tively similar to that[13] of the Mo(CH$_3$)$_8$$^{4-}$; the band corresponding to the δ–δ* transition occurs at 16.9 cm^{-1}, and this figure together with a W–W distance of 2.26 Å gives a point very close to Sattelberger and Fackler's[13] line.

(18) We have also confirmed that WCl$_5$, the reagent used by Mertls and Wilkinson,[16] is a suitable source of tungsten. When we used a CH$_3$Li/WCl$_5$ mole ratio of 8/1 and maintained the temperature $< -20°$, we obtained W$_2$Me$_{8-x}$4$_x$$^{4-}$ compounds; Mertis and Wilkinson use an 8/1 ratio.

(19) Setting angles for 15 strong reflections ($2\theta \sim 20°$) were used to calculate the lattice parameters (Mo Kα, λ 0.710 73 Å; −55 (3) °C) a = 11.403 (8), and c = 11.969 (5) Å of the tetragonal cell. Based on a crystal composition of Li$_4$W$_2$Cl$_4$(CH$_3$)$_4$·4C$_4$H$_8$O, a density of 1.89 g cm^{-3} is calculated when $Z = 2$.

Intensity data were collected using monochromatized Mo Kα radiation and θ–2θ scans of variable rate (3 to 24°/min depending on reflection intensity) and range. The range was varied to account for spectral dispersion, and background measurements were made at both limits of each scan. An initial examination of the data established the Laue group to be 4/*mmm*. Because the crystal was under mineral oil we were unable to measure the crystal faces accurately and no absorption correction was applied. Three standard reflections monitored throughout the diffraction experiment were stable.

(20) The systematic absence of significant intensity for reflections of the type $hk0$, $h + k = 2n + 1$, suggested (uniquely) the space group, $P4/nmm$. The Patterson map allowed placement of two independent tungsten atoms in special positions 2(c); refinement of their positions with assigned isotropic thermal parameters of 2.1 Å^2 led to $R_1 = 0.22$. So long as space group $P4/nmm$ was used, difference Fourier maps were uninterpretable. Nevertheless, by employing a disordered model which turned out to a superposition of half-weighted mirror-images of the correct idealized W$_2$X$_8$$^{4-}$ unit, it was possible to obtain by refinement a model for which $R_1 = 0.10$. These difficulties vanished when one image was placed in the correct space group, $P42_12$, and a Li atom and a tetrahydrofuran molecule were found in a difference map.

(21) Thermal instability precludes combustion analysis. Determinations of CH$_3$ (by CH$_4$ evolution), Cl (as AgCl), and W (as WO$_3$), performed on the crystalline substances, satisfied the relation (CH$_3$ + Cl)/W = 4 with the CH$_3$/Cl ratio varying from one preparation to another within the limits 2.8 to 4.6.

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μ-Allene-bis(cyclopentadienyl)tetracarbonyldimolybdenum; a Bridging Allene Ligand

Sir:

There is a current belief that transition metal cluster chemistry could lead to a new era in homogeneous hydrocarbon catalysis.[1] The reactivity of metal-to-metal bonds and the synthesis of new cluster compounds are clearly two topics requiring study if such aspirations are to be realized. Bimetallic compounds containing metal-to-metal multiple bonds[2] will surely occupy a unique position in this field of chemistry. They are the smallest examples of unsaturated metal cluster compounds and provide building blocks for the systematic synthesis of new cluster compounds. We have previously shown that an extensive coordination chemistry surrounds metal-to-metal triple bonds in the chemistry of molybdenum[3-7] and tungsten.[8-16] Others have shown[17] that acetylenes, but *not* olefins,[18] add across metal-to-metal triple bonds, although the same products can be obtained directly by reaction of the acetylenes with Cp$_2$Mo$_2$(CO)$_6$ without isolating the presumed Cp$_2$Mo$_2$(CO)$_4$ intermediates.[19] The structure of a representative product, Cp$_2$Mo$_2$(CO)$_4$(μ-EtCCEt), has been determined; the length of the Mo–Mo single bond is 2.977 (1) Å.[20] We now report the preparation and characterization of Cp$_2$Mo$_2$(CO)$_4$(allene) from the reaction between allene and the M–M triple-bonded compound Cp$_2$Mo$_2$(CO)$_4$,[17] thus providing the first instance in which an allene molecule, acting as a four-electron donor, bridges two directly bonded metal atoms.[21]

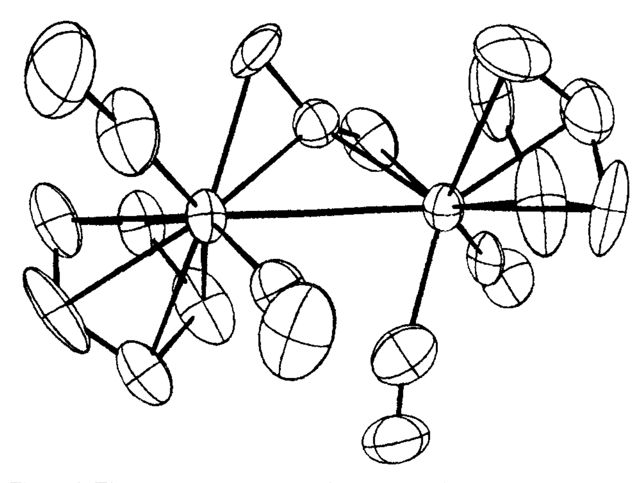

Figure 1. The molecular structure of Cp$_2$Mo$_2$(CO)$_4$(allene). Atoms are represented by thermal ellipsoids enclosing 50% of their electron density.

Addition of allene (1 equiv) to hydrocarbon solutions of Cp$_2$Mo$_2$(CO)$_4$ leads to a deep red solution and the formation (~10% yield) of a microcrystalline orange precipitate.[23] Deep red crystals of Cp$_2$Mo$_2$(CO)$_4$(allene) were the only product isolated from the solution. Mass spectrum (120 °C): parent ion, Cp$_2$Mo$_2$(CO)$_4$(C$_3$H$_4$)$^+$, strong; Cp$_2$Mo$_2$(CO)$_2$C$_3$H$_4$$^+$; Cp$_2Mo_2C_3H_4$$^+$. IR (cm^{-1}): 1995, 1960, 1915, 1860, 1830; these bands must be due to ν_{CO} and $\nu_{\mathrm{C=C}}$ but unequivocal assignment must await study of ^{13}C-labeled samples.

The crystal structure[24] was determined giving the molecular configuration shown in Figure 1. Some important dimensions are: Mo(1)–Mo(2), 3.117 (1) Å; Mo(1)–C(15), 2.23 (2) Å; Mo(1)–C(16), 2.11 (1) Å; Mo(2)–C(17), 2.23 (2) Å; Mo(2)–C(16), 2.13 (1) Å; C(15)–C(16), 1.44 (2) Å; C(16)–C(17), 1.41 (1) Å; ∠C(15)–C(16)–C(17), 146 (1)°, where C(15)–C(16)–(17) constitute the skeleton of the allene ligand. The M-to-C(terminal) distances are ca. 0.10 Å longer than M-to-C(central) distances as in other allene complexes.[22] The entire Mo(1)–Mo(2)–C(15)–C(16)–C(17) configuration is consistent with each of the two virtually orthogonal ethylenic portions of C$_3$H$_4$ interacting with one metal atom. The entire molecule has approximately C_2 symmetry, with the C_2 axis passing through C(16) and the mid-point of the Mo(1)–Mo(2) bond. The longer Mo–Mo bond here compared to Cp$_2$Mo$_2$(CO)$_4$(EtCCEt) is consistent with the use of a three-carbon chain rather than the two-carbon acetylene to bridge the metal atoms. The Mo–C–O chains are all a little bent, presumably due to intramolecular crowding (angles of 164° to 176°), but the longer Mo–Mo distance mitigates crowding and there is no semibridging CO ligand as in Cp$_2$Mo$_2$(CO)$_4$(EtCCEt).

NMR spectra (benzene-d_6, 40 °C, δ values in parts per million downfield from Me$_4$Si) are consistent with the same structure in solution. These spectra are unchanged by raising the temperature to 80 °C or by addition of allene to the solutions. The ^{1}H spectrum: 4.54, singlet, 10 H; 3.67, triplet, 2 H; 2.52, triplet, 2 H. The triplets are not of 1:2:1 relative intensities and can be assigned to a "deceptively simple" AA′BB′ multiplet,[25] consistent with the C_2 molecular symmetry. The ^{13}C[^{1}H] spectrum consists of five singlets: 237, 2 C, and 233, 2 C (carbonyl carbon atoms); 196, 1 C (central allenic C); 93, 10 C (Cp rings); 36, 2 C (terminal allenic C's). Without ^{1}H-decoupling the terminal allenic signal became four equally intense lines, assignable to the X portion of an X$_2$AA′BB′ spectrum, with $J_{\mathrm{AX}} \approx J_{\mathrm{BX}} \approx 160$ Hz, indicative[26] of approximately sp^2 hybridization at C.

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References and Notes

(1) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84,** 959 (1975); (b) R. Ugo, *Catal. Rev.*, **11,** 225 (1975).
(2) F. A. Cotton, *Chem. Soc. Rev.*, **4,** 27 (1975).
(3) M. H. Chisholm and W. Reichert, *J. Am. Chem. Soc.*, **96,** 1249 (1974).
(4) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. Reichert, and L. W. Shive, *J. Chem. Soc., Chem. Commun.*, 480 (1974).
(5) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4469 (1976).
(6) M. H. Chisholm, M. W. Extine, and W. W. Reichert, *Adv. Chem. Ser.* **No. 150,** 273 (1970).
(7) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *J. Am. Chem. Soc.*, in press.
(8) M. H. Chisholm, F. A. Cotton, M. W. Extine, B. R. Stults, and J. M. Troup, *J. Am. Chem. Soc.*, **97,** 1242 (1975).
(9) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97,** 5625, (1975).
(10) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4477 (1976).
(11) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Miller, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4486 (1976).
(12) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 5683 (1976).
(13) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Miller, and B. R. Stults, *Inorg. Chem.*, **15,** 2244 (1976).
(14) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **15,** 2252 (1976).
(15) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, in press.
(16) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, in press.
(17) R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97,** 3535 (1975).
(18) Thus there exists the potential for the catalytic hydrogenation of acetylenes to olefins. In the cluster compounds $Ni_4(CN\text{-}t\text{-}Bu)_4(RC{\equiv}CR)_3$ which contain acetylenic moieties bridging nickel atoms, this catalysis has been achieved. M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, **98,** 4645 (1976).
(19) (a) A. Nakamura and N. Hagahara, *Nippon Kagaku Zasski*, **84,** 344 (1963); A. Nakamura, *Mem. Inst. Sci. Ind. Res. Osaha Univ.*, **19,** 81 (1962); (b) W. I. Bailey, Jr., and F. A. Cotton, unpublished work.
(20) W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, **121,** C23 (1976).
(21) There is one reported structure[22a] of an allene bridging two metal atoms that are not bonded to each other, and, of course, several examples[22] of allenes serving as two-electron, 1,2-dihapto ligands have been structurally characterized.
(22) (a) P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *Chem. Commun.*, 361 (1969); (b) T. Kashawagi, N. Yasuoka, N. Kasai, and M. Kukudo, *ibid.*, 317 (1969); (c) T. G. Hewitt, K. Anzenhofer, and J. J. DeBoer, *ibid.*, 312 (1969).
(23) The nature of this compound, which is virtually insoluble in all the usual spectroscopic solvents, is uncertain. It does not appear to be formed by reaction of allene with $Cp_2Mo_2(CO)_4$(allene), but, rather, competitively upon reaction of allene with $Cp_2Mo_2(CO)_4$. Its elemental analysis is consistent with the formula $Cp_2Mo_2(CO)Q_4C_3H_4$ and its IR spectrum has bands at 1945, 1920, 1905, 1840, and 1720 cm^{-1}. The compound is essentially nonvolatile, although at 300 °C, ions corresponding to $Cp_2Mo_2(\text{allene})^+$ and $Cp_2Mo_2(\text{allene})(CO)_2{}^+$ together with weaker ions of *m/e* considerably greater than $Cp_2Mo(CO)_2(\text{allene})^+$ were observed in the mass spectrum. It has been shown by direct comparison that the compound is not $Cp_2Mo_2(CO)_4(MeCCH)$.
(24) The space group used was *Pn*, a nonstandard setting of *Pc*. Unit cell dimensions: $a = 10.932$ (2) Å, $b = 7.776$ (2) Å, $c = 10.015$ (1) Å, $\beta = 107.82$ (2)°, $V = 810.6$ Å^3. $d_{calcd} = 1.943$ for $Z = 2$ and FW = 474.18. A total of 2041 unique reflections with $0° < 2\theta(\text{Mo K}\alpha) \leq 55°$ were collected at 23 ± 2°. The structure was solved and refined by full-matrix least-squares using only the 1306 reflections with $I > 3\sigma(I)$. All C, O, and Mo atoms were treated anisotropically and anomalous scattering by Mo was included. Final *R* values were, $R_1 = 0.030$ and $R_2 = 0.046$.
(25) D. M. Grant, J. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38,** 470 (1963).
(26) Cf. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972, p 25, et seq.

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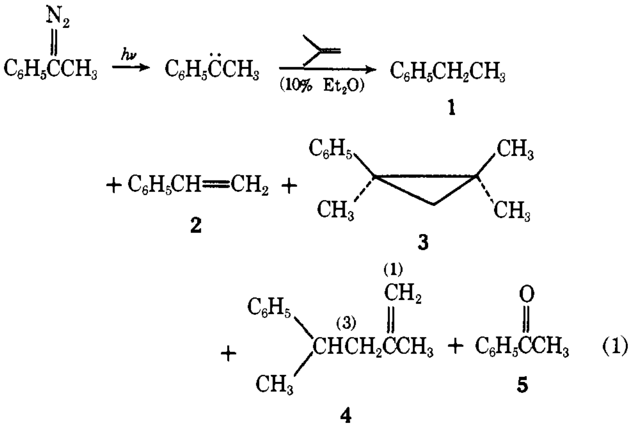
Reactions of Methylphenylcarbene and Phenylcarbene in Isobutene Matrices: Origins of the "Insertion" Products

Sir:

Phenylcarbene reacts with frozen *cis*-butene matrices (−196 °C) to yield olefins which apparently arise by abstraction-recombination reactions of the triplet carbene.[1] These observations, characterized as "most remarkable",[2] have led us to examine reactions of the title carbenes with isobutene matrices. Not only has our earlier finding of matrix-fostered olefin formation been confirmed, but using $(CH_3)_2C{=}^{13}CH_2$ matrices, we have obtained an even more remarkable glimpse into the origins of the olefins.

Equation 1 and Table I summarize the products from photolytically generated $PhCCH_3$ and isobutene.[4] Photolyses (6-8 h) were conducted in Pyrex tubes at 3000 Å, using the procedures described in ref. 1. Isobutene was degassed, and residual diazoalkane was destroyed with maleic anhydride.[5] Products **2**-**5** were identified by GC (18 ft × 0.25 in. 15% Carbowax 20M column, 160 °C) comparisons with authentic samples, and by GC-MS techniques. Ethylbenzene was identified by NMR. The identity of **4** was substantiated by GC comparisons with authentic **4** on three different 100 ft Golay columns (Apeizon-L, SF-96, Carbowax K-1540, all at 130 °C). Products were stable to all photolytic conditions. Authentic **3** was prepared from 1-bromo-1-phenyl-2,2-dimethylcyclopropane[6] with methyl iodide and methyllithium.[7] To prepare 2-methyl-4-phenyl-1-pentene (**4**),[8] 3-phenylbutanoic acid was converted to 4-phenyl-2-pentanone with methyllithium, and the ketone was treated with triphenylphosphonium methylide.



1-Phenyldiazoethane was photolyzed in a matrix (−196 °C) of $(CH_3)_2C{=}^{13}CH_2$,[9] to clarify the origin of **4**. ^{13}C NMR analysis of unlabeled **4** revealed resonances for C(1) and C(3) at δ ($CDCl_3$, Me_4Si) 112.0 and 37.8, respectively.[11] In the ^{13}C NMR spectrum of product **4** derived from the labeled isobutene matrix, the signal of C(3) was prominent; calculations indicated that >96% of the ^{13}C label was at C(3).

A parallel series of experiments was carried out with phenylcarbene, generated from phenyldiazomethane,[1,5] eq 2. In isobutene solutions (0 °C, −120 °C), addition product **6**[5]