Intramolecular C−C Bond Formation from β-Keto Phosphine and Allenylidene Ligands in Related Ruthenium(II) Cyclopentadienyl and Indenyl Complexes. X-ray Crystal Structure of (S_{Ru},R_C/R_{Ru},S_C)-[Ru(η^5-C_9H_7)(PPh_3){η^2(*P*,*O*)-$Ph_2PCH(Me)C(Bu^t)$=O}][PF_6] and (S_{Ru},R_C/R_{Ru},S_C)-[Ru{η^2(*C*,*P*)-C(=C=CPh_2)CH[C(=O)Bu^t]PPh_2}(η^5-C_9H_7)(PPh_3)]

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The reaction of β-keto phosphines $Ph_2PCH(R')C(=O)R$ (**a**, R = Bu^t, R′ = H; **b**, R = Ph, R′ = H; **c**, R = Bu^t, R′ = Me) with [$RuCl(\eta^5$-$C_nH_m)(PPh_3)_2$] complexes (**1**, C_nH_m = cyclopentadienyl; **1′**, C_nH_m = indenyl) affords neutral [$RuCl(\eta^5$-$C_nH_m)(PPh_3)$]{η^1(*P*)-keto phosphine}] (**2a,b** and **2′a**). Cationic derivatives, [$Ru(\eta^5$-$C_nH_m)(PPh_3)$]{η^2(*P*,*O*)-keto phosphine}][PF_6] (**3a,b** and **3′a**−**c**), are obtained by the reactions of complexes **1** and **1′** with the keto phosphines in the presence of NH_4PF_6. Complex **3′c** is diastereoselectively obtained as the S_{Ru},R_C/R_{Ru},S_C enantiomeric pair, as shown by an X-ray crystal structure analysis. Owing to the hemilabile ability of the keto phosphine ligand, complexes **3a** and **3′a** easily react with 1,1-diphenyl-2-propyn-1-ol to yield the allenylidene complexes [Ru(=C=C=CPh_2)(η^5-C_nH_m)(PPh_3){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}][PF_6] (**5a** and **5′a**, respectively). Treatment of complexes **3a** and **3′a** with K_2CO_3 in methanol leads to the deprotonation of the coordinated keto phosphine to give the neutral phosphino enolate derivatives [$Ru(\eta^5$-$C_nH_m)(PPh_3)$]{η^2(*P*,*O*)-Ph_2PCH=C-(Bu^t)O}] (**6a** and **6′a,** respectively). In contrast, allenylidene complexes **5a** and **5′a** react with K_2CO_3 or KOH in methanol to afford the alkynyl complexes [Ru{C≡CC(OMe)Ph_2}(η^5-C_nH_m)(PPh_3){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}] (**7a** and **7′a**), which are formed through the nucleophilic addition of the methoxy group to the C_γ atom of the allenylidene chain. Similarly, the ethoxy alkynyl derivative **8a** is obtained by the reaction of **5a** with KOH in ethanol. Under mild basic conditions (K_2CO_3/THF) complexes **5a** and **5′a** are deprotonated, resulting in conversion into the neutral derivatives [Ru{η^2(*C*,*P*)-C(=C=CPh_2)CH[C(=O)Bu^t]PPh_2}-(η^5-C_nH_m)(PPh_3)] (**9a** and **9′a**, respectively) through the generation of a novel phosphametallacyclobutane ring and in accord with a diastereoselective process. The molecular structure of **9′a**, determined by an X-ray crystal structure analysis, discloses a S_{Ru},R_C/R_{Ru},S_C configuration and shows a nearly planar Ru−P(2)−C(2B)−C(1) ring bearing an almost linear η^1(C)-coordinated allenyl group (C(1)−C(2A)−(3A) = 169.6(8)°). The formation of the four-membered ring probably takes place in a putative intermediate arising from the deprotonation of the η^1(*P*)-keto phosphine ligand in **5a** and **5′a**. The subsequent intramolecular carbon−carbon bond formation between the allenylidene group and the nucleophilic η^1(*P*)-phosphino enolate ligands is geometrically constrained to occur at the electrophilic C_α site of the allenylidene ligand, and the ruthenium fragment efficiently directs the configuration of the new stereogenic carbon atom in the resulting metallacycle ring.

Introduction

Organometallic chemistry of (cyclopentadienyl)ruthenium(II) complexes has very recently provided a noteworthy series of novel results: (i) generation of carbene complexes from aldehyde acetals[1a] or allenylidene ligands,[1b] (ii) formation of C- and O-bonded enolates from a coordinated γ-keto phosphine,[2] (iii) reactivity of neutral vinylidene complexes,[3] (iv) synthesis of amino

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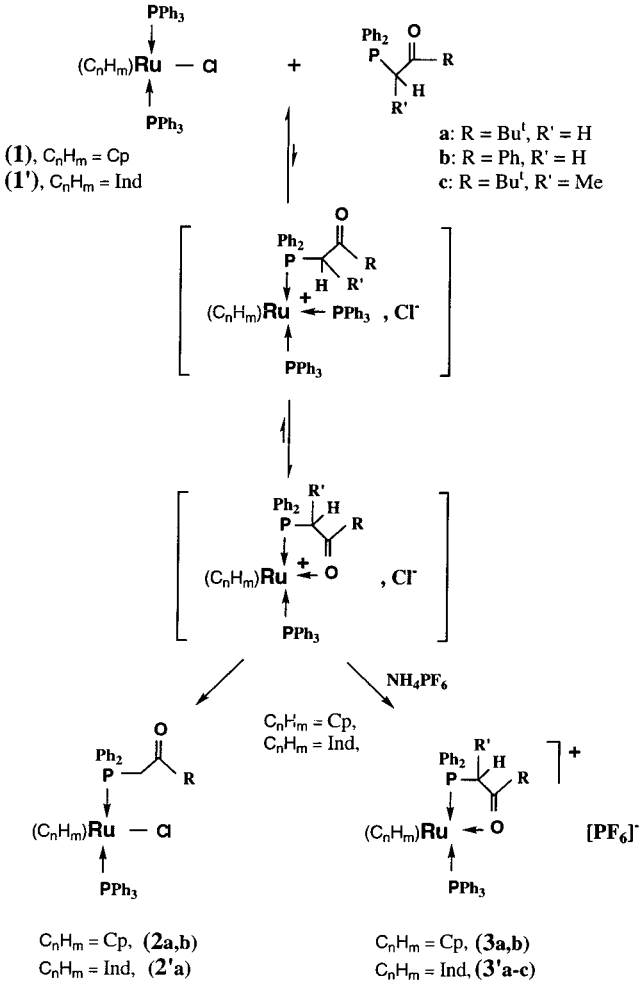
allenylidene complexes,[4] (v) cycloaromatization of a cationic vinylidene-ene-yne precursor,[5] and (vi) cyclopropanation of deprotonated vinylidene complexes.[6] Moreover, cyclopentadienyl and related ruthenium(II) complexes have revealed efficiency in several catalytic processes. The complexes $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ and $[RuCl(\eta^5\text{-}C_5H_5)(cod)]$ behave as catalyst precursors in several coupling reactions involving 1-alkynes,[7] whereas the parent complexes $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and $[RuCl(\eta^5\text{-}C_5Me_5)(L)H_3]$ are active in the redox isomerization of allyl and propargyl alcohols[8] and in the dimerization of terminal alkynes,[9] respectively. Such useful developments have generated renewed interest in extending the routes leading to (cyclopentadienyl)-ruthenium(II) and related derivatives.[10] We report herein (i) an efficient access to novel (cyclopentadienyl)- and (indenyl)ruthenium(II) complexes containing one β-keto phosphine ligand, (ii) the synthesis of allenylidene derivatives, which are easily obtained from the former complexes through the hemilabile ability of the coordinated β-keto phosphine ligand, and (iii) the intramolecular nucleophilic attack of the $\eta^1(P)$-coordinated phosphino enolate anion at the C_α atom of the allenylidene ligand, which leads to the formation of a phosphametallacyclobutane ring. Complexes containing the chiral β-keto phosphines $Ph_2PCH(Me)C(Bu^t)=O$ and the corresponding enolate derivative are obtained in a diastereoselective manner. The molecular structures of the complexes $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH(Me)C(Bu^t)=O\}][PF_6]$ and $[Ru\{\eta^2(C,P)\text{-}C(=C=CPh_2)CH[C(=O)Bu^t]PPh_2\}(\eta^5\text{-}C_9H_7)(PPh_3)]$ determined by X-ray diffraction reveal that they are obtained as the $S_{Ru},R_C/R_{Ru},S_C$ enantiomeric pair.

Results and Discussion

Reaction of β-Keto Phosphines with $[RuCl(\eta^5\text{-}C_nH_m)(PPh_3)_2]$ Complexes. The sparingly soluble precursor $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**1**) reacts with β-keto phosphines $Ph_2PCH_2C(=O)R$ (**a**, R = Bu^t; **b**, R = Ph) in methanol at reflux, to afford deep orange solutions which deposit orange crystals of the neutral derivatives $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)R\}]$ (**2a,b**) after standing at room temperature (Scheme 1). An analogous treatment in the presence of NH_4PF_6 immediately results in the formation of a yellow precipitate identified as the cationic derivatives $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH_2C(R)=O\}][PF_6]$ (**3a,b**), which were isolated in high yields (Scheme 1). The indenyl parent precursor $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1′**) showed a similar reactivity and yielded the analogous neutral and cationic complexes **2′a** and **3′a,b**, respectively (Scheme 1). The indenyl complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH(Me)C(Bu^t)=O\}][PF_6]$ (**3′c**) was similarly obtained by starting from **1′** and the PC_α-substituted keto phosphine $Ph_2PCH(Me)C(=O)Bu^t$ (**c**), but surprisingly, we failed to detect any reaction between **1** and keto phosphine **c**.

Scheme 1. Synthesis of $[RuCl(\eta^5\text{-}C_nH_m)(PPh_3)\{\eta^1(P)\text{-keto phosphine}\}]$ and $[Ru(\eta^5\text{-}C_nH_m)(PPh_3)\{\eta^2(P,O)\text{-keto phosphine}\}][PF_6]$ Complexes



All the complexes are air-stable in the solid state and have been characterized by IR and NMR spectroscopy and elemental analysis. The IR spectra (Table 1) of complexes **3a,b** and **3′a**−**c** show, besides the typical absorptions due to the presence of the PF_6^- anion, a strong ν(C=O) absorption in the range 1610−1552 cm^{-1} indicating the coordination of the oxygen atom from the keto phosphine ligand, whereas the IR spectra of complexes **2a,b** and **2′a** display the ν(C=O) absorption in the range 1702−1665 cm^{-1}, in accordance with an uncoordinated keto group.[11] The $^{31}P\{^1H\}$ NMR spectra (Table 1) exhibit two doublet resonances consistent with an AX spin system, as expected from two nonequivalent coordinating phosphorus atoms. Whereas the chemical shifts related to the two nuclei appear very close in the

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Table 1. IR and $^{31}P\{^1H\}$ NMR Data for the New Complexes

compd	IR[a] ν(C=O)	$^{31}P\{^1H\}$ NMR δ_P	$\delta_{P'}$	$^2J_{PP'}$
$[RuCl(C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}]$ **(2a)**	1697	44.2	39.7	42.1[c]
$[RuCl(C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Ph\}]$ **(2b)**	1665	43.9	43.2	42.1[d]
$[RuCl(C_9H_7)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}]$ **(2′a)**	1702	50.7	46.2	43.8[c]
$[Ru(C_5H_5)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH_2C(Bu^t)=O\}][PF_6]$ **(3a)**	1600	61.6	46.3	35.1[d]
$[Ru(C_5H_5)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH_2C(Ph)=O\}][PF_6]$ **(3b)**	1552	61.7	47.4	36.7[c]
$[Ru(C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH_2C(Bu^t)=O\}][PF_6]$ **(3′a)**	1610	72.6	46.4	31.7[d]
$[Ru(C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH_2C(Ph)=O\}][PF_6]$ **(3′b)**	1555	73.6	47.2	32.2[d]
$[Ru(C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH(Me)C(Bu^t)=O\}][PF_6]$ **(3′c)**	1587	95.5	42.7	30.5[d]
$[Ru(C_5H_5)(CO)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}][PF_6]$ **(4a)**	1704	45.2	35.1	27.2[c]
$[Ru(C{=}C{=}CPh_2)(C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}][PF_6]$ **(5a)**	1708	48.6	39.8	29.5[d]
$[Ru(C{=}C{=}CPh_2)(C_9H_7)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}][PF_6]$ **(5′a)**	1708	50.9	40.1	26.5[c]
$[Ru(C_5H_5)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH{=}C(Bu^t)O\}]$ **(6a)**	1491[b]	58.9	49.0	39.0[d]
$[Ru(C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH{=}C(Bu^t)O\}]$ **(6′a)**	1494[b]	73.8	46.9	34.3[c]
$[Ru\{C{\equiv}CC(OMe)Ph_2\}(C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}]$ **(7a)**	1699	54.4	47.5	34.1[c]
$[Ru\{C{\equiv}CC(OMe)Ph_2\}(C_9H_7)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}]$ **(7′a)**	1705	53.9	50.2	35.8[d]
$[Ru\{C{\equiv}CC(OEt)Ph_2\}(C_5H_5)(PPh_3)\{\eta^1(P)\text{-}Ph_2PCH_2C(=O)Bu^t\}]$ **(8a)**	1701	54.4	45.9	38.2[d]
$[Ru\{\eta^2(C,P)C(=C{=}CPh_2)CH[C(=O)Bu^t]PPh_2\}(C_5H_5)(PPh_3)]$ **(9a)**	1694	59.9	18.5	41.7[d]
$[Ru\{\eta^2(C,P)C(=C{=}CPh_2)CH[C(=O)Bu^t]PPh_2\}(C_9H_7)(PPh_3)]$ **(9′a)**	1677	55.7	13.1	31.0[d]

[a] ν in cm^{-1}. [b] ν(C=CO). [c] In $CDCl_3$. [d] In CD_2Cl_2.

case of complexes **2a,b** and **2′a** (δ 50.7−39.7 ppm), the ring formation in complexes **3a,b** and **3′a**−**c** results in a deshielding of the keto phosphine resonance (δ 95.5−61.6 ppm) but that attributable to the phosphorus nucleus from PPh_3 remains almost unaffected (δ 47.4−42.7 ppm). The ^1H and $^{13}C\{^1H\}$ NMR spectra are also in accordance with the proposed formulations. Along with the resonances attributable to the cyclopentadienyl and indenyl ligands, the ^1H NMR spectra of derivatives which contain the keto phosphine $Ph_2PCH_2C(=O)R$ (**a**, **b**) show the two PCH_2 protons to be diastereotopic, as expected from the presence of a chiral ruthenium center. Furthermore, the $^{13}C\{^1H\}$ NMR spectra provide evidence for the presence of two inequivalent Ph_2P phenyl groups.

The NMR data for complex **3′c**, wherein the keto phosphine **c** adds a second chiral P**C**(H)Me center, clearly indicates the presence of only one diastereomer. Further structural specification was inferred from the X-ray diffraction study.

Figure 1 shows the ORTEP drawing of the $S_{Ru}R_C$ diastereomer of **3′c**, and a listing of selected bond distances and angles is given in Table 2. The molecule has a pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is bonded to the indenyl group acting as an η^5 ligand, the phosphorus atom from PPh_3, and the oxygen and phosphorus atoms from the chelating keto phosphine ligand. The Ru−PPh_2 and Ru−PPh_3 bond lengths are similar to each other (2.239(2), 2.357(2) Å, respectively) and to those of **1** (2.337(1) and 2.335(1) Å).[12] The Ru−O bond length (2.129(4) Å) is normal relative to the simple σ-coordination of the keto function through the oxygen atom and is close to those (2.13(1) and 2.20(1) Å) in the typical cationic keto phosphine−ruthenium complex $[Ru(MeCN)_2\{\eta^2(P,O)\text{-}Ph_2PCH_2C(Ph)=O\}_2]^{2+}$.[13] The P−Ru−O angle in **3′c** (79.3(1)°) is similar to those in the bis-chelate complex (80.6(4) and 80.9(3)°), but the P−Ru−P value in **3′c** is significantly smaller (97.44(7)° *vs* 106.2(2)°), suggesting a lack of steric hindrance in

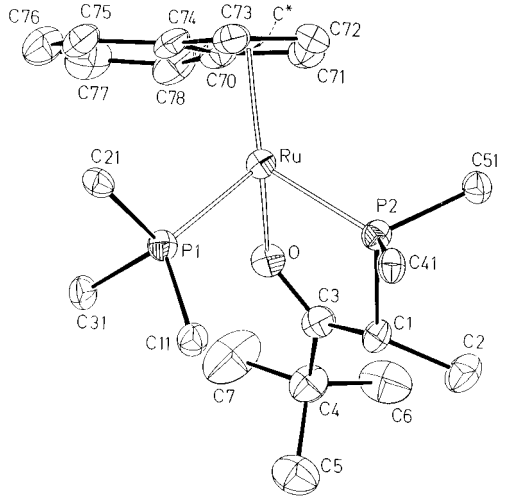

Figure 1. View of the molecular structure of $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\eta^2(P,O)\text{-}Ph_2PCH(Me)C(Bu^t)=O\}][PF_6]$ **(3′c**; only the enantiomer S_{Ru},R_C is shown). Priority order for the assignment of the absolute configurations: (a) for Ru, indenyl > PPh_3 > $CPPh_2$ > $(C=O)^tBu$; (b) for C(1), PPh_2 > $(C=O)^tBu$ > Me > H.

3′c. The value for the O−Ru−PPh_3 angle (89.9(1)°) is in accordance with an approximately octahedral environment around the metal center.

The reaction of keto phosphines **a**−**c** with complexes **1** and **1′**, which selectively results in the substitution of one triphenylphosphine ligand, occurs in refluxing methanol, and two chemical pathways may be considered: (i) a direct substitution of a triphenylphosphine ligand from complexes **1** and **1′** by the keto phosphine and (ii) a cleavage of the ruthenium−chloride bond in **1** and **1′** to generate initially a tris(phosphine) cationic intermediate. The first mechanism would lead directly to the neutral complexes **2** and **2′**. A subsequent cleavage of the ruthenium−chloride bond in **2** and **2′** allows the coordination of the keto oxygen atom from the functional ligand to achieve the formation of the cationic derivatives **3** and **3′**. The second mechanism is depicted in Scheme 1. The cleavage of the ruthenium−chloride bond in **1** and **1′** results in the $\eta^1(P)$ coordination (or alternatively $\eta^1(O)$ coordination) of the keto phosphine. Further removal of one triphenylphosphine

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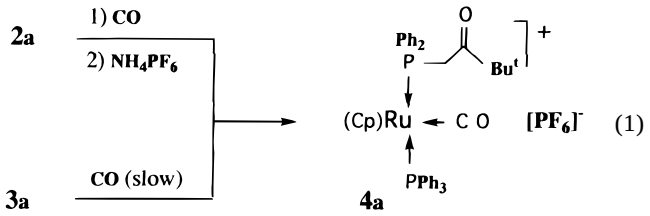
Table 2. Selected Bond Distances and Slip Parameter Δ[a] (Å) and Bond Angles and Dihedral Angles FA,[b] HA,[c] and CA[d] (deg) for [Ru(η^5-C_9H_7)(PPh_3){η^2-$Ph_2PCH(Me)C(Bu^t)$=O)}][PF_6] (3′c)

	Distances		
Ru−C*	1.892(6)	Ru−O	2.129(4)
Ru−P(1)	2.357(2)	C(3)−O	1.249(7)
Ru−P(2)	2.239(2)	C(3)−C(1)	1.500(9)
Ru−C(70)	2.315(7)	C(1) -P(2)	1.885(7)
Ru−C(71)	2.210(7)	C(70)−C(78)	1.43(1)
Ru−C(72)	2.165(7)	C(70)−C(74)	1.431(9)
Ru−C(73)	2.186(7)	C(70)−C(71)	1.43(1)
Ru−C(74)	2.351(6)	C(71)−C(72)	1.42(1)
P(1)−C(11)	1.834(7)	C(72)−C(73)	1.420(9)
P(1)−C(21)	1.824(7)	C(73)−C(74)	1.431(9)
P(1)−C(31)	1.828(7)	C(74)−C(75)	1.43(1)
P(2)−C(41)	1.808(7)	C(75)−C(76)	1.36(1)
P(2)−C(51)	1.832(7)	C(76)−C(77)	1.38(1)
Δ	0.135(7)	C(77)−C(78)	1.36(1)
	Angles		
C*−Ru−O	125.9(2)	C(78)−C(70)−C(74)	119.0(7)
C*−Ru−P(1)	123.8(2)	C(78)−C(70)−C(71)	131.3(8)
C*−Ru−P(2)	127.6(2)	C(74)−C(70)−C(71)	109.7(7)
O−Ru−P(1)	89.9(1)	C(72)−C(71)−C(70)	105.8(7)
O−Ru−P(2)	79.3(1)	C(71)−C(72)−C(73)	110.1(7)
P(1)−Ru−P(2)	97.44(7)	C(72)−C(73)−C(74)	107.2(7)
Ru−O−C(3)	126.6(4)	C(75)−C(74)−C(70)	120.6(7)
O−C(3)−C(1)	119.1(6)	C(75)−C(74)−C(73)	132.6(7)
C(3)−C(1)−P(2)	107.5(5)	C(73)−C(74)−C(70)	106.8(7)
C(1)−P(2)−Ru	104.7(2)	C(76)−C(75)−C(74)	117.1(8)
C(3)−C(1)−C(2)	118.7(6)	C(77)−C(78)−C(70)	117.8(8)
C(75)−C(76)−C(77)	122.6(8)	C(78)−C(77)−C(76)	122.7(8)
FA	173.3(5)	HA	174.0(5)
CA	164.4(3)		

[a] Δ = *d*[Ru−C(74), C(70)] − *d*[Ru−C(71), C(73)]. [b] FA (fold angle) is the angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78). [c] HA (hinge angle) is the angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71), C(74), C(70), C(73). [d] CA (conformational angle) is the angle between normals to least-squares planes defined by C**, C*, Ru and C*, Ru, P(2). C* is the centroid of C(70), C(71), C(72), C(73), C(74). C** is the centroid of C(70), C(74), C(75), C(76), C(77), C(78).

ligand allows the formation of the cationic derivatives **3** and **3′** to be completed. In this mechanism, the formation of the neutral complexes **2** and **2′** only arises through the competition between the chloride anion and the keto oxygen atom, in coordinating at the ruthenium center. The first mechanism appears unlikely when the conditions of the reaction are compared to the conditions where the straightforward substitution of triphenylphosphine in **1** by functional ether phosphines is achieved.[14] In this case, significantly more drastic conditions (prolonged reflux in toluene) are required and unavoidably result in mixtures consisting of mono- and disubstituted derivatives.[14] Of further interest, the chloride ligand in **1** is already known to be substituted in methanol by phosphorus ligands to afford cationic tris(phosphine) complexes, despite the fact that formation of the species [Ru(η^5-C_5H_5)(PPh_3)$_3$]$^+$ is believed to be sterically hindered.[15] Ketophosphines **a**−**c** are roughly comparable to triphenylphosphine, and the expulsion of one phosphorus ligand from the analogous species [Ru(η^5-C_nH_m)(PPh_3)$_2${η^1(*P*)-Ph_2PCHRC(=O)R′}]$^+$ may be expected. In such a key intermediate, the chelate effect is expected to favor the expulsion of a triphenylphosphine ligand relative to the η^1(*P*)-coordinated keto phosphine. Although only a minor steric effect might be expected in **3′c** as compared to **3′a** as a consequence of the introduction of a methyl group in the keto phosphine, the diastereoselectivity inherent in the formation of **3′c** becomes easier to understand if it is assumed that the intermediate complex [Ru(η^5-C_9H_7)(PPh_3)$_2${η^1(*P*)-$Ph_2PCH(Me)C$(=O)Bu^t}]$^+$ is formed. Steric repulsion between the PCMe methyl group and the triphenylphosphine ligands could probably induce diastereoselectively the substitution of one triphenylphosphine ligand by the keto oxygen atom of the keto phosphine and would be responsible for the S_{Ru},R_C/R_{Ru},S_C configuration. The lack of reactivity of the cyclopentadienyl complex **1** toward the keto phosphine **c**, in contrast to the case for indenyl complex **1′**, which gives **3′c**, although surprising since the cyclopentadienyl ring is smaller than the indenyl ligand, may be kinetically assisted according to the well-known indenyl effect.[16]

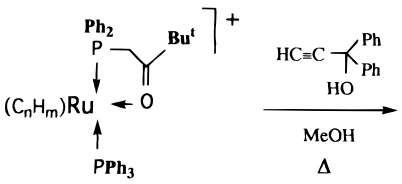
Hemilabile Reactivity of the Keto Phosphine Ligand in Complexes 3a and 3′a. Revealing the hemilabile character of the chelating η^2(*P*,*O*)-keto phosphine functional ligand, complex **3a** reacts with carbon monoxide (1 atm, room temperature) to yield the cationic derivative [Ru(η^5-C_5H_5)(CO)(PPh_3){η^1(*P*)-Ph_2PCH_2C(=O)Bu^t}][PF_6] (**4a**; eq 1).



(1)

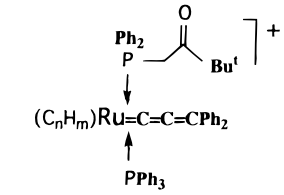
However, the formation of **4a** is peculiarly slow, since it remains uncompleted after more than 1 week, and the synthesis of **4a** under these mild conditions is more conveniently achieved by reacting **2a** with carbon monoxide. A subsequent exchange reaction of the chloride anion with NH_4PF_6 allows the process to be completed (eq 1). The IR spectrum of **4a** shows a strong ν(C≡O) absorption at 1977 cm^{-1}, providing evidence for the presence of coordinated carbon monoxide, together with a ν(C=O) absorption at 1704 cm^{-1} indicating the η^1(*P*)-coordinating mode of the keto phosphine. Hemilabile functional phosphine ligands have also proved useful in the access to complexes involving a cumulenic type ligand.[17] Analogously, complexes **3a** and **3′a** react with 1,1-diphenyl-2-propyn-1-ol in methanol at reflux, to efficiently yield the highly colored allenylidene derivatives [Ru(=C=C=CPh_2)(η^5-C_nH_m)(PPh_3){η^1(*P*)-Ph_2-PCH_2C(=O)Bu^t}][PF_6] (**5a** and **5′a**, respectively; eq 2). Significant IR and NMR spectroscopic characterization arises from the comparison of **5a** and **5′a** with the analogous complexes [Ru(=C=C=CPh_2)](η^5-C_5H_5)(PMe_3)$_2$]-

(14) De Klerk-Engels, B.; Groen, J. H.; Vrieze, K.; Möckel, A.; Lindner, E.; Goubitz, K. *Inorg. Chim. Acta* **1992**, *195*, 237.
(15) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.
(16) Gamasa, M. P.; Gimeno, J.; Gonzalez-Bernardo, C.; Martin-Vaca, B. M.; Monti, D.; Bassetti, M. *Organometallics* **1996**, *15*, 302 and references cited therein.
(17) (a) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49. (b) Braun, T.; Steinert, P.; Werner, H. *J. Organomet. Chem.* **1995**, *488*, 169. (c) Lindner, E.; Geprägs, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106. (d) Lindner, E.; Haustein, M.; Fawzi, R.; Steimann, M.; Wegner, P. *Organometallics* **1994**, *13*, 5021. (e) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126.



3a, 3′a

Counter anion: $[PF_6]^-$



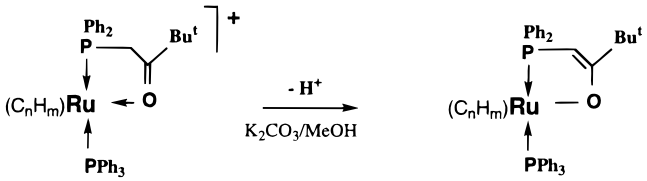
(2)

C_nH_m = Cp: **5a**
C_nH_m = Ind: **5′a**

$[PF_6]$ and $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$.[18,19] The main features are relevant to the presence of the allenylidene ligand: the IR spectra of **5a** and **5′a** show the typical very strong ν(C=C=C) absorption at *ca.* 1935 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectra disclose resonances at δ 294.4 (C_α), 207.0 (C_β), and 161.2 ppm (C_γ) for **5a** and at δ 290.2 (C_α), 205.7 (C_β), and 156.5 ppm (C_γ) for **5′a**, attributable to the carbon nuclei forming the cumulenic chain $Ru=C_\alpha=C_\beta=C_\gamma$.

In contrast, indicating an irreversible and strong coordination of carbon monoxide, complex **4a** was found to be unreactive toward the alkynol.

Reactivity of Complexes 3a and 3′a Related to the Ketone-to-Enol Tautomerism in the Keto Phosphine Ligand. Under mild basic conditions (K_2CO_3 in methanol), the 4e-donor keto phosphine ligand in complexes **3a** and **3′a** is deprotonated into the 3e-donor phosphino enolato ligand in the neutral derivatives [Ru(η^5-C_nH_m)(PPh_3){η^2(*P*,*O*)-Ph_2PCH=C(Bu^t)O}] (**6a** and **6′a**, respectively; eq 3).



3a, 3′a

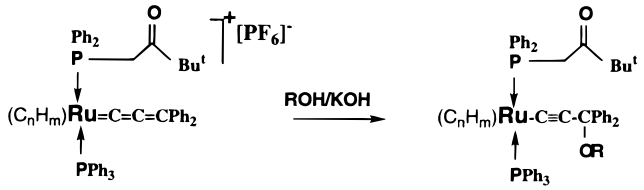
C_nH_m = Cp: **6a**

C_nH_m = Ind: **6′a**

(3)

The IR spectra of **6a** and **6′a** show the expected absorption attributable to the functionalized C=C(O) bond at 1491 and 1494 cm^{-1}, respectively. Both ^1H and ^{13}C NMR spectra indicate the presence of a PCH= bonding pattern. Of special interest, the broadness of the $^{13}C\{^1H\}$ NMR resonances attributable to the phenyl groups of the triphenylphosphine ligand in **6′a** likely arises from a sterically hindered rotation around the Ru−P bond on the NMR time scale.

Under similar reaction conditions (K_2CO_3 or KOH, in methanol) the allenylidene complexes **5a** and **5′a** afforded the methoxide acetylide derivatives **7a** and **7′a**, and the analogous ethoxide derivative **8a** was obtained by using ethanol instead of methanol (eq 4). Thus,



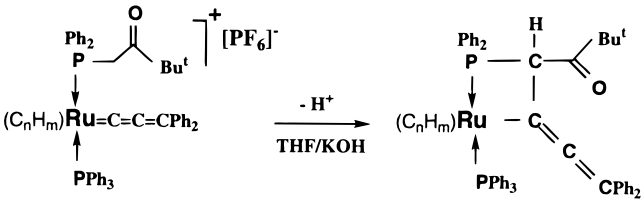
5a, 5′a

C_nH_m = Cp R = Me: **7a**
C_nH_m = Ind R = Me: **7′a**
C_nH_m = Cp R = Et: **8a**

(4)

under mild conditions, **5a** and **5′a** undergo the formal addition of an alkoxide anion to the electrophilic C_γ-carbon atom of the allenylidene ligand according to the reversible process that has been previously reported in the case of the parent complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$.[19] Furthermore, indicating a similar reversibility, the recrystallization of the methoxide derivative **7a** from dichloromethane and ethanol afforded a mixture of crystals of **8a** and **7a**. As expected, the IR spectra of the acetylide derivatives show a sharp absorption at *ca.* 2065 cm^{-1} that is attributable to the ν(C≡C) bond, and the ^1H NMR spectra clearly confirm the presence of the alkoxide group.

Phosphino enolato ligands have shown to react with coordinated 1-alkynes and thus to disturb the 1-alkyne-to-vinylidene rearrangement in generating phosphametallacyclic compounds.[20] Therefore, derivatives **5a** and **5′a** offered an unprecedented opportunity to examine the generation of a phosphino enolate anion within the coordination sphere of a metal center bearing a cumulenic-type ligand. In order to preclude the reaction consisting of alkoxide addition leading to acetylide complexes, the deprotonation of **5a** and **5′a** was attempted in THF. Under such conditions, the neutral derivatives **9a** and **9′a** were formed and subsequently isolated as yellow and red crystals, respectively (eq 5).



5a, 5′a

C_nH_m = Cp: **9a**
C_nH_m = Ind: **9′a**

(5)

The ^{13}C and ^1H NMR spectra of **9a** and **9′a** are structurally informative and unambiguously indicated a P**C**H sp^3 carbon atom resulting from the removal of one hydrogen atom in the keto phosphine ligand. Another interesting feature of the ^{13}C NMR spectrum

(18) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(19) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27.

(20) (a) Crochet, P.; Demerseman, B. *Organometallics* **1995**, *14*, 2173. (b) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048. (c) The molecular model of the corresponding diastereomer R_{Ru},R_C shows a significant steric hindrance of the phenyl and *tert*-butyl groups.

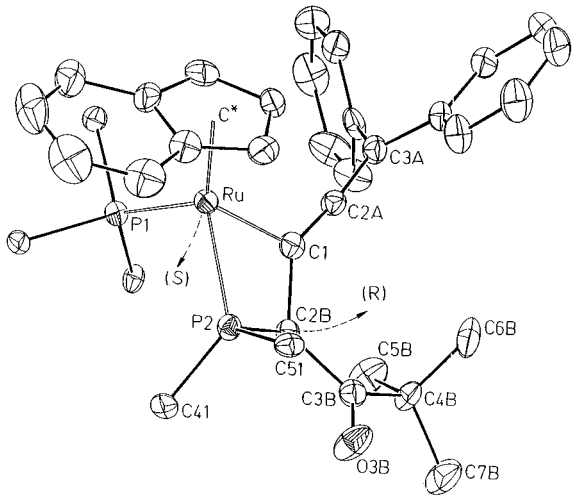


Figure 2. View of the molecular structure of [Ru{η^2(*C*,*P*)-C(=C=CPh$_2$)[CH(=O)Bu^t]PPh$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)] (**9′a**; only the enantiomer S_{Ru},R_C is shown). Priority order for the assignment of the absolute configurations: (a) for Ru, indenyl > PPh$_3$ > CPPh$_2$ > C=C=CPh$_2$; (b) for C(2B), PPh$_2$ > C(Ru)=C=C=CPh$_2$ > (C=O)^{t}Bu > H.

is the observation of resonances attributable to a σ-bonded allenyl ligand,[21] indicating that a carbon−carbon bond is formed from the coupling of the nucleophilic enolate carbon atom and the electrophilic C$_\alpha$-carbon atom of the allenylidene ligand to give a four-membered phosphametallacycle. The ^{31}P{^{1}H} NMR spectra (Table 1) consists of two doublet resonances, in accordance with the nonequivalence of the phosphorus nuclei. The location of one resonance at δ *ca.* 18 also suggests that the formation of a small ring has occurred.[22] The structure of **9a** and **9′a** involves two stereogenic centers, but only one diastereoisomer was detected by NMR spectroscopy. The X-ray structure determination of the indenyl complex **9′a** discloses the expected phosphametallacyclobutane ring and a S_{Ru},R_C/R_{Ru},S_C configuration.

The crystal structure consists of a molecule of **9′a** and one CH_2Cl_2 molecule of crystallization. An ORTEP drawing of the molecule displaying the R_C,S_{Ru} configuration is shown in Figure 2. Selected bond distances and angles are listed in Table 3. The molecular structure shows the typical pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is bonded to the indenyl group acting as an η^5 ligand, the phosphorus atom from PPh$_3$, and the phosphorus and one carbon atom from the phosphametallacyclobutane ring.

Of special interest, the orientation of the allenyl chain is almost *trans* relative to the benzo ring of the indenyl ligand. Such an orientation is in contrast with the *cis* orientation exhibited in allenylidene (indenyl) ruthenium(II) complexes but is similar to the orientation adopted in vinylidene (indenyl) ruthenium(II) complexes.[19a] As in **3′c**, the Ru−PPh$_2$ bond (2.266(2) Å) is slightly shorter than the Ru−PPh$_3$ bond (2.299(2) Å). The main features concerning the four-membered ring in **9′a** are the following: (a) the bonding distances Ru−C(1), P(2)−C(2B), and C(1)−C(2B) (2.121(8), 1.839(8),1.523(9) Å, respectively) are consistent with a simple σ-bond. The ring is almost planar, as inferred from the torsion angle Ru−C(1)−C(2B)−P(2) = 15.1(5)°. Accordingly, the sum of the four angles Ru−C(1)−C(2B), C(1)−C(2B)−P(2), Ru−P(2)−C(2B), and C(1)−Ru−P(2) in the ring (357°) is close to 360°. None of the four bond distances are exceptional,[21c] and the flatness of the phosphametallacyclobutane ring likely results from steric demand. The C=C bond distances (C(1)−C(2A) = 1.283(9), C(2A)−C(3A) = 1.33(1) Å) in the almost linear allenyl skeleton (C(1)−C(2A)−C(3A) = 169.6(8)°) compares fairly well with the values ($C_\alpha-C_\beta$ = 1.307(8), $C_\beta-C_\gamma$ = 1.302(9) Å; $C_\alpha-C_\beta-C_\gamma$ = 175.4(6)°) reported for the osmium complex [OsCl$_2$(CH=C=CPh$_2$)(NO)(PPr$^i_3$)$_2$], which is one of the rare examples[21a] of mononuclear complexes wherein an allenyl group simply acts as a σ-bonded ligand.[21b]

Table 3. Selected Bond Distances and Slip Parameter Δ[a] (Å) and Bond Angles and Dihedral Angles FA,[b] HA,[c] and CA[d] (deg) for [Ru{η^2(*C*,*P*)-C(=C=CPh$_2$)CH[C(=O)Bu^t]PPh$_2$}-(η^5-C$_9$H$_7$)(PPh$_3$)] (9′a)

Distances			
Ru−C*	1.935(8)	C(3B)−O	1.193(8)
Ru−P(1)	2.299(2)	C(1)−C(2A)	1.283(9)
Ru−C(1)	2.121(8)	C(2A)−C(3A)	1.33(1)
Ru−P(2)	2.266(2)	C(1)−C(2B)	1.523(9)
Ru−C(70)	2.338(7)	C(2B)−P(2)	1.839(8)
Ru−C(71)	2.222(8)	C(70)−C(78)	1.41(1)
Ru−C(72)	2.208(7)	C(70)−C(74)	1.41(1)
Ru−C(73)	2.246(7)	C(70)−C(71)	1.43(1)
Ru−C(74)	2.381(8)	C(71)−C(72)	1.41(1)
P(1)−C(11)	1.841(8)	C(72)−C(73)	1.40(1)
P(1)−C(21)	1.848(8)	C(73)−C(74)	1.44(1)
P(1)−C(31)	1.833(7)	C(74)−C(75)	1.42(1)
P(2)−C(41)	1.814(7)	C(75)−C(76)	1.35(1)
P(2)−C(51)	1.829(8)	C(76)−C(77)	1.39(1)
Δ	0.125(8)	C(77)−C(78)	1.34(1)

Angles			
C*−Ru−C(1)	125.2(3)	C(78)−C(70)−C(74)	119(1)
C*−Ru−P(1)	125.1(3)	C(78)−C(70)−C(71)	132.7(9)
C*−Ru−P(2)	129.2(2)	C(74)−C(70)−C(71)	107.8(8)
C(1)−Ru−P(1)	92.1(2)	C(72)−C(71)−C(70)	107.6(7)
C(1)−Ru−P(2)	68.8(2)	C(71)−C(72)−C(73)	109.1(8)
P(1)−Ru−P(2)	99.47(8)	C(72)−C(73)−C(74)	107.4(8)
Ru−C(1)−C(2A)	123.4(6)	C(75)−C(74)−C(70)	120(1)
Ru−C(1)−C(2B)	104.2(5)	C(75)−C(74)−C(73)	132(1)
C(1)−C(2A)−C(3A)	169.6(8)	C(73)−C(74)−C(70)	107.9(7)
C(1)−C(2B)−P(2)	94.7(5)	C(76)−C(75)−C(74)	119(1)
Ru−P(2)−C(2B)	89.3(2)	C(77)−C(78)−C(70)	118(1)
C(75)−C(76)−C(77)	120.(1)	C(78)−C(77)−C(76)	123(1)
FA	172.6(6)	HA	175.4(6)
CA	170.1(4)		

[a] Δ = *d*[Ru−C(74), C(70)] − *d*[Ru−C(71), C(73)]. [b] FA (fold angle) is the angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78). [c] HA (hinge angle) is the angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71), C(74), C(70), C(73). [d] CA (conformational angle) is the angle between normals to least-squares planes defined by C**, C*, Ru and C*, Ru, C(1). C* is the centroid of C(70), C(71), C(72), C(73), C(74). C** is the centroid of C(70), C(74), C(75), C(76), C(77), C(78).

(21) (a) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612. (b) As far as we are aware, this (σ-allenyl)ruthenium complex is the first to be crystallographically characterized. We have recently prepared a further example, namely: [Ru{η^3(*C*,*P*,*P*)-C(=C=CPh$_2$)(Ph$_2$PCHPPh$_2$)}(η^5-C$_9$H$_7$)]: Cadierno,V.; Gamasa, M. P.; Gimeno, J.; Lopez-Gonzalez, M. C.; Borge, J.; García-Granda, S. *Organometallics*, in press. The complex [Ru(η^5-C$_5$H$_5$)(CO)$_2$(CH=C=CH$_2$)] has been also described: Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185. (c) A similar four-membered phosphametallacycle has been described and crystallographically characterized: Bruce, M. I.; Cifuentes, M. P.; Humphrey, M. G.; Poczman, E.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *338*, 237.

(22) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

The C(3B)−O distance (1.193(8) Å) is typical of a C=O bond. The keto group is located far away from the metal center, as required by the $S_{Ru},R_C/R_{Ru},S_C$ configuration of **9′a**. We have recently reported the synthesis of the complexes [Ru(η^6-arene){η^3(*C,O,P*)-C(=CH_2)C(Me)-(COBu^t)PPh_2}][PF_6], which display a comparable four-membered phosphametallacyclobutane ring but differ from **9′a** in the supplementary coordination of the keto oxygen atom to the ruthenium center.[20a,b] This comparison seems to indicate that the diastereoselectivity of the formation of **9′a** is sterically required,[20c] since the alternative configuration would force the keto group to lie very close to the metal center that is coordinatively saturated.

Conclusions

The reaction of the complexes [RuCl(η^5-C_nH_m)(PPh_3)$_2$] with β-keto phosphines provides a convenient, high-yield access to (cyclopentadienyl)- and (indenyl)ruthenium(II) derivatives containing η^1(*P*)- and η^2(*P,O*)-β-keto phosphine ligands. The formation of only one diastereomer for complex **3′c**, containing two stereogenic centers at the ruthenium atom and at the chiral keto phosphine $Ph_2PCH(Me)C(=O)Bu^t$, emphasizes a noteworthy stereoselectivity. The complexes containing η^2-(*P,O*) keto phosphines proved to be excellent precursors for the straightforward synthesis of allenylidene derivatives through their reaction with 1,1-diphenyl-2-propyn-1-ol, due to the hemilabile ability of the keto phosphine ligand. The opening of the chelate η^2(*P,O*) ring is easily achieved, allowing the coordination of the alkynol and the subsequent favorable tautomerization to the allenylidene group. The deprotonation of the methylene group of the η^1(*P*)- $Ph_2PCH_2C(=O)R$ keto phosphines in allenylidene complexes **5a** and **5′a** generates a transient phosphino enolate ligand, which is subsequently added regioselectively to the electrophilic C_α-carbon atom of the allenylidene chain. This intramolecular coupling reaction results in the diastereoselective formation of complexes **9a** and **9′a**, which contain an unusual phosphametallacyclobutane ring. The formation of only one diastereomer for both **3′c** and **9′a** emphasizes a noteworthy stereoselectivity, likely promoted by the steric properties of the metal fragments.

Experimental Section

General Comments. The reactions were performed according to Schlenk type techniques under an inert atmosphere of argon or nitrogen, but only the handling of β-keto phosphines requires a rigorous exclusion of oxygen. Solvents were distilled under an inert atmosphere after drying according to conventional methods. Infrared spectra were recorded as Nujol mulls. NMR spectra (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{31}P, 121.50 MHz; absolute values of coupling constants in Hz) were recorded at 297 K and referenced internally to the solvent peak. The following abbreviations are used: s, singlet; d, doublet; t, triplet; t_a, apparent triplet; q, quadruplet; m, unresolved multiplet. The starting complexes [RuCl(η^5-C_5H_5)-(PPh_3)$_2$] (**1**)[23] and [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1′**)[24] and keto phosphines $Ph_2PCH(R')C(=O)R$ (**a**−**c**)[11,25] were prepared according to the literature.

[RuCl(C_5H_5)(PPh_3){(η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}] (2a). A mixture consisting of a 4.00 g (5.51 mmol) sample of **1**, 1.75 g (6.15 mmol) of $Ph_2PCH_2C(=O)Bu^t$, and methanol (100 mL) was heated at reflux for 1 h. The hot solution was filtered, and the orange filtrate was kept at room temperature to afford orange crystals of **2a**. Yield: 3.26 g, 79%. ^{1}H NMR ($CDCl_3$; δ): 7.94−7.19 (m, 25 H, Ph), 4.34 (dd, 1 H, $^2J_{HH}$ = 16.7, $^2J_{PH}$ = 2.2, PCH_2, H_a), 4.14 (s, 5 H, C_5H_5), 1.45 (dd, 1 H, $^2J_{PH}$ = 9.6, PCH_2, H_b), 0.57 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR (CD_2Cl_2; δ): 210.3 (d, $^2J_{PC}$ = 10.8, CO), 139.7 (dd, $^1J_{PC}$ = 38.6, $^3J_{PC}$ = 4.5, PhP, ipso), 138.3 (d, $^1J_{PC}$ = 39.5, Ph_3P, ipso), 137.9 (dd, $^1J_{PC}$ = 44.9, $^3J_{PC}$ = 2.2, PhP, ipso), 134.7 (d, $^3J_{PC}$ = 10.8, Ph_3P, meta), 134.1 (d, $^3J_{PC}$ = 10.8, PhP, meta), 132.3 (d, $^3J_{PC}$ = 9.0, PhP, meta), 129.6 (s, Ph_3P, para), 129.5 (d, $^4J_{PC}$ = 1.8, PhP, para), 129.2 (s, PhP, para), 128.2 (d, $^2J_{PC}$ = 9.0, PhP, ortho), 128.0 (d, $^2J_{PC}$ = 9.9, Ph_3P, ortho), 127.6 (d, $^2J_{PC}$ = 9.9, PhP, ortho), 81.3 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 1.8, C_5H_5), 45.7 (s, *C*Me$_3$), 29.0 (d, $^1J_{PC}$ = 14.4, PCH_2), 25.9 (s, C*Me*$_3$). Anal. Calcd for $C_{41}H_{41}ClOP_2Ru$: C, 65.81; H, 5.52; Cl, 4.74; P, 8.28. Found: C, 65.57; H, 5.28; Cl, 4.82; P, 8.06.

[RuCl(C_5H_5)(PPh_3){(η^1(*P*)-$Ph_2PCH_2C(=O)Ph$}] (2b). Dark orange crystals of **2b** were similarly obtained in 76% yield by starting from **1** and $Ph_2PCH_2C(=O)Ph$. ^{1}H NMR (CD_2Cl_2; δ): 7.70−6.94 (m, 30 H, Ph), 4.84 (dd, 1 H, $^2J_{HH}$ = 14.5, $^2J_{PH}$ = 7.1, PCH_2, H_a), 4.17 (s, 5 H, C_5H_5), 1.81 (dd, 1 H, $^2J_{PH}$ = 8.1, PCH_2, H_b). Anal. Calcd for $C_{43}H_{37}ClOP_2Ru$: C, 67.23; H, 4.85; Cl, 4.61; P, 8.06. Found: C, 66.74; H, 4.88; Cl, 4.40; P, 8.27.

[RuCl(C_9H_7)(PPh_3){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}] (2′a). Thin orange needles of **2′a** were obtained in 35% yield by starting from **1′** and $Ph_2PCH_2C(=O)Bu^t$. ^{1}H NMR ($CDCl_3$; δ): 7.87−6.29 [m, 29 H, Ph and C_9H_7 (4 H)], 4.83 (m, 1 H, C_9H_7), 4.77 (m, 1 H, C_9H_7), 4.50 (dd, 1 H, $^2J_{HH}$ = 17.2, $^2J_{PH}$ = 3.3, PCH_2, H_a), 3.07 (s, broad, 1 H, C_9H_7), 1.49 (dd, 1 H, $^2J_{PH}$ = 10.0, PCH_2, H_b), 0.60 (s, 9 H, Bu^t). Anal. Calcd for $C_{45}H_{43}ClOP_2Ru$: C, 67.70; H, 5.43. Found: C, 68.10; H, 5.36.

[Ru(C_5H_5)(PPh_3){η^2(*P,O*)-$Ph_2PCH_2C(Bu^t)$=O}][PF_6]·-CH_2Cl_2 (3a). As a typical procedure, a mixture consisting of a 10.0 g (13.8 mmol) sample of **1**, 4.00 g (14.1 mmol) of Ph_2-$PCH_2C(=O)Bu^t$, 2.50 g (15.3 mmol) of NH_4PF_6, and methanol (100 mL) was heated at reflux for 3 h. The resulting slurry was evaporated to leave a residue that was stirred with diethyl ether (70 mL). The yellow precipitate was collected by filtration, washed with diethyl ether, and then extracted with dichloromethane (45 mL). The solution was filtered and the filtrate covered with methanol (20 mL) and then diethyl ether (170 mL) to afford orange crystals of **3a**. Yield: 10.2 g, 79%. ^{1}H NMR (CD_2Cl_2, δ): 7.50−6.83 (m, 25 H, Ph), 4.50 (s, 5 H, C_5H_5), 3.80 (dd, 1 H, $^2J_{HH}$ = 18.9, $^2J_{PH}$ = 10.9, PCH_2, H_a), 2.14 (dd, 1 H, $^2J_{PH}$ = 7.9, PCH_2, H_b), 1.07 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 233.2 (d, $^2J_{PC}$ = 6.6, CO), 141.8 (dd, $^1J_{PC}$ = 43.9, $^3J_{PC}$ = 2.8, PhP, ipso), 134.7 (d, $^1J_{PC}$ = 42.7, Ph_3P, ipso), 134.3 (d, $^3J_{PC}$ = 12.9, PhP, meta), 134.0 (d, $^3J_{PC}$ = 10.9, Ph_3P, meta), 132.4 (d, $^4J_{PC}$ = 2.2, PhP, para), 131.1 (d, $^4J_{PC}$ = 1.8, Ph_3P, para), 130.8 (d, $^4J_{PC}$ = 2.0, PhP, para), 129.8 (d, $^3J_{PC}$ = 11.2, PhP, meta), 129.5 (d, $^2J_{PC}$ = 10.9, PhP, ortho), 129.3 (d, $^2J_{PC}$ = 10.9, PhP, ortho), 129.1 (d, $^3J_{PC}$ = 2.7, part of dd, PhP, ipso, the other part is overlapped), 128.9 (d, $^2J_{PC}$ = 9.7, Ph_3P, ortho), 80.5 (s, C_5H_5), 46.6 (d, $^3J_{PC}$ = 2.4, *C*Me$_3$), 45.6 (d, $^1J_{PC}$ = 25.8, PCH_2), 27.0 (s, C*Me*$_3$). ^{13}C NMR (CD_2Cl_2; δ (selected values)): 45.6 (ddd, $^1J_{HC}$ = 135 and 125, $^1J_{PC}$ = 25.8, PCH_2). Anal. Calcd for $C_{41}H_{41}F_6OP_3Ru{\cdot}CH_2Cl_2$: C, 53.51; H, 4.60; Cl, 7.52; P, 9.86. Found: C, 53.42; H, 4.76; Cl, 6.70; P, 9.58. The low chlorine value is likely attributable to easy loss of some dichloromethane.

[Ru(C_5H_5)(PPh_3){η^2(*P,O*)-$Ph_2PCH_2C(Ph)$=O}][PF_6] (3b). Red crystals of **3b** were obtained in 86% yield by starting from

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1 and $Ph_2PCH_2C(=O)Ph$. ^1H NMR ($CDCl_3$, δ): 7.85−6.79 (m, 30 H, Ph), 4.52 (s, 5 H, C_5H_5), 4.06 (dd, 1 H, $^2J_{HH} = 19.3$, $^2J_{PH} = 11.2$, PCH_2, H_a), 2.18 (dd, 1 H, $^2J_{PH} = 7.5$, PCH_2, H_b). Anal. Calcd for $C_{43}H_{37}F_6OP_3Ru$: C, 58.84; H, 4.25; P, 10.59. Found: C, 59.25; H, 4.32; P, 10.52.

[Ru(C_9H_7)(PPh$_3$){η^2(*P,O*)-$Ph_2PCH_2C(Bu^t)$=O}][PF_6] (3′a). Orange crystals of **3′a** were obtained in 75% yield by starting from **1′** and $Ph_2PCH_2C(=O)Bu^t$. ^1H NMR (CD_2Cl_2; δ): 7.53−6.59 [m, 29 H, Ph and C_9H_7 (4 H)], 4.86−4.33 (m, 3 H, C_9H_7), 3.74 (dd, 1 H, $^2J_{HH} = 18.9$, $^2J_{PH} = 11.3$, PCH_2, H_a), 2.21 (dd, 1 H, $^2J_{PH} = 8.5$, PCH_2, H_b), 1.08 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 232.1 (d, $^2J_{PC} = 4.5$, CO), 139.2 (dd, $^1J_{PC} = 46.7$, $^3J_{PC} = 2.7$, PhP, ipso), 133.8 (d, $^3J_{PC} = 10.8$, Ph_3P, meta), 133.6 (d, $^3J_{PC} = 11.7$, PhP, meta), 133.2 (d, $^1J_{PC} = 41.3$, Ph_3P, ipso), 132.3 (d, $^4J_{PC} = 2.7$, PhP, para), 130.9 (d, $^4J_{PC} = 2.7$, PhP, para), 130.8 (d, $^4J_{PC} = 2.7$, Ph_3P, para), 130.3 (s, CH, C_9H_7), 130.1 (d, $^3J_{PC} = 9.9$, PhP, meta), 129.5 (d, $^2J_{PC} = 10.8$, PhP, ortho), 129.4 (d, $^2J_{PC} = 10.8$, PhP, ortho), 129.4 (dd, $^1J_{PC} = 52.1$, $^3J_{PC} = 2.7$, PhP, ipso), 129.4 (s, CH, C_9H_7), 128.8 (d, $^2J_{PC} = 8.9$, Ph_3P, ortho), 124.8 (s, CH, C_9H_7), 123.4 (s, CH, C_9H_7), 110.7 (d, $^2J_{PC} = 3.5$, C_9H_7), 108.0 (d, $^2J_{PC} = 4.4$, C_9H_7), 87.8 (s, CH, C_9H_7), 65.3 (d, $^2J_{PC} = 8.4$, CH, C_9H_7), 61.8 (s, CH, C_9H_7), 46.6 (d, $^3J_{PC} = 2.8$, *C*Me$_3$), 45.7 (d, $^1J_{PC} = 27.5$, PCH_2), 27.1 (s, C*Me*$_3$). Anal. Calcd for $C_{45}H_{43}F_6OP_3Ru$: C, 59.53; H, 4.78. Found: C, 59.30; H, 4.61.

[Ru(C_9H_7)(PPh$_3$){η^2(*P,O*)-Ph_2PCH_2C(Ph)=O}][PF_6] (3′b). Red crystals of **3′b** were obtained in 75% yield by starting from **1′** and $Ph_2PCH_2C(=O)Ph$. ^1H NMR (CD_2Cl_2; δ): 7.77−6.72 [m, 34 H, Ph and C_9H_7 (4 H)], 4.89 (s, broad, 1 H, C_9H_7), 4.64 (s, broad, 1 H, C_9H_7), 4.52 (m, 1 H, C_9H_7), 4.04 (dd, 1 H, $^2J_{HH} = 18.9$, $^2J_{PH} = 11.7$, PCH_2, H_a), 1.99 (dd, 1 H, $^2J_{PH} = 7.9$, PCH_2, H_b). Anal. Calcd for $C_{47}H_{39}F_6OP_3Ru$: C, 60.84; H, 4.24; P, 10.02. Found: C, 60.88; H, 4.27; P, 10.02.

[Ru(C_9H_7)(PPh$_3$){η^2(*P,O*)-Ph_2PCH(Me)$C(Bu^t)$=O}][PF_6] (3′c). After a mixture consisting of **1′**, $Ph_2PCH(Me)C(=O)Bu^t$, and NH_4PF_6 in methanol was heated at reflux for 15 h, subsequent work allowed orange crystals of **3′c** to be obtained in 74% yield. ^1H NMR (CD_2Cl_2, δ): 7.81−6.31 [m, 29 H, Ph and C_9H_7 (4 H)], 5.13−3.55 (m, 3 H, C_9H_7), 2.93 (dq, 1 H, $^2J_{PH} = 11.5$, $^3J_{HH} = 7.3$, PCH), 1.29 (dd, 3 H, $^3J_{PH} = 11.2$, PCMe), 1.12 (s, 9 H, Bu^t). Anal. Calcd for $C_{46}H_{45}F_6OP_3Ru$: C, 59.93; H, 4.92; P, 10.08. Found: C, 59.77; H, 4.92; P, 9.94.

[Ru(CO)(C_5H_5)(PPh$_3$){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}][PF_6] (4a). From 3a. A 0.50 g (0.53 mmol) sample of **3a** was dissolved in a mixture of dichloromethane (15 mL) and methanol (15 mL). The solution was stirred for 2 weeks under a carbon monoxide atmosphere and then evaporated to dryness. The remaining solid was recrystallized from dichloromethane (10 mL) and diethyl ether (110 mL) to afford yellow crystals of **4a**. Yield: 0.37 g, 79%.

From 2a. A 2.50 g (3.34 mmol) sample of **2a** was dissolved in dichloromethane (20 mL), and methanol (80 mL) was then added. The resulting slurry was stirred for 1 week under a carbon monoxide atmosphere to obtain a clear yellow solution. NH_4PF_6 (0.60 g, 3.68 mmol) was then added, and the mixture was stirred overnight. Subsequent work as above afforded **4a**. Yield: 2.61 g, 88%. IR: ν(C≡O), 1977 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.70−6.93 (m, 25 H, Ph), 4.99 (s, 5 H, C_5H_5), 3.02 (dd, 1 H, $^2J_{HH} = 16.9$, $^2J_{PH} = 2.6$, PCH_2, H_a), 2.28 (dd, 1 H, $^2J_{PH} = 10.9$, PCH_2, H_b), 0.61 (s, 9 H, Bu^t). Anal. Calcd for $C_{42}H_{41}F_6O_2P_3Ru$: C, 56.95; H, 4.67. Found: C, 56.59; H, 4.55.

[Ru(=C=C=CPh_2)(C_5H_5)(PPh$_3$){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}][PF_6] (5a). A mixture consisting of a 2.00 g (2.12 mmol) sample of **3a**, 0.85 g (4.08 mmol, an excess) of 1,1-diphenyl-2-propyn-1-ol, and methanol (70 mL) was heated at reflux for 6 h. The resulting violet solution was evaporated, and the residue was washed with diethyl ether. The solid was dissolved in dichloromethane, and this solution was covered with diethyl ether to afford highly colored dark green crystals of **5a**. Yield: 1.83 g, 82%. IR: ν(Ru=C=C=C), 1938 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.75−6.93 (m, 35 H, Ph), 5.07 (s, 5 H, C_5H_5), 3.40 (dd, 1 H, $^2J_{HH} = 17.3$, $^2J_{PH} = 2.1$, PCH_2, H_a), 2.03 (dd, 1 H, $^2J_{PH} = 10.9$, PCH_2, H_b), 0.31 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 294.4 (ta, $^2J_{PC} \approx {}^2J_{P'C} \approx 18.0$, C_α), 207.5 (d, $^2J_{PC} = 10.5$, CO), 207.0 (s, C_β), 161.2 (s, C_γ), 144.2 (s, *Ph*$_2$C, ipso), 135.7 (d, $^1J_{PC} = 52.1$, PhP, ipso), 135.2 (d, $^1J_{PC} = 49.4$, Ph_3P, ipso), 134.1 (d, $^3J_{PC} = 10.8$, Ph_3P, meta), 133.0 (d, $^1J_{PC} = 48.5$, PhP, ipso), 133.0 (d, $^3J_{PC} = 10.8$, PhP, meta), 132.7 (s, *Ph*$_2$C, para), 132.6 (d, $^3J_{PC} = 9.9$, PhP, meta), 131.7 (d, $^4J_{PC} = 2.7$, PhP, para), 131.5 (d, $^4J_{PC} = 1.8$, Ph_3P, para), 131.2 (d, $^4J_{PC} = 2.7$, PhP, para), 130.8 (s, *Ph*$_2$C, meta), 129.9 (s, *Ph*$_2$C, ortho), 129.2 (d, $^2J_{PC} = 9.8$, PhP, ortho), 128.9 (d, $^2J_{PC} = 10.8$, Ph_3P, ortho), 128.5 (d, $^2J_{PC} = 11.7$, PhP, ortho), 93.7 (s, C_5H_5), 45.2 (s, C*Me*$_3$), 35.1 (d, $^1J_{PC} = 27.8$, PCH_2), 25.5 (s, C*Me*$_3$). Anal. Calcd for $C_{56}H_{51}F_6OP_3Ru$: C, 64.18; H, 4.91; P, 8.87. Found: C, 63.95; H, 4.86; P, 8.72.

[Ru(=C=C=CPh_2)(C_9H_7)(PPh$_3$){η^1(*P*)-$Ph_2PCH_2C(=O)Bu^t$}][PF_6] (5′a). With **3′a** as the starting material, the same procedure afforded dark violet crystals of **5′a** in 75% yield. IR: ν(Ru=C=C=C), 1932 cm^{-1}. ^1H NMR ($CDCl_3$; δ): 7.66−6.75 [m, 39 H, Ph and C_9H_7 (4 H)], 5.69−4.66 (m, 3 H, C_9H_7), 3.25 (dd, 1 H, $^2J_{HH} = 17.4$, $^2J_{PH} = 2.0$, PCH_2, H_a), 1.96 (dd, 1 H, $^2J_{PH} = 10.8$, PCH_2, H_b), 0.23 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ): 290.2 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx 17.9$, C_α), 207.4 (d, $^2J_{PC} = 10.3$, CO), 205.7 (s, C_β), 156.5 (s, C_γ), 140.3−86.0 (m, 7 Ph and C_9H_7), 45.4 (s, *C*Me$_3$), 35.8 (d, $^1J_{PC} = 30.2$, PCH_2), 25.8 (s, C*Me*$_3$). Anal. Calcd for $C_{60}H_{53}F_6OP_3Ru$: C, 65.63; H, 4.87; P, 8.46. Found: C, 65.83; H, 4.85; P, 8.04.

[Ru(C_5H_5)(PPh$_3$){η^2(*P,O*)-$Ph_2PCHC(Bu^t)$=O}] (6a). A mixture consisting of **3a** (or **2a**), an excess of K_2CO_3, and methanol was stirred overnight to afford a yellow slurry. The precipitate was collected by filtration then washed with water and methanol to afford **6a** in nearly quantitative yield. Despite the fact that **6a** is poorly soluble in common solvents, yellow crystals may be obtained by adding diethyl ether to a saturated solution in dichloromethane. ^1H NMR (CD_2Cl_2, δ): 7.48−6.97 (m, 25 H, Ph), 4.64 (dd, 1 H, $^2J_{PH} = 1.8$, $^4J_{PH} = 0.5$, PCH), 3.93 (s, 5 H, C_5H_5), 0.92 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 199.9 (d, $^2J_{PC} = 18.3$, =CO), 147.6 (dd, $^1J_{PC} = 42.7$, $^3J_{PC} = 2.4$, PhP, ipso), 138.4 (d, $^1J_{PC} = 37.8$, Ph_3P, ipso), 138.1 (dd, $^1J_{PC} = 47.6$, $^3J_{PC} = 5.5$, PhP, ipso), 134.3 (d, $^3J_{PC} = 11.6$, Ph_3P, meta), 132.9 (d, $^3J_{PC} = 11.0$, PhP, meta), 130.8 (d, $^3J_{PC} = 10.4$, PhP, meta), 128.9 (d, $^4J_{PC} = 1.8$, Ph_3P, para), 128.3 (d, $^4J_{PC} = 1.8$, PhP, para), 127.8 (d, $^2J_{PC} = 9.2$, PhP, ortho), 127.5 (d, $^2J_{PC} = 9.2$, Ph_3P, and overlapped, PhP, ortho), 79.0 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx 2.3$, C_5H_5), 75.2 (d, $^1J_{PC} = 58.0$, PCH=), 38.6 (d, $^3J_{PC} = 11.0$, *C*Me$_3$), 29.6 (s, C*Me*$_3$); a PhP-para resonance was not located. Anal. Calcd for $C_{41}H_{40}OP_2Ru$: C, 69.18; H, 5.66; P, 8.70. Found: C, 68.97; H, 5.69; P, 8.64.

[Ru(C_9H_7)(PPh$_3$){η^2(*P,O*)-$Ph_2PCHC(Bu^t)$=O}] (6′a). A mixture consisting of a 1.80 g (1.98 mmol) sample of **3′a**, 0.28 g (2.03 mmol) of K_2CO_3, and methanol (40 mL) was stirred overnight. The resulting mixture was evaporated, and the remaining solid was extracted with tepid toluene (30 mL). The solution was filtered and the filtrate covered with hexane (110 mL) to afford dark orange crystals of **6′a**. Yield: 1.16 g, 77%. ^1H NMR ($CDCl_3$, δ): 7.45−6.36 [m, 29 H, Ph and C_9H_7 (4 H)], 4.49 (d, 1 H, $^2J_{PH} = 2.9$, PCH), 4.23 (m, 1 H, C_9H_7), 4.14 (m, 1 H, C_9H_7), 3.36 (m, 1 H, C_9H_7), 0.93 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 199.5 (d, $^2J_{PC} = 15.3$, =CO), 145.7 (dd, $^1J_{PC} = 45.8$, $^3J_{PC} = 2.7$, PhP, ipso), 135.1 (dd, $^1J_{PC} = 53.0$, $^3J_{PC} = 5.4$, PhP, ipso), 134.2 (broad resonance, Ph_3P, ipso and meta), 132.5 (d, $^3J_{PC} = 9.9$, PhP, meta), 131.6 (d, $^3J_{PC} = 9.9$, PhP, meta), 128.8 (s, broad, Ph_3P, para), 128.5 (d, $^4J_{PC} = 2.7$, PhP, para), 128.1 (d, $^4J_{PC} = 2.7$, PhP, para), 127.8 (d, $^2J_{PC} = 9.9$, PhP, ortho), 127.7 (d, $^2J_{PC} = 9.9$, PhP, ortho), 127.4 (d, broad, $^2J_{PC} = 9.0$, Ph_3P, ortho), 126.9 (s, CH, C_9H_7), 125.5 (s, CH, C_9H_7), 124.8 (s, CH, C_9H_7), 122.5 (s, CH, C_9H_7), 112.1 (d, $^2J_{PC} = 4.5$, C_9H_7), 105.0 (d, $^2J_{PC} = 7.2$, C_9H_7), 86.4 (s, CH, C_9H_7), 75.5 (d, $^1J_{PC} = 60.1$, PCH=), 64.5 (s, CH, C_9H_7), 63.9 (d, $^2J_{PC} = 13.5$, CH, C_9H_7), 38.4 (d, $^3J_{PC} = 11.7$, *C*Me$_3$), 29.6 (s, C*Me*$_3$). ^{13}C NMR (CD_2Cl_2; δ (selected values)): 75.5 (dd, $^1J_{HC} = 161$, $^1J_{PC} = 60$, PCH=). Anal. Calcd for $C_{45}H_{42}OP_2Ru$: C, 70.95; H, 5.56; P, 8.13. Found: C, 71.08; H, 5.57; P, 8.20.

[Ru{C≡CC(OMe)Ph$_2$}(C$_5$H$_5$)(PPh$_3$){η^1(*P*)-Ph$_2$PCH$_2$C(=O)Bu^t}] (7a). A mixture consisting of a 0.93 g (0.89 mmol) sample of **5a**, 0.30 g (2.17 mmol, an excess) of K_2CO_3, and methanol (35 mL) was stirred overnight. The resulting slurry was evaporated to dryness, and the residue was extracted with dichloromethane (25 mL). The solution was filtered, and methanol (30 mL) was added to the filtrate. The mixture was slowly concentrated under reduced pressure to afford yellow crystals of **7a**. Yield: 0.65 g, 78%. IR: ν(C≡C), 2061 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.00−7.02 (m, 35 H, Ph), 4.41 (s, 5 H, C_5H_5), 4.21 (dd, 1 H, $^2J_{HH}$ = 16.8, $^2J_{PH}$ = 2.3, PCH_2, H_a), 3.39 (s, 3 H, OMe), 1.32 (dd, 1 H, $^2J_{PH}$ = 10.3, PCH_2, H_b), 0.51 (s, 9 H, Bu^t). Anal. Calcd for $C_{57}H_{54}O_2P_2Ru$: C, 73.29; H, 5.83; P, 6.63. Found: C, 73.49; H, 5.75; Cl, P, 6.67. Attempts to enhance the procedure by performing the recrystallization from dichloromethane and ethanol afforded a mixture of crystals of **8a** and **7a** (∼3/1 by ^{1}H NMR).

[Ru{C≡CC(OMe)Ph$_2$}(C$_9$H$_7$)(PPh$_3$){(η^1(*P*)-Ph$_2$PCH$_2$C(=O)Bu^t}] (7′a). A mixture consisting of a 0.50 g (0.46 mmol) sample of **5′a**, 0.05 g (0.5 mmol) of KOH, and methanol (30 mL) was stirred for 2 days. The resulting orange precipitate was collected by filtration and then washed with methanol. Yield: 0.38 g, 85%. IR: ν(C≡C), 2066 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.90−6.19 [m, 39 H, Ph and C_9H_7 (4 H)], 5.07 (m, 1 H, C_9H_7), 4.79 (s, broad, 1 H, C_9H_7), 4.43 (dd, 1 H, $^2J_{HH}$ = 17.8, $^2J_{PH}$ = 3.0, PCH_2, H_a), 3.91 (s, broad, 1 H, C_9H_7), 3.40 (s, 3 H, OMe), 1.57 (dd, 1 H, $^2J_{PH}$ = 9.6, PCH_2, H_b), 0.53 (s, 9 H, Bu^t). Anal. Calcd for $C_{61}H_{56}O_2P_2Ru$: C, 75.68; H, 5.83; P, 6.40. Found: C, 75.90; H, 5.92; P, 6.25.

[Ru{C≡CC(OEt)Ph$_2$}(C$_5$H$_5$)(PPh$_3$){η^1(*P*)-Ph$_2$PCH$_2$C(=O)Bu^t}] (8a). The reaction of **5a** in ethanol with KOH at room temperature or with K_2CO_3 at reflux (1 h) afforded a yellow precipitate of **8a** in a nearly quantitative yield. Recrystallization from dichloromethane and ethanol yielded yellow crystals. IR: ν(C≡C), 2065 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.90−7.02 (m, 35 H, Ph), 4.38 (s, 5 H, C_5H_5), 4.19 (dd, 1 H, $^2J_{HH}$ = 17.0, $^2J_{PH}$ = 2.2, PCH_2, H_a), 3.86 and 3.31 (2 dq, 2 H, $^2J_{HH}$ = 8.8, $^3J_{HH}$ = 7.1, C*H*$_2$Me), 1.37 (dd, 1 H, $^2J_{PH}$ = 10.0, PCH_2, H_b), 1.16 (t$_a$, 3 H, $^3J_{HH}$ = 7.1, CH_2*Me*), 0.47 (s, 9 H, Bu^t). Anal. Calcd for $C_{58}H_{56}O_2P_2Ru$: C, 73.47; H, 5.96; P, 6.53. Found: C, 73.56; H, 5.75; P, 6.36.

[Ru{η^2(*C,P*)-C(=C=CPh$_2$)CH[C(=O)Bu^t}PPh$_2$}(C$_5$H$_5$)(PPh$_3$)] (9a). A mixture consisting of a 0.77 g (0.73 mmol) sample of **5a**, 0.40 g (2.89 mmol) of K_2CO_3, and THF (60 mL) was stirred at room temperature for 3 days. The solvent was evaporated under vacuum, and the remaining solid was extracted with diethyl ether (50 mL). The solution was filtered and the filtrate evaporated to leave a yellow powder that was washed with hexane (35 mL). This crude product (yield 0.52 g, 79%) was recrystallized from toluene/hexane to obtain yellow crystals. Yield: 0.33 g, 50%. IR: ν(C=C=C), 1887 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.59−7.11 (m, 35 H, Ph), 4.28 (d, 1 H, $^2J_{PH}$ = 9.7, PCH), 4.13 (s, 5 H, C_5H_5), 0.63 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 209.3 (d, $^2J_{PC}$ = 9.0, CO), 196.3 (dd, $^3J_{PC}$ = 17.9 and 2.7, C$_\beta$), 141.6 (dd, $^5J_{PC}$ = 4.5 and 1.8, *Ph*C$_\gamma$, ipso), 140.6 (dd, $^5J_{PC}$ = 3.6 and 1.8, *Ph*C$_\gamma$, ipso), 139.3 (dd, $^1J_{PC}$ = 37.7, $^3J_{PC}$ = 1.8, PhP, ipso), 139.2 (d, $^1J_{PC}$ = 38.6, Ph_3P, ipso), 134.8 (d, $^3J_{PC}$ = 10.8, Ph_3P, meta), 134.7 (dd, $^1J_{PC}$ = 25.1, $^3J_{PC}$ = 1.8, PhP, ipso), 134.2 (d, $^3J_{PC}$ = 12.6, PhP, meta), 133.5 (d, $^3J_{PC}$ = 9.9, PhP, meta), 130.5 (d, $^4J_{PC}$ = 1.8, PhP, para), 129.9 (s, *Ph*C$_\gamma$, meta), 129.5 (d, $^4J_{PC}$ = 1.8, Ph_3P, para), 129.1 (d, $^4J_{PC}$ = 1.8, PhP, para), 128.4 and 128.3 (2 s, *Ph*C$_\gamma$, ortho and meta), 128.0 (d, $^2J_{PC}$ = 9.9, PhP, ortho), 127.9 (d, $^2J_{PC}$ = 9.0, Ph_3P, ortho), 127.6 (s, *Ph*C$_\gamma$, ortho), 126.9 (d, $^2J_{PC}$ = 9.0, PhP, ortho), 126.0 (s, *Ph*C$_\gamma$, para), 124.8 (s, *Ph*C$_\gamma$, para), 99.9 (t$_a$, $^4J_{PC} \approx {}^4J_{P'C} \approx$ 2.3, C$_\gamma$), 86.2 (dd, $^2J_{PC}$ = 53.9 and 15.3, C$_\alpha$), 83.4 (t$_a$, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 2.3, C_5H_5), 67.8 (d, $^1J_{PC}$ = 26.3, PCH), 44.5 (s, *C*Me$_3$), 26.6 (s, C*Me*$_3$). ^{13}C NMR (CD_2Cl_2; δ (selected values)): 86.2 (ddd, $^2J_{PC}$ = 53.9 and 15.3, $^2J_{HC}$ = 9.9, C$_\alpha$), 67.8 (dd, $^1J_{HC}$ = 133, $^1J_{PC}$ = 26.3, PCH). Anal. Calcd for $C_{56}H_{50}OP_2Ru$: C, 74.57; H, 5.59; P, 6.87. Found: C, 74.79; H, 5.50; P, 6.53.

Table 4. Crystallographic Data for the Structural Analysis of [Ru(η^5-C$_9$H$_7$)(PPh$_3$)[η^2(*P,O*)-Ph$_2$PCH(Me)C(Bu^t)=O)}][PF$_6$] (3′c) and [Ru{η^2(*C,P*)-C(=C=CPh$_2$)CH[C(=O)Bu^t]PPh$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)]·CH$_2$Cl$_2$ (9′a)

	3′c	**9′a**·CH_2Cl_2
formula	$C_{46}H_{45}F_6OP_3Ru$	$C_{61}H_{54}Cl_2OP_2Ru$
fw	921.80	1036.95
cryst syst	monoclinic	orthorombic
space group	$P2_1/c$	*Pbca*
a (Å)	11.469(8)	18.896(8)
b (Å)	20.985(6)	15.16(1)
c (Å)	17.913(4)	35.35(2)
α (deg)	90	90
β (deg)	91.73(3)	90
γ (deg)	90	90
V (Å^3)	4309(4)	10128(11)
Z	4	8
calcd density (g cm^{-3})	1.42	1.36
F(000)	1888	4288
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
cryst size (mm)	0.16 × 0.20 × 0.26	0.10 × 0.26 × 0.30
temp (K)	293	293
monochromator	graphite cryst	graphite cryst
μ (mm^{-1})	0.53	0.52
range of abs	0.52−1.00	0.57−1.00
diffraction geom	ω−2θ	ω−2θ
θ range for data collection (deg)	1.50−24.97	1.15−24.97
index ranges for data collection	$-13 \le h \le 13$	$0 \le h \le 20$
	$0 \le k \le 24$	$0 \le k \le 16$
	$0 \le l \le 21$	$0 \le l \le 38$
no. of rflns measd	9647	9707
no. of indep rflns	7567	8626
no. of variables	519	609
agreement between equiv rflns[a]	0.085	0.000
final *R* factors ($I > 2\sigma(I)$)	R1 = 0.052	R1 = 0.048
	wR2 = 0.115	wR2 = 0.090
final *R* factors (all data)	R1 = 0.173	R1 = 0.247
	wR2 = 0.153	wR2 = 0.138

[a] $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$.

[Ru{η^2(*C,P*)-C(=C=CPh$_2$)CH[C(=O)Bu^t]PPh$_2$}(C$_9$H$_7$)(PPh$_3$)] (9′a). Red crystals of **9′a** were similarly obtained in 89% yield by starting from **5′a**. IR: ν(C=C=C), 1876 cm^{-1}. ^{1}H NMR (CD_2Cl_2; δ): 7.62−6.20 [m, 39 H, Ph and C_9H_7 (4 H)], 4.96 (m, 1 H, C_9H_7), 4.40 (s, broad, 1 H, C_9H_7), 4.15 (d, 1 H, $^2J_{PH}$ = 9.9, PCH), 3.76 (s, broad, 1 H, C_9H_7), 0.54 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 209.0 (d, $^2J_{PC}$ = 9.0, CO), 195.6 (dd, $^3J_{PC}$ = 16.2 and 2.7, C$_\beta$), 141.3 (dd, $^5J_{PC}$ = 3.6 and 1.8, *Ph*C$_\gamma$, ipso), 140.5 (dd, $^5J_{PC}$ = 2.7 and 1.8, *Ph*C$_\gamma$, ipso), 138.7 (dd, $^1J_{PC}$ = 37.7, $^3J_{PC}$ = 1.8, PhP, ipso), 138.6 (d, $^1J_{PC}$ = 38.6, Ph_3P, ipso), 134.9 (d, $^3J_{PC}$ = 10.8, Ph_3P, meta, includes as a shoulder one part of dd, PhP, ipso), 134.5 (d, $^3J_{PC} \approx$ 1, second part of dd, PhP, ipso), 133.7 (d, $^3J_{PC}$ = 9.9, PhP, meta), 133.6 (d, $^3J_{PC}$ = 11.7, PhP, meta), 130.2 (d, $^4J_{PC}$ = 1.8, PhP, para), 129.4−129.2 (m, Ph_3P, para, and *Ph*C$_\gamma$, meta, and PhP, para), 128.6 (s, *Ph*C$_\gamma$, ortho), 128.4 and 128.3 (2 s, *Ph*C$_\gamma$, meta and ortho), 127.9 (d, $^2J_{PC}$ = 9.0, PhP, ortho), 127.7 (d, $^2J_{PC}$ = 9.0, Ph_3P, ortho), 127.1 (d, $^2J_{PC}$ = 9.9, PhP, ortho), 126.2, 125.5, 124.2, and 124.0 (4 s, *Ph*C$_\gamma$, para, 2 C, and C_9H_7, 2 C), 123.5, 123.3, 106.9, 105.1 (4 s, C_9H_7), 102.0 (d, $^4J_{PC}$ = 1.9, *Ph*C$_\gamma$), 96.2 (s, C_9H_7), 84.9 (dd, $^2J_{PC}$ = 51.2 and 13.6, C$_\alpha$), 77.6 (d, $^2J_{PC}$ = 9.9, C_9H_7), 74.2 (d, $^2J_{PC}$ = 9.1, C_9H_7), 68.6 (d, $^1J_{PC}$ = 25.1, PCH), 44.5 (s, *C*Me$_3$), 26.7 (s, C*Me*$_3$). ^{13}C NMR (CD_2Cl_2; δ (selected values)): 84.9 (ddd, $^2J_{PC}$ = 51.2 and 13.5, $^2J_{HC}$ = 9.9, C$_\alpha$), 68.6 (dd, $^1J_{HC}$ = 133, $^1J_{PC}$ = 25.0, PCH). Anal. Calcd for $C_{60}H_{52}OP_2Ru$: C, 75.69; H, 5.51; P, 6.51. Found: C, 75.96; H, 5.92; P, 6.07.

Crystal Structure Analysis of 3′c and 9′a·CH_2Cl_2. X-ray-quality suitable single crystals of complex **3′c** were obtained directly, while those of **9′a**·CH_2Cl_2 were elaborated through the slow diffusion of methanol into a concentrated solution in dichloromethane. Experimental data collection, crystal, and refinement parameters are collected in Table 4. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 10 and 12°). Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. Profile analysis was performed on all reflections.[26] Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|^2$ values. The structures were solved by DIRDIF (Patterson methods and phase expansion).[27] Isotropic full-matrix least-squares refinement on $|F_o|^2$ was performed using SHELX93.[28] At this stage an empirical absorption correction was applied using XABS2.[29] Hydrogen atoms (except H(1) in **3′c** and H(2B) in **9′a**) were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The geometrically placed hydrogen atoms were isotropically refined, riding on their parent atoms, with a common thermal parameter. H(1) in **3′c** and H(2B) in **9′a** were independently (and also isotropically) refined. Atomic scattering factors were taken from ref 30. Geometrical calculations were made with PARST.[31] The crystallographic plots were made with EUCLID.[32]

Complex 3′c. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (0.0610P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2)/3]$ and $\sigma^2(F_o^2)$ is derived from counting statistics. The maximum shift to esd ratio in the last full-matrix least-squares cycle was −0.001. The final difference Fourier map showed no peaks higher than 0.55 e Å^{-3} nor deeper than −0.74 e Å^{-3}.

Complex 9′a·CH_2Cl_2. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (0.0367P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2)/3]$ and $\sigma^2(F_o^2)$ is derived from counting statistics. The maximum shift to esd ratio in the last full-matrix least-squares cycle was −0.043. The final difference Fourier map showed no peaks higher than 0.43 e Å^{-3} nor deeper than −1.57 e Å^{-3}. The CH_2Cl_2 solvent molecule was affected by structural disorder and was anisotropically refined, showing the maximum hole on the final electronic density map. The CH_2Cl_2 hydrogen atoms were geometrically placed, fixing their thermal parameters to 0.40.

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Supporting Information Available: For **3′c** and **9′a**, text giving further details of the X-ray study and tables of bond distances and angles, atomic coordinates, positional and thermal parameters, and torsion angles (37 pages). Ordering information is given on any current masthead page.

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