Reversible Hydrogenation of Anthracene during Complexation to Cyclopentadienyliron: Change in Regioselectivity depending on the Steric Bulk of the Cyclopentadienyl Group

Véronique Guerchais and Didier Astruc*

Laboratoire de Chimie des Organométalliques, ERA CNRS n° 477, Université de Rennes I, Campus de Bealieu, 35042 Rennes Cedex, France

Anthracene and dihydroanthracene react with $(C_5Me_5)Fe(CO)_2Br$ and $AlCl_3$ to give a mixture of $[(C_5Me_5)Fe(\eta^6\text{-9,10-dihydroanthracene})]^+X^-$ and $[(C_5Me_5)Fe(\eta^6\text{-1,2,3,4-tetrahydroanthracene})]^+X^-$ (60:40) whereas under identical conditions, $(C_5H_5)Fe(CO)_2Cl$ gives only $[(C_5H_5)Fe(\eta^6\text{-9,10-dihydroanthracene})]^+X^-$.

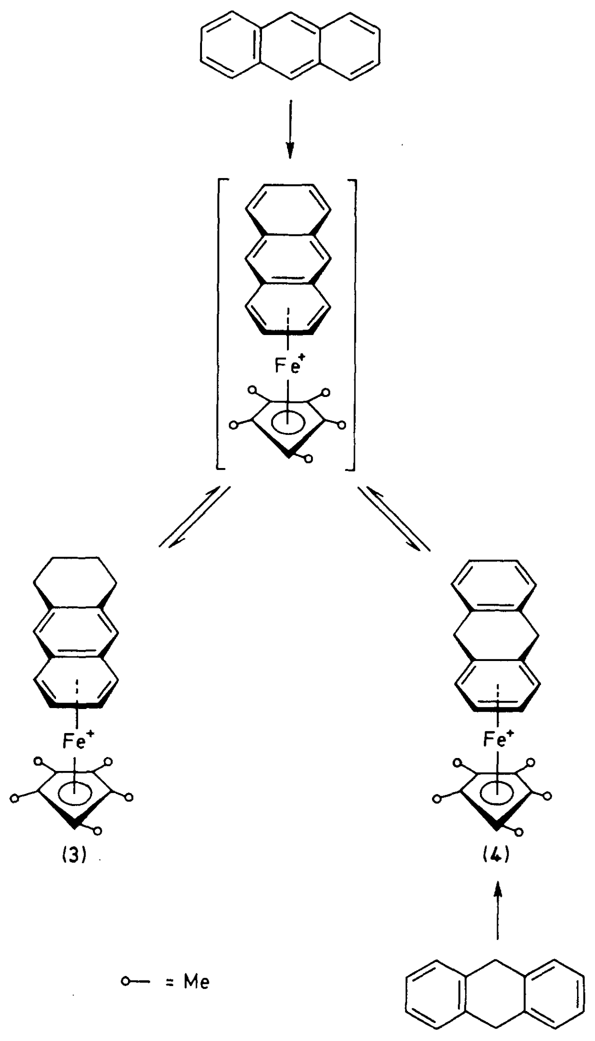
The discovery by Maitlis *et al.*[1] that a C_5Me_5–rhodium complex catalyses the selective hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene has resulted in an extensive search for other similar catalysts[2] as well as mechanistic studies[3] of this reaction. It is known that, upon complexation of anthracene by $(C_5H_5)Fe^+$ using ferrocene and aluminium chloride, hydrogenation at positions 9 and 10 always occurs.[4] We have found that, although the reaction with $(C_5H_5)Fe(CO)_2Cl$, (**1**), gives the 9,10-hydrogenated product, the use of $(C_5Me_5)Fe(CO)_2Br$, (**2**),[5] results in the formation of the 1,2,3,4-tetrahydroanthracene complex as the major reaction product (Scheme 1).

$(C_5H_5)Fe(CO)_2Cl$ (**1**) $(C_5Me_5)Fe(CO)_2Br$ (**2**)

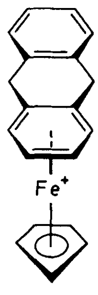
The reaction of (**2**) with $AlCl_3$ (2 mol) (commercial or twice-sublimed) and anthracene (1 mol) neat or in heptane at 80 °C for 12 h gives 10% of $[(C_5Me_5)Fe(arene)]^+X^-$ complexes ($X^- = PF_6^-$ after metathesis with aqueous HPF_6). ^1H N.m.r. spectroscopy before and after separation of the two complexes by fractional crystallization in acetone–ethanol indicates the formation of red (**3**) and yellow (**4**)† in the ratio 60:40. For (**3**), the ^1H n.m.r. spectrum (CD_3COCD_3) shows two distinct methylene patterns at δ 3.07 and 1.92 whereas only a singlet is found at δ 4.09 in the spectrum of (**4**). The complexed ring gives two sets of signals at δ 6.70 and 6.10. The chemical shift difference between the protons α and β to the orthocondensed ring is due to the aromaticity of this ring in (**3**) (as in the naphthalene complexes[4,6]), whereas in (**4**), as in $[(C_5H_5)Fe(\eta^6\text{-9,10-dihydroanthracene})]^+$, (**5**),[4] the complexed ring appears as a singlet at δ 6.07. The ^{13}C n.m.r. spectra (CD_3CN) confirms the structures (**3**) and (**4**): two distinct methylene signals (triplet in the off-resonance spectrum) are found at δ 30.6 (α) and 23.2 p.p.m. (β) for (**3**) whereas only one such signal is found at 32.5 p.p.m. in the spectrum of (**4**). Finally the red colour of (**3**) indicates strong conjugation as in $[(C_5H_5)Fe(\eta^6\text{-naphthalene})]^{+6}$ whereas non-conjugated complexes such as (**4**) and $[(C_5H_5)Fe(\eta^6\text{-9,10-dihydroanthracene})]^+$, (**5**), are yellow.† Under the same reaction conditions, (**1**) gives only

---

† Satisfactory spectroscopic (^1H and ^{13}C n.m.r. and u.v.–visible) and elemental analyses were obtained for complexes (**3**) and (**4**).



Scheme 1


(5)

complex (**5**), a finding which parallels the reaction using ferrocene, also reported to give (**5**).[4] Interestingly, dihydroanthracene reacts with (**2**) under these reaction conditions to give a mixture of (**3**) and (**4**) in the same proportions as anthracene. This indicates that both 9,10-dihydrogenation and 1,2,3,4-tetrahydrogenation of the intermediate complex $[(C_5Me_5)Fe(\eta^6\text{-anthracene})]^+$ are reversible (Scheme 1), the ratio between (**3**) and (**4**) resulting from an equilibrium. At high reaction temperatures, the bimetallic complex $[\{(C_5Me_5)Fe\}_2(\eta^6,\eta^6\text{-9,10-dihydroanthracene})]^{2+}$,[4] is formed, which shifts this equilibrium. We believe the changing site of *endo*‡ hydrogenation in $[(C_5Me_5)Fe(\eta^6\text{-anthracene})]^+$ results from the steric effect of the ligand C_5Me_5[8,9] which partly inhibits hydrogenation in the 9,10 positions. This finding should be useful in the design of selective catalysts for the hydrogenation of polyaromatic compounds.[1]

We are grateful to S. Sinbandhit (Centre de Mesures Physiques de l'Ouest) for carefully recording the n.m.r. spectra.

Received, 29th June 1983; Com. 867

References

1 M. J. Russel, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 427.
2 R. G. Grey, G. P. Pez, and A. Wallo, *J. Am. Chem. Soc.*, 1980, **102**, 5949.
3 R. Wilczynski, W. A. Fordyce, and J. Halpern, *J. Am. Chem. Soc.*, 1983, **105**, 2066.
4 R. G. Sutherland, S. C. Chen, J. Pannekoek, and C. C. Lee, *J. Organomet. Chem.*, 1975, **101**, 221.
5 J.-R. Hamon, D. Astruc, and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758.
6 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 1966, **166**, 607.
7 R. G. Sutherland, W. J. Pannekoek, and C. C. Lee, *Can. J. Chem.*, 1978, **56**, 1782.
8 J.-R. Hamon and D. Astruc, manuscript in preparation; J.-R. Hamon, State Thesis, Rennes, 1982; D. Astruc, *Tetrahedron*, in the press.
9 C. Lapinte and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1983, 430.

---

‡ Hydrogenation of 9,10-dimethylanthracene during ligand exchange with ferrocene was shown to proceed on the side of iron and the participation of the latter was invoked (ref. 7).

Printed by Heffers Printers Ltd Cambridge England