

Transformation of the Bis(diphenylphosphino)methane Ligand on the $\text{Ru}_3(\text{CO})_9$ Framework. Synthesis and Characterization of $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$, $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$, and $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$

Noël Lugan,^{1a} Jean-Jacques Bonnet,^{1a} and James A. Ibers*^{1b}

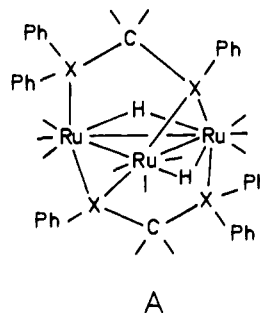
Contribution from the Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 31400 Toulouse, France, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received November 9, 1984

Abstract: Several transformations of the dppm ligand on Ru_3 clusters have been established (dppm = bis(diphenylphosphino)methane), starting from the parent complex $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dppm})$, **1**. In compound **2**, $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$, the $\text{Ru}_3(\text{CO})_9$ fragment is bridged by the six-electron tridentate phosphine ligand. In compound **3**, $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$, the $\text{Ru}_3(\text{CO})_9\text{H}$ fragment is bridged in a bidentate manner by the five-electron phosphine donor. In compound **4**, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$, the $\text{Ru}_3(\text{CO})_{10}$ fragment is bridged in a bidentate manner by the four-electron phosphine ligand. Thermolysis of **1** at 80 °C in cyclohexane affords **2** in high yield. Thermolysis of **2** in the presence of H_2 affords **3** in high yield. Compound **3** can also be produced directly from **1** at 90 °C in toluene. When CO is bubbled through a solution of **2** in refluxing cyclohexane, compound **4** is produced in high yield. Compound **4** reacts with H_2 under reflux in cyclohexane to yield compound **3**. When compound **4** is refluxed in cyclohexane under N_2 , compound **2** results. The nature of compounds **2**, **3**, and **4** has been established by spectroscopic means and by X-ray diffraction methods: crystal data, **2**, monoclinic, $C_{2h}^5\text{-}P2_1/c$, $Z = 4$, $a = 10.689$ (7) Å, $b = 11.936$ (7) Å, $c = 23.281$ (18) Å, $\beta = 90.18$ (8)° ($t = -85$ °C), final $R(F^2) = 3.8\%$, $\text{NO} = 7725$, $\text{NV} = 381$; **3**, monoclinic, $C_{2h}^5\text{-}P2_1/n$, $Z = 4$, $a = 10.593$ (2) Å, $b = 13.850$ (2) Å, $c = 20.720$ (3) Å, $\beta = 94.12$ (1)° ($t = -155$ °C), final $R(F^2) = 3.5\%$, $\text{NO} = 7037$, $\text{NV} = 384$; **4**, monoclinic, $C_{2h}^5\text{-}P2_1/n$, $Z = 4$, $a = 12.022$ (1) Å, $b = 15.266$ (1) Å, $c = 17.225$ (2) Å, $\beta = 105.56$ (1)° ($t = -155$ °C), final $R(F^2) = 3.5\%$, $\text{NO} = 6755$, $\text{NV} = 400$.

Current interest in transition-metal clusters arises in part from their possible utility in homogeneous catalysis. Perhaps clusters will induce unusual catalytic reactions as a result of cooperative interactions among adjacent metal centers.² But such studies are complicated by the relative ease with which clusters fragment under conditions appropriate for effective catalysis.³ Catalytic as well as stoichiometric reactivity of clusters requires coordinative unsaturation; this can be produced by loss of a ligand or by metal-metal bond scission.⁴ Therefore, for effective catalysis, a compromise must be reached between the stability of the cluster framework and the reactivity of the complex. One approach to such a compromise is to use bridging ligands to maintain the integrity of the polymetallic core and to ensure that possible metal-metal bond cleavages be reversible.⁵ Considerable attention has recently been focused on a variety of nonfluxional polydentate phosphines, arsines,^{6,7} and other bridging ligands.⁸

This strategy has been pursued in our group and has led us to the isolation of trinuclear ruthenium clusters stabilized by edge-bridging bis(diphenylphosphino)methane (dppm) or bis(diphenylarsino)methane (dpam) ligands.⁷ We have shown that these ligands can control the nuclearity of the complexes. For instance, $\text{Ru}_3(\text{CO})_8\text{L}_2$ ($\text{L} = \text{dppm}$ or dpam) reacts with molecular oxygen with retention of the trinuclear metal framework to afford the trinuclear μ_3 -oxo derivative $\text{Ru}_3(\text{CO})_6(\mu_3\text{-O})\text{L}_2$ ⁹ in which L behaves as a $\mu\text{-}\eta^2$ ligand as in the parent complexes $\text{Ru}_3(\text{CO})_8\text{L}_2$.

Previously we found that in the presence of H_2 , the edge-bridging ligand in the complexes $\text{Ru}_3(\text{CO})_8\text{L}_2$ can experience a facile oxidative cleavage to afford, for example, $(\text{C}_6\text{H}_5)\text{XCH}_2\text{X}(\text{C}_6\text{H}_5)_2$ ($\text{X} = \text{P}$ or As) bridging ligands as in $\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-X}(\text{C}_6\text{H}_5)\text{CH}_2\text{X}(\text{C}_6\text{H}_5)_2)$,¹⁰ A. These dihydrido species



(1) (a) Laboratoire de Chimie de Coordination. (b) Northwestern University.

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exhibit interesting catalytic hydrogenation properties and high stability under severe reaction conditions. Apparently there is stabilization of the metal framework by a single ligand in a $\mu_3\text{-}\eta^2$ coordination mode in which two faces of the cluster are capped by X atoms. In order to gain increased understanding of the oxidative cleavage process of the dpmm ligand, we have undertaken the present study of the behavior of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dpmm})$ under typical conditions encountered in catalysis, i.e., in the presence of heat, H_2 , or CO.

Experimental Section

General Remarks. All reactions at atmospheric pressure were performed under a prepurified dinitrogen atmosphere with the use of standard Schlenk-line techniques. However, since the compounds reported in this paper are not particularly air-sensitive at room temperature, chromatographic separations and recrystallizations were carried out in air. Solvents were purified by standard methods. Bis(diphenylphosphino)methane (dpmm) was purchased from Alfa Products and used as received. $\text{Ru}_3(\text{CO})_{12}$ ¹¹ and $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dpmm})$ ¹² were prepared by published procedures.

Microanalyses were performed by Gailbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on samples in cyclohexane solution on a Perkin-Elmer Model 283 grating spectrometer. ¹H and ³¹P NMR spectra were obtained on a JEOL JNM-FX 270 FTNMR spectrometer. All ¹H NMR chemical shifts are relative to TMS. ³¹P positive chemical shifts are downfield from 85% H_3PO_4 as an external reference.

Preparation of $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$ (2). A solution of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dpmm})$ (1) (300 mg, 0.31 mmol) in cyclohexane (40 mL) was refluxed (80 °C) under N_2 for 6 h. The initial light-red solution turned dark red. The solution was cooled, concentrated on a rotary evaporator, and finally chromatographed on silica gel (Merck 60). Elution with a mixture of dichloromethane/hexane (1/10) gave two bands. The first to elute contained the new compound 2 whereas the second band contained a small amount of unreacted starting material 1. A brown compound stayed on the top of the column and was not further characterized. The first band was evaporated to dryness under vacuum. Recrystallization of the residual red powder from benzene gave parallelepipedic crystals of 2 (220 mg, 82%). Anal. Calcd for $\text{C}_{28}\text{H}_{16}\text{O}_9\text{P}_2\text{Ru}_3$: C, 39.03%; H, 1.87%. Found: C, 38.99%; H, 1.97%. IR ($\nu(\text{CO})$) 2072 (m), 2038 (s), 2030 (s), 2010 (s), 1990 (m), 1985 (sh), 1967 (w), 1938 (w) cm^{-1} ; ¹H NMR (CD_2Cl_2) δ 6.3–7.9 (m), 6.80 (m), 6.78 (m), 6.32 (m, 14 H, C_6H_5 and C_6H_4), 4.13 (AB(XY) pattern, 2 H, CH_2); ³¹P{¹H} NMR (CD_2Cl_2) δ 117.3 (d, $J_{\text{PP}} = 85$ Hz, bridging P), 2.9 (d, terminal P).

Preparation of $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$, 3. (a) From $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$ (2). Hydrogen was bubbled through a solution of 2 (200 mg, 0.23 mmol) in refluxing cyclohexane (30 mL). After 90 min, the initially red solution turned yellow. The solution was cooled, concentrated on a rotary evaporator, and next chromatographed on silica gel (Merck 60). Elution with a dichloromethane/hexane mixture (1/5) afforded 3 as the only detectable product. Recrystallization from pentane at -30 °C gave yellow platelets of 3 (150 mg, 75%). Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{O}_9\text{P}_2\text{Ru}_3$: C, 38.84%; H, 2.10%. Found: C, 38.14%; H, 2.11%. IR ($\nu(\text{CO})$) 2081 (m), 2048 (s), 2028 (s), 2010 (m), 2000 (m), 1992 (m), 1985 (m), 1980 (m), 1960 (w) cm^{-1} ; ¹H NMR (toluene- d_6 , 253 K) δ 7.3–8.0 (m, C_6H_5), 4.77 (dd, CH_2 (isomer 3b, vide infra)), 3.74 (AB(XY) pattern, CH_2 (isomer 3a)), -16.07 (dd, $\mu\text{-H}$ (isomer 3b)), -16.72 (dd, $\mu\text{-H}$ (isomer 3a)); ³¹P{¹H} NMR (CD_2Cl_2 , 243 K) δ 134.6 (d, $J_{\text{PP}} = 100$ Hz, $\mu\text{-P}$ (isomer 3a)), 122.4 (d, $J_{\text{PP}} = 100$ Hz, $\mu\text{-P}$ (isomer 3b)), 20.4 (d, terminal P (isomer 3b)), 18.9 (d, terminal P (isomer 3b)).

(b) From $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dpmm})$ (1). With the same procedure as described above but at 90 °C, in toluene 3 can be prepared directly from 1 with approximately the same yield.

Preparation of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$ (4). In a typical experiment, CO was bubbled through a solution of 2 (200 mg, 0.23 mmol) in refluxing cyclohexane (40 mL) for 6 h. The initially dark-red solution gradually turned orange-red. The solution was concentrated and then chromatographed. Elution with a mixture of dichloromethane/hexane (1/9) afforded two red bands. The first one was the new compound 4 whereas the second was unreacted 2. Recrystalli-

zation of 4 from a mixture of dichloromethane/pentane at -30 °C gave bipyramidal red-orange crystals (125 mg, yield 80% based on 2 consumed). Anal. Calcd for $\text{C}_{29}\text{H}_{16}\text{O}_{10}\text{P}_2\text{Ru}_3$: C, 39.15%; H, 1.81%. Found: C, 39.56%; H, 2.38%. IR ($\nu(\text{CO})$), 2090 (m), 2032 (m), 2020 (s), 2008 (s), 1990 (m), 1968 (m) cm^{-1} ; ¹H NMR (CD_2Cl_2) δ 6.7–7.6 (m, 14 H, C_6H_5 and C_6H_4), 3.45 (AB(X₂) pattern, 2 H, CH_2); ³¹P{¹H} (CD_2Cl_2) δ 28.8 (s, terminal P).

Conversion of 4 to 2. A solution of 4 (100 mg, 0.11 mmol) in cyclohexane (20 mL) was refluxed under N_2 . The reaction was monitored by IR spectroscopy and was found to be complete in 2 h.

Reaction of 4 with H_2 to yield 3. Compound 4 (100 mg, 0.11 mmol) was dissolved in cyclohexane (30 mL), and the solution was heated under reflux. Hydrogen was bubbled through the solution. The reaction was monitored by IR spectroscopy ($\nu(\text{CO})$ region) and was complete in 4 h.

Attempted Reaction of 3 with CO. A solution of 3 (100 mg, 0.12 mmol) in cyclohexane (40 mL) was placed in an autoclave. The vessel was pressurized to 40 bar with CO and heated to 80 °C. After 18 h at this temperature, the autoclave was cooled and depressurized. The resulting solution was evaporated to dryness in vacuo, and an IR and NMR examination of the residual yellow powder showed only the starting material 3.

Crystallographic Studies. Crystals of 2 were grown from benzene/hexane (1/9) by slow evaporation of a solution at room temperature; crystals of 3 were obtained through recrystallization from hexane solution at -30 °C; crystals of 4 were formed from an acetone/ethanol solution (1/3) that was allowed to evaporate slowly at room temperature. Space groups and approximate cell parameters for the three compounds were determined from precession photographs taken at room temperature. Data were collected on a computer-controlled Picker FACS-1 diffractometer at -155 °C for compounds 3 and 4 and at -85 °C for compound 2.¹³ For each compound, accurate cell constants were obtained by the least-squares refinement of the setting angles of 15 reflections.¹⁴ Data collection and reduction were carried out as described previously.¹⁵ Table I presents further crystallographic information.

The positions of the Ru and P atoms in each structure were determined by direct methods (MULTAN). 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.¹⁶ Anomalous dispersion terms for the Ru and P atoms were included in F_o .^{16,17} All non-hydrogen atoms were allowed to vibrate anisotropically. The positions of the hydrogen atoms, except the μ -hydrido ligand in 3 whose position was determined from a difference electron density map and was refined, were idealized ($\text{C-H} = 0.95$ Å, $B = 1.0$ Å² 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^2 and involved all unique data, including those with $F^2 < 0$. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Final atomic parameters for the atoms of 2, 3, and 4 are listed in Tables IIa, IIIa, and IVa, respectively. Tables IIb, IIIb, and IVb list the hydrogen thermal parameters for all atoms of 2, 3, and 4, respectively.¹⁸ Structure amplitudes ($10|F_o|$ vs. $10|F_c|$) for the three structures are available as Tables V, VI, and VII.¹⁸ A negative entry for $|F_o|$ in these latter tables indicates that $F_o^2 < 0$.

Results

Scheme I sketches compounds 1–4. The parent compound 1 may be thought of as a $\text{Ru}_3(\text{CO})_{10}$ fragment bridged in a bidentate manner by the four-electron donor dpmm. Compound 2, similarly is the $\text{Ru}_3(\text{CO})_9$ fragment bridged by the six-electron tridentate ligand $(\text{C}_6\text{H}_5)_2\text{P}(\mu\text{-CH}_2)\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)$. Compound 3 is the $\text{Ru}_3(\text{CO})_9\text{H}$ fragment bridged in a bidentate manner by the five-electron donor ligand $(\text{C}_6\text{H}_5)_2\text{P}(\mu\text{-CH}_2)\text{P}(\text{C}_6\text{H}_5)_2$, while compound 4 may be thought of as the $\text{Ru}_3(\text{CO})_{10}$ fragment bridged in a bidentate manner by the four-electron donor ligand $(\text{C}_6\text{H}_5)_2\text{P}(\mu\text{-CH}_2)(\mu\text{-C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)$. In each instance the particular phosphine ligand is derived by various transformations of

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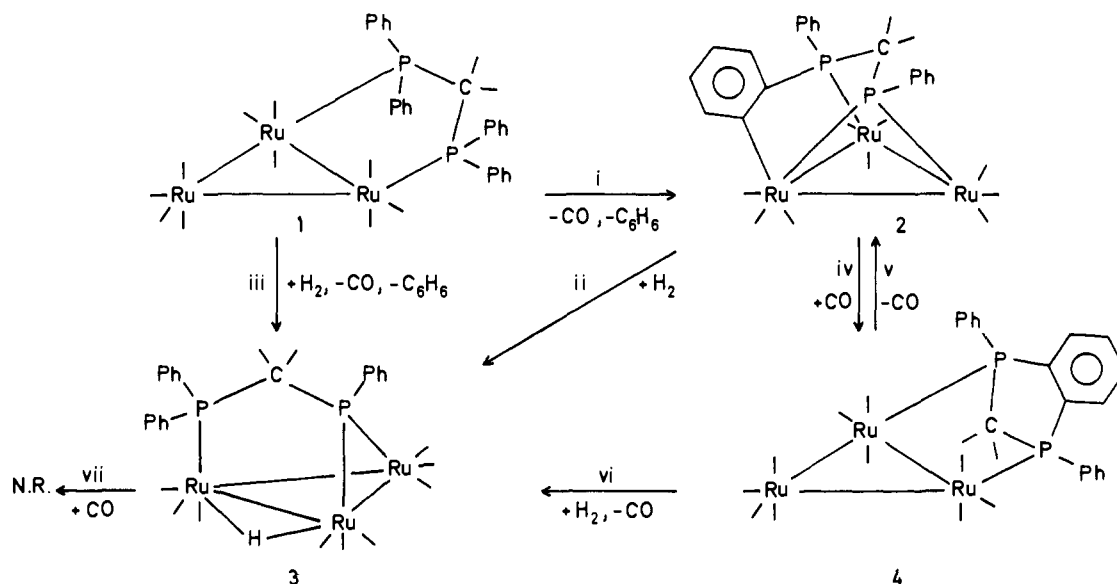
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Scheme I



the original dpmm ligand on the Ru₃ cluster as described below. But first we describe briefly the structures of 2, 3, and 4.

Description of the Structures. Perspective views of compounds 2, 3, and 4 are presented along with labeling schemes in Figures 1, 2, and 3, respectively, while Tables VIII and IX summarize important bond distances and angles.

In compound 2, each Ru atom of the Ru₃ triangle has two equatorial and one axial CO group. The tridentate phosphine ligand sits upon the Ru₃(CO)₉ fragment so that atom Ru(1) is bonded to one P atom, atom Ru(2) is bonded to the other P atom, and this P atom, along with atom C(12) of the C₆H₄ fragment, completes the coordination about atom Ru(3). The presence of three Ru–Ru single bonds completes the closed-shell electron configuration about each Ru atom.

In compound 3, each Ru atom of the Ru₃ triangle again has two equatorial and one axial CO group, but in addition there is an H bridge between atoms Ru(1) and Ru(3), as deduced from the crystallographic results. As discussed below, this H bridge is fluxional in solution. The bidentate phosphine ligand sits on top of this Ru₃(CO)₉H fragment so that one P atom is bonded to atom Ru(1) while the other P atom bridges atoms Ru(2) and Ru(3). Again the presence of Ru–Ru single bonds completes the closed-shell configuration about each Ru atom. This coordination mode of the dpmm fragment is similar to that observed for several organic molecules coordinated to a M₃(CO)₉H core (M = Ru, Os).¹⁹

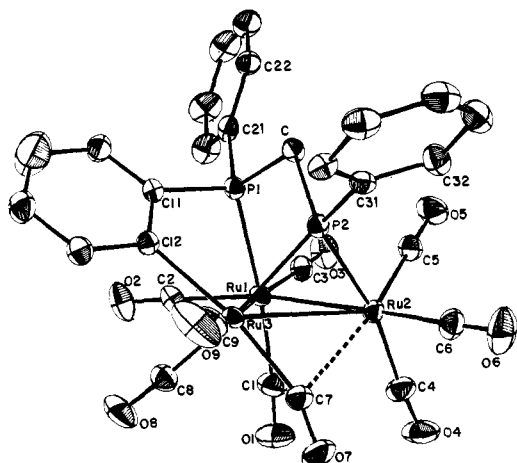


Figure 1. Perspective view of the complex Ru₃(CO)₉(μ-η³-P(C₆H₅)-CH₂P(C₆H₅)(C₆H₄)) (2). Here and in Figures 2 and 3, vibrational ellipsoids are given at the 50% probability level.

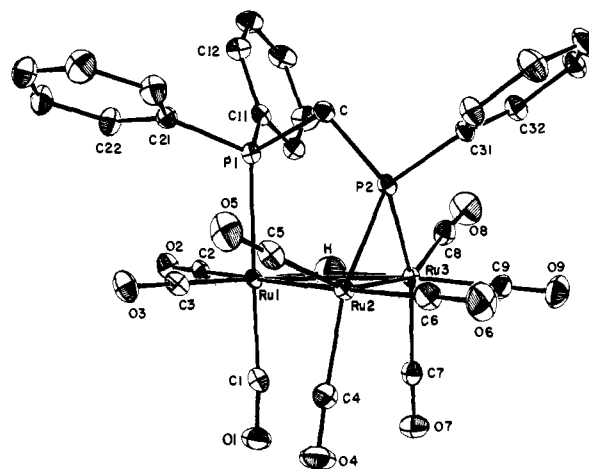


Figure 2. Perspective view of the complex Ru₃(CO)₉(μ-H)(μ-η²-P(C₆H₅)CH₂P(C₆H₅)₂) (3).

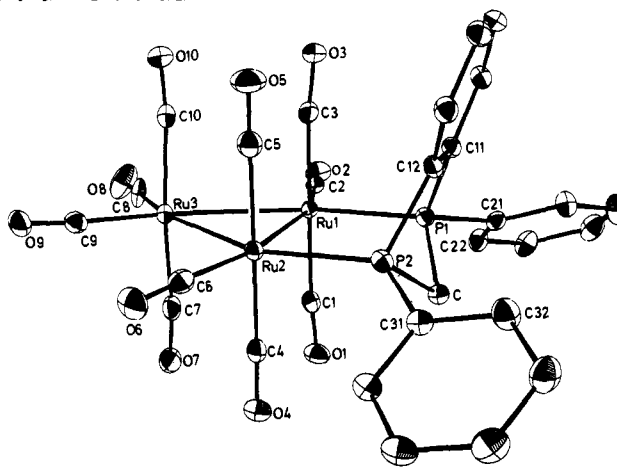


Figure 3. Perspective view of the complex Ru₃(CO)₁₀(μ-η²-P(C₆H₅)-CH₂P(C₆H₅)(C₆H₄)) (4).

Compound 4 has approximate C_s symmetry. Atom Ru(3) has two axial and two equatorial CO ligands while atoms Ru(1) and

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Table I. Experimental Data for X-ray Studies

	compound		
	2	3	4
formula	C ₂₈ H ₁₆ O ₉ P ₂ Ru ₃	C ₂₈ H ₁₆ O ₉ P ₂ Ru ₃	C ₂₈ H ₁₆ O ₁₀ P ₂ Ru ₃
F _w , amu	861.59	863.60	889.60
a, Å	10.689 (7)	10.593 (2)	12.022 (1)
b, Å	11.936 (7)	13.850 (2)	15.266 (1)
c, Å	23.281 (18)	20.720 (3)	17.225 (2)
β, deg	90.18 (8)	94.12 (1)	105.56 (1)
V, Å ³	2970	3032	3045
Z	4	4	4
ρ _{obsd} , g/cm ³ (23 °C)	1.82	1.75	1.80
ρ _{calcd} , g/cm ³	1.927 (-85 °C)	1.892 (-155 °C)	1.940 (-155 °C)
space group	C _{2h} ⁵ -P2 ₁ /c	C _{2h} ⁵ -P2 ₁ /n	C _{2h} ⁵ -P2 ₁ /n
crystal shape	9-sided, faces {001}, {011}, {102}, {102}	16-sided, faces {001}, {011}, {101}, {111}, {111}	18-sided, faces {011}, {101}, {110}, {111}, {001}
crystal vol, mm ³	0.078	0.14	0.012
t, °C	-85 ^a	-155	-155
radiation	graphite monochromated Mo Kα, λ(Mo Kα ₁) = 0.7093 Å	graphite monochromated Mo Kα, λ(Mo Kα ₁) = 0.7093 Å	graphite monochromated Mo Kα, λ(Mo Kα ₁) = 0.7093 Å
linear abs coeff, cm ⁻¹	16.35	15.48	15.98
transmission factor	0.60-0.67	0.43-0.66	0.68-0.75
receiving aperture, mm	4.2 high × 3.2 wide 32 cm from crystal	2.2 high × 3.7 wide 32 cm from crystal	4.3 high × 4.3 wide 32 cm from crystal
take-off angle, deg	4.0	2.5	2.6
scan speed, deg min ⁻¹	2.0 in 2θ	2.0 in 2θ	2.0 in 2θ
scan mode	θ-2θ	θ-2θ	θ-2θ
scan range	1.0 below Kα ₁ to 0.9 above Kα ₂	1.0 below Kα ₁ to 0.9 above Kα ₂	1.0 below Kα ₁ to 0.9 above Kα ₂
background counts	10 s at each end of scan with rescan option ^b	10 s at each end of scan with rescan option ^b	10 s at each end of scan with rescan option ^b
2θ limit, deg	3-58	3-56	3-55
unique data used in final refinement	7725	7037	6755
unique data, F _o ² > 3σ(F _o ²)	7261	6817	5812
final no. of variables	381	384	400
R (on F _o ² , all data)	3.8	3.5	3.5
R _w (on F _o ² , all data)	8.6	7.9	6.6
R (on F _o for F _o ² > 3σ(F _o ²))	2.6	2.1	2.5
R _w (on F _o for F _o ² > 3σ(F _o ²))	5.0	4.8	3.3
error in observ of unit weight, e ²	2.16	1.67	1.07

^a The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. ^b The diffractometer was run under the Vanderbilt disk-oriented system (Lenhart, P. G. *J. Appl. Crystallogr.* 1975, 8, 568-570).

Table IIa. Positional Parameters for Ru₃(CO)₉(μ₃-η³-P(C₆H₅)CH₂P(C₆H₅)(C₆H₄)) (2)

atom	x	y	z	atom	x	y	z
Ru(1)	0.320 513 (18)	0.012 167 (16)	0.182 187 (08)	C(16)	-0.050 44 (25)	-0.097 28 (23)	0.108 34 (12)
Ru(2)	0.423 407 (18)	0.204 305 (16)	0.130 230 (09)	C(21)	0.221 35 (23)	-0.181 80 (20)	0.073 37 (11)
Ru(3)	0.164 544 (18)	0.203 334 (15)	0.165 285 (08)	C(22)	0.215 67 (27)	-0.204 31 (22)	0.014 60 (13)
P(1)	0.203 77 (06)	-0.040 10 (05)	0.100 736 (25)	C(23)	0.237 4 (03)	-0.312 03 (26)	-0.005 68 (15)
P(2)	0.249 67 (06)	0.186 74 (05)	0.072 884 (26)	C(24)	0.262 9 (03)	-0.397 73 (26)	0.032 38 (17)
C(1)	0.393 14 (28)	0.068 32 (26)	0.252 13 (12)	C(25)	0.267 6 (03)	-0.376 85 (25)	0.090 84 (16)
O(1)	0.433 01 (27)	0.093 81 (26)	0.295 08 (10)	C(26)	0.245 9 (03)	-0.269 01 (24)	0.110 96 (13)
C(2)	0.206 08 (25)	-0.076 28 (24)	0.225 01 (11)	C(31)	0.227 57 (24)	0.279 80 (20)	0.012 05 (10)
O(2)	0.137 45 (23)	-0.129 13 (21)	0.250 95 (10)	C(32)	0.113 43 (25)	0.329 29 (23)	0.000 03 (11)
C(3)	0.449 50 (24)	-0.095 22 (22)	0.168 77 (11)	C(33)	0.099 1 (03)	0.393 87 (24)	-0.049 13 (13)
O(3)	0.524 83 (21)	-0.159 67 (20)	0.159 66 (11)	C(34)	0.198 3 (03)	0.407 95 (24)	-0.086 25 (12)
C(4)	0.545 33 (27)	0.220 10 (26)	0.192 27 (14)	C(35)	0.311 4 (03)	0.359 24 (24)	-0.074 78 (12)
O(4)	0.621 86 (23)	0.232 72 (25)	0.225 02 (11)	C(36)	0.327 06 (28)	0.295 17 (22)	-0.025 71 (12)
C(5)	0.510 99 (23)	0.098 66 (23)	0.087 09 (11)	H(1)C	0.295	0.030	0.016
O(5)	0.562 45 (20)	0.036 62 (20)	0.058 48 (09)	H(2)C	0.152	0.052	0.015
C(6)	0.473 35 (26)	0.343 55 (24)	0.095 02 (13)	H(13)	-0.128	0.175	0.179
O(6)	0.507 71 (24)	0.422 87 (20)	0.073 90 (12)	H(14)	-0.282	0.041	0.165
C(7)	0.282 00 (27)	0.314 34 (24)	0.196 99 (13)	H(15)	-0.236	-0.131	0.118
O(7)	0.317 61 (23)	0.387 05 (21)	0.223 99 (11)	H(16)	-0.029	-0.167	0.091
C(8)	0.111 90 (26)	0.167 09 (24)	0.242 49 (12)	H(22)	0.196	-0.145	-0.012
O(8)	0.073 15 (24)	0.146 54 (23)	0.286 84 (09)	H(23)	0.237	-0.327	-0.046
C(9)	0.051 97 (28)	0.322 95 (23)	0.146 23 (12)	H(24)	0.278	-0.472	0.018
O(9)	-0.013 44 (27)	0.392 56 (22)	0.134 91 (11)	H(25)	0.284	-0.437	0.117
C	0.224 74 (22)	0.051 02 (20)	0.039 05 (10)	H(26)	0.247	-0.255	0.151
C(11)	0.041 65 (22)	-0.016 98 (20)	0.118 25 (10)	H(32)	0.044	0.319	0.026
C(12)	0.017 28 (22)	0.086 23 (20)	0.144 63 (10)	H(33)	0.021	0.430	-0.057
C(13)	-0.106 77 (25)	0.105 04 (24)	0.160 59 (12)	H(34)	0.187	0.452	-0.121
C(14)	-0.199 46 (25)	0.025 90 (28)	0.151 87 (14)	H(35)	0.379	0.370	-0.101
C(15)	-0.172 37 (26)	-0.076 78 (27)	0.125 58 (15)	H(36)	0.407	0.261	-0.017

Table VIII. Interatomic Distances (Å) for Compounds 2, 3, and 4

	2	3	4
Ru(1)–Ru(2)	2.818 (1)	2.890 (1)	2.884 (1)
Ru(2)–Ru(3)	2.888 (1)	2.820 (1)	2.848 (1)
Ru(1)–Ru(3)	2.853 (1)	3.012 (1)	2.851 (1)
Ru(1)–P(1)	2.351 (1)	2.384 (1)	2.319 (1)
Ru(2)–P(2)	2.293 (1)	2.306 (1)	2.324 (1)
Ru(3)–P(2)	2.347 (1)	2.332 (1)	
Ru(1)–C(1)	1.922 (3)	1.938 (2)	1.934 (3)
Ru(1)–C(2)	1.901 (3)	1.915 (2)	1.899 (3)
Ru(1)–C(3)	1.909 (3)	1.905 (2)	1.936 (3)
Ru(2)–C(4)	1.952 (3)	1.938 (2)	1.921 (3)
Ru(2)–C(5)	1.866 (3)	1.916 (2)	1.947 (3)
Ru(2)–C(6)	1.929 (3)	1.892 (2)	1.891 (3)
Ru(3)–C(7)	1.968 (3)	1.953 (2)	1.942 (3)
Ru(3)–C(8)	1.934 (3)	1.929 (3)	1.911 (3)
Ru(3)–C(9)	1.918 (3)	1.892 (2)	1.917 (3)
Ru(3)–C(10)			1.927 (3)
Ru(1)–H		1.815 (32)	
Ru(3)–H		1.827 (32)	
Ru(3)–C(12)	2.158 (3)		
P(1)–C	1.816 (2)	1.822 (2)	1.835 (3)
P(2)–C	1.821 (2)	1.839 (2)	1.845 (3)
P(1)–C(11)	1.803 (2)	1.826 (2)	1.827 (3)
P(1)–C(21)	1.817 (2)	1.823 (2)	1.823 (3)
P(2)–C(31)	1.815 (3)	1.823 (2)	1.820 (3)
(C–O)	1.133 (8) ^a	1.136 (5)	1.140 (6)
(C–C)	1.390 (8)	1.391 (5)	1.390 (6)

^aHere and in Table IX the parenthetical value on a mean refers to the standard deviation of a single observation on the assumption that the values averaged are from the same population.

are worthy of comment. Based on the internal consistency among C–C distances in the C₆ rings, the standard deviations of the positional parameters, as deduced from the least-squares refinements, are reasonable; there is no apparent distortion of the orthometallated C₆H₄ fragment in compound 2. From the Ru–Ru distances, it is very clear that the bridging H ligand in compound 3 brings about a considerable lengthening of the Ru–Ru bond it bridges; in compounds 2 and 3, the Ru–P terminal bond is longer than the average Ru–P–Ru bridging bond, and in each instance the P atom is more or less trans to a CO ligand. The Ru(2)–C(5) bond in compound 2 is the shortest of all Ru–C bonds in the three structures, presumably because there is no ligand trans to the C(5)–O(5) group save for a weakly semibringing C(7)–O(7) group (Ru(2)···C(7) = 2.538 (3) Å).

Synthetic Aspects. Thermolysis of the cluster Ru₃(CO)₁₀(μ-η²-dppm) (1) in refluxing cyclohexane (80 °C) for 6 h affords the new complex Ru₃(CO)₉(μ₃-η³-P(C₆H₅)CH₂P(C₆H₅)(C₆H₄)) (2) in high yield (80%). Such a reaction occurs with evolution of 1 mol of CO and 1 mol of benzene per mole of cluster. The ³¹P{¹H} NMR spectrum of 2 is consistent with the structure established by X-ray analysis. Thus, a signal observed at 2.9 ppm is assigned to a terminal P atom while a low field one, centered at 117.3 ppm, is typical for a P atom bridging a metal–metal bond.²⁴ The ¹H NMR spectrum is also consistent with the structure found in the solid state. In particular, the chemical shifts characteristic of an orthometallated phenyl ring are observed.²⁵ The AB(XY) pattern observed for the methylene protons indicates also the stereorrigidity of the molecule, at least to 80 °C. The main feature of this thermolysis is the ease with which an intramolecular rearrangement of the bridging ligand occurs. Indeed the ligand is converted from a μ-η² four-electron donor that edge bridges in 1 into a μ₃-η³ six-electron donor that face bridges in 2. The mechanism of this transformation has not been established, but we believe that the following pathway is reasonable. Thermolysis of 1 results in the loss of 1 mol of CO from the Ru atom having no P atom attached; the resulting vacant site may be removed by orthometallation of a phenyl ring to afford an intermediate [Ru₃(CO)₉(μ-H)(μ-η³-P(C₆H₅)₂CH₂P(C₆H₅)(C₆H₄))] ([2']),

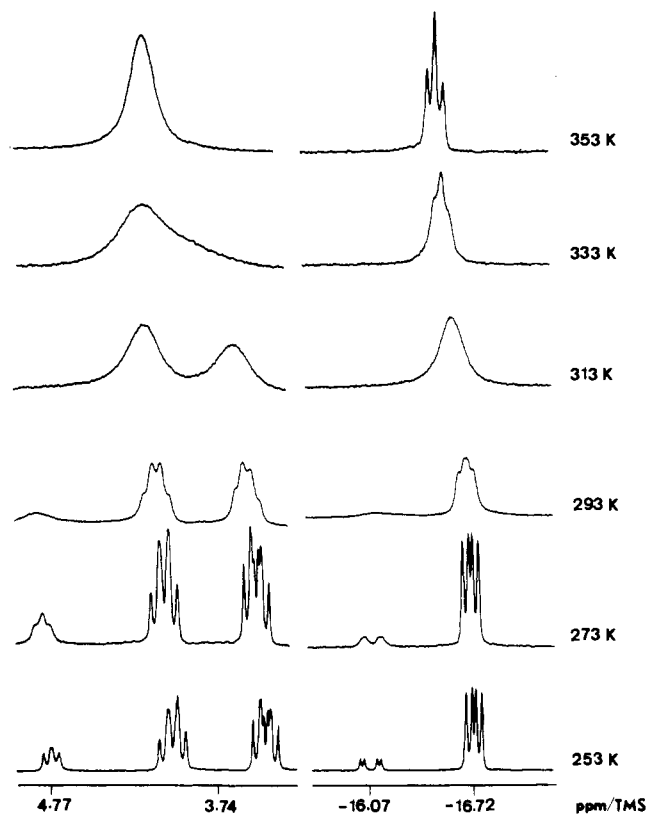
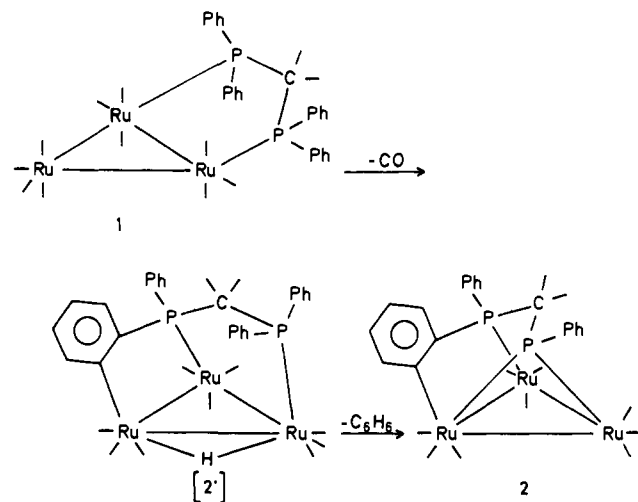


Figure 4. ¹H NMR spectra of Ru₃(CO)₉(μ-H)(μ₃-η²-P(C₆H₅)CH₂P(C₆H₅)₂) (3) in toluene-d₈ (270 MHz).

closely akin to known triosmium clusters involving triphenylphosphine²⁶ or dppm²⁷ ligands. The last step in the transformation



in 2 then involves oxidative cleavage of a P–C bond and reductive elimination of benzene via H transfer.

When a cyclohexane solution of complex 2 is heated at 80 °C for 90 min in the presence of H₂, compound 3, Ru₃(CO)₉(μ-H)(μ₃-η²-P(C₆H₅)CH₂P(C₆H₅)₂), is obtained in 75% yield.²⁸ The latter can also be prepared directly from 1 in the same manner. This reaction can be viewed as a demetallation of the orthometallated phenyl ring of the μ₃-η³ six-electron donor ligand in 2 to provide the μ₃-η² five-electron donor capping ligand in 3. The ¹H and ³¹P{¹H} NMR spectra show 3 to exist as a mixture of two

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(24) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, 19, 186–191.

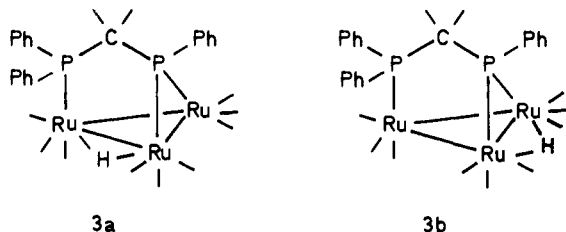
(25) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1972**, 2094–2099.

Table IX. Bond Angles (deg) for Compounds 2, 3, and 4

	2	3	4	2	3	4	
Ru(2)-Ru(1)-Ru(3)	61.22 (1)	57.04 (1)	59.54 (1)	Ru(2)-Ru(3)-C(8)	123.06 (8)	157.22 (7)	162.38 (9)
Ru(2)-Ru(1)-P(1)	94.40 (2)	93.08 (1)	89.11 (2)	Ru(2)-Ru(3)-C(9)	122.19 (9)	88.97 (8)	95.35 (8)
Ru(2)-Ru(1)-C(1)	85.57 (10)	87.17 (7)	90.02 (8)	Ru(2)-Ru(3)-P(2)	50.69 (2)	52.13 (1)	
Ru(2)-Ru(1)-C(2)	158.42 (8)	179.16 (6)	163.84 (8)	Ru(2)-Ru(3)-C(12)	129.69 (6)		
Ru(2)-Ru(1)-H		91 (1)		Ru(2)-Ru(3)-C(10)			91.24 (10)
Ru(3)-Ru(1)-P(1)	78.02 (2)	90.79 (1)	148.49 (2)	Ru(2)-Ru(3)-H		93 (1)	
Ru(3)-Ru(1)-C(1)	94.14 (9)	87.83 (7)	92.08 (8)	C(7)-Ru(3)-C(8)	89.38 (12)	100.52 (10)	90.04 (13)
Ru(3)-Ru(1)-C(2)	98.04 (8)	122.47 (6)	104.31 (8)	C(7)-Ru(3)-C(9)	89.12 (13)	92.03 (10)	95.95 (12)
Ru(3)-Ru(1)-C(3)	159.50 (8)	138.67 (7)	88.18 (8)	C(7)-Ru(3)-P(2)	98.74 (9)	153.60 (7)	
Ru(3)-Ru(1)-H		34 (1)		C(7)-Ru(3)-C(12)	169.68 (10)		
P(1)-Ru(1)-C(1)	170.98 (9)	178.18 (7)	90.90 (8)	C(7)-Ru(3)-C(10)			174.84 (12)
P(1)-Ru(1)-C(2)	86.27 (9)	86.24 (6)	107.05 (8)	C(7)-Ru(3)-H		85 (1)	
P(1)-Ru(1)-C(3)	94.11 (8)	90.30 (7)	88.65 (8)	C(8)-Ru(3)-C(9)	101.38 (11)	96.06 (11)	102.21 (12)
P(1)-Ru(1)-H		88 (1)		C(8)-Ru(3)-P(2)	161.40 (9)	105.81 (7)	
C(1)-Ru(1)-C(2)	90.47 (13)	93.49 (9)	90.11 (11)	C(8)-Ru(3)-C(12)	81.26 (11)		
C(1)-Ru(1)-C(3)	94.75 (12)	91.52 (9)	179.48 (11)	C(8)-Ru(3)-C(10)			90.54 (15)
C(1)-Ru(1)-H		90 (1)		C(8)-Ru(3)-H		83 (1)	
C(2)-Ru(1)-C(3)	100.33 (11)	98.83 (9)	90.27 (11)	C(9)-Ru(3)-P(2)	95.48 (8)	87.14 (7)	
C(2)-Ru(1)-H		88 (1)		C(9)-Ru(3)-C(12)	88.51 (11)		
C(3)-Ru(1)-H		173 (1)		C(9)-Ru(3)-C(10)			88.94 (13)
Ru(1)-Ru(2)-Ru(3)	59.98 (1)	63.67 (1)	59.66 (1)	C(9)-Ru(3)-H		176 (1)	
Ru(1)-Ru(2)-P(2)	81.90 (2)	79.09 (1)	88.81 (2)	P(2)-Ru(3)-C(12)	91.48 (6)		
Ru(1)-Ru(2)-C(4)	91.23 (10)	92.07 (7)	89.17 (8)	P(2)-Ru(3)-H		97 (1)	
Ru(1)-Ru(2)-C(5)	83.01 (8)	98.17 (7)	90.94 (8)	Ru(1)-P(1)-C(11)	106.57 (8)	116.03 (7)	112.98 (8)
Ru(1)-Ru(2)-C(6)	172.93 (8)	164.86 (8)	161.40 (9)	Ru(1)-P(1)-C(21)	118.33 (9)	111.97 (7)	123.42 (9)
Ru(3)-Ru(2)-P(2)	52.35 (2)	52.98 (1)	148.38 (2)	Ru(1)-P(1)-C	114.36 (8)	113.24 (7)	109.90 (9)
Ru(3)-Ru(2)-C(4)	115.44 (9)	103.64 (7)	91.14 (8)	C(11)-P(1)-C(21)	108.80 (11)	103.84 (10)	106.38 (12)
Ru(3)-Ru(2)-C(5)	129.23 (8)	151.76 (7)	88.09 (9)	C(11)-P(1)-C	102.02 (11)	102.63 (10)	93.28 (12)
Ru(3)-Ru(2)-C(6)	112.97 (8)	101.19 (8)	101.91 (9)	C(21)-P(1)-C	105.49 (11)	108.23 (10)	106.55 (12)
P(2)-Ru(2)-C(4)	167.78 (9)	156.56 (7)	90.78 (8)	Ru(2)-P(2)-Ru(3)	76.96 (2)	74.89 (2)	
P(2)-Ru(2)-C(5)	91.81 (8)	104.49 (7)	90.18 (9)	Ru(2)-P(2)-C(31)	120.10 (9)	121.98 (7)	123.63 (9)
P(2)-Ru(2)-C(6)	93.22 (9)	92.22 (7)	109.69 (9)	Ru(2)-P(2)-C	116.77 (8)	118.14 (7)	110.27 (9)
C(4)-Ru(2)-C(5)	97.39 (11)	98.20 (10)	179.04 (12)	Ru(2)-P(2)-C(12)			113.17 (9)
C(4)-Ru(2)-C(6)	92.65 (13)	91.17 (10)	88.70 (11)	Ru(3)-P(2)-C(31)	127.87 (8)	118.07 (7)	
C(5)-Ru(2)-C(6)	102.33 (12)	96.00 (11)	90.89 (12)	Ru(3)-P(2)-C	114.52 (8)	124.27 (7)	
Ru(1)-Ru(3)-Ru(2)	58.80 (1)	59.29 (1)	60.79 (1)	C(31)-P(2)-C	100.86 (11)	100.27 (10)	104.82 (12)
Ru(1)-Ru(3)-C(7)	96.60 (9)	91.38 (7)	86.38 (8)	C(31)-P(2)-C(12)			107.50 (12)
Ru(1)-Ru(3)-C(8)	82.21 (8)	114.45 (7)	101.74 (9)	C(12)-P(2)-C			92.78 (12)
Ru(1)-Ru(3)-C(9)	173.31 (9)	148.09 (8)	155.93 (8)	P(1)-C-P(2)	102.07 (11)	106.70 (11)	99.05 (12)
Ru(1)-Ru(3)-P(2)	80.26 (2)	76.13 (1)		P(1)-C(11)-C(12)	114.45 (18)	119.68 (16)	112.45 (18)
Ru(1)-Ru(3)-C(12)	86.46 (6)			C(11)-C(12)-Ru(3)	122.04 (17)		
Ru(1)-Ru(3)-C(10)			88.49 (9)	C(11)-C(12)-P(2)			112.36 (18)
Ru(1)-Ru(3)-H		34 (1)		<Ru-C-O>	177.2 (2.1) ^a	176.4 (1.8)	175.5 (2.4)
Ru(2)-Ru(3)-C(7)	59.49 (8)	101.49 (7)	86.67 (8)	<C-C-C>	120.0 (1.5)	120.0 (0.4)	120.0 (0.4)

^a Excluding Ru(3)-C(7)-O(7) = 159.07 (85)°.

isomers, **3a** and **3b**, that differ in the position of the H bridge on the Ru₃ triangle. At room temperature, these two isomers in-



terconvert rapidly on the NMR time scale (Figure 4). At 253 K, the two isomers are observed in a 8:1 ratio. In the solid state only isomer **3a** is observed. The ¹H NMR spectrum of **3** at different temperatures is displayed in Figure 4. The signals at 3.74 and 4.77 ppm we attribute to the methylene group in isomers **3a** and **3b**, respectively. A hydride bridge on one of the two initially equivalent Ru-Ru bonds (Ru(1)-Ru(2) or Ru(1)-Ru(3) of Figure 2) induces a magnetic inequivalence of the proton nuclei within the CH₂ group. The complex signal at 3.74 ppm is the AB part of an ABXY system (where X and Y are two inequivalent P atoms). On the other hand, the proton nuclei within the CH₂ group for isomer **3b**, where the H bridge is on the Ru(2)-Ru(3) bond, are magnetically equivalent. The doublet of doublets at 4.77 ppm is the A₂ part of an A₂XY system. The two signals observed at -16.72 and -16.07 ppm are attributed to the μ-H ligands within isomers **3a** and **3b**, respectively. They both appear

as a doublet of doublets since in each case they are coupled to two inequivalent P atoms.

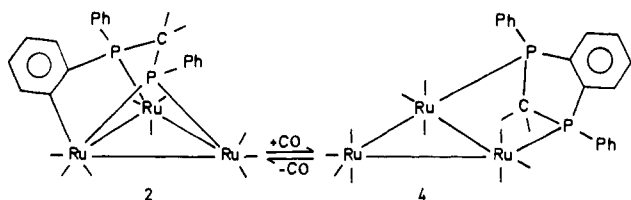
In refluxing cyclohexane, **2** reacts with CO at atmospheric pressure to give the new cluster compound Ru₃(CO)₁₀(μ-η²-P-(C₆H₅)CH₂P(C₆H₅)(C₆H₄)) (**4**) in 80% yield (based on **2** consumed). In the presence of CO, the tridentate μ₃-η³ six-electron donor ligand in **2** undergoes an intramolecular reductive elimination to afford the μ-η² four-electron donor ligand in **4**. ¹H and ³¹P{¹H} NMR spectra of **4** show that the structure in solution fits the one determined for the solid state (Figure 3). Indeed the chemical shifts for the P nuclei at 28.8 ppm are consistent with terminal P atoms, for instance, in Ru₃(CO)₁₀(μ-η²-dppm);¹³ the CH₂ protons appear as the AB part of an ABX₂ pattern centered at 3.45 ppm, consistent with the approximate C_s symmetry of the molecule.

Scheme I shows in addition that (i) **4** can give back **2** upon thermolysis and (ii) **4** can be converted into **3** by reaction with molecular hydrogen. The thermolysis reaction giving **2** from **4** could result from a loss of a CO ligand from the unique Ru atom followed by an oxidative addition of a P-C(C₆H₄) bond. The observed transformation of **4** into **3** could proceed via formation of **2** as the intermediate species, as **2** has been shown to give **3** by reaction with H₂.

Discussion

Although the dppm ligand, because of its stability, is widely used as a ligand in the chemistry of dinuclear complexes,²⁹ the

Scheme II



reactions described above show that it undergoes facile reactions on a Ru_3 cluster. Nevertheless, the dppm fragments thus formed have played their role in the stabilization of the Ru_3 triangle as it has been retained throughout all reactions investigated. For example, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-dppm})$ (**1**) reacts with H_2 to give the Ru_3H cluster $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$ (**3**),²⁸ whereas the Ru_3 cluster is not maintained in the reaction of $\text{Ru}_3(\text{CO})_{12}$ with H_2 .³⁰ Compound **3** exhibits remarkable stability as no change is observed when it is heated at 80 °C for 18 h under a pressure of 40 bar of CO. But the mobility of the hydrido ligand in **3** may be important in hydrogenation reactions.

The reaction of **2**, $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$, with CO to afford **4**, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4))$, is reversible. These reactions proceed through intramolecular reductive elimination or oxidative addition of the dppm fragment (Scheme II) that could give rise to an intermediate in which atom Ru(3) (Figures 1 and 3) is coordinatively unsaturated. Thus the activation of two-electron donor ligands other than CO in stoichiometric or catalytic carbonylation reactions might be possible.

Finally, the reaction $1 \rightarrow 2 \rightarrow 4$ can be viewed as the "synthesis" of a new bidentate phosphine ligand, $(\text{C}_6\text{H}_5)\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)$, on a Ru_3 core, starting from the well-known dppm ligand. The three Ru atoms take part in this process, which demonstrates a cooperative interaction of the metal centers in a cluster to transform an organic substrate.

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Registry No. **1**, 64364-79-0; **2**, 96502-43-1; **3a**, 95402-64-5; **3b**, 95402-64-5; **4**, 96482-75-6.

Supplementary Material Available: Tables IIb, IIIb, and IVb, anisotropic thermal parameters for compounds **2**, **3**, and **4**, respectively, and Tables V, VI, and VII, structure amplitudes ($\times 10$) for compounds **2**, **3**, and **4**, respectively (a negative entry for $|F_o|$ in these latter tables indicates that $F_o^2 < 0$) (92 pages). Ordering information can be obtained from any current masthead page.

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Cyclopropeniumdiazonium Systems: First Generation of a C-sp-Attached Diazonium Function

Robert Weiss,* Klaus-Georg Wagner, Claus Priesner, and Jürgen Macheleid

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany. Received August 20, 1984

Abstract: Synthesis of stable cyclopropeniumdiazonium salts via several independent pathways is reported. These systems represent the first authentic examples of a diazonium function attached to sp-hybridized carbon. Novel reaction types of these systems include (a) reversible protonation, (b) irreversible hydrolysis, and (c) thermal dediazonation. Experimental results are rationalized on the basis of MNDO model calculations.

I. Introduction

Despite the high standard of the contemporary synthetic art, not all important functional groups have been attached to carbon via all three main types of C-hybridization. A case in point is the diazonium function which hitherto has only been observed in conjunction with sp^3 or sp^2 orbitals of carbon.¹ Alkynyldiazonium salts, **A**, are the most obvious—though not exclusive (viz. below)—target molecules containing a C_{sp} -attached diazonium function. However, the attempt to synthesize such salts meets with tremendous difficulties. In a classical sense, for the synthesis of **A**, the existence of primary ynamines would be a prerequisite. These, however, are inaccessible as they are prototropic forms of much more stable nitriles. Other potential precursors (including alkynyl isocyanates^{2a} and thionylimines^{2b}) would only be accessible

via the corresponding amines. There is one isolated report in the literature³ which is directly concerned with synthesis and reactivity of a salt **A** ($\text{R} = n\text{-C}_4\text{H}_9$, $\text{A}^- = \text{NO}_3^-$). The authors claim to have generated this system by reacting the corresponding nitrosoalkyne with NO, thus making use of a very old aprotic diazotization technique.⁴ The diazonium salt itself was never directly observed but the authors report its successful trapping via diazo coupling. However, these results have been called in doubt very recently by M. Hanack et al.⁵ whose various verification attempts met with total failure. This latter group has approached the synthesis of salts **A** via dehydrohalogenation reactions of a suitable vinylidiazonium precursor.⁶ By working under carefully controlled conditions at low temperature, they were able to collect circumstantial evidence for the intermediacy of **A** ($\text{R} = \text{Ph}$, $\text{A}^- = \text{SbCl}_5\text{OTs}^-$) by way of various nucleophilic trapping reactions.

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