CHE-8109065). The computing expenses have been covered by grants from the University of Iowa, Graduate College.

Registry No. I, 76581-48-1; II, 76581-46-9; III, 82336-38-7; IV, 82311-91-9; $(Et_4N)_2MoS_4$, 14348-09-5; BzSSSBz, 6493-73-8; S, 7704-34-9; $(NH_4)_2MoS_4$, 15060-55-6; $(NH_4)_2S_3$, 12259-92-6; $(Ph_4P)_2MoS_4$, 14348-10-8.

Supplementary Material Available: Listings of structure factors for $(Et_4N)_2[(S_4)_2MoS]$, $(Et_4N)_2[(S_4)_2MoO]$, and $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]$ and a table of selected, weighted least-squares planes (53 pages). Ordering information is given on any current masthead page.

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Reaction of $[Fe_3(CO)_{12}]$ with Dicyclohexylcarbodiimide. Formation and Structure of $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$

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Received July 8, 1981

The reaction of the carbodiimide $C_6H_{11}NCNC_6H_{11}$ (C_6H_{11} = cyclohexyl) with $[Fe_2(CO)_9]$ in boiling hexane gives the same products as it does with $[Fe(CO)_5]$, i.e., $[Fe(CO)_4(CNC_6H_{11})]$ (I) and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II), but with $[Fe_3(CO)_{12}]$ in boiling heptane it also gives the previously unknown derivative $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$ (III). The molecular structure of III has been determined by a single-crystal X-ray diffraction study. This shows that the $Fe_2(CO)_6$ fragment has the familiar "saw horse" structure with each of the two N atoms of the coordinated carbodiimide molecule bridging its two iron atoms and the carbodiimide carbon atom acting as an axial carbene ligand to a distorted trigonal-bipyramidal $Fe(CO)_4$ moiety. The structure was solved by the heavy-atom method and refined by least squares to R = 0.074 for 1559 nonzero unique photographic reflections. Crystals of the compound are monoclinic, space group $P2_1/n$, with a = 10.876 (4) Å, b = 16.609 (7) Å, c = 14.982 (5) Å, and β = 90.7 (1)° for Z = 4. The IR spectrum of III is consistent with the presence of two isomers in solution arising from restricted rotation of the $Fe(CO)_4$ moiety about the Fe–C(carbene) bond. The X-ray structure determination shows that this behavior is probably due to steric interactions between the $Fe(CO)_4$ carbonyl ligands and the cyclohexyl groups. Although *i*-PrNCN-*i*-Pr reacts similarly with $[Fe_3(CO)_{12}]$ to give products analogous to I, II, and III, with the last again exhibiting rotational isomerism, *p*-MeC_6H_4NCN-*p*-MeC_6H_4 forms counterparts of I and II but not III.

Introduction

The thermal reaction of $[Fe(CO)_5]$ with an organocarbodiimide, RNCNR, has been shown to give two products, $[Fe(CO)_4(CNR)]$ and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(RN)_2CNR\}]$.[2,3] Three different mechanisms have been proposed for this interesting reaction.[2-4] They involve the following reactive intermediates: (a) a carbene complex, $[Fe_2(CO)_6\{\mu,\mu'\text{-}(RN)_2C\}]$,[2] (b) a metal–nitrene complex,[3] or (c) an intermediate containing a cyclic $Fe(C_2N_4R_4)$moiety[4] similar to those proposed, and sometimes observed, for the metal-promoted rearrangement reactions of other heterocumulenes such as RNCS, CS_2, or CO_2 (e.g., the references in ref 4).

In a continuation of previous work on the reaction of iron carbonyls with organocumulenes,[5] we have studied the reactions of dicyclohexylcarbodiimide, $C_6H_{11}NCNC_6H_{11}$ (C_6H_{11} = cyclohexyl), with the polynuclear carbonyls $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. We had hoped to be able to isolate mononuclear $[Fe(CO)_2(L)_2(\eta^2\text{-}RNCNR)]$ derivatives when the reaction was carried out in the presence of other ligands (cf. the analogous reaction with CS_2[5]). Unfortunately we have not, as yet, been successful, but we have shown that, whereas the reaction of $[Fe_2(CO)_9]$ with $C_6H_{11}NCNC_6H_{11}$ gave the same products as does $[Fe(CO)_5]$, $[Fe_3(CO)_{12}]$ also gave $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$. The structure of this complex has been determined by an X-ray diffraction study and is closely related to that of the reactive intermediate proposed by Farona et al.[2] in (a) above.

Experimental Section

$[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ were prepared as described elsewhere.[6] Other chemicals were purchased. The organocarbodiimides were used as received.

All reactions were carried out under an atmosphere of nitrogen with solvents that had been dried over calcium hydride and distilled prior to use.

A mixture of $[Fe_2(CO)_9]$ (1.5 g), $C_6H_{11}NCNC_6H_{11}$ (0.85 g), and PPh_3 (0.72 g) in tetrahydrofuran (50 mL) was stirred. When all of the $[Fe_2(CO)_9]$ had dissolved, the IR spectrum of the reaction mixture was measured. It showed that only $[Fe(CO)_4(PPh_3)]$, $[Fe(CO)_3(PPh_3)_2]$, and unchanged $C_6H_{11}NCNC_6H_{11}$ were present. These were separated (chromatography with alumina and C_6H_6) and identified unambiguously.

A mixture of $[Fe_2(CO)_9]$ (2 g) and $C_6H_{11}NCNC_6H_{11}$ (1.13 g) in hexane (50 mL) was heated to reflux. When all of the $[Fe_2(CO)_9]$ had dissolved, the solvent was removed from the mixture at reduced pressure. The residue was dissolved in benzene and chromatographed on alumina. Two compounds could be isolated, $[Fe(CO)_4(CNC_6H_{11})]$ (I) and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II). They were identified by IR spectroscopy and by analyses. Reaction yields were low and variable; that of II averaged 5%.

A solution of $[Fe_3(CO)_{12}]$ (5 g) and $C_6H_{11}NCNC_6H_{11}$ (2 g) in heptane (60 mL) was heated to reflux until the green color disappeared. The brown reaction mixture was filtered and the solvent removed at reduced pressure. The residue was redissolved in hexane and chromatographed on alumina. In order of elution, the products were $[Fe(CO)_4(CNC_6H_{11})]$ (I), $[Fe(CO)_3(CNC_6H_{11})_2]$ (a trace amount), yellow $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II), and a red material.

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This last was chromatographed for a second time and was identified as $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$ (III). The products were recrystallized from hexane. All were obtained in final yields of ca. 10%; the exact values depended on the amount of purification that proved necessary.

Reactions between $[Fe_3(CO)_{12}]$ and other RNCNR compounds were carried out as described above. When R = *i*-Pr, the counterparts of I, II, and III were isolated in yields of ca. 10%. When R = *p*-MeC_6H_4, only analogues of I and II could be detected and only II was identified by analyses. However, such was the difficulty we had in product separation and purification, we cannot claim unambiguously that a derivative of type III was not formed.

Infrared spectra were measured on a Perkin-Elmer 337 IR spectrometer equipped with a Hitachi Perkin-Elmer readout recorder. They were calibrated with DCl and water vapor[7] so that peak positions are accurate to ±1 cm^{-1}. Mass spectra were measured on a VG 70-70 M mass spectrometer. Analyses were carried out in the Analytical Laboratory of University College, Dublin.

Analyses and IR spectra (1600–2100-cm^{-1} region with relative peak heights in parentheses, hexane solution) are as follows.

$[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$: yellow crystals; mp 127–129 °C (lit.[2] mp 135 °C); ν(CO) 1988 (10, broad), 2033 (9.2), 2070 (5.4) cm^{-1}; ν(CN) 1676 (1.6) cm^{-1} (literature values:[2] 1981, 2030, 2070 cm^{-1}; 1676 cm^{-1}). Anal. Calcd: C, 51.5; H, 5.7; N, 7.2. Found: C, 51.2; H, 5.7; N, 7.1.

$[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$: red crystals; mp 131–133 °C; ν(CO) A 1923 (6.5), B 1935 (7.4), C 1958 (3.8), D 1971 (4.6), E 2005 (9.1), F 2014 (7.6), G 2042 (8.8), H 2051 (10), I 2084 (4.0) cm^{-1}. Anal. Calcd: C, 42.2; H, 3.4; N, 4.2. Found: C, 42.2; H, 2.9; N, 4.6.

$[Fe_2(CO)_6\{\mu,\mu'\text{-}(i\text{-}PrN)_2CN\text{-}i\text{-}Pr\}]$: yellow; identified by IR spectroscopy only: ν(CO) 1984 (10, broad), 2036 (7.8), 2070 (5.3) cm^{-1}; ν(CN) 1678 (2.0) cm^{-1} (literature values:[2] 1981, 2028, 2064 cm^{-1}; 1678 cm^{-1}).

$[Fe_2(CO)_6\{\mu,\mu'\text{-}(i\text{-}PrN)_2CFe(CO)_4\}]$: red crystals; ν(CO) A 1925 (4.3), B 1938 (5.6), C and D 1967 (6.6, broad), E 2006 (8.8), F 2014 (5.8), G 2043 (6.7), H 2053 (10), I 2083 (2.1) cm^{-1}. Anal. Calcd: C, 35.5; H, 2.4; N, 4.9. Found: C, 35.7; H, 3.4; N, 5.3.

$[Fe_2(CO)_6\{\mu,\mu'\text{-}(p\text{-}MeC_6H_4N)_2CN\text{-}p\text{-}MeC_6H_4\}]\cdot{}^1/_2C_6H_{14}$: yellow crystals; ν(CO) 1986 (10, broad), 2018 (9.1), 2059 (5.4) cm^{-1}; ν(CN) 1674 (1.9) cm^{-1}. Anal. Calcd: C, 57.3; H, 4.3; N, 6.5. Found: C, 57.5; H, 4.4; N, 7.3.

Structure Analysis. Crystal Data: $C_{23}H_{22}N_2O_{10}Fe_3$, M_r = 654.0, monoclinic, *a* = 10.876 (4) Å, *b* = 16.609 (7) Å, *c* = 14.982 (5) Å, β = 90.7 (1)°, *V* = 2706.1 $Å^{-3}$, D_m = 1.57 (by flotation), *Z* = 4, D_c = 1.605 g cm^{-3}, *F*(000) = 1328, μ(Mo Kα) = 1.69 mm^{-1}. Systematic absences *h*0*l* if $h + l \neq 2n$ and 0*k*0 if $k \neq 2n$, space group $P2_1/n$ (nonstandard No. 14).

The compound crystallizes as deep red rectangular parallelepipeds of poor quality which are elongated along [101] with pinacoids {101}, {$\bar{1}$01}, and {010}. Cell parameters were determined from precession photographs with Mo Kα radiation of λ = 0.71069 Å. Intensities were estimated visually from precession photographs for the layers 0–5 about [010] and [$\bar{1}0\bar{1}$] with use of Mo Kα radiation. They were corrected for Lorentz and polarization effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation, and 1559 nonzero reflections were obtained. Neutral-atom scattering factors were taken from ref 8 and were not corrected for anomalous dispersion. All calculations were carried out on a UNIVAC computer with programs written by F.S.S.

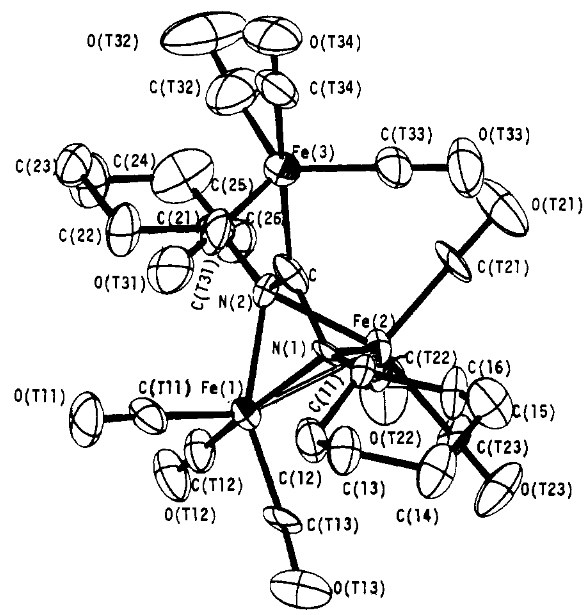

Figure 1. Perspective drawing of $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$ together with the atom-labeling scheme. Thermal ellipsoids are drawn to include 35% probability.

Table I. Final Atomic Coordinates (Fractional, ×10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

	x	*y*	*z*
Fe(1)	711 (2)	1701 (2)	1650 (1)
Fe(2)	596 (2)	1962 (2)	70 (1)
Fe(3)	2632 (2)	3915 (2)	995 (2)
N(1)	2058 (11)	2106 (7)	877 (8)
N(2)	385 (11)	2749 (8)	1060 (8)
C	1654 (15)	2893 (12)	990 (10)
C(11)	3367 (14)	1915 (10)	813 (9)
C(12)	3885 (16)	1442 (13)	1626 (10)
C(13)	5295 (14)	1330 (12)	1576 (11)
C(14)	5571 (14)	930 (13)	710 (13)
C(15)	5086 (16)	1390 (15)	−119 (13)
C(16)	3681 (14)	1508 (12)	−35 (10)
C(21)	−535 (15)	3392 (10)	1230 (10)
C(22)	−620 (14)	3606 (13)	2209 (11)
C(23)	−1572 (20)	4274 (13)	2381 (13)
C(24)	−2780 (20)	4043 (15)	2031 (15)
C(25)	−2726 (18)	3855 (15)	1051 (19)
C(26)	−1800 (18)	3173 (12)	844 (13)
C(T11)	1230 (15)	1943 (12)	2779 (12)
C(T12)	−828 (15)	1407 (12)	1944 (10)
C(T13)	1085 (17)	663 (12)	1617 (11)
O(T11)	1536 (13)	2078 (11)	3496 (8)
O(T12)	−1775 (12)	1211 (9)	2124 (8)
O(T13)	1399 (16)	2 (10)	1667 (13)
C(T21)	817 (20)	2566 (14)	−903 (12)
C(T22)	−1013 (17)	1702 (13)	−183 (10)
C(T23)	1027 (17)	993 (12)	−413 (13)
O(T21)	912 (15)	2942 (12)	−1530 (10)
O(T22)	−1951 (13)	1456 (13)	−358 (10)
O(T23)	1157 (14)	408 (10)	−718 (12)
C(T31)	3330 (18)	3538 (15)	1985 (12)
C(T32)	1524 (25)	4682 (15)	1098 (19)
C(T33)	3126 (18)	3676 (12)	−91 (12)
C(T34)	3756 (20)	4699 (14)	1051 (13)
O(T31)	3765 (15)	3324 (11)	2640 (10)
O(T32)	875 (18)	5246 (10)	1135 (20)
O(T33)	3497 (15)	3512 (11)	−776 (10)
O(T34)	4463 (15)	5217 (8)	1093 (12)

Structure Determination. The structure was solved by the heavy-atom method. Refinement was carried out by least-squares calculations in which $\sum w\Delta^2$ was minimized. The weight, *w*, for each reflection was initially unity and in the final cycles given by $w = (5.5 + 0.14|F_o| + 0.0045|F_o|^2)^{-1}$, a scheme chosen such that the average values for $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. The positions of the hydrogen atoms were calculated with assumption of tetrahedral environments about the carbon atoms and C–H of 1.0 Å. They were included in the calculations, but at no time were their parameters refined. Anisotropic refinement was carried out with the following five block matrices due to the large number of parameters (343) being refined: (1) the overall scale and thermal parameters, (2) the parameters for the $Fe_2(CO)_6NCN$ group, (3) the parameters for the $Fe(CO)_4$ group, and (4) and (5) the parameters for the cyclohexane rings. Refinement was terminated when the maximum shift in any parameter was $<0.2\sigma$. The final *R* was 0.074, and $R' = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ was 0.098. A final difference map showed no

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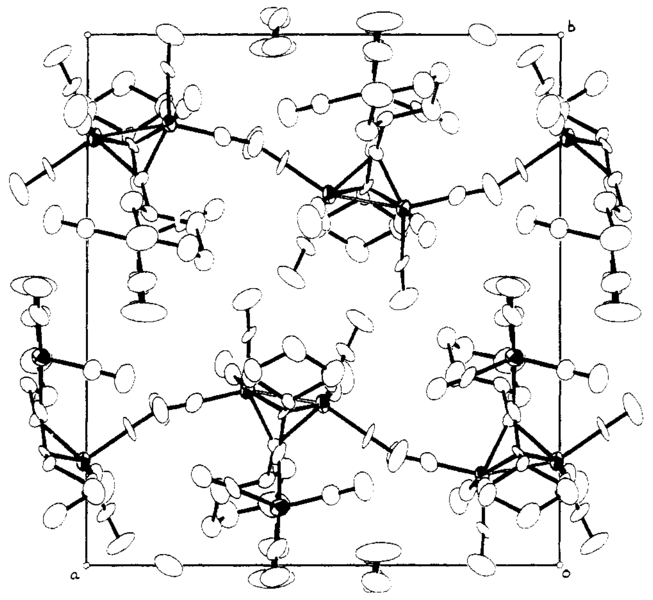

Figure 2. Packing of the molecule in the solid.

densities >|0.7| e Å^{-3}. Molecular structure and atom labeling are shown in Figure 1, and the packing of the molecule in the unit cell is shown in Figure 2. The final atomic coordinates are listed in Table I, and selected bond lengths and bond angles are contained in Table II. The following tables have been deposited as supplementary material: Table III, nonbonding interatomic contact distances; Table IV, observed and calculated structure factors; Table V, final atomic anisotropic thermal parameters; Table VI, atomic parameters for hydrogen atoms; Table VII, least-squares planes data.

Results and Discussion

Although dicyclohexylcarbodiimide did not react with $[Fe_2(CO)_9]$ in the presence of PPh_3 (only $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$ were obtained), it did react in the absence of PPh_3 and at elevated temperatures. The products, $[Fe(CO)_4(CNC_6H_{11})]$ (I) and $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CNC_6H_{11}\}]$ (II), were the same as those obtained from the reaction of $[Fe(CO)_5]$ and $C_6H_{11}NCNC_6H_{11}$, also at elevated temperatures.[2,3] On the other hand, $[Fe_3(CO)_{12}]$ and the carbodiimide not only gave I and II but also III, $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$. Analogues of I, II, and III were formed with use of *i*-PrNCN-*i*-Pr under the same conditions, but with *p*-MeC_6H_4NCN-*p*-MeC_6H_4 we were able to detect only the counterparts of I and II. The yields of purified products from these reactions were low. This was due, in part, to the formation of large amounts of insoluble and intractable tars and also to the necessary, repeated use of column chromatography in product purification.

Table II. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses

(a) Distances (Å)

Fe(1)···Fe(2)	2.409 (3)	Fe(3)–C	2.00 (2)
	$n = 1$	$n = 2$	$n = 3$
Fe(n)–N(1)	2.00 (1)	2.00 (1)	
Fe(n)–N(2)	1.98 (1)	1.99 (1)	
Fe(n)–C(Tn1)	1.82 (2)	1.79 (2)	1.77 (2)
Fe(n)–C(Tn2)	1.80 (2)	1.84 (2)	1.76 (3)
Fe(n)–C(Tn3)	1.77 (2)	1.83 (2)	1.76 (2)
Fe(n)–C(Tn4)			1.79 (2)
C(Tn1)–O(Tn1)	1.14 (2)	1.13 (2)	1.14 (2)
C(Tn2)–O(Tn2)	1.12 (2)	1.13 (2)	1.17 (3)
C(Tn3)–O(Tn3)	1.15 (2)	1.08 (2)	1.14 (2)
C(Tn4)–O(Tn4)			1.16 (2)
C–N(n)	1.39 (2)	1.41 (2)	
N(n)–C(n1)	1.46 (2)	1.49 (2)	
C(n1)–C(n2)	1.55 (2)	1.51 (2)	
C(n2)–C(n3)	1.55 (2)	1.54 (2)	
C(n3)–C(n4)	1.49 (2)	1.46 (3)	
C(n4)–C(n5)	1.55 (3)	1.50 (3)	
C(n5)–C(n6)	1.55 (3)	1.55 (3)	
C(n6)–C(n1)	1.48 (2)	1.53 (3)	

(b) Angles (Deg)

C–Fe(3)–C(T34)	169 (1)	C–Fe(3)–C(T32)	104 (1)
C(T31)–Fe(3)–C(T32)	118 (1)	C–Fe(3)–C(T33)	88 (1)
C(T31)–Fe(3)–C(T33)	124 (1)	C(T34)–Fe(3)–C(T31)	86 (1)
C(T32)–Fe(3)–C(T33)	117 (1)	C(T34)–Fe(3)–C(T32)	86 (1)
C–Fe(3)–C(T31)	86 (1)	C(T34)–Fe(3)–C(T33)	90 (1)
Fe(3)–C(T31)–O(T31)	177 (2)	Fe(3)–C(T33)–O(T33)	177 (2)
Fe(3)–C(T32)–O(T32)	173 (2)	Fe(3)–C(T34)–O(T34)	179 (2)
N(1)–C–N(2)	99 (1)		
N(1)–C–Fe(3)	129 (1)	N(2)–C–Fe(3)	132 (1)

	$n = 1$	$n = 2$
N(1)–Fe(n)–N(2)	64.8 (5)	64.5 (5)
N(1)–Fe(n)–C(Tn1)	104.1 (6)	108.2 (8)
N(1)–Fe(n)–C(Tn2)	157.4 (7)	154.3 (6)
N(1)–Fe(n)–C(Tn3)	98.1 (6)	98.0 (7)
N(2)–Fe(n)–C(Tn1)	105.8 (7)	104.9 (8)
N(2)–Fe(n)–C(Tn2)	100.7 (7)	100.9 (6)
N(2)–Fe(n)–C(Tn3)	151.8 (6)	154.8 (8)
C(Tn1)–Fe(n)–C(Tn2)	96.4 (7)	95.8 (9)
C(Tn1)–Fe(n)–C(Tn3)	99.9 (9)	97.7 (9)
C(Tn2)–Fe(n)–C(Tn3)	87.6 (8)	87.7 (9)
Fe(n)–C(Tn1)–O(Tn1)	178 (2)	177 (2)
Fe(n)–C(Tn2)–O(Tn2)	179 (2)	172 (2)
Fe(n)–C(Tn3)–O(Tn3)	173 (2)	173 (2)
Fe(1)–N(n)–Fe(2)	74.1 (4)	74.6 (4)
Fe(1)–N(n)–C	91 (1)	91 (1)
Fe(2)–N(n)–C	86 (1)	86 (1)
Fe(1)–N(n)–C(n1)	133 (1)	132 (1)
Fe(2)–N(n)–C(n1)	135 (1)	133 (1)
N(n)–C(n1)–C(n2)	114 (1)	113 (1)
N(n)–C(n1)–C(n6)	113 (1)	112 (1)
C(n6)–C(n1)–C(n2)	111 (1)	111 (1)
C(n1)–C(n2)–C(n3)	112 (1)	112 (1)
C(n2)–C(n3)–C(n4)	108 (1)	111 (2)
C(n3)–C(n4)–C(n5)	114 (2)	111 (2)
C(n4)–C(n5)–C(n6)	109 (1)	112 (2)
C(n5)–C(n6)–C(n1)	111 (1)	110 (2)

The IR spectrum of the red, air-stable crystalline solid III in the 1700–2100-cm^{-1} region is consistent with its molecular structure (see below). If it is superimposed on that of II, it is quite clear that definitely absorption bands A, B, C, and D and very probably F and G are due to the ν(CO) modes of the $Fe(CO)_4$ fragment. On the basis of a C_{3v} idealized symmetry, one would expect it to give rise to three IR absorption bands due to ν(CO) vibrations of e, a_1, and a_1^* symmetries (the asterisk only distinguishes the two modes of the same symmetry). For $[Fe(CO)_4\{C(NMe)_2C_2H_4\}]$ these have frequencies of 1938, 1963, and 2044 cm^{-1} respectively,[9] (cf. the proposed assignment for $[Fe(CO)_4(PEt_3)]$[10]). We suggest that the added complexity of the IR spectrum of III is due to isomerism arising from restricted rotation of the $Fe(CO)_4$ moiety about the Fe–C(carbene) bond as implied by the structure determination discussed below. Absorption bands C and D are assigned to the a_1 ν(CO) vibrations of the two rotational isomers while A and B with their irregular band envelopes are due to their e modes with each, perhaps, being split into two singly degenerate components as a consequence of reduction of the idealized C_{3v} local symmetry of the $Fe(CO)_4$ group by distortions (see below) or the presence of the remainder of the molecule. It is unlikely that the relative complexity of the IR spectrum of III is due solely to this lowering of effective symmetry; under such circumstances the singly degenerate a_1 vibration would still give rise to a single ab-

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sorption band. Absorption bands F and G are tentatively assigned to the a_1* vibrations of the rotational isomers. The $Fe_2(CO)_6$ fragment with its C_{2v} local symmetry would be expected to give rise to five IR-active, singly degenerate ν(CO) vibrations. Although only three IR absorption bands may be attributed to them in the spectra of both II and III (E, H, and I), the 1980-cm^{-1} band of II and E of III are broad and probably have more than one component. However, the rotational isomerism of the $Fe(CO)_4$ group does not appear to affect the ν(CO) vibrations of the $Fe_2(CO)_6$ moiety, which suggests that there are no significant interactions between the ν(CO) vibrations of the two parts of the molecule. The increase in the frequencies of the $Fe_2(CO)_6$ ν(CO) vibrations in going from II to III is a consequence of replacing the μ,μ'-$(C_6H_{11}N)_2CNC_6H_{11}$ ligand by the poorer electron-donating or better electron-withdrawing μ,μ'-$(C_6H_{11}N)_2CFe(CO)_4$.

The IR spectra of $[Fe_2(CO)_6\{\mu,\mu'$-(*i*-PrN)$_2$CN-*i*-Pr$\}]$, $[Fe_2(CO)_6\{\mu,\mu'$-(*i*-PrN)$_2$CFe(CO)$_4\}]$, and $[Fe_2(CO)_6\{\mu,\mu'$-(*p*-MeC$_6$H$_4$N)$_2$CN-*p*-MeC$_6$H$_4\}]$ are similar to those of their cyclohexyl counterparts II, III, and II, respectively. They need no further discussion.

The mass spectrum of II shows a molecular ion peak at m/e = 583.1 and others corresponding to consecutive loss of CO ligands. For III a molecular ion peak (m/e = 654) was not observed, but peaks corresponding to ions that have lost 1, 3, 5, 6, 7, 8, 9, and 10 CO ligands were detected.

The formation of III means that is is very unlikely that the $[Fe_2(CO)_9]/C_6H_{11}NCNC_6H_{11}$ reaction proceeds via the carbene-type intermediate $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)C\}]$[2] as this would be expected to react very readily with more $[Fe_2(CO)_9]$ to give III. Consequently we feel that the formation of III in the $[Fe_3(CO)_{12}]/C_6H_{11}NCNC_6H_{11}$ reaction does not involve prior breakdown of the Fe_3 triangle into reactive mono- or diiron fragments, but the formation of II may involve such breakdown (cf. the reaction of $C_6H_{11}NCNC_6H_{11}$ with $[Fe(CO)_5]$[2] or $[Fe_2(CO)_9]$). However, if both II and III have a common precursor, this must react with more $C_6H_{11}NCNC_6H_{11}$ if it is to give II, and varying the mole ratio of the reactants would be expected to affect the II:III product ratios. However, the reaction yields were so low and variable that we have not been able to confirm this.

Description of the Structure of $[Fe_2(CO)_6\{\mu,\mu'\text{-}(C_6H_{11}N)_2CFe(CO)_4\}]$. The bond lengths and angles are given in Table II. A drawing of the molecule and atomic labeling scheme is shown in Figure 1, and Figure 2 shows the molecular packing in the lattice.[11] The molecules are held in the crystal by van der Waals forces.

The carbodiimide bridges two $Fe(CO)_3$ groups with an Fe(1)···Fe(2) distance of 2.409 (3) Å. Both iron atoms are in a distorted-octahedral environment, each bonding to three carbonyl groups, two bridging nitrogen atoms, and the other iron atom. The carbodiimide is closely planar. Its carbon atom forms an Fe–C(carbene) bond of length 2.00 (2) Å with the $Fe(CO)_4$ group through an axial coordination position of a distorted trigonal bipyramid. The symmetry of the $Fe_2(CO)_6\{(CN)_2CFe\}$ fragment, almost C_{2v}-*mm*2, and the molecular dimensions within it are virtually identical with those found in related $[Fe_2(CO)_6\{\mu,\mu'\text{-}(RN)_2CO\}]$ complexes where R = Ph[12] or Me.[13] Another relevant molecule is $[Fe(CO)_4\{C(NMe)_2C_2H_2\}]$, which has an Fe–C(carbene) bond length of 2.007 (5) Å and axially monosubstituted trigonal-bipyramidal coordination about Fe.[14]

Both cyclohexyl rings of the coordinated carbodiimide adopt chair conformations. Steric interactions between these rings and the carbonyl ligands of both the $Fe_2(CO)_6$ and the $Fe(CO)_4$ groups are apparent. Those involving the hydrogen atoms of the ring carbon atoms C(12), C(11), and C(16) and C(22), C(21), and C(26) are particularly important. Although the first ring adopts a nearly symmetrical position with respect to both the $Fe_2(CO)_6$ group and the trigonal plane of the $Fe(CO)_4$ group, the second ring is rotated about the N(2)–C(21) direction in order to minimize the C(21)–H(21)···CO-(T32) interaction. However, the degree of rotation is small (~20°). It is restricted by the axial hydrogen atom contacts of C(22) and C(26) to carbonyl ligands of the $Fe_2(CO)_6$ group. For further alleviation of a close C(21)···C(T32) contact, the trigonal plane of the (carbene)$Fe(CO)_4$ moiety is tilted back from the second ring, thus increasing the C–Fe(3)–C(T32) angle to 104° and distorting the geometry about Fe(3). It is evident that rotation of the $Fe(CO)_4$ group about the Fe–C(carbene) bond will be restricted even in solution and will give rise to the rotational isomerism discussed above.

Registry No. I, 34871-29-9; II, 34871-26-6; III, 82044-62-0; $Fe_2(CO)_6\{\mu,\mu'$-(*i*-PrN)$_2$CN-*i*-Pr$\}$, 34871-27-7; $Fe_2(CO)_6\{\mu,\mu'$-(*i*-PrN)$_2$CFe(CO)$_4\}$, 82044-63-1; $Fe_2(CO)_6\{\mu,\mu'$-(*p*-MeC$_6$H$_4$N)$_2$CN-*p*-MeC$_6$H$_4\}$, 82056-42-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Table III, nonbonding interatomic contact distances, Table IV, observed and calculated structure factors, Table V, final atomic anisotropic thermal parameters, Table VI, atomic parameters for hydrogen atoms, and Table VII, least-squares planes data (14 pages). Ordering information is given on any current masthead page.

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