Role of the Reversible Opening of a Metal–Metal Bond in a Cluster-Assisted Transformation of Bis(diphenylphosphino)methane

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A reinvestigation of the reaction of $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**2**) with carbon monoxide (Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484–4491) under milder conditions shows that at room temperature **2** is in equilibrium with the adduct $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P\text{-}(C_6H_5)(C_6H_4))$ (**3a**), in which one Ru–Ru bond has been broken. **3a** has been isolated in 82% yield upon crystallization at −30 °C under a CO atmosphere. Similarly, **2** reacts at 0 °C with phosphines to afford compounds of general formula $Ru_3(CO)_9L(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**3b**, L = $P(C_6H_5)_3$; **3c**, L = dppm). Addition of triphenylphosphine to compound **2** at 25 °C or warming a solution of **3a** gives, among several compounds that have not been identified, the new dinuclear complex $Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}P(C_6H_5)\text{-}CH_2P(C_6H_5)(C_6H_4))$ (**5**). The nature of compounds **3a**, **3b** **3c**, and **5** has been established by spectroscopic means and for compound **3a**, **3c**, and **5** by X-ray diffraction methods. Crystal data: **3a**, triclinic, C_i^1—$P\bar{1}$, $Z = 2$, a = 13.435 (2) Å, b = 14.039 (2) Å, c = 9.839 (2) Å, α = 92.50 (1)°, β = 113.94 (1)°, γ = 92.86 (1)° (t = −165 °C), final $R(F)$ = 1.9%, NO = 5277, NV = 424; **3c**, monoclinic, C_{2h}^5—$P2_1/c$, $Z = 4$, a = 14.368 (2) Å, b = 25.612 (2) Å, c = 15.913 (2) Å, β = 108.09 (1)° (t = −150 °C), final $R(F)$ = 6.8%, NO = 6301, NV = 412; **5**, monoclinic, C_{2h}^5—$P2_1/c$, $Z = 4$, a = 13.625 (3) Å, b = 9.951 (2) Å, c = 18.917 (4) Å, β = 97.46 (2)° (t = −155 °C), final $R(F^2)$ = 4.8%, NO = 4404, NV = 316.

Introduction

One of the most attractive features of transition-metal clusters is their ability to transform various organic substrates through pathways that are not accessible to mononuclear species.[2]

The activation of phosphorus-containing ligands promoted by metal clusters is a typical example where the participation of adjacent metal centers seems to be required. Studies of the elementary steps involved in such transformations are important to our knowledge of "basic" cluster reactions.

In a previous publication,[3] we described the quantitative conversion of bis(diphenylphosphino)methane (dppm) into a new ligand upon interaction with a triangular ruthenium cluster (Scheme I).

While the first reaction (**1** → **2**) involved here is now well-documented,[4] the second one (**2** → **4**) is not. Related examples of the opening of phosphido bridges are rare and have been recently reported.[5] Since the elimination of the phosphorus bridge in the sequence **2** → **4** seemed to involve the activation of carbon monoxide, we were interested in how both events might be related. A reinvestigation of the reaction of **2** with carbon monoxide or phosphine ligands under mild conditions led us to establish a reactivity pattern for this kind of complex. The results are reported here.

Experimental Section

General Remarks. All reactions at atmospheric pressure were performed under a prepurified dinitrogen atmosphere with the use of standard Schlenk-line techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl, dichloromethane was distilled under dinitrogen from P_2O_5, and hexane was distilled by reflux over sodium and stored under dinitrogen. The following compounds were purchased and used as received: triphenylphosphine (Ega-Chemie), bis(diphenylphosphino)methane (Alfa), carbon monoxide (L'Air Liquide). Compound **2**, $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$, was prepared by a published procedure.[3]

Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrophotometer. These spectra were calibrated against water vapor absorption. ^1H and ^{31}P NMR spectra were obtained on a Brucker WM250 spectrometer. All ^1H NMR chemical shifts are relative to TMS. ^{31}P positive chemical shifts are downfield from 85% H_3PO_4 as external reference. Microanalyses of C, H, and P were made by the "Service Central de Microanalyse du CNRS".

Preparation of $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_4))$ (3a). Carbon monoxide was bubbled through a solution of **2** (200 mg) in CH_2Cl_2 (10 mL) at room temperature. The initial deep red

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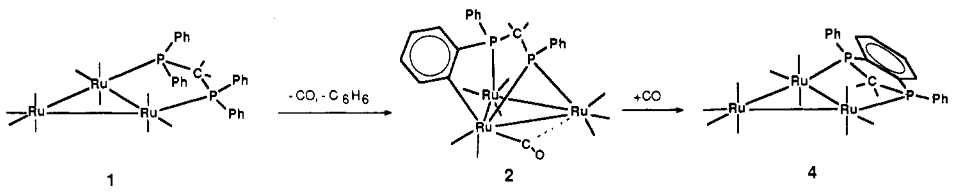
Scheme I



color turned red-orange within 5 min. An IR spectrum (ν(CO) region) of the solution showed two new bands at 2095 and 2050 cm^{-1} in addition to those of **2** (2066 (m), 2025 (s, br), 1998 (m), 1975 (w), 1920 (vw) cm^{-1}). Hexane (10 mL) was then added under a CO atmosphere. The new compound **3a** crystallized at −30 °C from this solution as yellow needles. The crystals were collected on a cold frit, washed with cold hexane, and dried (170 mg, yield 82%). Compound **3a** is relatively unstable, even as a solid, and no analytical results were obtained. The following NMR data are for compound **3a**, although under conditions of measurement compound **2** is also present (**2**/**3a** ≈ 1/2.5): $^1H\{^{31}P\}$ NMR ($CDCl_3$, 27 °C, under CO atmosphere) δ 6.0–8.0 (m, C_6H_5 and C_6H_4), 3.7 (AB pattern, $\Delta\nu_{AB}$ = 124 Hz, J_{AB} = 12.3 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 27 °C, under CO atmosphere) δ 17.9 (d, $^2J_{PP}$ = 77 Hz, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), −45.7 (d, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$).

Preparation of $Ru_3(CO)_9(P(C_6H_5)_3)$ $(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (3b). A tetrahydrofuran solution (20 mL) of complex **2** (250 mg, 0.29 mmol) and $P(C_6H_5)_3$ (76 mg, 0.29 mmol) was stirred at 0 °C in a Schlenk tube. A rapid color change from deep red to gold yellow was observed. The reaction was monitored by IR spectroscopy (ν(CO) region) and was complete in 10 min. The solution was then evaporated to dryness under vacuum. The solid residue was recovered and dissolved in 2 mL of cold CH_2Cl_2 and 10 mL of cold hexane at −10 °C. Slow crystallization of this solution at −30 °C gave yellow platelets (240 mg, yield 75%): IR (ν(CO), cm^{-1}, THF solution) 2065 (m), 2043 (m), 2015 (s), 1990 (m, br); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 0 °C, 1/1 cis and trans isomer mixture) δ 6.0–7.9 (m, C_6H_5 and C_6H_4), 3.8 (AB pattern, $\Delta\nu_{AB}$ = 175 Hz, J_{AB} = 12.3 Hz, CH_2), 3.6 (AB pattern, $\Delta\nu_{AB}$ = 86 Hz, J_{AB} = 12.5 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 0 °C) trans isomer δ 34.8 (dd, $^3J_{PP}$ = 7 Hz, $^2J_{PP}$ = 155 Hz, $P(C_6H_5)_3$), 10.8 (dd, $^2J_{PP}$ = 77 Hz, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), −41.1 (dd, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), cis isomer δ 25.1 (dd, $^3J_{PP}$ = 7 Hz, $^2J_{PP}$ = 13 Hz, $P(C_6H_5)_3$), 8.4 (dd, $^2J_{PP}$ = 89 Hz, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), −61.3 (dd, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$). Anal. Calcd for $C_{46}H_{31}O_9P_3Ru_3$: C, 49.16; H, 2.78; P, 8.27. Found: C, 49.13; H, 2.76; P, 8.27. If the above reaction is carried out at 25 °C or above, other compounds in addition to **3b** are formed. These include **5** (vide infra), $Ru(CO)_3(P(C_6H_5)_3)_2$, and undetermined products in ratios highly dependent on the temperature of the reaction.

Preparation of $Ru_3(CO)_9(\eta^1\text{-dppm})(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (3c). Under the same experimental conditions as for **3b**, the reaction of dppm (89 mg, 0.23 mmol) with complex **2** (200 mg, 0.23 mmol) was complete within 10 min. The new compound **3c** was recrystallized as yellow parallelepipedic platelets (yield 85%): IR (ν(CO), cm^{-1}, CH_2Cl_2 solution) 2065 (m), 2038 (m), 2010 (s), 1985 (m, br). $^1H\{^{31}P\}$ NMR (0 °C, $CDCl_3$) δ 6.0–7.9 (m, C_6H_5 and C_6H_4), 3.9 (AB pattern, $\Delta\nu_{AB}$ = 245 Hz, J_{AB} = 12.3 Hz, CH_2), 2.6 (AB pattern, $\Delta\nu_{AB}$ = 153 Hz, J_{AB} = 14.2 Hz, CH_2); $^{31}P\{^1H\}$ NMR (0 °C, $CDCl_3$) δ 17.2 (ddd, $^2J_{PP}$ = 91 Hz, $^3J_{PP}$ = 6 Hz, $^2J_{PP}$ = 13 Hz, $P(C_6H_5)_2CH_2P(C_6H_5)_2$), 9.8 (dd, $^2J_{PP}$ = 88 Hz, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), −30.0 (d, $P(C_6H_5)_2CH_2P(C_6H_5)_2$ (noncoordinated)), −60.1 (dd, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$). Anal. Calcd for $C_{53}H_{38}O_9P_4Ru_3$: C, 51.09; H, 3.07; P, 9.94. Found: C, 51.24; H, 3.50; P, 9.64.

A Route to $Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (5). If a dichloromethane solution (20 mL) of **2** (250 mg, 0.29 mmol) was allowed to react at room temperature with triphenylphosphine (76 mg, 0.29 mmol), a mixture of several products was obtained. A ^{31}P NMR spectrum of the crude solution shows (i) a set of major signals that are those of the isomers of **3b** (see above), (ii) a signal at 55 ppm (s) that is attributed to $Ru(CO)_3(P(C_6H_5)_3)_2$[6] (ν(CO) absorption band at 1900 cm^{-1} [6]), (iii) signals at 86.7 (d) and 0.9 (d) ppm that belong to the new compound **5**, and (iv) other weak signals that cannot be assigned unambiguously.

A suspension of **3b** (100 mg) in 15 mL of cyclohexane was warmed at 70 °C for 2 h. The resulting red solution was next concentrated under vacuum and then chromatographed on silica gel. Elution with dichloromethane/hexane (1/5) gave several bands, but only the major one, which was orange, could be worked up. This band contains a mixture of **2** and **5**; these can be separated upon crystallization: IR (ν(CO), cm^{-1}, C_6H_{12} solution) 2070 (s), 2032 (s), 2010 (s), 1992 (m), 1985 (m), 1975 (m); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 27 °C) δ 6.3–7.9 (m, C_6H_5 and C_6H_4), 4.0 (AB pattern, $\Delta\nu_{AB}$ = 79 Hz, J_{AB} = 12.1 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 27 °C) δ 86.7 (d, $^2J_{PP}$ = 71 Hz, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$), 0.9 (d, $P(C_6H_5)CH_2P(C_6H_5)(C_6H_4)$). Anal. Calcd for $C_{25}H_{16}O_6P_2Ru_2$: C, 44.39; H, 2.38; P, 9.16. Found: C, 44.62; H, 2.36; P, 9.17.

Crystallographic Studies. Crystals of **3a** were grown from dichloromethane/ethanol (1/3) at ambient temperature under a CO atmosphere; crystals of **3c** were obtained from a dichloromethane/hexane solution (1/5) at −30 °C; crystals of **5** were obtained from an acetone/ethanol solution (1/3) that was allowed to evaporate slowly at room temperature.

For compounds **3a** and **3c**, cell constants were obtained at low temperature[7] by the least-squares refinement of the setting angles of 25 reflections in the range 20° < 2θ(Mo $K\alpha_1$) < 30° obtained on an Enraf-Nonius CAD4 diffractometer; data collection and reduction were carried out as described previously.[8] For compound **5**, the cell parameters were determined at low temperature[9] from the setting angles of 15 centered reflections[10] obtained on a Picker FACS-1 diffractometer; the data were processed as previously described[10] with the use of a p value of 0.04. Table I presents further crystallographic information.

The positions of the Ru and P atoms in each structure were determined by direct methods. The combination of full-matrix least-squares refinement and difference electron density syntheses was used to locate the remaining non-hydrogen atoms. Atomic scattering factors were taken from the usual tabulations.[11] Anomalous dispersion terms for the Ru and P atoms were included in F_c.[12] All non-hydrogen atoms were allowed to vibrate anisotropically. The positions of the hydrogen atoms were idealized (C–H = 0.95 Å, B = 1 Å^2 greater than the equivalent B of the atom to which it is attached) and held fixed during refinements. The final refinements were carried out on F for **3a** and **3c** and on F^2 for **5**.[13] For **3a** and **3c** only reflections having $F_o^2 > 3\sigma(F_o^2)$ were used; for **5** all unique data were used. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ for **3a** and **3c**, and $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$ for **5**. Final atomic parameters for the atoms of **3a**, **3c**, and **5** are listed in Tables II, III, and IV, respectively. Tables S1, S2, and S3 list the thermal parameters for all atoms of **3a**, **3c**, and **5**, respectively.[14] Structure amplitudes

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Table I. Experimental Data for X-ray Studies

	3a	**3c**	**5**
formula	$C_{29}H_{16}O_{10}P_2Ru_3 \cdot CH_2Cl_2$	$C_{53}H_{38}O_9P_4Ru_3$	$C_{25}H_{16}O_6P_2Ru_2$
fw, amu	974.54	1245.99	676.49
a, Å	13.435 (2)	14.368 (2)	13.625 (3)
b, Å	14.039 (2)	25.612 (2)	9.951 (2)
c, Å	9.839 (2)	15.913 (2)	18.917 (4)
α, deg	92.50 (1)		
β, deg	113.94 (1)	108.09 (1)	97.46 (2)
γ, deg	92.86 (1)		
V, Å^3	1690	5567	2543
Z	2	4	4
ρ_{calcd}, g·cm^{-3}	1.915		1.770
space group	C_i^1—$P\bar{1}$	C_{2h}^5—$P2_1/c$	C_{2h}^5—$P2_1/c$
cryst shape			10-sided, faces {100}, {001}, {011}, (1$\bar{1}\bar{1}$), (11$\bar{1}$)
cryst vol, mm^3			0.0628
diffractometer	Nonius CAD4	Nonius CAD4	Picker FACS1
t, °C	−165	−150	−155
radiatn	graphite monochromated, Mo Kα, λ(Mo Kα_1) = 0.7093 Å		
linear abs coeff, cm^{-1}	16.05		13.25
transmissn factors	0.99–0.97^a		0.56–0.64^b
receiving aperture, mm	3.5 × 3.5	4 × 4	3.7 × 3.2
takeoff angle, deg	3.0	3.5	3.4
scan speed, deg min^{-1}	2.0	2.0	2.0
scan mode	ω–2θ	ω–θ	θ–2θ
scan range, deg	1.1 below Kα_1 to 1.1 above Kα_2	0.85 below Kα_1 to 0.85 above Kα_2	1.0 below Kα_1 to 1.0 above Kα_2
2θ limit, deg	3–50	3–49	3–50
unique data used in final refinement	5277	6301	4404
unique data, $F_o^2 > 3\sigma(F_o^2)$	5277	6301	4273
final no. of variables	424	412	316
R (on F_o^2, all data)			4.8
R_w (on F_o^2, all data)			8.8
R (on F_o, $F_o^2 > 3\sigma(F_o^2)$)	1.9	6.8	2.5
R_w (on F_o, $F_o^2 > 3\sigma(F_o^2)$)	2.6	10.7	5.2

^{a} Ψ-Scan method. ^{b} Analytical method.

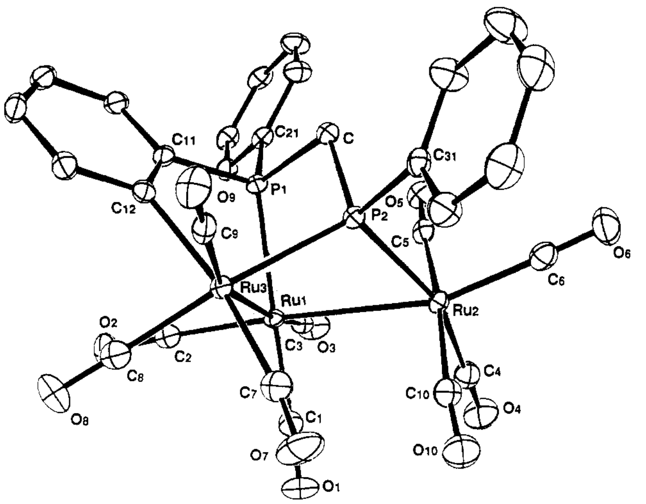

Figure 1. Perspective view of the complex $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$(**3a**). Here and in Figures 2 and 3 vibrational ellipsoids are drawn at the 50% probability level.

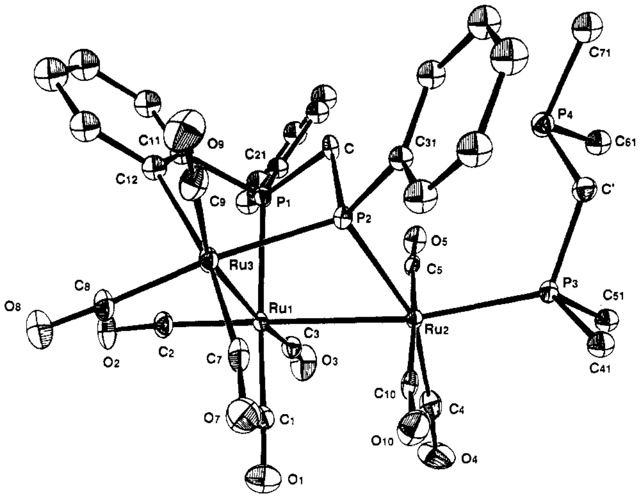

Figure 2. Perspective view of the complex $Ru_3(CO)_9(\eta^1\text{-}dppm)(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**3c**). Only the ipso carbon atoms of the phenyl rings attached to atoms P(3) and P(4) are shown.

(10|F_o| vs 10|F_c|) for the three structures are available in Tables S4–S6.[14] A negative entry for |F_o| in the last table indicates that $F_o^2 < 0$. Compound **3a** crystallizes with a molecule of dichloromethane per molecule of a trinuclear cluster. This solvent molecule has been located and refined. Compound **3c** also crystallizes with a solvent molecule, as shown for instance by residual peaks in the final difference electron density map. However all attempts to attribute these peaks to a disordered hexane molecule were unsuccessful. As a result the R values found for **3c** are rather high.

Results

Scheme II shows compounds **1**–**5**. The sequence **1** → **2** → **4** has been discussed previously.[3] Compounds **3a**, **3b**, and **3c** may be thought of as $Ru_3(CO)_9L$ fragments (**3a**, L = CO; **3b**, L = $P(C_6H_5)_3$; **3c**, L = dppm,) bridged by the six-electron tridendate ligand $(C_6H_5)PCH_2P(C_6H_5)(C_6H_4)$. They are thus 50e trinuclear clusters. In compound **5** the same six-electron ligand bridges the Ru–Ru bond.

Description of the Structures. Perspective views of compounds **3a** and **3c**, $Ru_3(CO)_9L(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (L = CO or dppm), are presented along with

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[14] See paragraph at the end of paper regarding supplementary material.

Table II. Final Atomic Parameters for Compound 3a

atom	x	y	z	B_{eq}, Å^2
Ru(1)	0.29360 (2)	0.37768 (1)	0.01734 (2)	0.957 (4)
Ru(2)	0.37763 (2)	0.20764 (1)	−0.06655 (2)	1.121 (4)
Ru(3)	0.32297 (2)	0.29075 (1)	0.29262 (2)	1.058 (4)
P(1)	0.11979 (5)	0.29552 (5)	−0.04400 (6)	1.03 (1)
P(2)	0.28525 (5)	0.17135 (5)	0.09394 (6)	1.03 (1)
C(1)	0.4457 (2)	0.4201 (2)	0.1064 (3)	1.49 (5)
O(1)	0.5353 (2)	0.4468 (2)	0.1599 (2)	2.38 (5)
C(2)	0.2568 (2)	0.4822 (2)	0.1112 (3)	1.51 (5)
O(2)	0.2379 (2)	0.5493 (1)	0.1627 (2)	2.36 (4)
C(3)	0.2578 (2)	0.4281 (2)	−0.1745 (3)	1.38 (5)
O(3)	0.2333 (2)	0.4612 (2)	−0.2853 (2)	2.32 (4)
C(4)	0.4463 (2)	0.2789 (2)	−0.1769 (3)	1.89 (6)
O(4)	0.4848 (2)	0.3212 (2)	−0.2403 (2)	2.86 (5)
C(5)	0.2394 (2)	0.2151 (2)	−0.2336 (3)	1.40 (5)
O(5)	0.1615 (1)	0.2167 (1)	−0.3383 (2)	1.78 (4)
C(6)	0.3924 (2)	0.0755 (2)	−0.1186 (3)	1.76 (6)
O(6)	0.3976 (2)	−0.0013 (1)	−0.1518 (2)	2.78 (5)
C(7)	0.4787 (2)	0.2833 (2)	0.3696 (3)	1.78 (6)
O(7)	0.5704 (2)	0.2809 (2)	0.4372 (2)	3.12 (5)
C(8)	0.3486 (2)	0.4111 (2)	0.4117 (3)	1.72 (6)
O(8)	0.3643 (2)	0.4795 (2)	0.4847 (2)	2.72 (5)
C(9)	0.3138 (2)	0.2027 (2)	0.4289 (3)	1.39 (5)
O(9)	0.3083 (2)	0.1486 (1)	0.5091 (2)	2.09 (4)
C(10)	0.5225 (2)	0.2185 (2)	0.1013 (3)	1.80 (6)
O(10)	0.6098 (2)	0.2230 (2)	0.1847 (2)	2.97 (5)
C	0.1383 (2)	0.1676 (2)	−0.0263 (3)	1.11 (5)
C(11)	0.0726 (2)	0.3184 (2)	0.1009 (3)	1.22 (5)
C(12)	0.1538 (2)	0.3123 (2)	0.2449 (3)	1.26 (5)
C(13)	0.1190 (2)	0.3253 (2)	0.3605 (3)	1.60 (6)
C(14)	0.0122 (2)	0.3420 (2)	0.3344 (3)	1.87 (6)
C(15)	−0.0655 (2)	0.3468 (2)	0.1913 (3)	1.83 (6)
C(16)	−0.0349 (2)	0.3352 (2)	0.0730 (3)	1.47 (5)
C(21)	0.0031 (2)	0.3080 (2)	−0.2186 (3)	1.23 (5)
C(22)	−0.0677 (2)	0.2311 (2)	−0.3013 (3)	1.73 (6)
C(23)	−0.1578 (2)	0.2460 (2)	−0.4299 (3)	2.04 (6)
C(24)	−0.1781 (2)	0.3373 (2)	−0.4762 (3)	1.67 (6)
C(25)	−0.1086 (2)	0.4139 (2)	−0.3946 (3)	1.63 (6)
C(26)	−0.0178 (2)	0.3997 (2)	−0.2663 (3)	1.43 (5)
C(31)	0.3039 (2)	0.0480 (2)	0.1502 (3)	1.31 (5)
C(32)	0.2238 (2)	−0.0261 (2)	0.0830 (3)	2.16 (6)
C(33)	0.2410 (3)	−0.1182 (2)	0.1282 (4)	2.77 (7)
C(34)	0.3376 (3)	−0.1382 (2)	0.2407 (3)	2.58 (7)
C(35)	0.4186 (2)	−0.0654 (2)	0.3075 (3)	2.47 (7)
C(36)	0.4012 (2)	0.0266 (2)	0.2629 (3)	1.95 (6)
C′	0.9692 (3)	0.1036 (2)	0.3246 (4)	3.87 (9)
Cl(1)	0.87209 (7)	0.02179 (6)	0.3435 (1)	3.60 (2)
Cl(2)	1.05581 (7)	0.04638 (6)	0.25793 (9)	3.65 (2)

Table III. Final Atomic Parameters for Compound 3c

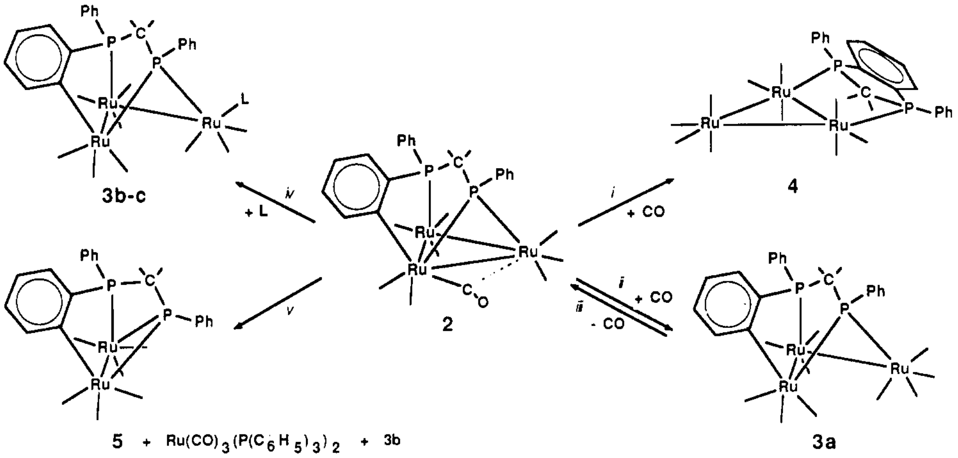
atom	x	y	z	B_{eq} or B_{iso}, Å^2
Ru(1)	0.51629 (7)	0.05256 (4)	0.30688 (7)	1.02 (2)
Ru(2)	0.68537 (7)	0.06094 (4)	0.24304 (7)	0.97 (2)
Ru(3)	0.41990 (8)	0.13222 (4)	0.18097 (7)	1.21 (2)
P(1)	0.5612 (2)	0.1307 (1)	0.3897 (2)	1.14 (7)
P(2)	0.5956 (2)	0.1429 (1)	0.2260 (2)	1.09 (7)
P(3)	0.8303 (2)	0.0810 (1)	0.2081 (2)	1.12 (7)
P(4)	0.8978 (3)	0.1748 (2)	0.3384 (2)	1.48 (7)
C(1)	0.478 (1)	0.0037 (5)	0.2115 (9)	1.4 (3)
O(1)	0.4526 (8)	−0.0264 (4)	0.1564 (7)	2.6 (2)
C(2)	0.397 (1)	0.0503 (6)	0.3336 (9)	1.7 (3)
O(2)	0.3259 (7)	0.0450 (4)	0.3500 (7)	2.6 (2)
C(3)	0.587 (1)	0.0050 (6)	0.3957 (9)	1.7 (3)
O(3)	0.6232 (8)	−0.0249 (5)	0.4494 (7)	3.0 (2)
C(4)	0.711 (1)	−0.0131 (6)	0.2572 (9)	1.9 (3)
O(4)	0.7182 (8)	−0.0573 (4)	0.2615 (8)	3.2 (3)
C(5)	0.7458 (9)	0.0712 (5)	0.3687 (8)	1.3 (3)
O(5)	0.7863 (7)	0.0746 (4)	0.4417 (6)	1.8 (2)
C(7)	0.411 (1)	0.0917 (6)	0.0771 (9)	1.7 (3)
O(7)	0.3885 (8)	0.0714 (4)	0.0083 (6)	2.5 (2)
C(8)	0.292 (1)	0.1082 (6)	0.1755 (9)	1.8 (3)
O(8)	0.2140 (7)	0.0960 (5)	0.1713 (7)	2.7 (2)
C(9)	0.392 (1)	0.1959 (6)	0.1151 (9)	1.8 (3)
O(9)	0.3771 (8)	0.2336 (4)	0.0774 (7)	2.8 (2)
C(10)	0.6168 (9)	0.0486 (6)	0.1175 (9)	1.5 (3)
O(10)	0.5844 (8)	0.0403 (5)	0.0452 (6)	2.6 (2)
C	0.632 (1)	0.1720 (5)	0.3369 (8)	1.2 (3)
C′	0.8812 (9)	0.1472 (5)	0.2270 (9)	1.4 (3)
C(11)	0.457 (1)	0.1716 (6)	0.3768 (9)	1.5 (2)*
C(12)	0.397 (1)	0.1776 (6)	0.2889 (9)	1.5 (2)*
C(13)	0.318 (1)	0.2122 (6)	0.272 (1)	2.1 (3)*
C(14)	0.300 (1)	0.2394 (7)	0.342 (1)	2.7 (3)*
C(15)	0.359 (1)	0.2337 (7)	0.428 (1)	2.6 (3)*
C(16)	0.438 (1)	0.1994 (6)	0.4462 (9)	2.1 (3)*
C(21)	0.627 (1)	0.1307 (5)	0.5073 (8)	1.4 (2)*
C(22)	0.600 (1)	0.0941 (6)	0.562 (1)	2.1 (3)*
C(23)	0.649 (1)	0.0933 (6)	0.653 (1)	2.3 (3)*
C(24)	0.724 (1)	0.1279 (6)	0.689 (1)	2.3 (3)*
C(25)	0.750 (1)	0.1644 (6)	0.636 (1)	2.5 (3)*
C(26)	0.703 (1)	0.1666 (6)	0.5462 (9)	1.8 (3)*
C(31)	0.635 (1)	0.1917 (5)	0.1606 (8)	1.2 (2)*
C(32)	0.687 (1)	0.2366 (6)	0.1959 (9)	1.6 (3)*
C(33)	0.715 (1)	0.2717 (6)	0.1423 (9)	2.0 (3)*
C(34)	0.690 (1)	0.2625 (6)	0.053 (1)	2.2 (3)*
C(35)	0.636 (1)	0.2190 (6)	0.015 (1)	2.0 (3)*
C(36)	0.609 (1)	0.1845 (6)	0.0669 (9)	2.1 (3)*
C(41)	0.818 (1)	0.0722 (5)	0.0919 (9)	1.5 (2)*
C(42)	0.818 (1)	0.0216 (7)	0.060 (1)	2.5 (3)*
C(43)	0.804 (1)	0.0127 (7)	−0.029 (1)	3.2 (3)*
C(44)	0.789 (1)	0.0527 (8)	−0.086 (1)	4.2 (4)*
C(45)	0.791 (2)	0.1037 (8)	−0.054 (1)	4.7 (4)*
C(46)	0.803 (1)	0.1124 (7)	0.034 (1)	2.9 (3)*
C(51)	0.937 (1)	0.0410 (5)	0.2614 (9)	1.4 (2)*
C(52)	1.014 (1)	0.0381 (6)	0.2249 (9)	1.6 (3)*
C(53)	1.098 (1)	0.0106 (7)	0.266 (1)	2.1 (3)*
C(54)	1.109 (1)	−0.0141 (6)	0.347 (1)	2.2 (3)*
C(55)	1.033 (1)	−0.0108 (6)	0.384 (1)	2.2 (3)*
C(56)	0.948 (1)	0.0142 (6)	0.3409 (9)	1.7 (3)*
C(61)	1.012 (1)	0.1462 (6)	0.4058 (9)	1.8 (3)*
C(62)	1.018 (1)	0.1321 (7)	0.493 (1)	2.7 (3)*
C(63)	1.105 (1)	0.1088 (8)	0.550 (1)	3.7 (4)*
C(64)	1.182 (1)	0.1007 (7)	0.521 (1)	3.5 (4)*
C(65)	1.178 (1)	0.1145 (7)	0.437 (1)	3.4 (4)*
C(66)	1.096 (1)	0.1373 (6)	0.380 (1)	2.6 (3)*
C(71)	0.936 (1)	0.2421 (6)	0.3194 (9)	2.1 (3)*
C(72)	0.901 (1)	0.2828 (7)	0.358 (1)	2.7 (3)*
C(73)	0.926 (1)	0.3341 (8)	0.346 (1)	3.9 (4)*
C(74)	0.979 (1)	0.3453 (8)	0.292 (1)	3.9 (4)*
C(75)	1.012 (1)	0.3047 (8)	0.249 (1)	3.8 (4)*
C(76)	0.991 (1)	0.2531 (7)	0.264 (1)	2.7 (3)*

[a] Atoms with an asterisk were refined isotropically.

labeling schemes in Figures 1 and 2, respectively, while Tables V and VI summarize important bond distances and angles. Compounds **3a** and **3c** are trinuclear 50e open clusters with a long Ru(2)···Ru(3) distance of 4.027(1) Å in **3a** and 4.064 (1) Å in **3c**. One face of these triruthenium complexes is capped by the six-electron tridendate $(C_6H_5)PCH_2P(C_6H_5)(C_6H_4)$ ligand. The coordination mode of the tridendate bridging ligand here is very similar to that found in the 48e parent **2**. This capping involves (i) a phosphido group that bridges the open edge (P(2)–Ru(2) = 2.427 (1) and 2.435 (2) Å, and P(2)–Ru(3) = 2.390 (1) and 2.417 (2) Å, respectively, in **3a** and **3c**), (ii) a terminal phosphorus atom (P(1)–Ru(1) = 2.382 (1) and 2.373 (2) Å, respectively, in **3a** and **3c**), and (iii) an orthometalated phenyl ring Ru(3)–C(12) = 2.166 (2) and 2.180 (6) Å, in **3a** and **3c**, respectively (Tables V and VI). While appropriate bond distances among **2**, **3a**, and **3c** are comparable (excluding Ru(2)–Ru(3)), some bond angles are not, as in **2** there are three Ru–Ru bonds and two of the three Ru atoms (Ru(2) and Ru(3)) are seven-coordinate, while in **3a** and **3c** there are only two Ru–Ru bonds and each Ru center is the more usual six-coordinated.

Octahedral geometry about the Ru atoms is completed by coordination of three terminal CO groups around atoms Ru(1) and Ru(3) in **3a** and **3c**, three terminal CO ligands about atom Ru(2) in **3a**, and two CO groups and a monodentate dppm ligand about atom Ru(2) in **3c**. The coordination site occupied by atom P(3) of the dppm ligand is trans to the Ru(1)–Ru(2) bond. This site is occupied

Scheme II[a]



[a] (i) CO bubbling, 80 °C, cyclohexane; (ii) CO bubbling, 25 °C, dichloromethane; (iii) upon redissolution; (iv) phosphine addition ($P(C_6H_5)_3$ or dppm), 0 °C, dichloromethane; (v) $P(C_6H_5)_3$, 25 °C, dichloromethane.

Table IV. Final Atomic Parameters for Compound 5

atom	*x*	*y*	*z*	B_{eq}, Å^2
Ru(1)	0.30468 (2)	−0.12991 (2)	0.38973 (1)	1.2
Ru(2)	0.16192 (2)	−0.04807 (2)	0.27253 (1)	1.3
P(1)	0.41180 (5)	−0.02837 (7)	0.31687 (4)	1.3
P(2)	0.25512 (5)	0.08837 (7)	0.35521 (4)	1.4
C(1)	0.2032 (2)	−0.1766 (3)	0.4486 (2)	1.8
O(1)	0.1446 (2)	−0.2037 (2)	0.4841 (1)	2.5
C(2)	0.4099 (2)	−0.1366 (3)	0.4678 (2)	1.8
O(2)	0.4752 (2)	−0.1480 (2)	0.5115 (1)	2.5
C(3)	0.3136 (2)	−0.3047 (3)	0.3464 (2)	1.7
O(3)	0.3219 (2)	−0.4047 (2)	0.3190 (1)	2.6
C(4)	0.0607 (2)	−0.0438 (3)	0.3359 (2)	1.9
O(4)	0.0013 (2)	−0.0432 (2)	0.3733 (1)	2.2
C(5)	0.0965 (2)	0.0786 (3)	0.2077 (2)	1.7
O(5)	0.0605 (2)	0.1588 (2)	0.1694 (1)	2.4
C(6)	0.1199 (2)	−0.2221 (3)	0.2338 (2)	2.2
O(6)	0.0955 (2)	−0.3251 (3)	0.2116 (2)	3.6
C(7)	0.3748 (2)	0.1464 (3)	0.3304 (1)	1.3
C(11)	0.3764 (2)	−0.0538 (3)	0.2224 (1)	1.3
C(12)	0.2735 (2)	−0.0602 (3)	0.2003 (2)	1.5
C(13)	0.2465 (2)	−0.0725 (3)	0.1266 (2)	1.8
C(14)	0.3158 (2)	−0.0753 (3)	0.0782 (2)	2.0
C(15)	0.4161 (2)	−0.0675 (3)	0.1021 (2)	1.7
C(16)	0.4473 (2)	−0.0568 (3)	0.1758 (2)	1.5
C(21)	0.5445 (2)	−0.0480 (3)	0.3362 (1)	1.3
C(22)	0.6082 (2)	0.0615 (3)	0.3421 (2)	1.8
C(23)	0.7101 (2)	0.0404 (3)	0.3559 (2)	2.1
C(24)	0.7472 (2)	−0.0895 (3)	0.3636 (2)	2.1
C(25)	0.6838 (2)	−0.1979 (3)	0.3583 (2)	2.3
C(26)	0.5819 (2)	−0.1774 (3)	0.3455 (2)	1.8
C(31)	0.1978 (2)	0.2276 (3)	0.3965 (1)	1.4
C(32)	0.1862 (2)	0.3503 (3)	0.3599 (2)	2.1
C(33)	0.1384 (2)	0.4552 (3)	0.3872 (2)	2.4
C(34)	0.1019 (2)	0.4407 (3)	0.4518 (2)	2.5
C(35)	0.1113 (3)	0.3201 (4)	0.4879 (2)	3.0
C(36)	0.1594 (3)	0.2132 (3)	0.4600 (2)	2.4

Table V. Interatomic Distances (Å) for Compounds 2, 3a, and 3c

	2	3a	3c
Ru(1)–Ru(2)	2.818 (1)	2.917 (1)	2.918 (1)
Ru(1)–Ru(3)	2.853 (1)	2.907 (1)	2.894 (1)
Ru(1)–P(1)	2.351 (1)	2.382 (1)	2.373 (2)
Ru(1)–C(1)	1.922 (3)	1.917 (2)	1.912 (7)
Ru(1)–C(2)	1.901 (3)	1.891 (2)	1.885 (7)
Ru(1)–C(3)	1.909 (3)	1.926 (2)	1.905 (7)
Ru(2)–Ru(3)	2.888 (1)	4.027 (1)	4.064 (1)
Ru(2)–P(2)	2.293 (1)	2.427 (1)	2.435 (2)
Ru(2)–P(3)			2.373 (2)
Ru(2)–C(4)	1.952 (3)	1.969 (2)	1.931 (7)
Ru(2)–C(5)	1.866 (3)	1.929 (2)	1.935 (7)
Ru(2)–C(6)	1.929 (3)	1.944 (2)	
Ru(2)···C(7)	2.538 (3)		
Ru(2)–C(10)		1.961 (2)	1.959 (7)
Ru(3)–P(2)	2.347 (3)	2.390 (1)	2.417 (2)
Ru(3)–C(7)	1.968 (3)	1.925 (2)	1.923 (7)
Ru(3)–C(8)	1.934 (3)	1.947 (2)	1.913 (7)
Ru(3)–C(9)	1.918 (3)	1.899 (2)	1.912 (7)
Ru(3)–C(12)	2.158 (3)	2.166 (2)	2.180 (6)
P(1)–C	1.816 (2)	1.832 (2)	1.841 (6)
P(1)–C(11)	1.803 (2)	1.803 (2)	1.786 (7)
P(1)–C(21)	1.817 (2)	1.818 (2)	1.815 (7)
P(2)–C	1.821 (2)	1.841 (2)	1.841 (6)
P(2)–C(31)	1.815 (3)	1.839 (2)	1.820 (6)
P(3)–C′			1.834 (6)
P(3)–C(41)			1.816 (6)
P(3)–C(51)			1.822 (7)
P(4)–C′			1.854 (6)
P(4)–C(61)			1.816 (7)
P(4)–C(71)			1.863 (7)
⟨C–O⟩[a]	1.133 [8]	1.133 [6]	1.14 [1]
⟨C–C⟩[b]	1.390 [8]	1.386 [8]	1.38 [5]

[a] Within carbonyl groups. [b] Within phenyl rings; estimated standard deviation of a single observation on the assumption that values averaged are from the same population.

by a CO ligand in the parent complex **2**. Accordingly, the formation of **3c** from **2**, via the opening of a Ru–Ru bond and concomitant addition of dppm, must involve a rearrangement of CO ligands about atom Ru(2).

A perspective view of **5**, $Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$, is shown along with labeling scheme in Figure 3. Important bond distances and angles are given in Tables VII and VIII, respectively. The molecule is a dinuclear compound in which the tridentate six-electron species $(C_6H_5)PCH_2P(C_6H_5)(C_6H_4)$ this time acts as an edge-bridging ligand through (i) a phosphido group (P(2)–Ru(1) = 2.342 (1) Å, P(2)–Ru(2) = 2.321 (1) Å), (ii) a terminal phosphorus atom (P(1)–Ru(1) = 2.361 (1) Å), and (iii) an orthometalation of a phenyl ring (Ru(2)–C(12) = 2.176 (3) Å). The structure of **5** is very similar[15] to that of the compound $Fe_2(CO)_6(\mu\text{-}\eta^3\text{-}(C_6H_5)PCHMeP(C_6H_5)(C_6H_4))$: this compound was obtained through oxidative addition of the $(C_6H_5)_2PCHMeP(C_6H_5)_2$ ligand to $Fe_2(CO)_7(\mu\text{-}(C_6H_5)_2PCHMeP(C_6H_5)_2)$.

Synthetic Aspects. The reaction of the ruthenium cluster **2** with CO at room temperature affords the new cluster $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**3a**). At room temperature, compounds **2** and **3a** are in equilibrium. Integration of the ^1H NMR signals from the CH_2

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[15] Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; MacPherson, K. A.; Melchior, F.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 540–542.

Table VI. Bond Angles (deg) for Compounds 2, 3a, and 3c

	2	**3a**	**3c**
Ru(2)–Ru(1)–Ru(3)	61.22 (1)	87.51 (1)	88.75 (2)
Ru(2)–Ru(1)–P(1)	94.40 (2)	91.71 (1)	91.11 (4)
Ru(2)–Ru(1)–C(1)	85.6 (2)	82.13 (5)	80.7 (2)
Ru(2)–Ru(1)–C(2)	158.42 (8)	168.51 (5)	172.6 (2)
Ru(2)–Ru(1)–C(3)	101.13 (8)	92.45 (5)	89.6 (2)
Ru(3)–Ru(1)–P(1)	78.02 (2)	77.49 (1)	77.25 (4)
Ru(3)–Ru(1)–C(1)	94.14 (9)	88.41 (5)	87.3 (2)
Ru(3)–Ru(1)–C(2)	98.04 (8)	82.40 (5)	84.6 (2)
Ru(3)–Ru(1)–C(3)	159.50 (8)	173.51 (5)	174.8 (2)
P(1)–Ru(1)–C(1)	170.98 (9)	164.88 (5)	162.7 (2)
P(1)–Ru(1)–C(2)	86.27 (9)	91.45 (5)	90.6 (2)
P(1)–Ru(1)–C(3)	94.11 (8)	96.03 (5)	97.8 (2)
C(1)–Ru(1)–C(2)	90.5 (2)	92.08 (7)	95.8 (3)
C(1)–Ru(1)–C(3)	94.8 (2)	98.02 (7)	97.3 (3)
C(2)–Ru(1)–C(3)	100.3 (2)	98.20 (7)	97.4 (3)
Ru(1)–Ru(2)–Ru(3)	59.98 (1)		
Ru(1)–Ru(2)–P(2)	81.90 (2)	68.46 (1)	68.46 (4)
Ru(1)–Ru(2)–P(3)			169.70 (4)
Ru(1)–Ru(2)–C(4)	91.23 (10)	93.32 (5)	91.9 (2)
Ru(1)–Ru(2)–C(5)	83.01 (8)	77.12 (5)	78.8 (2)
Ru(1)–Ru(2)–C(6)	172.93 (8)	161.75 (5)	97.7 (2)
Ru(1)–Ru(2)–C(10)		97.64 (5)	
Ru(3)–Ru(2)–P(2)	52.35 (2)		
Ru(3)–Ru(2)–C(4)	115.44 (9)		
Ru(3)–Ru(2)–C(5)	129.23 (8)		
Ru(3)–Ru(2)–C(6)	112.97 (8)		
P(2)–Ru(2)–P(3)			105.07 (6)
P(2)–Ru(2)–C(4)	167.78 (9)	161.52 (5)	159.0 (2)
P(2)–Ru(2)–C(5)	91.81 (8)	90.82 (5)	92.89 (2)
P(2)–Ru(2)–C(6)	93.22 (9)	95.96 (5)	
P(2)–Ru(2)–C(10)		92.56 (5)	86.8 (2)
P(3)–Ru(2)–C(4)			95.4 (2)
P(3)–Ru(2)–C(5)			93.9 (2)
P(3)–Ru(2)–C(10)			89.8 (2)
C(4)–Ru(2)–C(5)	97.4 (2)	87.89	90.3 (3)
C(4)–Ru(2)–C(6)	92.7 (2)	102.52	
C(4)–Ru(2)–C(10)		86.67 (8)	88.7 (3)
C(5)–Ru(2)–C(6)	102.3 (2)	94.26 (7)	
C(5)–Ru(2)–C(10)		172.23 (7)	176.3 (3)
Ru(1)–Ru(3)–Ru(2)	58.80 (1)		
Ru(1)–Ru(3)–P(2)	80.26 (2)	69.07 (1)	69.11 (4)
Ru(1)–Ru(3)–C(7)	96.60 (9)	97.86 (5)	95.97 (2)
Ru(1)–Ru(3)–C(8)	82.21 (8)	95.39 (5)	92.95 (2)
Ru(1)–Ru(3)–C(9)	173.31 (9)	161.92 (5)	162.6 (2)
Ru(1)–Ru(3)–C(12)	86.46 (6)	88.46 (4)	89.2 (2)
Ru(2)–Ru(3)–P(2)	50.69 (2)		
Ru(2)–Ru(3)–C(7)	59.49 (8)		
Ru(2)–Ru(3)–C(8)	123.06 (8)		
Ru(2)–Ru(3)–C(9)	122.19 (9)		
Ru(2)–Ru(3)–C(12)	129.69 (6)		
P(2)–Ru(3)–C(7)	98.74 (9)	94.14 (5)	95.6 (2)
P(2)–Ru(3)–C(8)	161.40 (9)	164.45 (5)	161.8 (2)
P(2)–Ru(3)–C(9)	95.48 (8)	94.51 (5)	94.89 (2)
P(2)–Ru(3)–C(12)	91.48 (6)	95.86 (4)	95.9 (2)
C(7)–Ru(3)–C(8)	89.4 (2)	88.38 (7)	89.12 (3)
C(7)–Ru(3)–C(9)	89.1 (2)	90.62 (7)	92.4 (3)
C(7)–Ru(3)–C(12)	169.7 (2)	169.58 (7)	168.4 (3)
C(8)–Ru(3)–C(9)	101.4 (2)	100.81 (7)	102.5 (3)
C(8)–Ru(3)–C(12)	81.3 (2)	82.76 (7)	80.3 (3)
C(9)–Ru(3)–C(12)	88.5 (1)	85.68 (7)	85.5 (3)
Ru(1)–P(1)–C	114.36 (8)	108.43 (6)	108.9 (2)
Ru(1)–P(1)–C(11)	106.57 (8)	110.82 (6)	111.0 (2)
Ru(1)–P(1)–C(21)	118.33 (9)	122.57 (6)	122.5 (2)
C–P(1)–C(11)	102.0 (2)	99.33 (7)	99.9 (3)
C–P(1)–C(21)	105.5 (2)	107.42 (8)	106.7 (3)
C(11)–P(1)–C(21)	108.8 (2)	105.76 (8)	105.4 (3)
Ru(2)–P(2)–Ru(3)	76.96 (2)	113.44 (2)	113.79 (6)
Ru(2)–P(2)–C	116.77 (8)	105.63 (5)	105.1 (2)
Ru(2)–P(2)–C(31)	120.10 (9)	110.93 (5)	114.1 (2)
Ru(3)–P(2)–C	116.77 (8)	107.65 (5)	106.9 (2)
Ru(3)–P(2)–C(31)	127.87 (8)	115.27 (5)	112.7 (2)
C–P(2)–C(31)	100.9 (2)	102.83 (8)	103.1 (3)
Ru(2)–P(3)–C′			119.7 (2)
Ru(2)–P(3)–C(41)			113.3 (2)
Ru(2)–P(3)–C(51)			116.3 (2)
C′–P(3)–C(41)			101.0 (3)
C′–P(3)–C(51)			102.0 (3)
C(41)–P(3)–C(51)			101.9 (3)
C′–P(4)–C(61)			103.7 (3)
C′–P(4)–C(71)			98.9 (3)
C(61)–P(4)–C(71)			102.1 (3)
Ru(3)–C(7)–O(7)	159.1 (9)		
P(1)–C–P(2)	102.1 (2)	102.1 (2)	100.0 (3)
⟨Ru–C–O⟩[a]	177 [2]	176 [3]	174 [3]
⟨C–C–C⟩[b]	120 [2]	120 [2]	120 [2]

[a] Within carbonyl groups excluding C(7)O(7) in **2**. [b] Within phenyl rings.

Table VII. Interatomic Distances (Å) for Compound 5

Ru(1)–Ru(2)	2.871 (1)	Ru(2)–C(6)	1.938 (3)
Ru(1)–P(1)	2.361 (1)	Ru(2)–C(12)	2.176 (3)
Ru(1)–P(2)	2.342 (1)	P(1)–C	1.837 (3)
Ru(1)–C(1)	1.940 (3)	P(1)–C(11)	1.808 (3)
Ru(1)–C(2)	1.921 (3)	P(1)–C(21)	1.808 (3)
Ru(1)–C(3)	1.933 (3)	P(2)–C	1.847 (3)
Ru(2)–P(2)	2.321 (1)	P(2)–C(31)	1.816 (3)
Ru(2)–C(4)	1.943 (3)	⟨C–O⟩[a]	1.141 [4]
Ru(2)–C(5)	1.898 (3)	⟨C–C⟩[b]	1.39 [1]

[a] Within carbonyl groups. [b] Within phenyl rings.

group within **2** and **3a** gives a ratio **2**/**3a** close to 1/2.5 at 27 °C in $CDCl_3$. Pure compound **3a** can be obtained upon crystallization at −30 °C under a CO atmosphere. It is stable for hours as a solid at room temperature. However, dissolution of **3a** in several solvents at room temperature yields **2** quantitatively, while evolution of CO is visible together with a change of color from orange to deep red. The $^{31}P\{^{1}H\}$ NMR spectrum of **3a** is consistent with the structure established by X-ray analysis. Thus the signal observed at 7.9 ppm is assigned to a terminal P atom while the high-field one, centered at −45.7 ppm, is typical for a P atom bridging a nonbonded metal–metal interaction.[16]

Table VIII. Bond Angles (deg) for Compound 5

Ru(2)–Ru(1)–P(1)	80.56 (2)	P(2)–Ru(2)–C(12)	95.15 (8)
Ru(2)–Ru(1)–P(2)	51.66 (2)	C(4)–Ru(2)–C(5)	94.2 (2)
Ru(2)–Ru(1)–C(1)	92.82 (8)	C(4)–Ru(2)–C(6)	93.1 (2)
Ru(2)–Ru(1)–C(2)	165.14 (8)	C(4)–Ru(2)–C(12)	177.9 (2)
Ru(2)–Ru(1)–C(3)	90.10 (9)	C(5)–Ru(2)–C(6)	104.9 (2)
P(1)–Ru(1)–P(2)	67.54 (2)	C(5)–Ru(2)–C(12)	86.5 (1)
P(1)–Ru(1)–C(1)	167.92 (9)	C(6)–Ru(2)–C(12)	84.8 (2)
P(1)–Ru(1)–C(2)	90.42 (9)	Ru(1)–P(1)–C	97.02 (9)
P(1)–Ru(1)–C(3)	93.45 (8)	Ru(1)–P(1)–C(11)	114.31 (9)
P(2)–Ru(1)–C(1)	100.42 (8)	Ru(1)–P(1)–C(21)	120.89 (9)
P(2)–Ru(1)–C(2)	113.94 (8)	C–P(1)–C(11)	103.1 (2)
P(2)–Ru(1)–C(3)	138.43 (9)	C–P(1)–C(21)	111.0 (2)
C(1)–Ru(1)–C(2)	93.8 (2)	C(11)–P(1)–C(21)	108.5 (2)
C(1)–Ru(1)–C(3)	96.7 (2)	Ru(1)–P(2)–Ru(2)	76.00 (2)
C(2)–Ru(1)–C(3)	102.3 (2)	Ru(1)–P(2)–C	97.38 (9)
Ru(1)–Ru(2)–P(2)	52.33 (2)	Ru(1)–P(2)–C(31)	135.40 (9)
Ru(1)–Ru(2)–C(4)	89.62 (9)	Ru(2)–P(2)–C	115.81 (9)
Ru(1)–Ru(2)–C(5)	154.36 (9)	Ru(2)–P(2)–C(31)	120.52 (9)
Ru(1)–Ru(2)–C(6)	100.1 (1)	C–P(2)–C(31)	108.3 (2)
Ru(1)–Ru(2)–C(12)	90.61 (8)	P(1)–C–P(2)	90.4 (2)
P(2)–Ru(2)–C(4)	86.63 (9)	⟨Ru–C–O⟩[a]	178 [2]
P(2)–Ru(2)–C(5)	102.53 (9)	⟨C–C–C⟩[b]	120.0 [9]
P(2)–Ru(2)–C(6)	152.5 (1)		

[a] Within carbonyl groups. [b] Within phenyl rings.

The $^{1}H\{^{31}P\}$ NMR spectrum is also consistent with the structure found in the solid state. In particular, the chemical shifts characteristic of an orthometalated phenyl ring are observed.[3,17]

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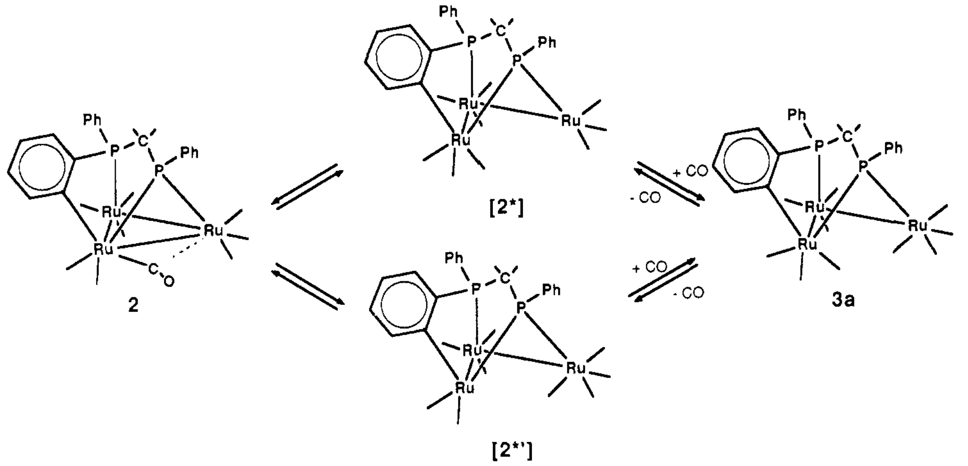
Scheme III



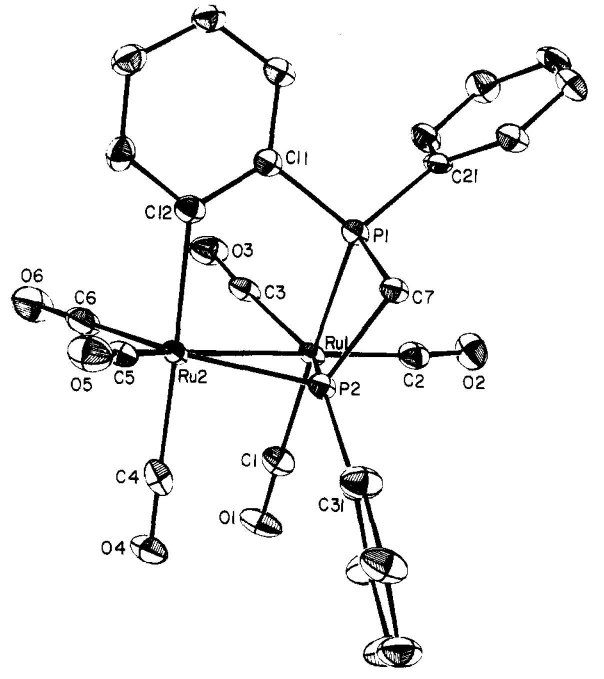


Figure 3. Perspective view of the complex $Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$(5).

The reaction of 2 at 0 °C with various phosphines affords in high yields compounds of general formula $Ru_3(CO)_9L(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$: L = $P(C_6H_5)_3$, **3b**, 75% yield; L = dppm, **3c**, 85% yield. The $^{31}P\{^1H\}$ NMR spectrum of **3c** is consistent with the structure established by X-ray analysis. Thus the two signals observed at 9.8 and 17.2 ppm are assigned to terminal P atoms (labeled P(1) and P(3), respectively, in Figure 2); the two high-field signals at -30.0 and -60.1 ppm are assigned to a noncoordinated P atom and to a P atom bridging a nonbonded metal–metal interaction (labeled P(4) and P(2), respectively, in Figure 2). The J_{PP} coupling constants found (see Experimental Section) are consistent with such assignments. The dppm ligand is found to be in a cis position with respect to the bridging P atom of the phosphido group (J_{PP} = 13 Hz), as in the solid state. The $^1H\{^{31}P\}$ NMR spectrum is also consistent with the structure found in the solid state, as exemplified by the chemical shifts characteristic of an orthometalated phenyl ring.

The $^{31}P\{^1H\}$ NMR spectrum of **3b** is consistent with a structure similar to that of **3c**, but now two isomers are observed in solution with a ratio close to 1/1. The cis isomer (terminal P atom of the $P(C_6H_5)_3$ ligand cis with respect to atom P(2)) exhibits a J_{PP} coupling constant of 13 Hz while the trans isomer exhibits a J_{PP} coupling constant of 155 Hz.[18]

Discussion

Compound 2 belongs to a growing family of saturated metal clusters that are able to add carbon monoxide reversibly.[19-22] For some compounds[19,20] (e.g. $Cp(CO)_2MnFe_2(CO)_6(\mu_3\text{-}P(C_6H_5))$[19a]) as for 2 the addition involves only metal–metal bond rupture. In one instance, $Ru_3(CO)_9$(c-Hx-DAB),[21] addition involves expansion of the cluster core without bond breaking. For others CO addition involves metal–metal bond rupture and ligand rearrangements[16c,22] (e.g. $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CC(C_6H_5))(\mu\text{-}P(C_6H_5)_2)$[22c]).

As previously pointed out,[3] in compound 2 the two ruthenium atoms that are bridged by the phosphido group are heptacoordinated so that a direct nucleophilic attack of CO on one metal center to afford **3a** is highly unlikely. From recent kinetic studies[19c,23] of related systems, we believe that the following pathway (Scheme III) is reasonable. The closed cluster 2 is in equilibrium with its unsaturated valence tautomer 2* (or 2*'), where the semibridging CO ligand in 2 is now terminal and the Ru–Ru bond is broken. This activated complex 2* (or 2*'), formed

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(20) The compound $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2)$, synthesized during the course of a study of the reactivity of $Ru_3(CO)_8(\mu\text{-}\eta^2\text{-}C(O)(C_6H_5))(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2H)$,[18b] also adds CO reversibly through a simple Ru–Ru bond opening to afford $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2$: Lugan, N.; Lavigne, G.; Bonnet, J.-J.; Réau, R.; Neibecker, D.; Tkatchenko, I., to be submitted for publication.

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in the preequilibrium, is trapped by CO to afford **3a**. Similarly, formation of **3b** and **3c** could arise from addition of the phosphines at low temperature to **2***. It is rather surprising that the reaction of triphenylphosphine with **2** at or above room temperature causes the rupture of the trinuclear unit to give the dinuclear complex **5**, since face-bridging dppm fragments have been shown to play their role in the stabilization of the Ru_3 triangle.[3,4a]

In conclusion, we believe that the previously reported[3] CO-induced transformation of $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**2**) into $Ru_3(CO)_{10}(\mu\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**4**) (see Scheme I) involves addition of CO as the initial reaction step to give $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**3a**) (Scheme II). Just as the addition of CO to bis(alkylidyne) clusters favors carbon–carbon coupling,[24] the addition of CO in the present case favors the coupling of a phosphido bridge with an adjacent aryl group. This illustrates a rather general principle in cluster chemistry: a closed metal cluster is prone to give a CO adduct via opening of a metal–metal bond; the resultant open cluster can isomerize to a closed species either by loss of ligand or by intramolecular reductive elimination and rearrangement within the ligand shell.

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Registry No. 2, 96502-43-1; **3a**, 114490-24-3; **3b**, 114466-60-3; *trans*-**3b**, 114466-61-4; **3c**, 114466-62-5; **5**, 114490-25-4; $Ru(CO)_3(P(C_6H_5)_3)_2$, 14741-36-7.

Supplementary Material Available: Tables S1, S2, and S3, anisotropic thermal parameters for compounds **3a**, **3c**, and **5**, respectively (3 pages); Tables S4, S5, and S6, structure amplitudes (×10) for compounds **3a**, **3c**, and **5**, respectively (88 pages). Ordering information is given on any current masthead page.

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From Germaphosphene to Germathia- (or Germaselena-) Phosphiranes

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Reaction of sulfur (or selenium) with the germaphosphene **1** leads to new stable three-membered heterocycles, the germathiaphosphirane **3** and the germaselenaphosphirane **14**. The structure of **3** was confirmed by X-ray crystal analysis (space group $P\bar{1}$; a = 11.098 (3) Å, b = 12.329 (3) Å, c = 16.050 (6) Å; α = 62.63 (2)°, β = 65.76 (2)°, γ = 70.05 (2)°; V = 1746 (1) Å^3; d_{calcd} = 1.180 g/cm^3 for Z = 2; R_w = 0.052, 5172 reflections with $I > 2.5\,\sigma(I)$). The Ge–P (2.316 (1) Å) and Ge–S (2.227 (1) Å) bond lengths are normal. The P–S bond is slightly elongated. Germanium is nearly planar (sum of the bond angles = 358.1°).

Introduction

Compounds of groups 14 and 15 with lower coordination numbers are of current interest because of their unusual structure and reactivity.[1] The only known kinetically stable germaphosphene **1** has been synthesized,[2] its X-ray structure recently determined[3] (the Ge=P double bond length (2.138 (3) Å) is shortened by about 8.5% in relation to the standard Ge—P single bond), and some of its chemical reactions investigated. The germaphosphene **1** readily undergoes electrophilic, nucleophilic, and radical addition reactions[4a] to the germanium–phosphorus double bond, and an unexpected thermolysis reaction has been reported.[4b]

Stable metal–group 14 three-membered heterocycles are still rare: some of them have recently been isolated,[5] but only two have been structurally characterized.[6]

In this paper we report [2 + 1] cycloaddition reactions between **1** and sulfur and selenium that lead to stable novel three-membered organogermanium heterocycles, the germathiaphosphirane **3** and the germaselenaphosphirane **14**. The X-ray structure of **3** has been determined.

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