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

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

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

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

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 ~36% C_{2s}, and the total spin density on the CO ligand is estimated as ~0.13 electron ($\rho_{CO} \sim 0.13$). Using $a_{^{14}N} \sim 15$ G and the CNDO(II) result of ~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 cobo-globin 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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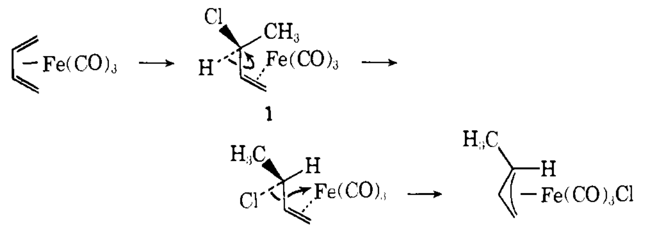
Stereochemistry and Mechanism of Protonation of Diene–Iron Tricarbonyl Complexes

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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[9] F.-D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).

[10] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.*, **112**, 1169 (1958).

[1] (a) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964); (b) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, 84, 4591 (1962).

[2] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *ibid.*, **91**, 6968 (1969).

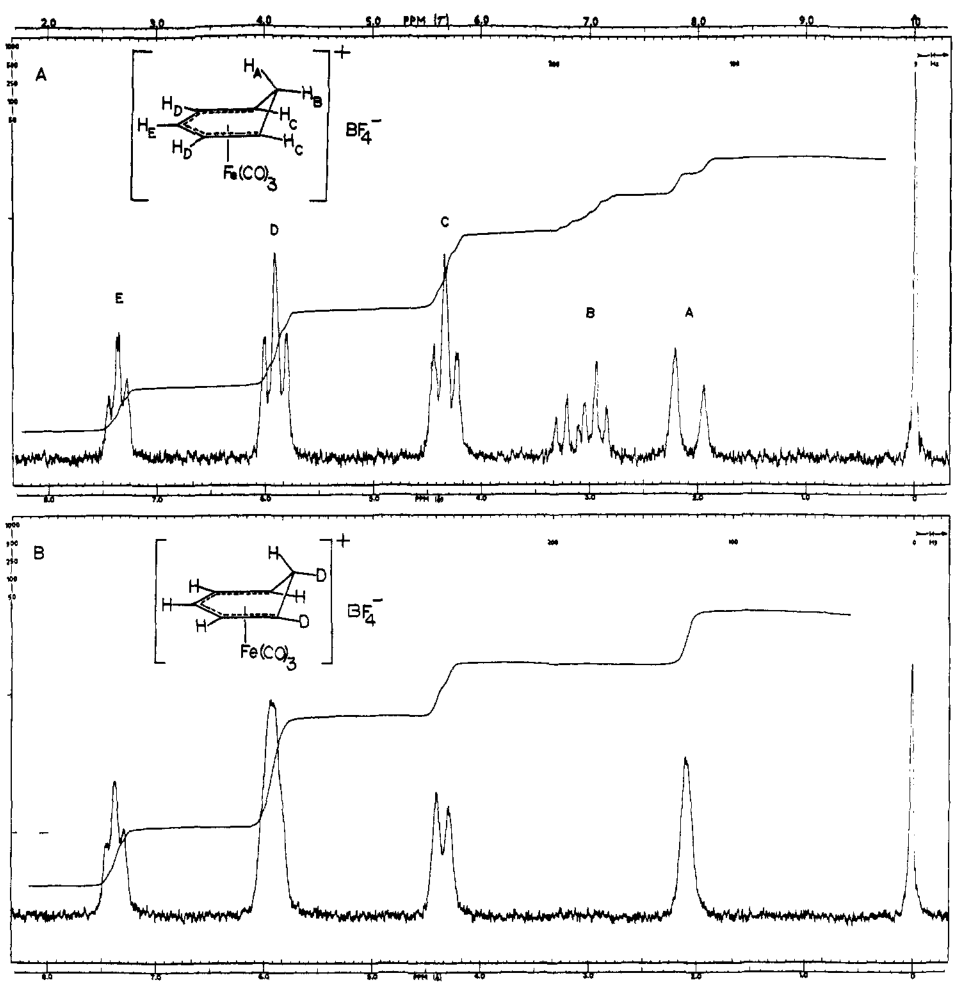
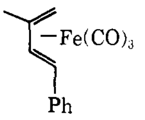


Figure 1. (A) Nmr spectrum of 5-h_2 in trifluoroacetic acid; (B) nmr spectrum of 5-d_2 in trifluoroacetic acid.

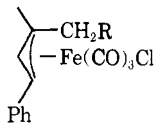
addition of acids with coordinating anions to diene–iron tricarbonyl complexes.

In this mechanism, protonation, followed by addition of chloride to the face of the olefin remote from the metal, results in a species 1, in which rotation about the C_2–C_3 bond may occur. Transfer of chlorine to iron then leads to preferential formation of the syn π-allyl complex.

We wish to report observations which indicate that this mechanism is not obligatory for the addition of acids to diene complexes. Treatment of 1,2,3,4-*tetrahapto*-(1-phenyl-3-methylbutadiene)iron tricarbonyl (**2**) with dry HCl (pentane, −78°) leads to π-allyl complex **3**-*h*. The ir of this complex showed three strong bands in the carbonyl region at 2085, 2040, and 2000 cm^{-1}, typical of π-allyl Fe(CO)$_2$X complexes.[1a,3] The nmr



2



3-*h*, R = H
3-*d*, R = D

spectrum, in addition to resonance due to the aromatic protons, showed a doublet (J = 12 Hz) at δ 5.65 (C_2H), a doublet (J = 12 Hz) at 4.68 (C_1H), and two singlets at 2.20 and 1.57 assigned, respectively, to the syn and anti methyl protons on C_3 (ratio $Me_{1.57}/Me_{2.20}$ = 0.97 ± 0.04). This assignment is made by analogy to several reported[1b,4] π-allyl complexes of iron, cobalt, and nickel in which the syn methyl resonance always occurs at lower field than the anti. When DCl was used under the same conditions the spectrum was identical except that the resonance at δ 1.57 was reduced to approximately two-thirds of its previous intensity (ratio $Me_{1.57}/Me_{2.20}$ = 0.71 ± 0.02). This result indicates that deuteration occurred exclusively and irreversibly on the anti methyl group. The mechanism in Scheme I predicts incorporation of deuterium into the syn methyl exclusively and is therefore inconsistent with the experimental result.

The π-allyl complex produced above was rather unstable, decomposing[3] to a mixture of starting diene complex and inorganic iron salts in a matter of hours at room temperature. In the interests of studying a more convenient system, we dissolved the complex **2** in neat trifluoroacetic acid at room temperature. Examination of the nmr spectrum of this solution indicated that a π-allyl complex had been formed. Evaporation

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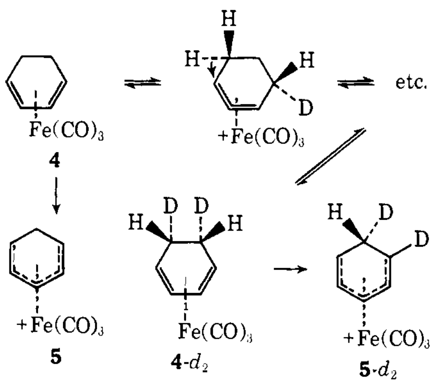
(4) (a) J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, **2**, 601 (1963); (b) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6785 (1970).

of the nmr solution led to recovery of the diene complex in about 85% yield. Use of trifluoroacetic-*O-d* acid led to the complete disappearance of the anti methyl signal within 1 min (the time necessary to run the spectrum). Thus, protonation is readily reversible under these conditions.[5]

The nmr spectrum of a solution of cyclohexadieneiron tricarbonyl (**4**) in CF_3CO_2H was essentially the same as that in benzene. Protonation of this compound nonetheless occurs, since a solution in CF_3CO_2D led to rapid incorporation of two atoms of deuterium into the methylene groups,[6] *via* the mechanism shown in Scheme II. That two, and only two, deuterium atoms are incorporated implies a *stereospecific*, reversible protonation.[7]

Scheme II



While it has been assumed[2,8] that protonation occurs on the side of the ligand near the metal (endo)[9] there is no direct proof of the stereochemistry of this process. We offer such proof. When **4** is treated with trityl fluoroborate in methylene chloride, the cyclohexadienyliron tricarbonyl cation **5** is formed.[8,12] The nmr spectrum of this compound is shown in Figure 1A; particularly noteworthy are the signals at δ 2.08 and 3.10, corresponding to the exo and endo methylene protons, respectively. This assignment is consistent with the coupling constants to the protons on C_1 and C_5; the coupling to the exo proton is close to 0 Hz, because the dihedral angle involved is approximately 90°,[13] while the endo coupling is larger (6.5 Hz). Similar hydride abstraction from **4**-d_2 gave **5**-d_2, whose spectrum is shown in Figure 1B. The endo proton at δ 3.10 is no longer visible, and the two-proton triplet at 4.35 has become a one-proton doublet, indicating, respectively, the presence of deuterium at C_1 and C_6 endo as indicated. The remaining changes in the spectrum are likewise consistent with this deuteration pattern. The spectrum demonstrates clearly that hydride abstraction and proton addition occur from opposite sides of the ligand, and that the protonation is endo. Confirmation of this conclusion comes from the work of Lewis and coworkers,[12b] who showed that hydride abstraction with Ph_3C^+ and hydride addition with BH_4^- occur on the same side of the ligand. Since there is ample evidence that nucleophilic attack on these systems occurs exo to the metal,[14] these results also imply endo protonation.

[5] Diene complex recovered from this solution showed deuterium at C-4 and, to a lesser extent, C-1. No deuterium could be detected in the methyl group.

[6] Determined by nmr and mass spectroscopy of the reisolated diene complex.

[7] Isomerization of diene complexes in acid has been observed: A. J. Birch and M. Haas, *Tetrahedron Lett.*, 3705 (1968).

[8] M. A. Haas, *Organometal. Chem. Rev., Sect. A*, **4**, 307 (1969).

[9] Protonation of complexes containing *noncoordinated* double bonds has been shown to occur endo to the metal.[10,11]

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[14] See ref 8 for examples.

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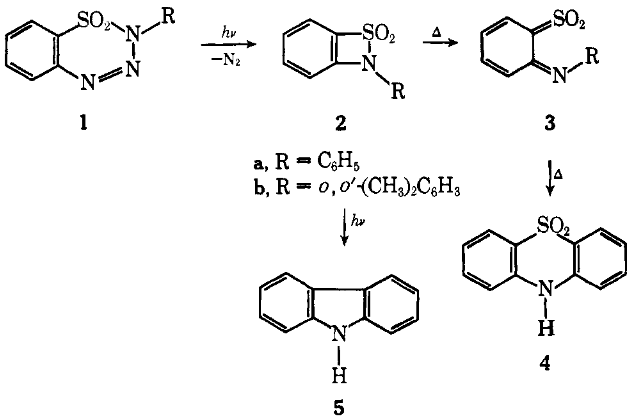
Benzothiazete 1,1-Dioxides

Sir:

Benzo-fused four-membered heterocycles containing two heteroatoms are currently unknown although a number of the monocyclic counterparts have been reported. However, the "ortho quinoid" valence isomers of such heterocycles are well-known stable organic reagents.[1] We wish to report the isolation and reactions of a derivative of the title structure as the first member of this new class of heterocycles.

2-Phenyl-2*H*-1,2,3,4-benzothiatriazine 1,1-dioxide (**1a**) derived from the nitrosation of *o*-amino-*N*-phenylbenzenesulfonamide[2] was irradiated[3] in toluene solution ($10^{-2}M$) at −78° and after the rapid evolution of nitrogen ceased a crude solid was isolated which resisted purification and spectroscopic analysis due to its thermal instability. Immediate reaction of this product at 30° with added nucleophiles such as water or aniline to give the conjugate addition products, *N*-phenyl-*o*-aminobenzenesulfonic acid and *N,N′*-diphenyl-*o*-aminoben-



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[1] A benzodioxete structure which was assigned by Wilstatter to a colorless modification of *o*-quinone remains an intriguing but as yet unsupported proposal: R. Wilstatter and A. Pfannenstiel, *Ber.*, **41**, 2508 (1908); W. M. Horspool, *Quart. Rev., Chem. Soc.*, **23**, 204 (1969).

[2] F. Ullman and C. Gross, *Ber.*, **43**, 2694 (1910).

[3] Photolyses were conducted using a 450-W Hanovia lamp in a Pyrex probe.