Contribution from the Department of Chemistry,
University Rochester, Rochester, New York 14627

Synthesis of Rhodium(I) A-Frame Complexes with Anionic Bridgehead Ligands, Structure of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$, and Reactivity with Electrophilic Reagents

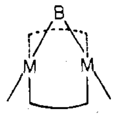
CLIFFORD P. KUBIAK and RICHARD EISENBERG*

Received January 30, 1980

The reaction of $[Rh_2Cl_2(CO)_2(dpm)_2]$, dpm = bis(diphenylphosphino)methane, with $Y^{n-} = S^{2-}$, Se^{2-}, and $PH(C_6H_{11})^-$ leads to new complexes, $[Rh_2(\mu\text{-}Y)(CO)_2(dpm)_2]^{(2-n)+}$. The sulfide $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ is found by a single-crystal X-ray analysis to have an A-frame type structure. In this arrangement, two square-planar coordinated Rh(I) ions are bridged by dpm ligands and share a common anionic ligand in the bridgehead position. The two coordination planes are inclined at a dihedral angle of 83.6°. The Rh···Rh separation is 3.154 (2) Å. IR, NMR, microanalytical, and conductivity data are used to characterize other A-frame molecules with Y = Se^{2-}, $PH(C_6H_{11})^-$, SH^-, SEt^-, and SCH_2Ph^-. Protonation or ethyl alkylation of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ with Et_2OR^+ (R = H, Et) occurs at the bridging sulfide. Benzyl bromide is also found to effect S-alkylation. In the case of alkyl iodides, sulfur removal is observed. $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ reacts with SO_2 to form a stable adduct, $[Rh_2(\mu\text{-}S)(\mu\text{-}SO_2)(CO)_2(dpm)_2]$. The reaction with methyl isocyanide results in CO substitution and $[Rh_2(\mu\text{-}S)(CNMe)_2(dpm)_2]$.

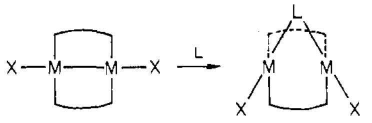
Introduction

The study of binuclear complexes in which both metal centers are accessible to a single substrate molecule is essential for the development of multicentered reagents and catalysts.[1] We have focused our studies on a class of binuclear complexes which have the A-frame structure I. Complexes of the A-frame type are characterized by two approximately square-planar coordinated metal ions which are bound together by two bridging diphosphines and further linked at a common corner of the two coordination planes by a bridgehead ligand, B. The bridging diphosphines preserve the integrity of the binuclear arrangement, while the relative inclination of the two square planes has the additional effect of directing the out-of-plane metal d and p functionalities into a "pocket" between the metal centers. A-frame complexes are therefore expected, and have recently been found,[2-5] to bind small molecules in the pocket between the metal centers.

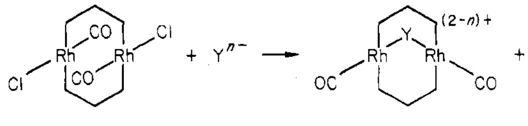


I

Since the initial reports in 1977 of complexes having the A-frame structure,[6,7] numerous other examples have appeared in the literature. Two general methods for the synthesis of A-frame complexes have been successfully employed. The first, shown in eq 1, has been used primarily by Balch,[7,8] Puddephatt,[9,10] and recently ourselves[4] and involves the introduction of a small molecule ligand, L, into the M–M bond of highly unsaturated $[M_2X_2(LL)_2]$ complexes (M = Pd(I) or Pt(I), X = Cl or Br, LL = dpm (bis(diphenylphosphino)methane) or dam (bis(diphenylarsino)methane); M = Rh(0), X = CO, LL = dpm). By this method, A-frame molecules have been prepared which contain CO,[4,7,11,12] CNR,[4,7] SO_2,[8] H^+,[4,10] and R_2NN^+[13] as bridghead ligands. The second method, eq 2, involves removal of chloride from $[Rh_2Cl_2(CO)_2(dpm)_2]$ to produce the μ-chloride A-frame $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)]^{+}$[2,14] or displacement of both chlorides by other anionic bridging ligands (Y^{n-}).[6]



(1)



(2)

We report herein the use of the second method to prepare A-frame complexes of rhodium(I) which have anionic bridgehead ligands (Y = S^{2-}, Se^{2-}, and PR_2^-). A partial report of this work has been previously communicated.[6] The full details of an X-ray crystallographic study of the sulfide-bridged A-frame complex $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ are now presented, as well as results of the reaction chemistry of this complex primarily with electrophilic reagents.

Experimental Section

Materials. Rhodium trichloride hydrate (Matthey Bishop), phosphines (Strem), triethyloxonium hexafluorophosphate, hexafluorophosphoric acid–diethyl ether, benzyl bromide, *n*-butyllithium (Aldrich), alkyl iodides (Eastman), sodium sulfide (Mallinckrodt), potassium selenide (Pfaultz and Bauer), silver hexafluorophosphate (Ventron), and the gases H_2, ethylene, SO_2, and CO (Matheson) were used as purchased. All solvents except nitromethane (Eastman Spectrograde) were dried and degassed before use.

Preparation of Complexes. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (COD = cyclooctadiene) was prepared by established procedures.[15] All syntheses were routinely performed under an atmosphere of dry nitrogen by using modified Schlenk techniques. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. ^{31}P and ^1H NMR spectra were recorded on a JEOL JNM-PS-100 instrument with Fourier transform abilities. Infrared spectra were recorded on a Perkin-Elmer 467 grating

---

(1) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. (b) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

(2) Cowie, M; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. Cowie, M. *Inorg. Chem.* **1979**, *18*, 286.

(3) Cowie, M.; Dwight, S. K.; Sanger, A. R. *Inorg. Chim. Acta* **1978**, *31*, L407.

(4) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.

(5) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.

(6) Kubiak, C. P.; Eisenberg R. *J. Am. Chem. Soc.* **1977**, *99*, 6129.

(7) Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502.

(8) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(9) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L33.

(10) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L27.

(11) Colton, R.; McCormick, M. J.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* **1977**, 823.

(12) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425.

(13) Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85.

(14) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.

(15) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

0020-1669/80/1319-2726$01.00/0

spectrometer. Samples were either KBr pellets or Nujol mulls on NaCl plates. Conductivities of the complexes in nitromethane solution were measured with a Barnstead PM-70CB conductivity bridge equipped with a Barnstead B-10 1.0-cm cell.[28] A working cell constant was determined from the ratio of the observed specific conductance of 0.02 N aqueous KCl with the literature value of 0.002 768 Ω^{-1} cm^{-1} at 25 °C.[16] Typically, equivalent conductances for the complexes in solution were determined at six concentrations from ca. 3–0.1 mM.

$[Rh_2Cl_2(CO)_2(PPh_2CH_2PPh_2)_2]$. $[Rh_2Cl_2(CO)_2(dpm)_2]$ is prepared by a slight modification of the method reported by Mague.[17] CO gas is bubbled through a stirred 50-mL toluene solution which contains 1.0 g of $[Rh_2(\mu\text{-}Cl)_2(1,5\text{-}COD)_2]$. After 30 min, the CO flow is discontinued and 2.0 g of bis(diphenylphosphino)methane (dpm) dissolved in 20 mL of toluene is added by syringe. The reaction solution is stirred vigorously for 10 min. CO is removed from the reaction flask under vacuum and replaced by N_2. The reaction flask which contains a thick orange precipitate is stored at −10 °C for 1 h. The precipitate is collected in air, washed first with toluene and then with diethyl ether to remove unreacted dpm and 1,5-cyclooctadiene, and dried in vacuo. Yields are typically 90–98%, and samples thus prepared are indistinguishable in their spectroscopic properties from those prepared by previously established methods.[17b]

$[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$. Sodium sulfide hydrate (0.044 g) is dissolved in 5 mL of anhydrous methanol. This solution is degassed and added by syringe to a stirred methanol slurry of 0.2 g of $[Rh_2Cl_2(CO)_2(dpm)_2]$. After 30 min, the bright red precipitate is collected, washed with methanol, and recrystallized from methanol–dichloromethane. Yields are typically 85–95%. Anal. Calcd for $C_{52}H_{44}P_4SO_2Rh_2$: C, 58.76; H, 4.14; P, 11.68; S, 3.01. Found: C, 58.17; H, 4.22; P, 11.50; S, 2.99. IR: ν(CO) 1933 s, 1920 vs cm^{-1} (Nujol).

$[Rh_2(\mu\text{-}Se)(CO)_2(PPh_2CH_2PPh_2)_2]$. Solid potassium selenide (0.03 g) is added to a 25-mL methanol slurry which contains 0.2 g $[Rh_2Cl_2(CO)_2(dpm)_2]$. After 30 min, the purple-brown precipitate is collected under nitrogen, washed with methanol, and recrystallized from methanol–dichloromethane (yield 52%). Anal. Calcd for $C_{52}H_{44}P_4SeO_2Rh_2$: C, 56.24; H, 3.97; P, 11.02. Found: C, 56.54; H, 4.00; P, 11.18. IR: ν(CO) 1930 s, 1918 vs cm^{-1} (Nujol).

$[Rh_2(\mu\text{-}PH(C_6H_{11}))(CO)_2(PPh_2CH_2PPh_2)_2]^+PF_6^-$. $[Rh_2Cl_2(CO)_2(dpm)_2]$ (0.1 g) is partially dissolved in 10 mL of dichloromethane. The addition of cyclohexylphosphine (12 μL) causes complete dissolution of the complex and leads to a faint red coloration of the solution. The addition of *n*-butyllithium–hexane solution (1 equiv with respect to phosphine) by syringe is accompanied by a solution color change to bright red. $NaPF_6$ (0.04 g) in 10 mL of ethanol is then added. Dichloromethane is removed on a rotary evaporator until a precipitate begins to appear. Storage of the solution of −10 °C for 12 h affords the product, which is recrystallized from dichloromethane–ethanol to give red microcrystals (yield ca. 75%). Anal. Calcd for $C_{58}H_{56}P_6F_6O_2Rh_2$: C, 53.95; H, 4.38; P, 14.42. Found: C, 54.14; H, 4.40; P, 14.40. Λ_{mM} = 80.4 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: ν(CO) 2014 s, 2000 vs; ν(P–H) 2310 w cm^{-1} (Nujol). ^1H NMR (relative to internal Me_4Si with relative intensity in parentheses): $\delta(C_6H_{11})$ 0.57 m, 1.27 m (11.2); $\delta(CH_2)$ 3.97 m, 3.67 m (4); $\delta(C_6H_5)$ 7.60 m (40). $^{31}P\{^1H\}$ NMR (relative to internal $(CH_3O)_3PO$): $\delta(PHC_6H_{11})$ 28.3 m; δ(dpm) 21.6 m, 22.4 m.

S-Alkylation of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$. Synthesis of $[Rh_2(\mu\text{-}SR)(CO)_2(PPh_2CH_2PPh_2)_2]^+PF_6^-$ (R = H, C_2H_5, CH_2Ph). The complexes with R = H or Et are synthesized as their hexafluorophosphate salts by the following method. $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (0.1 g) is dissolved in 10 mL of degassed dichloromethane. A 10% excess of triethyloxonium hexafluorophosphate (0.026 g) or hexafluorophosphoric acid–diethyl ether (0.023 g) is then added. The solution immediately changes from red to orange. Methanol (10 mL) is added to the solution. Dichloromethane is removed on a rotary evaporator until a precipitate begins to appear. Overnight storage at −10 °C leads to the product as orange crystals (yield 80–95%). Anal. Calcd for $C_{52}H_{45}P_5SF_6O_2Rh_2$ ($[Rh_2(\mu\text{-}SH)(CO)_2(dpm)_2]^+PF_6^-$): C, 51.66; H, 3.75; P, 12.83; S, 2.65. Found: C, 51.82; H, 3.89; P, 12.85; S, 2.58. Λ_{mM} = 90.3 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: ν(CO) 1991 s, 1978 vs cm^{-1} (Nujol). ^1H NMR (relative to internal Me_4Si with relative intensities in parentheses): δ(SH) 2.82 s (1); $\delta(CH_2)$ 4.64 br, 4.32 br (4); $\delta(C_6H_5)$ 7.62 (40). Anal. Calcd for $C_{54}H_{49}P_5SF_6O_2Rh_2$ ($[Rh_2(\mu\text{-}SC_2H_5)(CO)_2(dpm)_2]^+PF_6^-$): C, 52.43; H, 3.96; P, 12.54; S, 2.59. Found: C, 52.16; H, 3.91; P, 12.68; S, 2.73. Λ_{mM} = 86.8 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: ν(CO) 1992 s, 1976 vs cm^{-1} (Nujol). ^1H NMR: $\delta(CH_3$–Et) 0.56 t (2.9); $\delta(CH_2$–Et) 2.27 quar (partly obscured by solvent); $\delta(CH_2$–dpm) 4.31 br (4.1); $\delta(C_6H_5)$ 7.62 m (40).

$[Rh_2(\mu\text{-}SCH_2Ph)(CO)_2(PPh_2CH_2PPh_2)_2]^+PF_6^-$. Excess benzyl bromide (0.05 mL) is added to a 10 mL dichloromethane solution of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$. The solution gradually changes from red to orange over a period of 1 h. A 10-mL solution of $NaPF_6$ (0.04 g) in methanol is then added. Dichloromethane is removed on a rotary evaporator until a precipitate begins to appear. Storage of the solution at −10 °C for 6 h yields a microcrystalline product. Recrystallization from dichloromethane–methanol produces orange crystals (yield ca. 80%). Anal. Calcd for $C_{59}H_{51}P_5SF_6O_2Rh_2$: C, 54.55; H, 3.93; P, 11.94; S, 2.47. Found: C, 54.29; H, 3.85; P, 11.66; S, 2.35. Λ_{mM} = 86.6 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: ν(CO) 1993 s, 1963 vs cm^{-1} (Nujol). ^1H NMR: $\delta(CH_2$–PH) 3.37 s (2.2); $\delta(CH_2$–dpm) 4.36 br (4.2); $\delta(C_6H_5)$ 7.60 m (45).

Reaction of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$ with Alkyl Iodides and CO. Preparation of $[Rh_2I_2(CO)_x(PPh_2CH_2PPh_2)_2]$. $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (0.1 g) is dissolved in 10 mL of tetrahydrofuran, and an excess of methyl or ethyl iodide (ca 0.05 mL) is added. The solution rapidly changes to dark brown. CO gas is then bubbled through the solution for 30 min. The solution gradually becomes lighter in color, and a pale yellow solid is precipitated. The precipitate is recrystallized from dichloromethane–diethyl ether under an atmosphere of CO to give yellow crystals (yield ca. 90%). Anal. Calcd for $C_{54}H_{44}P_4I_2O_4Rh_2$: C, 48.37; H, 3.28; P, 9.26; I, 18.94. Anal. Calcd for $C_{53}H_{44}P_4I_2O_3Rh_2$: C, 48.48; H, 3.55; P, 9.45; I, 19.35. Found: C, 48.54; H, 3.50; P, 8.94; I, 18.84. Λ_{mM} = 75.2 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: ν(CO) 1962 vs, 1850 s (KBr); 1981 vs, 1860 s cm^{-1} (CH_2Cl_2).

Samples prepared by this method are in their spectroscopic and physical properties identical with those prepared as follows. $[Rh_2Cl_2(CO)_2(dpm)_2]$ (0.1 g) and lithium iodide (0.03 g) are dissolved together in 10 mL of tetrahydrofuran. After 10 min, the solution is dark brown. CO is then bubbled through the solution for 30 min. The pale yellow solid which is precipitated is recrystallized from dichloromethane–diethyl ether under an atmosphere of CO to give yellow crystals (yield ca. 90%).

Deprotonation of $[Rh_2(\mu\text{-}SH)(CO)_2(PPh_2CH_2PPh_2)_2]^+PF_6^-$. $[Rh_2(\mu\text{-}SH)(CO)_2(dpm)_2]^+PF_6^-$ (0.1 g) is dissolved in 10 mL of dichloromethane. One equivalent of *n*-butyllithium–hexane solution is added by syringe, and the solution immediately turns red. A red crystalline product is obtained by addition of 10 mL of methanol to the solution and removal of dichloromethane on a rotary evaporator. The product is identified as $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ by the characteristic red color and ν(CO) 1920 and 1933 cm^{-1} (Nujol).

Reaction of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$ with Methyl Isocyanide. Preparation of $[Rh_2(\mu\text{-}S)(CNMe)_2(PPh_2CH_2PPh_2)_2]$. $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (0.1 g) is dissolved in a minimal amount of dichloromethane. Methyl isocyanide (10 μL) is added to the solution. Over the period of 10 min, the solution becomes deep purple. Diethyl ether (10 mL) is then added, and the solution is stored at −10 °C overnight. The product is collected as purple microcrystals (yield ca. 70%). IR: ν(CN) 2152 s, 2183 vs cm^{-1} (KBr).

Reaction of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$ with Sulfur Dioxide. Preparation of $[Rh_2(\mu\text{-}S)(\mu\text{-}SO_2)(CO)_2(PPh_2CH_2PPh_2)_2]$. $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (0.1 g) is partially dissolved in 5 mL of toluene. A stream of SO_2 gas is passed over the mixture for ca. 5 min. The solution becomes deep purple and homogeneous. Diethyl ether (10 mL) is added, and the solution is stored at −10 °C for 24 h to obtain purple crystals (yield ca. 80%). Anal. Calcd for $C_{52}H_{44}P_4S_2O_4Rh_2$: C, 55.42; H, 3.91; P, 11.01; S, 5.68. Found: C, 55.00; H, 4.07; P, 11.04; S, 6.07. IR: ν(CO) 1990 s, 1972 vs; $\nu(SO_2)$ 1200 m, 1051 m cm^{-1} (Nujol).

Data Collection and Reduction. Red crystals of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ were obtained as above. On the basis of optical goniometry and precession photography it was determined that the crystals belong to the orthorhombic system. The observed systematic absences of $0kl$, $l = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h + k = 2n + 1$, uniquely determine the space group as $Pccn$ (D_{2h}^{10}).[18] The lattice

---

(16) Jones, G.; Bradshaw, B. C. *J. Am. Chem. Soc.* **1933**, *55*, 1780.

(17) (a) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975. (b) Mague, J. T.; Mitchener, J. P. *Ibid.* **1969**, *8*, 119.

(18) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1960; Vol. 1, p 144.

Table I

Final Positional and Thermal Parameters for $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.353 84 (5)	0.788 78 (4)	0.069 37 (4)	33.6 (4)	19.72 (25)	17.68 (22)	0.6 (3)	−0.7 (3)	−1.77 (23)
S	0.250 000 (0)	0.750 000 (0)	−0.022 12 (17)	40.6 (21)	26.9 (12)	16.8 (11)	−1.5 (16)	0.0 (0)	0.0 (0)
P(1)	0.436 81 (19)	0.677 27 (15)	0.044 69 (13)	36.4 (15)	25.1 (9)	22.6 (9)	4.7 (11)	−1.4 (10)	−2.3 (1)
P(2)	0.256 96 (20)	0.894 72 (12)	0.086 23 (13)	41.3 (16)	19.3 (8)	24.3 (9)	1.8 (11)	1.8 (11)	−2.6 (7)
C	0.438 9 (8)	0.827 5 (5)	0.132 0 (5)	62 (8)	25 (4)	24 (4)	3 (5)	−1 (5)	−2 (3)
O	0.492 6 (6)	0.858 1 (5)	0.169 4 (4)	103 (8)	47 (4)	41 (3)	−12 (4)	−31 (4)	−5 (3)
C(dpm)	0.351 0 (7)	0.596 6 (5)	0.030 9 (5)	39 (6)	21 (3)	30 (3)	−2 (4)	10 (5)	−3.6 (29)

Group Parameters

	x_c[b]	y_c	z_c	ϕ	θ	ρ	B, Å^2
P(1)C(1)	0.5610 (5)	0.67898 (24)	−0.0981 (3)	1.469 (7)	2.599 (6)	−1.484 (6)	0.0
P(1)C(2)	0.5935 (5)	0.6075 (5)	0.1524 (4)	3.129 (9)	2.629 (8)	2.326 (8)	0.0
P(2)C(1)	0.3725 (4)	1.0482 (3)	0.0463 (4)	2.188 (20)	1.847 (6)	−1.206 (20)	0.0
P(2)C(2)	0.1765 (4)	0.9185 (4)	0.2412 (3)	0.508 (5)	2.855 (5)	1.829 (5)	0.0

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Entries are $\times 10^4$. [b] x_c, y_c, and z_c are group center of mass coordinates; ϕ, θ, and ρ are angular parameters described previously;[26] B is the group thermal parameter which was not refined. In the numbering scheme for phenyl carbons, the number following P denotes the phosphorus bound to the ring, the first number following C denotes the phenyl ring, and the last number signifies the position of the carbon atom in the ring with 1 being bonded to phosphorus.

constants at 22 °C were determined from a least-squares refinement of the setting angles of 12 high-angle reflections ($(\sin\theta)/\lambda \geq 0.2772$).[19] The reflections were carefully centered, by using Mo Kα radiation ($\lambda = 0.7093$ Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are $a = 13.708$ (7) Å, $b = 17.504$ (9) Å, and $c = 19.302$ (11) Å. An experimental density of 1.51 (1) g/cm^3 determined by the flotation method agrees with a value of 1.525 g/cm^3 for $Z = 4$.

The mosaicity of the crystal used for intensity measurements was examined by means of a narrow-source, open-counter ω-scan technique.[20] The full widths at half-maximum for typical strong reflections were ≤0.12°.

The crystal dimensions were approximately 0.18 × 0.22 × 0.24 mm, and the crystal was mounted with the c^* axis offset by 4° from the ϕ axis of the diffractometer.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the X-ray tube was 1.8°. The scan was from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak. The scan speed was 1°/min, and backgrounds were counted for 10 s at each end of the scan range. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10 000 counts/s. The pulse height analyzer was set for a 90% window centered on Mo Kα radiation.

Data were collected in the range $3° \leq 2\theta \leq 45°$ from the octant with $h,k,l \geq 0$. The three standard reflections were monitored every 77 observations. The intensities of the standards varied by less than ±3%. A total of 3576 reflections were observed. The values of I and $\sigma^2(I)$[21] were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections. The linear absorption coefficient for Mo Kα radiation is 9.05 cm^{-1}, and no correction for absorption was made. The final data set consisted of 3062 independent relfections of which 1884 had $F_o^2 \geq 3\sigma(F_o^2)$.

Solution and Refinement of the Structure. The structure was solved by standard heavy-atom methods and partially confirmed by direct methods.[22] The position of the rhodium atom was determined from a three-dimensional Patterson map. The positions of two phosphorus atoms and a sulfur atom on the twofold symmetry axis ($^1/_4$, $^3/_4$, z) of the space group $Pccn$ were also deduced from the Patterson map. Application of the direct-methods program package MULTAN III, using the 300 largest normalized structure factors and the tangent formula result with the highest figure of merit, confirmed the rhodium, sulfur, and two phosphorus atom positions. Refinement of the scale factor, atomic positional, and isotropic thermal parameters of these four atoms resulted in residuals of $R_1 = 0.22$ and $R_2 = 0.31$.[23] In this and all subsequent refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights w were taken as $4F^2/\sigma^2(F^2)$. Only those reflections with $F^2 \geq 3\sigma(F^2)$ were included in the refinements. Scattering factors for neutral Rh, S, P, O, and C were those of Cromer and Mann.[24] The effects of anomalous dispersion were included in the calculation of $|F_c|$; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[25]

A difference Fourier synthesis phased by the rhodium, sulfur, and two phosphorus atoms revealed the positions of all remaining hydrogen atoms in the structure. The phenyl rings were treated as rigid groups with d(C–C) = 1.392 Å.[26] Refinement of a model in which all atoms were treated isotropically resulted in $R_1 = 0.074$ and $R_2 = 0.093$. During refinement, one of the four independent phenyl rings showed unusually high isotropic thermal parameters for three of its carbon atoms, specifically B values of 17.7, 24.3, and 12.0 Å^2 for P(1)C(22), P(1)C(23), and P(1)C(24), respectively. The other three carbon atoms in the ring showed nearly normal thermal motion, with isotropic thermal parameters B in the range 5–9 Å^2. The possibilities that the initial parameters for this phenyl ring had been incorrect or that the phenyl ring had wandered from its true position during refinement were eliminated by the following test. The six questionable carbon atoms were removed; and the remaining parameters were refined by least squares. A subsequent difference Fourier calculation returned the original six positions for the phenyl carbon atoms. A model which included the six recalculated positions with temperature factors fixed at $B = 5.0$ Å^2 was refined to convergence. The ensuing difference Fourier calculation did not show peaks of sufficient electron density or of reasonable resemblance to a phenyl ring to justify a disorder model. A subsequent refinement in which the temperature factors of the problematic phenyl carbon atoms were allowed to vary again led to high isotropic parameters for P(1)C(22), P(1)C(23), and P(1)C(24).

We concluded that the unusually large thermal motion exhibited by this ring would be best described by anisotropic thermal parameters. Initially, only nongroup atoms were refined anisotropically, leading

---

(19) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corp.

(20) Furnas, T. C. "Single Crystal Orienter Instruction Manual"; General Electric Co.: Milwaukee, Wis., 1957; Chapter 10.

(21) Goldberg, S. Z.; Kubiak, C.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* **1975**, *14*, 1650.

(22) All computations were performed on an IBM 360/65 computer. The data processing program was an extensively modified version of Raymond's URFACS. In addition, local versions of the following were used: Ibers' NUCLS, a group least-squares program; Zalkins' FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plotting program; Woolfson's MULTAN III direct methods package.

(23) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The estimated standard deviation of an observation of unit weight is given by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v are the number of observations and variables, respectively.

(24) Cromer, D. T.; Mann, B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(25) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(26) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773. LaPlaca, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1965**, *87*, 2851; *Acta Crystallogr.* **1965**, *18*, 511.

Table II. Derived Positional Parameters and Anisotropic Thermal Parameters of Group Atoms

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)C(11)	0.5081 (6)	0.6762 (4)	−0.0366 (4)	68 (8)	19 (4)	30 (4)	1 (5)	18 (5)	−3 (3)
P(1)C(12)	0.6095 (6)	0.6716 (5)	−0.0351 (4)	31 (8)	68 (7)	73 (7)	10 (6)	30 (6)	17 (6)
P(1)C(13)	0.6624 (5)	0.6744 (5)	−0.0966 (6)	59 (10)	65 (7)	83 (8)	19 (7)	34 (8)	27 (7)
P(1)C(14)	0.6139 (8)	0.6817 (5)	−0.1596 (5)	92 (13)	52 (6)	73 (8)	24 (7)	37 (8)	11 (6)
P(1)C(15)	0.5125 (8)	0.6863 (5)	−0.1611 (4)	143 (16)	91 (10)	34 (5)	18 (10)	22 (8)	−2 (6)
P(1)C(16)	0.4597 (5)	0.6836 (5)	−0.0996 (5)	99 (11)	88 (8)	22 (4)	9 (8)	13 (6)	−6 (5)
P(1)C(21)	0.5244 (6)	0.6366 (5)	0.1066 (4)	45 (7)	51 (5)	32 (4)	24 (5)	−8 (5)	−9 (4)
P(1)C(22)	0.5599 (9)	0.6821 (6)	0.1601 (7)	307 (28)	133 (14)	156 (15)	161 (17)	−190 (18)	−111 (12)
P(1)C(23)	0.6290 (11)	0.6529 (8)	0.2059 (7)	523 (52)	183 (20)	226 (23)	250 (28)	−295 (30)	−137 (18)
P(1)C(24)	0.6626 (8)	0.5784 (8)	0.1981 (6)	183 (21)	135 (14)	56 (8)	72 (14)	−54 (11)	−13 (8)
P(1)C(25)	0.6270 (8)	0.5329 (5)	0.1446 (6)	91 (13)	111 (10)	56 (7)	47 (10)	8 (8)	26 (7)
P(1)C(26)	0.5579 (7)	0.5621 (5)	0.0988 (5)	73 (10)	59 (6)	56 (6)	34 (7)	−6 (7)	28 (5)
P(2)C(11)	0.3191 (5)	0.9837 (3)	0.0647 (5)	40 (6)	21 (4)	41 (5)	4 (4)	9 (5)	0 (4)
P(2)C(12)	0.3653 (6)	1.0268 (5)	0.1156 (4)	63 (9)	28 (4)	64 (6)	−2 (6)	−24 (7)	−4 (4)
P(2)C(13)	0.4188 (6)	1.0913 (4)	0.0973 (6)	74 (10)	32 (5)	75 (7)	−14 (6)	−15 (7)	8 (5)
P(2)C(14)	0.4260 (6)	1.1127 (4)	0.0280 (6)	65 (10)	31 (6)	103 (9)	−9 (6)	16 (9)	10 (6)
P(2)C(15)	0.3797 (8)	1.0696 (6)	−0.0229 (4)	167 (18)	47 (6)	64 (7)	−38 (9)	36 (9)	6 (6)
P(2)C(16)	0.3263 (7)	1.0051 (5)	−0.0046 (4)	135 (14)	49 (6)	47 (6)	−32 (8)	29 (7)	2 (5)
P(2)C(21)	0.2127 (5)	0.9095 (4)	0.1743 (3)	37 (7)	32 (4)	31 (4)	2 (4)	3 (4)	−11 (4)
P(2)C(22)	0.2356 (5)	0.8563 (4)	0.2254 (5)	68 (9)	55 (5)	25 (4)	−22 (6)	12 (5)	−1 (4)
P(2)C(23)	0.1994 (7)	0.8653 (5)	0.2923 (4)	70 (10)	87 (8)	35 (5)	−27 (7)	13 (6)	−10 (5)
P(2)C(24)	0.1404 (6)	0.9276 (6)	0.3081 (4)	70 (11)	135 (13)	47 (7)	−58 (10)	34 (8)	−44 (8)
P(2)C(25)	0.1174 (5)	0.9808 (5)	0.2570 (5)	74 (11)	87 (9)	50 (6)	−14 (8)	11 (7)	−47 (6)
P(2)C(26)	0.1536 (6)	0.9717 (4)	0.1901 (4)	48 (8)	48 (5)	49 (5)	0 (6)	−8 (6)	−31 (4)

to $R_1 = 0.067$ and $R_2 = 0.080$. The least-squares program NUCLSA which permits anisotropic refinement of group and nongroup atoms was then used. In the final model, all group and nongroup atoms were refined anisotropically. The contributions of phenyl hydrogen atoms were not included in the calculation of $|F_c|$. The total of 228 variables was refined to convergence with residuals of $R_1 = 0.047$ and $R_2 = 0.055$. In the final cycle of refinement, no parameters shifted by more than 12% of their estimated standard deviations. The final estimated standard deviation for an observation of unit weight was 1.74 e.[23] The largest peak of a final difference Fourier map was 0.8 e/Å^3 or 25% of a typical carbon atom peak in this study and was <0.5 Å from P(1)C(23).

The final atomic positional and thermal parameters and phenyl group parameters are given in Table I. Derived positional and thermal parameters for the group atoms are given in Table II. A listing of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Synthesis of A-Frame Complexes. The reaction of $[Rh_2Cl_2(CO)_2(dpm)_2]$ with the chalcogenide ions S^{2-} or Se^{2-} leads to the displacement of both chlorides and formation of neutral complexes $[Rh_2(\mu\text{-}Y)(CO)(dpm)_2]$ (Y = S, Se). The structure of the sulfide has been determined by X-ray crystallography (vide infra) to be an A frame, $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$.

IR spectra of the sulfide and selenide are virtually superimposable, with only slight differences seen in values of ν(CO) 1920 vs and 1933 s cm^{-1} (Y = S) vs. 1918 vs and 1930 s cm^{-1} (Y = Se). The IR data and the analytical results indicate that the Y = Se complex possesses a completely analogous A-frame structure to that of the sulfide derivative.

The preparation of the μ-cyclohexyl phosphide A frame depends on the in situ generation of the highly nucleophilic cyclohexyl phosphide ion by deprotonation of cyclohexyl phosphine. The formulation as a μ-phosphide A-frame cation $[Rh_2(\mu\text{-}PH(C_6H_{11}))(CO)_2(dpm)_2]^+$ is based on microanalytical, conductivity, IR, and ^{1}H and $^{31}P\{^1H\}$ NMR data. We conclude that $[Rh_2(\mu\text{-}PH(C_6H_{11}))(CO)_2(dpm)_2]^+PF_6^-$ is a 1:1 electrolyte from conductivity measurements of nitromethane solutions. The Onsager plot of the equivalent conductance, Λ_e, vs. $c^{1/2}$, where c is the concentration in equiv/L, has a slope −589 cm^2 Ω^{-1} equiv$^{-3/2}$ L$^{1/2}$ which compares well with values for PF_6^- salts of similar 1:1 electrolytes in nitromethane solution (Table III). The appearance of two ν(CO) at 2000 and 2014 cm^{-1} is consistent with an A-frame structure in which the stretching frequencies increase due to the positive charge of the complex. Analysis of the $^{31}P\{^1H\}$ NMR is complicated by what appears to be extensively overlapped dpm and phosphide resonances. Two multiplets centered at δ 21.6 and 22.4 each show two intense principal lines separated by 124 and 130 Hz, respectively. These are assigned to two pairs of equivalent dpm phosphorus nuclei coupled to rhodium. A less intense five-line multiplet centered at δ 28.3 is assigned to the bridging cyclohexyl phosphide, coupled to four dpm phosphorus nuclei ($J_{P_{Cy}-P_{dpm}} \approx 30$ Hz). Additional upfield lines, nearly overlapping the dpm resonances, support an assignment of the five-line multiplet as one part of the A-spectrum of the ABB′CC′XX′ triplet of quintets ($J_{Rh-P_{Cy}} \approx 170$ Hz). In the ^{1}H NMR, the cyclohexyl protons appear at δ 0.57 and 1.27 (cf. cyclohexylphosphine, δ 1.07, 1.66) and show the expected 11:4:40 intensity ratio to the dpm methylene and phenyl proton resonances. We have been unable to assign an ^{1}H resonance to the phosphide proton and suspect that the split components from the expectedly large J_{P-H} are concealed by other resonances. However, in the IR spectrum, a characteristic weak absorption at 2310 cm^{-1} is observed and assigned to ν(P–H).[27] The presence of the phosphide proton is also suggested by the

Table III. Conductivity Data for Rhodium A-Frame Complexes

complex	Λ_0	slope[a]	Λ_{mM}[b]
$[Rh_2(\mu\text{-}SH)(CO)_2(dpm)_2]^+PF_6^-$	111.5	−670	90.3
$[Rh_2(\mu\text{-}SEt)(CO)_2(dpm)_2]^+PF_6^-$	108.0	−669	86.8
$[Rh_2(\mu\text{-}SCH_2Ph)(CO)_2(dpm)_2]^+PF_6^-$	104.6	−569	86.6
$[Rh_2(\mu\text{-}PHC_6H_{11})(CO)_2(dpm)_2]^+PF_6^-$	99.0	−589	80.4
$[Rh_2I_2(CO)_x(dpm)_2]$	89.7	−460	75.2
$[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]^+PF_6^-$	112.2	−751	88.5
$NH_4^+PF_6^-$	143.9	−546.5	126.6

[a] Units of slope are cm^2 ohm^{-1} equiv$^{-3/2}$ L$^{1/2}$ obtained by plotting the equivalent conductance, Λ_e, of nitromethane solutions vs. $c^{1/2}$, where c is the concentration in equivalents per liter.
[b] Equivalent conductance at 0.001 M concentration.

---

(27) Sanders, J. R. *J. Chem. Soc. A* **1971**, 2991.

(28) For NMR data: s = singlet, t = triplet, quar = quartet, quin = quintet, m = multiplet, br = broad. For IR data: vs = very strong, s = strong, m = medium, w = weak. For conductivity: Λ_{mM} = equivalent conductance at 0.001 M concentration.

(29) (a) Hoare, R. J.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2138. (b) Bonnet, J. J.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1977**, *16*, 1514. (c) Huq, F.; Skapski, A. C. *J. Cryst. Mol. Struct.* **1974**, *4*, 411.

overall charge of the complex. Attempts to deprotonate the phosphide with strong base to obtain a neutral Rh–PCy–Rh species, analogous to the aforementioned sulfide and selenide complexes, have proved unsuccessful. The extension of the synthetic route taken for the cyclohexyl phosphide A frame to the bulkier secondary phosphines, PPh_2H and PCy_2H, have led only to unstable mixtures.

S-Alkylation and Protonation of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)_2]$. The reaction of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ with R^+ (R = H, Et) leads to new A-frame cations $[Rh_2(\mu\text{-}SR)(CO)_2(dpm)_2]^+$ in which the bridgehead sulfide is protonated or alkylated. The hexafluorophosphate salts of the complexes are 1:1 electrolytes in nitromethane solution as evidenced by conductivity measurements. Conductivity data for these and related 1:1 electrolytes are given in Table III. Both complexes exhibit similar ν(CO) values of 1978 and 1991 cm^{-1} and 1976 and 1992 cm^{-1} for the protonated and ethylated derivatives, respectively. For R = H, the sulfhydryl proton resonance appears at δ 2.82 s in the ^1H NMR, while for R = Et, characteristic methylene and methyl resonances appear at δ 2.27 quar and δ 0.56 t. The fact that additional coupling to either phosphorus or rhodium is not observed is consistent with S-alkylation.

The cationic complexes $[Rh_2(\mu\text{-}SR)(CO)_2(dpm)_2]^+$ (R = H, Et) are isoelectronic with the cyclohexyl phosphide species $[Rh_2(\mu\text{-}PHCy)(CO)_2(dpm)_2]^+$. In contrast to the phosphide complex, however, the sulfhydryl proton in $[Rh_2(\mu\text{-}SH)(CO)_2(dpm)_2]^+$ can be removed by strong base, regenerating the sulfide $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$.

Besides the highly electrophilic reagents Et_2OR^+ (R = H, Et) benzyl bromide effects S-alkylation of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$. The hexafluorophosphate salt of $[Rh_2(\mu\text{-}SCH_2Ph)(CO)_2(dpm)_2]^+$, prepared by metathesis of the bromide salt initially formed, shows 1:1 electrolyte behavior similar to the protonated and ethylated derivatives. The benzyl mercaptide complex is obtained analytically pure and exhibits ν(CO) 1993 s and 1963 vs cm^{-1}. The α-methylene protons appear as a singlet at δ 3.37 in the ^1H NMR, consistent with S-alkylation.

Removal of Sulfide. Reaction with Alkyl Iodides and CO. The reaction of the sulfide A frame, $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$, with RI (R = Me, Et) followed by treatment with CO leads to removal of sulfur. While the reaction with benzyl bromide leads cleanly to the *S*-benzyl alkylated A frame, THF solutions which contain $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ rapidly turn dark brown when reacted with RI. The species in solution is characterized by ν(CO) 1940 cm^{-1} (THF) and has not been isolated in pure form. When CO is introduced, the solution becomes lighter in color, and a yellow complex is precipitated. The yellow complex shows both terminal and bridging ν(CO) at 1962 vs and 1850 cm^{-1} (KBr). Evidence for sulfur removal is found in microanalytical data and in the independent preparation of the complex from $[Rh_2Cl_2(CO)_2(dpm)_2]$, LiI, and CO. We originally formulated the yellow complex as $[Rh_2I_2(\mu\text{-}CO)_2(CO)_2(dpm)_2]$[6] on the basis of microanalysis, the appearance of only a single terminal and single bridging ν(CO), and somewhat weaker electrolytic behavior than that of related 1:1 electrolytes (Table III). Since that time it has come to our attention that a second reasonable formulation is $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dpm)_2]^+I^-$, similar to the recently reported μ-CO adduct of the chloride A-frame cation, $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$.[2] We have found some support for the second formulation in results of a spectrophotometric titration of the yellow complex with $AgPF_6$. Monitoring the 2200–1800-cm^{-1} carbonyl stretching region of the IR spectrum of a dichloromethane solution, we observe no change in ν(CO) 1982 and 1860 cm^{-1} when between 0 and 1 equiv of $AgPF_6$ is added. However, upon addition of between 1 and 2 equiv of $AgPF_6$, the peak at 1860 cm^{-1} diminishes proportionately in intensity, the region between 1970 and 1990 cm^{-1} broadens, and a new peak grows in at 2060 cm^{-1}. The results of the spectrophotometric titration suggest that in solution only one of the two iodides is coordinated to the complex.

The observations regarding the Ag^+ spectrophotometric titration and relatively low conductivity of solutions of the complex can be reconciled by a close ionic association of an iodide with a cationic complex. The results of microanalysis are slightly better for our original formulation but are not unreasonable for $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dpm)_2]^+I^-$. The observation of only a single ν(CO) in the terminal CO stretching region is inconsistent with the proposed μ-I, μ-CO structure, but may arise from a near degeneracy of the terminal ν(CO) vibrational modes. We conclude that the most reasonable formulation in solution is $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(dpm)_2]^+I^-$, similar to the structurally characterized chloride.[2] We have undertaken an X-ray study of the crystalline yellow solid $[Rh_2I_2(CO)_x(dpm)]$ but unfortunately have been unsuccessful in solving the structure.

Reactions of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ at the Metal Centers. Evidence for reactivity at the metal centers of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ is found in its reaction with SO_2. The product obtained, on the basis of microanalytical data, is a 1:1 SO_2 adduct. The reaction is easily reversed by warming a toluene solution of the adduct under a N_2 stream for 15 min. The values of $\nu(SO_2)$ (1200 m, 1051 m cm^{-1}) are consistent with reported values for bridging SO_2 complexes.[3,8,30-32] The values of ν(CO) (1972 vs, 1990 s cm^{-1}) are raised considerably over those for the starting material, $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ (1920 vs, 1933 s cm^{-1}). The separation between symmetric and asymmetric stretching absorptions, however, remains relatively constant. This mitigates against the possibility of an unsymmetrical adduct, with SO_2 bound to only one of the two metal centers. We find no evidence of intermediate species in this reaction; only the product and starting sulfide A frame are observable by IR in solution when SO_2 is added. The reaction of the sulfide A frame to form an endo μ-SO_2 adduct, $[Rh_2(\mu\text{-}S)(\mu\text{-}SO_2)(CO)_2(dpm)_2]$, is analogous to the formation of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)(CO)_2(dpm)_2]^+$[3] from the corresponding rhodium chloride A-frame cation. Sanger et al. claim the formation of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)(CO)_2(dpm)_2]^+$ proceeds by direct attack of SO_2 at the endo or pocket site of the A-frame structure.[3,14] Our IR observations of the reaction of the sulfide A frame with SO_2 suggest a similar direct formation of an endo adduct, $[Rh_2(\mu\text{-}S)(\mu\text{-}SO_2)(CO)_2(dpm)_2]$.

Although the chloride- and sulfide-bridged rhodium A frames exhibit parallel chemistry in their reactions with SO_2, only the chloride forms a stable endo μ-CO adduct.[2] Sanger et al. have reported CO labeling studies of the formation of the endo μ-CO adduct, $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$, which show that the bridging carbonyl originates as one of the two terminal carbonyls in $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]^+$. In contrast, we find no evidence of a reaction on the sulfide A frame with CO. Solutions of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ show no changes of their IR spectra when placed under 1 atm of CO. The reaction of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ with methyl isocyanide similarly does not lead to stable adducts. Instead, substitution of CO is observed, leading to $[Rh_2(\mu\text{-}S)(CNMe)_2(dpm)_2]$ with ν(CN) 2152 s and 2183 vs cm^{-1}. It is interesting to note that the species $[Rh_2(\mu\text{-}SR)(CO)_2(dpm)_2]^+$ (R = H, Et, CH_2Ph) which are analogous in both

---

(30) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

(31) Otsuka, S.; Tutsumo, Y.; Miki, M.; Aoke, T.; Matsumato, M.; Yoshioko, H.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1973**, 445.

(32) Angoletta, M.; Bellon, P. L.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1974**, *81*, C40.

(33) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

(34) Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840.

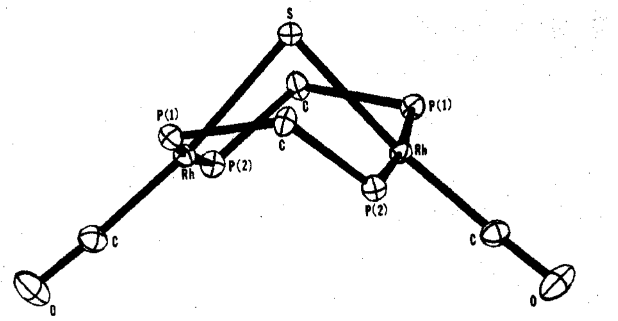


Figure 1. Perspective view of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$. Phenyl rings have been omitted.

their structure and charge to $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]^+$ also fail to form stable CO adducts.

The sulfide A frame does not react readily with H_2. We have been unable to detect a reaction between the complex and H_2 in solution. Indirect evidence for a reaction is found in the catalytic reduction of ethylene to ethane by toluene solutions of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ under a 1:1 H_2–ethylene atmosphere. This reaction, however, is exceedingly slow (4–6 turnovers/day at 25 °C), and studies of it have been abandoned.

Solid-State Structure of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$. The crystal structure is composed of discrete molecules of $[Rh_2(\mu\text{-}S)(CO)_2(PPh_2CH_2PPh_2)]$ exhibiting the A-frame arrangement. The asymmetric unit consists of one-half molecule with the bridging sulfur atom situated on a twofold rotation axis parallel to *c*. Each molecule is therefore twofold symmetric.

The molecular structure consists of two rhodium atoms bridged by two bis(diphenylphosphino)methane (dpm) ligands and a sulfur atom. The two carbon monoxides are approximately trans to sulfur (S–Rh–C = 172.8 (3)°). The phosphorus atoms of each of the two dpm ligands are also transoid in their coordination to rhodium (P(2)–Rh–P(1) = 173.49 (9)°). The cis relationship of both the sulfur and carbon monoxide to the phosphines (S–Rh–P(2) = 89.40 (7)°, S–Rh–P(1) = 84.25 (7)°, C–Rh–P(2) = 88.6 (3)°, C–Rh–P(1) = 97.9 (3)°) completes the approximately square-planar coordination about each rhodium. The largest displacement of an atom from the (Rh, P(1), P(2), S, C) least-squares plane is 0.17 (1) Å, for the carbonyl carbon. The two square planes are inclined at a dihedral angle of 83.3°. The Rh···Rh separation of 3.154 (2) Å is significantly longer than the separation between adjacent dpm phosphorus atoms (3.047 (4) Å). The stability of the square-planar geometry for discrete mononuclear d^8 complexes suggests that no M–M bond is required in the A-frame arrangement. Indeed, the Rh–Rh internuclear distance is much greater than those found for Rh–Rh electron pair bonds in polynuclear cluster compounds (2.6–2.8 Å).[35-37] The Rh–Rh distance, 3.154 (2) Å, of the sulfide A-frame, however, is shorter than that found in a dam-bridged complex in which the two square-planar units are parallel, $[Rh_2Cl_2(CO)_2(dam)_2]$ (3.396 (1) Å). The close proximity of the rhodium centers in $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ and red color of the complex suggest a significant, but nonbonding, Rh–Rh interaction. The red color represents a considerable absorption shift toward the visible compared to mononuclear square-planar rhodium complexes which are usually yellow. Similar shifts observed in the visible spectra of binuclear rhodium complexes have recently been explained as proximity shifted M–L charge-transfer transitions.[34]

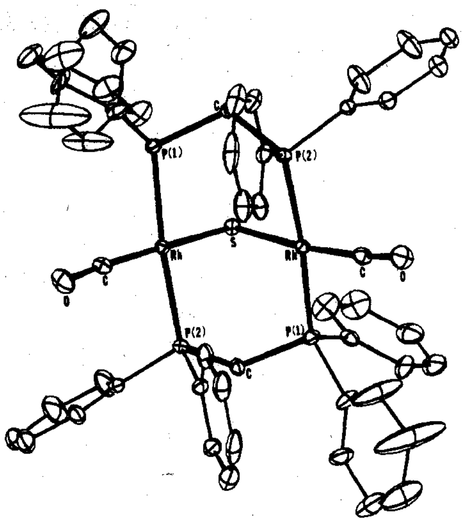


Figure 2. Perspective view of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ with phenyl rings. The thermal ellipsoids correspond to 50% probability distributions.

Table IV. Important Structural Parameters for $Rh_2(\mu\text{-}S)(CO)_2(dpm)_2$

Intramolecular Distances (Å)			
Rh–C	1.81 (1)	C–O	1.16 (1)
Rh–P(2)	2.304 (3)	C···P(2)	2.90 (1)
Rh–P(1)	2.309 (3)	C···P(1)C(22)	3.09 (1)
Rh–S	2.367 (3)	Rh···P(2)C(11)	3.446 (6)
Rh···Rh	3.154 (2)	P(1)···P(2)	3.047 (4)
P(1)–C(dpm)	1.858 (9)	C···P(1)H(22)	2.23
P(1)–P(1)C(21)	1.837 (9)	P(2)H(22)···P(2)H(22)	2.34
P(1)–P(1)C(11)	1.848 (8)	O···P(1)H(22)	2.27
P(2)–P(2)C(11)	1.823 (7)	S···P(1)H(16)	2.69
P(2)–P(2)C(21)	1.823 (7)	C···P(2)H(22)	2.75
P(2)–C(dpm)	1.83 (1)		
Intermolecular Distances (Å)			
O···P(1)C(15)	3.37 (1)	P(1)H(24)···P(2)H(12)	2.43
O···P(2)C(15)	3.56 (1)	P(2)H(13)···P(2)H(24)	2.47
P(1)C(13)···P(1)C(13)	3.57 (2)	P(2)H(16)···P(2)H(24)	2.51
P(1)C(24)···P(2)C(25)	3.57 (1)	O···P(1)H(15)	2.60
P(2)C(13)···P(2)C(24)	3.56 (1)	O···P(2)H(25)	2.67
P(2)C(25)···O	3.59 (1)		
Bond Angles (Deg)			
C–Rh–P(2)	88.6 (3)	P(1)C(21)–P(1)–P(1)C(11)	101.7 (4)
C–Rh–P(1)	97.9 (3)	P(1)C(21)–P(1)–C(dpm)	102.3 (4)
C–Rh–S	172.8 (3)	P(1)C(21)–P(1)–Rh	121.0 (3)
P(2)–Rh–P(1)	173.49 (9)	P(1)C(11)–P(1)–C(dpm)	101.9 (4)
P(2)–Rh–S	89.40 (7)	P(1)C(11)–P(1)–Rh	116.4 (3)
P(1)–Rh–S	84.25 (7)	P(2)C(11)–P(2)–P(2)C(21)	104.3 (4)
Rh–S–Rh	83.5 (1)	P(2)C(11)–P(2)–C(dpm)	100.0 (4)
C(dpm)–P(1)–Rh	116.7 (3)	P(2)C(11)–P(2)–Rh	112.7 (3)
O–C–Rh	174.3 (9)	P(2)C(21)–P(2)–C(dpm)	105.2 (4)
P(2)–C(dpm)–P(1)	111.4 (5)	P(2)C(21)–P(2)–Rh	115.9 (3)
Dihedral Angle between Planes (Deg)			
C, Rh, S, P(1), P(2) C′, Rh′, S, P(1)′, P(2)′	83.3 (3)		

Figure 1 presents a perspective view of the molecule in which the phenyl rings have been omitted. A second view, with phenyl rings, appears in Figure 2. Interatomic distances and angles are given in Table IV.

The bonding distances in the structure appear normal. The two Rh–P bond lengths of 2.309 (3) and 2.304 (3) Å are slightly shorter than or equal to those found in some related Rh–dpm structures (cf. 2.331 (8) in $[Rh_2(\mu\text{-}SO_2)Cl_2(dpm)_2]$,[3] 2.333 (8) in $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpm)_2]^+BPh_4^-$,[2] 2.321

---

(35) Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331. Mills, O. S.; Paulus, E. F. *Ibid.* **1968**, *11*, 587.

(36) Paulus, E. F.; Fischer, E. O.; Fritz, H. P.; Schuster-Woldan, H. *J. Organomet. Chem.* **1967**, *10*, 3.

(37) Wei, C. H.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 4792.

(2) in $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]^+BF_4^-$,[14] and 2.309 (4) Å in $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+(p\text{-}CH_3C_6H_4SO_3^-)$.[4] The Rh–C bond length of 1.81 (1) Å compares well with those of the carbonyl complexes above and with those of rhodium carbonyl complexes in general.[29] The Rh–S bond length of 2.367 (3) Å is near those reported for a dirhodium bis[μ-(phenylthiolato)] complex (2.372 (2) and 2.403 (2) Å).[29b] The P–C bond lengths in the dpm ligand range from 1.823 (7) to 1.859 (9) Å and are typical for dpm complexes.[2-4,14]

Unusually close intramolecular contacts occur between the carbon monoxide and phenyl hydrogen atoms. Although the contribution of phenyl hydrogens was not included in the calculation of $|F_c|$, idealized phenyl hydrogen positions were calculated to identify which portions of the overall structure might be affected by their presence. A C–H bond length of 0.95 Å was assumed. The closest approach of a phenyl hydrogen to other atoms involves P(1)H(22). P(1)H(22) is the hydrogen bound to phenyl carbon P(1)C(22) (see footnote to Table I for numbering scheme). The hydrogen is approximately equidistant to the carbonyl C and O atoms (C–P(1)-H(22) = 2.23 and O–P(1)H(22) = 2.27 Å). It should be noted that the phenyl carbon, P(1)C(22), to which this hydrogen is bound, was one which showed unusually large and anisotropic thermal motion in the refinement of the structure. We attribute the problems encountered in refinement to distortions of the phenyl ring (P(1)C(2)) caused by the P(1)H(22)···C—O interaction.

The closest intramolecular nonbonded H···H contact is between symmetry related P(2)H(22) hydrogens (2.34 Å). All other phenyl hydrogen distances are greater than the sum of van der Waals radii (2.4 Å). The three closest intermolecular H···H distances are 2.43 (P(1)H(24)···P(2)H(12)), 2.47 (P(2)H(13)···P(2)H(24)), and 2.51 Å (P(2)H(16)···P(2)H(24)). A partial tabulation of close intra- and intermolecular contacts is given in Table IV.

An unusual feature of the present structure is the high degree of twisting of the $Rh_2P_4C_2$ ring. This is manifested in a P(1)–Rh–Rh–P(2) torsion angle of 20.19 (9)° which contrasts with values of 0.16 (6)° and 3.70 (5)° for the closely related μ-chloride rhodium A frame $[Rh_2(\mu\text{-}Cl)(CO)_2(dpm)_2]^+BF_4^-$. Two gross structural effects are caused by the staggered phosphine conformation: (1) it places one pair of symmetry related phenyl rings (P(1)C(2)) in near proximity to the carbon monoxides, resulting in unusually close P—H···C—O contacts (vide supra), and (2) it places a second pair of phenyl rings within the endo pocket envisioned for binuclear substrate bonding. This placement of the phenyl rings blocks the pocket. There is no obvious explanation regarding the origin of the dpm twisting. A less pronounced twist has been observed recently in $[Rh_2(\mu\text{-}SO_2)Cl_2(dpm)_2]$, while most similar structures reported to date exhibit nearly eclipsed phosphine conformations.

Conclusions. The reactivity of the rhodium sulfide A frame, $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$, is generally localized at the bridgehead sulfur. Electrophilic reagents, Et_2OR^+ (R = Et, H), and alkyl halides react at sulfur leading to S-alkylated or protonated A-frame complexes. In the case of the reaction with alkyl iodides followed by CO, sulfur removal, presumably as R_2S, is observed.

The X-ray structure of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ suggests that the placement of two dpm phenyl rings effectively blocks the metal centers. This observation is consistent with, but may not be the cause of, the dominant role of sulfur in reactions with electrophilic reagents. The steric hindrance of the phenyl rings in access to the A-frame pocket is belied by the facile reaction of the complex with SO_2. In solution, the μ-S A-frame complex probably exhibits an interconvertibility of conformations of the $Rh_2P_4C_2$ ring. We therefore believe our inability to observe stable adducts of the complex with CO or H_2 is determined more by electronic factors affecting stability in solution than by structural effects in the solid. We find some support for this notion in our recent observation and structural characterization of stable adducts of the analogous iridium complex, $[Ir_2(\mu\text{-}S)(CO)_2(dpm)_2]$, with both CO and H_2, which will be reported separately.[5]

Acknowledgment. We wish to thank the National Science Foundation (Grants CHE76-17440 and 79-10390) for support of this work and Matthey Bishop Co., Inc., for a generous loan of precious metal salts. C.P.K. gratefully acknowledges Sherman Clarke and Elon Huntington Hooker Fellowships held over the course of this work.

Registry No. $Rh_2(\mu\text{-}S)(CO)_2(dpm)_2$, 64424-95-9; $Rh_2Cl_2(CO)_2(dmp)_2$, 22427-58-3; $Rh_2(\mu\text{-}Se)(CO)_2(dpm)_2$, 73972-16-4; $[Rh_2(\mu\text{-}PH(C_6H_{11}))(CO)_2(dpm)_2]^+PF_6^-$, 73972-18-6; $[Rh_2(\mu\text{-}SCH_2Ph)(CO)_2(dpm)_2]^+PF_6^-$, 73972-20-0; $[Rh_2(\mu\text{-}SC_2H_5)(CO)_2(dpm)_2]^+PF_6^-$, 64424-98-2; $[Rh_2(\mu\text{-}SH)(CO)_2(dpm)_2]^+PF_6^-$, 73972-22-2; $Rh_2I_2(CO)_3(dpm)_2$, 73972-23-3; $Rh_2(\mu\text{-}S)(CNMe)_2(dpm)_2$, 64424-96-0; $Rh_2(\mu\text{-}S)(\mu\text{-}SO_2)(CO)_2(dpm)_2$, 73971-84-3; $Rh_2(\mu\text{-}Cl)_2(LS\text{-}COD)_2$, 12092-47-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.