

Heterobimetallic Complexes. The Preparation, Solid-State Structure, and Fluxional Behavior of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$

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Abstract: The synthesis, solid-state crystal structure, cyclic voltammetry, and spectroscopic characterization of the first organobimetallic complex with a crystallographically demonstrated Rh to Mo bond, $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$, are reported. The X-ray diffracton structural analysis shows that the complex adopts a solid-state conformation with a tightly folded RhP_2Mo framework. The Rh-Mo metal-metal bond distance is 2.9212 (7) Å, and one of the carbonyl ligands on Mo is directed toward the Rh atom and C_5Me_5 ring causing unsymmetrical coordination of the ring. NMR studies show that the complex is highly fluxional with a surprisingly facile axial to equatorial carbonyl interchange mechanism.

Introduction

There is increasing evidence that binuclear transition-metal complexes will play at least two important roles in the systematic development of organotransition-metal chemistry. In one role, these relatively simple compounds can serve as models for more complex systems. Fundamental studies of binuclear oxidative additions, migratory insertions, and reductive eliminations should significantly aid the development and interpretation of polymetallic or cluster-catalyzed reactions. In a second role, the reactions of bimetallic compounds should prove unique and useful in their own right. This potential is suggested by recent studies revealing bimetallic mechanisms in reactions previously believed to take place at a single metal site.² Especially interesting are the recent applications of mixed-metal systems in organic synthesis³ and in CO and H_2 chemistry.⁴ For these reasons, bimetallic systems are of considerable current interest.⁵

Phosphido-bridged binuclear transition-metal complexes comprise an important subgroup of bimetallic compounds. The tenaciously bridging and chemically inert phosphido groups hold the metals in close proximity permitting study of various cooperative reactions including metal-metal bond formation and

cleavage.⁶ These compounds continue to be the focus of synthetic efforts,⁷ structure analyses,⁸ theoretical studies,⁹ and investigations of reactivity.^{6b,10} Especially noteworthy are the contributions of Vahrenkamp⁷ and Dahl.^{8a} The less easily prepared heterobinuclear members of this group¹¹ are not as well studied as the homobinuclear species. Such heterobinuclear phosphido-bridged complexes present new questions concerning their preparation, structural properties, fluxional behavior, and the little explored chemical reactivity of polar metal-metal bonds.^{10b,c}

Described herein are the synthesis, characterization, solid state structure determination, and fluxional behavior in solution of the heterobimetallic complex $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ (1). This is the first report of a complex having a Rh-Mo bond that has been both fully characterized in solution and crystallographically characterized in the solid state.¹²

Experimental Section

General Data. All manipulations were done under an inert atmosphere, either in standard schlenkware under N_2 freed from O_2 and H_2O by passage over Chemical Dynamics Corp. catalyst R3-11 and activated 4-Å molecular sieves or in a Vacuum Atmospheres Co. drybox. Solvents were distilled under N_2 from Na/benzophenone or CaH_2 . *n*-Butyllithium in hexane was obtained from Aldrich and titrated before use by the method of Kofron.¹³ Alumina was dried by heating at 180-200 °C under vacuum for at least 1 day.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian XL-100 spectrometer; chemical shift values (δ) (reported relative to Me_4Si for 1H and ^{13}C NMR) were measured by using the 1H residuals in the deuterated solvent (1H NMR), the ^{13}C signals of solvent (^{13}C NMR), or a sealed internal capillary tube containing 85% H_3PO_4 (^{31}P NMR) as standards. The ^{13}C and ^{31}P NMR spectra were broad-band proton decoupled. Variable-temperature NMR spectra were obtained by using a Varian variable-temperature controller modified by addition of an external variable resistance box; the probe temperature was calibrated by using a thermometer placed in the probe. Solution infrared

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Table I. Crystallographic Data for $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$

fw: 568.19	$d(\text{calcd}) = 1.64 \text{ g cm}^{-3}$
monoclinic	$d(\text{exptl}) = 1.63 (2) \text{ g cm}^{-3}$
space group $P2_1/n$	Mo $K\alpha$ radiation: $\lambda = 0.71069 \text{ \AA}$
$a = 8.984 (2) \text{ \AA}$	scan rate: variable $2-24^\circ/\text{min}$
$b = 17.497 (4) \text{ \AA}$	2θ limits: $3^\circ \leq 2\theta \leq 50^\circ$
$c = 14.698 (4) \text{ \AA}$	scan range: $\pm 0.7^\circ$
$\beta = 94.60 (2)^\circ$	data collected: 4217
$V = 2303.2 (8) \text{ \AA}^3$	data $F_o^2 > 3\sigma(F_o)^2$: 3178
$Z = 4$	$\rho = 0.04$
$\mu = 22.91 \text{ cm}^{-1}$	

spectra were recorded in CaF_2 cells under N_2 by using a Beckman IR-7 instrument. The UV/visible spectrum was recorded on a Cary 15 spectrophotometer. Cyclic voltammetry was carried out by using a E.G. and G. Princeton Applied Research Co. Model 175 universal programmer and a Model 173 potentiostat/galvanostat and by using a conventional three-electrode cell. Mass spectrum (CDC instrument Model 21-110) and elemental analysis were done by Dr. R. Wielesek at the University of Oregon's microanalytical lab.

Materials. $RhCl_3 \cdot H_2O$ and $Mo(CO)_6$ were obtained from Alfa and used as bottled. Pentamethylcyclopentadiene was prepared by the method of either Whitesides¹⁴ or of Bercaw.¹⁵ $[(C_5Me_5)RhCl_2]_2$,¹⁶ $Mo(CO)_4(NBD)$,¹⁷ and $Mo(CO)_4(HPMe_2)_2$ ¹⁸ were made by following literature procedures. Dimethylphosphine was prepared by our improved procedure.^{18b}

Preparation and Characterization of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ (1). In a dry schlenk tube under N_2 , a solution of $Mo(CO)_4(LiPMe_2)_2$ ¹⁹ was prepared from 274 mg (0.83 mmol) of $Mo(CO)_4(HPMe_2)_2$ in ca. 8 mL of THF by adding 1.16 mL of 1.4 M *n*-BuLi at $-78^\circ C$. After 15 min, this yellow solution was added dropwise by gas-tight syringe to a mixture of 240 mg (0.39 mmol) of $[(C_5Me_5)RhCl_2]_2$ in 20 mL of THF at $-78^\circ C$; the mixture became dark green during the addition. After 1.25 h at $-78^\circ C$, the mixture was allowed to warm slowly (about 1.5 h) to ca. $-5^\circ C$ and then the cold bath was removed. After an additional 0.5 h, the solvent was removed under vacuum. The material was transferred to the drybox, the dark residue was triturated with portions of hexane (total volume about 150 mL), and 230 mg of a red-brown powder was removed by filtration. The hexane-soluble fraction was chromatographed in the box over alumina. Elution with hexane followed by a hexane-benzene mixture with increasing portions of benzene and collection of the green band gave 135 mg (0.24 mmol, 30.6%) of 1. The compound may be recrystallized from hexane at low temperature under N_2 . Anal. ($C_{18}H_{27}P_2O_4MoRh$): C, H, N.

Solutions of 1 are moderately air sensitive; the crystalline solid may be exposed to air for short periods (up to about 1 h) with no noticeable decomposition. The solid partially melts (in a sealed capillary tube, N_2 atmosphere) at $155^\circ C$ and rapidly turns red-brown; the transformed solid persists to $195^\circ C$ where it melts to a red liquid: visible (hexane) λ_{max} 630 nm (ϵ 2600 $L \cdot mol^{-1} \cdot cm^{-1}$); IR (benzene) 2005 (s, sh), 1945 (s), 1915 (s, br) cm^{-1} ; 1H NMR (benzene- d_6) δ 1.59 (15 H, dt, $J_{P-H} = 2 \text{ Hz}$, $J_{Rh-H} = 0.9 \text{ Hz}$), 1.26 (12 H, $X_6AA'X_6'$, $N = |J_{A-X}| + |J_{A'-X}| = 11 \text{ Hz}$) (Figure 3) [with use of the high radio frequency power method,^{20b,c} $|J_{P-P}|$ was found to be ca. 40 Hz as measured from the separation of the inner and outer, weak intensity ($\chi = 1$) lines]; ^{31}P NMR (benzene- d_6) δ 167.6 downfield of H_3PO_4 (d, $J_{Rh-P} = 133 \text{ Hz}$); ^{13}C (benzene- d_6 with added $Cr(acac)_3$) δ 10.8 (s), 20.6 (AXX'), 99.6 (apparent doublet), 217 (s); mass spectrum, the molecular ion displays the characteristic pattern expected due to the seven naturally occurring isotopes of Mo, base peak m/e 570 for ^{98}Mo (23.8% natural abundance). The fragmentation pattern includes the successive loss of four CO units (m/e 28). Cyclic voltammetry (ca. 1.3 mM 1 in THF with 0.1 M *n*-Bu₄NPF₆, Pt wire electrode) gave two distinct one-electron, chemically reversible waves ($E_{1/2} = +0.455$ and -0.035 V vs. SCE , $i_{pc}/i_{pa} = 0.78$ and 0.93, respectively, with $\Delta E_p = 64$ and 72 mV, respectively (Figure 5). Plots of i_{pc} vs. (scan rate)^{1/2} were linear.

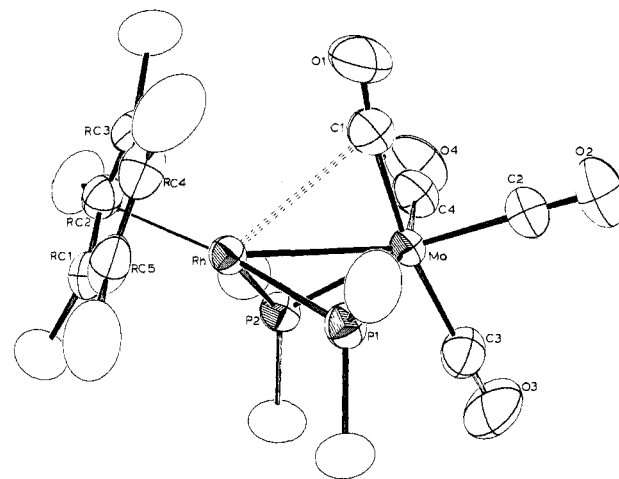
^{13}C NMR Data for *cis*-(Me_2PH)₂ $Mo(CO)_4$. Since a single carbonyl resonance was observed for 1, the ^{13}C NMR of *cis*-(Me_2PH)₂ $Mo(CO)_4$ was obtained as a control. (In benzene with added $Cr(acac)_3$): CO (*cis*) δ 210 (t, $J_{P-C(cis)} = \text{ca. } 8 \text{ Hz}$); CO (*trans*) δ 216 (m); $P-CH_3$ δ 13 (AXX', apparent triplet with a 12-Hz separation between the lines.)

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Figure 1. View of the $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ molecule.

Molecular Structure Determination of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$. Preliminary photographs taken on crystals obtained by using the procedure above indicated monoclinic symmetry. A crystal suitable for data collection was mounted and aligned on a Syntex P1 automated diffractometer equipped with a graphite crystal monochromator. The centered settings of 15 reflections with 2θ values greater than 18° (Mo $K\alpha$ radiation) were refined by least-squares procedures to give the cell constants listed in Table I. Intensity data were collected out to a 2θ value of 50° and processed in the usual way. The locations of the Mo and Rh atoms were determined from a Patterson map. Phases obtained from these heavy-atom positions were used to locate the remaining atoms of the structure. Complete anisotropic refinement of the complex molecule converged with $R = 0.042$, $R_w = 0.048$, and an error in an observation of unit weight of 1.36. Computer programs, calculational procedures, and sources of scattering factor tables have been referenced previously.²¹ Final positional and thermal parameters for all atoms are given in Table II. A table of $|F_o|$ and $|F_c|$ values is available as supplementary material.

Results

Synthesis of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$. The preparation of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ provides the heterobimetallic compound in a modest but unoptimized yield. Substitution of $[(C_5Me_5)Rh(THF)_3](PF_6)_2$ ²² for $[(C_5Me_5)RhCl_2]_2$ provided little or no 1. Substitution of $[(COD)RhCl]_2$ gave product(s) that were thermally unstable.

Description of the Structure. A view of the $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ molecule is shown in Figure 1. Tables III and IV contain bond lengths and angles.

The MoP_2Rh ring has a folded structure with a flap angle of 109.37° versus triangular RhP_2 and MoP_2 planes. This value compares well with $105.1 (4)-118.9^\circ$ for the $[(CO)_3Fe(\mu-PR_2)]_2$ series.²⁴ Related complexes prepared with group 6 metals, specifically $[(CO)_4Cr(\mu-AsMe_2)]_2$ and $[(CO)_4Mo(\mu-PET_2)]_2$,²⁵ have planar rings with angles of 180° . In view of these results a flap angle which is intermediate between the tightly folded structures and the planar group 6 complexes might be anticipated.

However, the heterobimetallic complex $(CO)_3Fe(\mu-AsMe_2)_2Cr(CO)_4$ has also been found to have a folded structure with an angle of 113.8° at the Fe-Cr bond. A Rh-Mo bond is required for $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ to give saturated metal centers. The Mo-Rh length of 2.9212 (7) Å is shorter than the Mo-Mo separation of 3.057 (6) Å reported for $[(CO)_4Mo(\mu-PET_2)]_2$.²⁶ It is also shorter than the Rh(II)-Rh(II) bond length

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Table II. Positional and Thermal Parameters for the Atoms of $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$

atom	x^a	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	-0.15163 (5)	0.21816 (3)	0.07153 (3)	26.92 (21)	30.45 (22)	26.68 (21)	-3.28 (16)	3.51 (15)	-0.10 (16)
Mo	-0.07828 (6)	0.36932 (3)	0.14668 (4)	31.79 (27)	28.72 (26)	27.16 (25)	-2.40 (19)	-1.92 (19)	-2.83 (18)
P1	-0.02523 (18)	0.30949 (10)	0.00069 (11)	28.4 (7)	35.1 (7)	33.2 (7)	-4.1 (5)	5.6 (5)	-0.9 (6)
P2	-0.31924 (17)	0.30866 (10)	0.09433 (11)	26.1 (6)	39.8 (8)	35.8 (7)	0.2 (6)	3.9 (5)	-0.1 (6)
P1M1	-0.0935 (9)	0.3433 (5)	-0.1138 (5)	51 (4)	63 (4)	36 (3)	-4 (3)	4 (3)	13 (3)
P1M2	0.1673 (8)	0.2824 (4)	-0.0215 (6)	31 (3)	51 (4)	79 (5)	-2 (3)	21 (3)	2 (3)
P2M1	-0.4589 (9)	0.2904 (5)	0.1768 (6)	43 (4)	74 (5)	57 (4)	1 (3)	24 (3)	3 (4)
P2M2	-0.4390 (8)	0.3508 (5)	-0.0001 (6)	35 (3)	77 (5)	61 (4)	8 (3)	-9 (3)	18 (4)
C1	0.0473 (11)	0.2863 (4)	0.2106 (6)	69 (5)	41 (4)	61 (4)	-2 (3)	-23 (4)	-1 (3)
O1	0.1267 (10)	0.2470 (4)	0.2512 (6)	124 (6)	59 (3)	126 (6)	12 (4)	-86 (5)	1 (4)
C2	0.1114 (10)	0.4295 (5)	0.1685 (6)	55 (4)	56 (4)	60 (4)	-21 (4)	-15 (3)	7 (3)
O2	0.2184 (8)	0.4639 (5)	0.1798 (6)	79 (4)	103 (5)	141 (6)	-50 (4)	-43 (4)	25 (4)
C3	-0.1748 (9)	0.4658 (5)	0.0867 (6)	49 (4)	41 (4)	63 (4)	-2 (3)	3 (3)	2 (3)
O3	-0.2253 (8)	0.5183 (3)	0.0537 (5)	99 (5)	45 (3)	122 (5)	13 (3)	-13 (4)	27 (3)
O4	-0.2177 (7)	0.4015 (5)	0.3315 (4)	73 (4)	126 (5)	49 (3)	-9 (3)	15 (3)	-21 (3)
C4	-0.1652 (9)	0.3920 (5)	0.2638 (5)	45 (4)	62 (4)	43 (4)	-6 (3)	4 (3)	-8 (3)
RC1	-0.2652 (8)	0.1163 (4)	0.214 (5)	48 (4)	33 (3)	50 (4)	-17 (3)	-5 (3)	4 (3)
RC2	-0.2564 (8)	0.1082 (4)	0.1177 (4)	49 (3)	33 (3)	34 (3)	-4 (3)	8 (3)	2 (2)
RC3	-0.1026 (9)	0.1019 (4)	0.1475 (5)	64 (4)	31 (3)	40 (3)	-0 (3)	-6 (3)	6 (2)
RC4	-0.0159 (8)	0.1086 (4)	0.0710 (6)	41 (3)	33 (3)	62 (4)	-0 (3)	13 (3)	0 (3)
RC5	-0.1167 (10)	0.1156 (4)	-0.0085 (5)	70 (5)	27 (3)	45 (4)	-6 (3)	20 (3)	-2 (3)
RM1	-0.4071 (11)	0.1118 (6)	-0.0425 (7)	72 (5)	71 (5)	70 (5)	-31 (4)	-29 (4)	14 (4)
RM2	-0.3842 (10)	0.0950 (5)	0.1738 (7)	60 (5)	53 (5)	88 (5)	-9 (4)	36 (3)	13 (4)
RM3	-0.0394 (12)	0.0851 (6)	0.2457 (6)	97 (5)	69 (4)	52 (3)	1 (4)	-18 (4)	21 (3)
RM4	0.1509 (10)	0.0971 (5)	0.0705 (8)	50 (3)	57 (3)	118 (4)	14 (5)	20 (4)	18 (3)
RM5	-0.0796 (14)	0.1146 (5)	-0.1064 (6)	130 (4)	55 (5)	48 (5)	-20 (4)	43 (3)	-16 (3)

^a The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})]$. The quantities given in the table are in units of \AA^2 .

Table III. Bond Lengths (\AA) for the $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$

Molybdenum-Ligand Bond Lengths			
Mo-Rh	2.9212 (7)	Mo-C2	2.007 (8)
Mo-P1	2.468 (2)	Mo-C3	2.058 (8)
Mo-P2	2.478 (2)	Mo-C4	1.987 (8)
Mo-C1	2.024 (8)		
Rhodium-Ligand Bond Lengths			
Rh-P1	2.262 (2)	Rh-RC2	2.269 (6)
Rh-P2	2.229 (2)	Rh-RC3	2.345 (7)
Rh-C1	2.865 (8)	Rh-RC4	2.273 (7)
Rh-RC1	2.155 (6)	Rh-RC5	2.181 (7)
Carbonyl Bond Lengths			
C1-O1	1.126 (9)	C3-O3	1.123 (9)
C2-O2	1.134 (9)	C4-O4	1.147 (9)
Phosphorus-Methyl Bond Lengths			
P1-P1M1	1.842 (7)	P2-P2M1	1.841 (7)
P1-P1M2	1.848 (7)	P2-P2M2	1.840 (8)
Pentamethylcyclopentadiene Bond Lengths			
RC1-RC2	1.42 (1)	RC1-RM1	1.52 (1)
RC2-RC3	1.42 (1)	RC2-RM2	1.48 (1)
RC3-RC4	1.42 (1)	RC3-RM3	1.54 (1)
RC4-RC5	1.42 (1)	RC4-RM4	1.51 (1)
RC5-RC1	1.44 (1)	RC5-RM5	1.50 (1)

of 2.936 (2) \AA found for $[Rh(dmg)_2(PPh_3)]_2$. Typical Rh(0)-Rh(0) lengths of 2.75-2.78 \AA are found in carbonyl clusters. Within the RhP_2Mo ring the Rh-Mo bond forms dihedral angles of 38.72 (4) and 31.90 (4) $^\circ$ with the RhP_2 and MoP_2 planes. The fold in the ring together with the octahedral coordination geometry about the Mo atom directs one of the axial carbonyl ligands, CO1 in Figure 1, toward the Rh atom along the Rh-Mo bond. As a consequence carbonyl carbon C1 is within 2.8 \AA of the Rh atom, a length which is probably nonbonding but close to values associated with semibridged carbonyl ligands.²¹ Oxygen atom O1 is oriented toward the C_5Me_5 ring and is within 3.2 \AA of the methyl group bonded to RC3. This separation is well within the sum of the methyl and oxygen van der Waals radii (3.4 \AA). Steric effects of this interaction can be found at both metal centers. At the molybdenum the C1-Mo-C2 bond angle of 82.4 (3) $^\circ$ and the Mo-C1-O1 angle of 171.7 (7) $^\circ$ both reflect the displacement of carbonyl CO1 out of the site ideally trans to CO3, toward CO2. Pentamethylcyclopentadienyl coordination to the Rh atom is quite

Table IV. Bond Angles (Deg) for the

 $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ Molecule

Bond Angles about the Rhodium and Molybdenum Atoms			
Mo-Rh-P1	55.12 (4)	P1-Mo-C2	98.1 (3)
Mo-Rh-P2	55.57 (5)	P2-Mo-C2	169.7 (2)
P1-Rh-P2	86.42 (6)	P1-Mo-C3	94.9 (2)
Mo-Rh-C1	40.9 (2)	P2-Mo-C3	83.8 (2)
Rh-Mo-P1	48.74 (4)	P1-Mo-C4	162.7 (2)
Rh-Mo-P2	47.90 (4)	P2-Mo-C4	87.7 (2)
Rh-Mo-C1	68.0 (2)	C1-Mo-C2	82.4 (3)
Rh-Mo-C2	134.3 (3)	C1-Mo-C3	170.1 (3)
Rh-Mo-C3	120.6 (2)	C1-Mo-C4	89.1 (4)
Rh-Mo-C4	114.6 (2)	C2-Mo-C3	87.7 (3)
P1-Mo-P2	76.88 (5)	C2-Mo-C4	98.3 (4)
P1-Mo-C1	87.7 (3)	C3-Mo-C4	91.2 (3)
P2-Mo-C1	106.1 (2)		
Carbonyl Ligand Bond Angles			
O1-C1-Mo	171.7 (7)	O3-C3-Mo	178.3 (8)
O2-C2-Mo	179.1 (8)	O4-C4-Mo	176.7 (8)
Angles about the Bridging Phosphorous Atoms			
Mo-P1-Rh	76.13 (5)	Mo-P2-Rh	76.53 (5)
P1M1-P1-P1M2	99.7 (4)	P2M1-P2-P2M2	100.2 (4)
P1M1-P1-Mo	125.8 (3)	P2M1-P2-Mo	119.6 (3)
P1M1-P1-Rh	120.3 (2)	P2M1-P2-Rh	118.7 (3)
P1M2-P1-Mo	120.7 (3)	P2M2-P2-Mo	120.4 (3)
P1M2-P1-Rh	114.3 (2)	P2M2-P2-Rh	122.2 (3)
Interior Angles of the C_5Me_5 Ligand			
RC1-RC2-RC3	106.9 (6)	RC4-RC5-RC1	107.2 (6)
RC2-RC3-RC4	109.3 (6)	RC5-RC1-RC2	108.9 (6)
RC3-RC4-RC5	107.6 (6)		

unsymmetrical as shown in Figure 2. The Rh-C lengths range over 0.2 \AA with the longest to RC3 (2.345 (7) \AA). Similar values of 2.269 (6) and 2.273 (7) \AA are found for RC2 and RC4. Lengths to RC1 and RC5 are 2.155 (6) and 2.181 (6) \AA , respectively. The plane of the C_5Me_5 ligand is tipped approximately 19.8 $^\circ$ out of the ideal plane perpendicular to the RhP_2 fragment.

Structural features within the RhP_2Mo ring are in accord with other phosphido- and arsenido-bridged bimetallic complexes. Mo-P lengths averaging 2.473 (2) \AA are typical of Mo(0) and are longer than the average Rh-P length of 2.249 (2) \AA . This difference contributes to a more open P1-Rh-P2 angle of 86.42 (6) $^\circ$ compared with the 76.89 (5) $^\circ$ angle for P1-Mo-P2. Both

Table V. Dihedral Angles (Deg) and Least-Squares Planes for the $(C_5Me_5)Rh(\mu-PMe_2)_2Mo(CO)_4$ Molecule

Plane 1: Atoms Rh, P1, P2			
$3.89x + 4.12y - 12.24z = 1.18$			
Plane 2: Atoms Mo, P1, P2			
$2.21x - 14.68y + 6.82z = -4.59$			
Plane 3: Atoms RC1, RC2, RC3, RC4, RC5			
$0.30x + 17.39y + 1.48z = 1.97$			
Least-Squares Planes			
atoms	distance, Å	atoms	distance, Å
RC1	0.002 (7)	RM2	-0.178
RC2	0.007 (6)	RM3	-0.142
RC3	-0.014 (7)	RM4	-0.137
RC4	0.015 (7)	RM5	-0.161
RC5	-0.010 (6)	Rh	1.882
RM1	-0.213		
Dihedral Angles			
Rh-Mo bond-plane 1	38.72 (4)	plane 1-plane 2	109.37 (5)
Rh-Mo bond-plane 2	31.90 (4)	plane 2-plane 3	104.9 (3)
Rh-Mo bond-plane 3	18.5 (2)	plane 1-plane 3	109.8 (2)

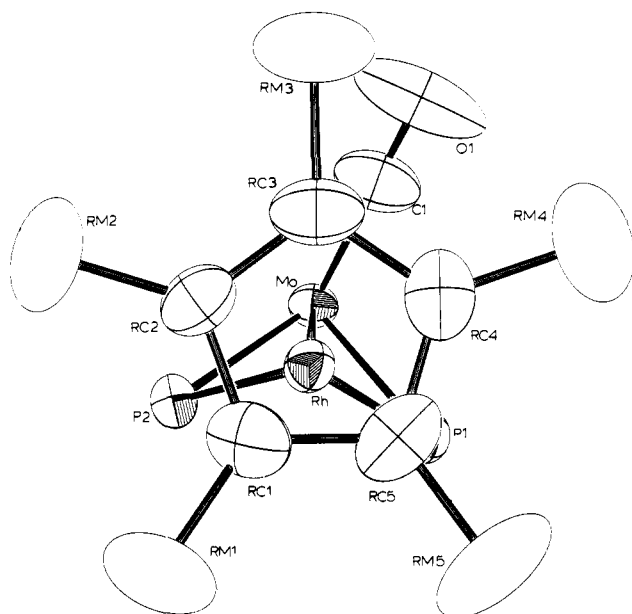


Figure 2. View down the plane of the C_5Me_5 ligand showing the locations of the Rh atom, the RhP_2Mo ring, and carbonyl ligand CO1 with respect to the ring carbon atoms.

values agree with interior angles found in folded structures and differ from the 104° values found for the planar Cr and Mo molecules. Interior angles at the phosphorus atoms average to $76.33 (5)^\circ$. Bond angles at this position remain relatively constant at the 75° value through the series of planar and folded structures containing metal-metal bonds with phosphido and arsenido bridges. Substituent bond angles to the bridging atoms also remain constant at 100° within the series. The carbon-phosphorus-carbon bond angles in this case average to $100.0 (4)^\circ$.

Stereochemical Nonrigidity. The ambient temperature NMR data together with the X-ray structure clearly indicate that the new compound is highly fluxional in solution. In the solid state, the methyl groups on phosphorus are clearly exo or endo, and the axial CO ligands on Mo are different from each other as well as from the equatorial CO ligands. However, the 1H NMR clearly shows only a single $X_6AA'X_6'$ pattern²⁰ for the phosphorus-bound methyl hydrogens (Figure 3) and, more remarkably, the ^{13}C NMR shows only a single, apparently uncoupled, carbonyl resonance ($J_{P-C} < 3$ Hz). Low-temperature NMR spectra confirm that the barrier to stereochemical nonrigidity is low. At $-87^\circ C$ in $CHClF_2/CD_2Cl_2$, coalescence of the $X_6AA'X_6'$ pattern to a broad

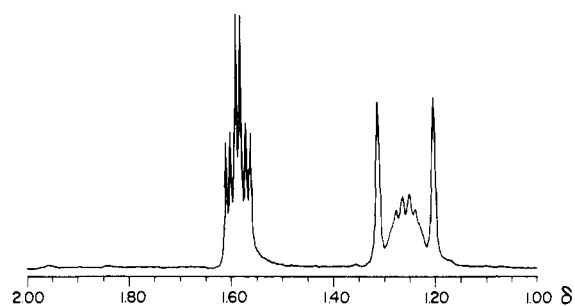


Figure 3. Ambient-temperature 100-MHz 1H NMR of 1: δ 1.59 (15 H, dt, $J_{P-H} = 2$ Hz, $J_{Rh-H} = 0.9$ Hz, C_5Me_5), 1.26 (12 H, $X_6AA'X_6'$, $N = 11$ Hz, PMe_2).

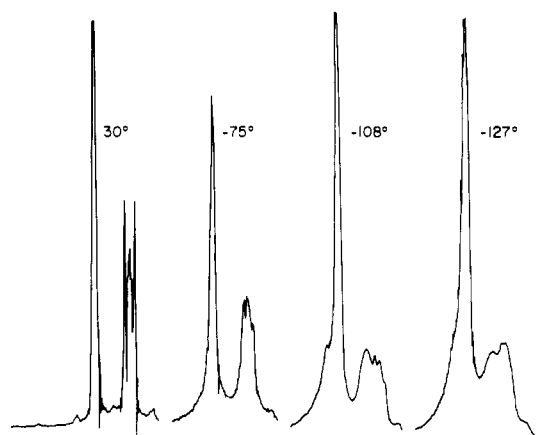


Figure 4. Variable-temperature 100-MHz 1H NMR of 1 in $CHClF_2/CD_2Cl_2$.

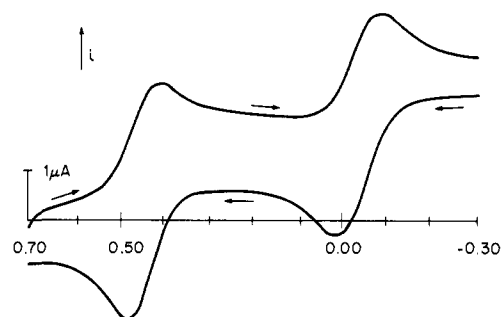


Figure 5. Cyclic voltammogram of 1 (ca. 1.3 mM 1 in THF with 0.1 M $n-Bu_4NPF_6$, Pt wire electrode, scan rate 50 $mV \cdot s^{-1}$, V vs. SCE).

peak was observed (Figure 4). Although some structure reappears at lower temperature, the slow-exchange limit of separate endo and exo methyl hydrogen resonances was not clearly observed even at $-140^\circ C$. On rewarming, the higher temperature patterns were regenerated and the peaks due to the $CHClF_2$ remained sharp throughout these experiments. This demonstrated that no irreversible decomposition had occurred and that good instrument resolution was being maintained. In the ^{13}C NMR, a single sharp CO resonance was observed down to $-60^\circ C$. As a check on this unexpected result, a control experiment on $cis-(Me_2PH)_2Mo(CO)_4$ exhibited the expected two-carbonyl ^{13}C NMR spectrum with $J_{P-C} = 8$ Hz.

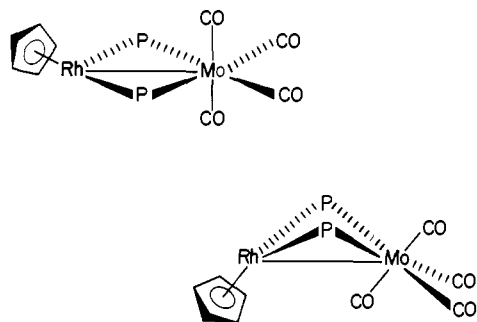
The electrochemical reduction of 1 shows two single-electron transfers cleanly separated by 490 mV (Figure 5). The linear i_p vs. (scan rate) $^{1/2}$ plots obtained demonstrate that the waves are uncomplicated by adsorption effects and are diffusion controlled.

Discussion

At the initiation of these studies, the Rh-Mo heterobimetallic, 1, posed several new questions concerning its method of synthesis, its solid-state structure, its solution structure, and potential stereochemical nonrigidity, as well as the completely unexplored reactivity of its heterobimetallic Rh-Mo bond. This study has focused on all but the last question, since the reactivity of polar

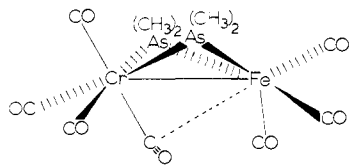
metal-metal bonds merits its own thorough investigation.²⁸

Two limiting structures, planar **2a** or folded **2b**, were plausible



a priori alternatives for the MoP₂Rh framework. (The methyl groups on phosphorous have been omitted for clarity.) Recent theoretical studies⁹ have determined that the observed geometries correspond to energy minima due to the interplay of M-M and M-P frontier orbital energies as a function of the M-P-M and P-M-P angles. A review of the structural features of metal-metal-bonded phosphido- and arsenido-bridged bimetallic complexes characterized crystallographically, in addition to our own results, shows that the M-A-M (A = P, As) angle remains relatively constant at approximately 74.4° and is independent of the planar/folded structure of the MA₂M' ring.²³⁻²⁶

In this case it is clear that steric factors significantly influence the value of the flap angle, which is limited by the contact between CO1 and the C₅Me₅ ligand. Vahrenkamp has noted a carbonyl interaction in (CO)₃Fe(μ-AsMe₂)₂Cr(CO)₄ (**3**)²⁵ which is similar



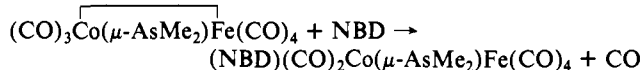
to that in (C₅Me₅)Rh(μ-PMe₂)₂Mo(CO)₄. In the Fe-Cr molecule the Fe-C separation is approximately 2.70 Å. Moreover, the planar structures found for the Cr₂As₂ and Mo₂P₂ rings of [(CO)₄Cr(μ-AsMe₂)₂]₂ and [(CO)₄Mo(μ-PEt₂)₂]₂ are virtually required to minimize axial carbonyl interactions between adjacent metal centers. The structural results on the Rh-Mo and Fe-Cr heterobimetallics emphasize the importance of steric effects in determining the flap angle in phosphido-bridged complexes.

The solution structure of the Rh-Mo complex, **1**, has been elucidated by using ¹H, ¹³C, and variable-temperature ¹H NMR. The methyl groups bound to phosphorus appear in the ¹H NMR at ambient probe temperature as a single X₆AA'X₆' pattern. The observation of this spin system rather than two X₃AA'X₃' systems and the variable-temperature data require a stereochemically nonrigid structure in solution. On the average, **1** has a folded structure in room-temperature solution on the basis of the observed correlation^{30b} of |J_{P-P}| and structurally confirmed^{8a} geometries. The |J_{P-P}| = 40 Hz value for **1** is intermediate to the low, |J_{P-P}| = 18 ± 2 Hz value for planar^{30b} [(CO)₄Mo(μ-PMe₂)₂]₂ and the relatively large |J_{P-P}| = 80 ± 10 Hz value^{30b} found in folded [(CO)₃M(μ-PMe₂)₂]₂ (M = Fe, Ru).

The fluxionality of **1** is interesting in several respects. Although many phosphido-bridged and related compounds are known to be fluxional in solution, the kinetic barrier in **1** is unusually low.² For example, the homobimetallic species [(CO)₃M(μ-PMe₂)₂]₂ (M = Fe, Ru)³⁰ and [CpCo(μ-PMe₂)₂]₂^{6b} show distinct endo and exo methyl resonances up to 38 and 100 °C and at ambient probe temperature, respectively. The behavior of the Rh-Mo hetero-

bimetallic, **1**, is consistent, however, with Vahrenkamp's recent observation²⁵ that (CO)₄Cr(μ-AsMe₂)₂Fe(CO)₃ has a highly folded CrAs₂Fe unit in the solid state yet shows a single sharp ¹H NMR methyl resonance down to -80 °C.

A simple bridge "flapping" or butterfly motion cannot, by itself, explain the fluxionality of **1**. In particular, bridge flapping does not interchange the axial and equatorial carbonyls on molybdenum as required by the observation of a single ¹³C NMR signal. The lack of an observable J_{P-C} is another surprising aspect of the ¹³C NMR of **1**. It may be that, given the rapid CO scrambling, J_{P-C} averages to J_{P-C} < 3 Hz, the estimated resolution limit of the experiment, and is manifest only as a slight broadening of the CO resonance. Alternatively, the single uncoupled ¹³C NMR carbonyl resonance is consistent with a CO or P dissociative mechanism. This would give a 5-coordinate molybdenum atom that could give a zero contribution to J_{P-C} (in the case where the lifetime of the intermediate is long relative to the nuclear relaxation times).³¹ Dissociation of CO was tested and appears unlikely, however, since **1** failed to react with added P(OMe)₃ over 6 h at 50 °C (as judged by ¹H NMR). At first glance, a P-dissociative pathway seems inconsistent with the low barrier to rearrangement. However, the possibility exists of forming a terminal phosphido ligand bound to rhodium that would be stabilized by d_π-p_π bonding, i.e., "(C₅Me₅)(Me₂P=)Rh(μ-PMe₂)Mo(CO)₄". Formally, this involves movement of a P-Mo electron pair toward Rh and movement of the Rh-Mo electron pair toward Mo to yield an 18-electron Rh(III) and 18-electron Mo(0) complex. The d⁶, 5-coordinate, probably³² square-pyramidal Mo(0) could interchange CO positions by a simple rotation of the square pyramid about the Mo-P bond. The only supporting evidence for this hypothetical intermediate is that it requires Rh-P coupling which is, in fact, observed. It is also intuitively appealing in that it incorporates the most novel feature of **1**, its polar Rh-Mo bond. Numerous examples are available of terminal phosphido ligands attached to metals,³³ and the following known^{10b} reaction provides precedent for ligand addition across a polar heterobimetallic bond with subsequent metal-metal bond cleavage.



The electrochemical results are readily accommodated by the Rh-Mo heteropolar bond. The two single-electron transfers are the expected result for the addition of electrons to a Rh-Mo orbital with unequal contributions from the two metals. Stated somewhat differently, the two single-electron transfers can be assigned to the formal reduction sequence primarily at rhodium of [Rh^{III}Mo⁰] to [Rh^{II}Mo⁰]⁻ and then to [Rh^IMo⁰]²⁻. The separate, one-electron waves in the cyclic voltammogram of **1** stand in sharp contrast to the single, two-electron reduction of, for example, the homobimetallic metal-metal-bonded complexes^{8a} [(CO)₃Fe(μ-PPh₂)₂]₂ and [(CO)_nM(μ-PMe₂)₂]₂ (M = Cr, Mo, W, n = 4; M = Fe, Ru, n = 3).^{30b}

Summary

The synthesis, solid-state structure, solution structure, fluxionality, and electrochemical properties of (C₅Me₅)Rh(μ-

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$\text{PMe}_2)_2\text{Mo}(\text{CO})_4$ have been presented. The pathway is now clear to explore the reactivity and properties of the heterobimetallic polar Rh–Mo bond²⁸ in 1.

Acknowledgment. Support for research at the University of Oregon from the National Science Foundation Grant CHE-78-11552, the Research Corp., and financial flexibility provided by

a Chevron Research grant is gratefully acknowledged. Research at the University of Colorado was supported by the Department of Energy through the Solar Energy Research Institute.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Intramolecular B–B Linkage between Polyhedral Cages in a *commo*-Metallacarborane. Synthesis and Structure of a Fluxional Metal–Boron Cluster, $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_3(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$

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Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received July 28, 1980

Abstract: The reaction of $\text{Li}^+\text{C}_5(\text{CH}_3)_5^-$, CoCl_2 , and $\text{Na}^+(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ in cold THF forms primarily *closo*-1,2,3- $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ (I), the triple-decker complex 1,7,2,3- $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_2(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_3$ (II), a structurally novel complex, $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_3(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$ (III), and traces of other products in a combined isolated yield of ~50%. Complexes I and II are $\text{C}_5(\text{CH}_3)_5$ analogues of C_5H_5 -substituted cobalt carboranes reported earlier, but III has no previous counterpart. An X-ray diffraction study of III disclosed a structure consisting of two identical $[\eta^5\text{-C}_5(\text{CH}_3)_5]$ units face coordinated to a third cobalt atom, with a direct B–B bond [1.758 (5) Å] between the two ligands; the linked boron atoms have no terminal hydrogen atoms in the solid-state structure. The “extra” hydrogen atom was not directly located, but its general position was indicated by a 3.5° fold in the molecule which creates a larger interligand pocket on one side than on the other. In the crystal, the unique hydrogen is proposed to reside in the larger pocket (in the vicinity of the central cobalt atom), but ¹¹B and ¹H FT NMR and infrared evidence indicates that, in solution, this hydrogen atom tautomerizes between equivalent terminal positions on the (formerly) linked boron atoms on the two ligands, with cleavage of the B–B link. Possible mechanisms of formation and stereochemical implications of the structure and fluxional behavior of III are presented. The chemistry of complex I resembles that of its C_5H_5 -substituted counterpart; thus, degradation of I in basic CH_3CN produces *nido*-1,2,3- $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5$ in 93% yield. Crystal data for III: space group *P*1, *Z* = 2, *a* = 8.555 (2) Å, *b* = 12.599 (2) Å, *c* = 16.268 (9) Å, α = 102.76 (4)°, β = 92.71 (3)°, γ = 99.15 (4)°, *V* = 1682 Å³, *R* = 0.073 for the 3739 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

The extraordinary richness of polyhedral borane chemistry is evident from the seemingly unlimited variety of structural features and bonding modes that have been found, with new ones continually being discovered. In addition to the many kinds of known polyhedral cage structures, numerous types of direct bonding between polyhedra have been established; indeed, ten distinguishable modes of interpolyhedral linkage in established compounds have been cited by Lipscomb¹ (if one also includes polyhedra connected by bridging atoms such as mercury, silicon, or tin, the list is even longer).

In this paper we describe a stereochemical phenomenon involving linked borane cages in which there are two aspects of interest: a novel solid-state molecular geometry and a curious form of fluxional behavior in solution which we believe implies reversible interpolyhedral boron–boron bond formation. These findings resulted from the serendipitous isolation of a byproduct in the preparation of the *closo*-carborane 1,2,3- $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$. In the course of this routine synthesis (which was based on the earlier preparation² of the corresponding cyclopentadienyl species 1,2,3- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ from 2,3- $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ ion, CoCl_2 , and NaC_5H_5), the new compound $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_3(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$ was obtained as a dark red,

air-stable, crystalline solid and subsequently characterized by spectroscopic and X-ray diffraction techniques. We report here the structural investigation of this complex as well as the synthesis and characterization of other $(\eta^5\text{-pentamethylcyclopentadienyl})_2\text{cobalt}$ complexes isolated from this reaction.

Experimental Section

Materials. 2,3-Dimethyl-2,3-dicarbaheptaborane(8), $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$, was prepared from B_5H_9 , $(\text{CH}_3)_2\text{C}_2$, and $(\text{C}_2\text{H}_5)_3\text{N}$ as described elsewhere.³ Pentamethylcyclopentadiene (Alfa) was used as received, and all other chemicals were reagent grade. Hygroscopic metal salts were dried at high temperature in vacuo, and tetrahydrofuran (THF) was rigorously dried over LiAlH_4 prior to use. *n*-Butyllithium was obtained from Alfa as a hexane solution and determined to be 1.8 M by the method of Silveira et al.⁴ Sodium hydride (50% in mineral oil, Alfa) was washed with pentane prior to use. Column chromatography was conducted with silica gel 60 (Merck), and thin-layer chromatography (TLC) was performed on precoated plates of silica gel F-254 (Brinkmann Instruments, Inc.)

Instrumentation. ¹¹B (32 MHz) and ¹H (100 MHz) pulse Fourier Transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL–Texas Instruments computer system. Broad-band heteronuclear decoupling was employed. ¹H NMR (90 MHz) spectra and some single-frequency homonuclear-decoupling ex-

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