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Preliminary communication

INTERACTION OF BENZENECYCLOPENTADIENYLIRON WITH OXYGEN

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Summary

Electroneutral benzenecyclopentadienyliron reacts with oxygen under strictly aprotic conditions to give a crystalline peroxidic dimer. The cyclohexadienyl-cyclopentadienyl structure of the latter, with a peroxide bridge between the six-membered ligands of the two moieties of the molecule, is determined by ^{1}H NMR spectroscopy. Reactions of this new peroxidic dimer with several reagents, i.e. HCl, H_2O, C_2H_5OH, C_6H_5SH, C_6H_5COCl, $CHCl_3$, CH_3COCH_3, are described.

Electroneutral arenecyclopentadienyliron derivatives, as is known [1], are oxidized by atmospheric oxygen in the presence of H_2O to form the corresponding cationic π-complexes.

$$2\ \text{AreneFeC}_5\text{H}_5 + O_2 + 2\ H_2O \rightarrow 2[\text{AreneFeC}_5\text{H}_5]^+ + 2\ OH^- + H_2O_2$$

In the case of $C_6H_6FeC_5H_5$, we were able to show that under strictly aprotic conditions the electroneutral π-complex reacts with oxygen to form the peroxidic dimer:

$$2\ C_6H_6FeC_5H_5 + O_2 \xrightarrow{\text{THF}} [C_6H_6FeC_5H_5]_2O_2$$

The reaction was carried out by bubbling dry air through an absolute THF solution (40 ml) of $C_6H_6FeC_5H_5$ (4 mmol) at –45°C. The dark-green mixture rapidly turned bright-orange. After the solvent was removed under reduced pressure and at –15 to –20°C an orange crystalline substance was obtained, which was purified by reprecipitation from THF with pentane. The IR spectrum of the orange product (Nujol; spectrometer UR-20) revealed a band at ~875 cm^{-1}, characteristic for a peroxide grouping [2].

Pyrolysis of 3.75 mmol of the resulting peroxide in decane at 60°C led to

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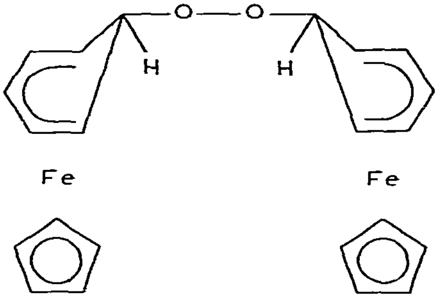
the formation of 43.3 cm^3 oxygen (identified by GLC) corresponding to the formula $[C_6H_6FeC_5H_5]_2O_2$. In addition, metallic iron, benzene (GLC) and ferrocene (~19%) are formed.

The structure of benzenecyclopentadienyliron peroxide was determined by ^{1}H NMR spectroscopy (in C_6H_5Cl, Bruker SXP 4-100). The ^{1}H NMR spectrum of the peroxide contains a signal of cyclopentadienyl (Cp) protons at δ 4.30 ppm (singlet) and signals of cyclohexadienyl (Chd) protons δ 5.66 (H^4, triplet), δ 4.54 (H^3 and H^5, triplet), δ 3.30 ppm (H^2 and H^6, triplet). The signal of H^1 is probably shifted to the region of the protons of Cp (singlet and triplet, H^3, H^5). Hence, the ratio of the integral intensities is: H^4/H^1, H^3, H^5, $H(Cp)/H^2$, $H^6 = 1/8/2$. The H^1 signal shift should be attributed to the influence of the peroxide grouping. The spin—spin coupling constants of the protons of the Chd ligands are $J_{3,4} = J_{4,5} = J_{5,6} = J_{3,2} = J_{1,6} = J_{1,2} \simeq 6$ Hz and no signal for coordinated benzene rings was detected. On the basis of this spectrum structure A is proposed for cyclopentadienyliron peroxide, with a peroxide bridge between the six-membered ligands of two initial π-complex molecules. The formation of the peroxide bridge is accompanied by the conversion of arene ligands into non-planar Chd ligands. A similar structure with an —O—O— bond between non-planar five-membered ligands was earlier assigned [3] to cobaltocene peroxide.

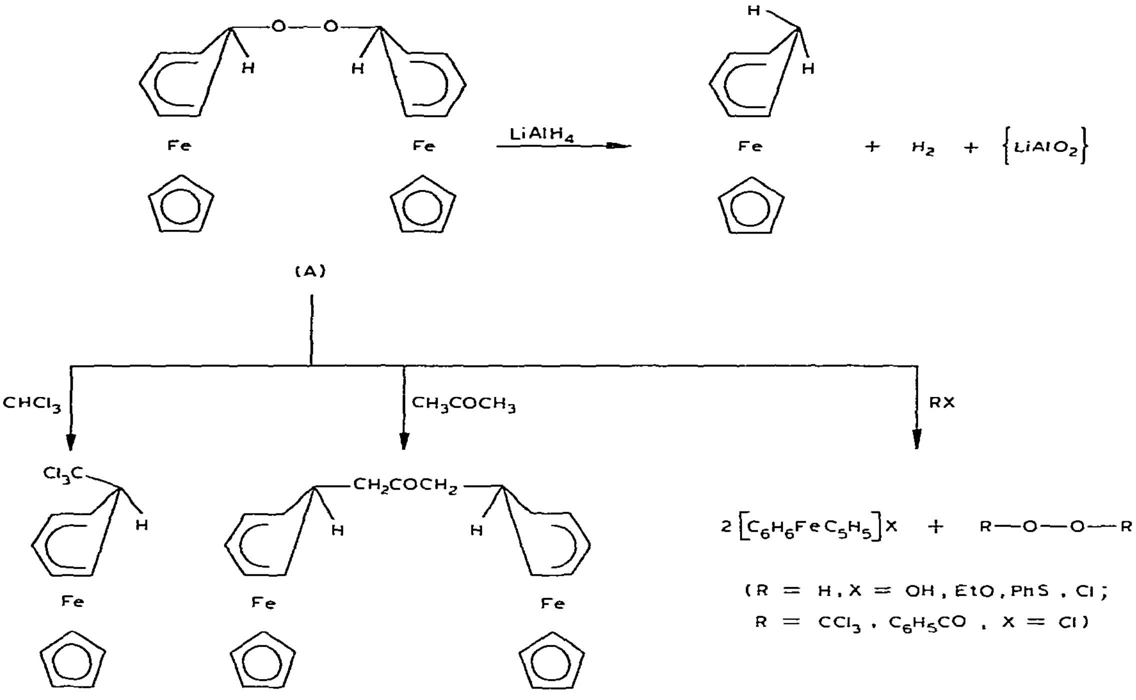


(A)

In the mass spectrum of $[C_6H_6FeC_5H_5]_2O_2$ no molecular ion was detected (AEI MS-30 mass spectrometer equipped with a DS-50 system for data-processing); while the following fragmentation products were recorded (m/e): 199 $C_6H_6FeC_5H_5^+$, 186 $C_5H_5FeC_5H_5^+$ (see [4]), 121 $C_5H_5Fe^+$, 78 $C_6H_6^+$, 65 $C_5H_5^+$, 56 Fe^+.

The reactivity of benzenecyclopentadienyliron peroxide is shown in Scheme 1. From Scheme 1 it can be seen that two types of reactions are characteristic for A: (a) those leading to the formation of the benzenecyclopentadienyliron cation; and (b) those leading to the formation of cyclohexadienylcyclopentadienyliron derivatives. Interaction with water, aqueous solution of acids, ethanol, thiophenol, carbon tetrachloride and benzoyl chloride belongs to type (a).

Interaction of $[C_6H_6FeC_5H_5]_2O_2$ (from 3.6 mmol $C_6H_6FeC_5H_5$) with 8.5 mmol H_3PO_4 in THF in the presence of 2 g KI, 20 ml H_2O and one drop of concentrated HCl (–78°C, vigorous stirring, gradual increase in temperature



SCHEME 1

up to 20°C) has led to the formation of $[C_6H_6FeC_5H_5]^+$ isolated as tetraphenylborate (1.72 g, 92%), m.p. 250—251°C (dec.). In addition, hydrogen peroxide was formed (92% from the theoretical), as was shown by titration of the iodine formed with a 1 *N* solution of $Na_2S_2O_3$. No formation of O_2 was observed under these conditions. The same results were obtained by interaction of $[C_6H_6FeC_5H_5]_2O_2$ with HCl in a dimethoxyethane/pentane mixture at −25°C.

Interaction of $[C_6H_6FeC_5H_5]_2O_2$ with water or ethanol in the absence of acids (DME) leads to a partial or full formation of oxygen, depending on the temperature, which can be explained by the rapid decomposition of hydrogen peroxide in alkaline solutions (pH = 9) in the presence of an iron salt.

$$[C_6H_6FeC_5H_5]_2O_2 + 2\,H_2O \rightarrow 2\,[C_6H_6FeC_5H_5]^+ + H_2O + 2\,OH^-$$

$$H_2O_2 \xrightarrow{OH^-} H_2O + \tfrac{1}{2}\,O_2$$

Partial formation of oxygen also takes place in an acidic solution (HCl) if the temperature is not strictly controlled. The quantitative determination of H_2O_2 is possible only in the presence of phosphoric acid. However, in all cases the interaction of $[C_6H_6FeC_5H_5]_2O_2$ with H_2O or C_2H_5OH has led to the formation of salts of benzene-cyclopentadienyliron cation in >90% yield, but no formation of ferrocene was observed.

Interaction of $[C_6H_6FeC_5H_5]_2O_2$ (1.7 mmol) with thiophenol (3.5 mmol) in a DME/pentane mixture at 0°C has resulted in the formation of a yellow crystalline $[C_6H_6FeC_5H_5]SC_6H_5$ salt, which was filtered off and decomposed with a mixture of an acidic $NaBF_4$ aqueous solution and ether. Then $[C_6H_6FeC_5H_5]BPh_4$ (90%) was precipitated from the water layer under the action of $NaBPh_4$. Diphenyl disulphide (37.5%), m.p. 60—61°C (from alcohol) was obtained from the ether layer after treatment with a 3% H_2O_2 aqueous solution. The dimethoxyethane filtrate was evaporated and the residue was washed with a 5% NaOH solution and then with ether, and $C_6H_5SSC_6H_5$ (37%) was obtained from the ether solution. The alkaline aqueous solution contained some thiophenol which was also oxidized (H_2O_2) to yield diphenyl disulphide (~4%).

We may conclude that benzenecyclopentadienyliron phenylmercaptide resulted from the interaction of $[C_6H_6FeC_5H_5]_2O_2$ with thiophenol, which is partially oxidized with hydrogen peroxide occurring in the same reaction.

$$[C_6H_6FeC_5H_5]_2O_2 + 2\ C_6H_5SH \rightarrow 2\ [C_6H_6FeC_5H_5]SC_6H_5 + H_2O_2$$

$$2\ [C_6H_6FeC_5H_5]SC_6H_5 + H_2O_2 \rightarrow 2\ [C_6H_6FeC_5H_5]OH + C_6H_5SSC_6H_5$$

Interaction of benzenecyclopentadienyliron peroxide with C_6H_5COCl (molar ratio 1/2) in DME at –20°C has led to 95% of benzene-cyclopentadienyliron cation isolated in the form of $[C_6H_6FeC_5H_5]BPh_4$. m.p. 250—251°C (dec.) and to benzoyl peroxide, m.p. 104—106°C. The IR spectrum revealed bands at 997, 1768, 1224 cm^{-1} [5].

The reaction of $[C_6H_6FeC_5H_5]_2O_2$ with CCl_4 (ratio 1/2; THF; –20°C) has led to decomposition of the π-complex, isolation of $C_6H_6FeC_5H_5BPh_4$ (~28%) and a colourless peroxidic compound (qualitative probe with KI), containing no iron (presumably CCl_3OOCCl_3).

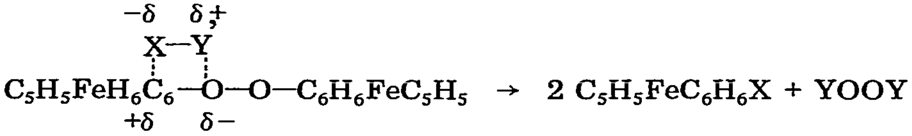
Interactions of benzenecyclopentadienyliron peroxide with lithium aluminium, chloroform and acetone belong to the reactions of type (b) occurring with retention of the Chd structure.

Interaction of 1.9 mmol $[C_6H_6FeC_5H_5]_2O_2$ with 10 mmol $LiAlH_4$ in DME at –2°C has led to the formation of hydrogen (99%, proved by GLC). Chd-FeCp (90%), m.p. 134—135°C (ref. 6: m.p. 135—136°C) was isolated from dimethoxyethane solution (see Scheme 1), the IR spectrum revealed a band at 2790 cm^{-1}, characteristic for *exo*-hydrogen of the Chd ligand [7]. The resulting precipitate contained Al and Li.

Interaction of 1.7 mmol $[C_6H_6FeC_5H_5]_2O_2$ with 5.5 mmol $CHCl_3$ in THF at –20°C has led to the formation of 85% (see Scheme 1) of *exo*-1-Cl_3CChd-FeCp, m.p. 91.5—92°C (from pentane) (Ref. 8: 90.5—92°C); the IR spectrum is identical with the spectrum of an authentic sample [8]. The mass spectrum of $Cl_3CC_6H_6FeC_5H_5$ revealed a molecular ion with m/e 316 and the fragmentation ions: 281 $[M - Cl]^+$, 246 $[M - 2\ Cl]^+$, 211 $[M - 3\ Cl]^+$, 199 $[C_6H_6FeC_5H_5]^+$, 186 $[C_5H_5FeC_5H_5]^+$ (see [4]), 121 $[C_5H_5Fe]^+$, 78 $[C_6H_6]^+$, 56 $[Fe]^+$. The ^1H NMR spectrum of $Cl_3CC_6H_6FeC_5H_5$ (in CS_2, Bruker SXP 4-100) contained signals of protons of the Cp ligand at δ 4.28 (singlet) and of the Chd ligand at 5.77 (H^4, triplet), 4.42 (H^3 and H^5, triplet), 3.42 (H^1, triplet), and 2.80 ppm (H^2 and H^6, triplet). The ratio of the integral intensities equals 5/1/2/1/2, the coupling constants for protons of the Chd ligand are: $J_{3,4} = J_{4,5} = J_{3,2} = J_{5,6} = J_{1,2} = J_{1,6} = 6$ Hz. Surprisingly, benzenecyclopentadienyliron peroxide does not react with methylene chloride (–30°C, THF).

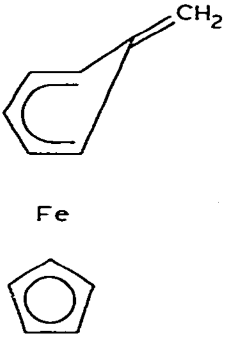
The reaction of $[C_6H_6FeC_5H_5]_2O_2$ (1.25 mmol) and acetone (3.5 mmol) in THF at −10°C has led to symmetric $C_5H_5FeC_6H_6CH_2COCH_2C_6H_6FeC_5H_5$, m.p. 43—44°C (from pentane containing toluene (20/1)). Found: Fe, 24.90, $C_{25}H_{26}Fe_2O_2$ calcd.: Fe, 24.59%. The IR spectrum (UR-20, CS_2) of this compound revealed the presence of a signal at 1728 cm^{-1} (ν(CO)), but no signal of an *exo*-H-atom (~2800 cm^{-1}). The ^1H NMR spectrum of the new π-complex (Bruker SXP 4-100; CS_2) showed signals of protons of the Cp ligand at δ 4.20, the Chd ligand at 5.74 (H^4, triplet), 4.06 (H^3 and H^5, triplet), 2.93 (H^1, quintet), 2.51 (H^2 and H^6, triplet) and of the methylene group at 1.32 ppm (doublet). The ratio of the integral intensities is 5/1/2/1/2/2; the coupling constants of the Chd ligand are $J_{3,4} = J_{4,5} = J_{2,3} = J_{5,6} = J_{1,6} = J_{1,2} = J((CH_2)—H^1) = 5.5$ Hz.

The reactivity of benzenecyclopentadienyliron peroxide may be interpreted as follows. First coordination of the reagent with the C—O bonds of the peroxide grouping occurs followed by the breaking of the two bonds and the formation of two new bonds. At the first stage the reaction always leads to a



$$\mathrm{C_5H_5FeH_6}\underset{+\delta}{\overset{\overset{-\delta}{X}}{\mathrm{C_6}}}—\underset{\delta-}{\overset{\overset{\delta+}{Y}}{\mathrm{O}}}—\mathrm{O—C_6H_6FeC_5H_5} \rightarrow 2\ \mathrm{C_5H_5FeC_6H_6X} + \mathrm{YOOY}$$

ChdFeCp derivative and to YOOY peroxide. The nature of the ChdCp complex and of the peroxide depends on the polarity of the X—Y bond in the reagent. The further fate of the ChdCp derivative depends on the nature of the X-grouping. If X is a hydrogen atom or a hydrocarbon radical, the ChdCp complex is stable (reaction type (b)). However, if the sp^3-hybridized carbon of the Chd ligand forms a bond with oxygen, sulphur or halogen (reaction type (a)), the ChdCp derivative is unstable. Heterolysis of the bond between an sp^3-hybridized C-atom and the substituent X takes place, with X becoming anionic at the $[C_6H_6FeC_5H_5]^+$ cation. That ChdFeCp derivatives are stable, provided the methylene carbon of the Chd ligand is bonded with C and H atoms only is known from the literature [9]. Benzenecyclopentadienyliron peroxide itself is the first example of a ChdFe complex with an sp^3-carbon bonded to oxygen. The interaction of hexamethylbenzenecyclopentadienyliron with



(B)

oxygen under aprotic conditions is described in ref. 10. A ChdFeCp derivative with an *exo*-cyclic double bond (B) results from this reaction.

References

1 A.N. Nesmeyanov, N.A. Sinitsyna, L.S. Kotova, V.S. Kolesov, V.F. Sizoi and N.A. Vol'kenau, Dokl. Akad. Nauk SSSR, 242 (1978) 1356.
2 L.A. Kazitsyna, N.B. Kupletskaya, Primenenie UF-, IK-, YaMR i mass-spectroscopii v organicheskoy chimii, Moskva, Izdatel'stvo MGU, 1979
3 H. Kojima, S. Takahashi and N. Hagihara, J. Chem. Soc. Chem. Commun., (1973) 230.
4 A.N. Nesmeyanov, N.A. Vol'kenau, P.V. Petrovskii, L.S. Kotova, V.A. Petrakova and L.I. Denisovich, J. Organometal. Chem., 210 (1981) 103.
5 S.S. Ivanchev, A.I. Yurzhenko and Yu.N. Anisimov, J. Fiz. Khim., 39 (1965) 1900.
6 I.U. Khand, P.L. Pauson and W.E. Watts, J. Chem. Soc., C, (1968) 2257.
7 I.U. Khand, P.L. Pauson and W.E. Watts, J. Chem. Soc., C, (1969) 2024.
8 A.N. Nesmeyanov, N.A. Vol'kenau and V.A. Petrakova, J. Organometal. Chem., 136 (1977) 363.
9 P.J.C. Walker and R.J. Mawby, J. Chem. Soc. Chem. Commun., (1972) 330.
10 D. Astruc, E. Román, J.R. Hamon and P. Batail, J. Amer. Chem. Soc., 101 (1979) 2240.