

A New Route to Binuclear and Trinuclear Ruthenium Carbonyl Derivatives: Structures of $[\text{Ru}_3(\text{CO})_6(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3]$ and Its Proton Adduct

Hameed A. Mirza, Jagadese J. Vittal, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received July 1, 1992

Reduction of ruthenium(III) acetate, prepared in situ from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and silver acetate, with NaBH_4 in the presence of $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ and CO gives a good route to $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$ (1) and also gives $[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$ (2) in low yield. Complex 2 is very readily protonated to give $[\text{Ru}_3(\mu\text{-H})(\text{CO})_6(\mu\text{-dppm})_3]^+$ (3). The structures of both 2 and 3 have been determined by X-ray diffraction: 2, space group $P2_1/n$, $a = 24.984(3)$ Å, $b = 19.433(3)$ Å, $c = 14.724(2)$ Å, $\beta = 90.747(9)^\circ$, $Z = 4$, $R(R_w) = 0.051(0.040)$; (3) $\text{BF}_4 \cdot \text{C}_2\text{H}_4\text{Cl}_2 \cdot 1.5\text{C}_5\text{H}_{12}$, space group $P\bar{1}$, $a = 14.810(2)$ Å, $b = 21.801(2)$ Å, $c = 13.847(1)$ Å, $\alpha = 107.67(1)^\circ$, $\beta = 91.54(4)^\circ$, $\gamma = 89.86(1)^\circ$, $Z = 2$, $R(R_w) = 0.075(0.082)$. The hydride ligand in 3 is shown to be edge-bridging, and the cluster cation 3 is fluxional with the hydride migrating rapidly between edges and from side to side of the Ru_3 triangle even at -80°C .

Introduction

Several diphosphine derivatives of the unstable binuclear ruthenium carbonyl $[\text{Ru}_2(\text{CO})_9]$ have been prepared and shown to have fascinating properties. The complex $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dmpm})_2]$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$), is easily prepared from $[\text{Ru}_3(\text{CO})_{12}]$ and dmpm and has been shown to have a very interesting chemistry with unsaturated reagents.² Several related complexes $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-R}_2\text{PN}(\text{Et})\text{PR}_2)_2]$ ($\text{R} = \text{OMe}$, $O\text{-}i\text{-Pr}$) are known and display unusual chemistry with electrophiles and in redox reactions, forming new carbon dioxide complexes, $\text{Ru}_2(\mu\text{-CO}_2)$, for example.³ However, $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (1) can only be prepared by photolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with dppm , and the recent synthesis of $[\text{Ru}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-dppm})]$ also involves a photochemical step.^{3,4} The thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with dppm may give $[\text{Ru}_3(\text{CO})_{12-2x}(\mu\text{-dppm})_x]$ ($x = 1\text{--}3$) or products arising from metalation of the dppm ligands, but fragmentation to Ru_2 complexes does not occur.⁴ This paper reports a simple one-step nonphotochemical synthesis of 1, which makes this complex readily available for studies of its reactivity. Also reported is a comparison of the structures of $[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$ (2) and its proton adduct (3), which displays interesting fluxionality.

Experimental Section

Reactions were carried out in the absence of air using standard Schlenk techniques. NMR spectra were recorded by using Varian XL200 (^1H) and XL300 (^{31}P) spectrometers.

Syntheses. $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$. Silver acetate (2.2 g) was added to a stirred solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 g) in EtOH (30 mL). The mixture was stirred for 10 min, allowed to stand overnight, and then filtered to remove AgCl . To the filtrate was added dppm (1.6 g) in toluene (30 mL), and the solution was saturated with CO. To this solution was added dropwise a suspension of NaBH_4 (1.2 g) in EtOH (25 mL), with rapid bubbling of CO through the solution. The mixture was stirred for a further 4 h, and then the orange precipitate of the product was isolated by filtration, washed with EtOH (20 mL) and pentane (10 mL), and dried under vacuum. Large yellow-orange needles were obtained on recrystallization from $\text{C}_2\text{H}_4\text{Cl}_2/\text{hexane}$. Yield: 62%. Mp: 238–240 $^\circ\text{C}$. NMR in CD_2Cl_2 : ^1H $\delta = 3.62$ [quintet, $J_{\text{obs}}(\text{PH}) = 4.7$ Hz]; ^{31}P $\delta = 34.4$ [s]. IR (Nujol): $\nu(\text{CO}) = 1966$ (s), 1923 (vs), 1898 (vs), 1883 (s), 1701 cm^{-1} (s).

trans- $[\text{RuH}(\text{CO})(\text{dppm})_2]\text{BPh}_4$. The solvent was evaporated from the mother liquor from the above synthesis. The residue was dissolved in EtOH (60 mL), and NaBPh_4 (0.3 g) was added to precipitate the product, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{ether}$. Yield: 9%. Mp: 247–250 $^\circ\text{C}$. NMR in CD_2Cl_2 : ^1H $\delta = -3.6$ [triplet of quintets, $^2J(\text{PH}) = 20.5$, $J(\text{HH}) = 3.2$ Hz], 4.97 [m, $^2J(\text{PH}) + ^4J(\text{PH}) = 9$, $^2J(\text{H}^a\text{H}^b) = 16$ Hz, CH^a], 5.30 [m, $^2J(\text{PH}) + ^4J(\text{PH}) = 9$, $^2J(\text{H}^a\text{H}^b) = 16$, $J(\text{H}^b\text{R}^u) = 3.2$ Hz, H^b]; ^{31}P $\delta = -6.2$ [s]. IR (Nujol): $\nu(\text{CO}) = 1999$ (sh), 1983 cm^{-1} (s).

$[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$. The mother liquor from the synthesis of $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ was allowed to stand for 3 weeks at room temperature, whereupon red crystals of the product slowly formed. Yield: 5%. NMR in CD_2Cl_2 : ^1H $\delta = 3.9$ [t, $^2J(\text{PH}) = 8.9$ Hz, CH_2]; ^{31}P $\delta = 17.7$ [s]. IR (Nujol): $\nu(\text{CO}) = 1937$ (vs), 1925 (vs), 1914 (vs), 1875 cm^{-1} (w).

$[\text{Ru}_3(\mu\text{-H})(\text{CO})_6(\mu\text{-dppm})_3][\text{PF}_6]$. To a solution of $[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$ (0.01 g) in CH_2Cl_2 (1 mL) was added aqueous $\text{H}[\text{PF}_6]$ (0.03 mL). Monitoring by ^{31}P NMR showed that conversion to the product was essentially quantitative. The solvent was evaporated, and the product was washed with ether. Anal. Calc for $\text{C}_{81}\text{H}_{67}\text{F}_6\text{O}_6\text{P}_7\text{Ru}_3$: C, 54.9; H, 3.8. Found: C, 54.4; H, 4.0. NMR in CD_2Cl_2 : ^1H $\delta = 3.87$ [t, 6H, $J_{\text{obs}}(\text{PH}) = 10$ Hz, CH_2P_2], -18.68 [s, 1H, RuH]; ^{31}P $\delta = 15.3$ [s, dppm]. IR: $\nu(\text{CO}) = 1999$ (sh), 1966 cm^{-1} (vs). The BF_4^- salt was prepared similarly, and the cation had identical spectroscopic properties.

$[\text{RuCl}_2(\text{dppm})_2]$. A solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5 g) and dppm (1.6 g) in toluene/ethanol (1:1, 60 mL) was saturated with CO. To this solution was added dropwise NaBH_4 (0.8 g) in EtOH (15 mL), and the mixture was stirred for 2.5 h. The yellow precipitate of the product was isolated by filtration and recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. Yield: 15%. NMR

- (1) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 4, Chapter 32.2.
- (2) (a) Johnson, K. A.; Gladfelter, W. L. *Organometallics* 1989, 8, 2866. (b) Johnson, K. A.; Gladfelter, W. L. *Organometallics* 1990, 9, 2101. (c) Johnson, K. A.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1991, 113, 5097. (d) Johnson, K. A.; Gladfelter, W. L. *Organometallics* 1991, 10, 376.
- (3) (a) de Leeuw, G.; Field, J. S.; Haines, R. J.; McCulloch, B.; Meintjies, E.; Monberg, C.; Olivier, G. M.; Ramdial, P.; Sampson, C. N.; Sigwarth, B.; Steen, N. D.; Moodley, K. G. *J. Organomet. Chem.* 1984, 275, 99. (b) Field, J. S.; Haines, R. J.; Sampson, C. N.; Sundermeyer, J.; Moodley, K. G. *J. Organomet. Chem.* 1987, 322, C7. (c) Engel, D. W.; Moodley, K. G.; Subramony, L.; Haines, R. J. *J. Organomet. Chem.* 1988, 349, 393. (d) Field, J. S.; Francis, A. M. A.; Haines, R. J.; Woollam, S. F. *J. Organomet. Chem.* 1991, 412, 383. (e) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Chem. Commun.* 1990, 985. (f) Kiel, G.-Y.; Takats, J. *Organometallics* 1989, 8, 839.
- (4) (a) Cartwright, S.; Clucas, J. A.; Dawson, R. H.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Organomet. Chem.* 1986, 302, 403. (b) Lukan, N.; Bonnet, J. J.; Ibers, J. A. *J. Am. Chem. Soc.* 1985, 107, 4484. (c) Bruce, M. I.; Shawkataly, O. B.; Williams, M. L. *J. Organomet. Chem.* 1985, 287, 127. (d) Manojlovic-Muir, L. J.; Brandes, D. A.; Puddephatt, R. J. *J. Organomet. Chem.* 1987, 332, 201.
- (5) Puddephatt, R. J.; Manojlovic-Muir, L. J.; Muir, K. W. *Polyhedron* 1990, 23, 2767 and references therein.

in CD_2Cl_2 : ^1H $\delta = 5.0$ [m, CH_2]; ^{31}P $\delta = -12.5$ [s]. MS: m/z 940, $\text{RuCl}_2(\text{dppm})_2^+$.

X-ray Structure Determinations. The data collections were carried out by using an Enraf-Nonius interCAD4F diffractometer at room temperature (296 K) using Mo $K\alpha$ radiation with a graphite monochromator for **2** and Cu $K\alpha$ radiation with a nickel filter for **3**. The density measurements were made by neutral buoyancy using a mixture of carbon tetrachloride and hexane. Photoindexing and automatic indexing routines, followed by least-squares fits of 21 accurately centered reflections ($30 \leq 2\theta \leq 35^\circ$ for **2** and $49.6 \leq 2\theta \leq 56.8^\circ$ for **3**) gave cell constants and an orientation matrix.⁶ Intensity data were recorded in the θ - 2θ mode, at variable scan speeds so chosen as to optimize counting statistics within a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side for **2**, and static background measurements were made at the end points of the width $(0.95 + \tan \theta)^\circ$ for **3**. Four standard reflections were monitored at regular intervals of time to check the stability of the crystal during the experiment. The structures were solved by a combination of SHELXS-86⁷ and difference Fourier techniques. Scattering factors for neutral and non-hydrogen atoms were taken from ref 8. All the phenyl ring carbon atoms were constrained to regular hexagons with C-C = 1.395 Å.

Compound 2. A red crystal (of approximate dimensions $0.31 \times 0.24 \times 0.15$ mm) was mounted inside a capillary tube under argon. A total of 9017 reflections were collected (of which 8481 were unique) over a period of 154 h. All the calculations (except where otherwise stated) were performed with the NRCVAX Crystal Structure programs⁹ running on a SUN 3/50 workstation. Corrections were made for Lorentz, monochromator, crystal polarization, and background radiation effects. An empirical absorption correction was applied,¹⁰ based upon the ψ scans of nine reflections with θ ranging from 3.2 to 16.8° . The maximum and minimum transmission factors were 0.9986 and 0.9403. The space group was deduced to be $P2_1/n$ from systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$).^{8b} Refinement on F was carried out by full-matrix least-squares techniques. The Ru, P, and six O atoms were assigned anisotropic thermal parameters. All the hydrogen atoms were located by difference Fourier techniques and were placed in idealized positions (C-H = 0.95 Å). The final $R = 0.051$ and $R_w = 0.040$ for 5119 ($I \geq 2.5\sigma(I)$) observations and 257 variables. In the final least-squares cycles the maximum shift/esd was zero. The final difference Fourier map contained no peaks greater than $0.77 \text{ e} \cdot \text{Å}^{-3}$.

Compound 3. Single crystals were obtained from a mixture of dichloroethane and *n*-pentane by slow diffusion. The wine-red crystals lost solvents quickly and became opaque; hence they were examined under paraffin oil. A suitable-quality crystal of dimensions $0.28 \times 0.12 \times 0.12$ mm was wedged inside a Lindeman capillary and flame-sealed on both ends. In all, 11 129 reflections were collected. Corrections were made for Lorentz, crystal polarization, and background radiation effects and decay using the Structure Determination Package¹¹ running on a PDPI 1/23+ computer. Six faces were identified for the data crystal, and the distances among them were measured on a microscope. An absorption correction was applied to the data using the program ABSCOR.¹² The maximum and minimum absorption values were 57.62 and 38.71%, respectively. A p value of 0.07 was applied to the data.¹³ Equivalent reflections were averaged ($R(F) = 0.024$) to give 10 681 data available for solution and refinement. Refinement was carried out by full-matrix least-squares techniques on I , using the SHELX-76 software¹⁴ running on a SUN 3/80 workstation. Anisotropic thermal parameters were assigned for all the Ru, P, and O atoms and were refined. The hydrogen atoms were placed in idealized positions with C-H = 0.95 Å and were

Table I. Summary of X-Ray Structure Determinations

	2 , $\text{C}_{81}\text{H}_{66}\text{O}_6 \cdot \text{P}_6\text{Ru}_3$	3 , $\text{C}_{81}\text{H}_{67}\text{O}_6\text{BF}_4\text{P}_6\text{Ru}_3 \cdot \text{C}_2\text{H}_4\text{Cl}_2 \cdot 1.5\text{C}_5\text{H}_{12}$
fw	1624.45	1919.4
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	24.984(3)	14.810(2)
b (Å)	19.433(3)	21.801(2)
c (Å)	14.724(2)	13.847(1)
α (deg)	90	107.67(1)
β (deg)	90.747(9)	91.54(4)
γ (deg)	90	89.86(1)
cell vol (Å^3), Z	7148(2), 4	4258.1(9), 2
density (g cm^{-3}): obs, calc	1.52(5), 1.51	1.52(5), 1.50
$F(000)$	3232	1864
radiation	Mo $K\alpha$	Cu $K\alpha$
wavelength (Å)	0.710 73	1.541 84
μ (cm^{-1})	7.9	61.4
R , R_w^a	0.051, 0.040	0.075, 0.082

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}.$$

included in the structure factor calculations only; a common thermal parameter was fixed at 0.100. The BF_4 anion was found to be disordered, having two different BF_4 models with occupancy factors 0.60 and 0.40. Each fragment was treated as an ideal tetrahedron with B-F = 1.370 Å; the individual isotropic thermal parameters were refined by the least-squares procedures. The solvent molecules (1 dichloroethane and 1.5 *n*-pentane) were located in the difference Fourier syntheses. The disorder found in dichloroethane (occupancy factors 0.80/0.20) and pentane (occupancy factors 0.50/0.50) molecules were successfully resolved. The C-Cl and C-C bond lengths in the $\text{C}_2\text{H}_4\text{Cl}_2$ molecule were fixed at 1.700 and 1.542 Å, respectively. Similarly, the C-C bond lengths and the C-C-C angles in the pentane molecules were fixed at 1.542 Å and 109.5° , respectively. A common thermal parameter was assigned for all the non-hydrogen atoms present in each disorder component of the pentane molecule and refined by the least-squares procedures. No hydrogen atoms were included for the solvent molecules. One bad reflection ($12, -3, 1$) was omitted in the least-squares cycles. In the final stages of least-squares refinements, the hydrogen atom near the Ru atoms was successfully located and refined (though the esd's are high) with a fixed thermal parameter ($U = 0.10$). Using 6003 observations with $I \geq 3\sigma(I)$ and utilizing weights of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 1.5330$ and $g = 0.0007$, refinement (on I) of 373 variables converged at agreement factors $R = 0.0748$ and $R_w = 0.0825$. In the final difference Fourier synthesis there were five peaks with electron density in the range 2.043 – $0.729 \text{ e} \cdot \text{Å}^{-3}$; of these, four were associated with the solvent molecules. The top three peaks (in the range 2.03 – $0.937 \text{ e} \cdot \text{Å}^{-3}$) were associated with the pentane carbon atoms C(33), C(21), and C(25a) at distances of 0.64, 0.48, and 0.71 Å, respectively, and the fourth peak was near C(62a) at 0.67 Å. Crystallographic data and the positional and U_{eq} thermal parameters for selected atoms are given in Tables I–III. Tables of anisotropic thermal parameters and root-mean-square amplitudes of vibration have been included in the supplementary material.

Results

Synthesis by Reduction of Ruthenium(III). The reduction of metal halides by sodium borohydride in the presence of carbon monoxide and bis(diphenylphosphino)methane, dppm, has proved to be a useful method for the synthesis of binuclear dppm-bridged metal carbonyl derivatives.¹⁵ This method was tested as a possible route to $[\text{Ru}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (**1**). Reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under these conditions always gave *trans*- $[\text{RuCl}_2(\text{dppm})_2]$ ¹⁶ as a significant product although, in some syntheses, the desired complex **1** was also formed in low yields. It seemed likely that the strong Ru-Cl bonds in $[\text{RuCl}_2(\text{dppm})_2]$ were responsible for the difficulty of reduction to the Ru(0) level, and so experiments were carried out in which 3 equiv of silver acetate

- (6) *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.
 (7) Sheldrick, G. M. SHELXS-86: Structure Solving Program. University of Göttingen, Germany, 1986.
 (8) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV. (b) *International Tables for X-ray Crystallography*; D. Reidel Publishing Co.: Boston, MA, 1983; Vol. A.
 (9) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. C. *J. Appl. Crystallogr.* **1989**, *22*, 384.
 (10) North, A. C. T.; Phillips, D. C.; Mathews, R. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.
 (11) *Enraf-Nonius Structure Determination Package, SDP-PLUS*, Version 3.0; Enraf-Nonius: Delft, The Netherlands, 1985.
 (12) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1968**, *18*, 1035.
 (13) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.
 (14) Sheldrick, G. M. SHELX-76: Program for Crystal Structure Determination. University of Cambridge, England, 1976.

- (15) Elliot, D. J.; Ferguson, G.; Holah, D. G.; Hughes, A. N.; Jennings, M. C.; Magnuson, V. R.; Potter, D.; Puddephatt, R. *J. Organometallics* **1990**, *9*, 1336 and references therein.
 (16) (a) Mason, R.; Meek, D. W.; Scollary, G. R. *Inorg. Chim. Acta* **1976**, *16*, L11. (b) Jung, C. W.; Garrou, P. E.; Hoffman, P. R.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 726.

Table II. Selected Atomic Positional ($\times 10^4$) and Thermal Parameters for Cluster 2

atom	x	y	z	U_{iso}/U_{eq} (\AA^2)
Ru(1)	2407.5(4)	7632.1(6)	4178.2(6)	2.15(5)
Ru(2)	1902.9(4)	7799.7(5)	5898.4(6)	2.24(5)
Ru(3)	1268.9(4)	7643.0(6)	4287.5(6)	2.40(5)
P(1)	2397.9(11)	7580(17)	2597.8(18)	2.46(15)
P(2)	1119.5(12)	7648.9(18)	2752.5(19)	2.56(15)
P(3)	475.2(12)	7661.1(19)	5084.5(19)	2.93(16)
P(4)	1174.9(12)	7825.8(18)	6840.0(19)	2.77(16)
P(5)	2685.5(12)	7766.5(18)	6746.4(19)	2.64(16)
P(6)	3242.2(11)	7794.0(18)	4820.1(19)	3.54(15)
O(1)	2246(3)	9188(4)	4015(5)	3.6(5)
O(2)	1862(3)	9373(4)	5864(5)	3.8(5)
O(3)	1072(3)	9190(5)	4296(5)	4.2(5)
O(4)	1435(3)	6104(4)	3970(6)	4.3(5)
O(5)	1882(4)	6218(4)	5850(6)	4.8(6)
O(6)	2678(3)	6100(4)	4391(6)	4.7(5)
C(1)	2271(5)	8596(7)	4107(8)	3.2(3)
C(2)	1889(5)	8775(6)	5827(8)	2.4(3)
C(3)	1189(5)	8614(7)	4310(8)	2.7(3)
C(4)	1400(5)	6687(7)	4140(8)	3.2(3)
C(5)	1886(6)	6819(7)	5808(9)	3.8(3)
C(6)	2544(5)	6661(7)	4320(8)	2.7(3)
C(10)	1726(4)	7375(6)	2120(6)	2.5(4)
C(20)	573(4)	8118(6)	6201(7)	2.8(3)
C(30)	3267(4)	7542(6)	6047(6)	2.9(3)

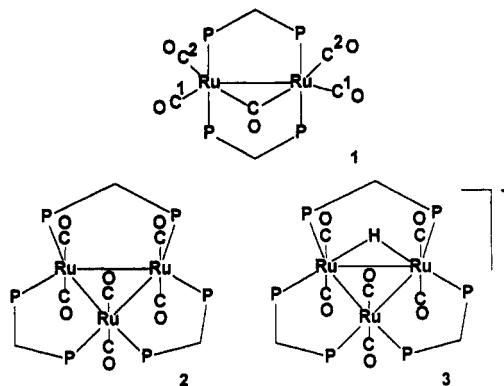
Table III. Selected Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters for (3)BF₄

atom	x	y	z	U_{eq} (\AA^2)
Ru(1)	2977.9(9)	7879.3(6)	5827.8(9)	41.2(4) ^a
Ru(2)	3079.0(9)	6994.7(6)	3837.1(9)	44.0(4) ^a
Ru(3)	4740.1(9)	7474.0(6)	4924.9(9)	40.7(4)
P(1)	3682(3)	8565(2)	7300(3)	45(1) ^a
P(2)	5577(3)	8034(2)	6385(3)	41(1) ^a
P(3)	5659(3)	6920(2)	3607(3)	47(1) ^a
P(4)	3854(3)	6356(2)	2441(3)	52(2) ^a
P(5)	1537(3)	6990(2)	3556(4)	54(2) ^a
P(6)	1421(3)	7787(2)	5915(4)	54(2) ^a
O(1)	2579(8)	8842(5)	4666(9)	64(5) ^a
O(2)	3191(8)	7981(6)	2669(9)	67(5) ^a
O(3)	4722(8)	8610(6)	4048(9)	69(5) ^a
O(4)	4634(9)	6322(6)	5738(11)	77(5) ^a
O(5)	2630(9)	5999(6)	4888(10)	77(5) ^a
O(6)	3144(8)	6918(6)	7046(9)	67(5) ^a
C(1)	2759(11)	8487(8)	5084(12)	46(4)
C(2)	3167(11)	7638(8)	3158(13)	49(4)
C(3)	4712(11)	8180(8)	4370(13)	50(4)
C(4)	4647(13)	6764(10)	5450(14)	66(5)
C(5)	2858(11)	6402(8)	4542(12)	49(4)
C(6)	3077(12)	7245(8)	6553(13)	54(5)
C(10)	4777(10)	8232(7)	7495(11)	47(4)
C(20)	4990(10)	6715(7)	2411(11)	47(4)
C(30)	943(11)	7185(8)	4751(12)	52(4)
H	4039(118)	8163(84)	5813(131)	100

^a Parameters were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$.

was added to the ruthenium(III) chloride solution to generate in situ a solution of ruthenium(III) acetate, which was then reduced in the usual way by borohydride in the presence of CO and dpmm. This synthesis routinely gave the desired product **1** in >60% yield in a single step from ruthenium(III) chloride and so is less expensive and more convenient than the previous method.³ This synthesis also gives some *trans*-[RuH(CO)(dpmm)]⁺ ion, conveniently isolated as the BPh₄⁻ salt, which is easily separated from **1**.¹⁷ In addition, the cluster complex [Ru₃(CO)₆(μ-dppm)₃], which is more conveniently prepared by reaction of dpmm with [Ru₃(CO)₁₂],^{4a} can be isolated in low yield from this reaction.

Properties of [Ru₂(CO)₄(μ-CO)(μ-dppm)₂]. The structure of **1** was deduced from the spectroscopic data and has also been



confirmed by X-ray structure analysis of its solvate [Ru₂(CO)₄(μ-CO)(μ-dppm)₂·C₂H₄Cl₂], details of which will be reported separately.¹⁸ The structure is similar to the structures of [Ru₂(CO)₄(μ-CO)(μ-LL)₂] with LL = Me₂PCH₂PMe₂, dpmm, and (MeO)₂PN(Et)P(OMe)₂, dmopn, determined previously.^{2,3} The trend in carbonyl stretching frequencies is dmopn > dpmm > dmpm, indicating that the π-acceptor property of the diphosphine ligands follow the same series. Thus the ranges for terminal carbonyls are 1913–1999, 1883–1966, and 1874–1954 cm⁻¹, and the frequencies for bridging carbonyls are 1703, 1701, and 1694 cm⁻¹ for LL = dmopn, dpmm, and dmpm, respectively.^{2,3} The spectroscopic properties of complex **1** are as expected except that the ¹H NMR spectrum contains only a single resonance for the CH₂ protons of the dpmm ligands. Since there is no plane of symmetry containing the Ru₂P₂C rings, due to the presence of the μ-CO ligand on one side only, the CH²H^bP₂ protons of each dpmm ligand are expected to be nonequivalent. The apparent equivalence is attributed to fluxionality of the carbonyl ligands.²

Structures and Properties of Trinuclear Complexes. A minor side product in the synthesis of **1** is the trinuclear cluster [Ru₃(CO)₆(μ-dppm)₃]^{4a} (**2**), which is electron-rich and is easily protonated to give [Ru₃(μ-H)(CO)₆(μ-dppm)₃]⁺ (**3**).

The product [Ru₃(CO)₆(μ-dppm)₃] (**2**) was characterized spectroscopically by comparison to an authentic sample.^{4a} However, the NMR spectra in chlorinated solvents contained a second set of resonances which were finally attributed to the protonated derivative [Ru₃(H)(CO)₆(μ-dppm)₃]⁺ (**3**). This hydridotrinuclear cation is easily formed by protonation of **2**; impurities of HCl in chlorinated solvents are sufficient for the purpose. In the ¹H NMR spectrum, cation **3** gives a broad singlet attributed to a ruthenium hydride proton at δ = -18.68 ppm and a single resonance due to the CH₂P₂ protons of the dpmm ligands at δ = 3.87 ppm, while the ³¹P NMR spectrum contains a sharp singlet due to the phosphorus atoms of dpmm. The spectra were unchanged at -80 °C. These data show that the cation has effective D_{3h} symmetry on the NMR time scale. Thus, 3-fold symmetry is necessary for equivalence of the six phosphorus atoms, and a plane of symmetry containing the Ru₃(μ-dppm)₃ unit is necessary for equivalence of the CH²H^bP₂ protons of each dpmm ligand. For a nonfluxional structure, this would indicate that an unprecedented planar Ru₃(μ₃-H) group is present. The alternative is a fluxional cluster containing either a nonplanar Ru₃(μ₃-H) group or a Ru₂(μ-H) group, the latter requiring a greater degree of fluxionality. The precedents are all for addition of electrophiles to an edge of Ru₃ clusters. For example, H⁺ adds to an unbridged edge in both [Ru₃(CO)₁₂] and [Ru₃(CO)₈(μ-dppm)₂].¹⁹ Since complex **2** has all edges bridged by μ-dppm ligands, edge protonation must lead to increased steric hindrance between the hydride and μ-dppm. In addition, cluster complexes containing the M₃(μ-dppm)₃ unit often prefer μ₃-X groups in the axial

(18) Kristof, E.; Taylor, N. J. Unpublished work.

(19) (a) Knight, J.; Mays, M. J. *J. Chem. Soc. A* 1970, 711. (b) Lavigne, G.; Lugan, N.; Bonnet, J. *J. Organometallics* 1982, 1, 1040. (c) Ladd, J. A.; Hope, H.; Balch, A. L. *Organometallics* 1984, 3, 1838.

(17) Ben Laarab, H.; Chaudret, B.; Dahan, F.; Devillers, J.; Poilblanc, R.; Sabo-Etienne, S. *New J. Chem.* 1990, 14, 321.

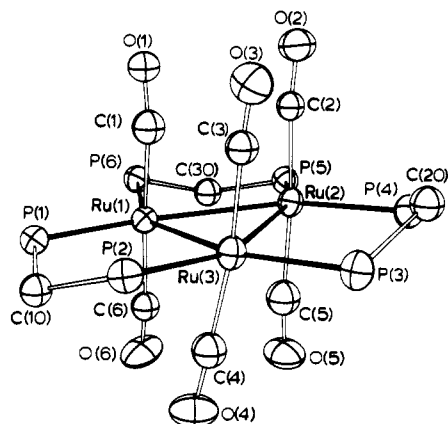


Figure 1. View of the structure of $[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$. Phenyl groups are omitted for clarity.

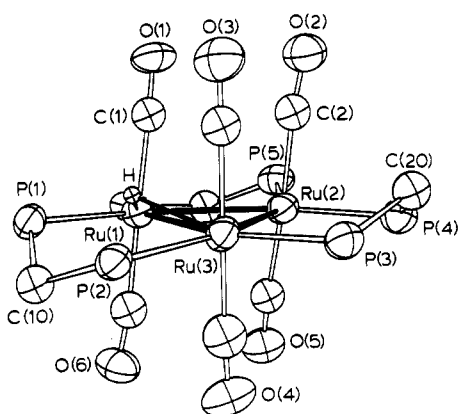


Figure 2. View of the structure of the cluster cation $[\text{Ru}_3(\mu\text{-H})(\text{CO})_6(\mu\text{-dppm})_3]^+$. The atom labeling is the same as in Figure 1; the envelope conformations of $\mu\text{-dppm}$ ligands are the same in each structure (see text). Phenyl groups are omitted for clarity.

position.⁵ It thus seemed possible that face bridging of the hydride might be preferred, although this is unprecedented in $[\text{Ru}_3(\text{CO})_{12}]$ or its phosphine-substituted derivatives.²⁰ Since NMR methods could not distinguish between the possibilities, X-ray structure determinations were carried out for both $[\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3]$ and $[\text{Ru}_3(\text{H})(\text{CO})_6(\mu\text{-dppm})_3][\text{BF}_4]$.

The structures of clusters **2** and **3** are shown in Figures 1 and 2, while selected distances, angles, and deviations from the Ru_3 plane are given in Tables IV and V.

Each structure contains a triangle of ruthenium atoms with equatorial $\mu\text{-dppm}$ ligands bridging each edge and with six axial carbonyl ligands, all of which are terminally bonded. The hydride ligand in **3** was successfully located and refined and found to bridge the $\text{Ru}(1)\text{-Ru}(3)$ bond as shown in Figure 2. The hydride is not in the Ru_3 plane but lies above the plane, and the associated $\mu\text{-dppm}$ ligand is displaced below, presumably because steric effects are unfavorable with the hydride and $\mu\text{-dppm}$ coplanar. The Ru-H distances found, while not accurately determined, are similar to those for other $\text{Ru}_2(\mu\text{-H})$ complexes.^{4,20} For example, $[\text{Ru}_3(\mu\text{-H})(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Me}_2\text{PCHPMe}_2)]$ has Ru-H distances of 1.66(5) and 1.75(5) Å.^{4d} Further evidence that the hydride location is correct was obtained from differences in bond distances and angles between the structures of **2** and **3** as discussed below.

Complexes containing the $\text{M}_3(\mu\text{-dppm})_3$ core do not have regular planar structures as a result of two different effects.⁵ First, the $\text{M}_2(\mu\text{-dppm})$ units adopt envelope conformations with the CH_2 group at the "flap". If the flap is up (i.e. CH_2 above the M_3P_6 plane), the phenyl groups above the plane are equatorial

Table IV. Selected Bond Distances (Å) and Angles (deg) for **2** and **3**

	2	3
Distances		
Ru(1)-Ru(2)	2.862(1)	2.852(2)
Ru(1)-Ru(3)	2.851(1)	2.940(2)
Ru(2)-Ru(3)	2.851(1)	2.876(2)
Ru(1)-P(1)	2.329(3)	2.349(4)
Ru(1)-P(6)	2.300(3)	2.325(5)
Ru(2)-P(4)	2.302(3)	2.339(5)
Ru(2)-P(5)	2.307(3)	2.306(5)
Ru(3)-P(2)	2.286(3)	2.343(4)
Ru(3)-P(3)	2.317(3)	2.329(4)
Ru(1)-C(1)	1.91(1)	1.93(2)
Ru(1)-C(6)	1.93(1)	1.94(2)
Ru(2)-C(2)	1.90(1)	1.92(2)
Ru(2)-C(5)	1.91(1)	1.87(2)
Ru(3)-C(3)	1.90(1)	1.92(2)
Ru(3)-C(4)	1.90(1)	1.91(2)
Ru(1)-H		1.7(2)
Ru(3)-H		1.9(2)
P-CH ₂	1.85(1)-1.88(1)	1.82(2)-1.91(2)
P-C(Ph)	1.828(8)-1.861(8)	1.82(2)-1.86(1)
C-O	1.14(2)-1.17(2)	1.12(2)-1.18(2)
Angles		
Ru(3)-Ru(1)-Ru(2)	59.87(3)	59.53(4)
Ru(3)-Ru(2)-Ru(1)	59.87(3)	61.77(4)
Ru(2)-Ru(3)-Ru(1)	60.26(3)	58.70(4)
Ru(3)-Ru(1)-C(1)	79.5(4)	94.4(5)
Ru(1)-Ru(3)-C(3)	96.5(4)	89.3(5)
Ru(3)-Ru(2)-C(2)	92.9(4)	89.1(5)
Ru(1)-Ru(2)-C(2)	94.2(3)	95.7(5)
C(6)-Ru(1)-C(1)	176.9(5)	174.5(7)
C(5)-Ru(2)-C(2)	172.5(5)	173.3(7)
C(4)-Ru(3)-C(3)	173.2(5)	174.5(8)
C(1)-Ru(1)-P(1)	89.3(4)	99.7(5)
C(6)-Ru(1)-P(1)	93.7(3)	83.8(5)
C(3)-Ru(3)-P(2)	89.8(4)	94.5(5)
C(4)-Ru(3)-P(2)	85.3(4)	89.1(6)
C(1)-Ru(1)-P(6)	92.8(4)	87.8(5)
C(6)-Ru(1)-P(6)	86.1(4)	86.9(5)
C(3)-Ru(3)-P(3)	83.4(4)	88.8(5)
C(4)-Ru(3)-P(3)	102.9(4)	93.6(6)
C(2)-Ru(2)-P(4)	89.8(4)	83.9(5)
C(2)-Ru(2)-P(5)	94.2(4)	88.0(5)
C(5)-Ru(2)-P(4)	92.7(4)	101.3(5)
C(5)-Ru(2)-P(5)	91.6(4)	86.1(5)
P-Ru-P	110.2(1)-114.5(1)	112.3(2)-114.7(2)
Ru-C-O	171(1)-174(1)	171(2)-178(2)
Ru-Ru-P	91.62(8)-95.50(8)	91.1(1)-94.7(1)
Ru-Ru-C	79.2(4)-100.2(4)	82.4(5)-96.7(5)
Ru(1)-H-Ru(3)		107.7(9)
C(1)-Ru(1)-H		79.8(6)
C(6)-Ru(1)-H		105.7(6)
C(3)-Ru(3)-H		71.9(5)
C(4)-Ru(3)-H		105.8(5)
P(1)-Ru(1)-H		58.6(6)
P(2)-Ru(3)-H		68.5(5)

Table V. Deviations (Å) of Selected Atoms from the Ru_3 Plane

	2	3	2	3	
P(1)	0.196(4)	0.067(4)	P(5)	-0.223(4)	0.234(5)
P(2)	0.299(4)	-0.174(4)	P(6)	0.192(4)	-0.272(5)
P(3)	-0.115(4)	0.069(5)	H		0.6(2)
P(4)	-0.127(4)	-0.033(5)			

and so cause less steric congestion than those below the plane, which are axial. This effect alone leads to six possible orientations of the $\text{Ru}_3(\mu\text{-dppm})_3$ unit. Since this is the major effect in determining overall steric hindrance, the numbering systems for structures **2** and **3** have been chosen so that the conformations of the $\mu\text{-dppm}$ ligands with the $\text{Ru}_3(\mu\text{-dppm})_3$ units are the same in each case. Thus, each structure has the flap atoms C(10) and C(30) below and C(20) above the $\text{Ru}(3)$ plane. The second type of distortion which occurs to minimize steric effects is a twisting of the $\mu\text{-dppm}$ ligands such that the phosphorus atoms are displaced

(20) (a) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984. (b) Yoshida, T.; Adachi, T.; Tanaka, T.; Goto, F. *J. Organomet. Chem.* **1992**, *428*, C12.

from the Ru_3 plane. Thus, in $[Ru_3(CO)_{12}]$ the equatorial carbonyls are displaced from the Ru_3 plane by a maximum of only 0.041 Å,²¹ but in **2** and **3** the analogous maximum displacements of phosphorus atoms are 0.299 and 0.272 Å, respectively. While the directions of the dppm twist in the structures of **2** and **3** are the same for P(3)C(20)P(4), they are opposite for P(1)C(10)P(2) and P(5)C(30)P(6). The greatest difference is for the dppm ligand P(5)C(30)P(6); thus, in complex **2** P(5) is 0.223 Å below and P(6) is 0.192 Å above the Ru_3 plane whereas in **3** P(5) is 0.234 Å above and P(6) is 0.272 Å below the Ru_3 plane. These distortions define the octahedral coordination axes for each ruthenium center,²² and so the orientations of the carbonyl ligands are also different in the structures of **2** and **3**. In $Ru_3(CO)_{12}$ the range of Ru–Ru–C(axial) angles is only 87.7–90.5°,²¹ but in **2** and **3** the ranges are much greater at 79.2–100.2 and 82.4–96.7°, respectively, and the patterns of distortion from 90° are different in each case. Because the dppm ligands are the major source of steric effects, the differences in orientations of these ligands in **2** and **3** will cause significant differences in other bond parameters, thereby complicating the interpretation of structural differences due to the hydride in **3**. This should be borne in mind in the following discussion.

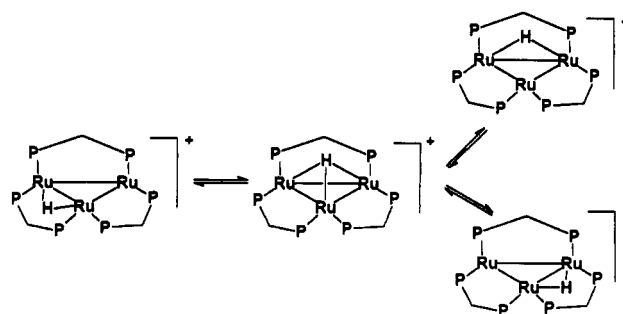
Considering trends in bond distances, both the average Ru–P and Ru–C distances are slightly greater in **3** than in **2**, and this could be due either to greater steric effects or to reduced back-bonding in the hydrido cation. The greatest difference is in the Ru(1)–Ru(3) distance, which is 0.089(2) Å longer in **3** than in **2**, consistent with this bond being the site of protonation.

As discussed above, differences in angles must be interpreted with caution. Thus, it is noted that the angles C(1)–Ru(1)–P(1) and C(3)–Ru(3)–P(2) increase by 10.4 and 4.7°, respectively, from **2** to **3**, as expected if the hydride is present above the Ru(1)–Ru(3) edge, but there are marked differences between many other C–Ru–P angles also (Table IV). More convincing evidence that the hydride is correctly located comes from a consideration of the displacements of phosphorus atoms from the Ru_3 plane. If we define this displacement for P(*n*) as $\delta[P(n)]$, then the values of $\sum\delta[P(n)]$ for **2** and **3** are 0.222 and –0.109 Å, respectively. That is, the net displacement of all P atoms is 0.222 Å above the plane in **2** but 0.109 Å below the plane in **3**. This is consistent with an overall repulsion by the hydride in **3**, which lies above the plane. The difference in net P displacement between the two structures is 0.331 Å, which can be factored as 0.602 [P(1) + P(2)] + 0.280 [P(3) + P(6)] – 0.551 [P(4) + P(5)] Å. Thus, the hydride repels the closest phosphorus atoms P(1) and P(2) most, while P(3) and P(6) are more weakly repelled. Since these displacements affect steric effects below the plane, P(4) and P(5), which are not directly affected by the hydride, are displaced above the plane in response. The overall differences in geometry of the dppm ligands between **2** and **3** thus follow naturally from the position of the hydride ligand and, in turn, provide strong evidence that the hydride ligand is located correctly by the X-ray structure determination.

Discussion

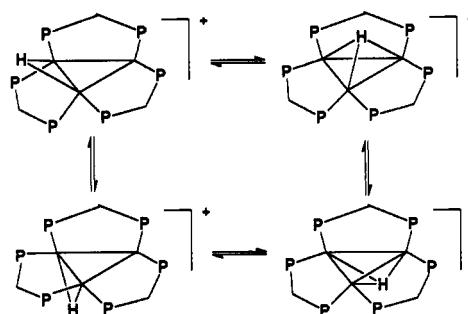
The mechanism of reduction of metal halides by sodium borohydride is difficult to determine, and the success or failure of the method in any particular case is difficult to predict.¹⁵ This work shows that easy reduction of ruthenium(III) to ruthenium(0) can occur, in the presence of CO and dppm, if good leaving groups are present on ruthenium(III) but not if chloride ligands are present. The easier reduction of metal carboxylates than of metal halides should be a general effect for soft metal ions, but

Scheme I^a



^a Carbonyl ligands are omitted.

Scheme II^a



^a Carbonyl ligands are omitted.

its success is still difficult to predict. For example, the attempted reduction of ruthenium(III) in the presence of CO and bis(dimethylphosphino)methane, dmpm, gave $[Ru(BH_3CN)_2(dmpm)_2]$ but failed to give any ruthenium(0) carbonyl even though both $[Ru_2(CO)_5(\mu-dmpm)_2]$ and $[Ru_3(CO)_8(\mu-dmpm)_2]$ are stable complexes,^{2,3} and attempted reduction of osmium(III) chloride in the presence of silver acetate, dppm, and CO failed to give any osmium(0) carbonyls. This unpredictability is certainly a major problem in further extension of the synthetic method. Nevertheless, the one-step synthesis of electron-rich binuclear carbonyls from metal halides is very attractive and the synthesis of **1** by this method is reproducible and convenient.

The new hydride cluster cation **3** has interesting structural and fluxional properties. The X-ray structure determination shows convincingly that the cation in the solid state should be formulated as $[Ru_3(\mu-H)(CO)_6(\mu-dppm)_3]^+$. However, the NMR spectra, even at –80 °C, indicate 3-fold symmetry, and so, assuming the preferred structures are the same in the solid and solution states, the compound is fluxional. The migration of hydride from edge to edge of the cluster must be particularly easy in **3**, and this is likely to occur by way of a $Ru_3(\mu_3-H)$ intermediate as shown in Scheme I.

In addition, the hydride must be able to migrate easily from one side of the Ru_3 triangle to the other. This could occur either on the outside of the triangle, through a transition state in which the $\mu-H$ and $\mu-dppm$ ligands are coplanar, or by tunneling through the center of the Ru_3 triangle, as has been suggested to occur for $[Pt_3(\mu_3-H)(\mu-dppm)_3]^+$.²³ The data cannot distinguish between the two mechanisms depicted in Scheme II.

The protonation of $[Ru_3(CO)_6(\mu-dppm)_3]$ occurs much more easily than for either $[Ru_3(CO)_{12}]$ or $[Ru_3(CO)_8(\mu-dppm)_2]$.¹⁹ This is of course expected in terms of electronic effects since substitution of dppm for carbonyls increases the electron density at ruthenium but is opposed by steric effects. For the proton, electronic effects are dominant, but attempts to add bulkier electrophiles such as Ag^+ or Ph_3PAu^+ to **2** have been unsuccessful, presumably due to unfavorable steric effects. The increase in

(21) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* 1977, 16, 2655.

(22) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Acta Crystallogr., Sect. B* 1982, B38, 1911.

(23) Lloyd, B. R.; Puddephatt, R. J. *J. Am. Chem. Soc.* 1985, 107, 7785.

electron density at the Ru₃ is also indicated by the decrease in values of $\nu(\text{CO})$ as more dppm ligands are introduced. The strong $\nu(\text{CO})/\text{cm}^{-1}$ bands are as follows: [Ru₃(CO)₁₂], 2066, 2026, 2004; [Ru₃(CO)₁₀(μ -dppm)], 2013, 2003, 1966; [Ru₃(CO)₈(μ -dppm)₂], 2023, 1981, 1970; [Ru₃(CO)₆(μ -dppm)₃], 1937, 1925, 1914.²⁴

(24) Bruce, M. I.; Matison, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.

Acknowledgment. We thank the NSERC (Canada) for financial support and Dr. N. C. Payne for access to crystallographic hardware and software.

Supplementary Material Available: Complete atomic and thermal parameters (Tables S1, S7), bond distances and angles (Tables S2, S8), general displacement parameter expressions (Tables S3, S9), calculated H atom positions (Tables S4, S10), weighted least-squares planes and dihedral angles (Tables S5, S11), and torsional angles (Tables S6, S12) for **2** and **3** (21 pages). Ordering information is given on any current masthead page.