Heterolytic C–O Cleavage in Arylethers Activated by [Fe(η^5-C_5H_5)]$^+$

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The C–O bond of Fe(η^5-C_5H_5)$^+$ complexes of aryl ethers is cleaved smoothly by reaction of Bu^{t}OK in THF or KOH in DME, yielding π-phenate complexes; transetherification can also be achieved *in situ* at room temperature.

The activation of aromatics by the cationic moiety [M(η^5-C_5H_5)]$^+$ (M = Fe or Ru) is well known for nucleophilic addition or substitution[1,2] and benzylic deprotonation reactions.[3] We now report a new type of aromatic reaction which is also activated by the [Fe(η^5-C_5H_5)]$^+$ fragment: heterolytic C–O cleavage of aryl ethers whose driving force is the formation of π-phenate complexes.[4–11] In the course of our project to develop the chemistry of organometallic molecular trees with multiple redox centres, we have serendipitously found that this cleavage reaction[12] is effected by Bu^{t}OK or KOH (Scheme 1).

When KOR^3 reacts with any complex of type **1** in DME (R^3 = H) or THF (R^3 = Bu^t) from −50 to 25 °C in the presence of one equiv. KBr or, even better, [Bu_4N]$^+$[PF_6]$^-$ (Scheme 1, path i, the zwitterion **2** is obtained as a monohydrate,† after work-up [as indicated by the elemental analyses of **2b** (R^5 = H)] featuring H bonding. The latter is also apparent in the ORTEP of the X-ray crystal structure of **2c** (Fig. 1) which shows a flat phenoxide ligand with a C–O distance of 1.25 Å and an angle between the C(1)–O vector and the ligand plane of 1.55°.‡

The parent complex **2a** was previously obtained by deprotonation of [Fe(η^5-C_5H_5)(C_6H_5OH)]$^+$ and formulated as an oxo-cyclohexadienyl complex.§ The solution structure is oscillating between the two forms [two mesomeric forms or two tautomers interconverting more rapidly than the IR time scale (10^{13} s^{-1}) as shown by the IR and NMR data].¶ The complexes **2** are stable except compound **2a** which is partly decomplexed in the course of the cleavage reaction (only *ca.* 10% yield of **2a** was obtained along with extensive formation of PhOK). We find that all the complexes **2** exhibit a strong infrared absorbtion at ν_{CO} 1545 cm^{-1} (film) inconsistent with a full double bond. Likewise, the ^{13}C NMR δ_{CO} chemical shift is located *ca.* 150 (CD_3CN–D_2O) whereas $\delta_{C=O}$ would be expected at *ca.* 190. The addition of Na$^+$$PF_6^-$ to acetone solutions of complexes **2** before removal of solvent causes strong changes in the IR spectra (film). In particular, the intensity of the $\nu_{C–O}$ bond at 1545 cm^{-1} is strongly diminished whereas the bond corresponding to $\nu_{C–O}$ at 1265 cm^{-1} is strongly increased. This indicates the formation of the hexahapto phenate complex in which the phenate oxygen is coordinated to Na$^+$. ^1H NMR spectra of CD_3CN or CD_3COCD_3 solutions of the complexes **2a–b** (but not **2c**) give very broad patterns, which progressively sharpen upon addition of D_2O until the signals become sharp at CD_3COCD_3 : D_2O 1 : 1 (or CD_3CN : D_2O 1 : 1). We believe these effects are due to intermolecular ion pairing involving the negatively charged oxygen atom (*cf.* the dimeric interaction in Fig. 1) inhibiting rotation of the arene ring about the (η^5-C_5H_5)–Fe–arene axis. Protonation of **2a** to give the phenol complex is achieved using CF_3CO_2D, the (η^5-C_5H_5) signal in ^1H NMR being shifted from δ 4.5 to 5. In summary, the stereoelectronic features of the phenate ligand strongly depend on the presence of solvent molecules giving rise to dimeric interaction and on potential coordination of the phenate oxygen to a metal.

Alkyl or phenyl groups can be cleaved from **1** by the nucleophile. For instance, a 61% (resp. 42%) yield of **2b** is obtained from **1b**, 1 equiv. Bu^{t}OK and 1 equiv. [Bu_4N]$^+$[PF_6]$^-$ (resp. KBr) in THF. These mild cleavage conditions strongly contrast with the drastic conditions required (200 °C, 10%

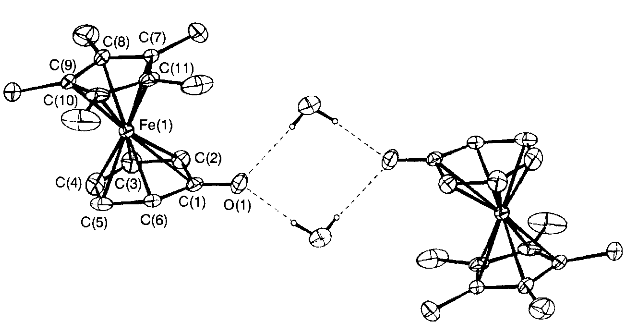
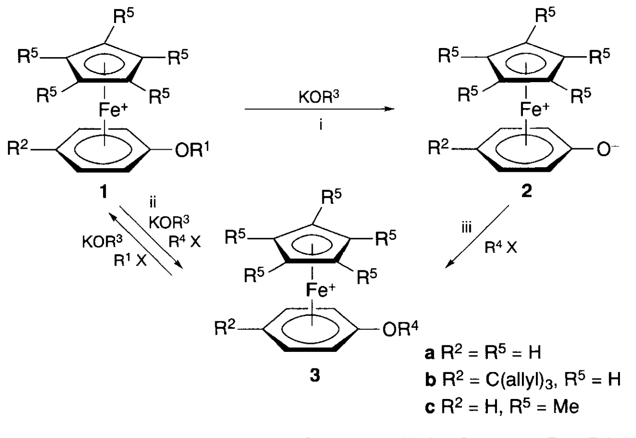


Fig. 1 CAMERON drawing of part of the molecular structure of **2c** showing the hydrogen bonds. Owing to OH···O hydrogen bonds between the water solvent molecule and the phenoxide ligand, the latter is disordered over two positions with 76 and 24% occupancies. For clarity, only one position of the phenoxide ligand has been drawn. Selected interatomic distances (Å): Fe–C(1) 2.269(9), Fe–C(2) 2.14(1), Fe–C(3) 2.09(2), Fe–C(4) 1.96(5), Fe–C(5) 2.05(2), Fe–C(6) 2.07(1), mean Fe–C(7–11) 2.043(6), C(1)–O(1) 1.250(1).



Scheme 1 R^1 = alkyl or phenyl; R^2 = H or alkyl; R^3 = H or Bu^t; R^4 = alkyl, allyl or benzyl; R^5 = H or Me; counter ion = PF_6^-. *Reagents and conditions*: i, DME (R^3 = H) or THF (R^3 = Bu^t), −50 °C → +20 °C, ii, DME (R^3 = H) or THF (R^3 = Bu^t), room temp; iii, DMF, K_2CO_3 (1 equiv.), room temp.

Table 1 Transetherification conditions (Scheme 1, path ii): 20 °C, 1–3 days; (3 mol of KOR^3 and 3 mol of R^{4}Br per mol of **1** (PF_6^- salt); reactions with R^{4}I gave close yields. Reported yields of iron complexes were obtained after work-up and purification

R^1	R^4	R^3	Yield **3** (%)
Me	allyl	H	71
Me	benzyl	H	76
(CH_2)$_3$Ph	benzyl	H	71
Ph	allyl	H	79
Ph	benzyl	Bu^t	81

yield) for the same reaction in the absence of the Fe(η^5-C_5H_5)$^+$ group.[13]

The transetherification is also achieved *in situ* when the complexes **1** are allowed to react with Bu^{t}OK (or KOH) and R^{4}X. At ambient temperature, these reactions yield 71–81% of the different arylether complexes (Table 1 and Scheme 1, R^{4}X = allylbromide or benzylbromide; R^1 = Me, $(CH_2)_3$Ph or Ph).[14]

Finally, alkylation of the phenate complexes can be achieved according to the path iii of Scheme 1. Reaction between **2b** and pentyl iodide in the presence of K_2CO_3 at 20 °C in DMF leads to the quantitative formation of the *O*-alkylated complex.[14] These reactions are thus of synthetic interest for the construction of organometallic molecular trees. The [Fe(η^5-C_5H_5)]$^+$ moiety serves as a protecting group in the air stable, easy to handle, zwitterions **2**, for the use of air-sensitive metal-free phenate derivatives.[3] Medium effects and their mechanistic features will be further investigated.

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Footnotes

† All new compounds gave satisfactory spectroscopic and analytical data.

‡ *X-Ray crystal data* for **2c**: space group $P2_1/n$, a = 14.653(6), b = 12.242(3), c = 8.237(2) Å, β = 92.56(5), V = 1476(2) Å^3, R = 0.036, Rw = 0.037 for 1184 reflections and 197 variables. Data at 20 °C were collected on a Philips PW 1100 diffractometer using Mo-Kα radiation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The formulation[11] of the deprotonated phenol complex [Fe$^+$(η^5-C_5H_5)(η^6-$C_6H_5O^-$)] as an oxocyclohexadienyl complex is presumably connected to the report of an infrared $\nu_{C=O}$ = 1651 cm^{-1} in that paper.

¶ This ambivalence of the π-phenate ligand in ruthenium complexes was well demonstrated in the seminal work by Wilkinson *et al.*[4]

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