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Hydrogen Bonding to Coordinated Imidazole. Association of 1,10-Phenanthroline and Other Bases with Bis(imidazole)metalloporphyrins

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Qualitative results are presented which indicate that halide ions, 1,10-phenanthroline, and substituted pyridines associate with the N–H group in bis(imidazole)metalloporphyrins. Electronic spectra indicate that 1,10-phenanthroline shifts the equilibrium $2B + FePCl \rightleftarrows (B)_2FeP^+ + Cl^-$ to favor the product when the base is imidazole (ImH) but not when it is 1-methylimidazole (1-MeIm). These spectra show no evidence for the formation of aromatic π complexes between 1,10-phenanthroline and the porphyrin. The preparation and proton NMR spectrum of $[(ImH)_2Co(TPP)][BF_4]$ are reported. Addition of halide ions, 1,10-phenanthroline, or substituted pyridines to dichloromethane solutions of $[(ImH)_2Co(TPP)][BF_4]$ causes the imidazole N–H resonance to shift to lower field due to the formation of hydrogen bonds. With 1,10-phenanthroline this interaction also causes an upfield shift of the 2,9 and 3,8 protons of 1,10-phenanthroline when the metalloporphyrin/1,10-phenanthroline ratio is high. This shift results from positioning the 1,10-phenanthroline so that it can chelate the imidazole NH unit and is caused by the ring current of the porphyrin.

Introduction

A number of recent studies have been concerned with the nature of the interactions of metalloporphyrins with molecules outside of the first coordination sphere of the metal ion. Much of the emphasis in this area has been on the formation of aromatic π complexes.[1-12] These interactions may be of considerable significance in the biological functioning of porphyrins because of the ability of such interactions to bind and position noncovalently attached porphyrins to macromolecules,[13] to alter the electronic environment of the porphyrin, and to facilitate electron transfer in and out of the porphyrin.[1]

We point out in this article that another type of external interaction of molecules with metalloporphyrins exists. Specifically, hydrogen bonding to axial imidazole ligands can result in binding some molecules to metalloporphyrins. Imidazole itself is well-known to participate in extensive hydrogen bonding since it can act as both a hydrogen bond donor and acceptor. In the solid state, imidazole forms one-dimensional chains with strong hydrogen bonding connecting the molecules.[14] In solution, evidence for the formation of aggregates formed by hydrogen bonding has come from both NMR[15,16] and infrared measurements.[17] Coordinated imidazole cannot act as a hydrogen bond acceptor, but it should act as a stronger hydrogen bond donor than free imidazole since the pK_a of coordinated imidazole exceeds that of free imidazole.[18]

It has been reported that addition of 1,10-phenanthroline to a dichloromethane solution containing imidazole and iron(III) deuteroporphyrin IX dimethyl ester chloride Fe(DP)Cl shifts equilibrium 1 in favor of the $(ImH)_2Fe(DP)^+$.[9]

$$2B + FePCl \rightleftarrows (B)_2FeP^+ + Cl^- \qquad (1)$$

B = an imidazole; P = a porphyrin dianion

This shift in the equilibrium has been attributed to the formation of a complex between $(ImH)_2Fe(DP)^+$ and 1,10-phenanthroline. The site of 1,10-phenanthroline binding to $(ImH)_2Fe(DP)^+$ was simply specified as "remote from the metal ion", but the interaction was implied to be the π charge-transfer type. Herein we demonstrate that the interactions responsible for the alteration of equilibrium 1 by 1,10-phenanthroline are hydrogen-bonding interactions.

Other independent evidence for hydrogen bonding to the N–H of coordinated imidazole is available. In the crystal structure of $[(ImH)_2Co(TPP)][CH_3COO]\cdot H_2O\cdot CHCl_3$ (TPP = anion of *meso*-tetraphenylporphyrin) the imidazole ligand is hydrogen bonded to the acetate anion,[19] while in the solid bis(imidazole)(octaethylporphinato)iron(III) perchlorate the imidazole is hydrogen bonded to a perchlorate ion.[20] The electron-spin resonance spectra of some bis(imidazole)ferric porphyrins are altered by the presence of fluoride ions, and these alterations have been ascribed to hydrogen bonding from the imidazole NH to fluoride.[21] Finally, Walker[22] has previously noted the importance of hydrogen bonding to coordinated imidazole on the magnitude of equilibrium constants for reaction 1 and has discussed the possibility that hydrogen bonding rather than π charge-transfer interaction is responsible for the apparent binding of four imidazole molecules by FeTPPCl in benzene solution.

Experimental Section

meso-Tetraphenylporphyrin (H_2TPP), its iron complex (TPPFeCl), and its cobalt(II) complex (TPPCo) were prepared by published routes.[23] Iron(III) deuteroporphyrin IX dimethyl ester chloride (Fe(DP)Cl) was obtained from Sigma Corp. Imidazole and 1,10-phenanthroline were dried under vacuum over phosphorus pentoxide and sublimed prior to use. 1-Methylimidazole was purified by distillation from barium oxide.

The cobalt(III) complexes bis(imidazole)(*meso*-tetraphenylporphyrin)cobalt(III) tetrafluoroborate, $[(ImH)_2Co(TPP)]BF_4$, and bis(1-methylimidazole)(*meso*-tetraphenylporphyrin)cobalt(III) tetrafluoroborate, $[(1\text{-}MeIm)_2Co(TPP)]BF_4$, were prepared by the same technique. In a typical preparation 1.34 g of Co(TPP) (2 mmol), 0.50 g of imidazole (7.35 mmol), 0.50 g of NH_4BF_4 (4.8 mmol), and 0.41 g of $AgBF_4$ (2.1 mmol) were mixed in 40 mL of methanol and 10 mL of chloroform. After being stirred in the open atmosphere, the mixture was heated under reflux with exposure to the atmosphere for 8 h. After the mixture was cooled, the solvent was removed by the use of a rotary evaporator. The solid was dissolved in 20 mL of dichloromethane and filtered. The filtrate was chromatographed on 200–300 mesh silicic acid which had dried at 130 °C. Three bands were eluted. The first and second bands were discarded, and the third, red-brown band, which contained $[(ImH)_2Co(TPP)][BF_4]$, was collected and evaporated to dryness. The product was obtained as blue crystals by slow addition of ether to a filtered acetone solution of the complex (yield: 1.45 g, 80%). The products were identified by their proton NMR spectra, which were nearly identical to those reported for $[(ImH)_2Co(TPP)]Br$ and $[(1\text{-}MeIm)_2Co(TPP)]Br$ previously.[24]

Proton NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer operating at 100 MHz. All chemical shifts were measured relative to internal tetramethylsilane. Dichloromethane was fractionally distilled from phosphorus pentoxide. Electronic spectra were recorded on a Cary 14 spectrophotometer.

Results and Discussion

Electronic Spectral Studies. A number of studies have shown that addition of imidazole or 1-methylimidazole to iron(III) porphyrin halides yields adducts via equilibrium 1.[24,25] The electronic spectral changes accompanying these reactions show no evidence for the formation of detectable quantities of a five-coordinate adduct. From these studies, equilibrium

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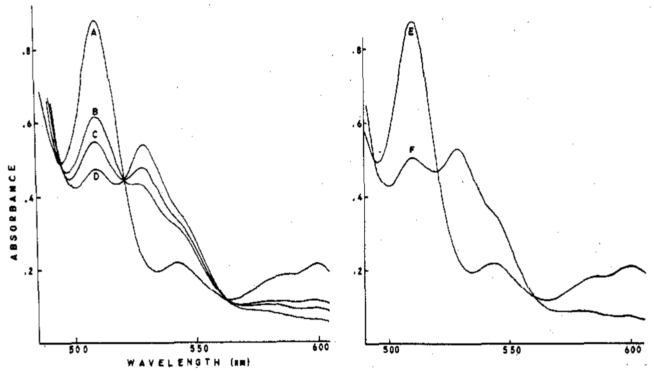

Figure 1. Electronic spectrum of 6.13 × 10^{-5} M FeTPPCl in dichloromethane solution in 1.0-cm path length cells in the presence of various bases. The following substances have been added: A, nothing; B, 1.30 × 10^{-3} M imidazole; C, 1.30 × 10^{-3} M imidazole and 1.55 × 10^{-3} M 1,10-phenanthroline; D, 1.30 × 10^{-3} M imidazole and 6.19 × 10^{-3} M 1,10-phenanthroline; E, 1.50 × 10^{-2} M 1,10-phenanthroline; F, 1.65 × 10^{-2} M 1-methylimidazole (the trace with 1.65 × 10^{-2} M 1-methylimidazole and 5.99 × 10^{-2} M 1,10-phenanthroline is coincident with trace F).

constants are available for reaction 1 in a variety of solvents. We have confirmed that the addition of 1,10-phenanthroline to solutions of imidazole and either Fe(TTP)Cl or Fe(DP)Cl does produce alterations in the electronic spectrum which indicates that equilibrium 1 is shifted to favor the product. Typical observations for Fe(TPP)Cl are shown in Figure 1. Similar results have been obtained with Fe(DP)Cl. Other than shifting equilibrium 1, no other spectral changes indicative of the formation of an adduct between 1,10-phenanthroline and either FePCl or $[B_2FeP]^+$ are observed. Specifically, if a π complex were to form, one could expect that the mixture would show alterations due to the formation of the 1,10-phenanthroline–porphyrin complex. Other such π complexes of metalloporphyrins are characterized by one or more of the following: new absorption bands, shifts in absorption maxima, alteration in the extinction coefficients of absorption bands due to broadening of the absorption bands.[3,4] No changes of this sort are evident in the 1,10-phenanthroline–imidazole–FePCl systems. Moreover 1,10-phenanthroline has no effect on equilibrium 1 when the base is 1-methylimidazole as may be seen by trace F of Figure 1. Consequently, the presence of a N–H unit in the imidazole base is critical in order for 1,10-phenanthroline to affect equilibrium 1. Thus we conclude that 1,10-phenanthroline perturbs equilibrium 1 through altering the hydrogen-bonding pattern. Now it may be argued that 1-methylimidazole is a poor model for imidazole since the equilibrium constant for eq 1 is about 100-fold less when B is 1-methylimidazole than when it is imidazole.[22] Therefore, further investigations of imidazole/1,10-phenanthroline interactions have been carried out by proton NMR spectroscopy.

Proton Nuclear Magnetic Resonance Studies. The N–H resonance of imidazole is affected by hydrogen bonding. In solutions of imidazole in inert solvents, dilution causes the N–H resonance to broaden and shift upfield as the hydrogen-bonded aggregates of imidazole are reduced in size.[15,16] It is a general characteristic of hydrogen-bonded systems to show a lower field resonance for a proton in a hydrogen-bonded state than for that same proton in a state where hydrogen bonding is absent.[26]

Addition of 1,10-phenanthroline to a dichloromethane solution of imidazole causes the N–H resonance to shift to lower field. The effect is shown in Figure 2. Other resonances of both imidazole and 1,10-phenanthroline are unperturbed under these conditions. These shifts are indicative of the formation of hydrogen bonds between imidazole and 1,10-phenanthroline.

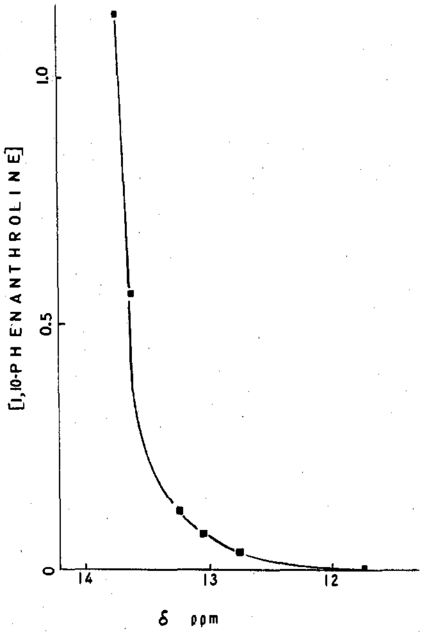

Figure 2. Chemical shift of imidazole N–H in dichloromethane solution as a function of 1,10-phenanthroline concentration. The imidazole concentration was 0.5 M.

In order to monitor the hydrogen bonding of coordinated imidazole, the diamagnetic and relatively nonlabile Co(III) d^6 complexes $[(ImH)_2Co(TPP)][BF_4]$ and $[(1\text{-MeIm})_2Co(TPP)][BF_4]$ have been prepared. The proton NMR spectrum of $[(Im)_2Co(TPP)](BF_4)$ in CD_2Cl_2 solution consists of a pyrrole peak at δ 9.00, a group of phenyl resonances at δ 7.99–7.71, and resonances of the imidazole C–H units at δ 4.52, 0.91, and 0.26. For comparison, Gouedard et al. report that $[(ImH)_2Co(TPP)]Br$ has the following resonances (δ): pyrrole, 8.87; phenyl, 7.73; 5 H (Im), 4.26; 2 H (Im), 0.72; 4 H (Im), 0.03 in $CDCl_3$ solution.[24] These imidazole resonances are shifted to higher field relative to their positions in free imidazole by the porphyrin ring current. The low-field portion of this spectrum is visible in Figure 3. No resonance assignable to the imidazole N–H proton is seen in the spectrum; it probably underlies the aromatic resonances at δ 7.99–7.71. Addition of a variety of substances, all of which are capable of accepting hydrogen bonds, to $[(ImH)_2Co(TPP)][BF_4]$ causes the N–H resonance to become visible at low fields, although it is quite broad. These substances include halide ions (Cl^-, Br^-, and I^-), 2,6-lutidine, 2,6-dimethyl-4-nitropyridine, 2,4,6-collidine, and 1,10-phenanthroline. 2,6-Di-*tert*-butylpyridine, which is too sterically hindered to act as a hydrogen-bond acceptor, has no effect on the spectrum of $[(ImH)_2Co(TPP)]_2[BF_4]$.

Proton NMR spectra of $[(ImH)_2Co(TPP)][BF_4]$ in the presence of varying quantities of 1,10-phenanthroline are shown in Figure 3. Two effects are evident. First, the N–H resonance of the coordinated imidazole shifts to lower field as 1,10-phenanthroline is added. Second, the 1,10-phenanthroline resonances are perturbed by the presence of the cobalt complex. Most noticeably, the lowest field group of four 1,10-phenanthroline resonances, which are assigned to the 2 and 9 protons, are shifted upfield by at least 1 ppm as the ratio of $[(ImH)_2Co(TPP)]$ to 1,10-phenanthroline is increased. The highest field group of four resonances also experiences a very much smaller upfield shift. These resonances have been assigned to the 3 and 8 protons of 1,10-phenanthroline. Only minor shifts occur in the remaining portions of the spectrum. The spectra clearly indicate that imidazole remains coordinated to cobalt and is not displaced by 1,10-phenanthroline. Addition of 1,10-phenanthroline to dichloromethane solutions of [(1-

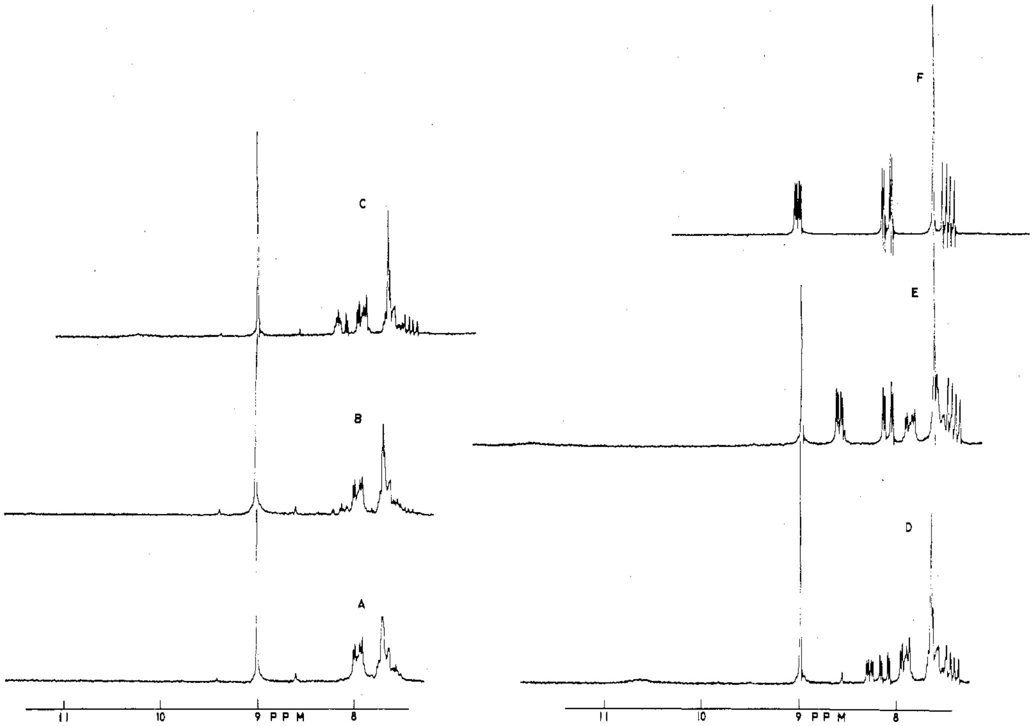

Figure 3. Proton magnetic resonance spectra of 1,10-phenanthroline in the presence of $[(Im)_2CoTPP][BF_4]$ in CD_2Cl_2. The concentration of $[(Im)_2CoTPP]^+$ is 0.025 M in spectra A through E. Ratio of 1,10-phenanthroline concentration to cobalt concentration: A, 0; B, 1.0; C, 1.6; D, 1.8; E, 4.6. Spectrum F is the spectrum of pure 1,10-phenanthroline.

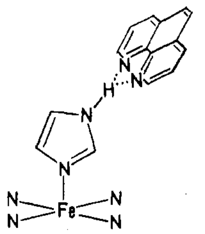

Figure 4. Proposed geometry of the 1,10-phenanthroline adduct of bis(imidazole)metalloporphyrins. The angle between the plane of the 1,10-phenanthroline and the porphyrin is about 145°. Only one imidazole is shown.

$MeIm)_2Co(TPP)][BF_4]$ causes no alteration of the proton NMR spectrum of either solute.

These proton NMR results are consistent with the model shown in Figure 4 in which the 1,10-phenanthroline binds to $[(ImH)_2Co(TPP)]$ by chelating the imidazole N–H unit so that the angle between the 1,10-phenanthroline and porphyrin planes is about 145°. This orientation places the 2 and 9 protons of 1,10-phenanthroline the closest of any 1,10-phenanthroline protons to the porphyrin plane. As a consequence of the porphyrin ring current, these resonances experience an upfield shift. The 3 and 8 protons of 1,10-phenanthroline are also shifted upfield by the porphyrin ring current, but to a lesser extent, because of their greater distance from the ring. The remaining 1,10-phenanthroline protons are too far from the ring to experience a shift.

We conclude that the imidazole N–H unit is the site of interaction of halides, 1,10-phenanthroline, and pyridines to bis(imidazole)metalloporphyrins. Although the electronic spectral studies with the iron porphyrins and the NMR studies with the cobalt porphyrins involve very different concentrations of reagents, we believe that the same general phenomenon is operating in both cases. Clearly, the interaction results in a dynamic situation since only single, site-averaged resonances are seen in the proton NMR studies. Another compound is known in which 1,10-phenanthroline interacts via hydrogen bonding with an axial ligand. In this case, the axial aquo ligands of a manganese(II) macrocyclic complex are involved.[27] In the case of the effect of 1,10-phenanthroline on the position of equilibrium 1, we suspect that the results presented in ref 9 are a composite of two effects: alteration of imidazole activity by interaction with 1,10-phenanthroline and alteration of the $[(ImH)_2FeP]^+$ activity by binding of 1,10-phenanthroline.

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Registry No. FeTPPCl, 16456-81-8; $[(Im)_2FeTPP]Cl$, 25442-52-8; $[(Im)_2CoTPP][BF_4]$, 69531-88-0; $[(1\text{-}MeIm)_2CoTPP][BF_4]$, 69531-90-4; 1,10-phenanthroline, 66-71-7; $[(1\text{-}MeIm)_2FeTPP]^+$, 52155-25-6; imidazole, 288-32-4.

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Synthesis of Cyclopentadienyldicarbonyl(dithiocarbene)iron Cations and Their Reactions with Amines

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Dithiocarbene complexes, $Cp(CO)_2Fe[C(SR)SR']^+$, are easily prepared by $R'SO_3F$ alkylation of the dithioester ligand of $Cp(CO)_2FeC(=S)SR$. The dimethyl derivative, $Cp(CO)_2Fe[C(SCH_3)_2]^+$, shows unusual reactivity toward nucleophilic amines to provide a variety of $Cp(CO)_2FeL^+$ derivatives. Primary amines produce isocyanide complexes, $Cp(CO)_2Fe(CNR)^+$; secondary amines give amino–thiocarbene complexes, $Cp(CO)_2Fe[\underline{C(NR_2)S}CH_3]^+$; diamines, amino alcohols, and amino thiols yield complexes with cyclic carbene ligands, $Cp(CO)_2Fe[\overline{CY(CH_2)_nN}R']^+$, where Y = NH, O, or S. The novel orthothioformate complex $Cp(CO)_2Fe[C(SCH_3)_3]$ is formed as a byproduct in some of the reactions. Spectral properties of the new complexes are discussed.

Introduction

Transition-metal carbene complexes have become a well-known class of organometallic compounds.[1-4] Only recently, however, have complexes with dithiocarbene ligands, M–C(SR)$_2$, been isolated. Such complexes have been reported for iron,[5] chromium,[6-8] tungsten,[7,8] osmium,[9] and platinum.[10,11] One route used to prepare dithiocarbene complexes has been alkylation of the thione sulfur atom in dithioester complexes, M–C(=S)SR, by CH_3SO_3F or $[Et_3O]BF_4$.[10] In the present paper, we extend this route to the preparation of $Cp(CO)_2Fe–C(SR)_2^+$ (Cp = η^5-C_5H_5) starting with the iron dithioester complexes $Cp(CO)_2Fe–C(=S)SR$ (R = CH_3,[12] $CH_2C_6H_5$).

Since there are no reports describing reactions of the dithiocarbene ligand itself, it was of interest to examine its reactions for the purpose of preparing novel ligands, as well as establishing general patterns of reactivity of this ligand.

Results and Discussion

Preparation and Characterization of $Cp(CO)_2Fe[C(SR)SR']^+$ Carbene Complexes. Iron dithioester complexes are readily available through the reaction of $Cp(CO)_2Fe^-$ with carbon disulfide and a suitable alkyl halide (eq 1).[12] Short reaction

$$Cp(CO)_2Fe^- \xrightarrow[(2)\ RX]{(1)\ CS_2} \underset{\text{Ia,b}}{Cp(CO)_2Fe—C(=S)SR} + X^- \qquad (1)$$

$$RX = CH_3I\ (\text{Ia}),\ C_6H_5CH_2Br\ (\text{Ib})$$

times are important since other products have been observed by using longer reaction times.[13] A ruthenium analogue of Ia has been prepared by the same route.[14] The dithioester complexes Ia,b are stable toward air in the solid state, but they decompose slowly when exposed to light.

Alkyl fluorosulfonates readily alkylate the thiocarbonyl sulfur atom of the dithioester ligand to give the corresponding cationic dithiocarbene complexes (eq 2). The yields are

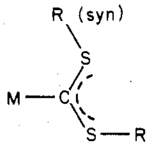
$$\text{Ia,b} \xrightarrow[(2)\ PF_6^-\ \text{exchange}]{(1)\ R'SO_3F} \{Cp(CO)_2Fe[C(SR)SR']\}PF_6 \qquad (2)$$

$$\text{IIa},\ R = R' = CH_3$$
$$\text{IIb},\ R = CH_3,\ R' = C_2H_5$$
$$\text{IIc},\ R = CH_2C_6H_5,\ R' = CH_3$$

generally in the range of 60–70%. Anion exchange is performed as the SO_3F^- salts of IIa–c are less stable and less readily crystallized than the PF_6^- salts. In the solid state the yellow crystalline carbene complexes IIa–c show no noticeable decomposition after several months of exposure to air. Complex IIa is slightly soluble in water; it is also stable toward water at room temperature and can be recovered almost quantitatively from aqueous solutions. The carbenes are soluble in polar solvents such as CH_2Cl_2, CH_3CN, and acetone, slightly soluble in $CHCl_3$ and THF, and insoluble in nonpolar solvents such as hexanes or Et_2O. Solutions of IIa exposed to air at room temperature are stable for several days. This stability differs markedly from that of a related carbene complex with no stabilizing heteroatomic groups, $\{Cp(CO)_2Fe[C(C_6H_5)H]\}PF_6$, solutions of which decompose completely within 1 h under similar conditions.[15]

The IR spectrum of IIa in CH_2Cl_2 shows two ν(CO) absorptions at 2058 and 2017 cm^{-1} with a calculated ν(CO) force constant[16a] of 16.8 mdyn/Å. Comparison of this value with the ν(CO) force constants of 17.6 and 17.1 mdyn/Å found for $\{CpFe(CO)_3\}PF_6$[16b] and $\{Cp(CO)_2FeCNCH_3\}PF_6$,[16b] respectively, indicates that the dithiocarbene ligand has a lower π-acceptor/σ-donor ratio than either the carbonyl or isocyanide ligand, which is consistent with conclusions drawn for other transition-metal carbene complexes.[3] The position of the carbene carbon resonance in the ^{13}C NMR (acetone-d_6) spectrum of IIa occurs at 303 ppm downfield relative to Me_4Si, which is also consistent with previous reports.[3]

A single line at τ 6.73 is observed for the two methyl groups of the carbene ligand in the ^1H NMR (acetone-d_6) spectrum of IIa. This is in contrast with spectra reported for $\{PtCl[C(SEt)_2](PPh_3)_2\}BF_4$,[10] $\{PtI[C(SMe)_2](PPh_3)_2\}I$,[11] and $\{PtI[C(SEt)_2](PPh_3)_2\}I$[11] which show different resonances for the two alkyl groups of the carbene ligands. The inequivalence of the alkyl groups is explained by the presence of syn and anti R groups



caused by restricted rotation around the C(carbene)–S bonds.[10,11] When an acetone-d_6 solution of IIa is cooled to −55

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