References and Notes

(1) E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3431, 3432 (1966); F. H. Westheimer, *Acc. Chem. Res.*, 1, 70 (1968).
(2) W. E. McEwen and K. D. Berlin, Eds., "Organophosphorus Stereochemistry", Vols. I and II, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1975.
(3) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967); F. Ramirez, A. J. Bigler, and C. P. Smith, *ibid.*, **90**, 3507 (1968); B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *ibid.*, **93**, 4004 (1971); D. J. Gorenstein, B. A. Luxon, J. B. Findley, and R. Momii, *ibid.*, **99**, 4170 (1977).
(4) D. I. Phillips, I. Szele, and F. H. Westheimer, *J. Am. Chem. Soc.*, **98**, 184 (1976).
(5) E. J. Behrman, M. J. Biallas, H. J. Brass, J. O. Edwards, and M. Isaks, *J. Org. Chem.*, **35**, 3063 (1970).
(6) K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **25**, 2006 (1960).
(7) I. Sigal, Thesis, Harvard University, 1978.
(8) P. C. Haake and G. Hurst, *J. Am. Chem. Soc.*, **88**, 2544 (1966).
(9) C. A. Bunton and S. J. Farber, *J. Org. Chem.*, **34**, 3396 (1969).
(10) P. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

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A Copper(I) Derivative of a Ferraborane: Preparation, Crystal, and Molecular Structure of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$

Sir:

Ferraborane analogues of hexaborane(10) represent a relatively new[1-3] and unexplored group of *nido*-metalloboranes[4] which are structural analogues[5] and isoelectronic[5,6] (in terms of electron counting rules) with B_6H_{10}.[7] We have prepared the bimetallic compound $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$, a derivative of $B_5H_9Fe(CO)_3$,[1] and have determined its crystal and molecular structure.

This compound is of special interest since it is unlike previously reported systems in which a metal is inserted into the basal boron-boron bond of a nido pyramid. In systems such as $Cu[P(C_6H_5)_3]_2B_5H_8$[8,9] and $Fe(CO)_4B_7H_{12}^-$ [10a] the metal replaces a bridge proton and in effect acts as a "pseudo" proton in accepting an electron pair from the boron-boron bond to form a three-center B-metal-B bond. The metal in its bridging position resides well below the basal plane of the pyramid, 1.5[9b] and 1.7 Å,[10b] respectively, for $Cu[P(C_6H_5)_3]_2B_5H_8$ and $Fe(CO)_4B_7H_{12}^-$, and there is no apparent metal-H-B bonding. In the present case, however, the inserted copper is relatively elevated (0.43 Å beneath the basal plane), not only giving a more open arrangement at the bonding site than previously observed for a metal inserted into a nido pyramid, but also bringing the copper within bonding distance of the exo hydrogen on at least one of the boron atoms adjacent to the metal. Figure 1 illustrates the coordination sphere around copper and iron in $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$, $Fe(CO)_3B_7H_{12}^-$,[11] and $Cu[P(C_6H_5)_3]_2B_5H_8$.[11]

The relatively "open" or "slipped" arrangement of copper at the bonding site in $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ is associated with the existence of Cu-H-B bonding.[12] In terms of the formalism of electron counting rules,[7] copper can be considered to be a vertex of the cluster, with the $Cu[P(C_6H_5)_3]_2$ unit contributing two skeletal electrons. In such terms the molecule is a formal analogue of B_7H_{11}, a long sought boron hydride.[15] It is not clear, however, that this extrapolation of electron counting rules is warranted. On the other hand, in the case of $Cu[P(C_6H_5)_3]_2B_5H_8$, the molecule is clearly an analogue of B_5H_9. Since there is no Cu-H-B bridge, the $Cu[P(C_6H_5)_3]_2$ unit can be treated, formally, as a replacement for a proton, thereby contributing no electrons to the skeletal electron count.

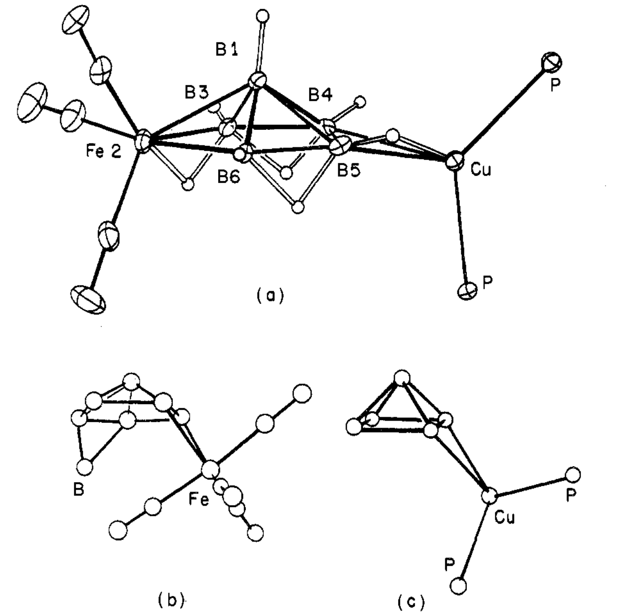

Figure 1. Comparison of the structure of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ (a) with the skeletal structure of $Fe(CO)_4B_7H_{12}^-$ (b) and $Cu[P(C_6H_5)_3]_2B_5H_8$ (c).

From the sequence of reactions

$$B_5H_9Fe(CO)_3 + KH \xrightarrow[-78\ °C]{(CH_3)_2O} K^+B_5H_8Fe(CO)_3^- + H_2 \qquad (1)$$

$$K^+B_5H_8Fe(CO)_3^- + Cu[P(C_6H_5)_3]_3Cl \xrightarrow[-45\ °C]{(CH_3)_2O} Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3 + KCl + P(C_6H_5)_3 \qquad (2)$$

the compound $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ was prepared and isolated. It is a yellow solid which is apparently stable at room temperature in the absence of air. It does not appear to be as photosensitive as its precursors $K^+B_5H_8Fe(CO)_3^-$ and $B_5H_9Fe(CO)_3$.[1]

Crystals of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ were grown by vapor diffusion of *n*-pentane into a toluene solution at 0 °C. They are triclinic (space group $P\bar{1}$); a = 11.113 (5), b = 14.670 (8), c = 15.034 (7) Å; α = 95.60 (4), β = 121.01 (3), δ = 106.29 (4)°; Z = 2; d_{calcd} = 1.36, d_{exptl} = 1.34 g cm^3. All X-ray data was collected at −90 °C.[16]

Bond distances in the borane unit of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ are normal:[19] B-B = 1.662 (11) to 1.783 (9), $B-H_{terminal}$ = 1.02 (7) to 1.13 (7), $B-H_{bridge}$ = 1.13 (7) to 1.30 (8) Å. Structural parameters for the $B_5H_8Fe(CO)_3$ unit are in excellent agreement with those observed for $B_5H_8Fe(CO)_3^-$.[1a] Iron-boron distances are Fe(2)-B(1) = 2.154 (7), Fe(2)-B(3) = 2.115 (10); Fe(2)-B(6) = 2.075 (7) Å. The Fe(2)-H(23) distance = 1.56 (6) Å. The site of copper insertion, the B(4)-B(5) bond is 1.662 (11) Å. Interestingly, this site is not the site of the boron-boron bond (B(3)-B(4)) in the parent anion $B_5H_8Fe(CO)_3^-$.[1] The significant difference in copper-boron distances is indicative of unsymmetrical binding of copper to the B(4)-B(5) system: Cu-B(4) = 2.274 (7), Cu-B(5) = 2.164 (8) Å.

As noted above, the remarkable structural feature of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ is the relatively open bonding site of the copper atom. There are no unsually short nonbonded contact distances or distorted angles to suggest a configuration forced by steric considerations. The angle P(1)-Cu-P(2) is 127.57 (8)°. The plane which is defined by B(4)-Cu-B(5) is

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12° from coplanarity with the basal plane of the $B_5H_8Fe(CO)_3$ pyramid (Figure 1). This angle is markedly smaller than the analogous angles for other nido pyramids which contain a metal inserted into a basal boron-boron bond: $Cu[P(C_6H_5)_3]_2B_5H_8$ (52°),[9b] $Fe(CO)_4B_7H_{12}^-$ (56°).[10b] The relatively elevated position of copper in $Cu[P(C_6H_5)_3]$-$B_5H_8Fe(CO)_3$ reflects and accommodates Cu-H-B bonding. Supportive evidence is provided by the infrared spectrum. It contains a band at 2292 cm^{-1} which is in the characteristic region for a Cu-H-B stretching mode.[8b,20] This band is absent from the infrared spectrum of $B_5H_8Fe(CO)_3^-$. Additionally, the Cu-H(5) distance, 1.96 (7) Å, falls within the range observed from X-ray studies of compounds which are said to have Cu-H-B bonding and also exhibit the characteristic Cu-H-B absorption in their infared spectra.[20] The Cu-H(4) distance, 2.25 (6) Å, is significantly longer than the longest Cu-H distance, 2.08 (7) Å, observed in Cu-H-B bonds.[20a] It is closer to the shortest Cu-H distance, 2.33 (9) Å, observed in $Cu[P(C_6H_5)_3]_2B_5H_8$,[9a] a compound which is said to possess no Cu-H-B bonding based upon the absence of a band in the infrared spectrum which is characteristic of the Cu-H-B stretching mode. In view of the significant difference in the Cu-B(4) and Cu-B(5) bond lengths, we believe that the difference in the Cu-H(4) and Cu-H(5) distances is real and that the Cu-H(5) distance is a bonding distance.

Copper is considered to possess a 16-electron configuration in $Cu[P(C_6H_5)_3]_2B_5H_8$.[8,9a] In $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ the presence of Cu-H-B bonding allows for an 18-electron configuration. The difference in these two arrangements is probably a function of the basal plane of the pyramid. The exo hydrogens in the pentagonal base might be more accessible than those in the square base. To test this point we are examining copper(I) derivatives of other nido pyramids: $Cu[P(C_6H_5)_3]_2B_4C_2H_7$ and $Cu[P(C_6H_5)_3]_2B_6H_9$.

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Supplementary Material Available: A listing of atom coordinates, bond distances, and bond angles (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Am. Chem. Soc.*, **98**, 7085 (1977); (b) S. G. Shore, J. D. Ragaini, R. L. Smith, C. E. Cottrell, and T. P. Fehlner, *Inorg. Chem.*, in press.

(2) R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 8087 (1977).

(3) The manganaborane analogue of B_6H_{10}, $B_5H_{10}Mn(CO)_3$, has also been reported: M. B. Fischer, D. F. Gaines, J. D. Kessler, the 174th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1977, INORG 167.

(4) Other *nido*-metalloboranes which are analogues of B_5H_9 are known: N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford. *J. Chem. Soc., Chem. Commun.*, 718 (1974); V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976); V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977); R. Weiss, J. B. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978).

(5) K. Wade, *Chem. Br.*, 11, 177 (1975).

(6) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976). See also R. E. Williams, *ibid.*, **18**, 67 (1976).

(7) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(8) (a) V. T. Brice and S. G. Shore, *J. Chem. Soc., Dalton Trans.*, 335 (1975); (b) G. G. Outtserson, Jr., V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **15**, 1456 (1976).

(9) (a) N. N. Greenwood, J. A. Howard, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 37 (1977). (b) Calculated from data suppled in ref 9a.

(10) (a) M. Mangion, W. R. Clayton, O. Hollander, and S. G. Shore, *Inorg. Chem.*, 16, 2110. (b) Calculated from data supplied in ref 10a.

(11) These skeletal drawings are based on ORTEP plots which employ published positional parameters.[9a,10a]

(12) This observation is a timely one in view of recent comments concerning certain metallocarborane systems which do not obey electron counting rules in that they adopt "open" or "slipped" structures instead of the expected closo arrangements. Explanations for such behavior range from the suggestion that the systems might contain unrecognized hydrogens which are not taken into account,[13] to possible electronic effects.[14] Although $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ is not related to such systems, in light of our results we suggest that systems which display extreme "slippage" could involve unanticipated interaction between the metal and exo hydrogens on adjacent boron atoms.

(13) D. A. Thompson, T. K. Hilty, and R. W. Rudolph, *J. Am. Chem. Soc.*, **99**, 6774 (1977).

(14) (a) H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 322 (1978); (b) D. M. Mingos, M. I. Forsyth, and A. J. Welch, *ibid.*, 605 (1977).

(15) R. J. Remmel, H. D. Johnson, II, I. S. Jaworiwsky, and S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5395 (1978).

(16) Of the 6945 reflections which were measured, 4760 unique reflections for which $I \geq 3\sigma(I)$ were considered as observed. Patterson and Fourier[17] techniques gave positions of nonhydrogen atoms. After refinement of positional and anisotropic thermal parameters of these atoms, phenyl hydrogens were located and their positional and isotropic thermal parameters were refined. From a weighted[18] difference map, borane hydrogens were located. In subsequent refinements, positional and isotropic thermal parameters of borane and phenyl hydrogens were allowed to vary. Full-matrix least-squares refinement converged with a conventional R of 0.050 and a weighted R of 0.056.[1] The average C–H distance on the phenyl rings is 0.94 (7) Å. The successful refinement of phenyl hydrogens lends credence to the refinement of borane hydrogens in this molecule.

(17) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall. "The X-ray System", Technical Report TR-192, Computer Science Center, University of Maryland, College Park, Md., June 1972.

(18) W. R. Clayton, M. Mangion, and E. A. Meyers, *Acta Crystallogr., Sect. A*, **28**, 743 (1975).

(19) A summary of distances is given by S. G. Shore, "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, p 88.

(20) (a) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975); (b) T. E. Paxton, M. F. Hawthorne, L. D. Brown, and W. N. Lipscomb, *Inorg. Chem.*, **13**, 2772 (1974); (c) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

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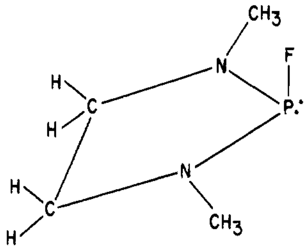
Carbon Monoxide Exchange in 1,2-Dimethyl-1,3,2-diazaphosphenium Tetracarbonyliron Cation

Sir:

In a recent paper[1] it was shown that the cyclic, fluorinated ligand (FL) coordinates to an $Fe(CO)_4$ group to give a trigonal-bipyramidal molecule, $(FL)Fe(CO)_4$, with the fluorinated ligand in the *axial position.* Treatment[2] of this neutral species,



(FL)

in CH_2Cl_2, with PF_5 results in transfer of the fluoride ion of the ligand to PF_5 to give PF_6^- and a cationic complex containing an axially coordinated cyclic phosphenium *cation*, $CH_3\overline{NCH_2CH_2N(CH_3)P}^+$ (L). The process can be represented by the equation

$$(FL)Fe(CO)_4 + PF_5 \xrightarrow[-80\ °C]{CH_2Cl_2} [(L)Fe(CO)_4]^+ + [PF_6]^-$$

The present communication establishes that the CO groups of the cationic $[LFe(CO)_4]^+$ are in labile equilibrium with free CO at temperatures above 0 °C, while the CO groups on neutral $(FL)Fe(CO)_4$ do *not* exchange with external CO at 25 °C. Both ^{13}C NMR and ^{13}C isotope exchange data are presented.

A. Carbon Monoxide Exchange as Indicated by ^{13}C NMR Line Shape. At −20 °C the ^{13}C spectrum of coordinated CO molecules in $[CH_3\overline{NCH_2CH_2N(CH_3)P}F]Fe(CO)_4$ shows a doublet of doublets resulting from $\overline{FPFeC}$ coupling, J_{FC} = 4.0

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