there is no good way to account for the observed P–Cu–P angle of 123.3°.[7] As a possible alternative approach which is also consistent with the molecular geometry, one might consider a more delocalized bonding scheme in which direct Cu–B overlap might be significant (as suggested by the short Cu–B distance of 2.18 ± 0.01 A). Such a description would require a greater fractional contribution of the copper 4s orbital to the bonding σ molecular orbitals, which would help to explain the large P–Cu–P angle.

The location of the hydrogen atoms in the present structure is evidence for the fact that, unlike $(CH_3)_3NAl(BH_4)_3$,[9] $\{[(C_6H_5)_3P]_2Cu(BH_4)\}$ is not disordered in the crystalline state at room temperature. In solution, however, it is possible that dynamic effects are operative, as suggested by recent proton nmr studies of other transition metal borohydride complexes.[10] Further work is currently in progress[11] to elucidate the structural and chemical properties of the present and related copper borohydride complexes in solution.

The geometry of the triphenylphosphine groups is very similar to that found in several other transition metal complexes[12] and will be reported in detail elsewhere.

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(7) A careful examination of the inter- and intramolecular nonbonded atomic distances did not reveal any obvious stereochemical interaction between the phenyl groups which might be completely responsible for this P–Cu–P angle. In certain other compounds containing *cis*-triphenylphosphine groups with metal–phosphorus distances comparable to that found here, considerably smaller P–M–P angles have been observed (*e.g.*, in $[(C_6H_5)_3P]_2Pt(CO_3)$, P–Pt–P = 98.2°, where the Pt–P bond length is 2.24 A).[8]

(8) F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Commun.*, 408 (1967).

(9) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 286 (1966).

(10) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc., Sect. A*, 182 (1966).

(11) S. J. Lippard and D. Ucko, unpublished work.

(12) *Cf.* S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965), and references contained therein.

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Chlorobis(π-cyclopentadienyldicarbonyliron)-(π-cyclopentadienyltricarbonylmolybdenum)tin(IV). A New Metal Cluster Compound

Sir:

Many metal cluster compounds which contain tin have been prepared[1] and the solid-state structures of a number of these compounds have been determined.[2] We wish to report the structure and properties of chlorobis(π-cyclopentadienyldicarbonyliron)(π-cyclopentadienyltricarbonylmolybdenum)tin(IV), a previously unreported metal cluster compound. This structural investigation provides the first experimental value for a tin–molybdenum bond length and is the first detailed report of the structure of a metal cluster which contains three different metal atoms.[3]

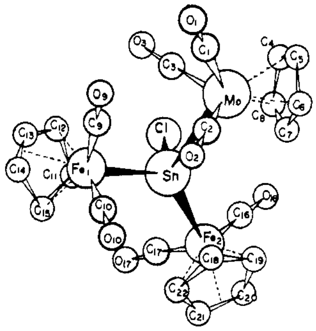

Figure 1. The molecular configuration of $[\pi\text{-}C_5H_5Fe(CO)_2]_2[\pi\text{-}C_5H_5Mo(CO)_3]SnCl$.

Chlorobis(π-cyclopentadienyldicarbonyliron)(π-cyclopentadienyltricarbonylmolybdenum)tin(IV) is a secondary reaction product in the preparation of bis-(π-cyclopentadienyldicarbonyliron)bis(π-cyclopentadienyltricarbonylmolybdenum)tin(IV).[4] $[\pi\text{-}C_5H_5Fe(CO)_2]_2[\pi\text{-}C_5H_5Mo(CO)_3]SnCl$ was recrystallized from dichloromethane under carbon monoxide; purple crystals suitable for X-ray analysis were deposited on the sides of the flask after several days. The compound decomposes between 128 and 136°. An analysis for chlorine definitely establishes the presence of this element. *Anal.* Calcd for $C_{22}ClFe_2H_{15}MoO_7Sn$: Cl, 4.71. Found: Cl, 4.42). The infrared spectrum in the C–O stretching region of $[\pi\text{-}C_5H_5Fe(CO)_2]_2[\pi\text{-}C_5H_5Mo(CO)_3]SnCl$ in dichloromethane shows the following bands (cm^{-1}): 1886 (m), 1921 (sh, m), 1949 (s), 1988 (vs), 2008 (s), 2029 (sh, m), 2057 (w).

Crystals of $[\pi\text{-}C_5H_5Fe(CO)_2]_2[\pi\text{-}C_5H_5Mo(CO)_3]SnCl$ belong to the orthorhombic system and the unit cell, which contains four molecules, has lattice parameters a = 10.57 ± 0.02, b = 12.14 ± 0.02, c = 22.04 ± 0.04 A. Systematic absences of $h00$, $0k0$, and $00l$ with odd indices indicate the space group $P2_12_12_1$.[5] Multiple-film equiinclination Weissenberg data were collected for the reciprocal levels $h0l$ through $h12l$ with Mo Kα radiation (λ 0.7107 A). The intensities of 1541 independent diffraction maxima were estimated visually and were corrected for Lorentz-polarization effects. Because the crystals decomposed slowly in the X-ray beam, four crystals of approximately the same size had to be used for collection of intensity data. The positions of the two heaviest atoms were determined from a Patterson synthesis, and all other nonhydrogen atoms were found in a series of difference Fourier syntheses. Isotropic least-squares refinement has yielded a discrepancy index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$, of 9.3%.

The molecular configuration is shown in Figure 1. The two iron atoms, the molybdenum atom, and the chlorine atom are bonded to the central tin atom in a distorted tetrahedral arrangement. The coordina-

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(1) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966), and references therein.

(2) J. E. O'Connor and E. R. Corey, *ibid.*, **6**, 968 (1967), and references therein.

(3) The solid-state structure of π-cyclopentadienyldicarbonyliron mercury tetracarbonylcobalt has been determined; however, the results have not been published as yet; *cf.* R. F. Bryan, *J. Chem. Soc., Sect. A*, 172 (1967).

(4) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **87**, 1146 (1965).

(5) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 105.

tion environment of each iron atom is octahedral with the cyclopentadienyl group occupying three coordination sites; the tin and two carbonyls are located at the three remaining sites. The bonding in the [π-C_5H_5-$Mo(CO)_3$] moiety is similar to that in [π-$C_5H_5Mo(CO)_3]_2$[6] and [(π-$C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4$][7] in which the metal atom is a seven-coordinated atom with the cyclopentadienyl group occupying three coordination sites.

Bond lengths and interatomic angles are given in Table I. The tin–molybdenum bond length of 2.891 A is the first such bond distance reported. It is considerably shorter than the expected distance of 3.00 A based on the sum of the covalent radii of tin (1.39 A)[8] and molybdenum (1.61 A).[6,7] The two tin–iron bond lengths agree well with other bond distances between these two metals.[2] The tin–chlorine bond length is exceptionally long and exceeds the distance of 2.43 A found in $Cl_2Sn[\pi$-$C_5H_5Fe(CO)_2]_2$.[2] The interatomic angles associated with the coordination environment of the tin atom are distorted considerably from the tetrahedral value. The greatest amount of tetrahedral angle distortion involves the lighter and less bulky chlorine atom. The Cl–Sn–M angle is decreased in each case in order to permit the M–Sn–M′ angles to increase. The orientations of the two cyclopentadienyl ligands bonded to the two iron atoms in this compound are almost identical with each other and are similar to the ring orientation observed in $Cl_2Sn[\pi$-$C_5H_5Fe(CO)_2]_2$.[2] The orientation of the cyclopentadienyl ligand bonded to the molybdenum atom is distinctly different from that found in [π-$C_5H_5Mo(CO)_3]_2$[6] and [π-$(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4$];[7] the ring is rotated approximately 36° from the orientation observed in the latter two compounds.

Table I. Bond Distances and Interatomic Angles and Their Estimated Standard Deviations[a]

Bond	Distance, A	Angle	Degrees
Sn–Mo	2.891 (5)	Mo–Sn–Fe_1	115.8 (2)
Sn–Fe_1	2.583 (7)	Mo–Sn–Fe_2	117.9 (2)
Sn–Fe_2	2.598 (7)	Mo–Sn–Cl	98.4 (3)
Sn–Cl	2.50 (1)	Fe_1–Sn–Fe_2	115.6 (2)
Mo–$C_{(ring)}$	2.35 (5)[b]	Fe_1–Sn–Cl	107.4 (3)
Mo–$C_{(CO)}$	1.96 (4)[b]	Fe_2–Sn–Cl	97.2 (3)
C–O	1.19 (5)[b]	Mo–C–O	173 (3)[b]
C–C	1.46 (7)[b]	C–C–C	106 (4)[b]
Fe_1–$C_{(ring)}$	2.14 (6)[b]	Sn–Fe_1–$C_{(CO)}$	91 (2)[b]
Fe_1–$C_{(CO)}$	1.68 (6)[b]	Fe_1–C–O	176 (4)[b]
C–O	1.20 (6)[b]	C–C–C	106 (5)[b]
C–C	1.45 (8)[b]	Sn–Fe_2–$C_{(CO)}$	87 (2)[b]
Fe_2–$C_{(ring)}$	2.12 (6)[b]	Fe_2–C–O	174 (5)[b]
Fe_2–$C_{(CO)}$	1.79 (6)[b]	C–C–C	107 (5)[b]
C–O	1.17 (6)[b]		
C–C	1.47 (8)[b]		

[a] Estimated standard deviations in the least significant figures are given in parentheses. [b] Indicates an average value.

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(6) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

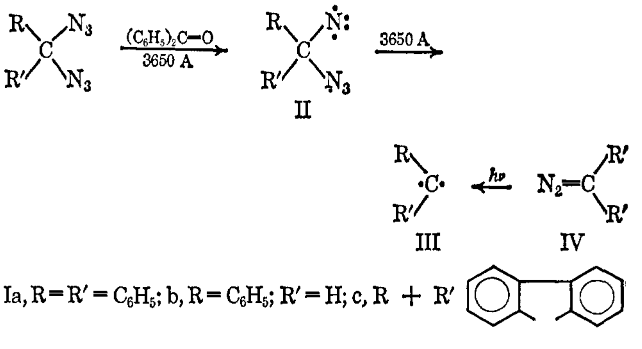
(7) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

(8) D. H. Olson and R. E. Rundle, *Inorg. Chem.*, **2**, 1310 (1963).

Generation of Methylenes from Geminal Diazides *via* Excited Nitrenes

Sir:

We have observed that sensitized photolysis of geminal diazides (I) at 77°K in rigid matrices yields the corresponding methylenes (III). By use of epr spectroscopy we find that the α-azidonitrenes (II) form initially and are then photolyzed to III. The epr spectra of IIIa–c, which should be very sensitive to the geometry of the methylenes, are identical with those obtained from the corresponding diazo compounds IVa–c in a variety of environments,[1] indicating that the observed structure is an intrinsic property of the methylene, independent of the geometry of the precursor. The I → II transformation is an example of the general preparation of ground-state triplet alkylnitrenes by sensitized photolysis of the corresponding azides, a procedure which has allowed the first observation of the parent methylnitrene.



Ia, R = R′ = C_6H_5; b, R = C_6H_5; R′ = H; c, R + R′

The diazides were prepared by treating the corresponding dihalomethanes with an alkali azide, usually in acetonitrile. Typically, Ia was prepared as follows: 0.01 mole of diphenyldichloromethane in 60 ml of dry acetonitrile was added dropwise to a stirred suspension of 0.05 mole of sodium azide in 30 ml of acetonitrile under dry nitrogen at −35°. The reaction mixture was allowed to warm to ambient temperature overnight. The acetonitrile was removed under vacuum at 30°. The solid residues were extracted with *n*-hexane, filtered, and dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure at 25°, yielding a white solid, mp 42–44° (88% yield). *The products should be handled with catuion as a 50-mg sample of Ib detonated when it came into contact with a hot glass surface during the sealing of an ampoule.*

Irradiation of a purified sample[2] of I in Fluorolube, tetrahydro-2-methylfuran, or other solvents at 77°K

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(1) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray *J. Chem. Phys.*, **40**, 2408 (1964); A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964).

(2) The sample of Ic available was less than 25% diazide. However, its behavior was completely parallel to that of the pure samples of Ia and Ib.