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Registry No. 1, 91781-59-8; **2**, 87555-82-6; **3**, 91781-60-1; **4**, 87555-81-5; **5**, 91781-61-2; **6**, 91781-62-3; **7**, 91781-63-4; $CoCl(PMe_3)_2(CO)_2$, 91840-41-4; *cis*-$Mo(CO)_4(PMe_3)_2$, 16027-45-5; $Cr(CO)_5$(*t*-Bu_2P)Li, 91781-64-5; $[Rh(COD)Cl]_2$, 12092-47-6; $CoCl(PMe_3)_3$, 55516-89-7; $Fe(CO)_5$, 13463-40-6; $CoCl_2(PMe_3)_2$, 53432-22-7; $(CO)_5Mo$(*t*-Bu_2P)Li, 91781-65-6; $NiCl_2(PMe_3)_2$, 19232-05-4; *t*-Bu_2PH, 819-19-2.

Supplementary Material Available: Tables of atomic thermal parameters and structure factors for **1**, **6**, and **7** (74 pages). Ordering information is given on any current masthead page.

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(18) See paragraph at end of text regarding supplementary material.

Lewis Acid Bonding to Triruthenium and Triosmium Clusters. The Crystal and Molecular Structure of $Ru_3(\mu\text{-}Ph_2PCH_2PPh_2)_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$ and Spectroscopic Studies of Related Adducts

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$Ru_3(\mu\text{-dpm})_2(CO)_8$ (dpm is bis(diphenylphosphino)methane) forms weakly bound adducts $Ru_3(\mu\text{-dpm})_2(CO)_8\cdot(\mu\text{-A})$ (A = AgO_2CCF_3, $Hg(O_2CCF_3)_2$, $Cu(NCCH_3)BF_4$, HO_2CCF_3) that have been characterized by electronic, infrared, and ^{31}P NMR spectroscopy. Equilibrium constants for adduct formation increase in the order $H^+ < Ag^+ < Hg^{2+} < Cu^+$. $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$ crystallizes in the orthorhombic space group $Pca2_1$ (No. 29) with four molecules per unit cell of dimensions a = 20.706 (9) Å, b = 15.693 (11) Å, and c = 18.447 (5) Å at 140 K. The structural study shows that the AgO_2CCF_3 unit binds through silver across the exposed edge of the triruthenium cluster. The adduct contains two adjacent, nearly coplanar triangles of the four metal atoms. The addition of Ag^+ to the Ru–Ru bond results in an 0.167 Å lengthening of the Ru–Ru separation and some bending of the in-plane carbonyl groups away from the silver binding site. Similar adducts of silver trifluoroacetate with $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and some substituted derivations of $Ru_3(CO)_{12}$ have been detected in solution.

Introduction

The structural similarity and isolobal relationship between the proton and the group 1B cations, particularly Au(I), has recently received wide recognition. As a consequence, there have been many reports on the ability of an Au(I) center, generally in the form $AuPPh_3^+$, to bind to anionic metal complexes and polynuclear clusters in a fashion that produces analogues of neutral metal hydrides.[1-15] The R_3PAu^+ group is a versatile ligand. It can act as a terminal ligand,[15] span a metal–metal bond,[2,4,7-13] coordinate to the triangular face of a metal cluster,[1,111,14] and add to a square face of a metal cluster.[5] However, extensions to the binding of group 1B metals to neutral clusters are rare.[16] Moreover, the use of related metal ions (Ag(I),[16-18] Cu(I),[18] and Hg(II),[19,20] which are all isoelectronic and isolobal with Au(I), for this type of mixed-metal cluster formation has been limited to a few isolated examples.

Here we report on the observation of binding of metal ions including Au(I), Cu(I), and Hg(II) to neural triruthenium and triosmium clusters and describe the detailed structure of one of these. It has been known for some time that $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ undergo reversible protonation in strongly acidic media.[21] Although

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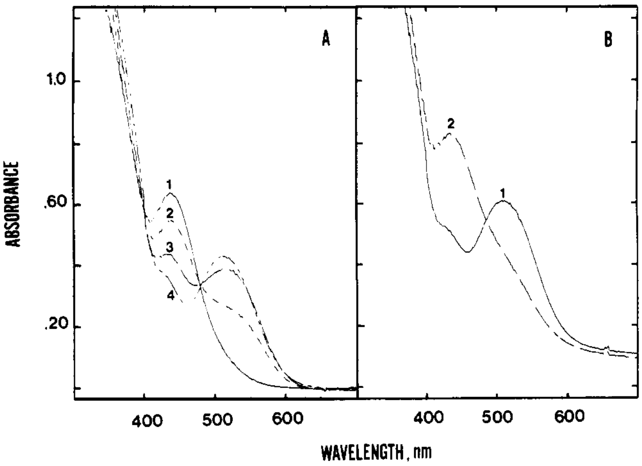
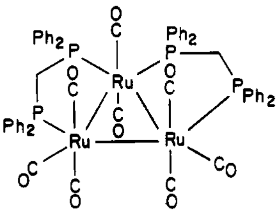


Figure 1. Electronic spectra showing in A the reaction between $Ru_3(\mu\text{-dpm})_2(CO)_8$ and silver trifluoroacetate and in B the removal of silver by the addition of bis(triphenylphosphine)nitrogen(1+) chloride. A: 1, 5.9×10^{-4} M solution of $Ru_3(\mu\text{-dpm})_2(CO)_8$ in dichloromethane, in successive traces silver trifluoroacetate has been added. 2, 0.50 equiv; 3, 1.0 equiv; 4, 2.0 equiv. B: 1, dichloromethane solution with 7.7×10^{-4} M $Ru_3(\mu\text{-dpm})_2(CO)_8$ and 1.0 equiv of silver trifluoroacetate; 2, that solution with 1 equiv of bis(triphenylphosphine)nitrogen(1+) chloride added after filtration to remove silver chloride. Cell path length: 1.0 mm throughout.

both edge- and face-bridged structures have been considered, infrared and NMR studies point to an edge-bridged structure.[22,23] Similarly 1, $Ru_3(\mu\text{-dpm})_2(CO)_8$[24] (dpm is bis(diphenylphosphino)methane), which should be more basic because of the phosphine substitution, is also known to under protonation.[25]



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Results and Discussion

Observation of the UV–visible spectra of the clusters in the presence of added metal ions offers a convenient method for monitoring adduct formation. The low-energy electronic transition in these clusters has been assigned as involving a transition from a metal cluster bonding to a cluster antibonding orbital.[26,27] Consequently, binding of cations to the ruthenium core would be expected to perturb the electronic spectrum. The data for the $Ru_3(\mu\text{-dpm})_2(CO)_8/AgO_2CCF_3$ system shown in Figure 1 are representative of our results. In part A of the figure, the effects of adding a silver trifluoroacetate to $Ru_3(\mu\text{-dpm})_2(CO)_8$ in dichloromethane solution are shown. The absorption band at 438 nm due to $Ru_3(\mu\text{-dpm})_2(CO)_8$ decreases in intensity as the silver trifluoroacetate concentration increases while a new absorption band centered at 512 nm grows. These data have been analyzed in terms of equilibrium 1 where $M_3L_{12} = Ru_3(\mu\text{-dpm})_2(CO)_8$ and $M'X = AgO_2CF_3$ to yield an equilibrium constant of 4.2×10^3 for the formation of the adduct. The formation of

$$M_3L_{12} + M'X \rightleftharpoons M_3L_{12}{\cdot}M'X \qquad (1)$$

the adduct is reversible under very mild conditions as shown by the data in Figure 1B. Treatment of the adduct with 1 equiv of chloride ion results in the precipitation of silver chloride, the loss of the absorption band at 512 nm, and the restoration of the spectrum of the $Ru_3(\mu\text{-dpm})_2(CO)_8$. The stability of the adduct $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$ is strongly solvent dependent. Although a sizable equilibrium constant has been measured in dichloromethane and the adduct is sufficiently stable to be isolated (vide infra), there is no evidence of adduct formation under corresponding conditions in either pure diethyl ether or benzene solution. We suspect that both of these solvents act as to solvate the silver ion so effectively that the weakly nucleophilic triruthenium complex cannot compete with the solvent for silver binding.

Similar data have been collected to show that trifluoroacetic acid, mercury(II) trifluoroacetate, and tetrakis(acetonitrile)copper(I) tetrafluoroborate form adducts with $Ru_3(\mu\text{-dpm})_2(CO)_8$. The equilibrium constants for adduct formation, which increase in the order $H^+ < Ag^+ < Hg^{2+} > Cu^+$, are given in Table I. Under analogous conditions, however, we find no evidence of bonding between $Ru_3(\mu\text{-dpm})_2(CO)_8$ and either lithium trifluoroacetate, thallium(I) acetate, thallium(III) trifluoroacetate, or (triphenylphosphine)gold(I) chloride. Qualitative evidence for the formation of an adduct resulting from the addition of bis(benzonitrile)palladium(II) chloride to 1 has been obtained but the adduct is very unstable. The factors influencing the stability of these adducts and the equilibrium constants for their formation are clearly complex. There is no apparent correlation between K_f and either the size of the ions (which increase in the order $H^+ < Cu^+ < Hg^{2+} < Ag^+\text{–}Au^+$), their oxidation potentials, or the cationic charge.

These adducts have also been characterized by infrared spectroscopy. The relevant data from the carbonyl stretching region are given in Table II. In general, adduct formation results in an increase in the complexity of this portion of the spectrum and a general shift of the bands to higher energies. However, only terminal carbonyl[11] absorptions are present. No shift from terminal to bridging mode of carbon monoxide binding accompanies adduct formation. Terminal-to-bridge conversion of carbonyl groups sometimes accompanies Lewis acid attack on carbonyl oxygen.[28] However, the nature of the infrared spectral changes indicates that the oxygen atoms of the carbonyl groups are not the site of the Lewis acid binding in these adducts.

Adduct formation can also be monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of $Ru_3(\mu\text{-dpm})_2(CO)_8$ belongs to the AA′BB′ spin system. The two chemical shifts and the prominent $J(P_AP_B)$ reported in Table III are readily obtained. Upon adduct formation the spectra are shifted to lower field and the magnitude of $J(P_AP_B)$ is reduced, but the basic pattern to the spectra is retained. Consequently, metal ion binding to $Ru_3(\mu\text{-dpm})_2(CO)_8$ does not lower the symmetry of the cluster in solution. Moreover, the similarity of the spectra of the four Lewis acid adducts indicates that these acids bind to the

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Table I. Electronic Spectral Data and Equilibrium Constants for Lewis Acid Adduct Formation

compound	λ_{max},[a] nm	ϵ,[a] $M^{-1}\ cm^{-1}$	K_f[a]
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$	512	$1.6\ (2) \times 10^4$	$4.2\ (7) \times 10^3$
	426	$1.4\ (2) \times 10^4$	
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Hg(O_2CCF_3)_2)$	554	$1.2\ (1) \times 10^4$	$5.4\ (5) \times 10^3$
	448	$9.8\ (9) \times 10^3$	
$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))]BF_4$	494	$9.9\ (2) \times 10^3$	$3.2\ (7) \times 10^4$
	346	$2.5\ (1) \times 10^4$	
$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)]O_2CCF_3$	498	$4.9\ (9) \times 10^3$	$1.5\ (3) \times 10^2$
$Ru_3(\mu\text{-dpm})_2(CO)_8$	438		
$Ru_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$	436	$1.2\ (3) \times 10^4$	$2.6\ (6) \times 10^3$
	382	$1.0\ (2) \times 10^4$	
$Ru_3(CO)_{12}$	393		
$Os_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$	406	$1.7\ (6) \times 10^4$	$1.7\ (6) \times 10^3$
	314	$1.5\ (5) \times 10^4$	
$Os_3(CO)_{12}$	389		
$Ru_3(\mu\text{-dam})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$[b]	370, 520		
$Ru_3(\mu\text{-dam})_2(CO)_8$[b]	370, 446		
$Ru_3(\mu\text{-dpm})(CO)_{10}(\mu\text{-}AgO_2CCF_3)$	356, 399, 490		
$Ru_3(\mu\text{-dpm})(CO)_{10}$	336 (sh), 422		

[a] In dichloromethane solution. [b] dam is bis(diphenylarsino)methane.

Table II. Infrared Stretching Frequencies

compound	$\nu(C{\equiv}O)$, cm^{-1}	medium
$Ru_3(\mu\text{-dpm})_2(CO)_8$	2038 (m), 1960 (vs), 1890 (w)	CH_2Cl_2
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)O_2CCF_3$	2082 (m), 2052 (m), 2022 (m), 2005 (s), 1982 (2), 1968 (w), 1910 (m)	Nujol mull
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$	2120 (w), 2089 (w), 2058 (m), 2016 (m), 1986 (s), 1950 (m, sh), 1905 (w)	CH_2Cl_2
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Hg(O_2CCF_3)_2)$	2070 (w), 2050 (w), 2030 (s), 1995 (vs), 1915 (m)	Nujol mull
$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))]BF_4$	2060 (w), 2017 (m), 1980 (s), 1968 (s, sh), 1945 (m, sh), 1907 (m)	CH_2Cl_2
$Ru_3(\mu\text{-dpm})_2(CO)_8(PdCl_2)$	2070 (w), 2014 (m), 1980 (s), 1960 (m, sh), 1897 (w), 1860 (vw)	Nujol mull
$Ru_3(CO)_{12}$	2060 (s), 2030 (m), 2007 (w)	CH_2Cl_2
$Ru_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$	2080 (vw), 2060 (s), 2030 (m), 2008 (w)	CH_2Cl_2
$Os_3(CO)_{12}$	2070 (s), 2034 (ms), 2013 (w)	CH_2Cl_2
$Os_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$	2094 (m), 2085 (m), 2068 (m), 2057 (ms), 2036 (m), 2011 (w)	CH_2Cl_2
$Ru_3(CO)_8(\mu\text{-dam})_2$	2040 (m), 1985 (m, sh), 1960 (s)	CH_2Cl_2
$Ru_3(CO)_8(\mu\text{-dam})_2(\mu\text{-}AgO_2CCF_3)$	2056 (w), 2035 (w), 1985 (s), 1970 (ms)	CH_2Cl_2
$Ru_3(CO)_{10}(\mu\text{-dpm})$	2080 (m), 2010 (s), 1995 (s), 1950 (m, br)	CH_2Cl_2
$Ru_3(CO)_{10}(\mu\text{-dpm})(\mu\text{-}AgO_2CCF_3)$	2100 (m), 2056 (w), 2028 (s), 1980 (m, br)	CH_2Cl_2

Table III. ^{31}P NMR Data

compound	solv	δ_A	δ_B	$J(P_AP_B)$, Hz
$Ru_3(\mu\text{-dpm})_2(CO)_8$	CD_3COCD_3	23.0	18.8	52.9
$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)](O_2CCF_3)$	CD_2Cl_2	16.6	12.9	35.3
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$	CD_2Cl_2	18.7	14.7[a]	43.9
$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu Hg(O_2CCF_3)_2)$	CD_2Cl_2	19.0	17.5	26.6
$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))]BF_4$	CD_2Cl_2	19.0	11.7	40.7
$Ru_3(\mu\text{-dpm})(CO)_{10}(\mu\text{-}AgO_2CCF_3)$	CD_2Cl_2	12.6	10.0[b]	36.9

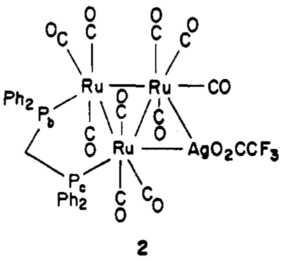
[a] Additional fine structure indicates that this is the phosphorus atom closest to the silver. Some splitting in the low-temperature spectrum may reflect the asymmetry in the silver binding seen in the solid-state structure. [b] $J(P_B\text{-}Ag)$ = 15.3 Hz at room temperature.

cluster at a common binding site. On the basis of the X-ray structure of the silver trifluoroacetate (vide infra) adduct, we propose that all four Lewis acids in this study add to the Ru–Ru bond at the exposed edge of the cluster.

Silver trifluoroacetate also binds to the unsubstituted $Ru_3(CO)_{12}$ and to $Os_3(CO)_{12}$. The electronic spectral changes for the $Os_3(CO)_{12}/AgO_2CCF_3$ system are shown in Figure 2. The spectra in part A show the effect of increasing silver ion concentration while the data in part B show that silver binding can be reversed through the addition of a chloride ion.

Qualitative evidence of silver trifluoroacetate binding to other substituted triruthenium clusters is given by the observation of the new electronic spectra bands recorded in Table II. These results are substantiated by the changes observed in the carbonyl stretching region of the infrared spectra of the parent clusters upon the addition of silver trifluoroacetate. These data are also collected in Table II.

The reaction beween $Ru_3(\mu\text{-dpm})(CO)_{10}$, with edge-bridging dpm, and silver trifluoroacetate has also been monitored by ^{31}P NMR spectroscopy. A spectrum is shown in Figure 3 for an equimolar mixture of the reactants. Under these conditions both free $Ru_3(\mu\text{-dpm})(CO)_{10}$ (peak labeled A) and $Ru_3(\mu\text{-dpm})(CO)_{10}(\mu\text{-}AgO_2CCF_3)$ (peaks labeled B and C) are present. These data clearly demonstrate that the adduct has the edge-bridged structure 2 rather than a face-bridged structure. Resonances B and C are assigned to phosphorus atoms b and c in 2. The magnitude of $J(P_bP_c)$ is consistent with the other values for similar coupling constants recorded in Table III. Resonance C contains additional splitting due to coupling



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to silver (^{109}Ag, 48.2% natural abundance, spin $^1/_2$; ^{107}Ag, 51.8% natural abundance, spin $^1/_2$). The magnitude of $J(P_cAg)$ is inconsistent with direct Ag–P bonding since one-bond Ag–P coupling constants are in the range 225–750 Hz.[29] The spectrum is essentially the same except for minor intensity changes at −75 and 25 °C so the exchange between free and bound silver trifluoroacetate is slow on the NMR time scale.

Adduct Isolation. The adducts $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$, $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Hg(O_2CCF_3)_2)$, $[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))]BF_4$, and $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)]O_2CCF_3{\cdot}HO_2CCF_3$ have been isolated in crystalline form by mixing a concentrated dichloromethane solution of 1 with concentrated solutions of the Lewis acids in dichloromethane or ethyl ether. The products either spontaneously crystallize or crystallize upon addition of more ether. Recrystallization of the adducts is made difficult by their ability to dissociate into their components. As a consequence, most of the spectroscopic data discussed in the preceding section were obtained from solutions containing excess Lewis acid.

The adduct with trifluoroacetatic acid has been formulated as an acid solvate, $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)(O_2CCF_3){\cdot}HO_2CCF_3$. There is no evidence for the formation of a doubly protonated complex in even very acidic solutions of the complex. However it is well-known that phosphine complexes crystallize with small molecules filling what would otherwise be voids in the structure: $Ru_3(\mu\text{-dpm})_2(CO)_8{\cdot}$acetone[24] and $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3){\cdot}{}^1/_2CH_2Cl_2$ offer pertinent examples.

The X-ray Crystal Structure of $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3){\cdot}{}^1/_2CH_2Cl_2$. This material crystallizes with one molecule of the adduct and half of a disordered molecule of dichloromethane in the asymmetric unit. There are no unusual contacts between these units. $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3){\cdot}{}^1/_2CH_2Cl_2$ is isomorphous with $Ru_3(\mu\text{-dpm})_2(CO)_8{\cdot}$acetone, which crystallizes to form a cylindrical cavity along the z axis that is partially filled with acetone molecules.[24] The structure of the silver adduct was solved by using the atomic coordinates of the heavy atoms from the $Ru_3(\mu\text{-dpm})_2(CO)_8{\cdot}$acetone structure as initial input parameters. Refinement established that the cluster core was similar in both structures and that the silver trifluoroacetate and the dichloromethane molecules occupied sites within the cylindrical cavity.

Atomic positional parameters are recorded in Table IV. Selected interatomic distances are collected in Table V. Table VI contains important interatomic angles.

An overall view of the adduct with the numbering scheme is shown in Figure 4. There is no imposed crystallographic symmetry. Figure 5 shows a side-on view of the inner coordination of the $AgRu_3$ portion of the structure. Figure 6 compares similar planar sections of the structures of $Ru_3(CO)_{12}$,[30] $Ru_3(\mu\text{-dpm})_2(CO)(CO)_8{\cdot}$acetone,[24] and $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3){\cdot}{}^1/_2CH_2Cl_2$.

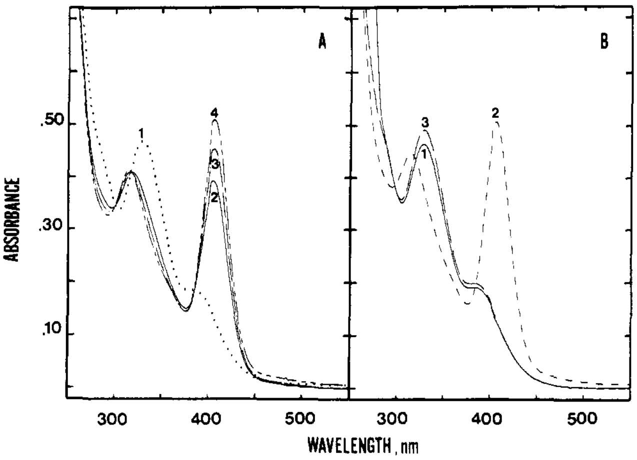

Figure 2. Electronic spectra of the $Os_3(CO)_{12}/AgO_2CCF_3$ system. A: 1, 4.3×10^{-4} M solution of $Os_3(CO)_{12}$ in dichloromethane, in *succeeding traces silver trifluoroacetate has been added*; 2, 1.1 equiv added; 3, 2.3 equiv added; 4, 5.6 equiv added. B: 1, same as A. 1; 2, same as A. 2; 3, solution from B. 2 after the addition of 6.2 equiv of bis(triphenylphosphine)nitrogen(1+) chloride and filtration to remove precipitated silver chloride. Cell path length: 1.0 mm throughout.

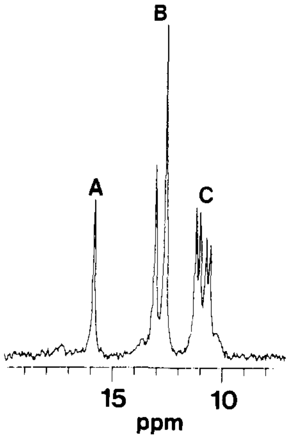

Figure 3. The ^{31}P NMR spectrum of an equimolar mixture of $Ru_3(\mu\text{-dpm})(CO)_{10}$ and silver trifluoroacetate in dichloromethane solution at −75 °C. See text for resonance assignments.

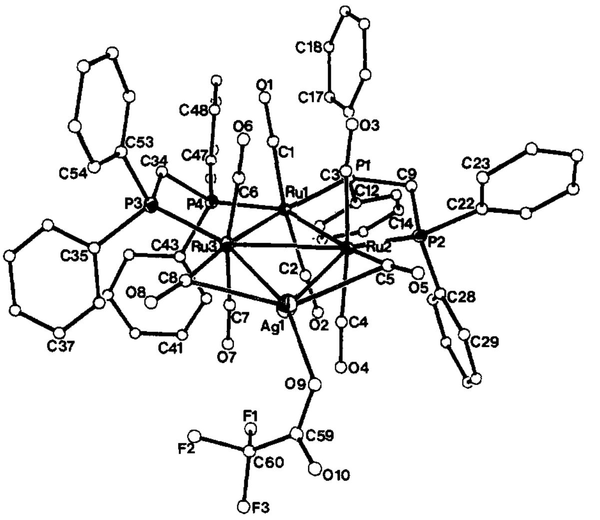

Figure 4. Molecular structure of $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$ with 50% probability thermal ellipsoids for the heavy atoms.

The silver trifluoroacetate has added across the otherwise exposed Ru(2)–Ru(3) edge of the cluster. The adjacent triangles making up the $AgRu_3$ core are nearly planar

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(29) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979; pp 107–109.

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

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
Ru(1)	1449 (1)	2243 (1)	0	10 (1)^a	C(24)	426 (6)	−1197 (8)	2153 (8)	23 (3)
Ru(2)	306 (1)	1360 (1)	418 (1)	12 (1)^a	C(25)	592 (7)	−2013 (10)	2007 (9)	35 (4)
Ru(3)	333 (1)	3279 (1)	266 (1)	13 (1)^a	C(26)	810 (7)	−2213 (10)	1306 (9)	38 (4)
P(1)	2153 (1)	1106 (2)	106 (2)	11 (1)^a	C(27)	868 (6)	−1584 (8)	781 (8)	30 (3)
P(2)	847 (1)	80 (2)	269 (2)	13 (1)^a	C(28)	719 (6)	−446 (7)	−596 (7)	16 (3)
P(3)	976 (1)	4494 (2)	272 (2)	14 (1)^a	C(29)	99 (7)	−788 (9)	−733 (8)	30 (3)
P(4)	2023 (1)	3413 (2)	−445 (2)	14 (1)^a	C(30)	−28 (7)	−1141 (9)	−1397 (8)	30 (3)
Ag(1)	−798 (1)	2388 (1)	331 (1)	30 (1)^a	C(31)	420 (7)	−1207 (10)	−1917 (9)	33 (4)
F(1)	−1434 (5)	2733 (10)	−1169 (8)	97 (6)^a	C(32)	1043 (7)	−883 (9)	−1787 (8)	30 (3)
F(2)	−2062 (8)	3657 (9)	−691 (12)	129 (8)^a	C(33)	1176 (6)	−515 (8)	−1124 (7)	19 (3)
F(3)	−2410 (7)	2836 (13)	−1500 (8)	135 (8)^a	C(34)	1842 (5)	4321 (7)	150 (6)	13 (2)
C(1)	1681 (5)	2596 (7)	959 (7)	13 (3)	C(35)	811 (5)	5334 (7)	−390 (7)	15 (3)
O(1)	1859 (4)	2820 (5)	1531 (5)	26 (2)	C(36)	435 (6)	5178 (8)	−1002 (7)	21 (3)
C(2)	1190 (5)	1753 (7)	−885 (7)	12 (2)	C(37)	372 (6)	5779 (8)	−1542 (8)	26 (3)
O(2)	1086 (4)	1447 (5)	−1444 (5)	20 (2)	C(38)	694 (6)	6538 (8)	−1494 (8)	23 (3)
C(3)	689 (6)	1528 (8)	1349 (7)	18 (3)	C(39)	1069 (6)	6706 (9)	−875 (8)	25 (3)
O(3)	892 (4)	1539 (6)	1942 (5)	26 (2)	C(40)	1121 (6)	6119 (8)	−341 (8)	22 (3)
C(4)	−58 (6)	1313 (8)	−529 (7)	20 (3)	C(41)	1653 (6)	3642 (9)	−2636 (8)	27 (3)
O(4)	−301 (4)	1238 (6)	−1098 (6)	32 (2)	C(42)	1714 (6)	3306 (8)	−1949 (7)	23 (3)
C(5)	−452 (6)	886 (8)	836 (8)	24 (3)	C(43)	1887 (6)	3841 (8)	−1358 (7)	17 (3)
O(5)	−868 (5)	542 (7)	1114 (6)	40 (3)	C(44)	2011 (6)	4713 (8)	−1507 (8)	23 (3)
C(6)	362 (6)	3246 (9)	1321 (8)	24 (3)	C(45)	1910 (6)	5012 (9)	−2204 (7)	24 (3)
O(6)	351 (4)	3278 (6)	1945 (6)	33 (2)	C(46)	1746 (7)	4468 (9)	−2765 (8)	30 (3)
C(7)	305 (6)	3095 (8)	−741 (7)	17 (3)	C(47)	2912 (6)	3433 (7)	−406 (7)	16 (3)
O(7)	239 (4)	3034 (6)	−1379 (5)	25 (2)	C(48)	3212 (5)	3465 (7)	297 (7)	17 (3)
C(8)	−423 (5)	3927 (7)	279 (7)	21 (3)	C(49)	3891 (6)	3428 (7)	312 (8)	25 (3)
O(8)	−849 (5)	4437 (7)	267 (7)	47 (3)	C(50)	4252 (6)	3342 (8)	−318 (7)	23 (3)
C(9)	1727 (5)	127 (7)	394 (7)	13 (2)	C(51)	3942 (7)	3303 (9)	−989 (8)	30 (3)
C(10)	2612 (6)	765 (7)	−688 (7)	17 (3)	C(52)	3274 (6)	3340 (8)	−1024 (8)	22 (3)
C(11)	2704 (5)	1325 (7)	−1240 (7)	13 (3)	C(53)	918 (5)	5062 (8)	1149 (7)	17 (3)
C(12)	3111 (6)	1129 (9)	−1826 (8)	26 (3)	C(54)	345 (6)	5450 (8)	1318 (7)	19 (3)
C(13)	3391 (6)	317 (8)	−1850 (8)	23 (3)	C(55)	229 (7)	5800 (9)	2008 (8)	28 (3)
C(14)	3303 (6)	−235 (9)	−1310 (8)	27 (3)	C(56)	731 (6)	5750 (9)	2534 (8)	28 (3)
C(15)	2916 (5)	−10 (8)	−719 (7)	20 (3)	C(57)	1301 (7)	5349 (10)	2380 (9)	39 (4)
C(16)	2795 (5)	1179 (7)	781 (7)	15 (3)	C(58)	1396 (7)	5014 (10)	1682 (8)	35 (4)
C(17)	3418 (5)	1425 (7)	562 (7)	18 (3)	O(9)	−1788 (5)	1976 (7)	50 (6)	42 (3)
C(18)	3917 (6)	1499 (8)	1084 (8)	23 (3)	O(10)	−2777 (6)	1996 (8)	−317 (7)	59 (3)
C(19)	3779 (6)	1352 (8)	1806 (8)	25 (3)	C(59)	−2224 (7)	2204 (10)	−349 (9)	36 (4)
C(20)	3175 (7)	1107 (9)	2009 (8)	30 (3)	C(60)	−2031 (9)	2813 (12)	−932 (11)	56 (5)
C(21)	2675 (6)	1040 (7)	1512 (7)	16 (3)	Cl(1)	3395 (4)	7394 (5)	1824 (4)	37 (2)
C(22)	689 (6)	−774 (8)	931 (7)	18 (3)	Cl(2A)	2398 (7)	8747 (9)	2110 (8)	32 (3)
C(23)	460 (6)	−575 (8)	1612 (7)	18 (3)	Cl(2B)	2548 (9)	6398 (11)	1123 (11)	54 (4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

as can be seen in Figure 5. The silver ion lies only 0.62 Å from the plane of the Ru_3 triangle. The dihedral angle between the Ru_3 triangle and the Ru_2Ag triangle is 15.5°. There is some asymmetry in the silver binding to the ruthenium cluster. The Ag–Ru(3) distance is 0.073 Å shorter than the Ag–Ru(2) distance. This places the silver ion also 0.09 Å closer to the equatorial carbonyl C(8)–O(8) on Ru(3) than to the corresponding carbonyl C(5)–O(5) on Ru(2). The coordination of the silver is completed by a bond to one oxygen of the monodentate trifluoroacetate group. This oxygen is also asymmetrically positioned with regard to the Ru_2Ag triangle. The Ru(3)–Ag–O(9) angle is 159.2 (3)° while the Ru(2)–Ag–O(9) angle is only 127.0 (3)°. The trifluoroacetate ion is also located so that O(9) is 0.57 Å out of the plane defined by Ag, Ru(2), and Ru(3) so that the environment of the silver ion is not quite planar. The other oxygen of the trifluoroacetate group is quite remote from the cluster. The nonbonded Ag–O(10) distance is 4.31 Å.

The Ag–Ru distances are comparable to those seen in the two other structurally characterized compounds with ruthenium–silver bonds. In $(\mu\text{-}Ph_3PAg)_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}$ the Ag–Ru distances that do not have hydride bridges are 2.842 and 2.857 Å while in $(\mu\text{-}Ph_3PAg)(\mu\text{-}Ph_3PCu)Ru_4(\mu_3\text{-}H)_2(CO)_{12}$ the corresponding values are shorter: 2.825 and 2.819 Å.[18] The Ag–Ru distances are also similar to the Au–Ru distances found in clusters where a Ph_3PAu group bridges an Ru–Ru edge. In $(\mu\text{-}Ph_3PAu)Ru_3(\mu\text{-}Cl)(CO)_{10}$ the Au–Ru distances are 2.7549 (6) and 2.7523 (6) Å.[13] For $(\mu\text{-}Ph_3PAu)Ru_3(\mu\text{-}COCH_3)(CO)_{10}$ the Au–Ru distances are 2.762 and 2.760 (or 2.762 and 2.782) Å,[11] while in $(\mu\text{-}Ph_3PAu)Ru_5C(CO)_{15}Cl$ the corresponding distances are 2.774 and 2.811 (or 2.764 and 2.841) Å.[8] The Ag–O distance is somewhat shorter than those found in the silver trifluoroacetate chains (with bridging trifluoroacetate) in bis(silver trifluoroacetate)benzene where the three Ag–O distances are 2.22 (1), 2.28 (1), and 2.41 (1) Å.[31] It is also shorter than the Ag–O distances found for the chelating trifluoroacetate in (2,2-dimethylbut-3-enyl methyl sulfide)(trifluoroacetato)silver(I) where the distances are 2.29 (2) and 2.99 (3) Å.[32]

The binding of silver causes relatively small perturbations in the geometry of the $Ru_3(\mu\text{-dpm})_2(CO)_8$ portion of the structure. These changes are best appreciated by comparing the in-plane sections shown in Figure 6. The largest change involves the 0.167 Å increase in the Ru(2)–Ru(3) distance along the edge where the silver ion is bound. This elongation causes the Ru(2)–Ru(1)–Ru(3) angle to open slightly (3.2°) and causes smaller decreases

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[31] Hunt, G. W.; Lee, T. C.; Amma, E. L. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 909.

[32] Alyea, E. C.; Ferguson, G.; McAlees, A.; McCrindle, R.; Myers, R.; Siew, P. Y.; Dias, S. A. *J. Chem. Soc., Dalton Trans.* **1981**, 481.

Table V. Selected Interatomic Distances (Å) for $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$

A. Metal Core			
Ru(1)-Ru(2)	2.849 (1)	Ru(1)-Ru(3)	2.869 (1)
Ru(2)-Ru(3)	3.025 (1)		
Ru(2)-Ag(1)	2.803 (1)	Ru(3)-Ag(1)	2.730 (1)
B. Ru-C and Ru···O (Axial)			
Ru(1)-C(1)	1.915 (12)	Ru(1)···O(1)	3.084 (12)
Ru(1)-C(2)	1.883 (12)	Ru(1)···O(2)	3.037 (12)
Ru(2)-C(3)	1.911 (13)	Ru(2)···O(3)	3.076 (13)
Ru(2)-C(4)	1.904 (13)	Ru(2)···O(4)	3.071 (13)
Ru(3)-C(6)	1.949 (14)	Ru(3)···O(6)	3.097 (14)
Ru(3)-C(7)	1.881 (13)	Ru(3)···O(7)	3.065 (13)
C. Ru-C and Ru···O (Equatorial)			
Ru(2)-C(5)	1.902 (13)	Ru(2)···O(5)	3.034 (13)
Ru(3)-C(8)	1.866 (12)	Ru(3)-O(8)	3.048 (12)
D. C-O (Axial and Equatorial)			
C(1)-O(1)	1.171 (15)	C(2)-O(2)	1.157 (15)
C(3)-O(3)	1.173 (16)	C(4)-O(4)	1.169 (17)
C(6)-O(6)	1.152 (18)	C(7)-O(7)	1.188 (16)
C(5)-O(5)	1.137 (17)	C(8)-O(8)	1.191 (15)
E. Ag-O, Ag···C, and Ag···O			
Ag(1)-O(9)	2.211 (10)	Ag(1)···C(5)	2.634 (12)
Ag(1)···O(10)	4.311 (10)	Ag(1)···C(8)	2.540 (12)
F. Ru-P			
Ru(1)-P(1)	2.312 (3)	Ru(1)-P(4)	2.336 (3)
Ru(2)-P(2)	2.317 (3)	Ru(3)-P(3)	2.327 (3)
G. P-C			
P(1)-C(9)	1.849 (11)	P(1)-C(10)	1.826 (13)
P(1)-C(16)	1.826 (12)	P(2)-C(9)	1.839 (10)
P(2)-C(22)	1.843 (13)	P(2)-C(28)	1.816 (13)
P(3)-C(34)	1.827 (11)	P(3)-C(35)	1.828 (12)
P(3)-C(53)	1.851 (13)	P(4)-C(34)	1.838 (11)
P(4)-C(43)	1.834 (13)	P(4)-C(47)	1.842 (12)

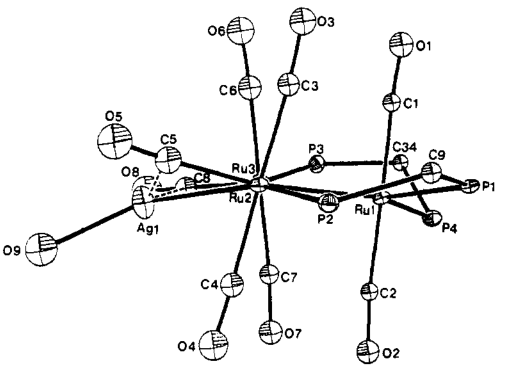


Figure 5. A side view of the inner coordination of $Ru_3(\mu\text{-}dpm)_2(CO)_8(\mu\text{-}AgO_2CCF_3)$.

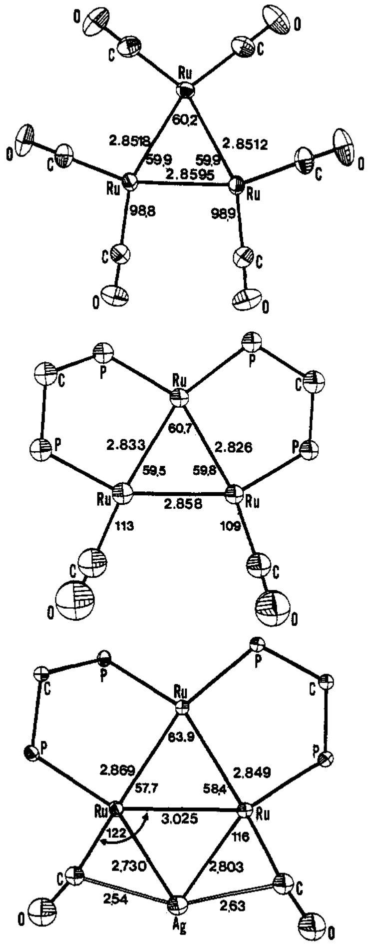
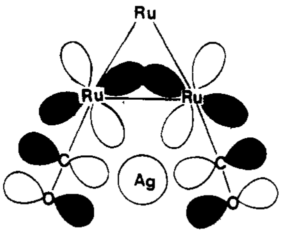
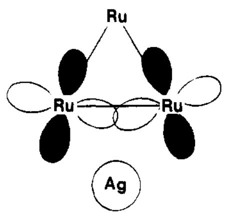


Figure 6. A comparison of corresponding sections of A, $Ru_3(CO)_{12}$,[30] B, $Ru_3(\mu\text{-dpm})_2(CO)_8$,[24] and C, $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$. For A the esd's are Ru-Ru (0.0004 Å), Ru-Ru-Ru (0.01°), and Ru-Ru-C (0.04°), and for B they are Ru-Ru (0.002 Å), Ru-Ru-Ru (0.04°), and Ru-Ru-C (0.06°).

in the other two Ru-Ru-Ru angles. The two equatorial carbonyl groups have spread apart somewhat upon coordination of the silver so that the Ru-Ru-C angles have expanded from 113° and 109° to 122° and 115°. Otherwise the Ru_3 core is similar to that in $Ru_3(\mu\text{-dpm})_2(CO)_8$ and in $Ru_3(CO)_{12}$. In particular the dpm-bridged Ru-Ru distances are similar in both dpm clusters and are similar to the Ru-Ru bond lengths in $Ru_3(CO)_{12}$.

In the binding within the adduct, the Ru_3 core must be acting as a nucleophile toward the silver ion. The silver ion, as a zero-electron donor, will not affect the overall electron count within the cluster. On the basis of overlap, it appears that the cluster core orbital **3** is more favorably disposed toward binding silver than is the edge orbital **4**.[27] The core orbital **3** has the appropriate symmetry to π bond with the carbonyl ligands, and calculations on the parent clusters $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ indicate that there is considerable π bonding in these orbitals. Consequently it is appropriate to examine the degree of interaction between the silver ion and the in-plane carbonyl groups.





The silver ion is rather close to the carbon atoms of two carbonyl groups. The Ag-C distances 2.54 and 2.63 Å are within the ranges found for silver(I) bonding to unsaturated hydrocarbons. In silver(I) olefin complexes the Ag-C bond distances fall in the range 2.34-2.59 Å,[32] while for complexes between silver(I) and aromatic hydrocarbons these distances occur in the range 2.45-2.92 Å.[33] Nevertheless, there does not appear to be a significant perturbation of the carbonyl groups. The in-plane Ru-C-O angles show little deviation from linearity, although for semibridging carbon monoxide considerable bending of these angles is expected. Likewise, although semibridging carbonyls show distinguishing, low-energy stretching fre-

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(33) Taylor, I. F.; Hall, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 5745.

Table VI. Selected Bond Angles (deg) for $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$

A. At Ru(1)

Ru(2)-Ru(1)-Ru(3)	63.9 (1)		
Ru(2)-Ru(1)-P(1)	97.2 (1)	Ru(2)-Ru(1)-P(4)	154.2 (1)
Ru(3)-Ru(1)-P(1)	158.6 (1)	Ru(3)-Ru(1)-P(4)	91.4 (1)
Ru(2)-Ru(1)-C(1)	95.7 (3)	Ru(2)-Ru(1)-C(2)	78.4 (3)
Ru(3)-Ru(1)-C(1)	83.1 (3)	Ru(3)-Ru(1)-C(2)	98.6 (3)
P(1)-Ru(1)-C(1)	89.3 (3)	P(1)-Ru(1)-C(2)	86.4 (3)
P(4)-Ru(1)-C(1)	88.3 (3)	P(4)-Ru(1)-C(2)	99.3 (4)
P(1)-Ru(1)-P(4)	108.4 (1)	C(1)-Ru(1)-C(2)	172.2 (5)

B. At Ru(2)

Ru(1)-Ru(2)-Ru(3)	58.4 (1)	Ru(3)-Ru(2)-C(5)	116.0 (4)
Ru(1)-Ru(2)-Ag(1)	112.5 (1)	Ag(1)-Ru(2)-Ru(3)	55.7 (1)
Ru(1)-Ru(2)-P(2)	89.3 (1)	P(2)-Ru(2)-Ag(1)	152.5 (1)
Ag(1)-Ru(2)-C(3)	108.0 (4)	Ru(1)-Ru(2)-C(3)	80.3 (4)
Ag(1)-Ru(2)-C(4)	69.3 (4)	Ru(1)-Ru(2)-C(4)	95.7 (4)
Ag(1)-Ru(2)-C(5)	64.8 (4)	Ru(1)-Ru(2)-C(5)	170.5 (4)
P(2)-Ru(2)-C(3)	91.5 (4)	C(3)-Ru(2)-C(4)	174.1 (5)
P(2)-Ru(2)-C(4)	92.8 (4)	C(4)-Ru(2)-C(5)	91.7 (6)
P(2)-Ru(2)-C(5)	96.2 (4)	C(3)-Ru(2)-C(5)	91.8 (6)

C. At Ru(3)

Ru(1)-Ru(3)-Ru(2)	57.7 (1)	Ru(2)-Ru(3)-C(8)	122.0 (6)
Ru(1)-Ru(3)-Ag(1)	114.1 (1)	Ag(1)-Ru(3)-Ru(2)	58.0 (1)
Ru(1)-Ru(3)-P(3)	90.2 (1)	P(3)-Ru(3)-Ag(1)	155.6 (1)
Ag(1)-Ru(3)-C(6)	88.3 (4)	Ru(1)-Ru(3)-C(6)	97.6 (4)
Ag(1)-Ru(3)-C(7)	86.5 (4)	Ru(1)-Ru(3)-C(7)	76.6 (4)
Ag(1)-Ru(3)-C(8)	63.9 (4)	Ru(1)-Ru(3)-C(8)	170.6 (4)
P(3)-Ru(3)-C(6)	89.9 (4)	C(6)-Ru(3)-C(7)	169.7 (6)
P(3)-Ru(3)-C(7)	98.5 (4)	C(6)-Ru(3)-C(8)	91.6 (6)
P(3)-Ru(3)-C(8)	91.9 (4)	C(7)-Ru(3)-C(8)	94.0 (6)

D. At Ag(1)

Ru(2)-Ag(1)-Ru(3)	66.3 (1)		
Ru(2)-Ag(1)-O(9)	127.0 (3)	Ru(3)-Ag(1)-O(9)	159.2 (3)
Ru(2)-Ag(1)-C(5)	40.8 (4)	Ru(3)-Ag(1)-C(8)	41.3 (4)

quencies in the infrared spectrum, none is present in the silver adduct and the spectral bands have shifted in the opposite direction. Finally it should be noted that the nonbonded C(5)···C(8) separations have increased from 3.46 Å in $Ru_3(CO)_{12}$ and 4.27 Å in $Ru_3(\mu\text{-dpm})_2(CO)_8$ to 4.88 Å in $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$. This effect, coupled with the increase in the in-plane Ru–Ru–C angles noted earlier, suggests that the presence of the silver ion is repelling, not attracting, the carbonyl groups.

The structural changes that occur upon addition of silver to $Ru_3(\mu\text{-dpm})_2(CO)_8$ resemble those observed when metal–metal bonds are protonated, an electronically analogous situation. The major effects of protonation involve the elongation of the metal–metal bond by about 0.15 Å and a bending of the adjacent ligands away from the site of protonation.[34] Similar changes are also seen in the one other case of addition of silver ion to a metal–metal bond. When silver perchlorate reacts with $Fe_2(CO)_6(\mu\text{-}CH(NHCH_3)Ph)(\mu\text{-}PPh_2)$, the silver ion adds to the Fe–Fe bond causing it to lengthen by ca. 0.12 Å.[16] In this adduct, as with $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$, the silver ion is three-coordinate with coordination completed by a rather long silver–oxygen bond (2.686 (6) Å).

Experimental Section

Preparation of Compounds. Trifluoroacetic acid (Aldrich), trifluoroacetic anhydride (Aldrich), and bis(diphenylphosphino)methane (Pressure Chemical Co.) were used without further purification. Silver trifluoroacetate (Aldrich) was recrystallized from diethyl ether/hexane before use. Mercuric trifluoroacetate was prepared from the oxide by reaction with trifluoroacetic anhydride in benzene and recrystallized from benzene/hexane.[35] The copper(I) complex $[Cu(CH_3CN)_4]BF_4$ was prepared by the procedure of Ho and Bau[36] and isolated as a solid before use. All of the clusters reported here can be prepared without protection from the atmosphere.

$Ru_3(\mu\text{-dpm})_2(CO)_8$. Three hundred milligrams (0.47 mmol) of $Ru_3(CO)_{12}$ were dissolved in 70 mL of boiling cyclohexane under a dinitrogen atmosphere, and 363 mg (0.94 mmol) of dpm was added. The solution was heated under reflux for 3.5 h and cooled overnight. The red needles were collected by filtration, washed with cyclohexane and pentane, and dried in vacuo. The yield, after recrystallization from dichloromethane/methanol, was 531 mg or 87%. The spectroscopic properties of the material agreed with those reported previously for material obtained from a slightly different route.[23] $Ru_3(\mu\text{-dam})_2(CO)_8$ was prepared similarly.

$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$. A solution containing 40 mg (0.18 mmol) of silver trifluoroacetate in 15 mL of diethyl ether was added dropwise to a solution of 200 mg (0.15 mmol) of $Ru_3(\mu\text{-dpm})_2(CO)_8$ in 8 mL of dichloromethane. The deep red, crystalline product formed immediately. After the solution was cooled at −15 °C for 1 h, the crystals were collected, washed with ether, and air dried. The yield, after recrystallization from dichloromethane/ether, was 193 mg or 82%. Anal. Calcd for $C_{60}H_{44}AgF_3P_4O_{10}Ru_3\cdot{}^1/_2CH_2Cl_2$: C, 46.89; H, 2.90; P, 8.00. Found: C, 46.84; H, 3.05; P, 9.00.

$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Hg(O_2CCF_3)_2)\cdot 2C_4H_{10}O$. Thirty-five milligrams of solid $Hg(O_2CCF_3)_2$ were added to a solution of 100 mg (0.08 mmol) of $Ru_3(\mu\text{-dpm})_2(CO)_8$ in 5 mL of dichloromethane. The color of the solution immediately changed from orange-red to deep purple. The solution was filtered to remove any unreacted solids. Dropwise addition of 3 mL of diethyl ether to the filtrate completely precipitated the product. It was rapidly filtered from solution and washed with ether. The solid was dried in vacuo. The yield was 105 mg or 78%. Attempts to recrystallize this solid from dichloromethane/ether led to significant decomposition. A microcrystalline material could be obtained in very low yield from

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Table VII. Summary of Crystallographic Data for $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$

formula	$C_{60.5}H_{45}AgClF_3P_4Ru_3$
fw	1548.40
cryst system	orthorhombic
space group based on conditions	$Pca2_1$ (No. 29); $0kl$ ($l = 2n$), $h0l$ ($h = 2n$)
cryst dimens, mm	0.28 × 0.26 × 0.41
cryst color and habit	red prisms
a, Å (140 K)	20.706 (9)
b, Å	15.693 (11)
c, Å	18.447 (5)
Z	4
V, $Å^3$	5994.2
$d(140\ K)_{calcd}$, g/cm^3	1.68
radiatn	Mo Kα (λ = 0.710 69 Å); graphite monochromator
linear abs coeff, cm^{-1}	12.54
temp, K	140
instrument	Syntex $P2_1$ diffractometer with modified LT-1 low temp apparatus
scan speed, deg/min	58.6
scan width, deg	1.0
type of scan	ω
ω offset for bkgds, deg	±1.0
2θ range, deg	0–45
range of transmissn factors	0.758, 0.653
octants	*h,k,l* positive
variables	391
data/variable ratio	9.50
programs	SHELXTL IV
check reflctns	2 measured every 200 reflections
no. of unique data	4071
no. of data $I \geq 3\sigma(I)$	3716
$R(F)$	0.043
$R_w(F)$	0.046
largest Δ/σ	0.005

concentrated dichloromethane solutions of the compound. Anal. Calcd for $C_{62}H_{44}F_6HgO_{12}P_4Ru_3\cdot 2C_2H_{10}O$: C, 45.17; H, 3.44; P, 6.66. Found: C, 45.57; H, 3.44; P, 6.56.

$[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))][BF_4]$. A slurry of 25 mg (0.08 mmol) of $[Cu(NCCH_3)_4]BF_4$ in 2 mL of dichloromethane was added to a solution of 100 mg (0.08 mmol) of $Ru_3(\mu\text{-dpm})_2(CO)_8$ in 4 mL of dichloromethane. The solution was stirred briefly to allow all the solids to dissolve, and then it was filtered. Diethyl ether was added dropwise (15 mL total) to the filtrate to induce crystallization. The rust-brown crystals were collected, washed with ether, and dried. The yield, after recrystallization from dichloromethane/ether, was 97 mg or 85%. Anal. Calcd for $C_{60}H_{47}BCuF_4NO_8P_4Ru_3$: C, 48.4; H, 3.15; N, 0.90; P, 8.30. Found: C, 46.7; H, 3.21; N, 0.72; P, 8.10.

$Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)(O_2CCF_3)\cdot HO_2CCF_3$. Approximately 0.5 mL (6.5 mmol) of CF_3CO_2H was added to a solution of 100 mg (0.08 mmol) of $Ru_3(\mu\text{-dpm})_2(CO)_8$ in 4 mL of dichloromethane with a concomitant color change from orange to red. Diethyl ether (10 mL total) was added to precipitate the adduct. The red crystalline solid was collected by filtration, washed with ether, and air dried. The yield was 95 mg or 87%. Attempts at recrystallization of the product from dichloromethane/ether resulted in significant decomposition. Anal. Calcd for $C_{62}H_{46}F_6O_{12}P_4Ru_3$: C, 49.17; H, 3.04; P, 8.19. Found: C, 49.04; H, 3.04; P, 8.00.

$Ru_3(\mu\text{-dpm})(CO)_{10}$. Under a dinitrogen atmosphere solid dpm (61 mg, 0.16 mmol) was added to a solution of 100 mg (0.16 mmol) of freshly distilled tetrahydrofuran. According to the procedures of Bruce and co-workers,[37] four drops of a tetrahydrofuran solution of sodium diphenyl ketyl were added. A color change from orange to deep red occurred. The volume of the solution was reduced to 7 mL, and hexane was slowly added. An initial yellow precipitate was removed by filtration and discarded. Further addition of hexane produced orange microcrystals of the product that were collected and washed with hexane. These were purified by recrystallization from dichloromethane/hexane: yield 62%. The spectroscopic properties agreed with those reported previously:[38] ^{31}P NMR 14.9 ppm (s).

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 180 infrared spectrometer. ^1H and proton-decoupled ^{31}P NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 200 and 81 MHz, respectively. An external, 85% phosphoric acid reference was used for ^{31}P NMR spectra, and the high-frequency positive convention, recommended by IUPAC, has been used in reporting chemical shifts. Electronic spectra were recorded on a Hewlett-Packard 8450A UV/visible spectrometer. Equilibrium constants were calculated from spectral titration data using a beer's law treatment.

X-ray Data Collection. Crystal and experimental data are given in Table VII. The deep red crystals were grown by slow vapor diffusion of diethyl ether into a dichloromethane solution of the complex. The crystal lattice was determined to be orthorhombic from axial photographs and the automatic indexing routine of the diffractometer software. The lattice constants are nearly identical with those for the related structure $Ru_3(\mu\text{-dpm})_2(CO)_8\cdot nCH_3COCH_3$ that crystallized in the space group $Pca2_1$ (No. 29).[24] Observed systematic absences in the data were consistent with the assignment of the space group as $Pca2_1$ for this structure as well. The data were collected at 140 K, and the usual Lorentz and polarization corrections were made. Neutral atom scattering factors were taken from a standard source. Corrections for anomalous dispersion were applied.[39]

Prior to data collection we were suspicious that perhaps the crystals we had obtained differed from the starting material only in the solvent (acetone or dichloromethane) present. It would have been valuable to have some values of F_o available for comparison. In this regard, the short list of axis reflections given below would be a useful addition to crystallographic reports, and in the present case, comparison of the two sets indicates that significant differences (larger than would result from variation in solvent molecules) exist between the two structures. F_o $Ru_3(\mu\text{-dpm})_2(CO)_8\cdot$(acetone)/$F_o$ $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$: $h00$, h = 4, 74/18; 6, 53/36; 8, 248/227; 10, 139/36; 12, 189/28; $0k0$, k = 2, 131/364; 3, 33/54; 4, 278/183; 5, 253/285; 6, 278/163; $00l$, l = 4, 239/318; 6, 467/692; 8, 237/381; 10, 228/340; 12, 157/342. We suggest that inclusion of such a list be made standard practice.

Solution and Refinement of the Structure. The coordinates for the three ruthenium atoms and the four phosphorus atoms for the $Ru_3(\mu\text{-dpm})_2(CO)_8\cdot n$acetone were taken from ref 24. After two cycles of least-squares refinement a medium-sized peak located 2.8 Å from Ru(2) and Ru(3) on a difference map was assigned to the Ag atom. Other atoms were located from successive difference maps. After isotropic refinement to $R = 0.0872$ ($R_w = 0.0872$) several peaks remained that were not attached to the parent molecule. These were connected to form a partially disordered dichloromethane molecule. An absorption correction (XABS) was applied. Hydrogen atoms were included at calculated positions that were recalculated with each cycle and with $U_{iso}(H)$ fixed at 1.2 times the U_{iso} for the bound carbon. Final cycles of refinement were carried out with anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the carbon and oxygen atoms. The final difference Fourier map was featureless in the vicinity of the adduct. A conventional R value of 0.043 ($R_w = 0.046$) was obtained.

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Registry No. 1, 77611-27-9; 2, 91782-22-8; $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$, 91782-13-7; $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Hg(O_2CCF_3)_2)$, 91782-14-8; $[Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}Cu(NCCH_3))][BF_4]$, 91782-16-0; $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}H)(O_2CCF_3)$,

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91782-18-2; $Ru_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$, 91782-19-3; $Os_3(CO)_{12}(\mu\text{-}AgO_2CCF_3)$, 91782-20-6; $Ru_3(\mu\text{-dam})_2(CO)_8(\mu\text{-}AgO_2CCF_3)$, 91782-21-7; $Ru_3(CO)_{12}$, 15243-33-1; $[Cu(NCCH_3)_4]BF_4$, 15418-29-8; $Ru_3(\mu\text{-dpm})(CO)_{10}$, 64364-79-0; Ag, 7440-22-4; Hg, 7439-97-6; Cu, 7440-50-8; Ru, 7440-18-8.

Supplementary Material Available: Listings of structure factor amplitudes, thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates (28 pages). Ordering information is given on any current masthead page.

Preparation and Structure of the [2]Ferrocenophane (η^5-$C_5H_4Fe(CO)Cp)Fe(\eta^5$-$C_5H_4PPh_2$) and Related Compounds

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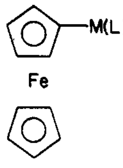
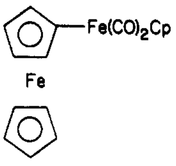
Reaction of (1,1′-ferrocenediyl)phenylphosphine with phenyllithium in diethyl ether at −78 °C followed by treatment of the product mixture with $Fe(CO)_2CpI$ gives a number of compounds including the ferrocenophanes (η^5-$C_5H_4Fe(CO)Cp)Fe(\eta^5$-$C_5H_4PPh_2$) (7) and (η^5-$C_5H_4C(O)Fe(CO)Cp)Fe(\eta^5$-$C_5H_4PPh_2$) (8). Treatment of an identical solution with $Fe(CO)(PPh_3)CpI$ also gives 7. The reaction of (1,1′-ferrocenediyl)phenylarsine with phenyllithium in a similar manner and subsequent reaction with $Fe(CO)_2CpI$ give primarily (η^5-$C_5H_4Fe(CO)_2Cp)Fe(\eta^5$-$C_5H_4AsPh_2$) (**10**). A synthetically useful ferrocenyl byproduct, (η^5-$C_5H_4I)Fe(\eta^5$-$C_5H_4PPh_2$) (**6**), was also isolated during these syntheses. The crystal and molecular structure of 7 has been determined by single-crystal X-ray diffraction analysis. The crystals are triclinic of space group $P\bar{1}$ with a = 10.540 (1) Å, b = 11.507 (2) Å, c = 9.737 (3) Å, α = 100.41 (1)°, β = 98.49 (1)°, γ = 88.95 (1), V = 1148.6 (5) Å^3, and Z = 2. The data were refined to R = 0.030 on the basis of 4765 reflections.

Introduction

A significant number of sigma bonded ferrocene-transition metal complexes of the type 1 are known,[1-4] for example, Fp–ferrocene 2,[4] which may readily be prepared by reaction of a haloferrocene with NaFp or by reaction of a metalated ferrocene with FpX (X = Cl, I; Fp = $Fe(CO)_2Cp$).

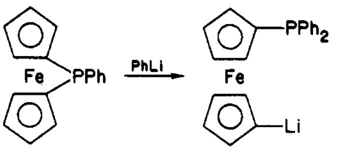


1



2

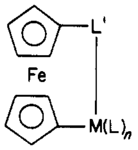
We have recently been concerned with ligand substitution reactions of 2 using acetylenes and phosphines[5] and also with the preparation of unsymmetrically, 1,1′-disubstituted ferrocene compounds such as (η^5-$C_5H_4PPh_2)Fe(\eta^5$-C_5H_4P-t-Bu_2) principally for use as ligands in catalysts and catalyst precursors. The ring opening reaction of (1,1′-ferrocenediyl)phenylphosphine[7,9] with phenyllithium discovered by Seyferth and Withers[10,11] has proven to be of great synthetic utility in this work (eq 1).



(1)

3 4

It seemed possible that convergence of these two lines of research could result in the preparation of ferrocenophane compounds such as 5 in which *intramolecular* ligand substitution has occurred. Such compounds would be of interest in view of our previous work and because these would be the first examples of [2]ferrocenophanes with transition metals in the bridge. This paper documents some work in this area utilizing 3 as a key reagent.



5

Experimental Section

All reactions were carried out under an inert atmosphere (Ar or N_2) using conventional Schlenk techniques. Phenyllithium was supplied by the Aldrich Chemical Co. as a 1.9 M solution in

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