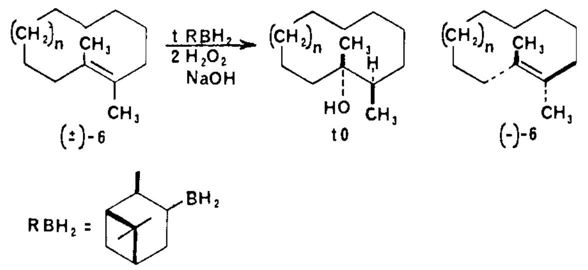
(+)-camphorsulfonate **1a** and products derived therefrom possess a high degree (>90%) of enantiomeric purity.

Following the above described sequence, the camphorsulfonate **1b** was prepared.[6] Fractional crystallization from ethyl acetate afforded material of mp 157-159 °C, $[\alpha]^{25}_D$ +6.4° (*c* 3.25, $CHCl_3$). Reduction-fragmentation with lithium aluminum hydride gave the diene **2b** [mp 59-61 °C, $[\alpha]^{22}_D$ −52.6° (*c* 6.45, EtOH)] and alcohol **5b.** Acetylation of **2b** and Li/NH_3 reduction yielded the diene **4b,** $[\alpha]^{22}_D$ −90° (*c* 3.28, $CHCl_3$). Selective hydroboration-oxidation followed by decarbonylation, as before, yielded (+)-*trans*-1,2-dimethylcycloundecene [**6b,** bp 190-205 °C at 750 Torr, $[\alpha]^{22}_D$ +29.1° (*c* 1.46, $CHCl_3$)].[13]

Enone **9b** [bp 80-85 °C at 0.2 Torr, $[\alpha]^{25}_D$ +109° (*c* 4.7, CH_3OH)], obtained through PCC oxidation of alcohol **5b,**[7] showed a similar ORD curve to that of **9a** indicating that it too possesses the *R* configuration. Thus olefins **2b-4b** and **6b-8b** must have the *S* configuration as shown.[3]

Efforts to prepare the bicyclo[7.3.1]tridecanediol **1c** (X = OH) met with unexpected problems, so we employed asymmetric hydroboration to assess the optical stability of *trans*-1,2-dimethylcyclododecene. Accordingly, treatment of racemic *trans*-1,2-dimethylcyclododecene (**6c**) with 0.5 mol equiv of monoisopinocampheylborane,[14] followed by oxidation with alkaline H_2O_2, afforded a mixture of alcohol **10c** [25% yield, mp 68-73 °C, $[\alpha]^{22}_D$ +14.9° (*c* 14.5, CH_2Cl_2)] and recovered racemic dimethylcyclododecene, $[\alpha]^{22}_D$ 0°. In contrast, racemic *trans*-1,2-dimethylcyclodecene (**6a**) afforded enriched (−)-*trans*-1,2-dimethylcyclododecene [33% yield, $[\alpha]^{22}_D$ −18° (*c* 1.3, CH_2Cl_2)] upon similar treatment. We therefore conclude that *trans*-1,2-dimethylcyclododecene must racemize at or below room temperature.



These results show that methyl substituents on the double bond permit optically stable *trans*-cycloundecenes to be prepared.[13] Presumably bulkier substituents such as *tert*-butyl would further increase the optical stability of *trans*-cycloalkenes and thus enable isolation of even larger ring optically active homologs.

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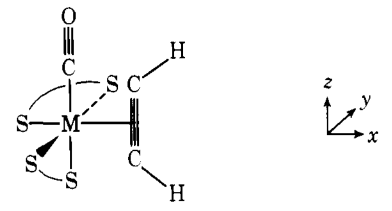
Carbon-13 Chemical Shifts of Alkyne Ligands as Variable Electron Donors in Monomeric Molybdenum and Tungsten Complexes

Sir:

The role of η^2-alkyne ligands in mononuclear metal complexes is commonly considered to parallel the Dewar-Chatt-Duncanson bonding model.[1] Properties of (η^2-alkyne)tungsten(II) complexes have recently been interpreted as manifesting electron donation not only from the acetylene $\pi_\parallel$ orbital but also from the filled acetylene $\pi_\perp$ orbital to tungsten.[2] We wish to communicate an empirical correlation between the number of electrons formally donated per alkyne ligand (*N*) compatible with an inert gas configuration for the metal center and the chemical shift of the bound alkyne carbon nuclei for a series of ten monomeric alkyne complexes of molybdenum and tungsten. The *N* values listed in Table I can be rationalized by molecular orbital considerations in each case.

The observed relationship between δ and *N* can be illustrated



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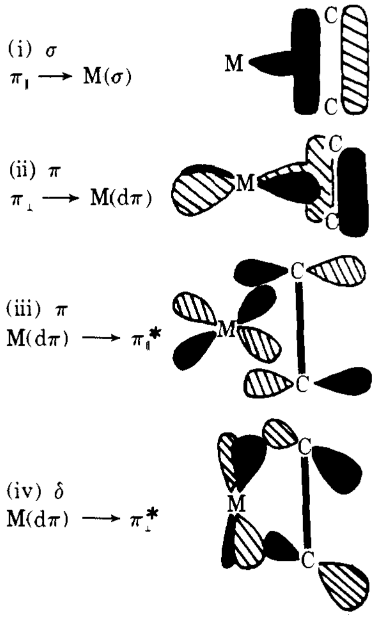


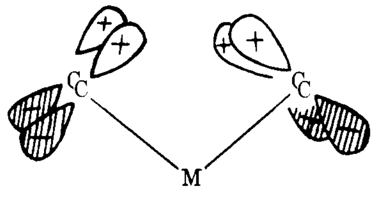
Table I. Carbon-13 Chemical Shifts of Alkyne Carbons Bound to Molybdenum(II) and Tungsten(II)

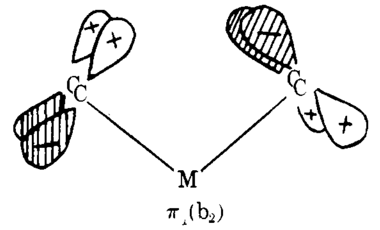
complex	$\delta(\mathrm{R^{13}C{\equiv}CR})$[a]	δ_{av}	N[b]	ref
$\mathrm{W(CO)(detc)_2(HC{\equiv}CH)}$ (**1**)	206.1, 207.1	206.6	4	this work
$\mathrm{W(CO)(detc)_2(HC{\equiv}CPh)}$[c] (**2**)	205.7	205.7	4	this work
$(\pi\text{-}\mathrm{C_5H_5})\mathrm{W(CO)(CH_3)(HC{\equiv}CH)}$ (**3**)	192.5, 187.4	190.0	4	*d*
$\mathrm{Mo(CO)(dmtc)_2(HC{\equiv}CH)}$ (**4**)	203.7	203.7	4	this work
$\mathrm{Mo(CO)(dmtc)_2(HC{\equiv}CPh)}$[c] (**5**)	205.3	205.3	4	this work
$\mathrm{W(CO)(CH_3CH_2C{\equiv}CCH_2CH_3)_3}$ (**6**)	191.1, 170.8	181.0	$3\frac{1}{3}$	this work
$[(\pi\text{-}\mathrm{C_5H_5})\mathrm{W(CO)(CH_3C{\equiv}CC_4H_9)_2}]^+$ (**7**)	162.2, 159.4, 144.8, 141.5	152.0	3	*e*
$\mathrm{Mo(detc)_2(HC{\equiv}CPh)_2}$[c] (**8**)	183.2, 177.1	180.2	3	this work
$(\pi\text{-}\mathrm{C_5H_5})_2\mathrm{Mo(HC{\equiv}CH)}$ (**9**)	117.7	117.7	2	*f*
$(\pi\text{-}\mathrm{C_5H_5})_2\mathrm{Mo(CH_3C{\equiv}CCH_3)}$ (**10**)	115.3	115.3	2	this work

[a] Relative to $\mathrm{Me_4Si}$. [b] Formal number of electrons donated per alkyne ligand (see text). [c] Only the $\mathrm{H^{13}C{\equiv}}$ was observed owing to NOE effects. [d] Alt, H. G. *J. Organomet. Chem.* **1977,** *127,* 349. [e] Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979,** *101,* 2055. [f] Thomas, J. L. *Inorg. Chem.* **1978,** *17,* 1507.

by considering three molybdenum(II)-alkyne complexes with N values of 2, 3, and 4, respectively. An apodictic case of two-electron donor behavior by acetylene is provided by **9**, while the 12-electron $\mathrm{Mo(dtc)_2}$ fragment of **8** requires an average of three electrons from each of the two alkyne ligands to conform to the effective atomic number rule. Similar reasoning requires that the single acetylene ligand in **4** donate four electrons to effectively complement the $\mathrm{Mo(CO)(dtc)_2}$ moiety. The C-13 chemical shifts of 117.7, 180.2, and 203.7 observed for these bound alkynes, respectively, span a range of >80 ppm and reflect a monotonic dependence on the number of electrons formally donated from the alkyne ligand to the metal. The correlation between δ and N is not linear, nor is there any reason to expect a linear relationship since a continuum of chemical shifts is possible while N is restricted to values calculated from the total number of acetylene electrons donated divided by the number of coordinated alkynes. Nonetheless a plot of δ vs. N (Figure 1) implies that δ is an observable which is highly sensitive to the nature of the metal-alkyne bond and provides experimental data which bears directly on the role of alkyne ligands in monomeric coordination complexes.

The N values listed in Table I are consistent with the results of elementary molecular orbital analyses. Two coparallel cis alkyne ligands can each donate two electrons from their respective $\pi_{\parallel}$ orbitals into vacant σ receptor metal orbitals. Donation from the two $\pi_{\perp}$ orbitals is restricted because both alkyne $\pi_{\perp}$ orbitals overlap the same metal $d\pi$ orbital and a three-center four-electron interaction results. From a group theoretical standpoint the local C_{2v} symmetry of the *cis*-$\mathrm{M(RC{\equiv}CR)_2}$ fragment produces $\pi_{\perp}$ orbital combinations of a_1 and b_2 symmetry (see below). The a_1 combination overlaps effectively with a single $d\pi$ orbital while the b_2 combination is nonbonding owing to the absence of a suitable metal orbital of b_2 symmetry. The net result is stabilization of $4\pi_{\parallel}$ and $2\pi_{\perp}$ electrons for an average donation of three electrons per alkyne.





$\pi_{\perp}(b_2)$

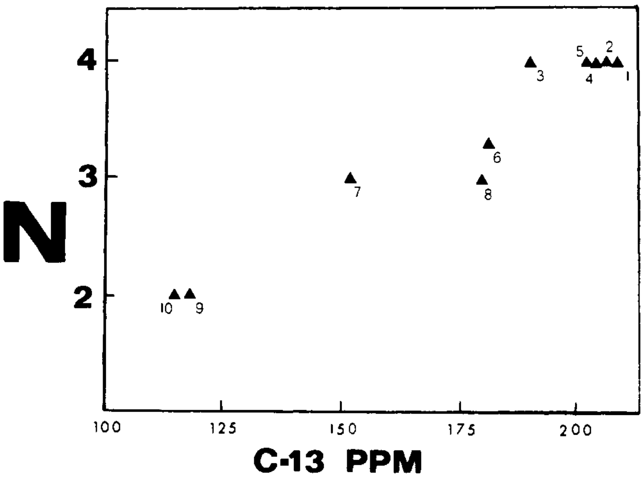


Figure 1. A plot of alkyne carbon-13 chemical shift (parts per million relative to $\mathrm{Me_4Si}$) vs. formal number of electrons donated per alkyne ligand (N).

King accurately described the bonding scheme applicable to **6** over a decade ago[3] (a total alkyne donation of ten electrons formally corresponds to $3\frac{1}{3}$ electrons per unsaturated ligand[4]), but the $\mathrm{W(CO)(RC{\equiv}CR)_3}$ structural unit[5] was too esoteric to substantially alter prevailing tenets concerning the possibility of realizing effective four-electron donation to a single metal center. Two-electron donation from an olefin or an alkyne involves only carbon p orbitals located in the metal-acetylene or metal-olefin plane and conveys the idea of $\pi_{\parallel}$ donation coupled with $\pi_{\parallel}{}^*$ acceptance. Four-electron donation retains these $\pi_{\parallel}$ and $\pi_{\parallel}{}^*$ interactions while π-type donation from $\pi_{\perp}$ occurs to supplement the olefinic type bonding. Overlap values responsible for σ, π, and δ metal-alkyne interactions have been calculated for $\mathrm{Mo(CO)(HC{\equiv}CH)(dtc)_2}$. As expected the σ overlap is greatest (derived from $\pi_{\parallel}$), but the overlap of d_{xy} with $\pi_{\perp}$ (0.10) is the same magnitude as the overlap of d_{xz} with $\pi_{\parallel}{}^*$. When one considers that the $d_{xz}-\pi_{\parallel}{}^*$ interaction corresponds to the retrodative bonding scheme invoked to account for the stability of metal-olefin complexes the potential impact of donation from $\pi_{\perp}$ is evident.[6]

Donation of electrons from both π orbitals of alkyne ligands to a single metal center is only significant to the extent that it constitutes a viable chemical concept which is reflected in molecular properties. Reactivity patterns of several complexes listed in Table I are noteworthy when viewed in the context of four-electron donation from alkyne ligands. (1) The ligand substitution reaction used to prepare $\mathrm{M(CO)(RC{\equiv}CR)(dtc)_2}$ involves the displacement of *two* classical two-electron donor ligands by a single acetylene molecule.[2] Note that phosphine substitution of $\mathrm{W(CO)_3(dtc)_2}$ under the same conditions leads 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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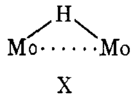
The μ-H[Mo(CO)$_4$PMePh$_2$]$_2^-$ Anion: An Example of Phosphine Enhancement of Metal-Metal Interaction

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 $J_{P\text{-}H}$ = 16.6 Hz for P = $PMePh_2$) or the ^{31}P NMR spectrum (doublet at 18.92 ppm upfield from 85% H_3PO_4, $J_{P\text{-}H}$ = 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