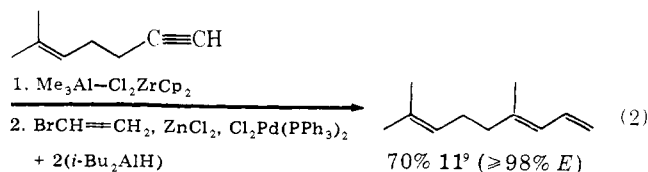


with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ produces 95:5 mixtures of two regioisomers,¹ the cross-coupled products obtained by using a minor excess (10%) of the alkenyl metal intermediates are regiochemically >99% pure, indicating that the alkenyl metal species represented by **3** ($\text{R}^2 = \text{Me}$) are considerably more reactive in the cross coupling than their regioisomers represented by **12**. Attempts are being made to further convert the conjugated dienes **9**, such as **11**, and enynes **10** into various natural products.



Although the exact role of ZnCl_2 remains to be clarified, the possible intermediacy of alkenylzinc species has been indicated by the observation that the formation of (*E*)-8-methyltridec-7-en-5-yne (**10**, $\text{R}^1 = \text{Pent-}n$; $\text{R}' = \text{Bu-}n$) in the reaction of (*E*)-2-methyl-1-heptenylzinc chloride¹¹ with 1-iodo-1-hexyne is at least as fast as that in the ZnCl_2 promoted reaction of **3** ($\text{R}^1 = \text{Pent-}n$; $\text{R}^2 = \text{Me}$) with 1-iodo-1-hexyne.

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References and Notes

- (1) Selective Carbon-Carbon Bond Formation via Transition Metal Catalysis. 9. Part 8: The accompanying paper, D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (2) (a) E. Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, 596 (1976); (b) S. Baba and E. Negishi, *J. Am. Chem. Soc.*, **98**, 6729 (1976); (c) E. Negishi and D. E. Van Horn, *J. Am. Chem. Soc.*, **99**, 3168 (1977); (d) N. Okukado, D. E. Van Horn, W. L. Klima, and E. Negishi, *Tetrahedron Lett.*, in press.
- (3) For a recent paper containing pertinent references, see E. Negishi, A. O. King, and N. Okukado, *J. Org. Chem.*, **42**, 1821 (1977).
- (4) This mechanistic scheme was proposed by Kumada (K. Tamao, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972)) for the Ni-catalyzed cross-coupling reaction, and has been supported by Parshall (G. W. Parshall, *ibid.*, **96**, 2360 (1974)) and Kochi (D. J. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975)).
- (5) The oxidative addition step does not involve the organometallic compound added as a carbon group transfer agent.
- (6) The Allred-Rochow electronegativity values (A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958)) for the metals used in this study including Pd and Ni are as follows: Pd (1.35), Ni (1.75), Al (1.47), Zr (1.22), Cu (1.75), Zn (1.66), Cd (1.46), In (1.49), Sn (1.72) and Ti (1.32).
- (7) The corresponding reaction of (*E*)-1-hexenyldiisobutylalane gave (*E*)-1-(*m*-tolyl)-1-hexene in 75% yield in 12 h at 25 °C. A similar sluggish reaction of an (*E*)-2-octenylzirconium derivative with phenyl iodide was reported earlier in ref 2c.
- (8) Various metals which have not been considered for different reasons include highly electropositive group 1a and 2a metals, highly electronegative metals of relatively small sizes (B, Si, etc.) and heavy metals (Hg, Tl, Pb, etc.) whose salts are readily reducible by Pd^0 or Ni^0 complexes.
- (9) All isolated products have been adequately characterized and identified by ^1H and ^{13}C NMR and IR.
- (10) A similar enyne synthesis via β,β -dialkyl-substituted alkenylcoppers has been reported recently (J. F. Normant, A. Commercon, and J. Villieras, *Tetrahedron Lett.*, 1465 (1975)). Although no difficulty was encountered in reproducing some of the reported results, our attempts to apply the procedure to the synthesis of dienes using alkenyl iodides, such as (*E*)-1-iodo-1-hexene, instead of alkenyl iodides have been almost totally un-

successful, no more than traces of the desired cross-coupled products being produced.

- (11) Prepared by treating (*E*)-1-iodo-2-methyl-1-heptene¹ with *n*- BuLi (-78°C) and ZnCl_2 .

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Reactions of Triply Bonded Dimetal Compounds. Reversible Addition of Carbon Monoxide to a Hexakis(alkoxy)dimolybdenum Compound. A Molecule with a Carbonyl-Bridged Metal-Metal Double Bond

Sir:

We report here our initial observations on a series of most remarkable reactions involving carbon monoxide and $\text{Mo}_2(\text{OR})_6$ compounds, which contain unbridged metal-metal triple bonds.¹

Alkane solutions of $\text{Mo}_2(\text{OR})_6$ compounds, where $\text{R} = \text{Me}_3\text{C}$, Me_2CH , and Me_3CCH_2 , rapidly absorb carbon monoxide at room temperature to give dark solutions.² Upon exposure to 2 equiv of CO, crystalline compounds have been obtained merely by cooling the alkane solutions to ca. -10°C . Black crystalline compounds of empirical formula $\text{Mo}(\text{OR})_3\text{CO}$ have been obtained³ for $\text{R} = \text{Me}_2\text{CH}$ and Me_3CCH_2 and a preliminary x-ray investigation has shown that the isopropoxide is tetranuclear, $\text{Mo}_4(\text{OPr}^i)_4(\text{CO})_4$. The IR spectrum of the latter compound shows four well-resolved and sharp bands of approximately equal intensity assignable to coordinated carbonyl ligands: 1957, 1882, 1837, and 1819 cm^{-1} . When $\text{R} = \text{Me}_3\text{C}$, a dark purple crystalline compound, $\text{Mo}_2(\text{OBu}^t)_6\text{CO}$ (I) was obtained which showed only one IR band, at 1670 cm^{-1} , assignable to a carbonyl group.

All the new carbonyl compounds are thermally labile. I readily loses CO on heating in vacuo and $\text{Mo}_2(\text{OBu}^t)_6$ is recovered. Carbon monoxide is also lost in solution under a nitrogen purge or under vacuum. This establishes the reversibility of reaction 1 below.



The black crystalline compounds, $\text{Mo}_4(\text{OR})_{12}(\text{CO})_4$, where $\text{R} = \text{Me}_2\text{CH}$ and Me_3CCH_2 , yield $\text{Mo}(\text{CO})_6$ at 50 °C (10^{-2} Torr) and $\text{Mo}_2(\text{OR})_8$ compounds at 80–100 °C (10^{-2} Torr). Other nonvolatile products are as yet uncharacterized in these thermal decomposition reactions.

Upon exposure to an excess of CO (1 atm), $\text{Mo}_2(\text{OR})_6$ compounds react further. For example, after exposing a hexane solution of $\text{Mo}_2(\text{OBu}^t)_6$ to an excess of CO (1 atm) for 12 h, the solvent was stripped, leaving a black powdery residue which showed the following IR bands assignable to carbonyl groups: 2022 (m), 1985 (vs), four overlapping bands at ~ 1930 (all strong), 1830 (w), 1690 (vw), 1670 (w), and 1630 (w) cm^{-1} . The band at 1985 cm^{-1} is assignable to $\text{Mo}(\text{CO})_6$ and, even at room temperature (1 atm), this compound slowly sublimates out of the black residue. Thus it appears that formation of I represents merely the first step in a chain of reactions which leads to $\text{Mo}(\text{CO})_6$ among other as yet uncharacterized products. We proceeded directly toward a full structural characterization of the novel carbonyl compound (I).

Crystals of I consist of discrete dinuclear molecules with the structure shown in Figure 1. Here we omit, for the sake of clarity, the $(\text{CH}_3)_3\text{C}$ groups. Each molecule possesses a crystallographically⁴ imposed mirror plane containing O1, C1, O2, and O3 and bisecting the Mo-Mo bond. The virtual symmetry of the molecule is C_{2v} . The coordination polyhedron about each

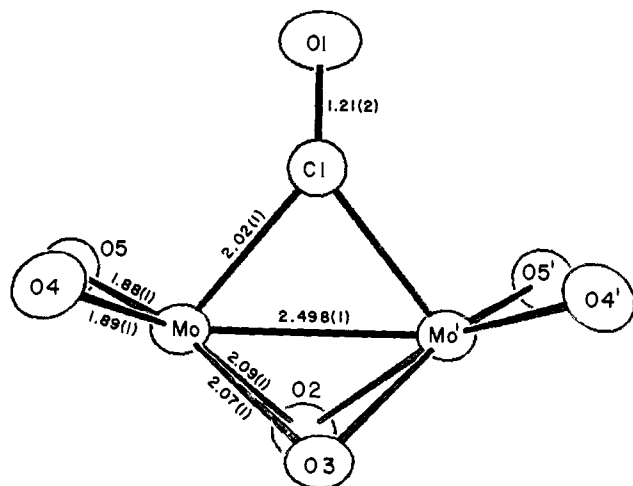


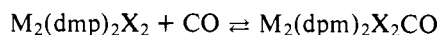
Figure 1. A view of the coordination geometry of **1**, $\text{Mo}_2(\text{OBu}')_6(\text{CO})$, showing the main internuclear distances. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density. The tertiary butyl groups are omitted for clarity.

metal atom is a distorted square pyramid with the Mo to carbonyl carbon bond at the apex.

We believe the Mo–Mo bond has a formal bond order of 2. The molecule is diamagnetic and the electron counting for each molybdenum atom may be conducted as follows: the neutral Mo atom has 6 electrons, each terminal RO group contributes 1 as does the bridging CO group, and the pair of bridging RO groups contribute 3 electrons to each metal atom. Thus, before metal–metal bond formation is considered, each metal atom has 12 electrons. To account readily for diamagnetism, an Mo–Mo bond of even order should be present. With a distance of 2.489 (1) Å, the most reasonable conclusion is a bond order of 2.

Metal–metal bonds of orders 1, 3, and 4 are, of course, very numerous and well known, but not many double bonds have been observed to date. For molybdenum there have not previously been any unambiguous cases⁵ except for that in $\text{Mo}_2(\text{OPr}')_8$,⁶ where the Mo–Mo distance, 2.523 (1) Å, is very similar to the one found here. It is noteworthy that in the isopropoxide also the metal atoms have formal 14-electron configurations, but the coordination polyhedron is a trigonal bipyramid.

In conclusion we emphasize the following. (1) This work provides the first synthesis and structural characterization of a compound in which a carbonyl ligand bridges a metal–metal double bond, as well as only the second unambiguous example of an Mo=Mo bond. (2) To our knowledge the only reactions comparable to (1) are the very recently reported^{7,8} reactions of platinum and palladium complexes of bis(diphenylphosphino)methane, dpm, viz.,



where X = Cl, Br. (3) The formation of $\text{Mo}(\text{CO})_6$ under the extremely mild conditions reported here is quite remarkable. Indeed, the reaction between $\text{Mo}_2(\text{OR})_6$ compounds and CO may prove synthetically useful for the synthesis of labeled compounds $\text{Mo}(\text{*CO})_6$.

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Supplementary Material Available: A table of atomic positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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 (2) Additions were made using standard vacuum line techniques.
 (3) Anal. Calcd for $\text{Mo}(\text{OCHMe}_2)_3\text{CO}$: C, 39.88; H, 7.03. Found: C, 39.88; H, 7.06.
 (4) Crystal data for $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\text{CO})$: $a = 17.827$ (3), $b = 9.335$ (2), $c = 19.447$ (4) Å; $\alpha = \beta = \gamma = 90.00^\circ$; $V = 3236$ (1) Å³; $Z = 4$. Space group $Cmcc_2$, (No. 36). Unique data (1532 reflections) having $0.0^\circ < 2\theta$ (Mo K α) $\leq 50.0^\circ$ were collected at 22 °C using Mo K α radiation ($\lambda = 0.710730$ Å) and the 1237 reflections having $I > 3\sigma(I)$ were retained as observed. The structure was solved using standard heavy-atom methods and refined to convergence using anisotropic thermal parameters for molybdenum and oxygen atoms and isotropic thermal parameters for the carbon atoms. Hydrogen atoms were not located. Final residuals are $R = 0.067$ and $R_w = 0.085$; the esd of an observation of unit weight was 1.958.
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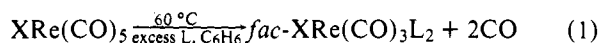
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Simultaneous Multiple Emissions from $\text{fac-XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$: $n\text{-}\pi^*$ Intraligand and Charge-Transfer Emission at Low Temperature

Sir:

We wish to report some interesting results concerning the excited-state decay of $\text{fac-XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$ (X = Cl, Br, I). These organometallics exhibit both long-lived and short-lived emissions at 77 K which are associated with an $n\text{-}\pi^*$ intraligand triplet excited state and a $\text{Re} \rightarrow 3\text{-benzoylpyridine CT}$ excited state, respectively. Aside from the fact that these are the first examples of species that exhibit $n\text{-}\pi^*$ intraligand emission, it is unusual that two emissions are observed at a similar energy. A similar phenomenon was observed in $\text{Ir}(1,10\text{-phenanthroline})_2\text{Cl}_2^+$ where two decay times were observed and associated with two states of different orbital configuration.¹ In another example of multiple emissions,² complexes of the type $\text{Rh}(2,2'\text{-bipyridine})_2(1,10\text{-phenanthroline})^{3+}$ exhibit two intraligand $\pi\text{-}\pi^*$ emissions associated with the two different ligands. Study of the excited-state decay of intraligand states is necessary for the development of phototemplate reactions of coordinated molecules.

Complexes $\text{fac-XRe}(\text{CO})_3\text{L}_2$ (L = 3-benzoylpyridine, 4-benzoylpyridine; X = Cl, Br, I) can be synthesized according to



following literature procedures for other pyridine complexes.³ Isolation of the solid product is by addition of *n*-pentane to concentrated C_6H_6 solutions. Repeated washing of the solid with alkane serves to remove any excess L or unreacted $\text{XRe}(\text{CO})_5$. Elemental analyses for two representative complexes are satisfactory. Calcd for $\text{ClRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$: C, 48.25; H, 2.70; N, 4.17. Found: C, 48.13; H, 2.78; N, 4.08. Found for $\text{ClRe}(\text{CO})_3(4\text{-benzoylpyridine})_2$: C, 48.41; H, 2.79; N, 4.25. All of the complexes exhibit the characteristic three-band infrared spectrum in the CO stretching region: 2030–2032, 1929–1932, 1894–1900 cm^{-1} . Further, the complexes exhibit a ketone carbonyl stretch with an integrated intensity twice (within 10%) that for the free ligand at the same concentration.