Volume 23
Number 5
February 29, 1984

Inorganic Chemistry

Communications

Metal Complexes of the Neutral Borane Adduct $B_2H_4{\cdot}2P(CH_3)_3$

Sir:

Bis(trimethylphosphine)–diborane(4) (I) reacted with zinc chloride and gave a complex with the formula $ZnCl_2{\cdot}B_2H_4{\cdot}2P(CH_3)_3$. Shown in Figure 1 is the structure of the complex as determined by single-crystal X-ray analysis.[1] I is coordinated to zinc through two hydrogen bridge bonds. Earlier, the formation of the triborane cation $B_3H_6{\cdot}2P(CH_3)_3^+$ was reported from this laboratory.[2] The cation was considered to be the result of the coordination of $B_2H_4{\cdot}2P(CH_3)_3$ to the cationic species BH_2^+. This formalism of $B_2H_4{\cdot}2P(CH_3)_3$ coordination was extended to that involving metals as the coordination centers and thus led to the isolation and characterization of the zinc complex. The coordination of two vicinal hydrogen atoms to a metal center, similar to that in Figure 1, has been observed commonly for the metal complexes of the octahydrotriborate ion[3,4] ($B_3H_8^-$). A similar mode of coordination was observed also in $HMn_3(CO)_{10}(BH_3)_2$,[5] which may be considered to be a coordination compound of the $B_2H_6^{2-}$ ion. A number of metal complexes of the BH_4^- ion are known. The BH_4^- ions in these complexes are bonded to the metal through the single or multiple B–H–M bridges.[4,6] However, the ability of a *neutral borane adduct* to form neutral metal complexes through the B–H–M bridge bonds had not been demonstrated.

The new complex $ZnCl_2{\cdot}B_2H_4{\cdot}2P(CH_3)_3$ is a stable solid at room temperature in the absence of air. The compound formed when $B_2H_4{\cdot}2P(CH_3)_3$ and $ZnCl_2$ were mixed in a 1:1 molar ratio in dichloromethane at room temperature. The complete conversion of the reactants into the complex was confirmed by the ^{11}B NMR spectrum of the reaction solution. The reaction could also be performed in diethyl ether as the solvent, whereupon the complex precipitated as a colorless solid. The precipitate could be purified by recrystallization from its dichloromethane solution. Trimethylphosphine displaced I from the complex. Treatment of the complex with hydrogen chloride in dichloromethane resulted in the rupture of the B–B bond of the ligand I, producing $(CH_3)_3PBH_3$ and $(CH_3)_3PBH_2Cl$. The proton-spin-decoupled ^{11}B NMR signal of the complex appeared as a doublet (peak separation 71 Hz) at −43.1 ppm ($BF_3{\cdot}O(C_2H_5)_2$ standard). The proton-spin-decoupled ^{31}P NMR signal was broad (half-height width 280 Hz) and trapezoid shaped, centered at −0.2 ppm (85% orthophosphoric acid standard), and appeared to have a slight dip at the center. In the ^{11}B-spin-decoupled proton NMR spectra, the methyl proton signal appeared as a doublet at δ 1.37 ($^2J_{HP}$ = 10.6 Hz) and the two borane proton signals were seen overlapped at δ 0.43 and 0.33. This spectral pattern remained unchanged in the temperature range from −40 to +55 °C. Below −40 °C the broadening of the signals became severe. The presence of the two borane proton signals indicated that the structure of the complex was rigid, on the NMR time scale, with respect to the hydrogen atom exchange between the terminal and bridge positions. The signal at 0.43 was a doublet ($^2J_{HP}$ = 4.2 Hz), and that at 0.33 was a broad singlet. These two signals were tentatively assigned to the terminal and bridge hydrogen atoms, respectively.

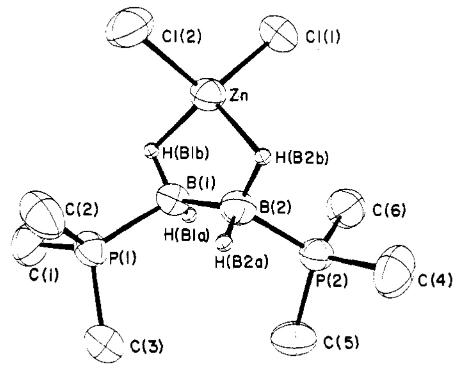


Figure 1. Molecular structure of $ZnCl_2{\cdot}B_2H_4{\cdot}2P(CH_3)_3$.

In addition to the zinc chloride complex described above, iodo- and chloro(triphenylphosphine)copper(I) complexes of I were isolated. These complexes could be prepared by the reactions of appropriate triphenylphosphine complexes of copper(I) halides with I in the manner similar to that described for the preparation of the zinc complex. They were characterized by their ^{11}B NMR signals, which appeared at −44.5 and −44.4 ppm, respectively, and by their infrared spectra, which were very similar to that of the $ZnCl_2$ complex in that two unique absorption bands appeared at 2310 ± 40 and 1970 ± 40 cm^{-1}. These two absorptions are attributed to the terminal B–H bonds and the B–H–M bridges, respectively. (IR data (cm^{-1}, KBr disk): $ZnCl_2$ complex, 2346 (s, br), 2010 (s, br); CuI complex, 2292 (m, br), 1925 (s, vbr); CuCl complex, 2280 (m, br), 1970 (s, vbr)). Thus the mode of $B_2H_4{\cdot}2P(C$-

---

(1) Crystallographic data for $ZnCl_2{\cdot}B_2H_4{\cdot}2P(CH_3)_3$: orthorhombic, space group $Pb2_1a$; a = 12.212 (1) Å; b = 13.700 (1) Å; c = 9.316 (1) Å; V = 1558.6 (2) $Å^3$; Z = 4; R = 0.031 on 1720 reflections with $I > 3\sigma(I)$. R = 0.034 when the inverse chirality was used. Details will be reported elsewhere.

(2) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

(3) Gaines, D. F.; Hildebrandt, S. J. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 3.

(4) Wegner, P. A. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1973; Chapter 12.

(5) Kaesz, H. D.; Fellmann, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753.

(6) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

0020-1669/84/1323-0511\$01.50/0 © 1984 American Chemical Society

Table I. Bond Lengths (Å) and Angles (deg) for $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)_3$

	Bond Lengths		
Zn–Cl(1)	2.213 (1)	B(1)–H(B1b)	1.08 (4)
Zn–Cl(2)	2.208 (1)	B(2)–H(B2b)	1.20 (4)
Zn–H(B1b)	1.87 (5)	B(1)–H(B1a)	0.99 (5)
Zn–H(B2b)	1.90 (4)	B(2)–H(B2a)	1.11 (5)
B(1)–B(2)	1.814 (6)	B(1)–P(1)	1.912 (4)
		B(2)–P(2)	1.910 (4)
	Bond Angles		
Cl(1)–Zn–Cl(2)	114.7 (1)	B(1)–B(2)–H(B2b)	123.6 (21)
H(B1b)–Zn–H(B2b)	106.7 (18)	B(2)–B(1)–H(B1b)	120.2 (24)
Zn–H(B1b)–B(1)	97.2 (29)	B(1)–B(2)–H(B2a)	116.6 (22)
Zn–H(B2b)–B(2)	91.3 (24)	B(2)–B(1)–H(B1a)	114.2 (25)

$H_3)_3$ coordination in these complexes appears similar. Other metal compounds are being tested for the possible complexation with the diborane(4) adduct.

The symmetry of the $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)_3$ molecule is approximately C_2. The positions of the two bridge hydrogen atoms deviate little (0.06 and 0.13 Å) from the plane defined by the two boron atoms and the zinc atom, and each of the two terminal hydrogen atoms lies on the plane defined by its vicinal phosphorus atom and the two boron atoms.[7] The bond lengths and angles pertinent to this communication are listed in Table I. It is noted that zinc chloride did not react with $BH_3 \cdot P(CH_3)_3$ under the conditions of the $ZnCl_2 \cdot B_2H_4 \cdot 2P(CH_3)_3$ formation. The diborane(4) adduct appears to provide a favorable vicinal H–H distance for the chelation. The chelation by the two geminal hydrogen atoms, however, may be unfavorable because of the shorter H–H distance. It is noted further that, when a 1:1 mixture of $B_2H_4 \cdot 2P(CH_3)_3$ and $B_3H_5 \cdot 3P(CH_3)_3$[8] was treated with a 1-equiv quantity of $ZnCl_2$ in dichloromethane, $B_3H_5 \cdot 3P(CH_3)_3$ preferentially complexed with $ZnCl_2$. This observation suggests that the coordination of neutral borane adducts to metal centers is a general type of reaction and may further be developed to include other higher borane adducts.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-81-K-0101.

Supplementary Material Available: A listing of final atomic coordinates and isotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

(7) The molecules of free diborane(4) adducts are in the staggered form, the two phosphines being trans to each other. $B_2H_4 \cdot 2P(C_6H_5)_3$: Van Doorne, W.; Cordes, A. W.; Hunt, G. W. *Inorg. Chem.* **1973**, *12*, 1686. $B_2H_4 \cdot 2PF_3$: Lory, E. R.; Porter, R. F.; Bauer, S. H. *Ibid.* **1971**, *10*, 1072.

(8) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

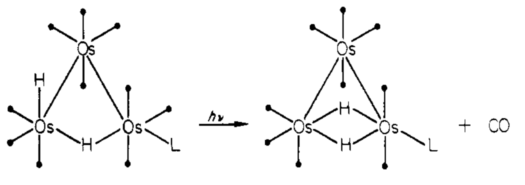
Steven A. Snow
Mamoru Shimoi
Calvin D. Ostler
Brian K. Thompson
Goji Kodama*
Robert W. Parry*

Received June 15, 1983

Photochemical Conversion of $H_2Os_3(CO)_{10}$(P-donor) to $H_2Os_3(CO)_9$(P-donor) in Solution and on High-Surface-Area Silica

Sir:

We wish to report our preliminary results concerning the photochemical generation of reactive intermediates from $H_2Os_3(CO)_{10}L$ (L = P-donor) in solution and on rigid oxide surfaces at 298 and 77 K. Our interest in these systems stems from that fact that the coordinatively unsaturated $H_2Os_3(CO)_9L$ species are well characterized[1] and are believed to be important in homogeneous catalytic reactions of olefins.[2] The relative importance of light-induced loss of CO from metal carbonyl clusters compared to metal–metal bond cleavage varies depending on the conditions under which the photochemistry is effected. Light-induced loss of CO from $Mn_2(CO)_{10}$[3] and *trans*-$(\eta^5\text{-}C_5R_5)Fe_2(CO)_4$ (R = H, $CH_2C_6H_5$, CH_3)[4,5] is the dominant photoreaction in rigid media at low temperature whereas net metal–metal bond cleavage dominates in fluid solution at 298 K. Relatively little is known regarding higher nuclearity clusters. The existence of both $H_2Os_3(CO)_{10}L$ and $H_2Os_3(CO)_9L$ complexes, therefore, provides an opportunity to investigate the mechanism of CO loss from these triangular clusters. Thus, the key issues in our study are establishment of (i) whether photoexcitation of $H_2Os_3(CO)_{10}L$ yields $H_2Os_3(CO)_9L$ and (ii) the mechanism for the light-induced chemistry. It has been previously established that $Os_3(CO)_{12}$ undergoes photosubstitution[6] and that $H_2Os_3(CO)_{10}(\eta^1\text{-SCHN-}p\text{-}C_6H_4F)$ undergoes light-induced loss of CO.[7] Our essential finding is that eq 1 represents the photochemistry at 298 K, but irradiation at low temperature does not result in CO loss as a primary photoreaction.



$H_2Os_3(CO)_{10}L$ $H_2Os_3(CO)_9L$ (1)

We have investigated three systems: $H_2Os_3(CO)_{10}(PPh_3)$, $H_2Os_3(CO)_{10}(PPh_2Et)$, and $[SiO_2]\text{–}L'Os_3(CO)_{10}H_2$ prepared from reaction of high-surface-area SiO_2 and $H_2Os_3(CO)_{10}(PPh_2CH_2CH_2Si(OEt)_3)$. The molecular species $H_2Os_3(CO)_nL$ (*n* = 9, 10; L = PPh_3, PPh_2Et, $PPh_2CH_2CH_2Si(OEt)_3$) were prepared according to the literature procedures or slight modifications thereof.[1,2,8] The modification of SiO_2 with $H_2Os_3(CO)_n(PPh_2CH_2CH_2Si(OEt)_3)$ (*n* = 9, 10) was carried out in a manner[9] similar to that previously reported.[10]

---

(1) (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313. (b) Benfield, R. E.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2210.

(2) (a) Brown, S. C.; Evans, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1049. (b) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056. (c) Ferrari, R. P.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta* **1978**, *31*, 177.

(3) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5534.

(4) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022.

(5) Hepp, A. F.; Paw-Blaha, J.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174.

(6) Tyler, D. R.; Altobelli, M.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *102*, 3022.

(7) Adam, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510.

(8) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975**, *88*, C21.

(9) High-surface-area SiO_2 (400 m^2/g) purchased from Alfa was pretreated by heating at ~250 °C under vacuum (10^{-2} torr) for 48 h. A typical preparation of $[SiO_2]\text{–}L'Os_3(CO)_nH_2$ involves the suspension of ~1 g of pretreated SiO_2 in 100 mL of hexane. The $H_2Os_3(CO)_nL'$ (*n* = 9, 10; L′ = $Ph_2PCH_2CH_2Si(OEt)_3$) was added to ~50 mM and the suspension stirred at 25 °C for 24 h under N_2. Elemental analysis establishes the coverage of cluster to be ~0.2 mmol/g or ~5 × 10^{-11} mol/cm^2 assuming that the surface area is 400 m^2/g. The solid was collected by filtration and washed repeatedly with hexane and dried under vacuum and under N_2. Control experiments using $H_2Os_3(CO)_n(PPh_2Et)$ (*n* = 9, 10) as the derivatizing agents yields no surface-confined metal carbonyls after washing with hexane.

0020-1669/84/1323-0512$01.50/0