N–H Activation by O_2 *via* $O_2^{\cdot -}$ in $Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_5NH_2)$ and Subsequent Formation of an Amino-acid Zwitterion by Mild Reaction with CO_2

Pascal Michaud and Didier Astruc *

Laboratoire de Chimie des Organométalliques, ERA n° 477, Université de Rennes, 35042 Rennes Cedex, France

The thermally unstable complex $Fe^I(cp)(C_6Me_5NH_2)$, (cp = $\eta^5\text{-}C_5H_5$) reacts with 1/4 mol of O_2 at −10 °C in toluene to give $Fe^{II}(cp)(\eta^5\text{-}C_6Me_5NH)$, the N–H being activated by O_2, consistent with an electron transfer mechanism $O_2 \rightarrow O_2^{\cdot -}$; the latter complex reacts with CO_2 (20 °C, 1 atm) providing $Fe^+(cp)(\eta^6\text{-}C_6Me_5NHCO_2^-)$.

We know that electron-rich neutral organometallic complexes bearing an even-hydrocarbon ligand with alkyl substituents may lose, for example, a benzylic H-atom upon reaction with O_2.[1,2] This type of C–H activation has been proposed to proceed by an outer-sphere electron transfer (ET) to O_2 giving the reactive superoxide radical anion $O_2^{\cdot -}$, equation (1) (cp = $\eta^5\text{-}C_5H_5$).

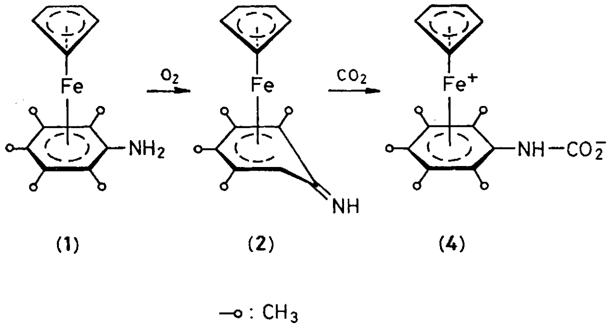
$$\mathrm{Fe^I(cp)(\eta^6\text{-}C_6Me_6)} \xrightarrow{O_2} [\mathrm{Fe^{II}\,(cp)(\eta^6\text{-}C_6Me_6)}]^+\mathrm{O_2}^{\cdot -} \xrightarrow{-\mathrm{HO_2}} \underset{(3)}{\mathrm{Fe^{II}(cp)(\eta^5\text{-}C_6Me_5CH_2)}} \quad (1)$$

We now report that an N–H bond is specifically activated by O_2 in the new d^7 19-electron complex $Fe^I(cp)(\eta^6\text{-}C_6Me_5NH_2)$, (**1**), and that this H-atom abstraction from NH_2 can be followed by reaction with CO_2 under ambient conditions to give an amino-acid zwitterion.

$[Fe^+(cp)(\eta^6\text{-}C_6Me_5NH_2)]\,[PF_6^-]$, (**1**)$^+$, is easily synthesized by the classical exchange reaction[3] between ferrocene and $C_6Me_5NH_2$[4,5] (15 h reflux, 60% crude yield, 53% yield of yellow needles after recrystallization from ethanol). Satisfactory elemental analysis and ^1H and ^{13}C n.m.r. spectra† indicate that no loss of a methyl group occurred. Upon Na/Hg reduction of (**1**)$^+$ in 1,2-dimethoxyethane (DME) at 20 °C, a transient dark green colour was observed and ferrocene, iron, and $C_6Me_5NH_2$ were formed rapidly, indicating that (**1**) is not stable under the reaction conditions whereas all other known $Fe^I(cp)(C_6R_6)$ complexes are.[6–8] A possible mode of decomposition is a shift $\eta^6 \rightarrow \eta^1$ of the ligation of $C_6Me_5NH_2$ to give a

---

† Spectral characteristics of (**1**)$^+$: ^1H n.m.r. (CD_3COCD_3, $SiMe_4$) δ 4.60 (s, cp, 5H), 5.23 (br, NH_2, 2H), 2.60 (s, CH_3, 6H), 2.53 (s, CH_3, 6H), and 2.50 (s, $p\text{-}CH_3$, 3H); $\{^1H\}^{13}C$ n.m.r. (CD_3CN, $SiMe_4$) δ 78.6 (cp), 121.2 ($C\text{-}NH_2$), 98.0, 93.5, and 82.0 (C_6 ring), and 17.4, 17.1, and 15.4 p.p.m. (CH_3). I.r. (Nujol) ν 567, 860 (s), 1650, 2000, 3475, and 3520 cm^{-1}. Mössbauer parameters (20 °C) I.S. = 0.46 mm s^{-1}; Q.S = 2.12 mm s^{-1}.



Scheme 1

17-electron species $\mathrm{Fe^{I}(cp)(\eta^1\text{-}C_6Me_5NH_2)(\eta^1\text{-}DME)}$. However (**1**) appeared to be indefinitely stable when the reduction (complete in 1 h) was carried out at −21 °C; it was characterized as a d^7 complex by the three *g* values close to 2 in the e.s.r. spectrum at −196 °C in frozen DME (2.0568, 1.9917, and 1.8460), typical of the orthorhombic distortion in this series.[9] After removing the DME *in vacuo* at −21 °C, (**1**) was extracted with cold toluene. This solution was titrated by I_2 and/or O_2. Upon addition of 1/4 mol O_2 at −10 °C, the dark green solution turned light red. Titration by $KMnO_4$ after hydrolysis shows that H_2O_2 is formed in trace amounts, consistent with equation (2) and dismutation of $O_2^{\bullet-}$.[1,2] Alternatively,

$$\underset{(\mathbf{1})}{\mathrm{Fe^{I}(cp)(\eta^6\text{-}C_6Me_5NH_2)}} + 1/4\,\mathrm{O_2} \xrightarrow{-21\,^{\circ}\mathrm{C}} \underset{(\mathbf{2})}{\mathrm{Fe^{II}(cp)(\eta^5\text{-}C_6Me_5NH)}} + 1/2\,\mathrm{H_2O} \qquad (2)$$

crystallization at −80 °C gave 86% of red crystals of Fe(cp)-(C_6Me_5NH), (**2**), the H atom abstraction product (Scheme 1). The structure of (**2**) was established by elemental analysis and ^1H and $\{^1H\}^{13}C$ n.m.r. and i.r. spectroscopy.‡ The $\{^1H\}^{13}C$ spectrum compares well with that of $\mathrm{Fe(cp)(\eta^5\text{-}C_6Me_5CH_2)}$, (**3**), the non co-ordinated cyclic carbon resonating at δ 156.5 p.p.m. [145 p.p.m. in (**3**)]. Contrary to (**3**), (**2**) is nearly insoluble in pentane. Its ionization potential (He I) [larger than that of (**3**)][10] and its Mössbauer parameters [close to those of the series $\mathrm{Fe^+(cp)(C_6Me_5NHR)\,X^-}$ (R = H, CO_2^-)] suggest that (**2**) has more zwitterionic character than (**3**), equation (3), *i.e.* the dihedral angle between the exocyclic

$$\mathrm{Fe(cp)(\eta^5\text{-}C_6Me_5NH)} \longleftrightarrow \mathrm{Fe^+(cp)(\eta^6\text{-}C_6Me_5NH^-)} \qquad (3)$$

double bond and the cyclohexadienyl plane could be less than 32°, the value found for (**3**).[11]

Note that the H-atom abstraction by O_2 is remarkably regiospecific, no C–H activation product being found in the ^1H and $\{^1H\}^{13}C$ n.m.r. spectra of the crude reaction product. Since N-bonded hydrogens are more acidic than C-bonded ones[12] in (**1**)$^+$ [confirmed by the reaction between (**1**)$^+$ and Bu^tOK in tetrahydrofuran (THF) which also gives (**2**)], this regiospecificity confirms the proposal of an ET mechanism $O_2 \rightarrow O_2^{\bullet-}$ followed by deprotonation of the side chain of the arene by $O_2^{\bullet-}$ in $\mathrm{Fe^I(cp)}$ arene complexes. The ET step must indeed be very fast since the redox potential of (**1**)$^+$/(**1**) is −1.9 V *vs.* standard calomel electrode (SCE) in aqueous LiCl (0.1 M) and −1.72 V/SCE in *NN*-dimethylformamide (+ $Bu^n_4N^+Br^-$ 0.1 M), over 1 V more negative than that of $O_2/O_2^{\bullet-}$.

Complex (**2**) reacts rapidly under 1 atm of CO_2 at 20 °C in THF to give a yellow precipitate of the water-soluble zwitterion $\mathrm{Fe^+(cp)(\eta^6\text{-}C_6Me_5NHCO_2^-)}$ (**4**), Scheme 1, (95% crude yield, 85% of microcrystals after recrystallization from acetone) identified by ^{13}C n.m.r. spectroscopy and by its strong absorption at 1640 cm^{-1} in the i.r. spectrum (Nujol).§ CO_2 cleavage occurs upon acidification to pH 1 by addition of aqueous HPF_6 to a water solution, which precipitates (**1**)$^+$ (90% yield). Whereas (**3**) reacts with I_2 to give $\mathrm{Fe^+(cp)(C_6Me_5CH_2I)I^-}$ or $\mathrm{[Fe^+(cp)(C_6Me_5CH_2^-)]_2(I^-)_2}$,[2,11] attempts to couple NH moieties by a similar reaction of (**2**) with I_2 gave instead the electron-transfer and H-atom-abstraction product (**1**)$^+$, equation (4), as the reaction between (**1**) and I_2 (after metathesis of the counter-anion with HPF_6).

$$\mathrm{Fe^+(cp)(C_6Me_5NH^-)} + 1/2\,\mathrm{I_2} \longrightarrow \mathrm{Fe^+(cp)(C_6Me_5NH^{\bullet})I^-} \xrightarrow[(\mathrm{H}^{\bullet})]{\text{solvent}} \mathrm{Fe^+(cp)(C_6Me_5NH_2)I^-} \qquad (4)$$

E.s.r. facilities provided by Professor J. H. Ammeter and L. Zoller (Zürich) are gratefully acknowledged. We also thank the CNRS for financial support and the DGRŚT for a pre-doctoral grant to P.M.

Received, 23rd December 1981; Com. 1464

References

1 D. Astruc, E. Román, J.-R. Hamon, and P. Batail, *J. Am. Chem. Soc.*, 1979, **101**, 2240.
2 D. Astruc, J.-R. Hamon, E. Román, and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 7502.
3 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedron Lett.*, 1963, **25**, 1725.
4 The synthesis of $\mathrm{[Fe^+(cp)C_6H_5NH_2)][PF_6^-]}$ by ligand exchange between ferrocene and aniline (6% yield) was reported by J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, 1979, **168**, 87.
5 C. Moinet, personal communication.
6 Note, however, that $\mathrm{Fe^I(cp)(C_6H_6)}$ decomposes in THF analogously (A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovstseva, and V. A. Petrakova, *J. Organomet. Chem.*, 1973, **61**, 329).
7 D. Astruc, J.-R. Hamon, G. Althoff, E. Román, P. Michaud, J.-P. Mariot, F. Varret, and D. Cozak, *J. Am. Chem. Soc.*, 1979, **101**, 5445.
8 J.-R. Hamon, D. Astruc, and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758.
9 M. V. Rajasekharan, S. Giesinski, J. H. Ammeter, N. Ostwald, J.-R. Hamon, P. Michaud, and D. Astruc., *J. Am. Chem. Soc.*, in the press.
10 J. C. Green, M. R. Kelly, M. P. Payne, E. A. Seddon, D. Astruc, and J.-R. Hamon, unpublished results.
11 J.-R. Hamon, D. Astruc, E. Román, P. Batail, and J. J. Mayerle, *J. Am. Chem. Soc.*, 1981, **103**, 2431.
12 C. C. Lee, U. S. Gill, and R. G. Sutherland, *J. Organomet. Chem.*, 1981, **206**, 89.

---

‡ Spectral characteristics of (**2**): ^1H n.m.r. (C_6D_6, $SiMe_4$) δ 3.56 (s, cp, 5H), 5.36 (br, NH, 1H), and 2.03, 1.93, and 1.80 (3s, CH_3, 15H); $\{^1H\}^{13}C$ (C_6D_6, $SiMe_4$) δ 75.4 (cp), 156.5 (C=NH), 93.1, 82.7, and 69.0 (C_6 ring), and 16.9 and 16.2 p.p.m. (CH_3). I.r. (toluene) ν_{NH} 1560 cm^{-1}. U.v. (toluene) λ nm (ε l mol^{-1} cm^{-1}) 420 (590), 350 (826), and 330 (934). Mössbauer parameters (20 °C) I.S. = 0.43 mm s^{-1}, Q.S. = 2.06 mm s^{-1}.

§ Spectral characteristics of (**4**) (satisfactory elemental analysis was obtained): ^1H n.m.r. (D_2O, TMPS) δ 4.63 (s, cp, 5H) and 2.45 and 2.48 (m, CH_3, 15H); $\{^1H\}^{13}C$ n.m.r. (D_2O, sodium 3-trimethylsilylpropanesulphonate) δ 80.2 (cp), 164.5 (CO_2), 106.9 (CN), 101.3, 101.4, and 101.7 (C_6 ring), and 16.9, 17.9 (*para*), and 19.0 p.p.m. (CH_3). Minute amounts of $\mathrm{Fe^+(cp)(C_6Me_5NH_2)\text{-}OH^-}$ and of D_2CO_3 are also found in the ^1H and ^{13}C n.m.r. spectra. Mössbauer parameters (20 °C) I.S. = 0.46 mm s^{-1}, Q.S. = 2.05 mm s^{-1}.