References and Notes

(1) T. E. Sloan and D. H. Busch, *Inorg. Chem.*, **17**, 2043 (1978).
(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.

Department of Chemistry
University of California
Berkeley, California 94720

Earl L. Muetterties

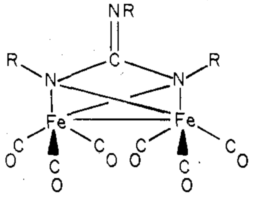
Received August 23, 1978

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

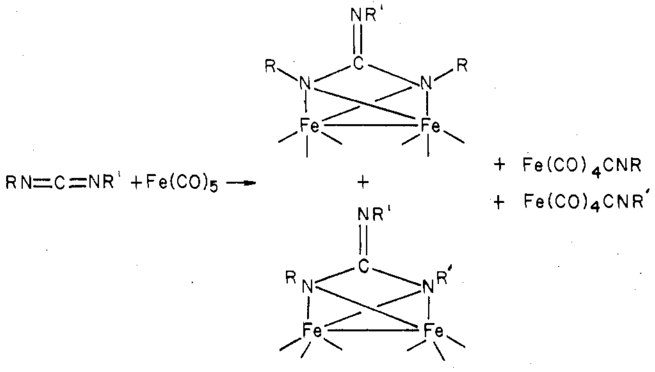
Sir:

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.

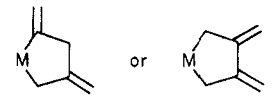


A mechanism was proposed where a carbene carbon is generated on carbodiimide by donor bond formation from *both* nitrogens to iron carbonyl moieties. This was recently ruled out by observations in Cotton's group[2] on *asymmetrically substituted* carbodiimides, where the iron bound nitrogens were found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

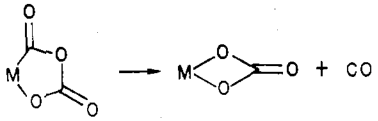
A simple mechanism for this carbodiimide coupling can be proposed that serves to illustrate the principle that metallocyclic intermediates are common in cumulene chemistry. These intermediates can be either symmetric or asymmetric, i.e.



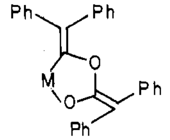
asymmetric symmetric

(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

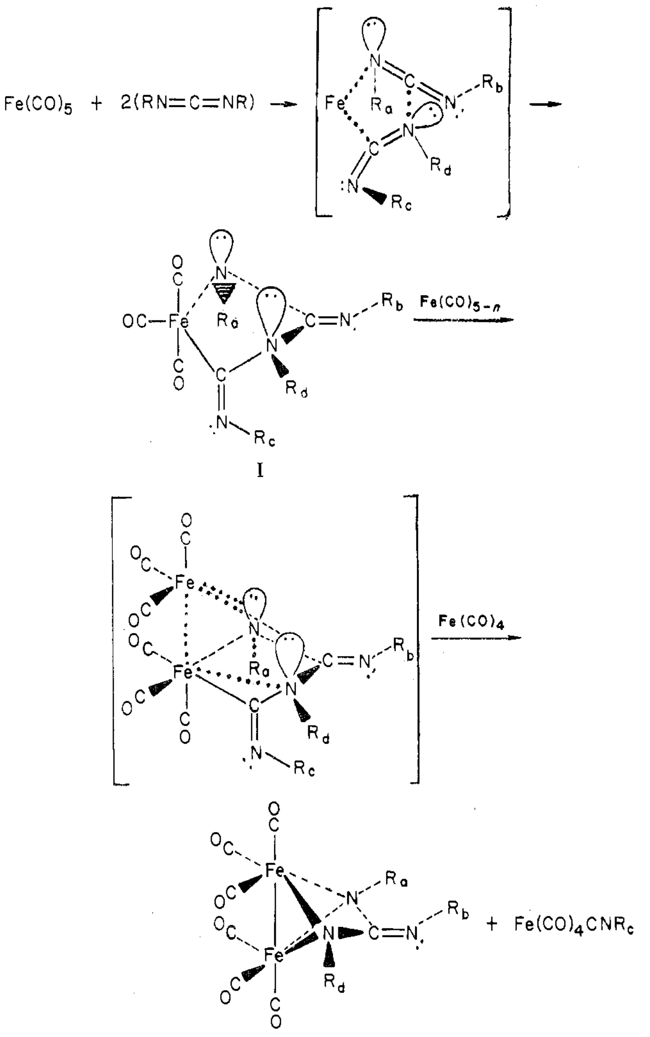
Clearly, the asymmetrically coupled bis(cumulene) metallocycle can be important in cumulene chemistry and cannot be ignored when considering carbodiimide chemistry. In fact the organometallic chemistry of carbodiimides seems to be analogous to that observed for carbon dioxide. Consider Chatt's molybdenum *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.

0020-1669/79/1318-0903$01.00/0

Scheme I



We shall show in future reports how the occurrence of asymmetric metallocycles also accounts for the isomeric distribution where two different cumulenes are coupled together.

References and Notes

(1) N. J. Bremer, A. B. Cutcliffe, M. F. Farona, and W. G. Kofron, *J. Chem. Soc. A*, 3264 (1971).
(2) J. D. Cotton and S. D. Zornig, *Inorg. Chim. Acta*, **25**, L133 (1977).
(3) T. Herskowitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, **98**, 1615 (1976).
(4) J. E. Bercaw and D. M. Duggan, submitted for publication.
(5) J. R. Schmidt and D. M. Duggan, submitted for publication.
(6) G. Fachimetti, C. Biran, C. Floriani, A. Chiese-Villa, and C. Guastini, *J. Am. Chem. Soc.*, **100**, 1921 (1978).
(7) J. Chatt, M. Kubota, G. J. Leigh, F. C. March, R. Mason, and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 1033 (1974).

Department of Chemistry
University of California
Irvine, California 92717

D. Michael Duggan

Received July 21, 1978

Nature of the Jahn–Teller Effect in the $Cu(C_5H_5NO)_6^{2+}$ Ion

Sir:

On the basis of recent independent studies, Carlin, O'Connor, and Sinn[1] and the present authors[2] have reported the single-crystal ESR spectra of the copper-doped hexakis(pyridine *N*-oxide) complex of zinc and have interpreted the results in terms of static and dynamic Jahn–Teller effects, respectively. Carlin and co-workers also report the results of complete X-ray structure analyses of the perchlorate and tetrafluoroborate salts of both copper and zinc complex ions, and these confirm the earlier conclusions[3] that these four compounds are isostructural with the cobalt and nickel complexes whose structures had previously been determined.[4,5] Since the metal ion site symmetry in all of these structures at ambient temperature is S_6 (space group $R\bar{3}$), the copper(II) salts afford additional examples of those hexacoordinated compounds of this ion whose structures apparently have a higher symmetry than that allowed by the Jahn–Teller theorem.

The single-crystal ESR spectra for such trigonal and cubic copper complexes are generally temperature dependent, indicating that the Jahn–Teller effect is dynamic on the ESR time scale at ambient temperature. As the temperature is reduced, however, the isotropic or near-isotropic signal corresponding to the "averaged" structure is usually replaced by spectra characteristic of three magnetically inequivalent sites related by the crystal threefold axis. This dynamic to static transition is generally interpreted in terms of the model proposed by Abragam and Pryce,[6] each site in the low-temperature spectra (i.e., below the transition point) representing a minimum in the Jahn–Teller potential wells and having magnetic parameters corresponding to the tetragonally elongated geometry typical for copper. The transition temperature is ligand dependent, ranging from 12–50 K for $Cu(H_2O)_6^{2+}$[7] to ca. 200 K for the tris(octamethylpyrophosphoramide)copper(II) ion[8] and the $Cu(NCH)_6^{2+}$[9] ion. The presence or absence of hyperfine structure in the higher temperature spectra is also ligand dependent.

Such features as described are evident in the spectra obtained for the $Cu(C_5H_5NO)_6^{2+}$ complex doped into the corresponding zinc lattice, and our initial studies, carried out on crystals grown from dimethylformamide–ethanol solutions and using spectra recorded over a temperature range at both X- and Q-band frequencies, were interpreted in the framework of this model.[2] The transition temperature, as derived from the spectra measured at X-band frequency, was found to be in the region of 50 K. However, the interpretation of these ESR spectra was made more complicated than for those reported for previous examples by the observation of additional sites, suggesting the presence of different types of copper ion geometry in the host crystal. The spectra indicated two sets of three magnetically inequivalent sites, related by the crystal threefold axis, together with the near-isotropic signal, characteristic of the dynamic Jahn–Teller effect, which in the crystals examined[10] accounted for the largest fraction of the total intensity of the spectra.

While the near-isotropic signal diminished in intensity on cooling, being replaced at ~50 K by signals for the three sites exhibiting a static Jahn–Teller effect, the additional sites (which, in contrast to the isotropic signal, showed the characteristic four-line hyperfine splitting pattern for copper) were affected very little by the temperature change but showed marked angular variations. The rotational behavior and line-width variation of the near-isotropic signal, on the other hand, parallel very closely that observed for the pure $Cu(C_5H_5NO)_6^{2+}$ complex, which at room temperature gives only an exchange-narrowed line.

In contrast with our interpretation of the main features of these spectra in terms of the dynamic ↔ static Jahn–Teller effect, however, Carlin, O'Connor, and Sinn[1] discuss their X-band room-temperature ESR results solely in terms of three statically distorted sites related by the crystal threefold axis.

0020-1669/79/1318-0904$01.00/0