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Reversible Phenyl Coordination of a Cluster-Bound Triphenylphosphine Ligand: $Ru_6C(CO)_{13}\{PPh_2(\mu\text{-}\eta^6\text{-}C_6H_6)\}$

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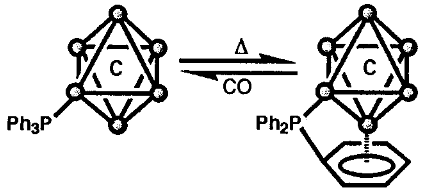
*Summary: In refluxing chlorobenzene, $Ru_6C(CO)_{16}PPh_3$ is converted to $Ru_6C(CO)_{13}\{PPh_2(\mu\text{-}\eta^6\text{-}C_6H_5)\}$ (**1**), in which one phenyl ring of the PPh_3 ligand is coordinated to an adjacent ruthenium atom. Treatment of **1** with CO at 25 °C regenerates $Ru_6C(CO)_{16}PPh_3$. An analogous derivative $Ru_6C(CO)_{13}\{PMe_2(\mu\text{-}\eta^6\text{-}C_6H_5)\}$ (**2**) can be prepared from $Ru_6C(CO)_{16}PMe_2Ph$.*

Introduction

Triphenylphosphine is a ubiquitous and useful ligand in organometallic chemistry. In addition to the primary coordination of the phosphorus atom, a variety of secondary bonding interactions[1] of a metal center with C−H or C═C bonds of the phenyl rings have been observed and these latter interactions are likely involved in degradative reactions of the ligand, including orthometalation and P−C bond cleavage. In one case, triphenylphosphine has been observed to bridge two metal centers, bonded by phosphorus to one metal and by a phenyl ring to the other in $\{Cr(CO)_2(\mu\text{-}PPh_2{-}C_6H_5)\}_2$.[2] The strong tendency of the hexanuclear Ru_6C framework to form arene complexes has been widely demonstrated in recent years.[3] We have found that this tendency can extend to a coordinated triphenylphosphine moiety, leading to (reversible) coordination of a phenyl ring to an adjacent ruthenium center in the cluster unit (see Scheme 1).

Scheme 1



Experimental Section

General Procedures. All reactions were conducted under an atmosphere of nitrogen with use of standard Schlenk techniques. Solvents for preparative use were dried and distilled before use. ^1H NMR spectra were recorded on General Electric GN-500 and QE 300 spectrometers and referenced to residual solvent resonance (7.24 ppm for $CDCl_3$). ^{31}P spectra were recorded on a General Electric GN-300NB spectrometer and referenced to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences. All *m/z* values are referenced to ^{102}Ru. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences. The starting materials $Ru_6C(CO)_{16}PPh_3$ and $Ru_6C(CO)_{16}PMe_2Ph$ were prepared by literature procedures.[4] Separation of products was accomplished by thin layer chromatography (TLC) using SiO_2 plates (Merck, Kieselgel 60 F_{254}, 0.25 mm).

Preparation of $Ru_6C(CO)_{13}PPh_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (1). A solution of $Ru_6C(CO)_{16}PPh_3$ (50 mg, 0.038 mmol) in chlorobenzene was heated under reflux for 24 h. The solvent was removed in vacuo, and the residue was separated by thin layer chromatography, eluting with chloroform/*n*-hexane (1:1) to yield brown $Ru_6C(CO)_{13}PPh_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (**1**) (26 mg, 0.021 mmol, 56% yield) and unreacted $Ru_6C(CO)_{16}PPh_3$ (10 mg). Black crystals of **1** were obtained by crystallization from chloroform/*n*-hexane.

$Ru_6C(CO)_{13}PPh_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (1). Anal. Calcd for $C_{32}H_{15}O_{13}PRu_6$: C, 30.88; H, 1.21; P, 2.49. Found: C, 30.74; H, 1.26; P, 2.17. MS (FAB^+): *m/z* 1249 (M^+). IR (CH_2Cl_2): ν(CO) 2065 (s), 2014 (vs), 1973 (m, br), 1847 (w, br), 1816 (w, br) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 ($4H_o$, dd, $J(H_o{-}H_m) = 8$ Hz, $J(H_o{-}P) = 13$ Hz), 7.58 ($6H_{m,p}$, m), 5.91 ($1H_p$, tr, $J(H_p{-}H_m) = 6$ Hz), 5.85 ($2H_m$, dd (app tr), $J(H_m{-}H_p) = 6$ Hz, $J(H_m{-}H_o) = 6$ Hz), 4.46 ($2H_o$, dd, $J(H_m{-}H_o) = 6$ Hz, $J(H_m{-}P) = 8$ Hz). $^{31}P\text{-}\{^1H\}$ NMR (121.6 MHz, $CDCl_3$): 41.19 ppm.

Reaction of 1 with CO. A solution of **1** (20 mg, 0.0161 mmol) in dichloromethane (30 mL) was placed in a 300 mL pressure bottle, which was then evacuated. Carbon monoxide was introduced to a pressure of 25 psig, and the solution was stirred under this atmosphere for 30 min at room temperature. The solution was dried under vacuum, and the residue was separated by thin layer chromatography, eluting with chloroform/*n*-hexane (1:1) to yield $Ru_6C(CO)_{16}PPh_3$ (7 mg, 0.0053 mmol, 33%) and $Ru_5C(CO)_{14}PPh_3$ (8 mg, 0.0068 mmol, 42%). The latter was identified by mass (FAB^+, *m/z* 1176 (M^+)) and IR[5] (CH_2Cl_2, n(CO), 2085 (w), 2057 (s), 2047 (m), 2032 (s), 2006 (m) cm^{-1}) spectra.

Preparation of $Ru_6C(CO)_{13}PMe_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (2). A solution of $Ru_6C(CO)_{16}PMe_2Ph$ (10 mg, 0.0083 mmol) in chlorobenzene was heated under reflux for 24 h. The solution was dried under vacuum, and the residue was separated by thin layer chromatography, eluting with chloroform/*n*-hexane (1:1) to yield brown $Ru_6C(CO)_{13}PMe_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (**2**) (7 mg, 0.0062 mmol, 75% yield) and unreacted $Ru_6C(CO)_{16}PMe_2Ph$ (1 mg).

$Ru_6C(CO)_{13}PMe_2(\mu\text{-}\eta^6\text{-}C_6H_5)$ (2). IR (CH_2Cl_2): ν(CO) 2065 (s), 2021 (s, sh), 2013 (vs), 1989 (m, br), 1823 (w, br), 1797 (w,

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Table 1. Crystallographic Data for 1

formula	$C_{32}H_{15}O_{13}PRu_6$	D_{calcd} (g cm^{-3})	2.336
fw	1244.83	μ(Mo Kα) (mm^{-1})	2.605
space group	$P2_1/a$	λ(Mo Kα) (Å)	0.710 73
temp (K)	298(2)	F(000)	2360
a (Å)	17.846(3)	θ range	1.08−24.47
b (Å)	10.548(8)	no. of reflns colld	6087
c (Å)	18.801(3)	no. of indep reflns	5872
β (deg)	90.680(10)	R_{int}	0.0432
V (Å^3)	3539(3)	R1[a]	0.0404 [$I > 2\sigma(I)$]
Z	4	wR$_2$[b]	0.1109

[a] $R1 = \sum|(F_o - F_c)|\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$.

br) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.92 (1H$_p$, app tr, J = 6 Hz), 5.79 (2H$_m$, app tr, J = 6 Hz), 4.69 (2H$_o$, app tr, J = 6 Hz), 2.06 (6H, d, J(CH_3−P) = 10 Hz). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$): 20.21 ppm.

X-ray Crystallography. A summary of selected crystallographic data for **1** is given in Table 1. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer. Correction for absorption[6] was applied by integration with 0.819 maximum and 0.687 minimum transmission. The structure was solved by direct methods;[7] correct positions for Ru atoms were deduced from an E-map. Several cycles of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for remaining non-H atoms. Hydrogen atoms were included as fixed idealized contributors. Successful convergence of the full-matrix least-squares refinement on F^2 (SHELXL-93)[8] was indicated by the maximum shift/error for the last cycle. The highest peaks in the final difference Fourier map were in the vicinity of Ru atoms. A final analysis of the variance between the observed and calculated structure factors showed no dependence on amplitude or resolution.

Results and Discussion

Thermolysis of $Ru_6C(CO)_{16}PPh_3$ in chlorobenzene gives $Ru_6C(CO)_{13}PPh_2(\mu\text{-}\eta^6\text{-}C_6H_6)$ (**1**), in which three carbonyl ligands have been replaced by one of the phenyl rings on the triphenylphosphine ligand. The positive ion FAB mass spectrum of **1** contains a parent ion multiplet followed by peaks corresponding to the loss of up to 13 carbonyl ligands. The carbonyl stretching frequencies range from 2065 to 1816 cm^{-1}, and the bridging carbonyl ligands appear at 1837 and 1816 cm^{-1} as broad peaks. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 41.2 ppm, which is shifted 9 ppm to higher field compared with the signal for $Ru_6C(CO)_{16}PPh_3$ at 50.0 ppm.

The ^{1}H NMR spectrum of **1** shows two groups of peaks. The first group, which integrates to 10 protons and has peaks at δ 8.01 and 7.58, within the range of normal phenyl protons on phosphine ligands, can be assigned to the protons of the two unaffected phenyl rings. The second group, corresponding to five protons, consists of three sets of peaks at δ 5.91, 5.85, and 4.46 with integrations of 1 (para), 2 (meta), and 2 (ortho) protons, respectively. The upfield shift of these latter signals is consistent with coordination of the third phenyl ring within the ruthenium cluster.

A single crystal X-ray structure study of **1** provided the ORTEP diagram shown in Figure 1. Selected bond distances and angles are listed in Table 2. The metal framework is a C-centered octahedron with the triphenylphosphine ligand coordinated by phosphorus to Ru(5) and by one of its phenyl rings to Ru(1). The Ru−Ru bond distances, 2.79−3.07 Å, are within the range of those for $Ru_6C(CO)_{17}$.[9] As observed in other η^6-arene Ru_6 complexes,[3b] the ruthenium atom bearing the arene ligand moves toward the carbide atom; Ru(1)−C(carbide) is the shortest among the six Ru−C(carbide) bonds. Among the four bonds of Ru(1) to adjacent Ru atoms, the Ru(1)−Ru(5) distance (2.789(1) Å) is the shortest compared to Ru(1)−Ru(2,4,6) (average 2.87 Å). However, the remaining bonds to Ru(5), especially Ru(4)−Ru(5) = 3.069(1) Å, are among the longest. This is apparently due to the strain caused by the bridging coordination of the phenyl ring. The coordinated phenyl ring is not symmetrically bonded to Ru(1); the Ru(1)−C(phenyl) bonds are longest to the para carbon (Ru(1)−C(94) = 2.28(1) Å) and shortest to the ipso carbon (Ru(1)−C(91) = 2.16(1) Å). The C−C distances of the coordinated phenyl ring do not show short−long alternation. The angle of C(91)−Ru(5)−P (100.1(3)°) is smaller than those of C(71,81)−Ru(5)−P (120.9(3)° and 119.3(3)°), which further indicates the structural distortions induced by the bridging configuration.

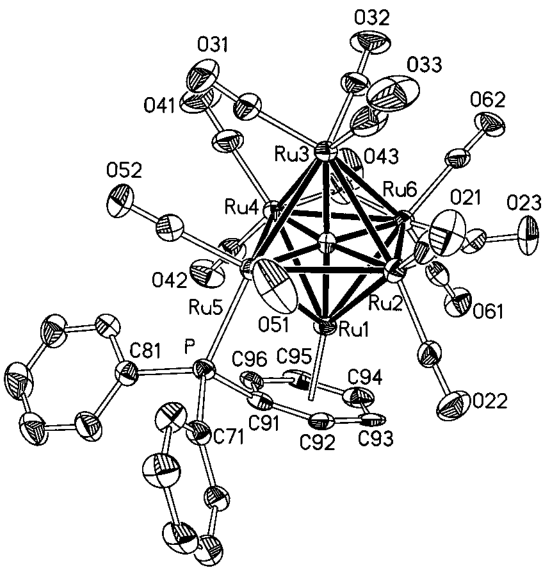

Figure 1. ORTEP drawing of the molecular structure of compound 1.

Placing a solution of **1** in CH_2Cl_2 under 25 psig of CO at room temperature for 30 min causes reformation of $Ru_6C(CO)_{16}PPh_3$ in 33% yield (Scheme 1), in addition to formation of pentanuclear $Ru_5C(CO)_{14}PPh_3$. To our knowledge, there have been no reports on replacing the arene ligand(s) by carbonyls in either face-capping or terminal arene clusters.[3b] It is significant also that the decapped Ru_5C compound is formed under such mild conditions compared to the formation of $Ru_5C(CO)_{15}$ from $Ru_6C(CO)_{17}$, which requires 80 atm of CO and heating to 70 °C for 3h.[10] The facile reactivity of **1** with CO is likely a direct manifestation of the strain in its structure.

We considered the possibility that the steric effect of the three phenyl rings in triphenylphosphine was the driving force for the formation of **1**. This led us to

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

		Ru−Ru			
Ru(1)−Ru(2)	2.880(1)	Ru(1)−Ru(4)	2.851(2)	Ru(1)−Ru(5)	2.789(1)
Ru(1)−Ru(6)	2.888(1)	Ru(2)−Ru(3)	2.908(2)	Ru(2)−Ru(5)	2.939(1)
Ru(2)−Ru(6)	2.829(1)	Ru(3)−Ru(4)	2.841(1)	Ru(3)−Ru(5)	2.915(1)
Ru(3)−Ru(6)	2.941(1)	Ru(4)−Ru(5)	3.069(1)	Ru(4)−Ru(6)	2.861(1)
		Ru−C(carbide)			
Ru(1)−C(1)	1.940(9)	Ru(2)−C(1)	2.088(8)	Ru(3)−C(1)	2.054(9)
Ru(4)−C(1)	2.032(8)	Ru(5)−C(1)	2.068(8)	Ru(6)−C(1)	2.091(8)
		Ru−C(phenyl), Ru−P, P−C			
Ru(1)−C(91)	2.163(8)	Ru(1)−C(92)	2.181(9)	Ru(1)−C(93)	2.265(10)
Ru(1)−C(94)	2.277(11)	Ru(1)−C(95)	2.264(10)	Ru(1)−C(96)	2.201(9)
Ru(5)−P	2.313(3)	P−C(71)	1.820(9)	P−C(81)	1.834(9)
P−C(91)	1.811(10)				
		Coordinated Phenyl C−C			
C(91)−C(92)	1.41(1)	C(92)−C(93)	1.42(1)	C(93)−C(94)	1.41(2)
C(94)−C(95)	1.39(2)	C(95)−C(96)	1.42(1)	C(96)−C(91)	1.45(1)
		Ru(5)−P−C(arene) Angles			
C(71)−P−Ru(5)	120.9(3)	C(81)−P−Ru(5)	119.3(3)	C(91)−P−Ru(5)	100.1(3)

examine the less crowded phosphine compound, $Ru_6C(CO)_{16}PMe_2Ph$, which we have demonstrated also yields an analogous thermolysis product. In particular, the ^1H NMR spectrum of **2** shows the same pattern as that of **1** in the coordinated phenyl ring region. This preparation suggests that the entropy gain upon loss of three CO molecules coupled with the stability of arene derivatives of the Ru_6 framework provides sufficient overall driving force to form these bridged derivatives.

Conclusion

We have prepared the first examples of cluster compounds in which a phenyl ring on a tertiary phosphine ligand becomes η^6-coordinated to an adjacent metal center, viz., $Ru_6C(CO)_{13}\{PR_2(\mu\text{-}\eta^6\text{-}C_6H_5)\}$ (**1**, R = Ph; **2**, R = Me). The formation of **1** is reversed by treating **1** with 25 psig of CO at room temperature. The analogous compound **2** shows that steric effects are not the primary driving force for the formation of these derivatives.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, thermal coefficients, bond distances, and bond angles from the structure determination of $Ru_6C(CO)_{13}\{PPh_2(\mu\text{-}\eta^6\text{-}C_6H_6)\}$ (10 pages). Ordering information is given on any current masthead page.

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