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 = $\eta^5\text{-}C_5H_5$).

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

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

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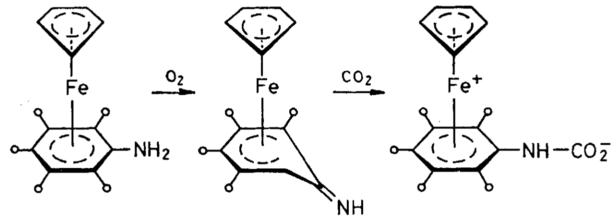
† Spectral characteristics of $(1)^{+}$: ^1H n.m.r. (CD_3COCD_3, $SiMe_4$) δ 4.60 (s, cp, 5H), 5.23 (br, NH_2, 2H), 2.60 (s, CH_3, 6H), 2.53 (s, CH_3, 6H), and 2.50 (s, *p*-CH_3, 3H); $\{^1H\}^{13}C$ n.m.r. (CD_3CN, $SiMe_4$) δ 78.6 (cp), 121.2 (C-NH_2), 98.0, 93.5, and 82.0 (C_6 ring), and 17.4, 17.1, 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}.



(1) (2) (4)

—o : CH_3

Scheme 1

17-electron species $Fe^{I}(cp)(\eta^1\text{-}C_6Me_5NH_2)(\eta^1\text{-}DME)$. 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,

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

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 $Fe(cp)(\eta^5\text{-}C_6Me_5CH_2)$, (**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 $Fe^+(cp)(C_6Me_5NHR)\ X^-$ (R = H, CO_2^-)] suggest that (**2**) has more zwitterionic character than (**3**), equation (3), *i.e.* the dihedral angle between the exocyclic

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

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 $Fe^{I}(cp)$ 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 $Fe^+(cp)(\eta^6\text{-}C_6Me_5NHCO_2^-)$ (**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 $Fe^+(cp)(C_6Me_5CH_2I)I^-$ or $[Fe^+(cp)(C_6Me_5CH_2^-)]_2(I^-)_2$,[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).

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

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‡ 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 $Fe^+(cp)(C_6Me_5NH_2)$-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}.