Notes

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Stereochemical Aspects of Iron Tricarbonyl 1,4-Dimethyltetraazabutadiene and Related Complexes

Curtis E. Johnson and William C. Trogler*

Stereochemical and fluxional properties of $LL'L''Fe(\eta^4\text{-}diene)$ compounds ($LL'L''$ = various combinations of CO and monodentate trivalent phosphorus ligands) continue to be of interest.[1-18] In contrast, only one study has appeared concerning the fluxional behavior of related σ,σ-bonded[19] heterodiene complexes.[20] The X-ray structure of the tetraazabutadiene complex[21] $Fe(CO)_3(N_4Me_2)$ reveals a distorted square-pyramidal (sq py) geometry with the metallacyclic group occupying two basal positions. Tricarbonyl(diene) complexes of iron(0) also adopt a sq py geometry where the diene occupies two basal coordination sties.[22] An understanding of steric congestion in these types of complexes may aid in the interpretation of thermal[23] and photochemical[24] reaction mechanisms. Herein is contained stereochemical information obtained from IR and NMR studies of iron tetraazabutadiene compounds. Activation energy barriers for an intramolecular fluxional process have been determined, and the results are compared with previous studies of $LL'L''Fe(\eta^4\text{-}diene)$ compounds.

Experimental Section

Procedures for the preparation of the complexes studied are the topic of a separate publication.[24] Iron tetraazabutadiene complexes
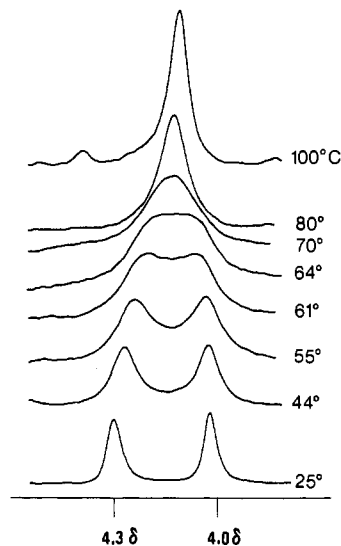
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Figure 1. Temperature dependence of the N-CH_3 resonances in the ^1H NMR spectra of $Fe(CO)(PMe_3)_2(N_4Me_2)$.

were handled by conventional vacuum-line and inert-atmosphere techniques. Samples were prepared in a nitrogen-filled glovebox, and the NMR tubes sealed with rubber septa.

A Varian CFT-20 spectrometer was employed to obtain ^1H (79.54 MHz), ^{13}C (20.0 MHz), and ^{31}P (32.199 MHz) NMR spectra. Free energies of activation at the coalescence temperature, T_c, were calculated by using the Eyring equation[25]

$$\Delta G_c^* = 2.3RT_c(10.32 + \log{(T_c/k_c)})$$

where $k_c = \pi(\Delta\nu)/2^{1/2}$ is the rate constant for the exchange process at coalescence, calculated from the frequency difference ($\Delta\nu$) in the absence of exchange.

IR spectra were recorded on Perkin-Elmer 283 and Nicolet 7199 FT-IR spectrometers in 0.1-mm path length NaCl cells. Relative infrared peak intensities were calculated with the cut and weigh method on expanded spectral traces recorded in the absorption mode. For these measurements, the peak maxima were less than 0.8 absorbance unit. Infrared spectroscopy can provide stereochemical information in the form of metal carbonyl bond angles calculated from integrated intensities of the CO stretching vibrations.[26-28] The angle between two neighboring CO groups (β) was calculated by using eq 1 and 2

$$\alpha = \arctan{(I_{as}/I_s)^{1/2}} \qquad (1)$$

$$\beta = 2\arcsin{(\cos{(90 - 180/n)}\sin{\alpha})} \qquad (2)$$

where α is the angle between the carbonyl groups and the n-fold axis and I_{as} and I_s are the integrated intensities of the asymmetric and symmetric carbonyl stretching vibrations.

Results and Discussion

Our study was prompted by the observation of two N-CH_3 resonances in the ^1H NMR spectrum of $Fe(CO)(PPh_3)_2$-(N_4Me_2) (Ph = C_6H_5). The parent tricarbonyl complex and several $Fe(CO)_2L(N_4Me_2)$ species (L = PMe_3, $P(OMe)_3$, PCy_3, $P(OPh)_3$, and $PMePh_2$, where Cy = c-C_6H_{11}) exhibit only a single N-CH_3 resonance. To test the hypothesis that

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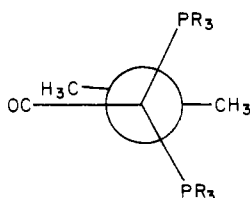(28) Kettle, S. F. A.; Paul, I. *Adv. Organomet. Chem.* **1972**, *10*, 199–236.

Table I. Summary of NMR Spectral Results for $Fe(CO)L_2(N_4Me_2)$ Complexes

ligand	$\delta_H(N\text{-}CH_3)^a$	$\Delta\delta_H$	cone angle, deg^b	T_c, °C^c	$\Delta G_c^{\ddagger}$, kcal/mol
PCy_3	4.22, 3.15	1.07	173		
PPh_3	4.05, 3.11	0.94	159	>90	>17.7
PMe_3	4.39, 4.09	0.30	118	64	17.2 ± 0.8
$P(OMe)_3$	4.25, 4.06	0.19	107	−60	10.9 ± 0.9
CO	3.89	0		<−105	

^{a} Benzene solvent is employed and chemical shifts are relative to external $SiMe_4$ at 35 °C except for L = $P(OMe)_3$; solvent = $THF\text{-}d_8$ and $T = -97$ °C. ^{b} Phosphorus ligand cone angles from: Tolman, C. A. *Chem. Rev.* 1977, 77, 313–348. Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* 1975, 14, 2942–2948. ^{c} Solvents proceeding down the column are C_6D_6, $C_6D_5CD_3$, $C_6D_5CD_3$, $THF\text{-}d_8$, and $THF\text{-}d_8$. For the L = PMe_3 in $C_6D_5CD_3$ $\delta_H(N\text{-}CH_3)$ were 4.30 and 4.03 in the absence of exchange.

the chemical shift nonequivalence might arise from a locked conformation in the disubstituted complexes, we studied the ^1H NMR spectra for several compounds as a function of temperature (Table I). With the smaller PMe_3 ligand the two *N*-methyl signals reversibly coalesce upon heating (Figure 1). With the even smaller trimethyl phosphite ligand, low temperatures were necessary to slow down the exchange process. Both the coalescence temperatures and the magnitude of the *N*-CH$_3$ chemical shift differences parallel the increase in the phosphorus-ligand cone angle[29] (Table I). The *P*-CH$_3$ resonance of $Fe(CO)(PMe_3)_2(N_4Me_2)$ provides evidence for a second-order splitting due to strong spin–spin coupling[30] of the two phosphorus nuclei. This coupling persists at the fast exchange limit, and therefore neither phosphine dissociation nor a bimolecular exchange process can account for the fluxional behavior. Since further substitution does not occur for these complexes in refluxing toluene,[23,24] a mechanism involving CO dissociation may be eliminated. Partial dissociation[31] of the tetraazabutadiene chelate also seems unlikely in view of (1) its instability when uncomplexed, (2) the lack of chemical evidence for Fe–N bond rupture in the thermal reaction mechanisms[23] of these complexes, and (3) the contrary evidence that the most sterically crowded complexes (which would promote Fe–N bond rupture) are the stereochemically most rigid.

In considering the conformation that leads to nonequivalent *N*-CH$_3$ groups, we note that the phosphorus atoms must be chemically indistinguishable on a similar time scale. At −50 °C the L = PCy_3, PPh_3, and PMe_3 complexes exhibit a single ^{31}P NMR resonance at δ 74.8, 68.5, and 23.9, respectively (4:1 THF/C_6D_6 solvent with 85% H_3PO_4 external reference). A static conformation (looking down the C_2 axis of the FeN_4 plane) consistent with these observations

corresponds to a distorted trigonal-bipyramidal structure. This permits a gauche disposition of bulky L and eclipses the small CO ligand with the FeN_4 plane. Alternatively a fast rocking motion may occur between two distorted sq py conformations:

Table II. Iron Carbonyl Bond Angles (β) from Infrared Intensities^a of the C–O Stretching Frequencies in $Fe(CO)_2L(N_4Me_2)$ Complexes

ligand	I_{as}/I_s	ν_{CO}, cm^{-1}	β, deg
CO	2.58	2068, 1995	95
$P(OMe)_3$	0.91	2009, 1952	87
PMe_3	0.93	1989, 1933	88
PPh_3	0.84	1988, 1935	85
PCy_3	0.93	1980, 1924	88

^{a} See text for discussion; in cyclohexane solvent.

Given the preference for sq py geometry in related $Fe(CO)L_2(\eta^4\text{-diene})$ complexes[1,4,7,9] (which exhibit facile exchange of apical and basal L), rapid rocking between the two isomers may be more likely.

Monosubstituted complexes show no signs of a conformational dependence upon steric properties. In this case NMR does not provide useful information, as the expected[32] sq py isomer with apical L does not yield an NMR nonequivalence. Fortunately, OC–Fe–CO bond angles, β, can be determined from the ratio of intensities of the symmetric and antisymmetric CO stretching vibrations[26-28] (Table II). For example, the 95° calculated for $Fe(CO)_3(N_4Me_2)$ agrees well with that (96°) derived in a single-crystal X-ray diffraction study.[21] Monosubstituted complexes exhibit β values of 85–88°, which show no dependence on the size of the phosphorus donor ligand. Steric effects do not appear to be as significant in the monosubstituted complexes. The decrease in β relative to the tricarbonyl complex must then be attributed to an electronic effect.[8]

We have also studied $Fe(CO)_3(N_4Me_2)$ and $Fe[P(OMe)_3]_3(N_4Me_2)$ by ^{13}C and ^{31}P NMR methods, respectively. The tricarbonyl complex undergoes fast CO exchange down to −105 °C in $THF\text{-}d_8$. If it is assumed that the ^{13}C chemical shift difference between apical and basal CO ligands is greater than 1 ppm (the difference is 6.8 ppm in $Fe(CO)_3(butadiene)^{12}$), then the free energy of activation for exchange must be less than 8 kcal/mol. Similarly, for $Fe[P(OMe)_3]_3(N_4Me_2)$ (studied by ^{31}P NMR to −85 °C in THF/C_6D_6) the barrier is less than 9 kcal/mol if one assumes an apical–basal ^{31}P chemical shift difference of at least 2 ppm (it is 22.4 ppm in $Fe[P(OMe)_3]_3(butadiene)^2$). The geometry of the trisubstituted tetraazabutadiene compound is probably distorted sq py, by analogy to the tricarbonyl complex and to known $Fe[P(OMe)_3]_3(\eta^4\text{-diene})$ complexes.[2,10,11] It is curious that the triphosphite derivative appears to possess a lower barrier to exchange than the diphosphite complex. This could occur if steric destabilization of the ground state exceeds that of the transition state for rearrangement. In $Fe(CO)_3(diazabutadiene)$ complexes the exchange was rapid at −80 °C and the barrier reported to be less than 9 kcal/mol.[20] Spectroscopic

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evidence[33-36] also suggests a sq py based structure in these complexes. It was suggested that the low barriers for the σ,σ-bonded diazabutadiene complexes may be related to the local C_{3v} symmetry of the $Fe(CO)_3$ group. The results for σ,σ-bonded tetraazabutadiene complexes, $FeL_3(N_4Me_2)$ (L = CO, $P(OMe)_3$), are also lower than has been found in corresponding diene complexes.[2,12,13]

Steric properties of L do not appear to be chemically significant in $Fe(CO)_2L(N_4Me_2)$ complexes; however, kinetic studies[23] have shown that severe steric crowding may occur in the 6-coordinate transition state that leads to their formation from $Fe(CO)_3(N_4Me_2)$. Ground-state steric effects are evident in the $Fe(CO)L_2(N_4Me_2)$ compounds and may partially account for the reluctance of these species to undergo either thermal[23] (associative) or photochemical[24] (dissociative) replacement of CO. Fluxional properties of these metallacyclic tetraazabutadiene complexes have analogues in the diazabutadiene and diolefin complexes. Available data suggest that the barriers for equilibration of sq py isomers in the metallacyclic systems are less than in the corresponding diolefin complexes.

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Contribution from the Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Molecular Structure of a Mixed-Valence Isopolyvanadate

Avi Bino,* Shmuel Cohen, and Carla Heitner-Wirguin

It is well-known that vanadium in its high oxidation states has a profound tendency to form isopolyions of various types.

Several vanadium(V) polyoxoions have been structurally characterized.[1] Among them few appear as a discrete unit like the decavanadate ion which occurs in salts such as K_2-$Zn_2V_{10}O_{28}\cdot16H_2O$.[2] The $V_{10}O_{28}^{6-}$ unit consists of ten VO_6 octahedra linked together. Recently, $HV_4O_{12}^{3-}$ has been prepared, and an X-ray structural analysis[3] shows that it has a cyclic arrangement of four tetrahedral VO_4 units formed by linking vertices.

One vanadium(IV) polyoxoion has been structurally characterized.[4] In that compound, $Na_{12}V_{18}O_{48}\cdot24H_2O$, the 18 vanadium(IV) atoms are in their usual geometry, i.e., the tetragonal pyramid, forming a rather symmetric sphere by sharing the edges of the VO_5 pyramids.

Mixed-valence vanadium(IV,V) compounds are scarce. One such compound, $K_2V_3O_8$, has been characterized.[5] The structure of that compound consists of infinite layers formed by V^VO_4 tetrahedra and $V^{IV}O_5$ tetragonal pyramids sharing vertices.

We report here the structure of the first mixed-valence isopolyvanadate ion $V_{10}O_{26}^{4-}$, which exists as a discrete entity.

The tetraethylammonium salt of this ion was synthesized by one of us several years ago.[6,7] It was obtained by the hydrolytic dissociation of vanadyl acetylacetonate in methylene chloride or chloroform. The formula $((C_2H_5)_4N)_4(V_{10}O_{28}H_4)$ was proposed for the compound, and it was found that of the ten vanadium atoms, eight were quinquivalent and two were quadrivalent. The results reported here require a revision of the above formula to $((C_2H_5)_4N)_4(V_{10}O_{26})\cdot H_2O$.

Experimental Section

Preparation. Details of preparation of this compound have been described in an earlier study.[6,7] A 3–5-g sample of the compound was dissolved in 100 mL of CH_3CN. The solution was filtered and partially evaporated in a Petri dish at 60 °C. The resulting needlelike, deep violet crystals were collected and washed with dichloromethane.

X-ray Crystallography. A crystal of dimensions $0.1 \times 0.1 \times 0.15$ mm was attached to the end of a glass fiber and mounted on a PW 1100 Philips four-circle computer-controlled diffractometer. Mo $K\alpha$ (λ = 0.710 69 Å) radiation with a graphite-crystal monochromator in the incident beam was used. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1/n$. The unit cell dimensions a = 19.182 (3) Å, b = 22.042 (5) Å, c = 13.856 (2) Å, β = 91.10 (4)°, and V = 5857 (3) Å^3 were obtained by a least-squares fit of 25 reflections in the range $12° < \theta < 16°$. With Z = 4 and a molecular weight of 1464, the calculated density is 1.66 g cm^{-3}.

Data were measured by using a ω–2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with scan time of 20 s. Background measurements were made at both limits of each scan.

A total of 7309 reflections in the range $3° < 2\theta < 45°$ were collected, 3839 of which having $I > 3\sigma(I)$ were used to solve and refine the structure. During data collection, three intensity standards were measured after every hour. No decay was observed. The data were corrected for Lorenz and polarization effects. The linear absorption coefficient is 15.11 cm^{-1}, no absorption correction was applied.

The vanadium atoms were located by using the results of MULTAN[8] direct-method analysis, and all nonhydrogen atoms were located in a series of difference Fourier maps. The structure was refined[9] in space group $P2_1/n$ to convergence by using anisotropic thermal parameters for all vanadium and oxygen atoms in the $V_{10}O_{26}^{4-}$ ion and isotropic ones for the rest of the atoms. The discrepancy index, R = $\sum||F_o| - |F_c||/\sum|F_o|$, had a final value of 0.092. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The positional parameters of all atoms are listed in Table I. Figure 1 shows the structure of the $V_{10}O_{26}^{4-}$ ion and the atomic numbering scheme used in the tables. The important interatomic distances and angles are listed in Table II. The asymmetric unit contains an entire $V_{10}O_{26}^{4-}$ ion; hence, there is no crystallographic symmetry imposed on this ion. However, the complex nearly possesses S_8 symmetry. The $(C_2H_5)_4N^+$ ions are of no particular interest and require no discussion. One $(C_2H_5)_4N^+$ ion was subjected to twofold disorder, but

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