Crystal and Molecular Structure of $Fe_3(N{\equiv}CCH_2CH_2CH_3)(CO)_9$. Characterization of a Cluster Complex with Triply Bridging Nitrile Ligand[1]

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Abstract: The title complex has been characterized by an X-ray crystal structure determination. The molecule crystallizes in the centrosymmetric space group $P2_1/m$ with $a = 9.003$ (1) Å, $b = 11.226$ (2) Å, $c = 8.986$ (2) Å, $\beta = 101.33$ (1)°, $V = 890.6$ Å^3, $Z = 2$, ρ(obsd) = 1.79 g cm^{-3}, and ρ(calcd) = 1.82 g cm^{-3}. Diffraction data were collected with a Syntex P$\bar{1}$ automated diffractometer using graphite monochromatized Mo Kα radiation. All atoms including hydrogen atoms have been located and refined by standard Patterson, Fourier, and least-squares techniques; the final discrepancy indices are $R_F = 2.8\%$ and $R_{wF} = 3.6\%$ for the 2584 independent reflections having $I \geq 3\sigma(I)$ in the range $0° < 2\theta < 65°$. The molecule is constrained to have a mirror plane. Each iron in the isosceles triangle (Fe(1)–Fe(2) = 2.6257 (5), Fe(2)–Fe(2′) = 2.4818 (7) Å) is bonded to three terminal linear carbonyl ligands and to an unprecedented triply bridging nitrile ligand. The nitrile ligand (C(CN)–N = 1.260 (3) Å) is σ bonded to Fe(1) via the nitrogen lone pair (Fe(1)–N = 1.795 (2) Å) and π bonded to Fe(2) and Fe(2′) (Fe(2)–N = 1.974 (2), Fe(2)–C(CN) = 2.076 (2) Å). The propyl substituent makes an angle of 135.1 (2)° with the C(CN)–N bond. The core of the complex is thus isostructural with $Fe_3(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_7$ and $HRu_3(C{\equiv}C\text{-}t\text{-}Bu)(CO)_9$, which contain isoelectronic acetylide ligands. These types of complexes are distinctly different from the electron-deficient acetylene complex $Fe_3(PhC{\equiv}CPh)(CO)_9$.

Introduction

As described in a previous paper,[1b] we have found that organic nitriles are hydrometalated by a variety of iron carbonyls including $[HFe_3(CO)_{11}]^-$ to give $HFe_3(RC{=}NH)(CO)_9$ and $HFe_3(N{=}CHR)(CO)_9$. Air oxidation of the former gives a complex whose mass spectrum and ^{1}H NMR are consistent with the formulation $Fe_3(N{\equiv}CR)(CO)_9$.[1d] The EAN rule suggested that the nitrile must be present as a triply bridging, six-electron donor with the nitrogen lone pair σ bonded to one metal and the two orthogonal nitrile π bonds bridging to the other two metals. Although this type of bonding mode has been observed for the isoelectronic acetylide ligand in $Fe_3(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_7$[2] and $HRu_3(C{\equiv}C\text{-}t\text{-}Bu)(CO)_9$,[3] no such nitrile complexes have as yet been reported. In fact, examples of the general classes of triply bridging hetero-unsaturated ligands[1c] and π-bonded nitriles[4] are scarce. A structural study of $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$ was therefore carried out and the results reported here confirm the presence of a triply bridging nitrile ligand.

Experimental Section

Data Collection. Crystals of $Fe_3(N{\equiv}CCH_3)(CO)_9$[1d] were grown from dichloromethane, but oscillation photographs showed that they were invariably polycrystalline. The n-propyl analogue, $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$[1d] was thus prepared and crystallized from hexane at −20 °C. Photographic and diffractometer data indicated a monoclinic crystal system with systematic $2n + 1$ absences on the b axis. These results are consistent with the space groups $P2_1$ and $P2_1/m$. The flotation density (1.79 g cm^{-3} in CCl_4-CH_2Br_2) together with the volume (890.6 Å^3) and molecular weight (488.76) indicated that Z was equal to 2. For the space group $P2_1/m$, this requires that the molecule lie on the crystallographic mirror plane. A well-formed single crystal bounded by the faces (00$\bar{1}$), (1$\bar{1}$0), (001), ($\bar{1}$10), (110), and ($\bar{1}\bar{1}$0) with perpendicular distances from a common point of 0.0, 0.295, 0.205, 0.0, 0.36, and 0.0 mm, respectively, was selected for data collection. The crystal was glued to a glass fiber and mounted on a Syntex P$\bar{1}$ automated diffractometer (equipped with scintillation counter and graphite monochromator) with the (001) and ($\bar{1}$10) faces roughly parallel to the instrumental ϕ axis.

Fifteen reflections selected from a random-orientation rotation photograph (13° < 2θ < 24°) were used as input to the automatic centering, autoindexing, least-squares, and axial photograph routines of the instrument to obtain an orientation matrix for data collection. After data collection, 15 new reflections with 39° < 2θ < 45° were centered to obtain an accurate set of lattice parameters for use in the refinement of the structure. These are given in Table I.

Intensity data were collected using the $\theta/2\theta$ scan technique with Mo K$\bar{\alpha}$ radiation, a scan rate of 2.4° min^{-1}, and a scan range of 1.2° below the Mo Kα_1 peak to 1.2° above the Mo Kα_2 peak with background counts of one-half the scan time at each end of the scan range. The intensities of three standard reflections, ($\bar{2}$03), (1$\bar{3}$2), and (104), were recorded after every 97 intensity measurements. The maximum deviations from their respective means were 1.4, 1.3, and 2.0%. A total of 3387 independent reflections were measured which constitute the entire quadrant $\pm h$, $+k$, $+l$ accessible with Mo K$\bar{\alpha}$ radiation and having $0° < 2\theta < 65°$. The 803 reflections having $I \leq 3\sigma(I)$ including the nine systematic absences ($0k0$), $k = 2n + 1$, were considered to be unobserved and omitted from the refinement. The 2584 observed reflections were corrected for Lorentz and polarization effects and processed as described previously.

Solution and Refinement of Structure. The programs used during the structure analysis have been described previously.[1c] The scattering factors for neutral iron, oxygen, nitrogen, and carbon were taken from Table 2.2A of ref 5 while those for hydrogen were those of Stewart et al.[6] Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for iron using the values in Table 2.3.1 of ref 5.

The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma(|F_o|)]^{-2}$. The discrepancy indices R_F (%) and R_{wF} (%) and the goodness of fit (GOF) were defined as given in an earlier paper.[1c]

A Patterson synthesis map was readily interpretable in terms of the space group $P2_1/m$ and yielded the positions of the two independent iron atoms, one (Fe(1)) on the crystallographic mirror plane, the other (Fe(2)) in a general position. The correctness of this space-group assignment is indicated by the subsequent successful refinement. A Fourier map phased on the two iron atoms revealed the positions of the 15 remaining independent nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of positional (excluding the y coordinate for atoms on the mirror plane) and isotropic thermal parameters converged at $R_F = 8.3\%$ and $R_{wF} = 11.3\%$.

The data were then corrected for the effects of absorption (μ = 24.56 cm^{-1}, maximum, minimum, and mean transmission factors of 0.802, 0.714, and 0.770). A cycle of least squares gave $R_F = 7.5\%$ and $R_{wF} = 10.6\%$. Several cycles of least squares with anomalous dispersion included for iron and anisotropic temperature factors for all atoms converged at $R_F = 3.3\%$ and $R_{wF} = 5.3\%$.

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Table I. Crystal Data for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$

crystal system: monoclinic
space group: $P2_1/m$
$a = 9.003$ (1) Å
$b = 11.226$ (2) Å
$c = 8.986$ (2) Å
$\beta = 101.33$ (1)°
radiation: Mo K$\bar{\alpha}$ = 0.710 69 Å
$V = 890.6$ (3) Å^3
$Z = 2$
$T = 25$ °C
mol wt 488.76
ρ(obsd) = 1.79 g cm^{-3}
ρ(calcd) = 1.82 g cm^{-3}

At this point a difference Fourier map indicated the positions of the propyl hydrogen atoms. While hydrogens H1, H31, and H32 were well behaved during a cycle of least squares, the H2-C2-H2′ angle expanded to 141°. H2 was thus placed in an idealized location prior to the next cycle of refinement which again included the positional parameters of all the hydrogen atoms and gave $R_F = 3.0\%$ and $R_{wF} = 4.0\%$. The position of H2 remained chemically reasonable. Two further cycles of least-squares refinement of positional parameters for all atoms, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for all hydrogen atoms converged at $R_F = 2.9\%$ and $R_{wF} = 3.8\%$

Examination of the intense, low-angle F_o and F_c values suggested that secondary extinction effects were present. A correction was made[7] and subsequent least-squares refinement led to the final discrepancy indices of $R_F = 2.8\%$ and $R_{wF} = 3.6\%$ and a GOF = 1.225 (N_o = 2584, N_v = 145). In the final least-squares cycle, the largest shift in any parameter was 0.03σ. Residuals between 0.21 and −0.23 e Å^{-3} were found on a final difference Fourier map. An analysis of $||F_o| - |F_c||/\sigma(F_o)$ for the 794 unobserved reflections (excluding the nine systematic absences) showed 77% to be less than 1, 16.5% in the range from 1 to 2, 4.5% in the range 2 to 3, and 2% greater than 3 (maximum value = 4.0).

The final atomic positions, thermal parameters, and root-mean-square amplitudes of vibration are given in Tables II, III, and IV, respectively, together with their estimated standard deviations based on the final least-squares correlation matrix and including contributions due to errors in the unit cell parameters. Interatomic distances and angles are given in Tables V and VI, respectively. The observed and calculated structure factor amplitudes are available as Table VII (supplementary material).

Results and Discussion

Overall Structure. The crystal consists of discrete molecular units of $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$ separated by normal van der Waals contacts. The overall geometry of the molecule and the system used for labeling the atoms are shown in Figure 1. A crystallographic mirror plane passing through the molecule bisects the Fe(2)-Fe(2′) bond and contains Fe(1), carbonyl (11), the propyl carbon atoms, and one hydrogen on the propyl methyl carbon. All three iron interactions are bonding (2.6257 (5), 2.6257 (5), and 2.4818 (7) Å) and define an exact isosceles triangle. Each iron atom is bonded to three terminal, linear carbonyl ligands, one quasi-axial and two quasi-equatorial (Figures 1 and 2). The open face of the $Fe_3(CO)_9$ cluster is capped by the triply bridging nitrile ligand. A top view of this is seen in Figure 1 and a side elevation is shown in Figure 2.

The Fe(2)-C(22) distance (1.816 (2) Å) is slightly longer (by 8σ) than the other four independent nearly equal iron-carbonyl carbon distances (1.796 ± 0.004 Å). The carbonyl carbon-oxygen bond distances are all equivalent within the statistical error (1.137 ± 0.007 Å). The parameters of the *n*-propyl group are unexceptional.

The Nitrile Ligand. The triply bridging nitrile ligand is σ bonded to Fe(1) via the nitrogen lone pair and μ bonded (π bonded) to both Fe(2) and Fe(2′) via the two orthogonal nitrile π bonds. The Fe(1)-N bond distance (1.795 (2) Å) is significantly shorter than the σ bond between the iminyl nitrogen and iron in $HFe_3(CO)_9(CH_3C{=}NH)$ (1.931 (2) Å)[1c] (discussion vide infra). The difference in Fe(2)-N and Fe(2)-C(CN) distances (1.974 (2) and 2.076 (2) Å, respectively) is nearly equal to the difference in covalent radii of nitrogen and carbon.

Table II. Final Atom Positions for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$[a]

atom	x	y	z
Fe(1)[b]	−0.741 66 (4)	0.25	0.077 01 (4)
Fe(2)	−0.782 77 (3)	0.360 53 (2)	−0.185 41 (3)
O(11)[b]	−1.0353 (3)	0.25	0.1709 (3)
O(12)	−0.6156 (2)	0.4476 (1)	0.2750 (2)
O(21)	−1.0924 (2)	0.4081 (2)	−0.1433 (2)
O(22)	−0.6537 (2)	0.5961 (2)	−0.0856 (2)
O(23)	−0.8570 (3)	0.4064 (2)	−0.5126 (2)
N[b]	−0.6324 (2)	0.25	−0.0699 (2)
C(CN)[b]	−0.6015 (3)	0.25	−0.2007 (3)
C(11)[b]	−0.9226 (3)	0.25	0.1336 (3)
C(12)	−0.6675 (2)	0.3717 (2)	0.1994 (2)
C(21)	−0.9710 (2)	0.3881 (2)	−0.1565 (2)
C(22)	−0.7020 (2)	0.5049 (2)	−0.1245 (2)
C(23)	−0.8260 (3)	0.3890 (2)	−0.3854 (3)
C(1)[b]	−0.4593 (3)	0.25	−0.2622 (3)
C(2)[b]	−0.4781 (5)	0.25	−0.4289 (4)
C(3)[b]	−0.3332 (5)	0.25	−0.4880 (5)
H(1)	−0.400 (2)	0.186 (2)	−0.221 (3)
H(2)	−0.533 (3)	0.199 (3)	−0.466 (3)
H(31)[b]	−0.352 (4)	0.25	−0.590 (4)
H(32)	−0.268 (3)	0.182 (3)	−0.445 (4)

[a] Positions of the atoms in the asymmetric unit are given in fractional coordinates followed in parentheses by the estimated standard deivation of the least significant digit. The remaining atoms in the molecule which are designated in the text by a prime are related to those of the basic asymmetric unit by the transformation (x', y', z') = (x, $\frac{1}{2} - y$, z). [b] Atom is required by symmetry to lie on the mirror plane at $y = \frac{1}{4}$.

The ligand carbon-nitrogen distance of 1.260 (3) Å is significantly longer than that of a nitrile triple bond (1.16 Å)[8] and is in fact nearly equal to that of a carbon-nitrogen double bond (1.28 Å).[8] A similar effect is observed for doubly π bonded acetylenes and acetylides for which carbon-carbon distances of 1.29-1.37 Å are typical[2,3,9] compared to 1.21 and 1.34 Å for carbon-carbon triple and double bonds, respectively.[8] It has been noted[2] that the carbon-carbon distance in doubly π bonded acetylides (1.29-1.30 Å)[2,3] is slightly shorter than in doubly π bonded acetylenes (1.31-1.37 Å).[9] Although no such comparison is presently possible for nitriles, it is known that the nitrogen lone pair molecular orbital in nitriles is somewhat antibonding with respect to the nitrile C-N bond.[10] Thus σ donation of this lone pair should tend to shorten the C-N bond slightly. The existence of a similar effect for acetylides would explain the observed difference in carbon-carbon bond distances between doubly π bonded acetylenes and acetylides.

For comparison, we note here that singly π bonded acetylenes typically have carbon-carbon bond lengths of 1.22-1.32 Å,[11] significantly shorter than those of doubly π bonded acetylenes (1.31-1.37 Å).[9] A similar comparison cannot be made for nitriles at this time since no studies of sufficient quality have been published for singly π bonded nitriles (vide infra). The C-N distance of 1.232 (6) Å in the related π bonded nitrilium cation complex $CpMo(CO)_2(CH_3C{\equiv}NPh)$,[12] however, is shorter than the C-N distance found here for a doubly bridging nitrile (1.260 (3) Å). This effect is also supported by infrared evidence. Single π coordination of acetonitrile in $Cp_2Mo(CH_3C{\equiv}N)$ results in a shift $\Delta\nu_{CN} = -494$ cm^{-1},[4i] while double π coordination of acetonitrile in $Fe_3(N{\equiv}CCH_3)(CO)_9$ results in an even larger shift, $\Delta\nu_{CN} = -610$ cm^{-1}.[1d]

A final observation regarding the nitrile ligand concerns the nonlinearity of the N-C(CN)-C(1) linkage. Bending back of the substituents on π-bonded acetylenes is of course well known and results from the rehybridization that occurs on π coordination.[11] The 45° deviation from linearity for N-C(CN)-C(1) (Figures 2 and 3B) is similar to that found for doubly π bonded

Table III. Final Thermal Parameters for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)[b]	0.873 (4)	0.632 (3)	0.824 (4)	0.0	0.227 (3)	0.0
Fe(2)	0.849 (3)	0.569 (2)	0.938 (3)	0.081 (2)	0.215 (2)	0.040 (2)
O(11)[b]	1.25 (3)	2.33 (5)	1.99 (4)	0.0	0.73 (3)	0.0
O(12)	2.04 (3)	0.77 (1)	1.41 (2)	−0.13 (2)	0.21 (2)	−0.22 (1)
O(21)	1.02 (2)	1.37 (2)	2.26 (3)	0.33 (2)	0.43 (2)	0.14 (2)
O(22)	1.68 (3)	0.77 (1)	2.58 (4)	−0.22 (2)	0.54 (2)	−0.19 (2)
O(23)	2.79 (4)	2.09 (3)	1.14 (2)	0.81 (3)	0.36 (2)	0.42 (2)
N[b]	0.75 (2)	0.54 (1)	0.91 (2)	0.0	0.14 (2)	0.0
C(CN)[b]	0.82 (3)	0.57 (2)	1.02 (3)	0.0	0.21 (2)	0.0
C(11)[b]	1.07 (3)	1.28 (3)	1.07 (3)	0.0	0.25 (3)	0.0
C(12)	1.24 (2)	0.66 (1)	0.99 (2)	0.07 (2)	0.28 (2)	0.05 (1)
C(21)	1.02 (2)	0.78 (2)	1.36 (3)	0.14 (2)	0.22 (2)	0.05 (2)
C(22)	1.06 (2)	0.65 (1)	1.44 (3)	0.05 (2)	0.35 (2)	0.06 (2)
C(23)	1.52 (3)	1.04 (2)	1.22 (3)	0.33 (2)	0.33 (2)	0.17 (2)
C(1)[b]	0.93 (3)	0.62 (2)	1.05 (3)	0.0	0.35 (2)	0.0
C(2)[b]	1.23 (5)	2.61 (9)	0.98 (4)	0.0	0.31 (3)	0.0
C(3)[b]	1.58 (6)	2.11 (7)	1.45 (5)	0.0	0.86 (4)	0.0
H(1)[c]	4.8 (5)					
H(2)[c]	7.1 (9)					
H(31)[c]	5.6 (9)					
H(32)[c]	10.0 (11)					

[a] Anisotropic temperature factors are given for the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\} \times 10^2$ followed in parentheses by the estimated standard deviation of the least significant digit. [b] The location of the atom on the mirror plane at $y = 1/4$ requires the β_{12} and β_{23} coefficients to be zero by symmetry. [c] Isotropic temperature factors B in Å^2.

Table IV. Root-Mean-Square Amplitudes of Vibration and Equivalent B Values for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$[a]

atom	rms amplitude/Å			equivalent B/Å^2		
	min	med	max	min	med	max
Fe(1)	0.1740 (4)	0.1888 (4)	0.2009 (5)	2.39	2.81	3.19
Fe(2)	0.1745 (3)	0.1878 (3)	0.2009 (3)	2.40	2.78	3.19
O(11)	0.195 (3)	0.288 (3)	0.386 (4)	3.00	6.55	11.76
O(12	0.200 (2)	0.253 (2)	0.289 (2)	3.16	5.05	6.59
O(21)	0.184 (2)	0.289 (2)	0.312 (2)	2.67	6.59	7.69
O(22)	0.208 (2)	0.261 (2)	0.321 (2)	3.42	5.38	8.41
O(23)	0.199 (2)	0.291 (3)	0.405 (3)	3.13	6.69	12.95
N	0.172 (2)	0.186 (3)	0.191 (2)	2.34	2.73	2.88
C(CN)	0.178 (3)	0.191 (3)	0.200 (3)	2.50	2.88	3.16
C(11)	0.200 (3)	0.209 (3)	0.286 (4)	3.16	3.45	6.46
C(12)	0.193 (2)	0.203 (2)	0.226 (2)	2.94	3.25	4.03
C(21)	0.191 (2)	0.228 (2)	0.234 (2)	2.88	4.10	4.32
C(22)	0.197 (2)	0.205 (2)	0.240 (2)	3.06	3.32	4.55
C(23)	0.209 (3)	0.220 (2)	0.284 (3)	3.45	3.82	6.37
C(1)	0.177 (3)	0.199 (3)	0.211 (3)	2.47	3.13	3.52
C(2)	0.191 (4)	0.222 (4)	0.408 (7)	2.88	3.89	13.14
C(3)	0.179 (4)	0.280 (5)	0.368 (6)	2.53	6.19	10.69

[a] The equivalent B values are related to the root-mean-square amplitudes of vibration, $(\overline{u}^2)^{1/2}$, by the expression $B = 8\pi^2(\overline{u}^2)$.

acetylenes and acetylides (33–40°)[2,3,9] but larger than that found for singly π bonded acetylenes (12–40°).[11] It is most interesting to note that the bending back about the nitrile nitrogen in the present compound is some 20°. It seems certain that some sort of bent bond must exist between Fe(1) and N. This also is consistent with the rather short Fe(1)–N distance noted previously.

In this context, a "bent" Ni–Ni bond in the doubly bridging acetylene complex $Cp_2Ni_2(C_2H_2)$ has been studied by preparing X–X valence electron density maps but the study was complicated by a disorder problem.[9c] The title complex would be an ideal candidate for either an X–X or X–N study. Large, well-formed, nearly cubical, X-ray stable crystals can be readily prepared. Even the present data set is very good; the R factor (2.8%) and residuals (0.2 e Å^{-3}) are low and the ratio of observations to parameters is high (owing in part to the crystallographic mirror plane).

Table V. Interatomic Distances (Å) for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$

Fe(1)-Fe(2)	2.6257 (5)	Fe(2)-Fe(2′)	2.4818 (7)
-N	1.795 (2)	-N	1.974 (2)
-C(11)	1.800 (3)	-C(CN)	2.076 (2)
-C(12)	1.798 (2)	-C(21)	1.792 (2)
		-C(22)	1.816 (2)
N-C(CN)	1.260 (3)	-C(23)	1.792 (2)
C(CN)-C(1)	1.491 (3)	C(1)-C(2)	1.474 (4)
		-H(1)	0.92 (2)
C(11)-O(11)	1.130 (4)		
C(12)-O(12)	1.132 (2)	C(2)-C(3)	1.503 (5)
C(21)-O(21)	1.144 (2)	-H(2)	0.78 (3)
C(22)-O(22)	1.140 (3)		
C(23)-O(23)	1.139 (3)	C(3)-H(31)	0.90 (4)
		-H(32)	0.99 (3)

Comparison with $Fe_3(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_7$ (A)[2] and $Fe_3(PhC{\equiv}CPh)(CO)_9$ (C).[13] A side elevation of each of the structures of derivatives A and C is shown in Figure 3 together with a similar profile, B, of the complex studied in the present work. A and B are both 48 e$^-$ complexes and are isostructural in the details of the metal triangle and the disposition of ligand

Table VI. Bond Angles (deg) for $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$[a]

Fe(2)-Fe(1)-Fe(2')	56.41 (2)	Fe(1)-Fe(2)-Fe(2')	61.80 (1)
-N	48.73 (5)	-N	43.10 (6)
-C(11)	106.15 (8)	Fe(1)-Fe(2)-C(21)	85.52 (7)
-C(12)	99.21 (6)	-C(22)	99.99 (7)
-C(12')	151.43 (6)	-C(23)	161.78 (9)
N-Fe(1)-C(11)	149.9 (1)	Fe(2')-Fe(2)-N	51.06 (4)
-C(12)	104.99 (7)	-C(CN)	53.29 (4)
C(11)-Fe(1)-C(12)	94.30 (9)	-C(21)	99.96 (7)
		-C(22)	153.17 (6)
Fe(1)-N-Fe(2)	88.17 (7)	-C(23)	100.29 (8)
-C(CN)	160.0 (2)	N-Fe(2)-C(CN)	36.13 (8)
Fe(2)-Fe(1)-Fe(2')	77.88 (7)	-C(21)	127.10 (9)
		-C(22)	102.10 (7)
Fe(2)-C(CN)-Fe(2')	73.41 (8)	-C(23)	129.13 (9)
-N	67.5 (1)	C(CN)-Fe(2)-C(21)	153.05 (8)
-C(1)	140.19 (8)	-C(22)	106.26 (7)
N-C(CN)-C(1)	135.1 (2)	-C(23)	93.4 (1)
C(CN)-C(1)-C(2)	116.1 (3)	C(21)-Fe(2)-C(22)	97.83 (9)
C(1)-C(2)-C(3)	115.1 (3)	-C(23)	95.1 (1)
		C(22)-Fe(2)-C(23)	98.0 (1)

[a] Bond angles about carbonyl carbons ranged from 177 to 179°; bond angles involving hydrogen atoms ranged from 92 to 112°.

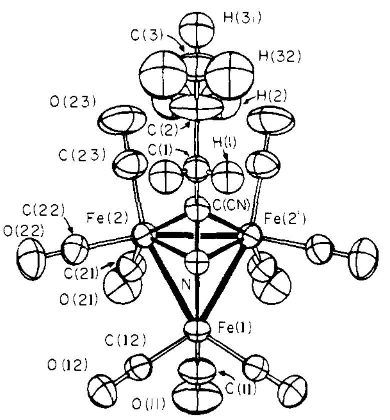

Figure 1. Overall view of the structure of $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$; thermal ellipsoids at 50% probability level.

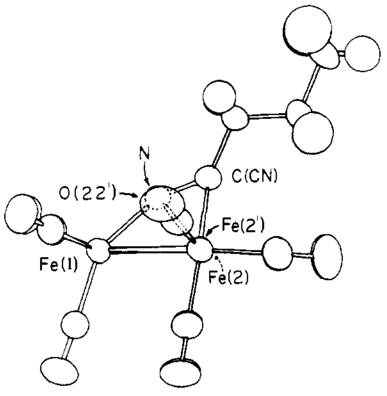

Figure 2. Side view in the direction of the Fe(2)-Fe(2') axis of $Fe_3(N{\equiv}C\text{-}n\text{-}Pr)(CO)_9$; thermal ellipsoids at 50% probability level.

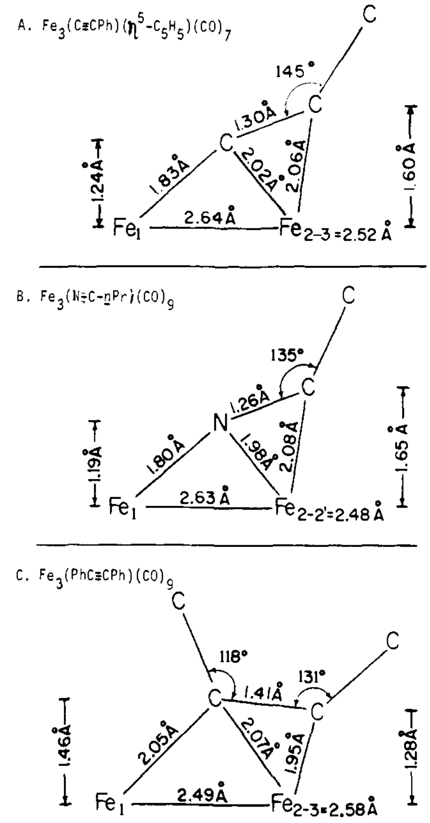

Figure 3. Comparison of selected structural parameters for related complexes in side view along analogous Fe-Fe axes.

to this triangle. These two complexes, however, are distinctly different from C, which is an electron-deficient (46 e^-) complex. The most obvious structural difference is the direction of the ligand tilt in A and B as compared to C. This results from two effects: (1) The σ bond between the ligand and Fe(1) is much shorter in A and B than in C (undoubtedly owing to the bent bond required in A and B; vide supra). (2) In A and B the ligand atom σ bonded to Fe(1) is closer to Fe(2) and Fe(3) than the other ligand atom which participates in the π bonding while the reverse is true for C.

Other important differences include the following. The Fe(1)-Fe(2) distance is greater than the Fe(2)-Fe(3) distance in A and B but vice versa in C. Within the ligand, the C-C and C-N distances in A and B are shorter than in C. (The C-C bond length in C is anomalously long (1.49 (2) Å) compared to other doubly π bonded acetylenes (1.31-1.37 Å), probably owing to the electron-deficient nature of C.) Correlated with this are the slightly larger intraligand angles in A and B over those in C.

Comparison with Other π-Bonded Nitriles. Although nitriles generally form σ-bonded adducts,[14] claims for π-bonded nitriles go back to 1957.[4,15] Some of these have subsequently been disproved,[16] and only two have been proven crystallographically. The first of these, $Ni_3(CO)_3(C_5H_{10}NC{\equiv}N)$, is of low quality ($R = 16\%$) and has only been published in communication form.[17] The C—N bond length found (1.13 Å) seems unreasonably short (cf. 1.16 Å for C≡N) even after allowance is made for the shortening effect of σ coordination (vide supra). The second complex which has been examined is $Ni(PPh_3)_2(CF_3C{\equiv}N)$,[18] but to our knowledge no published report has appeared. A structural determination for a simple singly π bonded nitrile would therefore be of great interest. We believe that the best candidate is $Cp_2Mo(CH_3CN)$[4i] since its spectral data are consistent with π coordination based on similar spectral data obtained for the $Fe_3(RCN)(CO)_9$ complexes whose structure has been established by the present work.[19]

Summary

The current study provides structural characterization of the first triply bridging nitrile ligand. Its features are entirely consistent with related acetylide complexes recently reported.

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Supplementary Material Available: Table VII, calculated and observed structure factors for the title compound (9 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 fourth 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.*, **101**, 7245 (1979). For the third paper see (d) M. A. Andrews and H. D. Kaesz, *ibid.*, preceding paper in this issue. (e) Following consultation with K. L. Loening, Nomenclature Director of Chemical Abstracts Service, Columbus, Ohio 43210, the following *Chemical Abstracts* index name is suggested for $Fe_3(N{\equiv}CCH_2CH_2CH_3)(CO)_9$: *triangulo*-[$\mu_3$-[($N$,1-$\eta$;$N$,1-$\eta$)-butyronitrile-$N$]]nonacarbonyltriiron. In line with IUPAC rules for inorganic chemistry[1f] the following systematic name is suggested: [μ_3-[(N-1-η:N-1-η)-butyronitrile-N]]nonacarbonyl-*triangulo*-triiron. (f) "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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(7) The correction that the program SECEXT uses is $F_{cor} = F_o(1 + C\beta J_o)^{1/2}$ with the symbols defined by W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963). In the present case, C has the value 1.6×10^{-6}.

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