

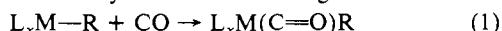
Stereochemistry at Iron during Carbonyl "Insertion" Reactions of $\text{FeMeI}(\text{CO})_2(\text{PMe}_3)_2$

Steven C. Wright and Michael C. Baird*

Contribution from the Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6.
Received April 26, 1985

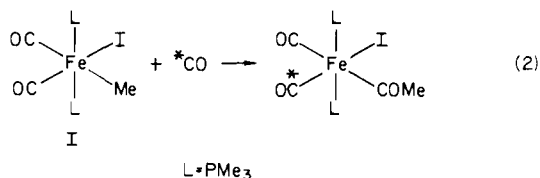
Abstract: Reaction of $\text{FeMeI}(\text{CO})_2(\text{PMe}_3)_2$ (I) with carbon monoxide at 250 K gives *cis*- $\text{Fe}(\text{MeCO})\text{I}(\text{CO})_2(\text{PMe}_3)_2$ (II), which in turn isomerizes at room temperature to give *trans*- $\text{Fe}(\text{MeCO})\text{I}(\text{CO})_2(\text{PMe}_3)_2$ (III). Reactions of I with ^{13}C -enriched (91.7%) carbon monoxide in CD_2Cl_2 were monitored at 250 K by using ^{13}C NMR spectroscopy (100.6 MHz), and selective enrichment was observed for both I and II. The sites of enrichment were identified for both compounds and were found to be compatible only with a mechanism involving (a) formal methyl migration and (b) a square-pyramidal intermediate. Restricted rotation of the acetyl group of III about the iron acetyl was also observed; an unexpectedly high free energy of activation for rotation of the acetyl group past the trimethylphosphine was calculated.

Carbonylation of alkyl-metal compounds, involving "insertion" of carbon monoxide into a metal-carbon σ bond (eq 1), is one of the most important and most extensively studied reactions of organometallic chemistry.^{1,2} Several investigations have dem-



onstrated that the reaction proceeds with retention of configuration at the migrating carbon atom,³ and there is currently considerable interest in obtaining relevant, complementary stereochemical data for metal centers. Early work, in which the stereochemical course of the reversible carbonylation of $\text{MeMn}(\text{CO})_5$ with ^{13}CO was followed by using IR spectroscopy, showed that the reaction of this compound, at least, proceeds via migration of the methyl group to a CO-coordinated to a *cis* site, i.e., involves a migratory insertion process. This result has been very recently confirmed by Flood et al., who utilized ^{13}C NMR spectroscopy to demonstrate that the ligand-induced "insertion" reaction of *cis*- $\text{MeMn}(\text{CO})_4$ (^{13}CO) must involve methyl migration proceeding through a square-pyramidal intermediate with a basal acetyl group.⁵ The migratory insertion mechanism was also shown to be consistent with the stereochemical change at iron accompanying photochemical decarbonylation of the chiral (at metal) compound $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COEt}$,⁶ and this mechanism was undoubtedly generally regarded by 1982 as being widely and even exclusively applicable to such reactions.

More recently, however, both Flood⁷ and Brunner⁸ have shown that ligand-induced carbonylation reactions of compounds of the type $\text{CpFe}(\text{CO})(\text{L})\text{R}$ can formally involve both alkyl and CO migration, the course of reaction depending on the nature of the solvent and the presence of Lewis acid catalysts. In a complementary study, Pańkowski and Bigorgne⁹ have reported that carbonylation of *cis*- $\text{FeMeI}(\text{CO})_2(\text{PMe}_3)_2$ (I) with ^{13}CO at 243 K proceeds as in eq 2. Again formal CO rather than formal alkyl migration seems implied.



The latter investigation, however, utilized only IR spectroscopy to identify the stereochemistry of the product, and the inability of this technique to distinguish the acetyl isomer shown in eq 2 from its isotopomer with the label *trans* to the acetyl group was not recognized.¹⁰ In view of the importance of such findings, we have investigated and report herein the carbonylation of I by utilizing ^{13}C NMR spectroscopy. During the course of our work, Cardaci et al.¹¹ reported the results of a similar, very elegant study of the carbonylation of the cyano and isothiocyanato analogues of I, demonstrating that there is, in fact, no evidence for formal CO migration (CO insertion) for these compounds. By implication, it would seem that the iodo compound I should behave similarly, but its carbonylation reactions were not studied in detail. Utilizing low-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, however, we have been able to investigate the still controversial iodo system more extensively than did Cardaci, finding that the carbonylation reactions of the iodo compound are similar to those of its cyano analogue. We have also obtained firm evidence that the reaction of eq 2 involves alkyl migration, a point left ambiguous by Cardaci's results.

Experimental Section

All reactions were carried out under nitrogen by using deoxygenated solvents which had been distilled prior to use: methylene chloride from P_2O_5 , *n*-hexane from sodium ribbon, and methanol from magnesium methoxide. Iron pentacarbonyl, iron nonacarbonyl, and trimethylphosphine were purchased from Strem Chemicals, methylene- d_2 chloride and ^{13}C -enriched (91.7%) carbon monoxide from MSD Isotopes.

Tricarbonylbis(trimethylphosphine)iron(0), $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$, was initially prepared as described in the literature¹² but was found to be contaminated with up to 75% of the monophosphine compound, $\text{Fe}(\text{CO})_4(\text{PMe}_3)$. A better route was therefore developed, involving reaction of a 3:1 molar ratio of trimethylphosphine with tricarbonyl(benzylideneacetone)iron(0)¹³ in tetrahydrofuran at 60 °C. Gram scale reactions were complete in 1-2 h; removal of the solvent under reduced pressure and recrystallization of the crude product from ethyl ether yielded pure $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ in 70-85% yield.

Dicarbonyliodomethylbis(trimethylphosphine)iron(II) ($\text{FeMeI}(\text{CO})_2(\text{PMe}_3)_2$, I) was prepared via a modification of the procedure described in the literature.¹² $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ (5 g) in 30 mL of methyl iodide was stirred at room temperature for 4 h. Unreacted methyl iodide was then removed under reduced pressure, and the solid residue was refluxed in *n*-hexane for 2 h. The resulting deep red crystalline product (70-80% yield) was recrystallized from ethyl ether, collected by filtration and dried; its spectroscopic properties showed that it was pure I.

^1H NMR spectra were run on Bruker HX 60 and AM 400 NMR spectrometers and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at 100.6 MHz on the latter instrument. IR spectra were run on a Bruker IFS 85 FTIR spectrometer.

- (1) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.
- (2) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.
- (3) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.
- (4) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.
- (5) Flood, T. C.; Jensen, J. E.; Stalder, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.
- (6) Davison, A.; Martinez, N. *J. Organomet. Chem.* **1974**, *74*, C17.
- (7) (a) Flood, T. C.; Campbell, K. D.; Downs, H. H.; Nakanishi, S. *Organometallics* **1983**, *2*, 1590. (b) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853.
- (8) Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595.
- (9) Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1983**, *251*, 333.

- (10) The rationale is presented clearly and succinctly in ref 11.
- (11) Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936.
- (12) Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227.
- (13) Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Organomet. Chem.* **1972**, *39*, 329.

Table I. $^{13}\text{C}\{^1\text{H}\}$ NMR Data

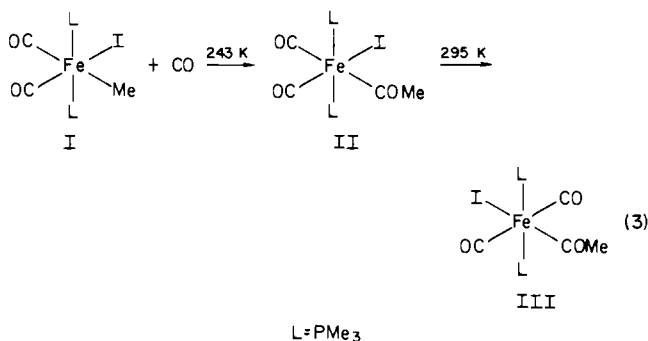
No.	Compound	$\delta_{\text{A}}(^2J_{\text{P-C}})$	$\delta_{\text{B}}(^2J_{\text{P-C}})$	$\delta_{\text{COMe}}(^2J_{\text{P-C}})$	$\delta_{\text{Me}}(^2J_{\text{P-C}})$	$J_{\text{A-B}}$	$J_{\text{A-COMe}}$	$J_{\text{B-COMe}}$	Ref.
1		204.7(15.7)	209.6(25.4)	—	NA ^a	4.8	—	—	10
2		207.3(18.4)	213.3(27.3)	—	-7.8(16.6)	NA ^a	—	—	16
3		208.0(15.6)	219.3(25.6)	—	-4.2(19.1)	NA ^a	—	—	This work
4		207.6(11.4)	216.3(25.4)	271.5(24.8)	48.8	NA ^a	15.3	NA ^a	This work
5		208.2(13)	213.3(26.7)	272.7(23.5)	NA ^a	7	15.5	8.9	10
6		209.0(11)	211.4(20)	272.9(22)	NA ^a	6	11	6	10

^a Not available.

The solvents used for spectroscopic measurements were CH_2Cl_2 or CD_2Cl_2 , as appropriate.

Results and Discussion

Stereochemistry of Carbonylation. Compound I is reported to react with CO (1 atm) in hexane and methylene chloride at 243 K to form *cis*- $\text{Fe}(\text{COMe})\text{I}(\text{CO})_2(\text{PMe}_3)_2$ ^{9,11} (II), which in turn converts to the *trans* isomer (III) at room temperature (eq 3).



Initial experiments designed to search for possible intermediates and to determine the relative rates of each step of eq 3 were therefore carried out by treating I with unenriched CO in CD_2Cl_2 at 225–270 K. Consistent with the literature, I was converted smoothly and cleanly to II at 250 K and then to III on warming to room temperature. The isomerization of II to III was complete within a few minutes in the presence of free carbon monoxide but took 12–15 min in the absence of free carbon monoxide. This type of behavior has been noted previously by Pańkowski and Bigorgne,⁹ who proposed as an intermediate the cationic $[\text{Fe}(\text{COMe})(\text{CO})_3(\text{PMe}_3)_2]^+$. Compounds II and III were identified on the basis of comparisons of their IR, ^1H NMR, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with data from the literature.^{9,11,12} Pertinent $^{13}\text{C}\{^1\text{H}\}$ NMR data are presented in Table I, and a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showing the carbonyl and trimethylphosphine resonances of an approximately 1:1 mixture of I and II is illustrated in Figure 1a.

On treatment of I with a deficiency of CO enriched in ^{13}C (91.7%) at 250 K, several unexpected observations were made (Figure 1b). As is shown, initial exposure of I to ^{13}C resulted in extensive enhancements of the resonances at 271.5 ppm (acetyl resonance of II), at 219.3 ppm (the downfield carbonyl resonance

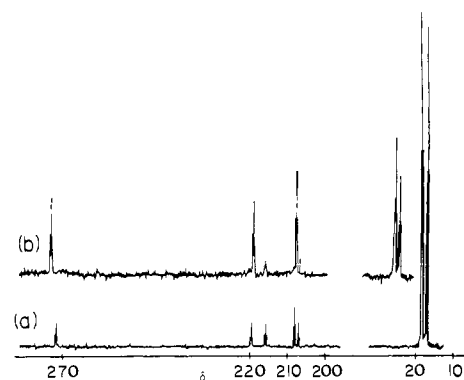


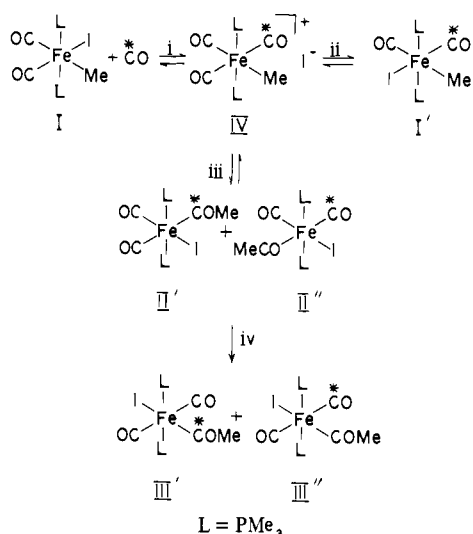
Figure 1. (a) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (natural abundance) of an approximately 1:1 mixture of I and II; (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of I treated with enriched CO at 270 K. (Note that the trimethylphosphine methyl resonances of (b) are offset to avoid overlap with the corresponding resonances of (a).)

of I), and at about 208 ppm (the upfield carbonyl resonance(s) of I and/or II).¹⁴ On warming to room temperature, II converted to III, and as the intense resonance at about 208 ppm disappeared, it follows that enrichment had occurred at the high-field resonance of II. There was essentially no enrichment of the downfield resonance of II (216.3 ppm), and only relatively slow enrichment of the upfield resonance of I (208.0 ppm). These results present interesting contrasts both with the results of Cardaci et al.¹¹ for the cyano system in methylene chloride and with observations^{9,11} that I initially undergoes only monolabeling at a terminal carbonyl site after treatment with enriched carbon monoxide in hexane. The latter difference can be rationalized on the basis of solvent effects (see below).

By working at low temperature and with a deficiency of enriched carbon monoxide, we have undoubtedly observed in situ the products of kinetic control. In order to understand the

(14) The degrees of enhancement of the carbonyl carbon resonances were assessed qualitatively by monitoring the changes in intensities of the carbonyl resonances relative to the intensities of the phosphine methyl resonances at 18.6 ppm (II) and 17.1 ppm (I). The procedure is very approximate, as the relaxation times and nuclear Overhauser enhancements may vary considerably, but the results were reasonably consistent over several runs. See Figure 1.

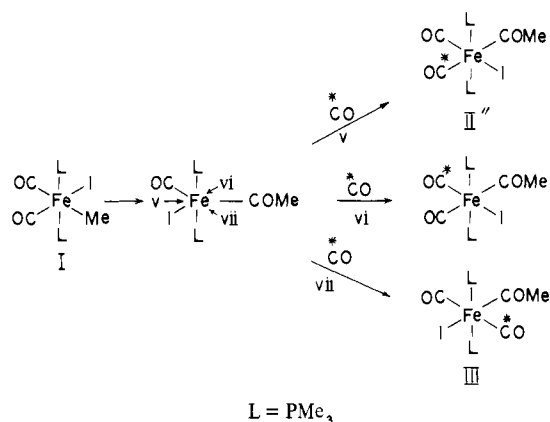
Scheme I



mechanism of the carbonylation process, however, it is necessary to identify the sites of enrichment of I and II. This was accomplished in two ways, the first of which assumes that trans influences are more important than are cis influences in determining the carbonyl chemical shifts and coupling constants.¹⁵ In Table I, we present pertinent data for a series of similar compounds. In the case of entry 1, the relative intensities of the carbonyl resonances leave no ambiguity concerning the assignments,¹¹ and it is clear that the high-field resonance (A) is to be assigned to the CO trans to the methyl group. Comparison of entries 1–3, in which the sole variable is the ligand cis to methyl, reveals a set of high-field carbonyl resonances (A) whose chemical shifts vary only 3.3 ppm and a lower field set of resonances (B) whose chemical shifts vary 9.7 ppm. Assuming a dominance of ligand trans influence on chemical shifts,^{15–18} the latter series of resonances, which vary relatively greatly, must be assigned to the carbonyl groups trans to the variable ligand. We note then that the resonances of the carbonyls trans to methyl exhibit the smaller values of $^2J(\text{C}-\text{P})$, as anticipated on the basis of relative positions in the trans influence series (alkyl, acyl > tertiary phosphine > CO).¹⁸ Furthermore, as the acetyl group also lies high in the trans influence series,¹⁸ entries 4–6 may also be considered as part of the above-mentioned series, and the resonances may be assigned as indicated. We note, finally, that trans carbon–carbon coupling constants (11–15.5 Hz) are considerably larger on average than are the corresponding cis coupling constants (5–9 Hz), as is also generally true for two-bond phosphorus–phosphorus coupling constants.¹⁹

In an effort to confirm the chemical shift assignments of I, attempts were made to measure nuclear Overhauser enhancements of the two carbonyl resonances during irradiation of the methyl proton resonance. As the magnitude of the NOE is proportional to r^{-6} , where r is the carbon–hydrogen internuclear distance,²⁰ the effect should be more pronounced for the carbonyl group cis to the methyl group. The experiments were not as definitive as we had anticipated, although selective irradiation of the methyl proton resonance of I did appear to cause an increase only in the peak height of the downfield carbonyl resonance. Unfortunately the signal-to-noise level was such that we cannot say with certainty

Scheme II



that the increase in peak height was significant. However the approach does have merit and gives a result which is compatible with the trans influence arguments, and we have confidence in the assignments proposed above.

Interestingly, the correlations of carbon chemical shifts and phosphorus–carbon coupling constants presented here appear to apply equally well to an analogous ruthenium system containing dimethylphenylphosphine.²¹

Mechanism of Carbonylation. The overall pattern of ^{13}C O enrichment of I and II in methylene chloride (and the routes by which we shall argue the observed specific labeling occurs) is as in Scheme I; it is clear that the labeling results reported here are quite different from those reported for the same reaction in *n*-hexane. Thus, both Pańkowski and Bigorgne⁹ and Cardaci et al.¹¹ noted only monolabeling of II in *n*-hexane at low temperatures; the latter group also reported total labeling of II after several hours of reaction. Interestingly, the cyano analogue of I, $\text{FeMeCN}(\text{CO})_2(\text{PMe}_3)_2$, was found to react sufficiently slowly in methylene chloride at room temperature that stepwise labeling of the acetyl analogue at the terminal carbonyl site trans to the acetyl group, as in II'', could be detected. In contrast to the iodo system, no labeling appeared in the acetyl position although subsequent labeling did appear in the carbonyl cis to the acetyl group. The isothiocyanato analogue behaved similarly, but in this case, prolonged exposure led to all sites being labeled. Thus, both compounds exhibit behavior which is quite different from that observed here for I.

Our observations seem best interpreted in terms of the sequence of steps outlined in Scheme I. Substitution of iodide by ^{13}C O would yield IV, a complex which was not detected but which has been reported elsewhere (unenriched).^{11,22,23} It is reasonable to suppose that the substitution would be reversible, thus leading to unlabeled I (route i) or to I' (route ii), as is observed. Unenriched intermediate IV is known^{11,22} to react reversibly with iodide to give II (unenriched). In our system, IV would be expected to give a 1:1 mixture of II' and II'' if the reactions involve methyl migration but *not if they involve CO migration*. If the latter occurred, the label of II'' would appear in the CO site cis to the acetyl group, and thus our results are in accord with the alkyl migration mechanism and rule out the formal CO migration (insertion) mechanism.

The pattern of enrichment of I', II', and II'' also appears to be inconsistent with the mechanism proposed by Cardaci,¹¹ which involves trigonal-bipyramidal intermediates, as in Scheme II. Here I would generate the five-coordinate intermediate V, which could in principle preferentially accept ^{13}C O along path v rather

(15) This argument is utilized by Cardaci¹¹ and is generally consistent with data in the literature. See, for instance, ref 16 and 17.

(16) Jablonski, C. R.; Wang, Y.-P. *Inorg. Chem.* **1982**, *21*, 4037.

(17) Pańkowski, M.; Chodkiewicz, W.; Simonnin, M.-P. *Inorg. Chem.* **1985**, *24*, 533.

(18) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(19) Pregosin, P. ^{31}P and ^{13}C NMR of Transition Metal Complexes"; Springer-Verlag: New York, 1979.

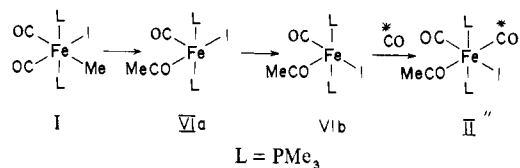
(20) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.

(21) Bernard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331. Professor Mawby informs us (private communication) of an error in Table 4 of this paper. The chemical shift of the carbonyl carbon with the 8.0-Hz coupling to phosphorus should be 190.8 ppm.

(22) Reichenbach, G.; Cardaci, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1982**, 847.

(23) Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2593.

Scheme III



than vi or vii, resulting in enrichment in the site trans to the acetyl group. While a species such as V appears to rationalize the pattern of labeling observed for the cyano system, however, it does not explain the simultaneous formation of II' and II'' in the iodo system in methylene chloride. The intermediacy of V also does not rationalize the introduction of label into I', and thus involvement of a trigonal-pyramidal species such as V must be rejected for the iodo system. Similar conclusions have been reached for the isoelectronic manganese system⁵, and have been justified theoretically.²⁴

A mechanism different from that of Scheme I may well apply for carbonylation of both I in the nonpolar solvent *n*-hexane at low temperatures and of the cyano analogue in methylene chloride at room temperature.^{9,11} Labeling at the acetyl carbonyl site does not appear to occur in either case in the initial stages of the reactions, and anion dissociation must therefore not occur prior to combination of the methyl and carbonyl ligands within the inner coordination spheres.²⁵ These reactions presumably proceed as in Scheme III, much as suggested by Cardaci¹¹ except that we favor square-pyramidal intermediates in order to be consistent with our findings presented above. The hypothesized rapid isomerization of VIa to VIb would be reasonable in view of the high trans influence of the acetyl group.¹⁸ We note also that the isoelectronic rhodium compound RhCl₂(MeCO)(PPh₃)₂ has an analogous structure.²⁷

(24) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(25) Iodide would be a relatively poor leaving group in the hydrocarbon solvent, and cyanide generally coordinates relatively strongly to transition-metal ions and thus would be a very poor leaving group.²⁶

(26) No obviously relevant equilibrium data are known to us, but stability constants for formation of cyano complexes of transition metals are generally larger than those of halo complexes. See: Martell, A. E.; Sillen, L. G. "Stability Constants"; 25, Chemical Society: London, 1964, 1971; Special Publications No. 17 and 25.

(27) Egglestone, D. L.; Lock, C. J. L.; Turner, G.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1977**, 1576.

Our results and interpretations appear to be largely consistent with the results of Mawby et al. for the chemistry of the analogous ruthenium system with dimethylphenylphosphine.²¹ Although detailed comparisons are clearly not justified, it seems likely that trigonal-bipyramidal intermediates need not be postulated here either.

Restricted Rotation of the Acetyl Group in III. While carrying out the low-temperature NMR experiments discussed above, we noted variations of the line width of the resonance of the terminal carbonyl group of III. We therefore carried out with enriched III a more extensive variable-temperature NMR experiment, in which the well-resolved (at room temperature) triplet at 213.4 ppm ($J(\text{P}-\text{C}) = 24.5$ Hz) was found to broaden at lower temperatures and finally split at about 225 K into two well-resolved triplets at 214.8 ppm ($J(\text{P}-\text{C}) = 23$ Hz) and 210.7 ppm ($J(\text{P}-\text{C}) = 26$ Hz). These results are clearly to be interpreted in terms of restricted rotation of the acetyl group about the iron-carbon bond, and as the two terminal carbonyl groups become non-equivalent at low temperature, the low-energy structure undoubtedly has the plane of the acetyl group lying in the FeI(CO)₂ plane. The coalescence temperature was found to be about 260 K, giving $\Delta G^\ddagger = 11.5 \pm 1.0$ kcal/mol²⁸ for eclipsing of the acyl group with the trimethylphosphines. This is considerably higher than barriers to rotation about the metal-acyl bonds of compounds of the type CFH₂COCo(CO)₃PPh₃²⁹ and CpFe(CO)(PPh₃)(COMe)³⁰ in which the barriers to acyl rotation are sufficiently low that different rotamers can be detected by IR but not by NMR spectroscopy. Somewhat higher barriers have been reported for rotation of aryl groups in the compounds $\eta^5\text{-C}_5\text{Me}_5\text{RhX(aryl)-PMe}_3$, but here the $\eta^5\text{-C}_5\text{Me}_5$ ligand undoubtedly contributes significantly to the barrier.³¹

Acknowledgment. Financial support from the Natural Sciences and Engineering Council of Canada (Operating Grant to M.C.B.) and Queen's University (scholarship to S.C.W.) made this research possible. We also thank D. Brandes for carrying out some of the preliminary experiments.

Registry No. I, 33542-07-3; II, 78306-61-3; III, 33542-06-2; Fe(CO)₃(PMe₃)₂, 25921-55-5; CO, 630-08-0; ¹³CO, 1641-69-6; tri-carbonyl(benzylideneacetone)iron, 53861-80-6; methyl iodide, 74-88-4.

(28) Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71.

(29) Lindner, E.; Zipper, M. *Chem. Ber.* **1974**, *107*, 1444.

(30) Pannell, K. H.; *J. Chem. Soc., Chem. Commun.* **1969**, 1346.

(31) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.

Binucleating Tetrapyrrole Macrocycles

Francis V. Acholla, Fusao Takusagawa, and Kristin Bowman Mertes*

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66045.
Received April 29, 1985

Abstract: Tetrapyrrolic bimetallic macrocyclic complexes have been synthesized in which the two metal ions are incorporated within one macrocyclic ring. The ligand, 4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo[28.2.1.1^{3,6}.1^{14,17}.1^{19,22}]hexatriaconta-1,3,5,7,12,14(35),15,17,19,21,23,28,30(33),31-tetradecane (bi-dptmd), can be obtained by Schiff base condensation of the precursor 5,5'-diformylidipyrromethane with trimethylenediamine. Related ligands can be synthesized by varying the diamine. Lead(II), zinc(II), and copper(II) complexes have been isolated. Copper(II) complexes with BF₄⁻, ClO₄⁻, Cl⁻, N₃⁻, and NCS⁻ as anions were investigated. Electrochemical studies using cyclic voltammetric techniques indicate a ligand-centered irreversible two-electron oxidation wave and two one-electron processes associated with the bicopper center. Crystals of Cu₂(bi-dptmd)(N₃)₂ are monoclinic, space group P2₁/n, with $a = 18.508$ (5) Å, $b = 12.311$ (3) Å, and $c = 20.185$ (6) Å, $\beta = 112.65^\circ$, and $Z = 4$. Refinement resulted in $R = 0.068$ and $R_w = 0.076$. The coordination sphere of each copper ion is distorted trigonal bipyramidal and consists of four ligand nitrogen atoms and a nitrogen from the azide. The ligand has folded so that the two dipyrromethane portions are facing each other, providing a hydrophobic walled-in cavity.

The quest for catalytic systems capable of activating species such as molecular oxygen and nitrogen has led to biomimetic models because of the ease with which certain biomolecules can

accomplish these feats. For example, the porphyrins and porphyrin-related ligands exhibit diverse chemistry, which includes oxygenase and oxidase activity as well as the complex reactions