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Aspects of the Chemistry of μ_3-Oxo Triruthenium Clusters Derived from $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$

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The title complex $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$ (dppm = bis(diphenylphosphino)methane) reacts reversibly with hydrogen in refluxing xylene solution to yield $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$. The X-ray structure of this complex is reported: crystal system trigonal; C_3^2—$P3_1$; a = 13.793 (5) Å, b = 13.800 (4) Å, c = 26.112 (7) Å; V = 4307 Å^3; Z = 3. Final R values are R_w = 0.048 and R = 0.048. The structure consists of a triangular ruthenium framework capped with a face-bridging oxygen atom (Ru(1)–Ru(2) = 2.801 (1) Å; Ru(1)–Ru(3) = 2.805 (1) Å; Ru(2)–Ru(3) = 2.670 (1) Å). The metal–metal vectors Ru(1)–Ru(2) and Ru(1)–Ru(3) are H-bridged and are supported by bridging dppm ligands. Reaction of this complex with iodine at room temperature yields the ionic complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}I)(\mu\text{-}H)_2(CO_5)(\mu\text{-}\eta^2\text{-dppm})_2]^+I^-$ which has been characterized by spectroscopic and crystallographic techniques: crystal system triclinic; $P\bar{1}$; a = 15.328 (4) Å, b = 17.168 (9) Å, c = 13.208 (5) Å; α = 95.66 (4)°, β = 90.83°, γ = 115.77 (3)°; V = 3108.6 Å^3, Z = 2. Final R values are R_w = 0.122 and R = 0.097. Oxidative addition of iodine to the cluster $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$ results in opening of the triangular structure. The bridging iodine atom spans the metal–metal vector Ru(2)–Ru(3) (nonbonding distance 3.273 (5) Å). This reaction has been extended to a variety of electrophiles, $E^+ = H^+$, $AuPPh_3{}^+$, or Ag^+, leading in all cases to cationic adducts $[Ru_3(\mu\text{-}E)(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(dppm)_2]^+$ which have been characterized spectroscopically.

Introduction

The complexation of metal clusters with polydentate phosphine ligands has been widely investigated in recent years.[1] While these ligands provide a satisfactory control of the nuclearity of clusters, they also induce significant modification of the reactivity of such species by increasing the basicity at metal centers. Besides, phosphine ligands are prone to a variety of cluster-assisted transformations involving oxidative cleavage of C–H and C–P bonds.[2] Such reactions are now well documented in the case of bis(diphenylphosphino)methane in $Ru_3(CO)_{10}(dppm)$,[3,4] $Ru_3(CO)_8(dppm)_2$ (**1**),[5-7] and $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppm)$.[7] By constrast, we have observed that dppm is chemically inert in trinuclear species $Co_3(\mu_3\text{-}C\text{-}CH_3)(CO)_7(dppm)$[8] or $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5\text{-}(dppm)_2$ (**2**),[9] both involving a face-bridging heteroatom.

In this paper, we focus on the chemistry of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(dppm)_2$ (**3**), derived from **2** upon treatment with H_2. This new complex combines the advantage of a high reactivity toward electrophiles along with a remarkable stability of the metal core. This is illustrated here in several cases, particularly in reaction with iodine, leading to a cationic cluster species which provides insight into the initial step of the oxidative addition of halogens to metal–metal bonded species.

Experimental Section

A. General Comments. Most reactions but those involving O_2 were routinely conducted under nitrogen atmosphere. Solvents were purified by distillation and were carefully deaerated prior to use. $RuCl_3{\cdot}3H_2O$ was generously supplied by Johnson Matthey Chemicals. Bis(diphenylphosphino)methane (dppm) was purchased from Ventron Chemicals. $Ru_3(CO)_{12}$[10] and $Ru_3(CO)_8(dppm)_2$[5] were prepared by published procedures.

Chromatographic workup was made by using silicagel columns filled with Kieselgel 60—Merck, ref 7734. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer. NMR data were recorded on Fourier transform spectrometers WH90 and WM250. ^1H chemical shifts were reported as δ values in parts per million downfield from internal Me_4Si. ^{31}P chemical shifts are reported as δ values (ppm) downfield from external H_3PO_4 (85%).

B. Preparation of the Complexes. Synthesis of $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$ (**2**). We report here a modification of the original procedure which was already mentioned in a brief communication.[9]

The reaction was conducted in a Schlenk flask equipped with a bubbler and connected with a reflux condenser. $Ru_3(CO)_8(dppm)_2{\cdot}2(CH_3)_2CO$ (**1**) (350 mg) was dissolved in 70 mL of ethoxyethanol. A continuous oxygen stream was then bubbled through the solution which was heated to 80–85 °C. The color

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[1] For examples of face-bridging tripod ligands, see: (a) De Boer, J. J.; Van Doorn, J. A.; Masters, C. *J. Chem. Soc., Chem. Commun.* **1978**, 1005. (b) Bahsoun, A. A.; Osborn, J. A.; Voelker, C.; Bonnet, J.-J.; Lavigne, G. *Organometallics* **1982**, *1*, 1114. (c) Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Organomet. Chem.* **1982**, *226*, C17. (d) Darensbourg, D. J.; Zalewski, D. J. *Organometallics* **1985**, *4*, 92. For examples of edge-bridging ligands, see: (e) Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380. (f) Reimann, W.; Abboud, W.; Basset, J.-M.; Mutin, R.; Rempel, G. L.; Smith, A. K. *J. Mol. Catal.* **1980**, *9*, 349. (g) Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, *19*, 1277. (h) Prest, D. W.; Mays, M. J.; Raithby, P. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 737. (i) Frew; A. A.; Hill, R. H.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 198. (j) Ceriotti, A.; Ciani, G.; Garlashelli, L.; Sartorelli, U.; Sironi, A. *J. Organomet. Chem.* **1982**, *229*, C9. (k) Foster, D. F.; Nicholls, B. S.; Smith, A. K. *J. Organomet. Chem.* **1982**, *236*, 395. (l) Braunstein, P.; Jud, J.-M.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 180. (m) See also some specific references cited and discussed below.

[2] (a) Humphries, A. P.; Kaesz, H. D. *Prog Inorg. Chem.* **1979**, *25*, 145. (b) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 11.

[3] Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484.

[4] Bruce, M. I.; Horn, E.; Snow, M. R.; Williams, M. L. *J. Organomet. Chem.* **1984**, *276*, C53.

[5] Lavigne, G.; Bonnet, J.-J. *Inorg. Chem.* **1981**, *20*, 2713.

[6] Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1982**, *1*, 1040.

[7] Bergounhou, C.; Bonnet, J.-J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F. *Organometallics* **1986**, *5*, 60.

[8] Balavoine, G.; Collin, J.; Bonnet, J.-J.; Lavigne, G. *J. Organomet. Chem.* **1985**, *280*, 429.

[9] Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Nouv. J. Chim.* **1981**, *5*, 423.

[10] Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47.

slowly changed from deep purple to orange brown, while a yellow precipitate appeared. After 2 h, the solution was cooled and filtered. The precipitate was chromatographed on silica gel. Elution with toluene allowed to separate traces of starting material (1). Further elution with dichloromethane afforded a yellow band containing the main reaction product **2**. The complex was recrystallized from acetone–ethanol mixtures and recovered in 65% yield.

$Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(dppm)_2$: IR ($\nu$(CO), cyclohexane) 2021 vs, 1992 m, 1961 vs, 1943 w, 1933 w, 1689 br cm^{-1}. The $^{31}P\{^1H\}$ spectrum exhibits a symmetric multiplet (AA′BB′) centered at 29.77 ppm. ^1H NMR data have been reported.[9] Anal. Calcd for $C_{56}H_{44}O_7P_4Ru_3$: C, 53.55; H, 3.53. Found: C, 53.07; H, 3.4.

Preparation of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2$ (3). A suspension of **2** (570 mg) in xylene (25 mL) was heated under reflux, while a continuous hydrogen stream was bubbled through the solution, using a gas dispersion tube. Slow dissolution of **2** was observed, and the color changed from light yellow to orange. After 4 h, the solution was cooled, allowing 536 mg of orange crystals to precipitate. These crystals were collected by filtration (they can be handled in air for a few minutes). Attempts to chromatograph this complex gave an untractable material at the top of the silica gel column. However, crystals obtained by the method outlined above are analytically and spectroscopically pure samples of **3** crystallizing with 1 mol of xylene/mol of complex.

$Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2\cdot C_6H_4(CH_3)_2$: yield 88%; IR ($\nu$(CO) cyclohexane) 2008 (s), 1973 (m), 1957 (s), 1938 (m) cm^{-1}; NMR data ($CDCl_3$), H nuclei are labeled as H_a, H_b (methylene), and H_c (equivalent hydride ligands); $^1H\{^{31}P\}$ NMR δ 3.70 (2 H_a, d, $J_{H_aH_b}$ = 12.89 Hz), 3.27 (2 H_b, d), −14.95 (2H_c, s); $^{31}P\{^1H\}$ NMR δ 22.75 (2 P, dd), 10.96 (2 P, dd), J_{PP} = 23.53 and 42.65 Hz. Anal. Calcd for $C_{63}H_{56}O_6P_4Ru_3$: C, 56.62; H, 4.23. Found: C, 56.76; H, 4.15.

Reaction of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2$ (3) with Carbon Monoxide. Crystals of **3** (50 mg) were dissolved in xylene (30 cm^3). A continuous stream of carbon monoxide was then bubbled through the solution. No reaction was observed at room temperature for 2 h. The solution was then heated under reflux, and samples were periodically examined by IR spectroscopy. After 15 min, disappearance of **3** was noticed. The solution was cooled and concentrated under vacuum. Chromatographic workup on silica gel afforded three bands. The first to elute with toluene/heptane (1/1) contained traces of the known complex $Ru_3(CO)_{10}(\mu\text{-}\eta^2\text{-}dppm)$[11] (<1 mg) and the second to elute with toluene contained traces of $Ru_3(CO)_8(\mu\text{-}\eta^2\text{-}dppm)_2$ (1) (~1 mg), while the third band to elute with dichloromethane was identified as $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2$ (2) (40 mg, yield 85%). Noticeably, longer reaction time gave improved yields of $Ru_3(CO)_{10}(\mu\text{-}\eta^2\text{-}dppm)$ and $Ru_3(CO)_8(\mu\text{-}\eta^2\text{-}dppm)_2$. For example, treatment of **3** with CO for 12 h at 85 °C gave $Ru_3(CO)_{10}(\mu\text{-}\eta^2\text{-}dppm)$ (10% yield), $Ru_3(CO)_8(\mu\text{-}\eta^2\text{-}dppm)_2$ (16% yield), and $Ru_3(\mu_3\text{-}O)(CO)_6(\mu\text{-}\eta^2\text{-}dppm)_2$ (48% yield).

Reaction of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2$ (3) with Electrophiles. 1. Acidification. A solution of **3** in CD_2Cl_2 was acidified with a slight excess of CF_3COOH in the NMR tube. Spectroscopic data for the resulting salt $[Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_3(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2]^+[CF_3COO^-]$ (4) are as follows: IR (ν(CO), CH_2Cl_2) 2080 (s), 2062 (vs), 2042 (m), 2003 (vs), 1978 (sh) cm^{-1}; NMR (CD_2Cl_2), labeling of H nuclei in the same way as for **3**, the additional hydrido ligand is labeled as H_d; ^1H NMR δ 4.13 (2 H_a, br), 3.55 (2 H_b, br), −14.10 (1 H_d, t, $J_{P\text{-}H}$ = 39.5 Hz), −15.55 (2 H_c, br); $^1H\{^{31}P\}$ NMR δ 4.13 (2 H_a, d, $J_{H_aH_b}$ = 13.75 Hz), 3.54 (2 H_b, d), −14.13 (1 H_d, s), −15.57 (2 H_c, s).

2. Reaction with $AuPPh_3Cl$. Complex **3** (100 mg, 0.075 mmol) was dissolved in 15 mL of CH_2Cl_2. The solution was stirred at room temperature in a Schlenk tube under nitrogen. Further addition of a slight excess of $AuPPh_3Cl$ (40 mg, 0.08 mmol) resulted in an instantaneous color change from orange to yellow. The solution was then evaporated to dryness. Ethanol (ca. 20 mL) was added, allowing rapid dissolution of the reaction product. Further addition of a saturated aqueous solution of NH_4PF_6 resulted in precipitation of a yellow complex. The addition was stopped as soon as complete decoloration of the solution was observed. The precipitate was then filtered and purified by chromatography, using dichloromethane/heptane as eluent. The complex was recovered as yellow crystals which were subsequently characterized as $[Ru_3(\mu_3\text{-}O)n(\mu\text{-}H)(\mu\text{-}AuPPh_3)(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2]^+[PF_6]^-$ (5) (126 mg, 0.069 mmol, 92% yield): IR (ν(CO), CH_2Cl_2) 2028 (s), 2003 (ms), 1969 (vs) cm^{-1}; NMR data, labeling of H nuclei as defined above; $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 3.54 (2 H_a, d, $J_{H_aH_b}$ = 13.75), 3.26 (2 H_b, d), −16.04 (2 H_c, s). Anal. Calcd for $AuC_{73}F_6H_{61}O_6P_6Ru_3$: C, 47.8; H, 3.35. Found: C, 47.8; H, 3.5.

3. Reaction with Iodine. Complex **3** (100 mg, 0.075 mmol) was dissolved in 10 mL of CH_2Cl_2. The solution was stirred at room temperature in a Schlenk tube. Crystals of iodine (19 mg, 0.075 mmol) were then added. Dissolution of these crystals was accompanied by a color change from orange to yellow. Cyclohexane was then added. The solution was reduced in volume under vacuum until the first crystals appeared. After the mixture cooled at −25 °C overnight, the complex was recovered by filtration and subsequently identified as $[Ru_3(\mu_3\text{-}O)(\mu\text{-}I)(\mu\text{-}H)_2(CO)_5(dppm)_2]^+I^-$ (6): IR (ν(CO), CH_2Cl_2) 2062 (vs), 2052 (s), 2005 (vs), 1974 (m) cm^{-1}; $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 3.48 (4 H, q, $J_{H_aH_b}$ 13.75 Hz, $\Delta\nu$ = 59 Hz), −10.98 (2 H_c, s, hydride signal); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 42.41 (2 P, d, $J_{P\text{-}P}$ 51.27 Hz), 33.42 (2 P, d). Anal. Calcd for $C_{55}H_{46}I_2O_6P_4Ru_3$: C, 44.52; H, 3.12. Found: C, 44.20; H, 3.1.

Metathesis of the anion was conducted by adding a saturated aqueous solution of NH_4PF_6. The resulting precipitate was chromatographed on silica gel (CH_2Cl_2 as eluent).

4. Reaction with $AgPF_6$. Complex **3** (50 mg, 0.037 mmol) was dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature in a Schlenk tube wrapped with an aluminum foil to avoid exposure to light. Excess of $AgPF_6$ (ca. 20 mg) was added. Formation of the yellow adduct was instantaneous. The complex was only characterized spectroscopically in solution. Crystals were unstable to air.

$[Ru_3(\mu\text{-}Ag)(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-}dppm)_2]^+[PF_6]^-$ (7): IR (ν(CO), CH_2Cl_2) 2075 (w), 2035 (vs), 2015 (s), 1985 (vs) NMR $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 3.70 (4 H, q, $J_{H_aH_b}$ = 13.5 Hz, $\Delta\nu$ = 77 Hz), −15.07 (2 H_c, s, hydride signal).

C. X-ray Structure Analysis of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_2(\mu\text{-}\eta^2\text{-}dppm)_2$ (3). Collection and Reduction of X-ray Data. Preliminary Laue and precession photographs showed the complex to crystallize in a trigonal cell. Systematic absences were consistent with space groups C_3^2—$P3_1$ and C_3^3—$P3_2$ (no. 144 and 145, respectively). The structure was successfully solved in the space group C_3^2—$P3_1$. The crystal selected for data collection was a prismatic needle with boundary planes of the form (010), (100), ($\bar{1}$10), and (001). The distances from these faces to arbitrary origin in the crystal were 0.046, 0.045, 0.049, and 0.226 mm, respectively. The crystal was glued on a glass fiber with Apiezon N grease and transferred to an Enraf-Nonius CAD4 diffractometer equipped with a low-temperature device. All intensity measurements were made at −152 ± 1 °C. The setting angles of 25 reflections in the range 24° < 2θ(Mo Kα) < 26° were refined by least-squares procedures, leading to the unit cell parameters. Experimental details are listed in Table I. The intensities of 4407 reflections were collected, up to 2θ = 46°. A slight linear intensity decay was observed and corrected by using standard reflections (the maximum correction factor was 1.049). Intensities were then corrected for Lorentz, polarization, and absorption effects and reduced to structure factor amplitudes.[12]

Solution and Refinement of the Structure. Solution, refinement, and analysis of the crystal structure were carried out with the SDP system[12] on a VAX 11/730 computer. Neutral atom scattering factors[13] were used with anomalous dispersion corrections[14] being applied to Ru, P, C, and O atoms. The coordinates

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(11) This complex has been already prepared by several routes: (a) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 3369. (b) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321. (c) Coleman, A. W.; Jones, D. F.; Dixneuf, P. H.; Brisson, C.; Bonnet, J.-J.; Lavigne, G. *Inorg. Chem.* **1984**, *23*, 952. (d) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

(12) *Enraf-Nonius Structure Determination Package*, 4th ed., August 1981; Frenz, B. A. & Associates: College Station, TX 77840, USA; and Enraf-Nonius: Delft, The Netherlands. Programs were implemented on a VAX 11/730 computer.

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

Table I. Experimental Crystal and Intensity Data for Compounds 3 and 6

	3	6
	Crystal Data	
formula	$C_{63}H_{56}O_6P_4Ru_3$	$C_{63}H_{56}I_2O_6P_4Ru_3$
mol wt	1336.25	1483.88
cryst system	trigonal	triclinic
space group	C_3^2—$P3_1$ (no. 144)	$P\bar{1}$ (no. 2)
Z	3	2
unit-cell parameters	at −152 ± 1 °C	at 25 °C
a, Å	13.793 (5)	15.328 (4)
b, Å	13.800 (4)	17.168 (9)
c, Å	26.112 (7)	13.208 (5)
α, deg	90.0	95.66 (4)
β, deg	90.0	90.83 (3)
γ, deg	120.0	115.77 (3)
V, Å^3	4307.7	3108.6
d(calcd), g cm^{-3}	1.42	1.58
μ, cm^{-1}	9.17	18.51
cryst vol, mm^3	3.4×10^{-3}	
	Intensity Data	
radiatn (Mo Kα) λ, Å	0.709 30	0.709 30
takeoff angle, deg	2.9	4.0
2θ limits, deg	1.6–46.0	2.0–40.0
scan mode	$\omega/2\theta$	
scan range, deg (θ)	0.4 below Kα_1 to 0.4 above Kα_2	0.6 below Kα_1 to 0.6 above Kα_2
scan speed, deg/min^{-1} (ω)	2	2
std reflctns	$0,3,\overline{17}$, $00\bar{6}$, $6,0,\overline{13}$, 5,1,11	$8\bar{6}\bar{2}$, 800, $7\bar{8}1$, $6\bar{9}3$
intensity decay, %	5	39.5
reflctns collected	4407	7447
unique data used	3218	2964
final no. of variable	395	230
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.048	0.097
$R_w = \sum\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\omega F_o^2)^{1/2}$	0.048	0.122

of Ru and P atoms were determined by direct methods, and the subsequent model was extended through standard combination of least-squares and difference Fourier calculations. A xylene molecule (solvent) was also located in the lattice and included to the model. In order to limit the number of variable parameters, carbon atoms of phenyl groups and xylene molecule were treated with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically. However, the flattened shape of the ellipsoids of C(1) and C(6) led us to prefer the use of isotropic thermal parameters in further refinements of both these atoms. Hydrogen atoms of organic ligands were entered in idealized position and not refined. The positions of the two hydride ligands were calculated[15] and included in the final model. The final cycle of full-matrix least-squares refinement on F_o involved 395 variables and 3218 unique data with $F_o^2 > 3\sigma(F_o^2)$. The final R values were $R_w(F) = 0.048$ and $R(F) = 0.048$. The error in an observation of unit weight was 1.5 e. The positional parameters for non-hydrogen atoms are listed in Table II. A complete listing of atomic coordinates and thermal parameters is available (Table S1).[16] Table S2[16] presents a listing of observed and calculated structure factor amplitudes.

D. X-ray Structure Analysis of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(\mu\text{-}I)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2]^+[I]^-$ (6). Collection and Reduction of X-ray Data. Crystals of complex 6 were seen to decompose in the X-ray beam. The crystal was glued on a glass fiber with Shellack and transferred to the diffractometer. Intensity measurements were made at 25 °C. Experimental details listed in Table I were obtained in the same manner as for the preceding compound. Intensities were not corrected for absorption since the main source of error was an important intensity decay. The decay observed was corrected by using standard reflections. Despite the poor quality of the resulting X-ray data, we were able to solve the structure with sufficient precision to ascertain the model.

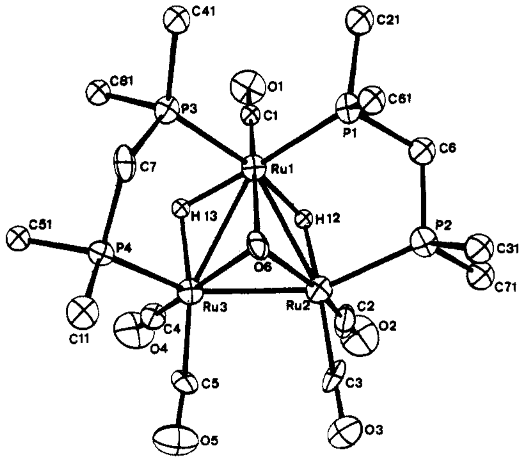

Figure 1. Perspective view of the complex $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2\cdot(C_6H_5)(CH_3)_2$ (3). Phenyl rings have been omitted for clarity.

Solution and Refinement of the Structure. The structure was solved by direct methods[17] in the usual manner (vide supra). Phenyl rings of the dppm ligands were treated as rigid groups (idealized D_{6h} symmetry, C–C = 1.395 Å; C–H = 0.95 Å); isotropic thermal parameters for H atoms were taken 1 Å^2 greater than those of adjacent carbon atoms). Ru, P, and I atoms were refined with anisotropic thermal parameters. The final cycle of full-matrix least-squares refinement on F_o involved 230 variables and 2964 unique data with $F_o^2 > 3\sigma(F_o^2)$. The final R values were $R(F) = 0.097$ and $R_w(F) = 0.122$. Such high R values are, indeed, due

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(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(15) Orpen, A. G. Hydex, A Program for Locating Hydrides (kindly supplied by the author), University of Bristol, England.

(16) Supplementary material.

(17) The main programs used for this structure determination were the following: main, Germain, and Woolfson's Multan; Zalkin's Fordap Fourier summation program; Busing and Levy's Orffe error function program; Ibers' Nucls full-matrix least-squares program, which in its nongroup closely resembles the Busing–Levy Orfls program; Johnson's Ortep, ORNL-3794, 1965. Calculations for the structure determination were performed on the Multics computer of the CICT.

(18) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Acta Crystallogr., Sect. B: Struct. Crytallogr. Cryst. Chem.* 1982, *B38*, 1911.

Table II. Atomic Coordinates for Complex 3[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Ru1	0.76132 (9)	−0.2141 (1)	−0.00677 (5)	1.43 (3)	C44	0.376 (1)	−0.335 (1)	−0.1593 (7)	3.6 (4)*
Ru2	0.98685 (9)	−0.15471 (9)	0.000	1.74 (3)	C45	0.353 (2)	−0.364 (2)	−0.1077 (8)	4.8 (5)*
Ru3	0.9323 (1)	0.0025 (1)	0.01763 (5)	1.65 (3)	C46	0.444 (1)	−0.304 (1)	−0.0738 (7)	3.1 (4)*
P1	0.7269 (3)	−0.3582 (3)	−0.0632 (2)	1.6 (1)	C51	0.784 (1)	0.161 (1)	0.0020 (6)	1.5 (3)*
P2	0.9625 (3)	−0.3131 (3)	−0.0440 (2)	2.0 (1)	C52	0.792 (1)	0.177 (1)	0.0543 (6)	2.8 (4)*
P3	0.6534 (3)	−0.1457 (3)	−0.0409 (2)	1.6 (1)	C53	0.743 (1)	0.232 (1)	0.0776 (7)	4.0 (5)*
P4	0.8507 (3)	0.0904 (3)	−0.0282 (2)	1.5 (1)	C54	0.689 (1)	0.274 (1)	0.0499 (6)	2.9 (4)*
O1	0.5797 (8)	−0.3698 (9)	0.0649 (4)	2.8 (3)	C55	0.679 (1)	0.259 (1)	−0.0022 (6)	2.2 (3)*
O2	1.067 (1)	−0.2186 (9)	0.0949 (4)	4.3 (4)	C56	0.729 (1)	0.203 (1)	−0.0251 (6)	2.4 (4)*
O3	1.2252 (9)	0.0024 (9)	−0.0341 (5)	3.9 (3)	C61	0.760 (1)	−0.326 (1)	−0.1315 (6)	1.7 (3)*
O4	0.947 (1)	0.073 (1)	0.1280 (4)	4.1 (4)	C62	0.813 (1)	−0.217 (1)	−0.1475 (6)	1.8 (3)*
O5	1.1649 (9)	0.197 (1)	0.0083 (5)	3.7 (3)	C63	0.844 (1)	−0.191 (1)	−0.2000 (6)	2.2 (3)*
O6	0.9030 (7)	−0.0992 (7)	−0.0449 (3)	1.6 (2)	C64	0.821 (1)	−0.278 (1)	−0.2323 (6)	2.5 (4)*
C1	0.647 (1)	−0.312 (1)	0.0375 (5)	1.2 (3)*	C65	0.768 (1)	−0.387 (1)	−0.2170 (7)	3.0 (4)*
C2	1.040 (1)	−0.193 (1)	0.0600 (7)	3.0 (4)	C66	0.738 (1)	−0.412 (1)	−0.1657 (6)	2.6 (4)*
C3	1.134 (1)	−0.056 (1)	−0.0216 (5)	1.6 (4)	C71	1.033 (1)	−0.378 (1)	−0.0110 (6)	2.2 (3)*
C4	0.941 (1)	0.048 (1)	0.0862 (6)	2.1 (4)	C72	0.976 (1)	−0.477 (1)	0.0176 (6)	2.7 (4)*
C5	1.077 (1)	0.120 (1)	0.0104 (6)	1.8 (4)	C73	1.036 (1)	−0.517 (1)	0.0438 (7)	2.9 (4)*
C6	0.816 (1)	−0.420 (1)	−0.0463 (6)	1.9 (3)*	C74	1.147 (1)	−0.462 (1)	0.0436 (6)	2.4 (4)*
C7	0.741 (1)	−0.013 (1)	−0.0722 (6)	2.0 (4)	C75	1.205 (1)	−0.366 (1)	0.0164 (7)	3.0 (4)*
C11	0.948 (1)	0.195 (1)	−0.0731 (6)	2.3 (3)*	C76	1.148 (1)	−0.323 (1)	−0.0112 (6)	3.1 (4)*
C12	0.988 (1)	0.305 (1)	−0.0677 (7)	3.4 (4)*	C81	0.573 (1)	−0.110 (1)	0.0029 (5)	1.6 (3)*
C13	1.066 (1)	0.381 (1)	−0.1017 (7)	4.2 (5)*	C82	0.503 (1)	−0.073 (1)	−0.0155 (6)	2.6 (4)*
C14	1.107 (1)	0.349 (1)	−0.1412 (7)	3.6 (4)*	C83	0.446 (1)	−0.042 (1)	0.0165 (7)	3.5 (4)*
C15	1.070 (2)	0.242 (2)	−0.1463 (8)	4.6 (5)*	C84	0.450 (2)	−0.053 (1)	0.0686 (7)	4.1 (5)*
C16	0.993 (1)	0.162 (1)	−0.1116 (7)	3.8 (4)*	C85	0.516 (1)	−0.089 (1)	0.0884 (6)	2.9 (4)*
C21	0.588 (1)	−0.481 (1)	−0.0625 (6)	2.1 (3)*	C86	0.579 (1)	−0.118 (1)	0.0573 (6)	2.3 (4)*
C22	0.511 (1)	−0.500 (1)	−0.1028 (6)	2.8 (4)*	C91	0.715 (1)	0.397 (1)	0.1832 (7)	3.8 (4)*
C23	0.408 (1)	−0.592 (1)	−0.1019 (7)	4.1 (5)*	C92	0.735 (1)	0.327 (1)	0.2062 (8)	4.4 (5)*
C24	0.373 (1)	−0.667 (1)	−0.0626 (7)	3.5 (4)*	C93	0.841 (2)	0.336 (2)	0.2116 (7)	4.5 (5)*
C25	0.446 (1)	−0.647 (1)	−0.0222 (7)	3.6 (4)*	C94	0.929 (1)	0.425 (1)	0.1885 (7)	4.0 (5)*
C26	0.553 (1)	−0.556 (1)	−0.0221 (7)	2.9 (4)*	C95	0.910 (1)	0.502 (1)	0.1635 (7)	3.0 (4)*
C31	1.010 (1)	−0.309 (1)	−0.1106 (6)	1.9 (3)*	C96	0.808 (2)	0.489 (2)	0.1589 (8)	5.2 (5)*
C32	1.060 (1)	−0.211 (1)	−0.1389 (6)	2.6 (4)*	C97	1.037 (2)	0.429 (2)	0.1893 (9)	6.0 (6)*
C33	1.095 (1)	−0.212 (1)	−0.1882 (7)	3.3 (4)*	C98	0.786 (2)	0.566 (2)	0.1319 (9)	6.1 (6)*
C34	1.082 (1)	−0.307 (1)	−0.2094 (7)	3.4 (4)*	HAC6	0.805	−0.477	−0.071	
C35	1.035 (1)	−0.407 (1)	−0.1816 (7)	3.9 (5)*	HBC6	0.793	−0.458	−0.014	
C36	0.996 (1)	−0.409 (1)	−0.1324 (7)	3.1 (4)*	HAC7	1.025	−0.201	0.231	
C41	0.546 (1)	−0.224 (1)	−0.0881 (6)	1.7 (3)*	HBC7	0.984	−0.322	0.249	
C42	0.566 (1)	−0.200 (1)	−0.1407 (6)	2.2 (3)*	H*1.2	0.854	−0.243	0.027	
C43	0.481 (1)	−0.257 (1)	−0.1759 (6)	2.7 (4)*	H*2.3	0.788	−0.090	0.024	

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Interatomic Distances (Å) with Esd's for $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2 \bullet (C_6H_5)(CH_3)_2$ (3)

Ru–Ru		Ru–O	
Ru(1)–Ru(2)	2.801 (1)	Ru(1)–O(6)	2.056 (8)
Ru(1)–Ru(3)	2.805 (1)	Ru(2)–O(6)	2.049 (8)
Ru(2)–Ru(3)	2.670 (1)	Ru(3)–O(6)	2.058 (7)
Ru–C		C–O	
Ru(1)–C(1)	1.87 (1)	C(1)–O(1)	1.14 (1)
Ru(2)–C(2)	1.90 (2)	C(2)–O(2)	1.12 (2)
Ru(2)–C(3)	1.88 (1)	C(3)–O(3)	1.15 (2)
Ru(3)–C(4)	1.88 (1)	C(4)–O(4)	1.14 (1)
Ru(3)–C(5)	1.85 (1)	C(5)–O(5)	1.15 (2)
Ru–P		P–C(methylene)	
Ru(1)–P(1)	2.326 (3)	P(1)–C(6)	1.86 (1)
Ru(1)–P(3)	2.305 (3)	P(2)–C(6)	1.81 (1)
Ru(2)–P(2)	2.341 (4)	P(3)–C(7)	1.80 (1)
Ru(3)–P(4)	2.353 (3)	P(4)–C(7)	1.87 (1)

to the observed decomposition of the crystal into the X-ray beam (vide supra). A full list of atomic coordinates along with thermal parameters is presented in Tables S3 and S4.[16] Rigid-group parameters are given in Table S5. A complete listing of observed and calculated structure factor amplitudes is also available (Table S6).[16]

Results and Discussion

Description of the Structure of 3. A perspective view of the structure is given in Figure 1. Selected interatomic distances and bond angles are listed in Tables III and IV, respectively. The structure of this 48e species consists of a triangular ruthenium framework involving three metal-metal bonds (Ru(1)–Ru(2) = 2.801 (1) Å; Ru(1)–Ru(3) = 2.805 (1) Å; Ru(2)–Ru(3) = 2.670 (1) Å). An oxygen atom is symmetrically bridging one face of the cluster (Ru(1)–O(6) = 2.056 (8) Å; Ru(2)–O(6) = 2.049 (8) Å; Ru(3)–O(6) = 2.058 (7) Å). Two metal–metal bonds are supported by edge-bridging dppm ligands, as referred to the parent complex $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(dppm)_2$ (2).[9] The main difference with the previously reported species consists in replacement of the face-bridging carbonyl ligand in 2 by two edge-bridging hydride ligands. These hydrides are found across the two equivalent metal–metal vectors Ru(1)–Ru(2) and Ru(1)–Ru(3) which are supported by the dppm ligands. The molecule has thus approximate (noncrystallographic) C_s symmetry (a pseudomirror plane is passing through O(6), Ru(1), and the middle of the Ru(2)–Ru(3) vector). The octahedral basis set of all three metal atoms are directed toward oxygen. Significantly, Ru–P vectors are out of the equatorial plane of the metal triangle, while all CO ligands also occupy positions which are intermediate between axial and equatorial.

A noticeable feature in this structure is the short value of the metal–metal bond Ru(2)–Ru(3) = 2.670 (1) Å, which is consistent with the electronegativity of oxygen and its small covalent radii.[19]

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[19] Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763.

Table IV. Selected Bond Angles (deg) for $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2\bullet(C_6H_4)(CH_3)_2$ (3)

Ru–Ru–Ru			
Ru(2)–Ru(1)–Ru(3)	56.89 (4)		
Ru(1)–Ru(2)–Ru(3)	61.63 (4)		
Ru(1)–Ru(3)–Ru(2)	61.48 (4)		
Ru–Ru–P			
Ru(1)–Ru(2)–P(2)	94.3 (1)	Ru(1)–Ru(3)–P(4)	94.00 (9)
Ru(2)–Ru(1)–P(1)	90.74 (9)	Ru(3)–Ru(1)–P(3)	91.30 (9)
Ru(2)–Ru(1)–P(3)	139.13 (9)	Ru(3)–Ru(1)–P(1)	132.42 (9)
Ru–Ru–C			
Ru(2)–Ru(1)–C(1)	125.8 (4)	Ru(3)–Ru(1)–C(1)	125.9 (3)
Ru(1)–Ru(2)–C(2)	119.6 (4)	Ru(1)–Ru(3)–C(4)	116.9 (4)
Ru(1)–Ru(2)–C(3)	146.6 (4)	Ru(1)–Ru(3)–C(5)	151.1 (3)
Ru(3)–Ru(2)–C(2)	112.4 (4)	Ru(2)–Ru(3)–C(4)	116.0 (4)
Ru(3)–Ru(2)–C(3)	96.0 (4)	Ru(2)–Ru(3)–C(5)	94.1 (4)
C–Ru–C			
C(2)–Ru(2)–C(3)	91.1 (6)	C(4)–Ru(3)–C(5)	86.7 (5)
Ru–O–Ru			
Ru(1)–O(6)–Ru(2)	86.1 (3)	Ru(1)–O(6)–Ru(3)	86.0 (3)
Ru(2)–O(6)–Ru(3)	81.1 (3)		
O–Ru–P			
O(6)–Ru(1)–P(1)	93.6 (2)	O(6)–Ru(1)–P(3)	93.2 (2)
O(6)–Ru(2)–P(2)	113.0 (2)	O(6)–Ru(3)–P(4)	88.1 (2)
O–Ru–C			
O(6)–Ru(1)–C(1)	170.8 (4)		
O(6)–Ru(2)–C(2)	159.7 (5)	O(6)–Ru(3)–C(4)	160.3 (5)
O(6)–Ru(2)–C(3)	99.7 (5)	O(6)–Ru(3)–C(5)	105.9 (4)
P–Ru–C			
P(1)–Ru(1)–C(1)	92.0 (4)	P(3)–Ru(1)–C(1)	92.8 (4)
P(2)–Ru(2)–C(2)	92.6 (4)	P(4)–Ru(3)–C(4)	106.2 (4)
P(2)–Ru(2)–C(3)	97.5 (4)	P(4)–Ru(3)–C(5)	94.9 (3)
Ru–P–C			
Ru(1)–P(1)–C(6)	109.9 (4)	Ru(1)–P(3)–C(7)	110.4 (4)
Ru(2)–P(2)–C(6)	110.8 (4)	Ru(3)–P(4)–C(7)	109.3 (4)
Ru–C–O			
Ru(1)–C(1)–O(1)	178 (1)		
Ru(2)–C(2)–O(2)	177 (1)	Ru(3)–C(4)–O(4)	178 (1)
Ru(2)–C(3)–O(3)	178 (1)	Ru(3)–C(5)–O(5)	175 (1)
P–C–P			
P(1)–C(6)–P(2)	114.4 (7)	P(4)–C(7)–P(3)	112.0 (6)

Description of the Structure of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(\mu\text{-}I)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2]^+I^-$ (6). Despite the observed decomposition of the crystal in the X-ray beam (see Experimental Section), we were able to solve the structure with sufficient precision to ascertain the model. The structure of this ionic species consists of the packing of well-separated cationic cluster units and iodide anions. A perspective view of the cation is given in Figure 2. Selected interatomic distances and bond angles are listed in Tables S7 and S8, respectively. While all these distances and angles are reasonable, the values of their esd's clearly point out the limitations of the X-ray data we have in hand.

The basic geometry of the parent cluster **3** is preserved in **6**. Electrophilic interaction of iodine with electron-rich metal centers has resulted in the formation of an iodo bridge (Ru(2)–I(1) = 2.815 (5) Å; Ru(3)–I(1) = 2.790 (4) Å). The corresponding metal–metal distance Ru(2)–Ru(3) = 3.273 (5) Å is clearly nonbonding, as compared with its former value in **3** (2.670 (1) Å).

Reactivity of $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(dppm)_2$. μ_3-Oxo carbonyl cluster complexes are relatively few in number,[9,19–23] and their chemistry has not been widely explored.

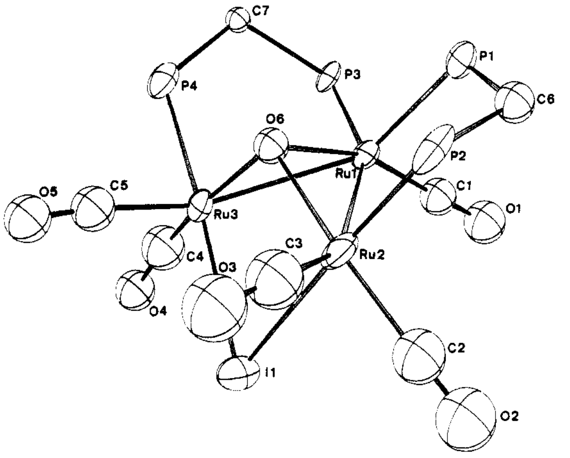

Figure 2. Perspective view of the complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(\mu\text{-}I)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2]^+I^-$. Phenyl rings have been omitted for clarity.

A prototype for this class of compounds in ruthenium chemistry is $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$ (**2**), available in high yield by direct reaction of O_2 with $Ru_3(CO)_8(\mu\text{-}\eta^2\text{-dppm})_2$ (**1**).[9]

In attempts to explore the reactivity of **2** we were first able to displace the bridging carbonyl ligand in the presence of hydrogen, generating the new complex $Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2$ (**3**).

$$\underset{\mathbf{2}}{Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2} + H_2 \rightleftharpoons \underset{\mathbf{3}}{Ru_3(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2} + CO$$

The reaction was shown to be reversible[24] since complex **2** could be recovered almost quantitatively under 1 atm of carbon monoxide in refluxing xylene.

In further studies, we attempted to check the ability of complex **3** to retain its trinuclear framework in the reaction with halogens which was known to involve metal–metal bonds.[25] Complete fragmentation was indeed observed in the case of $Ru_3(CO)_{12}$[26] and related derivatives $Ru_3(CO)_9(PR_3)_3$[27] and $Ru_3(CO)_8(dppm)_2$.[28]

By contrast, reaction of I_2 with **3** gave the new ionic cluster complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}I)(\mu\text{-}H)_2(CO)_5(dppm)_2]^+I^-$ (**6**). The bridging iodide atom in this complex spans the metal–metal vector which is not supported by bridging dppm ligands. The existence of this cationic complex is consistent with the previous expectation[29] that electrophilic attack of halogen to metal–metal bonded species proceeds via one end of the dihalogen molecule and that heterolytic cleavage of the halogen–halogen bond takes place to yield a free halide anion and an halogenium-bridged cationic

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(20) Ciani, G.; Sironi, A.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* 1977, 1667.

(21) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* 1983, 246.

(22) Ceriotti, A.; Resconi, L.; Demartin, F.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* 1983, *249*, C35.

(23) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* 1984, *106*, 1144.

(24) Related examples have been reported, although such reactions are rarely reversible: (a) Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1982, *104*, 6454. (b) Adams, R. D.; Horvath, I. T.; Kim, H. S. *Organometallics* 1984, *3*, 548.

(25) Deeming, A. J. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 6, pp 391–469.

(26) Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc., Chem. Commun.* 1968, 861.

(27) Kramer, G.; Poë, A.; Amer, S. *Inorg. Chem.* 1981, *20*, 1362.

(28) Colombié, A.; Lavigne, G.; Bonnet, J.-J. *J. Chem. Soc., Dalton Trans.*, in press.

(29) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* 1984, *106*, 1308.

metal complex. Related examples of addition of I^+ to polynuclear anions have been reported.[30–33]

Regarding the formation of **6** as the initial step of the reaction of iodine, we expected subsequent nucleophilic attack of the halide anion, with the following alternate possibilities, depending on the site of attack: (i) formation of a neutral dihalogen species similar to $Os_3(CO)_{12}I_2$,[34,35] (ii) abstraction of H^+ as HI,[33] and (iii) substitution of CO by I^- (reaction of I_2 with **3** might end up as the reaction of $SnCl_4$ with $Ru_3(\mu_3\text{-}S)(\mu\text{-}H)_2(CO)_9$, which gave $Ru_3(\mu_3\text{-}S)(\mu\text{-}H)_2(\mu\text{-}Cl)(CO)_8SnCl_3$[36]).

Actually, nucleophilic attack of the halide anion was not observed, even in refluxing tetrahydrofuran,[37] which accounts for a particular stability of the cationic complex.

Following this study, we attempted the reaction of **3** with a variety of electrophiles (E^+) as H^+, $AuPPh_3^+$, or Ag^+. Cationic adducts of general formula $[Ru_3(\mu\text{-}E)(\mu_3\text{-}O)(\mu\text{-}H)_2(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2]^+$ were isolated in all cases. This parallels recent observations of Lewis acid bonding to $Ru_3(CO)_8(dppm)_2$.[38]

While the bridging oxygen atom might be expected to have some nucleophilic character, no such evidence could be obtained. The presence of four donor phosphorus atoms increases the basicity at metal centers, in such a way that the privileged site for Lewis acid bonding is the metal–metal bond.

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Registry No. 1, 77611-27-9; 2, 79826-37-2; 3, 101835-50-1; 4, 101835-43-2; 5, 101835-45-4; 6, 101835-46-5; 7, 101835-48-7; $Ru_3(CO)_{10}(dppm)_2$, 64364-79-0; $AuPPh_3Cl$, 14243-64-2.

Supplementary Material Available: Table S1 (complete listing of atomic coordinates and thermal parameters for **3**), Table S2 (structure factors for **3**), Table S3 (atomic coordinated for **6**), Table S4 (anisotropic thermal parameters for **6**), Table S5 (rigid-group parameters for **6**), Table S6 (structure factors for **6**), Table S7 (selected interatomic distances for **6**), and Table S8 (selected bond angles for **8**) (129 pages). Ordering information is given on any masthead page.

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(30) Martinengo, S.; Chini, P.; Giordano, A.; Ceriotti, A.; Albano, V. G.; Ciani, G. *J. Organomet. Chem.* **1975**, *88*, 375.

(31) Farrar, D. H.; Jackson, P. G.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1009.

(32) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1979**, *170*, C15.

(33) Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *Inorg. Chem.* **1983**, *22*, 3115.

(34) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1969**, *17*, P40.

(35) Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

(36) Adams, R. D.; Katahira, D. A. *Organometallics* **1982**, *1*, 53.

(37) The nucleophilicity of the iodide anion is enhanced in tetrahydrofuran.

(38) Ladd, J. A.; Hope, H.; Balch, A. L. *Organometallics* **1984**, *3*, 1838.

Electrophilic Insertion of Terminal Phosphinidene Complexes into the C–H Bonds of Ferrocene

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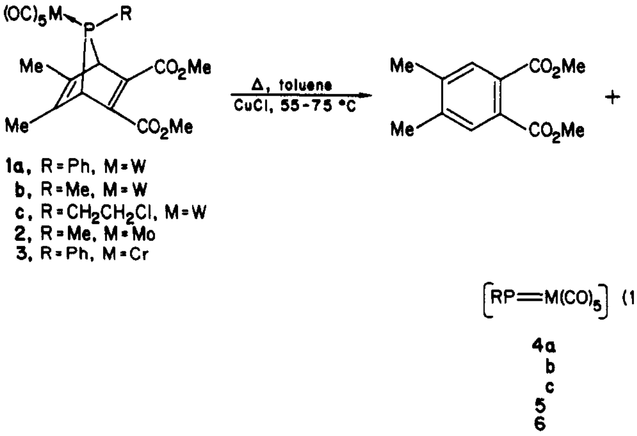
Terminal phosphinidene complexes, $[RP{=}M(CO)_5]$, as generated by catalytic decomposition of the corresponding 7-phosphanorbornadiene complexes at ca. 55–75 °C, insert into the C–H bonds of ferrocene to give secondary ferrocenylphosphine complexes $[FcP(H)R]M(CO)_5$ when M = Mo and W. The reaction fails when M = Cr. Metalation of the P–H bond of these ferrocenylphosphine complexes is easily achieved by *n*-butyllithium in THF at −78 °C. The anion thus formed can be alkylated or acylated. When R = CH_2CH_2Cl, the metalation affords a novel ferrocenylphosphirane complex.

According to experimental and theoretical data, terminal phosphinidene complexes, $RP{=}M(CO)_5$ (M = Cr, Mo, W), are highly electrophilic. For example, SCF calculations on HP and $HP{=}Cr(CO)_5$ gave a net charge on phosphorus of −0.05 e in the first case and +0.41 e in the second case.[1] On this basis, we thought that it would be perhaps possible to observe a reaction between these terminal phosphinidene complexes and electron-rich aromatic rings. This led us to investigate their reaction with ferrocene selected as a prototype of such rings. The results of this study are reported here.

Results and Discussion

As described previously,[2] the terminal phosphinidene complexes were generated by catalytic decomposition of the appropriate 7-phosphanorbornadiene complexes (eq 1). The reaction between these transient phosphinidene complexes and ferrocene was carried out by performing the decomposition of the 7-phosphanorbornadiene com-



1a, R = Ph, M = W
b, R = Me, M = W
c, R = CH_2CH_2Cl, M = W
2, R = Me, M = Mo
3, R = Ph, M = Cr

4a
b
c
5
6

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(1) Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133.

(2) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.