spectively. 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, $[HFe^{I}(\text{tetraeneN}_4)CH_3CN]$ 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 $Me_6[14]aneN_4$; 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 $[Fe(\text{tetraeneN}_4)Cl]^+$ 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 $[RFe(\text{tetraeneN}_4)]$, where R = CH_3, C_6H_5, according to the equations below.

$$[Fe(\text{tetraeneN}_4)Cl]^+ + LiR \rightarrow [Fe(\text{tetraeneN}_4)Cl] + Li^+ + 1/R\text{-}R$$

$$[Fe(\text{tetraeneN}_4)Cl] + LiR \rightarrow [Fe(\text{tetraeneN}_4)R] + LiCl$$

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 $C_6H_5Fe(\text{tetraeneN}_4)$ 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]

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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-

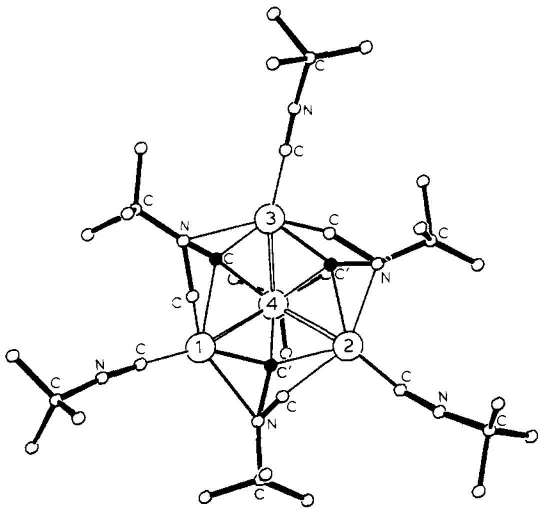

Figure 1. Perspective drawing (adapted from an ORTEP plot) of the $Ni_4[CNC(CH_3)_3]_7$ molecule viewed normal to the triangular base along the idealized threefold axis. Nickel atoms are represented by large numbered open circles. To show both possible modes of binding in the three bridging isocyanide groups, coordinated carbon atoms for edge-bridging isocyanide ligands are represented by small open circles and are designated C; face-bridging carbon atoms are represented by small blackened circles and designated C′.

hydrogen atoms has resulted in a conventional unweighted residual

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

of 0.107.

The structural analysis reveals that the crystal is composed of discrete $Ni_4[CNC(CH_3)_3]_7$ molecules (Figure 1) with the trigonally compressed tetrahedral cluster of nickel atoms approximately conforming to C_{3v} symmetry and the entire molecule, ideally to C_3 symmetry. The apical nickel atom, Ni(4), which lies on the pseudo-threefold axis is displaced by only 0.99 Å from the triangular base of the other three nickel atoms. The rather short 2.338 (7, 9, 13) Å[7] average length for the three apical-to-basal Ni-Ni bonds is comparable to short Ni-Ni bonds observed in other compounds[8a] and longer than the 2.508 Å value observed for a nearly regular tetrahedral, electron precise nickel cluster.[8b] Each nickel atom is bonded in a linear fashion to a terminal two-electron donating *tert*-butylisocyanide ligand having lengths of 1.17 (3, 3, 5) Å[7] and 1.42 (3, 5, 12) Å[7] for the C≡N and C—N bonds, respectively. Values of 175 (3, 3, 5) and 171 (4, 1, 3)° were determined for the average Ni-C-N and C-N-C bond angles of these four ligands. The 2.15 (3) Å apical Ni-C bond is 0.34 Å longer than the 1.81 (2, 5, 8) Å average for the three basal Ni-C bonds.

Each of the three remaining isocyanide ligands appears to have two possible bridging modes of bonding to the cluster as a four-electron donor. Both modes are illustrated in Figure 1. The first involves a spanning of the 3.67 (1, 3, 4) Å basal Ni···Ni edges by a "bent" isocyanide ligand to give Ni-N-C and Ni-C-N angles of 94 (3, 7, 11) and 168 (4, 9, 13)°, respectively. Average lengths of 2.24 (3, 6, 8), 1.64 (5, 28, 42), 1.23 (5, 24, 37), and 1.49 (3, 3, 4) Å were observed for the Ni—N, Ni—C, C=N, and N—C bonds, respectively. The other bridging mode involves a ~0.93 Å movement of the coordinated carbon atom from its position along the basal edge to a position equidistant (1.92 (5, 14, 35) Å) from the apical and two closest basal Ni atoms and ~0.63 Å out of the plane defined by the three nickel atoms. The C-N-C′ angle is 163 (4, 8, 12)° for this "face-bridging" mode of bonding. Carbon atoms with half occupancies at both coordinated positions for each bridging ligand were utilized in the least-squares refinement. Attempts to locate the benzene molecule, indicated by the analytical and crystal density data, from difference Fourier syntheses were unsuccessful.

Stereochemical nonrigidity is evident from the DNMR ^1H spectra for the nickel cluster. These data delineate a distinct two-step process whereby ligand atoms are permuted. In the less activated step, the ligands associated with the two high field resonances (intensities 27 and 9) are rendered equivalent on a time averaged basis as shown by their collapse into a single resonance while the low field resonance (intensity 27) remains unchanged. These "exchanging" sets are the terminal ligand sites. Bridge-terminal ligand site exchange becomes evident only at ~60°, and a final collapse of all CH_3 proton resonances is seen at 100° (60 MHz). A simple mechanistic rationale of the first exchange step comprises bridging-ligand traverse of tetrahedral edges or faces as the C_{3v} tetrahedron "breathes" to achieve an averaged T_d symmetry. In this scheme, terminal ligand transposition is slow on the NMR time scale in the low temperature transition region, *yet these terminal sites become equivalent because bridging ligands rapidly traverse all edges or faces* (There is a formally analogous mechanism[9] for bridge-hydrogen exchange in some *nido* boron hydrides). The second step of the process, which comprises terminal and bridge ligand exchange, perhaps proceeds by entry of a terminal ligand into a bridge position of an "open" face.

Without the Ni_x-N interaction for the three bridging ligands, the nickel cluster would appear to be six electrons short of an electron precise tetrahedral cluster. Alternatively, this deficit could be satisfied, at least partially, by the binding of an arene molecule parallel to the unique face, a point yet to be resolved with a better single crystal of $Ni_4[CNC(CH_3)_3]_7$·arene.[10] In any case, binding of the isocyanide nitrogen atom must be weak as evidenced by the DNMR studies. Thus the bridging ligands are electronically ambidentate ($\eta^2 \rightleftharpoons \eta^1$) in a fashion formally analogous to the trihapto-allyl ligand ($\eta^3 \rightleftharpoons \eta^1$) and inject a fluxional coordination feature that might be ideal for cluster catalysis chemistry. In fact, this nickel cluster, unlike mononuclear $Ni[CNC(CH_3)_3]_4$, is a catalyst for cyclization processes at 25°. Acetylene was selectively converted to benzene; no cyclooctatetraene was detected. Butadiene gave a mixture of 1,3, 1,4, and 1,5 cyclooctadienes, and in this case neither vinylcyclohexene nor linear octatriene was detected by GC MS analysis. We would like to presume that more than one metal atom (associated with a tetrahedral face) is involved in the cyclization transformation, as in a template synthesis, but have as yet no direct evidence in support of this type of reaction mechanism. We are now extensively developing the catalysis chemistry of this cluster and seeking extension of ligand electronic fluxionality in other types of clusters.

Acknowledgment. We acknowledge support of this research by the Advanced Research Projects Agency, Cornell Materials Science Center, by the National Science Foundation, Grant No. MPS73-08943 A02 (E.L.M.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society (V.W.D.)

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(2) Molecular weight (benzene cryscopic) determinations were consistently 20–30% low (theory: 897).
(3) The palladium compound prepared by a similar procedure[1] does in fact have the composition $Pd[CNC(CH_3)_3]_2$ by analysis and NMR, and we

find it to be a trimer.[4] The infrared spectrum indicates the presence of terminal and bridging isocyanide ligands (C═N) stretch. However, there was no evidence of ligand inequivalence from low temperature ^{1}H NMR studies.

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(5) The low field CH_3 proton NMR peak of relative intensity 27 is at τ 7.92 which is higher than the τ 6.23 value reported[6] for the bridging CH_3NC ligand in $(\eta^5-C_5H_5)_2Fe_2(CO)_2(NCCH_3)_2$. The two high field peaks at τ 9.59 and 9.37, respectively, are also higher than the reported[6] value of τ 7.48 for the terminal ligand in the aforementioned iron complex but are close to the value of τ 8.69 that we find for $Ni[CNC(CH_3)_3]_4$.

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Received February 24, 1975

Solid Phase Peptide Synthesis by Oxidation-Reduction Condensation

Sir:

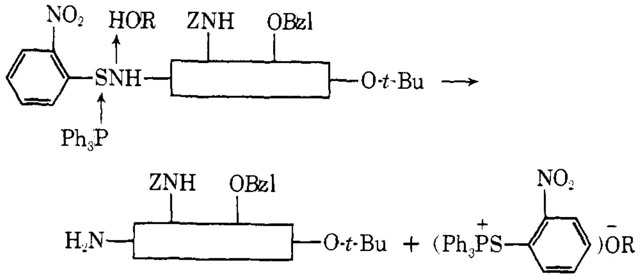
Several modifications on the solid-phase peptide synthesis toward fragment condensation[1] have been attempted to minimize erroneous sequences in the chain elongation from C-terminal amino acid to N-terminal amino acid (A-type elongation). On the other hand, there has been reported one instance[2] in which chain elongation via fragment condensation was carried out from N-terminal amino acid to C-terminal amino acid (B-type elongation) according to the azide method. However, some problems remained unsolved because of the limitations placed on solvents and of low yields in each coupling step. Recently it has been shown that the oxidation-reduction condensation can be successfully applied to the synthesis of LH-RH by B-type elongation via fragment condensation on a solid support.[3]

This communication reports a synthesis of ACTH(1-24) by the above mentioned method employing a new technique to monitor the amount of amino component in solution based on high pressure liquid chromatography. Furthermore, a novel, neutral cleavage technique of the *o*-nitrophenylsulfenyl (Nps-) protecting group was successfully employed in the preparation of peptide fragments.

The synthetic scheme for this method is shown in Figure 1.

In this strategy, the following precautions were taken: (1) the *tert*-butyl ester was selected for α-carboxyl protection since it is easily deprotected with trifluoroacetic acid; (2) the biologically active center was included in one fragment V in order to ensure the incorporation of this fragment which could be proved from the activity; (3) each fragment was designed to incorporate a uv absorbing moiety in order to detect any remaining fragment rapidly by way of high pressure liquid chromatography.

The syntheses of protected fragments were achieved stepwise in solution by oxidation-reduction condensation using the readily available benzyloxycarbonylamino acids except in the cases of the incorporation of *o*-nitrophenylsulfenyl (Nps-) amino acid residues which were coupled with *N,N'*-dicyclohexylcarbodiimide or by the active ester method. Selective removal of the Nps-protecting group from the protected fragments having benzyloxycarbonyl, benzyl ester, and *tert*-butyl groups was achieved under neutral conditions at room temperature through the phosphonium salt[4] by using triphenylphosphine and active hydrogen compounds such as phenol or water as shown in the following scheme.



Starting with 1.5 g of 2% cross-linked resin containing 0.046 mmol of *O*-benzylseryltyrosine,[5] coupling steps II and III were carried out with a three-fold excess of the added

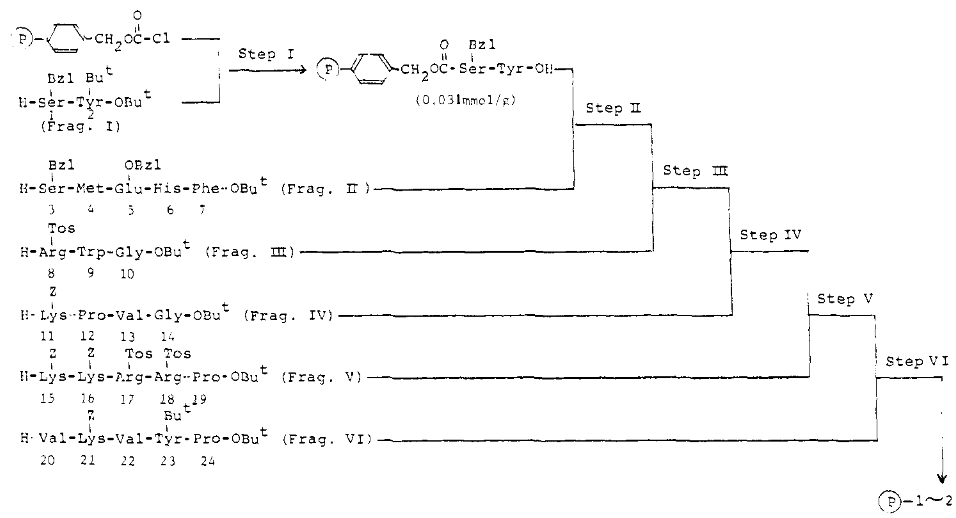


Figure 1. The scheme for the synthesis of ACTH(1-24).