Reversible Hydrogenation and Dehydrogenation of Cluster Bound Acimidoyl and Alkylidenimido Groups. Synthesis of Complexes Containing Triply Bridging Nitrene and Nitrile Ligands[1]

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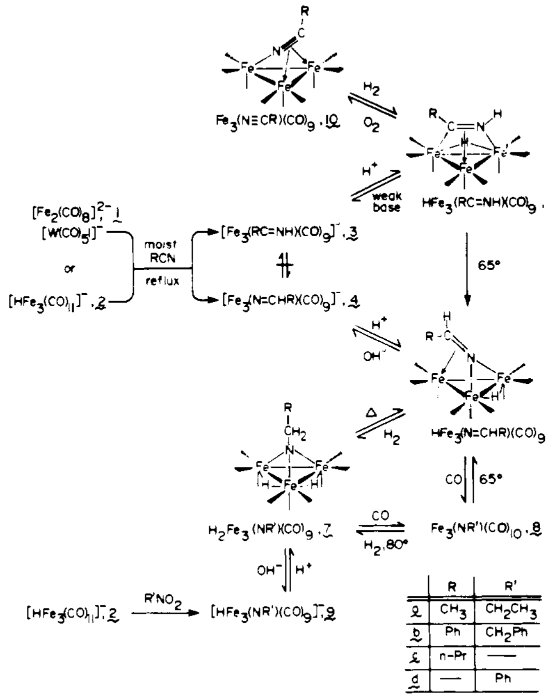
Abstract: $HFe_3(N{=}CHR)(CO)_9$ (**6a,b**)[2] reacts with H_2 or CO to give respectively the nitrene complexes $H_2Fe_3(NR')(CO)_9$ (**7a,b**) or $Fe_3(NR')(CO)_{10}$ (**8a,b**) (**a**, R = CH_3, R′ = CH_2CH_3; **b**, R = Ph, R′ = CH_2Ph). Thermolysis of **7a,b** or **8a,b** converts them back to **6a,b.** Complexes with no hydrogen on the α carbon atom, i.e., **7d** or **8d** (R′ = Ph), cannot form derivatives of type **6** but they are interconverted directly, i.e., treatment of **7d** with CO yields **8d** which can be reversed by heating **8d** in H_2. Treatment of **7a** with base gives $[HFe_3(NR')(CO)_9]^-$ (**9a**), which may also be prepared by reduction of **6a** with sodium borohydride. Furthermore, complexes **9a,d** may be prepared directly by reaction of $CH_3CH_2NO_2$ or $PhNO_2$, respectively, with $[HFe_3(CO)_{11}]^-$. Complex **9a** can be thermally dehydrogenated to $[Fe_3(N{=}CHCH_3)(CO)_9]^-$ (**4a**), but this is suppressed by carbon monoxide. Air oxidation of $HFe_3(RC{=}NH)(CO)_9$ (**5a,c**) gives $Fe_3(RC{\equiv}N)(CO)_9$ (**10a,c**) (**a**, R = CH_3; **c**, R = *n*-Pr) which possesses the first known triply bridging nitrile ligand. Complex **10a** can be reduced with hydrogen to give a mixture of **5a, 6a,** and **7a**, while **10c** is reduced by sodium borohydride to a 1:3 mixture of $[Fe_3(RC{=}NH)(CO)_9]^-$ (**3c**) and $[Fe_3(N{=}CHR)(CO)_9]^-$ (**4c**). An attempt to employ **3a** and **4a** as homogeneous catalysts for the hydrogenation of nitriles resulted in their decomposition to iron metal. Possible pathways for these transformations are discussed.

Introduction

The use of transition-metal clusters as homogeneous catalysts[3] and stoichiometric reagents[4] is currently of great interest.[5] Metal-atom clusters permit a greater variety of interactions with substrates than is possible in mononuclear complexes. Some examples can be cited for the cluster chemistry of iron,[6a,b] but an even richer field has been found for ruthenium and osmium.[6c,d,7] This greater diversity of interactions is also believed to be responsible for the ability of clusters to carry out reactions which mononuclear species generally cannot, such as the reduction of triple bonds.[5] It is often very difficult, however, to prove that the cluster is not merely the precursor to a mononuclear species or even to free metal which then acts as the actual catalyst or reagent.

In 1964 a patent was issued claiming $Fe(CO)_5$ as the catalyst precursor for the high-pressure hydrogenation of nitriles to amines.[8] In a previous paper,[1b] we noted that $Fe(CO)_5$ (probably via $[HFe_3(CO)_{11}]^-$ (**2**)) reacts with (moist) nitriles to give $[Fe_3(RC{=}NH)(CO)_9]^-$ (**3**) and $[Fe_3(N{=}CHR)(CO)_9]^-$ (**4**). We have therefore investigated the chemistry of these complexes to see how they might be related to the catalytic cycle responsible for the hydrogenation of nitriles. The original synthesis of the anions **3** and **4** and the neutral derivatives **5** and **6** isolated from these is summarized in Scheme I together with the interconversion reactions reported in this work. These include the stoichiometric reduction of the C–N triple bond of nitriles on the face of an intact $Fe_3(CO)_9$ cluster complex (transformations **10** to **5** to **6** to **7**). This provides a detailed model for the steps that might be involved in such a reduction on a metal surface. Complex **10a** and homologue **10c,** for which a structure has been determined,[1d] represent the first examples of derivatives containing a triply bridging nitrile.

Scheme I



Results

Hydrogenation and Carbonylation of $HFe_3(N{=}CHR)(CO)_9$ (6). We observed complex **6** to undergo facile reaction either with H_2 or CO at 25 °C (see Scheme I). Spectroscopic data for the products obtained in these and other reactions described in this section for derivatives in which R = CH_3 and R′ = CH_2CH_3 are listed in Table I; the infrared absorptions in the carbonyl stretching region are shown in Figures 1 and 2 (supplementary material). The reaction of H_2 with **6** is preceptible but slow at 1 atm pressure; preparative reactions for **7a** were carried out at 200 psi. Product **7a** was identified by its mass spectrum and ^1H NMR (Table I); the hydrogens are presumed to bridge different edges. In solution under nitrogen, **7a** gradually reverts to **6a.** In a facile manner, **6a** was also found to react with carbon monoxide to give $Fe_3(NCH_2CH_3)(CO)_{10}$ (**8a**) (Scheme I). This complex was also identified by spectroscopic means (Table I), especially by the similarity of its carbonyl IR to that of $Fe_3(NSiMe_3)(CO)_{10}$:[9] ν_{CO} in hexane solution (cm^{-1}) 2088 (w), 2048 (vs), 2019.5 (s), 2014 (m), 1999 (w) and 1743 (s). Gentle heating converts **7a** back to **6a.**

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Table I. Spectral Data for Complexes **7a-10a**

7a	ν_{CO} (C_6H_{12})[a]	2099 (9), 2060 (41), 2036 (100), 2031 (47), 2022 (8), 2003 (47), 1985 (20), 1972 (9) cm^{-1}
	^1H NMR ($CDCl_3$)[b]	τ 5.12, q (J = 7.0 Hz), 2 H; 8.28, t (J = 7.0 Hz), 3 H; 32.45, s, 2 H
	mass spectrum[a,c]	465 (42), 437 (11), 435 (29), 409 (8), 407 (14), 379 (41), 351 (88), 323 (100), 295 (44), 267 (26), 241 (11), 239 (21), 213 (14), 211 (23), 209 (22), 182 (4), 169 (7), 168 (8), 112 (4)
8a	ν_{CO} (C_6H_{12})[a]	2094 (1), 2049 (100), 2020 (51), 2014 (18), 1994 (7), 1730 (s) cm^{-1}
	^1H NMR ($CDCl_3$)	τ 5.32, q (J = 7.0 Hz), 2 H; 8.27, t (J = 7.0 Hz), 3 H
	mass spectrun[a,c]	491 (2), 463 (17), 435 (18), 407 (4), 379 (9), 351 (9), 323 (100), 295 (83), 267 (17), 239 (28), 211 (21), 209 (27), 168 (15); 112 (16), 56 (10)
9a	ν_{CO} (CH_3CN)[a,d]	2044 (8), 2002 (78), 1971 (100), 1954 (70), 1937 (sh), 1891 (12) cm^{-1}
	^1H NMR (CD_3CN)[b,e]	τ 5.45, q (J = 6.5 Hz), 2 H; 8.53, t (J = 6.5 Hz), 3 H; 30.63, s, 1 H
10a	ν_{CO} (C_6H_{12})[a]	2086 (11), 2037 (85), 2027 (100), 2015 (60), 1993 (13), 1983 (10), 1975 (3) cm^{-1}
	^1H NMR ($CDCl_3$)	τ 6.57, s, 3 H
	mass spectrum[a,c]	461 (20), 433 (14), 405 (10), 377 (3), 349 (8), 321 (100), 293 (45), 265 (27), 237 (36), 209 (45), 194 (9), 168 (23), 153 (14), 130 (9), 112 (12)

[a] Relative intensities in parentheses; infrared absorptions in the carbonyl stretching region for complexes **7a** and **9a** and for complexes **8a** and **10a** are given respectively in Figures 1 and 2 (supplementary material). [b] A 0.2-0.5-Hz coupling between N-CH_2 and Fe-H was apparent. [c] m/e values are given for ^{56}Fe only; fragments due to hydrogen loss are omitted unless they are a substantial component. [d] Bu_4N^+ salt. [e] Me_4N^+ salt.

We were interested to know whether transformation between **7** and **8** could occur without intervention by complexes such as **6**; such a direct interconversion would be observed for analogues of **7** or **8** which contain no hydrogen atoms on the α carbon atom, i.e., **7d** (R′ = Ph). Unlike its osmium analogue,[10] **7d** could not be prepared from the trimetal dodecacarbonyl and aniline. We found that it could, however, be prepared from $[HFe_3(CO)_{11}]^-$ and nitrobenzene (vide infra) and carbonylated to give **8d**. In turn, complex **8d** can be thermally hydrogenated back to **7d** but under much milder conditions than those required for the analogous transformation known for ruthenium.[11] It should be noted that for a trimethylsilyl analogue of **8**, namely, $Fe_3(NSiMe_3)(CO)_{10}$, photolysis under an H_2 atmosphere was required to convert it to the corresponding analogue of **7**, i.e., to $H_2Fe_3(NSiMe_3)(CO)_9$.[9b]

Synthesis and Characterization of $[HFe_3(NR')(CO)_9]^-$ (9). Complex **7a** is readily deprotonated by hydroxide to give $[HFe_3(NC_2H_5)(CO)_9]^-$ (**9a**) in a reaction analogous to that of hydride complexes **5a** and **6a**.[1b] The product was characterized by ^1H NMR (Table I) and by its clean reprotonation to **7a**. While anion **9a** is stable toward dehydrogenation at room temperature, it can be converted to **4a** in refluxing acetonitrile (80 °C). Under an atmosphere of carbon monoxide, however, the thermal dehydrogenation is completely suppressed. Complex **4a**, on the other hand, could not be hydrogenated back to **9a** at 1 atm pressure. The mechanistic implications of these observations are set forth in the Discussion section.

Two other methods for synthesizing **9a** and its analogues were also found. The first is the reaction of nitroethane or nitrobenzene with $[HFe_3(CO)_{11}]^-$ to give **9a** or **9d** directly in low to moderate yields. The second is the reduction of **6a** with sodium borohydride.

Attempted Reduction of $HFe_3(CH_3C{=}NH)(CO)_9$ (5a). Unlike **6a**, complex **5a** could not be hydrogenated under conditions less vigorous than those leading to isomerization. In addition, reaction with sodium borohydride leads primarily to deprotonation to give **3a**, rather than reduction of the C=N bond.

Synthesis and Chemistry of $Fe_3(N{\equiv}CR)(CO)_9$ (10). During routine studies of air stability, we found that air oxidation of hexane solutions of **5a** leads to a mixture of iron oxide, $Fe(CO)_5$, and a new complex, $Fe_3(N{\equiv}CCH_3)(CO)_9$ (**10a**) (Scheme I). Product **10a** was identified by its mass spectrum and ^1H NMR (Table I). The bonding in this complex was anticipated to be analogous to that found in the isoelectronic acetylide complexes $CpFe_3(C{\equiv}CR)(CO)_7$[12a] and $HRu_3(C{\equiv}CR)(CO)_9$.[12b] No crystals of **10a** suitable for X-ray structure determination could be obtained, but the butyronitrile analogue **10c** yielded satisfactory single crystals. The mode of bonding shown in Scheme I for the nitrile ligand of **10** has thus been confirmed crystallographically.[1d] It is interesting to note that complex **10a** could not be prepared directly from $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ and acetonitrile owing to decomposition and formation of $Fe(CO)_4(CH_3CH)$, respectively. Reaction of **10a** with hydrogen at 1 atm pressure at 80 °C slowly leads to the formation of a mixture of **5a**, **6a**, and **7a** (Scheme I). Reduction of **10c** with sodium borohydride gives a 3:1 mixture of **4c** and **3c**.

By contrast to the oxidation of **5a**, oxidation of complex **6a** gives only decomposition products.

Attempts to Employ $[Fe_3(CH_3C{=}NH)(CO)_9]^-$ (3a) and $[Fe_3(N{=}CHCH_3)(CO)_9]^-$ (4a) as Homogeneous Catalysts. As noted in the Introduction, we have found that clusters **3** and **4** are formed under the conditions previously patented for the catalytic hydrogenation of nitriles to amines.[8] A most important question therefore concerns the relevance of these clusters to the catalytic cycle. A "crossed" R group experiment was designed employing **3a** and **4a** (R = CH_3) as the catalysts for the hydrogenation of butyronitrile; if catalytic reduction were to take place and the cluster complexes could be recovered, the presence of propyl groups in these clusters would constitute evidence for at least one turnover by the cluster complexes. The conditions employed were milder (155 °C, 1800 psi, 20 h) than those typically employed in the patented process (200 °C, 4500 psi, 9 h)[8] because, if the clusters were indeed the catalysts, a higher specific activity could be anticipated. Also mild conditions would help to optimize recovery of at least a portion of the cluster complexes. Despite these precautions, the cluster complexes were found to be completely decomposed to iron metal, even at less than 5% conversion of the nitrile to amine.

Testing of the anions **3a** and **4a** is equivalent to testing of the neutral species **5a** and **6a** owing to their interconversion through solvent-induced disproportionation reactions.[1b]

Discussion

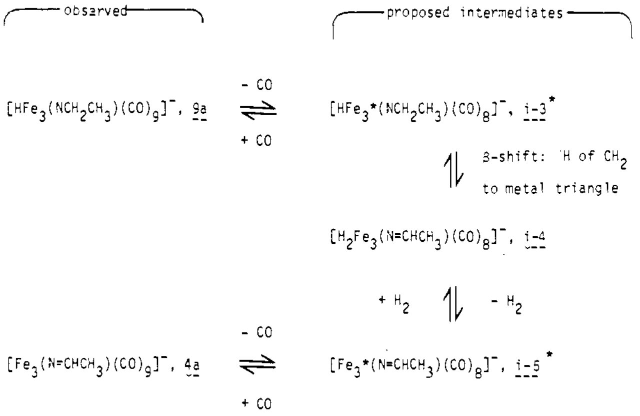
The synthesis of complexes **3-6** has enabled us to carry out the first chemical studies of cluster-bound acimidoyl and alkylidenimido ligands. It is interesting to note that the chemistry of the alkylidenimido complex **6** is based on reversible ligand reduction, while that of the C-iminyl complex **5** is based on reversible ligand oxidation. These results, together with the irreversible isomerization of **5** to **6**, provide a clear example of the elementary steps in the reduction of a nitrile triple bond on the face of an intact cluster. Although reduction of acetylenes has been observed on an osmium cluster complex, these interconversions have not yet been studied in any detail.[6c,d,7]

Interconversion of Alkylidenimido and Nitrene Groups. No triply bridged alkylidenimido complex was known previous to this study.[13] On the other hand, there are several known complexes containing a triply bridging nitrene ligand, e.g., $Fe_3(NSiMe_3)(CO)_{10}$,[9a] $Fe_3(NSiMe_3)(CO)_{10-x}L_x$ (L = PR_3 or $P(OR)_3$, x = 1, 2, or 3),[9b] $H_2Fe_3(NSiMe_3)(CO)_9$,[9b] $Ru_3(NPh)(CO)_{10}$,[11] $H_2Ru_3(NPh)(CO)_9$,[11] $H_2Os_3(NPh)(CO)_9$,[10] and Cp_3Ni_3NR.[14] However, the absence of hydrogens on the α carbon in all of these complexes precludes their conversion to alkylidenimido complexes. Thus the derivatives we have isolated in the present work offered the first opportunity to study the interconversion of these two functional groups. Our findings regarding these transformations suggest the presence of an electronically unsaturated intermediate, $^*Fe_3(NCH_2CH_3)(CO)_9$ (**i-2**),[1b,2] linking the products. Support for the existence of such as intermediate is derived from the facile interconversions with H_2 or CO of derivatives **7** and **8** containing triply bridging nitrene ligands, including those lacking hydrogen atoms on the α carbon. Additionally, intermediate **i-2** is consistent with hydrogen scrambling in **6a**, described in a previous paper.[1b] A hydrocarbon analogue of the transformation of **6** to **7** is observed in the hydrogenation of $H_2Os_3(C{=}CH_2)(CO)_9$ at 125 °C to give $H_3Os_3(CCH_3)(CO)_9$.[7d] When D_2 gas was used, the main product was a dideuterated derivative of the latter but tri- and tetradeuterated species were also present.[7d] NMR spectra showed that the ratio of methyl hydrogen to metal hydrogen was 0.67; thus, preferential attack directly on the carbon ligand was suggested.[7d] It is not clear, however, whether the 0.67 ratio is a kinetic or thermodynamic result. The improbability of direct attack by D_2 on the ligand and the known thermodynamic preference of the C-D and M-H bond pair[1b] over the C-H and M-D bond pair suggest that it may be the result of intramolecular H/D equilibration analogous to what has been observed for $DFe_3(N{=}CHCH_3)(CO)_9$.[1b] Although equilibration between metal- and ligand-bonded hydrogen atoms was not observed in $HDOs_2(C{=}CH_2)(CO)_9$ at temperatures up to 80 °C,[15] such might occur at the higher ranges required in the hydrogenation of the vinylidene complex. Further work will be needed to sort out these possibilities.

The complex $[HFe_3(NC_2H_5)(CO)_9]^-$ (**9a**) cannot dehydrogenate through an intermediate similar to **i-2**[1b,2] because it lacks one of the two cluster hydrogen atoms. It is in fact stable to dehydrogenation at room temperature but can be converted to **4a** by heating at 80 °C. This dehydrogenation is completely arrested in the presence of carbon monoxide. This suggests that the first step in the conversion of **9a** to **4a** is the loss of carbon monoxide to give the electronically unsaturated octacarbonyl derivative **i-3** depicted in Scheme II. The subsequent proposed steps are self-explanatory.

Reduction of Nitro Compounds by $[HFe_3(CO)_{11}]^-$ (2). Landesberg et al.[16] found that nitrobenzenes are reduced to anilines by **2**. Alper et al.[17] later proposed a mechanism for this, but some of the intermediates postulated are untenable because of the extremely electron-deficient iron centers present. Regardless of the correctness of the rest of the mechanism, Alper's complex **7** can be reformulated according to the EAN principle as our complex **9d** (see structure in Scheme II, R′ = Ph). This led us to reinvestigate the reaction of **2** with various nitro compounds under aprotic conditions. The reaction is not a clean one, but **9a** and **9d** are obtained in about 25 and 10% yield, respectively, from the treatment of **2** with the appropriate nitro compound. The low yields may be due to side reactions of **2**, namely, its cleavage to $[HFe(CO)_4]^-$ and its thermolysis to as yet unidentified species observed as byproducts. The mass spectrum of **7d** (the protonated derivative of **9d**) shows peaks due to free aniline.[18] These results implicate complex **9** as at least one of the intermediates in the reduction of nitrobenzenes to anilines by **2**. As noted by previous workers,[11] clusters of this type are probably also important in the $Ru_3(CO)_{12}$-catalyzed conversion of nitrobenzene to aniline and urea.[19]

Scheme II



Synthesis of $Fe_3(N{\equiv}CR)(CO)_9$ (10) by Oxidation of $HFe_3(RC{=}NH)(CO)_9$ (5). The air oxidation of **5** is a most unusual organometallic reaction; this complex is dehydrogenated to give **10**, the first η^3-nitrile cluster complex. Attempts to prepare **10a** directly from acetonitrile and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ were unsuccessful owing to predominance in this pathway of the Hieber disproportionation reaction.[20] We have not studied the oxidation of **5** in detail, but it seems likely that it is initiated by the abstraction of the N-H hydrogen as H^- by O_2. Subsequent loss of the highly acidic metal hydrogen as a proton together with a 30° ligand rotation would give complex **10**. The same cationic intermediate could also be reached in a two-step process by abstraction of H· followed by one-electron oxidation.

Hydrogenation of $Fe_3(N{\equiv}CR)(CO)_9$ (10). Complex **10a** is rather unreactive compared to the other neutral complexes reported here. At 80 °C and 1 atm of hydrogen gas pressure, however, it can be slowly converted to a mixture of **5a, 6a,** and **7a.** Because **5a** cannot be prepared from **6a** or **7a,** it must be a primary product of the hydrogenation of **10a.** Complexes **6a** and **7a** are probably secondary products resulting from the isomerization of **5a** to **6a** and the subsequent hydrogenation of **6a** to **7a.** The reluctance of low-valent complexes to exceed the EAN electron count requires that **10** undergo loss of CO or conversion of the six-electron donor nitrile to a four-electron donor prior to addition of hydrogen. The switch in nitrile bonding to a four-electron donor has structural precedence in the 46-electron complex $Fe_3(PhC{\equiv}CPh)(CO)_9$.[21] The hydrogenation of **10** to **7** is analogous to the known hydrogenation of the isoelectronic acetylide complex $HOs_3(C{\equiv}CH)(CO)_9$ to $H_3Os_3(CCH_3)(CO)_9$,[6d] except that the latter reaction may occur by a different mechanism owing to the presence of a metal hydride.

Borohydride Reductions. In the treatment of $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**) with borohydride, attack occurs as expected at the carbon of the alkylidenimido group in **6a** to give **9a.** A slight side reaction, namely, deprotonation of **6a,** is also observed, complicating isolation of pure **9a** by this route. This side reaction dominates when **5a** is treated with borohydride.

Reduction of $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$ (**10c**) with sodium borohydride gave a 1:3 mixture of **3c** and **4c.** This is distinctly different than the ratio of 4:1 observed in the original synthesis of anions **3a** and **4a.**[1b] Since the anions do not interconvert under these circumstances,[1b] these results may well reflect kinetic control of attack at nitrogen vs. carbon by BH_4^-. The fact that any attack at nitrogen is observed at all is probably related to the ability of the cluster to modify reactivity by serving as an electronic buffer through charge delocalization.

Conclusions

Despite the demonstration of the stepwise and, in some cases, reversible reduction of the carbon-nitrogen triple bond on the face of a triiron cluster, it is significant that none of the complexes isolated here is stable under the conditions required for the catalytic reduction of nitriles. Do these observations therefore have any relevance to the catalytic reaction? We believe that they do.

Clearly, the formation of iron metal from these cluster complexes indicates that carbon monoxide is too labile a ligand to maintain the integrity of the cluster under the catalytic conditions. The isolated species do, however, demonstrate how several metal atoms acting in concert can lead to the reduction of nitriles. As such, they serve as a model for what may be happening at the metal surface of the actual iron metal catalyst. The adjacent and subsurface metal atoms in the active metal particles may simply be thought of as less liable "ligands". Similar to the carbonyl groups in discrete clusters, these "ligands" stabilized the multimetal atom groupings required for the reduction and also help to delocalize electronic fluctuations.

Perhaps the most crucial point in a catalytic circle for the homogeneous species is the desorption of products. This is the point at which the present species failed to form a closed cycle. The conditions needed to displace amine from the dihydrodonitrene precursor complex are vigorous enough to lead to cluster decomposition, resulting in metallic iron. Although excess ligand (ancillary or reactant) can sometimes prevent this decomposition, the presence of such ligands often also leads to coordinative saturation which prevents the required transformations from occurring in the first place. Our work thus indicates some of the limitations of homogeneous systems for catalyst of reactions observed to occur with great facility in heterogeneous systems.

Experimental Section

The previous paper[1b] should be consulted regarding general information about chemicals, instrumentation, and reaction conditions. Tetrahydrofuran was dried by distillation from sodium benzophenone.

Syntheses of $H_2Fe_3(NCH_2R)(CO)_9$ (7) by Hydrogenation of $HFe_3(N{=}CHR)(CO)_9$ (6). A. R = CH_3. A solution of **6a** (0.266 g, 575 μmol) in hexane (150 mL) was treated with hydrogen (200 psi) in a Hoke bomb with occasional shaking for 48 h. The bomb was then vented by burning the slowly escaping hydrogen at the valve opening. The yellow-brown solution was concentrated, passed through a short silica gel column to remove any decomposition products, and collected under nitrogen. (This complex is the most air sensitive of the neutral ones prepared in this work.) Removal of solvent gave **7a** (0.231 g, 87%). Larger scale reactions employed benzene as solvent for greater solubility. The analytical sample was recrystallized from hexane. Anal. Calcd for $C_{11}H_7Fe_3NO_9$: C, 28.43; H, 1.52; N, 3.01. Found: C, 24.18; H, 1.63; N, 2.99.

B. R = Ph. Complex **7b** was prepared in an analogous manner. IR ν_{CO} in cyclohexane (cm^{-1}): 2099 (16), 2061 (83), 2040 (99), 2030 (100), 2024 (28), 2002 (77), 1985 (32), 1972 (15).

Attempted Synthesis of 7b from $Fe_3(CO)_{12}$ and Aniline. A solution of $Fe_3(CO)_{12}$ (0.470 g, 0.93 mmol) and aniline (0.1 mL, 1.10 mmol) in benzene (30 mL) was heated under reflux for 4 h. The solution turned from green to red and infrared spectra indicated the presence of unkonwn, air-sensitive neutral species but no **7b**.

Thermal Dehydrogenation of 7a to 6a. A solution of **7a** in hexane was allowed to stand overnight. Infrared spectra indicated that partial conversion to **6a** had occurred. The solution was then refluxed for 4.5 h, which completed the transformation.

Synthesis of $Fe_3(NC_2H_5)(CO)_{10}$ (8a) by Carbonylation of 6a. Carbon monoxide was bubbled through a solution of **6a** (36 mg, 78 μmol) in cyclohexane (35 mL) for 50 h. The solvent was then evaporated and the residue chromatographed on a short silica gel column to give **8a** (38 mg, 100%). The analytical sample was recrystallized from hexane. Anal. Calcd for $C_{12}H_5Fe_3NO_{10}$: C, 29.37; H, 1.03; N, 2.85. Found: C, 29.48; H, 0.97; N, 3.01.

Thermal Decarbonylation of 8a to 6a. A solution of **8a** in hexane was refluxed for 8 h, at which time infrared spectra showed complete conversion to **6a.**

Synthesis of $Fe_3(NPh)(CO)_{10}$ (8d) by Carbonylation of 7d. Carbon monoxide was bubbled through a solution of **7d** (99 mg) in refluxing cyclohexane for 3 h. The solvent was evaporated and the residue chromatographed on silica gel to remove traces of **7d** (band 1). Band 2 gave **8d** (58 mg, 55%). IR ν_{CO} in cyclohexane (cm^{-1}): 2095 (5), 2054 (100), 2049 (96), 2025 (76), 2016 (21), 1996 (9), 1988 (4), 1739 (~15). ^{1}H NMR ($CDCl_3$): τ (ppm) 3.52 (m).

Thermal Hydrogenation of 8d to 7d. Hydrogen was bubbled through a solution of **8d** in refluxing cyclohexane for 1 h, at which time infrared spectra indicated that complete conversion to **7d** had occurred.

Synthesis of $[HFe_3(NC_2H_5)(CO)_9]^-$ (9a) by Deprotonation of 7a. A solution of **7a** (0.261 g, 0.56 mmol) in methanol (25 mL) was treated with methanolic potassium hydroxide (1.7 mL of 0.36 M, 0.61 mmol) for 20 min. Addition of tetrabutylammonium iodide (0.244 g, 0.66 mmol) in water (50 mL) gave a black precipitate which was collected by filtration and washed with water. The product was dissolved in methanol, filtered, and concentrated. Addition of water to the cloud point and cooling at −20 °C gave **9a** (0.241 g, 61%). Anal. Calcd for $C_{27}H_{42}Fe_3N_2O_9$: C, 45.91; H, 6.01; N, 3.97. Found: C, 38.68; H, 6.63; N, 4.21.

Synthesis of $H_2Fe_3(NR')(CO)_9$ (7) from Nitroethane or Nitrobenzene and $[HFe_3(CO)_{11}]^-$ (2). A. R′ = C_2H_5. A solution of nitroethane (0.65 mL of a 1:10 tetrahydrofuran dilution, 904 μmol) and **2** (0.470 g, 853 μmol) in tetrahydrofuran (30 mL) was heated under reflux for 15 h, during which time the solution turned from violet to dark red-brown. The solvent was then evaporated and the residue extracted with diethyl ether until the extracts were pale red. The infrared spectrum of the ether-insoluble residue in acetonitrile showed only two bands, a weak one at 2008 cm^{-1} and a very strong, broad one at 1948 cm^{-1}. We have found that this complex can also be obtained from the thermolysis of **2** in tetrahydrofuran. Further attempts at characterization of this species have thus far not proved successful. The combined ether extracts were taken to dryness on an aspirator. Infrared spectra indicated that the residual solid consisted of $[HFe_3(NC_2H_5)(CO)_9]^-$ (**9a**) and $[HFe(CO)_4]^-$. This mixture was then treated with a few milliliters of water and acetic acid (30 mL). The red solution was extracted with hexane and then further acidified with water and excess phosphoric acid. Hexane extraction was continued until the aliquots were nearly colorless. Chromatography gave complex **7a** (91 mg, 23%), sometimes contaminated with $Fe_3(CO)_{12}$.

B. R′ = Ph. A solution of nitrobenzene (1.8 mL of a 1:10 tetrahydrofuran dilution, 1.75 mmol) and **2** (0.942 g, 1.71 mmol) in tetrahydrofuran (40 mL) was heated under reflux for 18 h and then worked up as described for R′ = C_2H_5, except that repeated chromatography could be used to remove $Fe_3(CO)_{12}$. This gave complex **7d** (99 mg, 11%). IR ν_{CO} in cyclohexane (cm^{-1}): 2101 (17), 2064 (91), 2041 (100), 2032 (62), 2028 (31), 2009 (75), 2002 (11), 1985 (32), 1975 (22).

Attempted Hydrogenation of $[Fe_3(N{=}CHCH_3)(CO)_9]^-$ (4a). Hydrogen was bubbled through a solution of **4a** in refluxing acetonitrile for 24 h. Infrared spectra indicated that no reaction had occurred.

Dehydrogenation of $[HFe_3(NC_2H_5)(CO)_9]^-$ (9a). A solution of **9a** in acetonitrile was refluxed for 18 h, which gave nearly complete conversion to **4a**. When repeated under carbon monoxide, no reaction occurred.

Reduction of $HFe_3(N{=}CHCH_3)(CO)_9$ (6a) with Sodium Borohydride. A solution of **6a** (80 mg) was treated with sodium borohydride (12 mg) in tetrahydrofuran (25 mL) for 1.5 h, at which time infrared spectra indicated that conversion to $[HFe_3(NC_2H_5)(CO)_9]^-$ had occurred. The solvent was evaporated and the resulting solid acidified with phosphoric acid to give $H_2Fe_3(NC_2H_5)(CO)_9$ (74 mg) contaminated with a little **6a**.

Attempted Hydrogenation of $HFe_3(CH_3C{=}NH)(CO)_9$ (5a). A solution of **5a** in hexane was treated with hydrogen (200 psi) in a Hoke bomb for 4 days. Infrared spectra at that time indicated that no reaction had occurred.

Reaction of 5a with Sodium Borohydride. A solution of **5a** (301 mg) was treated with sodium borohydride (31 mg) in tetrahydrofuran (40 mL) for 3 h, at which time infrared spectra indicated that conversion to $[Fe_3(CH_3C{=}NH)(CO)_9]^-$ had occurred. Acidification with phosphoric acid and extraction with hexane followed by chromatography gave two bands. The first band was a mixture of $Fe_3(CO)_{12}$, $H_2Fe_3(NC_2H_5)(CO)_9$, and a small amount of $HFe_3(N{=}CHCH_3)(CO)_9$. The bulk of the product was found in the second band, which consisted of **5a.**

Syntheses of $Fe_3(RCN)(CO)_9$ (10) by Oxidation of $HFe_3(RC{=}NH)(CO)_9$ (5). A. R = CH_3. A solution of **5a** (0.464 g, 1.00 mmol) in hexane was left exposed to air *without stirring* for about 50 h. A precipitate of iron oxide was present and infrared spectra showed that the solution contained about a 1:2 mixture of **5a** and **10a.** The solvent was evaporated and the residue chromatographed on a short silica gel column. The first band gave **10a** (86 mg, 19%). The analytical sample was recrystallized from dichloromethane at −20 °C. Anal. Calcd for $C_{11}H_3Fe_3NO_9$: C, 28.68; H, 0.66; N, 3.04. Found: C, 28.51; H, 0.61; N, 3.03. IR: ν_{CO}, see Table I; ν_{CN} in C_2Cl_4 (cm^{-1}) 1610.[22]

B. R = Ph. Complex **10b** was prepared in an analogous manner from **5b** (60 mg) in about 18% yield after a 3-day reaction. IR ν_{CO} in cyclohexane (cm^{-1}): 2086 (16), 2038 (72), 2029 (100), 2016 (45), 2004 (4), 1995 (14), 1984 (9).

C. R = Pr. Complex **10c** was prepared in an analogous manner from **5c** (0.7 g) in about 25% yield after a 5-day reaction. IR ν_{CO} in cyclohexane (cm^{-1}): 2086 (11), 2036 (81), 2027 (100), 2015 (56), 1992 (12), 1981 (11), 1974 (3). ν_{CN} in C_2Cl_4 (cm^{-1}): 1601.[22] ^1H NMR ($CDCl_3$, τ in ppm, J in Hz): 6.40, t (J = 7.5), 2 H; 7.97, sextet (J = 7.5), 2 H; 8.82, t (J = 7.5), 3 H.

Attempted Direct Synthesis of 10a. A. A solution of $Fe_3(CO)_{12}$ in benzene was treated with 1 equiv of acetonitrile at reflux for 2 h, during which time complete decomposition occurred.

B. $Fe_2(CO)_9$ was treated with acetonitrile in benzene solution. Infrared spectra indicated the formation of $Fe(CH_3CN)(CO)_4$ and trace amounts of an unidentified complex but no **10a.**

Hydrogenation of $Fe_3(CH_3CN)(CO)_9$ (10a). Hydrogen was bubbled through a solution of **10a** in refluxing cyclohexane for 20 h. Infrared spectra and chromatographic workup showed that a mixture of **10a, 5a, 6a,** and **7a** was present.

Reduction of $Fe_3(PrCN)(CO)_9$ (10c) with Sodium Borohydride. A solution of **10c** (123 mg) in tetrahydrofuran was treated with an excess of sodium borohydride for 20 h, at which time infrared spectra indicated that a mixture of **3c** and **4c** was present. The solvent was removed, the residue was acidified, and the hexane extracts were chromatographed. Band 1 gave **6c** (45 mg) contaminated with traces of **7c** and **10c.** Band 2 yielded **5c** (13 mg).

Attempted Catalytic Hydrogenation of Butyronitrile. Butyronitrile (30 mL, 340 mmol) containing a mixture of **3a** and **4a** (0.713 g, 1.33 mmol, prepared from **5a** by deprotonation with hydroxide) was placed in a glass-lined autoclave (previously flushed with nitrogen) and pressurized to 1800 psi with hydrogen. The autoclave was placed in a rocker and heated at 155 °C for 20 h. The hydrogen was then vented and the contents of the autoclave transferred to Schlenk flask. A large amount of iron metal was presented and the liquid had no red coloration indicating the absence of cluster complexes. Infrared spectra showed trace amounts (<50 mg) of $[HFe(CO)_4]^-$ and NMR spectra showed that less than 5% conversion of nitrile to amine had occurred.

A similar run using $Fe(CO)_5$ (0.5 mL) at 175 °C for 15 h gave 40% conversion but again only iron metal was present when the autoclave was opened.

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Supplementary Material Available: Infrared spectra, Figures 1 and 2 (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Taken in part from the Dissertation of M. A. Andrews, University of California, Los Angeles, 1977. This is the third of a series of papers relating to the reduction of acetonitrile on the face of a triiron cluster complex. For the first paper, see (b) M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, **101**, 7238 (1979). For the second paper, see (c) M. A. Andrews, G. van Buskirk, C. B. Knobler, and H. D. Kaesz, *ibid.*, preceding paper in this issue. For the next part see (d) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, *ibid.*, following paper in this issue.

(2) (a) In order to preserve continuity and facilitate correlation of the results in the present work with that of the other papers in this series, the numbering of derivatives in the first paper, ref 1b, is being retained in the present and succeeding works. (b) Proposed intermediates have been numbered with the prefix I to clearly distinguish them from isolated and characterized complexes. Electronically unsaturated clusters have been denoted by an asterisk. These contain 46 e^- as opposed to 48 e^- for the closed valence shell of a triangular metal cluster complex. (c) Following consultations with K. L. Loening, Nomenclature Director of Chemical Abstracts Service, Columbus Ohio 43210, the following *Chemical Abstracts* index name is suggested for the oxidation product **10a**, $Fe_3(N{\equiv}CCH_3)(CO)_9$: *triangulo*-[$\mu_3$-[(*N*,1-$\eta$;*N*,1-$\eta$)-acetonitrile-*N*]]nonacarbonyltriiron. In line with IUPAC rules for inorganic chemistry[2d] the following systematic name is suggested: [μ_3-[(*N*-1-η:*N*-1-η)-acetonitrile-*N*]]nonacarbonyl-*triangulo*-triiron. (d) "IUPAC Nomenclature of Inorganic Chemistry", 2nd ed., Crane Russak & Co., New York, 1970; see also *Pure Appl. Chem.*, **26**, 1 (1971).

(3) (a) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977); (b) R. C. Ryan, C. U. Pittman, Jr., and J. P. O'Connor, *ibid.*, **99**, 1986 (1977); (c) G. D. Mercer, J. S. Shu, T. B. Rauchfuss, and D. M. Roundhill, *ibid.*, **97**, 1967 (1975); (d) W. E. Walker, E. S. Brown, and R. L. Pruett, U.S. Patent 3 878 292 (April 15, 1975); *Chem. Abstr.*, **83**, 45426y–45428a (1975); (e) N. V. Kutepow and H. Kindler, *Angew. Chem.*, **72**, 802 (1960); but see F. Wada and T. Matsuda, *Chem. Lett.*, 197 (1974).

(4) (a) H. des Abbayes and H. Alper, *J. Am. Chem. Soc.*, **99**, 98 (1977); (b) T. Mitsudo, Y. Watanabe, M. Tanaka, S. Atsuka, K. Yamamoto, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **48**, 1506 (1975); (c) J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972); (d) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976); (e) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).

(5) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) *ibid.*, **85**, 451 (1976); (c) R. Ugo, *Catal. Rev. Sci. Eng.*, **11**, 225 (1975); (d) E. Band, W. R. Pretzer, M. G. Thomas, and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 7380 (1977).

(6) (a) W. Hubel in "Organic Synthesis via Metal Carbonyls", Vol. I, I. Wender and P. Pino, Eds., Interscience, New York, 1968, p 273; (b) G. Deganello, P. Uguagliati, L. Callagaro, P. L. Sandrini, and F. Zingales, *Inorg. Chim. Acta*, **13**, 247–289 (1975); (c) J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, **44**, 43–78 (1975); (d) A. J. Deeming, S. Hasso, and M. Underhill, *Proc. Int. Conf. Coord. Chem., 16th*, 4.35 (1974).

(7) (a) A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975); (b) W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.*, **87**, C27 (1975); (c) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1415 (1979); (d) A. J. Deeming and M. Underhill, *J. Chem. Soc., Chem. Commun.*, 277 (1973); (e) J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1978); (f) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977); (g) O. Gambino, R. P. Ferrari, M. Chinone, and G. A. Vaglio, *Inorg. Chim. Acta*, **12**, 155 (1975).

(8) D. R. Levering, U.S. Patent 3 152 184 (Oct 6, 1964); *Chem. Abstr.*, **62**, 427*g* (1965).

(9) (a) E. Koerner von Gustorf and R. Wagner, *Angew. Chem., Int. Ed. Engl.*, **10**, 910 (1971); (b) I. Fischler, R. Wagner, and E. A. Koerner von Gustorf, *J. Organomet. Chem.*, **112**, 155 (1976).

(10) C. C. Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1013 (1974).

(11) E. Sappa and L. Milone, *J. Organomet. Chem.*, **61**, 383 (1973).

(12) (a) K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **48**, 1616 (1975); (b) G. Gervasio and G. Ferraris, *Cryst. Struct. Commun.*, **3**, 447 (1973); see also M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 2260 (1977).

(13) Some μ_2-η^2-alkylidenimido complexes are known; see discussion and ref 20 in the preceding work.[1c]

(14) J. Muller, H. Dorner, and F. H. Kohler, *Chem. Ber.*, **106**, 1122 (1973).

(15) W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **90**, C13 (1975).

(16) J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972).

(17) H. des Abbayes and H. Alper, *J. Am. Chem. Soc.*, **99**, 98 (1977).

(18) Peaks and intensities due to free aniline in the mass spectrum of **9d** (70 eV, 90 °C) compared with the literature values (m/e, I_{obsd}, I_{lit}): 93, 100, 100; 66, 26, 33; 65, 15, 18; 39, 9, 18; 92, 11, 11; 46.5, 5, 9; 28, - - -, 8; 38, 3, 8. Cf. J. G. Grasselli and W. M. Ritchey, "Atlas of Spectral Data and Physical Constants for Organic Compounds", Vol. II, Chemical Rubber Publishing Co., Cleveland, Ohio, 1975, p 1429.

(19) F. L'Epplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970).

(20) See W. Hieber, *Adv. Organomet. Chem.*, **8**, 1 (1970), and references cited therein.

(21) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Am. Chem. Soc.*, **88**, 292 (1966).

(22) (a) ν_{CN} in **10a** and **10c** indicate a bond order close to two; $\nu_{C=N}$ is normally observed in the range 1640–1633 cm^{-1}.[22c] This observation is consistent with the C–N bond length of 1.260 (3) Å observed in **10c.**[1d] (b) For **10c** an additional band of intensity about the same as that of the 1601-cm^{-1} band is seen at 1515 cm^{-1}. Both these bands are well separated from the middle energy absorptions of the *n*-propyl group, the highest of which lies around 1450 cm^{-1} both in **10c** as well as in free butyronitrile. The origin of the 1515-cm^{-1} band is unknown at present. (c) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd ed., Wiley, New York, 1975, p 301.