mum possible value for $k$ with Cu(H$_{-2}$glyglygly)$^-$ because the proton-transfer reactions from general acids with p$K_a$ values near that of $H_2EDTA^{2-}$ are known to contribute to the rate. Hence, this third-order rate constant with the triglycine complex must be less than $5 \times 10^9$ $M^{-2}$ sec$^{-1}$ as indicated in Table I. Such proton-assisted nucleophilic pathways for Cu(H$_{-2}$glyglygly)$^-$ are much too slow to be observed with the trien or L-histidine reactions because the direct nucleophilic pathways are much more favorable for triglycine. The proton-assisted nucleophilic pathway is, however, the predominant one for the reactions of Cu$^{II}$ bound to bovine and to human serum albumin. We find the third-order rate constants corresponding to $k$ in eq 1 are $2 \times 10^7$ $M^{-2}$ sec$^{-1}$ for $H_2trien^{2+}$ and *ca.* $2 \times 10^6$ $M^{-2}$ sec$^{-1}$ for $HEDTA^{3-}$ with copper bound to human serum albumin.

**Acknowledgments.** This investigation was supported by Public Health Service Grant No. GM-12152 from the National Institute of General Medical Sciences and by a sabbatical leave to D.L.V. from the Naval Research Laboratory.

### References and Notes

(1) G. F. Bryce, R. W. Roeske, and F. R. N. Gurd, *J. Biol. Chem.*, **240**, 3837 (1965).
(2) H. Aiba, A. Yokoyama, and H. Tanaka, *Bull. Chem. Soc. Jap.* **47**, 1437 (1974).
(3) E. Breslow, *J. Biol. Chem.*, **239**, 3252 (1964).
(4) T. Peters, Jr., and F. A. Blumenstock, *J. Biol. Chem.*, **242**, 1574 (1967).
(5) W. T. Shearer, R. A. Bradshaw, F. R. N. Gurd, and T. Peters, Jr., *J. Biol. Chem.*, **242**, 5451 (1967).
(6) R. A. Bradshaw, W. T. Shearer, and F. R. N. Gurd, *J. Biol. Chem.*, **243**, 3817 (1968).
(7) J. C. Cassatt, *J. Biol. Chem.*, **248**, 6129 (1973).
(8) G. K. Pagenkopf and D. W. Margerum, *J. Amer. Chem. Soc.*, **90**, 6963 (1968).
(9) G. K. Pagenkopf and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2683 (1970).
(10) H. Hauer, G. R. Dukes, and D. W. Margerum, *J. Amer. Chem. Soc.*, **95**, 3515 (1973).
(11) D. W. Margerum and G. R. Dukes, "Metal Ions in Biological Systems," Vol 1, H. Sigel, Ed., Marcel Dekker, New York, N. Y., 1974, p 157.
(12) G. R. Dukes, G. K. Pagenkopf, and D. W. Margerum, *Inorg. Chem.*, **10**, 2419 (1971).
(13) D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, "Coordination Chemistry," Vol IIA, A. E. Martell, Ed., ACS Publications, Washington, D.C., submitted.

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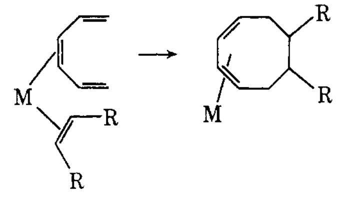
## $[_{2}\pi + {}_{6}\pi]$ Cycloaddition Reactions between Ligands Coordinated to an Iron Atom

*Sir:*

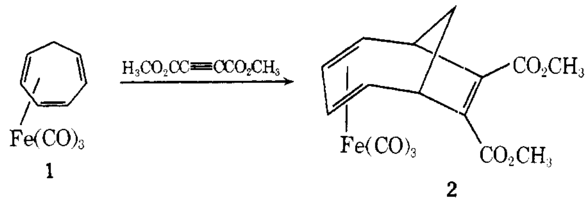
Both $[_{2}\pi + {}_{4}\pi]$ and $[_{2}\pi + {}_{6}\pi]$ concerted cycloaddition reactions are calculated to be exothermic processes and, on the basis of thermodynamic considerations alone, both processes might then be expected to occur with roughly similar facility. In practice, however, whereas there are hundreds of examples of the first of these processes known (*i.e.*, the Diels-Alder reaction), there is to our knowledge not a single example of the second of these reactions reported. The reason for this striking difference is that the latter reaction is a "forbidden" one according to the Woodward-Hoffmann classification of concerted reactions and associated with this is an additional high energy term in the reaction coordinate of the process.

It has earlier been shown in these laboratories that cycloaddition reactions can apparently take place between two ligands simultaneously bonded to a transition metal;[1] furthermore, from theoretical considerations[2] and the experimental results from other types of reactions,[3] we consider that "forbidden" reactions may become "allowed" when a transition metal is involved in the reaction. It therefore seemed possible that intramolecular cycloaddition reactions between a triene and trienophile, each being appropriately coordinated to a transition metal, may take place as indicated in eq 1. We now report examples of $[_{2}\pi + {}_{6}\pi]$ reactions which apparently are occurring by such a process.

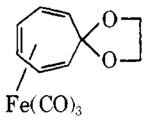


(1)

Irradiation of solutions of cycloheptatrieneiron tricarbonyl (**1**) and acetylene dicarboxylic ester in THF at 0° produced the complex **2** as yellow crystals, mp 109° (10%).[4,5] The structure of **2** was determined by X-ray analysis.[6] Of particular significance, in addition to demonstrating that $[_{2}\pi + {}_{6}\pi]$ addition had taken place, the X-ray study indicates that the acetylene moiety has added to the triene on the same face to which the iron atom is bonded, strongly suggesting that at some point in the reaction the acetylene was bonded to the Fe atom even though it is not in the product **2**.



The iron tricarbonyl complex of tropone ethylene ketal (**3**), upon similar irradiation at 0° in THF with acetylene carboxylic ester, produced the complex **4** (20% yield) as well as the uncomplexed free ligand **5** (5%).



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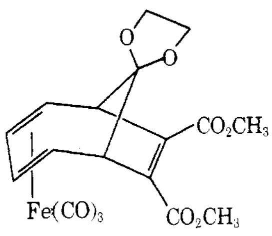

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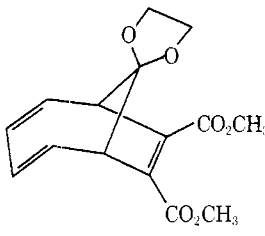
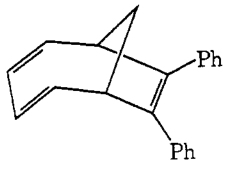


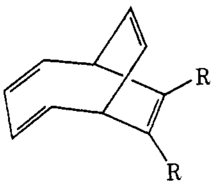
5

When solutions of the triene complex **3** in THF were irradiated at −78°, the lamp then turned off, and the acetylene added followed by warming to room temperature, the free [2 + 6] adduct **5** was isolated. This demonstrates that the formation of the new carbon bonds in the [2 + 6] process is a thermal, not photochemical, process.

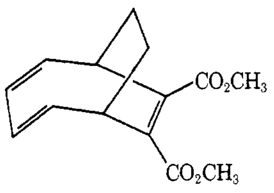
The cycloaddition reaction of triene Fe(CO)$_3$ complexes and the acetylenic trienophiles under such conditions appears to be fairly general and offers promise of synthetic utility. Thus irradiation of complex **1** in THF at −78°, removal of the light source followed by addition of diphenylacetylene, and warming to room temperature, afforded the hydrocarbon **6** in 25% yield.[4] (We refer to this procedure as the indirect method in contrast to the direct method where the irradiation is done in THF at 0° in the presence of the acetylene.) Likewise, cyclooctatetraene iron tricarbonyl when treated with acetylene carboxylic ester and diphenylacetylene by the same indirect photochemical process affords the adducts **7** (R = $COOCH_3$ and $C_6H_5$, respectively) each in yields of approximately 20%. Cyclooctatrieneiron tricarbonyl reacts with the acetylene carboxylic ester in the direct process to afford the adduct **8** (5%) together with its iron tricarbonyl complex (15%).[7]



**6**

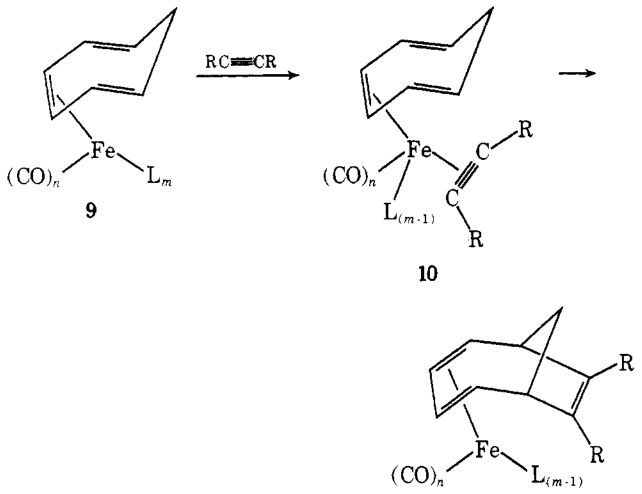


**7**



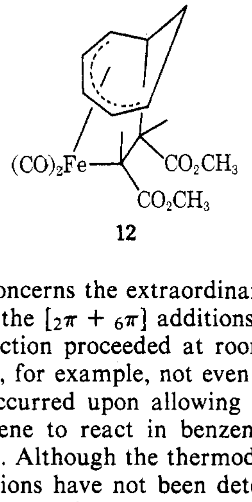
**8**

We suggest that the reactions leading to the formation of the [2 + 6] complexes and the corresponding free ligands proceed as follows. Irradiation of the triene complex, **1** for example, effects the replacement of one of the olefin bonds coordinated to iron by a solvent molecule to yield complexes of the type **9** ($L$ = THF, $n$ = 3, $m$ = 1) and/or a related species **9** ($n$ = 2, $m$ = 2) where an additional CO ligand has been displaced. The light then plays no further role in the reaction. A solvent ligand molecule is then thermally replaced by acetylene to produce **10** which undergoes intramolecular concerted addition to afford the adduct **11.** Dieneiron tricarbonyl products of the type **11** ($n$ = 3, $m$ = 1) are stable and are isolated as such, whereas the dicarbonyl monoetherate complex ($n$ = 2, $m$ = 2) are thermally unstable and result in the isolation of the uncomplexed ligand. The production of $(PPh_3)_3Fe(CO)_2$, albeit in low yield, upon addition of $PPh_3$ to a solution of the complex **1** after it had been irradiated at −78° supports the proposal that a dicarbonyl species such as **9** ($n$ = 2, $m$ = 2) is present in the irradiated solution used in the indirect method.



The stereochemistry of the complex **2** provides evidence for the intramolecular nature of the step in which the two new C–C $\sigma$ bonds are formed; whether they are formed in a concerted manner is a crucial question which remains to be answered. It should also be pointed out that the diene-$Fe(CO)_3$ complexes of the type **1** display *no* activity as a diene in a purely thermal Diels–Alder reaction.

When dimethyl maleate is added at −78° to a solution of cycloheptatriene $Fe(CO)_3$ which had been irradiated, no evidence for a [2 + 6] cycloaddition process is observed, although a novel complex **12**,[8] the structure of which was determined by X-ray analysis,[9] is isolated. Complex **12** is also obtained from dimethyl maleate iron tetracarbonyl and cycloheptatriene by both the direct and indirect method. The formation of **12** presumably involves initial steps analogous to the acetylene reactions cited above leading to a complex similar to **10** with dimethyl maleate coordinated to iron rather than the acetylene. Unlike the acetylene complex **10,** which has one set of $\pi$ bonds on the coordinated acetylene ligand free for intramolecular cycloaddition, the single $\pi$ bond in the analogous olefin complex is involved in coordination to iron and is not readily available for cycloaddition. A type of insertion process leading to the pentadienyl complex **12** is then apparently more favorable.



**12**

A final point concerns the extraordinary mild conditions required to effect the [$_2\pi$ + $_6\pi$] additions reported here. In each case the reaction proceeded at room temperature or below; in contrast, for example, not even an "allowed" [$_2\pi$ + $_4\pi$] reaction occurred upon allowing diphenylacetylene and cycloheptatriene to react in benzene for 3 weeks at room temperature. Although the thermodynamic factors of the [2 + 6] reactions have not been determined as yet, it seems likely that much of the difference in reactivity can be associated with entropy considerations. The Diels–Alder reaction typically involves large negative entropy factors (−30 to −40 eu); in the reactions described here the triene and trienophile, while held as ligands in the complex, are ideally positioned for reaction to occur and the entropy factors should be extremely small.

**Acknowledgment.** We thank the National Science Foundation, the U.S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. The Syntex $P2_1$ autodiffractometer was purchased with funds provided by the National Science Foundation (Grant GP37028).

## References and Notes

(1) J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, **93,** 262 (1971).
(2) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47,** 71 (1969); F. D. Mango, *Advan. Catal.*, **20,** 291 (1969), and references therein; M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **19,** 761 (1971).
(3) See, *inter alia*, J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92,** 7499 (1970); W. Slegeir, R. Case, J. S. McKennis, and R. Pettit, *ibid.*, **96,** 287 (1974).
(4) This compound as well as all other new compounds gave satisfactory elemental analyses and spectral data. In each reaction reported in this paper equimolar amounts of the triene complex and acetylene were used and yields reported are based on these amounts; varying amounts of unreacted complex and acetylene were recovered in each case. As yet no attempt has been made to maximize the conversion.

(5) The pertinent nmr data for the new compounds reported are as follows: compound **2** ($CS_2$), $\tau$ 8.50 (m, 2 H), 6.95 (t, 2 H), 6.64 (t, 2 H), 6.30 (s, 6 H), 4.46 (m, 2 H); compound **4** (acetone-$D_6$), $\tau$ 6.90 (d, 2 H), 6.70 (m, 2 H), 6.18 (m, 4 H), 6.20 (s, 6 H), 4.16 (m, 2 H); compound **6** ($CCl_4$), $\tau$ 8.19 (d, 1 H), 7.45 (m, 1 H), 6.43 (t, 2 H) 3.60–44.35 (m, 4 H), 2.92 (s, 10 H); compound **7** (R = Ph) ($C_6D_6$), $\tau$ 6.48 (m, 2 H), 3.65–4.40 (m, 6 H), 2.7–3.15 (m, 10 H); compound **7** (R = $COOCH_3$) ($CDCl_3$), $\tau$ 6.30 (m, 2 H), 6.25 (s, 6 H), 3.6–4.4 (m, 6 H); compound **8** ($CS_2$), $\tau$ 8.5–8.8 (m, 4 H), 6.40 (m, 2 H), 6.33 (s, 6 H), 4.2–4.8 (m, 4 H).

(6) Crystals of **2** from ether–pentane are monoclinic, $P2_{/}c$, $a = 12.360$ Å, $b = 9.295$ Å $c = 14.195$ Å, $\beta = 102.2°$, and $Z = 4$. Structure solution was by the heavy-atom method, followed by full-matrix least-squares refinement with 2583 reflections to a final $R = 0.056$, $R_w = 0.050$. Details of the structure will be reported elsewhere (T. A. Dodds and R. E. Davis, to be submitted for publication).

(7) In the formation of the free ligand an iron carbonyl fragment is released which conceivably could be reused in the reaction sequence. When diphenylacetylene and cycloheptatriene were added to an irradiated solution of **1**, the hydrocarbon **6** was obtained in 170% yield based on **1**. The configuration **10** can apparently also be reached in a purely thermal manner; when diphenylacetylene and cycloheptatriene are heated with 1,5-cyclooctadiene $Fe(CO)_3$ the hydrocarbon **6** is produced in low yield. These results suggest that some metal system could be found which would catalyze [2 + 6] addition under mild conditions.

(8) This compound is a yellow solid: mp 130–131°; nmr (acetone-$d_6$) 3.89 (m, 2), 4.72 (m, 2), 5.77 (d, 1), 5.88 (m, 1), 6.36 (s, 3), 6.45 (s, 3), 6.72 (d, 1), 6.92 (m, 1), 8.43 (t, 1), and 9.37 (m, 1); ir (KBr) 2010 (vs), 1955 (vs), 1720 (s), and 1675 (s) $cm^{-1}$.

(9) Crystals of **12** from ether–pentane are monoclinic, $a = 11.781$ Å, $b = 12.891$ Å, $c = 15.407$ Å, $\beta = 139.7°$, $Z = 4$. A disordered crystal structure has been partially refined in space group $P2_1/c$; the chemical structure **12** is firmly established on the basis of bond distances and angles. A report of the solution, refinement, and disordered structure will be published elsewhere (T.-H. Hseu and R. E. Davis, to be submitted for publication).

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## Molecular Sructure of Bis[(hydridotris(1-pyrazolyl)borato)copper(I)] and Implications for Certain Copper-Containing Proteins

*Sir:*

Polypyrazolylborate ligands have afforded a large number of interesting organometallic and coordination compounds.[1-3] In addition, they offer possible synthetic models of histidine chelating sites[4-6] in some metalloproteins. Among these are the copper-containing,[7,8] dioxygen-activating proteins hemocyanin[9] (a dioxygen carrier), tyrosinase[10] (an oxygenase), and possibly others[11] where copper atoms occur in pairs, histidine (imidazole) is implicated in metal ion binding,[9d] and a reduced form involves Cu(I). The fact that $Cu[HBpz_3]$[12] (I) is dimeric in solution and reacts with CO to form a carbonyl complex,[12,13] with $\nu$(CO) nearly as low as in carboxyhemocyanin,[14] has prompted us to investigate thoroughly the properties of I. We communicate here the first example of a pyrazolylborate ligand bridging two metals, of the pyrazolyl segment also bridging two metals, and of a new type of fluxional process for polypyrazolylborate complexes. We also report the oxygenation of I to produce what we formulate as a copper-dioxygen complex.

Crystals of I suitable for diffraction were grown from toluene solution at −40°. The compound crystallizes in the triclinic space group $P\bar{1}$ with one dimeric molecule in a unit cell of dimensions $a = 9.264$ (1) Å, $b = 7.638$ (1) Å, $c = 8.181$ (1) Å, $\alpha = 92.96$ (1)°, $\beta = 101.71$ (1)°, $\gamma = 89.40$ (1)°. Intensity data were collected on a diffractometer, and the structure was solved by standard Patterson and Fourier methods. It was refined by full-matrix least-squares techniques to an $R$ index of 0.037 for 2111 observations above background. The molecular structure consists of a centrosymmetric dimer with each $HBpz_3$ unit contributing two terminal pyrazole ligands (one to each copper) and one crosswise bridging pyrazole ligand (Figure 1). A listing of positional and thermal parameters will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material. The two bridging pyrazole rings lie in a noncrystallographic molecular mirror plane. Major features of the structure are (1) each copper ion is in a highly distorted tetrahedral environment, with N-Cu-N angles ranging from 93.74 (9) to 144.75 (10)°, (2) the Cu-Cu distance of 2.660 (1) Å is somewhat longer than in the ligand-bridged Cu(I) acetate structure (2.544 Å),[15] (3) the dimensions within the bridging pyrazole ring do not differ significantly from those in the terminal rings, and (4) the Cu-N bond distances are some 0.3 Å longer for the bridging nitrogen atoms (2.254 (2) and 2.224 (2) *vs.* 1.948 (2) and 1.946 (2) Å). In complexes containing both amino and bridging amido ligands, the corresponding metal-N distances are nearly equal.[16] Features (3) and (4) lead us to suggest that the bridge involves three-center two-electron bonding. These results also suggest that imidazole may be capable of functioning as a bridging ligand in bimetallic copper proteins.

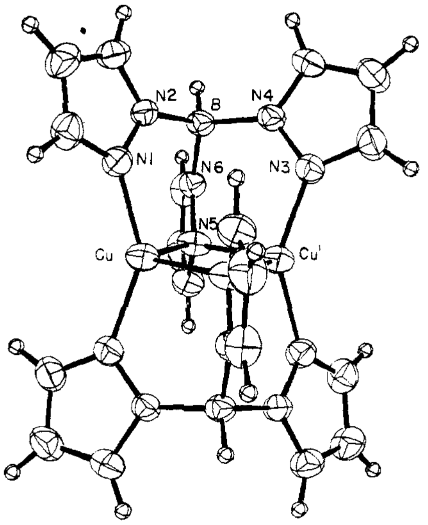

**Figure 1.** The molecular geometry of the centrosymmetric dimer $[Cu(HBpz_3)]_2$.

Despite the existence of two kinds of pyrazole rings in the solid state, the rings are magnetically equivalent in the solution pmr spectrum down to −130° (90 MHz).[17] Barring a major structural change on dissolution or accidental spectral degeneracy, the results can be interpreted in terms of rapid intramolecular rotational movement of the $HBpz_3$ ligand about the B-H bond axis, which serves to interconvert bridge and terminal pyrazole rings. This rearrangement involving nitrogen heterocycles represents a new and potentially large class of bridge-terminal ligand interchange processes.[18]

In nonprotonic solvents, I takes up (irreversibly) 1 mol of dry dioxygen to yield a green, paramagnetic substance (II), which analyzes (elemental analysis, mass spectrum, cryoscopic molecular weight in benzene) for $Cu_2(HBpz_3)_2O_2$. We have been unable to identify securely $\nu(^{16}O\text{-}^{16}O)$ or $\nu(^{18}O\text{-}^{18}O)$ in the vibrational spectra[19] (ir and laser Raman). However, we tentatively assign a $\nu(Cu\text{-}^{16}O)$[19b,20] in the infrared at 520 $cm^{-1}$ ($\nu(Cu\text{-}^{18}O)$ = 500 $cm^{-1}$). Compound II reacts with $(CH_3)(C_6H_5)_2P$ according to eq 1. Decomposition to, or equilibrium with, $Cu(HBpz_3)_2$ (detected *via* epr and visible spectroscopy) has hampered ef-