O)Ph$, 1d. The phosphine **1d** was obtained as white needles from 8.32 g (40.0 mmol) of chalcone and after recrystallization from a hot 1/1 mixture of toluene and ethanol (150 mL). Yield: 12.5 g, 79%. Mp: 168 °C. ^1H NMR, $CDCl_3$, 300.13 MHz, δ: 7.77–7.12 (m, 20 H, Ph), 4.33 (ddd, 1 H, $^2J_{PH}$ = 6.2 Hz, PCH), 3.72 (ddd, 1 H, $^2J_{HH}$ = 17.3, $^3J_{HH}$ = 10.9, $^3J_{PH}$ = 4.3 Hz, CH_2, H_a), 3.14 (ddd, 1 H, $^3J_{HH}$ = 2.8, $^3J_{PH}$ = 8.3 Hz, CH_2, H_b). Anal. Calcd for $C_{27}H_{23}OP$: C, 82.21; H, 5.88; P, 7.85. Found: C, 82.15; H, 5.88; P, 8.02.

Derivatives (η^6-arene)(keto phosphine)Ru^{II}, 2–4. (mesitylene)[$Ph_2PCH(Me)CH_2C(=O)Bu^t$]$RuCl_2$, 2a. A 1.00-g

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(1.71-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 1.10 g (3.53 mmol) of the phosphine **1a** in 30 mL of dichloromethane were stirred for 1 day, and the mixture was then evaporated to dryness. The residue was extracted with a toluene (15 mL)/chloroform (15 mL) mixture and the resulting solution filtered and then covered with 100 mL of hexane. The red crystals resulting from the natural diffusion of the solvents were separated from the mother solution by decantation, washed with hexane, and dried. Yield: 0.85 g, 41%. ^{1}H NMR, $CDCl_3$, 300.13 MHz, δ: 8.13–7.14 (m, 10 H, Ph), 4.53 (s, 3 H, C_6H_3), 3.86–3.73 (m, 2 H, PCH + CH_2, H_a), 1.84 (s, 9 H, C_6Me_3), 1.70 (m, 1 H, CH_2, H_b), 0.98 (s, 9 H, Bu^t), 0.86 (dd, 3 H, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 13.8 Hz, PCMe). Anal. Calcd for $C_{29}H_{37}Cl_2OPRu$: C, 57.61; H, 6.17; Cl, 11.73; P, 5.12. Found: C, 57.79; H, 6.37; Cl, 11.68; P, 4.98.

(*p*-cymene)[$Ph_2PCH(Me)CH_2C(=O)Bu^t$]$RuCl_2$, 2b. A mixture of 5.00 g (8.17 mmol) of [(*p*-cymene)$RuCl_2]_2$ and 5.30 g (17.0 mmol) of the phosphine **1a** in 80 mL of ethanol was stirred overnight at room temperature. The resulting slurry was filtered to collect the red precipitate that was then washed twice with 30 mL of diethyl ether. Yield: 9.42 g, 93%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.99–7.40 (m, 10 H, Ph), 5.06 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 4.75 (AB, 2 H, $^3J_{HH}$ = 5.9 Hz, C_6H_4), 3.75–3.60 (m, 2 H, PCH + CH_2, H_a), 2.47 (m, 1 H, C*H*Me_2), 1.83 (ddd, 1 H, $^2J_{HH}$ = 18.2, $^3J_{HH}$ = 11.0, $^3J_{PH}$ = 2.0 Hz, CH_2, H_b), 1.74 (s, 3 H, *Me*Ar), 0.96 (d, 3 H, $^3J_{HH}$ = 7.5 Hz, CH*Me*$_2$), 0.94 (s, 9 H, Bu^t), 0.93 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 0.82 (dd, 3 H, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 13.5 Hz, PCMe). Anal. Calcd for $C_{30}H_{39}Cl_2OPRu$: C, 58.25: H, 6.36; Cl, 11.46; P, 5.01. Found: C, 58.31; H, 6.38; Cl, 11.37; P, 5.06.

(hexamethylbenzene)[$Ph_2PC(Me)_2CH_2C(=O)Me$]$RuCl_2$, 2c. The stoichiometric amounts of [(hexamethylbenzene)$RuCl_2]_2$ and phosphine **1b** were stirred in dichloromethane, affording a red precipitate of **2c** in 50% yield. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.22–7.34 (m, 10 H, Ph), 2.88 (d, 2 H, $^3J_{PH}$ = 6.5 Hz, CH_2), 1.94 (s, 3 H, MeCO), 1.49 (s, 18 H, C_6Me_6), 1.01 (d, 6 H, $^3J_{PH}$ = 14.5 Hz, $PCMe_2$). Anal. Calcd for $C_{30}H_{39}Cl_2OPRu$: C, 58.25; H, 6.36; Cl, 11.46; P, 5.01. Found: C, 58.36; H, 6.37; Cl, 11.60; P, 5.04.

(mesitylene)[$Ph_2PC(Me)_2CH_2C(=O)Me$]$RuCl_2$, 2d. A mixture of 1.00 g (2.82 mmol) of (mesitylene)(Me_2S)$RuCl_2$ (used as a "soluble form" of [(mesitylene)$RuCl_2]_2$) and 1.00 g (3.52 mmol) of the phosphine **1b** in 50 mL of diethyl ether was stirred overnight. The resulting slurry was filtered and the collected orange red precipitate washed with hexane. Yield: 1.42 g, 87%. ^{1}H NMR, toluene-d_8, 300.13 MHz, δ: 8.32–6.98 (m, 10 H, Ph), 4.14 (s, 3 H, C_6H_3), 3.39 (d, 2 H, $^3J_{PH}$ = 7.1 Hz, CH_2), 1.83 (s, 3 H, MeCO), 1.52 (s, 9 H, C_6Me_3), 1.48 (d, 6 H, $^3J_{PH}$ = 14.8 Hz, $PCMe_2$). Complex **2d** could not be obtained in an analytical state of purity. Decomposition occurred while attempting to recrystallize the crude product. Interestingly, the slow evaporation of a solution in a CH_2Cl_2/EtOH mixture afforded some dark red crystals of **9e**.

(*p*-cymene)[$Ph_2PC(Me)_2CH_2C(=O)Me$]$RuCl_2$, 2e. A 3.06-g (5.00-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 3.0 g (10.6 mmol) of the phosphine **1b** were stirred overnight in 80 mL of ethanol. The resulting slurry was filtered and the collected orange precipitate washed with diethyl ether (60 mL). Yield: 4.96 g, 84%. Red crystals were obtained upon addition of diethyl ether to a dichloromethane saturated solution of the crude product (~1 g/40 mL). ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.95–7.45 (m, 10 H, Ph), 5.10 (AB, 4 H, $^3J_{HH}$ = 6.3 Hz, C_6H_4), 2.88 (d, 2 H, $^3J_{PH}$ = 6.6 Hz, CH_2), 2.40 (m, 1 H, C*H*Me_2), 1.97 (s, 3 H, MeCO), 1.58 (s, 3 H, *Me*Ar), 1.27 (d, 6 H, $^3J_{PH}$ = 15.1 Hz, $PCMe_2$), 0.95 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$). Anal. Calcd for $C_{28}H_{35}Cl_2OPRu$: C, 56.94; H, 5.97; Cl, 12.01; P, 5.25. Found: C, 56.92; H, 5.76; Cl, 12.38; P, 5.44.

(mesitylene)[$Ph_2PCH(Ph)CH_2C(=O)Me$]$RuCl_2$, 2f. A 3.05-g (5.22-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 3.50 g (10.5 mmol) of the phosphine **1c** were stirred for 2 days in 40 mL of dichloromethane. The solvent was removed under vacuum and the residue extracted with a hot toluene (20 mL)/dichloromethane (10 mL) mixture. The solution was filtered and the red filtrate covered with 100 mL of hexane to afford dark red crystals. Yield: 6.44 g, 99%. ^{1}H NMR, $CDCl_3$, 300.13 MHz, δ: 7.93–6.54 (m, 15 H, Ph), 5.06 (ddd, 1 H, $^2J_{PH}$ = 10.2 Hz, PCH), 4.45 (s, 3 H, C_6H_3), 4.08 (ddd, 1 H, $^2J_{HH}$ = 16.3, $^3J_{HH}$ = 3.0, $^3J_{PH}$ = 7.4 Hz, CH_2, H_a), 2.30 (ddd, 1 H, $^3J_{HH}$ = 13.0, $^3J_{PH}$ = 5.2 Hz, CH_2, H_b), 1.91 (s, 3 H, MeCO), 1.85 (s, 9 H, C_6Me_3). Anal. Calcd for $C_{31}H_{33}Cl_2OPRu$: C, 59.62; H, 5.33; Cl, 11.35; P, 4.96. Found: C, 59.35; H, 5.29; Cl, 11.66; P, 4.96.

(*p*-cymene)[$Ph_2PCH(Ph)CH_2C(=O)Me$]$RuCl_2$, 2g. A 1.10-g (1.80-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 1.35 g (4.07 mmol) of the phosphine **1c** were stirred overnight in 40 mL of ethanol to obtain a red precipitate. Yield: 2.14 g, 93%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.85–6.51 (m, 15 H, Ph), 5.30–4.38 (m, 5 H, C_6H_4 + PCH), 4.03 (ddd, 1 H, $^2J_{HH}$ = 17.0, $^3J_{HH}$ = 2.7, $^3J_{PH}$ = 8.0 Hz, CH_2, H_a), 2.55 (m, 1 H, C*H*Me_2), 2.31 (ddd, 1 H, $^3J_{HH}$ = 12.4, $^3J_{PH}$ = 4.5 Hz, CH_2, H_b), 1.83 (s, 3 H, MeCO), 1.75 (s, 3 H, *Me*Ar), 1.08 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 0.98 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$). Anal. Calcd for $C_{32}H_{35}Cl_2OPRu$: C, 60.19; H, 5.52; Cl, 11.10; P, 4.85. Found: C, 60.99; H, 5.71; Cl, 11.20; P, 4.85.

(mesitylene)[$Ph_2PCH(Ph)CH_2C(=O)Ph$]$RuCl_2 \cdot {}^2/_3CH_2Cl_2$, 2h. A 1.50-g (2.57-mmol) sample of [(mesitylene)$RuCl_2]_2$ and 2.10 g (5.32 mmol) of the phosphine **1d** in 40 mL of dichloromethane were stirred overnight. The red solution was filtered and the filtrate covered with 100 mL of diethyl ether to afford orange red needles. Yield: 3.00 g, 79%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.95–6.41 (m, 20 H, Ph), 4.99 (ddd, 1 H, $^2J_{PH}$ = 9.1 Hz, PCH), 4.83 (ddd, 1 H, $^2J_{HH}$ = 18.5, $^3J_{HH}$ = 2.5, $^3J_{PH}$ = 7.9 Hz, CH_2, H_a), 4.43 (s, 3 H, C_6H_3), 2.97 (ddd, 1 H, $^3J_{HH}$ = 12.3, $^3J_{PH}$ = 5.0 Hz, CH_2, H_b), 1.81 (s, 9 H, C_6Me_3). Anal. Calcd for $C_{36}H_{35}Cl_2OPRu \cdot {}^2/_3CH_2Cl_2$: C, 59.25; H, 4.93; Cl, 15.90; P, 4.17. Found: C, 59.37; H, 4.91; Cl, 16.02; P, 4.10.

(*p*-cymene)[$Ph_2PCH(Ph)CH_2C(=O)Ph$]$RuCl_2 \cdot {}^2/_3CH_2Cl_2$, 2i. A 0.85-g (1.39-mmol) sample of [(*p*-cymene)$RuCl_2]_2$ and 1.10 g (2.79 mmol) of the phosphine **1d** were stirred overnight in 60 mL of ethanol. The resulting slurry was filtered to collect the red precipitate that was then washed with ethanol (20 mL). Yield: 1.70 g, 87%. Recrystallization from dichloromethane/hexane afforded dark red crystals. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.93–6.44 (m, 20 H, Ph), 5.30–4.36 (m, 6 H, C_6H_4 + PCH + CH_2, H_a), 3.01 (ddd, 1 H, $^2J_{HH}$ = 18.4, $^3J_{HH}$ = 12.3, $^3J_{PH}$ = 4.5 Hz, CH_2, H_b), 2.56 (m, 1 H, C*H*Me_2), 1.78 (s, 3 H, *Me*Ar), 1.07 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 0.98 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$). Anal. Calcd for $C_{37}H_{37}Cl_2OPRu \cdot {}^2/_3CH_2Cl_2$: C, 59.74; H, 5.10; Cl, 15.61; P, 4.09. Found: C, 60.16; H, 5.18; Cl; 15.66; P, 4.04.

{(mesitylene)[$Ph_2PCH(Me)CH_2C(Bu^t)$=O]RuCl}(PF_6), 3a, from 2a. A 0.80-g (1.32-mmol) sample of complex **2a** and 0.22 g (1.35 mmol) of NH_4PF_6 were stirred overnight in 30 mL of methanol. The reaction mixture was evaporated to dryness and the residue extracted with 15 mL of dichloromethane. The orange solution was filtered and then covered with 100 mL of diethyl ether, affording light red crystals. Yield: 0.57 g, 60%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.71–7.53 (m, 10 H, Ph), 5.09 (s, 3 H, C_6H_3), 3.38 (m, 1 H, PCH), 3.15 (ddd, 1 H, $^2J_{HH}$ = 18.9, $^3J_{HH}$ = 3.7, $^3J_{PH}$ = 29.3 Hz, CH_2, H_a), 1.92 (s, 9 H, C_6Me_3 and m, 1 H, CH_2, H_b), 1.18 (s, 9 H, Bu^t), 0.74 (dd, 3 H, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 12.6 Hz, PCMe). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 232.2 (d, $^3J_{PC}$ = 2.5 Hz, C=O), 136.9–123.6 (m, Ar), 108.3 (s, *C*Me, mesitylene), 83.8 (d, $^2J_{PC}$ = 3.5 Hz, CH, mesitylene), 48.0 (s, *C*Me_3), 40.3 (s, CH_2), 26.4 (s, C*Me*$_3$), 23.0 (d, $^1J_{PC}$ = 26.9 Hz, P*C*H), 19.4 (s, C_6Me_3), 15.6 (d, $^2J_{PC}$ = 7.5 Hz, PC*Me*). Anal. Calcd for $C_{29}H_{37}ClF_6OP_2Ru$: C, 48.78; H, 5.22; Cl, 4.96; P, 8.68. Found: C, 49.34; H, 5.32; Cl, 5.19; P, 8.81.

{(*p*-cymene)[$Ph_2PCH(Me)CH_2C(Bu^t)$=O]RuCl}(PF_6), 3b, from 2b. A 0.50-g sample (0.81-mmol) of complex **2b** and 0.20 g (1.19 mmol) of $NaPF_6$ were stirred in a methanol (30 mL)/dichloromethane (5 mL) mixture for 1 day. The solvents were removed under vacuum, and the residue was extracted with 30 mL of dichloromethane. The solution was filtered and the orange filtrate covered with 100 mL of diethyl ether to afford orange red crystals. Yield: 0.14 g, 24%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.75–7.53 (m, 10 H, Ph), 5.92 (AB, 2 H, $^3J_{HH}$ = 6.6 Hz, C_6H_4), 5.42

(AB, 2 H, $^3J_{HH}$ = 5.9 Hz, C_6H_4), 3.32 (m, 1 H, PCH), 3.17 (ddd, 1 H, $^2J_{HH}$ = 19.4, $^3J_{HH}$ = 3.8, $^3J_{PH}$ = 29.2 Hz, CH_2, H_a), 2.25 (m, 1 H, C*H*Me_2), 1.89 (s, 3 H, *Me*Ar), 1.80 (ddd, 1 H, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 11.6 Hz, CH_2, H_b), 1.17 (s, 9 H, Bu^t), 0.92 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 0.78 (dd, 3 H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 12.5 Hz, PCMe), 0.72 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$). Anal. Calcd for $C_{30}H_{39}ClF_6OP_2Ru$: C, 49.49; H, 5.40; Cl, 4.87; P, 8.51. Found: C, 49.58; H, 5.59; Cl, 4.96; P, 7.92.

{(hexamethylbenzene)[$Ph_2PC(Me)_2CH_2C(Me)$=O]RuCl}(PF_6), 3c, from 2c. A 1.42-g (2.30-mmol) sample of complex **2c** and 0.40 g (2.45 mmol) of NH_4PF_6 were stirred overnight in a methanol (40 mL)/dichloromethane (10 mL) mixture. The solvents were removed, and the residue was extracted with dichloromethane (30 mL). The solution was filtered and the dark orange filtrate covered with 10 mL of methanol and then 120 mL of diethyl ether, to afford orange red crystals. Yield: 1.30 g, 78%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.83–7.54 (m, 10 H, Ph), 3.38 (dd, 1 H, $^2J_{HH}$ = 17.6, $^3J_{PH}$ = 16.0 Hz, CH_2, H_a), 3.20 (dd, 1 H, $^3J_{PH}$ = 13.5 Hz, CH_2, H_b), 2.65 (s, 3 H, MeCO), 2.06 (s, 18 H, C_6Me_6), 1.04 (d, 3 H, $^3J_{PH}$ = 10.5 Hz, PCMe), 0.78 (d, 3 H, $^3J_{PH}$ = 13.9 Hz, PCMe′). Complex **3c** was characterized only by spectroscopy.

{(mesitylene)[$Ph_2PC(Me)_2CH_2C(Me)$=O]RuCl}(PF_6), 3d. A 1.98-g (3.39-mmol) sample of [(mesitylene)$RuCl_2]_2$, 2.0 g (7.0 mmol) of the phosphine **1b**, and 1.15 g (7.06 mmol) of NH_4PF_6 were stirred for 2 days in a methanol (60 mL)/dichloromethane (20 mL) mixture. Orange crystals were obtained after extraction and recrystallization as above. Yield: 1.28 g, 28%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.92–7.58 (m, 10 H, Ph), 4.88 (s, 3 H, C_6H_3), 3.32 (dd, 1 H, $^2J_{HH}$ = 17.5, $^3J_{PH}$ = 19.9 Hz, CH_2, H_a), 3.24 (dd, 1 H, $^3J_{PH}$ = 14.2 Hz, CH_2, H_b), 2.65 (s, 3 H, MeCO), 1.90 (s, 9 H, C_6Me_3), 1.08 (d, 3 H, $^3J_{PH}$ = 10.8 Hz, PCMe), 0.94 (d, 3 H, $^3J_{PH}$ = 14.0 Hz, PCMe′). Anal. Calcd for $C_{27}H_{33}ClF_6OP_2Ru$: C, 47.27; H, 4.85; Cl, 5.17; P, 9.03. Found: C, 47.24; H, 4.85; Cl, 5.32; P, 9.04.

{(*p*-cymene)[$Ph_2PC(Me)_2CH_2C(Me)$=O]RuCl}(PF_6), 3e. A 3.06-g (5.00-mmol) sample of [(*p*-cymene)$RuCl_2]_2$, 3.0 g (10.6 mmol) of the phosphine **1b** and 1.80 g (11.0 mmol) of NH_4PF_6 were stirred for 2 days in 70 mL of methanol. The solvent was removed under vacuum, and the residue was washed with diethyl ether (100 mL). The solid was extracted with 50 mL of dichloromethane. The solution was filtered and then covered with 180 mL of diethyl ether to afford orange crystals. Yield: 4.21 g, 60%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.97–7.52 (m, 10 H, Ph), 5.62 (ABX, 2 H, $^3J_{HH}$ = 6.0, $^3J_{PH}$ = 1.2 Hz, C_6H_4), 5.18 (AB, 2 H, $^3J_{HH}$ = 6.1 Hz, C_6H_4), 3.47 (dd, 1 H, $^2J_{HH}$ = 18.2, $^3J_{PH}$ = 9.9 Hz, CH_2, H_a), 3.20 (dd, 1 H, $^3J_{PH}$ = 26.7 Hz, CH_2, H_b), 2.61 (s, 3 H, MeCO and m, 1 H, C*H*Me_2), 1.71 (s, 3 H, *Me*Ar), 1.28 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.20 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.13 (d, 3 H, $^3J_{PH}$ = 10.9 Hz, PCMe), 0.87 (d, 3 H, $^3J_{PH}$ = 14.2 Hz, PCMe′). Anal. Calcd for $C_{28}H_{35}ClF_6OP_2Ru$: C, 48.04; H, 5.04; Cl, 5.06; P, 8.85. Found: C, 47.79; H, 4.99; Cl, 5.28; P, 8.89.

{(mesitylene)[$Ph_2PCH(Ph)CH_2C(Me)$=O]RuCl}(PF_6)·$^1/_2CH_2Cl_2$, 3f, from 2f. A 1.80-g (2.88-mmol) sample of complex **2f** and 0.60 g (3.68 mmol) of NH_4PF_6 were dissolved in 20 mL of dichloromethane, and then 60 mL of methanol was added. The mixture was heated at reflux overnight and then evaporated under vacuum. The residue was extracted with 40 mL of dichloromethane and this solution filtered and then covered with 120 mL of diethyl ether to afford red crystals. Yield: 1.25 g, 56%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, mixture of two stereoisomers in a ~4/1 ratio, asterisk marked values for the major isomer, δ: 7.70–6.30 (m, 15 H, Ph), 4.96* and 4.88 (s, 3 H, C_6H_3), 4.19 (m, 1 H, PCH), 3.46 and 3.37* (m, 2 H, CH_2), 2.67 and 2.59* (s, 3 H, MeCO), 1.98 and 1.94* (s, 9 H, C_6Me_3). Anal. Calcd for $C_{31}H_{33}ClF_6OP_2Ru·^1/_2CH_2Cl_2$: C, 48.72; H, 4.41; Cl, 9.13; P, 7.98. Found: C, 48.73; H, 4.51; Cl, 9.29; P, 7.52.

{(*p*-cymene)[$Ph_2PCH(Ph)CH_2C(Me)$=O]RuCl}(PF_6), 3g. Complex **3g** was detected only, by $^{31}P\{^1H\}$ NMR spectroscopy from solutions of **4a** in CD_2Cl_2 (see Table 1 for $^{31}P\{^1H\}$ NMR data).

{(mesitylene)[$Ph_2PCH(Ph)CH_2C(Ph)$=O]RuCl}(BF_4), 3′h from 2h. A 0.39-g (0.52-mmol) sample of complex **2h** was dissolved in 20 mL of dichloromethane. The solution was cooled to −60 °C and 0.11 g (0.57 mmol) of $AgBF_4$ added. After being stirred overnight at room temperature, the reaction mixture was filtered and the filtrate covered with 60 mL of diethyl ether to afford red crystals. Yield: 0.33 g, 86%. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, mixture of two stereoisomers in a ~2/1 ratio, asterisk marked values for the major isomer, δ: 8.03–6.40 (m, 20 H, Ph), 5.07* and 4.99 (s, 3 H, C_6H_3), 4.38–3.69 (m, 3 H, $PCHCH_2$), 2.05 and 2.01* (s, 9 H, C_6Me_3). Anal. Calcd for $C_{36}H_{35}BClF_4OPRu$: C, 58.59; H, 4.78; Cl, 4.80; P, 4.20. Found: C, 58.70; H, 4.79; Cl, 4.64; P, 4.31.

{(*p*-cymene)(Me_2S)[$Ph_2PCH(Ph)CH_2C$(=O)Me]RuCl}(PF_6), 4a, from 2g. A 0.50-g (0.78-mmol) sample of complex **2g**, 0.13 g (0.80 mmol) of NH_4PF_6, and 1.0 mL (13.6 mmol, an excess) of Me_2S were stirred for 2 days in 30 mL of methanol. The reaction mixture was evaporated to dryness and the residue extracted with 20 mL of dichloromethane. The solution was filtered and then covered with 70 mL of diethyl ether to afford orange red crystals. Yield: 0.48 g, 76%. IR, ν(C=O): 1713 cm^{-1}. The dissociation of **4a** into **3g** and free Me_2S occurred in CD_2Cl_2 solution, resulting in an intricate ^{1}H NMR spectrum (see Table 1, complex **3g**, for $^{31}P\{^1H\}$ NMR data). Anal. Calcd for $C_{34}H_{41}ClF_6OP_2RuS$: C, 50.40; H, 5.10; Cl, 4.38; P, 7.65; S, 3.96. Found: C, 50.42; H, 5.12; Cl, 4.57; P, 7.86; S, 4.37.

Complexes [(η^2-keto phosphine-*P,O*)$_2$(L)RuCl](PF_6), L = PR_3 or $P(OMe)_3$, 5. {[$Ph_2PCH(Me)C(Et)$=O]$_2$[$P(OMe)_3$]RuCl}(PF_6), 5a. A 0.90-g (2.16-mmol) sample of (*p*-cymene)[$P(OMe)_3$]$RuCl_2$, 1.40 g (5.14 mmol) of the phosphine $Ph_2PCH(Me)C$(=O)Et, and 0.59 g (3.62 mmol) of NH_4PF_6 were stirred overnight in 40 mL of methanol. The orange mixture was evaporated to dryness and the residue extracted with 40 mL of dichloromethane. The solution was filtered and then covered with diethyl ether (130 mL) to afford orange crystals. Yield: 1.28 g, 63%. IR ν(C=O): 1625, 1590 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 140.1 (dd, P^1OMe), 65.6 (dd, P^2Ph_2), 51.6 (dd, P^3Ph_2); $^2J_{PP}$ = 38.4 (P^1, P^2), 45.3 (P^1, P^3), 323 (P^2, P^3) Hz. ^{1}H NMR, $CDCl_3$, 80 MHz, δ: 7.92–7.38 (m, 20 H, Ph), 4.26 (m, 2 H, PCH), 3.11 (d, 9 H, $^3J_{PH}$ = 10.7 Hz, POMe), 2.86 (m, 4 H, CH_2), 1.61–1.37 (m, 6 H, PCMe), 1.05 (t, 3 H, $^3J_{HH}$ = 6.9 Hz, CH_2*Me*), 0.62 (t, 3 H, $^3J_{HH}$ = 6.9 Hz, C′H_2*Me*). Anal. Calcd for $C_{37}H_{47}ClF_6O_5P_4Ru$: C, 46.97; H, 5.01; Cl, 3.75; P, 13.09. Found: C, 47.21; H, 4.86; Cl, 3.84; P, 13.27.

{[$Ph_2PCH(Me)C(Ph)$=O]$_2$(PPh_3)RuCl}(PF_6)·$^1/_2CH_2Cl_2$, 5b. A 2.21-g (3.89-mmol) sample of (*p*-cymene)(PPh_3)$RuCl_2$, 2.48 g (7.79 mmol) of the phosphine $Ph_2PCH(Me)C$(=O)Ph, and 0.70 g (4.29 mmol) of NH_4PF_6 were stirred for 3 days in 50 mL of methanol. Diethyl ether (50 mL) was added and the slurry filtered to collect the red precipitate that was then extracted with dichloromethane (50 mL). The solution was filtered and the filtrate covered with 150 mL of diethyl ether to afford red crystals. Yield: 2.10 g, 44%. IR, ν(C=O): 1565 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 76.0 (t, P^1), 46.4 (dd, P^2), 26.6 (dd, P^3); $^2J_{PP}$ = 25.7 (P^1, $P^{2,3}$), 308 (P^2, P^3) Hz. ^{1}H NMR, CD_2Cl_2, 80 MHz, δ: 7.57–6.97 (m, 45 H, Ph), 4.47–3.76 (m, 2 H, PCH), 1.22 (dd, 3 H, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 12.5 Hz, PCMe), 0.92 (dd, 3 H, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 11.5 Hz, P′CMe). Anal. Calcd for $C_{60}H_{53}ClF_6O_2P_4Ru·^1/_2CH_2Cl_2$: C, 59.42; H, 4.45; Cl, 5.84; P, 10.13. Found: C, 59.29; H, 4.74; Cl, 6.01; P, 10.36.

{[$Ph_2PCH(Me)C(Ph)$=O]$_2$[$P(OMe)_3$]RuCl}(PF_6), 5c. Dark red crystals of **5c** were similarly obtained by starting from 2.99 g (6.94 mmol) of (*p*-cymene)[$P(OMe)_3$]$RuCl_2$, 4.42 g (13.9 mmol) of the phosphine $Ph_2PCH(Me)C$(=O)Ph, and 1.30 g (7.98 mmol) of NH_4PF_6. Yield: 4.02 g, 56%. IR, ν(C=O): 1556 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 134.1 (dd, P^1OMe), 52.0 (dd, P^2Ph_2), 43.8 (dd, P^3Ph_2); $^2J_{PP}$ = 37.1 (P^1, P^2), 45.7 (P^1, P^3), 322 (P^2, P^3) Hz. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.13–6.91 (m, 30 H, Ph), 4.86–4.73 (m, 2 H, PCH), 3.22 (d, 9 H, $^3J_{PH}$ = 10.8 Hz, POMe), 1.50 (dd, 3 H, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 11.8 Hz, PCMe), 1.24 (dd, 3 H, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 11.9 Hz, P′CMe). Anal. Calcd for $C_{45}H_{47}$-

$ClF_6O_5P_4Ru$: C, 51.86; H, 4.55; Cl, 3.40; P, 11.89. Found: C, 52.07; H, 4.69; Cl, 3.20; P, 11.83.

{[$Ph_2PC(Me)_2C(Pr^i)$=O]$_2$(PMe_3)RuCl}(PF_6)·$^1/_3CH_2Cl_2$, 5d. A 1.31-g (3.44-mmol) sample of (*p*-cymene)(PMe_3)$RuCl_2$, 2.05 g (6.88 mmol) of the phosphine $Ph_2PC(Me)_2C(=O)Pr^i$ and 1.12 g (6.88 mmol) of NH_4PF_6 were stirred for 1 day in 60 mL of methanol. The orange mixture was evaporated to dryness and the residue extracted with 60 mL of dichloromethane. The solution was filtered and the filtrate covered with diethyl ether (120 mL) to afford orange crystals. Yield: 2.51 g, 74%. IR, ν(C=O): 1625, 1590 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 32.38 MHz, δ: 71.4 (d, P^1Ph_2), 70.9 (d, P^2Ph_2), 14.6 (t, P^3Me_3); $^2J_{PP}$ = 29.8 ($P^{1,2}$, P^3) Hz. ^1H NMR, $CDCl_3$, 80 MHz, δ: 8.47–7.39 (m, 20 H, Ph), 3.49 (m, 2 H, C*H*Me_2), 1.97 (t, 3 H, $|^3J_{PH} + {}^5J_{PH}|$ = 7.6 Hz, PCMe), 1.61 (t, 3 H, $|^3J_{PH} + {}^5J_{PH}|$ = 8.8 Hz, PCMe), unsolved 2 PCMe groups, 1.48 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.42 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.05 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.01 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 0.74 (d, 9 H, $^2J_{PH}$ = 9.8 Hz, PMe_3). Anal. Calcd for $C_{41}H_{55}ClF_6O_2P_4Ru·^1/_3CH_2Cl_2$: C, 50.52; H, 5.81; Cl, 6.01; P, 12.61. Found: C, 50.77; H, 5.16; Cl, 6.34; P, 12.96.

{[$Ph_2PC(Me)_2C(Pr^i)$=O]$_2$[$P(OMe)_3$RuCl}(PF_6), 5e. Following a similar procedure, orange crystals of **5e** were obtained starting from 1.70 g (4.09 mmol) of (mesitylene)[$P(OMe)_3$]$RuCl_2$, 2.50 g (8.39 mol) of the phosphine $Ph_2PC(Me)_2C(=O)Pr^i$, and 1.40 g (8.59 mmol) of NH_4PF_6 in 40 mL of methanol. Yield: 1.45 g, 35%. IR, ν(C=O): 1630, 1600 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, 32.38 MHz, δ: 132.5 (dd, P^1OMe), 74.7 (dd, P^2Ph_2), 62.5 (dd, P^3Ph_2); $^2J_{PP}$ = 38.4 (P^1, P^2), 41.9 (P^1, P^3), 317 (P^2, P^3) Hz. ^1H NMR, CD_2Cl_2, 80 MHz, δ: 8.40–7.45 (m, 20 H, Ph), 3.48 (m, 2 H, 2 C*H*Me_2), 3.17 (d, 9 H, $^3J_{PH}$ = 10.7 Hz, POMe), 1.82 (dd, 3 H, $^3J_{PH}$ = 6.3, $^5J_{PH}$ = 2.0 Hz, PCMe), 1.65 (dd, 3 H, $^3J_{PH}$ = 6.8, $^5J_{PH}$ = 2.2 Hz, PCMe), unsolved 2 PCMe groups, 1.46 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.23 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.11 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 0.93 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$). Anal. Calcd for $C_{41}H_{55}ClF_6O_5P_4Ru$: C, 49.13; H, 5.53; Cl, 3.54; P, 12.36. Found: C, 49.06; H, 5.40; Cl, 3.99; P, 12.77.

Reaction of (*p*-cymene)(PPh_3)$RuCl_2$ with $Ph_2PC(Me)_2CH_2C$(=O)Me. A 0.57-g (1.00-mmol) sample of (*p*-cymene)(PPh_3)$RuCl_2$, 0.70 g (2.46 mmol) of the phosphine **1b**, and 0.34 g (2.09 mmol) of NH_4PF_6 were stirred overnight in 30 mL of methanol. Similar treatment as above afforded red orange crystals of **3e** from dichloromethane/diethyl ether. Yield: 0.68 g, 97%. The product was identified as **3e** by IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR spectroscopies (see complex **3e** for the experimental data).

Complexes with Three η^2-*P,O* Ligands, 6. {[$Ph_2PCH(Me)C(Bu^t)$=O]$_2$[$Ph_2PC(Me)$=$C(Bu^t)O$]Ru}(PF_6)·$^1/_4CHCl_3$, 6a. A 1.80-g (3.17-mmol) sample of (*p*-cymene)[$Ph_2PC(Me)$=C(Bu^t)O]RuCl, 1.89 g (6.34 mmol) of the phosphine $Ph_2PCH(Me)C(=O)Bu^t$, and 1.10 g (6.74 mmol, an excess) of NH_4PF_6 were stirred for 3 days in 30 mL of methanol. The mixture was evaporated to dryness and the residue extracted with 20 mL of chloroform. The solution was filtered and then covered with 120 mL of diethyl ether, affording orange crystals. Yield: 2.45 g, 66%. IR: ν(C=O) 1610, 1582 cm^{-1}; ν(C=CO) 1518 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: major (2/3) isomer 83.2 (dd, P^1), 59.6 (dd, P^2), 53.6 (dd, P^3), $^2J_{PP}$ = 30.6 (P^1, P^2), 22.2 (P^1, P^3), 274 (P^2, P^3) Hz; minor (1/3) isomer: 69.0 (t, P^1), P^2 and P^3 partly overlapped by the major isomer, $^2J_{PP}$ = 28.6 (P^1, $P^{2,3}$) Hz. Anal. Calcd for $C_{57}H_{68}F_6O_3P_4Ru·^1/_4CHCl_3$: C, 58.78; H, 5.88; Cl, 2.27; P, 10.59. Found: C, 58.41; H, 6.06; Cl, 2.24; P, 10.65.

{[$Ph_2PCH(Me)C(Ph)$=O]$_2$[$Ph_2PC(Me)$=$C(Ph)O$]Ru}(PF_6)·$^1/_2CH_2Cl_2$, 6b. Complex **6b** was obtained similarly as dark red crystals, starting from (*p*-cymene)[$Ph_2PC(Me)$=C(Ph)O]RuCl and the phosphine $Ph_2PCH(Me)C(=O)Ph$. IR: ν(C=O) 1564 cm^{-1}; ν(C=CO) 1545 cm^{-1}. Anal. Calcd for $C_{63}H_{56}F_6O_3P_4Ru·^1/_2CH_2Cl_2$: C, 61.38; H, 4.62; Cl, 2.85; P, 9.97. Found: C, 61.31; H, 4.73; Cl, 3.30; P, 9.65.

{[$Ph_2PCH_2C(Bu^t)$=O][$Ph_2PCH(Me)C(Ph)$=O)][$Ph_2PC(Me)$=$C(Ph)O$]Ru}(PF_6)·$^3/_2CH_2Cl_2$, 6c. A 1.04-g (1.87-mmol) sample of (*p*-cymene)[Ph_2PCH=C(Bu^t)O]RuCl, 1.19 g (3.74 mmol) of the phosphine $Ph_2PCH(Me)C(=O)Ph$, and 0.31 g (1.87 mmol) of NH_4PF_6 were stirred for 2 days in 40 mL of methanol. The mixture was then evaporated to dryness and the residue extracted with 20 mL of dichloromethane. The solution was filtered and then covered with diethyl ether (100 mL) to afford dark red crystals. Yield: 1.00 g, 41%. IR: ν(Bu^tC=O) 1588 cm^{-1}; ν(PhC=O) 1566 cm^{-1}; ν(C=CO) 1531 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 61.9 (t, P^1), 55.1 (dd, P^2), 50.4 (dd, P^3); $^2J_{PP}$ = 28.5 (P^1, $P^{2,3}$), 290 (P^2, P^3) Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.85–6.32 (m, 40 H, Ph), 4.54 (m, 1 H, PC*H*Me), 3.74 (dd, 1 H, $^2J_{HH}$ = 18.2, $^2J_{PH}$ = 10.6 Hz, PCH_2, H_a), 2.57 (dd, 1 H, $^2J_{PH}$ = 10.2 Hz, PCH_2, H_b), 2.04 (dd, 3 H, $^3J_{PH}$ = 8.2, $^5J_{PH}$ = 1 Hz, MeC=), 0.93 (s, 9 H, Bu^t), 0.86 (dd, 3 H, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 11.7 Hz, PCH*Me*). Anal. Calcd for $C_{60}H_{58}F_6O_3P_4Ru·^3/_2CH_2Cl_2$: C, 57.11; H, 4.75; Cl, 8.22; P, 9.58. Found: C, 56.68; H, 4.76; Cl, 7.14 (some loss of dichloromethane occurred); P, 9.63.

Complexes (η^2-keto phosphine)(phosphino enolato)(CO)RuCl, 7. [$Ph_2PCH_2(Bu^t)$=O][Ph_2PCH=$C(Bu^t)O$](CO)RuCl, 7a. From (*p*-cymene)[Ph_2PCH=$C(Bu^t)O$]RuCl. A mixture of 1.30 g (2.35 mmol) of (*p*-cymene)[Ph_2PCH=C(Bu^t)O]RuCl and 0.68 g (2.39 mmol) of the phosphine $Ph_2PCH_2C(=O)Bu^t$ in 25 mL of methanol was stirred under a carbon monoxide atmosphere for 2 days. The resulting yellow precipitate (mixture of **7a** and **8a**) was recrystallized from dichloromethane/hexane to afford lemon yellow crystals. Yield: 0.58 g, 34%.

From 9a. A mixture of 2.22 g (3.00 mmol) of complex **9a** and 1.50 g (10.9 mmol, excess) of powdered K_2CO_3 in 50 mL of dichloromethane was stirred for 4 days under a carbon monoxide atmosphere. The solution was filtered, concentrated to 20 mL, and then covered with hexane (120 mL) to afford crystals of **7a**. Yield: 1.16 g, 53%. IR: ν(C≡O) 1943 cm^{-1}; ν(C=O) 1632 cm^{-1}; ν(C=CO) 1499 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 45.4 (d), 34.4 (d); $^2J_{PP}$ = 317 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.94–7.20 (m, 20 H, Ph), 4.60 (dd, 1 H, $^2J_{PH}$ = 2.9, $^4J_{PH}$ = 1.8 Hz, PCH=), 3.95 (ddd, 1 H, $^2J_{HH}$ = 17.1, $^2J_{PH}$ = 10.6, $^4J_{PH}$ = 2.0 Hz, PCH_2, H_a), 3.84 (dd, 1 H, $^2J_{PH}$ = 10.5 Hz, PCH_2, H_b), 0.92 (s, 9 H, Bu^t), 0.87 (s, 9 H, Bu^t). Anal. Calcd for $C_{37}H_{41}ClO_3P_2Ru$: C, 60.69; H, 5.64; Cl, 4.84; P, 8.46. Found: C, 60.98; H, 5.68; Cl, 4.80; P, 8.72.

[$Ph_2PCH(Me)C(Bu^t)$=O][Ph_2PCH=$C(Bu^t)O$](CO)RuCl, 7b. From (*p*-cymene)[$Ph_2PC(Me)$=$C(Bu^t)O$]RuCl. A solution of 1.60 g (2.81 mmol) of (*p*-cymene)[$Ph_2PC(Me)$=C(Bu^t)O]RuCl and 0.80 g (2.81 mmol) of the phosphine $Ph_2PCH_2C(=O)Bu^t$ in 30 mL of methanol, was stirred for 2 days under a carbon monoxide atmosphere. The resulting yellow slurry was evaporated to dryness under vacuum. The solid was washed with hexane, and recrystallization from chloroform/hexane afforded yellow needles. Yield: 1.30 g, 62%.

From (*p*-cymene)[Ph_2PCH=$C(Bu^t)O$]RuCl. A solution of 2.37 g (4.27 mmol) of (*p*-cymene)[Ph_2PCH=C(Bu^t)O]RuCl and 1.50 g (5.00 mmol) of the phosphine $Ph_2PCH(Me)C(=O)Bu^t$ in 40 mL of methanol, was stirred for 3 days under a carbon monoxide atmosphere. The resulting slurry was filtered to collect the yellow precipitate and then washed with hexane. Yield: 2.20 g, 70%. IR: ν(C≡O) 1951 cm^{-1}; ν(C=O) 1627 cm^{-1}; ν(C=CO) 1507 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 50.5 (d), 33.1 (d); $^2J_{PP}$ = 310 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.02–7.28 (m, 20 H, Ph), 4.55 (dd, 1 H, $^2J_{PH}$ = 2.5, $^4J_{PH}$ = 1.7 Hz, PCH=), 4.45 (m, 1 H, PC*H*Me), 1.36 (dd, 3 H, $^3J_{HH}$ = 7.6, $^3J_{PH}$ = 13.0 Hz, PCMe), 1.11 (s, 9 H, Bu^t), 0.65 (s, 9 H, Bu^t). Anal. Calcd for $C_{38}H_{43}ClO_3P_2Ru$: C, 61.16; H, 5.81; Cl, 4.75; P, 8.30. Found: C, 61.78; H, 5.97; Cl, 5.04; P, 8.45.

[$Ph_2PC(Me)_2C(Pr^i)$=O][Ph_2PCH=$C(Bu^t)O$](CO)RuCl, 7c. A solution of stoichiometric amounts of (*p*-cymene)[Ph_2PCH=C(Bu^t)O]RuCl and $Ph_2PCMe_2C(=O)Pr^i$ in methanol was stirred as above under a carbon monoxide atmosphere. The solvent was evaporated under vacuum to obtain a yellow solid that was washed with hexane. IR: ν(C≡O) 1948 cm^{-1}; ν(C=O) 1631 cm^{-1}; ν(C=CO) 1498 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 68.5 (d), 34.3 (d); $^2J_{PP}$ = 308 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.01–7.22 (m, 20 H, Ph), 4.68 (dd, 1 H, $^2J_{PH}$ = 3.1, $^4J_{PH}$ = 1.6 Hz, PCH), 3.16 (m, 1 H, C*H*Me_2), 1.51 (d, 3 H, $^3J_{PH}$ = 9.5 Hz, PCMe), 1.31 (d, 3 H, $^3J_{PH}$ = 10.5 Hz, PCMe′), 0.99 (s,

9 H, Bu^t), 0.92 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 0.89 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$). The high solubility of **7c** precluded easy recrystallization and the crude product was not analyzed.

[Ph$_2$PC(Me)$_2$CH$_2$C(Me)=O][Ph$_2$PCH=C(Bu^t)O](CO)RuCl, 7d. A solution of 0.77 g (1.39 mmol) of (*p*-cymene)[Ph$_2$PCH=C(Bu^t)O]RuCl and 0.45 g (1.58 mmol) of the phosphine **1b** in 30 mL of methanol, was stirred for 20 h under a carbon monoxide atmosphere. The solvent was removed under vacuum and the residue dissolved in 20 mL of hot ethanol. The slow cooling of the solution to −20 °C afforded first pale yellow crystals of **7d**, and then unreacted (*p*-cymene)[Ph$_2$PCH=C(Bu^t)O]RuCl. Yield: 0.15 g, 15%. IR: ν(C≡O) 1937 cm^{-1}; ν(C=O) 1675 cm^{-1}; ν(C=CO) 1500 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 42.1 (d), 32.9 (d); $^2J_{PP}$ = 309 Hz. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.05–7.26 (m, 20 H, Ph), 4.73 (dd, 1 H, $^2J_{PH}$ = 3.1, $^4J_{PH}$ = 1.0 Hz, PCH), 3.61 (dd, 1 H, $^2J_{HH}$ = 16.4, $^3J_{PH}$ = 15.2 Hz, CH_2, H_a), 3.13 (dd, 1 H, $^3J_{PH}$ = 24.4 Hz, CH_2, H_b), 2.05 (s, 3 H, MeCO), 1.42 (d, 3 H, $^3J_{PH}$ = 9.0 Hz, PCMe), 1.16 (s, 9 H, Bu^t), 0.96 (d, 3 H, $^3J_{PH}$ = 13.2 Hz, PCMe′). Anal. Calcd for $C_{37}H_{41}ClO_3P_2Ru$: C, 60.69; H, 5.64; Cl, 4.84; P, 8.46. Found: C, 60.63; H, 5.52; Cl, 4.80; P, 8.21.

[Ph$_2$PC(Me)$_2$C(Pr^i)=O][Ph$_2$PC(Me)=C(Bu^t)O](CO)RuCl, 7e. A solution of 0.68 g (1.20 mmol) of (*p*-cymene)[Ph$_2$PC(Me)=C(Bu^t)O]RuCl and 0.40 g (1.34 mmol) of the phosphine Ph$_2$PC(Me)$_2$C(=O)Pr^i in 30 mL of methanol was stirred for 20 h under a carbon monoxide atmosphere. The solvent was removed under vacuum and the residue washed with hexane. Recrystallization from acetone/hexane afforded yellow crystals. Yield: 0.80 g, 88%. IR: ν(C≡O) 1953 cm^{-1}; ν(C=O) 1625 cm^{-1}; ν(C=CO) 1513 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 68.8 (d), 58.0 (d); $^2J_{PP}$ = 305 Hz. ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.84–7.21 (m, 20 H, Ph), 3.12 (m, 1 H, C*H*Me$_2$), 1.89 (d, 3 H, $^3J_{PH}$ = 9.9 Hz, PCMe), 1.50 (d, 3 H, $^3J_{PH}$ = 8.2 Hz, PCMe), 1.12 (d, 3 H, $^3J_{PH}$ = 11.6 Hz, PCMe), 1.04 (s, 9 H, Bu^t), 0.94 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 0.85 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$). Anal. Calcd for $C_{39}H_{45}ClO_3P_2Ru$: C, 61.61; H, 5.97; Cl, 4.66; P, 8.15. Found: C, 61.33; H, 6.02; Cl, 4.89; P, 8.42.

Complexes (η^1-keto phosphine-*P*)(phosphino enolato)(CO)$_2$RuCl, 8. [Ph$_2$PCH$_2$C(=O)Bu^t][Ph$_2$PCH=C(Bu^t)O](CO)$_2$RuCl, 8a, from 7a. A solution of 0.50 g (0.68 mmol) of complex **7a** in 20 mL of acetone was stirred for 1 h under carbon monoxide and then covered with 120 mL of hexane under the carbon monoxide atmosphere to afford yellow prisms of **8a**. Yield: 0.18 g, 35%. In CD_2Cl_2 solution, complex **8a** showed partial dissociation into **7a** (and carbon monoxide) even under a carbon monoxide atmosphere. IR; ν(C≡O) 2016 cm^{-1}; ν(C=O) 1703 cm^{-1}; ν(C=CO) 1499 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 27.1 (d), 12.4 (d); $^2J_{PP}$ = 237 Hz. ^{1}H NMR, CD_2Cl_2, 300.13 MHz (mixture of **8a** and **7a**, available values), δ: 1.15 (s, 9 H, Bu^t), 1.09 (s, 9 H, Bu^t). Anal. Calcd for $C_{38}H_{41}ClO_4P_2Ru$: C, 60.04; H, 5.44; Cl, 4.66; P, 8.15. Found: C, 60.15; H, 5.60; Cl, 4.78; P, 8.08.

[Ph$_2$PCH(Me)C(=O)Bu^t][Ph$_2$PCH=C(Bu^t)O](CO)$_2$RuCl, 8b, from 7b. The stirring of **7b** in methanol under a carbon monoxide atmosphere (5 days) afforded a yellow precipitate consisting of a 4/1 mixture of **8b** and **7b**. IR: ν(C≡O) 2011 cm^{-1}; ν(C=O) 1694 cm^{-1}; ν(C=CO) 1496 cm^{-1}. Pure **7b** was recovered after recrystallization (from dichloromethane/hexane) under a carbon monoxide free atmosphere. A solution of **7b** in $CDCl_3$ was stirred for 20 h under carbon monoxide and then NMR spectra were recorded. The spectra showed residual **7b** and resonances attributable to **8b**. ^{31}P{^{1}H} NMR, $CDCl_3$, 121.50 MHz, δ: 31.3 (d), 27.3 (d); $^2J_{PP}$ = 229 Hz. ^{1}H NMR, $CDCl_3$, 300.13 MHz (mixture of **8b** and **7b**, the resonances of **7b** are omitted), δ: 7.87–7.28 (m, 20 H, Ph), 4.93 (m, 1 H, PC*H*Me), 4.70 (dd, 1 H, $^2J_{PH}$ = 3.2, $^4J_{PH}$ = 2.4 Hz, PCH=), 1.23 (s, 9 H, Bu^t), 1.02 (s, 9 H, Bu^t).

Complexes (η^2-keto phosphine-*P,O*)$_2$RuCl$_2$, 9. [Ph$_2$PCH$_2$C(Bu^t)=O]$_2$RuCl$_2$, 9a. A mixture of 1.26 g (2.06 mmol) of [(*p*-cymene)RuCl$_2$]$_2$ and 2.34 g (8.23 mmol) of the phosphine Ph$_2$PCH$_2$C(=O)Bu^t in 40 mL of ethanol, was heated at reflux for 1 day. The resulting solution was cooled to −20 °C to afford a crystalline precipitate that was collected by filtration and washed with diethyl ether. This crude product was used as complex **9a** for experimentation. Dark orange crystals of **9a**·(acetone) were obtained after recrystallization from acetone (40 mL)/pentane (120 mL). Yield: 2.17 g, 66%. IR: ν(C=O) 1622 cm^{-1}; ν(acetone) 1710 cm^{-1}. *trans*-dichloro isomer: ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.50 MHz, δ) 70.7 (s); ^{1}H NMR (CD_2Cl_2, 300.13 MHz, δ) 8.26–6.50 (m, 20 H, Ph), 4.11 (d$_f$, 4 H, $|^2J_{PH} + {}^4J_{PH}|$ = 11.5 Hz, PCH_2 + P′CH_2), 1.39 (s, 18 H, Bu^t). *cis*-dichloro isomer: ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.50 MHz, δ) 69.9 (d), 67.2 (d), $^2J_{PP}$ = 38.1 Hz; ^{1}H NMR (CD_2Cl_2, 300.13 MHz, δ) 8.26–6.50 (m, 20 H, Ph), 4.29 (dd, 1 H, $^2J_{HH}$ = 17.8, $^2J_{PH}$ = 10.7 Hz, PCH_2, H_a), 3.93 (d, 2 H, $^2J_{PH}$ = 10.7 Hz, P′CH_2), 3.77 (dd, 1 H, $^2J_{PH}$ = 10.0 Hz, PCH_2, H_b), 1.42 (s, 9 H, Bu^t), 0.90 (s, 9 H, Bu^t). Anal. Calcd for $C_{36}H_{42}Cl_2O_2P_2Ru$·(acetone): C, 58.65; H, 6.06; Cl, 8.88; P, 7.76. Found: C, 58.75, H, 5.98; Cl, 9.09; P, 7.83.

[Ph$_2$PCH$_2$C(Bu^t)=O]$_2$RuI$_2$, 9′a, from 9a. A 0.74-g (1.00-mmol) sample of complex **9a** and 0.34 g (2.04 mmol) of KI were stirred for 2 days in 25 mL of acetone. The mixture was then evaporated to dryness and the residue extracted with dichloromethane (20 mL). The solution was filtered and the dark filtrate covered with 120 mL of pentane to afford violet black crystals of **9′a**. Yield: 0.62 g, 67%. IR, ν(C=O): 1619 cm^{-1}. ^{31}P{^{1}H} NMR, $CDCl_3$, 121.50 MHz, δ: 74.2 (s). ^{1}H NMR, $CDCl_3$, 300.13 MHz, δ: 7.27–7.09 (m, 20 H, Ph), 4.21 (d$_f$, 4 H, $|^2J_{PH} + {}^4J_{PH}|$ = 10.3 Hz, PCH_2), 1.40 (s, 18 H, Bu^t). ^{13}C{^{1}H} NMR, CD_2Cl_2, 75.47 MHz, δ: 227.4 (s, C=O), 137.4 (m$_5$, $|^1J_{PC} + {}^3J_{PC}|$ = 47.7 Hz, C *ipso*), 134.7 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 10.2 Hz, C *ortho*), 130.3 (s, C *para*), 127.5 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 10.0 Hz, C *meta*), 51.9 (t, $|^1J_{PC} + {}^3J_{PC}|$ = 29.7 Hz, PCH_2), 45.5 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 7.1 Hz, CMe_3), 27.5 (s, C*Me*$_3$). Anal. Calcd for $C_{36}H_{42}I_2O_2P_2Ru$: I, 27.48. Found: I, 27.08.

[Ph$_2$PCH(Me)C(Bu^t)=O]$_2$RuCl$_2$, 9b. A mixture of 2.20 g (3.59 mmol) of [(*p*-cymene)RuCl$_2$]$_2$ and 4.29 g (14.4 mmol) of the phosphine Ph$_2$PCH(Me)C(=O)Bu^t in 50 mL of ethanol was heated at reflux for 1 day. The resulting red solution was filtered and then cooled to −20 °C to afford light red crystals. The mother solution was decanted, and the crystals were washed with diethyl ether. Yield: 4.40 g, 79%. IR, ν(C=O): 1621 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 79.6 (s). ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.41–6.92 (m, 20 H, Ph), 4.31 (m, 2 H, PCH), 1.55 (s, 18 H, Bu^t), 1.11 (dd$_f$, 6 H, $^3J_{HH}$ = 7.6, $|^3J_{PH} + {}^5J_{PH}|$ = 13.0 Hz, PCMe). Anal. Calcd for $C_{38}H_{46}Cl_2O_2P_2Ru$: C, 59.37; H, 6.03; Cl, 9.22; P, 8.06. Found: C, 59.54; H, 6.26; Cl, 9.52; P, 7.93.

[Ph$_2$PC(Me)$_2$C(Pr^i)=O]$_2$RuCl$_2$, 9c. Following the same procedure, complex **9c** was obtained as red crystals by starting from 0.95 g (1.55 mmol) of [(*p*-cymene)RuCl$_2$]$_2$ and 1.85 g (6.20 mmol) of the phosphine Ph$_2$PC(Me)$_2$C(=O)Pr^i that were heated at reflux in 30 mL of ethanol. Yield: 1.70 g, 71%. IR, ν(C=O): 1637 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 91.0 (s). ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.33–7.04 (m, 20 H, Ph), 3.37 (m, 2 H, C*H*Me$_2$), 1.42 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.32 (d$_f$, 12 H, $|^3J_{PH} + {}^5J_{PH}|$ = 10.2 Hz, PCMe$_2$). ^{13}C{^{1}H} NMR, CD_2Cl_2, 75.47 MHz, δ: 231.1 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 5.0 Hz, C=O), 136.5 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 8.9 Hz, C *ortho*), 130.9 (m$_5$, $|^1J_{PC} + {}^3J_{PC}|$ = 43.5 Hz, C *ipso*), 130.1 (s, C *para*), 127.1 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 9.6 Hz, C *meta*), 58.4 (t, $|^1J_{PC} + {}^3J_{PC}|$ = 22.7 Hz, P*C*Me$_2$), 36.6 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 6.2 Hz, *C*HMe$_2$), 24.4 (s, CH*Me*$_2$), 20.7 (s, PC*Me*$_2$). Anal. Calcd for $C_{38}H_{46}Cl_2O_2P_2Ru$: C, 59.37; H, 6.03; Cl, 9.22; P, 8.06. Found: C, 59.50; H, 6.13; Cl, 9.21; P, 8.31.

[Ph$_2$PCH(Me)CH$_2$C(Bu^t)=O]$_2$RuCl$_2$, 9d. A mixture of 1.96 g (3.20 mmol) of [(*p*-cymene)RuCl$_2$]$_2$ and 4.00 g (12.8 mmol) of the phosphine **1a** in 80 mL of ethanol was heated at reflux for 2 days to afford a red precipitate. Yield: 3.72 g, 73%. IR, ν(C=O): 1666 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, 121.50 MHz, δ: 65.1 (s). ^{1}H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.45–6.85 (m, 20 H, Ph), 2.96 (m, broad, 6 H, PCHCH_2), 1.26 (s, 18 H, Bu^t), 0.82 (dd$_f$, 6 H, $^3J_{HH}$ = 6.5, $|^3J_{PH} + {}^5J_{PH}|$ = 11.0 Hz, PCMe). The elemental analysis seems to indicate the retention of one molecule of water. Anal. Calcd for $C_{40}H_{50}Cl_2O_2P_2Ru·H_2O$: C, 58.97; H, 6.43; Cl, 8.70; P, 7.60. Found: C, 59.14; H, 6.68; Cl, 8.52; P, 7.22.

[Ph$_2$PC(Me)$_2$CH$_2$C(=O)Me]$_2$RuCl$_2$, 9e. A 2.00-g (4.00-mmol) sample of [(benzene)RuCl$_2$]$_2$ and 5.0 g (17.6 mmol) of the

phosphine **1b** were stirred overnight in 25 mL of dichloromethane, to afford a red solution that was concentrated under vacuum. Ethanol (30 mL) was added into the flask and the mixture was heated at reflux for 20 h. Diethyl ether (30 mL) was added after cooling, and the obtained pink precipitate was collected by filtration and then washed with diethyl ether. Yield: 4.65 g, 78%. Dark red crystals resulted from the slow evaporation of a solution of the product in a dichloromethane ($^1/_3$)/ethanol ($^2/_3$) mixture. IR, ν(C=O): 1678 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 70.0 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, 297 K, δ: 7.34–6.77 (broad, 20 H, Ph), 2.61 (s, 6 H, MeCO), 0.87 (broad, $PCMe_2$). ^1H NMR, CD_2Cl_2, 300.13 MHz, 213 K, δ: 4.26 (dd, 2 H, $^2J_{HH}$ = 16.8, $^3J_{PH}$ = 7.1 Hz, CH_2 + C'H_2, H_a), 3.13 (dd, 2 H, $^3J_{PH}$ = 26.2 Hz, CH_2 + C'H_2, H_b), 2.61 (s, 6 H, MeCO), 1.09 (d_f, 6 H, $|^3J_{PH}$ + $^5J_{PH}|$ = 5.6 Hz, PCMe + P'CMe), 0.52 (d_f, 6 H, $|^3J_{PH}$ + $^5J_{PH}|$ = 11.8 Hz, PCMe' + P'CMe'). Anal. Calcd for $C_{36}H_{42}Cl_2O_2P_2Ru$: C, 58.38; H, 5.72; Cl, 9.57; P, 8.36. Found: C, 58.24; H, 5.83; Cl, 9.71; P, 8.34.

[$Ph_2PC(Me)_2C(Pr^i)$=O][$Ph_2PC(Me)_2CH_2C(Me)$=O]$RuCl_2$, 9f. A mixture of 3.27 g (5.54 mmol) of (*p*-cymene)[$Ph_2PC(Me)_2CH_2C$(=O)Me]$RuCl_2$, **2e**, and 1.65 g (5.53 mmol) of the phosphine $Ph_2PC(Me)_2C$(=O)Pr^i in 40 mL of ethanol was heated at reflux for 20 h. After cooling, the mixture was filtered to collect the orange precipitate that was then washed with diethyl ether. Yield: 2.30 g, 55%. IR, ν(C=O): 1680, 1643 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 87.5 (d), 72.3 (d); $^2J_{PP}$ = 38.2 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.29–6.84 (m, 20 H, Ph), 3.73 (d, 2 H, $^3J_{PH}$ = 18.4 Hz, $PCCH_2$), 3.34 (m, 1 H, C*H*Me_2), 2.65 (s, 3 H, MeCO), 1.40 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.14 (d, 6 H, $^3J_{PH}$ = 10.6 Hz, $PCMe_2$), 1.05 (d, 6 H, $^3J_{PH}$ = 11.2 Hz, $P'CMe_2$). The NMR spectra showed the additional presence of little amounts of the symmetrical complexes **9c** and **9e**. The conversion of **9f** into **9c** and **9e** was completed while attempts were made to recrystallize the product.

Neutral Derivatives, 10–12, from Complexes 9. [$Ph_2PCH_2C(Bu^t)$=O][Ph_2PCH_2C(=O)Bu^t](CO)$RuCl_2$·CH_2Cl_2, 10a, from 9a. A solution of 1.00 g (1.35 mmol) of **9a** in 20 mL of dichloromethane was stirred overnight under a carbon monoxide atmosphere. The resulting yellow solution (containing mainly the derivative **11a**) showed under nitrogen the slow evolution of gas (presumably carbon monoxide) that became fast upon exposure to sunlight. After the formation of bubbles ceased, indicating completion of the **11a** → **10a** conversion, the solution was covered with hexane (120 mL) to afford yellow crystals. Yield: 0.78 g, 68%. IR: ν(C≡O) 1960 cm^{-1}; ν(C=O) 1708, 1631 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, 297 K, δ: 48.9 (d), 23.6 (d); $^2J_{PP}$ = 360 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, 297 K, δ: 7.59–7.34 (m, broad, 20 H, Ph), 4.05 (s, broad, 4 H, PCH_2), 0.90 (s, 18 H, Bu^t). ^1H NMR, CD_2Cl_2, 300.13 MHz, 253 K, δ: 7.77–7.41 (m, 20 H, Ph), 4.20 (dd, 2 H, $^2J_{PH}$ = 9.0, $^4J_{PH}$ = 1.2 Hz, PCH_2), 4.08 (dd, 2 H, $^2J_{PH}$ = 10.6, $^4J_{PH}$ = 0.8 Hz, $P'CH_2$), 1.00 (s, 9 H, Bu^t), 0.96 (s, 9 H, Bu^t). Anal. Calcd for $C_{37}H_{42}Cl_2O_3P_2Ru$·CH_2Cl_2: C, 53.46; H, 5.20; Cl, 16.61; P, 7.26. Found: C, 53.36; H, 5.29; Cl, 13.90 (some loss of dichloromethane occurred); P, 7.12.

[$Ph_2PCH(Me)C(Bu^t)$=O][$Ph_2PCH(Me)C$(=O)Bu^t](CO)$RuCl_2$·$^1/_2CH_2Cl_2$, 10b, from 9b. A solution of 1.00 g (1.30 mmol) of **9b** in 30 mL of acetone was stirred overnight under carbon monoxide. The resulting slurry was filtered to collect a yellow precipitate. Recrystallization from dichloromethane (20 mL)/hexane (100 mL) afforded yellow crystals. Yield: 0.76 g, 70%. IR: ν(C≡O) 1961 cm^{-1}; ν(C=O) 1696, 1625 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, 297 K, δ: 54.7 (d), 36.5 (d); $^2J_{PP}$ = 345 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, 297 K, δ: 7.90–7.20 (m, broad, 20 H, Ph), 5.09 (broad, 1 H, PCH), 4.38 (broad, 1 H, PCH), 1.29 (dd, 6 H, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 12.8 Hz, PCMe), 1.08 (s, broad, 18 H, Bu^t). Anal. Calcd for $C_{39}H_{46}Cl_2O_3P_2Ru$·$^1/_2CH_2Cl_2$: Cl, 12.67; P, 7.48. Found: Cl, 12.49; P, 7.38. A high carbon value obtained from elemental analysis likely indicated some retention of hexane to be also involved.

[$Ph_2PCH(Me)CH_2C(Bu^t)$=O][$Ph_2PCH(Me)CH_2C$(=O)Bu^t](CO)RuCl, 10c, from 9d. Complex **10c** was prepared similarly starting from 1.00 g (1.26 mmol) of **9d**, to obtain yellow crystals. Yield: 0.62 g, 60%. IR: ν(C≡O) 1945 cm^{-1}; ν(C=O) 1710, 1649 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, 297 K, δ: 36.0 (d), 31.4 (d); $^2J_{PP}$ = 342 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, 297 K, δ: 7.94–7.35 (m, 20 H, Ph), 3.84–2.27 (m, 6 H, $PCHCH_2$), 1.00–0.92 (m, 6 H, PCMe), 0.97 (s, 9 H, Bu^t), 0.94 (s, 9 H, Bu^t). Anal. Calcd for $C_{41}H_{50}Cl_2O_3P_2Ru$: C, 59.71; H, 6.11; Cl, 8.60; P, 7.51. Found: C, 59.26; H, 6.06; Cl, 9.09; P, 7.87.

[Ph_2PCH_2C(=O)Bu^t]$_2$(CO)$_2RuCl_2$, 11a, from 9a. A solution of 1.00 g (1.35 mmol) of **9a** in 20 mL of dichloromethane was stirred under carbon monoxide for 1 h and this solution covered with hexane (120 mL) under the carbon monoxide atmosphere (a syringe was used), to afford yellow crystals. Yield: 0.77 g, 72%. IR: ν(C≡O) 2028 cm^{-1}; ν(C=O) 1707 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 13.0 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.69–7.39 (m, broad, 20 H, Ph), 4.09 (t, 4 H, $|^2J_{PH}$ + $^4J_{PH}|$ = 7.4 Hz, PCH_2), 0.95 (s, 18 H, Bu^t). Anal. Calcd for $C_{38}H_{42}Cl_2O_4P_2Ru$: C, 57.29; H, 5.31; Cl, 8.90; P, 7.78. Found: C, 57.37; H, 5.29; Cl, 9.80; P, 7.99.

[$Ph_2PCH(Me)CH_2C$(=O)Bu^t]$_2$(CO)$_2RuCl_2$, 11b, from 9d. A solution of 0.60 g (0.75 mmol) of **9d** in 10 mL of dichloromethane was stirred under carbon monoxide and this solution covered with 100 mL of hexane under the carbon monoxide atmosphere, to obtain yellow crystals. Yield: 0.37 g, 58%. IR: ν(C≡O) 1993 cm^{-1}; ν(C=O) 1703 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 34.5 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.71–7.34 (m, 20 H, Ph), 3.73 (m, 2 H, PCH), 2.98 (m, 2 H, CH_2, H_a), 2.20 (m, 2 H, CH_2, H_b), 0.98 (m, 24 H, 2 PCMe + 2 Bu^t). Anal. Calcd for $C_{42}H_{50}Cl_2O_4P_2Ru$: C, 59.15; H, 5.91; Cl, 8.31; P, 7.26. Found: C, 59.07; H, 5.97; Cl, 9.09; P, 7.32.

[$Ph_2PC(Me)_2C(Pr^i)$=O](CO)$_2RuCl_2$, 12, from 9c. A 1.00-g (1.30-mmol) sample of **9c** was stirred in 30 mL of acetone under a carbon monoxide atmosphere, to give first an orange solution and then a yellow precipitate. After stirring overnight, the precipitate was separated by filtration and washed with diethyl ether. Yield: 0.54 g, 90%. Yellow crystals were obtained after recrystallization from dichloromethane/hexane under a carbon monoxide atmosphere. IR: ν(C≡O) 2078, 1991 cm^{-1}; ν(C=O) 1619 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 66.6 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.58–7.42 (m, 10 H, Ph), 3.34 (m, 1 H, C*H*Me_2), 1.55 (d, 6 H, $^3J_{PH}$ = 10.9 Hz, $PCMe_2$), 1.32 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$). Anal. Calcd for $C_{21}H_{23}Cl_2O_3PRu$: C, 47.92; H, 4.40; Cl, 13.47; P, 5.88. Found: C, 48.24; H, 4.46; Cl, 13.34; P, 6.26. The recrystallization of the crude complex but under a carbon monoxide *free* atmosphere resulted in the formation of a yellow solid. IR: ν(C≡O) 1955 cm^{-1}; ν(C=O) 1618 cm^{-1}. This complex was found insoluble in CD_2Cl_2. Anal. Calcd for $C_{20}H_{23}Cl_2O_2PRu$·$^2/_3CH_2Cl_2$: C, 44.01; H, 4.30; Cl, 21.29; P, 5.58. Found: C, 44.51; H, 4.46; Cl, 21.39; P, 5.57.

Cationic Derivatives, 13–15, from Complexes 9. {[$Ph_2PC(Me)_2C(Pr^i)$=O]$_2$(CO)RuCl}(PF_6), 13a, from 9c. A 0.77-g (1.00-mmol) sample of complex **9c** and 0.17 g (1.04 mmol) of NH_4PF_6 were stirred for 1 day in a methanol (20 mL)/dichloromethane (20 mL) mixture, under a carbon monoxide atmosphere. The solvents were removed under vacuum, and the residue was extracted with dichloromethane (20 mL). The solution was filtered and the filtrated covered with diethyl ether (100 mL) to afford orange yellow crystals. Yield: 0.68 g, 75%. IR: ν(C≡O) 1963 cm^{-1}; ν(C=O) 1612, 1597 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 70.7 (d), 66.4 (d); $^2J_{PP}$ = 309 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.95–7.16 (m, 20 H, Ph), 3.27 (m, 2 H, C*H*Me_2), 1.64 (d, 6 H, $^3J_{PH}$ = 8.4 Hz, 2 PCMe), 1.30 (d, 3 H, $^3J_{PH}$ = 8.4 Hz, PCMe), 1.20 (d, 3 H, $^3J_{PH}$ = 12.2 Hz, PCMe), 1.12 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.02 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 0.57 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 0.41 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$). Anal. Calcd for $C_{39}H_{46}ClF_6O_3P_3Ru$: C, 51.67; H, 5.12; Cl, 3.91; P, 10.25. Found: C, 52.07; H, 5.18; Cl, 4.33; P, 10.12.

{[$Ph_2PC(Me)_2CH_2C$(Me)=O]$_2$(CO)RuCl}(PF_6)·(acetone), 13b, from 9e. A 0.74-g (0.99-mmol) sample of **9e** and 0.17 g (1.04 mmol) of NH_4PF_6 were stirred for 20 h in a methanol (20 mL)/dichloromethane (10 mL) mixture, under a carbon monoxide

atmosphere. The resulting yellow slurry was evaporated to dryness and the residue extracted with 15 mL of dichloromethane. The solution was filtered and the filtrate evaporated to leave the crude product. Recrystallization from acetone (20 mL)/diethyl ether (120 mL) afforded a mixture of orange crystals of **13b** and a small amount of yellow needles of the acetone free complex. Yield: 0.37 g, 40%. IR: (orange crystals) ν(C≡O) 1963 cm^{-1}; ν(C=O) 1714 (acetone), 1667, 1649 cm^{-1}; (yellow needles) ν(C≡O) 1961 cm^{-1}; ν(C=O) 1668, 1652 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ, orange crystals or yellow needles: 40.2 (d), 37.4 (d); $^2J_{PP}$ = 305 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: (orange crystals) 7.95–7.39 (m, 20 H, Ph), 3.55–3.15 (m, 4 H, CH_2), 2.26 (s, 3 H, MeCO), 2.09 (s, 3 H, acetone), 1.96 (s, 3 H, MeCO), 1.34–1.14 (m, 12 H, $PCMe_2$); (yellow needles) identical except the resonance due to acetone. Anal. Calcd for $C_{37}H_{42}ClF_6O_3P_3Ru$·(acetone): C, 51.32; H, 5.17; Cl, 3.79; P, 9.92. Found: C, 51.50; H, 5.13; Cl, 4.54; P, 9.16.

{[$Ph_2PCH_2C(Bu^t)$=O]$_2$(Bu^tC≡N)RuCl}(PF_6), 14a, from 9a. A 0.74-g (1.00-mmol) sample of complex **9a**, 0.30 mL (2.71 mmol, an excess) of Bu^tC≡N, and 0.17 g (1.04 mmol) of NH_4PF_6 were stirred for 2 days in a methanol (20 mL)/dichloromethane (10 mL) mixture. The mixture was evaporated to dryness and the residue extracted with 15 mL of dichloromethane. The solution was filtered and the filtrate covered with diethyl ether (100 mL) to afford orange crystals. Yield: 0.67 g, 73%. IR, ν(C=O): 1628, 1602 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 64.2 (d), 63.1 (d); $^2J_{PP}$ = 38.2 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 8.23–6.72 (m, 20 H, Ph), 4.35 (ddd, 1 H, $^2J_{HH}$ = 18.2, $^2J_{PH}$ = 10.3, $^4J_{PH}$ = 1.0 Hz, PCH_2, H_a), 3.92 (dd, 1 H, $^2J_{HH}$ = 18.9, $^2J_{PH}$ = 10.2 Hz, P′CH_2, H_a), 3.78 (dd, 1 H, $^2J_{PH}$ = 10.1 Hz, PCH_2, H_b), 3.48 (dd, 1 H, $^2J_{PH}$ = 9.5 Hz, P′CH_2, H_b), 1.44 (s, 9 H, Bu^t), 1.20 (s, 9 H, Bu^t), 0.90 (s, 9 H, Bu^t). Anal. Calcd for $C_{41}H_{51}ClF_6NO_2P_3Ru$: C, 52.76; H, 5.51; Cl, 3.80; N, 1.50; P, 9.96. Found: C, 52.62; H, 5.61; Cl, 3.72; N, 1.34; P, 9.71.

{[$Ph_2PC(Me)_2C(Pr^i)$=O]$_2$(Bu^tC≡N)RuCl}(PF_6), 14b, from 9c. A 0.77-g (1.00-mmol) sample of **9c**, 0.30 mL (2.71 mmol, an excess) of Bu^tC≡N, and 0.17 g (1.04 mmol) of NH_4PF_6 were stirred for 20 h in a methanol (20 mL)/dichloromethane (10 mL) mixture. The mixture was evaporated to dryness and the residue extracted with 20 mL of dichloromethane. The orange solution was filtered and the filtrate covered with diethyl ether (120 mL) to afford **14b** as a mixture of yellow needles (trans-L,Cl isomer) and orange crystals (cis-L,Cl isomer). Yield: 0.74 g, 77%. Samples of each isomer were manually separated for the spectroscopic study. trans-L,Cl isomer: IR ν(C=O) 1617 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz, δ) 87.8 (s); ^1H NMR (CD_2Cl_2, 300.13 MHz, δ) 7.52–7.00 (m, 20 H, Ph), 3.46 (m, 2 H, C*H*Me_2), 1.44 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$ + C′H*Me*$_2$), 1.43 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$ + C′H*Me*$_2$), 1.41 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 11.2 Hz, PCMe + P′CMe), 1.22 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 10.6 Hz, PCMe′ + P′CMe′), 1.10 (s, 9 H, Bu^t). cis-L,Cl isomer: IR ν(C=O) 1623, 1589 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz, δ) 89.0 (d), 78.8 (d), $^2J_{PP}$ = 30.5 Hz; ^1H NMR (CD_2Cl_2, 300.13 MHz, δ) 8.34–6.58 (m, 20 H, Ph), 3.39 (m, 1 H, C*H*Me_2), 2.97 (m, 1 H, C*H*Me_2), 1.49 (s, 9 H, Bu^t), 1.48 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 1.36 (d, 3 H, $^3J_{PH}$ = 8.8 Hz, PCMe), 1.35 (d, 3 H, $^3J_{PH}$ = 9.3 Hz, PCMe), 1.34 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$), 1.12 (d, 3 H, $^3J_{PH}$ = 12.6 Hz, PCMe), 1.06 (d, 3 H, $^3J_{PH}$ = 12.3 Hz, PCMe), 0.97 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 0.20 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$). Anal. Calcd for $C_{43}H_{54}ClF_6NO_2P_3Ru$: C, 53.78; H, 5.67; Cl, 3.69; N, 1.46; P, 9.68. Found: C, 53.64; H, 5.82; Cl, 3.34; N, 1.47; P, 9.60.

{[$Ph_2PCH(Me)CH_2C(Bu^t)$=O]$_2$(Bu^tC≡N)RuCl}(PF_6)·$^1/_2$-CH_2Cl_2, 14c, from 9d. Following the procedure described for **14b**, orange crystals of **14c** were obtained by starting from 0.80 g (1.00 mmol) of **9d**, 0.30 mL (2.71 mmol, an excess) of Bu^tC≡N and 0.17 g (1.04 mmol) of NH_4PF_6. Yield 0.81 g, 78%. IR: ν(C≡N) 2258 cm^{-1}; ν(C=O) 1668, 1662 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 61.5 (d), 58.9 (d); $^2J_{PP}$ = 36.2 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.43–6.75 (m, 20 H, Ph), 3.52–2.72 (m, 6 H, $PCHCH_2$), 1.25 (s, 9 H, Bu^t), 1.24 (s, 9 H, Bu^t), 0.99 (s, 9 H, Bu^tCN), 0.81 (dd, 3 H, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 11.9 Hz, PCMe), 0.80 (dd, 3 H, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 12.0 Hz, P′CMe). Anal. Calcd for $C_{45}H_{59}ClF_6NO_2P_3Ru$·$^1/_2CH_2Cl_2$: C, 52.96; H, 5.86; Cl, 6.87; N, 1.36; P, 9.01. Found: C, 52.56; H, 5.77; Cl, 7.29; N, 1.38; P, 8.46.

{[$Ph_2PCH(Me)CH_2C(Bu^t)$=O]$_2$(MeC≡N)RuCl}(PF_6), 14′c, from 9d. According to the same procedure and using acetonitrile instead of Bu^tCN, orange crystals of **14′c** were obtained in 63% yield. IR: ν(C≡N) 2283 cm^{-1}; ν(C=O) 1667, 1660 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 63.0 (d), 58.4 (d); $^2J_{PP}$ = 37.1 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.73–6.68 (m, 20 H, Ph), 3.62–2.63 (m, 6 H, $PCHCH_2$), 1.83 (s, 3 H, MeCN), 1.29 (s, 9 H, Bu^t), 1.28 (s, 9 H, Bu^t), 0.85 (dd, 3 H, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 12.0 Hz, PCMe), 0.76 (dd, 3 H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 11.6 Hz, P′CMe). Anal. Calcd for $C_{42}H_{53}ClF_6NO_2P_3Ru$: C, 53.25; H, 5.64; Cl, 3.74; N, 1.48; P, 9.81. Found: C, 53.10; H, 5.86; Cl, 4.22; N, 1.56; P, 9.63.

{[$Ph_2PC(Me)_2CH_2C(Me)$=O]$_2$(Bu^tC≡N)RuCl}(PF_6)·$^2/_3$-CH_2Cl_2, 14d, from 9e. Starting from 0.74 g (0.99 mmol) of **9e**, 0.30 mL (2.71 mmol, an excess) of Bu^tC≡N, and 0.17 g (1.04 mmol) of NH_4PF_6, **14d** was obtained similarly as orange needles. Yield: 0.41 g, 42%. IR: ν(C≡N) 2242 cm^{-1}; ν(C=O) 1674 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 66.3 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.33–6.82 (m, 20 H, Ph), 3.92 (m, 2 H, CH_2 + C′H_2, H_a), 3.45 (m, 2 H, CH_2 + C′H_2, H_b), 2.68 (s, 6 H, MeCO), 1.36 (s, 9 H, Bu^t), 0.93 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 11.7 Hz, PCMe + P′CMe), 0.77 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 11.7 Hz, PCMe′ + P′CMe′). Anal. Calcd for $C_{41}H_{51}ClF_6NO_2P_3Ru$·$^2/_3CH_2Cl_2$: C, 50.56; H, 5.33; Cl, 8.36; N, 1.41; P, 9.39. Found: C, 50.27; H, 5.34; Cl, 8.00; N, 1.39; P, 9.18.

{[$Ph_2PC(Me)_2CH_2C(Me)$=O]$_2$(PhCH=C=)RuCl}(PF_6), 15, from 9e. A 0.74-g (0.99-mmol) sample of complex **9e**, 0.20 mL (1.82 mmol) of phenylacetylene, and 0.17 g (1.04 mmol) of NH_4PF_6 were stirred for 5 h in a methanol (20 mL)/dichloromethane (10 mL) mixture. The resulting brown solution was filtered and the filtrate covered with 120 mL of diethyl ether to afford red brown needles that were washed with diethyl ether. Yield: 0.44 g, 46%. IR, ν(C=O): 1671 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, 297 K, δ: 57.7 (s). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, 213 K, δ: 65.7 (d), 48.4 (d); $^2J_{PP}$ = 29.0 Hz. ^1H NMR, CD_2Cl_2, 300.13 MHz, 297 K, δ: 7.49–6.93 (m, 25 H, Ph), 5.05 (t, 1 H, $^4J_{PH}$ = 4.1 Hz, HC=), 3.86 (dd$_f$, 2 H, $^2J_{HH}$ = 19.6, $|^3J_{PH} + {}^5J_{PH}|$ = 17.8 Hz, PCH_2 + P′CH_2, H_a), 3.57 (dd$_f$, 2 H, $|^3J_{PH} + {}^5J_{PH}|$ = 17.2 Hz, PCH_2 + P′CH_2, H_b), 2.49 (s, 6 H, MeCO), 0.96 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 13.0 Hz, PCMe + P′CMe), 0.86 (d$_f$, 6 H, $|^3J_{PH} + {}^5J_{PH}|$ = 13.2 Hz, PCMe′ + P′CMe′). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, 297 K, selected values, δ: 313.1 (t, $^2J_{PC}$ = 16.9 Hz, C=Ru), 223.7 (s, CO), 117.0 (s, PhCH=). Anal. Calcd for $C_{44}H_{48}ClF_6O_2P_3Ru$: C, 55.50; H, 5.08; Cl, 3.72; P, 9.76. Found: C, 55.38; H, 5.30; Cl, 3.87; P, 9.40.

Complexes {(η^2-phosphino enolato-*P,O*)$_2$(L)$_2$Ru, 16, 17. [Ph_2PCH=C(Bu^t)O]$_2$(CO)$_2$Ru, 16, from 9a. A 0.50-g (0.68-mmol) sample of **9a** and 0.25 g (1.80 mmol, an excess) of powdered K_2CO_3 were stirred in 20 mL of methanol for 3 days under a carbon monoxide atmosphere. The reaction mixture was evaporated to dryness and the solid extracted with 15 mL of dichloromethane. The solution was filtered and the filtrate covered with pentane (100 mL) to afford cream colored crystals of **16**. Yield: 0.12 g, 24%. IR: ν(C≡O) 2004 cm^{-1}; ν(C=CO) 1489 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 27.3 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.75–7.27 (m, 20 H, Ph), 4.78 (t, 2 H, $|^2J_{PH} + {}^4J_{PH}|$ = 5.0 Hz, PCH), 1.15 (s, 18 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 204.1 (t, $^2J_{PC}$ = 10.3 Hz, C≡O), 196.8 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 12.2 Hz, =CO), 140.0 (t, $|^1J_{PC} + {}^3J_{PC}|$ = 50.1 Hz, C *ipso*), 131.4 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 6.2 Hz, C *ortho*), 129.8 (s, C *para*), 128.7 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 9.8 Hz, C *meta*), 69.0 (t, $|^1J_{PC} + {}^3J_{PC}|$ = 61.0 Hz, PCH), 39.7 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 11.0 Hz, CMe_3), 29.6 (s, CMe_3). Anal. Calcd for $C_{38}H_{40}O_4P_2Ru$: C, 63.06; H, 5.57; P, 8.56. Found: C, 63.44; H, 5.69; P, 8.38.

[Ph_2PCH=C(Bu^t)O]$_2$(MeC≡N)$_2$Ru·$^1/_3CH_2Cl_2$, 17a, from 9a. A 0.74-g (1.00-mmol) sample of **9a** and 0.50 g (3.62 mmol, an excess) of powdered K_2CO_3 were stirred in 15 mL of acetonitrile for 20 h. The reaction mixture was evaporated to dryness and the residue extracted with 15 mL of dichloromethane. The solution was filtered and the filtrate covered with hexane (100

Table 1. IR and $^{31}P\{^1H\}$ NMR Data for γ-Keto Phosphine Derivatives 2, 3, and 3′

phosphine, 1, and arene	η^1-*P* complexes, 2	IR[a] $\nu_{C=O}$	^{31}P[b] δ	η^2-*P,O* complexes, 3 or 3′	IR $\nu_{C=O}$	^{31}P δ	$\Delta\nu_{C=O}$[a]	^{31}P* δ
$Ph_2PCH(Me)CH_2C(=O)Bu^t$, **1a**		1698	−1.2[c]					
mesitylene	**2a**	1697	29.4[c]	**3a**	1646	37.7	51	27.4
p-cymene	**2b**	1708	24.6	**3b**	1637	35.9	71	
$Ph_2PC(Me)_2CH_2C(=O)Me$, **1b**		1706	20.9[c]					
hexamethylbenzene	**2c**	1708	20.6	**3c**	1665	46.1	43	
mesitylene	**2d**	1705	28.4[c]	**3d**	1662	49.4	43	
p-cymene	**2e**	1701	28.6	**3e**	1663	44.3	38	44.4
$Ph_2PCH(Ph)CH_2(=O)Me$, **1c**		1715	0.2[c]					
mesitylene	**2f**	1712	29.5[c]	**3f**	1667	45.0 37.9[d]	45	28.3
p-cymene	**2g**	1716	23.9	**3g**[e] (**4a**)		38.5 35.6[d]		29.3
$Ph_2PCH(Ph)CH_2C(=O)Ph$, **1d**		1686	0.0[c]					
mesitylene	**2h**	1689	31.0	**3′h**	1626	45.7 39.3[d]	63	45.6 39.3 28.8
p-cymene	**2i**	1690	25.3					

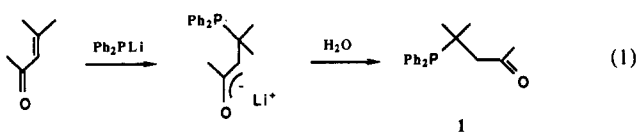
[a] IR as Nujol mulls, ν and Δν in cm^{-1}. [b] $^{31}P\{^1H\}$ NMR at 121.50 MHz in CD_2Cl_2. [c] ^{31}P NMR at 121.50 MHz in $CDCl_3$, ^{31}P* in CD_2Cl_2 + 10% Me_2S. [d] Major stereoisomer. [e] Complex **3g** was NMR detected only.

mL) to afford lemon yellow crystals. Yield: 0.56 g, 72%. IR: ν(C≡N) 2274 cm^{-1}; ν(C=CO) 1505 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 52.3 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.24–7.06 (m, 20 H, Ph), 4.78 (s, 2 H, $|^2J_{PH} + {}^4J_{PH}| \sim 0$ Hz, PCH), 1.56 (s, 6 H, MeCN), 1.31 (s, 18 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, 75.47 MHz, δ: 198.7 (t, $|^2J_{PC} + {}^4J_{PC}| = 6.6$ Hz, =CO), 139.2 (m_5, $|^1J_{PC} + {}^3J_{PC}| = 45.1$ Hz, C *ipso*), 132.8 (t, $|^2J_{PC} + {}^4J_{PC}| = 9.8$ Hz, C *ortho*), 128.6 (s, C *para*), 127.9 (t, $|^3J_{PC} + {}^5J_{PC}| = 8.8$ Hz, C *meta*), 120.5 (s, *MeCN*), 76.0 (m_5, $|^1J_{PC} + {}^3J_{PC}| = 59.3$ Hz, PCH), 38.9 (t, $|^3J_{PC} + {}^5J_{PC}| = 7.9$ Hz, *CMe*$_3$), 30.3 (s, C*Me*$_3$), 4.1 (s, *Me*CN). Anal. Calcd for $C_{40}H_{46}N_2O_2P_2Ru \cdot {}^1/_3CH_2Cl_2$: 62.26; H, 6.00; Cl, 3.04; N, 3.60; P, 7.96. Found: C, 62.23; H, 5.95; Cl, 3.12; N, 3.59; P, 7.97.

$[Ph_2PC(Me)=C(Bu^t)O]_2(MeC\equiv N)_2Ru \cdot {}^1/_6CH_2Cl_2$, 17b, from 9b. According to the same procedure, **17b** was obtained as yellow crystals starting from 0.95 g (1.23 mmol) of **9b** and 0.50 g (3.62 mmol, an excess) of K_2CO_3, that were stirred in a dichloromethane (10 mL)/acetonitrile (20 mL) mixture. Yield: 0.55 g, 56%. IR: ν(C≡N) 2267 cm^{-1}; ν(C=CO) 1505 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, 121.50 MHz, δ: 76.3 (s). ^1H NMR, CD_2Cl_2, 300.13 MHz, δ: 7.23–7.05 (m, 20 H, Ph), 1.71 (d_f, 6 H, $|^3J_{PH} + {}^5J_{PH}| = 9.9$ Hz, PCMe), 1.38 (s, 6 H, MeCN), 1.35 (s, 18 H, Bu^t). Anal. Calcd for $C_{42}H_{50}N_2O_2P_2Ru \cdot {}^1/_6CH_2Cl_2$: C, 63.94; H, 6.41; Cl, 1.49; N, 3.54; P, 7.82. Found: C, 63.89; H, 6.50; Cl, 1.52; N, 3.60; P, 7.49.

Results and Discussion

Syntheses of the γ-Keto Phosphines and Related $(\eta^6$-arene)Ru^{II} Derivatives. The formal 1,4-addition of Ph_2PLi to α,β-enones results in the formation of the γ-keto phosphines **1a–1d** after hydrolysis of the enolate intermediate (eq 1).



(1)

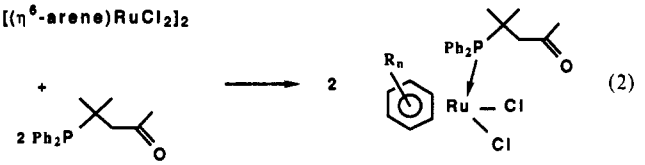
1

1a: $Ph_2PCH(Me)CH_2C(=O)Bu^t$
1b: $Ph_2PC(Me)_2CH_2C(=O)Me$
1c: $Ph_2PCH(Ph)CH_2C(=O)Me$
1d: $Ph_2PCH(Ph)CH_2C(=O)Ph$

The preparation and use of calibrated Ph_2PLi solutions in THF are particularly convenient, compared to the addition of Ph_2PH to α,β-unsaturated esters or nitriles which requires catalytic conditions,[20] or to the double assisted addition of Ph_2PH to α,β-unsaturated carbonyl compounds.[21]

The air sensitive γ-keto phosphines 1 were synthesized in yields up to 60% and isolated as recrystallized compounds of analytical purity, except **1b** which was obtained as an oil and used without attempts of further purification. The $^{31}P\{^1H\}$ NMR spectra of the γ-keto phosphines (Table 1) consisted of a single resonance in the range δ −1.2 (**1a**) to +20.9 (**1b**) ppm. The IR spectra (Table 1) showed the characteristic carbonyl absorption expected for a saturated ketone, and the ^1H NMR spectra were in agreement with the assigned structures. Owing to the chiral PC_α carbon atom, the CH_2 protons in the $Ph_2PCH(R)CH_2C(=O)R'$ phosphines **1a**, **1c**, and **1d** are diastereotopic. The ^1H NMR spectra of the phosphines **1c** and **1d** were well resolved, but due to the supplementary coupling between the PCH proton and those of the R = Me group, the interpretation of the spectrum of **1a** needed the comparison with the former.

The ability of the γ-keto phosphines 1 to behave as monodentate phosphorus ligands was shown by the easy access to their $(\eta^6$-arene)$(\eta^1$-keto phosphine-*P*)$RuCl_2$ derivatives, **2a–2i**, from $[(\eta^6$-arene)$RuCl_2]_2$ precursors (eq 2).



(2)

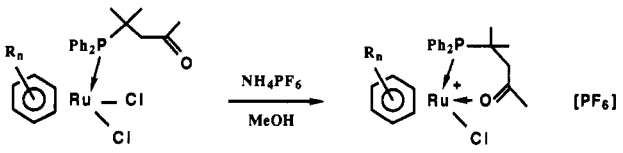
1a - 1d 2a - 2i

The air stable complexes **2a–2i** are listed in Table 1 and were found to be stable at ambient temperature in dichloromethane solution, except **2c**, **2d**, and **2e** where the PC_α permethylated phosphine **1b** was involved.

The analogous η^1-*P*-coordinated complexes obtained from β-keto phosphines were reported to undergo the substitution of one chloride ligand by the (keto) oxygen

(20) Blinn, D. A.; Button, R. S.; Farazi, V.; Neeb, M. K.; Tapley, C. L.; Trehearne, T. E.; West, S. D.; Kruger, T. L.; Storhoff, B. N. *J. Organomet. Chem.* **1990**, *393*, 143.
(21) Hashimoto, T.; Maeta, H.; Matsumoto, T.; Morooka, M.; Ohba, S.; Suzuki, K. *Synlett* **1992**, 340.

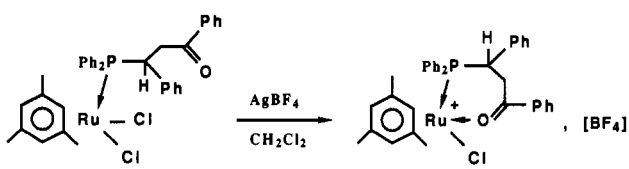
atom, when stirred in methanol with NH_4PF_6.[14] To compare the chelating abilities of γ- and β-keto phosphines, the reactivity of complexes **2** under the same conditions ($MeOH/NH_4PF_6$ or $NaPF_6$) was investigated. Except for starting from **2g**, **2h**, and **2i**, found to be inert under these conditions, the expected cationic derivatives, **3a–3f**, were obtained (eq 3).



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

In order to facilitate the comparison with the parent complexes **2**, complexes **3** are listed in Table 1. Relative to those of complexes **2**, the $^{31}P\{^1H\}$ NMR resonances observed for complexes **3** are downfield shifted and account for the chelate ring formation.[22] The occasional observation of two resonances (**3f**, **3g**, and **3'h**) likely indicated the presence of two diastereoisomers resulting from chirality at both the PC_α carbon and Ru centers. Reflecting the coordination of the oxygen atom, the IR carbonyl absorption is lowered in a $\Delta\nu$ range (38–71 cm^{-1}) centered around a $\Delta\nu$ = 50 cm^{-1} value (a $\Delta\nu$ close to 100 cm^{-1} was observed in the case of β-keto phosphines).

The ascertained inertness of complexes **2g**, **2h**, and **2i** might be the result of a deficient chelating ability of the keto phosphine or indicate a neighboring group effect resulting in the inertness of the ruthenium–chlorine bond. The η^2-*P,O*-coordination of the phosphine **1d** was achieved in **3'h**, obtained by reacting **2h** with $AgBF_4$ (eq 4).

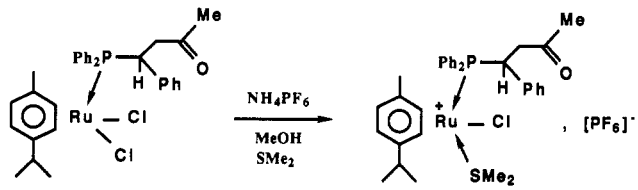


2h **3'h** (4)

The formation of the stable complex **3'h** is evidence of the chelating ability of the phosphine **1d**. In order to obtain further information related to the chelating ability of the γ-keto phosphines, the study of the competitive coordination (*vs* the keto function) of a neutral type L ligand such as dimethyl sulfide was undertaken. The $^{31}P\{^1H\}$ NMR spectra of complexes **3a**, **3f**, and **3'h** in CD_2Cl_2 + 10% Me_2S (Table 1) displayed resonances attributable to η^1-*P*-coordinated keto phosphines, but the spectrum of **3'h** indicated only a partial reaction and the one of **3e** was unaffected by the presence of Me_2S. However, the recrystallization of the involved complexes **3** from the slow diffusion of diethyl ether into a concentrated solution in a dichloromethane/Me_2S mixture, resulted selectively in their recovery. These observations suggested that the reaction of Me_2S with complexes **3** consisted of a reversible coordination of Me_2S to ruthenium according to the equilibrium in eq 5.

3 **4** (5)

Complex **2g** which was found inert under the simple $MeOH/NH_4PF_6$ conditions, reacted after the addition of dimethyl sulfide (in excess) to afford one example of isolable complex **4** incorporating dimethyl sulfide (eq 6).



2g **4a** (6)

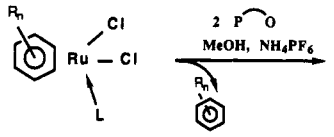
Complex **4a** was obtained as crystals of analytical purity. Both the IR spectroscopy in the solid state and the $^{31}P\{^1H\}$ NMR spectrum recorded from a CD_2Cl_2 + 10% Me_2S solution, indicated the keto phosphine in **4a** to be η^1-*P*-coordinated. However, the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 exhibited two resonances (δ = 38.5 and 35.6 ppm) attributable to diastereoisomers of complex **3g** which was not isolated. The formation of **3g** in solution is likely the result of competitive coordination of the keto function *vs* dimethyl sulfide. Noteworthy, complexes **2h** and **2i** obtained starting from the phosphine **1d**, remained inert under the $MeOH/NH_4PF_6$ conditions while Me_2S was added. The cleavage of the ruthenium chloride bond that is required to allow the coordination of Me_2S is mainly the result of a methanol induced polarization. The inertness of **2h** and **2i** suggested that the phosphine **1d** is structurally adjusted to protect the Ru—Cl bond from the methanol polarizing effect. Both the phosphines **1c** and **1d** bear a phenyl group at the PC_α position and distinct reactivities arising from different –C(=O)R groups. As previously observed in the case of β-keto phosphines,[14] the permethylation at the PC_α position in the γ-keto phosphine **1b** favored the η^2-*P,O*-coordinating mode.

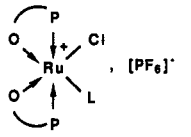
Replacement of the Arene Ligand in (η^6-arene)Ru^{II} Complexes with Keto Phosphines. In the course of our study of β-keto phosphines,[14] we had observed (but not yet reported) that strong enough chelating β-keto phosphines reacted in methanol with (η^6-arene)(L)$RuCl_2$ [L = PMe_3, PPh_3, or $P(OMe)_3$] complexes and NH_4PF_6. The reaction which occurred at ambient temperature consisted formally of the substitution of the arene and one chloride ligands by two molecules of keto phosphine, to afford the [(η^2-keto phosphine-*P,O*)$_2$(L)RuCl](PF_6) complexes, **5a–5e** (eq 7).

The $^{31}P\{^1H\}$ NMR spectra of the $P(OMe)_3$ derivatives **5a**, **5c**, and **5e** showed besides the low field resonance of the $P(OMe)_3$ ligand, two distinct keto phosphine ligands with a $^2J_{PP}$ coupling constant value of ~320 Hz, characteristic for *trans* phosphorus atoms.[23] Such an observation of distinct *trans* phosphorus requires a *cis* relative

(22) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (c) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(23) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294.



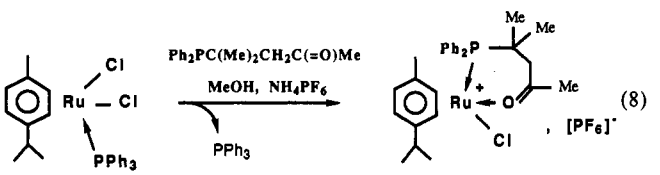


5a - 5e

5	P O ligand	L
5a:	$Ph_2PCH(Me)C(Et)=O$	$P(OMe)_3$
5b:	$Ph_2PCH(Me)C(Ph)=O$	PPh_3
5c:	$Ph_2PCH(Me)C(Ph)=O$	$P(OMe)_3$
5d:	$Ph_2PC(Me)_2C(Pr^i)=O$	PMe_3
5e:	$Ph_2PC(Me)_2C(Pr^i)=O$	$P(OMe)_3$

(7)

arrangement of the oxygen atoms. The PMe_3 derivative **5d** likely preserved the same structure despite the $^2J_{PP}$ constant value not being determined. The $^{31}P\{^1H\}$ NMR spectrum of **5b** incorporating the bulkier PPh_3 ligand indicated still a *mer* structure, but the observation of three so distinct chemical shifts (76.0, 46.4, and 26.6 ppm) suggested a less symmetrical structure. Therefore, a *cis* relative position of the phosphorus atoms of the chelating ligands in **5b** may be assumed. Surprisingly, the reaction of the γ-keto phosphine **1b** with (*p*-cymene)$(PPh_3)RuCl_2$ and NH_4PF_6 afforded exclusively the already described complex **3e** according to a phosphine exchange process (eq 8).

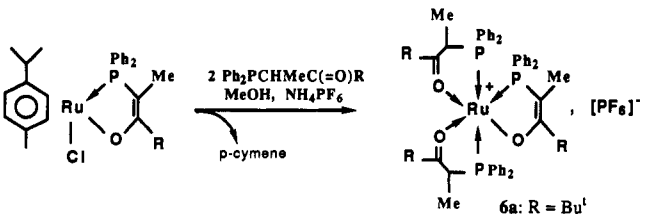


(8)

3e

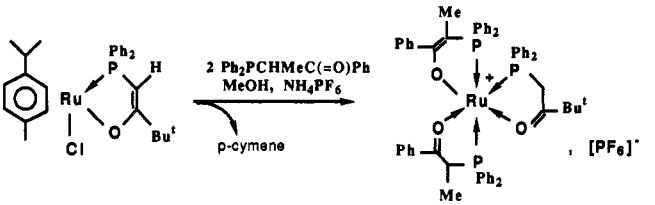
Such a selective removal of the PPh_3 ligand instead of the arene one, probably emphasized a directing effect from the structural constraints. Comparable with (η⁶-arene)$(PR_3)RuCl_2$ complexes, the (η⁶-arene)(η²-phosphino enolato-*P,O*)RuCl derivatives that were obtained from β-keto phosphines[14] reacted similarly. The cleavage of the ruthenium chlorine bond under the $MeOH/NH_4PF_6$ conditions, allowed the replacement of the arene ligand by two molecules of a β-keto phosphine. Such a process completed formally the coordination of three keto phosphine ligands on the ruthenium center and resulted in the formation of the [(η²-keto phosphine-*P,O*)₂(η²-phosphino enolato-*P,O*)Ru](PF₆) complexes, **6a–6c** (eq 9).

The three chelating ligands in **6a** and **6b** arose from the same β-keto phosphine, $Ph_2PCH(Me)C(=O)Bu^t$ and $Ph_2PCH(Me)C(=O)Ph$, respectively. These two almost homoleptic complexes were mainly characterized by IR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum of **6a** showed the presence of two isomers, but the peculiarly intricate $^{31}P\{^1H\}$ NMR spectrum of **6b** indicated a more complex unsolved mixture of several isomers. More interesting is the formation of the heteroleptic complex **6c** for which only one isomer involving a *mer* arrangement of the phosphorus atoms was observed in solution. The ^1H NMR spectrum of **6c** clearly indicated the three chelating ligands to be $Ph_2PCH(Me)C(Ph)=O$, $Ph_2PCH_2C(Bu^t)=O$, and $Ph_2PC(Me)=C(Ph)O^-$. Achieved by reacting (*p*-cymene)$[Ph_2PCH=C(Bu^t)O]RuCl$ with the phosphine $Ph_2PCH(Me)C(=O)Ph$, the formation of **6c** thus involved a proton transfer process from one entering



6a: R = Bu^t
6b: R = Ph

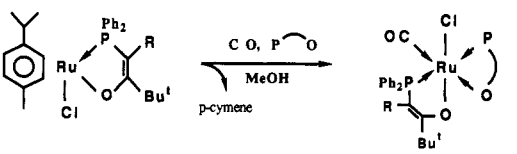
(9)



6c

keto phosphine to the initial phosphino enolato ligand $Ph_2PCH=C(Bu^t)O^-$.

The complexes (η⁶-arene)(η²-phosphino enolato-*P,O*)-RuCl were observed to react also with keto phosphines in methanol, while the mixture was stirred under a carbon monoxide atmosphere. The reaction which consists formally of the substitution of the arene ligand by one keto phosphine and one molecule of carbon monoxide, led to the neutral (η²-keto phosphine)(η²-phosphino enolato)-(CO)RuCl complexes, **7a–7e** (eq 10).



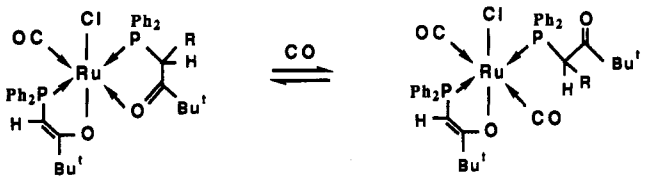
(10)

7a - 7e

7	R, P O ligand
7a:	H, $Ph_2PCH_2C(Bu^t)=O$
7b:	H, $Ph_2PCH(Me)C(Bu^t)=O$
7c:	H, $Ph_2PC(Me)_2C(Pr^i)=O$
7d:	H, $Ph_2PC(Me)_2CH_2C(Me)=O$
7e:	Me, $Ph_2PC(Me)_2C(Pr^i)=O$

Complex **7d** was obtained in a low yield but is an example of the involvement of a γ-keto phosphine. The $^{31}P\{^1H\}$ NMR spectra of complexes **7a–7e** exhibited a high $^2J \sim 300$ Hz coupling constant value accordant with a *trans* arrangement of the phosphorus atoms. The ^1H NMR spectroscopic data do not allow us to specify the relative arrangement of the other (all distinct) coordinating atoms. However, a *trans* arrangement of the C=O oxygen atom relative to carbon monoxide may be suggested with regard to the formation of derivatives 8 described below. Interestingly, complex **7b** was obtained by reacting either the phosphine $Ph_2PCH(Me)C(=O)Bu^t$ with (*p*-cymene)-$[Ph_2PCH=C(Bu^t)O]RuCl$ or the phosphine $Ph_2PCH_2C-(=O)Bu^t$ with (*p*-cymene)$[Ph_2PC(Me)=C(Bu^t)O]RuCl$. The preferential (and selective) formation of **7a** indicated that the basicity of the phosphino enolato ligand is significantly related to the presence of a methyl group at the PC_α position.

Owing to the hemilabile property of the keto phosphine chelate, the (η²-keto phosphine)(η²-phosphino enolato)-(CO)RuCl complexes **7a** and **7b**, added reversibly one molecule of carbon monoxide to afford the derivatives **8a** and **8b**, respectively (eq 11).



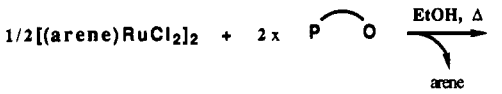
7a: R = H
7b: R = Me

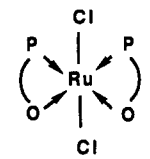
8a: R = H
8b: R = Me

(11)

The formation of complexes 8 preserved the *trans* relative arrangement of the phosphorus atoms, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. The *trans* relative arrangement of the carbon monoxide ligands was inferred from the observation of a single sharp C≡O absorption by IR spectroscopy.

Synthesis of (η^2-keto phosphine)$_2$RuCl$_2$ Complexes and Derivatives. The formation of the complexes **5–7** in methanol was achieved starting from (η^6-arene)(L)Ru(X)Cl (X = O or Cl) precursors and keto phosphines. The first step of the reactions likely consisted of the cleavage of the ruthenium chlorine bond and subsequent η^1-*P*-coordination of the keto phosphine. The reaction of the analogous (η^6-arene)(η^1-keto phosphine-*P*)RuCl$_2$ precursors with keto phosphines was then investigated and found to require a thermal activation. The precursors formed readily in ethanol and as a peculiarly convenient procedure, the mixture in ethanol of stoichiometric amounts of a keto phosphine and [(η^6-arene)RuCl$_2$]$_2$ derivative, was heated at reflux to obtain the air stable (η^2-keto phosphine-*P,O*)$_2$RuCl$_2$ complexes **9a–9d** (eq 12).





9a - 9e

9	P⌒O ligand
9a:	$Ph_2PCH_2C(Bu^t)$=O
9b:	$Ph_2PCH(Me)C(Bu^t)$=O
9c:	$Ph_2PC(Me)_2C(Pr^i)$=O
9d:	$Ph_2PCH(Me)CH_2C(Bu^t)$=O
9e:	$Ph_2PC(Me)_2CH_2C(Me)$=O

(12)

The complexes **9a–9d** were thus obtained in 66–79% yields from [(*p*-cymene)RuCl$_2$]$_2$ and the proper keto phosphine. Owing to the peculiarly low solubility of the intermediate (**2e**) where arene is *p*-cymene, complex **9e** was prepared using [(benzene)RuCl$_2$]$_2$ instead of [(*p*-cymene)RuCl$_2$]$_2$. Giving a supplementary indication of their weak chelating ability, the involvement of the γ-keto phosphines **1c** and **1d** resulted only in the formation of **2g** and **2i**, respectively. The synthesis of complexes **9** is straightforward, leading to the arene as the sole byproduct. The chelating mode of the keto phosphine in derivatives **9** appeared from the low frequency of the IR absorption corresponding to the keto function. Except for **9a** obtained as a mixture of isomers, the $^{31}P\{^1H\}$ NMR spectra of complexes **9** consisted of a single resonance of the two equivalent phosphorus nuclei. The ^1H NMR spectra indicated a high symmetry, requiring a *trans* relative arrangement of the chlorine atoms. Owing to virtual coupling, the resonances attributable to the PC$_\alpha$ and PC$_\beta$ protons were observed as filled-in doublets (noted d$_f$) and suggested low $^2J_{PP}$ coupling constant values[24] consistent with *cis* phosphorus nuclei in the case of ruthenium complexes.[23] To obtain an experimental measurement, the hybrid complex [η^2-Ph$_2$PC(Me)$_2$C(Pr^i)=O][η^2-Ph$_2$PC(Me)$_2$CH$_2$C(Me)=O]RuCl$_2$, **9f**, was prepared and a $^2J_{PP}$ = 38.2 Hz coupling constant value determined by $^{31}P\{^1H\}$ NMR spectroscopy.

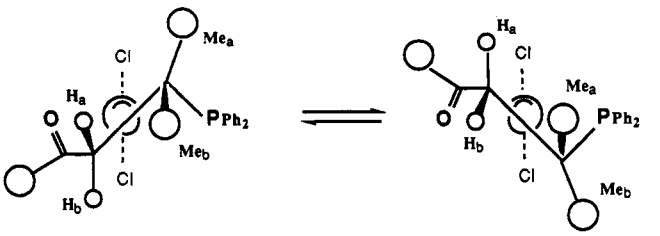


Figure 1. Representation of the fluxional behavior of the chelating γ-keto phosphine **1b** in complex **9e**.

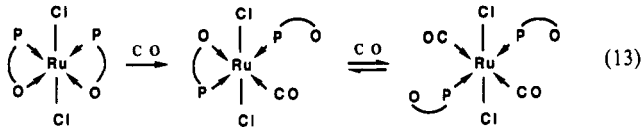
Of special interest is the ^1H NMR spectrum of [η^2-Ph$_2$PC(Me)$_2$CH$_2$C(Me)=O]$_2$RuCl$_2$, **9e**, that showed at 297 K, besides the broad phenyl and the single MeC(=O) resonances, the coalescence of the resonances expected for all the PCMe$_2$CH$_2$ protons. The spectrum is well resolved at 213 K, suggesting a fluxional behavior of the chelating γ-keto phosphine (**1b**) to occur at the ambient temperature. The fluxional process was interpreted as a "snakelike" torsion depicted in Figure 1 where the inequivalent H$_a$, H$_b$ protons and Me$_a$, Me$_b$ methyl groups exchange their magnetic environments, respectively.

Complex **9a** incorporating the β-keto phosphine Ph$_2$PCH$_2$C(=O)Bu^t displayed a mixture of two isomers in solution, both with *cis* phosphorus atoms but with *trans* or *cis* chlorine atoms. The ratio of the two isomers remained unchanged after attempts at separation by fractional crystallization, as monitored by NMR spectroscopy. Such an observation suggested the occurrence of a dynamic equilibrium in solution and noteworthy is the reaction of **9a** with KI which afforded solely the *trans* iodo derivative [η^2-Ph$_2$PCH$_2$C(Bu^t)=O]$_2$RuI$_2$, **9'a**. Both the $^{13}C\{^1H\}$ NMR spectra of **9'a** and **9c** showed the four phenyl groups to be equivalent and exhibit virtual five-line multiplets (noted m$_5$) and non-1:2:1 triplets consistent with a *cis* arrangement of the phosphorus.[25]

To compare the (η^2-keto phosphine)$_2$RuCl$_2$ complexes to known (η^2-*P,O*-functional phosphine)$_2$RuCl$_2$ complexes, the reaction with carbon monoxide was first investigated. A reaction occurred at ambient temperature while a solution of complex **9** in acetone or dichloromethane was stirred under a carbon monoxide atmosphere. The coordination of one molecule of carbon monoxide involves the cleavage of one O→Ru bond and resulted in the formation of the (keto phosphine)$_2$(CO)RuCl$_2$ derivatives **10a–10c** (eq 13).

According to a similar but reversible process, **10a** and **10c** added a second molecule of carbon monoxide to afford **11a** and **11b**, respectively. However, the β-keto phosphine Ph$_2$PCH(Me)C(=O)Bu^t is chelating enough to hinder the process in the case of **10b**. The $^{31}P\{^1H\}$ NMR spectra of complexes **10** exhibited high $^2J_{PP}$ ~ 350 Hz coupling constant values consistent with *trans* phosphorus nuclei. The formation of complexes **10** (and **11**) is closely similar to the reactions reported for both ether phosphine[2,26] and ester phosphine[27,28] (functional phosphine)$_2$RuCl$_2$ com-

(24) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1976**, *15*, 1128.
(25) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50.

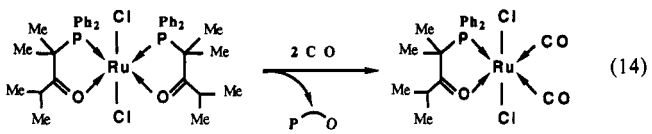


(9) (10) (11) (13)

P⌒O:

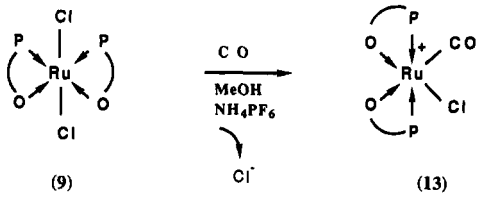
9a, $Ph_2PCH_2C(Bu^t)=O$	10a	11a
9b, $Ph_2PCH(Me)C(Bu^t)=O$	10b	
9d, $Ph_2PCH(Me)CH_2C(Bu^t)=O$	10c	11b

plexes and not surprising is the *cis* to *trans* rearrangement of the phosphorus atoms. Emphasizing the likeness, the ^1H NMR spectra of derivatives **10a–10c** reflected a fluxional process consistent with a fast exchange of the coordinating modes of the two keto phosphine ligands. Thus, the ^1H NMR spectrum of **10a** showed at room temperature the coalescence of the resonances attributable to the four PCH_2 protons and a single resonance attributable to the two *tert*-butyl groups. The spectrum was well resolved at −20 °C and disclosed two distinct keto phosphine ligands. The structure of the highly symmetrical derivatives **11a** and **11b** was inferred from the comparison of the spectroscopic data with that reported for ester phosphine and ether phosphine derivatives. More surprising is the reaction of **9c** that resulted in the loss of one keto phosphine ligand while the coordination of two molecules of carbon monoxide occurred (eq 14).



9c 12

The IR spectrum of the obtained complex **12** showed the two carbon monoxide ligands to be in a *cis* relative arrangement. The ^1H NMR spectrum indicated a symmetry requiring a *trans* relative arrangement of the chlorine atoms. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy by performing it in CD_2Cl_2. The spectrum of the resulting solution mainly consisted of two single resonances (δ 66.6 and 14.1 ppm) attributable to complex **12** and the free keto phosphine, respectively. Complex **12** is stable in the solid state but should be kept under a carbon monoxide atmosphere when dissolved in dichloromethane. The easy loss of one carbon monoxide ligand occurred under nitrogen, as indicated by both IR spectroscopy and elemental analysis of the resulting unsoluble yellow solid. The yellow solid was not studied further but a structure with halogen bridges may be suggested if compared to the reported formation of the dimeric complex $[(PMe_2Ph)_2(CO)RuCl_2]_2$.[29] The formation of **12** is likely the result of the inability of the PC_α permethylated keto phosphine $Ph_2PC(Me)_2C(=O)Pr^i$ to behave as a monodentate η^1-P ligand.[14] No tractable product was obtained starting from **9e** where the PC_α permethylated γ-keto phosphine $Ph_2PC(Me)_2CH_2C(=O)$-Me is involved, but both **9c** and **9e** reacted in methanol with carbon monoxide and NH_4PF_6 to afford the stable cationic complexes $[(\eta^2\text{-keto phosphine})_2(CO)RuCl](PF_6)$, **13a** and **13b**, respectively (eq 15).

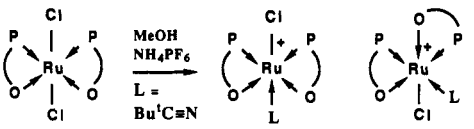


(9) (13)

P⌒O:

9c, $Ph_2PC(Me)_2C(Pr^i)=O$	13a
9e, $Ph_2PC(Me)_2CH_2(Me)=O$	13b

The $^{31}P\{^1H\}$ NMR spectra of **13a** and **13b** were consistent with two inequivalent *trans* phosphorus nuclei, and therefore a *cis* relative arrangement of the oxygen atoms is required. Thus, the removal of one chloride ligand under the $MeOH/NH_4PF_6$ conditions allowed the two chelating keto phosphines to be retained in **13a** and **13b**. The formation of complexes **13** consisted formally of a simple substitution of one chloride ligand, when the *cis* to *trans* rearrangement of the phosphorus atoms required the cleavage of one O→Ru bond.[2] Although such a cleavage may be assumed to occur temporarily, it is of interest to specify the structure of derivatives which arose from the simple substitution of the chloride by a neutral innocent ligand, in complexes **9**. The reaction of complexes **9** with nitriles and NH_4PF_6 in methanol was therefore investigated. The substitution of one chloride by a nitrile, such as $Bu^tC{\equiv}N$, resulted in the formation of the stable derivatives $[(\eta^2\text{-keto phosphine})_2(Bu^tC{\equiv}N)RuCl](PF_6)$, **14a–14d** (eq 16).



(9) (14)

P⌒O:

9a, $Ph_2PCH_2C(Bu^t)=O$	14a, (B)
9c, $Ph_2PC(Me)_2C(Pr^i)=O$	14b, (A) + (B)
9d, $Ph_2PCH(Me)CH_2C(Bu^t)=O$	14c, (B)
9e, $Ph_2PC(Me)_2CH_2(Me)=O$	14d, (A)

The ^1H and $^{31}P\{^1H\}$ NMR spectra of complexes **14** disclosed two isomeric structures A and B, both involving *cis* phosphorus atoms, as indicated by the observation of filled-in doublets (^1H NMR) in the case of the symmetrical structure A and low $^2J_{PP}$ values ($^{31}P\{^1H\}$ NMR) in the case of structure B. However, the coordinated atom (phosphorus or oxygen) located in a *trans* relative position to the nitrile in structure B, could not be specified by NMR spectroscopy. The derivative **14'c** incorporating MeCN (instead of Bu^tCN in **14c**) was similarly prepared. The comparison of the ^1H NMR spectra of **14c** and **14'c** allowed us to assign the Bu^tCN resonance of **14c**. Complex **14b** was obtained as a mixture of crystals of types A and B, which could be separated. Each so separated isomer was

(26) (a) Lindner, E.; Möckel, A.; Mayer, H. A.; Kübauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266. (b) Lindner, E.; Möckel, A.; Mayer, H. A.; Fawzi, R. *Chem. Ber.* **1992**, *125*, 1363. (c) Lindner, E.; Schober, U.; Fawzi, R.; Hilber, W.; Englert, U.; Wegner, P. *Chem. Ber.* **1987**, *120*, 1621.

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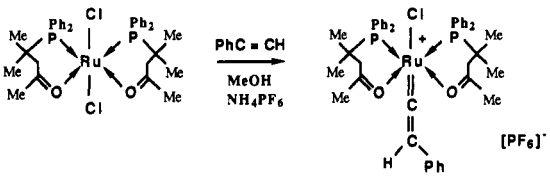
(28) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126.

(29) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 953.

found stable in solution by NMR spectroscopy, and no isomerization was detected after 1 day.

Starting from **9e**, the ease of the cleavage of one Ru–Cl bond in methanol allowed the coordination of phenylacetylene. The subsequent vinylidene rearrangement[30] resulted in the formation of the stable (vinylidene)ruthenium(II) derivative, **15** (eq 17).



9e 15 (17)

The $^{13}C\{^1H\}$ NMR spectrum of complex **15** exhibited a δ 313 ppm value, the low-field resonance expected for the Ru=C carbon nucleus. The ^1H NMR spectrum showed the two keto phosphine ligands to be equivalent. Some broadness of the $^{31}P\{^1H\}$ singlet resonance led us to record the spectrum at lower temperatures. A coalescence was observed at −20 °C, but the spectrum was well resolved at −60 °C and disclosed two distinct phosphorus nuclei. The related $^2J_{PP}$ = 29.0 Hz coupling constant value is evidence of their *cis* relative arrangement. The phosphorus atoms are likely diastereotopic at low temperature with respect to the vinylidene ligand, and a fast rotation around the Ru=C=C axis may account for the observation of a single resonance at ambient temperature.[31] The formation of neutral (vinylidene)ruthenium(II) derivatives from (ether phosphine)$_2$RuCl$_2$ or (ester phosphine)$_2$RuCl$_2$ complexes was recently reported.[28] A thermal or photochemical induced cleavage of one O→Ru bond allowed the coordination of phenylacetylene, and noteworthy is the subsequent *cis* to *trans* rearrangement of the phosphorus atoms.

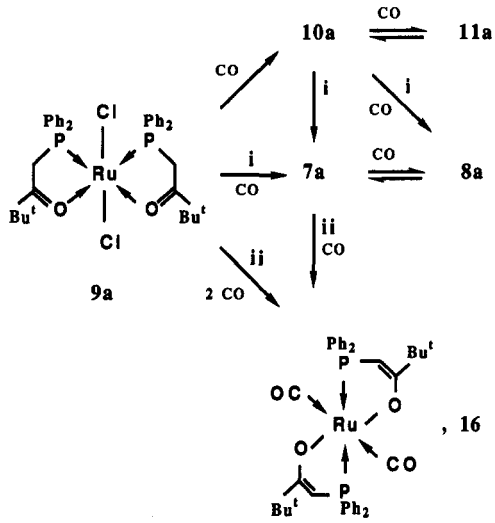
The formations of both complexes **14** and **15** emphasized the preservation of the *cis* arrangement of the phosphorus atoms. A *cis* relative arrangement of the C=O oxygen atoms is also retained but a *trans* to *cis* rearrangement of the positions which were occupied by the chlorine atoms was observed sometimes.

Synthesis of {(η^2-phosphino enolato-*P,O*)$_2$(L)$_2$Ru^{II} Complexes. One other interesting process consisted of the conversion of a β-keto phosphine ligand into a phosphino enolato one, according to the removal of a PC$_\alpha$ proton under basic conditions. In dichloromethane solution, the (η^2-keto phosphine)$_2$RuCl$_2$ complexes **9a** and **9b** reacted with carbon monoxide and K_2CO_3 to offer a more direct access to the phosphino enolato derivatives **7a** and **7b**, respectively. As described above, both **9a** and **9b** react with carbon monoxide to afford the corresponding complexes **10** which undergo the elimination of one molecule of hydrogen chloride in the presence of K_2CO_3. Starting from **9a** (or **7a**), the conversion of the two keto phosphine ligands into phosphine enolato chelates was achieved in methanol and afforded the highly symmetrical derivative **16**, as depicted in Scheme 1, where all the observed reactions are summarized.

The IR spectrum of **16** displayed a single sharp absorption consistent with *trans* carbon monoxide ligands, and the $^{31}P\{^1H\}$ NMR spectrum indicated the two phos-

(30) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
(31) Consiglio, G.; Morandini, F. *Inorg. Chim. Acta* **1987**, *127*, 79.

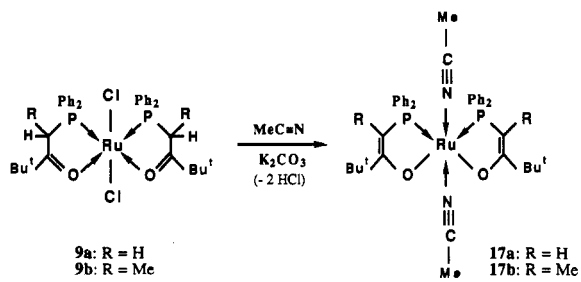
Scheme 1. Reactivity of 9a under a Carbon Monoxide Atmosphere[a]



[a] Key: (i) K_2CO_3 in CH_2Cl_2; (ii) K_2CO_3 in MeOH.

phorus atoms to be equivalent. The observation of a 1:2:1 virtual triplet attributable to the resonance of the two equivalent PCH protons is consistent with a *trans* relative position of the phosphorus atoms.[24] The $^{13}C\{^1H\}$ NMR spectrum of **16** exhibited only triplet resonances, as expected in the case of a high $^2J_{PP}$ value.[25] The deprotonation of the keto phosphine ligand leading to the phosphino enolato one likely required the chelating mode of the keto phosphine, as indicated by an experiment performed under a carbon monoxide pressure (100 bar) that afforded only a mixture of **11a** and **8a** (in a ~1:1 ratio) after a reaction time of 5 days, as monitored by NMR spectroscopy.

Complexes **9a** and **9b** were reacted also with K_2CO_3 in acetonitrile to obtain in high yields the novel bis(acetonitrile) derivatives **17a** and **17b**, respectively (eq 18).



9a: R = H
9b: R = Me

17a: R = H
17b: R = Me (18)

Noteworthy, the formation of **17a** and **17b** preserved the initial arrangement of the chelating ligands. The $^{31}P\{^1H\}$ NMR spectra of **17a** and **17b** consisted of a single resonance and indicated the phosphino enolato ligands to be equivalent. The ^1H NMR spectrum of **17b** exhibited a filled-in doublet attributable to the resonance of the six PCMe protons and also indicative of their virtual coupling with two *cis* phosphorus nuclei. A singlet attributable to the resonance of the two PCH protons indicated a $|^2J_{PH} + {}^4J_{PH}| \sim 0$ Hz value in the case of **17a**. Both ^1H (**17a** and **17b**) and $^{13}C\{^1H\}$ (**17a**) NMR spectra showed the four phenyl groups to be equivalent as evidence of the *trans* relative position of the nitrile ligands. Compared to the spectrum of **16**, the $^{13}C\{^1H\}$ NMR spectrum of **17a** exhibited the expected five-line multiplets consistent with *cis* phosphorus atoms, for both the C *ipso* and PCH carbon nuclei. Thus under mild basic conditions, the enolizable

complexes of type **9** undergo the nonreductive elimination of two molecules of hydrogen chloride, allowing the coordination of two molecules of acetonitrile.

Conclusions

Organic ketones provide convenient access to a large diversity of keto phosphines. The coordinating properties of β- and γ-keto phosphines are versatile and strongly related to their structure. The complexes (η^2-keto phosphine-*P,O*)$_2$RuCl$_2$ with *cis* phosphorus and *trans* chlorine atoms were obtained selectively in ethanol, from [(η^6-arene)RuCl$_2$]$_2$ precursors. The *cis* to *trans* rearrangement of the phosphorus atoms occurred subsequent to the cleavage of a C=O→Ru bond, and the *cis* arrangement is retained in processes where the hemilabile property of the keto phosphine chelates is not involved. The nonreductive elimination of hydrogen chloride from enolizable (β-keto phosphine)$_2$RuCl$_2$ derivatives occurred under mild basic conditions and resulted formally in the formation of coordinatively unsaturated (phosphino enolato)ruthenium(II) intermediates which added neutral ligands.

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