was measured for F_2 in these experiments, suggesting that these are similar vibrational modes of similar species. Of course, this depolarization ratio is too high for the Raman fundamental of F_2 and, likewise, it is probably higher than the true value for the 475-cm^{-1} scatterer. Apparently incomplete randomization of molecular orientations and scrambling of the polarized scattered light by the frosty matrix sample cause measured depolarization ratios to be too high in these experiments. The symmetric mode Raman bands for argon matrix isolated[6] OF_2 produced depolarization ratios which were much higher than those measured from the liquid spectrum.[9]

In order to provide a fluorine analysis of the new species at 475 cm^{-1}, similar reactions were done with sodium and Cl_2 in argon and a Cl_2–F_2 mixture in argon. With the chlorine–sodium reaction, an intense new band was observed at 225 cm^{-1} which is attributed to the chlorine counterpart, $M^+Cl_2^-$, of the 475-cm^{-1} fluorine band. The Cl_2–F_2 reaction with sodium showed only two new spectral features, the 475- and 225-cm^{-1} bands. Hence, the new species incorporates one halogen molecule or two halogen atoms and is most probably $M^+F_2^-$. The lack of intermediate spectral features between 475 and 225 cm^{-1} rules out a species containing three halogen atoms.

The Raman bands near 460 cm^{-1} reported here are assigned to the intraionic (F–F)$^-$ stretching mode in the $M^+F_2^-$ species. The interionic M^+–F_2^- mode is being sought in the infrared. The frequency position of this mode influences the Raman frequency of the intraionic (F–F)$^-$ mode. If we may approximate the M^+–F_2^- mode frequency with the analogous M^+–O_2^- modes, the frequencies 699, 391, 307, 255, and 236 cm^{-1} have been reported for Li^+, Na^+, K^+, Rb^+, and Cs^+ superoxides,[10-12] respectively. The significant point is that there is a frequency cross-over with the interionic and intraionic modes; for $Li^+F_2^-$ the interionic mode appears *above* the intraionic mode forcing it down (452 cm^{-1}) by interaction of vibrational modes of the same symmetry; for $Na^+F_2^-$ the interionic appears *below* the intraionic mode forcing it up (475 cm^{-1}). As the M^+ becomes heavier, the interionic mode rapidly drops diminishing the interaction and the intraionic mode frequency decreases (from 464 to 459 cm^{-1} for K^+ to Cs^+).

The additional electron in F_2^- is added to an antibonding σ molecular orbital thus reducing the number of net bonding electrons from two for F_2 to one for F_2^-. A casual approximation of the F_2^- vibrational frequency would be half that of F_2. It is gratifying that the F_2^- frequency falls near 50% of the F_2 fundamental. The $M^+F_2^-$ species observed here is, in many ways, analogous to the $M^+O_2^-$ species observed in alkali metal atom–O_2 matrix reactions.[10-13] In the superoxide species, oxygen isotopic mixtures showed the two oxygen atoms to be equivalent in an isosceles triangular structure and the O–O stretching modes corresponded to (O–O)$^-$ vibrations.

The evidence presented here strongly justifies the production and stabilization of F_2^- as the species $M^+F_2^-$ from the matrix reactions of alkali metal atoms and molecular fluorine. The ion–molecule is unstable as expected and it shows a bond similarity to F_2 from polarization data. The comparative vibrational frequencies of F_2 and F_2^- correspond to a rough molecular orbital prediction. Lastly, the frequency dependence upon the alkali metal reagent is not enough for a M–F vibration; it corresponds to a (F–F)$^-$ vibration slightly perturbed by its adjoining alkali cation partner.

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(9) D. J. Gardiner, N. J. Lawrence, and J. J. Turner, *J. Chem. Soc. A*, 400 (1971).

(10) L. Andrews, *J. Chem. Phys.*, **50**, 4288 (1969).

(11) L. Andrews, *J. Phys. Chem.*, **73**, 3922 (1969).

(12) L. Andrews, *J. Chem. Phys.*, **54**, 4935 (1971).

(13) R. R. Smardzewski and L. Andrews, *J. Chem. Phys.*, **57**, 1327 (1972).

Triple-Decked Sandwich Compounds. Planar $C_2B_3H_5^{4-}$ Cyclocarborane Ligands Analogous to $C_5H_5^-$

Sir:

The metallocarboranes, or metal–carborane π complexes,[1] are conveniently regarded as electronic analogs of the metallocenes, and a formal 6-electron donation from each carborane ligand (considered as a dianion) to the metal atom is normally assumed. With the following exception, all previously reported metallocarborane ligands are three-dimensional boron–carbon cages rather than planar ring systems. Recently, we prepared a diamagnetic (π-$C_2B_3H_7$)Fe(CO)$_3$ complex[2,3] and from spectroscopic data proposed a structure, subsequently confirmed by an X-ray study,[4] in which the formal c-$C_2B_3H_7^{2-}$ ligand (isoelectronic with $C_5H_5^-$) is planar except for two B–H–B bridging hydrogens which are directed away from the metal atom. This compound is thus a structural and electronic analog of the well known (π-C_5H_5)Fe(CO)$_3^+$ ion. The $C_2B_3H_7^{2-}$ ligand, which has not been prepared as a free anion, may be regarded as a bridge-diprotonated derivative of the cyclic planar $C_2B_3H_5^{4-}$ system, previously unknown. We describe here the first complexes containing the formal $C_2B_3H_5^{4-}$ ligand, which are also the first definitively characterized triple-decked sandwich species having three planar ring systems (Figure 1). These compounds have been characterized from their ^{11}B and ^1H nmr spectra, unit- and high-resolution mass spectra, infrared spectra, and an X-ray diffraction study of III. The close chemical and spectral similarity between III and the other compounds leaves no doubt as to the gross triple-decked structures of all three species. All of the compounds are diamagnetic air-stable crystalline solids in which the formal oxidation state of cobalt is conveniently assigned as +3.

Complex I was obtained from the reaction of 1,6-

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(1) For recent reviews, see M. F. Hawthorne, *Pure Appl. Chem.*, **29**, 547 (1972); R. Snaith, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci: Inorg. Chem., Ser. One*, **1**, 139 (1972); L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, Chapter 9.

(2) R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 261 (1971).

(3) D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972).

(4) See ref 3, footnote 11a. Also, J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, manuscript submitted for publication.

dicarba-*closo*-hexaborane(6), $C_2B_4H_6$, with sodium naphthalide in tetrahydrofuran, followed by addition of sodium cyclopentadienide and excess $CoCl_2$ and subsequent air oxidation. Complex II was prepared by treatment of sodium dicarba-*nido*-hexaborate(1−), $Na^+C_2B_4H_7^-$, with anhydrous NaC_5H_5 and $CoCl_2$ in THF followed by air oxidation, while III was obtained from $Na^+[2\text{-}CH_3C_2B_4H_6]^-$ in an analogous manner. Complexes I–III were minor products (3–4% yield) of these reactions, which also produced other metallocarboranes to be described later in a full paper. In addition, II has also been prepared directly from the sandwich compound $(\pi\text{-}C_2B_3H_7)Co(\pi\text{-}C_5H_5)$[5] (an analog of $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$, discussed above) by bridge deprotonation with NaH followed by reaction with $CoCl_2$ and NaC_5H_5.

$$\begin{tikzcd}
(\pi\text{-}C_2B_3H_7)Co(\pi\text{-}C_5H_5) \arrow[r, "NaH", "-H_2"'] & {[(\pi\text{-}C_2B_3H_6)Co(\pi\text{-}C_5H_5)]^-Na^+} \arrow[dl, "{CoCl_2, NaC_5H_5}"] \\
(\pi\text{-}2,3\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2 &
\end{tikzcd}$$

Each compound was purified by preparative-scale thin-layer chromatography on silica gel. The unit-resolution mass spectra of I, II, and III exhibit strong parent peaks at *m/e* 310 for I and II, and 324 for III, corresponding to the $^{59}Co_2{}^{12}C_{12}{}^{11}B_3{}^{1}H_{15}^+$ and $^{59}Co_2{}^{12}C_{13}{}^{11}B_3{}^{1}H_{17}^+$ ions, respectively; in each spectrum the profile in the parent region is nearly identical to that calculated for the composition indicated. The elemental formulas of I and II have been further confirmed by their high-resolution spectra (I, parent *m/e* 310.0138, II, 310.0115; calcd for I and II, 310.0112). The spectra of all three compounds contain intense $Co(C_5H_5)_2^+$ and $Co(C_5H_5)^+$ peaks at *m/e* 189 and 124, respectively. The ^{11}B and ^1H nmr data, presented in Tables I and II, are consistent with the indicated structures. In addition, the assignment of the carbon atoms in the central ring of I to nonadjacent positions is quite consistent with its synthesis from $1,6\text{-}C_2B_4H_6$, in which the carbons are separated.

Table I. 32.1-MHz ^{11}B Nmr Data

Compound	δ,[a] ppm (*J*, Hz)	Measd areas
I[b]	−22.8 (149)	2[c]
	−13.4 (155)	1[c]
II[d]	−57.3 (135)	1
	−6.3 (148)	2
III[d]	−53.2 (138)	1
	−7.0 (138)	2

[a] Chemical shifts relative to $BF_3\cdot O(C_2H_5)_2$. [b] CH_2Cl_2 solution. [c] Estimated from partially overlapped peaks. [d] $CHCl_3$ solution.

Table II. 100-MHz ^1H Nmr Data

	δ,[a] ppm		
Complex	C_5H_5	Carborane CH	Integrated areas
I[b]	−4.48	−2.40[c]	10,2
II[d]	−4.42	−5.52	10,2
III[d]	−4.35	−5.19[e]	10,1
		−2.74[f]	3

[a] Chemical shifts relative to $(CH_3)_4Si$. H–B quartets are weak and largely masked by H–C resonances. [b] CCl_4 solution. [c] Singlet with unresolved triplet-like fine structure. [d] $CDCl_3$ solution. [e] Doublet, $J = 3$ Hz, assigned to carborane CH. [f] CH_3 resonance.

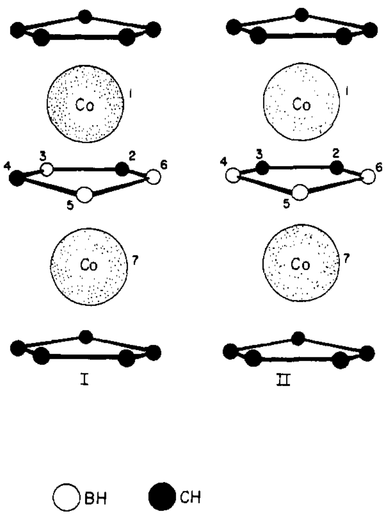

Figure 1. Schematic side view and numbering system of $(\pi\text{-}(1,7)\text{-}2,4\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2$ (I), $(\pi\text{-}(1,7)\text{-}2,3\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$ (II), and $(\pi\text{-}3\text{-}CH_3\text{-}(1,7)\text{-}2,3\text{-}C_2B_3H_4)Co_2(C_5H_5)_2$ (III). The relative ring orientation depicted is arbitrary; in each compound the C_5H_5 protons are nmr equivalent in solution at room temperature, and rapid rotation of the outer rings is assumed.

The carboranyl H–C resonance in the ^1H nmr spectrum of a carefully purified sample of III is a doublet with $J = 3$ Hz, and in the spectrum of I the corresponding peak appears as an unresolved triplet (fine structure has not yet been established in II, which exhibits a somewhat weaker spectrum due to low solubility). We have observed similar splitting, independent of field strength, in certain other small metallocarboranes containing four boron atoms or less and attribute it to H–B–C–H proton–proton coupling between hydrogens attached to neighboring boron and carbon atoms. Such coupling has apparently not been observed in larger carborane or metallocarborane systems. This effect is under further study and will be more fully discussed elsewhere.

The dark red crystals of III grown from pentane are monoclinic, space group *C*2/*c* with $a = 16.128$ (4), $b = 11.578$ (2), $c = 15.546$ (4) Å; and $\beta = 110.05$ (2)°. With eight molecules of $C_5H_5Co(2\text{-}CH_3C_2B_3H_4)CoC_5H_5$ per unit cell, no molecular symmetry is required. The intensity data were measured on a Syntex P$\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation and a θ–2θ scan technique. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. The usual residual *R* is 0.056 for the 1951 observed reflections used in the analysis. Location of the hydrogen atoms and further refinement is in progress.

A view of the molecule down the Co–Co vector is given in Figure 2. The rings are all planar but not parallel. The upper ring, C11–C15, is tipped 4.6° relative to the C_2B_3 plane and 10.0° relative to C21–C25; similarly, C21–C25 is tipped 5.5° relative to the C_2B_3 plane. The tip is such that C12 and C22 are furthest from the C_2B_3 plane. Since these two carbon atoms are furthest from the borons, there may be a correlation between the two observations. The other remarkable feature is that the upper (C11–C15) ring almost eclipses the C_2B_3 ring while the lower (C21–

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[5] L. G. Sneddon and R. N. Grimes, manuscript in preparation.

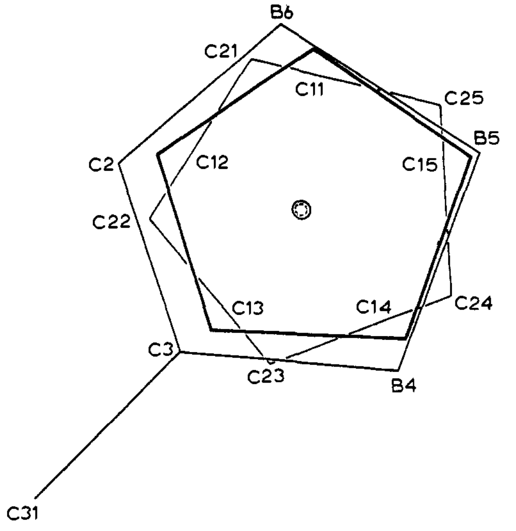

Figure 2. A view down the Co–Co bond in III, illustrating the crystal orientation of the three rings. The carbon atoms C11–C15 form the top ring and the carbons C21–C25 the bottom ring. The methyl group (C31) is only −0.008 Å from the plane of the C_2B_3 ring.

C25) ring is almost completely staggered relative to the other two rings. While the orientation of the C_5H_5 rings in metallocenes is still a subject of controversy, recent data suggest that in general the eclipsed configuration is the more stable. The presence of both eclipsed and staggered arrangements in III indicates that the factors determining the relative orientation of planar π-type rings may be more complex than anticipated. With the Co atoms situated 1.568 and 1.572 Å from the C_2B_3 plane all other distances are relatively normal.

The stability of the triple-decked compounds I–III is of interest in view of the scarcity of corresponding cyclopentadienyl species. Peaks attributed to $M_2(C_5H_5)_3^+$ ions, for which triple-decked structures were suggested, have been observed in the mass spectra of ferrocene and nickelocene[6] but structural data are lacking. The recently reported[7] $Ni_2(C_5H_5)_3^+$ system, for which a triple-decked structure has been proposed from nmr and ir data, is converted to nickelocene by water and other solvents; in contrast, compounds I–III are unreactive to water and air. Ligand–metal bonding in metallocarboranes has been discussed elsewhere,[1] but the situation in complexes I–III appears novel with respect to the simultaneous bonding of both faces of the central ring to metal atoms. The new complexes may be qualitatively similar to the pentagonal bipyramidal species $B_7H_7^{2-}$, $C_2B_5H_7$, and $CH_3GaC_2B_4H_6$, which have been described[8,9] in terms of delocalized π_{p_z} molecular orbitals on the ring combined with orbitals of appropriate symmetry on the apex atoms,[8] resulting in a set of filled bonding molecular orbitals for the cage system.

While it appears improbable that a free $C_2B_3H_5^{4-}$ ion would be stable, the chemistry of this ring system and its diprotonated form $C_2B_3H_7^{2-}$ in metal complexes is expected to be large in scope and may extend to unprecedented multiple-decked stacked compounds incorporating several metal atoms sandwiched between alternating carborane rings. We are presently examining such structural possibilities.

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(6) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 47, 1525 (1964).

(7) A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 11, 930 (1972); *Syn. Inorg. Metal-Org. Chem.* 2, 239 (1972).

(8) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36, 2179 (1962); (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (c) W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 47, 1791 (1961).

(9) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, 94, 1865 (1972).

Mössbauer Study of Stereochemistry Intermediate to Octahedral and Trigonal Prismatic

Sir:

The difficulty in distinguishing octahedral or trigonal antiprismatic (TAP) from trigonal prismatic (TP) coordination with conventional techniques (electronic spectra, nmr, magnetic susceptibility, etc.) is emphasized in low-spin iron(II) complexes. Such materials typically exhibit small, temperature-independent magnetic moments that are uninformative relative to variation in stereochemistry. The types of ligands capable of resulting in spin paired d^6 often lead to charge transfer absorptions, a complicating feature if one wishes to discern transitions of the "dd" type in electronic spectra. Using ordinary and magnetically perturbed Mössbauer spectroscopy, the problem of distinguishing TP from TAP coordination is considered for a series of tris diimine compounds for which some of the structures are known crystallographically. The coordination environment is varied from near regular octahedral (twist angle $\phi = 60°$) toward trigonal prismatic ($\phi = 0°$) as shown in Figure 1. In this figure only one chelate ring structure is illustrated for each complex and the drawings for compounds **2**, **5**, **6**, and **7** are not meant to be suggestive of a particular choice of ϕ. The compounds investigated are part of a group of clathro-chelate systems recently discussed in the literature[1–3] and the details of nomenclature as well as structure may be found in ref 3. As the twist angle is decreased from 60° toward 0° in this series the quadrupole splitting (ΔE) increases from near zero to $\approx$ 1 mm/sec. The respective ΔE's including sign for some of the complexes and isomer shifts (in parentheses) relative to iron metal are also shown in Figure 1. Application of

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(1) J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 3500 (1970).

(2) J. E. Parks, B. E. Wagner, and R. H. Holm, *Inorg. Chem.*, 10, 2472 (1971).

(3) G. E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 11, 2652 (1972).