in these cases are concerned, the tendency for rearrangement is not as pronounced as with the related lactones I and III. In both cases unrearranged acetoxy oxide is the major product along with products derived from rearrangement and solvolysis of the oxido group. Complete details of structures will be given in the full manuscript.

Finally, we wish to call attention to the potential application of the type of considerations put forth by Schleyer and Foote concerning systems where dipolar destabilization offers a common origin for both slowed rates of solvolysis and abnormally high carbonyl of the derived ketone.

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Transition Metal Borohydride Complexes. I. The Structure of Borohydridobis(triphenylphosphine)copper(I)

Sir:

At present, little is known about the mechanistic details of the reduction of transition metal ions by the borohydride ion, BH_4^-. Occasionally, it has been possible to isolate a stable transition metal borohydride complex, cogent examples being $[(\pi\text{-}C_5H_5)_2\text{-}Ti(BH_4)]$,[1] $[NiA(BH_4)_2]$,[2] and $\{[(C_6H_5)_3P]_2Cu(BH_4)\}$.[3,4] Recently we have begun to study the structures and reactivities of certain of these complexes as a first step toward understanding the detailed manner in which BH_4^- acts as a reducing agent. Here we report the first X-ray structural characterization[5] of a transition metal borohydride complex, borohydridobis(triphenylphosphine)copper(I).

Crystals suitable for X-ray studies, obtained by the method of Cariati and Naldini,[4] were found to have Laue symmetry 2/m with unit cell dimensions $a = 24.64 \pm 0.02$, $b = 9.058 \pm 0.008$, $c = 15.43 \pm 0.01$ A, and $\beta = 116.2 \pm 0.1°$. From the measured density, $\rho = 1.3$ g/cc, and observed systematic absences, hkl, $h + k \neq 2n$, $h0l$, $l \neq 2n$, the space group was ascertained to be C2/c or Cc, with $Z = 4$.

Three-dimensional intensity data were collected on a Picker automated diffractometer using Cu $K\alpha$ radiation. After applying the usual Lorentz, polarization, and absorption corrections, the data were placed on an approximately absolute scale by Wilson's method. A three-dimensional Patterson map revealed the copper and phosphorus atomic positions, and, from the first difference Fourier map, the 19 remaining nonhydrogen atoms in the asymmetric unit were located.[6] Isotropic
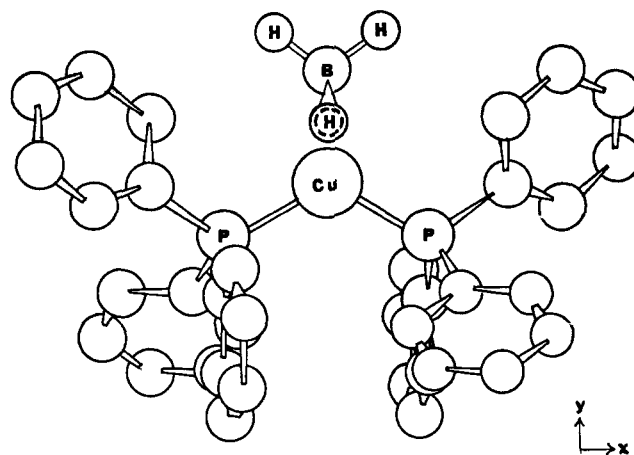
(1) R. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).
(2) N. F. Curtis, *J. Chem. Soc.*, 924 (1965), where A is a cyclic tetramine or a noncyclic Schiff base amine.
(3) J. M. Davidson, *Chem. Ind.* (London), 2021 (1964).
(4) F. Cariati and L. Naldini, *Gazz. Chim. Ital.* **95**, 3 (1965).
(5) Since the submission of this communication, a report describing the crystal structure of $Zr(BH_4)_4$ has appeared: P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

Figure 1. Geometry of borohydridobis(triphenylphosphine)copper(I): Cu-B, 2.18 ± 0.01 A, Cu-P, 2.276 ± 0.003 A, Cu-H, 2.02 ± 0.05 A, B-H, 1.31 ± 0.05 A, P-Cu-P, $123.3 \pm 0.2°$, P-Cu-B, $118.4 \pm 0.1°$. Carbon atoms are not labeled. Protons on the phenyl rings are not shown.

refinement of the 1750 independent observable reflections converged to values of 0.094 and 0.077 for the conventional unweighted and weighted factors, R_1 and R_2, respectively. Anisotropic refinement of all atoms further reduced these R factors to 0.077 and 0.066. Examination of a difference Fourier map, prepared by subtracting out the contributions of all nonhydrogen atoms, showed residual peaks in the regions expected for all hydrogen atoms attached to the benzene rings. In addition, the hydrogen atoms of the borohydride group were unambiguously located. No attempt was made to refine the hydrogen atom positional or thermal parameters.[6a]

The molecular structure of borohydridobis(triphenylphosphine)copper(I) is shown in Figure 1. From space group symmetry alone, the complex is required to have over-all twofold symmetry. This result is consistent with previous infrared spectral studies[3,4] of the molecule which suggest that, of the three possible orientations of the BH_4^- group shown below, I is correct. This conclusion is further supported by the
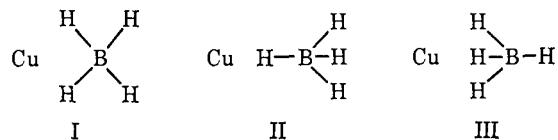
location of both the bridging and terminal hydrogen atoms at an average distance of 1.31 ± 0.05 A from the boron atom.

Both the boron and copper atoms may be considered as having quasi-tetrahedral configurations, in which two sp^3 orbitals from the copper atom participate in two three-center, two-electron bonds with the borohydride group. With this bonding scheme, however,

(6) The centrosymmetric space group, C2/c, was chosen after careful examination of the Patterson map and appears to be justified by the successful refinement of the structure.
(6a) NOTE ADDED IN PROOF: Subsequent refinement of all hydrogen atom positional and isotropic thermal parameters reduced R_1 to 0.059 and R_2 to 0.044. Slight changes in the molecular geometry of the copper-borohydride attachment resulted from the refinement, the details of which will be reported shortly (S. J. Lippard and K. Melmed, submitted for publication).

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 $(CH_3)_3$-$NAl(BH_4)_3$,[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.

(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

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

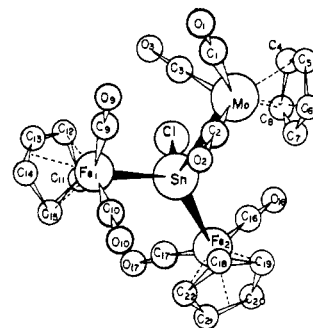(2) J. E. O'Connor and E. R. Corey, *ibid.*, **6**, 968 (1967), and references therein.

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

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]

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 $a = 10.57 \pm 0.02$, $b = 12.14 \pm 0.02$, $c = 22.04 \pm 0.04$ 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 non-hydrogen 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-

(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.