energy-rich benzvalene structure, even after it is excited by the absorption of a >110 kcal photon or by receiving 53 kcal of triplet energy, survives. Three other features—the quantum chain sequence,[10,12] the photosensitized adiabatic valence isomerization,[13] and the two independently reacting triplet states of one molecule—have been observed in other molecules only rarely.

Acknowledgment. The authors gratefully acknowledge the Air Force Office of Scientific Research (Grant AFOSR-74-2589), the National Science Foundation (Grant NSF-GP-40330X), and the National Institutes of Health (Grant GM-19173) for generous support of this work.

References and Notes

(1) Orbital symmetry forbiddenness has been proposed as an explanation. See (a) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1971, p 107; (b) R. Hoffman and R. B. Woodward, *Acc. Chem. Res.*, **1**, 17 (1968).

(2) Benzvalene was prepared by the procedure of T. J. Katz, E. J. Wang, and N. Acton, *J. Am. Chem. Soc.*, **93**, 3782 (1971).

(3) Review: *Photochemistry*, **4**, 636 (1973).

(4) Benzvalene and fulvene: K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).

(5) Dewar benzene: D. Bryce-Smith, A. Gilbert, and D. A. Robinson, *Angew. Chem., Int. Ed. Engl.*, **10**, 745 (1971); H. R. Ward and J. S. Wishnok, *J. Am. Chem. Soc.*, **90**, 1085, 5353 (1968).

(6) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **90**, 3291 (1968).

(7) H. Lutz and G. Stein, *J. Phys. Chem.*, **78**, 1909 (1974).

(8) Preparation of benzvalene-d_2: R. J. Roth and T. J. Katz, *J. Am. Chem. Soc.*, **94**, 4770 (1972). NMR signals at $\tau = 6.27$ due to the protons at C-5 and C-6 in benzvalene developed during the irradiation.

(9) The benzene-d_2 was recovered by GLPC and analyzed by infrared spectroscopy. For quantitative analysis, the three dideuteriobenzenes were synthesized and use was made of their differing absorptions: ortho at 1476 and 1449 cm^{-1}, meta at 1445 and 1420 cm^{-1}, and para at 1469, 1406, and 595 cm^{-1}. After 100% photoconversion the amount of meta isomer was less than 10% and the amount of para isomer was equal to or less than 0.5%.

(10) P. Lechtken, A. Yekta and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3027 (1973).

(11) This experiment is made possible by the weak quenching of benzophenone triplets by the pentene ($k_q \sim 10^7\ M^{-1}\ \mathrm{sec}^{-1}$) and the strong quenching of benzophenone triplets by benzvalene ($k_q \sim 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$) which allows us to employ a high concentration of pentene and low concentration of **2.** Benzene triplets are quenched by olefins at a diffusion controlled rate: R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965).

(12) With the exception of 1,2-dioxetanes,[10] only one other example of a documented quantum chain sequence is reported: J. Saltiel, D. E. Townsend, and A. Sykes, *J. Am. Chem. Soc.*, **95**, 5968 (1973). A cationic chain sequence involving a Dewar benzene was discovered: T. R. Evans, R. W. Wake, and M. M. Sifain, *Tetrahedron Lett.*, 701 (1973).

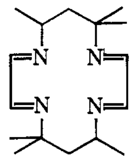
(13) To our knowledge the only other reported adiabatic valence isomerizations involve direct excitation: see N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *J. Am. Chem. Soc.*, **95**, 2035 (1973) and references therein.

Carl A. Renner, Thomas J. Katz,* Joseph Pouliquen
Nicholas J. Turro,* Walter H. Waddell
Department of Chemistry, Columbia University
New York, New York 10027
Received December 28, 1974

Stabilization of Low Valent Iron and Alkyl and Hydride Derivatives of Iron(I) by Macrocyclic Ligands Having Nitrogen Donors

Sir:

Recent studies on the complexes of macrocyclic ligands have revealed a rich oxidation-reduction chemistry that far exceeds expectation, particularly for transition metal derivatives with rings having the common nitrogen donor atoms.[1-4] We report here a series of derivatives of iron(I) that are stabilized by chelation of the iron atom to the unsaturated tetraaza macrocycle of structure I. The ligand also facilitates the synthesis of hydride and alkyl derivatives of the iron(I) atom, and such species are of potential significance to homogeneous catalysis. These products are all highly reactive but readily subject to handling in the absence of oxygen and moisture.



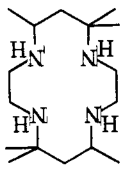
I

On the basis of our earlier electrochemical studies,[3,5] the ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated $\mathrm{Me_6[14]1,3,8,10\text{-}tetraeneN_4}$ or more simply $\mathrm{tetraeneN_4}$, structure I)[6] was chosen as the member of the family of tetraazamacrocycles that should be most effective in stabilizing both low oxidation state iron complexes and their alkyl and hydride derivatives. In acetonitrile solutions, $[\mathrm{Fe(tetraeneN_4)(CH_3CN)_2}]^{2+}$ exhibits three well-defined reduction waves at −0.80, −1.41, and −1.83 V vs. $\mathrm{Ag\text{-}AgNO_3^-}$ (0.1 *M*) (0.1 *M* $n\text{-}\mathrm{Bu_4NBF_4}$ supporting electrolyte).[3] Controlled potential electrolysis on the first reduction plateau (−1.2 V) produces purple $[\mathrm{Fe^I(tetraeneN_4)}]^+$ which was isolated in 80% yield as the $\mathrm{CF_3SO_3^-}$ salt. Anal. Calcd for $\mathrm{C_{17}H_{28}N_4SO_3F_3Fe}$: C, 42.42; H, 5.82; N, 11.65; S, 6.67. Found: C, 41.92; H, 6.02; N, 11.47; S, 6.70.

Magnetic susceptibility measurements indicate an effective moment of 2.3 BM.[7] The anisotropic ESR spectrum of a frozen acetonitrile solution of the iron(I) complex is characteristic of a low-spin d^7 system subject to a rhombic distortion from octahedral symmetry (*g* values: 2.516, 2.059, 1.933). The quasi-reversible Fe(I)/Fe(II) couple is observed at −0.69 V.

Although all Fe(I) derivatives containing nitrogen and/or oxygen donors must be considered rare, earlier reports include $\mathrm{Na[Fe^I(salen)]}$, which is reported[8] to contain high-spin Fe(I), and the product of one-electron reduction of $[\mathrm{Fe(Me_6[14]aneN_4)CH_3CN)_2}]^{2+}$ (see structure II for the ligand $\mathrm{Me_6[14]aneN_4}$), which exhibited properties inconsistent with those expected for a simply related Fe(I) derivative.[9] $\mathrm{Na[Fe^I(TTP)]}$, where TPP is tetraphenylporphyrin, has been fairly well characterized.[10]

II



Considerable attention has also been given to the second reduction process that $[\mathrm{Fe^{II}([14]tetraeneN_4)(CH_3CN)_2}]^{2+}$ undergoes. Controlled potential electrolysis of $[\mathrm{Fe^{II}(tetraeneN_4)(CH_3CN)_2}]^{2+}$ on the second reduction plateau (−1.6 V) produced, in solution, the two-electron reduction product, formally $\mathrm{Fe^0tetraeneN_4}$. Further reaction of this highly reactive species was followed by repeated scanning of the current-potential curve. It has been found that this process involves abstraction of a hydrogen atom, presumably from the supporting electrolyte $n\text{-}\mathrm{Bu_4NBF_4}$, to form an iron(I) hydride derivative, $\mathrm{H\text{-}Fe^I(tetraeneN_4)(CH_3CN)}$. Anal. Calcd for $\mathrm{(C_{16}H_{28}N_4)Fe(H)CH_3CN}$: C, 57.77; H, 8.56; N, 18.73. Found: C, 57.65; H, 8.46; N, 18.64. The purple-black isolated product (10–15% yield) has two quasi-reversible oxidation waves at −0.73 and −0.01 V. These are assigned to the Fe(I)/Fe(II) and Fe(II)/Fe(III) couples, respectively. A single irreversible reduction process occurs at −1.97 V. The anisotropic ESR spectrum is again representative of a low-spin d^7 system (g values: 2.302, 2.074, 2.006); μ_{eff} (benzene solution) = 2.1 BM. A sharp band at 1890 cm^{-1} in the infrared spectrum of the complex is assigned to $\nu_{\text{Fe-H}}$. Reaction with CCl_4 yields $CHCl_3$ (85% recovery).[11] Although the stabilization of the Fe-H linkage is well established in complexes with such ligands as phosphines, $[HFe^{I}(\text{tetraene}N_4)CH_3CN]$ is unique among well-characterized iron species having nitrogen donors. Olson and Vasilevskis[9] have offered evidence for a much more reactive but related species with the iron complex of $Me_6[14]\text{ane}N_4$; however, the extent of reduction of the iron remains in question. The well-demonstrated existence of low-valent Fe-H species in systems based on tetraaza macrocycles offers the strong possibility of their eventual significance in homogeneous catalysis processes.

The existence of the stable hydride posed the possibility for the existence of stable alkyl derivatives of iron(I). Indeed, paramagnetic iron(I) alkyl and aryl derivatives containing the same macrocyclic ligand have also been isolated. The iron(II) complex $[Fe(\text{tetraene}N_4)Cl]^+$ is reduced by one equivalent of a lithium alkyl or aryl to the corresponding iron(I) species. Addition of a second equivalent of LiR produces $[RFe(\text{tetraene}N_4)]$, where R = CH_3, C_6H_5, according to the equations below.

$$[Fe(\text{tetraene}N_4)Cl]^+ + LiR \rightarrow [Fe(\text{tetraene}N_4)Cl] + Li^+ + 1/R\text{–}R$$

$$[Fe(\text{tetraene}N_4)Cl] + LiR \rightarrow [Fe(\text{tetraene}N_4)R] + LiCl$$

Mass spectral data on the products for the case where R = C_6H_5 confirms the formation of both the aryl derivative (*m/e* 409) and the expected by-product, biphenyl (*m/e* 154). Anal. Calcd for $C_{22}H_{33}N_4Fe$: C, 64.57; H, 8.09. Found: C, 64.56; H, 8.91. Yield, (purified) 70%.

The organometallic compounds decompose above ~95° and are sensitive to ultraviolet light. The reactivities of the complexes are reflected by their cathodic half-wave potentials. The reversible Fe(I)/Fe(II) couple for $C_6H_5Fe(\text{tetraene}N_4)$ is observed at −0.80 V and the reversible Fe(II)/Fe(III) couple occurs at −0.16 V. Magnetic data indicate a moment of 2.1 BM, and ESR data confirm that the unpaired electron is in a molecular orbital of significant metal ion character (g values: 2.206, 2.070, 2.002). The electronic ground state of the five-coordinate iron(I) derivatives is proposed to be $d_{yz}{}^2$, $d_{xz}{}^2$, $d_{z^2}{}^2$, $d_{x^2-y^2}{}^1$, d_{xy} (for a coordinate system with xy axes which bisect the chelate rings of the macrocyclic ligand).[12] While a number of earlier reports claim the formation of alkyl and aryl derivatives of complexes of Fe(III)[5,13-16] and Fe(II),[17,18] the Fe(I) derivatives reported here are unique and serve to further illustrate the ability of macrocyclic ligands to stabilize unusual structures.[18,19]

References and Notes

(1) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969); D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *ibid.*, **10**, 1739 (1971); E. S. Gore and D. H. Busch, *ibid.*, **12**, 1 (1973).

(2) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

(3) J. C. Dabrowiak, V. L. Goedken, F. V. Lovecchio, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 5502 (1972).

(4) N. Takvoryan, K. Farmery, V. Katovic, F. V. Lovecchio, E. S. Gore, L. B. Anderson, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 731 (1974).

(5) M. C. Rakowski, Thesis, The Ohio State University, 1974.

(6) J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, in press.

(7) Moment determined by an NMR technique in solution. Accuracy does not exceed some 5%. See, for example, A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, N.Y., 1968, p 97ff.

(8) C. Floriani and F. Calderazzo, *Coord. Chem. Rev.*, **8**, 57 (1972).

(9) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **11**, 980 (1972).

(10) I. A. Cohen, D. Ostfeld, and B. Lichtenstein, *J. Am. Chem. Soc.*, **94**, 4522 (1972).

(11) R. A. Schunn, "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, N.Y., 1971, p 246.

(12) W. J. Horrocks, Jr., G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

(13) R. S. Wade and C. E. Castro, *J. Am. Chem. Soc.*, **95**, 226 (1973).

(14) D. A. Clark, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc. C*, 88, (1968).

(15) V. L. Goedken, S. M. Peng, and Y. Park, *J. Am. Chem. Soc.*, **96**, 284 (1974).

(16) F. Calderazzo and C. Floriani, *J. Chem. Soc. A*, 3665 (1971).

(17) R. Taube, H. Drevs, and T. Duc-Hup, *Z. Chem.*, **9**, 115 (1969).

(18) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misoni, *J. Am. Chem. Soc.*, **87**, 4652 (1965).

(19) These studies were supported in part by Grant GM10040 from the National Institute of General Medical Sciences of the U.S. Public Health Service. M.C.R. expresses appreciation for fellowship support from the Graduate School, OSU.

Mary C. Rakowski, Daryle H. Busch*
The Evans Chemical Laboratory, The Ohio State University
Columbus, Ohio 43210

Received September 27, 1974

A Fluxional, Catalytically Active Metal Cluster, $Ni_4[CNC(CH_3)_3]_7$

Sir:

In pursuing an analogy between metal surfaces and discrete metal clusters in the specific areas of surface chemistry and heterogeneous catalysis, we have discovered a metal cluster that has not only unusual structural and fluxional features but also a rather extensive catalytic chemistry primarily based on cyclodi- and -trimerization reactions. We report here on the solid- and solution-state structure, dynamic stereochemical facets, and catalytic chemistry of $Ni_4[CNC(CH_3)_3]_7$ which from stoichiometry appears to be a six-electron deficient cluster.

Reaction of bis(cyclooctadiene)nickel(0) with about 2 equiv of *tert*-butylisocyanide yields,[1] after recrystallization from benzene, dark red crystals that analyze precisely for $Ni_4[CNC(CH_3)_3]_7 \cdot C_6H_6$.[2,3] Solutions of the complex in toluene-d_8 show, at 0° and below, three types of CH_3 ^1H NMR resonances in the intensity ratio of 27:27:9 and an aromatic resonance with a relative intensity of 6.[5] A tetrahedral nickel cluster in which there are three bridging isocyanide ligands would seem the only plausible structural possibility.[5] Infrared data showed a very low energy C═N stretch for the bridging isocyanide ligands (1605, 1610 cm^{-1}) which suggested a face-bridging situation, a bonding situation not as yet established for isocyanides. Consistent cocrystallization of arenes with the cluster also suggested that an arene molecule might be π bonded to the unique face of the tetrahedron. It remained, however, for the X-ray crystallographic data to reveal the unexpected structural features of this cluster. Although the poor diffractive properties of the crystals resulted in a very low yield of data, it was possible by optimization of data collection procedures to obtain data of sufficient quality to allow a qualitative and semiquantitative description of the solid-state structure.

Single crystals of $Ni_4[CNC(CH_3)_3]_7 \cdot C_6H_6$ obtained by slow diffusion of pentane vapor into a benzene solution of the nickel cluster are monoclinic, space group $P2_1/c\text{-}C^5_{2h}$ with a = 11.236(5) Å, b = 11.036(4) Å, c = 36.637(7) Å, β = 101.39(3)°, and Z = 4 (d_{calcd} = 1.33, d_{measd} = 1.5 g cm^{-3}). Data collection on a Syntex P$\bar{1}$ autodiffractometer with slow θ-2θ scans and graphite monochromated Cu K$\bar{\alpha}$ radiation yielded 1656 independent reflections with $2\theta_{\text{CuK}\bar{\alpha}}$ < 84° (0.3 limiting Cu K$\bar{\alpha}$ sphere) and $I > 2\sigma(I)$. The four nickel atoms were located through direct methods (MULTAN) and the remaining atoms by standard difference Fourier techniques. Unit-weighted full-matrix least-squares refinement with anistropic thermal parameters for all non-