

Preliminary communication

Preparation and characterization of $(\eta^5\text{-C}_5\text{H}_5\text{Co})_2\text{-}(\mu\text{-PPh}_2)\text{B}_2\text{H}_5$: evidence for multicenter cluster bonding in $\sigma\text{-}\pi$ vinyl transition metal complexes

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(Received February 25th, 1988)

Abstract

The structural and spectroscopic properties of the new cobaltaborane, $\text{Cp}_2\text{Co}_2(\text{PPh}_2)\text{B}_2\text{H}_5$, show that this compound, a formal analogue of a dinuclear transition metal complex containing a C_2H_3 ligand in a $\sigma\text{-}\pi$ bonding mode, exhibits a geometry characteristic of an arachno tetranuclear cluster framework. Comparison with analogous $\sigma\text{-}\pi$ vinyl complexes suggests a significant component of multicenter cluster bonding character in the carbon–metal interaction in the organometallic compounds.

There are now a significant number of metallaboranes that are isoelectronic analogues of organo-transition metal compounds where the CH fragments in the latter are formally replaced by either BH_2 or $[\text{BH}]^-$ [1]. Alternatively these metallaboranes, or the organometallic compounds, can be formally viewed as heteronuclear clusters in which the main group atoms (boron or carbon) are taken to be an integral part of the cluster framework [2]. The complete characterization of the new cobaltaborane, $\text{Cp}_2\text{Co}_2(\text{PPh}_2)\text{B}_2\text{H}_5$ (**1**), which contains a B_2H_5 fragment formally equivalent to a $\sigma\text{-}\pi$ allyl ligand (C_2H_3), provides another comparison of the bonding of carbon and boron to transition metals.

By varying conditions, the reaction of CpCo(L)_2 with $\text{BH}_3 \cdot \text{THF}$ has been used to produce a number of cobaltaboranes with three and four CpCo units [3]. Here we report the first dinuclear product of the reaction. In a typical reaction, 23.6 mmol of $\text{BH}_3 \cdot \text{THF}$ were added dropwise to 7.9 mmol of $\text{CpCo}(\text{PPh}_3)_2$ in 30 ml toluene at 23°C over a period of 0.5 h. The reaction mixture was then stirred at 90°C for 6 h, concentrated and cooled thereby precipitating colorless $\text{BH}_3 \cdot \text{PPh}_3$ crystals. After

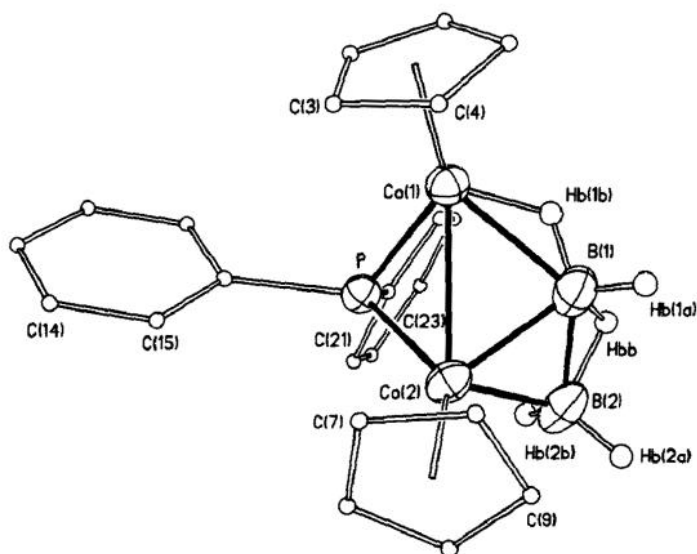


Fig. 1. Molecular structure of **1**. The η^5 -C₅H₅ and C₆H₅ rings are shown with arbitrary spheres to enhance clarity. CNT(1–5)–Co(1), 1.698(6); CNT(6–10)–Co(2), 1.715(6); Co(1)–Co(2), 2.472(1); Co(1)–P, 2.138(2); Co(2)–P, 2.165(2); Co(1)–B(1), 2.110(9); Co(2)–B(1), 2.025(8); Co(2)–B(2), 2.138(9); B(1)–B(2), 1.79(2) Å. Co(1)–P–Co(2), 70.1(1); Co(1)–B(1)–Co(2), 73.4(3); P–Co(1)–B(1), 87.1(3); P–Co(2)–B(2), 90.4(3); B(1)–Co(2)–B(2), 50.9(4); B(1)–B(2)–Co(2), 61.3(4); B(2)–B(1)–Co(2), 67.8(4); Co(1)–B(1)–B(2), 123.3(6); P–Co(2)–B(1), 88.6(3)°.

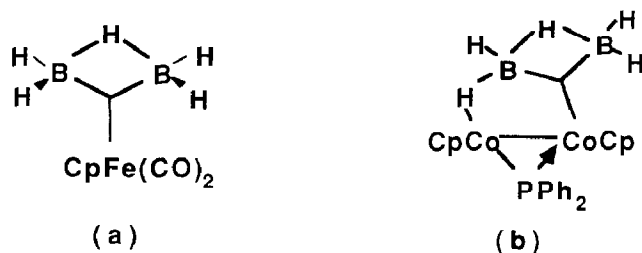
filtering, chromatography on silica gel (hexane/toluene (1/1)) resulted in a dark brown band, $R_f = 0.2$, which was collected and crystallized (dark red crystals) from toluene/hexane. The isolated yield was 0.72 mmol (18%). The air stable compound is soluble in toluene, benzene, THF and acetone.

A single crystal grown from toluene-hexane was subjected to X-ray diffraction analysis [15*]. The structure of **1** (Fig. 1) exhibits a PPh₂ bridged (CpCo)₂ fragment which is also asymmetrically bridged by a B₂H₅ ligand. One boron, B(1), is bound to both cobalt atoms while the other, B(2), is bound to only one cobalt atom. The hydrogen atoms of the borane fragment were crystallographically located. Two terminal H's are found on B(2), one terminal H on B(1), one bridge H between B(1) and B(2), and one bridge H between B(1) and Co(1). All the Co–B and B–H distances, as well as the other atom–atom distances, are within the expected ranges [4]. The gas phase molecular mass and spectroscopic data in solution are in full accord with the solid state structure [16*].

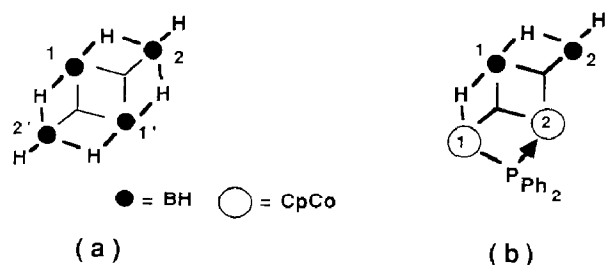
A complex metallaborane, Pt₂(PMe₂Ph)₂(B₂H₅)(B₆H₉) (**2**) has already been shown to contain a η^3 -B₂H₅ fragment similar to that in **1** [5]. Although the hydrogen atoms were not located in the structure determination of **2**, the ¹H NMR evidenced the same arrangement shown in Fig. 1. These authors pointed out that the B₂H₅ ligand could be considered either as a σ - π allyl analogue or part of a dimetallatetraborane fused to a dimetallaocaborane through the metal atoms. The structure of the dimetallatetraborane, Co₂(BH₄)₂(Ph₂P[CH₂]₅PPh₂)₂, with separated boron atoms has been reported [6].

* Reference number with asterisk indicates a note in the list of references.

The B_2H_5 moiety has also been structurally characterized in $CpFe(CO)_2B_2H_5$ (**3**), a compound which is analogous to $(CO)_4FeC_2H_4$, and we have compared the metal-main group bonding in these two compounds in detail [7]. In essence, the metal-boron bonding in **3** is primarily σ in character with little back donation from the metal to the borane. The B-H-B hydrogen compensates for the absence of a low-lying orbital analogous to the π^* orbital of C_2H_4 by directing the boron orbitals towards the iron atom thereby producing a strongly bonding three-center two-electron bond (scheme 1a). If **1** were analogous to a σ - π allyl complex, then a proper representation of the bonding would be that in Scheme 1b where the BH bond of the borane is considered to be a two-electron donor to the cobalt atom. The B-M distances between the two borons and cobalt atom joined by the three-center



Scheme 1



Scheme 2

bond would be expected to be equal and about 2.2 Å. In fact, in **1** the Co(2)-B(1,2) distances are shorter than 2.2 Å and there is a significant asymmetry in the two with the central distance being shorter (2.025(8) vs. 2.138(9) Å). The same holds true for **2** (2.158(26) vs. 2.244(26) Å).

This asymmetry can be rationalized if one considers **1** as an arachno, 14 skeletal electron cluster analogous to B_4H_{10} [8]. The latter molecule, (Scheme 2a) when viewed in terms of a localized MO model, contains 6, two-center, two-electron BH bonds, 4 three-center, two-electron BHB bonds and one orbital associated exclusively with the framework borons [9]. This four center orbital is represented as 2 three-center, one-electron bonds in Scheme 2a to emphasize the enhanced interaction of the 1-1' borons vs. the 2-2' borons in this framework orbital. An analogous representation of **1** is shown in Scheme 2b where the three-center framework bonds now contain two electrons each. The short Co(2)-B(1) distance requires a significant contribution from structure **2b** in a representation of the overall bonding. Although other methods can be used to express the bonding, the important fact is that the difference in the Co(2)-B(1) and Co(2)-B(2) distances is indicative of multicenter cluster bonding.

We have previously argued that a polyhapto borane “ligand” will be more intimately incorporated into a metal bonding network than an equivalent carbon ligand [10]. It is significant, then, that in almost all structurally characterized σ - π allyl complexes the bonding is also asymmetric with the metal-carbon distance analogous to the Co(2)-B(1) distance in **1** about 0.1 Å shorter than that analogous to the Co(2)-B(2) distance [11]. In addition, the ^{11}B NMR chemical shifts of **1** correlate well with the ^{13}C NMR shifts of an allyl complex [11,12]. Likewise the ^1H shifts of the terminal hydrogens of **1** are very similar to those of the CH hydrogens of $\text{HO}_3(\text{CO})_{10}\text{C}_2\text{H}_3$ [13]. All this indicates that the C_2H_3 ligand must also have significant cluster character, i.e., structure **2b** is an important contributor to the metal-ligand bonding. The existence of multicenter bonding has been postulated as a factor contributing to the facility of E-E and E-H bond making and breaking in EM_3 clusters [14]. The evidence presented above for multicenter bonding in a C_2M_2 system provides additional support for such a model.

Acknowledgement. The support of the National Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References

- 1 C.E. Housecroft and T.P. Fehlner, *Adv. Organomet. Chem.*, 21 (1982) 57. T.P. Fehlner, *N.J. Chem.*, in press.
- 2 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 18 (1976) 1.
- 3 J. Feilong, T.P. Fehlner and A.L. Rheingold, *J. Am. Chem. Soc.*, 109 (1987) 1860; J. Feilong, T.P. Fehlner and A.L. Rheingold, *J. Chem. Soc. Chem. Commun.*, (1987) 1395; J. Feilong, T.P. Fehlner and A.L. Rheingold, *Angew. Chem. Intern. Ed. Engl.*, 27 (1988) 424.
- 4 R.N. Grimes (Ed.), *Metal Interactions with Boron Clusters*, Plenum, N.Y., 1985.
- 5 R. Ahmad, J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc. Chem. Commun.*, (1981) 1019. R. Ahmad, J.E. Crook, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc. Dalton Trans.*, (1986) 2433.
- 6 D.G. Holah, A.N. Hughes, S. Maciaszek and V.R. Magnuson, *J. Chem. Soc. Chem. Commun.*, (1983) 1308.
- 7 J.S. Plotkin and S.G. Shore, *J. Organomet. Chem.*, 182 (1979) C15; R.L. DeKock, P. Deshmukh, T.P. Fehlner, C.E. Housecroft, J.S. Plotkin and S.G. Shore, *J. Am. Chem. Soc.*, 105 (1983) 815.
- 8 W.N. Lipscomb, *Boron Hydrides*, Benjamin, N.Y., 1963.
- 9 G.W. Adamson and J.W. Linnett, *J. Chem. Soc. A*, (1969) 1697.
- 10 C.E. Housecroft and T.P. Fehlner, *Inorg. Chem.*, 21 (1982) 1739.
- 11 R.E. Colborn, A.F. Dyke, S.A.R. Knox, K.A. Mead and P. Woodward, *J. Chem. Soc. Dalton Trans.*, (1983) 2099. A.D. Claus, M. Tachikawa, J.R. Shapley and C.G. Pierpont, *Inorg. Chem.*, 20 (1981) 1528. P. Caddy, M. Green, L.E. Smart and N. White, *J. Chem. Soc. Chem. Commun.*, (1978) 839.
- 12 R.E. Williams and L.D. Field in R.W. Parry and G. Kodama (Eds.), *Boron Chemistry-4*, Pergamon, N.Y., 1980, p. 131; B.F. Spielvogel, W.R. Nutt and R.A. Izydore, *J. Am. Chem. Soc.*, 97 (1975) 1609; B.F. Spielvogel and M.J. Purser, *ibid.*, 93 (1971) 4418; H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 107 (1974) 3089.
- 13 A.J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc. Dalton Trans.*, (1975) 1614.
- 14 M.M. Lynam, D.M. Chipman, R.D. Barreto and T.P. Fehlner, *Organometallics*, 6 (1987) 2405.
- 15 Crystal data for **1**: $\text{C}_{22}\text{H}_{25}\text{B}_2\text{Co}_2\text{P}$, monoclinic, $P2_1/c$, a 15.107(3), b 8.871(1), c 16.806(3) Å, β 111.11(2)°, V 2101.1(7) Å³, $Z = 4$, $D(\text{calc}) = 1.385 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) 16.55 \text{ cm}^{-1}$, T 295 K. Of 4529 reflections collected (Nicolet R3m/ μ , $4^\circ \leq 2\theta \leq 48^\circ$), 4099 were independent ($R_{\text{int}} = 2.7\%$) and corrected for absorption (empirical, $T_{\text{max}}/T_{\text{min}} = 1.14$). The structure was solved by direct methods and completed by difference Fourier syntheses. All hydrogen atoms were located, but those for the $\eta^5\text{-C}_5\text{H}_5$ and C_6H_5 rings were treated as idealized isotropic contributions. The remaining

hydrogen atoms were refined isotropically. All nonhydrogen atoms were refined anisotropically. The C_6H_5 rings were treated as rigid bodies to conserve data. At convergence: $R(F)$ 6.00%, $R(wF)$ 6.66%, $GOF=1.566$, $\Delta/\sigma(\max)=0.063$, $\Delta(\rho)$ $0.73 \text{ e}\text{\AA}^{-3}$, $N_0/N_v=11.6$. All computations and sources of scattering factors from the SHELXTL (5.1) library (G.W. Sheldrick, distributed by Nicolet XRD, Madison, WI).

- 16 MS, EI: P^+ m/e 460. Prominent loss of 1 and 2 H_2 from the parent ion is observed. The m/e 458 ion signal is the base peak of the parent ion cluster. IR (toluene); BH region; 2500 w, 2400 m, 2420 sh cm^{-1} . NMR: ^{31}P (C_6D_6 , 20°C); δ 259, s; ^{11}B (C_6D_6 , 20°C); δ 24.2, d, $J \approx 80 \text{ Hz}$; 7.35, t, $J \approx 90 \text{ Hz}$; ^1H ($C_6D_5CD_3$, -30°C); δ 7.45–7.02, m, 10H, Ph; δ 6.47, br, 1H, Hb(1a); δ 5.38, br, 1H, Hb(2a); δ 4.92, s, 5H, Cp; δ 4.38, s, 5H, Cp; δ 3.01; br, 1H, Hb(2b); δ -5.51, br, 1H, Hbb; -21.15, br, 1H, Hb(1b). The assignments of the BH protons are based on selective, boron decoupled proton spectra. Selective decoupling of the boron at δ 7.35 was only successful at -30°C .