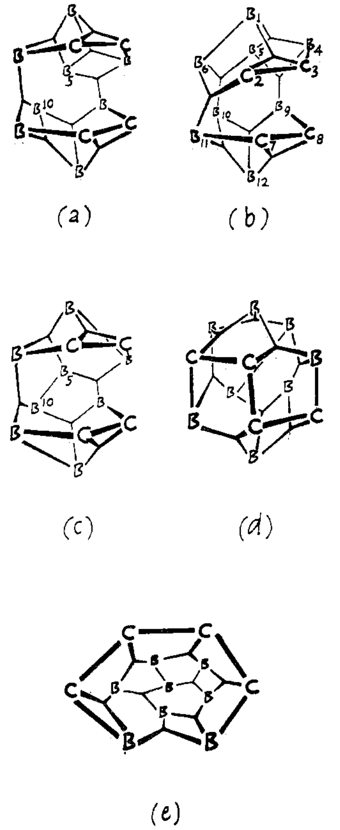

Figure 1. Hypothetical structure for $C_4B_8H_{12}$ (0860) opened up from the $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ analogue (b) in which the two $\eta^5\text{-}C_5H_5Co$ units are replaced by BH. The close relation of (a) to two $C_2B_4H_8$ valence structures leaves B(5) and B(10) unconnected, and hence (a) is expected to collapse to (b) or to take up an electron pair to give (c) as hypothetical $C_4B_8H_{12}^{2-}$ (0670). Structure (b) and hypothetical structures (a) and (c) are dominated[1] by $\eta\text{-}C_5H_5Co$ units (in place of BH) at positions 1 and 12, while the actual geometrical structure of $(CH_3C)_4B_8H_8$ (idealized as $C_4B_8H_{12}$) is shown in (d) in its dominant valence description. Here, in (d), a dominant localized structure is the zigzag C_4 group, while the single B–B bond is very delocalized. The valence structure of the nido-like form of $C_4B_8H_{12}$[3] (e) which is analogous to $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$[1b] is dominated by single bonds B–C–C–C–C–B around the open face, while there are alternative ways to place the remaining bonds.

established crystallographically for the 12-vertex, 28-electron system, I comment here on the severe distortion shown by one structure type[1] exemplified by $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ and $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6OC_2H_5$. This structure is idealized, for ease of discussion, as $(C_2B_4H_6)_2$, in order to exhibit the relationship of its framework bonds to those[2] in $C_2B_4H_8$ (4,5-dicarbahexaborane(8)).

First, open the structure to C_2 symmetry (Figure 1a). If we deploy the C=C double bonds each as a single and three-center bond, and the single bonds C(2)–B(6), C(3)–B(4), C(7)–B(11), and C(8)–B(9) as in $C_2B_4H_8$, and if we then require three framework bonds (omitting external BH or CH bonds) to each apex atom B(1) and B(12), there remain only two electron pairs for the equatorial region to bond B(4), B(5), and B(6) to B(9), B(10), and B(11) (Figure 1a). One way of placing these two equatorial bonds leaves B(5) and B(10) unconnected as shown in the open structure (Figure 1a). Any other placement of these two equatorial bonds would leave other pairs of boron atoms unconnected. Thus this molecular geometry could be stabilized by addition of two electrons to make a bond between B(5) and B(10) in the hypothetical ion $C_4B_8H_{12}^{2-}$ (Figure 1c).

The observed geometry for the analogue of neutral $C_4B_8H_{12}$ is therefore somewhat collapsed, so that C(2) is 2.02 Å from B_{11}. Hence, with few changes other than those associated with the conversion of a single C(2)–B(6) bond toward a three-center bond involving B(11), the framework bonding pattern of the two $C_2B_4H_6$ moieties is largely maintained. While there are other valence structures contributing to the resonance hybrids of these geometrical structures, the main features of the distortion of (a) to (b) and of the opening from the nearly icosahedral structure seem reasonable in terms of the bonding arrangement in $C_2B_4H_8$.

Relationships of these analogues (Figure 1a,b) to other known structures of $C_4B_8H_{12}$ or its analogues[3] are shown in Figure 1c–e the emphasis is on local dominant valence structures.

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A Comment on Ligand Designators

Sir:

I read with interest the recent article by Sloan and Busch[1] on proposed nomenclature for the "Designation of Coordination Sites for Ambidentate and Flexidentate Ligands". Especially pleasing was the apparent consistency of their proposed kappa (κ) notation with the enormously useful and simple *hapto* (η) notation introduced by Cotton[3]—allowing for minor changes in the *hapto* notation. However, in a following article, Leigh[2] proposed an alternative, ostensibly simpler system in which a single designator, Ω, could suffice for the η and κ designators. I fully appreciate the need for nomenclature with designators that are universal, simple, and unambiguous. However, it is the rare case that proposed systems can fully anticipate the problems that will be encountered in future structures, especially in the complex inorganic and organometallic area. I strongly urge that the Cotton *hapto* system be retained and remain unmodified. It is an elegant and widely used system. Just imagine the bewilderment of the chemistry student in the year 2052 as he reads "inorganic chemistry" articles in the 1960–2040 period if a succession of Greek letters were to parade by as designators.[4]

The *hapto* system as originally formulated[3] was free of electronic ambiguities. It was to be a topological designator that specified metal–ligand atom connexities subject to a precise[5] determination from crystallographic analysis and was to clearly avoid the ambiguities associated with "subjective judgements about bonding details".[3] It has succeeded well to date.

0020-1669/79/1318-0902$01.00/0

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(2) G. J. Leigh, *Inorg. Chem.*, **17**, 2047 (1978).
(3) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).
(4) As a case in point, consider the polyhedral borane story where the polyhedral vertex numbering sequence appears in the literature in three different forms over a 15-year period.
(5) There is a gray area in that some metal–ligand atom separations do not clearly fall within bonding distance or within nonbonding distance ranges.

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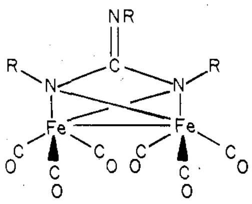
Cumulene-Derived Metallocyclic Complexes. 1. A Mechanism for Carbodiimide Rearrangements

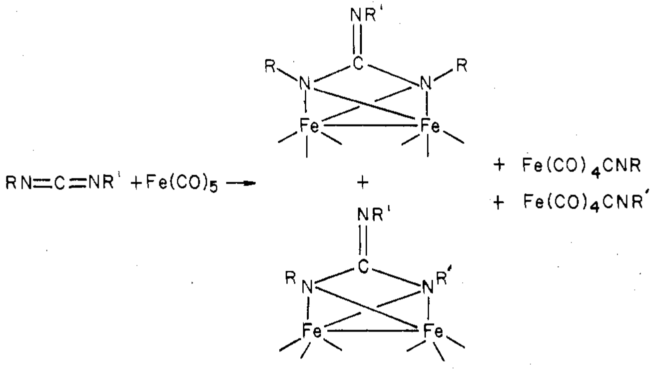
Sir:

Our studies, as part of a program to develop the organometallic chemistry of cumulenes, can provide a convenient explanation for the unexpectecd products obtained from the reaction of carbodiimides with iron carbonyl. A mechanism can be proposed in which the transition-state structure is consistent with chemistry observed for reactions of organometallic complexes with heterocumulenes such as carbon dioxide and diphenylketene, and also for allenes.

Farona's group reported in 1971[1] that dialkyl carbodiimides, RN=C=NR, react with $Fe(CO)_5$ to form dehydroguanidinoiron carbonyl complexes.

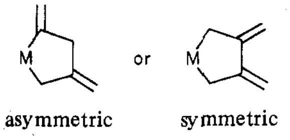


A mechanism was proposed where a carbene carbon is generated on carbodiimide by donor bond formation from *both* nitrogens to iron carbonyl moieties. This was recently ruled out by observations in Cotton's group[2] on *asymmetrically substituted* carbodiimides, where the iron bound nitrogens were found to be equivalently substituted in only one of the two dehydroguanidinodiiron complexes isolated, i.e.



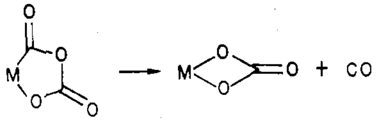
A mechanism was proposed in which a metal nitrene intermediate was created by attack of $Fe(CO)_5$ on the carbodiimide to release isocyanide.

A simple mechanism for this carbodiimide coupling can be proposed that serves to illustrate the principle that metallocyclic intermediates are common in cumulene chemistry. These intermediates can be either symmetric or asymmetric, i.e.

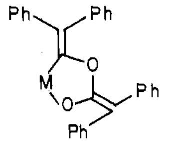


(only one symmetric form is shown and heteroatoms are not indicated but may be present).

The organometallic chemistry of carbon dioxide indicates the frequent occurrence of an intermediate involving an asymmetric bis CO_2 metallocycle, as indicated by Herskowitz[3] and our work on stoichiometric reactions of CO_2 with permethylmetallocenes.[4] The asymmetric bis CO_2 metallocycle decomposes to coordinated carbonate and free CO as follows



We have isolated more stable asymmetric bis(allene) metallocyclic products[4,5] and are carrying out a sequence of studies on these. Very recently, the first asymmetric bis(ketene) metallocycle was reported by Floriani.[6]



M = Cp_2Ti

Clearly, the asymmetrically coupled bis(cumulene) metallocycle can be important in cumulene chemistry and cannot be ignored when considering carbodiimide chemistry. In fact the organometallic chemistry of carbodiimides seems to be analogous to that observed for carbon dioxide. Consider Chatt's molybdenum *cis*-bis(dinitrogen) complex, $Mo(PMe_2Ph)_4(N_2)_2$, which upon reaction with CO_2 yields a product with bridging carbonate,[7] and coordinated CO. For carbodiimide reaction with $Fe(CO)_5$ a bridging dehydroguanidine is found, which is the CO_3^{2-} analogue, while CNR is released, equivalent to the loss of CO from CO_2 systems.

A detailed carbodiimide–$Fe(CO)_5$ mechanism will then quite possibly involve an asymmetric metallocycle. A suggested mechanism is shown in Scheme I. (Concerted metallocycle formation is shown only for illustrative purposes. The time of loss of isocyanide is not known, but shown as most convenient.) This mechanism easily accounts for all of Cotton's observations for reactions of $Fe(CO)_5$ with unsymmetrical carbodiimides. For *t*-BuN=C=NMe only two of the four possible products were found, [$R_a = R_d =$ Me, $R_b =$ *t*-Bu] and [$R_a =$ Me, $R_d = R_b =$ *t*-Bu]. The imine nitrogen always has the larger alkyl group and the coordinated nitrogens apparently cannot both have the larger substituent. The metallocycle substituent most sterically crowded by the carbonyl ligands is R_a. If this substituent is required to be the smallest, then R_b must always be the larger group, as observed. Neither R_c nor R_d are sterically encumbered and therefore either orientation will do, giving rise to the two products found. Cotton's nitrene mechanism still allows formation of the product with the smaller substituent in the R_b position.

It may also be noted that the metallocycle, I, is formally a 16-electron system and was formed with the amine lone pairs on the same side, facilitating interaction with a coordinatively unsaturated iron carbonyl species. Due to rapid inversion at nitrogen it makes no difference whether the combination of optical isomers of carbodiimide is as shown or otherwise; any pairing can produce the *RR* or *SS* metallocycle required.

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