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Iron-57 Mössbauer Study of Iron(II)-Carbene Compounds. Bonding Characteristics of Carbenes

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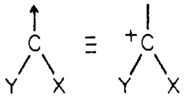
^{57}Fe Mössbauer spectra are reported for a number of six-coordinate iron(II) isocyanide-carbene complexes of the type $[Fe(CNMe)_5(carbene)](PF_6)_2$ and $[Fe(CNMe)_4(carbene)_2](PF_6)_2$. The signs of the ^{57}Fe QS for $[Fe(CNMe)_5[C(NH_2)NHMe]](PF_6)_2$ and $[Fe(CNMe)_4[(CNHMe)_2N_2HPh]](PF_6)_2$ are negative and positive, respectively. The derived partial center shift (pcs) and partial quadrupole splittings (pqs) for carbenes indicate that they are very good σ donors relative to all neutral ligands and poor π acceptors. In particular, our carbenes are better σ donors and worse π acceptors than MeNC. Using the point charge model including distortions, we attempt to explain the larger quadrupole splittings for the compounds containing chelating carbenes, and the unusual quadrupole splittings for "*trans*"- and *cis*-Fe(*o*-phen)$_2$(CN)$_2$ and $K_2[Fe(o\text{-phen})(CN)_4]$.

Introduction

Many recent papers and reviews have discussed the structure and bonding of metal-carbene compounds. The bonding in these compounds is considered to be a hybrid of the structures I-III[1] (where X and Y are heteroatoms such as O or N with nonbonding electrons).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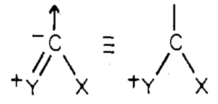
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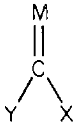

III

Cardin et al.[2] and Cotton et al.[1] have discussed X-ray structural and other data which indicate that the carbene is a hybrid mainly of structures I and II; i.e., there is little π back-bonding from the metal to the carbene as in III.

A number of spectroscopic techniques have been used to compare the bonding of carbenes with other neutral ligands—with a wide variety of conclusions. Thus, Darensbourg and Darensbourg[3] in an infrared study of $Cr(CO)_5L$ compounds suggested that carbenes were comparable to phosphines as donors and were strong π acceptors. The very recent photoelectron study of Jolly et al.[4] supported this view by suggesting that structure III contributed 45% to the overall hybrid. In striking contrast, ^{13}C NMR studies[5,6] suggest that there is electron deficiency on the carbene carbon. These workers have characterized such compounds as transition metal stabilized carbonium ions. More specifically, Clark and Manzer[7] suggested that carbenes are stronger σ donors and/or

Table I. ^{57}Fe Mössbauer Results for Iron(II) Carbene and Related Compounds[a] (mm s^{-1})

No.	Compd	Center shift (CS)[b]	Quadrupole splitting (QS)	Line width (Γ)
1	$[Fe(CNMe)_6](PF_6)_2$	0.18	0	0.28
2	$[Fe(CNMe)_4((CNHMe)_2NMe)](PF_6)_2$	0.16	0.37	0.26
3	$[Fe(CNMe)_5(C(NH_2)NHMe)](PF_6)_2$	0.17	−0.36	0.32
4	$[Fe(CNMe)_5(C(NC_4H_8)NHMe)](PF_6)_2$	0.19	0.40	0.31
5	$[Fe(CNMe)_4((CNHMe)_2N_2H_2)](PF_6)_2$	0.14	0.67	0.27
6	$[Fe(CNMe)_4((CNHMe)_2N_2HPh)](PF_6)_2$	0.17	+0.68[d]	0.28
7	$[Fe(CNMe)_4((CNMe)_2NH_2C(NH)Me)](PF_6)_2$	0.16	0.58	0.28
8	$[Fe(o\text{-phen})_2(CNMe)_2](PF_6)_2$	0.44	0.47	0.24
9	$[Fe(o\text{-phen})_2((CNHMe)_2N_2H_2)](PF_6)_2$	0.40	1.17	0.33
10	*cis*-$Fe(o\text{-phen})_2(CN)_2$[c]	0.43	+0.63	
11	"*trans*"-$Fe(o\text{-phen})_2(CN)_2$[c]	0.49	+0.62	
12	$K_2[Fe(o\text{-phen})(CN)_4]$[c]	0.34	+0.61	

[a] Errors ±0.02 mm sec^{-1}. [b] With respect to sodium nitroprusside at room temperature. [c] Magnitudes from N. E. Erickson, Ph.D. Thesis, University of Washington, 1964. Signs of QS from R. E. B. Garrod, Ph.D. Thesis, University of Cambridge, 1970. [d] $\eta = 0.7$.

weaker π acceptors than isocyanides from infrared evidence in bis(isocyanide)- and carbene-platinum(II) compounds. In addition, a comparison of the coupling constants J(Pt-C-H) in the complexes *trans*-$[PtMe(PMe_2Ph)_2L][PF_6]$ (where L = methoxycarbene and EtNC) gives J = 51 and 63 Hz, respectively, suggesting that the carbene is indeed a much better σ donor than isocyanide. Combined with the above infrared data, this evidence indicates that there is little π acceptance from the metal to the carbene.

Several iron(II)-carbene compounds have been prepared recently.[8,9] These compounds enable us to use the ^{57}Fe Mössbauer center shifts and quadrupole splittings to derive bonding properties of carbenes using methods outlined in previous papers.[10-12] Our results show that the carbenes in this study are better donors than isocyanides and poorer π acceptors toward Fe^{II}—entirely consistent with Clark and Manzer's work as well as the X-ray results. In addition, we have examined in more detail the effect of structural distortions on quadrupole splittings for sterically hindered ligands such as chelating carbenes and phenanthroline.

Experimental Section

Except for the new pyrrolidine complex, the complexes studied in this paper were prepared by literature methods[8,9] and were characterized by their infrared spectra. The narrow Mössbauer line widths (vide infra, Table I) also are a good indication of their purity.

The new pyrrolidine complex was prepared as follows. $[Fe(CNMe)_6](HSO_4)_2$ (575 mg) was dissolved in 25 ml of methanol, and an approximately tenfold excess of pyrrolidine was added (0.75 ml). The resulting solution was refluxed under nitrogen for 1 hr. During this period the color changed to yellow. After filtration, 0.5 g of NH_4PF_6 in 5 ml of methanol was added. A white precipitate appeared and was filtered off, and the resulting yellow solution was partially evaporated and cooled. Pale yellow crystals formed. The infrared spectrum of these showed the following bands (cm^{-1}): ν(N—H) 3341 (m); ν(C≡N) 2242 (m), 2197 (s).

By analogy with the reaction of NH_3 with $Fe(CNMe)_6{}^{2+}$, the compound formed should be $[Fe(CNMe)_5[C(NC_4H_8)NHCH_3]](PF_6)_2$. The analysis confirmed this expectation. Anal. Calcd: C, 28.97; H, 4.07; N, 14.78. Found: C, 29.08; H, 3.96; N, 14.84. If two isocyanides had reacted to give carbenes, the calculated carbon percentage increases to 32.84.

Mössbauer spectra were obtained at 110 K using methods described in a recent book[13] and paper.[12] A typical spectrum is shown in Figure 1. Spectra were calibrated using a 99.99% Fe foil absorber and center shifts are quoted relative to sodium nitroprusside. A 50-mCi ^{57}Co in Cu source was used at room temperature. All spectra were fitted to lorentzian line shapes using the updated version of A. J. Stone's program.

The magnetic spectra of $[Fe(CNMe)_4[(CNHMe)_2N_2HPh](PF_6)_2$ and $[Fe(CNMe)_5[C(NH_2)NHMe]](PF_6)_2$ were run at the PCMU, Harwell. The spectra are shown in Figure 2. For the former compound, the sign of the QS is positive with $\eta = 0.7 \pm 0.1$.[14] For the latter compound, the narrower triplet lines at positive velocities show that the sign of the QS is negative with $\eta \approx 0$.

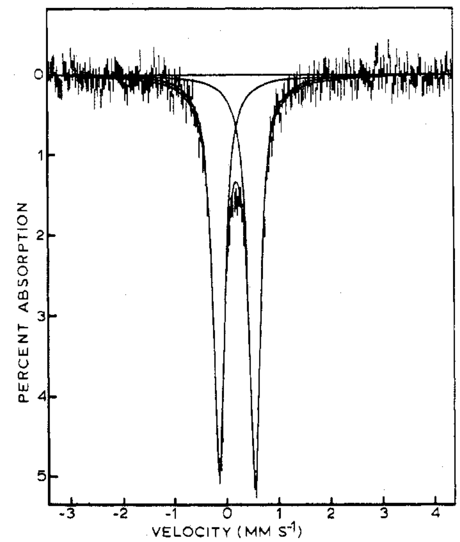


Figure 1. ^{57}Fe Mössbauer spectrum of $[Fe(CNMe)_4[(CNHMe)_2N_2HPh]](PF_6)_2$ at 110 K.

Results and Discussion

(a) Bonding Properties of Carbenes. The ^{57}Fe Mössbauer parameters for the seven carbene compounds, the two isocyanide precursors, and the three iron(II) phenanthroline cyanide complexes are given in Table I. The Mössbauer spectrum of the species $Fe(CNMe)_6{}^{2+}$ has been recorded previously (as the HSO_4 salt),[15] and our center shift (CS) is in good agreement with that given previously after correction for the standard and temperature. The previous CS of −0.02 mm sec^{-1} [15] was quoted with respect to stainless steel at room temperature. Adding 0.22 mm sec^{-1} to correct to sodium nitroprusside standard at liquid N_2 temperatures,[12] we obtain 0.20 mm sec^{-1}, in good agreement with our value of 0.18 mm sec^{-1}.

The methylamine compound (**2**, Table I) is known to be very distorted from octahedral symmetry with a carbene C-Fe-C angle of 67°.[16] Because such distortions are known to affect the magnitudes and especially the signs of quadrupole splittings for Fe^{II},[17] Co^{III},[18] and Sn^{IV} [19] compounds, consideration will first be given to complexes **3** and **4**, which are believed to involve the monodentate carbenes $:C(NH_2)NHCH_3$ and $:C(NC_4H_8)NHCH_3$, respectively. The center shifts for these two compounds are slightly smaller than the hexakis(isocyanide) percursor. Using the expression given previously[12]

$$CS = 0.22 + \sum_i (pcs)_i \tag{1}$$

we can readily derive the partial center shift (pcs) for the carbene as −0.01 mm sec^{-1}, taking the pcs of isocyanide as

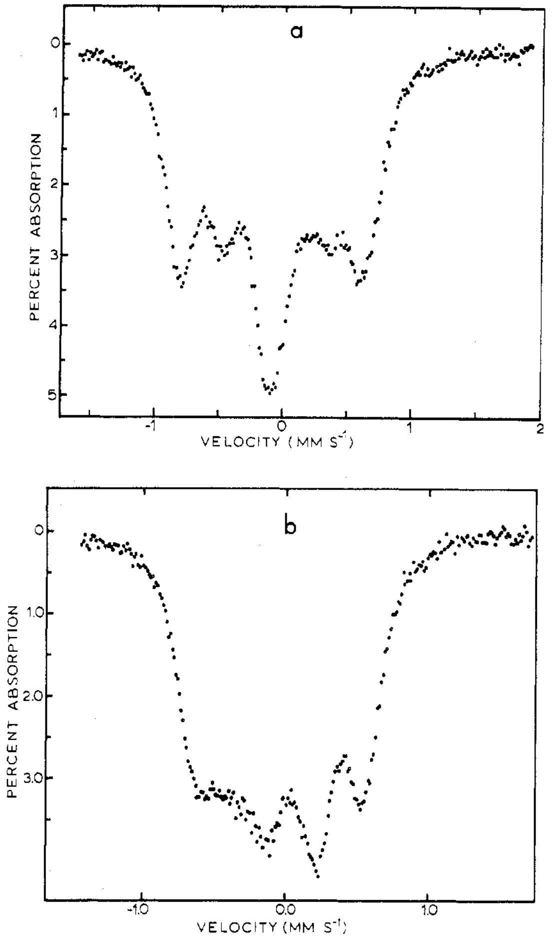


Figure 2. Mössbauer spectra of (a) $[Fe(CNMe)_4[(CNHMe)_2N_2HPh]](PF_6)_2$ and (b) $[Fe(CNMe)_5[C(NH_2)NHMe]](PF_6)_2$ at 4 K in a magnetic field of 3*T* (≡30 kG).

−0.005 mm sec^{-1} from the hexakis(isocyanide) complexes. However, both compounds show similar small but well-resolved quadrupole splittings, indicating that the bonding of the carbene is significantly different from that of the isocyanide. This difference can be readily expressed by deriving a partial quadrupole splitting value for the carbene. For an $FeAB_5$ species, the QS can be expressed as[10]

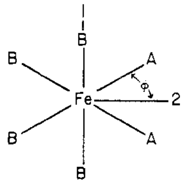
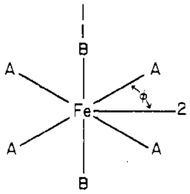
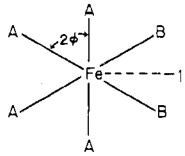
$$QS = 2(pqs)_{carbene} - 2(pqs)_{MeNC} \qquad (2)$$

Averaging the two QS values for compounds **3** and **4**, taking the sign to be negative as observed, and taking $(pqs)_{ArNC} = -0.70$ mm sec^{-1},[12] we obtain

$$-0.38 = 2(pqs)_{carbene} + 1.40 \qquad (3)$$

Solving, $(pqs)_{carbene} = -0.89$ mm sec^{-1}. Our other QS results are consistent with the negative QS for these compounds and the resulting very negative pqs value. First, the positive QS for the chelating carbene species (compound **6**) is expected, since the QS for an $FeAB_5$ species should be opposite to that of *cis*-FeA_2B_4.[10] Second, consider the two species (**8** and **9**, Table I) *cis*-$[Fe(o\text{-}phen)_2(CNMe)_2]^{2+}$ (**8**) and *cis*-$[Fe(o\text{-}phen)_2[C(NHMe)_2N_2H_2]^{2+}$ (**9**), where the two isocyanides in **8** are replaced by a chelating carbene in **9**. Since the pqs values for nitrogen donors such as NH_3 and C_5H_5N are in the −0.5-mm sec^{-1} range,[12] an increase in QS from **8** to **9** implies that the carbene has a more negative pqs value than isocyanide. It is interesting to note here that, as expected by the additivity model, the replacement of two isocyanides for a carbene causes the same *change* in QS when the other four ligands are isocyanides (compounds **1** and **5**) or phenanthrolines (compounds **8** and **9**). Thus, the increase in QS from **1** to **5** (0.67 mm sec^{-1}) is very similar to the increase from **8** to **9** (0.70 mm sec^{-1}).

Table II. EFG Expressions for Distorted $FeB_4(A\text{-}A)$, *trans*-$Fe(A\text{-}A)_2B_2$, and *cis*-$Fe(A\text{-}A)_2B_2$ Structures (A-A = Chelating Ligand)

No.	Compd	EFG expressions[a]
1		$V_{11}/e = 2[B] - 2[A]$ $V_{22}/e = (1 + 3\cos 2\phi)[A] - [B]$ $V_{33}/e = (1 - 3\cos 2\phi)[A] - [B]$
2		$V_{11}/e = 4[B] - 4[A]$ $V_{22}/e = (1 + 3\cos 2\phi)\{2[A]\} - 2[B]$ $V_{33}/e = (1 - 3\cos 2\phi)\{2[A]\} - 2[B]$
3		$V_{11}/e = A_1$ $V_{22}/e = {}^1/_2A_1(3\cos\chi - 1) + A_2\sin\chi$ $V_{33}/e = -{}^1/_2A_1(3\cos\chi + 1) - A_2\sin\chi$

[a] Where $A_1 = [B] - [A]$, $A_2 = -3(2^{1/2})[A]\cos 2\phi$, and $\chi = \tan^{-1}(-2A_2/3A_1)$.

From the pcs and pqs values,[10,12] we conclude that the carbenes are slightly better ($\sigma + \pi$) ligands than isocyanides and that the carbenes are appreciably better σ donors and poorer π acceptors than isocyanides. This conclusion is consistent with the conclusions given by Clark and Manzer[7] and the X-ray evidence which indicate little π acceptance by carbenes and a very small contribution of structure III to the overall hybrid. It is also apparent[12] that our carbenes are very much better donors than phosphines or phosphites to Fe^{II}.

(b) The Distorted Chelating Carbene Structures. Except for compound **2**, the quadrupole splittings for the isocyanide compounds containing chelating carbenes (compounds **2**, **5–7**, Table I) are substantially larger than the quadrupole splittings for compounds **3** and **4** which contain just the one carbene carbon. In addition, η for compound **6** is very large. For undistorted species, the magnitudes of both $FeAB_5$ and *cis*-FeA_2B_4 quadrupole splittings should be the same and η should be zero. The similar magnitudes for both species have been confirmed.[10,14] Since the monodentate carbene carbon and the chelating carbene carbons are both bonded to two N heteroatoms, it seems likely that the bonding properties of the carbene carbons are similar in both cases. The change in QS from ~0.3 to ~0.6 mm sec^{-1} and the large η value are thus probably associated mainly with distortions of the carbene C–Fe–C moiety from 90° bond angles. We do not know what these bond angles are for compounds **5–7**, but a rough calculation for compounds **5** and **6** taking the bond lengths 2.02 Å (Fe–C),[16] 1.35 Å (C–N,[16] and 1.41 Å (N–N) and assuming sp^2-hybridized N gives C–Fe–C of ~85.8° ($\phi = 42.9°$).

Using the point charge expressions (Table II, no. 1), we can rationalize very qualitatively the above QS and η for compounds **5–7**. We set the EFG axes for the carbene compounds [B = MeNC; A-A = carbene] as in Table II and calculate the QS and η as a function ϕ using the pqs values for MeNC and carbene carbon of −0.70 and −0.89 mm sec^{-1}, respectively. The results (Figure 3) show that the QS increases slowly as ϕ decreases, while η increases very rapidly. At $\phi \approx 43°$, $\eta \approx 1$ while the QS has increased only to ~0.45 mm sec^{-1}. It is

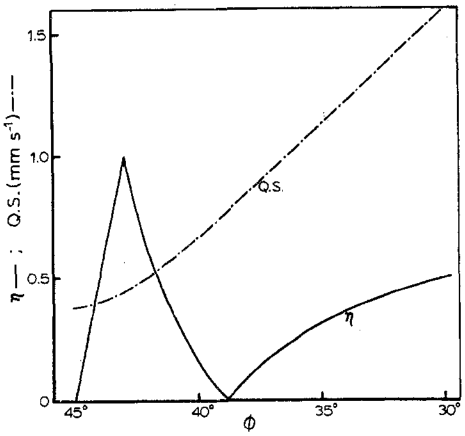


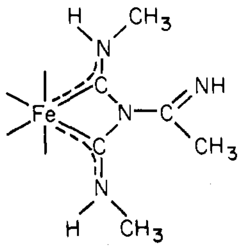
Figure 3. Plot of QS and η vs. ϕ (see text and Table II) for a carbene compound of the type $Fe(CNMe)_4(carbene)^{2+}$.

apparent that at no value of ϕ do both the calculated QS and η quantitatively match the observed QS and η.

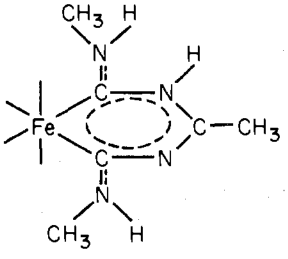
We believe that such distortion calculations will never have more than qualitative significance except when one pqs value is much larger than another.[20] The use of the distortion treatment requires absolute pqs values because of the different numerical coefficients in front of [A] and [B], while the pqs values used here are only relative values. As pointed out several times before,[10,13,17] absolute values are not required for predictive purposes for undistorted species. In addition to the above fundamental difficulty, we have assumed that the isocyanide ligands remain in their undistorted positions. Also, the carbene carbons can only π bond to one set of Fe t_{2g} orbitals, and this affects the expected relative QS for $FeAB_5$ and *cis*-FeA_2B_4.[10]

Because of the difficulty in obtaining a semiquantitative or quantitative QS model for the chelating carbene species, we are unable to explain the small QS for compound **2** which has a C–Fe–C angle of 67°.[16] Because of the great distortion, it is possible that the carbene carbons will no longer overlap well with the Fe $d_{x^2-y^2}$ orbital, and the carbene carbon then becomes effectively a poorer donor.

Compound **7** could have one of the structures a or b.[9] Our



a



b

quadrupole splittings suggest structure b as the correct one since the four-membered ring structure a should give a QS similar to that of compound **2**, and our distortion treatment suggests that the six-membered ring structure (b) should have a smaller QS than the five-membered ring structures in compounds **5** and **6** as observed.

(c) The Phenanthroline Compounds. Consideration of the distortions in the carbene compounds lead us to consider the effect of distortions on other Fe^{II} complexes with chelating ligands having a small bite, such as phenanthroline. A particular problem[17] involves the phenanthroline compounds *cis*-$Fe(o\text{-phen})_2(CN)_2$, "*trans*"-$Fe(o\text{-phen})_2(CN)_2$, and $K_2[Fe(o\text{-phen})(CN)_4]$ (**10–12**, Table I). All quadrupole splittings have the same sign and almost the same magnitude, whereas the predicted ratio is –1:2:1, respectively. The EFG expressions

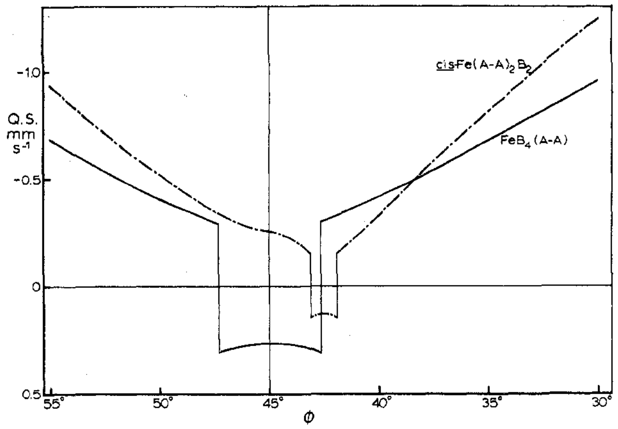


Figure 4. Plot of QS vs. ϕ for *cis*-$Fe(A\text{-}A)_2B_2$ and $FeB_4(A\text{-}A)$ complexes (A-A is a bidentate chelate). Note that at $\phi = 45°$, the two have QS values of different sign, but at $\phi \approx 42$ or 48°, they have the same sign.

for the three species are given in Table II, where A-A could be phenanthroline and B could be CN^-. We consider the effect of the A–Fe–A angle ($=2\phi$) on the QS, taking pqs values of –0.53 and –0.66 mm sec⁻¹ for [A] and [B], respectively. These are not meant to be accurate values for phenanthroline and CN^- but rather are considered to be representative values. The pqs for phenanthroline is not known, but it should be more positive than that of CN^-.[17]

The effect of the change of ϕ on the QS is seen in Figure 4. The QS for *trans*-$Fe(A\text{-}A)_2B_2$ is not shown because it should be double that for $FeB_4(A\text{-}A)$ at all ϕ values. At $\phi = 45°$, the theoretical ratio of –1:2:1 for cis:trans:B_4(A-A) is predicted. However between 43 and 42°, all signs change, with the cis sign changing twice within little over 1°. Thus at $\phi \approx 42°$ (a reasonable angle for the N–Fe–N species), *all* signs are positive as is observed. As shown by La Rossa and Brown,[18] these calculations indicate that the sign of small QS values can change abruptly for small distortions from octahedral symmetry.

Although the distortion treatment can rationalize the equal signs for the three compounds, the model does not explain the similar magnitudes. As pointed out above, the "*trans*"-$Fe(o\text{-phen})_2(CN)_2$ should always have twice the magnitude of $Fe(o\text{-phen})(CN)_4^{2-}$. This discrepancy could be due to one or all of the three reasons outlined in the previous section: lack of absolute pqs values, distortion of the CN^-, and π bonding to only one Fe t_{2g} orbital. However, it is more probable that the trans compound (isolated in the same way as by Schilt[21]) is in fact the cis compound. Thus, the CN stretching band at 2075 cm⁻¹ is broad and all well-characterized M(diimine)$_2X_2$ systems[22,23] appear to have cis X groups.

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Registry No. 1, 34821-77-7; **2**, 41654-40-4; **3**, 49716-69-0; **4**, 56292-60-5; **5**, 34823-42-2; **6**, 34977-39-4; **7**, 56292-62-7; **8**, 49664-77-9; **9**, 56292-63-8; $[Fe(CNMe)_6](HSO_4)_2$, 15334-25-5; pyrrolidine, 123-75-1.

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Complexes of Ferrous Phthalocyanine with Aromatic Nitroso Compounds, Isocyanides, and Phosphites

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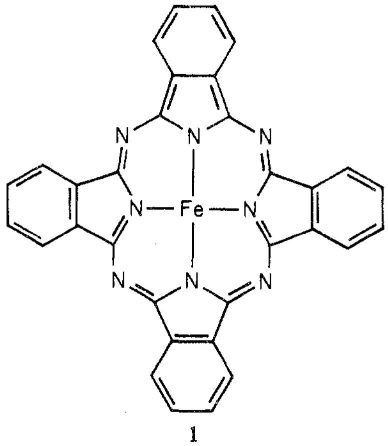
A number of new adducts of ferrous phthalocyanine (FePc) have been isolated. These include mixed-ligand complexes LFePcL' [L = a nitroso aromatic group, L' = *n*-butylamine or *N*-methylimidazole; L = cyclohexyl isocyanide, L' = *N*-methylimidazole; L = a phosphite, L' = *n*-butylamine] and bis adducts L_2FePc [where L is an isocyanide or a phosphite]. The complexes have been characterized by elemental analysis, electronic spectra, infrared spectra, and proton magnetic resonance spectra. The ring-current-induced shifts found for coordinated nitrosobenzene have been analyzed and it is concluded that this ligand coordinates iron through the nitrogen lone pair. The rate of exchange between free and complexed nitrosotoluene in $(CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$ has been determined by observing the ^1H NMR spectrum under intermediate exchange conditions. The exchange occurs via a dissociative path and the activation parameters for exchange are $\Delta H^\ddagger = 20.1 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = 14.2 \pm 0.2$ eu.

Introduction

The nitroso group is isoelectronic with two classes of ligands—dioxygen and diazenes—which are of considerable current interest to chemists. However, relatively few examples of metal–nitroso complexes are known, and there is only limited structural work in this area. The substitution product from the reaction of nitrosobenzene and ferrocyanide has been known for some time[1] and it also has been shown that aromatic nitroso compounds will complex ferrous hemoglobin and ferrous myoglobin.[2-6] Although these last two reactions undoubtedly involve axial coordination of the heme iron by nitrosobenzene, little is known in detail about the iron–nitroso bonding. Nitrosobenzene could coordinate iron in several fashions; the most obvious are (1) through the nitrogen lone pair, (2) through an oxygen lone pair, or (3) through the nitrogen–oxygen π bond. Additionally nitrosobenzene could coordinate as its dimer[7] or it could act as a bridging ligand. The best characterized, simple nitroso complex $(C_6H_5NO)_2PdCl_2$[8] has been shown by an X-ray structure determination[9] to have the palladium coordinated to the nitrogen lone pair. The only other nitroso complex which has been characterized by an X-ray structure determination[10] is the dimer $[C_6H_5NOFe(CO)_3]_2$ in which the nitroso group bridges two irons by forming both iron–nitrogen and iron–oxygen bonds.

The interaction of aromatic nitroso compounds with ferrous phthalocyanine (FePc), **1**, has been examined in order to study the coordination of a nitroso group with iron in a porphyrin-like environment. The ring currents produced by the phthalocyanine macrocycle induce significant shifts in the proton magnetic resonance spectra of ligands above and below the phthalocyanine plane.[11] An analysis of these shifts may be used to estimate molecular geometry. In the course of this work some other new adducts of FePc have been prepared and the range of bases which have been shown to add to FePc has been enlarged.



1

Experimental Section

Preparation of Compounds. Ferrous phthalocyanine was sublimed under vacuum before use. Bis(*n*-butylamine)ferrous phthalocyanine was prepared as described previously[11] and recrystallized from acetonitrile. Aromatic nitroso compounds were prepared via standard procedures.[12,13]

$(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$. Nitrosobenzene (200 mg, 1.87 mmol) was added to a stirred, filtered solution of 500 mg (0.70 mmol) of $(n\text{-}C_4H_9NH_2)_2FePc$ in 50 ml of dichloromethane. The volume of the deep blue solution was reduced by distillation to 20 ml, and 20 ml of diethyl ether was added. Upon further reduction of the solvent volume, the product formed purple crystals. The product was collected and recrystallized from 1:1 v/v of dichloromethane–diethyl ether containing additional nitrosobenzene; yield, 67%. Anal. Calcd for