EPR Characterization of the Products Formed after Photolysis of [Co^{III}(Salen)(CH$_3$)(H$_2$O)] and [Co^{III}(SaltMe)(CH$_3$)(H$_2$O)] in the Presence of N- and P-donor Bases

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Introduction

Organocobalt(III) complexes with Schiff base equatorial units have been extensively used as models of organocobalamins,[1,2] which are important cofactors in many enzymatic processes. Structural, kinetic, and spectroscopic studies have been performed in organocobalamins and in several model compounds to assess the steric and electronic contributions that labilize the cobalt−carbon bond.[1−5] Organocobalt(III) complexes with 3- and 4-substituted pyridines have been extensively studied to probe electronic effects, and those with phosphines to probe steric contributions.[1a,3]

Previous studies concerning EPR characterization of photolysis products of cobalamins and model compounds have shown that the reactivity of the cobalt(II) fragments depends largely on the equatorial moiety, and an understanding of the determining factors in the formation of 1:1 or 1:2 adducts has been the objective of intense research.[4−7] The purpose of this work is to use EPR spectroscopy to understand the photolysis mechanism of anaerobic solutions of [Co^{III}(Schiff base)(CH$_3$)(H$_2$O)] in aprotic solvents and in the presence of several N- and P-donor bases and to characterize the behavior of the cobalt(II) fragments formed upon photolysis. Two Schiff base ligands were used, salen = *N*,*N*′-ethylenebis(salicylideneiminato) and saltMe = *N*,*N*′-(1,2-dimethyl)butanebis(salicylideneiminato), in an attempt to correlate the reactivity of the cobalt(II) complexes formed upon irradiation with the electronic and steric effects of the axial ligands.

Experimental Section

Solvents were purchased from Merck, and all other chemicals from Aldrich. All solvents used in EPR experiments were purified by standard methods[8] and stored under nitrogen. The cobalt(II) complexes were prepared from CoCl$_2$ and the corresponding Schiff base ligand using published procedures.[9] All manipulations were carried out under nitrogen; the solvents were deoxygenated with nitrogen, and all solids were degassed under vacuum. The samples to be irradiated were prepared by adding the N- or P-donor base to solutions of the aqua(methyl)cobalt(III) complexes in toluene/dichloromethane (2:1). Photolysis was performed with a Hg lamp (250 W Philips HP/T; $\lambda = 560-580$ nm), and X-band EPR spectral measurements were made on a Bruker ESP E-300 instrument. EPR spectral simulations were performed using a program based on Pilbrow's formalism.[10] The best fit was observed for collinear **g** and **A(Co)** tensors, neglecting any quadrupolar interactions and assuming **g** and **A(P)** to have the same principal axes. The spin Hamiltonian parameters were calculated assuming an $^2A_1$ ground state.[11]

Results and Discussion

Reaction of [Co^{III}(Schiff Base)(CH$_3$)(H$_2$O)] with N- and P-Donor Bases. The addition of N- and P-donor bases to solutions of [Co^{III}(Schiff base)(R)(H$_2$O)] results in the rapid replacement of water molecules,[1,12] and with excess base, typically only base-bound alkylcobalt(III) species are present in solution.[13] This methodology provides a means for obtaining base-bound alkylcobalt(III) complexes that avoids the need to isolate these compounds.[1−5] In the present study, the extent of water replacement was found to depend on the type and amount of base and on the equatorial ligand. For solutions with a less than 10-fold molar excess of base, the optical electronic spectra are consistent with partial or no water replacement, and the solutions contain, most often, a mixture of [Co^{III}(Schiff base)(CH$_3$)(H$_2$O)], [Co^{III}(Schiff base)(CH$_3$)], and [Co^{III}(Schiff base)(CH$_3$)(L)]. In the presence of base:metal complex ratios greater than 10:1, water replacement is complete for pyridines; for phosphines, even with a base:metal ratio of 20:1, water replacement is not complete.

Photolysis in Frozen Matrix (77 K). Solutions of [Co^{III}(Schiff base)(CH$_3$)(H$_2$O)] irradiated and observed at 77 K are EPR silent, even after relaxation to fluid solutions and re-cooling to 77 K. These results suggest that, under these conditions, homolysis of the cobalt−carbon bond is not accomplished by photolysis with visible light.

EPR spectra, recorded at 77 K, of irradiated frozen solutions in toluene/dichloromethane of [Co^{III}(Schiff base)(CH$_3$)(H$_2$O)] in the presence of a 10-fold excess of base show one signal that is ascribed to a five-coordinate cobalt(II) complex, [Co^{II}(Schiff base)(L)], and a strong and much narrower signal centered at $g \approx 2.00$ that is attributed to an alkyl radical or to

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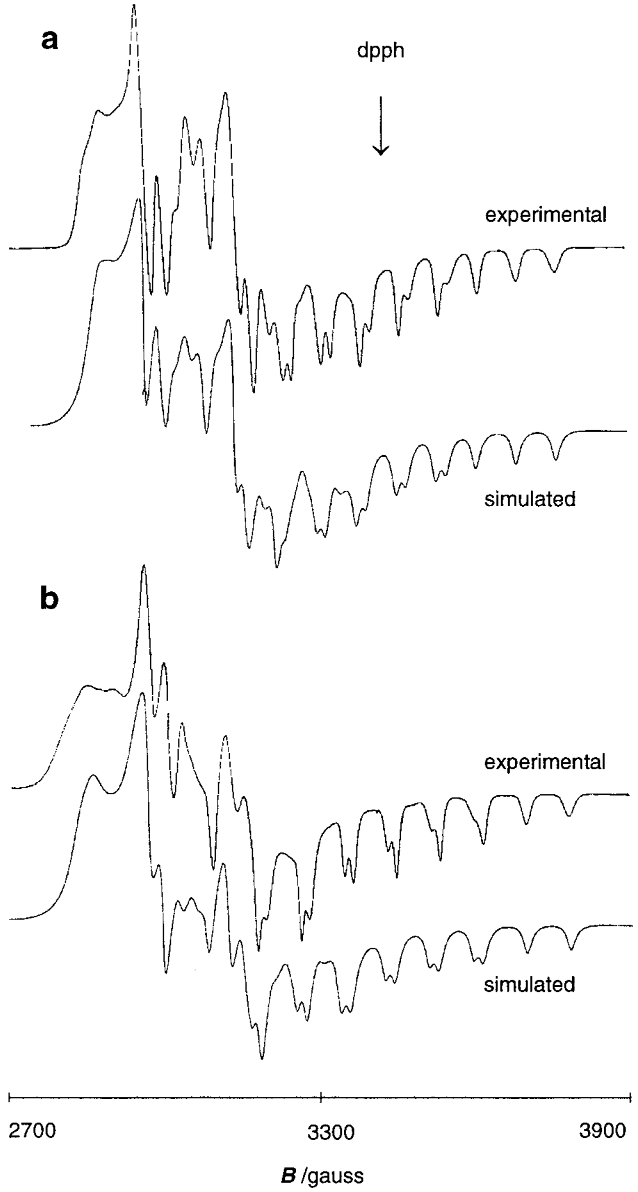

Figure 1. Experimental and simulated EPR spectra in frozen solution (77 K) observed after room-temperature photolysis of a toluene/dichloromethane solution of [Co^{III}(salen)(CH$_3$)(H$_2$O)] to which were added in a 20:1 molar ratio (a) phenyldimethylphosphine and (b) triphenylphosphine.

a product of the reaction of the alkyl radicals with solvent molecules.[14] This latter signal is lost just above the softening point of the glass, and the spectra of re-cooled frozen solutions exhibit only the signal of the five-coordinate cobalt(II) complex.

In the high-field region, spectra with phosphines exhibit hyperfine coupling to cobalt (^{59}Co, $I = {}^7/_2$) and to *one* phosphorus atom (^{31}P, $I = {}^1/_2$) (Figure 1), implying coordination of one molecule of the P-donor base (type B) and formation of five-coordinate complexes. In spectra with pyridines, each cobalt hyperfine line is split into three lines with relative intensity 1:1:1 (type C), implying formation of a five-coordinate compound as each cobalt atom interacts with *one* molecule of nitrogen base (^{14}N, $I = 1$) (Figure 2a).

Photolysis in Fluid Solutions. Room-temperature irradiation of [Co^{III}(Schiff base)(CH$_3$)(H$_2$O)] solutions results in frozen EPR spectra with large **g**-tensor anisotropy (type A), which are identical to spectra attributed to the species [Co^{II}(Schiff base)], probably weakly solvated.[15]

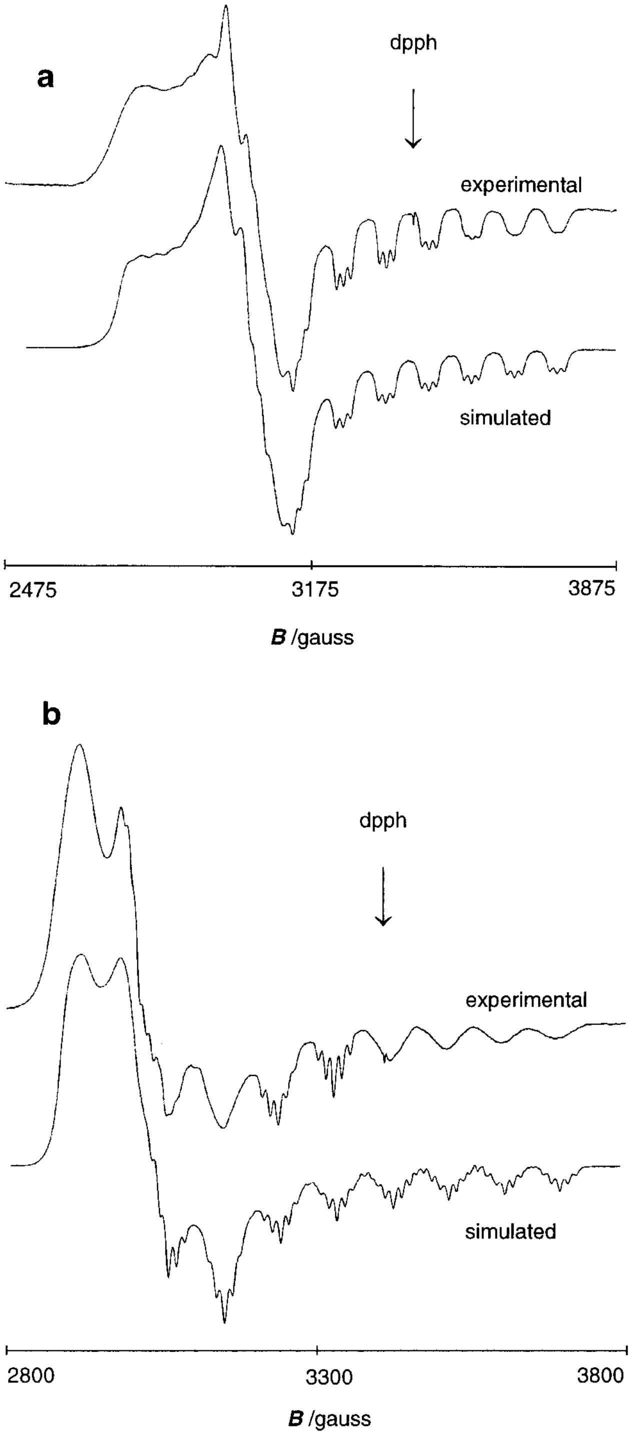

Figure 2. Experimental and simulated EPR spectra in frozen solution (77 K) observed after room-temperature photolysis of a toluene/dichloromethane solution of [Co^{III}(salen)(CH$_3$)(H$_2$O)] to which pyridine was added in (a) a 1:1 molar ratio and (b) a 10:1 molar ratio.

Pyridine Adducts. For photolyzed solutions of [Co^{III}(saltMe)(CH$_3$)(H$_2$O)] with pyridines, the type of complex formed is *independent* of the amount of N-donor base added (Table 1). EPR spectra are identical to those observed after photolysis at 77 K (type C), implying the formation of a five-coordinate compound.

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Table 1. Stoichiometry of the Cobalt(II) Complexes Formed after Room-Temperature Photolysis of [Co^{III}(Schiff base)(CH_3)(H_2O)] in Toluene/Dichloromethane Solutions to Which a Lewis Base Was Added in Different Molar Ratios

complex	axial ligand	PA[a]	TCA[b]	number of bases coordinated axially to Co(II)			
				1:1 Co:axial ligand	1:2 Co:axial ligand	1:10 Co:axial ligand	1:30 Co:axial ligand
[CH_3Co(salen)H_2O]	py	924		1	1	2	2
	4-CNpy	882		1	1 + 2	2	2
	4-Mepy	940		1	1	2	2
	4-Etpy	942		1	1	2	2
	4-N(Me)$_2$py	970		1	1	1 + 2	1 + 2
	3-CNpy	882		1	1 + 2	2	2
	3-Clpy	899		1	1 + 2	2	2
	3-Brpy	900		1	1 + 2	2	2
	3-Mepy	937		1	1	1 + 2	1 + 2
	3-Etpy	938		1	1	1 + 2	1 + 2
	PMe_2Ph		125	1	1	1	1
	PEt_3		130	1	1	1	1
	PBu_3		132	1	1	1	1
	$PMePh_2$		137	1	1	1	1
	$PBuPh_2$		145	1	1	1	1
	PPh_3		152	1	1	1	1
[CH_3Co(saltme)H_2O]	py	924		1	1	1	1
	4-CNpy	882		1	1	1	1
	4-Mepy	940		1	1	1	1
	4-Etpy	942		1	1	1	1
	4-N(Me)$_2$py	970		1	1	1	1
	3-CNpy	882		1	1	1	1
	3-Clpy	899		1	1	1	1
	3-Brpy	900		1	1	1	1
	3-Mepy	937		1	1	1	1
	3-Etpy	938		1	1	1	1
	PMe_2Ph		125	1	1	1	1
	PEt_3		130	1	1	1	1
	PBu_3		132	1	1	1	1
	$PMePh_2$		137	1	1	1	1
	$PBuPh_2$		145	0 + 1	0 + 1	1	1
	PPh_3		152	0 + 1	0 + 1	0 + 1	1

[a] Proton affinity (PA), values in kJ mol^{-1}, from ref 21. [b] Tolman cone angle (TCA), from ref 26.

In contrast, solutions of [Co^{III}(salen)(CH_3)(H_2O)] with pyridines yield three types of EPR spectra, depending on the amount of added base (Table 1). With equimolar ratios of [Co^{III}(salen)(CH_3)(H_2O)]:base, spectra of type C were always observed (Figure 2a), whereas for higher amounts of base, different results were obtained. For a 10-fold excess of base [except for 3-Etpy, 3-Mepy, and 4-(NMe_2)py], each cobalt hyperfine line in the EPR spectra is split into five lines with relative intensity 1:3:5:3:1 (type D), a pattern indicative of an interaction of the cobalt atom with two pyridine molecules (Figure 2b), thus supporting formation of [Co^{II}(salen)(L_2)]. For intermediate molar ratios, the observed spectra exhibit a superposition of two signals, one of type C and another of type D, implying the simultaneous existence of complexes with one and two pyridines bound to the metal. However, for 3-Mepy, 3-Etpy, and 4-(NMe_2)py, even in the presence of a 20-fold excess of base, the EPR spectra always show a mixture of signals arising from [Co^{II}(salen)(L)] and [Co^{II}(salen)(L_2)].

Phosphine Adducts. For [Co^{III}(salen)(CH_3)(H_2O)], the spectra are independent of the amount of base added (Table 1) and are identical to those observed for photolyzed solutions at 77 K (type B). Solutions of [Co^{III}(saltMe)(CH_3)(H_2O)] irradiated in the presence of any amount of PMe_2Ph, PEt_3, PBu_3, or $PMePh_2$ exhibit EPR spectra of type B, thus indicating formation of [Co^{II}(saltMe)(L)]. However, EPR spectra of photolyzed solutions of [Co^{III}(saltMe)(CH_3)(H_2O)] with *equimolar* ratios of the bulkier phosphines, $PBuPh_2$ and PPh_3, exhibit signals assigned to [Co^{II}(saltMe)(L)] (type B) and to a complex with *no* axially bound phosphine (type A). Increasing the amount of phosphine decreases the intensity of the type A signal, and in the presence of a 20-fold excess of base, only type B spectra are observed. EPR data provide a clear indication that cobalt(II) complexes with the Schiff bases studied do not form species with two axially bound phosphines.

Photololysis Mechanism. Photolysis of frozen solutions of alkylcobalamins[9,14,16] and model compounds[4,5,14−19] with bound pyridine or phosphine molecules has been extensively studied. The resulting products have been found to originate from homolytic fission of the Co−C bond after light absorption that moves an electron from the equatorial ligand into the antibonding Co(d_{z^2}) σ^* orbital.[14] Photolyzed solutions of the alkyl−Schiff base−cobalt(III) system studied in this work exhibit EPR spectra similar to those reported, thus implying that irradiation with visible light induces homolytic cleavage of the Co−C bond.

The same mechanism must be operative for photolysis in a fluid matrix, as solutions irradiated at 77 K, warmed to room temperature, and re-cooled exhibit only EPR signals due to cobalt(II) species, which are *identical* to those obtained when the photolysis is performed in a fluid matrix. For fluid solutions of salen complexes with excess N-donor base, the five-coordinate cobalt(II) binds a second base molecule, whereas for all other cases, five-coordinate cobalt(II) species do not react

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with excess base in solution. This latter behavior is similar to that observed for the final photolysis products of alkylcobaloximes in the presence of phosphines, for which stable five-coordinate cobalt(II) complexes were observed, even in the presence of large excesses of base.[4,5] In contrast, solutions of alkyl(pyridine)cobaloximes exhibit EPR bands due to a Co(II) complex with two bound pyridine molecules.[4,5] The different behavior of cobalt(II) phosphine and pyridine complexes was attributed to strong steric interactions between the phosphine and the equatorial system, which induce structural modifications that hinder binding of a second molecule of base.

Structural Information from EPR Data. The X-ray structures of [Co^{II}(salen)(py)],[20a] [Co^{II}(salen)(NO)],[20b] [Co^{II}(salen)(py)],[20c] and [Co^{II}(3-MeOsalen)(H_2O)][20d] have been reported. In all of these structures, the cobalt atom lies 0.20−0.43 Å above the equatorial plane, and the two salicylaldehyde fragments are bent away from the axial ligand. On the basis of structural data, it can be suggested that stabilization of five-coordinate species occurs by moving the metal atom away from the equatorial plane and by bending the equatorial ligand away from the axial ligand.

For five-coordinate complexes with pyridines, a plot of $g_\perp$ or g_z against base strength, as quantified by the base proton affinities (PA),[21] shows different relations for 3- and 4-substituted pyridines. For 4-substituted pyridines, we observed a linear decrease of $g_\perp$ and a linear increase of g_z with increasing PA. This result implies shorter Co−N bond lengths for the stronger bases, as a decrease in the axial bond length increases the antibonding d_{z^2} orbital energy.[6,22] In contrast, for 3-substituted pyridines, a linear dependence of both $g_\perp$ and g_z with PA is observed only for the weaker bases; 3-methyl- and 3-ethylpyridines do not fall in line with the other pyridines. This behavior can be ascribed to steric repulsions of the alkyl groups with the equatorial moiety, which do not allow the expected short Co−N distances as observed for sterically nondemanding 4-substituted pyridines.

EPR data are thus compatible with a decrease in the Co−N_{axial} bond length for stronger bases, which must impose structural modifications in the complex. The proximity of the two atoms must promote a longer displacement of the cobalt atom from the equatorial plane, thus rendering the sixth position less accessible for binding a second molecule. Stronger steric repulsions are expected for compounds with the bulkier equatorial ligand, [Co^{II}(saltMe)L], arising from interactions between the axial base and the methyl groups on the equatorial ligand ethylenic bridge, thus implying weaker axial base interactions and more extensive structural distortions.

We stress that there is a relationship between the total spin density on cobalt (or on the axial nitrogen) and the axial base strength for pyridines, and it is of interest to assess the applicability of the LFER models developed in organic chemistry. We used the dual parameter approach (DSP) and tried to fit the values of A_{av}(Co) and A_z(N) to an equation of the form $\Delta R = \rho_I\sigma_I + \rho_R\sigma_{R+}$, where ΔR is the difference between A_{av}(Co), or A_z(N), in pyridine and substituted pyridines, and σ_I and σ_{R+} have their usual meaning.[23,24] Straight lines were obtained for 4-substituted pyridines, and the ratios ρ_R/ρ_I were close to 1. This ratio for proton affinity values is 1.16, which indicates that inductive and resonance effects are of similar magnitude in proton affinities and in unpaired spin densities.

Application of the above equation to 3-substituted pyridines failed for salen complexes and was only marginally acceptable for A_{av}(Co) of saltMe complexes. Introduction of the steric parameter proposed by Brown[25] provides the more complex equation $\Delta R = \rho_I\sigma_I + \rho_R\sigma_{R+} + \rho_S\sigma_S$, which does fit our data. The results show that steric effects are important and that they are markedly different for saltMe and salen complexes, with the paradoxical observation that the latter are more sensitive to steric effects. Possibly, saltMe complexes with one bound pyridine are already extensively distorted, and as such, the possibility of being good indicators of subtle steric effects is lost.

For five-coordinate adducts with phosphines, no correlation between spin Hamiltonian parameters and Tolman's electronic parameter, χ, could be found. However, these parameters correlate with Tolman's cone angle (TCA),[26] an indication that steric effects are dominant. For complexes with salen, the values of $g_\perp$ increase with phosphine bulkiness, thus implying longer Co−P bonds for the bulkier axial ligands. This interpretation is supported by the observation that bulkier phosphines exhibit smaller phosphorus hyperfine coupling constants: as A(P) decreases, so does the unpaired spin density on the phosphorus s orbital. A similar behavior was observed for complexes with saltMe, but only for phosphines with TCA smaller than ∼140°; above this value, an increase in TCA does not change $g_\perp$ or A, an apparent indication that the Co−P bond length does not increase above a certain limit. A rationale for the observed behavior can be obtained by proposing that the deformation imposed on the equatorial ligand has reached a limit and that longer bonds would preclude bond formation. Bulky phosphines induce more extensive steric repulsions with the equatorial moiety, resulting in greater displacements of the cobalt atom toward the axial base and/or higher tilt of the equatorial moiety and, consequently, less reactive five-coordinate adducts.

Our results on photolysis of [Co^{III}(Schiff base)(CH_3)(H_2O)] in the presence of N-donor and P-donor bases indicate that the reactivity and stability of the homolysis fragments is largely dependent on electronic and steric effects for N-donor bases and on steric effects for P-donor bases. The stronger 4-substituted pyridines, pyridines with alkyl groups in position 3, and bulky phosphines induce distortions in the equatorial moiety that promote stabilization of the five-coordinate species formed upon homolysis.

Supporting Information Available: Details of the DSP analysis of spin density data; EPR parameters for the photolysis products in the presence of N-donor (Table S1) and P-donor (Table S2) bases; EPR spectra, 77 K, of [Co^{III}(salen)(CH_3)(H_2O)] after room-temperature photolysis (Figure S1); plots of $g_\perp$ and g_z vs proton affinity of pyridines (Figure S2); and plots of $g_\perp$ and A_{av}(P) vs proton Tolman's cone angle (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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