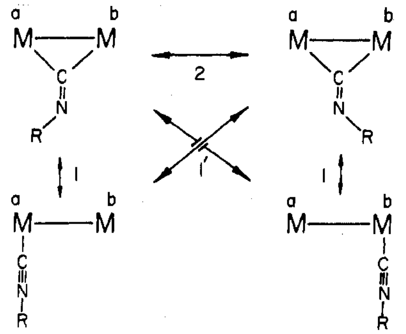

Figure 5. A schematic representation of the mechanism through which a terminal isocyanide ligand exchanges coordination sites between two metal atoms.

comparison of the bridge-terminal rearrangement barriers (15-20 kcal) to the nitrogen inversion barriers (10 kcal) shows the inversion process will have very little influence on that exchange rate. A simple comparison of the relative exchange rates supports this conclusion. The rate of bridge-terminal exchange as a function of temperature in *cis*-(η^5-$C_5H_5)_2Fe_2(CO)_3(\mu$-$CNCH_3$) has been measured.[9] It seems reasonable that the nitrogen inversion rates in this molecule will be approximately the same as those in compounds **1** and **2**. At −85° the rate of bridge-terminal rearrangement for this molecule is approximately 1×10^{-4} sec^{-1}. The nitrogen inversion rate will be approximately 20 sec^{-1}. The ratio of inversions to bridge-terminal rearrangements is thus approximately 2×10^5 inversions per bridge-terminal rearrangement.

Experimental Section

Solid samples were placed in nmr tubes adapted for serum stoppers. Following evacuation and admission of nitrogen, degassed solvents were transferred to the tubes with a syringe. The pmr spectra were recorded on a Varian Associates HA-100 equipped with variable-temperature accessory. Temperature calibrations were obtained from a methanol standard. Temperatures below −80° were obtained by calibrating the variable-temperature unit dial settings at higher temperatures and extrapolating to the lower values. The values are expected to be fairly reliable, ±3°, since a CS_2 sample was observed to freeze at the appropriate dial setting. Resonance shift positions were measured directly from a tetramethylsilane reference signal.

The free energies of activation were computed by the method of Shanan-Atidi and Bar-Eli.[11] There has recently been confirmation of the validity of this approximation.[18] The ratio of the syn to anti isomers in **1** was 1.0:0.653 with a coalescence temperature of −80°. The ratio of the two stereoisomers of isomer B of compound **2** was 1.0:0.326 with a coalescence temperature of −85°.

Acknowledgement. This work was supported by the National Science Foundation (Grant No. 33142X). We thank Dr. Bertram A. Frenz for a helpful discussion of the structure of (η^5-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$.

Registry No. **1**, 42892-72-8; **2A**, 42892-73-9; **2B**, 42892-74-0.

(18) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

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Low-Valent Metal Isocyanide Complexes. IV.[1] Crystal and Molecular Structures of *cis-anti*-Bis(*pentahapto*cyclopentadienyl)dicarbonylbis(μ-methyl isocyanide)-diiron(*Fe*-*Fe*), (η^5-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CNCH_3)_2$[2]

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One of the two tautomers postulated to be present in a solution of (η^5-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ has been isolated in crystalline form and its structure determined in detail. The tautomer has the cis conformation and an anti relationship of the two bent $CHCH_3$ groups in the bridging positions. The detailed shape of the molecule is closely similar to that of *cis*-(η^5-$C_5H_5)_2Fe_2(CO)_4$, thus validating the idea that $CNCH_3$-substituted polynuclear metal carbonyls can be used to gain information on the dynamical properties of their unsubstituted analogs. Using the present structure it can be shown that a bridging $CNC(CH_3)_3$ ligand would encounter severe steric strain. This explains why there is no detectable amount of a bridged isomer of (η^5-$C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$ while (η^5-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CNCH_3)_2$ is stable enough to be observed in solution. The crystallographic data are as follows: space group $P\bar{1}$; $Z = 2$; $a = 8.660$ (2) A; $b = 12.682$ (4) A; $c = 7.993$ (2) A; $\alpha = 101.72$ (2)°; $\beta = 116.28$ (1)°; $\gamma = 83.28$ (2)°. Unit cell dimensions and intensity data were measured at 15°, using Mo Kα radiation monochromatized by a graphite crystal. A total of 2050 independent reflections were collected in the 2θ range 0-45° and 1370 of these with $I_0 > 3\sigma(I_0)$ were used to refine the structure anisotropically to $R_1 = 0.039$ and $R_2 = 0.047$.

Introduction

As reported in the previous paper in this series, the infrared and variable-temperature nmr studies of the molecule (η^5-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ lead to certain explicit conclusions concerning the tautomers which could be present and interconverting among themselves. These conclusions followed rigorously from postulates made earlier by Adams and Cotton[3] as to the preferred pathways of rearrangement for binuclear metal carbonyls. The high degree of internal consistency within the body of spectroscopic data afforded very strong, but not incontrovertible, evidence that the two spectroscopically detectable isomers had been correctly identified. However, it was considered important to obtain direct evidence for at least one of them. The most effective way to do this is to isolate crystalline material and establish the structure crystallographically.

(1) Part II: R. D. Adams and F. A. Cotton, *Inorg. Chem.*, **13**, 249 (1974).

(2) This research was supported by the National Science Foundation (Grant No. 33142X) and by the Robert A. Welch Foundation which provided funds for purchase of the X-ray diffractometer.

(3) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).

Table II. Positional Parameters for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CNCH_3)_2$

Atom	x	y	z
Fe(1)	0.0981 (1)	0.21313 (7)	0.0495 (1)
Fe(2)	0.3937 (1)	0.29194 (8)	0.2509 (1)
O(1)	0.0223 (7)	0.1596 (4)	0.3387 (8)
O(2)	0.4231 (7)	0.2742 (5)	0.6159 (8)
N(1)	0.1066 (7)	0.4400 (5)	0.2539 (8)
N(2)	0.3786 (7)	0.0509 (5)	0.1713 (9)
C(1)	0.1661 (8)	0.3549 (6)	0.2023 (9)
C(2)	0.3198 (8)	0.1435 (6)	0.1625 (9)
C(3)	0.0528 (8)	0.1819 (6)	0.2222 (10)
C(4)	0.4135 (8)	0.2796 (6)	0.4687 (10)
C(5)	−0.0774 (10)	0.4606 (7)	0.2096 (15)
C(6)	0.5575 (11)	0.0177 (8)	0.2809 (16)
C(7)	−0.0977 (9)	0.1163 (7)	−0.1687 (11)
C(8)	−0.1560 (9)	0.2243 (7)	−0.1530 (10)
C(9)	−0.0581 (11)	0.2860 (7)	−0.1913 (11)
C(10)	0.0637 (10)	0.2165 (8)	−0.2294 (10)
C(11)	0.0376 (10)	0.1111 (7)	−0.2161 (11)
C(12)	0.6570 (8)	0.2898 (7)	0.3096 (11)
C(13)	0.6024 (9)	0.3968 (7)	0.3618 (11)
C(14)	0.4744 (9)	0.4305 (6)	0.1987 (11)
C(15)	0.4465 (9)	0.3467 (7)	0.0468 (10)
C(16)	0.5607 (10)	0.2591 (6)	0.1148 (11)
H(5,1)	−0.099 (9)	0.516 (5)	0.327 (10)
H(5,2)	−0.132 (9)	0.403 (6)	0.183 (10)
H(5,3)	−0.141 (9)	0.502 (5)	0.074 (10)
H(6,1)	0.630 (8)	0.021 (5)	0.170 (9)
H(6,2)	0.619 (9)	0.070 (6)	0.363 (10)
H(6,3)	0.559 (9)	−0.044 (6)	0.341 (10)

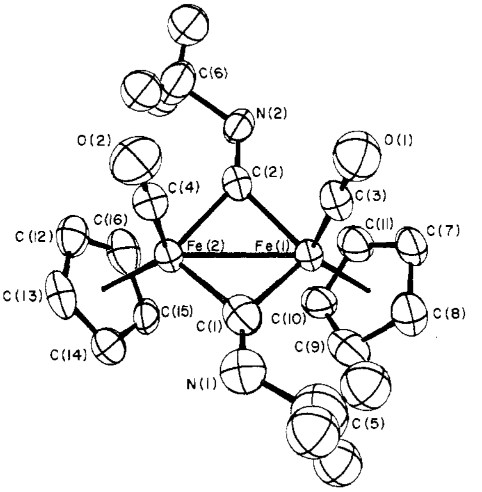

Figure 1. A perspective view of the molecular structure. The ellipsoids of thermal motion enclose 50% of the electron density. Hydrogen atoms are omitted for the sake of clarity. The atom-numbering scheme used in all tables is defined.

Table V. Bond Distances (Å)

Fe–Fe 2.538 (1)			
Fe(1)–C(1)	1.947 (7)	Fe(2)–C(1)	1.937 (7)
Fe(1)–C(2)	1.917 (7)	Fe(2)–C(2)	1.948 (7)
Fe(1)–C(3)	1.718 (8)	Fe(2)–C(4)	1.710 (8)
Fe(1)· · ·C(5)	3.574 (9)	Fe(2)· · ·C(5)	4.288 (8)
Fe(1)· · ·C(6)	4.293 (9)	Fe(2)· · ·C(6)	3.612 (9)
Fe(1)–C(7)	2.104 (7)	Fe(2)–C(12)	2.113 (6)
Fe(1)–C(8)	2.086 (7)	Fe(2)–C(13)	2.118 (7)
Fe(1)–C(9)	2.124 (8)	Fe(2)–C(14)	2.143 (7)
Fe(1)–C(10)	2.123 (7)	Fe(2)–C(15)	2.133 (7)
Fe(1)–C(11)	2.125 (7)	Fe(2)–C(16)	2.125 (6)
Fe(1)–Ct(1)[a]	1.749	Fe(2)–Ct(2)[b]	1.758
C(1)–N(1)	1.216 (8)	C(2)–N(2)	1.226 (8)
N(1)–C(5)	1.475 (9)	N(2)–C(6)	1.463 (10)
C(3)–O(1)	1.167 (8)	C(4)–O(2)	1.158 (8)
C(7)–C(8)	1.405 (11)	C(12)–C(13)	1.426 (10)
C(8)–C(9)	1.380 (11)	C(13)–C(14)	1.396 (10)
C(9)–C(10)	1.393 (11)	C(14)–C(15)	1.392 (10)
C(10)–C(11)	1.414 (11)	C(15)–C(16)	1.422 (11)
C(11)–C(7)	1.373 (10)	C(16)–C(12)	1.397 (10)
C(5)–H(5,1)	1.13 (7)	C(6)–H(6,1)	1.30 (7)
C(5)–H(5,2)	0.85 (7)	C(6)–H(6,2)	0.86 (7)
C(5)–H(5,3)	1.18 (7)	C(6)–H(6,3)	0.99 (7)

[a] Ct(1) refers to the centroid of the C(7)· · ·C(11) cyclopentadienyl ring. [b] Ct(2) refers to the centroid of the C(12)· · ·C(16) cyclopentadienyl ring.

Table VI. Bond Angles (deg)

C(1)–Fe(1)–Fe(2)	49.0 (2)	C(1)–Fe(2)–Fe(1)	49.4 (2)
C(1)–Fe(1)–C(2)	96.1 (3)	C(1)–Fe(2)–C(2)	95.4 (3)
C(1)–Fe(1)–C(3)	88.7 (3)	C(1)–Fe(2)–C(4)	87.1 (3)
C(2)–Fe(1)–Fe(2)	49.5 (2)	C(2)–Fe(2)–Fe(1)	48.4 (2)
C(2)–Fe(1)–C(3)	88.3 (3)	C(2)–Fe(2)–C(4)	88.0 (3)
C(3)–Fe(1)–Fe(2)	100.3 (2)	C(4)–Fe(2)–Fe(1)	98.8 (2)
C(1)–N(1)–C(5)	124.1 (6)	C(2)–N(2)–C(6)	126.8 (7)
Fe(1)–C(1)–Fe(2)	81.6 (3)	Fe(1)–C(2)–Fe(2)	82.1 (3)
Fe(1)–C(1)–N(1)	141.8 (5)	Fe(1)–C(2)–N(2)	137.2 (6)
Fe(2)–C(1)–N(1)	136.5 (5)	Fe(2)–C(2)–N(2)	140.7 (5)
Fe(1)–C(3)–O(1)	179.3 (6)	Fe(2)–C(4)–O(2)	177.7 (7)
C(7)–C(8)–C(9)	109.4 (7)	C(12)–C(13)–C(14)	108.0 (7)
C(8)–C(9)–C(10)	106.9 (7)	C(13)–C(14)–C(15)	108.4 (7)
C(9)–C(10)–C(11)	108.4 (7)	C(14)–C(15)–C(16)	108.3 (6)
C(10)–C(11)–C(7)	107.8 (7)	C(15)–C(16)–C(12)	107.7 (7)
C(11)–C(7)–C(8)	107.5 (7)	C(16)–C(12)–C(13)	107.6 (7)
Ct(1)[a]–Fe(1)–Fe(2)	135.9	Ct(2)[b]–Fe(2)–Fe(1)	135.5
Ct(1)–Fe(1)–C(1)	124.3	Ct(2)–Fe(2)–C(1)	125.2
Ct(1)–Fe(1)–C(2)	125.2	Ct(2)–Fe(2)–C(2)	124.3
Ct(1)–Fe(1)–C(3)	123.8	Ct(2)–Fe(2)–C(4)	125.8

[a] Ct(1) refers to the centroid of the C(7)· · ·C(11) cyclopentadienyl ring. [b] Ct(2) refers to the centroid of the C(12)· · ·C(16) cyclopentadienyl ring.

A high-precision structure of one of the isomers was desired for another reason. In our recent studies[1,3-5] it was assumed that replacement in $(\eta^5\text{-}C_5H_5)_2M_2(CO)_x$ of one or more CO ligands by CNR groups does not affect the basic structure of the molecule. This has been verified in the case of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$,[5] where $CNCH_3$ replaces a terminal CO group. The structure of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNC_6H_5)$ has been communicated;[6] apparently the replacement of a bridging CO group by a CNC_6H_5 group does not significantly change the structure. However a full paper, with structural details, has not appeared.

Crystallographic Procedures

Data Collection. Crystals of the compound were kindly supplied by Dr. R. D. Adams. An irregularly shaped dark brown-black crystal of approximate dimensions 0.11 × 0.18 × 0.25 mm was examined on a Syntex $P\bar{1}$ four-circle automatic diffractometer. From ω scans of several intense reflections, a peak width at half-height of 0.2° was measured. Cell constants and an orientation matrix for the triclinic unit cell were determined from least-squares refinement of the setting angles of 15 computer-centered reflections. The cell parameters are $a = 8.660$ (2), $b = 12.682$ (4), $c = 7.993$ (2) Å; $\alpha = 101.72$ (2), $\beta = 116.28$ (1), $\gamma = 83.28$ (2)°; and $V = 770.3$ (3) Å^3. For $Z = 2$ and mol wt 380.01, the calculated density is 1.638 g cm^{-3}.

Data were collected at 15° using Mo Kα radiation filtered by means of a graphite-crystal monochromator. The θ-2θ scan technique with a scan rate varying from 2 to 24°/min, depending on the intensity of the reflection, was used to collect 2050 independent reflections in the range $0° < 2\theta \leq 45°$. The scan range was from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak. No significant change in the intensities of three reference reflections, monitored every 100 reflections, was observed. Additional details of data collection have been given previously.[7]

No effects owing to secondary extinction were observed in the

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(4) R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 5, 153 (1973).

(5) R. D. Adams, M. D. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 6594 (1973).

(6) K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

(7) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, 50, 227 (1973).

Table VII. Equations of Weighted Least-Squares Planes[a] and Distances (A) of Atoms from These Planes

Plane I: cyclopentadienyl ring, C(7)· · ·C(11)
Equation: $2.10x + 0.287y + 6.00z + 1.18 = 0$

Atom	C(7)	C(8)	C(9)	C(10)	C(11)
Distance	0.000 (7)	0.002 (7)	−0.004 (7)	0.004 (7)	−0.002 (7)

Plane II: cyclopentadienyl ring, C(12)· · ·C(16)
Equation: $7.81x + 6.33y - 4.87z - 5.46 = 0$

Atom	C(12)	C(13)	C(14)	C(15)	C(16)
Distance	0.000 (7)	−0.003 (7)	0.004 (6)	−0.004 (7)	0.002 (6)

Plane III: bridging coordination, Fe(1), Fe(2), C(1), C(2)
Equation: $4.13x + 4.62y - 7.87z - 0.995 = 0$

Atom	Fe(1)	Fe(2)	C(1)	C(2)
Distance	0.005 (1)	0.006 (1)	−0.262 (6)	−0.289 (7)

Plane IV: bridging group, Fe(1), Fe(2), C(1), N(1), C(5)
Equation: $-3.30x - 6.73y + 7.48z + 1.39 = 0$

Atom	Fe(1)	Fe(2)	C(1)	N(1)	C(5)
Distance	−0.0002 (9)	−0.0007 (9)	−0.036 (4)	−0.027 (6)	0.110 (11)

Plane V: bridging group, Fe(1), Fe(2), C(2), N(2), C(6)
Equation: $4.80x + 2.24z - 7.92z - 0.557 = 0$

Atom	Fe(1)	Fe(2)	C(2)	N(2)	C(6)
Distance	−0.0003 (9)	0.0000 (9)	0.013 (6)	0.017 (6)	−0.067 (11)

Plane VI: bridging group, Fe(1), Fe(2), C(1)

Plane VII: bridging group, Fe(1), Fe(2), C(2)

Plane VIII: bridging group, Fe(1), C(1), C(2)

Plane IX: bridging group, Fe(2), C(1), C(2)

Dihedral Angles, Deg

Planes	Angles	Planes	Angles
I-II	87.0	IV-V	24.1
I-III	46.9	VI-VII	22.2 (3)
II-III	46.1	VIII-IX	24.9 (4)

[a] The equation of the plane is in the form $Ax + By + Cz + D = 0$, where x, y, and z are fractional triclinic coordinates.

data set. The linear absorption coefficient of the compound is 19.37 cm^{-1} for Mo Kα radiation. The transmission factors for the minimum and maximum path lengths within the bounds of the experiment are 0.80 and 0.70. No absorption correction was applied.

Solution and Refinement of Structure.[8] The positions of the two Fe atoms, one terminal C atom, and one bridging C atom were obtained from a three-dimensional Patterson function. The positions were varied, with fixed temperature parameters, in one cycle of full-matrix least-squares refinement resulting in agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.295$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.378$. In a succeeding difference Fourier synthesis all remaining nonhydrogen atoms were located. Least-squares refinement of these positions along with isotropic, and later anisotropic, temperature parameters led to R factors of 0.052 and 0.063. However, high correlation coefficients between parameters of each atom suggested that the initial choice of cell constants ($a = 8.809$, $b = 8.660$, $c = 12.683$ A; $\alpha = 96.72$, $\beta = 93.98$, $\gamma = 125.55°$) was a poor one. Therefore the data were transformed according to the cell given above and additional least-squares refinements showed no significant correlations among the parameters.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ showed that the original choice (0.04) for the parameter p, used in the calculation of the standard deviation of the intensity, was too small.[7] A more suitable choice of 0.05 was used in the final cycles of refinement.

All hydrogen atoms were located in a difference Fourier map. The positional parameters of the six methyl hydrogen atoms were refined with isotropic thermal parameters fixed at 5.0 A^2. Hydrogen atoms associated with the cyclopentadienyl rings were included in the structure factor calculation but were not refined; the positions included were those calculated assuming a C-H distance of 0.95 A along a twofold axis of a planar pentagonal C_5H_5 ring. Thermal parameters were fixed at 5.0 A^2.

Least-squares refinement of the 217 variables converged at $R_1 = 0.039$ and $R_2 = 0.047$. The error in an observation of unit weight is 1.23. Only the 1370 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were employed in the refinement. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weight w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors of Cromer and Waber[9] were used, with H scattering factors from Stewart, Davidson, and Simpson.[10] Anomalous dispersion for Fe was included in calculations of F_c,[11] with values taken from Cromer and Liberman.[12]

No unusual trends were observed in an analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of reflection number, $\lambda^{-1} \sin \theta$, $|F_o|$, or various classes of Miller indices. A final difference Fourier synthesis showed no peaks greater than 0.43 e A^{-3}, compared to the highest hydrogen peak of 0.56 e A^{-3} on the previous map.

The observed and calculated structure factor amplitudes in the form of $10|F_o|$ and $10|F_c|$ in electrons are given in Table I.[13] The final positional parameters are given in Table II; anisotropic thermal parameters for the nonhydrogen atoms are listed in Table III.[13] Table IV tabulates root-mean-square amplitudes of thermal vibration.[13]

Results

The structure of the molecule, shown in Figure 1, is clearly one of the two tautomers previously postulated[3] to be present in solution. In the drawing the atoms are represented by thermal vibration ellipsoids enclosing 50% of the electron density; the atom-numbering scheme is also shown, but the

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(8) Calculations were performed on an IBM 360 computer using the following programs: DATARED by Frenz for data reduction; FOURIER by Robinson and Dellaca and based on Zalkin's FORDAP; NUCLS, a full-matrix least-squares program by Ibers and Doedens based on Busing and Levy's ORFLS program; a modified version of SADIAN by Baur for calculating atomic distances and angles; PERFACT by Frenz for analyzing structure factors and weighting schemes; ORTEP by Johnson for illustrations; the function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen; LIST by Snyder for listing the data.

(9) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press.

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(11) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(13) See paragraph at end of paper regarding supplementary material.

cyclopentadienyl hydrogen atoms have been omitted for clarity. Tables V and VI list the important bond distances and angles, respectively. There are no nonhydrogen intermolecular contacts less than 3.20 Å. Table VII gives information about various least-squares planes. The conformational properties of the folded bridge system are also given in this table. It is clear that the system of two three-membered rings, joined along the Fe–Fe bond is far from planar. This folding is probably a result of the preference of each Fe atom for a tripod arrangement of the two bridging carbon atoms and the carbon atom of the terminal CO group, with C–Fe–C angles as close to 90° as allowed by the ring system.

The only previously reported structure with a pair of bridging isocyanide ligands is that of $(\eta^5\text{-}C_5H_5)_2Ni_2(CNCH_3)_2$.[14] Detailed comparison of the two structures is not useful since the difference in metal-metal distances (2.32 Å for Ni–Ni, *vs.* 2.54 Å for Fe–Fe) will have a quantitative effect on other structural parameters. There is, however, one qualitative point of comparison which merits discussion.

For each of the crystallographically independent bridging systems in the nickel compound the Ni–C and Ni′–C bonds to a given isocyanide ligand are significantly different in length. The Ni–C bond anti to the methyl group is shorter by 0.047 (6) and 0.024 (6) Å in the two bridging systems. The question naturally arose as to whether this sizable inequality of M–C bond lengths would be a characteristic feature of all bridging isocyanide ligands or a peculiarity of the $(\eta^5\text{-}C_5H_5)_2Ni_2(CNCH_3)_2$ molecule.

The present results suggest that this feature probably is a general one, though subject to considerable variation in magnitude. For one of the $CNCH_3$ bridges a significant difference of 0.031 (10) Å exists, while for the other the apparent difference, in the proper direction, is too small (0.010 (10) Å) to be considered significant.

Discussion

The first important result of this investigation is that it corroborates the interpretation, developed in this laboratory, of the dynamical properties of binuclear metal carbonyls. The molecule which has been isolated and structurally characterized is one of the two tautomers postulated to exist in solution on the basis of ir and nmr data and on the basis of the proposed interconversion mechanism[3] for these and similar molecules.

The structure also supports the assumption that when one CO group or a few CO groups are replaced by the least sterically demanding isocyanide group, $CNCH_3$, the structure of the molecule will change only in a few minor, inevitable ways. Table VIII gives a comparison between the average bond lengths and angles in *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and those in *cis-anti*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CNCH_3)_2$. Aside from the slight inequality of one pair of the bridge bonds, essentially nothing has changed significantly upon replacing the two μ-CO groups by μ-$CNCH_3$ groups.

Table VIII. Comparison of Structural Data for *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2L_2$ (L = μ-CO,[a] μ-$CNCH_3$[b]): Average Bond Distance (Å) or Bond Angle (deg)[c]

Atoms[d]	L = μ-CO	L = μ-$CNCH_3$
Fe–Fe	2.531 (2)	2.538 (1)
Fe–C_t	1.745 (21)	1.714 (8)
Fe–C_b	1.917 (7)	1.937[e]
Fe–centroid	1.746 (5)	1.754 (6)
Fe–C_b–Fe	82.6 (3)	81.9 (4)
C_b–Fe–C_t	90.5 (25)	88.0 (7)
C_b–Fe–C_b	96.0 (3)	95.8 (5)
Dihedral angle	16	22.1 (3)

[a] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3068 (1970). [b] This work. [c] Numbers in parentheses are the esd from the mean or the esd on an individual value, whichever is larger. [d] C_t = terminal carbon atom; C_b = bridging carbon atom; centroid = centroid of cyclopentadienyl ring; dihedral angle = angle between Fe_2C_b planes. [e] The esd is not defined because nonequivalent bonds are averaged.

Finally, the results obtained here provide a starting point to examine the severity of steric strain engendered when a *tert*-butyl isocyanide ligand is placed in a bridging position while keeping other parts of the molecule essentially fixed. This problem cannot be examined directly since the strain is at least enough to keep the concentration of any $CNC(CH_3)_3$-bridged species below the limit of observation either spectroscopically in solution or crystallographically.[15] When the CH_3 groups in the present structure are replaced by $C(CH_3)_3$ groups, some very close contacts are produced, mainly between the hydrogen atoms of the *tert*-butyl groups and the C and H atoms of the cyclopentadienyl groups. From estimates made using a three-dimensional scale model, even with the most favorable rotational orientation of the *tert*-butyl group, there exist at least four contacts of *ca.* 2.3 ± 0.2 Å between *tert*-butyl hydrogen atoms and cyclopentadienyl hydrogen atoms. In addition there are short contacts between *tert*-butyl H atoms and the C atom of a CO group and between *tert*-butyl H atoms and the Fe atom.

These contacts are short, but not prohibitive. By way of comparison, in the present structure there is one short H· · ·H contact of 2.2 Å between H(10) and H(15) of different cyclopentadienyl rings. Thus, at the expense of some asymmetry in the bridging system, it may be structurally possible for the μ-$CNC(CH_3)_3$ derivative to form, at least as a transient species in solution. However it seems unlikely that the structure is stable enough to crystallize out of solution. In view of these results it is not surprising that for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$ no isomer with a bridging $CNC(CH_3)_3$ ligand is detectable in solution and that the rate of transit of this ligand from one iron atom to the other (which must occur by way of an intermediate with a μ-$CNC(CH_3)_3$ group) is slow compared to the corresponding process in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNCH_3)$.

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Registry No. $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CNCH_3)_2$, 42892-73-9.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, Table III, showing anisotropic thermal parameters, and Table IV, showing rms amplitudes of thermal vibration, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-253.

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(15) R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.* 12, 257 (1973).