only in the presence of excess carboranyllithium it is possible that the deprotonation of a coordinated phosphine is responsible for their formation.

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Synthesis of Triiron Carbonyl Cluster Complexes Containing Isomeric Triply Bridging Acimidoyl or Alkylidenimido Group Derived from the Reduction of Organic Nitriles[1]

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Abstract: Reaction of various iron carbonyls such as $[Fe_2(CO)_8]^{2-}$ (**1**) in the presence of $[W(CO)_5I]^-$, $[HFe_3(CO)_{11}]^-$ (**2**), or $Fe(CO)_5$ in the presence of NaI with refluxing nitriles gives $[Fe_3(RC=NH)(CO)_9]^-$ (**3**) and $[Fe_3(N=CHR)(CO)_9]^-$ (**4**) (**a**, R = CH_3; **b**, R = Ph; **c**, R = *n*-Pr). These products contain triply bridging acimidoyl or alkylidenimido groups and may be protonated to give the neutral complexes $HFe_3(RC=NH)(CO)_9$ (**5**) and $HFe_3(N=CHR)(CO)_9$ (**6**), respectively. Deprotonation of **6a** gives pure **4a** but deprotonation of **5a** gives either pure **3a** or a mixture of both **3a** and **4a**, depending on the base employed. Anions **3a** and **4a** do not interconvert but the neutral complex **5a** isomerizes irreversibly to **6a** at 65 °C. The complexes have been characterized by infrared, ^1H NMR, mass spectroscopy, and single-crystal X-ray structure determination (see paper immediately following). The C–N stretching absorptions of **5a** and **6a** have been identified at 1353 and 1325 cm^{-1}, respectively. An intramolecular H/D exchange is observed for monodeuterated complex **6a**: $DFe_3(N=CHCH_3)(CO)_9 \rightleftharpoons HFe_3(N=CDCH_3)(CO)_9$ ($CDCl_3$, 35 °C). For this exchange, $k_f = 6 \times 10^{-4} s^{-1}$ and $K_{eq} = 1.2 \pm 0.2$. Complex **5a** forms hydrogen-bonded adducts via the N–H hydrogen with a variety of bases. The average shift in ν_{CO} upon adduct formation is correlated with the base strength.

Introduction

The π coordination chemistry of ligands containing carbon–carbon multiple bonds is vast.[2] In contrast, the π coordination chemistry of ligands containing carbon–nitrogen multiple bonds is limited, primarily owing to the preferential formation of σ-bonded adducts. Thus, imine, nitrile, alkylidenimino ($N=CR_2$), and pyridine ligands form nitrogen-bonded adducts,[3] while isonitriles form carbon-bonded adducts.[4] Although a few π-bonded nitriles[3,5] and heteroaromatics[3] are known, π bonding is more common when there are no lone pairs present on nitrogen such as in the iminium[6] $[R_2C=NR_2]^+$, nitrilium (iminoacyl),[7] $[RC\equiv NR]^+$, and keteniminium[3,8] $[R_2C=C=NR_2]^+$ cations.

In theory the use of clusters should provide a means for synthesizing complexes of π coordinated ligands containing carbon–nitrogen multiple bonds or, for that matter, other hetero-unsaturated linkages such as $C=O$ or $N=N$. The presence of several metal atoms in the cluster allows for a greater diversity of bonding interactions than is possible for an isolated metal atom.[9] This is demonstrated by the increasingly rich cluster chemistry of unsaturated hydrocarbon ligands.[10] In the case of a hetero-unsaturated ligand, one metal could be used to tie up the heteroatom lone pair through a σ bond, permitting one (or more) other metal atom(s) to coordinate in a π fashion to the ligand multiple bond.[11] In practice, a number of clusters are known which contain σ-bonded nitrile,[12] pyridine,[13] isonitrile,[12] acimidoyl ($RC=NR$),[13] or alkylidenimido ($:N=CR_2$),[14] and *C,C*-iminylidenium ($\cdot C=NR_2$)[13,15] ligands. However, we are aware of only a few cases where π coordination is present in addition to σ coordination, namely, in $HOs_3(RC=NR')(CO)_9$ (R = H, R' = CH_3;[13a] R = Ph, R' = CH_3;[13b] R = H, R' = Ph)[13c] and $Ni_4(CNR)_7$.[16]

Since to date most studies of hydridocarbonyl cluster compounds have involved the precious metals (primarily Re, Ru, and Os), we have been attempting to extend our studies to that of the more common metals. An unexpected result has led us to the preparation of several novel iron cluster complexes containing π-bonded acimidoyl or alkylidenimido groups; see Scheme I. Because the clusters reported here can be readily prepared in gram quantities, it has been possible to study a wide range of their physical and chemical properties. These results are detailed in this and the following papers.[1]

Results

Synthesis of the Neutral Complexes $HFe_3(CH_3C=NH)(CO)_9$ (5a) and $HFe_3(N=CHCH_3)(CO)_9$ (6a). One approach to the synthesis of cluster complexes is the reaction of a metal anion with a complex which contains a readily displaceable ligand. For example, the reaction of $[Mn(CO)_5(CH_3CN)]^+$ with $[Fe_2(CO)_8]^{2-}$ (**1**) gives $[MnFe_2(CO)_{12}]^-$.[17] By analogy we treated $[W(CO)_5I]^-$ with **1** in refluxing acetonitrile, hoping to obtain $[WFe_2(CO)_{12}]^{2-}$. No mixed metal products were obtained; however, a mixture of anions (later shown to consist of $[Fe_3(CH_3C=NH)(CO)_9]^-$ (**3a**) and $[Fe_3(N=CHCH_3)(CO)_9]^-$ (**4a**)) together with $W(CO)_3(CH_3CN)_3$ was produced. In order to facilitate separation and product identification, the anionic species were acidified with phosphoric acid. The resulting neutral material was readily resolved into two components by column chromatography. With the aid of a variety of spectroscopic data (Table I and vide infra) it was possible to deduce that the two complexes are $HFe_3(CH_3C=NH)(CO)_9$ (**5a**, 31% yield) and $HFe_3(N=CHCH_3)(CO)_9$ (**6a**, 8% yield). The structures of both of these represented in Scheme I have been confirmed by single-crystal

Table I. Spectral Data for Compounds **3a–6a**

	[Fe$_3$(CH$_3$C=NH)(CO)$_9$]$^-$ (**3a**)	[Fe$_3$(N=CHCH$_3$)(CO)$_9$]$^-$ (**4a**)
ν_{CO}(CH$_3$CN)^{a,b}	2032 (16), 1972 (100), 1965 (90), 1942 (55), 1917 (24) cm^{-1}	2037 (8), 1975 (100), 1949 (32), 1930 (11), 1919 (sh) cm^{-1}
ν_{NH}(CD$_3$CN)^c	3250 cm^{-1}	
^{1}H NMR (CD$_3$CN)^c	τ 7.41, s, 3 H; 6.85, q (J = 7 Hz), 8 H; 8.80, t (J = 7 Hz), 12 H	τ 3.73, q (J = 5 Hz), 1 H; 8.00, d (J = 8 Hz), 3 H; 6.85, q (J = 7 Hz), 8 H; 8.80, t of t (J = 7, 2 Hz),^{d} 12 H

	HFe$_3$(CH$_3$C=NH)(CO)$_9$ (**5a**)	HFe$_3$(N=CHCH$_3$)(CO)$_9$ (**6a**)
ν_{CO}(C$_6$H$_{12}$)^a	2088 (10), 2050 (56), 2022 (100), 2014 (62), 2003 (23), 1991 (8), 1971 (7), 1964 (5) cm^{-1}	2089 (9), 2051 (66), 2028 (100), 2013 (67), 2001 (22), 1995 (9), 1972 (7) cm^{-1}
ν_{NH}	3272 (s) cm^{-1}	
ν_{CH}	2974 (w), 2934 (w), 2900 (m), 2820 (w) cm^{-1}	3020 (w), 2970 (w), 2911 (m), 2849 (w) cm^{-1}
δ_{CH}^e	1429 (m), 1368 (s) cm^{-1}	1464 (w), 1419 (m), 1372 (s) cm^{-1}
ν_{CN}^e	1353 (s) cm^{-1}	1325 (s) cm^{-1}
^{1}H NMR (CDCl$_3$)	τ 7.38, s, 3 H; 36.72, s, 1 H	τ 3.55, d of q (J = 5, 2 Hz), 1 H; 7.76, d (J = 5 Hz), 3 H; 28.98, d (J = 2 Hz), 1 H
mass spectrum^{a,f}	463 (34), 435 (28), 407 (23), 379 (13), 351 (22), 323 (100), 295 (100), 280 (8), 267 (68), 239 (40), 211 (23), 209 (25), 169 (6), 168 (11), 155 (8), 153 (6), 149 (9), 112 (13)	463 (28), 435 (30), 407 (7), 379 (20), 351 (16), 323 (100), 295 (91), 267 (33), 239 (61), 211 (47), 209 (58), 169 (23), 168 (36), 154 (7), 153 (21), 138 (11), 113 (20), 112 (43), 98 (12), 84 (18), 56 (32)

^{a} Relative intensities in parentheses; infrared absorptions in the carbonyl stretching region for anions **3a** and **4a** and the neutral complexes **5a** and **6a** are given respectively in Figures 1 and 2 (supplementary material). ^{b} (CH$_3$)$_4$N$^+$ salt. ^{c} (C$_2$H$_5$)$_4$N$^+$ salt. ^{d} 1:1:1 triplets of 1:2:1 triplet due to ^{14}N coupling. ^{e} Assignment determined by deuterium labeling (see text). ^{f} m/e values are given for ^{56}Fe ions only; fragments due to hydrogen loss are omitted unles they are a substantial component.

Scheme I
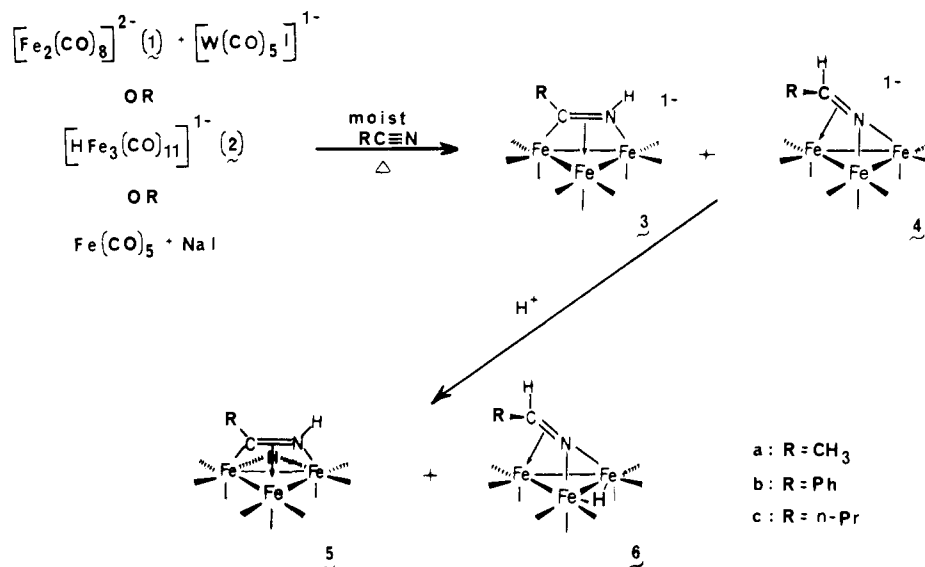
X-ray study, which included location of the metal hydride.[1b]

Investigations into Factors Controlling the Yields of 5a and 6a. The absence of tungsten-containing cluster complexes in the isolated products led us first to examine whether **5a** and **6a** could be synthesized from acetonitrile and reagents containing only iron such as Fe(CO)$_5$, [HFe(CO)$_4$]$^-$, Fe$_2$(CO)$_9$, [HFe$_2$(CO)$_8$]$^-$, Fe$_3$(CO)$_{12}$, [HFe$_3$(CO)$_{11}$]$^-$, and [Fe$_3$(CO)$_{11}$]$^{2-}$. Results of these and other experiments discussed in this section are presented in Appendix I, Tables A–E, as supplementary material. The results starting only with iron carbonyls are shown in Table A; the yields of **5a** were significantly lower, ranging from trace quantities up to 7% compared to the 31% obtained under optimum conditions ([Fe$_2$(CO)$_8$]$^{2-}$ and [W(CO)$_5$I]$^-$; see Table D). A further problem when working with only the iron carbonyls is the presence in the final mixture of Fe$_3$(CO)$_{12}$, which elutes together with **6a** and interferes with a determination of its yield. The Fe$_3$(CO)$_{12}$ is

produced from the decomposition of [HFe(CO)$_4$]$^-$ during the acidification step. This and other ionic byproducts are formed even when neutral carbonyls are employed owing to the base-catalyzed disproportionation reaction.[18,19] The only example of nitrile-induced base disproportionation of iron carbonyls known to us is in a patent claiming Fe(CO)$_5$ as a catalyst precursor for the hydrogenation of nitriles to amines.[20] It is noted in this patent that the reaction of Fe(CO)$_5$ in refluxing nitriles leads to infrared spectral changes, but no complexes were isolated. Our studies (Table A, Appendix I) show that intermediate complexes **3a** or **4a** and neutral complexes **5a** or **6a** formed after acidification are present in only very small amounts under these conditions. A great deal of metallic iron is also observed. The relevance of these observations to the patented catalytic hydrogenation is discussed in a subsequent paper.[21]

The effect of group 6 metal carbonyls was also tested by addition of complexes such as W(CO)$_6$, Mo(CO)$_{6-n}$-

Scheme II
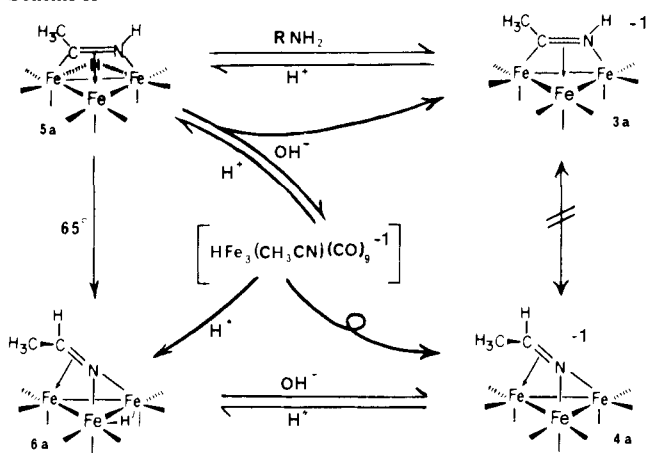
$(CH_3CN)_n$, and $W(CO)_3(CH_3CN)_3$; see Table B, Appendix I. Yield of **5a** was improved (11–15%), but again the presence of $Fe_3(CO)_{12}$ in the product mixture interfered with the separation of **6a**. We then turned to the effect of halogen (Table C, Appendix 1) since the optimum reaction mixture had contained some iodide.[22] Addition of various salts such as Et_4NBr, NaI, and Bu_4NI to reaction mixtures containing only iron carbonyl complexes gave **5a** in the range 0–11%; the latter was from a mixture starting with NaI and $Fe(CO)_5$. Though this yield is not optimal, the starting materials are cheap and convenient. Infrared spectra taken during the early stages of this reaction show that $[HFe_3(CO)_{11}]^-$ is formed. The hydrogen required for this most likely comes from the small amounts of water present.[23] The generality of this method is indicated by the preparation of the analogous complexes $HFe_3(PhC=NH)(CO)_9$ (**5b**) and $HFe_3(N=CHPh)(CO)_9$ (**6b**) (from $[HFe_3(CO)_{11}]^-$ and benzonitrile in refluxing tetrahydrofuran) and *n*-propyl complexes **5c** and **6c** (from $Fe(CO)_5$ and neat butyronitrile in the presence of water and sodium iodide).

The effects of combined cofactors in the treatment of various iron carbonyl starting materials were also investigated; see Table D, Appendix I (supplementary material). Cofactors such as $[W(CO)_5I]^-$ or $Mo(CO)_6$–NaI and $Mo(CO)_6$–Bu_4NI were added. The yields in this series of experiments were the highest observed by us and were optimum (31%) for the mixture $[Fe_2(CO)_8]^{2-}$ and $[W(CO)_5I]^-$. Finally, effects of varying the proton source or of attempting rigorously to dry the acetonitrile before use were also tested (Table E, Appendix 1 (supplementary material)). We tested both anhydrous and aqueous acetic acid, aqueous ammonium chloride, and acetonitrile dried over CaH_2. In each case yields less than the optimum were obtained.

Deprotonation of 5a and 6a. Synthesis of the Anionic Complexes $[Fe_3(CH_3C=NH)(CO)_9]^-$ (3a) and $[Fe_3(N=CHCH_3)-(CO)_9]^-$ (4a). Anions **3a** and **4a** can be isolated from the above reaction mixtures prior to acidification but are not easily separated from each other. A preferable route to these complexes is deprotonation of the separated and purified neutral complexes **5a** and **6a** as shown in Scheme II. Thus **4a** is readily prepared by treatment of **6a** with methanolic potassium hydroxide. Assignment of structure **4a** is confirmed by its ^1H NMR (Table I and vide infra) and by its clean conversion back to **6a** on acidification. In contrast, **3a** cannot be prepared in pure form from **5a** by deprotonation with hydroxide because partial isomerization occurs giving a mixture of **3a** and **4a**; see Scheme II. However, when a weaker base, such as *n*-butylamine, is employed, **3a** is obtained in pure form. Its structure is confirmed by spectroscopic data (Table I and vide infra) and by its clean conversion back to **5a** on acidification; **5a** does not isomerize at an appreciable rate at room temperature (see

section immediately following). Anion **3a** can also be prepared in pure form by base disproportionation, namely, the dissolution of **5a** in acetonitrile containing tetraethylammonium bromide. While the metal-bonded hydrogen in **5a** is thermodynamically acidic ($pK_a \sim -1.5$), it is sterically hindered. Its removal by bulky bases such as aniline requires several hours' time. Pure **3a** or **4a** do not isomerize thermally (80 °C, $CH_3=N$) nor do they isomerize at room temperature either under acidic (H_3PO_4) or basic (*t*-BuO^-) conditions.

Isomerization Reactions. $HFe_3(CH_3C=NH)(CO)_9$ (**5a**) gradually isomerizes irreversibly to $HFe_3(N=CHCH_3)(CO)_9$ (**6a**) in hexane at 65 ° C. In fact, this is the best method for preparing **6a** free of all traces of $Fe_3(CO)_{12}$. The nonisomerization observed for the anions **3a** or **4a** mentioned above indicates that the partial isomerization which occurs when **5a** is deprotonated with hydroxide ion to give both **3a** and **4a** must involve a different species, such as $[HFe_3(CH_3C\equiv N)(CO)_9]^-$ a product of kinetic as opposed to thermodynamic control; see section above. Evidence to support such a species is the observation that **5a** undergoes base-catalyzed hydrogen–deuterium exchange at the acimidoyl nitrogen; however, an attempt to trap the intermediate with methyl iodide was unsuccessful.

Spectral Determination of Structures. Spectral data for complexes **3a–6a** are listed in Table I. The mass spectra of $HFe_3(CH_3C=NH)(CO)_9$ (**5a**) and $HFe_3(N=CHCH_3)-(CO)_9$ (**6a**) are virtually identical. They show the parent ion together with ions due to loss of up to nine carbonyl groups. Further fragmentation involves loss of H_2 and CH_3CN to give Fe_3^+. Owing to the triply bridging group, only a few mono- and dinuclear fragments are observed, primarily $Fe_2(CH_3CN)^+$, Fe_2^+, and Fe^+. These results strongly suggest that **5a** and **6a** are isomers with the empirical composition $H_2Fe_3(CH_3CN)-(CO)_9$, confirmed by the other data presented below.

The full-range infrared spectrum of **5a** shows only one readily assignable characteristic feature, an N–H stretch at 3272 cm^{-1}. The ^1H NMR spectrum of **5a** shows a singlet due to the methyl group and a metal hydride singlet of area one. The N–H proton is not observed (search extending to δ 16 ppm), presumably owing to the effect of ^{14}N quadrupole broadening. These results establish the skeletal structure **5** shown in Scheme I, which has subsequently been confirmed crystallographically.[1b]

The full-range infrared spectrum of **6a** shows no clearly assignable features but the ^1H NMR is very characteristic of a $CHCH_3$ group (quartet plus triplet) with the methine hydrogen also coupled to a single metal hydride. This virtually requires the isomeric skeletal structure **6a**, which has also been confirmed crystallographically.[1b]

The infrared spectra of **5a** and **6a** in the carbonyl stretching region are very similar; see Figure 2 (supplementary material). A slight difference is found in the position of the band near 2025 cm^{-1} and the number of weak bands at lowest energy, **5a** having two and **6a** (which has a pseudo-mirror plane of symmetry) having only one. They are both remarkably similar to the spectrum of $HFe_3(S-i-Pr)(CO)_9$:[24] 2084 (m), 2046 (s), 2023 (s), 2011 (s), 2001 (m), 1995 (m), 1969 (sh), 1965 (w) cm^{-1}. This complex is structurally similar to **6** but has a nearly symmetrical triply bridging thiolate ligand in place of the ethylidenimido group.[1b]

Complexes $[Fe_3(CH_3C=NH)(CO)_9]^-$ (**3a**) and $[Fe_3-(N=CHCH_3)(CO)_9]^-$ (**4a**) are readily identified as analogues of the neutral complexes **5a** and **6a** by their spectroscopic features: the former by the presence of the N–H stretching absorption and ^1H NMR methyl resonance and the latter by a $CHCH_3$-type ^1H NMR resonance. The absence of a metal hydride signal and integration of the cation resonance against that of the methyl group in both **3a** and **4a** prove that monodeprotonation has occurred at the metal.

Determination of ν_{CN} in 5a and 6a. A C–N stretching frequency is not readily assignable in the full-range spectra of **5a** and **6a**, owing to overlap with the C–H bending modes. The prohibitive cost of $CH_3{}^{13}CN$ ($750/g) or $CH_3C^{15}N$ ($350/g) led us to attempt assignment of ν_{CN} via appropriate deuterated complexes. Infrared spectra of **5a** in the region 1500–1200 cm^{-1} are shown in Figure 3 (supplementary material). With R = CH_3, three bands are observed: a, 1429; b, 1368; c, 1353 cm^{-1}. When R = CD_3, only one band remains, that at 1353 cm^{-1}; hence it is assigned as ν_{CN} while a and b can be identified as deformation modes of the methyl group. Further evidence in support of these assignments comes from the spectrum of *N*-deuterio-**5a**; see Figure 3C (supplementary material). Absorptions a and b are again observed as in spectrum A but band c is replaced with band d, which is shifted slightly to lower energy at 1344 cm^{-1}. This is paralleled by the presence of ν_{ND} at 2438 cm^{-1} higher energy than 2390 cm^{-1}, its position calculated from ν_{NH} at 3272 cm^{-1}. Both effects are due to interaction of ν_{ND} with ν_{CN}. A similar but larger effect is observed in HCN, where a shift of 183 cm^{-1} to lower energy occurs for ν_{CN} upon deuteration.[25a] An unambiguous δ_{NH} mode was not observed for **5a**.

Infrared spectra of $HFe_3(N\!=\!CHCH_3)(CO)_9$ (**6a**) in the region 1500–1200 cm^{-1} are shown in Figure 4 (supplementary material). Four maxima are observed in the top scan (for R = CH_3): a, 1464; c, 1419; d, 1372; e, 1325 cm^{-1}. For the derivative R = CD_3, bands a, c, and d are essentially removed and replaced by a single absorption, b, at 1439 cm^{-1}; band e remains unchanged at 1325 cm^{-1}. From this behavior, we assign band e as ν_{CN}. Bands a, c, and d are assigned as δ_{CH} or δ_{CH_3} in the derivative R = CH_3 and band b as δ_{CH}' in the derivative R = CD_3.

The C–N stretching frequencies ν_{CN} 1353 cm^{-1} in **5a** and ν_{CN} 1325 cm^{-1} in **6a** are at positions intermediate between that expected for ν_{C-N} at 1100 cm^{-1} and $\nu_{C=N}$ at 1640 cm^{-1}.[25b,c] The C$\equiv$N stretching frequencies in **3a** and **4a** were not determined owing to overlap with vibrations of the alkylammonium cations.

Kinetics of Hydrogen Exchange in $HFe_3(N\!=\!CHCH_3)(CO)_9$ (6a). In order to determine whether the N–H or Fe–H hydrogen of **5a** is transferred to the ligand carbon during isomerization of **5a** to **6a**, we undertook deuterium-labeling studies. Rather than providing information regarding this question, the experiments showed that a facile hydrogen exchange takes place in **6a**. Thus NMR spectra show that $DFe_3(N\!=\!CHCH_3)(CO)_9$ (prepared from **4a** and D_3PO_4) readily equilibrates Fe–D and methine C–H positions. The experimental details of the kinetic study are shown in Figures 5 and 6 and Table II (all supplementary material). These indicate a reversible first-order reaction:

$$DFe_3(N\!=\!CHCH_3)(CO)_9$$

$$\underset{35\,°C}{\overset{CDCl_3}{\rightleftharpoons}} HFe_3(N\!=\!CDCH_3)(CO)_9$$
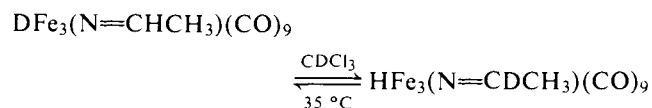
For this reaction, $k_f = 6 \times 10^{-4}\,s^{-1}$ and $K_{eq} = 1.2 \pm 0.2$. The half-life of the forward reaction is ca. 20 min. The greater stability of the C–D and Fe–H bond pair over the C–H and Fe–D bond pair is qualitatively consistent with a calculation by Collman et al. for a related case.[26]

Significantly, no hydrogen–deuterium scrambling was observed in the monodeuterio-**5a**, $DFe_3(CH_3C\!=\!NH)(CO)_9$, even at 65 °C.

Hydrogen Bonding by $HFe_3(CH_3C\!=\!NH)(CO)_9$ (5a). Occasionally, various reactions of **5a** led to the production of a complex whose carbonyl infrared spectrum was nearly identical with that of **5a** except that all the bands were shifted toward slightly lower energy. This was eventually traced to the reversible interaction of **5a** with traces of basic solvents. The
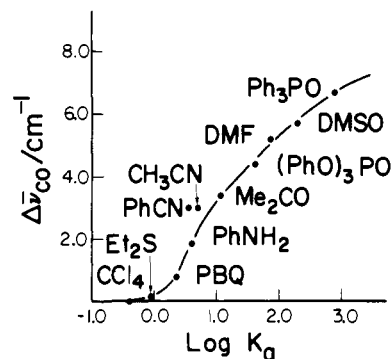
Figure 7. Plot of average shift to lower energy in carbonyl stretching frequency upon adduct formation between $HFe_3(CH_3C\!=\!NH)(CO)_9$ and various bases vs. logarithm of the association constant for the base with phenol. PBQ = *p*-benzoquinone, DMF = dimethylformamide, DMSO = dimethyl sulfoxide.

shifts in ν_{CO} observed in a variety of solvents are given in supplementary Table III and shown graphically in Figure 7, plotted against the logarithm of the association constants of the various bases with phenol.[27]

In addition to the changes in ν_{CO}, the N–H stretch is shifted to lower energy with concomitant broadening (ν_{NH} for dimethyl sulfoxide adduct 3103 cm^{-1}, $\Delta\nu_{1/2} = 140\,cm^{-1}$). This confirms that the interaction is a result of hydrogen bonding between the N–H hydrogen and the base.

The weakly acidic nature of the hydrogen of the triply bridging acimidoyl group in $HFe_3(CH_3C\!=\!NH)(CO)_9$ is paralleled by the hydrogen bonding observed for triply bridging hydroxide groups in adducts such as $W_4(CO)_8(NO)_4(OH)_4$·4B (B = H_2O, OPR_3).[28] For hydrogen-bonded adducts of **5a** the carbonyl stretching frequencies are observed to shift toward lower energy. This is undoubtedly due to transmission of electron density from the base to the carbonyls via the triply bridging acimidoyl ligand. The sigmoidal nature of the correlation between average ν_{CO} shift and base strength is shown in Figure 7. This is no doubt due to a saturation effect, i.e., a decrease in the ability of the cluster to accept further electron density when it has already become electron rich. The very good quantitative fit observed for most of the bases raises questions concerning the marked deviation of points **4** and **6** corresponding to benzonitrile and acetonitrile. The $\Delta\nu_{CO}$ values in Table III (supplementary material) for benzonitrile are reproducible to within a few tenths of a wavenumber, and the literature K_{eq} value vs. phenol appears to have been carefully determined.[29] We tentatively propose that dipole–dipole coupling between ν_{CN} of the nearby nitrile and ν_{CO} of the cluster carbonyls is responsible for the extra 1–1.5-cm^{-1} shift to lower energy.

Discussion

The complexes reported here represent a novel and, we believe, significant addition to the π coordination chemistry of ligands with carbon–nitrogen multiple bonds. The triply bridging acimidoyl ligand found in **3** and **5** has only one known analogue, $HOs_3(HC\!=\!NCH_3)(CO)_9$, which was prepared in very low yield by the oxidative addition of trimethylamine to $Os_3(CO)_{12}$ at 150 °C.[13] The triply bridging ethylidenimido ligand found in **4** and **6** is thus far unique, although terminal and doubly bridging forms of this ligand have been observed.[3,13] The isomerism observed for complexes **5** and **6** is paralleled in the alkenylene and alkenylidene complexes $H_2Os_3(HC\!=\!CH)(CO)_9$ (A) and $H_2Os_3(C\!=\!CH_2)(CO)_9$ (B), respectively.[10a,b,30] The π-bonded vinyl complex, H_2Os_3-$(CH\!=\!CHR)(CO)_{10}$ (C),[30a-c] which is obtained as a precursor in pyrolytic formation of B, also provides useful precedent in

Scheme III
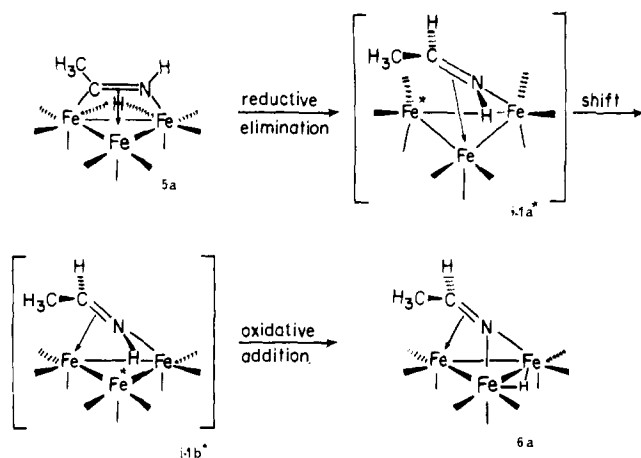
discussion of the interconversions between the iminyl complexes presented below.
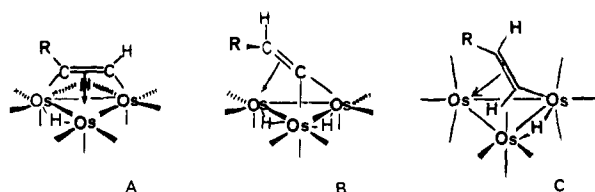
Isomerization of 5a to 6a. The facile exchange between cluster-bonded and carbon-bonded hydrogen atoms in **6a** masks information about the isomerization pathway we were hoping to obtain by thermal conversion of the cluster-deuterated complex, $DFe_3(CH_3C=NH)(CO)_9$. The absence of thermal isomerization in anions **3a** and **4a** (up to 80 °C), however, strongly implicates involvement of the metal-bonded hydrogen in **5a**. We thus propose Scheme III for the isomerization pathway based on well-established elemental steps in organometallic transformations. Precedent for a $\sigma-\pi$ bonded iminyl group in **i-1a** and **i-1b** comes from the $\sigma-\pi$ vinyl complex C shown above.[30a,b,e] The proposed reaction path is also consistent with the observed lack of H–D exchange in DFe_3-$(CH_3C=NH)(CO)_9$ under isomerization conditions. Attempts to trap the unsaturated species **i-1a** and **i-1b** with CO were unsuccessful, perhaps owing to steric crowding in $\sigma-\pi$ bonded acimidoyl derivatives which would cause rapid reversion to **5a** or **6a** under the thermal reaction conditions. The analogous relationship of derivatives **5a** and **6a** to the osmium complexes A and B, respectively, has already been noted above. By contrast, however, derivatives A and B are *not* observed to isomerize even at 100 °C. [30a,c] This is probably due to the much greater osmium–carbon and osmium–hydrogen bond strengths compared to Fe–C and Fe–H. This difference would inhibit the initial reductive elimination required for the formation of osmium **i-1a** and **i-1b** type intermediates. A further noteworthy difference is the lack of low-temperature exchange between metal-bonded and carbon-bonded hydrogen in the derivative $HDOs_3(C=CH_2)(CO)_9$.[32] There is a possibility that exchange can occur at higher temperature as reaction of D_2 with this osmium complex at 125 °C leads to d_n-$H_3Os_3(CCH_3)(CO)_9$ with some deuterium on carbon;[30d] this point is taken up again in a subsequent paper.[21]

Exchange of Carbon-Bonded with Metal-Bonded Hydrogen in 6a. This facile exchange at 35 °C is rather unique. We propose that equilibration of these two hydrogen atoms occurs through the coordinatively unsaturated cluster complex, **i-2**.[31]

$$DFe_3(N=CHCH_3)(CO)_9 \rightleftharpoons *Fe_3(NCHDCH_3)(CO)_9$$

$$\mathbf{i\text{-}2}^{31}$$
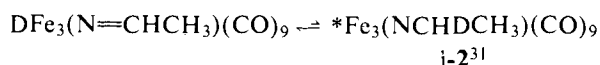
The latter would also account for the facile interconversion of **6a** into the nitrene complexes $Fe_3(NCH_2CH_3)(CO)_{10}$ and

$H_2Fe_3(NCH_2CH_3)(CO)_9$ by CO or H_2, respectively. These reactions are presented and discussed in a succeeding paper.[21]

Comments on the Formation of $[Fe_3(RC=NH)(CO)_9]^-$ (3) and $[Fe_3(N=CHR)(CO)_9]^-$ (4). To our knowledge, anions **3** and **4** represent the first isolated derivatives resulting from the hydrometalation of an unactivated organic nitrile by a transition-metal complex.[33,34] We are at present very far from understanding the path(s) by which these products are formed and the role of the cofactors in the optimum yield syntheses. For the present we would like to restrict our comments to two observations from the literature which we believe are pertinent to this work.

The first has to do with the enhanced reactivity of coordinated nitrile toward nucleophilic attack.[35] Prior coordination of nitrile to iron or to tungsten would greatly facilitate hydrometalation by a second metal center either intramolecularly within a cluster complex or intermolecularly with the nitrile serving as a template for cluster formation. The template effect for cluster formation is illustrated in the work of Yasufuku.[36] In this, a mononuclear acetylide complex is converted to a cluster complex by treatment with $Fe_2(CO)_9$. It should be

$$CpFe(CO)_2(C≡CPh) + Fe_2(CO)_9 \longrightarrow$$
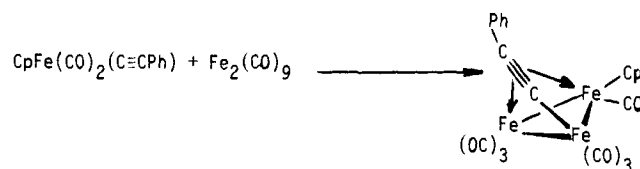
noted that in the cited example the acetylide σ bond is transferred away from the iron atom of the starting material. Although $W(CO)_5(CH_3CN)$ is present in our highest yield reaction mixture,[22] no mixed iron–tungsten clusters could be isolated. This could be due to the incompatible steric and electron requirements for tungsten in a mixed iron–tungsten cluster.

Summary

The hydrometalation of nitriles appears to require the modification of normal nitrile reactivity patterns through the cooperative interaction of more than one metal center. This cooperation may originate either from intramolecular sources as in a cluster complex or intermolecular sources with substrate (nitrile) serving as a template around which a cluster may be formed. We believe that these concepts are not limited to the case in point, but may have great significance in relationship to the hydrometalation and subsequent reduction of other unsaturated species bearing nonbonding lone pairs such as CO and N_2.

Experimental Section

Solvents and reagents were of commercial reagent grade which were used without further purification unless otherwise noted. Mallinckrodt reagent grade acetonitrile had a stated maximum impurity analysis of 0.3% water, 0.05% acetic acid, and 0.001% ammonia. $[C_5H_5NCH_3][W(CO)_5I]$,[37] $[(C_2H_5)_4N]_2[Fe_2(CO)_8]$,[19] and $[(CH_3)_4N][HFe_3(CO)_{11}]$[38] were prepared according to the literature methods cited. Reactions, filtrations, and recrystallizations were carried out under nitrogen using Schlenkware techniques. Chromatographic separations and handling of neutral complexes can be done in air if exposure is limited to a few hours. Carbonyl infrared spectra were recorded on a Beckman IR-4 spectrometer equipped with LiF optics and were calibrated against the cyclohexane peak at 2138.5 cm^{-1}. Full-range infrared spectra were recorded on a Perkin-Elmer 521 spectrometer in carbon tetrachloride, carbon disulfide, tetrachloroethylene, or perdeuterioacetonitrile solution. ^1H NMR spectra were recorded on a Varian A-60D spectrometer and calibrated against internal tetramethylsilane at τ 10.00. Mass spectra were obtained by Dr. K. Fang on an AEI MS-9 spectrometer using a direct inlet probe temperature of 90–100 °C and an ionizing voltage of 70 eV. Elemental

analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Syntheses of HFe₃(RC≡NH)(CO)₉ (5) and HFe₃(N≡CHR)(CO)₉ (6). Method A, R = CH₃. A solution of [C₅H₅NCH₃][W(CO)₅I] (0.255 g, 468 μmol) and [(C₂H₅)₄N]₂[Fe₂(CO)₈] (1, 0.253 g, 424 μmol) in acetonitrile (60 mL) was heated under reflux for 15 h. The solvent was then evaporated on an aspirator and the resulting solid treated with a mixture of phosphoric acid (30 mL) and hexane (40 mL). The red hexane layer was transferred to another flask and the phosphoric acid layer extracted with further aliquots of hexane until the extracts were nearly colorless. The combined hexane extracts were taken to dryness on a rotary evaporator and then chromatographed on a 1.9 by 22 cm silica gel column. Hexane eluted a yellow band containing tungsten hexacarbonyl and triiron dodecacarbonyl, followed closely by a dark red band which yielded **6a** (9 mg, 7%). Hexane–ether (9:1) eluted a second dark red band which gave **5a** (40 mg, 31%).

Method B, R = CH₃. A solution of [(CH₃)₄N][HFe₃(CO)₁₁] (2, 0.082 g, 149 μmol) in acetonitrile (70 mL) was heated under reflux for 4.5 h, during which time the solution turned from violet to red. The reaction mixture was worked up as described for method A. The first band off the column was greenish-brown and consisted of a mixture of triiron dodecacarbonyl and **6a**. The second band yielded **5a** (5 mg, 7%).

Method B, R = Ph. A solution of [(CH₃)₄N][HFe₃(CO)₁₁] (2, 1.252 g, 2.27 mmol) and benzonitrile (0.24 mL, 2.35 mmol) in tetrahydrofuran (25 mL) was heated under reflux for 64 h. After the solvent was removed on an aspirator, the resulting solid was dissolved in acetone (5 mL) and acidified with phosphoric acid (20 mL). Extraction with hexane and chromatography as in method A gave a mixture of triiron dodecacarbonyl, **6b** (band 1, 0.358 g), and **5b** (0.060 g, 5%). The material from the first band was rechromatographed. (With care most of **6b** can be placed on the column while most of the less soluble, green triiron dodecacarbonyl can be discarded.) This gave pure **6b** (0.149 g, 13%). IR (ν_{CO} in cyclohexane solution) **5b**, 2087 (19), 2050 (68), 2024 (100), 2015 (71), 2003 (26), 1992 (9), 1974 (9), 1965 (6); **6b**, 2088 (12), 2052 (71), 2028 (100), 2014 (68), 2006 (19), 1998 (13), 1976 (7), 1973 (4) cm⁻¹.

Method C, R = CH₃. A solution of iron pentacarbonyl (10 mL, 74.4 mmol) and sodium iodide (11.1 g, 74.0 mmol) in acetonitrile (300 mL) was heated under reflux for 48 h. The solution rapidly became dark red and vigorous carbon monoxide evolution occurred (*Caution*!). The solution was then cooled and the solvent removed on an aspirator. The resulting solid was partially dissolved in acetone (30 mL) and then treated with phosphoric acid (40 mL) and water (50 mL). (*Caution, the mixture becomes slightly warm and hydrogen is evolved as the iron metal present reacts with the acid*). The resulting precipitate was extracted with aliquots of hexane until the extracts were no longer red. The combined extracts were taken to dryness on a rotary evaporator (*Caution, some iron pentacarbonyl distills over with the hexane*) and the residue was chromatographed on a 4 by 40 cm silica gel column. Hexane eluted a dark red band which gave **6a** (sometimes contaminated with small amounts of triiron dodecacarbonyl and complexes **7, 8,** and **10** described in a succeeding paper)²¹ in about 4% yield (0.45 g). The analytical sample was recrystallized from hexane at −20 °C. Anal. Calcd for C₁₁H₅Fe₃NO₉: C, 28.55; H, 1.09; N, 3.03. Found: C, 28.40; H, 1.09; N, 2.83.

Hexane–ether or hexane–dichloromethane (9:1) eluted complex **5a** in about 11% yield (1.20 g) which was recrystallized from hexane–dichloromethane at −20 °C. Anal. Calcd for C₁₁H₅Fe₃NO₉: C, 28.55; H, 1.09; N, 3.03. Found: C, 28.51; H, 1.08; N, 2.96.

Method C, R = n-Pr. A solution of iron pentacarbonyl (10 mL, 74.4 mmol), sodium iodide (11 g, 74 mmol), and water (1 mL) in butyronitrile (250 mL) was heated under reflux for 9 h. The reaction mixture was worked up as described for R = CH₃ to give **6c** (1.0 g, 8%) and **5c** (0.7 g, 6%). IR (ν_{CO} in cyclohexane solution): **5c**, 2087 (14), 2050 (66), 2022 (100), 2014 (70), 2001 (27), 1990 (9), 1970 (7), 1964 (6); **6c**, 2087 (8), 2050 (63), 2027 (100), 2012 (59), 2006 (20), 1994 (12), 1971 (6) cm⁻¹.

Method C, R = CD₃. A solution of iron pentacarbonyl (5.0 mL), sodium iodide (5.0 g), and D₂O (0.3 mL) in CD₃CN (20 g) was heated under reflux for 48 h and worked up as described for R = CH₃.

Thermal Isomerization of 5a to 6a. A solution of **5a** (1.00 g, 2.16 mmol) in benzene (100 mL) was heated under reflux for 29 h. The solvent was then evaporated on a rotary evaporator and the resulting solid chromatographed as described above to remove traces of **5a**, giving pure **6a** (0.59 g, 60%).

Attempted Thermal Isomerization of 6a to 5a. A solution of **6a** in hexane was heated under reflux for 48 h (conditions under which **5a** can be converted to **6a**). Infrared spectra and chromatographic workup showed that no **5a** had been formed.

Reaction of 5a with Carbon Monoxide. A. A solution of **5a** in hexane was treated with carbon monoxide at 45 psi in a Hoke bomb for 9 days. Infrared spectra showed that no reaction had occurred.

B. A solution of **5a** in cyclohexane was heated under reflux with carbon monoxide bubbling through. Infrared spectra and chromatographic workup indicated that the only species present were **5a, 6a,** and **8a** described in a following paper.²¹

Synthesis of [Fe₃(CH₃C≡NH)(CO)₉]⁻ (3a). HFe₃(CH₃C≡NH)-(CO)₉ (**5a**, 0.47 g, 1.0 mmol) was dissolved in a solution of tetraethylammonium bromide (0.26 g, 1.2 mmol) in acetonitrile (20 mL) and stirred for 18 h. The solvent was then evaporated on an aspirator, and the solid was dissolved in methanol and precipitated with an equal volume of water. The precipitate was collected by filtration, washed with water, redissolved in methanol, and filtered. The filtrate was treated with water to the cloud point and cooled at −20 °C to give the black tetraethylammonium salt of **3a** (0.39 g, 66%). Anal. Calcd for C₁₉H₂₄Fe₃N₂O₉: C, 38.55; H, 4.09; N, 4.73. Found: C, 38.62; H, 4.15; N, 4.62.

Synthesis of [Fe₃(N≡CHCH₃)(CO)₉]⁻ (4a). A solution of HFe₃(N≡CHCH₃)(CO)₉ (**6a**, 0.712 g, 1.54 mmol) in methanol (10 mL) was treated with methanolic potassium hydroxide (10 mL, 0.16 M) for 30 min. Addition of aqueous tetraethylammonium bromide (0.468 g, 2.23 mmol, in 10 mL of water) gave a red precipitate which was collected by filtration and washed with water and hexane. The precipitate was redissolved in methanol and filtered, and water was added to the cloud point. Cooling at −20 °C gave the tetraethylammonium salt of **4a** (0.42 g, 46%). Anal. Calcd for C₁₉H₂₄Fe₃N₂O₉: C, 38.55; H, 4.09; N, 4.73. Found: C, 40.87; H, 4.24; N, 5.46.

Attempted Thermal Isomerization of 3a and 4a. Solutions of **3a** and **4a** heated under reflux in acetonitrile for 2 days showed no signs of isomerization. Some decomposition to iron metal occurred and in the case of **3a** a small amount of [HFe(CO)₄]⁻ formed.

Acid–Base-Induced Isomerizations. A. Acidification (acetone–phosphoric acid–hexane) of **3a** and **4a** cleanly gave **5a** and **6a**, respectively, as determined by infrared spectra and chromatographic workup.

B. Deprotonation of **6a** (see synthesis of **4a**) cleanly gave **4a**. Deprotonation of **5a** under similar conditions gave a mixture of **3a** and **4a** in about a 3:2 ratio. Deprotonation of **5a** (0.147 g, 0.32 mmol) in acetonitrile (25 mL) with *n*-butylamine (0.1 mL, 1.01 mmol) gave pure **3a**.

C. A solution of **5a** in acetone treated with phosphoric acid gave no detectable isomerization to **6a** after 24 h. Similarly, a solution of **3a** in tetrahydrofuran treated with sodium *tert*-butoxide gave no rearrangement to **4a**.

D. Treatment of **3a** with 14.8 equiv of phosphoric acid in acetonitrile gave only trace conversion to **5a**. Treatment with 6.8 equiv of nitric acid gave about a 65:35 equilibrium mixture of **5a** to **3a** before decomposition occurred. Treatment with 10 equiv of sulfuric acid gave complete conversion to **5a**.

E. Complex **5a** (0.145 g, 0.31 mmol) was treated with NaOH (28 mg, 0.7 mmol) in D₂O (8 mL)-acetone-*d₆* (2 mL) for 3 h. The mixture was then acidified with deuteriophosphoric acid and extracted with hexane to give DFe₃(CO)₉(CH₃C≡ND). Upon chromatography, the *N*-deuterio label reverted to the proteo form. (The fate of the metal label was not determined.)

Hydrogen Scrambling in 6a. NMR spectra of DFe₃-(N≡CHCH₃)(CO)₉ (prepared from **4a** and D₃PO₄-acetone-hexane) were recorded at periodic intervals. The relative concentrations of DFe₃(N≡CHCH₃)(CO)₉ and HFe₃(N≡CDCH₃)(CO)₉ were determined by comparing peak heights due to the methyl doublet of the former with the methyl singlet of the latter. These were used to determine k_f according to standard kinetic treatment for a reversible first-order reaction.³⁹ The equilibrium constant was determined for a sample prepared similarly except that acetone-*d₆* was used in the acidification. The sample was estimated to be 95% $d_1 \pm 5\%$ (due to NMR integration). Because of overlap in CH₃ resonances in the isotopomers DFe₃(N≡CHCH₃)(CO)₉ and HFe₃(N≡CDCH₃)(CO)₉, peak heights rather than signal areas were used to estimate their ratio at equilibrium. We thus place an error limit of 15%, or ±0.2, on K_{eq}.

Hydrogen-Bonding Studies. Carbonyl infrared spectra of **5a** in carbon tetrachloride containing ~5% by volume of various bases were

recorded and carefully calibrated. The data so obtained is reported in Table III (supplementary material).

Supplementary Material Available: Figures of infrared and ¹H NMR spectra and a plot of kinetic data (Figures 1–6), tables of kinetic data for hydrogen scrambling and shift in ν_{CO} upon adduct formation (Tables II and III), and Appendix I containing yield and byproduct data for the syntheses of **5a** and **6a** (Tables A–E) (11 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. (b) This is the first of a series of papers relating to the reduction of acetonitrile on the face of a triiron cluster complex; for the next part see M. A. Andrews, G. Van Buskirk, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, following paper in this issue. (c) Following consultations with K. L. Loening, Nomenclature Director of Chemical Abstracts Service, Columbus, Ohio 43210, the following *Chemical Abstracts* index names are suggested for the isomeric reduction products: for HFe₃-(CH₃C=NH)(CO)₉ (**5a**), *triangulo*-nonacarbonyl-μ-hydro[μ₃-[(N,1-η)-1-iminoethyl-C:N]]triiron; for HFe₃(N=CHCH₃)(CO)₉ (**6a**), *triangulo*-nonacarbonyl[μ₃-[(N,1-η)-ethaniminato-N:N]]-μ-hydrotriiron. In line with IUPAC rules for inorganic chemistry[1d] the following systematic names are suggested: for **5a**, [μ₃-[(N-1-η)-acetimidoyl-N,C]]nonacarbonyl-μ-hydrido-*triangulo*-triiron; for **6a**, nonacarbonyl[μ₃-[(N-1-η)-ethylidenimido-N,N]]-μ-hydrido-*triangulo*-triiron. (d) "IUPAC Nomenclature of Inorganic Chemistry", 2nd ed., Crane Russak & Co., New York, 1970; see also *Pure Appl. Chem.*, **28**, 1 (1971).
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