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## References and Notes

- (1) To be presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975.
- (2) The only other examples (to our knowledge) of a cluster system of five transition metal atoms are the  $[\text{M}_2\text{Ni}_3(\text{CO})_{13}(\mu_2\text{-CO})_3]^{2-}$  dianions (M = Mo, W),<sup>3</sup> which have a trigonal bipyramidal  $\text{M}_2\text{Ni}_3$  core, and the unique  $\text{Fe}_5(\text{CO})_{15}(\mu_5\text{-C})$  molecule,<sup>4</sup> which possesses a tetragonal pyramid with the carbide-like atom positioned slightly below the basal iron plane at essentially equal bonding distances from the five iron atoms.
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- (8)  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}_5(\text{CO})_9(\mu_2\text{-CO})_3$ : triclinic;  $A1$ ;  $a = 13.309$  (7),  $b = 23.804$  (14),  $c = 12.577$  (7) Å;  $\alpha = 91.73$  (5),  $\beta = 95.30$  (4),  $\gamma = 77.63$  (4)°;  $V = 3875.3$  Å<sup>3</sup>;  $\rho(\text{obsd}) = 1.47$  vs.  $\rho(\text{calcd}) = 1.46$  g cm<sup>-3</sup> for  $Z = 2$ . Least-squares refinement gave  $R_1(F) = 7.5$  and  $R_2(F) = 9.7\%$  for 3482 independent diffractometry data ( $I > 2\sigma(I)$ ). The conventional reduced unit cell has  $P1$  symmetry with  $a = 13.293$ ,  $b = 13.309$ ,  $c = 12.577$  Å;  $\alpha = 95.30$ ,  $\beta = 116.49$ ,  $\gamma = 98.52$ °;  $V = 1937.6$  Å<sup>3</sup>;  $Z = 1$ . The centrosymmetric space group requires the anion to possess site symmetry  $C_2$  which is caused by a crystal disorder involving the anion being randomly distributed between two orientations related by an average center of symmetry. This disorder, which superimposes the two centrosymmetrically related  $\text{Ni}(\text{CO})_3$  fragments on each other to give whole-weighted atoms, produces six half-weighted nickel atoms at the vertices of a "Star of David" in an analogous fashion to that found in the solid state for the  $[\text{M}_2\text{Ni}_3(\text{CO})_{16}]^{2-}$  dianions (M = Mo, W)<sup>3</sup> and for  $\text{Fe}_5(\text{CO})_{12}$ .<sup>9</sup> Our refinement of the  $[\text{Ni}_5(\text{CO})_9(\mu_2\text{-CO})_3]^{2-}$  dianion assumed for the central  $\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3$  fragment that the corresponding half-weighted terminal carbonyl carbon and the half-weighted bridging carbonyl oxygen atoms were completely superimposed for the two orientations.
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- (10) For the computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal; see paragraph at end of paper regarding supplementary material.
- (11) Cf. L. F. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7327 (1970).
- (12) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **96**, 7601 (1974).
- (13) The triphenylcyclopropenyl ring in the solid-state structure of  $\text{Ni}[(\eta^3\text{-C}_3(\text{C}_6\text{H}_5)_3)\text{C}(\text{py})_2]\text{-py}$  has been assumed to occupy one coordinated position of a distorted tetrahedral geometry about the central nickel atom.<sup>14</sup>
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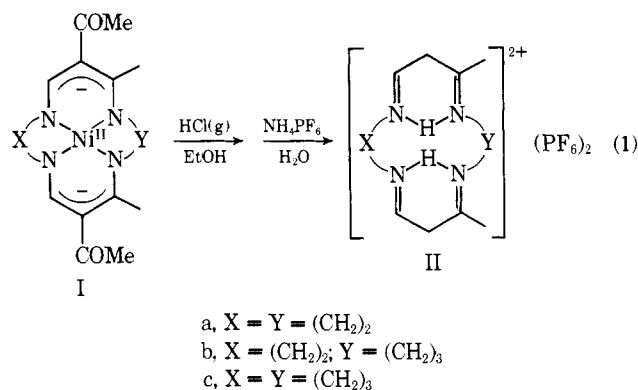
## Synthesis and Structures of New Sexadentate Complexes Produced by Electrophilic Reactions of Macroyclic Ligands in Their Transition Metal Complexes

Sir:

Increasing attention is turning toward the generation of ligand structures, based on macrocyclic frameworks, that facilitate the total control of the chemical environment in the vicinity of the metal ion. In natural systems the extra-macrocyclic role is often played by the protein. Earlier studies in this laboratory produced the first synthetic example of a ligand having a fifth donor atom held in a favorable posi-

tion for coordination at one of the axial sites remaining after planar tetradentate chelation by the parent macrocyclic.<sup>1</sup> Others have appended an imidazole ligand to a porphyrin ring<sup>2</sup> and built a picket fence structure to limit the closeness of approach of iron porphyrin units,<sup>3</sup> as well as added a hydrocarbon moiety to a tetradentate macrocyclic structure in such a way as to shield the region directly above the metal ion site.<sup>4,5</sup> Cytochrome *c* exemplifies the case where the two coordination sites not filled by a tetradentate macrocyclic ligand are occupied by donor groups propitiously arrayed by the protein portion of a natural product. We report here the fortuitous synthesis, characterization, and structural determination of a simple example of a structure that is analogous to the latter case.

A series of 14-, 15-, and 16-membered tetraaza, tetraene, macrocyclic ligands devoid of functional substituents has been prepared. Their syntheses utilize complexes of structure I.<sup>6,7</sup> This preparative route is based on the facile deacylation<sup>8</sup> and subsequent demetalation of the complexes of structure I with acid (dry HCl gas) in ethanol solvent. The macrocyclic ligands having structure II are isolated as their dihydrohexafluorophosphate salts after the evaporation of the ethanol and redissolution in water, followed by the addition of  $\text{NH}_4\text{PF}_6$  (eq 1). Deprotonation of the ligand salts



with 2 equiv of base ( $\text{NEt}_3$  or  $\text{OR}^-$ ) in the presence of solvated ferrous ion in acetonitrile results in rapid formation of the red-orange complexes, which can be isolated as orange-red crystals (75% yield) by reducing the solution volume, followed by the addition of hot absolute ethanol. All reactions were carried out in an inert atmosphere.

Although all of the complexes conform to the stoichiometry  $\text{Fe}(\text{MAC})(\text{PF}_6)_2 \cdot 2\text{CH}_3\text{CN}$ , only the 14-membered ring derivative has the obvious structure wherein the macrocycle is coordinated in a planar fashion about the  $\text{Fe}^{2+}$  ion with the acetonitrile molecules occupying axial sites. During preliminary characterization of the 15- and 16-membered ring derivatives the weak  $\text{C}\equiv\text{N}$  stretch was found to be absent from their infrared spectra and an N-H vibration at  $3310\text{ cm}^{-1}$  was observed. The NMR spectrum showed related complexities. The compounds were also found to be remarkably inert toward bases, and this observation was particularly difficult to rationalize. At this stage an X-ray crystallographic study was performed on one of the compounds (Ic), thereby revealing an unusual structure and a most interesting and novel ligand reaction as well.

The reaction and structure of the final products are given in Scheme I. *cis*-[3,11-Bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,8,12-tetraeneiron(II)] hexafluorophosphate was isolated as orange crystals from an acetonitrile-methanol solution. Both analytical data and the results of physical measurements are readily reconciled with the solid state structure, indicating the integrity of that structure in solution. Anal. Calcd: C, 31.96; H, 4.42; N, 12.43. Found: C, 32.06; H, 4.47; N, 12.47. The compound

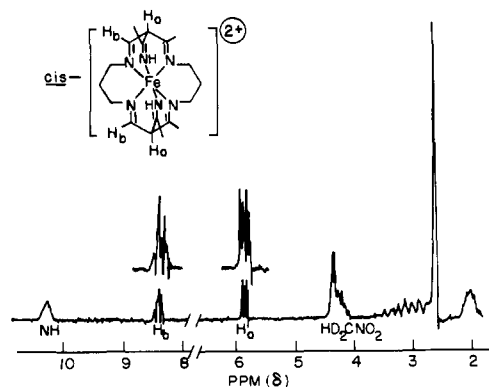
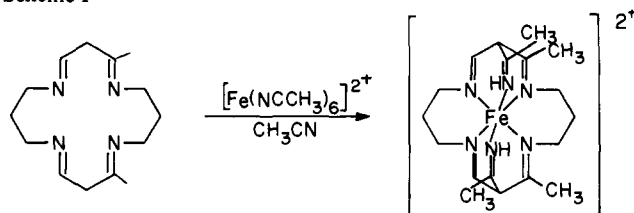


Figure 1.  $^1\text{H}$  NMR spectrum of the sexadentate complex.

Scheme I



has the spin paired  $d^6$  electronic configuration (magnetic susceptibility) and exists as a 2:1 electrolyte in acetonitrile solutions ( $\Lambda_m = 305$ ). Its  $^1\text{H}$  NMR spectrum and the appropriate assignments of the observed resonances are shown in Figure 1. The assignments are based on decoupling experiments and integration data.

The formation of these complexes is remarkable because of the mild conditions employed and the general sluggishness toward nucleophilic additions of the nitrile functions. In a simple mechanistic model, both the ring and the acetonitrile molecule coordinate to a single iron center. The ionization of a proton from the apical carbon of one of the  $\beta$ -diimine linkages produces a nucleophile adjacent to the coordinated, and perhaps electrophilically activated, acetonitrile. Intramolecular condensation completes the process. It is significant that these species are stable in neutral or acidic media, but that they are destroyed by strong base. Removal of protons from the NH groups is followed by elimination of acetonitrile to produce the complex of the planar dianionic ligands. The latter will be the subject of a later report.<sup>6</sup>

The dihexafluorophosphate salt of the complex is obtained as orange crystals belonging to the orthorhombic space group  $P2_12_12_1$  with  $a = 21.647$  (9) Å,  $b = 11.077$  (11) Å,  $c = 11.115$  (20) Å, and  $V = 2665.2$  Å<sup>3</sup>. The observed density of 1.68 g/cm<sup>3</sup> agrees well with that calculated for  $Z = 4$ . Data were collected on a Picker FACS III four-circle diffractometer using Mo  $K\alpha$  radiation. The structure was solved by superposition techniques and refined to an  $R$  of 0.064 for 2787 reflections.

The coordination sphere of the iron (Figure 2) consists of an octahedral array of nitrogen atoms distorted by an 8° trigonal twist. Goedken observed a 39° trigonal twist distortion for an iron clathrochelate.<sup>7</sup>

The rather normal Fe-N bond distances vary from 1.936 (5) to 1.971 (5) Å (Figure 3), perhaps reflecting strain within the chelating ligand. While an Fe-N bond of 1.97 Å is the predicted sum of the covalent radii for low spin iron(II) bound to nitrogen donors, distances as short as 1.90 Å have been reported.<sup>8,9</sup> The two iminoethyl groups, derived from acetonitriles, are bound in cis positions. The six C-N bonds in the unsaturated rings are localized as evidenced by the short C-N length which averages 1.256 (8) Å. Any

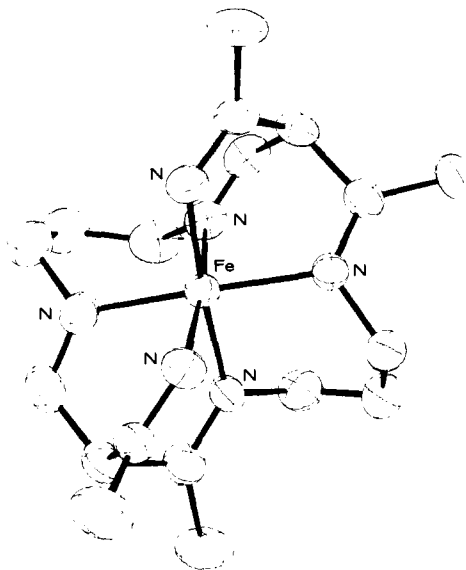


Figure 2. Structure of the sexadentate chelate.

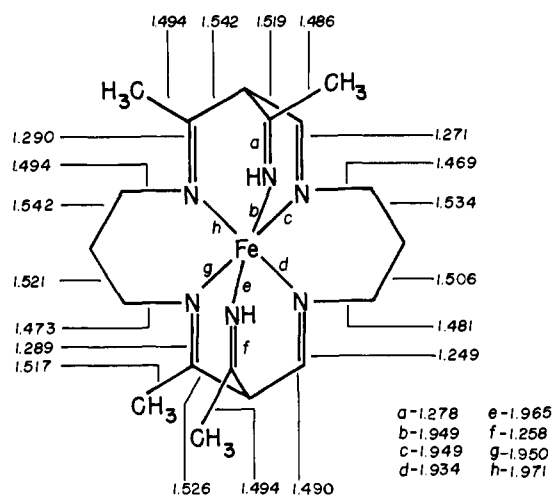


Figure 3. Bond distances in the sexadentate chelate.

given imine radiating from a common bridgehead carbon is nearly coplanar with each of the adjacent imines (maximum deviation  $\sim \pm 0.02$  Å). Furthermore, each triangular array of imine nitrogens is essentially equilateral (av angle 60.3 (5)°) with the bridgehead carbon situated above the approximate center of the triangle. Both of the saturated six-membered rings exhibit the twist conformation.

One of the two  $\text{PF}_6^-$  counterions is disordered about a fourfold axis extending through two trans fluorines. The disorder results from a  $\pi/4$  rotation with an occupancy ratio of 3:1 for the two configurations. A similar phenomenon was observed in the structure of  $[\text{Ru}(\text{NH}_3)_6][\text{PF}_6]_2$ .<sup>10</sup>

Materials having structures of the kind reported here are expected to play an important role in the continuing development of such areas as bioinorganic chemistry and homogeneous catalysis. It is particularly true of the element iron that the richness of its aqueous chemistry falls far short of that observed in natural systems because of the limiting and overriding effects of well-known solvent related processes. It is hoped that the types of structures just described will eventually overcome these limitations.<sup>11</sup>

References and Notes

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 (11) These studies were supported in part by a grant from the U.S. National Science Foundation and in part by Grant No. GM10040 from the National Institute of General Medical Sciences of the U.S. Public Health Services.

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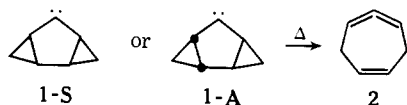
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### Thermolysis of *syn*- and *anti*-Tricyclo[4.1.0.0<sup>2,4</sup>]heptan-5-ylidene. *cis*-1-Ethynyl-2-vinylcyclopropane

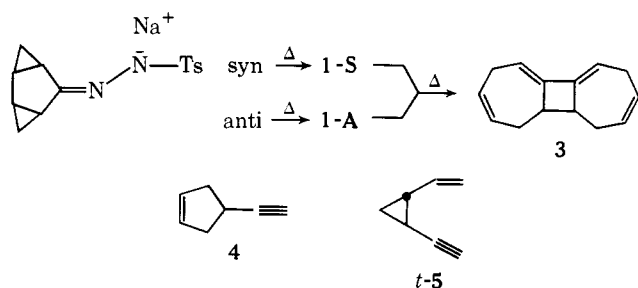
Sir:

Carbenes undergo a myriad of rather unique reactions, including a number of unusual unimolecular,  $\sigma$ -bond fragmentation processes.<sup>1</sup> These include the conversion of cyclopropylidene to allene<sup>2</sup> and the cleavage of cyclopropylcarbene into ethylene and acetylene.<sup>3</sup> Another potential fragmentation process is the conversion of cyclopentylidene into allene and ethylene. Heretofore such a process has been observed only in the case of oxycarbenes where a ketene rather than an allene is extruded.<sup>4</sup>

It was anticipated that *syn*- and *anti*-tricyclo[4.1.0.0<sup>2,4</sup>]heptan-5-ylidene (1-S and 1-A) might fragment in such a manner to yield the highly strained 1,2,5-cycloheptatriene (2). Indeed, when the tosylhydrazone sodium



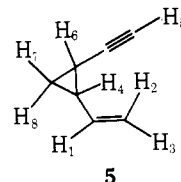
salt precursors of 1-S and 1-A<sup>5</sup> were pyrolyzed using static (S), drop-static (D-S), or hot tube (T) techniques,<sup>7</sup> up to 94% yield of a dimeric hydrocarbon material was produced. This dimer was demonstrated spectroscopically to have the



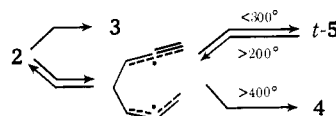
structure 3.<sup>9</sup> Dimer 3 was a white crystalline solid, mp 46–47°, which showed only broad multiplets in the NMR at  $\delta$  5.55 (6 H), 3.02 (4 H), 2.90–2.45 (2 H), and 2.33 (4 H). 3 had a characteristic uv absorption at  $\lambda_{\max}$  254 nm ( $\epsilon$

8120)<sup>10</sup> and it absorbed 4 equiv of H<sub>2</sub> when subjected to catalytic hydrogenation.<sup>12</sup> Yields of 3 remained between 84 and 94% in the temperature range 250–500°, using the S or D-S techniques, the only other products being variable amounts of *trans*-1-ethynyl-2-vinylcyclopropane (*t*-5) (0–11%), obtained at relatively low temperatures (<300°), and 4-ethynylcyclopentene (4),<sup>13</sup> obtained only at high temperatures (4% at 500°). In cases where the hot tube technique was utilized at 500°, yields of 3 and 4 were 39 and 26%, respectively, while no *t*-5 was detected.

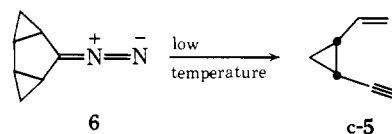
*t*-5 evidenced characteristic ir absorptions at 3320 ( $\equiv\text{C}-\text{H}$ ) and 2120 ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ , and its NMR (CDCl<sub>3</sub>, 100 MHz) showed peaks at  $\delta$  1.40–0.80 (m) (H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub>), 1.85 (d) (H<sub>5</sub>) ( $J_{5,6} = 2.0$  Hz), and 1.94–1.58 (m) (H<sub>4</sub>) and an ABX system with multiplets centered at  $\delta$  4.96 (H<sub>3</sub>), 5.12 (H<sub>2</sub>), and 5.40 (H<sub>1</sub>) with  $J_{1,2} = 16.8$ ,  $J_{1,3} = 9.5$ ,  $J_{1,4} = 7.5$ , and  $J_{2,3} = 2.5$  Hz:



It seems probable that products 3, 4, and *t*-5 derive from the highly strained cyclic allene, 1,2,5-cycloheptatriene (2), *t*-5 being formed reversibly at temperature >200°. Indeed it was found that in solution at temperatures >200°, *t*-5 converted quantitatively to dimer 3.



The significance of these results revolves around the question of the role played by the 1,2,5-cycloheptatriene. Is it formed *directly* from 1-A and 1-S via synchronous C<sub>2</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>6</sub> fragmentation or does it derive from another pathway? The total lack of dependence of product ratios upon the *syn* or *anti* nature of 1 speaks against a synchronous pathway for formation of 2. Strong evidence in favor of a more conventional pathway was obtained when significant amounts of *cis*-1-ethynyl-2-vinylcyclopropane, *c*-5 were isolated from low-temperature (160–200°) static pyrolyses of either salt. The isolation of *c*-5 apparently derived from the ability to distill the diazo compound 6 from the hot region *prior* to its loss of N<sub>2</sub>. Condensed on the sublimator cold finger at –80°, the reddish species then decomposed slowly yielding the highly unstable *c*-5 in up to 25% yield with the remainder of the products consisting of dimer 3 and azine formed from 6.



*cis*-1-Ethynyl-2-vinylcyclopropane gave an ir spectrum similar to that of the *trans* isomer (i.e., peaks at 3310 and 2120  $\text{cm}^{-1}$ ) and an NMR spectrum (100 MHz, CDCl<sub>3</sub>) which showed two one-proton multiplets at  $\delta$  0.78 (H<sub>8</sub>) and 1.20 (H<sub>7</sub>), a two-proton multiplet region at 1.48–1.84 (H<sub>4</sub> and H<sub>6</sub>), doublet at 1.88 (H<sub>5</sub>), and an ABX pattern with multiplets centered at  $\delta$  5.10 (H<sub>3</sub>), 5.24 (H<sub>2</sub>), and 5.64 (H<sub>1</sub>). Coupling constants were  $J_{1,2} = 15.8$ ,  $J_{1,3} = 8.5$ ,  $J_{1,4} = 7.5$ ,  $J_{2,3} = 2.5$ , and  $J_{5,6} = 2.0$  Hz.

It was found that *c*-5 underwent conversion rapidly ( $t_{1/2} = 4.3$  hr at 30°) to the dimer 3, ostensibly via a Cope rear-