Organometallics 1988, 7, 1036–1046

A small almost cubic crystal of 0.08 mm on the side was selected under inert-atmosphere conditions. The crystal was transferred to the goniostat where it was cooled to −137 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited orthorhombic symmetry and systematic extinction of $h00$ for $h = 2n + 1$ and of $0k0$ for $k = 2n + 1$, uniquely identifying the space group as the noncentrosymmetric $P2_12_12$. Data were collected in the manner detailed in Table III. A total of 3163 reflections were collected; after the usual data processing and averaging of equivalent reflections a unique set of 3041 reflections remained. A total of 2644 reflections considered observed by the criterion $F > 3.0\sigma(F)$ were used in the final least-squares refinement of the structure.

The structure was solved by a combination of direct methods and heavy-atom Fourier techniques. All non-hydrogen atoms were readily located. Initial full-matrix least-squares refinement leads to an R of 0.059. Since the space group is noncentrosymmetric, the other enantiomer was tested, the R was 0.054, and the refinement was continued by using this enantiomer. The least-squares refinement was completed by using anisotropic thermal parameters on all W and Cl atoms, while the C and O atoms were isotropic. Hydrogen atoms were introduced in calculated fixed positions on all of the C atoms in the OR groups. A difference map showed the position of two of the hydrogen atoms on C(43), and the third one was calculated. The final R was 0.050 for 2644 reflections.

The final difference Fourier was essentially featureless. The maximum peak was 1.5 e/Å^3, and several peaks of approximately 1.2–1.5 e/Å^3 were located in close proximity to the heavy atoms. No absorption correction was deemed necessary due to the almost cubic shape of the crystal.

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Registry No. 1, 113220-80-7; A, 92054-28-9; $(PhCn)_2PdCl_2$, 14220-64-5; $(PhCN)_2PtCl_2$, 14873-63-3; C_2Cl_6, 67-72-1; $HgCl_2$, 7487-94-7; W, 7440-33-7.

Supplementary Material Available: Tables of calculated H-atom positions, anisotropic thermal parameters, and complete bond distances and angles and alternate ball-and-stick drawings (9 pages); a listing of F_o and F_c values (7 pages). Ordering information is given on any current masthead page.

How Dioxygen Activates C–H Bonds of Simple Arenes in Unstable CpFe^I(arene) Complexes and the Versatile Reactivity of Superoxide Anion Generated from Dioxygen and Organoiron "Electron Reservoirs"[1]

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The reactivity of $O_2^{\bullet -}$ generated in inert solvents and ethers from dioxygen and electron reservoirs such as CpFe^I(arene) complexes has been examined with the aim of activating benzylic C–H bonds in simple arenes coordinated to CpFe^I. The C–H activation by O_2 in pentane, THF, or DME, known for $C_5R_5Fe^I(C_6R'_6)$ (R and R′ = alkyls), is investigated for unstable CpFe^I(arene) complexes with one to six methyl groups on the arene ligand. A dramatic salt effect is found when the reactions are carried out in THF; in the presence of Na^+X^-, the formation of yellow diagmagnetic salts $[CpFe(arene)]^+X^-$ and of $^1/_2$ mol of Na_2O_2 is general; it is quantitative with $X^- = PF_6^-$ upon reaction with $^1/_2$ mol of O_2 at −80 °C. When Na^+X^- is removed, the unstable CpFe^{II}(η^5-benzyl) complexes are obtained in high yield and characterized by the downfield resonance (140 ppm) observed in the $^{13}C\{^1H\}$ spectra for the ring carbon bound to the exocyclic double bond; they can be alkylated or functionalized in situ at −50 °C with CH_3I or PhCOCl. Primary, secondary, and tertiary C–H bonds can be activated in this way by O_2 in the 19-electron CpFe^I(arene) complexes. The rapid H-atom abstraction from methyl and ethyl substitutents at −80 °C is an outer-sphere electron transfer to dioxygen followed by deprotonation by superoxide anion, the latter process being inhibited by the salt effect (Na^+). The formation of dimeric peroxides is a general phenomenon in the reactions of $^1/_2$ mol of O_2 in pentane or toluene with CpFe^I complexes of arenes such as C_6H_6 or 1,3,5-t-$Bu_3C_6H_3$ which do not bear benzylic hydrogens. The competition between formation of a dimeric peroxide and benzylic H abstraction is exemplified by the behavior of CpFe^I(i-PrC_6H_5); reaction of O_2 with the latter in toluene gives the dimeric peroxide as the kinetic product (−80 °C), transformed into the thermodynamic H abstraction product at −17 °C. The salt effect in THF with M^+X^- (M^+ = n-Bu_4N^+, K^+, Na^+, X^- = PF_6^-, BF_4^-, F^-) also inhibits the formation of dimeric peroxide, and the salts $[CpFe(arene)]PF_6$ and Na_2O_2 are formed instead of the dimer. The salt effect is all the more important in the series M^+X^- as the size of the cation M^+ decreases and as that of the anion X^- increases. In all the reactions, formation of superoxide anion in ion pairs is the first step and its versatile reactivity (proton abstraction, nucleophilic addition, reduction or dismutation) accounts for the variety of reactions observed.

Introduction

The reactivity of superoxide radical anion has recently attracted considerable attention from chemists[2-8] and biochemists.[9,10] Some years ago it was reported[11,12] that the reactions of the stable 19-electron complexes CpFe^I(C_6R_6) (R = Me, Et) with O_2 formally give H-atom ab-

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(1) Organometallic Electron Reservoirs. 27. For part 26, see: Lacoste, M.; Toupet, L.; Varret, F.; Astruc, D. *J. Am. Chem. Soc.* 1987, *109*, 6504.

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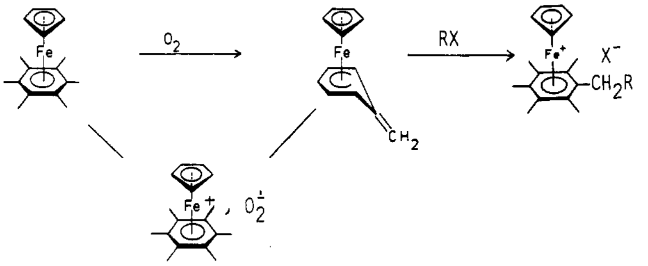
straction via the intermediacy of $O_2^{\bullet -}$. Details of this chemistry, summarized below



were reported in a full paper.[13] Later, we attempted to extend this C–H activation to more simple arenes although the CpFe^I complexes of the latter are unstable above −10 °C. This led to the finding that Na^+ salts inhibit the H-atom abstraction reaction.[14] It was found that Na^+ salts inhibit the formation of a dimeric peroxide upon reaction of $CpFe^IC_6H_6$ with O_2. These salt effects on the basic and nucleophilic properties of $O_2^{\bullet -}$ generated from Fe^I complexes and $O_2^{\bullet -}$ were reported in a preliminary communication.[14] In this paper, we report full details on these salt effects and how to avoid them in the perspective of activating C–H bonds by O_2 in unstable CpFe^I(arene) complexes.[15–22] Thus, we also describe cage reactions of O_2 with several new substrates: the Fe^I complexes of ethylbenzene, isopropylbenzene, mesitylene, and pentamethylbenzene; i.e., four classes of arenes having between zero and three benzylic hydrogen are examined. This allows us to discuss kinetic versus thermodynamic product formation and regioselectivity.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry N_2 using Schlenk techniques and a HE 493 Vacuum Atmosphere drybox. Reagent grade tetrahydrofuran (THF), dimethoxyethane (DME), diethyl ether, toluene, and pentane were predried over Na foil and distilled from sodium benzophenone ketyl. Benzoyl chloride was purified by using standard procedures.[23] CH_3I was distilled from P_2O_5. Magic methyl, CH_3SO_3F, was distilled prior to use. All other chemicals were used as received. ^1H NMR spectra were obtained with a Varian EM 360 (60-MHz) spectrometer. The low-temperature ^1H NMR spectra and the ^{13}C NMR spectra were recorded at 80 and 20.115 MHz, respectively, in the pulse Fourier transform mode with a Brucker WP 80 spectrometer, by Dr. S. Sinbandhit. All chemical shifts are reported in parts per million (ppm) relative to Me_4Si. Mass spectra were recorded by Dr. P. Guénot[24] at the "Centre de Mesures Physiques pour la Chimie" of Rennes using a Varian MAT 311 spectrophotometer.

Infrared spectra were recorded with a Pye-Unicam SP 1100 infrared spectrophotometer which was calibrated with polystyrene. Samples were prepared between KBr disks in Nujol or in 0.1-mm thick cells in solutions. Elemental analyses were performed by the CNRS Center for Microanalyses at Lyon-Villeurbanne. In the reaction of O_2 with frozen THF solution of Fe^I (containing a salt or not), $O_2^{\bullet -}$ was characterized by ESR as already reported.[13]

1. Reactions of O_2 with CpFe^I(arene) Complexes in Pentane, Toluene, or THF. (a) CpFe^I(C_6H_5Me) (7). (i) The complex 7^+BF_4 (1.80 g, 6 mmol) in 5 mL of DME is stirred with 69 g of Na/Hg (1%, 30 mmol) for 1 h at −20 °C. Then 100 mL of cold toluene is added to the dark green DME solution, and the mixture is filtered into a Schlenk flask at −80 °C. Next, 35 mL of O_2 (1.55 mmol) is added by syringe to this green solution which becomes deep red with a small quantity of yellow precipitate (7% of 7^+OH^- characterized by its ^1H NMR spectrum in D_2O). The deep red solution is again filtered at −80 °C into another Schlenk flask containing an excess of PhCOCl. The benzoylation occurs at −50 °C giving a yellow precipitate. After metathesis with aqueous HPF_6, the solid is dried over $MgSO_4$ in acetone, the solution is concentrated, and addition of excess dry ether provides 1.39 g (50%) of $[CpFe(C_6H_5CH_2COC_6H_5)]PF_6$.[12] Recrystallization from hot ethanol gives 1.35 g (48.7%) of canary yellow microcrystals: IR (Nujol) 1700 cm^{-1} (CO); ^1H NMR (CD_3COCD_3) δ 7.70 (m, PhCO, 5 H), 6.50 (s, C_6H_5, 5 H), 5.26 (s, Cp, 5 H), 4.86 (s, CH_2, 2 H); ^{13}C NMR (CD_3CN) δ 196.7 (CO), 137.3, 135.2, 131.0, 129.8, (Ph), 101.6 (C, ipso C_6H_5), 91.2, 90.5, 90.0, (C_6H_5, p, m, o), 41.7 (CH_2), 78.8 (Cp). Anal. Calcd for $C_{19}H_{17}F_6FeOP$: C, 49.35; H, 3.68. Found: C, 48.92; H, 3.53.

(ii) In another reaction done on a smaller scale, 8 could be generated in toluene-d_8 which allowed us to record a $^{13}C\{^1H\}$ NMR spectrum at −90 °C:[11] ^{13}C NMR ($C_6D_5CD_3$) δ 134.8 (C uncoordinated), 91.4 (C para), 80.6 (C meta), 52.5 (C ortho), 72.5 (Cp), 73.2 (CH_2).

(iii) Stoichiometry of the Reaction. To a dark green solution of 7 in toluene, obtained as above, is added 35 mL of O_2 (1.56 mmol) by syringe. The color changes to deep red. After hydrolysis followed by acidification by H_2SO_4 to pH 1, 19.2 mL of a 3.15 × 10^{-2} M solution of $KMnO_4$ is added for the titration of the 1.51 mmol of H_2O_2 formed in this reaction. The complex 7^+ is then

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(2) For reviews, see: (a) Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195. (b) Fee, J. A.; Valentine, J. S., ref 9, p 19. (c) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471. (d) Sawyer, D. T. *Acc. Chem. Res.* **1979**, *12*, 105. (e) Sawyer, D. T.; Valentine, J. S. *Ibid.* **1981**, *14*, 393.

(3) Photooxygenation: Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1982**, *104*, 1454.

(4) For the syntheses of models of prostaglandins, see: Corey, E. J.; Nicolaou, K. C.; Shibasaki, M.; Machida, Y.; Shiner, C. S. *Tetrahedron Lett.* **1975**, *37*, 3183.

(5) Properties as a base: Sawyer, D. T.; Gibian, M. J.; Morrison, M. M.; Sev, E. T. *J. Am. Chem. Soc.* **1978**, *100*, 627.

(6) Nucleophilic properties. (a) Reference 2a, p 209. (b) Reference 5. (c) Schmidt, M.; Bipp, H. *Z. Anorg. Chem.* **1960**, *303*, 190. (d) Le Berre, A.; Berguer, Y. *Bull. Soc. Chim. Fr.* **1966**, 2368. (e) San Filippo, J., Jr.; Chern, C. I.; Valentine, J. S. *J. Org. Chem.* **1975**, *40*, 1680.

(7) Disproportionation. (a) Klug-Roth, D.; Fridovitch, I.; Rabani, J. *J. Am. Chem. Soc.* **1973**, *95*, 2786. (b) Haliwell, B. *FEBS Lett.* **1974**, *56*, 34. (c) Reference 2e. (d) Reference 2b.

(8) Coordination chemistry: (a) Ellis, J.; Pratt, J. M.; Green, M. *J. Chem. Soc., Chem. Commun.* **1973**, 781. (b) Hill, H. A. O.; Turner, D. R.; Pillizer, G. *Biochem. Biophys. Res. Commun.* **1974**, *56*, 739. (c) Reference 2e.

(9) For reviews, see: Michelson, A. M.; McCord, J. M.; Fridovitch, I. *Superoxide and Superoxide Dismutase*; Academic: New York, 1977.

(10) Destruction of cells and membranes: (a) Fridovitch, I. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1976; p 239. (b) McCord, J. M.; Fridovitch, I. *J. Biol. Chem.* **1969**, *244*, 6049.

(11) Astruc, D.; Roman, E.; Hamon, J.-R.; Batail, P. *J. Am. Chem. Soc.* **1979**, *101*, 2240.

(12) Hamon, J.-R.; Astruc, D.; Român, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431.

(13) Astruc, D.; Hamon, J.-R.; Român, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502. This paper shows the slow deprotonation of 1^+ by KO_2 to give 2; thus this reaction would work as well with other complexes $CpFe(C_6H_nMe_{6-n})^+$ (n < 6). However the deprotonated complexes would not be stable nor isolable at the reaction temperature (20 °C).

(14) Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1983**, *105*, 5951.

(15) (a) For reports on the synthesis and electronic structure of CpFe^I(arene) complexes (arene = $C_6H_{6-n}Me_n$), see ref 16–21. The analogous ethylbenzene and isopropylbenzene complexes have not yet been reported but are made in the same fashion; they are unstable in the THF solution resulting from their synthesis above −15 °C. The tri-*tert*-butylbenzene complex is known[22] and is stable at 25 °C.

(16) Astruc, D.; Hamon, J.-R.; Althoff, G.; Român, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5545.

(17) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

(18) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J.; Ostwald, N.; Hamon, J.-R. Michaud, P.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400.

(19) For a photoelectron spectroscopic study of the stable Fe^I complexes, see: Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211.

(20) (a) Nesmeyanov, A. N.; Solodovnikov, S. P.; Vol'kenau, N. A.; Kotova, L. S.; Sinitsyna, N. A. *J. Organomet. Chem.* **1978**, *148*, C5. (b) Nesmeyanov, A. N.; Sinitsijna, N. A.; Kolesov, V. S.; Sizoi, V. F.; Vol'kenau, N. A. *Dokl. Akad. Nauk SSSR* **1978**, *242*, 1356.

(21) Astruc, D. *Tetrahedron* **1983**, *39*, 4027 (Report No. 157).

(22) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549.

(23) Perrin, D. D.; Amarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Compounds*; Pergamon: New York and Oxford, 1966.

(24) We thank Dr. P. Guénot (Centre de Mesures Physiques, Rennes) for recording this spectrum and for helpful discussions.

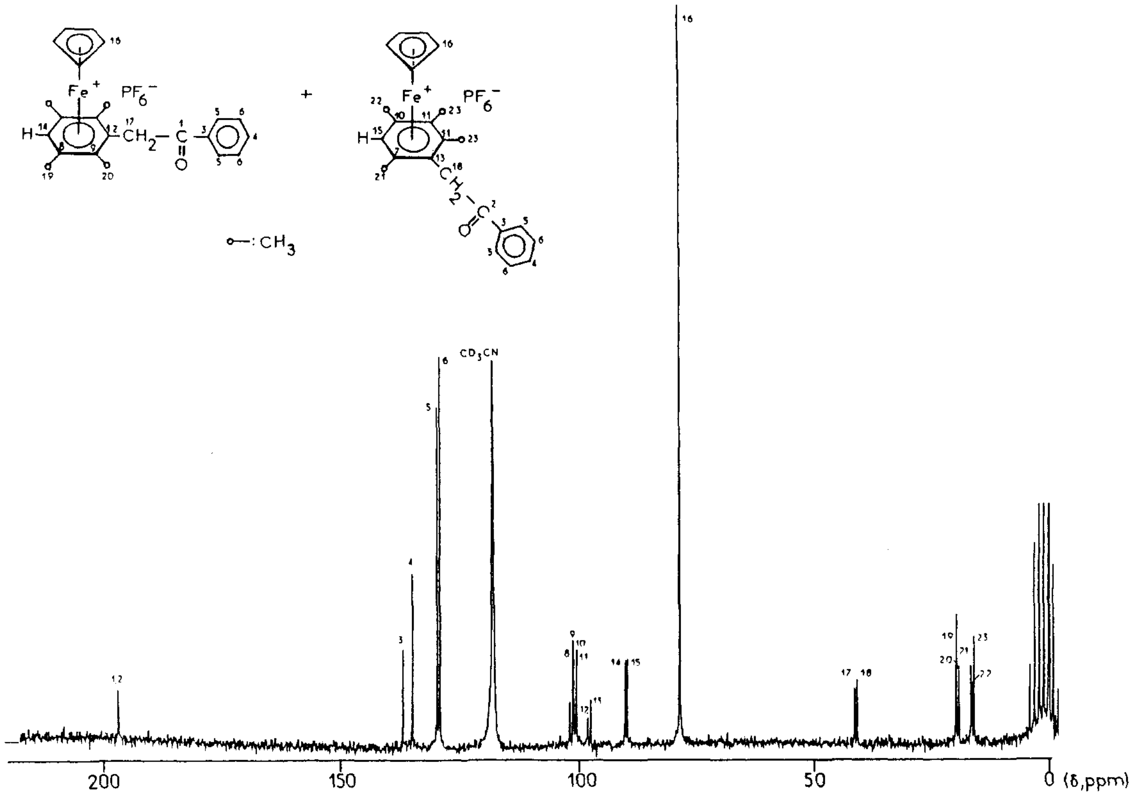

Figure 1. ^{1}H NMR spectrum in CD_3CN of the benzoylation products obtained after reaction of O_2 with Fe^{I}Cp(C_6Me_5H). The ortho structure cannot be discarded for the meta isomer, based on NMR spectra. Since the reaction of O_2 is not selective, it is probable that the ortho product formed decomposes before benzoylation because of the lack of stabilization by two adjacent Me groups (only one is present).

precipitated as the PF_6^- salt and the workup as above provides 1.065 g (2.97 mmol) of **7**$^+PF_6^-$.

Titration by I_2. To a dark green solution of **7** in toluene is added a solution of 381 mg of I_2 (1.5 mmol) in toluene. A yellow precipitate appears immediately. This solid is filtered, washed twice with 10 mL of toluene, and dried in vacuo. The complex **7**$^+I^-$ (1.01 g, 2.97 mmol) is collected.

For the reaction in THF, complex **7** is isolated in the solid state after DME is removed in vacuo at −20 °C, the solution extracted with cold pentane, and this solvent removes in vacuo again at low temperature. Thereafter, THF is added, and the reaction with O_2 proceeds using toluene.

(b) CpFe^I(C_6H_5Et) (25). All the reactions with **25** are carried out as in 1(a)(i). The complex [CpFe(η^5-C_6H_5CHMe)] obtained by reaction of O_2 with **25** in pentane at −80 °C is characterized by alkylation with CH_3I, giving a 60% yield of [CpFe($C_6H_5CHMe_2$)]PF_6, characterized by its ^{1}H NMR spectrum.[25]

(c) CpFe^I($C_6H_3Me_3$) (29). As in 1(a) the complex [CpFe(η^5-$C_6H_3Me_2CH_2$)] resulting from the reaction with **29** at −80 °C in pentane is acylated with PhCOCl at −50 °C. The workup as in 1(a)(i) provides a 44% yield of yellow microcrystals of {CpFe[C_6H_3(Me)$_2CH_2COC_6H_5$]}PF_6 after recrystallization from hot ethanol: IR (Nujol) 1695 cm^{-1} (CO); ^{1}H NMR (CD_3COCD_3) δ 7.78 (m, PhCO, 5 H), 6.44 (s, C_6H_3, 3 H), 5.18 (s, Cp, 5 H), 3.42 (s, CH_2, 2 H), 2.60 (s, CH_3, 6 H). Anal. Calcd for $C_{21}H_{21}F_6FeOP$: C, 51.43; H, 4.28; Fe, 11.43. Found: C, 51.13; H, 4.30; Fe, 11.12.

(d) CpFe^I(C_6HMe_5) (28). The complex **28**$^+PF_6^-$ (1.035 g, 2.5 mmol) in 5 mL of THF is stirred with 29 g of Na/Hg (1%, 13 mmol) for 2 h at −20 °C. Then 50 mL of cold pentane is added and the dark green solution filtered into a Schlenk flask containing 50 mL of pentane at −80 °C. At this temperature, 25 mL of O_2 (1.11 mmol) is added by syringe and the solution becomes deep red with formation of a small amount of yellow precipitate. The solution is filtered at −60 °C. Next, 2 mL of PhCOCl (17 mmol) is added at −50 °C. Immediately, the deep red solution becomes colorless and a yellow precipitate appears. Workup as in 1(a) provides 225 mg (18%) of yellow microcrystals of [CpFe($C_6HMe_4CH_2COC_6H_5$)]PF_6 after recrystallization from hot ethanol (mixture of the two isomers, see Figure 1). IR (Nujol): 1702 cm^{-1} (CO). For the sake of clarity we use the unconventional terms ortho, meta, para, and ipso, referenced to the unsubstituted carbon in C_5Me_5H. ^{1}H NMR (CD_3COCD_3): δ 7.80, 7.70 (m, PhCO), 5.26, 5.20 (s, Cp), 6.56, 6.51 (s, C_6H), 3.41 (s, CH_2), 2.65, 2.58, 2.49, 2.46 (s, C_6HMe_4). ^{13}C NMR (CD_3CN): δ 196.9, 196.8 (CO), 137.2, 135.1, 130.0, 129.4 (Ph), 102.2, 101.6, 101.5, 101.4, 100.9, 100.8 (C_6Me_4), 98.4, 97.8 (C ipso), 90.6, 90.1 (C_6H), 79.0 (Cp), 41.9, 41.4 (CH_2), 20.2, 20.1, 19.6, 17.0, 16.6, 16.3 (Me). Anal. Calcd for $C_{23}H_{25}F_6FeOP$: C, 53.28; H, 4.82; Fe, 10.81. Found: C, 53.30; H, 4.85; Fe, 11.00.

The mixture of the two isomers of CpFe(η^5-$C_6HMe_4CH_2$) can be generated in toluene-d_8, and a ^{13}C{^{1}H} NMR spectrum is recorded at −60 °C: δ 74.8, 74.5 (Cp), 86.5, 86.3 (C para), 83.2, 82.6, 82.4 (C meta), 59.3, 59.2, 58.0 (C ortho), 17.9, 17.6, 16.8, 16.6, 16.0 (Me), 143.5, 142.6 (C uncoordinated), 75.8, 75.6 (CH_2).

2. Reaction of O_2 with RCpFe^I(C_6H_6) in Toluene or THF. (a) R = H: CpFe^I(C_6H_6) (10). The complex **10**$^+BF_4^-$ (1.15 g, 4 mmol) in 5 mL of DME is stirred with 46 g of Na/Hg (1%, 20 mmol) for 2 h at −20 °C. Then the solvent is removed in vacuo and the neutral complex extracted with 100 mL of toluene at −80 °C. At this temperature, 30 mL of O_2 (1.34 mmol) is added by syringe and the initial dark green solution becomes orange. The toluene is removed in vacuo; workup and crystallization from pentane give 980 mg (2.46 mmol) of orange microcrystals (92% yield based on O_2, 61.5% overall yield) characterized by its ^{1}H and its ^{13}C{^{1}H} NMR spectrum as the dimeric peroxide [CpFe(η^5-C_6H_6O–)]$_2$:[20] ^{1}H ^{13}C{^{1}H} NMR (C_6D_6) δ 72.8 (Cp), 79.8 (C para), 77.9 (C meta), 73.3 (sp^3 C), 37.1 (C ortho); mass spectrum, *m/e* 199 ($CpFeC_6H_6^+$), 186 (Cp_2Fe^+), 121 ($CpFe^+$), 78 ($C_6H_6^+$), 56 (Fe^+). No oxygenated fragments were found.[24] Kojima et al. have reported in a short communication[26] that the isoelectronic d^7 complex Cp_2Co reacts with $^1/_2$ mol of O_2 at −78 °C to give a neutral d^6 peroxide [CpCo(η^4-C_5H_5O–)]$_2$, thermally stable up to 0 °C. We have repeated this reaction and found peaks corresponding to

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[25] Astruc, D.; Dabard, R. *Bull. Soc. Chim. Fr.* **1975**, 2571.

[26] Kojima, H.; Takahashi, S.; Nagihara, N. *J. Chem. Soc., Chem. Commun.* **1973**, 230.

oxygenated fragments in the mass spectrum of the reaction product.[24] Our results are similar to those reported by Vol'kenau and Petrakova.[27]

For the reaction in THF, the complex CpFe^I(C_6H_6) is isolated by precipitation from a concentrated solution of toluene by addition of a large excess of cold pentane. Thereafter, the manipulation proceeds using toluene.

(b) R = Me: $C_5H_4MeFe^I(C_6H_6)$ (13). The reaction with **13** is carried out as in 2(a) and provides 93% yield (based on O_2) of an orange complex characterized by its ^1H NMR spectrum as the dimeric peroxide $[C_5H_4MeFe(\eta^5\text{-}C_6H_6O–)]_2$.[27,28]

3. Reaction of O_2 with $C_5Me_5Fe^I(C_6H_6)$ (15) in Toluene. The complex $\mathbf{15}^+BF_4^-$ (1.07 g, 3 mmol) in 3 mL of DME is stirred with 35 g of Na/Hg (1%, 15 mmol) at −20 °C for 1 h. Then, at −80 °C, 150 mL of toluene is added by cannula, and the green solution is filtered. Injection of 28 mL of O_2 (1.25 mmol) changes the green color to orange. At 20 °C, this solution is concentrated to 20 mL and addition of 100 mL of cold pentane precipitates 600 mg of $[C_5Me_5Fe(\eta^5\text{-}C_6H_6O–)]_2$ (89% yield based on O_2, 74% overall yield), characterized by its ^1H NMR spectrum.[27,28]

4. Reaction of O_2 with $CpFe^I[C_6H_3(CMe_3)_3]$ (17) in Pentane. The complex $\mathbf{17}^+PF_6^-$ (0.88 g, 1.72 mmol) in 10 mL of DME is stirred with 20 g of Na/Hg (1%, 9 mmol) at 0 °C for 1 h. Then the DME is removed in vacuo, the green complex extracted with pentane, and, at −80 °C, 18 mL of O_2 (0.8 mmol) is added by syringe. The color immediately turns red. The solvent is removed, and the oily complex is dried under vacuum. $[CpFe(\eta^5\text{-}C_6H_3(CMe_3)O–)]_2$: 546 mg, 93% yield based on O_2, 86% overall yield; ^1H NMR (C_6D_6) δ 5.43 (s, meta H, 2 H), 4.10 (s, Cp, 5 H), 3.92 (s, CHO, 1 H), 1.55 (s, Me, 18 H), 1.50 (s, Me, 9 H); ^{13}C NMR (C_6D_6, 15 °C) δ 74.9 (Cp), 88.0 (para C), 77.9 (meta C), 53.9 (ortho C), 37.9 (para $C(Me)_3$), 37.6 (ortho $C(Me)_3$), 74.7 (sp^3 C), 31.9, 31.6 ($C(Me)_3$). Anal. Calcd for $C_{46}H_{70}Fe_2O_2$: C, 72.06; H, 9.13; Fe, 14.62; mol wt, (cryoscopy in benzene), 766. Found: C, 72.20; H, 9.15; Fe, 14.92; mol wt, 788.

5. Reaction of O_2 with $CpFe^I(C_6H_5CHMe_2)$ (20). (a) In Toluene. The complex $\mathbf{20}^+PF_6^-$ (770 mg, 2 mmol) in 5 mL of DME is stirred with 23 g of Na/Hg (1%, 10 mmol) at −20 °C for 2 h. Then 150 mL of cold toluene is added, and the green solution is filtered. At −80 °C, 17 mL of O_2 (0.76 mmol) is added by syringe and the solution immediately becomes orange. An IR spectrum of this solution at −80 °C shows a stretch at 810 cm^{-1} (peroxide). Half of the solution is hydrolyzed with HPF_6 in ether and allowed to warm up to room temperature, and acidification is completed to pH 1 by addition of H_2SO_4. Next, 4.55 mL of a 3.15×10^{-2} M solution of $KMnO_4$ is added for the titration of the 0.36 mmol of H_2O_2 formed. The complex $\mathbf{20}^+PF_6^-$ (270 mg, 0.70 mmol) is also collected, and this compound is characterized by ^1H NMR spectroscopy.[25] The other half of the solution is allowed to warm up, and, at −17 °C, the orange color turns deep red; at −10 °C, an excess of freshly distilled CH_3SO_3F is added, giving a yellow precipitate which is filtered; workup as in 1(a) provides 275 mg of $[CpFe(C_6H_5CMe_3)]PF_6$ (0.69 mmol) characterized by its ^1H NMR spectrum.[25]

(b) In Pentane. In an experiment similar to that of 5(a), a green solution of pentane is obtained. When it is warmed from −80 °C to room temperature, the color does not change to deep red as in 5(a). The solution is concentrated, and crystallization in pentane provides 351 mg (0.73 mmol) of a mixture of isomers of $[CpFe(\eta^5\text{-}C_6H_5CHMe_2O–)]_2$ (81% yield based on O_2): ^1H NMR (C_6D_6) δ 5.68 (m, H para), 4.67 (m, H meta), 4.03, 4.00 (s, Cp), 2.29 (m, H ortho and H endo), 1.50, 1.40, 1.33, 1.27, 1.17, 1.03 (m, Me), 3.37 (m, $C\mathit{H}Me_2$); ^{13}C NMR (C_6D_6) δ 104.3, 102.0 (C_6CHMe_2), 77.0, 75.9, 75.7, 75.6, 75.1, 74.8, 74.7 (C_6H_4), 72.8 (Cp), 46.1, 46.0, 45.6 (C_6H), 34.1, 33.7 ($\mathit{C}HMe_2$), 29.2, 28.1, 27.7, 24.9, 24.0, 22.6 ($CH\mathit{Me}_2$). Anal. Calcd for $C_{28}H_{34}Fe_2O_2$: C, 65.36; H, 6.61; Fe, 21.79. Found: C, 65.50; H, 6.82; Fe, 22.00.

When the reaction of O_2 with **20** was carried out in toluene-d_8 at −80 °C, ^1H and ^{13}C NMR spectra of **21** (−60 °C) and **22** (−10 °C) were recorded. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **21** are identical with those of the mixture of isomers isolated above. **22**: ^1H NMR ($C_6D_5CD_3$, −10 °C) δ 5.64 (t, para H, 1 H), 4.17 (t, meta H, 2 H), 2.23 (t, ortho H, 2 H), 4.01 (s, Cp, 5 H), 1.56 (s, Me, 6 H); $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, −10 °C) δ 148.8 (C uncoordinated), 101.3 ($\mathit{C}Me_2$), 77.0, 78.3, 54.4 (para, meta, ortho C ring), 72.7 (Cp), 24.2 ($C\mathit{Me}_2$).

6. Salt Effect on the Reactivity of $O_2^{\bullet-}$ as a Base. (a) Stoichiometry of the Reaction Using the $Na^+PF_6^-$ Salt in THF. To 6 mL of a 0.164 M solution (1 mmol) of $Na^+PF_6^-$ in THF is added 283 mg (1 mmol) of $CpFe^I(C_6Me_6)$ in 30 mL of THF, and the solution is cooled. At −80 °C, 11.5 mL (0.51 mmol) of O_2 is added by syringe, and immediately the starting deep green solution becomes colorless with the formation of a yellow, powdery precipitate. Workup as in 1(a)(i) gives 35 mg (0.45 mmol) of Na_2O_2 characterized by its infrared spectrum [(Nujol) ν(0–0) 800 cm^{-1}) and 425 mg (0.99 mmol) of $\mathbf{1}^+PF_6^-$ characterized by its ^1H NMR spectrum.

Two other experiments with 0.5 mmol and 0.25 mmol of $Na^+PF_6^-$/mol of **1** were carried out and give 0.48 and 0.70 mmol of $CpFe(\eta^5\text{-}C_6Me_5CH_2)$, 0.4 and 0.22 mmol of $\mathbf{1}^+PF_6^-$, and 0.20 and 0.10 mmol of Na_2O_2, respectively. The same procedure applied to the other CpFe^I(arene) complexes (arene = C_6H_5Me, C_6H_5Et, C_6H_5 *i*-Pr, $C_6H_3Me_3$, C_6HMe_5) also gives 90–100% yields of [CpFe(arene)]PF_6 and Na_2O_2 characterized similarly.[25]

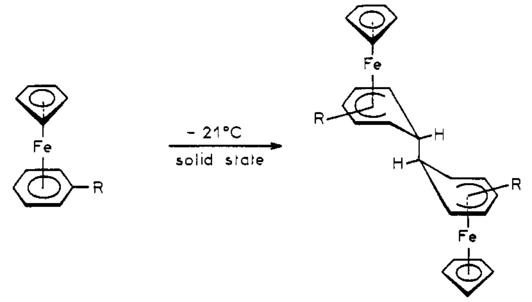
(b) Experiments with Other Salts. With all the salts used, the same procedure described above was used starting with 1 mmol of **1** with the following results: *n*-$Bu_4N^+PF_6^-$, 239 mg (0.85 mmol) of **2** and 63 mg (0.15 mmol) of $\mathbf{1}^+PF_6^-$; $K^+PF_6^-$, 125 mg (.44 mmol) of **2** and 232 mg (0.54 mmol) of $\mathbf{1}^+PF_6^-$; $K^+PF_6^-$ + 18-crown-6 (stoichiometry), 230 mg (0.81 mmol) of **2** and 50 mg (0.11 mmol) of $\mathbf{1}^+PF_6^-$; $Na^+BF_4^-$, 80 mg (0.28 mmol) of **2** and 265 mg (0.72 mmol) of $\mathbf{1}^+BF_4^-$; Na^+F^-, 192 mg (0.68 mmol) of **2** and 100 mg (0.33 mmol) of $\mathbf{1}^+F^-$.

7. Salt Effect on the Reactivity of $O_2^{\bullet-}$ as a Nucleophile. Complex **1** is isolated as in 2(a) and stored in the solid state at −40 °C. All the reactions were carried out in THF as described in 6 starting with 2 mmol of **1**: $Na^+PF_6^-$, quantitative yield of $\mathbf{10}^+PF_6^-$; $K^+PF_6^-$, 250 mg (0.58 mmol) of **11** and 492 mg (1.43 mmol) of $\mathbf{10}^+PF_6^-$; $K^+PF_6^-$ + 18-crown-6 (stoichiometry), 538 mg (1.25 mmol) of **11** and 260 mg (0.75 mmol) of $\mathbf{10}^+PF_6^-$.

The same procedure ($Na^+PF_6^-$, 1 equiv; THF, −80 °C) applied to the other CpFe^I(arene) complexes which do not bear benzylic hydrogens ($CpFe^I[C_6H_3(CMe_3)_3]$, $C_5H_4MeFe^I(C_6H_6)$, $C_5Me_5Fe^I(C_6H_6)$) also gives quantitative yields of [CpFe(arene)]PF_6 and Na_2O_2 characterized similarly.[17,22,25]

Results

1. Reactions of O_2 with CpFe^I(arene) Complexes Bearing Less Than Six Alkyl Substituents in the Presence of $Na^+PF_6^-$. THF or DME solutions of CpFe^I(arene) complexes prepared by Na/Hg reduction of [CpFe$^+$(arene)]PF_6^- at −21 °C are stable. Removal of the solvent or crystallization at −21 °C is known to give $[CpFe^{II}(\eta^5\text{-cyclohexadienyl})]_2$ as powders or crystals, respectively[17] (eq 1, mixture of isomers).



(1)

Upon addition of $^1/_2$ mol of O_2 at −80 °C to a THF or DME solution of the Fe^I complexes which still contains $Na^+PF_6^-$ from the synthetic procedure, the dark green solutions become colorless and give rise to yellow precipitates. These yellow powders show the characteristic

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(27) Vol'kenau, N. A.; Petrakova, V. A. *J. Organomet. Chem.* **1982**, *233*, C7.

(28) (a) Astruc, D. *Abstracts of Papers* 180th National Meeting of the American Chemical Society, Las Vegas; American Chemical Society: Washington, DC, 1980; INOR 311. (b) Hamon, J. R. 3rd Cycle Thesis, Rennes, 1981.

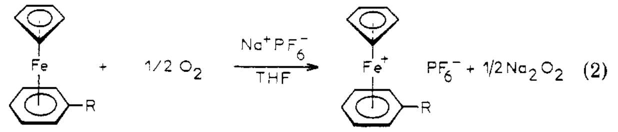
Table I. Salt Effect on the Reactivity of $O_2^{\cdot -}$ as a Base in the Reaction

$$\underset{1}{CpFe^{I}(C_6Me_6)} \xrightarrow[-80\ °C,\ THF]{O_2} \underset{2}{CpFe^{II}(C_6Me_5CH_2)} + \underset{1^+X^-}{[CpFe^{II}(C_6Me_6)]^+X^-}$$

M^+X^-	2^a	$1^+X^{-\,a}$
without	92	8
n-$Bu_4N^+PF_6^-$	85	15
$K^+PF_6^-$	45	55
$K^+PF_6^-$ + 18-crown-6^b	83	17
$Na^+PF_6^-$	0	100
$Na^+BF_4^-$	30	70
Na^+F^-	65	35

[a] Percent of 2 and 1^+X^- determined by weight (reactions are immediate). At 20 °C, the crude yields are 97% for 2 and 3% for $1^+PF_6^-$. Concentrations of both 1 and the salt in THF (30 mL) are 0.033 mol L^{-1}. With other CpFe^I(arene) complexes (arene = toluene, mesitylene, pentamethylbenzene, ethylbenzene, fluorene), analogues of 2 are not formed in the presence of 1 equiv of $Na^+PF_6^-$ under identical conditions 90–100% yield of [CpFe(arene)$^+$]PF_6^-. Superoxide ion was characterized by its characteristic ESR spectra at 77 K in reaction of O_2 with 1 in frozen THF solution as in ref 13 at 150–170 K in the presence or absence of salts. [b] Stoichiometry.

properties of the [CpFe^{II}(arene)]$^+$ cations in ^{1}H NMR[29] (DMSO-d_6 or acetone-d_6) and Mössbauer spectra.[21,30] They are diamagnetic, and their infrared spectra exhibit strong bands at 805 cm^{-1} characteristic of the peroxide ion O_2^{2-}.[14] Elemental analysis and the stoichiometry of these clean reactions confirm the general structure [CpFe^{II}(arene)]$^+PF_6^-$ together with the presence of $^1/_2$ mol of Na_2O_2. The reactions also give these ionic peroxides in DME in the presence of $Na^+PF_6^-$, although not so cleanly. The reactions in THF (eq 2) are quantitative and general,

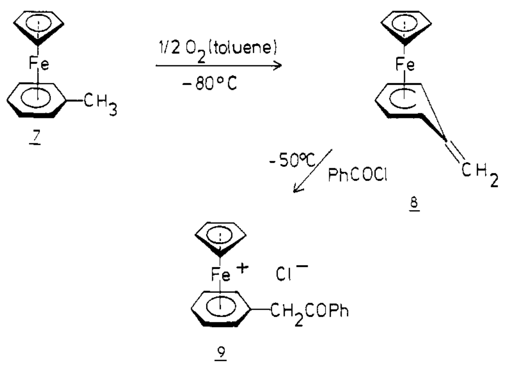


(2)

proceeding with various CpFe^I(arene) complexes (arene = benzene, toluene, mesitylene, pentamethylbenzene, ethylbenzene, isopropylbenzene, tri-*tert*-butylbenzene, fluorene, hexamethylbenzene, and hexaethylbenzene).

2. Reactions of O_2 with CpFe^{I}C$_6$Me$_6$ (1) in THF in the Presence of Various Added Salts M^+X^-: Influence of the Size of M^+ and X^-. A detailed study of the salt effect on the reaction of O_2 with the Fe^I compound was undertaken by using the easily handled, crystalline compound 1. As with all the other CpFe^I(arene) compounds, the reaction of O_2 in the presence of $NaPF_6$ in a THF solution provided by Na/Hg reduction of the PF_6^- precursor salt leads to the formation of the latter and of Na_2O_2. A similar result is obtained if fresh $NaPF_6$ is added stoichiometrically to a THF solution of 1 prepared from isolated crystals and if O_2 is allowed to react with this solution at 20 or −80 °C. If the size of the cation is increased or/and if the size of the anion is decreased, the salt effect is weaker and the reaction leads to mixtures of 2 and of 1^+X^- (see Table I). For instance using KPF_6 instead of $NaPF_6$ decreases the yield of $1^+PF_6^-$ from 100% to 55%, and, in the presence of 18-crown-6, the yield is decreased to 17%. All the results obtained are consistent with the salt effect (vide supra) without anomaly. The magnitude of the salt effect is thus reflected by the amount of 1^+X^-, noted in Table I for various salts.

Scheme I



3. Reactions of O_2 in the Absence of Salt with CpFe^I(arene) Bearing Benzylic Methyl or Methylene Groups. Filtered THF solutions of the Fe^I complexes, prepared at −21 °C by using a minimum volume of solution (ca. 5 mL) followed by addition of a 10–20-fold excess of pentane or toluene, also reacted with $^1/_2$ mol of O_2 at −80 °C, but the dark green color now turned dark red and only minute amounts of precipitate formed. Dark red solutions are typical of H abstraction products in this series, but they were found to be unstable above −50 °C. However, the exocyclic double bonds could be characterized by the peak at 140 ppm in $^{13}C\{^1H\}$ NMR spectra[13] at −90 °C, even in the simplest case of CpFe^{II}(η^5-$C_6H_5CH_2$) (8). The spectra indicate the formation of polymers even at low temperature (−50 °C). Hydrolysis of these polymers regenerates the cation [CpFe^{II}(arene)]$^+$. The structure of these polymers was not further investigated but possibly results from the intermolecular attack of the exposed methylene on the cyclohexadienyl para carbon. Reactions of the dark red solutions with excess PhCOCl in THF at −50 °C effected immediately after reaction with O_2 instantaneously provide yellow precipitates. These were characterized as the benzoylation product arising from attack on the methylene group. The overall yield for reaction of CpFe^I(toluene) (7) is 50% from $7^+PF_6^-$ (three steps). Analogous reactions proceed with CH_3I.

C–H activation by O_2 was found to be general for CpFe^I complexes of polymethylbenzenes and of ethylbenzene and characterized by alkylation with CH_3I.[31] In the case of CpFe^I(C_6Me_5H), three isomers may be formed if the reaction of O_2 is not regiospecific. The ^{1}H $^{13}C\{^1H\}$ NMR spectra of the H-atom abstraction product and of its benzoylation products indicate that two isomers (para and meta or ortho) are present in similar amounts (Figure 1).

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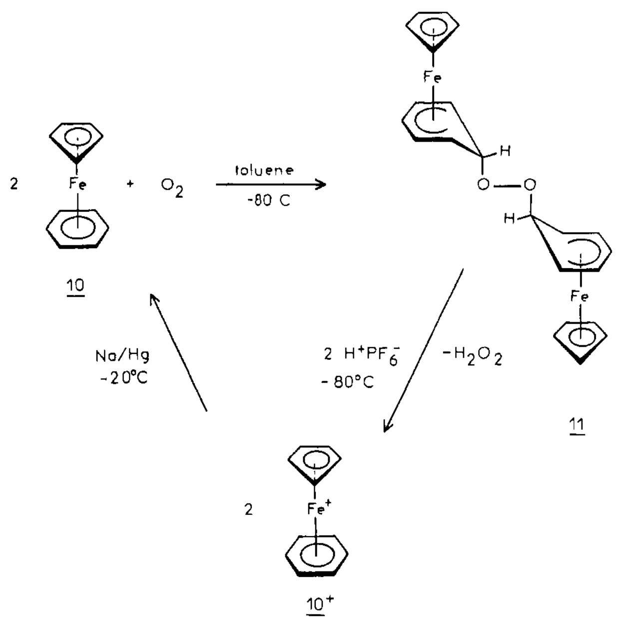
(29) Astruc, D.; Dabard, R. *Bull. Soc. Chim. Fr.* **1976**, 228.

(30) Stukan, R. A.; Vol'kenau, N. A.; Nesmeyanov, A. N.; Gold'danskii, *Izv. Akad. Nauk SSSR Ser. Khim.* **1966**, *8*, 1472.

(31) (a) The [CpFe^{II}(η^5-cyclohexadienyl)] complexes with an exocyclic double bond, resulting from the H atom abstraction by O_2 from [CpFe^I(arene)] are identical with those obtained by deprotonation of [CpFe^{II}(arene)]$^+$ using a base such as t-BuOK.[12] The acidity of benzylic hydrogens is considerably increased when the arene is bonded in a π-complex to an electron-withdrawing transition-metal moiety. This point has first been shown by Trahanovski[31b] using $Cr(CO)_3$ and applied by others to benzylic activation[31c–g] (deprotonation followed by alkylation or both steps in one-pot reactions). It has also been applied to [CpFe^{II}(arene)]$^+$ complexes.[11,31i–k] (b) Trahanovski, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897. (c) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36. (d) Jaouen, G. *Ibid.* **1977**, *295*, 59. (e) Jaouen, G.; Meyer, A.; Simmoneaux, G. *J. Chem. Soc.* **1975**, 813. (f) Boudeville, M.-A.; Des Abbayes, H. *Tetrahedron Lett.* **1975**, 2727. (g) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677. (h) Nesmeyanov, A. N.; Ustynuk, N. A.; Makarova, S.; Ustynuk, Y. A.; Novikova, L. N.; Luzikov, Yu *J. Organomet. Chem.* **1978**, *154*, 45. (i) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 688; *J. Am. Chem. Soc.* **1977**, *99*, 1427; (j) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1977**, *141*, 99. (k) Lee, C. C.; Steele, B. R.; Demchuk, K. J.; Sutherland, R. G. *Can. J. Chem.* **1979**, *57*, 946; *J. Organomet. Chem.* **1979**, *181*, 411.

Scheme II



The same reaction of O_2 proceeds in pure THF as well. When the solvent is carefully removed in vacuo at −21 °C from the above-filtered pentane solution of 7, addition of pure THF followed by $^1/_2$ mol of O_2 gives the dark red solution of 8. Alkylation by PhCOCl proceeds similarly, giving **9** (Scheme I).

4. Reactions of O_2 with CpFe^I(arene) Complexes Lacking Benzylic Hydrogens. (a) CpFe^I(C_6H_6) (10). The reactions in THF giving peroxides Na_2O_2 + [CpFe(arene)]$^+X^-$ in the presence of Na^+X^- do not depend on whether the arene bears benzylic hydrogen(s) or not. For instance, the parent complex **10** gives 10^+X^- + $^1/_2Na_2O_2$ rapidly and cleanly upon reaction with $^1/_2$ mol of O_2 at −80 °C. Since **10** is thermally stable up to 0 °C in the solid state, it was prepared and crystallized; a toluene- or Na^+X^--free THF solution of **10** reacts with $^1/_2$ mol of O_2 at −80 °C giving a soluble orange peroxide, **11**, which appeared to be thermally stable at 20 °C. ^1H and $^{13}C\{^1H\}$ NMR and mass spectra show that the structure is of the type CpFe(cyclohexadienyl) dimer but also indicate that it is different from that of the known dimer [CpFe(η^5-C_6H_6)]$_2$ (**12**).[32] This peroxide explodes upon contact with a spatula. The compared $^{13}C\{^1H\}$ NMR spectra of [CpFe(η^5-C_6H_6–)]$_2$ (**12**)[32,33] and of [CpFe(η^5-C_6H_6O–)]$_2$ (**11**) indicate a large difference in the chemical shifts of the sp^3 carbon (respectively 44.8 and 73.3 ppm, the latter value being characteristic of COO–). A weak infrared (forbidden) band if found at 810 cm^{-1}, characteristic of the peroxo bridge.[26,28,33] This complex **11** has also been reported by Vol'kenau and Petrakova.[27] Since the yield is nearly quantitative and the reaction stoichiometrically reproducible ($^1/_2$ mol of O_2/mol of **10**), we investigated the fate of dioxygen in this reaction. After reaction at −80 °C, the homogeneous orange solution was hydrolyzed with HPF_6 at this temperature. A yellow precipitate, [CpFe^{II}(C_6H_6)]$^+PF_6^-$, was obtained quantitatively. Titration of the filtrate by $KMnO_4$ indicate the presence of $^1/_2$ mol of H_2O_2,[34] which confirms that a peroxide is formed.

(b) CH_3CpFe^I(C_6H_6) (13) and $C_5(CH_3)_5$Fe^I(C_6H_6) (15). The reaction of **13** with O_2 was examined because of the possibility that the Cp methyl might lose an H atom to give [η^4-$C_5(CH_3)_4CH_2$]Fe^0(η^6-C_6H_6).[35] However, formation of the dimer [CH_3CpFe^{II}(η^5-C_6H_6O–)]$_2$ (**14**), analogous to **11**, is observed upon reaction with $^1/_2$ mol of O_2 in toluene. The behavior of **15** toward O_2 is completely analogous to those of **10** and **13**.

Table II. **Salt Effect on the Reactivity of $O_2^{\bullet-}$ as a Nucleophile in the Reaction**

$$\underset{10}{\mathrm{CpFe^I(C_6H_6)}} \xrightarrow{O_2} \underset{11}{[\mathrm{CpFe^{II}(\eta^5\text{-}C_6H_6O\text{–})}]_2} + \underset{10^+X^-}{[\mathrm{CpFe^{II}(C_6H_6)}]^+X^-}$$

M^+X^- [b]	11 [a]	$10^+PF_6^-$ [a]
without	100	0
$K^+PF_6^-$ + 18-crown-6 [c]	60	40
$K^+PF_6^-$	30	70
$Na^+PF_6^-$	0	100

[a] Percent of **11** and $10^+PF_6^-$ determined by weight (reactions are immediate). [b] Concentrations of both **10** and the salt in THF (30 mL) are 0.067 mol L^{-1}; $Na^+PF_6^-$ produces the same salt effect in DME. The intermediacy of superoxide ion is indicated by its characteristic ESR spectrum at 77 K in the reaction of O_2 with **10** in frozen THF solution as in ref 13 at 150–170 K in the presence or absence of a salt. [c] Stoichiometry.

As expected from the behavior of **10**, **13** reacts with $^1/_2$ mol of O_2 in THF + $Na^+PF_6^-$ to give a virtually quantitative amount of $13^+PF_6^-$ + $^1/_2Na_2O_2$. Compound **15** similarly gives $15^+PF_6^-$ and $^1/_2Na_2O_2$.

(c) CpFe^I(1,3,5-*t*-$Bu_3C_6H_3$) (17). Complex **17** is the only thermally stable Fe^I complex in which the arene bears less than six alkyls.[22] It does not dimerize even in the solid state at 20 °C. On the other hand, the dimeric peroxide **18** is obtained by contact of a solution of **17** with $^1/_2$ mol of O_2 in pentane (Scheme VII).

5. Reactions of O_2 with CpFe^I(C_6H_6) in THF in the Presence of Various Added Salts: Influence of the Size of M^+ and X^-. Whereas all CpFe^I(arene) compounds react with O_2 in THF in the presence of 1 equiv of $Na^+PF_6^-$ to give Na_2O_2 and [CpFe$^+$(arene)]PF_6^-, the type of reaction in the absence of $Na^+PF_6^-$ depends on whether the arene bears benzylic hydrogen(s). Thus, we undertook to also study the influence of the sizes of the cation and of the anion of the salt in the salt effect when the arene does not bear benzylic hydrogen(s). In the reaction of O_2 with a suitable Fe(I) compound, we replaced $NaPF_6$ by other salts, especially those having larger cations and smaller anions, in accord with the mechanism proposed (see below). We choose to effect reactions with CpFe^IC_6H_6 which can easily be isolated and is reasonably stable below ca. −5 °C. Table II summarizes the results obtained with various salts and indicates that the salt effect is no longer quantitative when cations larger than Na^+ or/and anions smaller than PF_6^- are used (mixtures of dimeric peroxides and of CpFe$^+$(arene)X^- are obtained). This conclusion is of the same nature as that found in the reactivity of CpFe^IC_6Me_6. As expected for such a salt effect, its magnitude is all the greater as the size of the cation of the salt decreases and as that of the anion increases. The maximum magnitude (quantitative salt effect: no dimeric peroxide formed) is found with $Na^+PF_6^-$ (as with other salts having a smaller cation or larger anion than $Na^+PF_6^-$).

6. Reactions of O_2 with a CpFe^I(arene) Complex Bearing a Sterically Hindered Benzylic Hydrogen:

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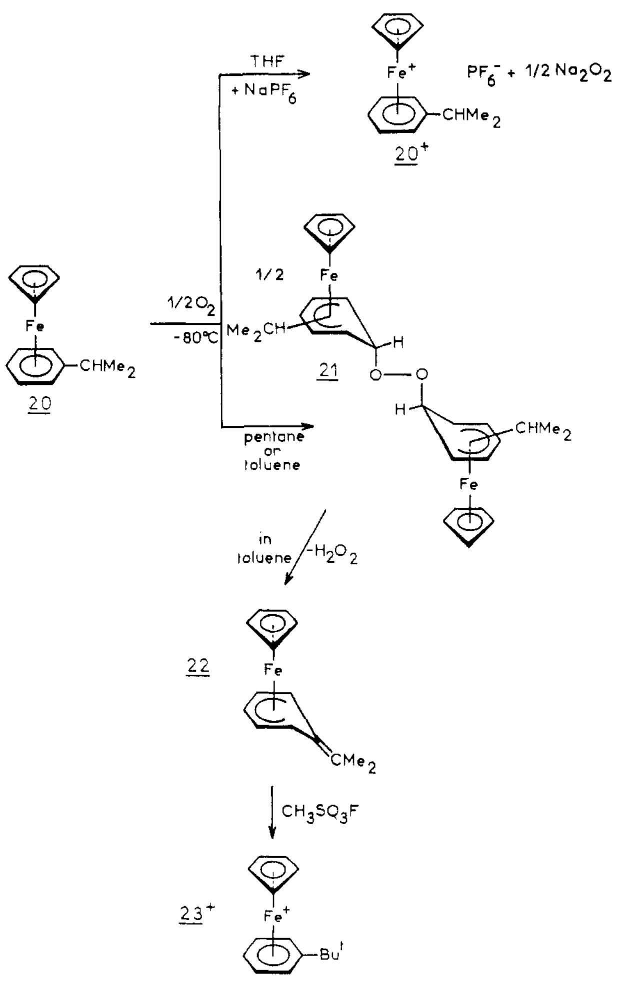
[32] Nesmeyanov, A. N.; Solodovnikov, S. P.; Vol'kenau, N. A.; Kotova, L. S.; Sinitsyna, N. A. *J. Organomet. Chem.* **1978**, *148*, C5.

[33] Nesmeyanov, A. N.; Sinitsijna, N. A.; Kolesov, V. S.; Sizoi, V. F.; Vol'kenau, N. A. *Dokl. Akad. Nauk SSSR* **1978**, *242*, 1356.

[34] For titration of H_2O_2 with $KMnO_4$ in organometallic reactions, see ref 13.

[35] (a) Decamethylcobaltocene should react with O_2 to give such a η_4-fulvalene compound by a similar H atom abstraction. However, in mixed sandwiches, the deprotonation step requires reaction at the more acidic even ligand.[5b] (b) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 20.

Scheme III



$CpFe^I(i\text{-}PrC_6H_5)$ (20). With **20**, three specific reactions are now observed (Scheme III). In THF + $Na^+PF_6^-$, $^1/_2$ mol of O_2 reacts with **20** giving $\mathbf{20}^+PF_6^-$. If $Na^+PF_6^-$ is removed by addition of excess pentane and filtration, contact with $^1/_2$ mol of O_2 gives the mixture of isomeric dimers **21** with the same stoichiometry as for **11**. In toluene (containing 10% DME or THF) a more unexpected and interesting behavior is reproducibly observed. Reaction with $^1/_2$ mol of O_2 at −80 °C gives a light orange homogeneous solution which upon warming subsequently becomes dark red at −17 °C, characteristic of H-atom abstraction. Monitoring this reaction by $^{13}C\{^1H\}$ NMR in toluene-d_8 indicates a $CpFe^{II}$(cyclohexadienyl) structure for the orange complex (−60 °C) and a similar structure with appearance of the characteristic signal of the ring carbon of the exocyclic double bond at 149 ppm for the dark red solution. A peroxy absorption of medium intensity in the IR spectrum at 810 cm^{-1} is also recorded for the orange complex, attributable to the asymmetric isomers; this band vanishes upon warming and is replaced by another absorption at 1600 cm^{-1} characteristic of the exocyclic double bond in the dark red complex. Addition of a THF solution of CH_3SO_3F at −10 °C causes the immediate precipitation of the yellow salt $CpFe(t\text{-}BuC_6H_5)FSO_3^-$, which is metathesized to the PF_6^- salt **23**; the overall yield from $\mathbf{20}^+PF_6^-$ is 50%. Thus, H-atom abstraction from **20** by O_2 giving **22** is restricted to toluene solutions. The nature of the toluene-soluble orange complex **21** is of interest in view of the further C–H activation observed. It is similar to the orange peroxides formed by reaction between O_2 and $CpFe^I$(arene) complexes lacking benzylic hydrogens. It is also hydrolyzed by HPF_6 at −80 °C to give $\mathbf{20}^+PF_6^-$ and H_2O_2. Thus the dimer **21** is the precursor of the H-atom abstraction product in toluene (Scheme III).

Mechanisms and Discussion

(a) Electron Transfer and Deprotonation by $O_2^{\bullet-}$ in Ion Pairs. We have shown that the reaction between O_2 and **1** is an outer-sphere electron transfer giving $\mathbf{1}^+O_2^{\bullet-}$ followed by deprotonation of $\mathbf{1}^+$ by $O_2^{\bullet-}$.[13] The intermediacy of $O_2^{\bullet-}$ is indicated by the characteristic EPR spectrum of this species. This pathway is a result of the large potential difference (ca. 1 V) between the two reversible redox systems $1/1^+$[36] and $O_2/O_2^{\bullet-}$.[2c] Since analogous H-atom abstractions by O_2 in various solvents is obtained with related $CpFe^I$(arene) complexes, it is reasonable to assume that the electron transfer mechanism is also operative in the latter. Indeed when reactions between O_2 and the Fe^I complexes were performed by diffusion of O_2 in frozen toluene solutions in EPR tubes, it is still possible to observe the spectrum of $O_2^{\bullet-}$ at 77 K.[17,18] The acidity of methyl protons in $[CpFe(C_6H_nMe_{6-n})]^+$ is greater than in $\mathbf{1}^+$ and that of methylene protons in $[CpFe(C_6H_5Et)]^+$ ($\mathbf{25}^+$) is also greater than in $[CpFe(C_6Et_6)]^+$ ($\mathbf{26}^+$). Of interest is the fact that H abstraction is obtained in various solvents but only in the absence of Na^+X^-. This electron-transfer mechanism followed by deprotonation by $O_2^{\bullet-}$ is also consistent with the rapid H-atom abstraction by O_2 at −80 °C found for both $CpFe^I$(*exo*-methylfluorene) and $CpFe^I$(*endo*-methylfluorene).[37]

(b) Salt Effect[38–40] and Disproportionation of $O_2^{\bullet-}$. The formation of $[CpFe^{II}(arene)]^+X^- + {}^1/_2M_2O_2$ is general when a salt, M^+X^-, is added. It is observed in THF and DME, whether the complexes (various M^+ and/or X^-) bear benzylic hydrogens or not and whatever their corresponding reactions in pentane and toluene. The ion exchange between the cages is known to be extremely fast even at low temperature,[38] indeed even faster than the various reactions of $O_2^{\bullet-}$. In addition, solvents with weak dielectric constants favor salt effects because ions of opposite signs are associated.[38–40] Thus the concentration of each ion pair, resulting from the equilibrium between the four cage ion pairs, is the most important factor that governs the observed chemistry.

In the absence of added salt, the cage formed by the cationic sandwich and $O_2^{\bullet-}$ is the only one in THF solution and $O_2^{\bullet-}$ cannot escape from this cage without reacting. Reaction of $O_2^{\bullet-}$ out of the cage is kinetically disfavored. On the other hand, the reactions in the cage are fast even at low temperature. Superoxide is a small, charged (hard) species that is not stabilized by a large (soft) cation:[2a] it is expected to be very reactive and it is indeed (Scheme IV). When the salt effect occurs (in THF), ionic peroxides are formed rather than superoxides. Since dioxygen is added to solutions of the Fe^I donor, the metal complex is present in excess in the reactions and thus a further oxidation state of O_2 may be attained, reduction of $O_2^{\bullet-}$ to

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(36) (a) Astruc, D.; Dabard, R. *Bull. Soc. Chim. Fr.* **1976**, *228*. (b) Moinet, C.; Román, E.; Astruc, D. *J. Electroanal. Interfacial Electrochem.* **1981**, *121*, 241.

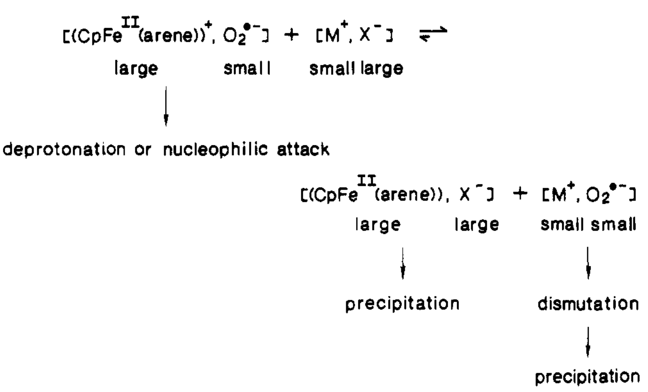
(37) Catheline, D.; Astruc, D. *Nouv. J. Chim.* **1984**, *8*, 381.

(38) Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277; *J. Am. Chem. Soc.* **1982**, *104*, 6142; **1981**, *103*, 6403; **1983**, *105*, 4875.

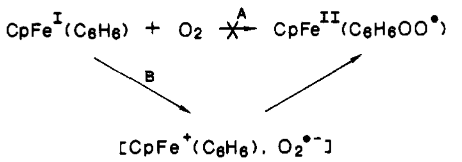
(39) Winstein, S.; Savedoff, L. G.; Smith, S. *Tetrahedron Lett.* **1960**, *9*, 24.

(40) For the special salt effects, see ref 38 and 39 and (a) Swarc, M., Ed.; *Ions and Ion Pairs in Organic Reactions*; Wiley: New York, 1974; Vol. 2. (b) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; Wiley: New York, 1975. (c) Loupy, A.; Tchoubar, B. *Effet de sels en Chimie Organique*; Bordas, Ed.; Paris, in press.

Scheme IV



Scheme V

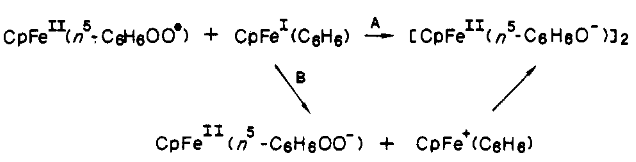


O_2^{2-}. However, the potential of the system $O_2^{\bullet -}/O_2^{2-}$ has been reported to be very negative (ca. −2 V/SCE),[41] and thus $O_2^{\bullet -}$ may be difficult to reduce in aprotic media.[42] On the other hand, fast disproportionation of superoxide anion is catalyzed not only by superoxide dismutase enzyme but also by some transition-metal ions and by protons.[43] We know that the alkyl groups of the sandwiches are available as a source of protons[31] but the formation of Na_2O_2 is quantitative as well in the absence of benzylic hydrogen. Although such a disproportionation is not known to be induced by alkali cations, it may be envisaged to proceed via the solvent separated ion pair and contact ion pair of NaO_2.[44]

One may view the role of Na^+ in this disproportionation as another salt effect. The first salt effect is to inhibit the cage chemistry, and the second one consists in inducing electron transfers among the oxygen species. This proposition follows our recent finding that Na^+ salts induce the disproportionation of Fe^I complexes to Fe^0 and Fe^{II} species in other reactions[45] where iron(I) plays the role of $O_2^{\bullet -}$ here. (Note that, in the present case, Na^+ salts have no effect on the oxidation states of the iron complexes because the electron transfer from Fe^I is extremely exergonic.) Finally the possibility that the Fe^I complex directly reduces the contact ion pair $[Na^+,O_2^{\bullet -}]$ cannot be discarded although the overpotential is around 0.7 V. Additional driving forces are the formation of precipitates of $[CpFe(arene)]^+PF_6^-$ and Na_2O_2. One should note that this latter factor is not the major one in the salt effect, however, given the variation of effects obtained upon variation of the sizes of the ions of the added salt.

(c) O_2-Induced Dimerization of $CpFe^I$(arene) Complexes and the Nucleophilic Properties of $O_2^{\bullet -}$.

Scheme VI



$CpFe^I$(arene) complexes lacking benzylic hydrogens react rapidly with $^1/_2$ mol of O_2 at −80 °C in pentane or toluene to give neutral dimeric peroxides such as **11**. The structure of these dimers resemble that of the dimer obtained by slow thermal dimerization, the only difference between the two kinds of dimers being the peroxo bridge. $CpFe^I$(arene) with methyl groups on the arene ligand gives only the type of dimer without peroxo bridge whereas $CpFe^I(1,3,5\text{-}t\text{-}Bu_3C_6H_3)$ only gives the type of dimer with the peroxo bridge. $CpFe^I(C_6R_6)$ (R = alkyl) cannot give any of these types of dimer. Two families of Fe(I) give both types of dimers: (i) the benzene complexes $CpRFe^I(C_6H_6)$ (R = H, Me, Me_5) and (ii) the monosubstituted arene complexes $CpFe^I(C_6H_5CR_1R_2R_3)(R_1 \text{ and } R_2 \neq H)$ (Table III).

A major question is whether the neutral peroxides are formed by coupling of the Fe^I complexes with dioxygen (Scheme VA) or by electron transfer to O_2 followed by nucleophilic attack (Scheme VB).

The reaction of radicals with O_2 is the well-known autooxidation process, and rates are usually high or are diffusion-controlled[47] (eq 3).

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (3)$$

$CpFe^I$(arene) complexes can be considered as organometallic radicals[22] in some respects, as exemplified by their dimerization. Note, however, that the spin density is essentially metal based as indicated by the Mössbauer[49] and EPR data[18] and EHT calculations (those based on Mössbauer data indicate about 80% of metal character for the e^*_1 HOMO). Indeed dimerization is extremely slow as compared to that of organic radicals and sometimes does not occur. Radicals can also transfer electrons even in media of low dielectric constants,[50] and we know that, due to the very large potential difference with O_2, electron transfer is rapid[51] at −80 °C in inert solvents as well as in ethers. In this competition between coupling and electron transfer, no reaction products that would result from the coupling with O_2 are found with $CpFe^I(C_6R_6)$ complexes although the spin density is higher on the unsubstituted Cp than on the benzene ring.[17] Thus we believe a direct coupling with O_2 is less probable than electron transfer followed by nucleophilic attacks of $O_2^{\bullet -}$ on the benzene ring of the cation. Such a nucleophilic attack on $(CpFe^{II}arene)^+$ complexes by anionic nucleophiles are classical[52] reactions (even those of neutral nucleophiles are known).[53] Finally electron transfer in this O_2-induced dimerization was ascertained by observation of the EPR spectra of $O_2^{\bullet -}$ ob-

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(41) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 83.

(42) Sawyer, D. T., Gibian, M. J.; Morrison, M. M., Sev, E. T. *J. Am. Chem. Soc.* **1978**, *100*, 627.

(43) (a) Reference 2b. (b) Chen, D. H.; Chiericato, G., Jr.; Nanni, E. J., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* **1982**, *104*, 1296.

(44) For examples of counterion dependence of reduction potentials in quinone series, see the works by H. Bock et al.: (a) Bock, H.; Solouki, B.; Rosmus, P.; Dammel, R.; Hänel, P.; Hierholzer, B.; Lechner-Knoblauch, U.; Wolf, H. P. In *Organo-silicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood Limited: Chichester, 1985; pp 45–73. (b) Bock, H. L'actualité Chimique, March 1986, p 33.

(45) Lacoste, M.; Astruc, D., submitted for publication.

(46) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Petrakova, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim* **1974**, *9*, 2159.

(47) (a) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193. (b) Davies, A. G. *J. Organomet. Chem.* **1980**, *200*, 87.

(48) Moinet, C.; Román, E.; Astruc, D. *J. Electroanal. Interfacial Electrochem.* **1981**, *121*, 241.

(49) Mariot, J.-P.; Michaud, P.; Lauer, S.; Astruc, D.; Trautwein, A. X.; Varret, F. *J. Phys. (Les Ulis, Fr.)* **1983**, *44*, 1377.

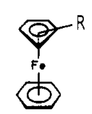
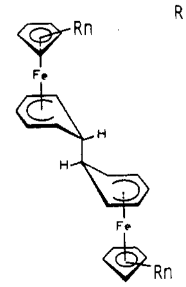
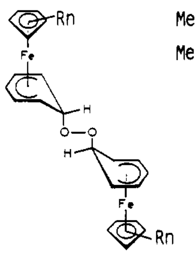
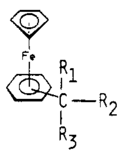
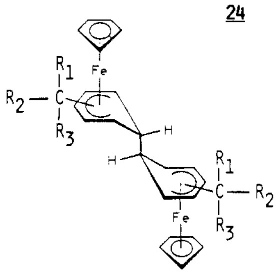
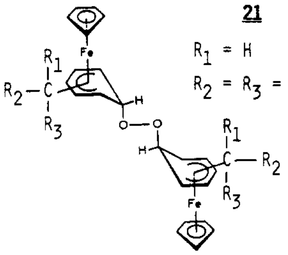
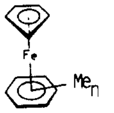
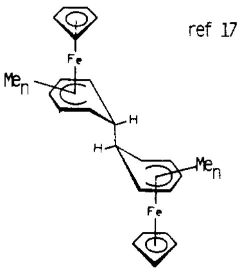
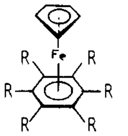
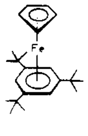
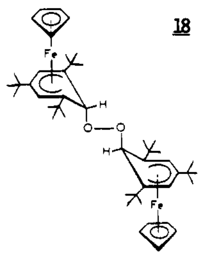
(50) Lawler, R. G.; Barbara, P. F.; Jacobs, D. *J. Am. Chem. Soc.* **1978**, *100*, 4912.

(51) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265 and references cited therein.

(52) (a) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. (b) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257.

(53) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 606.

Table III. Dimers $[Fe^{II}Cp(\eta^5\text{-cyclohexadienyl})]_2$ Obtained from $CpFe^{I}$(arene) Complexes Thermally or by Contact with O_2[a]

Fe^{I} complex	Fe^{II} dimer obtained thermally from Fe^{I}	Fe^{II} dimer with a peroxo-bridge obtained by contact of Fe^{I} with O_2
R = H 10[19] Me 13 Me_5 15[17] 	 R = H 12[46] Me 19 Me_5 27[17]	 R = H 11[27,28] Me 14 Me_5 16
20 	24 	 21 R_1 = H R_2 = R_3 = Me accessible if at most one R is H
 1≤n≤5 also one Et	 ref 17	NO (H atom abstraction)
R = Me 1[17] Et 26[22] 	NO (steric inhibition)	NO (H atom abstraction)
17[22] 	NO (steric inhibition)	18 

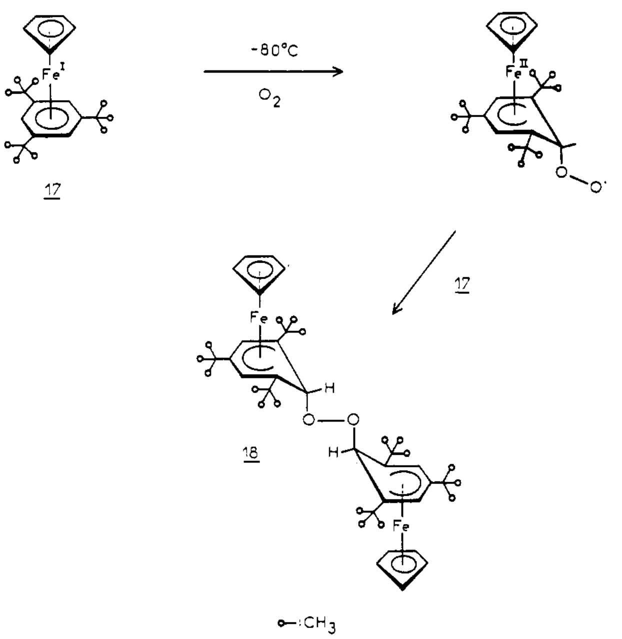
[a] The table indicates the conditions for substituents to provide a given type of dimer: the thermal dimerization is inhibited by bulky arene ligands whereas the dimerization with O_2 cannot occur if the arene bears primary or secondary benzylic hydrogens (H atom abstraction by O_2 is faster).

tained for gels of the Fe^{I} complexes into which O_2 was allowed to diffuse.

Further reaction of $CpFe(\eta^5\text{-}C_6H_6OO^\bullet)$ with $CpFe^{I}(C_6H_6)$ (**10**) poses a similar problem, i.e., it may be a direct coupling between the peroxy radical and **10** (Scheme VIA) or follow an electron-transfer path from **10** to the peroxo radical.

In only one particular instance (**17**), the Fe^{I} complex is thermally stable and does not dimerize at any temperature, except upon contact with $^1/_2$ mol of O_2. The bulk of the *tert*-butyl groups in positions 1, 3, and 5 about the benzene ligand obviously prevents the unsubstituted benzene carbons of two complexes from approaching each other. The reaction with the small species $O_2^{\bullet-}$ is possible, how-

Scheme VII



ever, and switches the ring geometry from planar to bent (cyclohexadienyl-like) with the peroxo substituent in an exo position. This peroxo “tail” is located far enough below the cyclohexadienyl plane to escape the steric inhibition so that it can react with an unsubstituted benzene carbon of another molecule of **17** to form the cyclohexadienyl peroxo dimer **18** (Scheme VII).

It is not certain that the mechanism is the same as in the reported case of cobaltocene:[26]

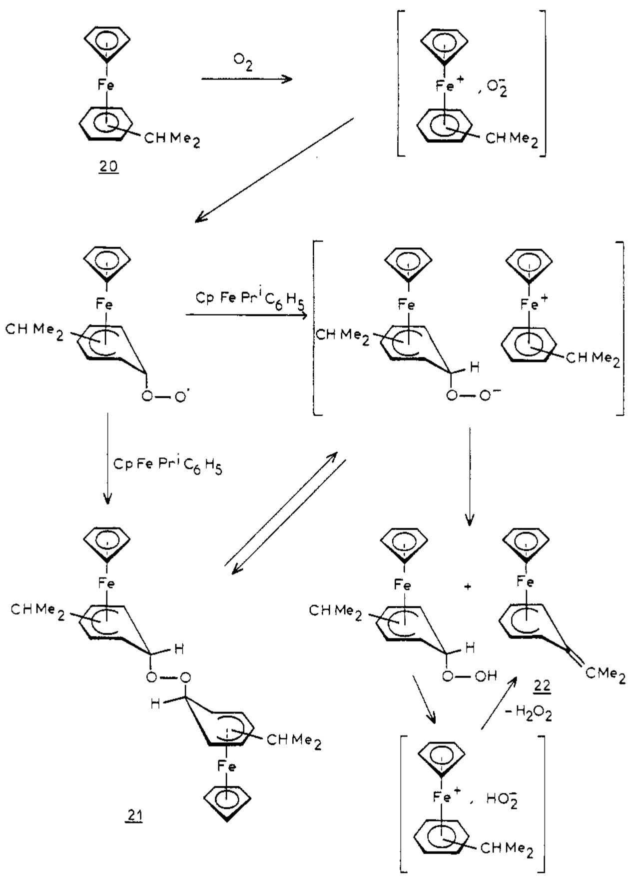
$$2CoCp_2 + O_2 \rightarrow [CpCo(\eta^4\text{-}CpO\text{-})]_2$$

Since its oxidation potential is much lower than those of CpFe^I(arene) (-1.3 V to -1.6 V versus SCE in nonaqueous solvents), cobaltocene is not likely to transfer easily an electron to O_2, the difference between the redox potentials of $CoCp_2/CoCp_2^+$ (~-0.9 V versus SCE) and $O_2/O_2^{\bullet -}$ (-0.7 V versus SCE) being small. Thus, a simple coupling in a persistent charge-transfer complex $[CoCp_2,O_2]$ is also possible. Nucleophilic attack of $O_2^{\bullet -}$ on an odd- (five-) electron Cp ligand is also more difficult than that of an even- (six-) electron benzene ligand.[35b]

(d) Formation and Decomposition of the Peroxo Dimers [CpFe^{II}(η^5-C$_6$H$_5$-*i*-PrO–)]$_2$ (21). In the absence of primary or secondary benzylic hydrogens, CpFe^I(arene) complexes react with O_2 to give dimeric peroxides **11**. This type of structure is known for cobaltocene, and their formation is indicated by the stoichiometry of the reaction, their hydrolysis to H_2O_2, and their spectroscopic characteristics.

A peculiar case is that of CpFe^I(*i*-PrC$_6$H$_5$) (**20**) which gives a mixture of dimers **21** on contact with $^1/_2$ mol of O_2 at -80 °C in pentane. It seems that a tertiary hydrogen such as that in **20** is not abstracted because of the steric bulk about this benzylic position. Superoxide anion can either react as a nucleophile or as a base, and the former process appears to proceed faster in pentane at -80 °C. It is probable that the balance between these two properties of superoxide in the cage is reached at this point because the reaction in toluene is not so clear-cut. The orange mixture of dimeric peroxide formed in this solvent at -80 °C is transformed suddenly at -17 °C to the deep red η^5-dimethylbenzyl species which can further be alkylated by CH_3SO_3F at the benzylic carbon to yield the *tert*-butylbenzene complex. The latter spectacular transformation is best taken into account by the formation of the kinetically disfavored thermodynamic deprotonation product.

Scheme VIII



This result implies a certain degree, even small, of reversibility of the carbon–oxygen bond formation, i.e., in other terms, heterolytic cleavage of this bond:

$$[CpFe(\eta^5\text{-}ArO\text{-})]_2 \rightarrow [CpFe^+(\eta^6\text{-}Ar,\eta^5\text{-}{}^-OOAr)FeCp]$$

Indeed, it is well-known that the addition of many nucleophiles to the arene ligand of organometallic arene cations is reversible.[54] It is logical to find this phenomenon occurring in toluene, a solvent which is better able to disperse charges than pentane. The above equilibrium is then shifted to the right by the deprotonation of the cation by the peroxide anion in the cage ion pair. The same fate can be attributed to the intermediate monomeric peroxide CpFe[(η^5-$C_6H_5CHMe_2OOH$)], HO_2^- being more basic than (η^5-$^-OOC_6H_5CHMe_2$)FeCp.

Summary, Conclusion, and Prospect

The reactions of dioxygen with thermally stable or unstable CpFe^I complexes of simple arenes dramatically depend on the presence and nature of M^+X^- salts. These complexes react with O_2 in ethers plus $Na^+PF_6^-$ to give only [CpFe^{II}(arene)]$^+PF_6^-$ and Na_2O_2. However, C–H activation by O_2 proceeds in good yields for CpFe^I complexes of simple arenes when a 10–20-fold excess of a cold inert solvent is added to the THF solution to remove Na^+X^- prior to contact with $^1/_2$ mol of O_2 at -80 °C. In this fashion, primary and secondary benzylic hydrogens are abstracted by $O_2^{\bullet -}$, following its generation from O_2, as in the reactions of $C_5R_5Fe^I$ complexes of arenes such as C_6H_6 and C_6H_3-*t*-Bu$_3$ lacking benzylic hydrogens give neutral

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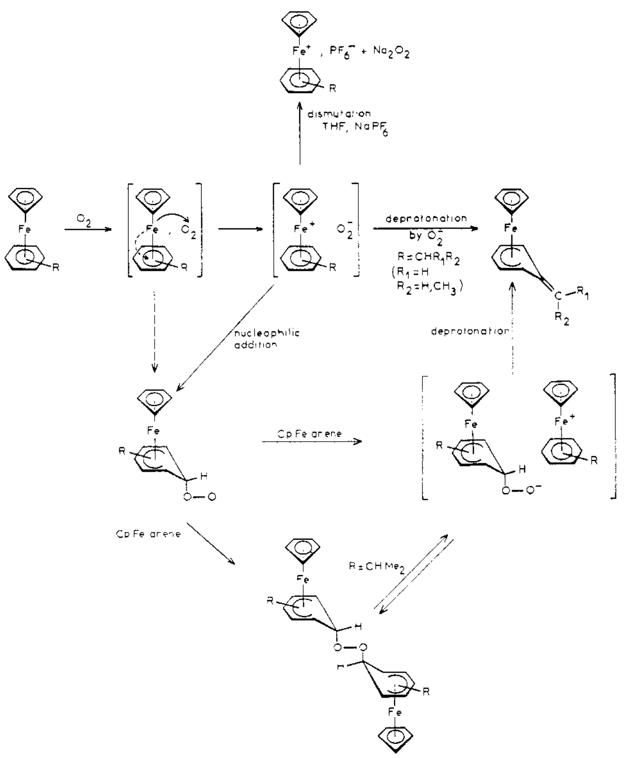
(54) (a) Davies, S. G.; Gelfand, L. S.; Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* 1979, 762. (b) Sweigart, D. A. *Ibid.* 1980, 1159.

Scheme IX



Fe^{II} peroxides. The balance between these two reactions is reached in the case of a tertiary hydrogen (the isopropylbenzene complex): the kinetic product (peroxide) is characterized at low temperature and transformed to the thermodynamic product (resulting from a formal H abstraction) at −17 °C.

The salt effect is best explained in terms of the versatile reactivity of $O_2^{\bullet-}$ in the ion pair [CpFe$^+$(arene),$O_2^{\bullet-}$] always formed in the first reaction step subsequent to interaction via a charge-transfer complex. In this ion pair, $O_2^{\bullet-}$ can act as a base (deprotonation of an alkyl substituent of the arene activated by CpFe$^+$) and as a nucleophile (in the absence of benzylic H, nucleophilic addition to the benzene ring of the cation) or it can disproportionate to O_2 and O_2^{2-}. The latter process may itself be induced by the salt effect (Na$^+$). Scheme IX accounts for these various possibilities of reaction of $O_2^{\bullet-}$ following the initial outer-sphere electron transfer.

The present study not only emphasizes the versatile reactivity of $O_2^{\bullet-}$ but also illustrates our concept aimed at obtaining reactive radical anions (such as $O_2^{\bullet-}$) by electron transfer from an organometallic electron reservoir in common solvents of low dielectric constants such as ethers or hydrocarbons. In the present case, this concept led to a remarkable C–H activation, extremely sensitive to the presence of salts and generalized to primary, secondary, and tertiary hydrogens of the entire series of arenes which can be complexed to CpFe$^+$. Application of this activation to more sophisticated aromatic structures can now be envisaged.

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Registry No. **7**, 69022-30-6; **7**$^+$BF$_4^-$, 32758-59-1; **7**$^+$OH$^-$, 112596-51-7; **7**+PF$_6^-$, 33435-42-6; **7**$^+$I$^-$, 112596-52-8; **8**, 72576-18-2; **10**, 51812-05-6; **10**$^+$BF$_4^-$, 1277-51-6; **11**, 83617-47-4; **13**, 70414-97-0; **14**, 112596-57-3; **15**$^+$BF$_4^-$, 112621-10-0; **16**, 112596-58-4; **17**$^+$PF$_6^-$, 83528-74-9; **18**, 86584-13-6; **20**, 98162-09-5; **20**$^+$PF$_6^-$, 32760-80-8; **21** (isomer 1), 112596-59-5; **21** (isomer 2), 112596-60-8; **22**, 72585-91-2; **25**, 78230-46-3; **27**, 112596-53-9; **28**$^+$PF$_6^-$, 112596-54-0; THF, 109-99-9; 18-crown-6, 17455-13-9; [CpFe($C_6H_5CH_2COC_6H_5$]PF$_6$, 86584-12-5; [CpFe($C_6HMe_4CH_2COC_6H_5$)]PF$_6$ (isomer 1), 112621-12-2; CpFe(η^5-$C_6HMe_4CH_2$) (isomer 2), 112596-56-2; n-Bu$_4$N$^+$PF$_6^-$, 3109-63-5; K$_+$PF$_{6-}$, 17084-13-8; Na$^+$PF$_6^-$, 21324-39-0; Na$^+$BF$_4^-$, 13755-29-8; Na$^+$F$^-$, 7681-49-4; O_2, 7782-44-7; $O_2^{\bullet-}$, 11062-77-4; toluene, 108-88-3; pentane, 109-66-0; CpFe^I($C_6H_3Me_3$), 51812-08-9.

Formation of a Tungsten Vinylvinylidene Complex from Addition of Alkyne to (dppe)$(OC)_3W{=}C{=}CHPh$

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Reaction of *mer*-(dppe)$(OC)_3W{=}C{=}CHPh$ with dimethyl acetylenedicarboxylate (DMAC) results in formation of *Z* and *E* isomers of a vinylvinylidene product, (dppe)$(OC)_3W{=}C{=}C(COOCH_3)C(COOCH_3){=}CHPh$. The reaction presumably proceeds through an η^1-cyclobutenyl complex prior to forming the final product which reflects net insertion of the added alkyne into the C_α–C_β bond of the vinylidene reagent. The kinetically formed *Z* isomer is rapidly converted to the *E* isomer by light, with a photostationary state ratio of 1:8 *Z*/*E*. Infrared and ^{1}H and ^{13}C NMR data are reported for both isomers. The X-ray crystal structure of the *Z* isomer shows an octahedral tungsten environment and an approximate cisoid geometry for the vinylvinylidene fragment. The compound crystallizes in space group $P2_1/c$ with four molecules per unit cell (a = 11.140 (4) Å, b = 18.047 (6) Å, c = 19.850 (7) Å; β = 94.87 (3)°; V = 3976.3 Å^3; ρ(calcd) = 1.521 g/cm^3). Full-matrix least-squares refinement of 358 variables using 4146 data with $I \geq 3\sigma(I)$ converged with unweighted and weighted residuals of 4.1% and 3.1%, respectively.

Introduction

The chemistry of metal vinylidene complexes has blossomed during the past decade. An excellent review by Bruce and Swincer[1] provides a comprehensive overview of this area. Rearrangement of terminal alkyne ligands to vinylidene ligands is common for octahedral d^6 deriv-

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(1) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.