to replacement of only one two-electron ligand. (2) Acetylene reacts with $W(CO)_3(dtc)_2$ quantitatively in minutes; no detectable reaction occurs with ethylene over a period of days. (3) Sixteen-electron complexes of Mo(II) and W(II) carbonyls are expected to behave as very reactive electrophiles;[7] $M(CO)(RC{\equiv}CR)(dtc)_2$ compounds resist nucleophilic attack even in refluxing THF. Examples of olefin analogs of alkyne complexes are known only for cases where N is equal to 2: $(\pi\text{-}C_5H_5)_2M(C_2H_4)$,[8] $[(\pi\text{-}C_5H_5)Mo(\pi\text{-}C_6H_6)(C_2H_4)]^+$,[9] $[PtCl_3(C_2H_4)]^-$[10], and $PtL_2(C_2H_4)$.[11] No olefin analogs of the "electron deficient" [12] alkyne complexes ($N > 2$) have been synthesized.

We are not aware of any other ligand which exhibits C-13 chemical shifts spanning a range of nearly 100 ppm when bound to the same transition metal ion in the same oxidation state. In our judgment the major factor responsible for the extraordinary chemical-shift variations of metal-bound acetylenic carbon nuclei stems from the unique ability of the alkyne ligand to function as a variable electron donor. The implications of variable electron donation from alkyne ligands are of potential importance in organometallic reactions involving facile interplay between 16- and 18-electron complexes. Known examples of variable electron donor ligands include nitrosyl[13] and allyl,[14] and the role of these ligands in catalytic reaction cycles[15] underscores the significance of identifying and investigating the electronic flexibility of acetylenic ligands.

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Joseph L. Templeton,* Bennett C. Ward
W. R. Kenan, Jr., Laboratory
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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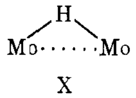
The μ-H[Mo(CO)$_4$PMePh$_2$]$_2^-$ Anion: An Example of Phosphine Enhancement of Metal-Metal Interaction

Sir:

Previous studies on the mechanism of $\mu\text{-}H[Mo(CO)_5]_2^-$ dimer disruption yielding neutral disubstituted $Mo(CO)_4P_2$ products led to the conclusion that at least one substitution of carbonyl by P on the *intact dimer* (anion **1** of Scheme I) must occur prior to dissociation of the X grouping.[1-3] Primary

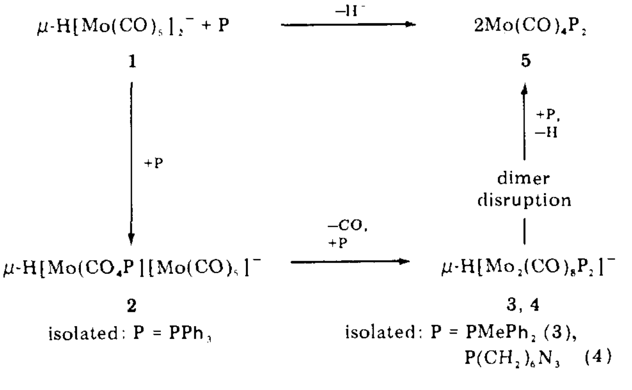


substantive evidence for this conclusion was afforded by the isolation and exhaustive analytical, X-ray structural, and kinetic characterization of the PPh_3 monosubstituted dinuclear anion (**2**) as its Et_4N^+ salt.[2] Although the fragments $[Mo(CO)_4P]$ and $HMo(CO)_5^-$ might be proposed as reasonable precursors to the disubstituted neutral products from **2**, there was no spectroscopic evidence for the possibly observable latter fragment and in fact kinetic data[2] supported the conversion of **2** into **3** via a CO dissociation—again from an intact dimer, **2**.[4,5] The intriguing possibility of isolation of disubstituted dinuclear bridging hydrides motivated an attempt at their syntheses, making use of the sterically less demanding ligands, $PMePh_2$ and $P(CH_2)_6N_3$.[6]

Compounds chemically analyzing as Et_4N^+ $[HMo_2(CO)_8P_2]^-$ were obtained from the reaction of Et_4N^+ $\mu\text{-}H[Mo(CO)_5]_2^-$ with a 10-fold excess of $PMePh_2$ or $P(CH_2)_6N_3$ in refluxing THF after reaction periods of 2–3 h. [Longer reaction periods led to the production of $P_2Mo(CO)_4$ neutral compounds.] Crystalline products in isolated yields of 10% for the $PMePh_2$ derivative and ~60% for the $P(CH_2)_6N_3$ derivative were obtained after filtration under N_2, addition of hexane, and cooling. The ν(CO) IR spectrum [P = $PMePh_2$; ν (CO) 2021 (w), 1989 (w), 1906 (s), 1875 (sh), 1822 (m)] was not straightforwardly interpretable by symmetry arguments[7,8] nor could the NMR hydride pattern (triplet centered at 11.75 ppm upfield from Me_4Si; with J_{P-H} = 16.6 Hz for P = $PMePh_2$) or the ^{31}P NMR spectrum (doublet at 18.92 ppm upfield from 85% H_3PO_4, J_{P-H} = 16.6 Hz)[9] differentiate between disubstitution on one Mo center or monosubstitution of two Mo centers. An X-ray crystal structure analysis has confirmed the latter arrangement. The structural parameters given below demonstrate a singular facility of the μ-H-dinuclear anions to accommodate both the added electron density and the steric crowding resulting from two $PMePh_2$ substitutents in a manner advantageous to the Mo···Mo interaction.

A bright orange plate-like crystal of the compound was sealed under nitrogen in a thin-walled glass capillary. The space group is $P2_1/c$, the lattice parameters are a = 14.940

Scheme I



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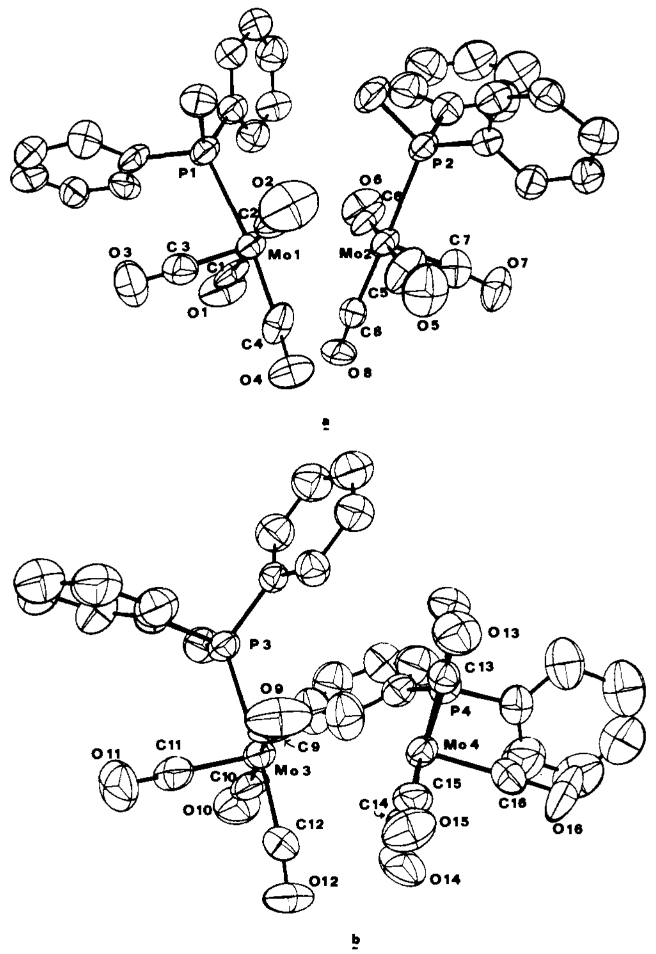

Figure 1. Structure of the two crystallographically independent anions (a, b) of $Et_4N^+[HMo_2(CO)_8P_2]^-$ with the atoms represented by their 50% probability ellipsoids for thermal motion. Important bond lengths in a include Mo(1)-P(1) = 2.540 (4), Mo(1)-C(1) = 2.05 (2), Mo(1)-C(2) = 2.00 (2), Mo(1)-C(3) = 1.90 (2), Mo(1)-C(4) = 1.97 (1), Mo(2)-P(2) = 2.543 (4), Mo(2)-C(5) = 2.04 (2), Mo(2)-C(6) = 2.02 (2), Mo(2)-C(7) = 1.97 (2), and Mo-C(8) = 1.94 (2) Å; bond angles in a are P(1)-Mo(1)-C(4) = 173.3 (5), P(1)-Mo(1)-C(3) = 87.0 (5), P(2)-Mo(2)-C(8) = 177.3 (5), and P(2)-Mo(2)-C(7) = 93.5 (5)°; The distance Mo(1)-Mo(2) = 3.443 (1) Å. For b, Mo(3)-Mo(4) = 3.442 (1), Mo(3)-P(3) = 2.553 (4), Mo(3)-C(9) = 2.04 (2), Mo(3)-C(10) = 2.05 (2), Mo(3)-C(11) = 1.94 (2), Mo(3)-C(12) = 1.99 (1), Mo(4)-P(4) = 2.541 (4), Mo(4)-C(13) = 2.00 (1), Mo(4)-C(14) = 2.05 (2), Mo(4)-C(15) = 1.95 (1), and Mo(4)-C(16) = 1.95 (1) Å; bond angles are P(3)-Mo(3)-C(12) = 175.4 (4), P(3)-Mo(3)-C(11) = 87.2 (5), P(4)-Mo(4)-C(15) = 172.7 (4), and P(4)-Mo(4)-C(16) = 88.2 (5)°.

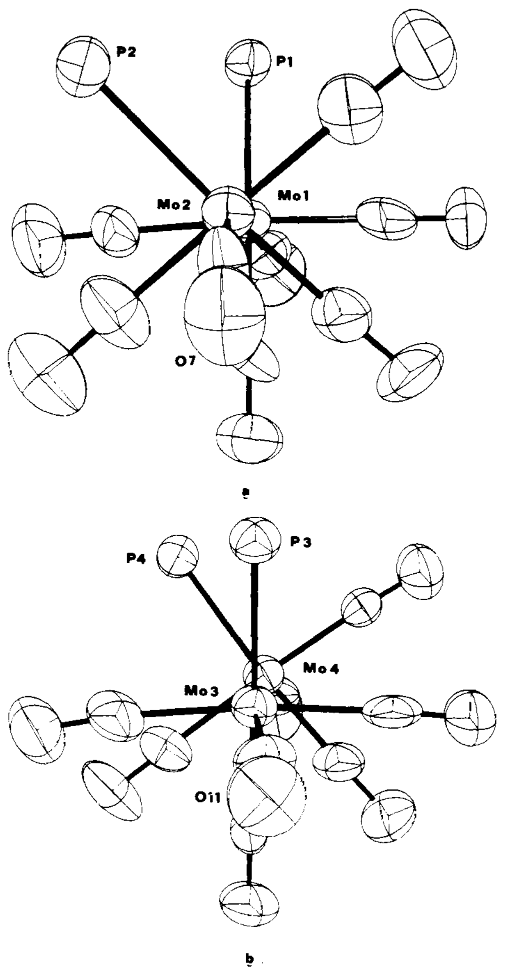

Figure 2. View along the Mo- - -Mo vectors for **3a** and **3b** illustrating the two independent molecular anions distinguished by the torsion angles P(1)-Mo(1)-Mo( )-P(2) = +43 and P(3)-Mo(3)-Mo(4)-P(4) = −38°. Note the positioning of the phosphine ligands exo to the bent molecular anion framework as defined by the intersection of vectors connecting O(7)-C(7)-Mo(2) and O(3)-C(3)-Mo(1) for **3a** and, for **3b**, vectors connecting O(11)-C(11)-Mo(3) and O(16)-C(16)-Mo(4). In accordance with the earlier structure,[2] the bridging hydride ligand is assumed to lie just off this intersection point.

(5), $b = 40.366$ (9), $c = 14.690$ (5) Å; $\beta = 90.56$ (2)°; $\rho_{calcd} = 1.42$ g cm^{-3} for $Z = 8$. Data (Mo Kα radiation) collected out to $\theta = 20°$ yielded 8134 independent observed reflections. The four independent molybdenum atoms were located via the direct methods MULTAN 74[10] system and subsequent difference Fourier maps yielded the position of the remaining nonhydrogen atoms. Full-matrix least-squares refinement produced a final agreement factor of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.076$. Hydrogen atoms on the phenyl groups were included at calculated positions and all nonhydrogen atoms were refined with anisotropic thermal parameters. The bridging hydrides were not evident on a difference Fourier and hydrogen atoms on the cation and methyl groups were not included.

The μ-H[Mo(CO)$_4$(PMePh$_2$)]$_2^-$ (**3**) dinuclear anion is of the (bent, staggered) configuration and the phosphine substituent on each pseudooctahedral molybdenum center is, as was noted for the μ-H[Mo$_2$(CO)$_9$PPh$_3$]$^-$ (**2**) molecular anion,[2] cis to the hydride bridge. As Figures 1 and 2 show, both PMePh$_2$ ligands are exo to the bent (OC)$_{ax}$-Mo-Mo(CO)$_{ax}$ molecular anion backbone and the staggering of separate Mo(CO)$_4$P units of +43 and −38° [the P(1)-Mo(1)-Mo(2)-P(2) and P(3)-Mo(3)-Mo(4)-P(4) torsion angles, respectively] accounts for the presence of two distinct molecular anions in the unit cell. The molecular anion **3** responds to the presence of two phosphine substituents as compared with one in **2** by exhibiting a greater framework bend; i.e., the angle of intersection defined by the two (OC)$_{ax}$-M vectors is 163° for the monosubstituted anion[2] and 148° for the disubstituted anion **3**. The greater bend coincides with a Mo-Mo distance [3.443 (1) Å] significantly shorter than that of **2** [3.4736 (1) Å][2] and only 0.02 Å longer than the Mo-Mo distance of (bent, staggered) μ-H[Mo(CO)$_5$]$_2^-$ [3.4213 (9) Å, PPN$^+$ salt].[11] The steric crowding of the two asymmetric ligands is minimized by a meshing of substituents. As Figure 1 shows, the methyl groups are oriented inwardly toward the M-H-M bridge which allows the large phenyl groups to fan out over the Mo(CO)$_4$ groups.

Other structural parameters of note are as follows. The Mo-P average bond length of 2.54 Å is from 0.02 to 0.06 Å longer than the typical Mo-P distance in neutral molecules.[12] Furthermore, an interesting parity exists in the M-C distances to carbonyls trans to PMePh$_2$ and to the bridging hydride.

Thus there are only two sets of M–C distances in the molecular anion; the shorter averages to 1.95 (2) Å and the longer [the Mo–C distance to equatorial carbonyls trans to each other] averages to 2.05 (2) Å. It should be stated that there are no significant intermolecular or interionic interactions which might influence molecular geometry.

Appropriate and interesting comparisons may be made between disubstituted, dinuclear species containing full metal–metal bonds and the title compound. Phosphine ligands are attached *diaxially* in the staggered dimers $[Mn(CO)_4L]_2$ (L = $PMePh_2$,[13] PPh_3,[14] $AsPh_3$,[14] and PEt_3[15]). Although the less bulky (aided by a longer M–L bond) $AsMe_2Ph$ ligands are attached *diequatorially* in eclipsed $[Mn(CO)_4(AsMe_2Ph)]_2$,[13] the As(1)–Mn(1)–Mn(2)–As(2) torsion angle is around 180°; i.e., the ligands are on opposite sides of the molecule. Earlier solid-state structural studies of VIB bridging hydride complexes have shown an impressive ease of interconversion between bent and linear forms of $\mu\text{-H}[W(CO)_5]_2^-$.[16,17] For that anion a simple change in counterion from Et_4N^+ to PPN^+ or PPh_4^+ effects a change in molecular anion structure from (linear, eclipsed) to (bent, staggered), respectively. (Notably the bending leads to a decrease in W–W distance of ~0.15 Å.) If steric factors only dictated the structure of $\mu\text{-H}[Mo_2(CO)_9PPh_3]^-$ or $\mu\text{-H}[Mo(CO)_4(PMePh_2)]_2^-$, then we would expect a linear geometry with substituents positioned to minimize interactions, analogous to the manganese dimers. The observed geometry defined above for $\mu\text{-H}[Mo(CO)_4(PMePh_2)]_2^-$ strongly suggests that this anion actually profits from steric interactions. Not only does the greater electron-donating ability of the two substituents provide for greater Mo–Mo overlap in the three-center, two-electron bridged hydride bond,[18] as compared to the $\mu\text{-H}[Mo_2(CO)_9PPh_3]^-$ case, but the positioning of both substituents on the same side of the molecular anion allows for steric strain to be applied to greatest advantage with regards to the Mo···Mo interaction.

Finally, the orientation of the phosphine methyl groups towards the X grouping suggested the possibility of linking the phosphorus donor sites. Reactions of Et_4N^+ $\mu\text{-H}[Mo(CO)_5]_2^-$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3) have yielded nicely crystalline, yellow, carbonyl-containing salts. Elemental analyses as well as infrared and NMR data suggested these salts to contain phosphine substituted, bridging hydride, dinuclear anions, analogous to the title anion, i.e.,

$$\mu\text{-H}[(OC)_4Mo \leftarrow PPh_2(CH_2)_nPh_2P \rightarrow Mo(CO)_4]^-$$

The bridging diphos ligands are apparently much less labile than the monodentate ligands. For example, Et_4N^+ $\mu\text{-H}[Mo(CO)_4)PMePh_2]_2^-$ in refluxing THF solution reacted with CO in a matter of minutes to produce $\mu\text{-H}[Mo_2(CO)_9PMePh_2]^-$ and, over the course of a day, to produce $\mu\text{-H}[Mo(CO)_5]_2^-$. The propylenediphos linked dinuclear anion however under similar reaction conditions showed no production, of $\mu\text{-H}[Mo_2(CO)_9PPh_2(CH_2)_3PPh_2]^-$, but rather a slow production (slower by a factor of 2 than the analogous reaction described above) of $\mu\text{-H}[Mo(CO)_5]_2^-$ was obtained.

Currently, chemical studies of these systems are being extended to include protonation and other reactions which would probe the hydride functionality.

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(19) (a) Tulane University; (b) University of Alabama.

Marcetta Y. Darensbourg,*[19a] J. L. Atwood*[19b]
W. E. Hunter,[19b] R. R. Burch, Jr.[19a]
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118, and
Department of Chemistry, University of Alabama
University, Alabama 35486

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Intermolecular Reduction of Coordinated Ligands by Transition Organometallic Hydride Reagents

Sir:

Transition organometallic hydride complexes[1] are of immense importance to the development of organometallic chemistry. Their most prevalent reactivity mode, alkene insertion,[2] corresponds to a concerted addition of a metal hydride across a substrate multiple bond within the same coordination sphere. Intermolecular modes of reactivity are also available and entail either proton transfer,[3] hydrogen atom donation,[4] or nucleophilic attack by the metal–H bond.[5] Relatively little, however, is known of the formal transfer of hydride from a transition organometallic hydride complex to an electrophile, irrespective of their hydridic nomenclature and the localization of negative charge on the hydrogen end of neutral metal carbonyl hydrides.[6] Both trityl carbocation[7a,b] and the proton[7b,c] abstract hydride from the limited number of transition metal hydrides examined. Several early transition metal hydride complexes $Cp_2Zr(H)X$ (X = Cl, R;[8a] Cp = $\eta^5\text{-}C_5H_5$), $(\eta^5\text{-}C_5Me_5)_2ZrH_2$,[8b] and Cp_2NbH_3[8c] additionally transfer hydride to water, organic ketones, and even coordinated CO.

We now report that first row, group 8 transition organometallic hydride reagents effect intermolecular hydride addition to coordinated alkene and carbene ligands. The readily available $CpFe(CO)Ph_3P(H)$[9] quantitatively reduces, as evidenced by IR monitoring, several $CpFe(CO)_2\text{-}\eta^2$-alkene salts