Reactivity of Diphenylphosphino Enolato Ligands in Ruthenium(II) Complexes and Related Processes Involving Easy Cleavage of a Phosphorus−Carbon Bond in Functionalized Phosphine Ligands

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The migration of a phenyl group from phosphorus to the coordinated ruthenium center in complexes (η^6-arene)[η^2-$Ph_2PC(R)$═$C(R')O$]RuCl, **2** [arene = 1,3,5-$Me_3C_6H_3$ or C_6Me_6; R = H or Me; R′ = Bu^t], occurs in methanol at reflux. The reaction is favored by the addition of KOAc and affords selectively the stable phosphinito enolato derivatives (η^6-arene)[η^2-Ph-(**MeO**)PC(R)═C(R′)O]Ru**Ph**. In contrast, the reaction of complexes **2** with methanol and K_2CO_3 preserves the functional ligand and affords selectively the hydride derivatives (η^6-arene)[η^2-$Ph_2PC(R)$═$C(R')O$]Ru**H**. The cleavage of the ruthenium−chlorine bond in complexes **2** is also the preliminary step involved in the coupling process of functional phosphino enolato ligands with 1-alkynes HC≡CR″. The reaction results in the formation of complexes {(η^6-arene)Ru[η^3-**CH═C(R″)**C(R)(PPh_2)C(R′)═O]}(PF_6) [R = H or Me, R′ = Bu^t or Ph, R″ = H, Me, Ph, *p*-MeC_6H_4, or $SiMe_3$], the isomerization of which into complexes {(η^6-arene)Ru-[η^3-CH(PPh_2)C(R″)═C(R)C(R′)═O]}(PF_6), [R′ = Bu^t, R″ = H, Me, Ph, or *p*-MeC_6H_4] occurs only when R = H. The isomerization consists of an intramolecular [1,3]-migration of a phosphorus−carbon bond and is catalyzed by the fluoride anion. When R″ = H, a subsequent cleavage of the ruthenium−carbon bond foreshadows the formation of (η^6-C_6Me_6)[η^1-Ph_2-PCH_2CH═CHC(═O)Bu^t]$RuCl_2$, **11**. Thus, starting from the precursor (η^6-C_6Me_6)[η^1-Ph_2-PCH_2C(═O)Bu^t]$RuCl_2$, the process achieves formally an insertion of ethyne into the starting functionalized phosphorus−carbon bond. The scarcely isolable complexes {(η^6-arene)Ru-[η^3-C(═CH_2)C(R)(PPh_2)C(R′)═O]Ru}(PF_6) [R = H or Me, R′ = Bu^t or Ph] reveal an easy cleavage of the functionalized phosphorus−carbon bond. This cleavage is the preliminary step involved in the formation of metallafuran complexes {(η^6-arene)(Ph_2PX)Ru[η^2-$C(CH_3)$═$CRC(R')$═O]}(PF_6) [X = Cl or F, R = H or Me, R′ = Bu^t or Ph], which implies also the capture of a halide anion by phosphorus in a transient intermediate.

Introduction

The involvement of organometallic complexes containing phosphine ligands in homogeneous catalysis has initiated a considerable research effort aimed at the discovery and improvement of catalytic processes. Often undesirable with respect to catalysis are side reactions resulting in the deactivation of catalysts.[1] The detection of byproducts wherein a fragment had arisen from a phosphine ligand through the cleavage of a phosphorus−carbon bond implies damage in the organometallic catalyst.[1,2] However, scission of phosphorus−carbon bonds in phosphine ligands has provided access to numerous phosphido-bridged polymetallic complexes.[3] The retention of a stable metal−carbon bond resulting from the migration of an alkyl (or aryl) group from a phosphine ligand to the coordinated metal is rare but frequent enough to highlight the fundamental interest of this simple [1,2]-sigmatropic shift of an alkyl group.[4] Theoretical calculations predict easy migration, and such activation of a phosphorus−carbon bond formally consists of an oxidative addition to a coordinatively unsaturated metal center.[5] The [1,2]-sigmatropic shift may occur under very mild conditions and is presumably a general and reversible process.[6] The process is responsible of the phenyl/alkyl exchange between a phosphine ligand and the metal center, resulting in an alkyl group interchange between phosphorus ligands or further interference in catalytic coupling reactions.[6,7] The [1,2]-sigmatropic shift was invoked also to account for several stoichiometric but intricate reactions.[8] A schematic summation is attempted in Chart 1. The oxidative addition of a phosphorus−carbon bond to a 16-electron metal center allows the achievement of the commonly favored 18-electron stabilization when the resulting PR_2 ligand is considered to act as a three-electron donor.[9] The shift of an alkyl group is assumed to occur between two highly reactive species, namely **A**

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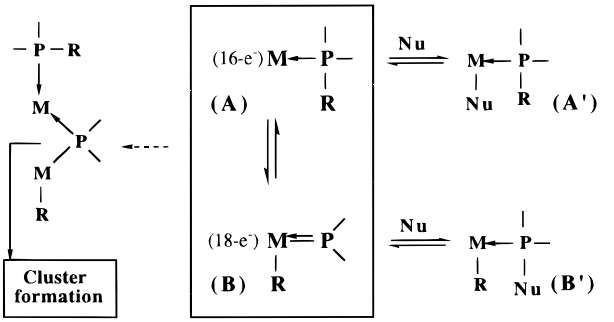
Chart 1. Behavior of a Phosphine Ligand Induced by a 2-Electron Deficiency at the Metal Center

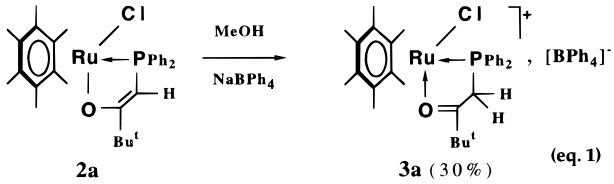


and **B** in Chart 1. The generation of a PR_2 arm in **B** offers easy access to bi- and then multimetallic complexes through the formation of phosphido bridges. Besides other processes such as ortho metalation,[1] a nucleophilic attack on the metal center in **A** or alternatively on the phosphorus atom in **B** achieves the deactivation of the **A** ↔ **B** system. However the deactivation is only apparent when a further **A′** ↔ **B′** transformation remains easy. Such transformations have been reported, and peculiarly noteworthy are a reversible transformation conducted through the protonation of a nitrogen center,[10] a metal−alkoxide/phosphorus−aryl metathesis,[11] or a migration of a phenyl group from the metal to phosphorus initiated by the cleavage of a phosphorus−alkoxide bond.[12]

Our interest focused on β-keto phosphine or related phosphino enolato ligands is rewarded again through the observation of several reactions wherein a cleavage of a phosphorus−carbon bond is undoubtedly involved. We report herein, as depicted in Chart 2, (i) a [1,2]-migratory process of a phenyl group from a diphenylphosphino enolato ligand to a ruthenium center, (ii) a [1,3]-migratory process of a phosphorus−carbon bond catalyzed by the fluoride anion, (iii) an example of a formal insertion of ethyne into a functionalized phosphorus−carbon bond, and (iv) a reaction where the cleavage of a phosphorus−carbon bond induced the formation of a metallafuran derivative.

Results and Discussion

1. Easy Migration of a Phenyl Group from a Phosphino Enolato Ligand to a Ruthenium Center. Whereas the P**C**$_\alpha$-carbon atom in diphenylphosphino enolato ligands in functionalized ruthenium complexes (η^6-arene)[η^2-Ph_2P**C**(R)═C(R′)O]RuCl, **2**, is a nucleophilic reactive site, the metal center becomes an electrophilic site when a cleavage of one metal−ligand bond results in a 16-electron intermediate. The dissociation of a chloride−metal bond in a polar solvent such as methanol is peculiarly common. A fast process occurs when $NaBPh_4$ is added to a solution of **2a** in methanol as monitored by the formation of an orange precipitate. Subsequent work was disappointing and resulted only in the isolation of bright red crystals of the parent complex **3a**, in 30% yield relative to ruthenium (eq 1).

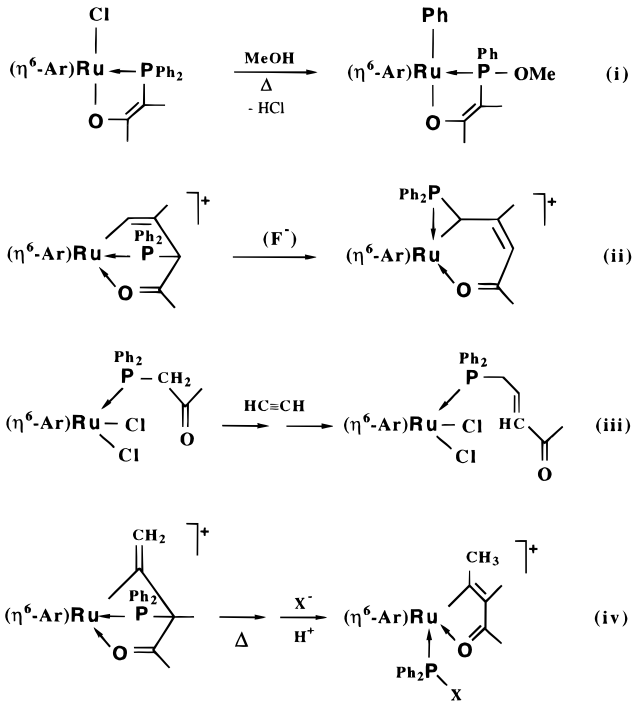


(eq. 1)

That the formation of **3a** consisted of a protonation of the phosphino enolato ligand in **2a** is evident. The source of protons is less clear but may occur through the decomposition of a speculated intermediate. In order to obtain further information, the simple substitution of the chloride in complexes **2** by a carboxylate anion was then attempted. Unexpectedly, the reaction of complexes **2a**−**d** with KOAc in methanol at reflux afforded the yellow phosphinito enolato derivatives (η^6-arene)[η^2-Ph(MeO)PC(R)═C(R′)O]RuPh, **4a**−**d**, in 45−70% yields (eq 2).

Of importance with respect to mechanistic considerations, the formation of a substantial amount of **4d** was obtained after heating **2d** in pure methanol. A soft base such as KOAc is adequate[13] to remove HCl from complexes (η^6-arene)(η^1-*P*-keto phosphine)$RuCl_2$, **1**, to achieve the formation of complexes **2**. Accordingly, derivatives **4a**−**d** were obtained more straightforwardly starting from **1a**−**d**. Providing a supplementary evidence of the involvement of methanol in the process, the reaction of **1a** with KOAc in ethanol at reflux

Chart 2. Reactions Examined in This Report



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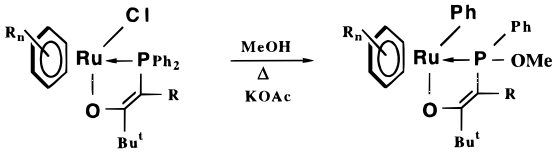


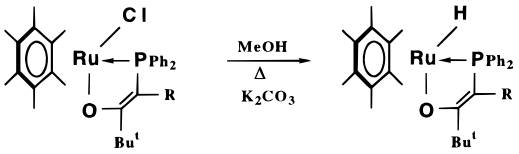
2a, 2b, 2c, 2d **4a, 4b, 4c, 4d**

Key: **a**: R = H, arene = hexamethylbenzene
b: R = Me, arene = hexamethylbenzene
c: R = H, arene = mesitylene
d: R = Me, arene = mesitylene

(eq. 2)

afforded the ethoxy derivative (hexamethylbenzene)[η^2-Ph(**EtO**)PCH═C(Bu^t)O]RuPh, **4′a**. Elemental analysis of complexes **4** indicated a negligible abundance of chlorine in agreement with the structural information provided by spectroscopic studies. The IR spectra of complexes **4** exhibited a strong absorption close to 1500 cm^{-1} (within 1514 in **4b** and 1496 cm^{-1} in **4a**) and attributable to the C═CO vibration according to the retention of the enolato pattern. ^{1}H NMR spectroscopy indicated clearly the presence of both an arene ligand and two phenyl groups, but also the additional presence of a methoxy group (ethoxy in **4′a**) relative to complexes **2**. The coupling of the OMe protons with the phosphorus nucleus ($^3J_{PH} \sim 12$ Hz) and the ^{31}P{^{1}H} NMR chemical shifts [δ = 172.2 (in **4d**)−143.0 ppm (in **4′a**)] indicated unambiguously that a phosphorus−oxygen bond was generated. The coordination at phosphorus in a phosphinito enolato ligand requires only one of the two phenyl groups detected by ^{1}H NMR spectroscopy, but a coordinatively saturated ruthenium is achieved only when the formation of a ruthenium−carbon σ-bond involving the second phenyl group is assumed. Further experimental support was provided by ^{13}C NMR spectroscopy. Besides the resonance expected for the ═**C**O enolato−carbon nucleus, a second low-field resonance is attributable to the *ipso*-carbon of a phenyl group σ-bonded to ruthenium.[4c] Some other resonances in the phenyl range displayed a broadness likely attributable to hindered rotation of the phenyl group σ-bonded to the metal.[14] The phosphorus atom and the metallic center are both stereogenic in complexes **4**, but only one diastereoisomer was detected in accordance with a diastereoselective reaction of formation.

A distinct reaction was observed when complexes **2** were reacted with K_2CO_3 in methanol at reflux and afforded in good yields the yellow hydride derivatives **5a**,**b** (eq 3).



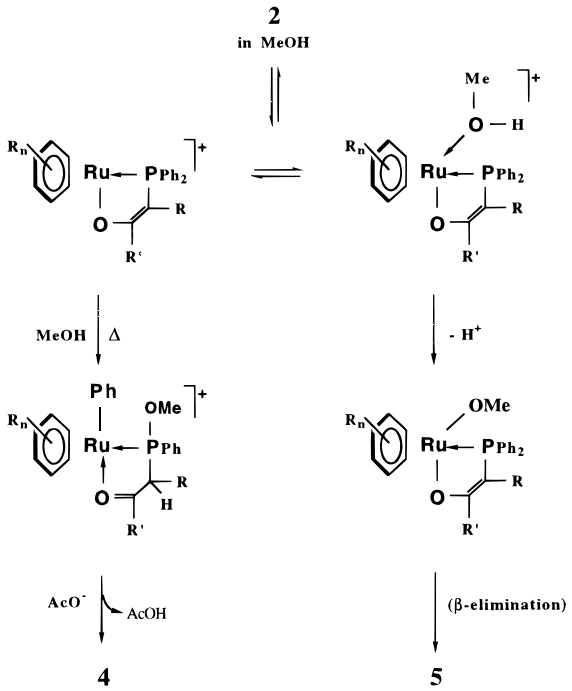
2a, 2b **5a, 5b**

Key: **a**: R = H
b: R = Me

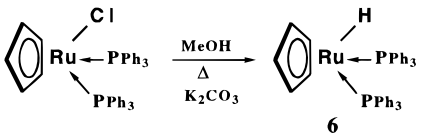
(eq. 3)

Unstable products formed starting from **2c** or **2d**; however, ^{1}H NMR spectroscopy suggested a similar hydride formation. The structures of complexes **5a**,**b** were assigned from spectroscopic studies and elemental analyses. Peculiarly charasteristic of hydride formation, the ^{1}H NMR spectra exhibited a high-field resonance (δ = −8.78 in **5a** and −8.76 ppm in **5b**) attributable to the Ru−H proton. The IR absorption corresponding to the Ru−H vibration was located at ν = 1948 in **5a** and 1923 cm^{-1} in **5b**. The hydride derivatives **5** in the solid state are less stable than the phenyl complexes **4** and darkened slowly while they were kept several weeks at room temperature.

Scheme 1. Rationale Accounting for the Formation of Complexes 4 and 5



The formation of a metal−hydrogen bond from a methoxy intermediate was already established and involves a β-elimination process. Thus, the substitution of the chloride ligand in Cp(PPh$_3$)$_2$RuCl by a methoxy anion under anhydrous conditions affords the hydride derivative Cp(PPh$_3$)$_2$RuH, **6**.[15] However, an alternative pathway accounting for the formation of the required methoxy intermediate may consist of the deprotonation of the solvated cationic species [Cp(PPh$_3$)$_2$Ru(MeOH)]$^+$, the formation of which occurs after simple dissolution of the chloro precursor in methanol.[16] Accordingly, we obtained the hydride **6** in 81% yield by reacting the chloro complex with K_2CO_3 in methanol at reflux (eq 4).



6 **(eq. 4)**

This result suggested strongly that the formation of the hydride complexes **5** occurred similarly, through the fast decomposition of a methoxy intermediate. As depicted in Scheme 1, the deprotonation of a [Ru-

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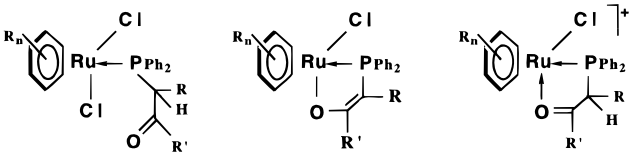
$(MeOH)]^+$ species by K_2CO_3 would generate a methoxy intermediate allowing the subsequent formation of the ruthenium−hydrogen bond. Of obvious interest, the involved ruthenium−methoxy neutral intermediate is an isomeric form of a complex **4** but affords selectively the corresponding hydride complex **5**.

The formation of complexes **4** is expected to involve a 16-electron intermediate. Such a coordinatively unsaturated intermediate may result from a labile methanol to ruthenium coordination allowing an easy bond breaking. The loss of the coordinated methanol would generate a cationic $\{(\eta^6\text{-arene})[\eta^2\text{-}Ph_2PC(R)=C(R')O]Ru\}^+$ 16-electron species wherein a reversible [1,2]-sigmatropic shift of a phenyl group from phosphorus to ruthenium may occur according to the process detailed in Chart 1. The nucleophilic attack of methanol on phosphorus and further deprotonation of methanol mediated by the enolato function drive the irreversible formation of **4**. Moreover, the nucleophilic attack of methanol on a chiral intermediate where the migratory phenyl group would bridge phosphorus to ruthenium may account for the diastereospecificity observed in the formation of **4**. Thus, the ability of the enolato function to deprotonate methanol selectively after the migration of a phenyl group had occurred is likely the key of the formation of complexes **4**. Such a functionality is unavailable when starting from $Cp(PPh_3)_2RuCl$, which remains unaffected in methanol at reflux.[16a] Furthermore, we have checked the persistence of this behavior in the presence of KOAc (3 days in methanol at reflux). The deprotonation of methanol is achieved when K_2CO_3 was added, but under such basic conditions, the deprotonation of the 18-electron $[Ru(MeOH)]^+$ intermediate had become the favored process and overshadows the formation of any complex **4**. Of general interest, the reversibility of the [1,2]-shift process accounts for the relative scarcity of reports of migration of an aryl group from phosphorus to the metal: the [1,2]-shift occurs when the metal becomes coordinatively unsaturated, but the metal center generally remains a favored electrophilic site relative to phosphorus.

2. Empirical Selection from Complexes (η^6-arene)(η^2-diphenylphosphino enolato)RuCl, 2. A large variety of neutral enolato complexes $(\eta^6\text{-arene})[\eta^2\text{-}Ph_2PC(R)=C(R')O]RuCl$, **2**, is conceivable through the variation of three structural parameters, namely the R and R′ groups and the arene ligand. The palette of complexes **2** synthesized is displayed in Chart 3 and involves some new complexes **2** where the arene ligand is hexamethylbenzene [**2b**, R = Me, R′ = Bu^t; **2a′**, R = H, R′ = Ph; **2b′**, R = Me, R′ = Ph], mesitylene [**2d′**, R = Me, R′ = Ph], or benzene [**2g**, R = Me, R′ = Bu^t]. A parallel numbering defines the structural parameters in the parent neutral complexes $(\eta^6\text{-arene})[\eta^1\text{-}Ph_2PCH(R)C(=O)R']RuCl_2$, **1** [new compounds: **1a**, **1b**, **1b′**, **1g**], and in the related cationic derivatives $\{(\eta^6\text{-arene})[\eta^2\text{-}Ph_2PCH(R)C(R')=O]RuCl\}^+$, **3** [new compounds: **3a**, **3b**, **3b′**, **3g**, **3g′**].

The stability of the cationic complexes **3** involving a chelating β-keto phosphine is noteworthy but prevents any observation of variation related to the structural parameters. The metallic center and the PC_α carbon atom are both stereogenic in complexes **3** where R = Me. A similar 3/2 ratio of stereoisomers was determined by ^{1}H NMR spectroscopy from solutions in CD_2Cl_2 of

Chart 3. Structure of Complexes 1−3 and Palette of Complexes 2 Providing the Key Determining R, R′ Groups and Arene Ligand in Derivatives or Related Complexes 1 and 3



1 2 3

Palette of complexes 2

Arene ligand:	(hexamethylbenzene)	(mesitylene)	(p-cymene)	(benzene)
R = H, R′ = Bu^t:	2a*	2c*	2e*	
R = H, R′ = Ph:	2a′		2e′*	
R = Me, R′ = Bu^t:	2b	2d*	2f*	2g
R = Me, R′ = Ph:	2b′	2d′	2f′*	

List of complexes **1**:
1a, 1b, 1b′, 1c*, 1c′*, 1d*, 1d′*, 1e*, 1e′*, 1f*, 1f′*, 1g
List of complexes **3**:
3a, 3b, 3b′, 3d*, 3e*, 3e′*, 3f*, 3g, 3g′

* The asterisk-marked complexes were reported previously.[13,17]

3b,**g** [R′ = Bu^t, arene = hexamethylbenzene or benzene]. An enhanced stereoselectivity (7/1 ratio) was determined when a solution of **3b′** [R′ = Ph, arene = hexamethylbenzene] was examined, but a 4/3 ratio was observed starting from **3g′** [R′ = Ph, arene = benzene]. Phosphino enolato complexes **2** are noticeably more labile than complexes **3**. Solutions in chloroform of the benzene derivative **2g** or of a *p*-cymene complex (except **2f** where R = Me and R′ = Bu^t) turned green within some hours at ambient temperature. Subsequently, the presence of free arene was detected by ^{1}H NMR spectroscopy. In contrast, stable orange solutions were obtained from complexes **2** wherein the arene ligand is hexamethylbenzene. Emphasizing a relationship between stability of complexes **2** and structure of the functional ligand, solutions of the mesitylene complexes where R = Me were found stable when R′ = Bu^t (**2d**) but rapidly turned green when R′ = Ph (**2d′**). As an empirical but useful rule, the stability of complexes **2** is favored when R = Me compared to R = H, to a lesser extent when R′ = Bu^t compared to R′ = Ph, and when there is an increased number of alkyl substituents at the arene ring.

3. Coordination of 1-Alkynes and Subsequent [1,3]-Shift of a Phosphorus−Carbon Bond Catalyzed by the Fluoride Anion. The enolate-carbon atom in complexes **2** is nucleophilic enough to participate in the 1-alkyne-to-vinylidene rearrangement which occurs subsequent to the coordination of a terminal alkyne at the ruthenium center.[13,17] To take advantage further of the formation of a polyfunctional ligand in the process and to avoid the use of a silver salt that

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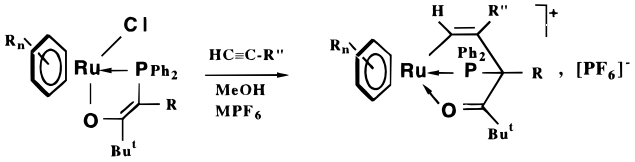
complicates experimental work,[13] the reaction of complexes **2b**,**d**, where R = Me, with some 1-alkynes was carried out in methanol and in the presence of NH_4PF_6 to afford good yields of the expected coupling products (eq 5).



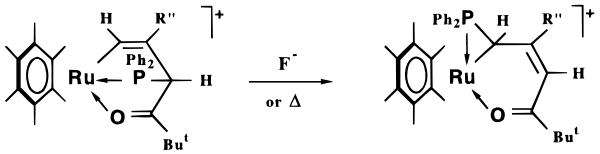
2a, 2b, 2d

R" = Me: 7a, 7b, 7d
R" = Ph: 8a, 8b, 8d
R" = p-MeC$_6$H$_4$: 9a

Key: **a**: R = H, arene = hexamethylbenzene
b: R = Me, arene = hexamethylbenzene
d: R = Me, arene = mesitylene

(eq. 5)

Thus, complexes **7b**,**d** were obtained from propyne and complexes **8b**,**d** from phenylacetylene, but attempts to obtain such complexes from *tert*-butylacetylene invariably failed. Coupling products where R = H (**7a**, **8a**, and **9a**) were isolated only when starting from **2a** wherein the arene ligand is hexamethylbenzene (eq 5). Despite these limitations, the reaction of 1-alkynes with precursors **2** provides an easy access to a variety of coupling products. The orange complexes **7**−**9** were obtained as racemates and characterized by elemental analysis and spectroscopic studies. Peculiarly characteristic of their structure are the $^{31}P\{^1H\}$ NMR resonance and the ^1H NMR resonance attributable to the Bu^tCH═ proton which are strongly deshielded.[13] Complexes **7**−**9** were unreactive toward strong acids but decomposed slowly when stirred in methanol with bases such as KOH or K_2CO_3. A solution of **7a** in dichloromethane was unaffected after $HBF_4{\cdot}OEt_2$ was added. The thermal stability of complexes **7** and **8**, where R = Me, is noteworthy. These complexes are inert in boiling ethanol and were conveniently recrystallized from hot methanol. In contrast, complexes **7a**, **8a**, and **9a**, where R = H, isomerize in ethanol at reflux to afford the dark-purple complexes **7′a**, **8′a**, and **9′a**, respectively (eq 6).



7a, R" = Me
8a, R" = Ph
9a, R" = p-MeC$_6$H$_4$

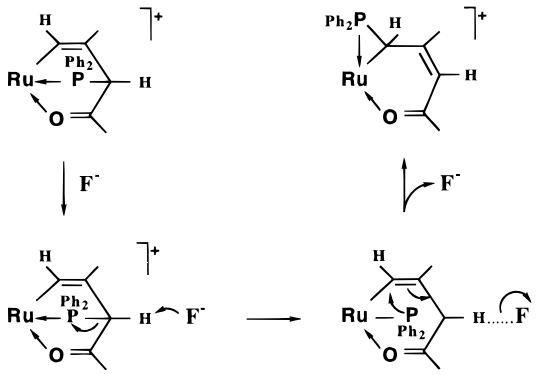
7'a, R" = Me
8'a, R" = Ph
9'a, R" = p-MeC$_6$H$_4$

Counter anion: **[PF$_6$]$^-$**

(eq. 6)

As specified previously,[13] such an isomerization consists of a [1,3]-migration of the functionalized phosphorus−carbon bond and results in a spectacular shift of the $^{31}P\{^1H\}$ resonance (from δ 142.2−124.2 to 4.3−5.5 ppm). Whereas the reaction occurred easily when starting from **7a**, the conversion of **8a** is incomplete and the removal of residual **8a** from **8′a** is difficult. Furthermore, **8a** is almost insoluble in ethanol and remains unaffected after heating in chloroform (or dichloromethane) at reflux for several days. However, the transformation of **8a** into **8′a** occurred when **8a** was heated in a mixture of ethanol and dichloromethane. The involvement of *p*-ethynyltoluene (instead of phenylacetylene) in complex **9a** is not sufficient to significantly increase the solubility. With a fresh sample of NH_4PF_6, **8′a** was straightforwardly obtained at room temperature from **7a** instead of the expected **8a**. Fluoride contamination was suspected, and we examined the behavior of solutions of complex **8a** after a fluoride salt was added. Despite that solubility of NaF in organic solvents is almost negligible, the addition of NaF to an orange solution of **8a** in a mixture of methanol and dichloromethane resulted in the formation of the dark-purple complex **8′a**. However, solutions of **8a** are stable in the absence of NaF or in the presence of another salt such as NaI. The isomerization is fast (less than 1 h) when $[Bu_4N]F$ is used as a soluble catalyst, but this salt is more difficult to remove on completion of the reaction. Not surprisingly, similar results were obtained when starting from **9a**. Substantiating furthermore the requirement of R = H, attempts to achieve the transformation starting from a complex **7** or **8**, where R = Me, were unsuccessful. Moreover, the thermally induced isomerization became ambiguous: unavoidable residual moisture may be suspected to generate fluoride by hydrolysis of the $(PF_6)^-$ anion present while the mixture is heated. The fundamental requirement with respect to the mechanism of the isomerization is the presence of a PCH hydrogen atom. The enolization of the keto function in complexes **7a**−**9a** is forbidden for geometrical reasons, but the PCH hydrogen atom is likely acidic enough to coordinate a fluoride anion according to the basicity of the fluoride anion.[18] As suggested in Scheme 2, the coordination of the fluoride anion would mediate a formal P−C → $P^{-/+}$C cleavage (or a simple weakening if the mechanism of the isomerization is a concerted one) of the phosphorus−carbon bond involved in the process: a 2-electron contribution from fluoride through coordination at hydrogen preserves the 8-electron stabilization at the carbon center.

Scheme 2. Simple Mechanism Accounting for the Isomerization Process Catalyzed by the Fluoride Anion[a]



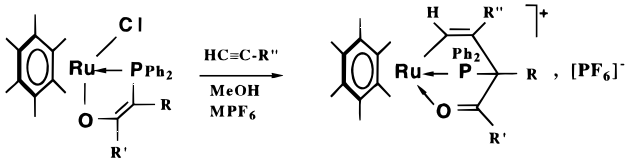
[a] The arene ligand is omitted for clarity.

Thus the temporary coordination of the fluoride anion contributes to the energy of activation allowing the progress of the reaction.

4. Coordination of Ethyne and Formal Insertion of Ethyne into the Functional Phosphorus−Carbon Bond. The involvement of ethyne in the coupling reaction of 1-alkynes with phosphino enolato ligands

(18) Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.

where R = Me or H resulted in the formation of the expected products (eq 7).

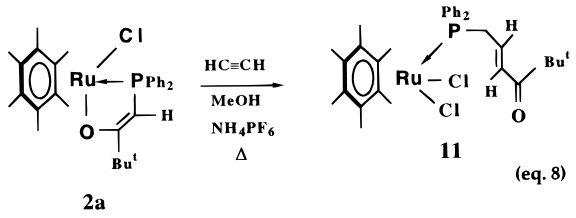


2a, 2a', 2b, 2b' **R'' = H: 10a, 10b, 10b'** **R'' = $SiMe_3$: 12a, 12a'**

Key: **a**: R = H, R' = Bu^t; **a'**: R = H, R' = Ph; **b**: R = Me, R' = Bu^t; **b'**: R = Me, R' = Ph

(eq. 7)

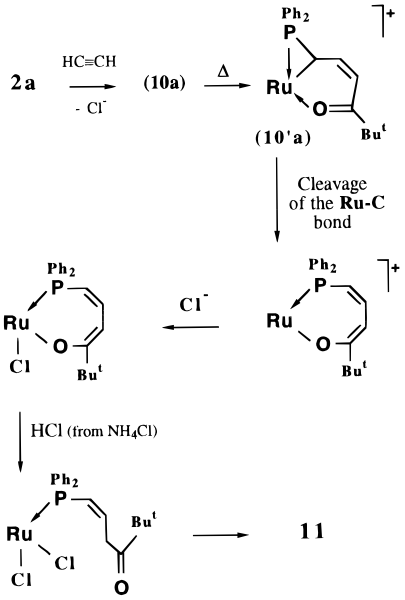
The stable derivatives **10b** and **10b′** were obtained in high yields starting from **2b** and **2b′** where R = Me. Already reported was the coupling product close to **10b** but wherein the arene ligand was a mesitylene one.[17] Emphasizing their thermal stability, well-formed crystals resulted from the slow cooling of a saturated solution in hot methanol. The coupling reaction of ethyne with **2a**, where R = H, afforded a product of markedly decreased thermal stability. In anticipation that the thermal isomerization of **10a** would generate a product of increased stability, heating of **10a** was attempted *in situ* but resulted in the formation of the novel complex **11** (eq 8).



2a (eq. 8)

The conversion of **10a** into **11** requires two chloride anions, but only one is available, as the ammonium chloride produced from the consumption of **10a**. However, this lack of chloride is inconsequential with respect to the yield of the reaction. Intentional addition of NH_4Cl to the reaction mixture before heating does not affect the yield in **11** (23%), implying that the low productivity of the process is attributable to competitive decomposition. Elemental analysis of **11** provided the direct evidence for two chorines *per* ruthenium atom. In agreement with the recorded $^{31}P\{^1H\}$ NMR chemical shift (δ = 31.9 ppm), the examination of both the ^1H and ^{13}C NMR spectra of **11** allows unambiguous confirmation that a *trans* $-CH_2C\mathbf{H}{=}C\mathbf{H}C(=O)Bu^t$ functional organic group R completes the arrangement around the phosphorus center in a common (arene)(Ph_2-PR)$RuCl_2$ structure. Thus, the ^1H NMR spectrum of **11** shows two vinylic protons ($^3J_{HH}$ = 15.1 Hz) consistent with their mutual *trans* arrangement. The ^{13}C NMR spectrum exhibited resonances expected from the PCH_2 moiety. As depicted in Scheme 3, a cleavage of the ruthenium−carbon bond arising from the isomerization of **10a** into the feasible intermediate **10′a** may account for the formation of **11**. We were unable to isolate **10′a** as its PF_6 salt, but NMR spectroscopy is highly suggestive of the formation of such a structure (see complex **10′a** in the Experimental Section). The speculated cleavage would result in the formation of a 16-electron cationic species able to gain a 18-electron stabilization

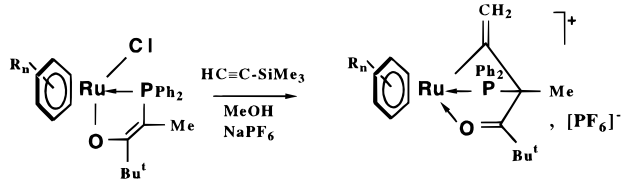
Scheme 3. Proposal of Mechanism Accounting for the Formation of Complex 11[a]



[a] The arene ligand is omitted for clarity.

through the coordination of a chloride anion. The following step between the acidic NH_4Cl and the basic enolato function achieves an addition of HCl releasing a β,γ-enone organic chain. A classical reorganization of the organic function into a conjugated α,β-enone one allows one to complete the formation of **11**. Complex **1a**, namely (hexamethylbenzene)[η^1-$Ph_2PCH_2C(=O)Bu^t$]-$RuCl_2$, is the precursor of **2a**, involved in the synthesis of **11**. The overall transformation **1a** → **11** simply consists of the formal insertion of ethyne into the functional phosphorus−carbon bond in **1a**, followed by a common enone isomerization into a conjugated one.

5. Formation of 2-Metallafuran Complexes Subsequently to the Coordination of (Trimethylsilyl)-acetylene. The coupling products **12a** and **12a′**, where an R″ = $SiMe_3$ group is preserved, were isolated after reacting (trimethylsilyl)acetylene with the precursors **2a** and **2a′**, respectively (eq 7). When we start from the precursors **2b**,**d** where R = Me instead of R = H, the simple coupling reaction between the functional ligand and the alkyne is hindered presumably for steric reasons and a different process occurred. As reported previously,[17] 1-alkyne-to-vinylidene rearrangement followed by methanolysis (or hydrolysis) of the carbon−silicon bond generates a reactive electrophilic $[Ru{=}C{=}CH_2]^+$ intermediate which allows further coupling with the functional ligand. This process results in the formation of complexes **13b**,**d**, respectively (eq 9).

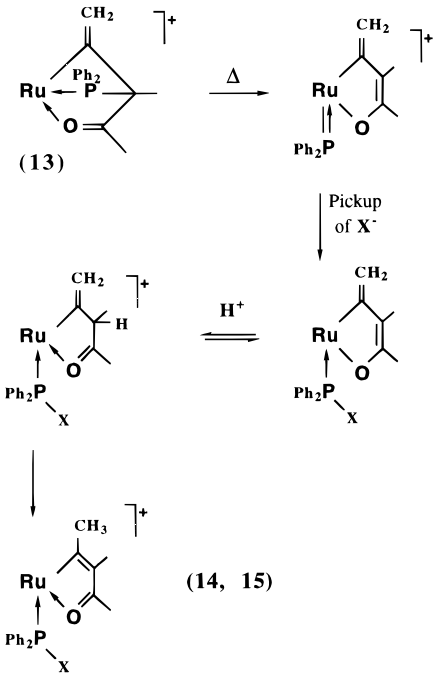


2b, 2d **13b, 13d**

Key: **b**: arene = hexamethylbenzene; **d**: arene = mesitylene

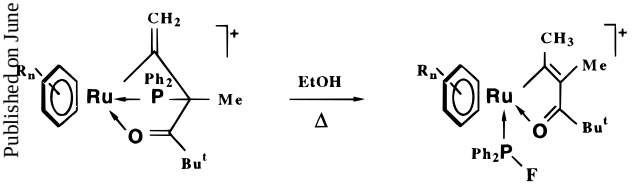
(eq. 9)

Scheme 4. Phosphorus−Carbon Bond Cleavage as a Key Step in the Formation of Complexes 14 and 15[a]



[a] The R, R′ groups and the arene ligand are omitted for clarity.

We failed to isolate **13b** in a pure state despite a ~90% yield in the crude product, as inferred from ^{1}H NMR spectroscopy. Unavoidable simple protonation of **2b** takes place simultaneously to generate **3b** as a tenacious impurity, inseparable by simple crystallization. Thus, derivative **13d** remains the sole compound of structure **13**, isolable in an analytical state of purity.[17] In ethanol at reflux **13b**,**d** undergo rearrangement to the metallafuran derivatives, **14b**,**d**, respectively (eq 10).

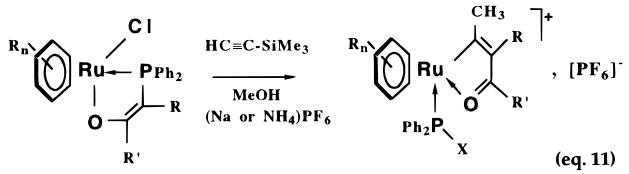


13b, 13d **14b, 14d**

Key: **b**: arene = hexamethylbenzene
d: arene = mesitylene
Counter anion: $[PF_6]^-$

(eq. 10)

Of peculiar interest related to this report, the structure of derivatives **14** clearly indicated that the cleavage of the functional phosphorus−carbon bond in precursors **13** was involved in the process as briefly mentioned previously.[17] As depicted in Scheme 4, such a cleavage would result in the formation of a five-membered metallacycle together with a reactive (three electron donor) Ph_2P ligand. A subsequent reaction with a fluoride anion[12] results in the formation of a neutral intermediate. Further protonation of the basic enolate function and subsequent stabilization through the isomerization of the β,γ-enone arrangement into a conjugate α,β-enone one achieve a process which was investigated recently.[19] Supporting the assumption of a $[RuPPh_2]^+$ intermediate, the preferential formation of the parent chloro complex **15d** (eq 11) occurred when a chloride anion is available. Failure to add an ethoxy group from ethanol (see formation of complexes **4**) is not unexpected.



(eq. 11)

2a, 2d, 2d' **14a, 14d': X = F**
15a, 15d: X = Cl

Key: **a**: R = H, R' = Bu^t, arene = hexamethylbenzene
d: R = Me, R' = Bu^t, arene = mesitylene
d': R = Me, R' = Ph, arene = mesitylene

The easy cleavage of the functional phosphorus−carbon bond implies significant steric constraints in complexes **13**. Interestingly, attempts to isolate a complex of type **13** starting from **2d′** failed but afforded straightforwardly the corresponding derivative **14d′** (eq 11).

The formation of **14d′** may be reasonably believed to involve a transient derivative of type **13**. Similarly, derivatives **14a** and **15a** were detected as byproducts from the reaction of (trimethylsilyl)acetylene with **2a**, which yields also the coupling product **12a** as already reported (see eq 7). As detailed in the Experimental Section and with the exception of **15a**, we succeeded in isolating pure samples of each complex. Their simultaneous formation provided evidence of a kinetic competition relevant to the interference of the reactivity of phosphino enolato ligands, in the 1-alkyne-to-vinylidene rearrangement.[17]

Conclusions

The results which frame this report emphasize the reactivity of the phosphorus center in diphenylphosphino enolato ligands. In the mediation of the nucleophilic addition of methanol on phosphorus, the enolate function is able to lock the migration of an aryl group at the metal center location. Besides this typical reaction of [1,2]-shift of a phenyl group from phosphorus to a transition metal, the transformation catalyzed by the fluoride anion underlines the diversity of reactions involving an activation of a phosphorus−carbon bond. The facility of this transformation is noteworthy when compared to the immutability of complexes where a methyl group is enough to hinder the process. Not of negligible interest, our results provide clear evidence that the fluoride anion hidden as an impurity in an inorganic salt may develop a catalytic activity resulting in a rearrangement of an organometallic structure. The formation of metallafuran derivatives is likely induced by a preliminary cleavage of a phosphorus−carbon bond, weakened owing to geometrical constraints. Such a cleavage may be considered as the first step of a process

(19) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Beatty, A. M. *Organometallics* **1995**, *14*, 5127.

of decomposition, and not surprisingly lower yields were encountered in the formation of the 2-metallafuran complexes.

Experimental Section

All chemicals were reagent grade and were used as received or synthesized as described below. 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.[13] Solvents were distilled under inert atmosphere after drying according to conventional methods. Infrared spectra were recorded as Nujol mulls. NMR spectra (^{1}H, 300.13; ^{13}C, 75.47; ^{19}F, 282.41; ^{31}P, 121.50 MHz; coupling constant values 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_4, quadruplet; q_5, quintuplet; m, unresolved multiplet.

Complexes (η^6-arene)(η^1-*P*-keto phosphine)RuCl$_2$, 1. Most of the complexes **1**−**3** were described previously.[13,17] New complexes **1** and **2** are required mainly as starting materials, and some procedures favored efficiency in yields relative to a high purity of compounds.

Synthesis of [(η^6-hexamethylbenzene)RuCl$_2$]$_2$. The synthesis of [(hexamethylbenzene)RuCl$_2$]$_2$ was adapted from a previously reported procedure.[20] A mixture consisting of a 10.0 g (16.3 mmol) sample of [(*p*-cymene)RuCl$_2$]$_2$ and 30 g (185 mmol) of hexamethylbenzene was coarsely powdered and then heated at 205 °C for 20 h. The solid obtained after cooling was stirred in hot toluene (250 mL) for 1 h. The powder that remains insoluble was separated from the hot solution by filtration and then washed with toluene (100 mL) and diethyl ether (150 mL). The orange powder so obtained was conveniently used as [(hexamethylbenzene)RuCl$_2$]$_2$ despite that this crude product retains some insoluble impurities. Yield: 10.5 g, 96%.

(hexamethylbenzene)[Ph$_2$PCH$_2$C(=O)Bu^t]RuCl$_2$, 1a. A mixture consisting of a 11.8 g (17.7 mmol) sample of [(hexamethylbenzene)RuCl$_2$]$_2$ and 10.1 g (35.5 mmol) of keto phosphine Ph$_2$PCH$_2$C(=O)Bu^t in dichloromethane (100 mL) was stirred for 6 h. The resulting dark red solution was filtered and the filtrate evaporated slowly to dryness. The weight of the residue (>24 g) indicated a retention of dichloromethane. Further stirring of the solid with ethanol (120 mL) afforded a red precipitate that was isolated by filtration and then washed with diethyl ether (50 mL) and dried. Yield: 19.5 g, 89%. The complex **1a** was checked simply by spectroscopy. IR, ν(C=O): 1698 cm^{-1}. ^{31}P{^{1}H} NMR, CDCl$_3$, δ: 26.9 (s). ^{1}H NMR, CDCl$_3$, δ: 8.03−7.39 (m, 10 H, Ph), 4.03 (d, 2 H, $^2J_{PH}$ = 9.1, PCH$_2$), 1.70 (d, 18 H, $^4J_{PH}$ = 0.9, C$_6$Me$_6$), 0.61 (s, 9 H, Bu^t). Indefinitely stable in air in the solid state, **1a** is a peculiarly convenient precursor of the well-characterized key-compound **2a**[13] but provides also a straightforward access to derivatives **4a** and **5a**.

(hexamethylbenzene)[Ph$_2$PCH(Me)C(=O)Bu^t]RuCl$_2$, 1b. A mixture consisting of a 9.97 g (14.9 mmol) sample of [(hexamethylbenzene)RuCl$_2$]$_2$ and 8.90 g (29.8 mmol) of keto phosphine Ph$_2$PCH(Me)C(=O)Bu^t in dichloromethane (80 mL) was stirred for 2 h. The resulting dark red solution was filtered and the filtrate evaporated to dryness. The residue was stirred with diethyl ether (100 mL) to afford a red precipitate that was collected by filtration and then washed with diethyl ether (50 mL) and dried. Yield: 17.3 g, 92%. IR, ν(C=O): 1696 cm^{-1}. ^{31}P{^{1}H} NMR, CDCl$_3$, δ: 32.5 (s). ^{1}H NMR, CDCl$_3$, δ: 8.35−7.30 (m, 10 H, Ph), 5.36 (dq$_4$, 1 H, $^2J_{PH}$ = 1.7, $^3J_{HH}$ = 7.2, PCH), 1.64 (d, 18 H, $^4J_{PH}$ = 0.5, C$_6$Me$_6$), 1.06 (s, 9 H, Bu^t), 0.92 (dd, 3 H, $^3J_{PH}$ = 16.5, $^3J_{HH}$ = 7.2, PCMe). Anal. Calcd for C$_{31}$H$_{41}$Cl$_2$OPRu: C, 58.86; H, 6.53; Cl, 11.21; P, 4.90. Found: C, 59.19; H, 6.63; Cl, 11.47; P, 4.91.

(hexamethylbenzene)[Ph$_2$PCH(Me)C(=O)Ph]RuCl$_2$·$^3/_4$CH$_2$Cl$_2$, 1b′. A mixture consisting of a 3.90 g (5.83 mmol) sample of [(hexamethylbenzene)RuCl$_2$]$_2$ and 3.76 g (11.8 mmol) of keto phosphine Ph$_2$PCH(Me)C(=O)Ph in dichloromethane (100 mL) was stirred for 20 h. The resulting solution was filtered and the dark red filtrate covered with hexane (400 mL) to afford orange red crystals. Yield: 6.20 g, 74%. IR, ν(C=O): 1670, 1665 cm^{-1}. ^{31}P{^{1}H} NMR, CDCl$_3$, δ: 32.8 (s). ^{1}H NMR, CDCl$_3$, δ: 8.37−7.13 (m, 15 H, Ph), 5.93 (dq$_4$, 1 H, $^2J_{PH}$ = 5.1, $^3J_{HH}$ = 7.1, PCH), *5.28 (s, CH$_2$Cl$_2$)*, 1.65 (s, 18 H, C$_6$Me$_6$), 1.00 (dd, 3 H, $^3J_{PH}$ = 16.1, $^3J_{HH}$ = 7.1, PCMe). Anal. Calcd for C$_{33}$H$_{37}$Cl$_2$OPRu·$^3/_4$CH$_2$Cl$_2$: C, 56.59; H, 5.42; Cl, 16.83; P, 4.32. Found: C, 56.88; H, 5.45; Cl, 17.59; P, 4.62. The high carbon and low chlorine values likely indicate an easy partial loss of dichloromethane.

(benzene)[Ph$_2$PCH(Me)C(=O)Bu^t]RuCl$_2$, 1g. A mixture consisting of a 2.19 g (4.38 mmol) sample of [(benzene)RuCl$_2$]$_2$[21] and 2.61 g (8.75 mmol) of keto phosphine Ph$_2$PCH(Me)C(=O)Bu^t in dichloromethane (50 mL) was stirred for 1 day. The resulting solution was filtered and the dark orange filtrate evaporated under vacuum. The addition of methanol (30 mL) to the residue and subsequent stirring of the mixture resulted in the formation of a crystalline precipitate. Diethyl ether (30 mL) was then added, and the slurry was kept overnight at −20 °C. The orange precipitate was collected by filtration and then washed with diethyl ether (30 mL) and dried. Yield: 3.00 g, 63%. IR, ν(C=O): 1692 cm^{-1}. ^{31}P{^{1}H} NMR, CDCl$_3$, δ: 30.6 (s). ^{1}H NMR, CDCl$_3$, δ: 8.34−7.32 (m, 10 H, Ph), 5.19 (s, 6 H, C$_6$H$_6$), 5.09 (dq$_4$, 1 H, $^2J_{PH}$ = 3.0, $^3J_{HH}$ = 7.3, PCH), 1.09 (s, 9 H, Bu^t), 1.03 (dd, 3 H, $^3J_{PH}$ = 16.8, $^3J_{HH}$ = 7.3, PCMe). Anal. Calcd for C$_{25}$H$_{29}$Cl$_2$OPRu: C, 54.75; H, 5.33; Cl, 12.93; P, 5.65. Found: C, 54.27; H, 5.36; Cl, 13.17; P, 5.89.

Complexes (η^6-arene)(η^2-*P*,*O*-phosphino enolato)RuCl, 2. (hexamethylbenzene)[Ph$_2$PCH=C(Ph)O]RuCl·$^1/_2$CH$_2$Cl$_2$, 2a′. A mixture consisting of a 4.08 g (6.10 mmol) sample of [(hexamethylbenzene)RuCl$_2$]$_2$ and 3.72 g (12.2 mmol) of keto phosphine Ph$_2$PCH$_2$C(=O)Ph in dichloromethane (50 mL) was stirred overnight, and the resulting red slurry was evaporated to dryness. Ethanol (80 mL) and then 0.70 g (12.5 mmol) of KOH were added to the residue to obtain a mixture that was heated at reflux overnight. The resulting slurry was filtered to isolate a yellow precipitate that was washed with ethanol (40 mL) and then extracted with dichloromethane (60 mL). The solution was filtered and the filtrate covered with hexane (150 mL) to afford orange crystals. Yield: 4.90 g, 62%. IR, ν(C=CO): 1517 cm^{-1}. ^{31}P{^{1}H} NMR, CDCl$_3$, δ: 52.5 (s). ^{1}H NMR, CDCl$_3$, δ: 7.85−7.18 (m, 15 H, Ph), *5.29 (s, 1 H, CH$_2$Cl$_2$)*, 4.98 (d, 1 H, $^2J_{PH}$ = 1.6, PCH), 1.84 (s, 18 H, C$_6$Me$_6$). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ: 182.7 (d, $^2J_{PC}$ = 17.9, =CO), 140.3 (d, $^1J_{PC}$ = 42.4, PhP, ipso), 138.4 (d, $^3J_{PC}$ = 14.1, PhC, ipso), 134.5 (d, $^2J_{PC}$ = 9.8, PhP, ortho), 133.2 (d, $^1J_{PC}$ = 60.2, PhP, ipso), 132.7 (d, $^3J_{PC}$ = 10.0, PhP, meta), 129.9 (d, $^4J_{PC}$ = 2.5, PhP, para), 129.8 (d, $^4J_{PC}$ = 2.3, PhP, para), 129.0 (s, PhC, para), 128.6 (d, $^3J_{PC}$ = 9.8, PhP, meta), 128.2 (s, PhC, ortho), 128.1 (d, $^2J_{PC}$ = 10.8, PhP, ortho), 127.4 (s, PhC, meta), 96.1 (d, $^2J_{PC}$ = 3.0, *C*$_6$Me$_6$), 78.3 (d, $^1J_{PC}$ = 62.0, PCH), 15.4 (s, C$_6$*Me*$_6$). ^{13}C NMR, CD$_2$Cl$_2$, δ (selected values): 182.7 (dd, $^2J_{HC}$ = 3.6, $^2J_{PC}$ = 17.6, =CO), 78.3 (dd, $^1J_{HC}$ = 164, $^1J_{PC}$ = 62.0, PCH). Anal. Calcd for C$_{32}$H$_{34}$ClOPRu·$^1/_2$CH$_2$Cl$_2$: C, 60.56; H, 5.47; Cl, 11.00; P, 4.81. Found: C, 60.58; H, 5.47; Cl, 10.91; P, 4.65.

(hexamethylbenzene)[Ph$_2$PC(Me)=C(Bu^t)O]RuCl, 2b. A mixture consisting of a 5.04 g (7.54 mmol) sample of [(hexamethylbenzene)RuCl$_2$]$_2$ and 4.50 g (15.1 mmol) of keto phosphine Ph$_2$PCH(Me)C(=O)Bu^t in dichloromethane (80 mL) was stirred overnight. The resulting red solution was filtered and the filtrate evaporated to dryness. Ethanol (120 mL) and then 0.85 g (15.2 mmol) of KOH were added to the residue. The mixture was stirred overnight, and the resulting orange

(20) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

(21) Winkhaus, G.; Singer, H. *J. Organomet. Chem.* **1967**, *7*, 487.

slurry was evaporated under vacuum. The residue was extracted with dichloromethane (50 mL) and the solution filtered to afford a dark orange filtrate that was slowly evaporated to dryness. The crude product so obtained was stirred with hot ethanol (60 mL), and the resulting slurry was cooled to −20 °C. The orange precipitate was collected by filtration and then washed with hexane (50 mL). Yield: 6.50 g, 72%. IR, ν(C═CO): 1525 cm^{-1}. ^{31}P{^{1}H} NMR, C_6D_6, δ: 66.8 (s). ^{1}H NMR, C_6D_6, δ: 8.05−7.05 (m, 10 H, Ph), 1.93 (d, 3 H, $^3J_{PH}$ = 10.9, PCMe), 1.60 (s, 18 H, C_6Me_6), 1.47 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ: 189.8 (d, $^2J_{PC}$ = 17.1, ═CO), 138.0 (d, $^1J_{PC}$ = 38.5, PhP, ipso), 136.4 (d, $^2J_{PC}$ = 10.4, PhP, ortho), 133.1 (d, $^3J_{PC}$ = 9.8, PhP, meta), 131.5 (d, $^1J_{PC}$ = 53.7, PhP, ipso), 130.0 (d, $^4J_{PC}$ = 2.4, PhP, para), 129.6 (d, $^4J_{PC}$ = 2.4, PhP, para), 128.7 (d, $^3J_{PC}$ = 9.8, PhP, meta), 127.7 (d, $^2J_{PC}$ = 10.4, PhP, ortho), 95.9 (d, $^2J_{PC}$ = 3.0, C_6Me_6), 79.3 (d, $^1J_{PC}$ = 56.2, PCMe), 38.9 (d, $^3J_{PC}$ = 11.6, CMe_3), 29.4 (s, CMe_3), 15.1 (s, C_6Me_6), 14.9 (s, $^2J_{PC}$ ∼ 0, PC*Me*). ^{13}C NMR, CD_2Cl_2, δ (selected values): 15.1 (q$_4$, $^1J_{HC}$ = 129, C_6Me_6), 14.9 (q$_4$, $^1J_{HC}$ = 126, PC*Me*). Anal. Calcd for $C_{31}H_{40}ClOPRu$: C, 62.46; H, 6.76; Cl, 5.95; P, 5.20. Found: C, 62.36; H, 6.93; Cl, 6.00; P, 5.08.

(hexamethylbenzene)[$Ph_2PC(Me)═C(Ph)O$]-RuCl·CH_2Cl_2, 2b′, from 1b′. A mixture consisting of a 3.60 g (5.03 mmol) sample of **1b′** and 0.35 g (6.25 mmol) of KOH in ethanol (80 mL) was stirred overnight and then heated at reflux for 2 h to afford an orange yellow slurry. The precipitate was collected by filtration and washed with water (50 mL) and then with ethanol (30 mL) and diethyl ether (30 mL). Yield: 3.40 g, 77%. Orange red crystals where one molecule of dichloromethane is retained were obtained after recrystallization from dichloromethane/hexane. IR, ν(C═CO): 1533 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 63.5 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.79−7.27 (m, 15 H, Ph), *5.28 (s, CH_2Cl_2)*, 1.80 (d, 18 H, $^4J_{PH}$ = 0.6, C_6Me_6), 1.71 (d, 3 H, $^3J_{PH}$ = 9.7, PCMe). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ: 181.0 (d, $^2J_{PC}$ = 20.8, ═CO), 141.2 (d, $^3J_{PC}$ = 13.4, PhC, ipso), 137.2 (d, $^1J_{PC}$ = 40.2, PhP, ipso), 136.4 (s, PhC, para), 136.3 (d, $^2J_{PC}$ = 9.8, PhP, ortho), 133.1 (d, $^3J_{PC}$ = 9.8, PhP, meta), 130.9 (d, $^1J_{PC}$ = 54.9, PhP, ipso), 130.4 (d, $^4J_{PC}$ = 2.4, PhP, para), 129.9 (d, $^4J_{PC}$ = 2.4, PhP, para), 128.9 (d, $^3J_{PC}$ = 9.8, PhP, meta), 128.8 (s, PhC, ortho), 127.9 (s, PhC, meta), 127.9 (d, $^2J_{PC}$ = 9.8, PhP, ortho), 96.1 (d, $^2J_{PC}$ = 3.3, C_6Me_6), 84.9 (d, $^1J_{PC}$ = 53.7, PCMe), 15.3 (s, PC*Me*), 15.2 (s, C_6Me_6). Anal. Calcd for $C_{33}H_{36}ClOPRu·CH_2Cl_2$: C, 58.25; H, 5.46; Cl, 15.17; P, 4.42. Found: C, 58.23; H, 5.46; Cl, 14.79; P, 4.49.

(mesitylene)[$Ph_2PC(Me)═C(Ph)O$]RuCl, 2d′. A mixture consisting of a 4.78 g (8.18 mmol) sample of [(mesitylene)-$RuCl_2]_2$[22] and 5.21 g (16.4 mmol) of keto phosphine Ph_2PCH-(Me)C(═O)Ph in dichloromethane (50 mL) was stirred for 2 days. The resulting dark red solution was filtered and the filtrate evaporated to dryness. The addition of ethanol (100 mL) to the residue and subsequent stirring of the mixture resulted in the formation of an orange slurry. KOH (0.93 g, 16.6 mmol) was added to the slurry, and the mixture was stirred overnight and then evaporated under vacuum to leave a brown residue that was extracted with dichloromethane (50 mL). The solution was filtered and the filtrate evaporated to leave the crude product. Recrystallization from hot ethanol (50 mL) afforded an orange pink powder that was collected by filtration and then washed twice with hexane (50 mL). Yield: 5.30 g, 56%. The product was found pure by NMR spectroscopy, but further recrystallization from hot toluene is required to obtain a sample of analytical purity. IR, ν(C═CO): 1542 cm^{-1}. ^{31}P{^{1}H} NMR, C_6D_6, δ: 65.0 (s). ^{1}H NMR, C_6D_6, δ: 8.14−7.05 (m, 15 H, Ph), 4.29 (s, 3 H, C_6H_3), 1.78 (d, 3 H, $^3J_{PH}$ = 10.2, PCMe), 1.74 (s, 9 H, C_6Me_3). Anal. Calcd for $C_{30}H_{30}$-ClOPRu: C, 62.77; H, 5.27; Cl, 6.18; P, 5.40. Found: C, 62.86; H, 5.18; Cl, 6.16; P, 5.49.

(22) (a) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605. (b) Bennett, M. A.; Ennett, J. P. *Organometallics* **1984**, *3*, 1365.

(benzene)[$Ph_2PC(Me)═C(Bu^t)O$]RuCl, 2g, from 1g. A mixture consisting of a 1.75 g (3.19 mmol) sample of **1g** and 0.20 g (3.57 mmol) of KOH in methanol (30 mL), was stirred for 1 h. The resulting brown solution was evaporated to dryness, and the residue was extracted with dichloromethane (30 mL). The solution was filtered and the filtrate evaporated to leave a crude product that was stirred for 5 h in a mixture of diethyl ether and hexane (1/1, 100 mL). The resulting orange precipitate was isolated by filtration and then washed with hexane (40 mL). Yield: 1.17 g, 72%. IR, ν(C═CO): 1524 cm^{-1}. ^{31}P{^{1}H} NMR, C_6D_6, δ: 70.1 (s). ^{1}H NMR, C_6D_6, δ: 8.07−7.07 (m, 10 H, Ph), 4.74 (s, 6 H, C_6H_6), 1.92 (d, 3 H, $^3J_{PH}$ = 11.5, PCMe), 1.49 (s, 9 H, Bu^t). Anal. Calcd for $C_{25}H_{28}$-ClOPRu: C, 58.65; H, 5.51; Cl, 6.92; P, 6.05. Found: C, 58.25; H, 5.58; Cl, 7.16; P, 6.12.

Complexes [(η^6-arene)(η^2-*P*,*O*-keto phosphine)RuCl]$^+$, 3. Formation of {(hexamethylbenzene)[Ph_2PCH_2C-(Bu^t)═O]RuCl}(BPh_4), 3a, from 2a. A mixture consisting of a 0.35 g (0.60 mmol) sample of **2a** and 0.21 g (0.61 mmol) of $NaBPh_4$ in methanol (30 mL) was stirred for 20 h. The resulting orange yellow slurry was evaporated under vacuum, and the residue was extracted with dichloromethane (20 mL). The solution was filtered and the filtrate covered with diethyl ether (100 mL) to afford orange red crystals of **3a**. Yield: 0.18 g, 33%. IR, ν(C═O): 1604 cm^{-1}. ^{31}P{^{1}H} NMR, $CDCl_3$, δ: 59.5 (s). ^{1}H NMR, $CDCl_3$, δ: 7.61−6.77 (m, 30 H, Ph), 3.92 (dd, 1 H, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 10.9, PCH_2, H_a), 3.44 (dd, 1 H, $^2J_{PH}$ = 9.7, PCH_2, H_b), 1.77 (d, 18 H, $^4J_{PH}$ = 0.7, C_6Me_6), 1.21 (s, 9 H, Bu^t). Anal. Calcd for $C_{54}H_{59}BClOPRu$: C, 71.88; H, 6.59; Cl, 3.93; P, 3.43. Found: C, 72.05; H, 6.65; Cl, 3.97; P, 3.32.

{**(hexamethylbenzene)[$Ph_2PCH(Me)C(Bu^t)$═O]RuCl**}-**(PF_6)·$^1/_4CH_2Cl_2$, 3b.** A mixture consisting of a 2.49 g (3.72 mmol) sample of [(hexamethylbenzene)$RuCl_2]_2$, 2.22 g (7.44 mmol) of keto phosphine $Ph_2PCH(Me)C(═O)Bu^t$, and 1.34 g (8.22 mmol) of NH_4PF_6 in methanol (40 mL) and dichloromethane (20 mL) was stirred overnight. The solvents were removed under vacuum, and the residue was extracted with dichloromethane (50 mL). The solution was filtered and the filtrate covered with diethyl ether (150 mL) to afford bright red crystals of **3b**. Yield: 5.00 g, 88%. IR, ν(C═O): 1598 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 77.7 (s, minor stereoisomer), 62.7 (s, major stereoisomer). ^{1}H NMR, CD_2Cl_2, δ, asterisk-marked values corresponding to the major (3/2) stereoisomer: 7.80−6.90 (m, 10 H, Ph), 4.09* and 3.86 (2 dq$_4$, 1 H, $^2J_{PH}$ = 11.1* and 12.7, $^3J_{HH}$ = 7.7* and 7.4, PCH), 1.86 and 1.84* (2 d, 18 H, $^4J_{PH}$ = 1.0 and 0.9*, C_6Me_6), 1.63 and 1.33* (2 dd, 3 H, $^3J_{PH}$ = 11.2 and 12.9*, $^3J_{HH}$ = 7.4 and 7.7*, PCMe), 1.38* and 1.30 (2 s, 9 H, Bu^t). Anal. Calcd for $C_{31}H_{41}ClF_6OP_2Ru·^1/_4CH_2Cl_2$: C, 49.16; H, 5.48; Cl, 6.97; P, 8.12. Found: C, 48.90; H, 5.54; Cl, 7.36; P, 8.04.

{**(hexamethylbenzene)[$Ph_2PCH(Me)C(Ph)$═O]RuCl**}-**(PF_6), 3b′, from 1b′.** A mixture consisting of a 1.30 g (1.81 mmol) sample of **1b′** and 0.32 g (1.96 mmol) of NH_4PF_6 in methanol (40 mL) and dichloromethane (15 mL) was stirred overnight. The resulting orange slurry was evaporated to dryness to leave a solid that was extracted with dichloromethane (35 mL). The solution was filtered and the filtrate covered with diethyl ether (100 mL) to afford bright orange red crystals of **3b′**. Yield: 1.36 g, 99%. IR, ν(C═O): 1561 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 79.1 (s, minor stereoisomer), 60.0 (s, major stereoisomer). ^{1}H NMR, CD_2Cl_2, δ, asterisk-marked values corresponding to the major (8/7) stereoisomer, available data: 8.09−7.00 (m, 15 H, Ph), 4.61* and 4.35 (2 dq$_4$, 1 H, $^2J_{PH}$ = 11.8*, $^3J_{HH}$ = 7.8*, PCH), 1.91 and 1.88* (2 d, 18 H, $^4J_{PH}$ = 0.8, C_6Me_6), 1.58 and 1.40* (2 dd, 3 H, $^3J_{PH}$ = 12.6*, $^3J_{HH}$ = 7.8*, PCMe). Anal. Calcd for $C_{33}H_{37}ClF_6OP_2$-Ru: C, 52.01; H, 4.89; Cl, 4.65; P, 8.13. Found: C, 52.12; H, 4.98; Cl, 4.95; P, 8.39.

{**(benzene)[$Ph_2PCH(Me)C(Bu^t)$═O]RuCl**}**(PF_6)·$^1/_2CH_2Cl_2$, 3g, from 1g.** According to a similar procedure, bright red crystals of **3g** were obtained in 52% yield starting from **1g**. IR, ν(C═O): 1567 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ:

76.5 (s, minor stereoisomer), 63.4 (s, major stereoisomer). ^{1}H NMR, CD_2Cl_2, δ, asterisk-marked values corresponding to the major (3/2) stereoisomer: 7.75−7.04 (m, 10 H, Ph), 5.81 and 5.65* (2 d, 6 H, $^3J_{PH}$ = 0.9 and 0.9*, C_6H_6), 4.17* and 3.91 (2 dq$_4$, 1 H, $^2J_{PH}$ = 11.7* and 12.3, $^3J_{HH}$ = 7.6* and 7.3, PCH), 1.52 and 1.37* (2 dd, 3 H, $^3J_{PH}$ = 12.0 and 13.8*, $^3J_{HH}$ = 7.3 and 7.6*, PCMe), 1.49* and 1.29 (2 s, 9 H, Bu^t). Anal. Calcd for $C_{25}H_{29}ClF_6OP_2Ru\cdot{}^1/_2CH_2Cl_2$: C, 43.72; H, 4.32; Cl, 10.12; P, 8.84. Found: C, 44.26; H, 4.20; Cl, 9.86; P, 9.08. The high carbon value resulted likely from some loss of dichloromethane.

{(mesitylene)[Ph$_2$PCH(Me)C(Ph)=O]RuCl}(PF$_6$), 3g′, from 2g′. To a stirred slurry of a 1.00 g (1.74 mmol) sample of **2g′** in ethanol (30 mL) was added 2.0 mL (an excess) of aqueous HPF_6 solution (60% in weight), resulting immediately in the formation of a yellow precipitate. The precipitate was collected by filtration and then washed with diethyl ether and dried. Yield: 0.88 g, 70%. Recrystallization of this crude product from a mixture of dichloromethane (20 mL) and methanol (60 mL) afforded bright red crystals of **3g′**. Yield: 0.48 g, 38%. IR, ν(C=O): 1550 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 78.4 (s, minor stereoisomer), 62.6 (s, major stereoisomer). ^{1}H NMR, CD_2Cl_2, δ, asterisk-marked values corresponding to the major (4/3) stereoisomer: 8.15−7.04 (m, 15 H, Ph), 5.16 and 5.02* (2 s, 3 H, C_6H_3), 4.61* and 4.40 (2 dq$_4$, 1 H, $^2J_{PH}$ = 10.8 and 12.1*, $^3J_{HH}$ = 7.7 and 7.8*, PCH), 2.09 and 2.06* (s and d*, 9 H, $^4J_{PH}$ = 0.8*, C_6Me_3), 1.51 and 1.46* (2 dd, 3 H, $^3J_{PH}$ = 11.2 and 13.0*, $^3J_{HH}$ = 7.7 and 7.8*, PCMe). Anal. Calcd for $C_{30}H_{31}ClF_6OP_2Ru$: C, 50.04; H, 4.34; Cl, 4.93; P, 8.60. Found: C, 50.22; H, 4.47; Cl, 4.87; P, 8.83.

Complexes (η^6-arene)(η^2-*P,O*-phosphinito enolato)-RuPh, 4. (hexamethylbenzene)[Ph(MeO)PCH=C(Bu^t)O]-RuPh, 4a, from 2a (or 1a). A mixture consisting of a 2.00 g (3.44 mmol) sample of **2a** and 0.50 g (5.09 mmol, an excess) of KOAc in methanol (50 mL) was heated at reflux for 25 h. After cooling, a yellow precipitate was collected by filtration. Recrystallization from a mixture of dichloromethane (15 mL) and methanol (70 mL) afforded yellow crystals of **4a**. Yield: 1.30 g, 65%. According to the same procedure, complex **4a** was obtained in a close yield, starting from **1a** and KOAc in methanol. IR, ν(C=CO): 1496 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 146.8 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.25−6.48 (m, broad, Ph), 5.30 (s, 1 H, PCH), 3.28 (d, 3 H, $^3J_{PH}$ = 10.9, OMe), 1.91 (d, 18 H, $^4J_{PH}$ = 0.5, C_6Me_6), 1.13 (s, 9 H, Bu^t). Anal. Calcd for $C_{31}H_{41}O_2PRu$: C, 64.45; H, 7.15; Cl, 0.00; P, 5.36. Found: C, 64.74; H, 7.14; Cl, 0.09; P, 5.57.

(hexamethylbenzene)[Ph(EtO)PCH=C(Bu^t)O]RuPh, 4′a, from 1a. A mixture consisting of a 2.00 g (3.23 mmol) sample of **1a** and 0.95 g (10.1 mmol, an excess) of KOAc in ethanol (50 mL) was heated at reflux for 30 h. The resulting yellow precipitate was collected by filtration, and subsequent recrystallization from a mixture of dichloromethane (15 mL) and methanol (80 mL) afforded yellow crystals of **4′a**. Yield: 1.07 g, 56%. IR, ν(C=CO): 1498 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 143.0 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.22−6.46 (m, 10 H, Ph), 4.28 (s, 1 H, PCH), 3.63 (ddq$_4$, 1 H, $^2J_{HH}$ = 9.8, $^3J_{PH}$ = 6.4, $^3J_{HH}$ = 7.0, OCH_2, H_a), 3.39 (ddq$_4$, 1 H, $^2J_{HH}$ = 9.8, $^3J_{PH}$ = 7.0, $^3J_{HH}$ = 7.0, OCH_2, H_b), 1.91 (s, 18 H, C_6Me_6), 1.23 (t, 3 H, $^3J_{HH}$ = 7.0, OCH_2*Me*), 1.12 (s, 9 H, Bu^t). Anal. Calcd for $C_{32}H_{43}O_2PRu$: C, 64.95; H, 7.32; Cl, 0.00. Found: C, 64.74; H, 7.27; Cl, 0.08.

(hexamethylbenzene)[Ph(MeO)PC(Me)=C(Bu^t)O]-RuPh, 4b, from 1b. A mixture consisting of a 2.00 g (3.16 mmol) sample of **1b** and 0.93 g (9.87 mmol, an excess) of KOAc in methanol (50 mL) was heated at reflux for 24 h. The resulting yellow precipitate was collected by filtration. Recrystallization from a mixture of dichloromethane (15 mL) and methanol (80 mL) afforded yellow crystals of **4b**. Yield: 1.00 g, 53%. IR, ν(C=CO): 1514 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 166.9 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.18−6.47 (m, 10 H, Ph), 3.29 (d, 3 H, $^3J_{PH}$ = 11.5, OMe), 1.80 (s, 18 H, C_6Me_6), 1.45 (d, 3 H, $^3J_{PH}$ = 10.4, PCMe), 1.14 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ: 193.7 (d, $^2J_{PC}$ = 20.5, =CO), 168.3 (d, $^2J_{PC}$ = 21.1, PhRu, ipso), 142.7 (broad, PhRu, ortho, 1-C), 136.8 (d, $^1J_{PC}$ = 64.5, PhP, ipso), 135.8 (broad, PhRu, meta, 2-C), 132.5 (d, $^3J_{PC}$ = 8.9, PhP, meta), 128.6 (d, $^4J_{PC}$ = 1.8, PhP, para), 127.2 (d, $^2J_{PC}$ = 9.7, PhP, ortho), 125.5 (broad, PhRu, ortho, 1-C), 120.6 (s, PhRu, para), 99.0 (d, $^2J_{PC}$ = 3.1, C_6Me_6), 84.5 (d, $^1J_{PC}$ = 52.3, P*C*Me), 51.5 (d, $^2J_{PC}$ = 5.3, OMe), 39.1 (d, $^3J_{PC}$ = 11.1, *C*Me$_3$), 28.9 (s, C*Me*$_3$), 15.8 (s, C_6*Me*$_6$), 13.8 (s, PC*Me*). Anal. Calcd for $C_{32}H_{43}O_2PRu$: C, 64.95; H, 7.32; P, 5.23. Found: C, 64.85; H, 7.35; P, 5.32.

(mesitylene)[Ph(MeO)PCH=C(Bu^t)O]RuPh, 4c, from 2c. A mixture consisting of a 1.96 g (3.63 mmol) sample of **2c** and 1.00 g (10.2 mmol, an excess) of KOAc in methanol (50 mL) was heated at reflux for 20 h. The hot solution was filtered, and the dark filtrate was cooled to −20 °C to afford yellow crystals that were washed twice with methanol (10 mL). Yield: 0.87 g, 45%. IR, ν(C=CO): 1494 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 154.8 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.22−6.42 (m, 10 H, Ph), 4.81 (s, 3 H, C_6H_3), 4.16 (d, 1 H, $^2J_{PH}$ = 0.7, PCH), 3.42 (d, 3 H, $^3J_{PH}$ = 11.8, OMe), 1.87 (s, 9 H, C_6Me_3), 1.16 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ: 201.4 (d, $^2J_{PC}$ = 16.9, =CO), 165.9 (d, $^2J_{PC}$ = 22.5, PhRu, ipso), 140.1 (very broad, PhRu, ortho and meta), 138.4 (d, $^1J_{PC}$ = 71.0, PhP, ipso), 131.6 (d, $^3J_{PC}$ = 9.1, PhP, meta), 129.1 (d, $^4J_{PC}$ = 2.2, PhP, para), 127.4 (d, $^2J_{PC}$ = 10.0, PhP, ortho), 125.5 (s, PhRu, para), 107.1 (d, $^2J_{PC}$ = 2.3, *C*Me, mesitylene), 84.8 (d, $^2J_{PC}$ = 4.5, CH, mesitylene), 77.3 (d, $^1J_{PC}$ = 56.9, PCH), 51.1 (d, $^2J_{PC}$ = 6.3, OMe), 38.2 (d, $^3J_{PC}$ = 11.5, *C*Me$_3$), 30.0 (s, C*Me*$_3$), 19.8 (s, C_6*Me*$_3$). Anal. Calcd for $C_{28}H_{35}O_2PRu$: C, 62.79; H, 6.59; Cl, 0.00; P, 5.78. Found: C, 62.69; H, 6.68; Cl, 0.09; P, 6.04.

(mesitylene)[Ph(MeO)PC(Me)=C(Bu^t)O]RuPh, 4d, from 1d. A mixture consisting of a 2.00 g (3.39 mmol) sample of **1d** and 1.66 g (16.9 mmol, an excess) of KOAc in methanol (50 mL) was heated at reflux for 25 h. After cooling, a yellow precipitate was separated by filtration from a dark green solution. This crude product was dissolved in dichloromethane (50 mL). The solution was filtered and the filtrate concentrated to ∼15 mL and then covered with methanol (90 mL) to afford large yellow crystals of **4d**. Yield: 1.30 g, 70%. IR, ν(C=CO): 1510 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 172.2 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.20−6.55 (m, 10 H, Ph), 3.46 (s, 3 H, C_6H_3), 3.46 (d, 3 H, $^3J_{PH}$ = 12.2, OMe), 1.85 (s, 9 H, C_6Me_3), 1.45 (d, 3 H, $^3J_{PH}$ = 11.0, PCMe), 1.23 (s, 9 H, Bu^t). ^{13}C{^{1}H} NMR, CD_2Cl_2, δ: 194.3 (d, $^2J_{PC}$ = 19.8, =CO), 166.5 (d, $^2J_{PC}$ = 21.4, PhRu, ipso), 137.2 (d, $^1J_{PC}$ = 73.6, PhP, ipso), 135.7 (broad, PhRu, ortho or meta), 131.9 (d, $^3J_{PC}$ = 8.8, PhP, meta), 128.6 (d, $^4J_{PC}$ = 2.3, PhP, para), 127.1 (d, $^2J_{PC}$ = 9.9, PhP, ortho), 125.5 (broad, PhRu, meta or ortho), 120.9 (s, PhRu, para), 106.9 (d, $^2J_{PC}$ = 1.9, *C*Me, mesitylene), 85.2 (d, $^2J_{PC}$ = 4.2, CH, mesitylene), 83.4 (d, $^1J_{PC}$ = 53.8, P*C*Me), 50.3 (d, $^2J_{PC}$ = 1.5, OMe), 39.5 (d, $^3J_{PC}$ = 11.4, *C*Me$_3$), 28.9 (s, C*Me*$_3$), 19.1 (s, C_6*Me*$_3$), 12.2 (s, PC*Me*). Anal. Calcd for $C_{29}H_{37}O_2PRu$: C, 63.37; H, 6.79; P, 5.64. Found: C, 63.30; H, 6.71; P, 5.87.

Hydride Complexes (η^6-arene)(η^2-*P,O*-phosphino enolato)RuH, 5, and Cp(PPh$_3$)$_2$RuH, 6. (hexamethylbenzene)-[Ph$_2$PCH=C(Bu^t)O]RuH, 5a, from 2a (or 1a). A mixture consisting of a 1.00 g (1.72 mmol) sample of **2a** and 0.36 g (2.61 mmol) of K_2CO_3 in methanol (50 mL) was heated at reflux overnight. The resulting yellow solution was evaporated under vacuum, and the residue was extracted with diethyl ether (30 mL). The solution was filtered and the filtrate evaporated to leave the crude product. Recrystallization from hot methanol (30 mL) afforded yellow crystals of **5a**. Yield: 0.67 g, 71%. According to the same procedure, complex **5a** was obtained in a similar yield starting from **1a** and K_2CO_3 in methanol. IR: ν(Ru−H), 1948 cm^{-1}; ν(C=CO), 1506 cm^{-1}. ^{31}P{^{1}H} NMR, CD_2Cl_2, δ: 60.4 (s). ^{1}H NMR, CD_2Cl_2, δ: 7.62−7.12 (m, 10 H, Ph), 4.27 (d, 1 H, $^2J_{PH}$ = 3.3, PCH), 1.85 (s, 18 H, C_6Me_6), 1.07 (s, 9 H, Bu^t), −8.78 (d, 1 H, $^2J_{PH}$ = 52.0, RuH). Anal. Calcd for $C_{30}H_{39}OPRu$: C, 65.79; H, 7.18; Cl, 0.00; P, 5.66. Found: C, 65.49; H, 7.06; Cl, 0.14; P, 5.60.

(hexamethylbenzene)[Ph$_2$PC(Me)=C(Bu^t)O]RuH, 5b, from 2b. A mixture consisting of a 1.24 g (2.08 mmol) sample

of **2b** and 0.43 g (3.12 mmol) of K_2CO_3 in methanol (50 mL) was heated at reflux for 3 h. The resulting yellow precipitate was separated by filtration and then washed twice with methanol (20 mL) and dried. Yield: 0.93 g, 80%. IR: ν(Ru−H), 1923 cm^{-1}; ν(C═CO), 1522 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 77.7 (s). ^1H NMR, CD_2Cl_2, δ: 7.79−7.15 (m, 10 H, Ph), 1.83 (s, 18 H, C_6Me_6), 1.66 (d, 3 H, $^3J_{PH}$ = 10.4, PCMe), 1.13 (s, 9 H, Bu^t), −8.76 (d, 1 H, $^2J_{PH}$ = 49.0, RuH). Anal. Calcd for $C_{31}H_{41}OPRu$: C, 66.29; H, 7.36; P, 5.51. Found: C, 66.19; H, 7.28; P, 5.39.

Cp(PPh$_3$)$_2$RuH, 6. A mixture consisting of a 0.51 g (0.70 mmol) sample of $Cp(PPh_3)_2RuCl$[23] and 0.12 g (0.89 mmol) of K_2CO_3 in methanol (25 mL) was heated at reflux for 0.5 h and then cooled to 0 °C. The resulting yellow precipitate was separated by filtration and then washed with methanol (15 mL) and dried. Yield: 0.39 g, 81%. The product was identified as $Cp(PPh_3)_2RuH$ from spectroscopic analysis.[15] IR, ν(Ru−H): 1969 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 68.1 (s). ^1H NMR, CD_2Cl_2, δ: 7.27−7.03 (m, 30 H, Ph), 4.26 (s, 5 H, Cp), −11.8 (t, 1 H, $^2J_{PH}$ = 33.6, RuH).

Complexes {(η^6-arene)Ru[η^3-*C,P,O*-CH═C(R″)C(R)(PPh$_2$)C(R′)═O]}(PF$_6$), 7−9. {(hexamethylbenzene)Ru[CH═C(Me)CH(PPh$_2$)C(Bu^t)═O]}(PF$_6$)·$^1/_4$CH$_2$Cl$_2$, 7a, from 2a. A ∼100 mL Schlenk flask containing a 0.40 g (0.69 mmol) sample of **2a** and 0.13 g (0.80 mmol) of NH_4PF_6 was filled with propyne (1 atm), and methanol (30 mL) was added *via* a syringe. The mixture was stirred overnight and then evaporated to dryness. The residue was extracted with dichloromethane (20 mL) and the solution filtered. The filtrate was covered with diethyl ether (100 mL) to afford orange yellow crystals of **7a**. Yield: 0.32 g, 62%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 124.2 (s). ^1H NMR, CD_2Cl_2, δ: 8.07 (m, 1 H, $RuCH_a$), 7.59−7.18 (m, 10 H, Ph), 4.76 (dd, 1 H, $^2J_{PH}$ = 10.1, $^4J_{H_aH}$ = 2.2, PCH), 2.11 (d, 18 H, $^4J_{PH}$ = 0.9, C_6Me_6), 1.85 (t_a, 3 H, $^4J_{H_aH}$ ∼ $^3J_{PH}$ ∼ 1.2, Me), 0.89 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 227.9 (d, $^2J_{PC}$ = 6.3, CO), 167.8 (d, $^2J_{PC}$ = 13.3, RuC), 134.9 (d, $^2J_{PC}$ = 13.0, ═*C*Me), 133.3 (d, $^3J_{PC}$ = 9.4, PhP, meta), 132.9 (d, $^4J_{PC}$ = 2.4, PhP, para), 132.6 (d, $^3J_{PC}$ = 11.5, PhP, meta), 132.3 (d, $^4J_{PC}$ = 2.2, PhP, para), 130.8 (d, $^1J_{PC}$ = 18.9, PhP, ipso), 129.9 (d, $^2J_{PC}$ = 9.0, PhP, ortho), 129.3 (d, $^2J_{PC}$ = 10.0, PhP, ortho), 127.3 (d, $^1J_{PC}$ = 51.4, PhP, ipso), 100.5 (d, $^2J_{PC}$ = 9.1, C_6Me_6), 70.0 (d, $^1J_{PC}$ = 27.9, PCH), 45.1 (d, $^3J_{PC}$ = 2.4, CMe_3), 26.0 (s, C*Me*$_3$), 23.3 (d, $^3J_{PC}$ = 4.7, ═C*Me*), 16.4 (s, C_6Me_6). ^{13}C NMR, CD_2Cl_2, δ (selected values): 167.8 (dm, $^1J_{HC}$ = 152, RuCH), 70.0 (dddq_4, $^1J_{HC}$ = 156, $^1J_{PC}$ = 28.0, $^3J_{HC}$ = 7.8 and 3.7, PCH). Anal. Calcd for $C_{33}H_{42}F_6OP_2Ru\cdot{}^1/_4CH_2Cl_2$: C, 53.04; H, 5.69; Cl, 2.35; P, 8.23. Found: C, 53.06; H, 5.81; Cl, 2.41; P, 7.84. Crystals free of dichloromethane were obtained after recrystallization from a methanol/diethyl ether mixture. Anal. Calcd for $C_{33}H_{42}F_6OP_2Ru$: C, 54.17; H, 5.79; P, 8.47. Found: C, 54.57; H, 5.80; P, 8.36.

{(hexamethylbenzene)Ru[CH═C(Me)C(Me)(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 7b, from 2b. According to the same procedure, a 0.81 g (1.36 mmol) sample of **2b** was reacted with propyne and 0.25 g (1.53 mmol) of NH_4PF_6 in methanol (40 mL). The resulting light yellow slurry was evaporated to dryness, and the residue was extracted with dichloromethane (35 mL). The solution was filtered, and diethyl ether (120 mL) was added to the filtrate. This solution was kept overnight at −20 °C to afford yellow crystals of **7b**. Yield: 0.60 g, 59%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 141.9 (s). ^1H NMR, $CDCl_3$, δ: 8.26 (m, 1 H, RuCH), 7.62−7.25 (m, 10 H, Ph), 2.00 (d, 18 H, $^4J_{PH}$ = 0.8, C_6Me_6), 1.82 (d, 3 H, $^4J_{HH}$ = 0.9, ═CMe), 1.71 (d, 3 H, $^3J_{PH}$ = 12.3, PCMe), 0.97 (s, 9 H, Bu^t). Anal. Calcd for $C_{34}H_{44}F_6OP_2Ru$: C, 54.76; H, 5.95; P, 8.31. Found: C, 54.42; H, 5.84; P, 8.69.

{(mesitylene)Ru[CH═C(Me)C(Me)(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 7d, from 2d. According to a similar procedure, a 0.38 g (0.69 mmol) sample of **2d** was reacted with propyne and 0.14 g (0.86 mmol) of NH_4PF_6 in methanol (30 mL) to afford orange crystals of **7d**. Yield: 0.41 g, 84%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 141.7 (s). ^1H NMR, $CDCl_3$, δ: 8.55 (m, 1 H, RuCH), 7.60−7.42 (m, 10 H, Ph), 5.25 (s, 3 H, C_6H_3), 2.12 (s, 9 H, C_6Me_3), 1.86 (s, broad, 3 H, ═CMe), 1.78 (d, 3 H, $^3J_{PH}$ = 12.4, PCMe), 0.99 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 228.0 (d, $^2J_{PC}$ = 8.5, CO), 167.5 (d, $^2J_{PC}$ = 13.4, RuC), 136.3 (d, $^2J_{PC}$ = 14.2, RuC═*C*), 134.5 (d, $^3J_{PC}$ = 8.9, PhP, meta), 133.2 (d, $^3J_{PC}$ = 10.7, PhP, meta), 133.1 (d, $^4J_{PC}$ = 2.4, PhP, para), 132.8 (d, $^4J_{PC}$ = 2.6, PhP, para), 129.9 (d, $^2J_{PC}$ = 8.9, PhP, ortho), 129.3 (d, $^2J_{PC}$ = 9.9, PhP, ortho), 129.1 (d, $^1J_{PC}$ = 17.5, PhP, ipso), 126.6 (d, $^1J_{PC}$ = 49.7, PhP, ipso), 109.8 (d, $^2J_{PC}$ = 1.2, C_6Me_3), 85.7 (d, $^2J_{PC}$ = 4.0, C_6H_3), 76.3 (d, $^1J_{PC}$ = 29.7, P*C*Me), 47.2 (d, $^3J_{PC}$ = 2.6, *C*Me$_3$), 26.3 (s, C*Me*$_3$), 20.7 (d, $^3J_{PC}$ = 5.3, ═C*Me*), 19.4 (s, C_6Me_3), 15.2 (d, $^2J_{PC}$ = 5.2, PC*Me*). ^{13}C NMR, CD_2Cl_2, δ (selected values): 167.4 (dm, $^1J_{HC}$ = 154, RuCH), 76.3 (dm, $^1J_{PC}$ ∼ 30, P*C*Me), 20.7 (q_4t_a, $^1J_{HC}$ = 127, $^3J_{HC}$ ∼ $^3J_{PC}$ ∼ 5.2, ═C*Me*), 15.2 (q_4d, $^1J_{HC}$ = 129, $^2J_{PC}$ = 5.1, PC*Me*). Anal. Calcd for $C_{31}H_{38}F_6OP_2Ru$: C, 52.92; H, 5.45; P, 8.80. Found: C, 52.88; H, 5.61; P, 8.85.

{(hexamethylbenzene)Ru[CH═C(Ph)CH(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 8a, from 2a. A mixture consisting of a 2.10 g (3.61 mmol) sample of **2a**, 0.60 g (3.68 mmol) of NH_4PF_6, and 1.30 mL (11.8 mmol) of phenylacetylene in methanol (80 mL) was stirred for 1 day. The mixture was then evaporated under reduced pressure and the residue extracted with dichloromethane (60 mL). The solution was filtered and the filtrate covered with diethyl ether (150 mL) to afford orange crystals of **8a**. Yield: 2.39 g, 83%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 125.2 (s). ^1H NMR, CD_2Cl_2, δ: 9.09 (dd, 1 H, $^3J_{PH}$ ∼ $^4J_{HH}$ ∼ 2.3, RuCH), 7.53−7.13 (m, 15 H, Ph), 5.51 (dd, 1 H, $^2J_{PH}$ = 10.2, $^4J_{HH}$ = 2.3, PCH), 2.12 (d, 18 H, $^4J_{PH}$ = 0.8, C_6Me_6), 0.79 (s, 9 H, Bu^t). Anal. Calcd. for $C_{38}H_{44}F_6OP_2Ru$: C, 57.50; H, 5.59; P, 7.80. Found: C, 57.80; H, 5.68; P, 8.10.

{(hexamethylbenzene)Ru[CH═C(Ph)C(Me)(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 8b, from 2b. Orange crystals of **8b** were similarly obtained in 68% yield by reacting **2b** with phenylacetylene and $NaPF_6$ in methanol. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 147.0 (s). ^1H NMR, CD_2Cl_2, δ: 8.71 (d, 1 H, $^3J_{PH}$ = 2.7, RuCH), 7.55−6.39 (m, 15 H, Ph), 2.02 (d, 18 H, $^4J_{PH}$ = 0.8, C_6Me_6), 1.70 (d, 3 H, $^3J_{PH}$ = 12.4, PCMe), 1.06 (s, 9 H, Bu^t). Anal. Calcd for $C_{39}H_{46}F_6OP_2Ru$: C, 57.99; H, 5.74; P, 7.67. Found: C, 58.03; H, 5.74; P, 7.89.

{(mesitylene)Ru[CH═C(Ph)C(Me)(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 8d, from 2d. A mixture consisting of a 0.51 g (0.92 mmol) sample of **2d**, 0.20 g (1.23 mmol) of NH_4PF_6, and 0.15 mL (1.37 mmol) of phenylacetylene in methanol (30 mL) was stirred for 1 day and then evaporated to dryness. The residue was extracted with dichloromethane (15 mL). The solution was filtered and the filtrate covered with diethyl ether (100 mL) to afford orange crystals of **8d**. Yield: 0.64 g, 91%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 147.9 (s). ^1H NMR, $CDCl_3$, δ: 8.87 (d, 1 H, $^3J_{PH}$ = 2.8, RuCH), 7.64−6.40 (m, 15 H, Ph), 5.35 (s, 3 H, C_6H_3), 2.11 (s, 9 H, C_6Me_3), 1.73 (d, 3 H, $^3J_{PH}$ = 12.4, PCMe), 1.10 (s, 9 H, Bu^t). Anal. Calcd for $C_{36}H_{40}F_6OP_2Ru$: C, 56.47; H, 5.27; P, 8.09. Found: C, 56.24; H, 5.13; P, 7.80.

{(hexamethylbenzene)Ru[CH═C(*p*-tolyl)CH(PPh$_2$)C(Bu^t)═O]}(PF$_6$), 9a, from 2a. Orange crystals of **9a** were similarly obtained in 66% yield by reacting **2a** with 4-ethynyltoluene and NH_4PF_6 in methanol. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 124.2 (s). ^1H NMR, $CDCl_3$, δ: 8.99 (dd, 1 H, $^3J_{PH}$ = 1.8, $^4J_{HH}$ = 2.2, RuCH), 7.55−7.00 (m, 14 H, Ph and C_6H_4), 5.50 (dd, 1 H, $^2J_{PH}$ = 10.2, $^4J_{HH}$ = 2.2, PCH), 2.28 (s, 3 H, C_6H_4Me), 2.14 (s, 18 H, C_6Me_6), 0.75 (s, 9 H, Bu^t). Anal. Calcd for $C_{39}H_{46}F_6OP_2Ru$: C, 57.99; H, 5.74; P, 7.67. Found: C, 57.60; H, 5.63; P, 7.86.

Complexes {(η^6-arene)Ru[η^3-*C,P,O*-CH(PPh$_2$)C(R″)═CHC(Bu^t)═O]}(PF$_6$), 7′a−9′a. {(hexamethylbenzene)Ru[CH(PPh$_2$)C(Me)═CHC(Bu^t)═O]}(PF$_6$), 7′a, from 7a. A mixture consisting of a 0.29 g (0.39 mmol) sample of **7a** in ethanol (30 mL) was heated at reflux for 20 h and then evaporated to dryness. The residue was dissolved in chloro-

(23) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

form (10 mL) and this solution covered with diethyl ether (100 mL) to afford dark orange crystals of **7′a**. Yield: 0.16 g, 56%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 4.3 (s). ^1H NMR, $CDCl_3$, δ: 7.54−7.39 (m, 10 H, Ph), 4.78 (d, 1 H, $^4J_{PH}$ = 12.2, =CH), 2.33 (s, 3 H, Me), 2.10 (d, 18 H, $^4J_{PH}$ = 0.9, C_6Me_6), 1.64 (d, 1 H, $^2J_{PH}$ = 11.0, PCH), 0.71 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 212.2 (s, CO), 134.4 (d, $^3J_{PC}$ = 12.4, PhP, meta), 133.3 (d, $^4J_{PC}$ = 3.2, PhP, para), 132.6 (d, $^4J_{PC}$ = 3.1, PhP, para), 131.9 (d, $^3J_{PC}$ = 10.8, PhP, meta), 130.2 (d, $^2J_{PC}$ = 12.4, PhP, ortho), 130.1 (d, $^2J_{PC}$ = 12.5, PhP, ortho), 124.9 (d, $^1J_{PC}$ = 68.8, PhP, ipso), 121.4 (d, $^1J_{PC}$ = 52.0, PhP, ipso), 107.3 (d, $^2J_{PC}$ = 4.8, =*C*Me), 102.4 (d, $^2J_{PC}$ = 1.4, *C*$_6$Me$_6$), 51.0 (d, $^3J_{PC}$ = 5.6, =CH), 47.0 (d, $^1J_{PC}$ = 34.6, PCH), 45.0 (s, *C*Me$_3$), 26.3 (s, C*Me*$_3$), 17.3 (d, $^3J_{PC}$ = 7.9, =C*Me*), 16.7 (s, C$_6$*Me*$_6$). ^{13}C NMR, CD_2Cl_2, δ (selected values): 51.0 (dm, $^1J_{HC}$ = 154, =CH), 47.0 (ddq$_5$, $^1J_{HC}$ = 173, $^1J_{PC}$ = 35, $^3J_{HC}$ ∼ 5, PCH). Anal. Calcd for $C_{33}H_{42}F_6OP_2Ru$: C, 54.17; H, 5.79; P, 8.47. Found: C, 54.19; H, 5.67; P, 8.00.

{(hexamethylbenzene)Ru[CH(PPh$_2$)C(Ph)=CHC(Bu^t)=O]}(PF$_6$), 8′a, from 8a. Isomerization Induced Thermally. A solution consisting of a 2.39 g (3.01 mmol) sample of **8a** in a mixture of dichloromethane (15 mL) and ethanol (45 mL) was heated at reflux for 4 days to afford a dark red solution. The solvents were removed under vacuum and the crude product recrystallized fractionally from dichloromethane (20 mL)/diethyl ether (100ml) to afford dark purple crystals of **8′a**. Yield: 1.94 g, 81%.

Isomerization Catalyzed by the Fluoride Anion. Dichloromethane (10 mL) and then methanol (30 mL) were added into a mixture consisting of a 0.48 g (0.60 mmol) sample of **8a** and 0.17 g (large excess) of powdered NaF. This reaction mixture was stirred for 10 days, but a change in color was already observed after 1 day. The mixture was then evaporated under vacuum, and the residue was extracted with dichloromethane (30 mL). The solution was filtered and the dark filtrate covered with diethyl ether (110 mL) to afford dark purple crystals of **8′a**. Yield: 0.34 g, 71%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 5.4 (s). ^1H NMR, CD_2Cl_2, δ: 7.71−7.06 (m, 15 H, Ph), 6.02 (dd, 1 H, $^4J_{HH}$ = 1.3, $^4J_{PH}$ = 2.0, =CH), 3.75 (dd, 1 H, $^2J_{PH}$ = 6.7, PCH), 2.02 (d, 18 H, $^4J_{PH}$ = 0.9, C_6Me_6), 0.72 (s, 9 H, Bu^t). Anal. Calcd for $C_{38}H_{44}F_6OP_2Ru$: C, 57.50; H, 5.59; P, 7.80. Found: C, 57.43; H, 5.37; P, 7.87.

{(hexamethylbenzene)Ru[CH(PPh$_2$)C(*p*-tolyl)=CHC(Bu^t)=O]}(PF$_6$), 9′a, from 9a. Isomerization Induced Thermally. Starting from **9a**, dark purple crystals of **9′a** were obtained in 63% according to the procedure detailed above.

Isomerization Catalyzed by the Fluoride Anion. A 0.81 g (1.00 mmol) sample of **9a** was dissolved in dichloromethane (15 mL). Methanol (45 mL) was added and then 10 mL of a saturated aqueous solution of NaF (∼1 mmol). The mixture was stirred for 8 days, but a change in color was already observed after 1 h. Subsequent work as detailed above afforded dark purple crystals of **9′a**. Yield: 0.59 g, 73%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 5.5 (s). ^1H NMR, $CDCl_3$, δ: 7.62−7.05 (m, 14 H, Ph and C_6H_4), 5.96 (dd, 1 H, $^4J_{HH}$ = 1.2, $^4J_{PH}$ = 1.8, =CH), 3.78 (dd, 1 H, $^2J_{PH}$ = 7.0, PCH), 2.46 (s, 3 H, Me), 2.03 (s, 18 H, C_6Me_6), 0.71 (s, 9 H, Bu^t). Anal. Calcd for $C_{39}H_{46}F_6OP_2Ru$: C, 57.99; H, 5.74; P, 7.67. Found: C, 58.12; H, 5.71; P, 7.65.

Coupling Products Involving Ethyne. {(hexamethylbenzene)Ru[CH=CHCH(PPh$_2$)C(Bu^t)=O]}[PF$_6$ or BPh$_4$], 10a, from 2a. As the PF$_6$ Salt. A ∼150 mL Schlenk flask containing a 1.00 g (1.72 mmol) sample of **2a** and 0.30 g (1.84 mmol) of NH_4PF_6 was filled with ethyne (1 atm), and methanol (50 mL) was added *via* a syringe. After being stirred for 1 day, the mixture was evaporated under reduced pressure and the residue was extracted with dichloromethane (40 mL). The solution was filtered and the solvent was then removed under vacuum to afford an orange solid (1.22 g) containing ∼75% of the expected product as monitored by ^1H NMR spectroscopy. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 129.5 (s), additional weaker resonances at δ 58.9 (s) and 32.6 (s). ^1H NMR, $CDCl_3$, δ: 8.71 (ddd, 1 H, $^3J_{HH}$ = 6.3, $^4J_{HH}$ = 1.7, $^3J_{PH}$ = 2.5, RuCH), 7.56−7.22 (m, 10 H, Ph), 6.30 (ddd, 1 H, $^3J_{HH}$ = 6.3 and 4.7, $^3J_{PH}$ = 16.7, =CH), 5.08 (ddd, 1 H, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.7, $^2J_{PH}$ = 10.4, PCH), 2.14 (s, 18 H, C_6Me_6), 0.83 (s, 9 H, Bu^t). Attempts of recrystallization from dichloromethane/diethyl ether invariably failed.

As the BPh$_4$ Salt. A ∼150 mL Schlenk flask containing a 0.49 g (0.84 mmol) sample of **2a** and 0.30 g (0.88 mmol) of $NaBPh_4$ was filled with ethyne (1 atm), and methanol (20 mL) was added. The mixture was stirred for 1 day, and the resulting yellow precipitate was separated by filtration and washed with water (20 mL) and then with ethanol (20 mL) and diethyl ether (50 mL). Yield: 0.62 g, 83%. This crude product was found pure by NMR spectroscopy. Bright yellow crystals were obtained after cooling a satured solution in tepid methanol (60 mL) to −20 °C. Yield: 0.38 g, 51%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 129.7 (s). ^1H NMR, CD_2Cl_2, δ: 8.79 (ddd, 1 H, $^3J_{HH}$ = 6.3, $^4J_{HH}$ = 1.6, $^3J_{PH}$ = 2.4, RuCH), 7.60−6.87 (m, 30 H, Ph), 6.28 (ddd, 1 H, $^3J_{HH}$ = 6.3 and 4.7, $^3J_{PH}$ = 16.8, =CH), 5.01 (ddd, 1 H, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.6, $^2J_{PH}$ = 10.3, PCH), 2.12 (d, 18 H, $^4J_{PH}$ = 0.5, C_6Me_6), 0.87 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 227.2 (d, $^2J_{PC}$ = 6.6, CO), 177.6 (d, $^2J_{PC}$ = 10.9, RuC), 164.5 (q$_4$, $^1J_{BC}$ = 49.2, PhB, ipso), 136.4 (m, PhB, ortho), 133.3 (d, $^3J_{PC}$ = 9.2, PhP, meta), 133.2 (d, $^4J_{PC}$ = 2.1, PhP, para), 132.9 (d, $^3J_{PC}$ = 11.7, PhP, meta), 132.5 (d, $^4J_{PC}$ = 2.6, PhP, para), 130.4 (part of d, PhP, ipso), 130.1 (d, $^2J_{PC}$ = 9.7, PhP, ortho), 129.4 (d, $^2J_{PC}$ = 10.0, PhP, ortho), 126.7 (d, $^1J_{PC}$ = 49.0, PhP, ipso), 126.1 (q$_4$, $^3J_{BC}$ = 2.7, PhB, meta), 125.3 (d, $^2J_{PC}$ = 12.2, RuC=*C*), 122.2 (s, PhB, para), 101.0 (d, $^2J_{PC}$ = 3.0, *C*$_6$Me$_6$), 65.9 (d, $^1J_{PC}$ = 28.7, PCH), 45.1 (d, $^3J_{PC}$ = 2.6, *C*Me$_3$), 25.7 (s, C*Me*$_3$), 16.6 (s, C$_6$*Me*$_6$). ^{13}C NMR, CD_2Cl_2, δ (selected values): 177.6 (ddd, $^1J_{HC}$ = 155, $^2J_{HC}$ ∼ $^1J_{PC}$ ∼ 10.0, RuCH), 125.3 (dddd, $^1J_{HC}$ = 173, $^2J_{PC}$ = 12.2, $^2J_{HC}$ = 4.6 and 3.3, RuC=*C*H), 65.9 (dm, $^1J_{HC}$ = 147, PCH). Anal. Calcd for $C_{56}H_{60}BOPRu$: C, 75.41; H, 6.78; P, 3.47. Found: C, 75.22; H, 6.86; P, 3.34.

{(hexamethylbenzene)Ru[CH(PPh$_2$)CH=CHC(Bu^t)=O]}(PF$_6$), 10′a, from 10a. A sample of crude **10a** as the PF_6 salt was heated in ethanol at reflux for 20 h. The resulting mixture was evaporated under vacuum to leave a dark residue, the ^1H and $^{31}P\{^1H\}$ NMR spectra of which were found promising, but we failed to obtain a more tractable material. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 6.1 (s). ^1H NMR, CD_2Cl_2, δ: 7.57−7.34 (m, 10 H, Ph), 5.59 (ddd, 1 H, $^3J_{HH}$ = 7.7 and 5.6, $^3J_{PH}$ = 25.8, PCCH=), 4.57 (ddd, 1 H, $^3J_{HH}$ = 5.6, $^4J_{HH}$ = 1.0, $^4J_{PH}$ = 12.2, =CHCO), 2.10 (s, 18 H, C_6Me_6), 1.89 (ddd, 1 H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.0, $^2J_{PH}$ = 9.6, PCH), 0.80 (s, 9 H, Bu^t).

{(hexamethylbenzene)Ru[CH=CHC(Me)(PPh$_2$)C(Bu^t)=O]}(PF$_6$), 10b, from, 2b. A ∼120 mL Schlenk flask containing a 1.00 g (1.68 mmol) sample of **2b** and 0.30 g (1.84 mmol) of NH_4PF_6 was filled with ethyne (1 atm), and methanol (50 mL) was then added. After being stirred for 1 day, the mixture was evaporated to dryness. The remaining solid was extracted with dichloromethane (20 mL) to obtain a yellow solution that was filtered and then covered with diethyl ether (100 mL) to afford yellow crystals of **10b**. Yield: 1.07 g, 87%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 145.0 (s). ^1H NMR, CD_2Cl_2, δ: 8.78 (dd, 1 H, $^3J_{HH}$ = 6.3, $^3J_{PH}$ = 2.6, RuCH), 7.62−7.24 (m, 10 H, Ph), 5.92 (dd, 1 H, $^3J_{PH}$ = 18.2, =CH), 2.00 (d, 18 H, $^4J_{PH}$ = 0.9, C_6Me_6), 1.79 (d, 3 H, $^3J_{PH}$ = 11.7, Me), 0.99 (s, 9 H, Bu^t). Anal. Calcd for $C_{33}H_{42}F_6OP_2Ru$: C, 54.17; H, 5.79; P, 8.47. Found: C, 53.92; H, 5.85; P, 8.33.

{(hexamethylbenzene)Ru[CH=CHC(Me)(PPh$_2$)C(Ph)=O]}(PF$_6$), 10b′, from 2b′. Starting from **2b′** instead of **2b**, dark orange crystals of **10b′** were similarly obtained in 53% yield. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 150.2 (s). ^1H NMR, CD_2Cl_2, δ: 9.02 (dd, 1 H, $^3J_{HH}$ = 6.2, $^3J_{PH}$ = 2.9, RuCH), 7.63−7.17 (m, 15 H, Ph), 5.89 (dd, 1 H, $^3J_{PH}$ = 17.6, =CH), 2.04 (s, 18 H, C_6Me_6), 1.74 (d, 3 H, $^3J_{PH}$ = 11.5, PCMe). Anal. Calcd for $C_{35}H_{38}F_6OP_2Ru$: C, 55.92; H, 5.10; P, 8.24. Found: C, 55.65; H, 5.11; P, 8.08.

(hexamethylbenzene)[$Ph_2PCH_2CH{=}CHC(=O)Bu^t$]-$RuCl_2 \cdot {}^1/_4CH_2Cl_2$, 11, from 2a. A ~150 mL Schlenk flask containing a 0.69 g (1.19 mmol) sample of **2a** and 0.21 g (1.29 mmol) of NH_4PF_6 was filled with ethyne (1 atm), and methanol (30 mL) was then added. After being stirred overnight at room temperature, the mixture was heated at reflux for 20 h. The resulting dark brown solution was cooled to −20 °C to obtain a red crystalline precipitate that was separated by filtration and then washed with ethanol (30 mL) and diethyl ether. Yield: 0.18 g, 23%. The yield was unchanged when NH_4Cl (1 mol/Ru) was added to the mixture before heating. Bright red needles were obtained after recrystallization from dichloromethane (20 mL)/diethyl ether (120 mL). IR, ν(C=CC=O): 1686, 1611 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 31.9 (s). ^1H NMR, $CDCl_3$, δ: 7.81−7.33 (m, 10 H, Ph), 6.47 (ddt, 1 H, $^3J_{PH} = 4.1$, $^3J_{HH} = 15.1$ and 8.3, PCCH), 5.93 (ddt, 1 H, $^4J_{PH} = 3.7$, $^3J_{HH} = 15.1$, $^4J_{HH} = 1.0$, HCCO), 3.56 (ddd, 2 H, $^2J_{PH} = 10.1$, $^3J_{HH} = 8.3$, $^4J_{HH} = 1.0$, PCH_2), 1.66 (s, 18 H, C_6Me_6), 0.81 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 203.0 (d, $^4J_{PC} = 2.3$, CO), 140.5 (d, $^2J_{PC} = 13.0$, PC*C*H), 134.9 (d, $^3J_{PC} = 8.8$, PhP, meta), 131.4 (d, $^4J_{PC} = 2.3$, PhP, para), 129.4 (d, $^1J_{PC} = 39.2$, PhP, ipso), 128.5 (d, $^3J_{PC} = 8.1$, H*C*CO), 128.3 (d, $^2J_{PC} = 9.4$, PhP, ortho), 96.7 (d, $^2J_{PC} = 3.1$, C_6Me_6), 42.8 (s, *C*Me_3), 32.0 (d, $^1J_{PC} = 24.1$, PCH_2), 26.0 (s, C*Me*$_3$), 15.5 (s, C_6*Me*$_6$). ^{13}C NMR, CD_2Cl_2, δ (selected values): 140.5 (ddq$_4$, $^1J_{HC} = 157$, $^2J_{PC} = 12.8$, $^2J_{HC} = 6.1$, PC*C*H), 32.0 (tddd, $^1J_{HC} = 135$, $^1J_{PC} = 24.2$, $^2J_{HC} = 5.7$, $^3J_{HC} = 3.7$, PCH_2). Anal. Calcd for $C_{32}H_{41}PCl_2ORu \cdot {}^1/_4CH_2Cl_2$: C, 58.17; H, 6.28; Cl, 13.31; P, 4.65. Found: C, 57.90; H, 6.29; Cl, 12.83; P, 4.88.

Coupling Products Involving (Trimethylsilyl)acetylene, 12 and 13. {(hexamethylbenzene)Ru[CH=C($SiMe_3$)-CH(PPh_2)C(Bu^t)=O]}(PF_6), 12a, from 2a. A mixture consisting of a 1.24 g (2.13 mmol) sample of **2a**, 0.36 g (2.15 mmol) of $NaPF_6$, and 0.50 mL (3.54 mmol) of (trimethylsilyl)acetylene in methanol (40 mL), was stirred for 20 h. The mixture was then evaporated under vacuum and the residue extracted with dichloromethane (30 mL). The solution was filtered and the filtrate evaporated to leave a solid that was dissolved in hot methanol (30 mL). This solution was cooled and then kept at −20 °C for several days to obtain yellow brown crystals of **12a**. Yield: 0.32 g, 19%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 136.8 (s). ^1H NMR, CD_2Cl_2, δ: 9.30 (dd, 1 H, $^3J_{PH} = 3.0$, $^4J_{HH} = 1.7$, RuCH), 7.57−7.12 (m, 10 H, Ph), 5.09 (dd, 1 H, $^2J_{PH} = 9.4$, PCH), 2.07 (d, 18 H, $^4J_{PH} = 0.8$, C_6Me_6), 1.07 (s, 9 H, Bu^t), −0.20 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 228.6 (d, $^2J_{PC} = 6.3$, CO), 191.1 (d, $^2J_{PC} = 10.8$, RuC), 141.6 (d, $^2J_{PC} = 9.0$, =CSi), 134.9 (d, $^3J_{PC} = 9.9$, meta), 132.8 (d, $^4J_{PC} = 2.7$, para), 132.7 (d, $^4J_{PC} = 2.7$, para), 131.9 (part of d, ipso), 131.6 (d, $^3J_{PC} = 10.8$, meta), 129.9 (d, $^2J_{PC} = 9.0$, ortho), 129.2 (d, $^2J_{PC} = 9.9$, ortho), 126.3 (d, $^1J_{PC} = 52.1$, ipso), 101.6 (d, $^2J_{PC} = 2.7$, C_6Me_6), 68.4 (d, $^1J_{PC} = 22.4$, PCH), 45.1 (d, $^3J_{PC} = 2.7$, *C*Me_3), 27.4 (s, C*Me*$_3$), 16.3 (s, C_6*Me*$_6$), −0.3 (s, $SiMe_3$). ^{13}C NMR, CD_2Cl_2, δ (selected values): 191.1 (dt$_a$, $^1J_{HC} = 153$, $^3J_{HC} \sim {}^2J_{PC} \sim 10.3$, RuC), 68.4 (ddd, $^1J_{HC} = 147$, $^3J_{HC} = 12.6$, $^1J_{PC} = 21.5$, PCH). Anal. Calcd for $C_{35}H_{48}F_6OP_2RuSi$: C, 53.22; H, 6.13; P, 7.84. Found: C, 53.55; H, 6.19; P, 7.41.

Recovery of Supplementary Product as the BPh_4 Salt. Additional crystals of **12a** (0.21 g) were obtained after addition of diethyl ether to the mother solution, but they were contaminated with a small amount of a yellow crystalline powder analyzed by NMR spectroscopy as a mixture of **14a** and **15a**. This material was dissolved in a concentrated (0.35 g/30 mL) solution of $NaBPh_4$ in methanol. The slow evaporation of the resulting yellow solution afforded orange yellow crystals of the pure BPh_4 salt (0.12 g). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 137.3 (s). ^1H NMR, $CDCl_3$, δ: 9.26 (dd, 1 H, $^3J_{PH} = 3.0$, $^4J_{HH} = 1.7$, RuCH), 7.60−6.84 (m, 30 H, Ph), 5.05 (dd, 1 H, $^2J_{PH} = 9.4$, PCH), 1.98 (d, 18 H, $^4J_{PH} = 0.8$, C_6Me_6), 1.08 (s, 9 H, Bu^t), −0.18 (s, 9 H, $SiMe_3$). Anal. Calcd for $C_{59}H_{68}BOPRuSi$: C, 73.50; H, 7.11; P, 3.21. Found: C, 73.55; H, 6.96; P, 3.13.

{(hexamethylbenzene)Ru[CH=C($SiMe_3$)CH(PPh_2)C-(Ph)=O]}(PF_6), 12a′, from 2a′. A mixture consisting of a 1.05 g (1.63 mmol) sample of **2a′**, 0.30 g (1.79 mmol) of $NaPF_6$, and 0.60 mL (4.25 mmol, an excess) of (trimethylsilyl)acetylene in dichloromethane (20 mL) was diluted with methanol (40 mL) and then stirred for 20 h. The resulting orange slurry was evaporated to dryness and the residue extracted with dichloromethane (30 mL). The solution was filtered and the filtrate covered with diethyl ether (120 mL) to afford dark orange crystals of **12a′**. Yield: 0.65 g, 49%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 134.1 (s). ^1H NMR, CD_2Cl_2, δ: 9.42 (dd, 1 H, $^3J_{PH} = 2.9$, $^4J_{HH} = 1.6$, RuCH), 8.04−7.03 (m, 15 H, Ph), 5.51 (dd, 1 H, $^2J_{PH} = 9.5$, PCH), 2.10 (d, 18 H, $^4J_{PH} = 0.8$, C_6Me_6), −0.42 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 208.5 (d, $^2J_{PC} = 6.6$, CO), 190.5 (d, $^2J_{PC} = 10.9$, RuC), 141.0 (d, $^2J_{PC} = 9.0$, =CSi), 136.4 (s, *Ph*C, para), 134.0 (d, $^3J_{PC} = 10.3$, PhP, meta), 133.1 (d, $^1J_{PC} = 20.5$, PhP, ipso), 133.0 (d, $^4J_{PC} = 2.4$, PhP, para), 132.5 (d, $^3J_{PC} = 3.6$, *Ph*C, ipso), 132.3 (d, $^4J_{PC} = 1.7$, PhP, para), 130.4 (d, $^3J_{PC} = 9.1$, PhP, meta), 130.3 (s, *Ph*C, ortho), 130.2 (s, *Ph*C, meta), 129.9 (d, $^2J_{PC} = 8.2$, PhP, ortho), 129.1 (d, $^2J_{PC} = 10.8$, PhP, ortho), 126.3 (d, $^1J_{PC} = 53.1$, PhP, ipso), 102.0 (d, $^2J_{PC} = 2.9$, C_6Me_6), 65.5 (d, $^1J_{PC} = 23.5$, PCH), 16.3 (s, C_6*Me*$_6$), −1.6 (s, $SiMe_3$). ^{13}C NMR, CD_2Cl_2, δ (selected values): 190.5 (ddd, $^1J_{HC} = 154$, $^3J_{HC} = 10.1$, $^2J_{PC} = 10.9$, RuC), 132.5 (dt, $^3J_{PC} = 3.5$, $^2J_{HC} = 8.1$, *Ph*C, ipso). Anal. Calcd for $C_{37}H_{44}F_6OP_2SiRu$: C, 54.88; H, 5.48; P, 7.65. Found: C, 54.48; H, 5.51; P, 7.59.

{(hexamethylbenzene)Ru[C(=CH_2)C(Me)(PPh_2)C-(Bu^t)=O]}(PF_6), 13b, from 2b. To a solution of a 1.50 g (2.52 mmol) sample of **2b** in dichloromethane (10 mL) were added 0.54 g (3.22 mmol) of $NaPF_6$ and then methanol (40 mL) and 0.50 mL (3.54 mmol) of (trimethylsilyl)acetylene, and this mixture was stirred overnight. Diethyl ether (60 mL) was added to the resulting yellow slurry, and the yellow precipitate was collected by filtration. Yield: 1.11 g, ~60%. The ^1H NMR spectrum is very similar to the spectrum of the related complex **13d**[17] but revealed the presence (~10%) of **3b** as its PF_6 salt. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 67.8 (s). ^1H NMR, $CDCl_3$, δ: 7.69−7.44 (m, 10 H, Ph), 5.70 (dd, 1 H, $^2J_{HH} = 2.0$, $^4J_{PH} = 8.3$, $=CH_2$, H_a), 5.51 (dd, 1 H, $^4J_{PH} = 5.3$, $=CH_2$, H_b), 2.11 (d, 18 H, $^4J_{PH} = 1.0$, C_6Me_6), 1.78 (d, 3 H, $^3J_{PH} = 12.3$, PCMe), 0.70 (s, 9 H, Bu^t). The contaminant was retained after a fast recrystallization from a dichloromethane/diethyl ether mixture, whereas a slow recrystallization from a dichloromethane/methanol mixture afforded crystals but of **14b** in 16% yield (0.30 g).

Metallafuran Complexes {(η^6-arene)(Ph_2PX)Ru[η^2-*C*,*O*-C(Me)=C(R)C(R′)=O]}(PF_6), 14 and 15. {(hexamethylbenzene)(Ph_2PF)Ru[C(Me)=CHC(Bu^t)=O]}(PF_6), 14a, from 2a. A mixture consisting of a 1.24 g (2.13 mmol) sample of **2a**, 0.35 g (2.15 mmol) of NH_4PF_6, and 0.50 mL (3.54 mmol) of (trimethylsilyl)acetylene in methanol (40 mL) was stirred for 20 h. The mixture was heated to dissolve the resulting yellow precipitate and the hot solution filtered. Orange yellow crystals of **14a** formed while the filtrate was kept overnight at room temperature. Yield: 0.19 g, 12%. IR, ν(C=CC=O): 1520 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 182.6 (d, $^1J_{FP} = 923$). $^{19}F\{^1H\}$ NMR, CD_2Cl_2, δ: −73.4 (d, $^1J_{PF} = 710$, PF_6), −149.3 (d, $^1J_{PF} = 923$, Ph_2PF). ^1H NMR, CD_2Cl_2, δ: 7.66−7.00 (m, 10 H, Ph), 6.47 (t$_a$, 1 H, $^4J_{PH} \sim {}^4J_{HH} \sim 1.1$, =CH), 2.80 (d, 3 H, $^4J_{HH} = 1.0$, RuCMe), 2.04 (s, 18 H, C_6Me_6), 1.02 (s, 9 H, Bu^t). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 256.0 (d, $^2J_{PC} = 19.8$, RuC), 222.5 (s, CO), 134.7 (dd, $^1J_{PC} = 46.2$, $^2J_{FC} = 13.9$, PhP, ipso), 133.8 (dd, $^1J_{PC} = 51.6$, $^2J_{FC} = 15.7$, PhP, ipso), 133.0 (d, $^4J_{PC} = 1.8$, PhP, para), 132.3 (s, RuC=*C*), 131.9 (d, $^4J_{PC} = 1.8$, PhP, para), 130.1 (dd, $^2J_{PC} = 15.3$, $^3J_{FC} = 3.6$, PhP, ortho), 129.7 (d, $^3J_{PC} = 11.7$, PhP, meta), 128.9 (d, $^3J_{PC} = 10.8$, PhP, meta), 128.9 (dd, $^2J_{PC} = 12.6$, $^3J_{FC} = 3.6$, PhP, ortho), 106.3 (d, $^2J_{PC} = 1.9$, C_6Me_6), 41.6 (s, *C*Me_3), 34.7 (d, $^3J_{PC} = 4.5$, RuC*Me*), 28.1 (s, C*Me*$_3$), 16.2 (s, C_6*Me*$_6$). Anal. Calcd for $C_{32}H_{41}F_7OP_2Ru$: C, 52.10; H, 5.60; P, 8.40. Found: C, 51.88; H, 5.61; P, 8.56.

{(hexamethylbenzene)(Ph_2PF)Ru[C(Me)=C(Me)C-(Bu^t)=O]}(PF_6), 14b, from 13b. As reported above, yellow crystals of **14b** were obtained when a slow crystallization of crude **13b** was attempted. Under the same conditions, the

close complex **13d** (arene = mesitylene instead of hexamethylbenzene) was detected to undergo the same transformation in affording the previously described complex **14d**.[17] $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 182.0 (d, $^1J_{FP}$ = 925). ^1H NMR, $CDCl_3$, δ: 7.58−6.86 (m, 10 H, Ph), 2.67 (s, 3 H, RuCMe), 1.98 (d, 18 H, $^4J_{PH}$ = 0.3, C_6Me_6), 1.56 (s, 3 H, RuCCMe), 1.02 (s, 9 H, Bu^t). Anal. Calcd for $C_{33}H_{43}F_7OP_2Ru$: C, 52.73; H, 5.77; P, 8.24. Found: C, 52.72; H, 5.87; P, 8.12.

{(mesitylene)(Ph_2PF)Ru[C(Me)=C(Me)C(Ph)=O]}(PF_6), 14d′, from 2d′. A mixture consisting of 0.75 g (1.31 mmol) of **2d′**, 0.22 g (1.35 mmol) of NH_4PF_6, and 0.30 mL (2.12 mmol) of (trimethylsilyl)acetylene in ethanol (30 mL) was stirred for 20 h and then evaporated under vacuum. The residue was extracted with dichloromethane (30 mL), and the resulting solution was filtered and then evaporated to leave a crude product that was recrystallized from hot methanol to afford orange crystals of **14d′**. Yield: 0.10 g, 10%. IR, ν(C=CC=O): 1520 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 184.4 (d, $^1J_{FP}$ = 931). $^{19}F\{^1H\}$ NMR, CD_2Cl_2, δ: −73.1 (d, $^1J_{PF}$ = 711, PF_6), −144.7 (d, $^1J_{PF}$ = 931, Ph_2PF). ^1H NMR, CD_2Cl_2, δ: 7.73−6.91 (m, 15 H, Ph), 5.39 (s, 3 H, C_6H_3), 2.97 (s, 3 H, RuCMe), 2.18 (s, 9 H, C_6Me_3), 1.59 (s, 3 H, RuCCMe). Anal. Calcd for $C_{32}H_{33}F_7OP_2Ru$: C, 52.68; H, 4.56; P, 8.49. Found: C, 52.90; H, 4.58; P, 8.54.

{(hexamethylbenzene)(Ph_2PCl)Ru[C(Me)=CHC(Bu^t)=O]}(PF_6), 15a, from 2a. A mixture consisting of a 1.24 g (2.13 mmol) sample of **2a**, 0.36 g (2.15 mmol) of $NaPF_6$, and 0.50 mL (3.54 mmol) of (trimethylsilyl)acetylene in dichloromethane (20 mL) was diluted with ethanol (40 mL). After being stirred for 2 days, the mixture was evaporated to leave a solid that was extracted with dichloromethane (30 mL). The solution was filtered and the filtrate evaporated. The residue was dissolved in 25 mL of hot methanol to afford a brown solution that deposited a mixture of orange crystals consisting of **15a** and **14a** in a 9/1 ratio, while standing overnight at room temperature. Yield: 0.14 g, 9%. The addition of diethyl ether (25 mL) to the mother liquor and subsequent cooling at −20 °C resulted in the formation of crystals of **12a** together with a little amount of **15a**. IR, ν(C=CC=O): 1524 cm^{-1}. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 126.1 (s). ^1H NMR, $CDCl_3$, δ: 7.72−6.92 (m, 10 H, Ph), 6.48 (q_4, 1 H, $^4J_{HH}$ = 0.9, =CH), 2.93 (d, 3 H, $^4J_{HH}$ = 0.9, RuCMe), 1.92 (d, 18 H, $^4J_{PH}$ = 0.7, C_6Me_6), 0.88 (s, 9 H, Bu^t). Owing to the presence of **14a** (∼10%), elemental analysis is provided only as the evidence of the presence of chlorine. Anal. Calcd for $C_{32}H_{41}ClF_6OP_2Ru$: Cl, 4.70; P, 8.21. Found: Cl, 4.27; P, 8.21.

{(mesitylene)(Ph_2PCl)Ru[C(Me)=C(Me)C(Bu^t)=O]Ru}(PF_6), 15d, from 2d. A mixture consisting of a 1.02 g (1.84 mmol) sample of **2d**, 0.32 g (1.96 mmol) of NH_4PF_6, and 0.40 mL (2.83 mmol) of (trimethylsilyl)acetylene in methanol (30 mL) was stirred for 2 h. The mixture was then heated at reflux for 15 h to obtain a yellow brown solution that was evaporated to dryness. The residue was extracted with dichloromethane (30 mL). The resulting solution was filtered, and the filtrate was covered with diethyl ether (140 mL) to afford yellow brown crystals of **15d**. Yield: 0.37 g, 28%. IR, ν(C=CC=O): 1527 cm^{-1}. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 126.1 (s). ^1H NMR, CD_2Cl_2, δ: 7.90−6.98 (m, 10 H, Ph), 5.17 (s, 3 H, C_6H_3), 2.95 (s, 3 H, RuCMe), 2.09 (s, 9 H, C_6Me_3), 1.69 (s, 3 H, RuCCMe), 0.91 (s, 9 H, Bu^t). Anal. Calcd for $C_{30}H_{37}ClF_6OP_2Ru$: C, 49.63; H, 5.14; Cl, 4.88; P, 8.53. Found: C, 49.66; H, 5.19; Cl, 4.70; P, 8.43.

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