to $(DH)_2$ should be in the vicinity of the Schiff base double bonds. The Me_3Bzm compound is of some interest in this connection. The H4 signal is 0.74 ppm further upfield for the Costa model than for the $(DH)_2$ complex (Figure 4, Table VIII). The H4 nucleus should lie out over the double bonds of the equatorial ligands. The 1D NOE data clearly show that the propylene protons are not near the H4 proton of coordinated Me_3Bzm. In contrast, the H2 signal is enhanced by irradiation of propylene $N-CH_2$ protons lying on the L side of the equatorial plane. Indeed, the α-H signals of the $PhNH_2$ and py compounds also gave an NOE with the most downfield multiplet assigned to these CH_2 groups of the propylene bridge. These results suggest that the L ligand is rotating relatively freely. Clearly, more studies are needed to (i) resolve the issue of the reasons for the greater anisotropy of the $Co((DO)(DOH)pn)CH_3^+$ group compared to the $Co(DH)_2CH_3$ group and (ii) assess the relative contributions of effects a and b to the shifts of the axial ligand signals.

The above NOE studies suggest that the downfield multiplet in all cases is assignable to the H's on the terminal CH_2 groups of the propylene bridge which lie on the L side of the equatorial plane. Indeed, when L is an aniline type ligand, this multiplet is relatively upfield (3.8 to 3.9 ppm). The multiplet of most of the complexes in Table VII appears at ca. 4.0 ppm or to even lower field. This observation is consistent with the effect of the anisotropic ring of the aniline-type ligands. The $2NH_2py$ compound follows the trend, and this result supports NH_2 binding by this ligand. Likewise, the shifts of the equatorial CH_3 groups are ca. 0.2 ppm more upfield than for most other compounds in Table VIII for both the aniline-type ligands and $2NH_2py$—again, consistent with NH_2 binding in the Costa system.

In conclusion, our extensive comparison of the $[LCo((DO)(DOH)pn)CH_3]X$ and $LCo(DH)_2CH_3$ compounds for L = N-donor ligand does not indicate any major differences in structure or properties comparable in magnitude to those found between these systems and cobalamins on the one hand and Schiff base models such as Cosaloph compounds on the other hand. Clearly, compared to cobaloximes, steric effects are more important in the Costa-type models, which also exhibit greater anisotropy. The basis for the anisotropic effect is still uncertain but it seems clear that the Co center in the Costa-type models is more electrophilic than that of the cobaloxime. Since the Co center in cobalamins has relatively low electrophilicity for a Co compound, the Costa-type models are clearly deficient. On the other hand, Co–N-(axial) bond lengths are somewhat longer for Costa type compounds—a result more in keeping with cobalamin structures.[30,31] Although comparable to cobaloximes, the lower symmetry of the Costa-type compounds leads to more complex NMR spectra, the very complexity of the spectra eventually could be useful in evaluating the various contributions of a–c in influencing NMR shifts. In turn, such information could prove useful in interpreting the relationship of NMR spectra of cobalamins to their conformation—a subject of vital importance in unraveling B_{12}-dependent enzymatic processes.[30,36]

Acknowledgment. This research was supported by NIH Grant GM29225 to L.G.M. and by a grant from the MPI (Rome) to L.R. The purchase of the 360-MHz NMR instrument was supported in part by an NSF departmental grant to Emory. We are grateful to these organizations. The research was also supported, in part, by an Emory Research Grant.

Supplementary Material Available: Tables of elemental analyses, anisotropic thermal parameters, hydrogen atom coordinates, and complete bond lengths and bond angles (12 pages). Ordering information is given on any current masthead page.

Contribution from the Institut de Recherches sur la Catalyse, CNRS conventionné à l'Université Claude Bernard,
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Cationic Metal Nitrosyl Complexes. 6. Characterization of the 19-Electron Radical Cation $[Fe(NO)_2LL'_2]^+$

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Received February 20, 1986

The reaction of $[Fe(NO)_2Cl]_2$ with $AgPF_6$ in THF or MeCN leads to the formation of a radical cation that initiates the cationic polymerization of activated olefins. On the bases of ESR and IR experiments in the presence of PPh_3, $P(OPh)_3$, *trans*-$PPh_2(CH{=}CH)PPh_2$, or $PPh_2CH_2CH_2PPh_2$, the radical cation corresponds to the 19-electron complex $[Fe(NO)_2LL'_2]^+$ in a trigonal-bipyramid arrangement with two equivalent NO and L ligands in the equatorial plane (L = L' = THF, MeCN, PPh_3; L = PPh_3, L' = THF, MeCN). EHMO calculations agree with the ESR features. This five-coordination (19-electron configuration) is relevant to the electrophilic behavior of the iron ion, which is induced by the presence of the cationic charge and of the two NO ligands.

The structure determinations of mononuclear metal–nitrosyl complexes have shown that the M–N–O bond angles vary in the range 180–120°.[2] Conversion of linear into bent NO is a feasible process[3] and corresponds formally to the withdrawal of two electrons from the metal. Such a situation generates coordinatively unsaturated metal centers, a prerequisite for catalysis. In this context our interest has been focused toward the catalytic properties of $[Fe(NO)_2Cl]_2$ (**1**). Vinyl compounds are polymerized when a cocatalyst such as $AgPF_6$ (BF_4 or ClO_4) is added to a solution of **1**.[4] The conversion is optimum for Fe:Ag = 1, and AgCl quantitatively precipitates. These observations suggest that Cl^-–PF_6^- (BF_4^-, ClO_4^-) anion exchange has occurred, leaving in solution the solvated cationic complex **3** (eq 1) acting as the

$$\underset{\mathbf{1}}{{}^1/_2[Fe(NO)_2Cl]_2} \xrightarrow{L} \underset{\mathbf{2}}{Fe(NO)_2ClL_n} \xrightarrow[-AgCl]{AgPF_6} [Fe(NO)_2L_m]^+PF_6^- \quad (1)$$

3a, L = MeCN
3b, L = THF

initiator for the polymerization at low temperature (≤25 °C).

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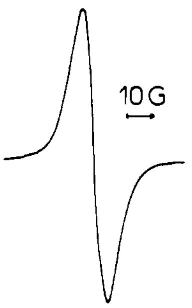

Figure 1. Isotropic ESR spectrum of **2** in THF at 20 °C.

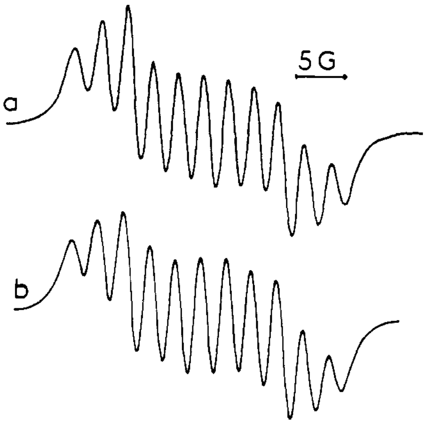

Figure 2. Isotropic ESR spectra of **3a**: (a) taken in MeCN–PhMe (1:9) at −40 °C; (b) computer simulated with $A_{N1} = A_{N2} = 2.5$ G, $A_{N3} = 7.5$ G, and a line width of 1 G.

Species **3** is a radical cation so that polymerization can occur either through a radical or a cationic mechanism. A mechanistic study of the system has shown that the cationic properties of **3** are predominant in initiating the chain growth through a carbenium ion.[4] It was therefore of interest to characterize species **3** in solution, e.g., coordination number and geometry, and to examine its reactivity toward stabilizing ligands such as phosphanes.

In this paper, we report the structural characterization of the above mentioned complexes in solution by electron spin resonance (ESR) and infrared (IR) spectroscopies.

Results

Reaction of $[Fe(NO)_2Cl]_2$ (1) with $AgPF_6$ in THF or MeCN. The diamagnetic dimer **1**, when dissolved in tetrahydrofuran (THF) or in acetonitrile (MeCN), affords the solvated paramagnetic monomer $Fe(NO)_2Cl$ (**2**). Its ESR spectrum at 20 °C (Figure 1) consists of a single line 10 G wide ($g_{av} = 2.0362$ in THF and 2.0387 in MeCN). At lower temperature, a nonresolved hyperfine structure (hfs) appears, probably due to ^{14}N ($I = 1$) and $^{35,37}Cl$ ($I = {}^3/_2$) nuclei.

Addition of equimolecular amounts of $AgPF_6$ to **2** led to the quantitative formation of AgCl and to the complete conversion of **2** into one paramagnetic compound, **3**, which decomposes within 4 h at 25 °C whereas **2** is stable under reflux in THF or MeCN for hours under inert atmosphere. However, at −30 °C, **3** is stable over a period of 16 h. Its ESR spectrum displays a hyperfine structure that is solvent-dependent.

In MeCN, the ESR signal of **3a** exhibits 11 lines separated by 2.5 G (Figure 2a). The relative intensities of these lines are 1.0:2.0:3.5:2.8:2.7:2.8:2.7:2.6:3.2:2.0:1.0 at −40 °C. The symmetry of the structure allows us to determine $g_{av} = 2.0276$. In agreement with the computer simulation using an 80% Lorentzian–20% Gaussian line shape, this pattern corresponds to the coupling of the unpaired electron with two equivalent ^{14}N nuclei and with another ^{14}N nucleus ($A_{N1} = {}_{AN2} = 2.5$ G; $A_{N3} = 7.5$ G; line width = 1 G; Figure 2b). The IR spectrum of the solution shows two absorption bands in the ν_{NO} region centered at 1805 and 1735 cm^{-1}. Moreover, coordinated MeCN is evidenced by ν_{CN} frequency shift: 2305 and 2290 cm^{-1} vs. 2255 cm^{-1} for free MeCN.[5]

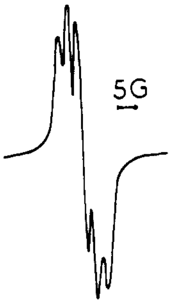

Figure 3. Isotropic ESR spectrum of **3b** in THF–PhMe (1:5) at −30 °C.

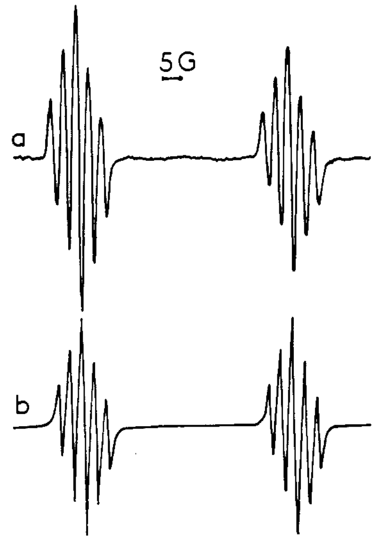

Figure 4. Isotropic ESR spectra of **4a**: (a) taken in MeCN–PhMe (1:9) at −10 °C; (b) computer simulated with $A_{N1} = A_{N2} = 3$ G, $A_P = 52.5$ G, and a line width of 1 G.

In THF, the ESR spectrum of **3b** exhibits five lines separated by 2.5 G. This spectrum is not well resolved so that it is difficult to measure the line intensities (Figure 3). However, this pattern is in agreement with the coupling of the unpaired electron with two equivalent ^{14}N nuclei ($A_N = 2.5$ G; $g_{av} = 2.0280$; −30 °C). The IR spectrum of the solution shows two absorption bands in the ν_{NO} region centered at 1810 and 1735 cm^{-1}.

Reaction of 3a or 3b with PR_3 Ligands. When a solution of **3a** or **3b** was reacted at −30 °C with PPh_3 or $P(OPh)_3$ fast exchange of coordinated solvent molecules occurred, leading to new paramagnetic species.

(a) Addition of PPh_3 To Give 4a. The ESR spectrum presents a doublet of five lines (1:2:3:2:1) separated by 3 G. The centers of the two groups of the five lines are separated by 52.5 G and the g_{av} factor equals 2.0256 (Figure 4a). This pattern corresponds to the interaction of the unpaired electron with one ^{31}P nucleus ($A_P = 52.5$ G) and two equivalent ^{14}N nuclei ($A_N = 3$ G), as shown by computer simulation (line width = 1 G; 80% Lorentzian–20% Gaussian line shape; Figure 4b). The IR spectrum shows two ν_{NO} bands centered at 1800 and 1725 cm^{-1}.

(b) Addition of $P(OPh)_3$ To Give 4b. Only a small amount of a paramagnetic complex similar to **4a** is formed even with a large excess of phosphite in the solution ($A_{N1} = A_{N2} = 3$ G; $A_P = 102$ G; $g_{av} = 2.0268$; −40 °C). The predominant paramagnetic species has the ESR parameters of **3a** (11 lines separated by 2.5 G; $g_{av} = 2.0283$; −40 °C).

Interpretation of the ESR and IR Results

For all the cationic complexes of **3** and **4**, the hfs of the ESR spectra indicates the presence of two equivalent ^{14}N (NO) nuclei For **3a** the distinction between ^{14}N of NO and MeCN was made

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[5] Ballivet, D.; Tkatchenko, I. *Inorg. Chem.* **1977**, *16*, 945–947 and references therein.

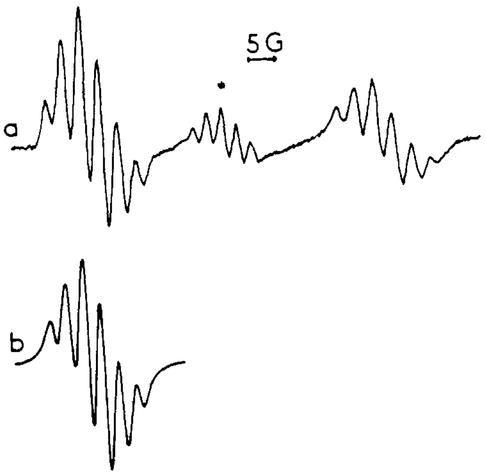
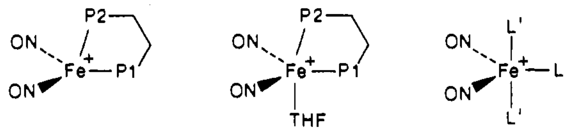


Figure 5. Isotropic ESR spectra of **7**: (a) taken in THF–PhMe (1:5) at −45 °C; (b) computer simulated for the low-field signal with $A_{N1} = A_{N2} = 3.2$ G, $A_{P2} = 2.8$ G, and a line width of 1.9 G. The asterisk denotes impurity.

possible by examining the modification of the hfs when THF replaces MeCN as the solvent or when PPh_3 ($P(OPh)_3$) was added to a solution of **3a**. Moreover, the IR results point out the presence of two NO ligands. In this class of complexes, where the coligands are respectively MeCN, THF, PPh_3, or $P(OPh)_3$, the $A_{N(NO)}$ value lies in the range 2.5–3 G. The additional hfs features show that the complexes can be formulated as $[Fe(NO)_2MeCN]^+$, $[Fe(NO)_2THF_n]^+$ (*n* unknown due to the unobservable coupling with THF), $[Fe(NO)_2PPh_3]^+$, and $[Fe(NO)_2P(OPh)_3]^+$. This formulation is quite unexpected on the basis of the electron configuration of the iron center. If one takes the NO ligand as a 3-electron donor, it leads to 15-electron complexes in solution. In the formalism developed by Enemark and Feltham, they correspond to $\{Fe(NO)_2\}^9$ moieties.[6] Two of them have been previously characterized by single-crystal X-ray diffraction techniques. The structures exemplify two coordination number possibilities in the solid state. A pseudotetrahedral arrangement was found for $Fe(NO)_2PPh_3Cl$ (**5**),[7] while a trigonal-bipyramidal one (TBP) was observed for $Fe(NO)_2[Me_2Ga(N_2C_5H_7)(OCH_2CH_2NMe_3)]$ (**6**).[8] In both complexes the NO are equivalent with a more pronounced Fe–N–O bending in the TBP geometry (158 vs. 166°). For our complexes **3**, **4a**, and **4b** one would have expected either a 17-electron configuration, $[Fe(NO)_2L_2]^+$, or a 19-electron configuration, $[Fe(NO)_2L_3]^+$, by analogy with **5** or **6**, respectively. The ESR silence of eventual additional coligands can be ascribed either to the lack of resolution in the hfs or to symmetry restriction.

Interestingly, in the presence of $PPh_2(CH_2)_2PPh_2$ (dppe) the ESR spectrum of **7** presents a doublet (55 G) of six lines with $g_{av} = 2.0209$ (Figure 5a). The computer simulation for the six lines indicated that this hfs corresponds to the presence of two equivalent ^{14}N nuclei (NO ligands), $A_{N1} = A_{N2} = 3.2$ G, and one nucleus of $I = {}^1/_2$, 2.8 G (line width 1.9 G; Figure 5b). Whereas the 55-G coupling constant is easily attributed to the ^{31}P nucleus (A_{P1}) by comparison to the spectrum of **4a**, the 2.8-G coupling constant is due either to another ^{31}P or to one ^1H nucleus[9] from dppe. If ^1H was involved, one should detect at least the presence of two protons arising from the CH_2 groups of the phosphine. Moreover, when dppe was replaced by *trans*-$PPh_2(CH{=}CH)PPh_2$, this additional coupling disappeared (see text below). These arguments lead to an interpretation of the hfs of **7** as arising from two equivalent ^{14}N and two nonequivalent ^{31}P nuclei. It is worth noting that **7** could not be obtained by addition of dppe to a solution of **3a** or **3b**. Species **7** was prepared by the one-electron oxidation of $Fe(NO)_2dppe$ with $NOPF_6$ at −45 °C.[10] In our opinion, this different reactivity pathway for dppe is relevant to its coordination modes. It acts as a chelating ligand in $Fe(NO)_2dppe$,[11] whereas when it is added to **3a** or **3b**, it could behave as a bridging ligand[12] leading to diamagnetic complexes (see Experimental Section). Of course dppe could also be monodentate[12] but a spectrum similar to that of **4a** should be obtained, as was observed when *trans*-$PPh_2(CH{=}CH)PPh_2$ was added to **3b**, giving **4c**, ($A_{N1} = A_{N2} = 3$ G; $A_P = 52$ G; $g_{av} = 2.0253$; −20 °C). The fact that the A_N and A_{P1} values with dppe are equivalent to those with PPh_3 or *trans*-$PPh_2(CH{=}CH)PPh_2$ strongly suggests that no important structural modification had occurred. The presence of an additional ^{31}P coupling, A_{P2}, with $A_{P2} << A_{P1}$, is attributed to a slight distortion of the geometry encountered with MeCN, THF, PPh_3, $P(OPh)_3$, and *trans*-$PPh_2(CH{=}CH)PPh_2$. In this context, the pseudotetrahedral arrangement of the complexes formulated as $[Fe(NO)_2L_2]^+$ in a C_{2v} symmetry can be discarded just because the two ^{31}P nuclei of dppe should exhibit the same couplings. The difference observed between the A_P's of dppe indicates a lower symmetry for the complex. The limiting case is Fe, $(NO)_2$, and one P (P1) coplanar and the other P nucleus (P2) out of this plane. Hence, we can consider P2 as a perturbation of the trigonal geometry (I, Chart I). If the SOMO is σ with respect to the Fe, $(NO)_2$, P1 plane, P2 is weakly coupled, as experimentally observed.

Chart I



I II: **7** III: **3a**, **3b**, **4a**, **4b**, **4c**

The ligand arrangement depicted in I gives the possibility for additional ligand coordination, leading to a distorted TBP geometry (II, Chart I). In the experiment, THF used as the solvent could occupy this fifth coordination site.

The replacement of the bidentate ligand, dppe, by monodentate ligands L, MeCN, PPh_3, or $P(OPh)_3$, is accompanied by the occurrence of only one A_L coupling in the ESR spectra of **3** and **4** while the two equivalent $A_{N(NO)}$'s remain. This result is explained in terms of constraint release going from a distorted TBP (II) to a nondistorted one with C_{2v} symmetry (III, Chart I), the SOMO being σ with respect to the Fe, $(NO)_2$, L plane. More confidence in this pentacoordinated possibility in solution was gained by carrying out noniterative extended Hückel calculations. Three models were taken into account. Two of them were with a perfect TBP geometry like III with both FeNO bond angle values of either 180 or 150° and with $L = L' = PH_3$. The third one considers the case of nonequivalent FeNO bond angles (180 and 120°). The calculations[13] unequivocally demonstrate that, as far as the C_{2v} symmetry is maintained in the TBP geometry, no axial ligand couplings can be observed.

In structure III with $L = PR_3$ (Chart I), the axial positions can be occupied either by the solvents THF, MeCN ($L \neq L'$) or by excess PR_3 ($L = L'$). For PPh_3, the evidence for its axial coordination came from the changes in g_{av} value as PPh_3:Fe was varied. This effect was better controlled by studying the ESR spectrum of $[Fe(NO)_3PPh_3]^+PF_6^-$[11] when dissolved in THF. This complex is diamagnetic in noncoordinating solvents such as CH_2Cl_2 or $MeNO_2$, but in THF or MeCN one NO ligand is displaced by solvent molecules,[14] leading to ESR signals even at temperatures

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as low as −50 °C. The ESR spectrum obtained is characteristic of the formation of species III (Chart I). A doublet of five lines is observed ($A_{N1} = A_{N2} = 3$ G; $A_P = 54$ G; $g_{a'} = 2.0204$; −20 °C) and is straightforwardly assigned to $[Fe(NO)_2PPh_3(THF)_2]^+PF_6^-$. Species **3b** ($[Fe(NO)_2(THF)_3]^+PF_6^-$) is also present in trace amounts probably due to PPh_3–THF competition for coordination. This behavior has been confirmed by the following experiments. Addition of $AgPF_6$ to the solution led to the presence of only species **3b** by trapping free PPh_3 in the solution. Further addition of PPh_3 restored the doublet of five lines. Independently, a THF solution of $[Fe(NO)_3PPh_3]^+$ in the presence of PPh_3 produced an ESR spectrum where two doublets of five lines can be distinguished. One of these doublets corresponds to $[Fe(NO)_2PPh_3(THF)_2]^+$. The other doublet is obtained pure for an initial PPh_3:Fe ratio of 3, and its parameters are unchanged as the amount of PPh_3 is increased ($A_{N1} = A_{N2} = 3$ G; $A_P = 52$ G; $g_{av} = 2.0250$; −20 °C). This signal is assigned to $[Fe(NO)_2(PPh_3)_3]^+$. This set of results points out that, in the TBP complexes, THF–PPh_3 competition occurs according to eq 2.

$$[Fe(NO)_2(THF)_3]^+ \xrightleftharpoons{PPh_3} [Fe(NO)_2PPh_3(THF)_2]^+ \xrightleftharpoons{2PPh_3} [Fe(NO)_2(PPh_3)_3]^+ \quad (2)$$

Discussion

Several evidences for the TBP structure of the $\{Fe(NO)_2\}^9$ radical cation in the presence of MeCN, THF, PPh_3, $P(OPh)_3$, and *trans*-$PPh_2CH{=}CHPPh_2$ have been presented.

The SOMO is confined in the equatorial plane of the TBP. Competition in the equatorial position was evidenced by MeCN–$P(OPh)_3$ and THF–PPh_3 experiments. $P(OPh)_3$ appears to be much less basic than MeCN as it could not totally displace the coordinated solvent. In the axial position, it has been shown that either THF or PPh_3 can be present.

The more interesting feature of the $[Fe(NO)_2LL'_2]^+$ complexes is their pentacoordination with a 19-electron configuration. Such a configuration was already reported for complex **6**.[8] However, one can argue that for **6** the presence of the tripod gallate ligand forces the pentacoordination. The tetracoordination has also been described for the 17-electron $Fe(NO)_2PPh_3Cl$ complex (**5**), which only has monodentate ligands.[7] Formally, the $[Fe(NO)_2LL'_2]^+$ species are issued from **5** by Cl^-–PF_6^- exchange so that one could have expected, for the new series **3** and **4**, the tetracoordination with a 17-electron configuration with the replacement of Cl^- by one ligand L. This is not the case. The presence of the cationic charge strongly modifies the electronic properties of the iron center. It creates a highly electrophilic iron ion that expands its coordination sphere and is able to induce the formation of a carbenium ion from a coordinated olefin.[4] The coordination of the olefin in the axial position is a favorable situation for the delocalization of the cationic charge onto the organic substrate.

It is known that NO ligands are strong π-acceptors so that they can accommodate the electron excess. Examples of this behavior have been recently reported for the 19-electron $Fe(NO)_2(CO)_2^-$,[15] $Fe(NO)_3CO$,[16] $Co(NO)_2(CO)_2$,[17] and $CpW(NO)_2P(OPh)_3$[18] complexes. For the four compounds, two NO ligands are equivalent. The molecular orbital schemes discussed show that the SOMO's have substantial NO 2π character. The X-ray structure of the tungsten complex reveals that the W–N–O bond angles are not far from linearity (170.3° average). Therefore this 19-electron configuration does not promote the bending of one NO ligand in order to get formally a 17-electron complex. The same behavior was found for the $[Fe(NO)_2LL']^+$ complexes described in this paper. On the bases of the ESR and IR results, the two NO ligands are equivalent and not far from linearity. A study by EDGE/EXAFS spectroscopies was undertaken to obtain more structural information on these 19-electron complexes in solution.[19]

Experimental Section

The complexes here studied are air- and moisture-sensitive. All syntheses and subsequent manipulations were conducted with exclusion of air and water by using Schlenk techniques.

Materials. Acetonitrile was distilled from CaH_2. Toluene and THF were distilled from sodium benzophenone ketyl.

The preparations of $[Fe(NO)_2Cl]_2$, $Fe(NO)_2(PPh_3)_2$, and $Fe(NO)_2$dppe are described in ref 3 and 20.

$AgClO_4$, $AgPF_6$, $AgBF_4$, and $NOPF_6$ were purchased from Alfa Inorganics and used as received.

PPh_3 and dppe were purified by repeated recrystallizations from ethanol. $P(OPh)_3$ was distilled under reduced pressure.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 597 spectrometer with CaF_2 or AgCl windows.

ESR spectra were recorded on a Varian E9 X-band instrument equipped with a variable-temperature accessory. Diphenylpicrylhydrazyl radical ($g = 2.0036$) was used as the external standard in a dual-cavity arrangement. Relative errors of the **g** tensor are ca. ±0.0003. The splitting patterns of the spectra were analyzed by computer simulation technique using the program SUPERB (CISI library) with an 80% Lorentzian–20% Gaussian line shape. Samples for the ESR studies were prepared by diluting the mother solutions with toluene in a quartz tube maintained under argon.

Preparation of the Radical Cations 3. A solution of 305 mg (1 mmol) of **1** in 20 mL of MeCN was added to 506 mg (2 mmol) of $AgPF_6$ in 20 mL of MeCN at −30 °C. After ca. 3 h of reaction, the ESR signal of the monomer $Fe(NO)_2Cl$ had disappeared and AgCl was separated from the solution by filtration, washed, and dried. The AgCl yield was 92%. The solution contained complex **3a** and was studied by ESR. Conductometric measurements performed at −30 °C in MeCN showed that **3a** behaves as a 1:1 electrolyte.[21] Attempts to get reproducible elemental analysis of **3a** failed due to its instability. Precipitation with Et_2O followed by drying under vacuum led to the progressive disappearance of the IR ν_{NO} bands at 1805 and 1735 cm^{-1} whereas two new ν_{NO} bands appeared at 2290 and 1830 cm^{-1}. The 2290-cm^{-1} band was due to the formation of $NOBF_4$.

The same procedure was followed when THF replaced MeCN as the solvent. The solution contained complex **3b** and was studied by ESR.

When $AgPF_6$ was replaced by $AgBF_4$, $AgClO_4$, or $TlBF_4$, the same radical cation **3a** or **3b** was formed, and AgCl or TlCl precipitated quantitatively.

At −30 °C, the ESR signal of species **3** was stable over a period of 16 h whereas, at 25 °C, it disappeared within 4 h.

Preparation of the Radical Cations 4. The addition of PPh_3 to the above mentioned solution of **3a** or **3b** at −30 °C in a 3:1 molar ratio afforded complex **4a** instantaneously. At 25 °C, **4a** decomposed into diamagnetic complexes after 40 min of reaction. $Fe(NO)_2(PPh_3)_2$ could be identified as one of the products.

The addition of $P(OPh)_3$ to a solution of **3a** at −30 °C in a 3:1 molar ratio afforded complex **4b** in small amounts. Neither a prolonged reaction time (19 h) nor a large excess of phosphite (10-fold excess) increased the ESR signal of **4b**.

Reaction of 3a or 3b with dppe. The addition of dppe to a solution of **3a** or **3b** led, even at −65 °C, to a diamagnetic solution. With a 1.5:1 molar ratio, equimolar amounts of $Fe(NO)_2$dppe (yield 50%) and of $[Fe(NO)(dppe)_2]^+PF_6^-$ (yield 50%) were isolated after 3 h of reaction at 25 °C and characterized by IR, ^{31}P NMR, and elemental analyses.

Reaction of $Fe(NO)_2$dppe with $NOPF_6$. A solution of 57.6 mg (0.11 mmol) of $Fe(NO)_2$dppe in 20 mL of THF was added to 29.1 mg (0.16 mmol) of $NOPF_6$ in 4 mL of THF at −45 °C. After 30 min of reaction, the ESR spectrum was recorded. After the experiment, the mother solution was evaporated to dryness at 25 °C. No phosphine oxide was detected by IR and TLC techniques.

Reaction of $Fe(NO)_2(PPh_3)_2$ with $NOPF_6$. A solution of 77 mg (0.1 mmol) of $Fe(NO)_2(PPh_3)_2$ in 20 mL of THF was added to 18 mg (0.1 mmol) of $NOPF_6$ in 4 mL of THF at −40 °C. After 15 min of reaction,

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the ESR spectrum was recorded at increasing temperatures (−40 to +25 °C). After the experiment, the mother solution was evaporated to dryness at 25 °C. No phosphine oxide was detected.

Acknowledgment. We thank Dr. I. Tkatchenko and Dr. H. Faucher for helpful discussions and J. F. Dutel for technical assistance in the ESR experiments.

Registry No. **1**, 21576-91-0; **3a**, 103437-84-9; **3b**, 103437-86-1; **4a**, 103437-89-4; **4b**, 103437-87-2; $[\mathrm{Fe(NO)_2(PPh_3)_3}]^+$, 103437-88-3; $\mathrm{Fe(NO)_2}$dppe, 15683-28-0; $[\mathrm{Fe(NO)(dppe)_2}]^+\mathrm{PF_6}^-$, 52194-32-8; $\mathrm{Fe(NO)_2(PPh_3)_2}$, 14056-98-5.

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Effect of Arene Methylation on Photochemical Arene Replacement Reactions of $[(\eta^5\text{-}\mathrm{C_5(CH_3)_5})\mathrm{M}(\eta^6\text{-arene})]^+$ (M = Fe, Ru) Complexes

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Received October 28, 1985

The quantum yields (ϕ) for the photochemical arene release from $[\mathrm{Cp^*M}(\eta^6\text{-arene})]^+$ complexes (Cp* = η^5-pentamethylcyclopentadienyl) have been measured for M = Fe(II) and Ru(II) in acetonitrile solutions at room temperature. (Fe: arene = toluene (ϕ = 0.007), hexamethylbenzene (ϕ = 0.00002). Ru: arene = benzene (ϕ = 0.19), mesitylene (ϕ = 0.025), hexamethylbenzene (ϕ = 0.0019).) For both M = Fe and Ru, permethylation of the cyclopentadienyl ligand decreases the arene release quantum yields as compared to those of the analogous cyclopentadienyl compounds. For M = Fe, the decreases are factors of 113 and 20 500, respectively, for arene = toluene and hexamethylbenzene. The very large decrease observed for the (pentamethylcyclopentadienyl)(hexamethylbenzene)iron complex is consistent with an important steric blocking effect of the five pentamethylcyclopentadienyl methyl groups. For the three (pentamethylcyclopentadienyl)ruthenium compounds studied, decreases are more modest relative to the cyclopentadienyl compounds (1.8, 3.4, and 7.4 for M = Ru, where arene = benzene, mesitylene, and hexamethylbenzene). In this case, a linear correlation persists between log ($\phi/(1-\phi)$) and σ_p, the Hammett parameter for methyl substituents. The linearity of the log ($\phi/(1-\phi)$) vs. σ_p plot indicates that steric effects are not present to hinder the participation of acetonitrile in the transition state of the highly methylated Ru complexes studied. The increase in the Hammett ρ parameter from +1.38 to +2.05 upon cyclopentadienyl methylation of the Ru complexes suggests a slight increase in negative charge occurs at the arene in the arene release transition state of the pentamethylcyclopentadienyl complexes relative to the cyclopentadienyl complexes.

Introduction

A recent investigation of the mechanism of photochemical arene release from $[\mathrm{CpM}(\eta^6\text{-arene})]^+$ complexes (Cp = η^5-cyclopentadienyl; M = Fe, Ru; arene = alkyl- or Cl-substituted benzenes) revealed electronic and steric inhibition of the arene release quantum yield for alkyl arene substituents.[1] The electronic effect exists for complexes of both metals but was slightly more important for the ruthenium compounds. The steric effect that results either from a high degree of arene methylation (five or six methyl groups) or from very bulky (ethyl or *tert*-butyl) arene substituents protects the excited metal center from nucleophilic attack. This steric effect is much more pronounced in the iron complexes. We have now extended our studies to the η^5-pentamethylcyclopentadienyl (Cp*) complexes of iron and ruthenium. These studies show that the decreases in the arene replacement quantum yields that occur on permethylation of the cyclopentadienyl ring in the ruthenium complexes result from an electronic effect, while the larger decreases observed for the iron systems result from a steric effect.

Experimental Section

General Considerations. All solvents were of spectroscopic grade and were used without further purification unless otherwise noted.

Dichloromethane and acetonitrile were dried over activated alumina or activated 4-Å molecular sieves prior to use. $\mathrm{NH_4PF_6}$ was purchased from Pennwalt Inc. $\mathrm{Ru_3(CO)_{12}}$ was purchased from Strem Chemicals. All other reagents were purchased as reagent grade and used as received. UV-visible spectra were obtained on either a Cary 17D or a Hewlett-Packard 8450 A spectrophotometer. ^{1}H NMR spectra were obtained for acetone-d_6 solutions of the compounds with a Varian CFT 20 spectrometer equipped with a proton accessory.

Synthesis of $[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]\mathrm{PF_6}$ Compounds. $[\mathrm{Cp^*Fe(CO)_3}]\mathrm{PF_6}$ was synthesized by the method of Catheline and Astruc.[2] $[\mathrm{Cp^*Fe}(\eta^6\text{-HMB})]\mathrm{PF_6}$ (HMB = hexamethylbenzene) was synthesized by the method of Hamon et al.,[3] with the improvement suggested by Roman[4] for the corresponding Cp complexes.

$[\mathrm{Cp^*Fe}(\eta^6\text{-tol})]\mathrm{PF_6}$ (tol = toluene) was obtained by metal atom techniques[5] as a gift of the 3M Co. The complete details of the synthesis and characterization of this compound will be reported later.

Synthesis of $[\mathrm{Cp^*Ru}(\eta^6\text{-arene})]\mathrm{PF_6}$ Compounds. $[\mathrm{(C_6H_6)RuCl_2}]_2$,[6] $(n\text{-Bu})_3\mathrm{Sn(C_5(CH_3)_5)}$,[7] and $[\mathrm{Cp^*Ru(CO)_2}]_2$[8] were prepared by literature procedures.

$[\mathrm{Cp^*Ru}(\eta^6\text{-C_6H_6})]\mathrm{PF_6}$. (a) Method I. A sample of 0.9577 g (1.915 mmol) of $[\mathrm{(C_6H_6)RuCl_2}]_2$ was placed under nitrogen in 75–100 mL of freshly distilled acetonitrile. Approximately 2 mL (~3.4 mmol) of $(n\text{-Bu})_3\mathrm{Sn(C_5(CH_3)_5)}$ was then added, and the solution was refluxed for 18.5 h. The resultant solution was dark red-brown. The solvent was removed under vacuum to leave a dark oily residue. Distilled water (~500 mL) was added to this residue, and the mixture was filtered to give a pale yellow filtrate. Excess $\mathrm{NH_4PF_6}$ was added, causing precipitation of a brown solid, which was collected by filtration. Elution of the brown solid through a short alumina column with acetone gave a mixture of yellow $(n\text{-Bu})_3\mathrm{SnCl}$ and a white solid. Two recrystallizations from acetone/ether gave 0.5456 g (1.188 mmol) of white microcrystalline $[\mathrm{Cp^*Ru}(\eta^6\text{-C_6H_6})]\mathrm{PF_6}$ (31% yield). Mp: 310–313 °C dec. ^{1}H NMR (solvent acetone-d_6): δ 606 (s, $\mathrm{C_6H_6}$, 6 H), 2.08 (s, Cp*, 15 H). Anal. Calcd for $\mathrm{C_{16}H_{21}RuPF_6}$: C, 41.83; H, 4.61. Found: C, 42.01; H, 4.67.

(b) Method II. A stirred solution of 0.363 g (0.621 mmol) of $[\mathrm{Cp^*Ru(CO)_2}]_2$ in 30 mL of dry dichloromethane was cooled in an ice bath. A solution of 0.33 mL (6.44 mmol) of $\mathrm{Br_2}$ dissolved in 10 mL of dry, degassed dichloromethane was slowly added by cannula. After the solution was stirred for an additional 40 min, the solvent was evaporated

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