$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]Cl$ could be detected. This indicates that Fp undergoes CO replacement with phosphine much faster than Cl abstraction from chloroform, consistent with earlier observations.[21] It also suggests that the reaction of Fp′· with chloroform is an outer-sphere electron transfer rather than an inner-sphere atom abstraction, since the latter would lead to Fp′Cl which would undergo chloride substitution to the observed product only slowly.[23]

A substantial body of chemistry of (unsaturated alkyl) metal complexes, especially Fp(allyl), has been generated by taking advantage of the capacity of the unsaturated group to undergo electrophilic attack.[24] The homolytic displacement mechanism shown here offers the potential for further expanding the scope of such systems, with regard to both mechanistic understanding[25] and new synthetic methods.

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(4) A small initial acceleration of Fp′Cp formation (~5% in 5 min) is observed, but this quickly ceases. In the presence of a small amount of added galvinoxyl—an effective radical scavenger—even this initial enhancement is suppressed. All irradiations were carried out in thin-walled Pyrex NMR tubes, using a low-intensity, long-UV (λ_{max} ~3600 Å) lamp.
(5) With 10% Fp_2 (based on FpCp) added, a 25% conversion into Fp′Cp after 5 min is observed. On further irradiation, disappearance of FpCp continues at about the same rate, but appearance of Fp′Cp slows while ferrocene formation increases, indicating the rate of photoconversion of Fp′Cp into ferrocene has become nearly equal to the rate of its formation. Irradiation for very prolonged periods gives virtually complete conversion into ferrocene.
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(16) Formation of this product is believed to arise from an intramolecular Arbuzov-like rearrangement of the intermediate substitution product, with a free double bond on the η^1-C_5H_5 acting as nucleophile; $C_5H_5CH_3$ is also formed.[1] A model for this transformation can be seen in the rearrangement of $CpM(CO)_2(EMe_2)[P(OMe)_3]$ to $CpM(CO)_2(EMe_3)[PO(OMe)_2]$ (M = Mo, W; E = As, Sb) which similarly involves transformation of trimethyl phosphite to a phosphonate ligand.[17]
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(21) Based upon data obtained from competition experiments,[22] the rate constant for the reaction of Fp· with chloroform is estimated as ~1 mol^{-1} s^{-1}; under conditions used here, this would give a pseudo-first-order rate constant of 2.5 s^{-1}. The rates for substitution of Fp· have not been measured, but the corresponding first- or pseudo-first-order rate constant for phosphine substitution in $Mn(CO)_5$· is at least several orders of magnitude higher.[6] Reaction with chloroform involves net oxidation of the metal and hence should be much more facile for the more electron-rich phosphine-substituted radical.
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(25) For example, it has been noted that $Fp(CH_2CH{=}CD_2)$ readily equilibrates under mild conditions to a 1:1 mixture with its isomer $Fp(CD_2CH{=}CH_2)$;[26] while no mechanism was proposed, it is tempting to ascribe this loss of regiochemistry to the homolytic displacement process, since in an addition–elimination mechanism for displacement each transfer would change the end of the allyl group bonded to iron. Also, the insertion of SO_2 into M–R bonds has recently been found to go by a closely related radical-chain path in certain cases.[27]
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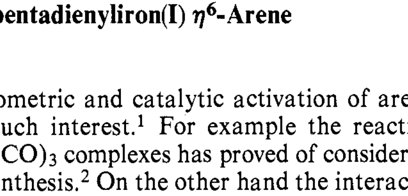
Novel Reactions of Dioxygen in Organometallic Chemistry. Hydrogen Atom Abstraction vs. Dimerization of the 19-Electron Complexes η^5-Cyclopentadienyliron(I) η^6-Arene

Sir:

Stoichiometric and catalytic activation of arenes has attracted much interest.[1] For example the reactivity of η^6-arene-$Cr(CO)_3$ complexes has proved of considerable help in organic synthesis.[2] On the other hand the interaction of $^3O_2$, $^1O_2$, and O_2^-· with organic and organometallic compounds is becoming a subject of increasing attention since it is relevant to synthesis of models and biological processes. Yet the known modes of reaction involve the attachment of one or two oxygen atoms onto the metal or onto an organic moiety. In particular when simple electron transfer occurs with a complex (A) according to $A + {}^3O_2 \rightarrow A^+ + O_2^-\cdot$, further interaction between these two latter species is not known.[3] We report now two peculiar reactions of O_2 on the 19-electron complexes η^5-CpFe-η^6-arene: the hydrogen atom abstraction by O_2 from a methyl group in η^5-C_5H_5Fe-η^6-$C_6(CH_3)_6$ and the O_2-induced dimerization of η^5-C_5H_5Fe-η^6-arene when the benzene ligand bears less than six methyl groups.

The green 19-electron complex η^5-C_5H_5Fe-η^6-$C_6(CH_3)_6$[4] (**1**) instantaneously reacts with 0.25 mol of O_2 or more simply contact with dry air (25 °C) in pentane or DME affords 0.5 mol of H_2O and the novel red diamagnetic complex (**2**) (eq 1)



in 90% crude yield (60% of crystals by slowly cooling down the filtered pentane solution to −40 °C). Anal. Calcd for $FeC_{17}H_{22}$: Fe, 19.79; C, 72.35; H, 7.86. Found: Fe, 19.61; C, 72.32; H, 8.07.

Minute amounts of H_2O_2 and of a precipitate of η^5-C_5H_5Fe-η^6-$C_6(CH_3)_6{}^+OH^-$ (≃10%) are also formed. The

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mass spectrum of **2** exhibits a molecular peak at 282.106 consistent with the loss of one hydrogen atom from **1** (calcd for $FeC_{17}H_{22}$, 282.107).

The singularity of the C_5H_5 peak (^1H and decoupled ^{13}C), the presence of three singlets for the methyl groups (^1H, 3:6:6; ^{13}C, 1:2:2:) and of four singlets for the C_6 ring (decoupled ^{13}C), and the intensity 2 of the singlet at δ 3.60 ppm (^1H)[5] show that dehydrogenation of **1** took place at a CH_3 group attached to the benzene ring. Thus the structure of the new complex **2** is best represented in terms of a cyclohexadienyl ligand coordinated in a pentahapto fashion to C_5H_5Fe and bearing an exocyclic double bond (eq 1). That the ring carbon bound to the methylene is essentially decoordinated from the metal[6] is shown by its position in the ^{13}C spectrum (δ 145 ppm) far downfield from the five other cyclohexadienyl carbons (57–90 ppm). The preliminary X-ray structure of **2**[7] shows a dihedral angle of 40° in the cyclohexadienyl ligand and a length of 1.36 Å for the exo double bond.

The reaction of **1** with O_2 proceeds at −78 °C in pentane in a few minutes; 0.5 mol of O_2 is necessary (color change from dark green **1** to bright red **2**) and 0.5 mol of H_2O_2 is formed (large ν_{OH} (IR) band at ~3400 cm^{-1}, titration by $KMnO_4$ after hydrolysis), so that the stoichiometries are

$$\mathbf{1} + \tfrac{1}{4}O_2 \rightarrow \mathbf{2} + \tfrac{1}{2}H_2O \ (25\ °C)$$

$$\mathbf{1} + \tfrac{1}{2}O_2 \rightarrow \mathbf{2} + \tfrac{1}{2}H_2O_2 \ (-78\ °C)$$

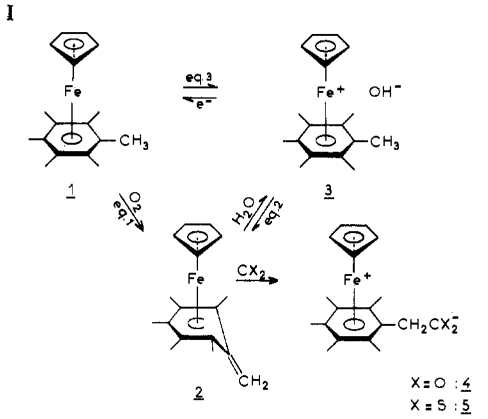
The formation of **2** from **1** also occurs rapidly with air in the solid state.

Since **2** proved to be air sensitive, but stable under N_2, we checked an alternative route by deprotonation of the 18-electron cationic complex $[C_5H_5FeC_6(CH_3)_6]^+X^-$. There has been very recently a great deal of interest for deprotonation of the alkyl chains of conjugated complexed arenes.[8] In particular, fluorene,[8a-c] diphenylamine,[8c] carbazole,[8c] benzimidazole,[8c] and triphenylmethane[8c] coordinated with the η^5-$C_5H_5Fe^+$ moiety have been deprotonated. That no arenes with simple alkyl chains have been examined[9] seems to suppose that conjugation would be necessary to stabilize organometallic complexes of arenes that have been deprotonated in the α position.

Indeed, we find that stoichiometric addition of *t*-BuOK to $[C_5H_5FeC_6(CH_3)_6]^+$ ($X^- = BF_4^-$;[10] for **3b**; PF_6^- for **3c**) in DME or THF at room temperature immediately affords **2** which is isolated quantitatively. **2** is hygroscopic. If a moderate excess of water is added to an acetone solution of **2**, the red color immediately turns yellow and $[C_5H_5FeC_6(CH_3)_6]^+OH^-$ (**3a**) can be precipitated by addition of ether and isolated;[10b] alternatively metathesis with $NaBF_4$ or $NaPF_6$ affords **3b** or **3c** (respectively). In contrast to the analogous complex of fluorenyl[8a,b] which does not react with water alone,[8b] **2** is a strong base in water. When excess D_2O (100:1) is added to **2**, a Gaussian distribution of D (0–4; average for two runs, 1.3) is recorded in the mass spectrum. The cycle on Scheme I is demonstrated as follows: if excess D_2O is added to **3a**, no deuteration is recorded after 4 days, but, when D_2O and Na/Hg amalgam are added to the otherwise extremely air-sensitive dark green DME solution of the 19-electron complex **1**, air can be admitted without color change and after 2-h extensive (90%) labeling by 18 D is recorded by ^1H NMR and mass spectrum (the same result is obtained starting from **3c** or **2**).

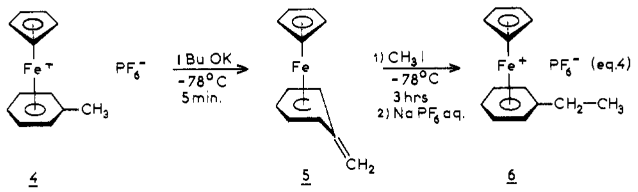
The nucleophilic properties of the exocyclic carbon of **2** are also exemplified by the reactions with CO_2 and CS_2: a pentane solution of **2** immediately reacts at room temperature or at −78 °C with 1 equiv of CO_2 or CS_2 to yield quantitatively the zwitterions $C_5H_5Fe^+C_6(CH_3)_5CH_2CX_2^-$ (X = O, **4**; S, **5**),[11] in which the hexahapto coordination of the arene is now recovered.

Scheme I

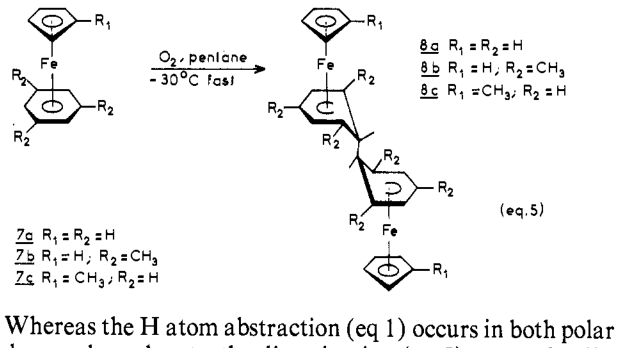


This stepwise benzylic activation shows that **2** is a good model for intermediates in benzylic activation processes.

Although *t*-BuOK does react with the complex of toluene $(\eta^5\text{-}C_5H_5Fe\text{-}\eta^6\text{-}C_6H_5CH_3)^+PF_6^-$ (**4**) at −78 °C in THF (eq 4) in the same fashion as that of hexamethylbenzene **3b** to provide the unstable complex **5** as demonstrated by reacting **5** in situ at −78 °C (3 h) with CH_3I to form **6**[12] (70% yield),



hydrogen atom abstraction by O_2 from the 19-electron complexes η^5-C_5H_5Fe-η^6-$C_6H_5CH_3$ (**7d**) does not proceed. Instead dioxygen induces the dimerization of **7** to the dimers **8** quantitatively in pentane[13] (eq 5) (stoichiometry: 30–40% O_2/mol of **7**, 5% H_2O_2 found for runs at 0 °C). The reaction is fast for **7a** at −47 °C[13] and for **7b–c** at −37 °C.



Whereas the H atom abstraction (eq 1) occurs in both polar and nonpolar solvents, the dimerization (eq 5) proceeds efficiently only in nonpolar solvents such as pentane. If, for instance, DME is used, the major product of the reaction of **7** and O_2 is the cationic complex $(\eta^5\text{-}C_5H_4R_1Fe\text{-}\eta^6\text{-}C_6H_3R_2)^+$ (**9**), along with minor amounts of the dimer **8**. This suggests that the O_2-induced dimerization of **7** follows a radical mechanism, whereas the H atom abstraction from **1** is at least partly ionic.

We believe the peculiar reaction of O_2 or air on $C_5H_5FeC_6(CH_3)_6$ (**1**) can be explained in terms of the deprotonation of the cation **3**. Taking into account the low potential of reduction of O_2

$$O_2 \overset{e^-}{\rightleftharpoons} O_2^{-\cdot}$$

$E°' = -0.75$ vs. SCE, and the high potential of reduction of **3**

$$[C_5H_5FeC_6(CH_3)_6]^+ \overset{e^-}{\rightleftharpoons} C_5H_5FeC_6(CH_3)_6$$

$E^{\circ\prime} = -1.8$ V vs SCE,[14] the electron-transfer proceeds readily:

$$C_5H_5FeC_6(CH_3)_6 + O_2 \rightarrow C_5H_5FeC_6(CH_3)_6^+ + O_2^-\cdot$$

It has recently been shown[15] that electron transfer occurs in media of low dielectric constant between two radicals of greatly different electronegativities, yielding ion pairs.

Although $O_2^-\cdot$ is a weak base on the grounds that the pK_a of $HO_2\cdot$ is 4.88, a solution of $O_2^-\cdot$ behaves as if it is strongly basic and can promote proton transfer from acids with an approximate pK_a value of 23 as has been emphasized recently.[16]

As further evidence, KO_2 reacts with **3b** in Me_2SO or with equimolar 18-crown-6 in THF to give **2** in 30 min at room temperature.[17] Also note that the mass spectrum of **1** shows an important peak at $[M - 1]^+$, 282.106, consistent with an easy deprotonation of the cation **2**.

A reaction between cobaltocene and O_2 has been reported to produce an oxygen bridge between two η^4-C_5H_5 groups,[18a] but this and other radical-type reactions of cobaltocene[18b] can be understood on the basis of their low redox potential (−1.2 V/SCE)[19] and the important ligand character of its e_{1g}^* HOMO.[20] The interaction of η^5-C_5H_4RFe-η^6-arene with $^3O_2$ is probably not relevant to this latter reaction. An endoperoxide can be involved if $^1O_2$ is the interacting species or alternatively an Fe^I-O_2 bond (or Fe^{II}-$O_2^-\cdot$, depending on one's point of view) as an intermediate would imply a partial decoordination of the arene ligand. We plan to investigate this mechanism in more detail since the peculiar reactions of dioxygen described here usefully mimic the reactivity of $O_2^-\cdot$ vs. $^1O_2$ in biologically significant systems.

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(4) Full characterization of 1 will be published separately.

(5) ^1H NMR (δ, C_6D_6): C_5H_5, 3.48 (s, 5), CH_2; 3.60 (s, 2); CH_3, 2.07 (s, 9) 1.76 (s, 6). ^{13}C NMR (δ, ppm, C_6D_6): C_5H_5, 75.64; CH_3, 16.31 16.9; cyclohexadienyl, 145.0, 90.1, 83.5, and 57.05 J(=CH_2) = 156, 5 Hz.

(6) Treichel et al. have recorded the crystal structure of η^6-fluorenyl Fe–η^5-C_5H_5,[6a,b] showing that it is a zwitterion (A) in which no carbon atom is decoordinated from the η^6-benzene ligand. However all reported complexes with deprotonated arenes give NMR shifts showing that neither of the two following mesomeric structures (A and B) is present in a pure form.[6]

(A) (B)

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(13) The dimerization of 7a with formation of some ferrocene has been reported to proceed in pentane in 15 h under an inert atmosphere (A. N. Nesmeyanov, N. A. Vol'kenau, and V. A. Petrakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 2159 (1974)). We have found the same product distribution in both this reaction and the reaction of O_2 at −47 °C. On the other hand **7b** does not produce any ferrocene but only the dimer **8b** by reaction with O_2 at −47 °C or 25 °C nor does it dimerize at 25 °C in pentane under N_2 unlike **7a**, We therefore believe that the dimerization of **7a** can be induced by moieties formed during the thermal decomposition, if any, in the same way as by O_2. See also C. Moinet, E. Roman, and D. Astruc, *J. Organomet. Chem.*, **128**, C45 (1977).

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Intramolecular Kinetic Isotope Effect in Gas-Phase Proton-Transfer Reactions

Sir:

In spite of the potential usefulness of kinetic isotopic effects (KIE) toward the detailed understanding of energy surfaces of ion-molecule reactions and the dynamics of these processes, there has been little activity in this area. An early study of the intramolecular KIE in the reaction of rare gas ions with HD revealed that at near-thermal energies an inverse isotope effect is observed ($k_H/k_D < 1$).[1] This fact has been interpreted as arising from the unimolecular decomposition of a long-lived intermediate XHD^+. At higher ion translational energies, where $k_H/k_D > 1$, a direct reaction model provides satisfactory agreement with experiment.[2]

In the present communication, we report preliminary results on intramolecular kinetic isotope effects of a series of gas-phase proton-transfer reactions, where variation of R and X provides a convenient way of varying the exothermicity of the reaction.

$$RO^- + XC_6H_4CH_2D \begin{array}{l} \xrightarrow{2k_H} ROH + XC_6H_4CHD^- \\ \xrightarrow[k_D]{} ROD + XC_6H_4CH_2^- \end{array} \qquad (1)$$

Previous measurements by ICR of the absolute rate constant for the methoxide–toluene reaction show that it is an order of magnitude smaller than a typical ion–molecule collision rate constant.[3] On the other hand, excitation function measurements for this same reaction suggest that there is no activation energy for the process.[4] These gas-phase reactions are also very useful for comparison with primary KIE observed in slow proton transfer reactions in solution, typical of carbon acids. The solution processes apparently exhibit a maximum effect when ΔpK ~ 0,[5,6] an observation which has been rationalized

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