

Reactions of Ruthenium(0) Phosphine Complexes with Diphenylacetylene

Anthony F. Hill,* Madeleine Schultz, and Anthony C. Willis

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory, Australia

Received July 7, 2004

Heating diphenylacetylene with $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ in toluene under reflux provides the 2-phenylindenone complex $[\text{Ru}(\eta^4\text{-O}=\text{CCPh}=\text{CHC}_6\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$, arising from C–H activation of one *ortho*-proton of diphenylacetylene, hydroruthenation of the triple bond, and cyclization incorporating one carbonyl ligand. Both phosphines are replaced by 1,2-bis-(diphenylphosphino)ethane to provide $[\text{Ru}(\eta^4\text{-O}=\text{CCPh}=\text{CHC}_6\text{H}_4)(\text{CO})(\text{dppe})]$. In contrast, heating diphenylacetylene with $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ in toluene under reflux generates the tetraphenylcyclopentadienone complex $[\text{Ru}(\eta^4\text{-O}=\text{CC}_4\text{Ph}_4)(\text{CO})_2(\text{PPh}_3)]$ in high yield, via [2+2+1] alkyne and CO cyclization. The crystal structures of $[\text{Ru}(\eta^4\text{-O}=\text{CCPh}=\text{CHC}_6\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ru}(\eta^4\text{-O}=\text{CCPh}=\text{CHC}_6\text{H}_4)(\text{CO})(\text{dppe})]$, $[\text{Ru}(\eta^4\text{-O}=\text{CC}_4\text{Ph}_4)(\text{CO})_2(\text{PPh}_3)]$, and $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ solvates are reported.

Introduction

The ruthenium(0) complex $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**) has been shown to undergo facile substitution of one phosphine by diphenylacetylene to yield the simple alkyne complex $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**).¹ A similar reaction occurs with diphenylbutadiyne;² however, with the α,ω -diyne 4,7,10-trithiatrideca-2,11-diyne (TTDD) remarkably facile (ambient conditions) co-cyclization of the diyne with coordinated CO occurs to provide a coordinated cyclopentadienone complex, $[\text{Ru}\{\kappa\text{-S},\eta^4\text{-O}=\text{C}(\text{CMe}=\text{CSC}_2\text{H}_4)_2\text{S}\}(\text{CO})(\text{PPh}_3)]$ (**3**).³ In contrast, the less labile starting material $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ (**4**) has been reported to react with diphenylacetylene only in refluxing benzene in the presence of carbon dioxide, to form the coordinated tetraphenylcyclopentadienone complex $[\text{Ru}(\eta^4\text{-O}=\text{CC}_4\text{Ph}_4)(\text{CO})_2(\text{PPh}_3)]$ (**5**) apparently as a mixture of isomers.⁴ Given this disparity in the reaction conditions required for the formation of **3** and **5**, the curious use of CO_2 to activate **4**, and the apparent neglect of **2** as a mechanistic candidate en route to **5**, we have now reinvestigated the reactions of diphenylacetylene with both **1** and **4**. Under thermal conditions (toluene reflux) these two compounds react very differently.

Results and Discussion

As reported by Roper,¹ under ambient conditions the complex **1** reacts cleanly with diphenylacetylene to provide the zerovalent alkyne complex $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**). Given the importance of this

complex to further discussions, we have acquired $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR data in addition to placing the compound on a firm structural footing through a crystallographic analysis. Indeed, despite an enormously rich chemistry of alkynes on ruthenium carbonyl clusters,⁵ there exist remarkably few structural data for simple mononuclear ruthenium(0) alkyne adducts, these being limited to the complexes $[\text{Ru}(\eta\text{-F}_3\text{CC}\equiv\text{CCF}_3)(\text{CO})_4]$ ⁶ and $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PEt}_3)_2]$,⁷ the latter being most akin to **2**. The geometry at ruthenium can be deduced from the appearance of two $\nu(\text{CO})$ IR absorptions [Nujol: 1959, 1895 cm^{-1}] and one $^{31}\text{P}\{^1\text{H}\}$ NMR signal ($\delta = 42.5$, C_6D_6) as being trigonal bipyramidal with axial phosphines and the alkyne lying in the equatorial plane to maximize retrodonation from the π -basic ruthenium center. The *trans* disposition of the phosphines is further confirmed by the characteristic virtual triplets observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the carbon atoms (*ipso*, *ortho/meta*) of the PC_6H_5 groups. Infrared data for a range of complexes of the form $[\text{Ru}(\text{L})(\text{CO})_2(\text{PPh}_3)_2]$ have been previously collated,⁸ and from these it is apparent that in this system $\text{PhC}\equiv\text{CPh}$ is a weaker *net* acceptor ligand than a range of carbon π -acids, such as CS_2 . The dichotomy between alkynes acting as two- or four-electron donors is normally discussed in terms of the $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of the alkyne carbon nuclei, because these are known to be particularly sensitive to the electronic environment. The alkyne carbon nuclei in **2** resonate at $\delta = 109.3$, in a region typical of two-electron alkyne ligands,⁹ to low field of that for free $\text{PhC}\equiv\text{CPh}$ (CDCl_3 : $\delta = 89.4$).

* To whom correspondence should be addressed. E-mail: a.hill@anu.edu.au.

(1) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60–61.

(2) Alcock, N. W.; Hill, A. F.; Melling, R. P.; Thompsett, A. R. *Organometallics* **1993**, *12*, 641–648.

(3) Hill, A. F.; Rae, A. D.; Schultz, M.; Willis, A. C. *Organometallics* **2004**, *23*, 81–85.

(4) Yamazaki, H.; Taira, Z. *J. Organomet. Chem.* **1999**, *578*, 61–67.

(5) Sappa, E. *J. Cluster Sci.* **1994**, *5*, 211–263.

(6) Marinelli, G.; Streib, W. E.; Huffman, J. C.; Caulton, K. G.; Gagné, M. R.; Takats, J.; Dartiguenave, M.; Chardon, C.; Jackson, S. A.; Eisenstein, O. *Polyhedron* **1990**, *9*, 1867–1881.

(7) Ogasawara, M.; Maseras, F.; Gallego-Planas, N.; Kawamura, K.; Ito, K.; Toyota, K.; Streib, W. E.; Komiya, S.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 1979–1993.

(8) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1990**, *395*, 195–206.

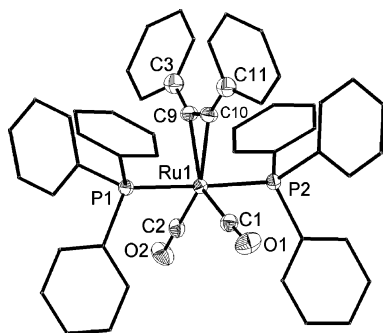


Figure 1. Molecular geometry of **2** in the crystal of $2 \cdot C_6H_6$ (40% probability ellipsoids, phenyl groups simplified). Selected bond distances (Å) and angles (deg): Ru1–P1 2.3666(6), Ru1–P2 2.3718(6), Ru1–C1 1.901(2), Ru1–C2 1.906(2), Ru1–C9 2.159(2), Ru1–C10 2.161(2), C9–C10 1.273(3), P1–Ru1–P2 177.13(2), C1–Ru1–C2 108.0(1), P1–Ru1–C1 93.47(7), P2–Ru1–C1 90.77(7), P1–Ru1–C2 89.16(7), P2–Ru1–C1 89.28(7), Ru1–C3–C9 141.0(2), Ru1–C10–C11 141.3(2).

The molecular structure of **2** is depicted in Figure 1, which confirms the geometry suggested by spectroscopic data. The geometry of the “Ru(CO)₂(PPh₃)₂” fragment calls for little comment, with interphosphine and intercarbonyl angles of 177.13(2)° and 108.0(1)°, respectively, and Ru–P and Ru–C bond lengths that fall within existing norms for ruthenium(0). Interest centers on the alkyne ligand, data for which are presented in Table 1, along with those for [M(η -F₃CC≡CCF₃)(CO)₄] (M = Ru, Os)⁶ and [Ru(η -PhC≡CPh)(CO)₂(PEt₃)₂].⁷ The ruthenium π -basicity increases in the order RuL₄ = Ru(CO)₄ < Ru(CO)₂(PPh₃)₂ < Ru(CO)₂(PEt₃)₂, and so it might be expected that the geometric parameters for the alkyne coordination in **2** would be intermediate, given simple Dewar–Chatt–Duncanson arguments. However, the replacement of PEt₃ with the less basic PPh₃ does not result in statistically significant (3–4 σ) changes in either the C≡C or Ru–C bond lengths. Structural data for the perfluorobut-2-yne complex⁶ reveal significantly shorter Ru–C bond lengths, though not at the expense of the C≡C bond; however it should be emphasized that perfluorobut-2-yne is an exceptionally π -acidic and poorly σ -basic alkyne. Thus, for the complexes in Table 1 it appears that the crystallographic data are insufficiently precise to assess the minimal geometric response of subtle electronic variations in the ligand set basicity.

Prolonged reflux of a toluene solution of **1** with excess PhC≡CPh results in a color change from pale yellow to deep red and the formation of two major ruthenium-containing products. The predominant product **6** precipitates from the reaction, and a minor product identified as **5** may be purified by column chromatography (Scheme 1). The formation of **5** results from ligand redistribution on ruthenium under these conditions and is discussed further below. The major product **6** is obtained in over 75% yield (both by ³¹P{¹H} NMR spectroscopy and isolated) upon heating a toluene solution of preisolated **2** under reflux, with insignificant

formation of **5**. Heating a toluene solution of **2** under reflux in the presence of additional PhC≡CPh also leads to the formation of **6**, as might be expected, in addition to small amounts of **5**. The compound **6** was also the only tractable material isolated in small amounts from the complex reaction mixture obtained from [Ru(CO)(CNC₆H₃Me₂-2,6)(PPh₃)₃] and PhC≡CPh under similar conditions. The spectroscopic data for **6** did not unequivocally suggest a formulation for the product, in part due to the complexity of the aryl region of both the ¹H and ¹³C{¹H} NMR spectra. Curiously, the infrared spectrum included absorptions in regions typical of both terminal [CH₂Cl₂: 1931] and ketonic carbonyl groups [1583 cm⁻¹]. The formulation of **6** as an indenone complex, [Ru(η^4 -O=CCPh=CHC₆H₄)(CO)(PPh₃)₂], eventually followed from a crystallographic study, the results of which are summarized in Figure 2. It is of note that **6** is a structural isomer of **2**, with identical chemical composition.

The geometry of the “Ru(CO)(PPh₃)₂” fragment of **6** is unremarkable, with parameters falling within conventional norms for a piano-stool geometry.^{10–16} Some steric congestion is expected with *cis*-PPh₃ groups, and the P1–Ru–P2 angle is 105.74(3)°. This congestion is manifest in both the ³¹P{¹H} NMR spectra and the reactivity of the complex (see below). The germane structural features concern the effect of coordination on the indenone ligand. Free 2-phenyl-1-indenone¹⁷ has not been structurally characterized; however the crystal structure of 2,3-diphenyl-1-indenone¹⁸ provides a point of reference for assessing the geometrical perturbations accompanying complexation. Figure 3 displays structural data for the indenone skeletons of both 2,3-diphenyl-1-indenone and **6** (ring numbering as for Figure 2), and it is immediately apparent that the somewhat localized bonds of the five-membered ring in the free ligand become delocalized upon coordination to the metal, the most dramatic change being to the bond C(9)–C(10), which increases by 0.1 Å. In contrast, the bonding in the six-membered benzo ring appears to become more localized upon coordination relative to the conventional aromatic nature of the benzo ring of free

(10) Structural data for piano stool complexes of the “*fac*-Ru(0)(CO)(PPh₃)₂” fragment are limited to the complexes [Ru(CO)(PPh₃)₂(L)] (L = Me₂Si(CH₂)₂)¹¹ and H₂C=CMeCH=O).¹² Divalent examples include the neutral complex [Ru(CO)(PPh₃)₂(η^5 -C₂B₉H₁₁)]¹³ and the cationic examples [Ru(CO)(PPh₃)₂(L)]⁺ (L = η -C₅H₅^{14,15} and η^5 -C₉H₇¹⁶). For these complexes, Ru–P and Ru–C distances span the ranges 2.322–2.402 and 1.8331–1.890 Å, respectively, with the shorter Ru–C distances being associated with the Ru(0) complexes and no obvious correlation between Ru–P bond length and oxidation state or charge. The P–Ru–P angles span the range 97.8–104.9°, while P–Ru–C angles are generally smaller (86.1–97.8°). The angle-sums for the three angles of each complex range from 280.5° to 296.7°, reflecting geometries between pseudooctahedral and tetrahedral.

(11) Paulasaari, J. K.; Moiseeva, N.; Bau, R.; Weber, W. P. *J. Organomet. Chem.* **1999**, *587*, 299–303.

(12) Hiraki, K.; Nonaka, A.; Matsunaga, T.; Kawano, H. *J. Organomet. Chem.* **1999**, *574*, 121–132.

(13) Ellis, D. D.; Couchman, S. M.; Jeffery, J. C.; Malget, J. M.; Stone, F. G. A. *Inorg. Chem.* **1999**, *38*, 2981–2988.

(14) Doyle, G.; van Engen, D. *J. Organomet. Chem.* **1985**, *280*, 253–259.

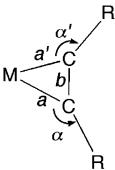
(15) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, *100*, 115–123.

(16) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117–131.

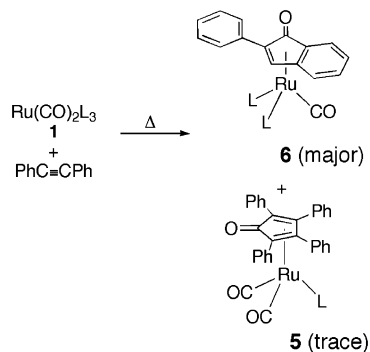
(17) Free 2-phenylindenone is unstable with respect to pyrolytic dimerization: Wawzonek, S.; Hansen, G. R.; Zigman, A. R. *Chem. Commun.* **1969**, 6.

(18) Watson, W. H.; Nagl, A. *Acta Crystallogr. C* **1987**, *43*, 2444–2445.

(9) For discussions of ¹³C{¹H} NMR chemical shifts for coordinated alkynes see: (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1–100. (b) Cooke, J.; Takats, J. *J. Am. Chem. Soc.* **1997**, *119*, 11088–11089. (c) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oro, L. A.; Valero, C. *J. Organomet. Chem.* **1994**, *468*, 223–228.

Table 1. Comparison of Geometric Parameters for Mononuclear Alkyne Complexes of Ruthenium


complex	α	α'	a	a'	b
$[\text{Ru}(\text{PhC}\equiv\text{CPh})(\text{CO})_2(\text{PEt}_3)_2]^7$	138.0(2)	139.4(2)	2.1538(2)	2.1538(2)	1.286(3)
$[\text{Ru}(\text{PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$	141.0(2)	141.3(2)	2.159(2)	2.161(2)	1.273(3)
$[\text{Ru}(\text{F}_3\text{CC}\equiv\text{CCF}_3)(\text{CO})_4]^6$	145.4(3)	145.3(3)	2.128(4)	2.121(4)	1.276(6)
$[\text{Os}(\text{F}_3\text{CC}\equiv\text{CCF}_3)(\text{CO})_4]^6$	146.2(11)	146.2(11)	2.149(12)	2.135(12)	1.276(2)

Scheme 1. Reaction of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ with $\text{PhC}\equiv\text{CPh}$ in Refluxing Toluene ($L = \text{PPh}_3$)

indenone. Thus, an alternation of long and short bonds emerges around the C(3)–C(8) ring. These observations presumably reflect significant involvement of the π -system of the five-membered ring with the ruthenium center at the expense of the aromaticity of the six-membered ring, which develops 4,6-cyclohexadiene character. Notably, the 2-phenyl group is oriented so as to allow conjugation with the indenone π -system.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** reflects its planar chirality, such that two distinct resonances are observed for the two diastereotopic phosphorus nuclei at all temperatures (–80 to +100 °C) around δ 43 and 44. However, rather than the anticipated AB system of two doublets, the resonances appear as broad peaks at room temperature (CDCl_3 : $\nu_{1/2} = 70$; CD_2Cl_2 : $\nu_{1/2} = 25$; $(\text{CDCl}_2)_2$: $\nu_{1/2} = 85$; C_6D_6 : $\nu_{1/2} = 100$ Hz). Heating or cooling the sample does not lead to resolution of the coupling; the chemical shifts and line widths change with temperature, while the resonances remain broad. The broadness of these resonances is presumably related to synchronous rotation of the triphenylphosphine ligands being sterically hindered by their adjacent disposition. A plot of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** in CD_2Cl_2 from –80 to 40 °C is shown in Figure 4, while the corresponding plot in $(\text{CDCl}_2)_2$ from 25 to 100 °C is included in the Supporting Information. In the ^1H NMR spectrum in CD_2Cl_2 at room temperature, the unique olefinic proton is observed at δ 5.04. This appears as a doublet ($^3J(\text{PH}) = 4$ Hz, 298 K), presumably showing coupling only to the phosphorus atom that is *pseudo-trans* to this proton, the implication being that the “Ru(CO)(PPh₃)₂” fragment does not freely rotate about the axis normal to the indenone ligand plane. This resonance broadens as the sample is heated or cooled. The $^{13}\text{C}\{^1\text{H}\}$ spectrum at room temperature displays resonances for metal-bound (δ 210.1) and ketonic (δ 164.8) carbonyl carbon nuclei, the former resonance showing

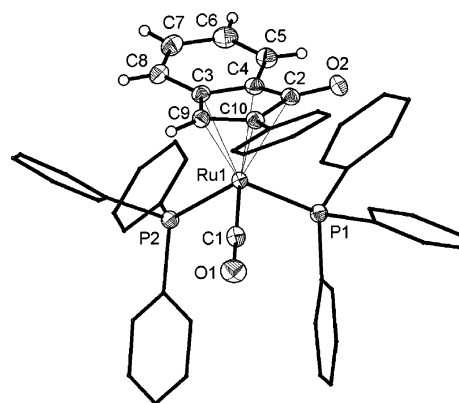


Figure 2. Molecular geometry of **6** in the crystal of **6**·CH₂Cl₂ (40% probability ellipsoids, phenyl groups simplified). Selected bond distances (Å) and angles (deg): Ru1–P1 2.3591(8), Ru1–P2 2.3522(7), Ru1–C1 1.825(3), Ru1–C3 2.382(3), Ru1–C4 2.456(3), Ru1–C9 2.163(3), Ru1–C10 2.268(3), O1–C1 1.161(4), O2–C2 1.241(3), C2–C4 1.492(4), C2–C10 1.470(4), C3–C4 1.419(4), C3–C8 1.423(4), C3–C9 1.438(4), C4–C5 1.422(4), C5–C6 1.378(5), C6–C7 1.411(5), C7–C8 1.366(5), C9–C10 1.450(4), P1–Ru1–P2 105.74(3), C1–Ru1–P1 91.6(1), C1–Ru1–P2 87.8(1).

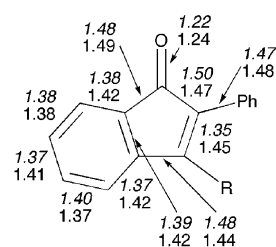


Figure 3. Schematic diagram showing the effects of metal coordination upon the bond lengths in the 2-phenyl-1-indenone fragment. The upper distances in italics are for the free molecule, 2,3-diphenyl-1-indenone ($R = \text{Ph}$),¹⁸ while the lower distances are for the coordinated ligand in **6** ($R = \text{H}$; ring numbering as for Figure 2).

apparent triplet structure as expected due to coupling to two inequivalent though similar phosphorus nuclei.

The mechanism by which **6** forms remains open to speculation; however a plausible route is suggested in Scheme 2. The alkyne complex **2** is stable at ambient temperature, and so the requisite thermal activation is presumably associated with the development of a vacant coordination site via phosphine dissociation. Orthometallation of one of the alkyne phenyl rings could then generate a ruthenium(II) hydride complex. Examples of the orthometallation of ligand aryl substituents are numerous within the chemistry of ruthenium,¹⁹ although

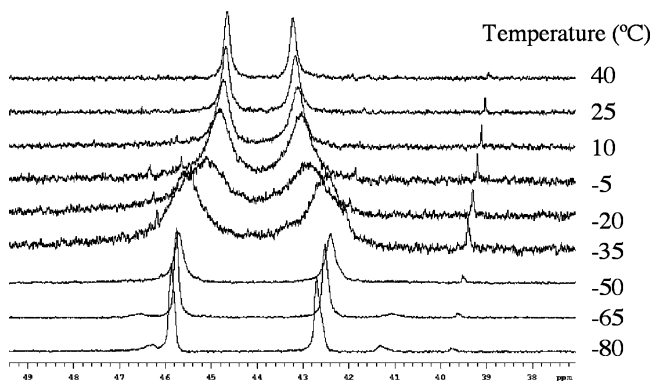
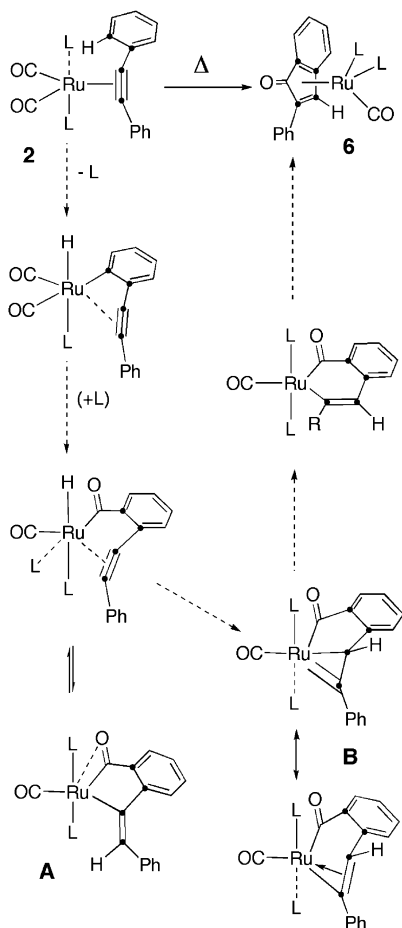


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** in CD_2Cl_2 over the temperature range -80 to $+40$ °C.

Scheme 2. Suggested Mechanism for the Formation of 6 (L = PPh_3)



by far the majority involve the aryl group being tethered to a classical donor, e.g., phosphines, azobenzenes, bipyridyls, and phosphites. Indeed, the intermediacy of orthometalated phosphines in catalytic hydrogenations mediated by $[\text{RuHCl}(\text{PPh}_3)_3]$ has long been recognized.²⁰ More recently, Murai has shown that acyl groups may serve to tether aryl groups proximal to ruthenium for the purpose of orthometalation;²¹ however, the adoption

of such a role by alkynes is less well documented. The haptotropic shift of $[\text{Os}(\text{NH}_3)_5]^{n+}$ ($n = 2, 3$) groups between the $\text{C}\equiv\text{C}$ and *ipso-ortho* multiple bond of diphenylacetylene is documented²² and provides an alternative route for the ruthenium center to access the *ortho* C–H bond, without requiring variations in valence electron count (ligand dissociation). The 2-alkynylphenyl class of ligand resulting from orthometalation has been implicated on a number of occasions though no structural data exist for transition metal derivatives. Thus, the insertion of benzyne into the metal–alkynyl bond of $[\text{Ni}(\text{C}\equiv\text{CPh})(\text{C}\equiv\text{C}\text{Cl}_2)(\text{PETe}_3)_2]$ has been invoked to account for the resulting formation of *ortho*- $\text{PhC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}\text{Cl}_2$.²³ A similar benzyne insertion mechanism has been suggested for the formation of $\text{PhC}\equiv\text{CC}_6\text{H}_4\text{SnBu}_3$ from 2- $\text{Me}_3\text{SiC}_6\text{H}_4\text{OTf}$ and $\text{PhC}\equiv\text{CSnBu}_3$ catalyzed by $[\text{Pd}_2\text{Cl}_2(\eta\text{-C}_3\text{H}_5)_2]$.²⁴ While these processes appear to generate the 2-alkynylphenyl ligand, the sequence is distinct from that proposed *en route* to **6**. However, such an activation has been suggested for the formation of the complex tentatively formulated as $[\text{Co}(\sigma, \eta^2\text{-C}_6\text{F}_4\text{C}\equiv\text{CPh-2})\{\eta^4\text{-O}=\text{CC}_4\text{Ph}_2(\text{C}_6\text{F}_5)_2\}]$, arising from the thermolysis of $[\text{Co}_2(\text{PhC}\equiv\text{CC}_6\text{F}_5)(\text{CO})_6]$.²⁵

The remaining steps in the mechanistic proposal involve migratory insertion of a carbonyl ligand, alkyne hydrometallation to generate a metallacyclic alkenyl complex, and reductive elimination of the indenone ligand. None of these steps are contentious; however two points are noteworthy: First, we have no evidence as to whether alkyne hydrometallation precedes or follows carbonyl insertion. Second, in the vast majority of cases alkyne hydrometallation proceeds via a concerted mechanism to place Ru and H in *cis* positions on the resulting alkene. Products resulting from the addition regiochemistry **A** in Scheme 2 are not observed, so if hydrometallation with this regiochemistry occurs, it must be reversible. A mechanism involving concerted *cis* addition with the regiochemistry inferred from the structure of the product **6** leads to an energetically unfavorable, strained *trans* cyclohexene structure. Instead, it is necessary to invoke a σ, π (three-electron) vinyl coordination (**B** in Scheme 2), with attendant geometric (and entropic) demands. In the event that carbonyl insertion precedes alkyne hydrometallation, a greater degree of conformational flexibility is introduced, easing access to this otherwise strained alkyne insertion transition state.

An iron compound with an indenone ligand related to that of **6** has been observed in low yield as one of a mixture of six products obtained from the reaction of bis(4-chlorophenyl)acetylene with $\text{Fe}_3(\text{CO})_{12}$ in refluxing petroleum (bp 80 °C) (Scheme 3).²⁶ When the same reaction was carried out with unsubstituted $\text{PhC}\equiv\text{CPh}$, none of the corresponding 2-phenylindenone complex was detected in the product mixture.²⁷ Further literature precedent for orthometalation of diphenylacetylene

(22) Harman, W. D.; Wishart, J. F.; Taube, H. *Inorg. Chem.* **1989**, *28*, 2411–2413.

(23) Miller, R. G.; Kuhlman, D. P. *J. Organomet. Chem.* **1971**, *26*, 401–406.

(24) Yoshida, H.; Honda, Y.; Shirakawa, E.; Hiyama, T. *Chem. Commun.* **2001**, 1880–1881.

(25) Dickson, R. S.; Michel, L. J. *Aus. J. Chem.* **1975**, *28*, 1957–1969.

(26) Braye, E. H.; Hübel, W. *J. Organomet. Chem.* **1965**, *3*, 38–42.

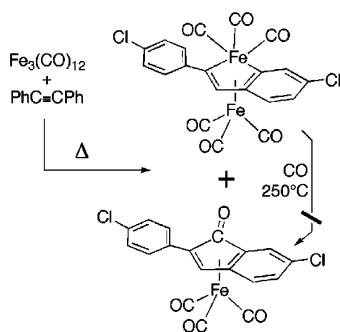
(27) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250–268.

(19) Hill, A. F. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd: Oxford, 1995; Vol. 7.

(20) James, B. R.; Markham, L. D.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* **1974**, 439–440.

(21) Murai, S.; Chatani, N.; Kakiuchi, F. *Pure Appl. Chem.* **1997**, *69*, 589–594.

Scheme 3. Reported Reaction of Bis(4-chlorophenyl)acetylene with $\text{Fe}_3(\text{CO})_{12}$ ²⁶



is provided by the formation 2-phenylindanone from $\text{PhC}\equiv\text{CPh}$, CO, and water catalyzed by a mixture of $[\text{Co}_2(\text{CO})_8]$ and PPh_3 , for which intermediate cobaltaindene and indenone complexes were proposed.²⁸ A similar orthometalation is implicit in the aryl indenone formation arising from the reaction of $\text{PhC}\equiv\text{CPh}$ with $[\text{Fe}(\text{2-chlorophenyl})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$.²⁹ Notably, earlier work by Hübel and co-workers demonstrated that a diferraindene did not react with CO up to 250 °C under CO pressure to form the coordinated indenone (Scheme 3).²⁶ Rhoda³⁰ and ruthenaindenes³¹ have similarly been obtained from $\text{PhC}\equiv\text{CPh}$, though in neither case do subsequent insertion or elimination processes ensue.

When **2** was heated in an NMR tube in d_8 -toluene, after 5 min at reflux the $^{31}\text{P}\{^1\text{H}\}$ resonance due to **2** was observed in addition to resonances attributable to $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ **1** and $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ **4** (approximate ratio **1**:**2**:**4** 1:10:5). After 18 h heating under reflux, the characteristic broad resonances due to the indenone complex **6** were observed, as well as a minor resonance at δ 38 corresponding to the tetraphenylcyclopentadienone complex **5**. This last complex is presumably formed from the reaction of $\text{PhC}\equiv\text{CPh}$ with **4**, the latter arising from ligand redistribution (see below). A minor and as yet unidentified resonance was observed at δ 47. Further heating did not alter the $^{31}\text{P}\{^1\text{H}\}$ spectrum of the reaction mixture, which contained **5**, **6**, **4**, and **1** in the approximate ratio 1:20:1:2. In contrast, heating a mixture of **2** and $\text{PhC}\equiv\text{CPh}$ in d_6 -benzene under reflux (bp ca. 79 °C) did not result in appreciable formation of **5** or **6** but rather led to the eventual accumulation of **4**, which is presumably the thermodynamic minimum of possible ligand redistribution products of the starting material.

The product **6** reacts with 1,2-bis(diphenylphosphino)ethane (dppe) in refluxing toluene to substitute both triphenylphosphine ligands and form the corresponding dppe complex $[\text{Ru}(\eta^4\text{-O}=\text{CC}_6\text{H}_4\text{CH}=\text{CPh})(\text{CO})(\text{dppe})]$ (**7**), which is noticeably more soluble than **6**. Spectroscopic data for the derivative are as expected, and most notably the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum comprises a simple conventional AB system [CD_2Cl_2 : δ = 76.5, 60.6; $^2J(\text{P}_\text{A}\text{P}_\text{B})$ = 3.2 Hz], lending credence to our assumption

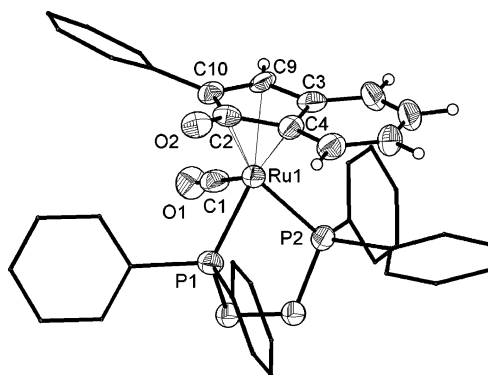


Figure 5. Molecular geometry of **7** in the crystal of **7**· CH_2Cl_2 (40% probability ellipsoids, phenyl groups simplified). Selected bond distances (Å) and angles (deg): Ru1–P1 2.315(2), Ru1–P2 2.307(2), Ru1–C1 1.86(1), Ru1–C3 2.279(9), Ru1–C4 2.344(9), Ru1–C9 2.173(7), Ru1–C10 2.271(9), O1–C1 1.14(1), O2–C2 1.26(1), C2–C4 1.51(1), C2–C10 1.46(1), C3–C4 1.41(1), C3–C8 1.43(1), C3–C9 1.44(1), C4–C5 1.45(1), C5–C6 1.37(1), C6–C7 1.41(1), C7–C8 1.37(1), C9–C10 1.45(1), P1–Ru1–P2 83.07(9), P1–Ru1–C1 89.7(3), P2–Ru1–C1 88.0(3).

that the peculiarities in the spectrum of **6** were due to hindered rotation about the Ru–P bonds (entirely precluded for **7**). These values may be compared with that reported for the complex $[\text{Ru}\{\eta^4\text{-O}=\text{C}(\text{MeCCSC}_2\text{H}_4)_2\text{-S}\}(\text{CO})(\text{dppe})]$ (C_6D_6 : δ = 60.5),³ which in contrast to **7**, has a molecular plane of symmetry. Complex **7** was also characterized crystallographically, and the results of this study are summarized in Figure 5. The geometric parameters for the indenone ligand are comparable to those for **6**, again reflecting the development of cyclohexadiene character for the benzo ring, which lodges in the cleft provided by the two phosphine phenyl groups positioned *anti* to the carbonyl ligand. The remaining phenyl group bound to P1 lies between the indenone carbonyl and the 2-phenyl substituents, but remains in an orientation allowing conjugation with the indenone system. Each of these placements appears to arise from a minimization of interligand steric interactions since there are no obvious intramolecular C–H $\cdots\pi$ or π -stacking interactions. The strength of indenone coordination in both **6** and **7** is noteworthy in that no $[\text{Ru}(\text{CO})(\text{dppe})_2]$ ³² was observed during the reaction, and neither does **6** react with carbon monoxide under mild conditions (ambient temperature, 1 atm).

The alternative ruthenium(0) starting material **4** is, in contrast to **1**, essentially inert to ligand substitution under ambient conditions. However, when treated with excess $\text{PhC}\equiv\text{CPh}$ in refluxing toluene over 2 weeks, a [2+2+1] cyclization of CO and alkyne is observed to provide the tetraphenylcyclopentadienone adduct **5** in good yield (85% by $^{31}\text{P}\{^1\text{H}\}$ NMR). This contradicts the reported and curious requirement of CO_2 for the reaction to occur,⁴ an observation that was rationalized in terms of the supposed formation of $[\text{Ru}(\text{CO})_4(\text{PPh}_3)_2]\text{O}_2\text{-CO}$ among other intriguing mechanistic candidates. Of more concern are inconsistencies between the spectroscopic data we obtained for **5** and those previously

(28) Joh, T.; Doyama, K.; Fujiwara, K.; Maeshima, K.; Takahashi, S. *Organometallics* **1991**, *10*, 508–513.

(29) Butler, I. R.; Cullen, W. R.; Lindsell, W. E.; Preston, P. N.; Rettig, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 439–441.

(30) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327–356.

(31) Burns, R. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9514–9520.

(32) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1982**, *234*, C5–C8.

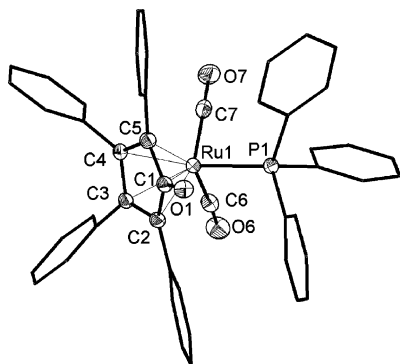
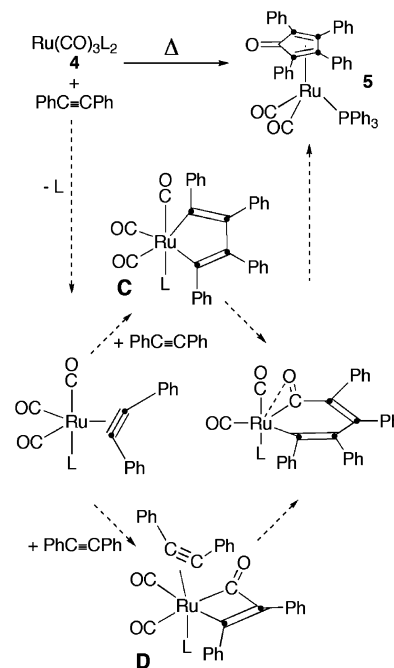


Figure 6. Molecular geometry of **5** in the crystal of **5**·C₇H₈ (40% probability ellipsoids, phenyl groups simplified). Selected bond distances (Å) and angles (deg): Ru1–P1 2.3673(7), Ru1–C2 2.268(2), Ru1–C3 2.203(2), Ru1–C4 2.204(2), Ru1–C5 2.280(2), Ru1–C6 1.884(3), Ru1–C7 1.891(3), C1–O1 1.240(3), C6–O6 1.151(3), C7–O7 1.146(3), C1–C2 1.488(3), C1–C5 1.481(3), C2–C3 1.452(3), C3–C4 1.411(3), C4–C5 1.444(3), P1–Ru1–C6 91.16(8), P1–Ru1–C7 90.99(8), C6–Ru1–C7 93.9(1).

reported.^{4,33} Because of these uncertainties, an X-ray structural determination was performed to confirm the identity of the product. The structure of **5**·C₆H₆ was published; the present study used crystals of **5**·PhMe obtained from toluene. The results of this study are summarized in Figure 6. In the previous study **5** was reported to form as a mixture of isomers arising from rotation of the “Ru(CO)₂(PPh₃)” group about an axis normal to the cyclopentadienone plane, though it might be expected that such a rotation is rapid. We, however, observe only one isomer with $\delta(^{31}\text{P}) = 38.9$ and $\nu(\text{CO}) = 2012$ and 1958 cm^{-1} (toluene). It is implausible that two isomers would be distinctly observable on the NMR time scale but not on the infrared time scale. Germane geometric parameters associated with the cyclopentadienone of both **5**·C₆H₆ and **5**·PhMe are, as expected, comparable and fall within norms for such ligands bound to ruthenium.^{3,4,34–36} The general impact of coordination of the cyclopentadienone ring may be assessed with reference to the crystal structure of free tetraphenylcyclopentadienone,³⁷ the primary perturbation being that the C=C and C–C bond lengths within the butadiene component of the cyclopentadienone ring become more similar as a result of association of the π -system with the ruthenium center.

Two alternative mechanisms for the formation of **5** are proposed in Scheme 4. The starting complex **4** is relatively unreactive, in contrast to **1**, but in refluxing toluene, must lose either one carbonyl or one triphenylphosphine ligand. Because neither **6** nor **2** is observed in the reaction of **4** with PhC≡CPh, the ligand lost appears to be PPh₃. Coordination of the alkyne to the

Scheme 4. Suggested Mechanism for the Formation of **5** (L = PPh₃)



“Ru(CO)₃(PPh₃)” fragment would then provide [Ru(η -PhC≡CPh)(CO)₃(PPh₃)]. This complex differs from **4** in having an extra π -acceptor ligand, which might be expected to activate the complex to migratory insertion involving coupling of the alkyne with one carbonyl ligand (path **D**). Some support for this interpretation comes from the observation that the thiocarbonyl complex [Os(η -PhC≡CPh)(CS)(PPh₃)₂] reacts with carbon monoxide to provide the osmacyclobutenthione complex [Os{C(=S)CPh=CH}(CO)₂(PPh₃)₂],³⁸ via CS/alkyne coupling of the presumed intermediate [Os(η -PhC≡CPh)(CS)(CO)(PPh₃)₂]. Formation of the ruthenacyclobutene depletes the ruthenium center of two valence electrons, which allows coordination of a second alkyne unit that then inserts into the ruthenium alkenyl linkage. Santos has shown that activated alkynes insert into nonmetallacyclic coordinatively unsaturated ruthenium alkenyls.^{39,40} More relevant to the present situation, the formation of the metallacyclohexadienes [Ru{C(=CHR)CR=CHCR=CH}(CO)(PPh₃)₂] (R = CO₂Me)⁴¹ and [Os{C(=S)CH=CHCH=CH}(CO)(PPh₃)₂]⁴² may be interpreted in terms of alkyne insertion into the metal alkenyl bonds of the metallacyclobutene intermediates [Ru{C(=CHR)CR=CH}(CO)(PPh₃)₂] and [Os{C(=S)CH=CH}(CO)(PPh₃)₂]. In both of these cases, the metallacyclohexadiene ring is stabilized by a further interaction (sulfur or ester) with the metal center and reductive elimination does not proceed under the reaction conditions. In the present case, however, no such

(33) Most notably, the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance reported for one of the suggested isomers of **5** ($\delta = 26.5$) is identical with that for triphenylphosphine oxide.

(34) Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25–L26.

(35) Smith, T. P.; Kwan, K. S.; Taube, H.; Bino, A.; Cohen, S. *Inorg. Chem.* **1984**, *23*, 1943–1945.

(36) Rüba, E.; Mereiter, K.; Soldouzi, K. M.; Gemel, C.; Schmid, R.; Kirchner, K.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 5384–5391.

(37) Alvarez-Toledano, C.; Baldovino, O.; Espinoza, G.; Toscano, R. A.; Gutiérrez-Pérez, R.; García-Mellado, O. *J. Organomet. Chem.* **1997**, *540*, 41–49.

(38) Elliot, G. P.; Roper, W. R. *J. Organomet. Chem.* **1983**, *250*, C5–C8.

(39) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091–1095.

(40) Castaño, A. M.; Echavarren, A. M.; López, J.; Santos, A. *J. Organomet. Chem.* **1989**, *379*, 171–175.

(41) Yamazaki, H.; Aoki, K. *J. Organomet. Chem.* **1976**, *122*, C54–C58; the same compound was obtained in low yield from a different route: Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H.; Zaitseva, N. N. *Aus. J. Chem.* **2000**, *53*, 99–107.

(42) Elliot, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811–813.

interaction is possible, and thus reductive elimination of the cyclopentadienone occurs.

We have no firm evidence to exclude the alternative sequence of events represented in path **C**, viz., coordination of two alkynes followed by cyclization to a ruthenacyclopentadiene, which then inserts a CO ligand. However, the only route to a coordinatively unsaturated intermediate for coordination of the second alkyne would require dissociation of either a second phosphine or carbonyl ligand to provide $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_x(\text{PPh}_3)_{3-x}]$ ($x = 2, 3$). It should be noted that the ability of alkynes to act as four-electron donors does provide a mechanism for stabilization of such intermediates, a situation that has been addressed by Caulton in related systems.^{6,7}

The observation of **5** from the reaction of **1** with $\text{PhC}\equiv\text{CPh}$ is presumably due to the initial formation of some **4** (observed spectroscopically) through ligand redistribution under the harsh reaction conditions. Notably, **1** reacts immediately with CO (1 atm) to form **4** quantitatively. Comparing the mechanisms proposed in Schemes 2 and 4, it is apparent that the significant difference between these two reactions is the “ $(\text{CO})_2(\text{PPh}_3)_2$ ” versus “ $(\text{CO})_3(\text{PPh}_3)$ ” ligand sets. Given that the reactions are both high yielding, and form only the product described regardless of the stoichiometry of the reagents, common intermediates may be excluded. Thus, the electronic nature of the fragment “ $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$ ” is fundamentally different to that of “ $\text{Ru}(\text{CO})_3(\text{PPh}_3)$ ”.

Conclusions

The thermal reactions of the two ruthenium(0) starting materials **1** and **4** with excess diphenylacetylene both proceed in good yield, forming dramatically different products, both of which contain Ru(0). The former reaction proceeds via the alkyne adduct **2**, which undergoes an *ortho*-C–H activation reaction to subsequently deliver this hydrogen atom to the alkyne triple bond. Reductive elimination leads to the coordinated indenone complex **6**. In contrast, **4** reacts via carbonyl and alkyne coupling with reductive elimination of a tetraphenylcyclopentadienone fragment to yield the complex **5**. Common intermediates can be excluded, leading to the inference that the electronic properties of the “ $\text{Ru}(\text{CO})_x(\text{PPh}_3)_{4-x}$ ” ($x = 2, 3$) fragments are sufficiently distinct to direct the course of the reactions profoundly.

Experimental Section

General Procedures. All air-sensitive manipulations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk and vacuum line techniques, using dried and degassed solvents. NMR spectra were recorded on a Varian Inova 300 (^1H at 300.75, ^{13}C at 75.4, ^{31}P at 121.4 MHz) instrument. The chemical shifts (δ) for ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are given in ppm relative to residual signals of the solvent and for $^{31}\text{P}\{^1\text{H}\}$ spectra to an external 85% H_3PO_4 reference. The coupling constants (J) are given in Hz with an estimated error of ± 0.5 Hz. Mass spectra of the complexes were obtained on a Micromass ZMD spectrometer using the APCI technique in acetonitrile by the Mass Spectrometry service of the Research School of Chemistry, Australian National University. The microanalyses were carried out by the microanalytical

service of the Research School of Chemistry, Australian National University.

Synthesis of $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ (2**).** The complex was prepared as described previously. A mixture of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**: 1.5 g, 1.6 mmol) and diphenylacetylene (0.60 g, 3.4 mmol) in toluene was stirred overnight under a nitrogen atmosphere. Completion of the reaction was evident by the disappearance of the infrared absorption at 1900 cm^{-1} and appearance of bands at 1959 and 1891 cm^{-1} . The solvent volume was reduced under reduced pressure and the residue crystallized from a mixture of toluene and hexane. Yield: 1.2 g (88%). Crystallographic grade crystals of the benzene monosolvate were obtained by slow evaporation of a benzene solution of the complex. IR C_6H_6 : $1963, 1875$ (RuCO) cm^{-1} . Nujol: $1959, 1895$ (RuCO), 1777 ($\text{C}\equiv\text{C}$) cm^{-1} . NMR (C_6D_6 , 298 K) ^1H (300 MHz): δ 7.71 (m, 12 H), 7.28 (m, 2 H), 7.26 (m, 2 H), 6.97–6.87 (m, 24 H). $^{13}\text{C}\{^1\text{H}\}$ (75.5 MHz): δ 135.7 [vt, $J_{\text{CP}} = 21$, $\text{C}^4(\text{PC}_6\text{H}_5)$], 134.3 [vt, $J_{\text{CP}} = 6$, $\text{C}^{2,3}(\text{PC}_6\text{H}_5)$], 131.9 [s, $\text{C}^4(\text{C}_6\text{H}_5)$], 130.9 [s, $\text{C}^{2,3}(\text{C}_6\text{H}_5)$], 129.6 [s, $\text{C}^{2,3}(\text{C}_6\text{H}_5)$], 124.9 [s, $\text{C}^1(\text{C}_6\text{H}_5)$], 109.3 (t, $^2J_{\text{CP}} = 4$ Hz, $\text{C}\equiv\text{C}$); other peaks obscured by solvent peak. $^{31}\text{P}\{^1\text{H}\}$ (121 MHz): 42.5 (s). Crystal data for $2\cdot\text{C}_6\text{H}_6$: $\text{C}_{58}\text{H}_{46}\text{O}_2\text{P}_2\text{Ru}$, $M_w = 938.02$, triclinic, $P\bar{1}$ (#2), $a = 11.5764(1)\text{ \AA}$, $b = 13.5638(2)\text{ \AA}$, $c = 16.9036(2)\text{ \AA}$, $\alpha = 82.5692(5)^\circ$, $\beta = 72.9256(6)^\circ$, $\gamma = 66.1848(6)^\circ$, $V = 2321.00(5)\text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.342\text{ g cm}^{-3}$, $T = 200\text{ K}$, yellow block, 11 423 independent measured reflections [$2\theta \leq 55^\circ$], $R_1 = 0.0319$, $wR_2 = 0.0366$, 7616 absorption-corrected reflections [$I > 3\sigma(I)$], 568 parameters, CCDC 237864.

Synthesis of $[\text{Ru}\{\eta^4\text{-OC}(\text{CPh})_4\}(\text{CO})_2(\text{PPh}_3)]$ (5**).** The complex $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ (**4**) (0.010 g, 1.4×10^{-2} mmol) and $\text{PhC}\equiv\text{CPh}$ (0.075 g, 4.2×10^{-2} mmol) were weighed into a flask, and toluene was added. The mixture was heated to reflux until the $^{31}\text{P}\{^1\text{H}\}$ spectrum indicated complete consumption of **4** (2 weeks). Slow evaporation of the solvent led to the formation of X-ray quality crystals of **5**, which crystallized with one molecule of toluene in the lattice. The complex **5** can also be obtained by chromatography (SiO_2 , THF) of the supernatant of the reaction of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ with excess $\text{PhC}\equiv\text{CPh}$ in refluxing toluene (see below). IR (toluene): 2012, 1958 (RuCO), 1613 ($\text{C}=\text{O}$) cm^{-1} (cf 2011, 1956, and 1606 $^\circ$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K, 121 MHz): δ 38.9 (s) (cf δ 26.5, 32.7 $^\circ$ NB: OPPh_3 has $\delta = 26.5$). Crystal data for $5\cdot\text{C}_7\text{H}_8$: $\text{C}_{56}\text{H}_{43}\text{O}_3\text{PRu}$, $M_w = 895.94$, monoclinic, $P2_1/n$ (#14), $a = 12.871(3)\text{ \AA}$, $b = 18.419(4)\text{ \AA}$, $c = 18.401(4)\text{ \AA}$, $\beta = 95.94(3)^\circ$, $V = 4338(1)\text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.372\text{ g cm}^{-3}$, $T = 200\text{ K}$, yellow block, 9929 independent measured reflections [$2\theta \leq 55^\circ$], $R_1 = 0.0382$, $wR_2 = 0.0864$, 7477 absorption-corrected reflections [$I > 2\sigma(I)$], 551 parameters, CCDC 237866.

Synthesis of $[\text{Ru}(\text{CO})(\text{PPh}_3)_2\{\eta^4\text{-O}=\text{C}(\text{Ph})\text{CC}(\text{H})\text{C}_6\text{H}_4\}]$ (6**).** (a) A mixture of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**: 2.15 g, 2.27 mmol) and $\text{PhC}\equiv\text{CPh}$ (1.21 g, 6.80 mmol) in toluene (50 mL) was heated under reflux for 2 days, during which time the color changed from yellow to deep red. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which revealed that after 2 days, no further product (toluene/ C_6D_6 $\delta = 42, 43$) was formed and that the starting ruthenium complex **1** (δ 50.9) had been completely consumed. Upon cooling to room temperature, **6** precipitated as an orange solid. The supernatant was chromatographed on silica gel, eluting initially with dichloromethane to remove triphenylphosphine and its oxide, and subsequently eluting with tetrahydrofuran to give the byproduct **5** (0.20 g). The orange solid was recrystallized from dichloromethane to provide an orange powder of the dichloromethane monosolvate of **6**. Mp: 178–180 $^\circ\text{C}$. Crystallographic grade crystals of the dichloromethane solvate were grown by the slow evaporation of a solution of the complex in dichloromethane. Yield: 0.88 g (44%). (b) A solution of $[\text{Ru}(\eta\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**: 2.4 g, 2.79 mmol) in toluene (300 mL) was heated under reflux in an atmosphere of prepurified nitrogen for 3 days. The complex **6** was isolated by column chromatography, eluting first with dichloromethane

to remove triphenylphosphine and its oxide, then with THF to remove **6** (no **5** is formed under these conditions). Yield: 1.80 g (75%). IR Nujol: 1925s (RuCO), 1595m, 1581m (C=O); CH₂Cl₂: 1931s (RuCO), 1583brm (C=O) cm⁻¹. NMR (CD₂Cl₂, 298 K) ¹H (300 MHz): δ 8.22 [d, 2 H, ³J_{HH} = 11, (C₆H₄)], 7.47–7.15, 6.90–6.75 [m × 2, 35 H, PC₆H₅ and (CC₆H₅)], 6.26 [d, ³J_{HP} = 8, 1 H, (C₆H₄)], 5.95 [br, 1 H, (C₆H₄)], 5.04 [d, ³J_{HP} = 4 Hz, 1 H, (PhC=CH)]. ¹³C{¹H} (75 MHz): δ 210.1 (dd, M-CO, ²J_{PAC} = ²J_{PBC} = 12), 164.8 (O=C), 138.1 [C⁴(CC₆H₅)], 136.5, 135.4 [d × 2, C¹(PC₆H₅)], ¹J_{CP} = 60], 134.2, 133.9 [d × 2, C^{3,5}(PC₆H₅)], ³J_{CP} = 14], 131.4 (s, C₆H₄), 129.8 [d, C^{2,6}(PC₆H₅)], ²J_{CP} = 28], 129.2 [d, C^{2,6}(PC₆H₅)], ²J_{CP} = 23] 128.69, 128.43, 128.32, 128.22, 128.14, 129.09, 127.8 (8 lines, PC₆H₅, C₆H₄ and CC₆H₅), 127.3 [s, C^{2,6}(CC₆H₅)], 127.1 (s, C₆H₄), 125.8, 125.5 [C⁴(PC₆H₅)], 125.2 (CC₆H₅), 124.9, 121.2 (s, C₆H₄), 110.5 (CC₆H₅), 92.0 [br × 2, C^{8,9}(O=CC₄)], 77.4 [dd, ²J_{CP} = 8, ²J_{CP} = 3 Hz, C²(O=CC₄)], 64.0 [br, C³(O=CC₄)]. ³¹P{¹H} (121 MHz): δ 44.5 (br), 43.0 (br). MS (APCI, +ve ion): 861 [M]⁺. Anal. Satisfactory data not obtained, presumably due to desolvation. Found: C, 67.96; H, 4.74; P, 6.35. Calcd for C₅₂H₄₀O₂P₂Ru·CH₂Cl₂: C, 67.37; H, 4.48; P, 6.56. Crystal data for **6**·CH₂Cl₂: C₅₂H₄₂Cl₂O₂P₂Ru, *M*_w = 944.78, monoclinic, *P*2₁/*n* (#14), *a* = 10.2089(1) Å, *b* = 19.1137(2) Å, *c* = 22.0738(2) Å, β = 93.636(1)°, *V* = 4298.59(7) Å³, *Z* = 4, ρ_{calc} = 1.460 g cm⁻³, *T* = 200 K, orange block, 9864 independent measured reflections [2θ ≤ 55°], *R*₁ = 0.0448, *wR*₂ = 0.1092, 8116 absorption-corrected reflections [*I* > 2σ(*I*)], 541 parameters, CCDC 237863.

Synthesis of [Ru(CO)(dppe){η⁴-(OC(Ph)CC(H)C₆H₄)}] (7). A mixture of [Ru{η⁴-(OCCPh=CHC₆H₄)(CO)(PPh₃)₂] (**6**): 0.22 g, 0.25 mmol) and 1,2-bis(diphenylphosphino)ethane (0.20 g, 0.50 mmol) in toluene (40 mL) was heated under reflux. The reaction progress was monitored by infrared spectroscopy, which indicated that after 2 h all the starting material (*ν*(CO) = 1931 cm⁻¹) had been converted to **7** (*ν*(CO) = 1943 cm⁻¹). The solvent was removed under reduced pressure, and the residue was washed with benzene to remove triphenylphosphine and unreacted dppe. The residue was then crystallized from a mixture of dichloromethane and hexane to provide

orange microcrystals. Yield: 0.13 g (71%). Mp: 150–155 °C (dec). Crystallographic grade crystals of the dichloromethane monosolvate were obtained by slow diffusion of hexane into a dichloromethane solution. IR CH₂Cl₂: 1943s (RuCO), 1585m (C=O) cm⁻¹. NMR (CD₂Cl₂, 298 K) ¹H (300 MHz): δ 7.91 [d, 2 H, H^{2,6}(CC₆H₅)], ³J_{HH} = 7.2], 7.73–7.61, 7.51 (m × 2, 10 H, PC₆H₅), 7.37–7.07 (m, 12 H, PC₆H₅ and CC₆H₅), 6.62 [d, 1 H, H^{4,7}(C₆H₄)], ³J_{HH} = 8.4], 6.39 [dd, 2 H, H^{2,6}(PC₆H₅)], ³J_{HP} = ³J_{HH} = 7.8] 6.20, 6.11 [t, × 2, 2 H × 2, H^{5,6}(C₆H₄)], ³J_{HH} = 7.4], 5.68 (d, 1 H, ³J_{HP} = 2.7 Hz, H³(O=CC₄)), 2.68–1.93 (m × 2, 4 H × 2, PCH₂). ¹³C{¹H} (121 MHz): δ 205.8 (br, RuCO), 164.8 (CO), 137.1 [C¹(CC₆H₅)], 135.3 [d, ¹J_{CP} = 49, C¹(PC₆H₅)], 134.8 [d, ¹J_{CP} = 40, C¹(PC₆H₅)], 133.8 [d, ²J_{CP} = 11, C^{2,6}(PC₆H₅)], 133.5 [C⁴(PC₆H₅)], 132.8, 132.3 [d × 2, ³J_{CP} = 11, C^{3,5}(PC₆H₅)], 132.1 [d, ²J_{CP} = 15, C^{2,6}(PC₆H₅)], 131.1 [C⁴(PC₆H₅)], 130.5, 129.4 [C^{5,6}(C₆H₄)], 128.8, 128.6 [d × 2, ³J_{CP} = 7, C^{3,5}(PC₆H₅)], 128.1 [C⁴(PC₆H₅)], 127.9 [d, ³J_{CP} = 10, C^{3,5}(PC₆H₅)], 126.5, 125.6, 125.2 [C²⁻⁶(CC₆H₅)], 123.2, 120.7 [C^{4,7}(C₆H₄)], 105.6, 93.5 [C^{8,9}(O=CC₄)], 76.9 [br, C²(O=CC₄)], 61.0 [C³(O=CC₄)], 30.6 (dd, ¹J_{CP} = 46, ²J_{CP} = 13, PCH₂), 29.6 (dd, ¹J_{CP} = 32, ²J_{CP} = 13 Hz, PCH₂). ³¹P{¹H} (121 MHz): δ 76.5, 60.6 (AB, ²J_{AB} = 3.2 Hz). MS (APCI, +ve ion): 734 [M]⁺, 706 [M - CO]⁺. Anal. Found: C, 68.48; H, 4.33; P, 8.44. Calcd for C₄₂H₃₄O₂P₂Ru: C, 68.75; H, 4.67; P, 8.44. Crystal data for **7**·CH₂Cl₂: C₄₃H₃₆Cl₂O₂P₂Ru, *M*_w = 818.68, monoclinic, *P*2₁/*n* (#14), *a* = 13.0957(5) Å, *b* = 21.3537(9) Å, *c* = 14.4418(6) Å, β = 100.305(2)°, *V* = 3973.4(3) Å³, *Z* = 4, ρ_{calc} = 1.368 g cm⁻³, *T* = 200 K, orange plate, 5513 independent measured reflections [2θ ≤ 46°], *R*₁ = 0.0572, *wR*₂ = 0.0511, 2645 absorption-corrected reflections [*I* > 1.5σ(*I*)], 451 parameters, CCDC 237865.

Supporting Information Available: Tables giving crystallographic details for **2**, **5**, **6**, and **7**; stacked plot of ³¹P{¹H} NMR spectra of **6** in C₂D₂Cl₄ from 25 to 100 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0400954