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Low-Valent Metal Isocyanide Complexes. V.¹ Structure and Dynamical Stereochemistry of Bis(pentahapto cyclopentadienyl)tricarbonyl(*tert*-butyl isocyanide)diiron(*Fe-Fe*), $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]^2$

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Studies of the infrared and proton nmr spectra of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$ have indicated that the molecule exists in solution primarily as a rapidly interconverting mixture of *cis* and *trans* isomers. The terminal isocyanide ligand can pass from one metal atom to the other *via* a bridging position. The *cis-trans* isomerization remains rapid ($>600 \text{ sec}^{-1}$) at -120° and is thus estimated to have a free energy of activation of $<7.0 \text{ kcal/mol}$. The exchange of the isocyanide ligand between metal atoms is a much slower process, for which the coalescence temperature is about -10° and the Arrhenius activation energy is $14.4 \pm 0.7 \text{ kcal/mol}$. From a solution in pentane, a homogeneous crystalline solid is obtained and has been identified, by X-ray crystallography, as the *cis* isomer with a terminal isocyanide group. The crystals belong to the monoclinic space group $P2_1/c$ with unit cell parameters $a = 15.571 (8) \text{ \AA}$, $b = 9.518 (9) \text{ \AA}$, $c = 12.162 (7) \text{ \AA}$, $\beta = 101.74 (4)^\circ$, and $Z = 4$. Except for the replacement of one terminal CO group by $\text{CNC}(\text{CH}_3)_3$, the structure is essentially identical with that of *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$.

Introduction

We report here the dynamic and structural properties of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$ in solution, as a function of temperature, and in the crystalline phase. This work constitutes an extension of our previous investigations in the field of stereochemical nonrigidity of polynuclear metal carbonyls^{1,3-9} as well as a further contribution to our studies of metal isocyanide complexes.¹⁰⁻¹² The preparation of this particular compound has been reported by others as well,^{13,14} but its structural and dynamical properties have not heretofore been reported and interpreted in detail. The results presented here help to refine our understanding of the relative importance of various factors in the dynamical behavior of binuclear metal carbonyl species.

Procedure

Spectroscopic Measurements. Infrared spectra of the compound, prepared by the method of Jetz and Angelici,¹³ were recorded on a Perkin-Elmer Model 451 spectrophotometer and calibrated with polystyrene. Pmr spectra were recorded on a Varian Associates Model T-60 or HA-100 spectrometer equipped with a variable-temperature accessory. Temperature calibration was obtained from either methanol or ethylene glycol standards and is expected to be within $\pm 2^\circ$.

Nmr line shape calculations were carried out using the program

EXCHSYS written by G. M. Whitesides and J. K. Krieger.¹⁵ This was a routine analysis treating the process as a one-for-one exchange between uncoupled sites.

Collection of X-Ray Data. Red-black crystals of the compound were grown from a solution in pentane. From visual examination most of the crystals appeared twinned. However, a single crystal measuring $0.15 \times 0.13 \times 0.07 \text{ mm}$ was found and mounted on a thin glass fiber. Preliminary X-ray examination of the crystal and data collection were performed on a Syntex PI computer-controlled diffractometer equipped with a graphite-crystal monochromator. The operation of the diffractometer and other details of data collection have been described elsewhere,¹⁶ and only deviations from this description are included here.

The crystal was found to be monoclinic and of good quality with an ω scan peak width at half-height of 0.20° for several strong reflections. Eleven reflections were carefully centered and their setting angles refined by least-squares to obtain unit cell dimensions and an orientation matrix for data collection. Unit cell dimensions and other crystal data are given in Table I.

Data were collected at 22° using the θ - 2θ scan technique and a variable scan rate ranging from 1.0 to $24.0^\circ/\text{min}$ depending on the intensity of the reflection. Standard reflections, collected every 100 reflections, showed no evidence for crystal decomposition or crystal movement. Unique data were collected up to $2\theta(\text{Mo K}\alpha)$ of 45.8° using a scan range from $2\theta(\text{Mo K}\alpha) - 0.9^\circ$ to $2\theta(\text{Mo K}\alpha) + 0.9^\circ$. No absorption correction was made in view of the small variation in transmission factors of $84.8 \pm 4.5\%$ through the extreme directions of the crystal during data collection. Lorentz and polarization corrections were made;¹⁷ no evidence for secondary extinction was observed. A total of 1658 reflections were collected and only the 907 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used for the refinement of the structure.

Solution and Refinement of the Structure. The two iron atoms were located using a three-dimensional Patterson function. The positions of the iron atoms were refined by least squares to give the agreement factors

$$R_1 = (\sum \|F_o\| - |F_c|) / \sum |F_o| = 0.314$$

$$R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.408$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given by $4|F_o|^2/\sigma^2$ where σ

(15) Cf. J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

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

(17) Computer programs used in data reduction and in the solution and refinement of the structure were as follows. DATARED by Frenz was used for data reduction. The Fourier program JIMDAP by Ibers is a version of Zalkin's FORDAP. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\sum w(|F_o| - |F_c|)^2$. ORTEP by Johnson was used for drawing illustrations on a Gerber plotter. Atomic distances, angles, and errors were calculated using program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen.

(1) Part IV: F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, **13**, 253 (1974).

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

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(12) R. D. Adams and F. A. Cotton, *Inorg. Chem.*, **13**, 249 (1974).

(13) W. Jetz and R. J. Angelici, *J. Organometal. Chem.*, **35**, C37 (1972).

(14) M. J. Boylan, J. Bellerby, J. Newman, and A. R. Manning, *J. Organometal. Chem.*, **47**, C33 (1973).

Table I. Crystal Data for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNCC}(\text{CH}_3)_3]$

FW 408.89	Monoclinic
$a = 15.571$ (8) Å	Space group $P2_1/c$
$b = 9.518$ (9) Å	$F(000) = 840$
$c = 12.162$ (7) Å	Mo $K\alpha$ radiation
$\beta = 101.74$ (4) $^\circ$	$\mu = 17.8$ cm $^{-1}$
$V = 1764.8$ Å 3	$d_{\text{calcd}} = 1.54$ g cm $^{-3}$

is the esd of $|F_o|^2$. Scattering factors were taken from ref 18. Anomalous dispersion effects were included for the iron atoms using $\Delta f'$ and $\Delta f''$ values by Cromer and Liberman.¹⁹ A difference Fourier map based on the iron atom positions revealed the coordinates of all the remaining nonhydrogen atoms. The positions of these atoms were refined isotropically by two cycles of full-matrix least squares to give the residuals of $R_1 = 0.079$ and $R_2 = 0.092$. All of the hydrogen atoms on the *tert*-butyl group were located on a difference Fourier map after two anisotropic cycles of refinement on the nonhydrogen atoms. The positions of the hydrogen atoms on the cyclopentadienyl rings were calculated and were added as a constant contribution throughout the remainder of the refinement. All hydrogen atoms were given a constant thermal parameter of 5.0 Å 2 . Three full-matrix least-squares cycles, refining nonhydrogen atoms anisotropically and the positional parameters of the *tert*-butyl group hydrogen atoms, converged to the following agreement indices: $R_1 = 0.031$ and $R_2 = 0.035$. In the final cycle, no parameter shift exceeded the standard deviation of the parameter. The esd in an observation of unit weight is 0.98.

A final difference Fourier map showed no peaks greater than 0.30 e Å $^{-3}$; the hydrogen atoms were located on a previous map at 0.40 e Å $^{-3}$.

A list of observed and calculated structure factor amplitudes is given in Table II.²⁰ The atomic coordinates and their estimated standard deviations are given in Table III. Anisotropic thermal parameters are given in Table IV. Root-mean-square amplitudes of thermal vibration are given in Table V.¹⁸

Results

The infrared spectrum for a solution in hexane contains two bands, at 2108 and 2067 cm $^{-1}$, which we assign to C \equiv N stretching in terminal CNR ligands, one band at 1952 cm $^{-1}$ which we assign to CO stretching in a terminal carbonyl ligand and, finally, a multiple absorption in the region of bridging CO groups. The latter consists of a strong band with a peak at 1776 cm $^{-1}$ and a somewhat weaker band at 1779 cm $^{-1}$ which usually appears as an unresolved shoulder but which can be barely resolved under optimum instrumental conditions. These observations are in general agreement with those reported by Manning, *et al.*¹⁴

At room temperature the pmr spectrum in CS $_2$ shows only a single sharp cyclopentadienyl resonance at τ 5.55 and a single resonance for the *tert*-butyl group at τ 8.90. Upon cooling, the cyclopentadienyl resonance collapses and reforms as two peaks of equal intensity, which are sharp at -50° (Figure 1). The *tert*-butyl resonance remains unchanged throughout this temperature range. The spectral changes have been analyzed by line shape calculations, and the results are as follows: $E_a = 14.4 \pm 0.7$ kcal mol $^{-1}$, $\log A = 13.1 \pm 0.5$, $\Delta G^\ddagger = 13.9 \pm 1.0$ kcal mol $^{-1}$, $\Delta H^\ddagger = 13.9 \pm 0.7$ kcal mol $^{-1}$, $\Delta S^\ddagger = 0.0 \pm 3.0$ cal deg $^{-1}$ mol $^{-1}$.

The cyclopentadienyl resonances show no signs of additional broadening when the solution is cooled further, even to -120° . However, at -120° the methyl resonance is slightly, but definitely, broadened.

The molecular structure, as it exists in the crystal, is depicted in Figure 2. Important molecular dimensions are presented in Tables VI-VIII. There were no abnormal intermolecular contacts in the crystal.

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

(19) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).

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

Table III. Atomic Positional Parameters^a

Atom	x	y	z
Fe(1)	0.2171 (1)	0.3325 (1)	0.1473 (1)
Fe(2)	0.1906 (1)	0.5835 (1)	0.1980 (1)
O(1)	0.3139 (4)	0.4265 (7)	0.3638 (6)
O(2)	0.1293 (5)	0.5107 (7)	-0.0350 (6)
O(3)	0.3753 (6)	0.3628 (9)	0.0606 (7)
N(1)	0.3428 (6)	0.7136 (8)	0.1254 (7)
C(1)	0.1242 (11)	0.1870 (13)	0.0655 (10)
C(2)	0.2024 (10)	0.1252 (11)	0.0923 (13)
C(3)	0.2310 (9)	0.1267 (12)	0.2112 (17)
C(4)	0.1628 (13)	0.1945 (14)	0.2497 (12)
C(5)	0.0979 (8)	0.2313 (12)	0.1598 (16)
C(6)	0.1517 (9)	0.6627 (19)	0.3441 (8)
C(7)	0.1575 (8)	0.7684 (12)	0.2711 (15)
C(8)	0.0995 (10)	0.7485 (17)	0.1737 (12)
C(9)	0.0557 (7)	0.6234 (18)	0.1833 (14)
C(10)	0.0905 (9)	0.5732 (11)	0.2906 (14)
C(11)	0.2650 (6)	0.4479 (9)	0.2768 (8)
C(12)	0.1655 (6)	0.4899 (10)	0.0592 (9)
C(13)	0.3119 (7)	0.3528 (10)	0.0957 (8)
C(14)	0.2841 (6)	0.6618 (10)	0.1550 (7)
C(15)	0.4243 (7)	0.7596 (11)	0.0922 (8)
C(16)	0.4139 (8)	0.7373 (13)	-0.0339 (10)
C(17)	0.4995 (9)	0.6744 (14)	0.1538 (12)
C(18)	0.4351 (9)	0.9143 (14)	0.1190 (11)
H(1)	0.364 (5)	0.795 (9)	0.927 (6)
H(2)	0.396 (5)	0.626 (9)	0.944 (6)
H(3)	0.473 (5)	0.756 (8)	0.943 (6)
H(4)	0.555 (5)	0.713 (9)	0.155 (7)
H(5)	0.500 (7)	0.583 (9)	0.147 (8)
H(6)	0.497 (5)	0.706 (8)	0.243 (7)
H(7)	0.491 (5)	0.941 (9)	0.088 (7)
H(8)	0.435 (5)	0.932 (9)	0.198 (7)
H(9)	0.382 (6)	0.976 (9)	0.910 (7)
H(10)	0.090	0.201	-0.007
H(11)	0.235	0.085	0.039
H(12)	0.281	0.091	0.256
H(13)	0.161	0.214	0.328
H(14)	0.043	0.280	0.161
H(15)	0.182	0.650	0.418
H(16)	0.199	0.846	0.289
H(17)	0.090	0.809	0.111
H(18)	0.010	0.585	0.126
H(19)	0.073	0.485	0.321

^a Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables.

Discussion

Structure. The structure of the molecule as it occurs in the crystal presents no unusual features. Aside from the replacement of one terminal CO group by CNC(CH $_3$) $_3$, its structure is essentially identical with that of *cis*-($\eta^5\text{-C}_5\text{H}_5$) $_2\text{Fe}_2(\text{CO})_4$ as reported by Bryan, *et al.*²¹ Thus the corresponding bond lengths and angles in the bridging systems all agree within twice the sum of their esd's, including the Fe-Fe distances, which are 2.523 (2) and 2.531 (2) Å. The dimensions of the terminal isocyanide ligand are very close to those for the one in ($\eta^5\text{-C}_5\text{H}_5$) $_2\text{Mo}_2(\text{CO})_5(\text{CNCH}_3)$,⁹ except that in the present case there is a more pronounced deviation from linearity (C-N-C = 172 (1) $^\circ$). This appears to be the result of repulsion from the C $_5\text{H}_5$ ring which is bound to the same iron atom.

Dynamical Stereochemistry. From the infrared spectrum, we conclude that there are two tautomers present in solution, each one having a terminal isocyanide ligand. This conclusion seems to follow inescapably from the appearance of two bands in the region characteristic of C \equiv N stretching in terminal RNC ligands. It is then necessary to accept the postulate that the terminal CO stretching bands in the two tauto-

(21) R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3069 (1970).

Table IV. Anisotropic Thermal Parameters for Nonhydrogen Atoms^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0040 (1)	0.0077 (2)	0.0069 (1)	-0.0077 (1)	0.0023 (1)	-0.0008 (1)
Fe(2)	0.0035 (1)	0.0080 (2)	0.0063 (1)	-0.0001 (1)	0.0018 (1)	-0.0006 (1)
O(1)	0.006 (1)	0.016 (1)	0.009 (1)	0.002 (1)	0.000 (1)	-0.001 (1)
O(2)	0.008 (1)	0.016 (1)	0.006 (1)	-0.001 (1)	-0.000 (1)	0.000 (1)
O(3)	0.008 (1)	0.022 (2)	0.023 (1)	-0.002 (1)	0.010 (1)	-0.004 (1)
N(1)	0.004 (1)	0.009 (1)	0.012 (1)	-0.002 (1)	0.004 (1)	-0.000 (1)
C(1)	0.007 (1)	0.012 (2)	0.010 (1)	-0.003 (1)	0.000 (1)	-0.000 (1)
C(2)	0.008 (1)	0.007 (2)	0.015 (2)	-0.001 (1)	0.005 (1)	-0.002 (1)
C(3)	0.008 (1)	0.006 (2)	0.017 (2)	-0.001 (1)	-0.002 (1)	0.006 (1)
C(4)	0.012 (1)	0.012 (2)	0.009 (1)	-0.006 (1)	0.006 (1)	-0.002 (1)
C(5)	0.005 (1)	0.012 (2)	0.017 (2)	-0.002 (1)	0.005 (1)	-0.001 (2)
C(6)	0.007 (1)	0.020 (2)	0.007 (1)	0.004 (1)	0.002 (1)	-0.004 (2)
C(7)	0.005 (1)	0.009 (2)	0.019 (2)	0.000 (1)	0.005 (1)	-0.003 (1)
C(8)	0.005 (1)	0.023 (3)	0.010 (1)	0.006 (1)	0.001 (1)	0.002 (2)
C(9)	0.002 (1)	0.026 (3)	0.014 (2)	0.005 (1)	0.011 (2)	0.000 (1)
C(10)	0.005 (1)	0.011 (2)	0.014 (1)	-0.000 (1)	0.005 (1)	0.000 (1)
C(11)	0.004 (1)	0.008 (1)	0.006 (1)	-0.001 (1)	0.001 (1)	0.000 (1)
C(12)	0.004 (1)	0.012 (2)	0.006 (1)	-0.002 (1)	0.002 (1)	-0.000 (1)
C(13)	0.006 (1)	0.010 (2)	0.011 (1)	-0.000 (1)	0.005 (1)	-0.003 (1)
C(14)	0.003 (1)	0.008 (1)	0.007 (1)	-0.002 (1)	0.002 (1)	-0.001 (1)
C(15)	0.005 (1)	0.010 (1)	0.008 (1)	0.001 (1)	0.001 (1)	0.000 (1)
C(16)	0.005 (1)	0.019 (2)	0.010 (1)	0.001 (1)	0.003 (1)	0.000 (1)
C(17)	0.006 (1)	0.018 (2)	0.012 (1)	0.001 (1)	0.002 (1)	0.003 (2)
C(18)	0.006 (1)	0.014 (2)	0.014 (1)	-0.000 (1)	0.005 (1)	0.000 (2)

^a The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Root-Mean-Square Amplitudes of Thermal Vibration (Å)

Atom	Min	Intermed	Max
Fe(1)	0.18 (1)	0.19 (1)	0.25 (1)
Fe(2)	0.18 (1)	0.19 (1)	0.23 (1)
O(1)	0.23 (1)	0.25 (1)	0.31 (1)
O(2)	0.20 (1)	0.27 (1)	0.33 (1)
O(3)	0.17 (1)	0.30 (1)	0.45 (1)
N(1)	0.15 (2)	0.23 (1)	0.31 (1)
C(1)	0.21 (2)	0.27 (2)	0.31 (2)
C(2)	0.18 (2)	0.26 (2)	0.35 (2)
C(3)	0.13 (3)	0.27 (2)	0.42 (2)
C(4)	0.19 (2)	0.23 (2)	0.41 (2)
C(5)	0.20 (2)	0.26 (2)	0.36 (2)
C(6)	0.17 (2)	0.27 (2)	0.34 (2)
C(7)	0.18 (2)	0.23 (2)	0.38 (2)
C(8)	0.17 (2)	0.28 (2)	0.37 (2)
C(9)	0.15 (2)	0.21 (2)	0.42 (2)
C(10)	0.20 (2)	0.23 (2)	0.34 (2)
C(11)	0.18 (2)	0.21 (2)	0.23 (2)
C(12)	0.19 (2)	0.21 (2)	0.26 (2)
C(13)	0.18 (2)	0.22 (2)	0.32 (1)
C(14)	0.16 (2)	0.20 (2)	0.24 (1)
C(15)	0.20 (2)	0.24 (2)	0.24 (2)
C(16)	0.22 (2)	0.25 (2)	0.33 (2)
C(17)	0.25 (2)	0.26 (2)	0.32 (2)
C(18)	0.22 (2)	0.28 (2)	0.30 (2)

Table VI. Bond Lengths (Å)

Fe(1)-Fe(2)	2.523 (2)	N(1)-C(14)	1.16 (1)
Fe(1)-C(11)	1.94 (1)	N(1)-C(15)	1.47 (1)
Fe(1)-C(12)	1.92 (1)	C(15)-C(16)	1.52 (1)
Fe(1)-C(13)	1.73 (1)	C(15)-C(17)	1.49 (2)
Fe(2)-C(11)	1.86 (1)	C(15)-C(18)	1.51 (1)
Fe(2)-C(12)	1.88 (1)	C(1)-C(2)	1.33 (1)
Fe(2)-C(14)	1.81 (1)	C(1)-C(5)	1.36 (1)
Fe(1)-C(1)	2.10 (1)	C(2)-C(3)	1.42 (2)
Fe(1)-C(2)	2.08 (1)	C(3)-C(4)	1.40 (2)
Fe(1)-C(3)	2.10 (1)	C(4)-C(5)	1.37 (2)
Fe(1)-C(4)	2.10 (1)	C(6)-C(7)	1.36 (1)
Fe(1)-C(5)	2.12 (1)	C(6)-C(10)	1.34 (1)
Fe(2)-C(6)	2.13 (1)	C(7)-C(8)	1.35 (1)
Fe(2)-C(7)	2.08 (1)	C(8)-C(9)	1.39 (2)
Fe(2)-C(8)	2.10 (1)	C(9)-C(10)	1.39 (2)
Fe(2)-C(9)	2.11 (1)	C(16)-H(1)	0.99 (8)
Fe(2)-C(10)	2.10 (1)	C(16)-H(2)	1.11 (8)
O(1)-C(11)	1.19 (1)	C(16)-H(3)	1.02 (8)
O(1)-C(11)	1.19 (1)	C(17)-H(4)	0.94 (8)
O(2)-C(12)	1.19 (1)	C(17)-H(5)	0.87 (8)
O(3)-C(13)	1.16 (1)	C(17)-H(6)	1.13 (8)
		C(18)-H(7)	1.04 (8)
		C(18)-H(8)	0.98 (8)
		C(18)-H(9)	1.02 (8)

mers are unresolved. Furthermore, the antisymmetric stretching modes of the bridging CO groups of the isomers are of nearly the same frequency. Such coincidences, or near coincidences, however, need not be considered unusual or surprising, since similar ones occur, beyond any doubt, in the unsubstituted system composed of *cis*- and *trans*-(η^5 -C₅H₅)₂Fe₂(CO)₄^{4,22} as Manning²² was the first to realize. The two species present here must be the analogous *cis* and *trans* isomers.

The appearance of only a single C₅H₅ proton resonance at room temperature requires us to postulate two dynamical processes: (1) the *cis* and *trans* isomers rapidly interconvert; (2) the isocyanide ligand passes rapidly from one metal atom to the other.

Process 1. The process by which the *cis* and *trans* isomers are interconverted in this system is presumably very similar to that which occurs for the parent molecule (η^5 -C₅H₅)₂Fe₂(CO)₄^{4,7,8}

Table VII. Selected Bond Angles (deg)

Fe(1)-Fe(2)-C(14)	98.0 (3)	C(16)-C(15)-C(17)	109.9 (10)
Fe(2)-Fe(1)-C(13)	100.2 (3)	C(16)-C(15)-C(18)	109.7 (10)
Fe(1)-C(11)-Fe(2)	83.0 (4)	C(17)-C(15)-C(18)	112.3 (10)
Fe(1)-C(12)-Fe(2)	83.2 (4)	C(1)-C(2)-C(3)	109.0 (11)
Fe(1)-C(11)-O(1)	134.2 (7)	C(2)-C(3)-C(4)	104.0 (11)
Fe(1)-C(12)-O(2)	137.1 (8)	C(3)-C(4)-C(5)	109.6 (12)
Fe(1)-C(13)-O(3)	178.3 (9)	C(4)-C(5)-C(1)	107.1 (11)
Fe(2)-C(11)-O(1)	142.6 (8)	C(5)-C(1)-C(2)	110.3 (11)
Fe(2)-C(12)-O(2)	139.5 (8)	C(6)-C(7)-C(8)	110.4 (11)
Fe(2)-C(14)-N(1)	178.5 (8)	C(7)-C(8)-C(9)	107.4 (12)
C(14)-N(1)-C(15)	171.5 (9)	C(8)-C(9)-C(10)	105.6 (11)
N(1)-C(15)-C(16)	108.2 (9)	C(9)-C(10)-C(6)	109.8 (11)
N(1)-C(15)-C(17)	109.4 (9)	C(10)-C(10)-C(7)	106.8 (10)
N(1)-C(15)-C(18)	107.1 (9)		

As shown schematically in Figure 3, the *cis* and *trans* isomers, A and A', are converted to the nonbridged tautomers C by shifting the bridging carbonyl ligands to terminal positions. The nonbridged tautomers probably exist

Table VIII. Weighted Least-Squares Planes and Dihedral Angles

Plane		Atoms defining plane				Equation of mean plane ^a					
I		C(1)-C(2)-C(3)-C(4)-C(5)				7.30x + 8.39y - 1.87z = 2.35					
II		C(6)-C(7)-C(8)-C(9)-C(10)				12.25x - 4.806y - 6.19z = -3.45					
III		Fe(1)-C(11)-Fe(2)				-13.04x - 2.87y + 7.39z = 2.69					
IV		Fe(1)-C(12)-Fe(2)				-14.82x - 2.44y + 4.33z = 3.39					
V		Fe(1)-Fe(2)-C(13)				5.65x - 1.396y + 9.83z = 2.21					
VI		Fe(1)-Fe(2)-C(14)-N(1)-C(15)				5.57x - 1.41y + 10.00z = 2.26					
Displacement of Atoms from Mean Plane, A											
Plane I		Plane II		Plane III		Plane IV		Plane V		Plane VI	
C(1)	-0.002	C(6)	-0.008	O(1)	0.068	O(2)	0.078	C(11)	1.408	Fe(1)	0.000
C(2)	0.001	C(7)	0.007	C(12)	-0.431	C(11)	-0.432	C(12)	-1.402	Fe(2)	0.001
C(3)	0.000	C(8)	-0.005					C(14)	-0.004	C(14)	-0.002
C(4)	-0.002	C(9)	0.000					N(1)	-0.037	N(1)	-0.032
C(5)	0.002	C(10)	0.004					O(3)	-0.001	C(15)	0.041
										C(13)	0.002
										C(17)	1.211
										C(18)	0.153
Dihedral Angles between Planes, deg											
Planes		Planes		Planes		Planes		Planes		Planes	
I-II	93.1	II-III	132.0	III-IV	17.7	IV-V	99.3				
I-III	133.4	II-IV	132.8	III-V	81.6						
I-IV	133.0	II-V	87.8								
I-V	90.7										

^a Equations have the form $Ax + By + Cz = D$ where x , y , and z are fractional coordinates.

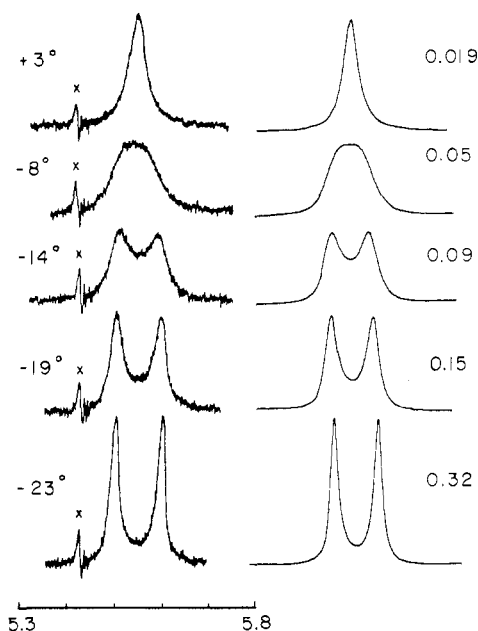


Figure 1. Observed and calculated pmr spectral changes of the cyclopentadienyl resonances of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$ in CS_2 solvent. The values associated with the calculated spectra are the average lifetimes in seconds. The peak marked \times is from $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ impurity.

as gauche and trans staggered rotamers,^{4,8} but this is not explicitly shown for simplicity (*cf.* Figure 4). A partial internal rotation around the metal-metal bond interconverts the isomers and the rearrangement is completed by returning a pair of carbonyl ligands to bridging positions.

If one assumes that cyclopentadienyl signals for cis and trans isomers would be separated by about 10 Hz (as they are in $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ ⁴), then the failure to observe separate resonance from the two isomers at -120° allows us to put an approximate upper limit of about 7.0 kcal/mol on the free energy of activation for cis-trans interconversion. This may be compared with ΔG^\ddagger for the cis-trans interconversion in $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ which is about 10.5 kcal/mol.⁴

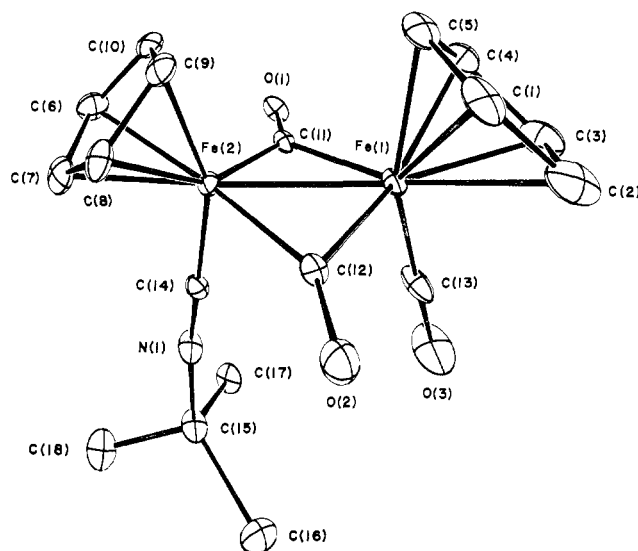


Figure 2. The molecular structure of $\text{cis}-(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$ as it occurs in the crystalline state. The atom-numbering scheme used in the tables is defined.

While it is not possible to specify with certainty the reason for this difference in the free energies of activation, either or both of two factors seem likely to be critical. This may best be appreciated by examination of Figure 5, which is a qualitative potential energy diagram for cis-trans interconversion in such a system.⁸ The height of the overall barrier for passing from one bridged isomer to the other is determined by the energies ΔG_1 and ΔG_2 . The former is the energy difference between a bridged structure and the nonbridged rotamer which arises directly from it upon opening the bridges. The second is the barrier to that rotation which is required to interconvert the two rotamers shown. Lessening either one or both of these energies would reduce the activation energy for cis-trans interconversion. There is insufficient evidence for determining in any greater detail exactly what is happening.

Process 2. Let us now consider the spectral changes in the C_5H_5 resonance which occur between temperatures of about

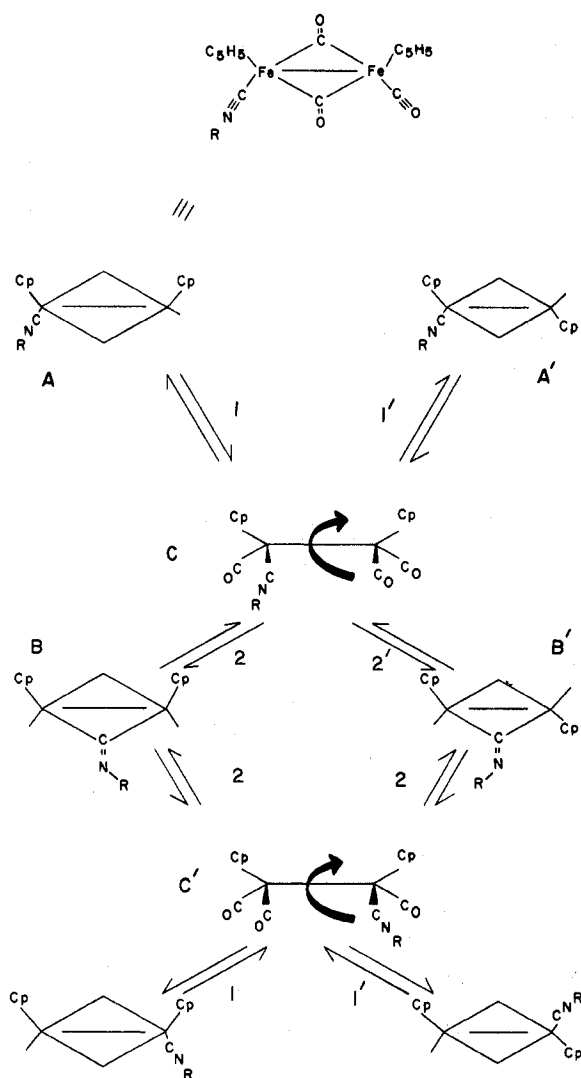


Figure 3. A schematic representation of the rearrangement pathways available to monosubstituted isocyanide derivatives of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

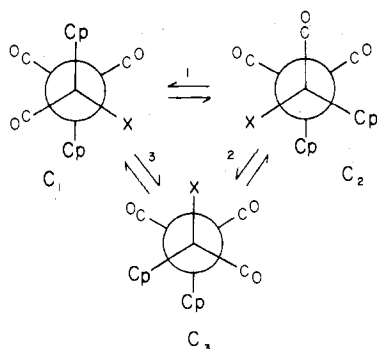


Figure 4. Newmann projections of nonbridged tautomers C. The trans rotamer C_1 is generated from the trans-bridged isomer A. The diastereotopic gauche rotamers C_2 and C_3 may be generated from the cis isomer A' . The three rotamers may be interconverted by internal rotations 1, 2, and 3 around the metal-metal bond. Cp = C_5H_5 and X = $t\text{-BuNC}$.

+25 and about -50° , keeping in mind the fact that in this same temperature region there is no change in the methyl resonance. We attribute these observations to the overall process in which the isocyanide ligand passes from one metal atom to the other.

As can be seen in Figure 3, process 2 is an alternative rearrangement available to the nonbridged tautomers C. In-

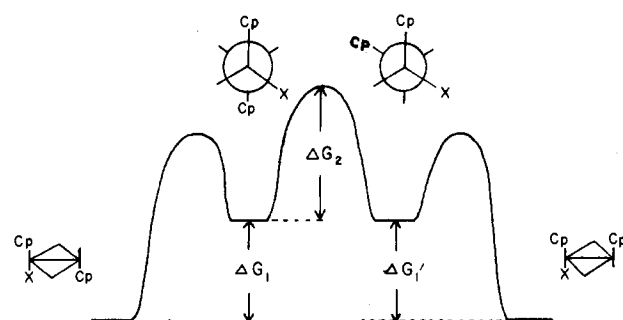


Figure 5. A qualitative potential energy diagram for the cis-trans isomer interconversion process. X = $\text{CNC}(\text{CH}_3)_3$.

stead returning directly to a relatively stable structure with two bridging carbonyl ligands, A or A' , the isocyanide ligand on one metal atom and a carbonyl ligand on the other metal atom can shift into bridging positions. There are two such relatively unstable isomers, namely, cis (B) and trans (B'), which are analogous to the bis(carbonyl)-bridged structures, A and A' . Once the B or B' structure has been established, the foregoing sequence of steps can reverse itself, whereby the isocyanide ligand can either return to the metal atom whence it came or pass to the other one. Finally, the molecule can return from one of these C configurations to a doubly CO-bridged structure.

It has previously been reported that in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\text{CNCH}_3)_2$, the isocyanide ligands have a greater preference for the bridging position than do the CO ligands. This is shown by the fact⁷ that of the three readily interconvertible isomers, *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CNCH}_3)_2$, *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})(\text{CNCH}_3)(\mu\text{-CO})(\mu\text{-CNCH}_3)$, and *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CNCH}_3)_2(\mu\text{-CO})_2$, only the first two are observed in the equilibrium mixture. Similarly, in the system $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{CNCH}_3)$, the isomers with a bridging isocyanide ligand are somewhat more abundant at equilibrium than those with two bridging CO groups.²³ In the present case there is no detectable amount of a bridged isomer. This means that the equilibrium constant $K = \{(\mu\text{-CO})[\mu\text{-CNC}(\text{CH}_3)_3] \text{ isomer(s)}\} / \{(\mu\text{-CO})_2 \text{ isomer(s)}\}$ must be $<10^{-2}$. This, in turn, means that $\mu\text{-CNCC}(\text{CH}_3)_3$ -containing species are less stable by about 3 kcal/mol or more, whereas, with CNCH_3 isocyanide-bridged species are slightly more stable than those with CO bridges, by roughly 1 kcal/mol.

The disfavoring of the $\text{CNC}(\text{CH}_3)_3$ ligand from a bridging position by at least 4 kcal/mol as compared with the CNCH_3 ligand is most likely a steric effect. As shown in the preceding paper, there are some noticeably close nonbonded contacts when a $\text{CNC}(\text{CH}_3)_3$ ligand occupies a bridging position in a $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n(\text{CNR})_{4-n}$ type molecule. However, these close contacts do not appear to be severe enough to render the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})[\mu\text{-CNC}(\text{CH}_3)_3]$ structure inaccessible as a transient intermediate or transition state for the passage of the $\text{CNC}(\text{CH}_3)_3$ ligand from one metal atom to the other. For that process, as reported above, the ΔG^\ddagger is about 14 kcal/mol.

Registry No. *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$, 42892-76-2; *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]$, 42892-77-3.

Supplementary Material Available. Table II, a listing of structure factor amplitudes, 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

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Transition Metal Chemistry of Quinuclidinone-Containing Ligands. II. Spectral and Magnetic Properties of Some Transition Metal Complexes Containing 2-(*N*-Morpholinylmethyl)-3-quinuclidinone and Related Ligands¹

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Complexes of cobalt(II), nickel(II), and iron(II) halides with the title compound were prepared by adding the appropriate metal salt to the ligand in alcoholic solutions. The complexes have pseudotetrahedral microsymmetry around the central metal ion as indicated by their spectral and magnetic properties; the coordination sphere contains one bidentate nitrogen-bonded ligand and two halide atoms. Ligand field band assignments, metal-halide stretching frequencies, and magnetic susceptibility data are given for each of the complexes. The cobalt(II) and nickel(II) perchlorate complexes of the title compound were also prepared, and each contains two bidentate ligands which provide a tetrahedral ligand field that is stronger than for the halide complexes. It is suggested that the apparent preference of the ligand for one-to-one metal-to-ligand coordination and the consequent tetrahedral structures result from a combination of the size of the quinuclidine group and the rigidity of the five-membered chelate ring formed by the coordinated ligand. In addition to these pseudotetrahedral complexes, an octahedral nickel chloride complex which apparently contains bridging chloride ligands is reported. A cobaltous thiocyanate complex is also found to have an octahedral structure in the solid state and a tetrahedral structure in solution.

Introduction

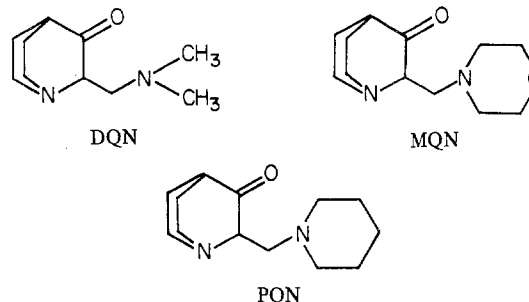
As a part of an investigation of ligands which produce tetrahedral or distorted tetrahedral complexes with transition metal ions, we examined the coordinating ability of several potentially bidentate 2-(*N*-aminomethyl)-3-quinuclidinone ligands.

The study of the transition metal complexes which contain quinuclidinone and its derivatives has to date been limited. Yoke and his coworkers studied complexes involving quinuclidine and AgNO_3 ,² CuCl_2 ,³ and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.⁴ The $\text{CuCl}_2 \cdot \text{Quin}$ and $\text{CoCl}_2 \cdot 2\text{Quin}$ complexes (where Quin represents quinuclidine) were reported³ stable and magnetically normal and the cobalt was found to have an electronic spectrum typical of pseudotetrahedral coordination. The copper acetate complex $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Quin}$ shows the antiferromagnetic behavior typically found in the dimeric copper(II) acetate systems.⁵ Clark and Natile⁶ prepared five- and six-coordinate vanadium(III) and chromium(III) halide complexes with quinuclidine. Complexes of the type $\text{VX}_3 \cdot 2\text{Quin}$ (where X represents Cl or Br) were found to have trans trigonal-bipyramidal structures. Both $\text{CrCl}_3 \cdot 3\text{Quin}$ and $\text{CrCl}_3 \cdot 2\text{Quin}$ were prepared; the former was found to have an octahedral structure and the latter a trans bipyramidal structure. The five-coordinate compound $\text{CrBr}_3 \cdot \text{Quin}$ was the only isolable adduct found for chromium(III) bromide. The electron spin resonance spectra of one-to-one adducts of copper(II) bis(acetylacetonate) and copper(II) bis(hexafluoroacetylacetonate) with pyridine and quinuclidine have been examined.⁷

A series of positive transition metal complexes containing the quinuclidinium ion was reported by Quagliano, *et al.*⁸

The only complexes with a bidentate quinuclidine-containing ligand appear to be those of Coffen and McEntee,¹ who reported several cobalt(II), nickel(II), and copper(II) complexes containing *trans*-2-(2'-quinoly)methylene-3-quinuclidinone and its 6-methoxy derivative.

This paper reports the preparation and properties of several transition metal complexes containing the new ligands 2-(*N*-morpholinylmethyl)-3-quinuclidinone (MQN), 2-(*N*-dimethylaminomethyl)-3-quinuclidinone (DQN), and 2-(*N*-piperidinylmethyl)-3-quinuclidinone (PQN). Fisher-Hirschfelder models of MQN indicate a bulky, rigid structure which has considerable steric hindrance at the two nitrogen coordination sites. We anticipated that these ligands would coordinate through both nitrogen atoms to form complexes of the type MLX_2 in which L is the bidentate ligand, and X is a halide or pseudohalide. In view of the rigid five-membered ring which could be formed with the central metal ion and the steric factors present in these ligands, we further expected tetrahedral



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