Volume 13
Number 2
February 1974

Inorganic Chemistry

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Low-Valent Metal Isocyanide Complexes. III.[1] Inversion at the Nitrogen Atoms of Bridging Isocyanide Ligands

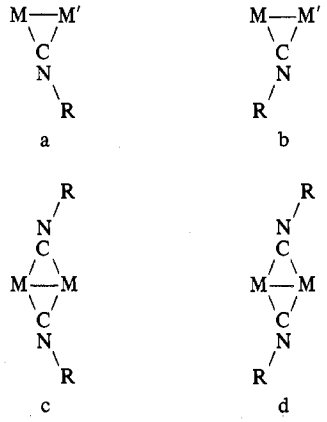
R. D. ADAMS and F. A. COTTON*

Received June 12, 1973

The existence of isomers which differ in the orientations of bent bridging isocyanide ligands has been demonstrated in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNCH_3)_3$, **1**, and $(\eta^5\text{-}C_5H_5)Fe_2(CO)_2(CNCH_3)_2$, **2**, and their interconversions have been studied by nmr spectroscopy at low temperatures. For **1** three isomers, two syn and one anti, are possible; the anti and one syn isomer predominate and interconvert rapidly on the nmr time scale at 25°. At −100° sharp signals due to the separate isomers can be observed.

Introduction

It is well established that isocyanide ligands which bridge two metal atoms have nonlinear CNC chains.[2,3] The overall structure of a M(μ-CNR)M′ group is therefore grossly similar to those of organic imines RC=NR′R″, with R′ and R″ corresponding to M and M′. This situation is of interest in two ways. First, there is the possibility that isomers may arise when the two metal atoms, M and M′, are chemically nonequivalent, *e.g.*, **a** and **b**. With doubly bridged systems of syn and anti isomers, **c** and **d** are possible even when M and M′ are identical.



Moreover, the possibility of dynamic rearrangement, interconverting such isomers, also has to be considered. Dynamic rearrangements of this type are well known in organic imine chemistry.[4] In some binuclear molecules containing one or more isocyanide ligands, it has been shown that the isocyanide ligand(s) can pass rapidly from a terminal position on one metal atom to a terminal position on the other by traversing an intermediate in which the isocyanide ligand occupies a bridging position.[5-7] Inversion of the configuration at the nitrogen atom of the bridging isocyanide ligand must be an essential step in the complete mechanism of such an end-to-end transposition of the isocyanide group. Since the nitrogen inversion barriers in *N*-alkylimines are very high,[8] it seemed possible that the nitrogen inversion step might play a significant role in determining the rate of the metal-to-metal exchange of isocyanides.

In this paper the results of some studies of the isomers and isomerizations characteristic of bridging isocyanide ligands are discussed.

Results

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNCH_3)_3$, 1. The preparation, characterization and dynamical behavior of this compound will be fully reported elsewhere.[9,10] These other studies have shown that the molecule exists in solution entirely in one tautomeric form, which must be either the cis or the trans isomer having two bridging isocyanide ligands. On this basis, it might be supposed that there would be only a single infrared absorption band in the region characteristic of terminal CO ligands.

It was, therefore, interesting to observe the presence of two strong, distinct bands (1938, 1947 cm^{-1}) as well as a weak shoulder (1955 cm^{-1}) in the terminal carbonyl absorption region of the infrared spectrum of **1**. The presence of isomers, formed by different relative orientations of the methyl groups on the bridging ligands, was the suspected cause of this and a study of the low-temperature pmr spectra

(1) Part II: R. D. Adams and F. A. Cotton, *Syn. Inorg. Metal-Org. Chem.*, 2, 277 (1972).
(2) (a) K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965); (b) R. D. Adams, F. A. Cotton, and G. A. Rusholme, *J. Coord. Chem.*, 1, 275 (1971).
(3) F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 13, 253 (1974).
(4) C. G. McCarty in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, London, 1970, Chapter 9.
(5) R. D. Adams and R. A. Cotton, *J. Amer. Chem. Soc.*, 94, 6193 (1972).
(6) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 6589 (1973).
(7) R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 6594 (1973).
(8) G. Binsch, *Top. Stereochem.*, 3, 150 (1968).
(9) R. D. Adams and F. A. Cotton, article in preparation, dealing with the series $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNCH_3)_n$, n = 1-3. See in the meantime ref 10.
(10) R. D. Adams, Ph.D. Thesis, Massachusetts Institute of Technology, 1973.

was, therefore, undertaken. The room-temperature pmr spectrum of **1** in CS_2 solvent shows two sharp cyclopentadienyl singlets at τ 5.38 and 5.54, relative intensity 5, a sharp singlet at τ 6.41, relative intensity 6, assigned to methyl resonances from two bridging methyl isocyanide ligands, and a sharp singlet at τ 7.22, relative intensity 3, attributed to the methyl resonance of a terminal methyl isocyanide ligand.

The low-temperature pmr spectra of the compound are shown in Figure 1. As the temperature is lowered, the cyclopentadienyl and bridging methyl isocyanide resonances show significant broadening, while the terminal methyl isocyanide resonance remains fairly sharp. At $-85°$ each of the cyclopentadienyl resonances is beginning to re-form as two peaks, the bridging methyl isocyanide resonance is asymmetrically broad, but the terminal methyl isocyanide resonance is still relatively sharp. At about $-100°$ each of the cyclopentadienyl resonances has re-formed as two sharp peaks, resulting in two pairs of lines with different intensities. The bridging methyl isocyanide resonance has re-formed as three peaks, one large singlet and two smaller peaks of equal intensity. The terminal methyl isocyanide resonance is now significantly broadened. Addition of 10% by volume of $CDCl_3$ to the solvent greatly reduces the relative intensity of the inner pair of cyclopentadienyl resonances. At the same time, the two equally intense bridging methyl isocyanide resonances are reduced in size, and the terminal methyl isocyanide resonance changes shape yielding a singlet with a small shoulder on the high-field side.

The pmr spectral changes have been interpreted in terms of the interconversion of two of three possible stereoisomers formed by different relative orientations of the methyl groups on the bridging isocyanide ligands. As shown in Figure 2, these isomers include two syn forms, isomers 1 and 3, and one anti form, isomer 2. Furthermore, the inner pair of cyclopentadienyl resonances at τ 5.48 and 5.58, the pair of methyl resonances at τ 6.48 and 6.57, and one of two terminal methyl isocyanide resonances at τ 7.40 (the high field shoulder in the 10% $CDCl_3$-CS_2 solvent) can definitely be assigned to the anti isomer 2. The pair of cyclopentadienyl resonances at τ 5.42 and 5.67, the single methyl isocyanide resonance at τ 6.54, and the remaining terminal methyl isocyanide resonance at τ 7.40 can be assigned to one of the two syn forms. There is no basis to determine which one. At ambient temperatures these two isomers are rapidly interconverting. The spectra changes could not be the result of bridge–terminal coordination rearrangement since in the room-temperature spectrum (fast-exchange limit) there is no evidence for exchange of the bridging methyl isocyanide resonance with the terminal methyl isocyanide resonance. The presence of a third, small, terminal carbonyl absorption in the room-temperature infrared spectrum implies existence of a small amount of the third stereoisomer. Presumably, this isomer has been depopulated below the limits of observation at $-100°$.

Line shape calculations on the spectral changes in the cyclopentadienyl region gave rates which did not give a satisfactorily linear Arrhenius plot. The difficulty was traced to the fact that the resonances in the region of intermediate exchange rates were disproportionately broad on the assumption that the only source of spectral change was the exchange between the two observed isomers. We feel that the most likely explanation is that a trace amount (increasing in concentration at higher temperatures) of the third isomer is present and is undergoing exchange with the other two. The net effect on the spectra will be additional broadening with only a minor change in the peak shapes. No great difference would be expected between the observed coalescence temperature and the true coalescence temperature associated with the predominant exchange process. As a result, we have used an approximate equation[11] to determine the exchange rate at the coalescence temperature. From this rate we can calculate the free energies of activation, $\Delta G_A^{\ddagger} = 10.4 \pm 0.5$ kcal/mol and $\Delta G_B^{\ddagger} = 10.0 \pm 0.5$ kcal/mol, where

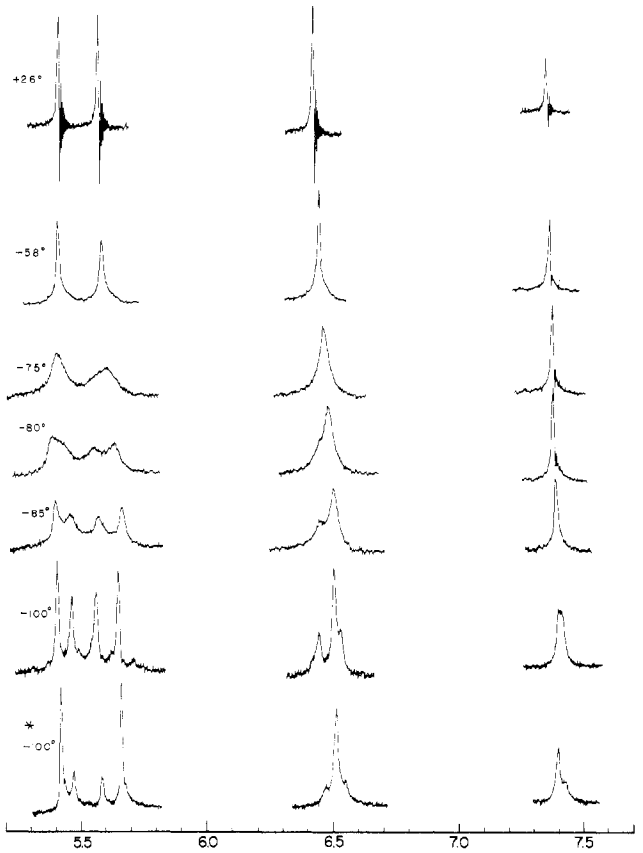


Figure 1. The low-temperature pmr spectra of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNCH_3)_3$ recorded in CS_2 solvent, except for the spectrum labeled with an asterisk which was recorded in a 10% $CDCl_3$-CS_2 solvent.

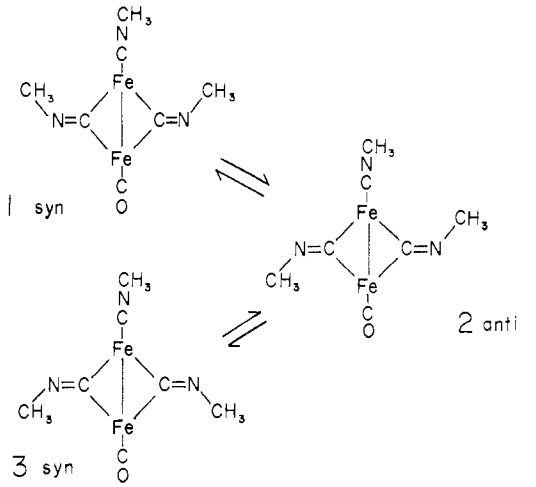


Figure 2. Stereoisomers resulting from different relative orientations of the methyl groups on the bridging isocyanide ligands in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNCH_3)_3$. The cyclopentadienyl rings have been omitted for clarity.

(11) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 74, 961 (1970).

A and B refer to the syn (1 or 3) and anti isomers, respectively. The coalescence temperature was taken as −80°.

Since there are two bridging isocyanide ligands with nitrogen inversions occurring on each, we considered the possibility that the rearrangement on one ligand might be correlated to the rearrangement on the second ligand. The effect might be such that a concerted motion, simultaneously inverting the configurations on both bridging ligands, would have a lower activation barrier than an uncorrelated motion, wherein the nitrogens on each bridging ligand invert independently. Evidence for such an effect is potentially available from the data at hand. If the concerted rearrangement occurred significantly faster than the independent rearrangement, the two bridging methyl isocyanide resonances from the anti isomer would average to a singlet before coalescing with the resonance from the syn isomer. Since this is obviously not observed in the spectra, it is concluded that the predominant mode of rearrangement occurs *via* independent inversions on the two nitrogen atoms. Owing to the quality of the spectra, however, the possibility that a concerted mechanism might be operative to a small extent cannot be ruled out.

$[(\eta^5\text{-}C_5H_5)Fe(CO)CNCH_3]_2$, 2. It has been shown[6] that this molecule exists in solution as a mixture of two isomers: a cis form having two bridging isocyanide ligands and two terminal carbonyl groups (isomer A, Figure 3) and a trans form having one bridging and one terminal isocyanide ligand and one bridging and one terminal carbonyl group (isomer B, Figure 3). In view of the results described above, it was decided to investigate this compound further in hope of obtaining additional evidence for nitrogen inversion rearrangements in the bridging isocyanide ligands. The pmr spectra at several temperatures in CS_2 solvent are shown in Figure 4. In the −45° spectrum the smaller sharp cyclopentadienyl resonance at τ 5.38 and the smaller sharp bridging methyl isocyanide resonance at τ 6.47 can be assigned to isomer A. The pair of sharp cyclopentadienyl resonances at τ 5.49 and 5.63 and the sharp pair of methyl isocyanide resonances at τ 6.43 (bridging ligand) and 7.33 (terminal ligand) can be assigned to isomer B. At −85° the cyclopentadienyl and bridging methyl isocyanide resonances from isomer B show significant broadening. Between −87° and −90° a broad peak forms between the two cyclopentadienyl resonances, and a small, broad peak forms on the low-field side of the bridging methyl isocyanide resonance. In addition, the cyclopentadienyl resonance from isomer A is beginning to broaden. In this solvent the equilibrium between geometric isomers A and B lies largely in favor of B at these low temperatures. At −100° a small broad singlet at τ 5.58 has formed between the pair of equally intense cyclopentadienyl resonances of isomer B. These resonances are once again sharp, and the bridging methyl isocyanide resonance has re-formed as a small singlet at τ 6.42 and a large singlet at τ 6.50. The cyclopentadienyl resonance from isomer A is small and broad and the bridging methyl isocyanide resonance seems to be slightly broadened.

The spectral changes in isomer B can be attributed to a slowing of the rate of interconversion of two isomers which differ in the orientation of the methyl group on the single bridging isocyanide ligand. Since each isomer of this type should show two cyclopentadienyl resonances, we must assume that the newly formed broad singlet is actually an unresolved composite of two closely spaced singlets. Since chemical shifts are known to depend on the solvent medium, especially when the molecule forms a solvated complex,[12] we anticipated that slight changes in the solvent might cause

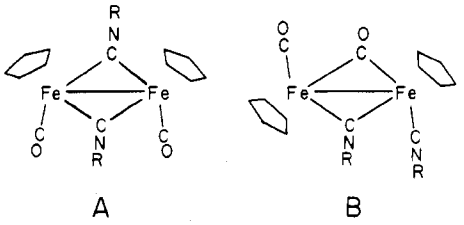


Figure 3. The two isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ which exist in equilibrium in solution. The bridging CH_3NC ligands are deliberately drawn so as not to show any particular orientation.

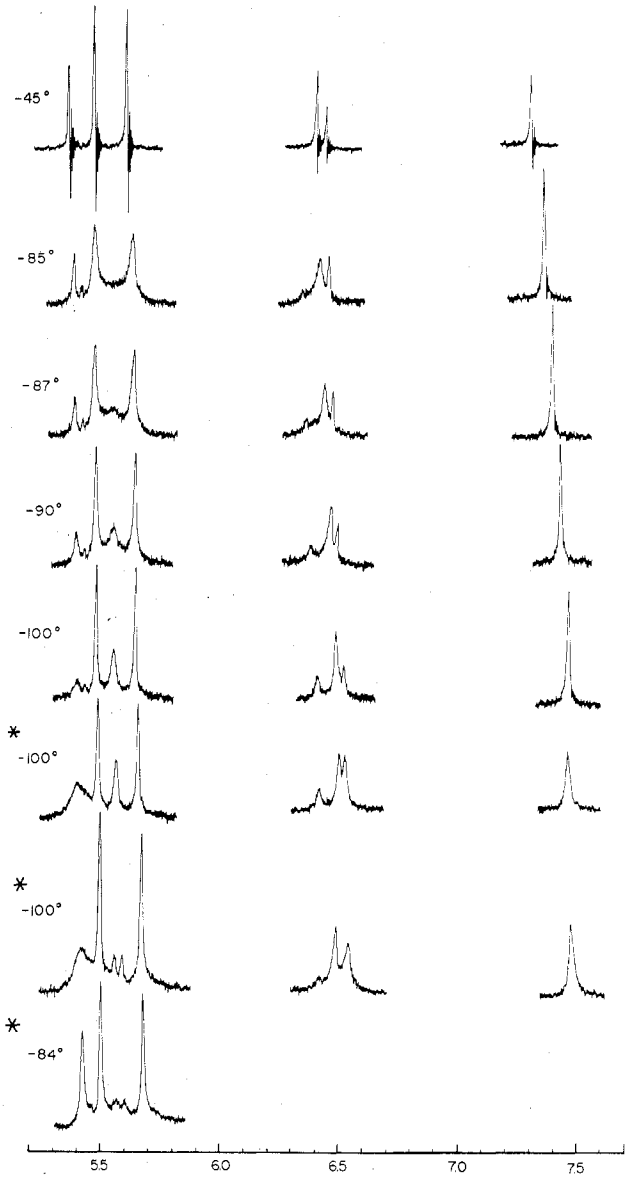


Figure 4. Pmr spectra in the low-temperature range for $[(\eta^5\text{-}C_5H_5)Fe(CO)CNCH_3]_2$ in CS_2 solvent. The lower three spectra, marked with an asterisk, were taken on a room-temperature sample placed in a precooled nmr probe. The lower two spectra were taken in 10% $CDCl_3$–CS_2 solvent.

a separation of two overlapping signals. The second spectrum from the bottom in Figure 4 was recorded on a sample dissolved in a solvent mixture $CDCl_3$–CS_2 (10:90 by volume), and two small peaks lying between the two large peaks now are resolved, the isomer equilibrium is also affected, and an

(12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 104.

appropriate change in the relative intensities of the bridging methyl isocyanide resonances also occurs. When the sample is slightly warmed (the bottom spectrum), the small resonances collapse, as expected.

There are other interesting features to be seen in the lower three spectra in Figure 4. A sample which has come to equilibrium at room temperature contains a relatively large concentration of isomer A, compared to the equilibrium proportion at lower temperatures. Moreover, when a sample at equilibrium at 25° is rapidly cooled to −100°, the low-temperature equilibrium distribution is only very slowly established. To obtain the spectrum third from the bottom, a sample at 25° was placed directly in a probe precooled to −100°. Interestingly, the cyclopentadienyl resonance from isomer A is very broad. Addition of $CDCl_3$ slightly shifts the bridging methyl isocyanide resonances and we can now clearly see that the bridging methyl isocyanide resonance of isomer A, τ 6.53, is substantially broadened. However, the solvent change does not affect the shape of the cyclopentadienyl resonance from isomer A. With warming (bottom spectrum) this cyclopentadienyl resonance changes to a relatively sharp singlet. Instrumental limitations prevented us from obtaining spectra at lower temperatures, but it seems quite plausible that the pronounced broadening of the resonances in isomer A is also due to the slowing of inversions at the nitrogen atoms. This molecule, with two bridging isocyanide ligands and two terminal carbonyl groups, can obviously exist as syn and anti forms similar to those shown in Figure 2 for compound **1**.

Line shape calculations pertaining to the spectral changes which occur in isomer B yielded spectra very similar to the observed spectra. However, an Arrhenius plot of the rates at the respective temperatures produced an exceptionally high frequency factor. Sources of this error lie predominantly in the small temperature range (25°) of the exchange region. This greatly limited the number of different spectra which could be recorded. In addition, it seems that the temperature assignments could be highly susceptible to error, and at these low temperatures this could greatly affect the energy parameters. Furthermore, the shift positions and natural line widths of the two resonances which constitute the broad singlet at τ 5.58 can be only tentatively assigned. Therefore, to obtain useful results we have bypassed the complete analysis and once again employed the equation.[11] Assuming the coalescence temperature to be −85°, we calculate $\Delta G_A^{\ddagger}$ to be 11.0 ± 1.0 kcal/mol and $\Delta G_B^{\ddagger}$ to be 9.8 ± 1.0 kcal/mol, where A and B refer to the more and less populated isomers, respectively.

An additional comment on the spectral changes observed in isomer B is in order. If there are two isomers as proposed, there should also be two terminal methyl isocyanide resonances. At all temperatures, the terminal methyl isocyanide resonance is a relatively sharp singlet. The chemical shifts for these resonances must be nearly identical for both isomers. This is not intuitively unreasonable since the methyl group on the terminal isocyanide ligand is remote from the isomerization center, and its magnetic shielding might be insensitive to the positioning of the methyl group on the bridging ligand. This idea is supported by the observation that terminal methyl isocyanide resonances in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNCH_3)_3$ varied only slightly from one isomer to another.

Discussion

Nitrogen inversion isomerizations in imines are a thoroughly investigated phenomenon,[4] but the barriers to nitrogen inversions in *N*-alkylimines are so high as to be generally inaccessible to study by dynamic nmr methods.[4,8] The corresponding *N*-arylimines have substantially lower barriers and have been extensively studied through the variable-temperature nmr technique.

Two distinct mechanisms have been proposed to explain the rearrangement. The bond rotation mechanism involves weakening of the CN double bond, through either a homolytic type rupture or bond polarization, followed by rotation around the CN bond. The inversion mechanism entails a simple, direct inversion at the nitrogen atom, whereby a linear transition state is traversed. In a very clever experiment, Kessler and Liebfritz[13] have recently shown that in *N*-arylguanidines the inversion mechanism is the overwhelmingly favored process.

The very short CN bond distances in bridging isocyanide ligands[14] indicate these bonds possess a high degree of triple-bond character. Thus, passage through a linear transition state seems energetically quite reasonable. Conversely, weakening of the multiple bond toward a single bond, sufficient to allow the bond rotation mechanism, seems highly unlikely. We think that there can be but little doubt that the rearrangement mechanism in bridging isocyanides is one of inversion at the nitrogen atom with a linear transition state.[15] Furthermore, it is by virtue of the high multiple-bond order that these arrangements are so facile, with $G^{\ddagger} \approx 10$ kcal, whereas in the corresponding *N*-alkylimines $E_a > 25$ kcal.[16]

Reversal of configuration in bridging isocyanide ligands is an essential step in the overall rearrangement mechanism whereby a terminal isocyanide ligand passes from one metal atom to another *via* a bridged intermediate. We shall now discuss the details of this mechanism. Figure 5 shows the possible rearrangement steps by which a terminal isocyanide ligand can be intramolecularly exchanged between two metal atoms. The first step involves shifting the terminal ligand into the bridging position. This can occur by two processes. In process 1, the bridging ligand is so positioned that the alkyl group is oriented syn to the metal to which it was originally terminally coordinated. In process 1′, it is positioned anti to the metal to which it was originally terminally coordinated. Next, the bridging ligand must invert at the nitrogen atom. Finally, the ligand must shift to a terminal position on the second metal atom. In this last step, it is important to note that the shift from bridging to terminal coordination must be identical in character with the step in which it shifted into the bridging position. If the ligand shifts to the bridging position by process 1, it must return to a terminal position by a process similar to 1. This follows from the principle of microscopic reversibility.[17] The question, then, is by which of the two processes, 1 or 1′, does the ligand shift into the bridging position. We can see no way, at present, to determine which of these paths is the actual one.

Although the nitrogen inversion rearrangement is an essential component of the bridge–terminal exchange mechanism,

(13) H. Kessler and D. Liebfritz, *Chem. Ber.*, 104, 2143 (1971).

(14) The mean distance in $(\eta^5\text{-}C_5H_5)_2Ni_2(CNCH_3)_2$ is 1.194 (5) Å; that in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CNCH_3)_2$ is 1.221 (8) Å.

(15) Another mechanism, which might be considered, is a 180° rotation of the entire isocyanide ligand around the C=N axis. Although this cannot easily be given a detailed electronic formulation within the formalized bonding description, the details of bonding in bridging carbonyl type ligands are not clearly understood, and this mechanism cannot necessarily be dismissed with the data at hand.

(16) D. Y. Curtin, and J. W. Hausser, *J. Amer. Chem. Soc.*, 83, 3474 (1961).

(17) T. L. Brown, *Inorg. Chem.*, 7, 2673 (1968).

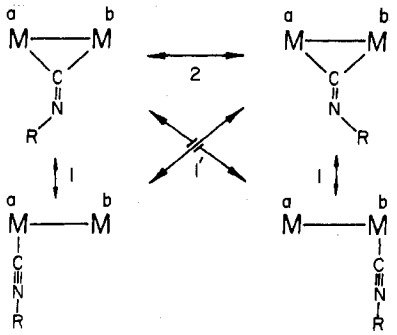


Figure 5. A schematic representation of the mechanism through which a terminal isocyanide ligand exchanges coordination sites between two metal atoms.

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*-$(\eta^5$-$C_5H_5)_2Fe_2(CO)_3(\mu$-$CNCH_3)$ 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, $\pm 3°$, 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 $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$.

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).

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

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

F. A. COTTON* and B. A. FRENZ

Received June 12, 1973

One of the two tautomers postulated to be present in a solution of $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ 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*-$(\eta^5$-$C_5H_5)_2Fe_2(CO)_4$, 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 $(\eta^5$-$C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$ while $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CNCH_3)_2$ 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 $I_o > 3\sigma(I_o)$ 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 $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ 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).