stopped-flow spectrometer was purchased under P.H.S. Grant RR-7058-09 to Rutgers University. We thank Professor U. Tonellato (Università di Padova, Italy) for useful discussions. R.A.M. is grateful to NATO (Grant 1619) for travel support to the Università di Padova.

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(21) Colgate-Palmolive Fellow, 1979–1980.

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Metal Clusters with Exposed and Low-Coordinate Nitride Nitrogen Atoms

Sir:

In pursuing possible analogies between metal surfaces and metal clusters,[1] we have sought nitride clusters with exposed and possibly reactive nitrogen atoms to allow experimental comparisons between ammonia synthesis on metal surfaces and the possible stoichiometric or catalytic hydrogenation of nitrogen with metal clusters. To date, only two nitride clusters have been reported,[2] namely, the isostructural and trigonal-prismatic $[Co_6N(CO)_{15}^-]$ and $[Rh_6N(CO)_{15}^-]$, both of which contained interstitial rather than exposed nitride nitrogen atoms. We describe here the synthesis and structural characterization of a prototypic series of iron nitride clusters in which the nitrogen atoms are exposed and of low coordination number, namely, four and five. The term nitride is used to denote species in which a nitrogen atom is only within bonding distance of metal atoms.

An extension of our synthetic methods for low-coordinate carbide clusters[3] was successfully modified for the analogous nitrides. The Fe_4N cluster anion $[Fe_4N(CO)_{12}^-]$ (**1**) was prepared by the reaction of $NOBF_4$ with $Na_2Fe_2(CO)_8$ in the presence of excess iron pentacarbonyl (diglyme solution at 130 °C).[4] This anionic nitride was protonated by strong acids in toluene solution to form the neutral nitride $HFe_4N(CO)_{12}$ (**2**).[5] In these solutions, excess acid, e.g., CF_3SO_3H, did not yield the cation $[HFe_4NH(CO)_{12}^+]$.

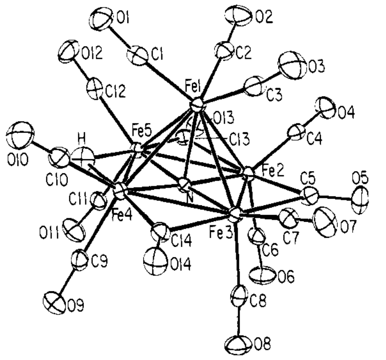

Figure 1. Atom labeling scheme for $HFe_5N(CO)_{14}$.

It is important to note that the synthesis of $[Fe_4N(CO)_{12}^-]$ is very temperature sensitive; below 130 °C, a nitrosyl complex was formed, and above, an Fe_5N cluster was the major product. When the synthesis mixture of $NOBF_4$, $Na_2Fe_2(CO)_8$, and $Fe(CO)_5$ was heated for either prolonged periods or at temperatures above 130 °C, the cluster $[Fe_5N(CO)_{14}^-]$ (**3**) was formed.[6] This anion was converted to $HFe_5N(CO)_{14}$ (**4**) on dissolution in a sulfuric acid-toluene mixture.[7] A third derivative in this Fe_5N system, $[HFe_5N(CO)_{13}^{2-}]$ (**5**), was obtained from **3** by reaction with $LiB(C_2H_5)_3H$.[8]

By analogy to the iron carbide structures[3,9] and from the general molecular orbital calculations of Lauher,[10a] our 62-electron four-iron nitrides should have butterfly structures, and our 74-electron five-iron nitrides should have square-pyramidal structures. Spectroscopic data for the Fe_4N complexes **1** and **2**, in comparison with those of the precise carbide analogues $[HFe_4C(CO)_{12}^-]$ and $[Fe_4C(CO)_{12}^{2-}]$,[3,10b] strongly implicate an Fe_4 butterfly with the nitride nitrogen atom centered above the wings. Infrared studies established that for **2** all CO ligands were terminal (as in the carbides), and the hydride ^1H NMR resonance at 40.2 ppm was in a characteristic range for such iron hydride clusters.[3] The carbonyl ^{13}C NMR spectrum for **2** consisted of a sharp singlet and two very broad resonances at 25 °C and a set of four resonances of 4:4:2:2 intensity ratios at -80 °C.[11] These resonances can be assigned to the four CO environments of **2** as shown in A. An X-ray crystallographic analysis of $HFe_4N(CO)_{12}$ established the proposed butterfly structure with a 4-coordinate nitride atom.[12a] Average iron–iron distances were 2.62 (1) (apical–basal)

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(1) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).

(2) S. Martinengo, G. Ciani, A. Sironi, B. T. Heaton, and J. Mason, *J. Am. Chem. Soc.*, **101**, 7095 (1979).

(3) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).

(4) The tetraethylammonium salt of **1** was prepared by reaction of $Na_2Fe(CO)_4{\cdot}{}^3/_2C_4H_8O_2$ (4.5 g) with $Fe(CO)_5$ (9 mL) to which was added 60 mL of diglyme. After formation of $Na_2Fe_2(CO)_8$, $NOBF_4$ (1.5 g) was slowly added. The solution was heated to 130 °C for 1 h and then cooled. A black precipitate, which formed after addition of hexane, was triply washed with water. $(C_2H_5)_4NCl{\cdot}H_2O$ (2.0 g) was added to the precipitate, and the product, $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$, was extracted with dichloromethane. An equal volume of ethanol was added to the extract, and the volume of the resulting solution was reduced to $^1/_2$ under vacuum. After the solution was cooled to -25 °C, black crystals of $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$ (300 mg, 3.3%) were formed: IR [ν(CO)/tetrahydrofuran] 2063 (vw), 2015 (s), 1990 (vs), 1967 (m), 1933 (w) cm^{-1}; ^{13}C NMR (dichloromethane, 0 °C) 215.6 (s, 6 CO), 218.2 (s, 6 CO) ppm. Anal. Calcd: C, 34.13; H, 2.86; N, 3.98. Found: C, 34.22; H, 3.09; N, 3.86.

(5) The tetraethylammonium salt $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$ (200 mg) was added to a Schlenk flask containing 50 mL of toluene and 2 mL of H_2SO_4, and the two-layer system was stirred rapidly. The red-brown toluene layer was collected through Celite, and the toluene was removed under vacuum. The $HFe_4N(CO)_{12}$ product was recrystallized from CH_2Cl_2 at -30 °C: IR [ν(CO)/hexane] 2053 (s), 2035 (m), 2023 (m), 2015 (vw), 1994 (w) cm^{-1}; mass spectrum, 575 (p^+) followed by successive loss of 12 CO, 183 $(HFe_3N)^+$; ^{13}C NMR (tetrahydrofuran, -88 °C) 215.1 (s, 2 CO), 214.7 (d, $J = 8.7$ Hz, 4 CO), 211.2 (s, 4 CO), 206.1 (s, 2 CO) ppm. Anal. Calcd: C, 25.08; H, 0.18; N, 2.44. Found: C, 25.09; H, 0.26; N, 2.44.

(6) $[(C_2H_5)_4N][Fe_5N(CO)_{14}]$ was prepared analogously to **1** except that the reaction temperature was increased to 145 °C and reaction time to 2 h (yield, 66% based on $NOBF_4$): IR [$\nu(CO)/CH_2Cl_2$] 2062 (w), 2001 (vs, br), 199] (vs, br), 1970 (m, sh), 1805 (w, br) cm^{-1}; ^{13}C NMR (dichloromethane, 0 °C) 221.4 (s, 11 CO), 215.9 (s, 3 CO) ppm. Anal. Calcd: C, 32.39; H, 2.47; N, 3.43. Found: C, 32.47; H, 2.56; N, 3.40.

(7) $HFe_5N(CO)_{14}$ prepared in the same manner as **2** had the following spectra: mass spectrum, 687 (p^+) followed by ions corresponding to loss of carbon monoxide molecules; IR [ν(CO)/hexane] 2053 (vs), 2034 (s), 2012 (w), 1981 (vw, br), 1871 (vw) cm^{-1}.

(8) To a tetrahydrofuran solution of $[(C_2H_5)_4N][Fe_5N(CO)_{14}]$ (**4**) (900 mg in 30 mL) was added 3.0 mL of 1 M $LiBEt_3H$ in tetrahydrofuran at -78 °C. After being warmed to ambient temperature, the solvent was removed under reduced pressure. $(C_2H_5)_4NCl{\cdot}H_2O$ (205 mg) was added to the resultant solid, and $[(C_2H_5)_4N]_2[HFe_5N(CO)_{13}]$ was obtained from methanol as deep brown plates (440 mg, 44%): IR [$\nu(CO)/CH_3CN$] 1958 (vs), 1947 (s), 1912 (s), 1776 (w) cm^{-1}; ^1H NMR (CD_3CN) 3.11 (methylene), 1.15 (methyl), -12.28 (hydride at -40 °C) ppm. ^{13}C NMR (tetrahydrofuran, -80 °C) 213.5 (d, 2 CO), 221.6 (s, 3 CO), 223.0 (d, 2 CO), 232.5 (br, s, 6 CO) ppm. Anal. Calcd: C, 37.90; H, 4.50; N, 4.57. Found: C, 37.72; H, 4.51; N, 4.60.

(9) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962).

(10) (a) J. W. Lauher, *J. Am. Chem. Soc.*, **100**, 5305 (1978). (b) The cluster $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ was shown by X-ray studies to have an Fe_4C butterfly geometry with the carbon atom above the wings. M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *ibid.*, **102**, 4542 (1980).

(11) The CO ^{13}C resonance for **1** consisted of two singlets from +20 to -80 °C. Facile CO site exchange had been observed[3] for the $[Fe_4C(CO)_{12}^{2-}]$ analogue.

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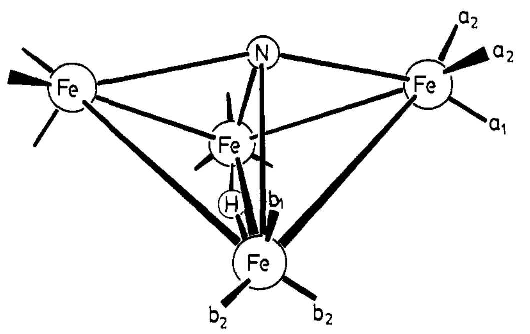

(A)

and 2.54 (2) Å (basal–basal), and the average iron–nitrogen distances were 1.77 (1) (apical iron) and 1.92 (2) Å (basal iron). The dihedral angle between the two Fe(apical)-2Fe(basal) planes was 101°, and the Fe(apical)–N–Fe(apical) angle was 178.4 (6)°. The basicity of the nitrogen atom in **2** was not high.[12b] However, this complex did dissolve in pure CF_3SO_3H, indicating protonation of the cluster, but the site of protonation could not be established by NMR because of fast intermolecular proton exchange.

All three Fe_5N clusters, **3–5**, appeared to have square-pyramidal geometry. An X-ray crystallographic analysis[13] of $HFe_5N(CO)_{14}$ (**5**) established a square-pyramidal arrangement of iron atoms, Fe–Fe = 2.58 (2) Å average, with the nitride nitrogen atom located near the basal plane (Figure 1). Actually, the nitrogen atom was precisely 0.093 (2) Å below the basal plane away from the apical iron atom, a slightly greater extension than for the carbide carbon atom in the isoelectronic carbide analogue, $Fe_5C(CO)_{15}$.[9] With respect to the disposition of peripheral ligands in **5**, the apical iron atom had three terminal carbonyls, the basal iron atoms each had two terminal carbonyls, three of the basal edges were unsymmetrically bridged by one carbonyl, and the remaining edge was bridged by a hydride ligand. By taking into account the smaller nitrogen atom radius, there was a close parallel in the iron–nitrogen distances of this nitride cluster to the iron–carbon distances in the $Fe_5C(CO)_{15}$[9] analogue: apical Fe–N = 1.913 (2) Å, Fe–C = 1.96 (3) Å and basal Fe–N = 1.836 (3) Å, Fe–C = 1.88 (1) Å. In the only other first row cluster nitride,[2] $[Co_6N(CO)_{15}^-]$, the average Co–N distance was 1.938 Å.

The anionic nitride, $[Fe_5N(CO)_{14}^-]$ (**3**), is isoelectronic with $[Fe_5C(CO)_{14}^{2-}]$, and the dynamic ^{13}C NMR spectra of these two species were analogous; both showed two ^{13}C resonances of relative intensities 3:11 of which the more intense resonance broadened at low temperatures. These patterns of ^{13}C CO resonances can be rationalized in terms of an intermediate exchange system in which CO exchange between basal and apical iron atom sites is slow on the NMR time scale while interiron CO exchange is fast among the basal set of iron atoms. A precise structural model for **3** is $[RhFe_4C(CO)_{14}^-]$, whose tetraethylammonium salt was crystallographically defined earlier.[15] The metal atom framework was square pyramidal with a CO bridging a basal edge and two terminal CO ligands at these two basal metal atom sites and with three terminal CO ligands at the remaining metal atom sites. Presumably, the $[HFe_5N(CO)_{13}^{2-}]$ cluster ion (**5**) has a structure similar to that established for $HFe_5N(CO)_{14}$ (**4**), where the bridging carbonyl opposite the bridging hydride in **4** is absent.

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Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements, structure factor tables, and relevant bond angles and lengths (31 pages). Ordering information is given on any current masthead page.

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[12] (a) X-ray analysis for $HFe_4N(CO)_{12}$: mol wt 574.5 amu; triclinic space group $P\bar{1}$, $Z = 2$, $a = 7.491$ (2), $b = 9.214$ (3), $c = 13.974$ (6) Å, $\alpha = 88.09$ (3), $\beta = 86.98$ (3), $\gamma = 73.76$ (3)°, and $V_{\text{calcd}} = 924.5$ (6) Å^3 at 298 K. Unit-cell parameters were determined from 17 reflections. With a Syntex $P2_1$ automated diffractometer, 2169 independent reflections were collected ($4.0° \leq 2\theta \leq 40.0°$). A total of 1415 unique reflections had $F_o^2 \geq \sigma F_o^2$. Absorption corrections were made ($\mu_c = 31.38$ cm^{-1}), and transmission factors ranged from 0.80 to 0.83. The structure was solved with MULTAN and Patterson functions. The structure of $HFe_4N(CO)_{12}$ was disordered with disordered molecules related by a near twofold rotation inversion axis which resulted in a superposition of the molecules. The iron cluster core was resolved by using least-squares refinements in which the iron–iron superposition gave a site separation of ~0.50 Å. The difference maps contained iron ellipsoids which also indicated disorder. Final refinement led to $R(F_o) = 0.071$, $R_w(F_o^2) = 0.078$, and GOF = 1.40. The successful least-squares refinement yielded a structural model with chemically reasonable distances and angles (a full discussion of Fe_4X butterfly structures will be published by us). (b) This is expected because in the analogous and neutral complex $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ the C–H hydrogen atom is removed as a proton by methanol (M. Tachikawa, unpublished data).

[13] X-ray analysis for $HFe_5N(CO)_{14}$: mol wt 686.4 amu; monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.473$ (2), $b = 15.056$ (3), $c = 16.048$ (3) Å, $\beta = 95.42$ (2)°, $\mu(\text{Mo K}\alpha) = 36.38$ cm^{-1}. One quadrant, 4945 reflections, of data was collected on a Syntex $P2_1$ automated diffractometer at 173 K. Solution of the structure was accomplished by using MULTAN,[14] and the hydrogen atom was located in a difference Fourier synthesis. All atomic positional and thermal parameters refined successfully (anisotropic temperature factors except for hydrogen atoms) and convergence were realized at an agreement factor of $R_w(F_o) = 0.031$ for 3967 reflections where $F_o^2 > \sigma F_o^2$.

[14] A. Germain, P. Main, and M. M. Wolfson, *Acta Crystallogr.*, **19**, 1014 (1954).

[15] M. Tachikawa, A. C. Sievert, E. L. Muetterties, M. R. Thompson, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, **102**, 1725 (1980).

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Bisannelation of Arenes with Bisaryne Equivalents

Sir:

We have found that tetrabromo derivatives[1] of 1,4-disubstituted benzenes function as bisaryne equivalents,[2,3] allowing one to readily convert benzenes to anthracenes in two steps. The method is broad in scope and is generally useful for synthesizing polynuclear aromatic compounds and for other novel structures. Table I gives illustrative examples.

In a typical procedure, 10 mmol of the bisaryne equivalent and 20 mmol (or excess) of the diene in 100 mL of carefully dried solvent are cooled to −78 °C[4] and stirred (argon atmosphere) as *n*-butyllithium (30 mL in hexane, approximately 0.8 M) is added

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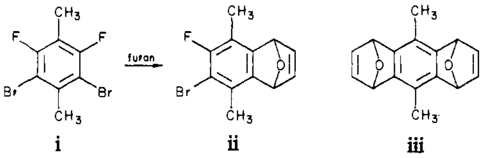
[1] Other halo drivatives, such as dibromo–diiodo or tetraiodo, also work, and other possibilities are being explored. The tetrabromo derivatives, however, are usually the most easily accessible.

[2] The only previous similar reaction of which we are aware is the conversion of i to iii: Wittig, G.; Hārle, H. *Justus Liebigs Ann. Chem.* **1959**, *623*, 17. With magnesium in THF, i gave mainly the monoadduct ii (34%) and only 5% of the bisadduct iii. With butyllithium, the yield of iii increased to 15%, but no ii was isolated.



i ii iii

[3] Bisarynes have been postulated as intermediates in certain mass spectral fragmentations and to rationalize products from the copyrolysis of benzene with pyromellitic or mellophanic dianhydrides (Fields, E. K.; Meyerson, S. *Adv. Phys. Org. Chem.* **1968**, *6*, 18–21), but alternate explanations are possible.

[4] Often some of the bisaryne equivalent crystallizes out during this cooling, but dissolves as the butyllithium is added.

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