was present at the C-6 syn position (which overlaps the signals of the C-5 and the methoxy protons). That is, the addition of deuterium proceeded with 60% retention and 40% inversion in the formation of **3**-*d*.

These results are quite different from most ground-state electrophilic and nucleophilic ring openings of cyclopropanes where predominant or exclusive inversion at the site of nucleophilic attack is the rule,[3a,b] in contrast to the predominant retention in the present case. In this respect our observations are somewhat similar to those on the addition of HBr to **1** which proceeds with retention of configuration at both sites of attack.[3b] However, the preferential formation of the more hindered syn product here and the pattern of the substituent effects observed in the diphenylcyclopropane case which indicate ionic intermediates are probably not involved[1] suggest a pathway for the photochemical addition different from the carbonium ion mechanism postulated in the HBr and other electrophilic additions.

We prefer a mechanism involving attack of methanol on an excited polarizable arylcyclopropane, the addition of proton and nucleophile being concerted and not involving any highly charged intermediates.[11] The reason for the intriguing predominance of retention of configuration in the attack is unknown. We are currently investigating the photochemical addition of other hydroxylic solvents of varying size, acidity, and polarity to **1** in order to probe this matter further.

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(11) The bonds to proton and nucleophile need not be formed to the same extent throughout the course of the addition. Moreover, the proton and nucleophile need not come from the same molecule. Such would be the case where inversion is observed.

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Cobalt(II)-Tetraphenylporphyrin Complex with Carbon Monoxide

Sir:

Planar low-spin cobalt(II) complexes have recently served as models for reversible O_2 carrying systems[1–4] and in understanding aspects of vitamin B_{12} chemistry.[4–6] The cobalt(II) analog of hemoglobin (coboglobin) has recently been synthesized and reported to form O_2 complexes reversibly, but attempts to observe an interaction of carbon monoxide with coboglobin and with the separated metalloporphyrin, cobalt(II) protoporphyrin IX dimethyl ester, were unsuccessful.[3] Reactions of CO with vitamin B_{12} derivatives and cobaloximes have been extensively studied. The reduction of cobaloxime(III) by CO is catalyzed by cobaloxime(II).[5] This reaction is thought to involve an interaction of CO with cobaloxime(II), but no direct evidence for an adduct has been reported. Complexes of CO with methylcobaloxime(III)[7] and cobaloxime(I)[8] have been identified, but to our knowledge no carbon monoxide adduct of a cobalt(II) corrin, oxime, or porphyrin complex has been reported.

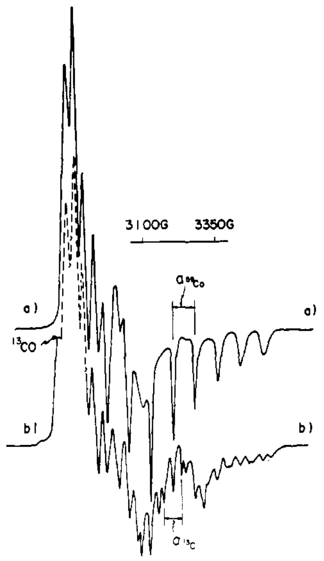

Figure 1. Epr spectra for the 1:1 carbon monoxide adduct of cobalt(II) tetraphenylporphyrin: (a) ^{12}CO; (b) 55% ^{13}CO, 45% ^{12}CO.

We wish to report that cobalt(II) tetraphenylporphyrin [Co(TPP)] forms a 1:1 adduct with CO which can be conveniently studied by epr in frozen solutions. In addition to the possible biological interest in the interaction of CO with cobalt(II) porphyrins, paramagnetic low-spin d^7 complexes of this type have a single unpaired electron in the d_{z^2} used in σ bonding with CO and provide an unusual opportunity to examine the σ spin delocalization to carbon monoxide.

Samples for epr studies were prepared in a vacuum line by subjecting degassed toluene solutions of cobalt(II) tetraphenylporphyrin to CO gas (155 mm, 296°K) and cooling to N_2 temperature. Representative epr spectra for both ^{12}CO and enriched ^{13}CO adducts of Co(TPP) appear in Figure 1. Measurements of the epr line intensities in the 55% ^{13}CO sample show that each peak in the ^{12}CO adduct splits into two equal intensity components in the ^{13}CO adduct which demonstrates the presence of a 1:1 complex with carbon monoxide (theoretical intensity ratio $^{13}C/^{12}C = 0.61$; observed ratio $= 0.64 \pm 0.05$). The epr parameters for Co(TPP) and 1:1 adducts with CO and CH_3CN in frozen toluene solution (90°K) appear in Table I. Epr data for the CO adduct are consistent with an axially symmetric complex with a $(d_{xz,yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Solving the relationships for

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Table I. Epr Parameters for Frozen Toluene Solutions of CoTPP and 1:1 Adducts of CO and CH_3CN (90 °K)

Complex	$g_{\parallel}$	$A(^{59}Co)$,[b] G	$a(^{13}C$ or $^{14}N)$, G	$g_{\perp}$	$B(^{59}Co)$,[b] G	$b(^{13}C)$, G
CoTPP[a]	1.97	161 (0.0141)		2.80	153 (0.0210)	
CoTPP–CO	2.017	+77.6 (0.00734)	62	2.217	−33 (0.0034)	54
CoTPP–$NCCH_3$	2.028	+91.6 (0.00866)	15.6	2.364	−23 (0.0026)	

[a] Epr parameters from second-order analysis including quadrupole effects. [b] Values in parentheses are in cm^{-1}. A and B are the ^{59}Co hyperfine coupling components along and normal to the principal magnetic axis.

axially symmetric complexes with the $(d_{z^2})^1$ configuration

$$g_{\perp} = 2.002 - 6\xi_{\text{eff}}/\Delta E_{xz,yz\rightarrow z^2}$$

$$A = P[-K + (4/7) - (1/7)(g_{\perp} - 2.002)]$$

$$B = P[-K - (2/7) - 45/7)]\xi_{\text{eff}}/\Delta E_{xz,yz\rightarrow z^2}]$$

gives physically acceptable results (P is intrinsically positive) only when A is positive and B negative. The resulting parameters for the CO adduct ($P = 0.017$ cm^{-1}, $K = 0.119$, $\Delta E_{xz,yz\rightarrow z^2} = 10{,}500$ cm^{-1}) are comparable to other square-pyramidal low-spin Co(II) complexes such as $[Co(CN)_5]^{3-}$.[9]

Carbon-13 hyperfine coupling ($\langle a_{^{13}C}(CO)\rangle = 56$ G) in the Co(TPP)–CO adduct is large compared to the methyl radical ($\langle a_{^{13}C}(CH_3\cdot)\rangle = 41$ G)[10] where a full unpaired electron occupies the C_{2p} orbital. This indicates a substantial CO C_{2s} spin density ($a_{C_{2s}} = 1190$ G/e; $\rho_{C_{2s}}(CO) \sim 0.047$). CNDO(II) eigenvectors for CO indicate the highest occupied σ donor level is $\sim$36% C_{2s}, and the total spin density on the CO ligand is estimated as $\sim$0.13 electron ($\rho_{CO} \sim 0.13$). Using $a_{^{14}N} \sim 15$ G and the CNDO(II) result of $\sim$17% N_{2s} character for the highest σ donor level of CH_3CN ($a_{N_{2s}} = 553$ G/e) gives $\rho_{N_{2s}}(CH_3CN) \sim 0.027$ and $\rho_{CH_3CN} \sim 0.16$. Similar ligand spin densities can be estimated for many nitrogen donors from data available in the literature.[2] Although the many necessary approximations used in estimating the ligand spin densities reduce the significance of quantitative comparisons, it is clear that there is a substantial σ interaction of CO with CoTPP and the σ spin delocalization to CO is comparable with the donor molecules CH_3CN and C_5H_5N.

The interactions of CO and O_2 with the CH_3CN and C_5H_5N adducts of CoTPP have also been studied. Carbon monoxide is found at low temperature to displace CH_3CN but not C_5H_5N from the 1:1 adducts. The CH_3CN adduct re-forms upon degassing the solution. There is no evidence for any six-coordinate species that contains CO. The behavior of CO can be contrasted with that of O_2 which we find adds reversibly to the Co(TPP)–CH_3CN adduct to form a six-coordinate complex. The epr parameters for the CoTPP(CH_3CN)–O_2 complex are virtually identical with the analogous pyridine complex reported by Walker.[2]

The inability of CO to displace pyridine from Co(TPP)–pyridine or to form a six-coordinate complex suggests that the absence of CO adducts with coboglobin and vitamin B_{12r} is a consequence of histidine and benzimidazole, respectively, occupying the fifth coordination sites in these complexes. A systematic reexamination of the interaction of low-spin cobalt(II) complexes with CO is in progress.

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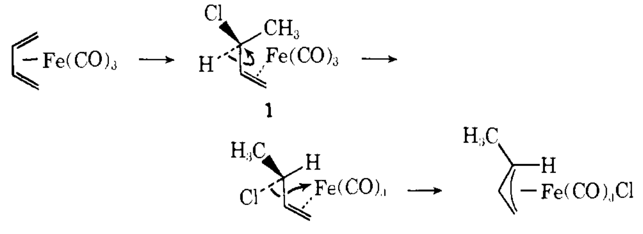
Stereochemistry and Mechanism of Protonation of Diene–Iron Tricarbonyl Complexes

Sir:

Fundamental to the understanding of the reactivity of metal π complexes are their reactions with simple electrophiles, particularly the proton. Recent investigations of the protonation of diene–iron tricarbonyl complexes[1,2] have shown that, depending on the conditions, a variety of reactions may occur: addition of both proton and anion[1a] to give a covalent, coordinatively saturated π-allyl complex; addition of a proton[1b] only, to give a coordinatively unsaturated cationic complex; or, in strongly acid media, diprotonation.[2] The fact that a change in the configuration of the diene was observed to accompany the addition of HCl to piperylene-iron tricarbonyl, while no change was observed with noncoordinating acids,[1b,2] together with the observation that cyclohexadieneiron tricarbonyl did not give a π-allyl complex under the same conditions, led Pettit[1a] to propose the mechanism shown in Scheme I for the

Scheme I



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