Crystal and Molecular Structures of $HFe_3(CH_3C{=}NH)(CO)_9$ and $HFe_3(N{=}CHCH_3)(CO)_9$, Isomeric Cluster Complexes Derived from the Reduction of Acetonitrile[1]

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Abstract: The complexes $HFe_3(CH_3C{=}NH)(CO)_9$ (**5a**)[2] and $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**)[2] have been characterized by low-temperature X-ray crystal structure determination. Molecule **5a** crystallizes (in part) in the $P\bar{1}$ space group with a = 9.276 (3) Å, b = 9.190 (2) Å, c = 9.099 (2) Å, α = 92.40 (2)°, β = 90.79 (2)°, γ = 83.45 (3)°, and V = 770.0 (4) Å^3 at −158 °C and Z = 2, $\rho_{\text{obsd}}^{25\,°\text{C}}$ = 1.89 g cm^{-3} and $\rho_{\text{calcd}}^{25\,°\text{C}}$ = 1.92 g cm^{-3}. Molecule **6a** also crystallizes in the $P\bar{1}$ space group with a = 13.620 (2) Å, b = 7.822 (2) Å, c = 7.554 (1) Å, α = 72.19 (1)°, β = 92.71 (1)°, γ = 89.60 (1)°, and V = 765.2 (2) Å^3 at −158 °C; Z = 2, $\rho_{\text{obsd}}^{25\,°\text{C}}$ = 1.99 g cm^{-3}, $\rho_{\text{calcd}}^{25\,°\text{C}}$ = 2.01 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 were located and refined by standard Patterson, Fourier, and least-squares techniques. The final discrepancy indices are for **5a**, R_F = 2.9% and R_{wF} = 4.2% for 4849 independent reflections having $I \geq 3\sigma(I)$ in the range $0° < 2\theta < 65°$; for **6a**, R_F = 4.1% and R_{wF} = 4.8% for 3260 independent reflections having $I \geq 3\sigma(I)$ in the range $0° < 2\theta < 60°$. In **5a**, the iron atoms form a nearly isosceles triangle, Fe(1)-Fe(2) = 2.5173 (7), Fe(1)-Fe(3) = 2.5672 (7), and Fe(2)-Fe(3) = 2.7537 (8) Å. The latter two iron atoms are bridged by a hydrogen atom, Fe(2)-H(FE) = 1.72 (3) and Fe(3)-H(FE) = 1.70 (4) Å. The acetimidoyl group, $CH_3{=}NH$, is triply bridging on the iron triangle; the carbon-nitrogen distance in this group is 1.344 (2) Å, similar to that of π-bonded iminium cations. The degree of bending of the substituents on this group, however, is not pronounced. The acetimidoyl group appears attached to the iron triangle through two σ interactions, Fe(2)-N = 1.931 (2) and Fe(3)-C(CN) = 1.933 (2) Å, and one π interaction, Fe(1)-N = 2.001 (2) and Fe(1)-C(CN) = 2.096 (2) Å. The closest intermolecular contact, 2.33 Å, is between the acetimidoyl N-H hydrogen atom and a carbonyl oxygen atom of an adjacent molecule. In **6a**, the iron atoms approach an equilateral triangle, Fe(1)-Fe(2) = 2.5457 (8), Fe(1)-Fe(3) = 2.5521 (9), and Fe(2)-Fe(3) = 2.5879 (8) Å. The latter two iron atoms are bridged by a hydrogen atom, Fe(2)-H(FE) = 1.59 (6) and Fe(3)-H(FE) = 1.71 (6) Å. The ethylidenimido group, $N{=}CHCH_3$, is triply bridging on the iron triangle. The carbon-nitrogen distance in this group is 1.321 (5) Å, intermediate between a double and a single carbon-nitrogen bond. The $N{=}CHCH_3$ group is attached to the iron triangle through two σ bonds to the nitrogen atom, Fe(2)-N = 1.878 (3) and Fe(3)-N = 1.877 (3) Å, and a π bond displaying a pronounced asymmetry to the third iron atom, Fe(1)-C(CN) = 2.223 (4) and Fe(1)-N = 1.960 (3) Å. The closest intermolecular contact, 2.58 Å, is between the C-H hydrogen atom of the ethylidenimido group and a carbonyl oxygen atom of an adjacent molecule.

Introduction

A variety of triply bridging unsaturated hydrocarbon ligands is now known and many have been structurally characterized.[3] In contrast, triply bridging hetero-unsaturated ligands are virtually unknown. The only examples that we are aware of are an isonitrile in $Ni_4(CN\text{-}t\text{-}Bu)_7$,[4] a carbonyl in $[HFe_4(CO)_{13}]^-$,[5] and the *N*-methyl-[6a,c] or *N*-phenyl-[6b] formidoyl group in $HOs_3(HC{=}NR)(CO)_9$. Our studies of carbonyl hydride cluster chemistry have led us to the preparation of derivatives containing three new types of triply bridging heterounsaturated ligands:[1b,c] an acetimidoyl group in $HFe_3(CH_3C{=}NH)(CO)_9$, **5a**[2] (and in its anion $[Fe_3(CH_3{=}NH)(CO)_9]^-$), an ethylidenimido group in $HFe_3(N{=}CHCH_3)(CO)_9$, **6a** (and in its anion $[Fe_3(N{=}CHCH_3)(CO)_9]^-$), and a nitrile in $Fe_3(N{\equiv}CR)(CO)_9$.[1c] We felt that the unique character of these new complexes warranted study by single-crystal X-ray methods. The structure determinations of **5a** and **6a** are the subject of this paper.

Experimental Section

Data Collection for $HFe_3(CH_3C{=}NH)(CO)_9$ (5a). Crystals of **5a**[1b] were grown from ether-hexane at −20 °C. Preliminary oscillation and Weissenberg photographs indicated the presence of two crystal systems, a triclinic form and an orthorhombic form. Crystals of the latter type were mounted about the c axis and showed $2n + 1$ systematic absences on the a and b axes indicating the space group $P2_12_12_1$ or $P2_12_12$ with a = 9.71, b = 18.8, and c = 9.01 Å. Carbonyl infrared spectra of each of the two types taken in cyclohexane solution were identical. The photographically determined volumes were 815 Å^3 for the triclinic form and 1640 Å^3 for the orthorhombic form. The flotation density determined for a mixture of the two types in CCl_4-CH_2Br_2 was 1.89 g cm^{-3}. The triclinic crystals were more nearly cubical and had fewer and better formed faces than the orthorhombic type; thus a triclinic crystal was selected for the structure determination. The crystal chosen was bounded by the faces $(\bar{1}\bar{1}0)$, (110), (101), $(\bar{1}0\bar{1})$, (100), $(10\bar{1})$, and $(1\bar{1}0)$ with perpendicular distances from a common point of 0.0, 0.17, 0.15, 0.085, 0.0, 0.0, and 0.39 mm, respectively. The crystal was glued to a thin glass fiber and mounted on a Syntex $P\bar{1}$ automated diffractometer (equipped with scintillation counter and graphite monochromator) with the crystal (110) and (101) faces roughly parallel to the instrumental ϕ axis.

Fifteen high-angle reflections were used as input to the automatic centering, autoindexing, least-squares, and axial photograph routines of the instrument to obtain a set of room temperature lattice parameters. Based on Mo K$\bar{\alpha}$ = 0.710 69 Å, the results were a = 9.368 (4) Å, b = 9.289 (3) Å, c = 9.278 (3) Å, α = 91.92 (3)°, β = 90.41 (3)°, γ = 83.59 (3)°, and V = 801.9 (5) Å^3. The calculated density of 1.92 g cm^{-3} for Z = 2 agrees with the flotation density of 1.89 g cm^{-3} observed for the mixture of crystalline types. The crystal was then cooled to −158 °C[7] and recentered using the same 15 reflections to give the final low-temperature unit cell parameters listed in Table 1.

Intensity data were collected at this temperature using the $\theta/2\theta$ scan technique with Mo K$\bar{\alpha}$ radiation, a scan rate of 3° min^{-1}, and a scan range of 1.6° below the Mo Kα_1 peak to 1.4° above the Mo Kα_2 peak with background counts of one-half the scan time taken at each end of the scan range. The intensities of three standard reflections, $(1\bar{2}2)$, $(\bar{1}13)$, and (231), were recorded after every 97 intensity measurements. The maximum deviations from their respective means were 1.7, 1.8, and 1.0%. A total of 5593 independent reflections were measured which constitute the entire hemisphere $+h$, $\pm k$, and $\pm l$ accessible with Mo K$\bar{\alpha}$ radiation having $0° < 2\theta < 65°$. The 744 re-

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Table I. Crystal Data

molecule	$HFe_3(CH_3C{=}NH)(CO)_9$[a]	$HFe_3(N{=}CHCH_3)(CO)_9$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a	9.276 (3) Å	13.620 (2) Å
b	9.190 (2) Å	7.822 (2) Å
c	9.099 (2) Å	7.554 (1) Å
α	92.40 (2)°	72.19 (1)°
β	90.79 (2)°	92.71 (1)°
γ	83.45 (3)°	89.60 (1)°
V	770.0 (4) Å^3	765.2 (2) Å^3
Z	2	2
T	−158 °C	−158 °C
mol wt	462.72	462.72
$\rho_{obsd}^{25°C}$	1.89 g cm^{-3} [b]	1.99 g cm^{-3}
$\rho_{calcd}^{25°C}$	1.92 g cm^{-3}	2.01 g cm^{-3}
radiation (Mo $K\bar{\alpha}$)	0.710 69 Å[c]	0.710 73 Å

[a] This unit cell was chosen for convenience sake owing to its nearly cubical shape. The reduced unit cell parameters at −158 °C are a = 9.276 Å, b = 12.291 Å, c = 12.659 Å, α = 117.73°, β = 94.18°, γ = 132.02°. [b] For a mixture of triclinic and orthorhombic, see Experimental Section. [c] The new value of 0.710 73 Å became known to us after completion of the structure of **5a.** Recalculations are not warranted.

flections having $I \leq 3\sigma(I)$ were considered to be unobserved and omitted from the refinement. The 4849 observed reflections were corrected for Lorentz and polarization effects and converted to $|F_o|$ and $\sigma(|F_o|)$ by means of the equations

$$I = SC - \tau(B_1 + B_2) \quad (1)$$

$$\sigma(I) = [SC + \tau^2(B_1 + B_2) + p^2I^2]^{1/2} \quad (2)$$

$$|F_o| = k[I/(Lp)]^{1/2} \quad (3)$$

$$\sigma(|F_o|) = (k/2)[\sigma(I)]/[I(Lp)]^{1/2} \quad (4)$$

where SC is the count during the scan, τ is the ratio of scan time to background time (= 1 here), B_1 and B_2 are the two background counts, p is the "ignorance factor" (set to 0.04 here), and Lp is the Lorentz and polarization factor. Absorption and secondary extinction corrections were applied during refinement (vide infra).

Data Collection for $HFe_3(N{=}CHCH_3)(CO)_9$ (6a). Crystals of **6a** were sublimed under a vacuum of 15 μm at 50 °C. Carbonyl spectra showed the crystals to be the desired complex, unaltered by the sublimation. The crystal selected for structure determination was shown through oscillation and Weissenberg photography to be triclinic, with axial lengths of 7.40, 8.05, and 13.93 Å and a volume of 823 Å^3. The flotation density (1.99 g/cm^3 in aqueous ZnI_2) indicated that Z was equal to 2, consistent with the $P\bar{1}$ space group. The crystal was bounded by the faces $(\bar{1}00)$, (100), (001), $(00\bar{1})$, $(0\bar{1}\bar{1})$, and (021) with perpendicular distances from a common point of 0.15, 0.0, 0.0, 0.125, 0.0, and 0.22 mm, respectively. The crystal was glued to a thin glass fiber and painted with a thin layer of epoxy to prevent air oxidation observed with other crystals. This was mounted on a Syntex $P\bar{1}$ automated diffractometer equipped with scintillation counter and graphite monochromator with the crystal (100) and (001) faces roughly parallel to the instrumental ϕ axis.

Fifteen reflections were used as input to the automatic centering, autoindexing, least-squares, and axial photograph routines of the instrument to obtain a set of room temperature lattice parameters. Based on Mo Kα = 0.710 73 Å, the results were a = 13.631 (8) Å, b = 7.827 (5) Å, c = 7.554 (5) Å, α = 72.33 (5)°, β = 92.69 (5) °, γ = 87.59 (5)°, and V = 766.9 (8) Å^3. The crystal was then cooled to −158 °C[7] and recentered, using 15 reflections with $25° < 2\theta < 30°$ collected in a fast scan. An accurate set of lattice parameters for use in the refinement of the structure was obtained, and is given in Table I.

Intensity data were collected at this temperature using the $\theta/2\theta$ scan technique with Mo $K\bar{\alpha}$ radiation, a scan rate of 3° min^{-1}, and a scan range of 1.3° below the Mo Kα_1 peak to 1.3° above the Mo Kα_2 peak with background counts of one-half the scan time taken at each end of the scan range. The intensities of three standard reflections, $(4\bar{1}0)$, $(\bar{1}01)$, and (001), were recorded after every 97 intensity measurements. These showed no significant change during data collection. A

Table II. Final Atom Positions[a]

	$HFe_3(CH_3C{=}NH)(CO)_9$			$HFe_3(N{=}CHCH_3)(CO)_9$		
atom	x	y	z	x	y	z
Fe(1)	0.226 77(3)	0.224 51(3)	0.422 79(2)	0.730 97(4)	1.021 94(7)	0.863 72(7)
Fe(2)	0.257 09(3)	0.026 07(2)	0.222 76(3)	0.846 91(4)	0.800 12(7)	0.786 45(7)
Fe(3)	0.161 55(3)	0.312 61(3)	0.163 65(3)	0.658 77(4)	0.756 34(7)	0.778 72(7)
O(11)	−0.0764(2)	0.1652(2)	0.4414(2)	0.7422(2)	0.8038(4)	1.2566(4)
O(12)	0.2008(2)	0.5105(2)	0.5826(2)	0.8704(2)	1.2893(4)	0.9161(5)
O(13)	0.3336(2)	0.0621(2)	0.6813(2)	0.5525(2)	1.2319(4)	0.8759(5)
O(21)	−0.0300(2)	−0.0763(2)	0.1773(2)	0.9236(2)	0.5559(4)	1.1463(4)
O(22)	0.3683(2)	−0.2050(2)	0.4217(2)	0.9176(2)	0.6073(4)	0.5344(4)
O(23)	0.4092(2)	−0.1336(2)	−0.0279(2)	1.0170(2)	1.0318(4)	0.7566(5)
O(31)	−0.1479(2)	0.2813(2)	0.0983(2)	0.6086(4)	0.4863(4)	1.1282(2)
O(32)	0.2755(2)	0.3647(2)	−0.1259(2)	0.4662(2)	0.9406(5)	0.7064(4)
O(33)	0.0954(2)	0.6215(2)	0.2574(2)	0.6170(3)	0.5391(5)	0.5269(4)
N	0.3929(2)	0.1600(2)	0.2884(2)	0.7406(2)	0.9381(4)	0.6456(4)
C(CN)	0.3506(2)	0.3001(2)	0.2572(2)	0.7255(3)	1.1103(6)	0.5543(5)
C(ME)	0.4575(2)	0.4110(2)	0.2729(2)	0.8018(3)	1.2328(6)	0.4485(6)
C(11)	0.0413(2)	0.1902(2)	0.4298(2)	0.7376(3)	0.8857(5)	1.1026(5)
C(12)	0.2127(2)	0.3990(2)	0.5207(2)	0.8170(3)	1.1848(5)	0.8925(5)
C(13)	0.2917(2)	0.1245(2)	0.5803(2)	0.6212(3)	1.1495(5)	0.8705(6)
C(21)	0.0823(2)	−0.0404(2)	0.1968(2)	0.8967(3)	0.6529(5)	1.0061(6)
C(22)	0.3229(2)	−0.1140(2)	0.3470(2)	0.8912(3)	0.6817(5)	0.6324(5)
C(23)	0.3488(2)	−0.0696(2)	0.0660(2)	0.9485(3)	0.9464(5)	0.7652(6)
C(31)	−0.0292(2)	0.2929(2)	0.1246(2)	0.6255(3)	0.5921(5)	0.9925(5)
C(32)	0.2264(2)	0.3449(2)	−0.0151(2)	0.5415(3)	0.8702(6)	0.7352(5)
C(33)	0.1201(2)	0.5007(2)	0.2212(2)	0.6341(3)	0.6224(5)	0.6230(6)
H(FE)	0.187(4)	0.140(4)	0.088(4)	0.758(5)	0.643(8)	0.848(9)
H(N)	0.484(3)	0.134(4)	0.335(4)	0.657(4)	1.151(6)	0.517(7)
H(ME1)	0.410(3)	0.505(3)	0.309(3)	0.778(4)	1.354(7)	0.445(7)
H(ME2)	0.526(3)	0.394(3)	0.344(3)	0.805(4)	1.220(7)	0.322(8)
H(ME3)	0.509(3)	0.407(3)	0.173(4)	0.870(4)	1.201(7)	0.500(7)

[a] Positions are given in fractional coordinates followed in parentheses by the estimated standard deviation of the least significant digit.

Table III. Final Thermal Parameters[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$HFe_3(CH_3C{=}NH)(CO)_9$						
Fe(1)	0.312(3)	0.315(3)	0.286(2)	−0.033(2)	−0.002(2)	0.027(2)
Fe(2)	0.327(3)	0.269(2)	0.354(3)	−0.056(2)	0.035(2)	−0.002(2)
Fe(3)	0.477(3)	0.300(3)	0.312(3)	−0.057(2)	−0.043(2)	0.034(2)
O(11)	0.42(1)	0.64(2)	0.68(2)	−0.08(1)	0.09(1)	0.00(1)
O(12)	1.00(2)	0.47(2)	0.58(2)	−0.08(1)	−0.04(1)	−0.11(1)
O(13)	0.60(2)	0.76(2)	0.54(2)	0.11(1)	−0.01(1)	0.24(1)
O(21)	0.47(1)	0.51(1)	0.76(2)	−0.15(1)	0.01(1)	−0.06(1)
O(22)	0.56(2)	0.53(2)	0.84(2)	−0.01(1)	−0.03(1)	0.25(1)
O(23)	0.86(2)	0.83(2)	0.92(2)	−0.41(2)	0.48(2)	−0.45(2)
O(31)	0.61(2)	0.84(2)	0.97(2)	−0.14(2)	−0.21(2)	−0.01(2)
O(32)	1.39(3)	0.94(2)	0.50(2)	−0.25(2)	0.14(2)	0.17(2)
O(33)	1.02(2)	0.42(1)	0.78(2)	0.04(1)	−0.19(2)	−0.01(1)
N	0.38(1)	0.38(1)	0.43(1)	−0.09(1)	0.07(1)	−0.02(1)
C(CN)	0.44(2)	0.37(2)	0.41(2)	−0.08(1)	0.06(1)	0.05(1)
C(ME)	0.57(2)	0.46(2)	0.72(2)	−0.21(2)	0.07(2)	−0.01(2)
C(11)	0.42(2)	0.39(2)	0.42(2)	−0.02(1)	0.03(1)	0.01(1)
C(12)	0.53(2)	0.48(2)	0.37(2)	−0.04(1)	−0.02(1)	0.06(1)
C(13)	0.41(2)	0.49(2)	0.44(2)	0.01(1)	0.03(1)	0.06(1)
C(21)	0.44(2)	0.34(2)	0.46(2)	−0.03(1)	0.03(1)	−0.01(1)
C(22)	0.37(2)	0.40(2)	0.56(2)	−0.07(1)	0.04(1)	0.03(1)
C(23)	0.58(2)	0.49(2)	0.63(2)	−0.22(2)	0.16(2)	−0.08(2)
C(31)	0.68(2)	0.46(2)	0.53(2)	−0.08(2)	−0.09(2)	0.02(2)
C(32)	0.78(2)	0.51(2)	0.43(2)	−0.14(2)	−0.04(2)	0.07(1)
C(33)	0.60(2)	0.44(2)	0.47(2)	−0.03(1)	−0.16(1)	0.09(1)
H(FE)[b]	5.0(8)					
H(N)[b]	3.8(7)					
H(ME1)[b]	2.3(5)					
H(ME2)[b]	1.6(5)					
H(ME3)[b]	3.5(7)					
$HFe_3(N{=}CHCH_3)(CO)_9$						
Fe(1)	0.184(3)	0.602(9)	0.570(9)	−0.058(4)	0.002(4)	−0.269(7)
Fe(2)	0.152(3)	0.806(10)	0.704(10)	−0.058(4)	0.012(4)	−0.386(8)
Fe(3)	0.161(3)	0.656(9)	0.597(10)	−0.083(4)	−0.001(4)	−0.250(8)
O(11)	0.44(2)	1.27(6)	0.70(6)	−0.15(3)	0.01(3)	−0.24(5)
O(12)	0.40(2)	0.92(6)	1.58(7)	−0.24(3)	−0.90(3)	−0.49(5)
O(13)	0.32(2)	1.26(6)	1.45(7)	0.09(3)	0.16(3)	−0.47(5)
O(21)	0.41(2)	1.12(6)	0.88(6)	−0.08(3)	0.02(3)	−0.22(5)
O(22)	0.40(2)	1.28(6)	0.97(6)	0.11(3)	0.03(3)	−0.56(5)
O(23)	0.27(2)	1.13(6)	1.73(8)	−0.21(3)	−0.03(3)	−0.25(5)
O(31)	0.43(2)	1.00(6)	0.85(6)	−0.17(3)	0.01(3)	−0.21(5)
O(32)	0.23(2)	1.60(7)	1.23(6)	0.05(3)	−0.09(2)	−0.44(5)
O(33)	0.60(2)	1.49(7)	1.07(6)	−0.39(3)	0.14(3)	−0.80(6)
N	0.24(2)	0.74(6)	0.57(5)	−0.08(2)	0.03(2)	−0.35(5)
C(CN)	0.30(2)	0.93(7)	0.72(7)	−0.06(3)	−0.02(3)	−0.27(6)
C(ME)	0.27(2)	0.90(7)	0.75(7)	−0.10(3)	0.03(3)	−0.10(6)
C(11)	0.26(2)	0.90(7)	0.80(7)	−0.10(3)	0.08(3)	−0.38(6)
C(12)	0.30(2)	0.66(6)	0.77(7)	−0.04(3)	−0.02(3)	−0.29(5)
C(13)	0.26(2)	0.80(7)	0.89(7)	−0.02(3)	0.02(3)	−0.35(6)
C(21)	0.25(2)	0.84(7)	0.96(7)	−0.13(3)	0.07(3)	−0.50(6)
C(22)	0.23(2)	0.90(7)	0.66(7)	−0.05(3)	−0.04(3)	−0.15(6)
C(23)	0.22(2)	0.75(7)	0.92(7)	−0.03(3)	−0.02(3)	−0.18(6)
C(31)	0.24(2)	0.79(7)	0.85(7)	−0.09(3)	−0.02(3)	−0.42(6)
C(32)	0.25(2)	1.08(8)	0.71(7)	−0.07(3)	0.01(3)	−0.28(6)
C(33)	0.27(2)	0.92(7)	0.81(7)	−0.21(3)	0.08(3)	−0.27(6)
H(FE)[b]	5.8(1.6)					
H(C)[b]	2.2(0.9)					
H(ME1)[b]	3.4(1.2)					
H(ME2)[b]	3.3(1.2)					
H(ME3)[b]	3.0(1.1)					

[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] Isotropic temperature factors B in Å^2.

total of 4507 independent reflections were measured, which constitute the entire hemisphere $+h, \pm k, \pm l$ accessible with Mo $K\alpha$ radiation having $0° < 2\theta < 60°$. The 1247 reflections having $I \leq 3\sigma(I)$ were considered to be unobserved and omitted from the refinement. The 3260 observed reflections were corrected for Lorentz and polarization effects and converted to $|F_o|$ and $\sigma(|F_o|)$ by means of eq 1-4 given and defined above. An absorption correction was applied during refinement (vide infra).

Solution and Refinement of Structures. Programs used during the structural analysis included the data reduction program P1BAR for the Syntex diffractometer by Bell and Murphy; JBPATT, JBFOUR, and PKLIST, modified versions of Fourier programs by Blount; local versions of ORFLS and ORXFFE by Busing, Martin, and Levy for full-matrix least-squares and error analysis; ABSN by Coppens for absorption correction; SECEXT (Christensen's program modified by Knobler) for secondary extinction correction; MGTL by Gantzel and Trueblood for least-squares planes; HPOSN by Hope for calculating idealized hydrogen positions; ORTEP by Johnson for structure plots;

Table IV. Root-Mean-Square Amplitudes of Vibration and Equivalent B Values[a]

atom	rms amplitude/Å			equivalent B/Å^2		
	min	med	max	min	med	max
			$HFe_3(CH_3C{=}NH)(CO)_9$			
Fe(1)	0.1081(5)	0.1159(5)	0.1162(5)	0.92	1.06	1.07
Fe(2)	0.1045(5)	0.1143(5)	0.1266(4)	0.86	1.03	1.27
Fe(3)	0.1088(5)	0.1149(5)	0.1450(4)	0.93	1.04	1.66
O(11)	0.130(2)	0.163(2)	0.173(2)	1.33	2.10	2.36
O(12)	0.126(2)	0.167(2)	0.209(2)	1.25	2.20	3.45
O(13)	0.122(2)	0.159(2)	0.203(2)	1.18	2.00	3.25
O(21)	0.126(2)	0.155(2)	0.182(2)	1.25	1.90	2.62
O(22)	0.129(2)	0.158(2)	0.199(2)	1.31	1.97	3.13
O(23)	0.127(3)	0.144(2)	0.268(2)	1.27	1.64	5.67
O(31)	0.144(2)	0.189(2)	0.214(2)	1.64	2.82	3.62
O(32)	0.132(3)	0.201(2)	0.247(3)	1.38	3.19	4.82
O(33)	0.130(2)	0.169(2)	0.224(2)	1.33	2.26	3.96
N	0.117(3)	0.123(3)	0.145(2)	1.08	1.19	1.66
C(CN)	0.115(3)	0.132(3)	0.143(3)	1.04	1.38	1.61
C(ME)	0.119(3)	0.162(3)	0.180(3)	1.12	2.07	2.56
C(11)	0.125(3)	0.132(3)	0.139(3)	1.23	1.38	1.53
C(12)	0.121(3)	0.143(3)	0.153(3)	1.16	1.61	1.85
C(13)	0.128(3)	0.133(3)	0.153(3)	1.29	1.40	1.85
C(21)	0.119(3)	0.136(3)	0.143(3)	1.12	1.46	1.61
C(22)	0.121(3)	0.132(3)	0.154(3)	1.16	1.38	1.87
C(23)	0.120(3)	0.143(3)	0.188(3)	1.14	1.61	2.79
C(31)	0.139(3)	0.144(3)	0.176(3)	1.53	1.64	2.45
C(32)	0.131(3)	0.146(3)	0.186(3)	1.35	1.68	2.73
C(33)	0.116(3)	0.143(3)	0.174(3)	1.06	1.61	2.39
			$HFe_3(N{=}CHCH_3)(CO)_9$			
Fe(1)	0.1059(11)	0.1290(10)	0.1401(9)	0.89	1.31	1.55
Fe(2)	0.1096(11)	0.1262(10)	0.1565(9)	0.95	1.26	1.93
Fe(3)	0.1049(11)	0.1272(10)	0.1446(9)	0.87	1.28	1.65
O(11)	0.134(5)	0.177(5)	0.217(5)	1.42	2.47	3.72
O(12)	0.120(6)	0.196(5)	0.224(5)	1.14	3.03	3.96
O(13)	0.148(5)	0.194(5)	0.206(5)	1.73	2.97	3.35
O(21)	0.151(5)	0.177(5)	0.200(5)	1.80	2.47	3.16
O(22)	0.139(5)	0.179(5)	0.208(5)	1.53	2.70	3.58
O(23)	0.132(5)	0.189(5)	0.229(5)	1.38	2.82	4.14
O(31)	0.148(5)	0.158(5)	0.212(4)	1.73	1.97	3.55
O(32)	0.139(5)	0.185(5)	0.213(5)	1.53	2.70	3.58
O(33)	0.124(6)	0.183(5)	0.262(5)	1.21	2.64	5.42
N	0.104(6)	0.139(5)	0.160(5)	0.85	1.53	2.02
C(CN)	0.133(7)	0.157(6)	0.174(6)	1.40	1.95	2.39
C(ME)	0.132(7)	0.152(6)	0.181(6)	1.38	1.82	2.59
C(11)	0.133(7)	0.142(6)	0.172(6)	1.40	1.59	2.33
C(12)	1.26(7)	0.144(6)	0.171(6)	1.25	1.64	2.31
C(13)	0.138(7)	0.156(6)	0.157(6)	1.50	1.92	2.07
C(21)	0.118(7)	0.147(6)	0.179(6)	1.10	1.71	2.53
C(22)	0.126(7)	0.146(6)	0.171(6)	1.25	1.68	2.31
C(23)	0.140(6)	0.144(7)	0.165(6)	1.55	1.64	2.15
C(31)	0.115(7)	0.156(7)	0.162(6)	1.04	1.92	2.07
C(32)	0.134(7)	0.151(6)	0.179(6)	1.42	1.80	2.53
C(33)	0.124(7)	0.146(6)	0.189(6)	1.21	1.68	2.82

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

and PUBLIST by Hoel for structure factor table listing. All calculations were performed on the UCLA Campus Computing Network's IBM 360/91.

The scattering factors for neutral iron, oxygen, nitrogen, and carbon were taken from Table 2.2A of ref 8a while those for hydrogen were those of Stewart et al.[8b] 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 8a.

The function minimized during least-squares refinement was $\Sigma w||F_o| - |F_c||^2$ where $w = [\sigma(|F_o|)]^{-2}$. The discrepancy indices were defined as

$$R_F\ (\%) = \left[\frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}\right] \times 100$$

$$R_{wF}\ (\%) = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100$$

and the goodness of fit (GOF) was given by

$$\mathrm{GOF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{(N_o - N_v)}\right]^{1/2}$$

where N_o is the number of observations and N_v is the number of variables.

Structure of 5a. The positions of the three independent iron atoms were determined from a Patterson synthesis and found to be consistent with the space group $P\overline{1}$. The correctness of this space-group assignment is indicated by the subsequent successful refinement. A Fourier map phased on the iron atoms revealed the positions of the 21 remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters converged at $R_F = 7.7\%$ and $R_{wF} = 10.1\%$.

The data were then corrected for the effects of absorption (μ = 28.35 cm^{-1}, maximum, minimum, and mean transmission factors of 0.832, 0.688, and 0.778). A cycle of least squares gave $R_F = 5.8\%$ and $R_{wF} = 8.5\%$, indicating the validity of the correction. Three more

Table V. Interatomic Distances (Å) for $HFe_3(CH_3C{=}NH)(CO)_9$ (**5a**) and $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**)

parameter	**5a**	**6a**
Fe(1)-Fe(2)	2.5173(7)	2.5521(9)
-Fe(3)	2.5672(7)	2.5457(8)
-N	2.001(2)	1.960(3)
-C(CN)	2.096(2)	2.223(4)
-C(11)	1.787(2)	1.791(4)
-C(12)	1.794(2)	1.792(4)
-C(13)	1.795(2)	1.802(4)
Fe(2)-Fe(3)	2.7537(8)	2.5879(8)
-N	1.931(2)	1.877(3)
-C(21)	1.806(2)	1.804(4)
-C(22)	1.798(2)	1.815(4)
-C(23)	1.814(2)	1.784(4)
-H(FE)	1.72(3)	1.71(6)
Fe(3) N		1.878(3)
-C(CN)	1.933(2)	
-C(31)	1.828(2)	1.809(4)
-C(32)	1.790(2)	1.789(4)
-C(33)	1.785(2)	1.821(4)
-H(FE)	1.70(4)	1.59(6)
C(11)-O(11)	1.148(2)	1.142(5)
C(12)-O(12)	1.143(2)	1.146(5)
C(13)-O(13)	1.144(2)	1.142(5)
C(21)-O(21)	1.137(2)	1.140(5)
C(22)-O(22)	1.140(2)	1.141(5)
C(23)-O(23)	1.134(2)	1.144(5)
N-C(CN)	1.344(2)	1.321(5)
-H(N)	0.95(3)	
C(CN)-C(ME)	1.502(3)	1.504(6)
-H(C)		0.98(5)
C(31)-O(31)	1.139(3)	1.138(5)
C(32)-O(32)	1.142(2)	1.141(5)
C(33)-O(33)	1.144(2)	1.132(5)
C(ME)-H(ME1)	0.97(3)	0.99(5)
-H(ME2)	0.90(3)	0.99(6)
-H(ME3)	1.03(3)	0.99(5)

cycles of least-squares refinement with anomalous dispersion included for iron and anisotropic thermal parameters for all but the carbonyl carbon atoms led to convergence at $R_F = 3.5\%$ and $R_{wF} = 5.2\%$.

At this point, a difference Fourier map clearly indicated the positions of the five hydrogen atoms at heights of 0.7-0.9 e Å^{-3} (peaks 2, 3, 4, 6, and 8 based on height; peaks 1, 5, and 7 being in chemically unreasonable locations, i.e., 0.71 Å from Fe(3) or 0.50 Å from C(23)). Least-squares refinement of positional parameters for all atoms and anisotropic temperature factors for all nonhydrogen atoms but with fixed isotropic temperature factors for hydrogen atoms (2.0 for H(FE) and 2.4 for others) converged at $R_F = 2.9\%$ and $R_{wF} = 4.2\%$.

Examination of the intense, low-angle F_o and F_c values suggested that secondary extinction effects were present. A correction was thus applied[9] but it had a negligible effect on the refinement.

A low-angle data set ($\sin\theta/\lambda < 0.30$, 345 reflections) was then used to refine only the scale factor and hydrogen positional and isotropic thermal parameters. The final low angle based discrepancy indices were $R_F = 3.2\%$ and $R_{wF} = 5.2\%$.[10] With the hydrogen atoms omitted ($R_F = 4.4\%$ and $R_{wF} = 8.7\%$), a low angle based difference Fourier map showed the five hydrogen atoms (in the positions found previously) as the five largest peaks (0.4-0.3 e Å^{-3}) with the remaining peaks (<0.25 e Å^{-3}) in chemically unreasonable positions.

Final least-squares refinement with the full data set of all atom position parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms gave the final discrepancy indices $R_F = 2.9\%$ and $R_{wF} = 4.2\%$ and a GOF = 1.585 ($N_o = 4849$, $N_v = 237$). In the final least-squares cycle, the largest shift in a nonhydrogen parameter was 0.09σ and for a hydrogen parameter 0.53σ. Residuals between 1.08 and −1.04 e Å^{-3} were found on a final difference Fourier map. None of the large positive residuals found on this map appeared on the low angle difference map.

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 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).

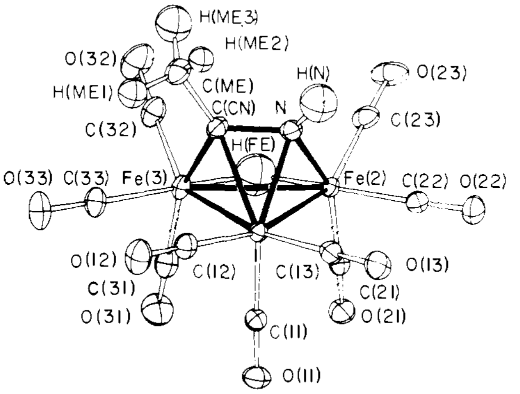


Figure 1. Overall view of the structure of $HFe_3(CH_3C{=}NH)(CO)_9$; thermal ellipsoids at the 50% probability level.

Structure of 6a. The positions of the three independent iron atoms were determined from a Patterson synthesis and were found to be consistent with the space group $P\bar{1}$. The correctness of this space group assignment is indicated by the subsequent successful refinement. A Fourier map phased on the iron atoms revealed the positions of the 21 remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters converged at $R_F = 7.7\%$ and $R_{wF} = 8.8\%$.

The data were then corrected for the effects of absorption (μ = 29.17 cm^{-1}, maximum, minimum, and mean transmission factors of 0.861, 0.806, and 0.843). A cycle of least squares gave $R_F = 7.1\%$ and $R_{wF} = 8.2\%$, indicating the validity of the correction. Three more cycles of least-squares refinement with anomalous dispersion included for iron and anisotropic thermal parameters for all nonhydrogen atoms led to convergence at $R_F = 4.4\%$ and $R_{wF} = 5.3\%$. At this point, a difference Fourier map indicated the positions of the five hydrogen atoms at heights of 0.5-0.6 e Å^3 (peaks 13, 14, 15, 16, 18, and 19 based on height; peaks 14 and 16 were 0.008 Å apart, and were consequently assumed to be the same atom; peaks 1-12 and 17 were in chemically unreasonable positions, e.g., 0.95 Å from Fe(1)). Four additional cycles of least-squares refinement of positional parameters for all atoms, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for the hydrogen atoms converged at $R_F = 4.1\%$ and $R_{wF} = 4.8\%$.

Examination of the intense, low-angle F_o and F_c values suggested that no secondary extinction corrections were necessary. In addition, since the hydrogen atoms were readily found, no low-angle data set was used to refine the hydrogen positional and thermal parameters.

Final least-squares refinement with the full data set of all atom positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms gave the final discrepancy indices $R_F = 4.1\%$ and $R_{wF} = 4.8\%$ and a GOF = 1.414 ($N_o = 3260$, $N_v = 237$). In the final least-squares cycle, the largest shift in a nonhydrogen parameter was 0.02σ and for a hydrogen parameter 0.15σ.

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 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 VIII (supplementary material).

Results and Discussion

Overall Structure of 5a. The crystal consists of discrete molecular units of $HFe_3(CH_3C{=}NH)(CO)_9$ with only one intermolecular distance (H(N)-O(13), vide infra) significantly shorter than normal van der Waals contacts. The overall geometry of the molecule and the system used for labeling the atoms are shown in Figure 1. All three iron interactions are

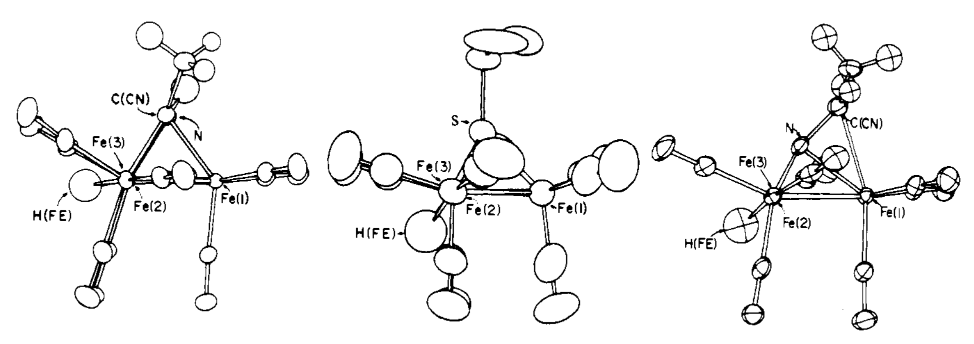
Table VI. Interatomic Angles (deg) for $HFe_3(CH_3C{=}NH)(CO)_9$ (**5a**) and $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**)

parameter	**5a**[a]	**6a**[b]
Fc(1)-Fe(2)-Fe(3)	58.09(2)	57.37(2)
-N	51.44(5)	49.72(9)
-C(21)	106.64(6)	106.4(1)
-C(22)	93.69(6)	152.5(1)
-C(23)	153.46(6)	92.8(1)
-H(FE)	93.9(12)	88.2(21)
Fc(3)-Fe(2)-N	67.50(5)	46.46(10)
-C(21)	95.46(6)	107.1(1)
-C(22)	151.75(6)	104.1(1)
-C(23)	111.50(7)	149.4(1)
-H(FE)	36.1(12)	36.6(21)
N-Fe(2)-C(21)	156.83(7)	149.1(2)
-C(22)	94.79(8)	102.8(2)
-C(23)	102.45(8)	106.8(2)
-H(FE)	92.6(12)	81.7(21)
C(21)-Fe(2)-C(22)	94.08(8)	99.4(2)
-C(23)	98.37(9)	92.1(2)
-H(FE)	80.5(12)	77.7(21)
C(22)-Fe(2)-C(23)	93.26(9)	95.7(2)
-H(FE)	171.7(12)	88.1(21)
C(23)-Fe(2)-H(FE)	81.4(12)	169.5(21)
Fc(1)-Fe(3)-Fe(2)	56.34(2)	59.61(2)
-N		49.84(9)
-C(CN)	53.27(5)	
-C(31)	109.24(7)	107.5(1)
-C(32)	146.61(7)	89.0(1)
-C(33)	94.84(6)	153.9(1)
-H(FE)	92.6(11)	91.1(24)
Fe(2)-Fe(3)-N		46.42(10)
-C(CN)	69.67(6)	
-C(31)	99.01(7)	109.7(1)
-C(32)	107.05(7)	144.4(1)
-C(33)	151.12(6)	106.1(1)
-H(FE)	36.6(12)	40.0(23)
C(CN)-Fe(3)-C(31)	162.28(8)	
-C(32)	94.92(9)	
-C(33)	92.37(8)	
-H(FE)	94.4(12)	
N-Fe(3)-C(31)		151.3(2)
-C(32)		101.4(2)
-C(33)		104.2(2)
-H(FE)		85.0(3)
C(31)-Fe(3)-C(32)	101.59(9)	94.5(2)
-C(33)	92.09(9)	97.8(2)
-H(FE)	82.7(12)	77.4(23)
C(32)-Fe(3)-C(33)	96.58(9)	95.4(2)
-H(FE)	78.6(12)	171.6(23)
C(33)-Fe(3)-H(FE)	172.0(12)	88.1(24)
Fe(2)-Fe(1)-Fe(3)	65.57(2)	61.02(2)
-N	48.98(5)	46.94(10)
-C(11)	86.67(6)	89.7(1)
-C(12)	163.10(6)	100.2(1)
-C(13)	101.10(6)	160.7(1)
-C(CN)	72.87(5)	76.3(1)
Fe(3)-Fe(1)-N		47.10(9)
-C(CN)	47.66(5)	
-C(11)	84.86(6)	88.5(1)
-C(12)	98.94(6)	160.8(1)
-C(13)	166.31(6)	101.2(1)
-C(CN)		75.9(1)
N-Fe(1)-C(CN)	38.22(6)	36.1(1)
-C(11)	134.95(7)	126.6(2)
—C(12)	121.36(8)	117.8(2)
-C(13)	98.23(8)	116.1(2)
C(CN)-Fe(1)-C(11)	132.46(8)	162.7(2)
-C(12)	91.83(8)	96.4(2)
-C(13)	127.51(8)	92.8(2)
C(11)-Fe(1)-C(12)	99.07(9)	96.0(2)
-C(13)	97.91(8)	97.7(2)
C(12)-Fe(1)-C(13)	93.87(8)	96.7(2)
C(32)-Fe(1)-C(33)		95.4(2)
-H(FE)		171.6(23)
C(33)-Fe(1)-H(FE)		88.1(24)
Fe(1)-N-Fe(2)	79.58(6)	83.3(1)
-Fe(3)	64.39(5)	83.1(1)
-C(CN)	74.7(1)	82.8(2)
-H(N)	115.8(20)	
Fe(2)-Fe(1)-Fe(3)		87.1(1)
-C(CN)	113.7(1)	135.8(3)
-H(N)	125.8(20)	
Fe(3)-Fe(1)-C(CN)		133.2(3)
C(CN)-Fe(1)-H(N)	120.5(20)	
Fe(1)-C(CN)-Fe(3)	79.07(7)	
-N	67.09(9)	61.0(2)
-C(ME)	127.6(1)	120.8(3)
-H(C)		104.8(32)
Fe(3)-C(CN)-N	109.1(1)	
-C(ME)	130.5(1)	
C(ME)-C(CN)-H(C)		115.0(28)
N-C(CN)-C(ME)	119.4(2)	124.7(4)
-H(C)		116.9(28)
Fe(2)-H(FE)-Fe(3)	107.3(20)	103.3(34)

[a] Interatomic angles about carbonyl carbon atoms ranged from 176 to 179°; angles about C(ME) ranged from 100 to 117°. [b] Interatomic angles about carbonyl carbons ranged from 176 to 179°; angles about C(ME) ranged from 102 to 115°.

bonding (2.5173 (7), 2.5672 (7), and 2.7537 (8) Å) and define a nearly isosceles triangle. Each iron atom is also bonded to three terminal linear carbonyl ligands. A vertical profile of the molecule is shown in Figure 2a together with similar profiles of $HFe_3(S\text{-}i\text{-}Pr)(CO)_9$ (Figure 2b)[11] and **6a** (Figure 2c). These will serve for comparisons in the three related structures discussed below. The two projections of **5a**, Figures 1 and 2a, show that three of the carbonyl groups extend axially below the triiron plane, four of the carbonyl groups are equatorially disposed, while the remaining two (which we will denote as dihedral) intersect the triiron plane at an angle of 30°. The open face of the $Fe_3(CO)_9$ cluster is capped by the triply bridging CH_3CNH group which is discussed in detail below. Finally, the metal hydride ligand lies slightly below the triiron plane symmetrically bridging Fe(2) and Fe(3). It is thus sandwiched between the axial and dihedral carbonyls of Fe(2) and Fe(3) (see Figure 2a).

Overall Structure of 6a. The crystal consists of discrete molecular units of $HFe_3(N{=}CHCH_3)(CO)_9$ with normal van der Waals contacts. The overall geometry of the molecule and the system used for labeling the atoms are shown in Figure 3. The numbering of the metal atoms was chosen so as to place hydrogen between iron atoms labeled (2) and (3), similar to that selected in the structure of **5a**; no specific structure relationship is implied. All three iron interactions are bonding (2.5457 (8), 2.5521 (9), 2.5879 (8) Å), and define a nearly equilateral triangle. Each iron atom is also bonded to three terminal carbonyl ligands. The two projections of **6a**, Figures 2c and 3, show that three of the carbonyl groups extend axially below the triiron plane and only two carbonyl groups are equatorially disposed, CO(12) and (13). The two carbonyl groups which appear pseudotrans to the bridging hydrogen, CO(23) and (32), intersect the triiron plane at an angle of 30°. The remaining two, CO(22) and (33), we will denote as dihedral; these intersect the triiron plane at an angle of 25°. The open face of the $Fe_3(CO)_9$ cluster is capped by the triply bridging $NCHCH_3$ group, which is discussed in detail below. Finally, the hydride ligand lies significantly below the triiron



(a) $HFe_3(CH_3C{=}NH)(CO)_9$ (b) $HFe_3(S\text{-}\underline{i}Pr)(CO)_9$ (c) $HFe_3(N{=}CHCH_3)(CO)_9$

Figure 2. Side view in the direction of the Fe(2)-Fe(3) axis of related hydridotriiron cluster complexes; thermal ellipsoids at the 50% probability level.

plane, and nearly symmetrically bonded between Fe(2) and Fe(3).

The Acetimidoyl Group in 5a. The C—N bond length of 1.344 (2) Å in the $CH_3C{=}NH$ group is between that of a C—N single bond (1.47 Å) and of a C—N double bond (1.28 Å).[12] The C-N stretching frequency of 1353 cm^{-1} [1b] is in agreement with this apparent bond order of ~1.5. The bonding of the triply bridging $CH_3C{=}NH$ group to the metal triangle could be described as two σ bonds, Fe(2)-N = 1.931 (2) and Fe(3)-C(CN) = 1.933 (2) Å, and a π bond, Fe(1)-N = 2.001 (2) and Fe(1)-C(CN) = 2.096 (2) Å. The lengthening of the C=N double bond upon π coordination is entirely analogous to the effect observed for olefins[13] and iminium cations.[14] Illustrative examples of the latter are 1.392 (6) Å for C=N in $[Ni(PPh_3)_2(H_2C{=}NMe_2)]^+$,[14a] 1.42 (1) Å in $(FcCH_2(CH_3)N{=}CH_2)Mn(CO)_4$ (Fc = ferrocenyl),[14b] 1.43 (2) Å in a nickel(II) salicylaldiminium complex,[14c] and 1.45 (2) Å in $Mn(CO)_4(H_2C{=}NC_2H_4)$.[14d] The C—N distance in $HFe_3(CH_3C{=}NH)(CO)_9$ (1.344 (2) Å) is *shorter* than the corresponding distance of 1.415 (11) Å observed in $HOs_3(HC{=}NPh)(CO)_9$.[6b,c] The metal-metal distance of the hydrogen-bridged metal-metal bond which is also bridged by the hetero-π group could in part be responsible for this difference; cf. Fe(2)-Fe(3) = 2.7537 (8) Å while Os(1)-Os(2) = 2.956 (1) Å.[6b,c] Without a π interaction to the third metal atom as in the osmium complexes cited below, the C-N distance is observed markedly to shorten, i.e., $d(C_{17}\text{-}N)$ = 1.278 (10) Å in $HOs_3(PhC_{17}{=}NMe)(CO)_{10}$[15a] or $d(C_{17}\text{-}N)$ = 1.320 (10) Å in $HOs_3(HC{=}NPh)(CO)_9P(OMe)_3$.[6b,c]

It is puzzling to note that, despite the apparent C-N bond order of ~1.5 in the π-bonded acetimidoyl group in **5a**, the geometries about C(CN) and N hardly deviate from pure sp^2. Thus Fe(2), N, H(N), C(CN), C(ME), and Fe(3) are nearly coplanar[16] and the angles about N (113.7 (1), 115.8 (20), 120.5 (20), and 125.8 (20)°) and C(CN) (109.1 (1), 119.4 (2), 127.6 (1), and 130.5 (1)°) are close to 120°.[17a] This contrasts with the usual rehybridization toward sp^3 with concomitant bending back of the substituents found for π-bonded olefins and iminium cations. This bending back is more commonly measured by the angles α and β.[13,17b] For an uncomplexed olefin these are 0 and 90°, respectively. For π-bonded olefins typical values are α = 35-85° and β = 40-75°,[13] and for π-bonded iminium cations β = 47-79°.[14] In the present structure α = 14°, β = 88° (for the H(N) and Fe(2) substituents) and β = 79° (for the C(ME) and Fe(3) substituents).

Although the C-C distance and degree of bending back in olefins are not strictly correlated,[13] the present case would definitely seem to be anomalous.[18] The small degree of bending back here cannot be attributed to the presence of two metal substituents which are in a constrained geometry since significant bending back is observed in complexes containing isostructural triply bridging alkenylene (RC=CR) ligands such as $Cp_3Rh_3(CO)(PhC{=}CPh)$ (α = 26, β = 74, 80°)[19a] and $Fe_3(CO)_8(PhC{=}CPh)_2$ (α = 31, 33; β = 77, 78, 72, 69°).[19b] This observation warrants further structural and theoretical investigations.

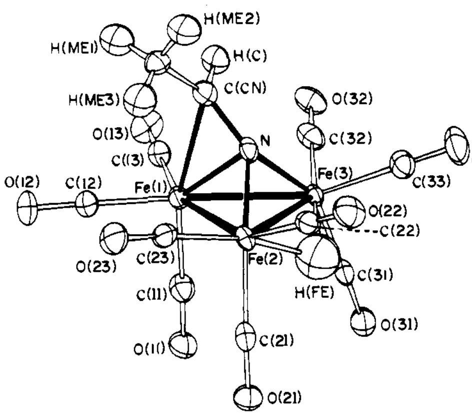


Figure 3. Overall view of the structure of $HFe_3(N{=}CHCH_3)(CO)_9$; thermal ellipsoids at the 50% probability level.

A final note concerning the acetimidoyl group is the observation that there is a slight twist about the C(CN)-N bond. This is apparent in Figure 2a from the 10° dihedral angle of C(ME)-C(CN)-N-H(N). Similar twists have been observed in olefin complexes.[13] The twist is correlated with a slight asymmetry in the bonding of the bridging acetimidoyl group; the N atom is about 0.1 Å closer than C(CN) is to Fe(1). This may result from the 0.1-Å difference in covalent radii of carbon and nitrogen.

The Ethylidenimido Group in 6a. The carbon-nitrogen bond distance in the $N{=}CHCH_3$ group is 1.321 (5) Å, intermediate between that of a C—N single (1.47 Å) and double (1.28 Å) bond; this is also reflected in the position of ν_{CN} 1325 cm^{-1}.[1b] This C-N bond, however, is slightly shorter than that in the acetimidoyl group in **5a**, cf. C-N = 1.344 (2) Å and ν_{CN} 1353 cm^{-1}.[1b] This no doubt results from less electron withdrawal in the asymmetrically and possibly less intimately bonded ethylidenimido group; see discussion following. The disposition of atoms about C(CN) strongly suggests sp^2 hybridization for carbon: N, C(CN), C(ME), and H(C) are nearly coplanar, and the angles about C(CN) (124.7 (4), 116.9 (28), and 115.0 (28)°) are nearly 120°. The C—N distance of 1.321 (5) Å in the triply bridging $N{=}CHCH_3$ group in **6a** is markedly and understandably longer than in η^2-alkilidenimido groups not π bonded to a third metal center as, for instance, $d(N{=}CR_2)$ = 1.24 (2) and 1.29 (2) Å in $Fe_2(N{=}CR_2)(CO)_6$, R = *p*-tolyl,[20a] $d(N{=}CR_2)$ = 1.258 (9) and 1.259 (9) Å in $Mn_2(N{=}CR_2)(CO)_7$, R = CF_3,[20b] and $d(N{=}CR_2)$ = 1.280 (6) and 1.279 (5) Å in $HRu_3(N{=}CR_2)(CO)_{10}$, R = Me.[20c]

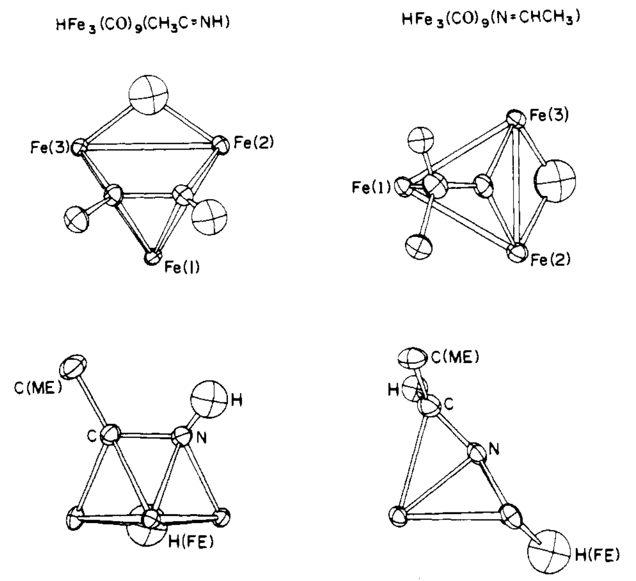
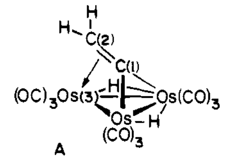
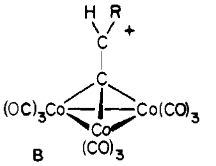


Figure 4. Side elevation (lower drawings) and top view (upper drawings) of cluster complexes. For clarity, only the hydrogen atom bonded to the metal triangle, the three metal atoms, the carbon atom of the methyl group, and the carbon, nitrogen, and hydrogen of the iminyl group are shown; thermal ellipsoids at 50% probability. The side elevations show the molecules with the central carbon to nitrogen axis of the iminyl ligands parallel to the plane of the paper; the top view is a projection of each of the molecules onto the plane defined by the metal triangle.

In **6a** the ethylidenimido group is attached to the metal triangle through two σ bonds to nitrogen, Fe(2)–N = 1.878 (3) and Fe(3)–N = 1.877 (3) Å, and by a π bond of pronounced asymmetry, Fe(1)–C(CN) = 2.223 (4) and Fe(1)–N = 1.960 (3) Å. The difference in the latter two distances far exceeds that which can be attributed to the difference of 0.1 Å between the covalent radii of carbon and nitrogen. A similar asymmetry in bonding is reported in the structure of the isoelectronic complex $H_2Os_3(C{=}CH_2)(CO)_9$ (A):[21a] Os(3)–C(1) = 2.17, Os(3)–C(2) = 2.35 Å. The asymmetry in the π bond in **6a** (or in A) must derive from the geminal attachment



A



B

of the *N*-iminyl (or the vinylidene) group to two of the metal atoms of the triangle while it is also π bonded to the third. In Figure 2c (as well as in Figure 4) the geometry of this attachment is shown in profile. For purposes of discussion it is convenient to define a reference plane for the ethylidenimido group as that plane which contains the C(CN)–N axis and which is normal to the plane defined by C(CN), N, and Fe(1). This reference plane is also normal to the plane of the paper in Figure 2c (and in Figure 4). It is seen that the substituents on C(CN), namely, H(C) and C(ME), are positioned slightly out of the reference plane on the side *away* from Fe(1). Although it is less, it is in the usual direction for substituents of an unsaturated system which is π bonded to a metal.[13] The geminally bonded iron atoms Fe(2) and Fe(3), however, are below the reference plane, on the side *toward* Fe(1). This must place considerable strain on the π bond between the ethylidenimido group and Fe(1) and approach of the nitrogen atom toward Fe(1) would tend to relieve this strain. Thus, while also remaining bonded to Fe(2) and Fe(3), the N atom would tend to become a triply bridging nitrene. This must in turn be accompanied by developing positive charge on C(CN) which would limit the motion of N to Fe(1). The same considerations would apply by analogy to the movement of C(1) to Os(3) in A.

These structural features should be discussed together with the isoelectronic cluster complexes $[Co_3(CCHR)(CO)_9]^+$ (B).[21b,c] In these, a carbonium ion has been generated on the carbon α to the one triply bridging the metal triangle. Owing to the marked stability of such carbonium ion complexes, it has been suggested[21c-e] that the α carbon atom in B may well be bent significantly over toward the cluster. This would tend toward the same structure as in the vinylidene complex A, but from the opposite extreme. One may thus envisage the structures with asymmetrically bonded alkylidenimido (or vinylidene) groups as occupying energy minima in a Walsh diagram connecting two extreme higher energy forms: a structure on the one hand containing a symmetric but considerably strained π-bond between the unsaturated center and the unique metal atom (in the ideal represented by structure A) and a structure on the other hand containing a symmetric NM_3 (or CM_3) tetrahedron with positive charge localized on the α carbon atom (represented by structure B). When motion toward a triply bridging nitrene is accompanied by hydride shift from the metal cluster to the α carbon atom we form $^*Fe_3(NCH_2CH_3)(CO)_9$, intermediate **i-2**[1b] required for the facile exchange of carbon-bonded and metal-bonded hydrogen atoms observed for **6a**.[1b] It is noteworthy that the same tautomerism is not observed at low temperature in the vinylidene complex A (see discussion in ref 1b).

Comparison of the Position of Bridging Hydrogen and Related Structural Features in 5a, 6a, and $HFe_3(S\text{-}i\text{-}Pr)(CO)_9$. Although hydrogen atoms were successfully located and refined in these three structures, it is worthwhile to examine the effects of hydrogen on other structural features, a matter of some importance in situations where the hydrogen must be inferred from indirect evidence.[22] Even at the point of the first Fourier maps in **5a** and **6a**, the disposition of the carbonyl groups clearly indicated the position of the metal hydride. In **5a** carbonyl groups (21), (23), (31), and (32) extend at angles of 96–112° with the Fe(2)–Fe(3) vector (see Figure 1 and Table VI). The common angle of a carbonyl group with a metal–metal vector not bridged by another atom lies in the range 85–101°, as observed for carbonyl groups (11), (12), (13), (22), and (33) with their appropriate iron–iron vectors. In the structure of **6a** the disposition of the metal carbonyls at the point of the first Fourier map similarly indicated the position of the metal hydride: carbonyl groups (21), (22), (31), and (33) extend at angles of 104–110° with the Fe(2)–Fe(3) vector while carbonyl groups (11), (12), (13), (23), and (32) extend at angles of 88–101° with their appropriate iron–iron vectors. This swing back of the carbonyl ligands is well documented and is probably the best method of inferring metal hydride positions in the absence of actual refinement.[23-25]

For both **5a** and **6a**, vectors drawn through the carbonyl ligands pseudotrans to the metal hydride do not intersect at the hydride ligand, but slightly within the Fe(2)–H(Fe)–Fe(3) triangle. This effect has been noted previously and is ascribed to closed three-center-two-electron bonding between the metal atoms and the bridging hydride.[24]

A final observation concerns the Fe(2)–Fe(3) bond lengths. A hydrogen atom bridging between two metal atoms not bridged by any other atoms is observed to lengthen the metal–metal bond over its normal value.[22] When metals bridged by a hydrogen atom are also bridged by a second ligand, the effect of the metal hydride may be masked by the steric requirements of the second bridging group.[13,24,25] Metal–metal distances are thus generally a poor indicator of hydride location unless a suitable reference structure is available. The rather long Fe(2)–Fe(3) separation of 2.7537 (8) Å in **5a** may be attributed principally to the steric requirement of the two-atom iminyl group bridging these two

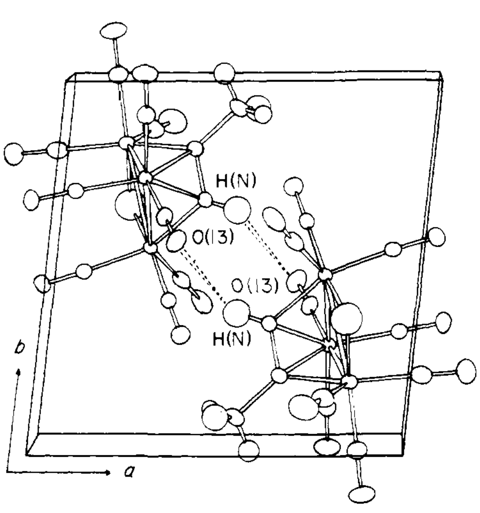


Figure 5. Unit cell of $HFe_3(CH_3C{=}NH)(CO)_9$ showing hydrogen bonding between H(N) and O(13).

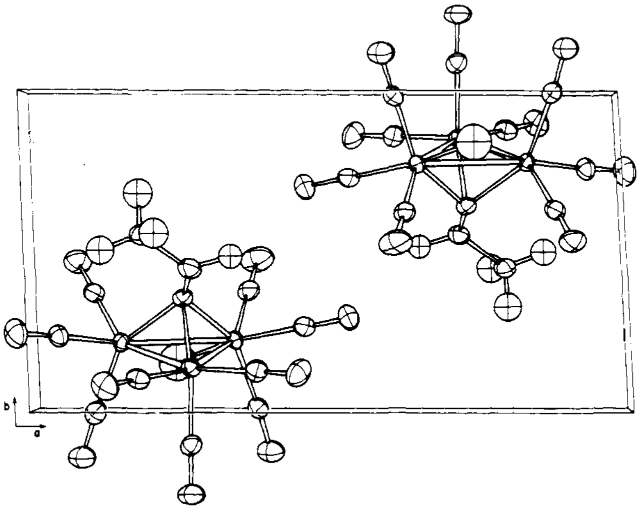


Figure 6. Unit cell of $HFe_3(N{=}CHCH_3)(CO)_9$.

metal atoms. Indeed, in **6a**, the edge Fe(2)-Fe(3) at 2.5879 (8) Å is only slightly longer than the other two edges of the metal triangle, while in $HFe_3(S\text{-}i\text{-}Pr)(CO)_9$, the metal triangle is nearly equilateral (2.640 (2), 2.653 (2), and 2.678 (2) Å).[11] Indeed, in the anion $[HFe_3(CO)_{11}]^-$, the edge of the metal triangle bridged by hydrogen is *shorter* (2.577 (3) Å) than the unbridged sides (2.685 (3), 2.696 (3) Å);[25a] in this case, the edge bridged by hydrogen is also bridged by a CO group. A similar situation is found in $HRu_3(C{=}NMe_2)(CO)_{10}$, in which the edge of the metal triangle is bridged by hydrogen and also bridged by the $C{=}NMe_2$ group; this edge is also shorter (2.801 (1) Å) than the unbridged edges of the metal triangle (2.822 (1) Å).[25b]

Finally, it is interesting to note that, in **6a**, with a nearly equilateral metal triangle, the hydrogen on the cluster is observed to be distinctly below the plane of the metal triangle, as it is in $HFe_3(S\text{-}i\text{-}Pr)(CO)_9$;[11] see Figure 2. In the latter, the metal triangle is also very nearly equilateral. This contrasts markedly with **5a**, in which H(FE) is nearly coplanar with the metal triangle; in this derivative, the metal triangle is nearly isosceles. These structural differences are also accompanied by rotational orientation of the carbonyl and hydride ligands about the H-bridged Fe–Fe axis. This effect is apparent in Figure 2; the ligands in the thiolate complex about the H-bridged Fe–Fe axis are rotated further counterclockwise than in **5a**; **6a** appears intermediate between these two but closer to the thiolate than to **5a**.

Comparison of the Orientations of the Isomeric ($CH_3C{=}NH$) and ($N{=}CHCH_3$) Groups toward the Metal Triangle to Which They Are Bonded. Differences in the orientations of the isomeric groups are illustrated in Figure 4. For the sake of clarity the carbonyl groups and the hydrogen atoms on the methyl groups have been omitted. For each of the complexes the lower drawing represents a vertical elevation in which the axis joining the central carbon and nitrogen atoms of the iminyl groups has been placed parallel to the plane of the paper. The upper drawings represent a top view of each of the lower structures. One then sees the orientation of the heteroatom groups in their relation both to the plane of the metal triangle (lower drawings) as well as to each of the metal atoms in these triangles (top drawings). Studies described in the previous paper[1b] have indicated that **6a** is the thermodynamically more stable isomer and can be obtained by thermal isomerization of **5a**. A pathway for this transformation was proposed. This involved first reductive elimination of C—H in **5a** to give an intermediate containing a σ–π bonded $CH_3CH{=}NH$ group. Oxidative addition of NH to the metal cluster in this intermediate would lead to **6a**. The drawings of the two isomers shown in Figure 4 suggest this to be an intramolecular least motion pathway between the two isomers. If this pathway is traversed, the following transformation matrix would apply to the iron atoms in each of the isomers:

5a		**6a**
Fe(1)	→	Fe(2)
Fe(2)	→	Fe(3)
Fe(3)	→	Fe(1)

The exchange of H(FE) with H(C) in the ethylidenimido group in **6a**[1b] has thus far prevented us from obtaining experimental evidence regarding this transformation pathway.

Intermolecular Contacts in the Unit Cells for 5a and 6a. We have shown that **5a** forms hydrogen-bonded adducts with a variety of bases via the acetimidoyl N-H hydrogen.[1b] It is not therefore surprising that the closest intermolecular contact in its crystal is between H(N) and a carbonyl oxygen (O(13)) (Figure 5). The extent of the interaction is quite weak (H(N)-O(13) = 2.33 Å vs. van der Waals distance of ~2.7 Å and N-H(N)-O(13) angle = 136°) in keeping with the poor basicity of terminal carbonyl oxygen atoms. Much stronger hydrogen bonds have been observed between triply bridging hydroxide hydrogens and phosphine oxides in $H_4W_4(CO)_{12}(OH)_4{\cdot}4(OPR_3)$.[26]

The unit cell in **6a** is shown in Figure 6. The closest intermolecular contact is 2.58 Å between O(32) and H(C). This is somewhat below the van der Waals distance of ~2.7 Å, but not as short as the intermolecular separation in **5a**. No hydrogen-bond effects were noted in **6a** as observed in **5a**.[1b] Other intermolecular contacts below 3 Å are O(33)-H(ME1) = 2.82, O(22)-H(ME1) = 2.96, and O(22)-O(22)′ = 2.953 Å.

Summary

The present study is the first elucidation of isomeric acimidoyl and alkylidenimido groups triply bridging on a metal cluster. Low-temperature data collection has permitted us to locate and refine the position of the hydrogen atoms both on the metal clusters as well as the hetero-unsaturated groups bonded to them. Important insights into the nature of the bonding and reactivity of unsaturated substrates with metal clusters are provided.

Acknowledgment. We thank the National Science Foundation (Grant 76 15436) for support of this work, the UCLA Computing Center for partial support of the computational expenses, and Ms. Sharon R. Kantor for assistance in data collection for the structure determination of **6a**. The Syntex diffractometer was purchased with NSF Grant GP 28248.

Supplementary Material Available: Tables VII and VIII, observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) The structure determination of $HFe_3(CH_3C{=}NH)(CO)_9$ has been taken from the Dissertation of M. A. Andrews, University of California, Los Angeles, 1977. This is the second of a series of papers relating to the reduction of acetonitrile on the face of a triiron cluster complex. For the first part see (b) M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, preceding paper in this issue. For the third part see (c) M. A. Andrews and H. D. Kaesz, *ibid.*, following paper in this issue.

(2) (a) In order to preserve continuity and facilitate correlation of the results reported in the present work with that of the preceding paper, ref 1b, the numbering of the derivatives in that paper is being retained in the present and succeeding works, ref 1c and references cited therein. (b) 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 $HFe_3(CH_3C{=}NH)(CO)_9$ (**5a**), *triangulo*-nonacarbonyl-μ-hydro[μ_3-[(N,1-η)-1-iminoethyl-*C:N*]]triiron; for $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**), *triangulo*-nonacarbonyl[μ_3-[N,1-η)-ethaniminato-*N:N*]]-μ-hydrotriiron. In line with IUPAC rules for inorganic chemistry[2c] the following systematic names are suggested: for **5a**, [μ_3-[(N-1-η)-acetimidoyl-*N,C*]]nonacarbonyl-μ-hydrido-*triangulo*-triiron; for **6a**, nonacarbonyl[μ_3-[(N-1-η)-ethylidenimido-*N,N*]]-μ-hydrido-*triangulo*-triiron. (c) "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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(9) 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, the value of C is 0.35×10^{-6}.

(10) (a) The final low angle based hydrogen parameters are (atom, x, y, z, B) H(FE), 0.192 (7), 0.156 (7), 0.081 (7), 3.7 (23); H(N), 0.474 (7), 0.145 (8), 0.346 (8), 6.4 (26); H(ME1), 0.413 (7), 0.506 (8), 0.314 (8), 3.5 (21);[11] H(ME2), 0.535 (6), 0.391 (6), 0.352 (6), −0.1 (18);[11] H(ME3), 0.508 (8), 0.403 (8), 0.182 (10), 5.0 (24).[11] (b) The thermal parameters for the methyl hydrogens are affected by the significant residual motion of the methyl group even at the −158 °C temperature as judged from the smeared out electron density distribution near C(ME) in the difference maps.

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(17) (a) This is especially true of those not subject to constraints, i.e., N–C(CN)–C(ME) and C(CN)–N–H(N). (b) For the system (A)(B)C═D(E)(F), α is the angle between the normals to planes ABC and DEF. The angle β is the angle between the normal to the ABC plane and the CD bond, and β' is the angle between the normal to the DEF plane and the CD bond.[13]

(18) Since part of the observed effect depends upon the position of H(N), it is important to note that H(N) is fairly well located (errors in angles involving H(N) $\approx 2°$), although perhaps its position is affected slightly by the presence of weak intermolecular hydrogen bonding. In any case the effect is clearly apparent without data concerning the position of H(N).

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