carbonyl group can "reserve" an iron coordination site needed for a later step of the reaction).

In summary this work indicates that benzalacetonetricarbonyliron, although it can serve as a convenient source of $Fe(CO)_3$ groups under mild conditions for reactions with dienes[6] and acetylenes,[15] can undergo more complicated reactions involving the benzalacetone unit in the cases of other ligands as exemplified by $CH_3N(PF_2)_2$ in this work. There are thus some clear limitations in the use of benzalacetonetricarbonyliron as a source of $Fe(CO)_3$ groups in synthetic transition metal organometallic chemistry.

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Structural and Chemical Characterization of a Phosphine Bound M–H–M Bridged Carbonylate: $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$

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Abstract: An X-ray crystal structure determination of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ (**1**) has affirmed the positioning of PPh_3 to be cis to the hydride bridge in a (bent, staggered) molecular anion framework. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters of a = 16.386 (6) Å, b = 13.470 (5) Å, c = 17.085 (8) Å, and β = 92.10 (7)°; ρ_{calcd} = 1.48 g cm^{-3} for Z = 4. The refinement led to a final R value of 0.034 based on 3518 observed reflections. The Mo–Mo separation is 3.4736 (7) Å, the bend of the molecular anion framework is 162.7°, the Mo–H–Mo angle is 127 (3)°, and the hydride is located asymmetrically between the Mo atoms, the shorter Mo–H distance (by 0.5 Å) being to the $Mo(CO)_5$ moiety. The quite long Mo–P bond (2.565 (1) Å) corroborated the solution chemistry of **1**, which was kinetically dominated by a labile Mo–PPh_3 bond. The kinetically determined Mo–P bond enthalpy in **1** is 23 ± 2.4 kcal/mol. The title compound may be used as precursor to more highly substituted dimer anions and/or neutral complexes, $L_2Mo(CO)_4$.

Introduction

Previous investigations of $(\mu\text{-}H)[M(CO)_5]_2^-$ (M = group 6B) and related compounds have placed particular emphasis on the structural chemistry of such M–H–M bridged systems, while investigations of the dynamic chemistry of these carbonylates have remained limited. We have recently reported ligand lability studies of $Et_4N^+(\mu\text{-}H)[M(CO)_5]_2^-$ and have suggested that simple CO dissociation from an equatorial position is rate determining in ligand substitution reactions.[2,3] Group 5A donor ligands react with $(\mu\text{-}H)[M(CO)_5]_2^-$ in refluxing THF or EtOH to form $L_2M(CO)_4$ products. A kinetic investigation of this process implicated coordinatively unsaturated intermediates of the type $(OC)_5M\text{-}H\text{-}M(CO)_4^-$, with dimer disruption occurring only after substitution onto the available coordination site. For the reaction of $Et_4N^+(\mu\text{-}H)[Mo(CO)_5]_2^-$ with PPh_3 in THF, an intermediate, $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ (**1**), was isolated prior to dimer disruption and was tentatively identified as an equatorially substituted Mo dimer.[3]

Subsequent work has intimated that the effects of M–M interaction in these bridged hydride-dinuclear carbonylates make tenuous the local symmetry approximation used in the ν(CO) infrared-based structure assignment.[4] An X-ray crystal structure determination was initiated to ascertain the geometry of the substituted anion as well as the details of structural modification on substitution of CO by the relatively enormous PPh_3 ligand. The refined structure of **1** (including the hydride position), the kinetic determination of the Mo–P bond strength in **1**, and the use of **1** as a precursor to other substituted dinuclear hydrides are reported here.

A recent review of structural transition metal hydride chemistry included an excellent and clarifying section on the six or so structures of 6B M–H–M carbonylates and derivatives.[5] A brief synopsis of the current status of these structural

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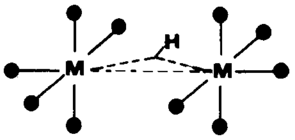
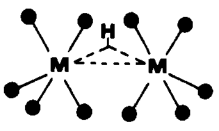
findings is appropriate to our later discussion. The structures may be classified according to the $(OC)_{ax}M$- - -$M(CO)_{ax}$ "backbone" (linear or bent) and the relative orientation of equatorial carbonyls on each metal center (eclipsed or staggered). Basically two combinations, (linear, eclipsed) (**2**) and (bent, staggered) (**3**), have been reported to date. The (linear, eclipsed) has been established as the structure of μ-H[Cr(CO)$_5$]$_2^-$ as its Et$_4$N$^+$ and (Ph$_3$P)$_2$N$^+$ (or PPN$^+$) salts[6-8] and also of μ-H[W(CO)$_5$]$_2^-$ as its Et$_4$N$^+$ salt.[9] The (bent, staggered) structure (**3**) exists for μ-H[W(CO)$_5$]$_2^-$ as its PPN$^+$ and Ph$_4$P$^+$ salts[9] and for the neutral derivatives μ-H[W(CO)$_5$][W(CO)$_4$(NO)] and μ-H[W(CO)$_5$][W(CO)$_3$(NO)(P(OMe)$_3$]].[10,11] The H is positioned off the M- - -M axis in linear arrangements (**2**) or off the intersection point of the $(OC)_{ax}$-M vectors which define the bent arrangement (**3**). The M-H-M angle in **2** ranges from 137° to 160° and in **3** is around 125-130°.



2
(linear, eclipsed)



3
(bent, staggered)

The M-H-M bond in these systems is best described as a "closed three-center, two-electron bond,"[6-11] for which qualitative molecular orbital schemes have been developed.[12,13] The importance of metal-metal interactions to the changes in the ν(CO) infrared spectra of (μ-H)[Mo(CO)$_5$]$_2^-$ and (μ-H)[W(CO)$_5$]$_2^-$ was determined via stereospecific ^{13}CO labeling studies.[4,13] Further, a complete vibrational analysis of such carbonylates is underway.[14,15]

Despite such substantial contributions to the structural and electronic descriptions of (μ-H)[M(CO)$_5$]$_2^-$ species, some uncertainties remain. Bau and co-workers[5b,9b] have recently reported results of a low-temperature (14 K) neutron-diffraction study of (μ-H)[W(CO)$_5$]$_2^-$, concluding that there is extensive asymmetry in the W-H-W bridge (W$_1$-H = 1.718 (12) Å, W$_2$-H = 2.070 (12) Å); i.e., either substantial crystal packing forces are perturbing the anion or government of the hydride location is by a double minimum potential, corroborative of earlier interpretations of vibrational spectral results.[12] This asymmetry of the M-H-M bridge in the otherwise symmetrical (μ-H)[W(CO)$_5$]$_2^-$ species as well as the substantive symmetry of the M-H-M bridge in the quite asymmetric (μ-H)[W(CO)$_5$][W(CO)$_3$(P(OMe)$_3$)(NO)] compound gives even more cause for the elucidation of the structure of **1**.

The structure of Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$PPh$_3$]$^-$ as determined by single-crystal X-ray diffraction methods is the first of a protonated Mo-Mo carbonyl framework and to our knowledge the first of a complex containing a phosphine bond in an anion. The structure is of type **3** and the hydride is asymmetrically located between the Mo atoms. The Mo-P bond is long compared to that found in neutral analogues and the solution chemistry has indicated it to be quite weak. Activation energy parameters for phosphine dissociation are reported as well as an extensive investigation of ligand exchange reactions of **1**.

Experimental Section

All syntheses and kinetic studies were carried out under a dry nitrogen atmosphere using solvents freshly distilled under N$_2$ and purified by standard techniques; tetrahydrofuran was distilled from Na/benzophenone and hexane was distilled from CaSO$_4$. Triphenylphosphine was recrystallized from EtOH. Carbon monoxide gas (Matheson) was used as received. Infrared spectra were recorded in sealed NaCl cells on a Perkin-Elmer 521 grating infrared spectrophotometer equipped with a linear absorbance potentiometer and calibrated against CO and H$_2$O vapor spectra.

Table I. Crystal Data

compd	Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$PPh$_3$]$^-$
mol wt	837.5
linear abs coeff μ, cm^{-1}	7.53
calcd density, g cm^{-3}	1.48
max crystal dimensions, mm	0.20 × 0.26 × 0.54
space group	monoclinic, $P2_1/n$
molecules/unit cell	4
cell constants[a]	
a, Å	16.386 (6)
b, Å	13.470 (5)
c, Å	17.085 (8)
β, deg	92.10 (7)
cell vol, Å^3	3768.5

[a] Mo Kα radiation, λ 0.210 69 Å, ambient temperature of 23 ± 1 °C.

Preparations. Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$PPh$_3$]$^-$ (**1**) was prepared by the reaction of Et$_4$N$^+$(μ-H)[Mo(CO)$_5$]$_2^-$ and PPh$_3$ as previously described.[3] Crystals for X-ray structure analysis were grown from THF/hexane. Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$P(p-tolyl)$_3$]$^-$ was analogously synthesized by the reaction of Et$_4$N$^+$(μ-H)[Mo(CO)$_5$]$_2^-$ with P(p-tolyl)$_3$ and was isolated as air-stable, pale yellow crystals. Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for C$_{38}$H$_{42}$Mo$_2$NO$_9$P: C, 51.94; H, 4.67. Found: C, 51.73; H, 4.80. The infrared spectrum in the ν(CO) region showed bands in tetrahydrofuran at 2056 (vw), 2000 (w), 1963 (vw), 1927 (s), 1873 (w, br), and 1838 cm^{-1} (w, br).

Alternatively Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$P(p-tolyl)$_3$]$^-$ was prepared by phosphine metathesis which was effected by refluxing for 15 min a 50-mL THF solution of 0.40 g of Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$PPh$_3$]$^-$ (0.48 mmol) and 4.46 g of P(p-tolyl)$_3$ (14.4 mmol). The solution was cooled to room temperature and was filtered through a medium-porosity frit. Hexane (100 mL) was added. After standing overnight at −5 °C, yellow crystals precipitated from solution and were collected and washed with hexane. This product had a ν(CO) infrared spectrum and an ^{1}H NMR spectrum in the δ 10-0 region identical with those of Et$_4$N$^+$(μ-H)[Mo$_2$(CO)$_9$P(p-tolyl)$_3$]$^-$ prepared by CO replacement of Et$_4$N$^+$(μ-H)[Mo(CO)$_5$]$_2^-$, yield 0.14 g, 32%.

Kinetic Measurements. Rates of reaction of **1** with PPh$_3$ in refluxing THF were determined by the previously described method[3] in which the disappearance of the carbonylate in the presence of a 8-100-fold excess of ligand was monitored over 75% of the reaction lifetime utilizing a minimum of 15 points per reaction by following the band at 1928 cm^{-1}, the most intense band in the ν(CO) infrared spectrum. Samples for infrared analysis were periodically withdrawn from the reaction vessel by means of a long syringe needle inserted through the serum cap of the condenser.

The rate of reaction of **1** with CO gas in THF solution at various temperatures was measured in a similar fashion, although, in these studies, solutions were saturated with CO gas and its concentration was maintained constant by the following procedure. The reaction vessel containing the dry components was flushed with N$_2$; following addition of THF, CO gas was bubbled through the solution via a needle inserted through the serum-capped side arm of the flask. Pressure relief was through a mineral oil outlet at the condenser top. Exciting CO gas was oxidized by passing the stream of exiting gases from the mineral oil bubbler into a bubbler containing aqueous KMnO$_4$. To ensure minimal solvent loss, the CO flow was slow, and the reaction vessel was equipped with a condenser jacketed with water cooled to 1 °C. Following dissolution of the reactants, the flask was immersed in a Precision Scientific Temptrol Bath regulated to ±0.5 °C. In order to circumvent difficulties with overlapping bands for **1** and the product Et$_4$N$^+$(μ-H)[Mo(CO)$_5$]$_2^-$, rates of reaction were obtained by following the disappearance of the isolated absorbance at 2001 cm^{-1}.

Plots of ln (A_t − A_∞) vs. time, where A_t is the absorbance of the isolated band of **1** at either 2001 or 1928 cm^{-1} and A_∞ is the absorbance at time infinity, were found to be linear. Thus, all reactions were first order in carbonylate. Data were treated by the method of least squares, and each individual rate constant represents one kinetic run in which the error is the confidence limit at the 95% level. The acti-

Table II. Atomic Positions in Fractional Coordinates and Thermal Parameters for $[Et_4N]^+(\mu\text{-}H)[(CO)_5Mo][(CO)_4(PPh_3)Mo])^-$

Atom	x/a	y/b	z/c	B11	B22	B33	B12	B13	B23
Mo(1)	0.17956(3)	0.12578(3)	0.01027(3)	0.00321(2)	0.00367(3)	0.00298(2)	-0.00023(2)	0.00052(1)	-0.00028(2)
Mo(2)	0.30593(3)	0.33095(3)	-0.00766(3)	0.00361(2)	0.00295(3)	0.00279(2)	-0.00021(2)	0.00024(1)	-0.00027(2)
P	0.35043(8)	0.28092(10)	-0.14242(8)	0.00280(6)	0.00273(8)	0.00249(5)	-0.00000(5)	-0.00012(4)	0.00027(5)
N(1)	0.2722(3)	0.2161(4)	0.4021(3)	0.0053(3)	0.0045(3)	0.0050(3)	-0.0009(2)	0.0007(2)	-0.0005(2)
O(1)	0.0668(3)	-0.0533(3)	0.0478(3)	0.0041(2)	0.0050(3)	0.0064(2)	-0.0006(2)	0.0010(2)	0.0013(2)
O(2)	0.0609(3)	0.2076(4)	-0.1265(3)	0.0061(3)	0.0072(4)	0.0055(2)	-0.0000(3)	-0.0011(2)	0.0010(2)
O(3)	0.0769(3)	0.2727(4)	0.1147(3)	0.0077(3)	0.0095(4)	0.0064(3)	0.0028(3)	0.0023(2)	-0.0020(3)
O(4)	0.2902(4)	0.0585(5)	0.1558(3)	0.0081(3)	0.0140(6)	0.0053(3)	0.0044(4)	-0.0024(2)	-0.0013(3)
O(5)	0.2523(3)	-0.0355(3)	-0.1022(3)	0.0066(3)	0.0061(3)	0.0054(2)	0.0003(2)	0.0014(2)	-0.0021(2)
O(6)	0.1425(3)	0.4353(4)	-0.0584(4)	0.0054(3)	0.0092(5)	0.0094(4)	0.0030(3)	-0.0012(2)	-0.0009(3)
O(7)	0.2547(4)	0.3655(4)	0.1611(3)	0.0119(4)	0.0084(4)	0.0043(2)	-0.0037(3)	0.0033(2)	-0.0022(3)
O(8)	0.3869(5)	0.5395(3)	-0.0595(3)	0.0058(2)	0.0035(3)	0.0052(2)	-0.0011(2)	0.0004(2)	-0.0006(2)
O(9)	0.4630(3)	0.2417(4)	0.0793(3)	0.0076(3)	0.0080(4)	0.0083(3)	0.0010(3)	-0.0043(3)	0.0000(3)
C(1)	0.1051(3)	0.0163(5)	0.0343(3)	0.0033(3)	0.0052(4)	0.0037(3)	0.0004(3)	0.0007(2)	0.0002(3)
C(2)	0.1051(4)	0.1779(4)	-0.0792(4)	0.0041(3)	0.0045(4)	0.0038(3)	-0.0009(3)	0.0001(2)	-0.0003(3)
C(3)	0.1170(4)	0.2225(5)	0.0791(4)	0.0040(3)	0.0070(5)	0.0039(3)	0.0004(3)	0.0007(2)	-0.0003(3)
C(4)	0.2521(4)	0.0836(5)	0.1018(4)	0.0043(3)	0.0063(5)	0.0046(3)	0.0006(3)	0.0005(2)	-0.0016(3)
C(5)	0.2290(3)	0.0254(4)	-0.0626(3)	0.0037(3)	0.0050(4)	0.0033(2)	-0.0010(3)	0.0009(2)	-0.0001(3)
C(6)	0.2011(4)	0.3951(4)	-0.0534(4)	0.0042(3)	0.0045(4)	0.0052(3)	0.0002(3)	0.0002(3)	-0.0012(3)
C(7)	0.2712(4)	0.3634(5)	0.0982(4)	0.0065(4)	0.0043(4)	0.0040(3)	-0.0015(3)	0.0011(3)	-0.0003(3)
C(8)	0.3597(3)	0.4611(4)	-0.0092(3)	0.0036(3)	0.0041(4)	0.0032(2)	0.0002(3)	0.0003(2)	-0.0005(2)
C(9)	0.4059(4)	0.2715(4)	0.0462(4)	0.0055(3)	0.0036(4)	0.0042(3)	-0.0003(3)	-0.0012(3)	-0.0004(3)
C(10)	0.4168(3)	0.3743(4)	-0.1932(3)	0.0031(2)	0.0027(3)	0.0030(2)	0.0002(2)	0.0002(2)	0.0002(2)
C(11)	0.4069(4)	0.3936(4)	-0.2726(3)	0.0042(3)	0.0045(4)	0.0030(2)	-0.0005(3)	-0.0001(2)	0.0010(2)
C(12)	0.4567(4)	0.4632(5)	-0.3076(4)	0.0048(3)	0.0061(5)	0.0040(3)	-0.0005(3)	0.0003(2)	0.0022(3)
C(13)	0.5148(4)	0.5136(5)	-0.2641(4)	0.0047(3)	0.0049(5)	0.0054(3)	-0.0009(3)	0.0006(3)	0.0021(3)
C(14)	0.5258(4)	0.4942(4)	-0.1853(4)	0.0039(3)	0.0044(4)	0.0051(3)	-0.0009(3)	0.0004(2)	0.0002(3)
C(15)	0.4769(3)	0.4241(4)	-0.1497(3)	0.0034(2)	0.0040(3)	0.0034(2)	0.0001(3)	0.0002(2)	0.0002(2)
C(16)	0.4244(3)	0.1729(4)	-0.1484(3)	0.0027(2)	0.0031(3)	0.0027(2)	-0.0000(2)	-0.0002(2)	-0.0001(2)
C(17)	0.4739(4)	0.1603(4)	-0.2118(4)	0.0051(3)	0.0039(4)	0.0041(3)	0.0005(3)	0.0014(2)	0.0005(3)
C(18)	0.5199(4)	0.0750(5)	-0.2196(4)	0.0063(4)	0.0059(5)	0.0055(4)	0.0014(4)	0.0030(3)	-0.0033(3)
C(19)	0.5165(4)	0.0004(4)	-0.1641(4)	0.0043(3)	0.0039(4)	0.0056(3)	0.0011(3)	0.0012(3)	-0.0003(3)
C(20)	0.4689(4)	0.0120(4)	-0.1013(4)	0.0038(3)	0.0034(4)	0.0044(3)	0.0004(3)	-0.0005(2)	0.0004(3)
C(21)	0.4225(3)	0.0990(4)	-0.0919(3)	0.0032(2)	0.0035(3)	0.0031(2)	0.0001(2)	-0.0002(2)	-0.0000(2)
C(22)	0.2753(3)	0.2481(4)	-0.2143(3)	0.0031(2)	0.0042(4)	0.0024(2)	-0.0007(2)	-0.0002(2)	0.0003(2)
C(23)	0.2182(4)	0.3190(5)	-0.2369(4)	0.0036(3)	0.0053(4)	0.0043(3)	0.0000(3)	-0.0006(2)	0.0011(3)
C(24)	0.1541(4)	0.2957(5)	-0.2886(4)	0.0040(3)	0.0052(5)	0.0042(3)	0.0003(3)	-0.0008(2)	0.0019(3)
C(25)	0.1461(4)	0.1981(6)	-0.3183(4)	0.0048(3)	0.0098(6)	0.0041(3)	-0.0030(4)	-0.0014(3)	0.0018(4)
C(26)	0.2012(4)	0.1296(5)	-0.2956(4)	0.0064(4)	0.0061(5)	0.0049(3)	-0.0019(4)	-0.0018(3)	0.0002(3)
C(27)	0.2649(4)	0.1527(4)	-0.2442(4)	0.0046(3)	0.0042(4)	0.0038(3)	-0.0009(3)	-0.0011(2)	0.0003(3)
C(28)	0.2137(4)	0.1489(5)	0.3547(4)	0.0057(4)	0.0054(5)	0.0053(3)	-0.0019(3)	-0.0005(3)	-0.0005(3)
C(29)	0.1776(5)	0.1948(6)	0.2794(4)	0.0075(5)	0.0089(6)	0.0042(3)	-0.0013(4)	-0.0002(3)	0.0004(4)
C(30)	0.3467(5)	0.2433(6)	0.3540(5)	0.0053(4)	0.0097(7)	0.0077(5)	-0.0025(4)	0.0026(3)	-0.0027(5)
C(31)	0.3976(6)	0.1428(9)	0.3323(7)	0.0066(5)	0.017(1)	0.0153(9)	-0.0000(6)	0.0024(5)	-0.0108(9)
C(32)	0.2334(5)	0.3158(5)	0.4191(4)	0.0073(4)	0.0047(5)	0.0061(4)	0.0009(4)	0.0015(3)	-0.0011(3)
C(33)	0.1533(5)	0.3073(7)	0.4636(5)	0.0067(5)	0.0129(9)	0.0068(5)	0.0015(5)	0.0013(4)	-0.0019(3)
C(34)	0.2934(5)	0.1604(6)	0.4769(5)	0.0082(5)	0.0068(5)	0.0066(4)	-0.0008(4)	-0.0029(4)	0.0017(4)
C(35)	0.3552(6)	0.2170(8)	0.5334(5)	0.0092(6)	0.0124(9)	0.0073(5)	-0.0021(6)	-0.0036(4)	0.0001(3)
H(1)	0.4806	0.2168	-0.2493	5.0000					
H(2)	0.5568	0.0668	-0.2638	5.0000					
H(3)	0.5475	-0.0627	-0.1720	5.0000					
H(4)	0.4647	-0.0395	-0.0571	5.0000					
H(5)	0.3256	0.1065	-0.0461	5.0000					
H(6)	0.2219	0.3899	-0.2166	5.0000					
H(7)	0.1148	0.3471	-0.3073	5.0000					
H(8)	0.0969	0.1817	-0.3538	5.0000					
H(9)	0.1954	0.0617	-0.3165	5.0000					
H(10)	0.3050	0.0997	-0.2245	5.0000					
H(11)	0.3642	0.3574	-0.3046	5.0000					
H(12)	0.4481	0.4781	-0.3664	5.0000					
H(13)	0.5492	0.5667	-0.2854	5.0000					
H(14)	0.5731	0.5251	-0.1553	5.0000					
H(15)	0.4839	0.4106	-0.0930	5.0000					
H(16)	0.264(3)	0.178(4)	-0.026(3)	2.8(5)					

vation parameters for the reaction of **1** with CO in THF at various temperatures were also calculated via the method of least squares. Each individual rate constant was given equal weight, and the confidence limits are also expressed at the 95% level.

X-ray Data Collection and Structure Determination. Single crystals of the air-stable compound were sealed in thin-walled, glass capillaries. The final lattice parameters as determined from a least-squares refinement of 13 reflections with $\theta > 20°$ are given in Table I. The space group was uniquely determined as $P2_1/n$ from the systematic absences, $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$.

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast 20°/min prescan. Calculated speeds based on the net intensities gathered in the prescan ranged from 7.0 to 0.3°/min. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity, the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0.9°$ and $B = 0.2°$. Aperture settings were determined in a like manner with $A = 4.00$ mm and $B = 2.11$ mm. Other diffractometer parameters and the method of estimation of the standard deviation have been described previously.[16] As a check on the stability of the instrument and the crystal, two reflections were measured after every 45 reflections. Only a random fluctuation of ±2% was noted. One independent quadrant of data was measured out to $2\theta = 50°$. A slow scan was performed on a total of 3518 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 50 was obtained in the prescan. On the basis of these considerations, the data set of 3518 reflections used in the subsequent structure determination and refinement was considered observed and consisted in the main of those reflections for which $I \geq 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but no absorption correction was applied.

Full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS.[17] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Mo, P, N, O, and C were taken from Cromer and Waber.[18] The scattering factor for molybdenum was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[19] Scattering factors for H were taken from ref 20.

The existence of four molecules per unit cell in the space group $P2_1/n$ imposed no crystallographic symmetry on the molecule. The position of one of the molybdenum atoms was revealed by the inspection of a Patterson map and subsequent difference Fourier maps phased on the molybdenum atom readily afforded the positions of all the remaining nonhydrogen atoms. Anisotopic refinement led to a discrepancy factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.056$. The hydrogen atoms on the phenyl groups were then placed at calculated positions 1.0 Å from the bonded carbon atoms. The R_1 factor was lowered to 0.046 and further anisotropic refinement led to a value of $R_1 = 0.034$. At this point examination of a difference Fourier map revealed the location of the bridging hydrogen atom (ca. 0.7 $e^-/Å^3$ compared to residual peaks near the molybdenum atom of ca. 0.9 $e^-/Å^3$). Refinement of the positional and thermal parameters of the

Table III. Bond Lengths (Å) and Angles (deg) for $Et_4N^+(\mu\text{-}H)[Mo(CO)_5][Mo(CO)_4PPh_3]^-$

		Bond Lengths	
Mo(1)-Mo(2)	3.4736 (7)	Mo(2)-C(6)	2.034 (7)
Mo(1)-C(1)	1.967 (6)	Mo(2)-C(7)	1.966 (6)
Mo(1)-C(2)	2.044 (6)	Mo(2)-C(8)	1.963 (6)
Mo(1)-C(3)	2.054 (6)	Mo(2)-C(9)	2.014 (7)
Mo(1)-C(4)	2.011 (7)	Mo(2)-P	2.565 (1)
Mo(1)-C(5)	2.027 (6)	P-C(10)	1.837 (5)
Mo(1)-H(16)	1.68 (5)	P-C(16)	1.838 (5)
Mo(2)-H(16)	2.19 (6)	P-C(22)	1.831 (5)
		Bond Angles	
Mo(1)-H(16)-Mo(2)	127 (3)	C(3)-Mo(1)-C(4)	91.6 (2)
C(10)-P-C(16)	100.2 (2)	C(3)-Mo(1)-C(5)	173.6 (2)
C(10)-P-C(22)	100.2 (2)	C(4)-Mo(1)-C(5)	92.9 (2)
C(16)-P-C(22)	101.5 (2)	C(6)-Mo(2)-H(16)	95 (1)
C(10)-P-Mo(2)	116.1 (2)	C(7)-Mo(2)-H(16)	104 (1)
C(16)-P-Mo(2)	118.3 (2)	C(8)-Mo(2)-H(16)	168 (1)
C(22)-P-Mo(2)	114.5 (2)	C(9)-Mo(2)-H(16)	86 (1)
C(1)-Mo(1)-H(16)	156 (2)	P-Mo(2)-H(16)	75 (1)
C(2)-Mo(1)-H(16)	93 (2)	P-Mo(2)-C(6)	94.9 (2)
C(3)-Mo(1)-H(16)	112 (2)	P-Mo(2)-C(7)	176.8 (2)
C(4)-Mo(1)-H(16)	86 (2)	P-Mo(2)-C(8)	93.6 (1)
C(5)-Mo(1)-H(16)	73 (2)	P-Mo(2)-C(9)	91.2 (2)
C(1)-Mo(1)-C(2)	93.2 (2)	C(6)-Mo(2)-C(7)	88.1 (3)
C(1)-Mo(1)-C(3)	91.7 (2)	C(6)-Mo(2)-C(8)	89.4 (2)
C(1)-Mo(1)-C(4)	88.8 (3)	C(6)-Mo(2)-C(9)	173.8 (3)
C(1)-Mo(1)-C(5)	83.9 (2)	C(7)-Mo(2)-C(8)	87.7 (2)
C(2)-Mo(1)-C(3)	85.0 (2)	C(7)-Mo(2)-C(9)	85.8 (3)
C(2)-Mo(1)-C(4)	176.1 (2)	C(8)-Mo(2)-C(9)	90.2 (2)
C(2)-Mo(1)-C(5)	90.6 (2)		

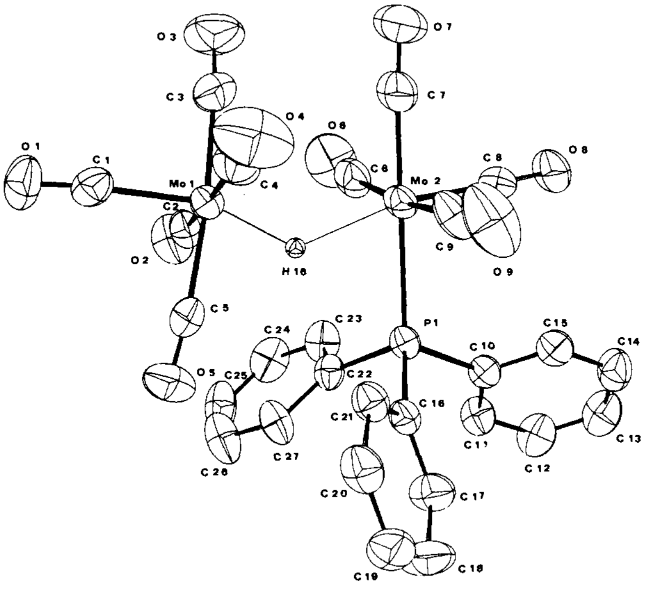


Figure 1. ORTEP plot of the structure of the $(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ molecular anion illustrating the numbering scheme.

hydrogen atom led to convergence at values of $R_1 = 0.032$ and $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2\}^{1/2} = 0.036$. The hydrogen atoms of the tetraethylammonium cation were not located. Unobserved reflections were not included, and unit weights were used at all stages. The largest parameter shifts in the final cycle of refinement were less than 0.03 of their esd's. The standard deviation of an observation of unit weight was 2.21. The final values of the positional and thermal parameters are given in Table II.[21]

Results and Discussion

A perspective view of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ (**1**) is presented in the ORTEP drawing given in Figure 1. Figure 2 illustrates the packing of **1** in the unit cell. A list of bond angles and bond lengths for the anion is given in Table III.

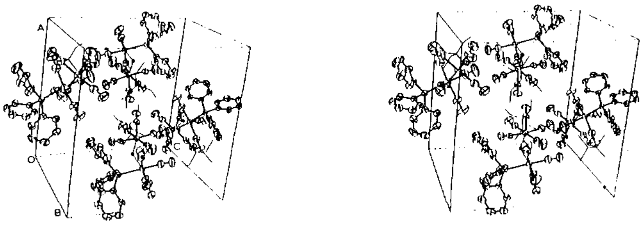


Figure 2. Stereoscopic view of the crystal packing of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$.

The anion exists as a bent dimer of pseudooctahedra, sharing a common hydrogen ligand, which does not itself strictly occupy the sixth octahedral site of each Mo. The bulky PPh_3 is positioned cis to the hydride bridge and exo to the bent $(OC)_{ax}Mo$- - -$Mo(CO)_{ax}$ backbone. The bend in the molecular anion framework, as defined by the angle of intersection of extensions of the C_1-Mo_1 and C_8-Mo_2 vectors, is 162.7 (5)°; the Mo-H-Mo angle is 127 (3)°. The equatorial carbonyls of Mo(1), C(2), C(3), C(4), and C(5) are all staggered with respect to their counterparts on Mo(2). This staggering is 24°; that is the C(4)-Mo(1)-Mo(2)-C(9) dihedral angle.

These gross structural features, which place **1** into structural type **3** (vide supra), are very similar to those of compounds determined previously by both X-ray and neutron diffraction techniques,[5] particularly the $(\mu\text{-}H)[W(CO)_5][W(CO)_3(P(OMe)_3)(NO)]$ compound, in which the $P(OMe)_3$ ligand is cis and the NO ligand is trans to the hydride bridge.[11] There are, however, unique details and details of definite dissimilarity which provide interesting comparisons to earlier structures and/or which are of importance to the dynamical chemistry of this anion. These include (a) the Mo-Mo distance and extent of the Mo-Mo interaction; (b) the notable asymmetry of the Mo-H-Mo bridge; (c) the long Mo-P bond distance.

As demonstrated in Table IV, for nonsubstituted dimeric carbonylates the distance between metals varies in the order "linear" $(\mu\text{-}H)[M(CO)_5]_2^-$ > "bent" $(\mu\text{-}H)[M(CO)_5]_2^-$ > $M_2(CO)_{10}^{2-}$, where "linear" and "bent" refer to the $(OC)_{ax}M$- - -$M(CO)_{ax}$ backbone as demonstrated in structures

Table IV. M-M Bond Distances

M-M	distance, Å[a]		ref	comments
Cr-Cr	3.386 (6)	$Et_4N^+(\mu\text{-H})[Cr(CO)_5]_2^-$	6	D_{4h}[b]
Cr-Cr	2.97 (1)	$[PPN^+]_2Cr_2(CO)_{10}^{2-}\cdot CH_2Cl_2$	7a	D_{4d}
Cr-Cr	4.1[c]	$PPN^+(\mu\text{-}I)[Cr(CO)_5]_2^-$	22	bent, eclipsed
Mo-Mo	3.123 (7)	$[PPN^+]_2Mo_2(CO)_{10}^{2-}\cdot CH_2Cl_2$	7a	D_{4d}
Mo-Mo	3.4736 (7)	$Et_4N^+(\mu\text{-H})[Mo_2(CO)_9PPh_3]^-$	[d]	bent, staggered
W-W	3.504 (1)	$Et_4N^+(\mu\text{-H})[W(CO)_5]_2^-$	5b, 9	D_{4h}
W-W	3.391 (1)	$PPN^+(\mu\text{-H})[W(CO)_5]_2^-$	9	bent, staggered
W-W	3.329	$HW_2(CO)_9NO$	10	bent, staggered
W-W	3.393 (4)	$HW_2(CO)_8P(OMe)_3NO$	11	bent, staggered
W-W	3.0162 (11)	$[Et_4N^+]_2H_2W_2(CO)_8^{2-}$	23	
Mn-Mn	2.923 (3)	$Mn_2(CO)_{10}$	24	D_{4d}
Tc-Tc	3.036 (6)	$Tc_2(CO)_{10}$	25	D_{4d}

[a] All error analyses are as presented in the respective references. [b] This and subsequent symmetry labels of anions ignore the position of the hydride bridge. [c] This distance was calculated from the Cr-I-Cr bond angle and Cr-I bond length data. [d] This work.

2 and **3**, *not* to the M-H-M fragment (as *all* of the latter have been shown to be bent). When positioned cis to the hydride bridge, substituents bulkier than CO are expected to loosen the dimeric structure according to the extent of steric interactions. The electronic effects to be considered, one of which definitely opposes and the second aligns with the direction of the steric effect, are as follows. The flexibility of the M-H-M linkage allows for bending of the dimer structure, and, as noted earlier, a staggering of equatorial carbonyls seems to accompany this bend thereby allowing for a closer approach of the metals. In the nonsubstituted $(\mu\text{-H})[W(CO)_5]_2^-$, where both (linear, eclipsed) and (bent, staggered) forms are known,[9] a decrease in W-W distance of ca. 0.15 Å is coincident with the bend. Secondly, accumulating evidence in favor of a double minimum potential well for the hydride position in $\mu\text{-H}[M(CO)_5]_2^-$ systems[12,14] leads to the quite reasonable physical interpretation of tautomeric forms of donor-acceptor complexes of the type $^-(OC)_5MH \rightarrow M(CO)_5$ and $(OC)_5M \leftarrow HM(CO)_5^-$.[5b] Substitution of CO by the better donor ligand PPh_3 decreases the ability of the $Mo(CO)_4PPh_3$ moiety to serve as an acceptor, and this effect by itself would lengthen the distance to its sixth ligand, $HMo(CO)_5^-$.

In the $(\mu\text{-H})[W(CO)_5][W(CO)_4(NO)]$[10] and $[W(CO)_5][\mathit{mer}\text{-}(\mu\text{-H})W(CO)_3(P(OMe)_3)NO)]$[11] structures, steric and electronic factors combine so as to only slightly lengthen (by ~0.06 Å) the W-W distance in the phosphite-substituted dimer. There is no substantial difference in the W-H-W angle (being 125° for the former and 129° for the latter) nor in the bend of the molecular anion framework, 151 and 153°, respectively. Although the PPh_3 ligand is sterically more demanding than $P(OMe)_3$, the substitution of PPh_3 for CO evidently causes even less change in the Mo-Mo distance. That is, the Mo-Mo separation in (bent, staggered) $\mu\text{-H}[Mo(CO)_5]_2^-$ as its PPN^+ salt was determined by X-ray analysis to be 3.4213 (9) Å.[26] Thus a steric factor for PPh_3 on the Mo-Mo distance of only 0.05 Å is obtained.

Note that the asymmetry of the Mo-H-Mo fragment is also consistent with the formulation of **1** as a donor-acceptor complex $[(CO)_5MoH \rightarrow Mo(CO)_4PPh_3]^-$. The hydride ligand itself interacts more strongly with the more electron-deficient moiety, $Mo(CO)_5$. The asymmetry observed here (Mo(1)-H = 1.68 (5) Å, Mo(2)-H = 2.19 (6) Å) is much more pronounced than that of $\mu\text{-H}[W(CO)_5][W(CO)_3(P(OMe)_3)(NO)]((OC)_5W\text{-}H$ = 1.859 (6) Å and $(ON)((MeO)_3P)(OC)_3W\text{-}H$ = 1.894 (6) Å), suggesting that the electron-withdrawing ability of NO and the donating ability of $P(OMe)_3$ combine in $W(CO)_3(POMe)_3)(NO)$ to effect an electronic environment very similar to that of $W(CO)_5$.

As the discussion in the last paragraph implies, it is not necessary to invoke the term "double minimum potential" to explain the asymmetry of the hydride position in this inherently electronically asymmetric complex anion. Nor can any persuasive argument be made for cation or intermolecular contacts as determinative of the hydride position or indeed any aspect of the anion's geometry. There is no intermolecular separation involving the bridging hydride that is less than 3.75 Å. The seven closest contacts of anion and cation are defined by the ethyl carbon-carbonyl oxygen distances and are as follows: C(29)- - -O(3), 3.377 (9); C(29)- - -O(4), 3.394 (10); C(29)- - -O(7), 3.530 (9); C(31)- - -O(2′), 3.354 (11); C(31)- - -O(4), 3.644 (12); C(33)- - -O(5″), 3.494 (10); C(35)- - -O(1″), 3.642 (11) Å.[27]

A combination of features, the asymmetric hydride and the substituent basic PPh_3 ligand, leads to an interesting structural effect. Essentially there are only two different Mo-C bond distances in the anion. The average equatorial Mo-C bond lengths for Mo(1)-C_{eq}, Mo(2)-C(6), and Mo(2)-C(9) are very nearly the same (ca. 2.03 Å). The Mo-C bond lengths to those carbonyls which are trans either to the bridging hydride or to the PPh_3 group, although shorter as expected, are practically identical (1.97 Å).

The Mo-P distance reported here, 2.565 (1) Å, is longer than that known for any neutral complexes. For example, the longest Mo-P distances are reported for rather rigid ligands where steric factors might account for a long bond: 2.522 Å for $Mo(CO)_4\text{-}[P(C_2H_5)]_5$[28] and 2.518 Å for $Mo(CO)_4\text{-}[CH_2(PPh_2)_2]$.[29] An Mo-P distance of 2.479 (5) Å was determined for $Mo(CO)_5[P(CH_2)_6N_3]$;[30] in that case of a "tied-back" phosphine ligand, steric interactions are minimal. Apparently this is the first structural report of a complex carbonylate anion containing an Mo-P bond. Since the predominant binding of PPh_3 to metals lies in the σ-donor ability of PPh_3, the effect of the anionic charge is to diminish the Mo-P interaction. In this case the steric factor reinforces the electronic situation; however, the latter is expected to be paramount in determining Mo-P bond length. In contrast, the Mo-C bond distances of this anion are scarcely altered from those of neutral analogues; the unique ability of CO to achieve a charge balance through its σ-donor and π-acceptor ability is again documented.

That the long Mo-P distance suggests a weak Mo-PPh_3 bond is borne out by the chemical characterization of **1**. The following experimental results have aided in qualitatively and quantitatively establishing the lability of the phosphine ligand

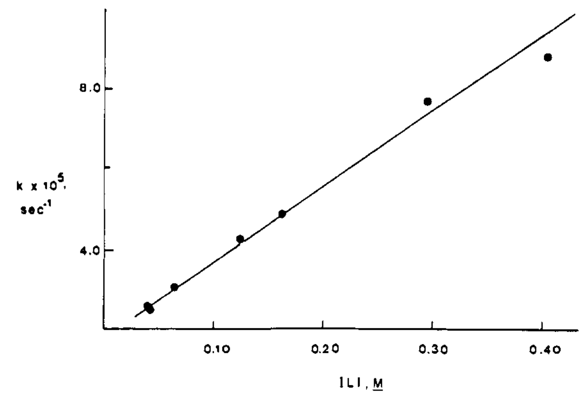


Figure 3. The rate constant, k_{obsd}, dependency on ligand concentration is illustrated by this plot of the data from Table V.

and also have provided insight into the mechanistic role of **1** in the reaction of $Et_4N^+(\mu\text{-}H)[Mo(CO)_5]_2^-$ with PPh_3 to produce *cis*-$Mo(CO)_4(PPh_3)_2$: (1) the dependence of the rate of reaction 1 on PPh_3 concentration; (2) the low activation energy for reaction 2, whose barrier reflects the Mo-P cleavage process; (3) the retardation of (2) by PPh_3; (4) the ready metathesis of PPh_3 in **1** by $P(p\text{-tolyl})_3$ and CO.

$$\mathbf{1} + PPh_3 \rightarrow cis\text{-}Mo(CO)_4(PPh_3)_2 \tag{1}$$

$$\mathbf{1} + CO \rightleftharpoons \mu\text{-}H[Mo(CO)_5]_2^- \xrightarrow[H^+/CO]{\Delta} Mo(CO)_6 + H_2 \tag{2}$$

The rate expression for reaction 1 shows a dependence on the concentration of PPh_3 as well as on **1** (Table V and Figure 3):

$$\text{rate} = k_{obsd}[\mathbf{1}] \tag{3}$$

$$k_{obsd} = k + k'[PPh_3] \tag{4}$$

If an associative or dissociative interchange mechanism were to be of importance to the substitution reactions of bridging hydride carbonylates, one would reasonably expect that an even more prominent ligand-dependent term would be present in the rate expression for the analogous reaction of the sterically less hindered and electronically less rich $\mu\text{-}H[M(CO)_5]_2^-$ with donor ligands. Since there is *no* rate dependence on ligand concentration for the reaction of $\mu\text{-}H[Mo(CO)_5]_2^-$ with PPh_3[3] and much evidence for the facile metathesis of PPh_3 in **1** (vide infra), the $[PPh_3]$ dependence observed for (1) is probably best ascribed not to a mechanism involving coordinative expansion of **1** but rather to the existence of a nonproductive equilibrium (i.e., nonproductive in the sense of eq 1, a reaction of higher energy than (5)):

$$\mathbf{1} \rightleftharpoons [(\mu\text{-}H)Mo_2(CO)_9(THF)^-] + PPh_3 \tag{5}$$

An increase of the concentration of PPh_3 shifts equilibrium 5 toward the left and leads to higher concentrations of **1**. *It is the complete dimer,* **1**, *coordinatively saturated, which is the kinetically active species toward further substitution or dimer disruption in the process that leads to neutral* $L_2Mo(CO)_4$ (eq 1).[3]

Table V. First-Order Rate Constants for the Reaction of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ [a] with PPh_3 in Refluxing THF under N_2

$L^a \times 10^2$, M	$k \times 10^5$, s^{-1}	$L^a \times 10^2$, M	$k \times 10^5$, s^{-1}
4.21	2.63 ± 0.62	16.2	4.42 ± 0.31
4.24	2.53 ± 0.16	29.4	7.83 ± 0.69
6.51	3.05 ± 0.21	40.5	8.75 ± 0.90
12.4	4.12 ± 0.21		

[a] [Carbonylate] = 4.2×10^{-3} M.

Table VI. First-Order Rate Constants for the Reaction of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ with CO and PPh_3 in CO-Saturated THF at 51.6 °C[a]

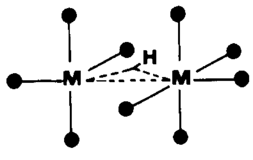
$[PPh_3] \times 10^2$, M	$k \times 10^4$, s^{-1}	$[PPh_3] \times 10^2$, M	$k \times 10^4$, s^{-1}
0	5.08 ± 0.30	4.46	1.59 ± 0.24
0	4.82 ± 0.24	8.73	1.16 ± 0.04
1.25	3.47 ± 0.40	11.0	0.67 ± 0.04

[a] [Carbonylate] = 1.1×10^{-2} M, [CO] estimated at 8.8×10^{-3} M.[34,35]

The maximum rate constant experimentally obtained for the disappearance of **1**, according to eq 1, which requires a dissociation of CO, was measured at a $[PPh_3]$ excess of 100-fold. That value, 8.75×10^{-5} M, is about five times smaller than that for the loss of CO from $Et_4N^+(\mu\text{-}H)[Mo(CO)_5]_2^-$ under the same conditions of solvent and temperature.[3] These data imply that PPh_3 does not promote CO loss from **1**, contrary to its apparent cooperative behavior in $Ir_4(CO)_{12n}(PPh_3)_n$ (n = 2, 3).[31]

Disubstituted dimers, $(\mu\text{-}H)[Mo_2(CO)_8L_2^-$, have been prepared for the smaller phosphines (L), $PMePh_2$, $P(CH_2)_6N_3$, and $(Ph_2P)_2(CH_2)_n$ (n = 1, 2, 3).[32] Spectroscopic (NMR, IR) data suggest that each Mo bears a phosphorus donor ligand in these compounds. Which CO is dissociated from **1** or similar $(\mu\text{-}H)[Mo_2(CO)_9L]^-$ anions en route to the more highly substituted compounds is uncertain. Loss of CO from the $Mo(CO)_5$ moiety in **1** could directly lead to the observed products. On the other hand, phosphines are termed by Atwood and Brown[33] as "cis labilizers" and as such might promote loss of CO from the $-Mo(CO)_4L$ moiety. If such were the case, CO migration from the $Mo(CO)_5$ group to the thus formed $Mo(CO)_3L$ would precede the addition of a second L. Evidence capable of distinguishing between these and other possible mechanisms will require the careful monitoring of isotopically labeled CO groups on stereospecifically labeled molecules.

The reaction of **1** with ^{13}CO in refluxing THF proceeds with stereospecific incorporation of ^{13}CO cis to the hydride bridge. Consistent with this result, it was suggested that the $HMo_2(CO)_9^-$ intermediate afforded by PPh_3 dissociation had one coordinatively unsaturated molybdenum center which was square pyramidal in geometry with the bridging hydride ligand being in an equatorial position (**4**). Alternatively, such an intermediate could involve a bridging carbonyl (structure **5**).



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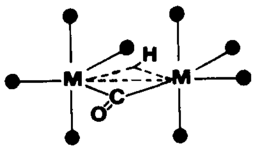

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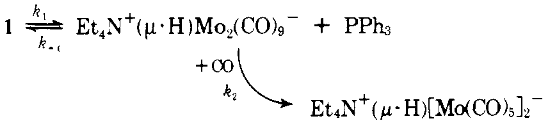
The relative reactivities of the $HMo_2(CO)_9^-$ intermediate, produced by phosphine dissociation from **1**, toward recombination with CO or with PPh_3 have been compared. In a series of competition experiments **1** was reacted with CO and PPh_3 in CO-saturated THF[34,35] at 51.6 °C with varying PPh_3 concentration. As seen from the data in Table VI, PPh_3 retards the rate of the forward reaction of eq 6. It has previously been



$$\mathbf{1} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Et_4N^+(\mu\text{-}H)Mo_2(CO)_9^- + PPh_3 \xrightarrow[k_2]{+CO} Et_4N^+(\mu\text{-}H)[Mo(CO)_5]_2^- \tag{6}$$

Table VII. Reactions of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ with CO in CO-Saturated THF at Various Temperatures[a]

temp, °C	$k^b \times 10^4, s^{-1}$	temp, °C	$k^b \times 10^4, s^{-1}$
37.3	1.00 ± 0.06	51.6	4.82 ± 0.24
46.7	2.93 ± 0.18	58.6	9.75 ± 1.82
51.6	5.08 ± 0.30		

[a] [Carbonylate] = 1.1×10^{-2} M, [CO] estimated at 8.8×10^{-3} M.[34,35] [b] Activation parameters calculated from these data: E_{act} = 23.8 ± 2.4 kcal/mol, $\Delta H^{\ddagger}$ = 23.2 ± 2.4 kcal/mol, $\Delta S^{\ddagger} = -8.0 \pm 7.7$ eu.

shown[36] from a steady-state solution of equations of the same form as eq 6 that $1/k_{obsd}$ is linearly related to $[PPh_3]/[CO]$. The slope of such a plot is k_{-1}/k_1k_2. Since k_1 is known to be $5.0 \times 10^{-4}\ s^{-1}$ (Table VI), the competition ratio, k_{-1}/k_2, for the reaction given by eq 6 is 0.46, indicating that the coordinatively unsaturated intermediate is fairly nondiscriminating with respect to reestablishing its complete coordination number (although a slight preference for CO perhaps exists). Similar studies of such reactive intermediates as $[Mo(CO)_4PPh_3]$ and $[Mo(CO)_5]$ have likewise shown an insensitivity to the nature of the incoming ligand.[37,38]

The competition experiment described above is compelling evidence for the highly dissociative nature of the reaction of **1** with CO. The transition state looks very much like the intermediate, $\mu\text{-}HMo_2(CO)_9^-$, hence activation energy parameters for this reaction may be utilized to measure the Mo–P bond strength. The first-order rate constants determined for eq 6 at various temperatures are given in Table VII. The enthalpy of activation for PPh_3 loss is 23.2 ± 2.4 kcal/mol, and the corresponding entropy of activation is −8.0 ± 7.7 eu. These data are aptly compared with those obtained for the reaction of *cis*-$Mo(CO)_4(PPh_3)_2$ with CO to yield $Mo(CO)_5PPh_3$.[39] The activation parameters for this process were determined to be $\Delta H^{\ddagger}$ = 29.7 kcal/mol and $\Delta S^{\ddagger}$ = 14.2 eu. The difference in $\Delta H^{\ddagger}$ for PPh_3 loss in **1** and in *cis*-$Mo(CO)_4(PPh_3)_2$ is due to the Mo–P bond energy difference whereas the difference in $\Delta S^{\ddagger}$ is probably dominated by the greater solvent reorganization required in the case of the anion than in the case of the neutral intermediate.

Triphenylphosphine in **1** is readily metathesized under mild conditions with $P(p\text{-tolyl})_3$ to produce $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9P(p\text{-tolyl})_3]^-$. Reaction of **1** with 20-fold or greater excesses of L, where L = $P(OEt)_3$ or $P(OPh)_3$, gives rise to species which have infrared spectra indicative of a mixture of $\mu\text{-}HMo_2(CO)_{10-x}L_x^-$ (x = 1, 2) complexes, none of which have been isolated. Nevertheless, the low selectivity of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9]^-$ implies that the metathesis of other phosphines for PPh_3 in **1** is quite a general reaction.

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Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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