

### Preliminary communication

---

## BIFUNCTIONALIZATION OF HEXAMETHYLBENZENE VIA TEMPORARY COORDINATION TO $\text{Fe}^{2+}$

DOMINIQUE MANDON and DIDIER ASTRUC\*

*Laboratoire de Chimie des Organométalliques, UA CNRS 415, 35042 Rennes Cédex (France)*  
and

*Laboratoire de Chimie Organique et Organométallique, UA CNRS 35, Université de  
Bordeaux I, 351 cours de la Libération, 33405 Talence Cédex (France)*

(Received March 3rd, 1986)

### Summary

Complexation of  $\text{C}_6\text{Me}_6$  by  $\text{Fe}^{2+}$  in  $(\text{C}_6\text{Me}_6)_2\text{Fe}^{2+}$  followed by (i) addition of hydride, (ii) subsequent addition of a carbanion, (iii) removal of hydride by  $\text{Ph}_3\text{C}^+$  by an electron-transfer pathway, (iv) deprotonation, (v) acylation, (vi) deprotonation, and (vii) decomplexation by  $\text{Al}_2\text{O}_3/\text{O}_2$  gives a regio- and stereo-specifically controlled cyclohexadiene.

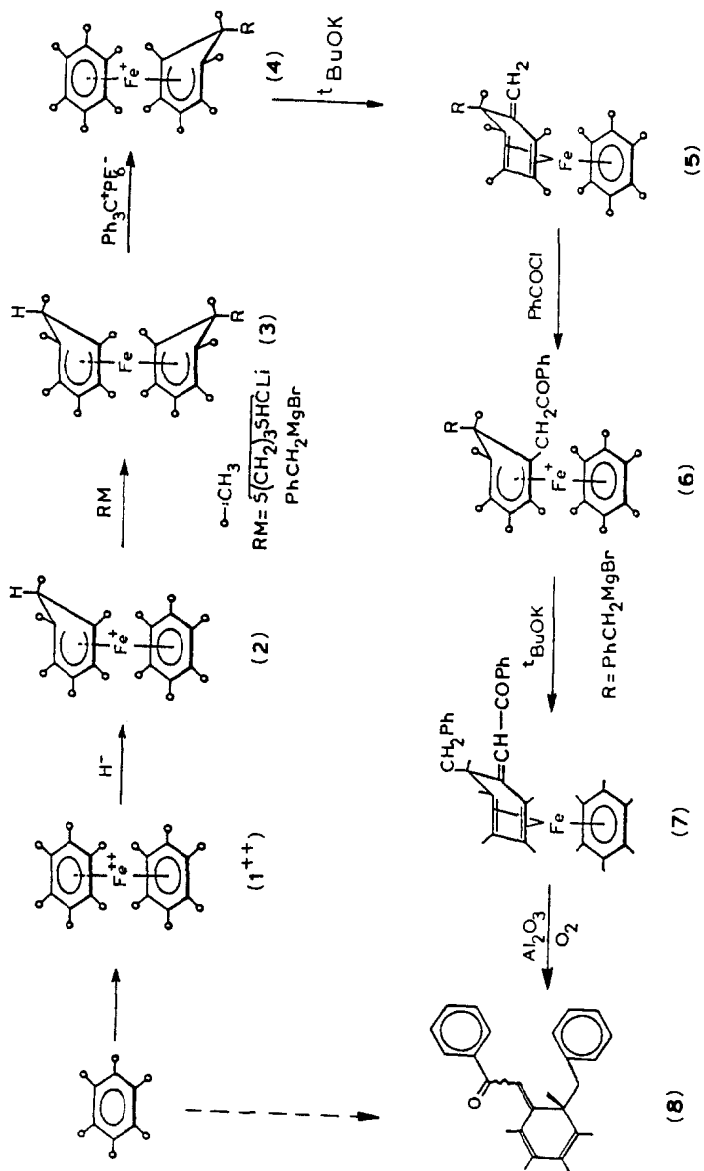
---

Although modification of aromatic reactivity upon complexation to a transition metal group is a well understood concept [1], bicationic activation has been little studied [1a]. In principle double nucleophilic attack on bicationic arene complexes provides cyclohexadiene complexes, and this is essentially the case for hydrides [1a, 2]. However a variety of carbanions react with arene-cyclohexadienyliron monocations [3, 4] produced by hydride addition to bis-(arene)iron dications [5, 6]. This communication demonstrates that  $\text{C}_6\text{Me}_6$  can be bifunctionalized to cyclohexadiene products using a series of nucleophilic and electrophilic reactions on iron complexes.

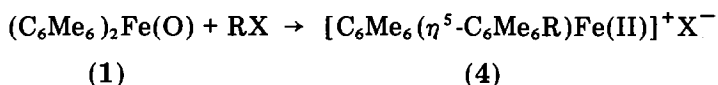
The overall transformation of  $\text{C}_6\text{Me}_6$  (Scheme 1) involves six reactions of the iron complexes in addition to the complexation and decomplexation procedures. The eight steps proceed in high (overall 32%) yield for  $\text{R} = \text{CH}_2\text{Ph}$ . The robust *exo*-substituted  $\eta^5$ -hexamethylcyclohexadienyl- $\eta^6$ -hexamethylbenzene-iron cations are made either from the dication  $1^{2+}$  by hydride protection/deprotection and nucleophilic attack of  $\text{RM}$  on 2 or from the 20-electron complex 1 and  $\text{RX}$  [7]. The latter procedure saves one step but gives around 50% yield:

---

\*Correspondence to be addressed to this author at the University of Bordeaux I.



SCHEME 1. (i)  $FeCl_2$ ,  $AlCl_3$ , heptane, reflux overnight [12]; (ii)  $NaBH_4$ , THF, 20°C [6]; (iii)  $PhCH_2MgBr$  or  $LiCHS(CH_2)_3S$ , THF, -80°C [3a]; (iv)  $Ph_3C^+PF_6^-$ ,  $CH_2Cl_2$ , 20°C, ([3a], see text for E.T. mechanism); (v)  $t-BuOK$  or  $NaOMe$ , THF (-80–0°C, [3a]), (vi)  $PhCOCl$ , THF, -50–0°C; (vii)  $t-BuOK$ , THF, -80–0°C; (viii) ether,  $Al_2O_3$  (suspension),  $O_2$  (1 atm), 20°C, 1 min.



In the deprotonation reaction 3→4, (Scheme 1), both the 17-electron cation  $3^+$  and the radical  $\text{Ph}_3\text{C}^\cdot$  can be observed by EPR. Since the potential of the nearly reversible redox system  $3 \rightleftharpoons 3^+$  ( $-0.5$  V vs SCE at  $0.1$  V  $\text{s}^{-1}$  (DMF);  $E_A - E_C \approx 0.12$  V;  $i_a/i_c \approx 0.8$ ) is  $0.8$  V more negative than that for  $\text{Ph}_3\text{C}^+ \rightleftharpoons \text{Ph}_3\text{C}^\cdot$  ( $+0.3$  V) [8], electron transfer proceeds to give the observed organometallic and organic radical. H atom transfer between these two species follows. It should be noted that this is the only possible mechanism, since the bulk of  $\text{Ph}_3\text{C}^+$  and 3 is far too large to allow a direct  $\text{H}^-$  transfer [9]. Although all the intermediates in Scheme 1 have been isolated and identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and infrared spectroscopy\*, the air-sensitive neutral iron(0) complexes show little stability in solution, and for preparative purposes are benzoylated "in situ". Interestingly, the infrared spectra of 7 do not exhibit the carbonyl stretch owing to the high proportion of the zwitterionic enolate mesomer\*. However, the carbonyl stretch ( $1695$   $\text{cm}^{-1}$ ) appears in the infrared spectrum of the ligand 8 after its removal from the metal (ether,  $\text{Al}_2\text{O}_3$ ,  $\text{O}_2$ , rapid)\*\*. After separation from  $\text{C}_6\text{Me}_6$  by TLC, 8 is recrystallized from ether (yellow crystals, m.p.  $36\text{--}38^\circ\text{C}$ ) and identified by mass,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and infrared spectroscopies\*\*\*. Although the stereochemistry of the exocyclic double bond was not determined, it would be expected that the acyl group would lie, as in Scheme 1, on the less bulky side.

The type of activation by dications which is described complementarily to that known for the monocation  $\text{CpFe}^+ \text{C}_6\text{Me}_6$  [11] in respect to synthetic applications.

We are grateful to S. Sinbandhit and P. Guénot (Centre de Mesures Physiques, Rennes) for their valuable assistance with mass and NMR spectroscopies.

## References

- 1 (a) S.R. Grunde and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1982) 379; (b) P.M. Maitlis, *Chem. Soc. Rev.*, 10 (1981) 1; (c) M.F. Semmelhack, *Ann. N.Y. Acad. Sci.*, 295 (1977) 36.
- 2 (a) D. Jones, L. Pratt and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, (1962) 4458; (b) D.A. Sweigart, *J. Chem. Soc. Chem. Commun.*, (1979) 762.

\*7:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 0.87, 0.92, 1.17, 1.21, 1.31 ( $5 \times s$ ,  $5 \times 3\text{H}$ ,  $\text{CH}_3$  cyclohexadiene); 1.76 (s, 18H,  $\text{C}_6\text{Me}_6$ ); 2.46 (d, 1H,  $^2J(\text{H-H})$  12.4 Hz,  $\text{CH}_2\text{Ph}$ ); 3.86 (d, 1H,  $^2J(\text{H-H})$  12.4 Hz,  $\text{CH}_2\text{Ph}$ ); 6.18 (s, 1H, C=CH); 6.98, 7.23 ( $2 \times m$ ,  $2 \times 5\text{H}$ ,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ): 14.6, 15.1, 15.9, 18.1, 26.0 ( $\text{CH}_3$  cyclohexadiene); 15.6 ( $\text{C}_6\text{Me}_6$ ); 44.0 ( $\text{CH}_2\text{-Ph}$ ); 46.6 (*C-*ipso** cyclohexadiene); 66.2, 68.9 ( $\text{C}_{sp}^2$ ,  $\alpha$  diene); 85.8, 86.9 ( $\text{C}_{sp}^2$ ,  $\beta$  diene); 93.5 ( $\text{C}_6\text{Me}_6$ ); 96.6 ( $\text{C}=\text{CH}_2$  *exo*); 125.3, 127.1, 128.2, 128.9, 130.6, 141.9, 146.2 ( $\text{C}_6\text{H}_5$ ); 142.8 ( $\text{C}=\text{CH}_2$ ); 180.9 (C=O). Infrared (KBr, Nujol, ether,  $\text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}=\text{C})$ : 1620  $\text{cm}^{-1}$  broad, not intense, no carbonyl stretch. Mass spectrum:  $m/z$  266 ( $\text{C}_6\text{Me}_5\text{CH}_2\text{COPh}^+$ ), 162 ( $\text{C}_6\text{Me}_6^+$ ), 91 ( $\text{C}_6\text{H}_5\text{CH}_2^+$ ), 56 (Fe).

\*\*8:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) 1.58 (m, 6 H,  $\text{CH}_3$ ); 2.05 (s, 3H,  $\text{CH}_3$ ); 2.08 (s, 3H,  $\text{CH}_3$ ); 2.12 (s, 3H,  $\text{CH}_3$ ); 2.52 (d, 1H,  $^2J(\text{H-H})$  12.9 Hz,  $\text{CH}_2\text{Ph}$ ); 2.85 (s, 1H,  $^2J(\text{H-H})$  12.9 Hz,  $\text{CH}_2\text{Ph}$ ); 6.00 (s, 1H, C=CH); 7.07, 7.70, 7.90 ( $3 \times m$ , 10H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ) 20.6, 27.3, 28.9 ( $\text{CH}_3$ ); 54.6 ( $\text{CH}_2\text{Ph}$ ); 69.8 (*C-*ipso** cyclohexadiene); 125.1 ( $\text{C}=\text{CH}$ ); 123.9, 126.4, 127.6, 128.4, 128.5, 128.8, 129.9 ( $\text{C}_6\text{H}_5$ ,  $\text{C}_{sp}^2$  cyclohexadiene); 155.9 (C=CH); 201.8 (C=O). Infrared (film)  $\nu(\text{C}=\text{O})$  1695;  $\nu(\text{C}=\text{C})$  1595, 1610  $\text{cm}^{-1}$ . Mass spectrum:  $m/z$  356 ( $\text{C}_6\text{Me}_5\text{CH}_2\text{PhCHCOPh}^+$ ), 265 ( $M - \text{CH}_2\text{Ph}^+$ ), 251 ( $M - \text{COPh}^+$ ), 105 ( $\text{COPh}^+$ ), 91 ( $\text{CH}_2\text{Ph}^+$ ).

\*\*\*Satisfactory elemental analyses for C and H were obtained for 7 and 8.

- 3 A.M. Madonik, D. Mandon, P. Michaud, C. Lapinte and D. Astruc, *J. Am. Chem. Soc.*, 106 (1984) 3381.
- 4 D. Astruc, P. Michaud, A.M. Madonik, J.-Y. Saillard and R. Hoffmann, *Nouv. J. Chim.*, 9 (1985) 41.
- 5 A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova and L.S. Polkovnikova, *Dokl. Akad. Nauk SSSR*, 236 (1977) 1130.
- 6 P. Michaud, D. Astruc and J.H. Ammeter, *J. Am. Chem. Soc.*, 104 (1982) 3755.
- 7 A.M. Madonik and D. Astruc, *J. Am. Chem. Soc.*, 106 (1984) 2437.
- 8 (a) H. Volz and W. Lotsch, *Tetrahedron Lett.*, (1969) 2275; (b) G. Kothe, W. Süermann, H. Baumgärtel and H. Zimmermann, *Ibid* (1969) 2185; (c) M.F. Asaro, G.S. Bodner, J.A. Gladysz, S.R. Cooper and N.J. Cooper, *Organometallics*, 4 (1985) 1020.
- 9 (a) A.J. Birch, K.B. Chamberlain, M.A. Haas and D.J. Thompson, *J. Chem. Soc. Perkins Trans.*, 1 (1973) 1882; (b) A.J. Pearson, *Acc. Chem. Res.*, 13 (1980) 463; *Transition Met. Chem.*, 6 (1981) 67; (c) D. Mandon, L. Toupet and D. Astruc, *J. Am. Chem. Soc.*, in press.
- 10 D. Astruc, J.-R. Hamon, E. Roman and P. Michaud, *J. Am. Chem. Soc.*, 103 (1981) 7502.
- 11 J.-R. Hamon, J.-Y. Saillard, A. Le Beuze, M. Mc Glinchey and D. Astruc, *J. Am. Chem. Soc.*, 104 (1982) 7549.
- 12 (a) E.O. Fischer and R. Böttcher, *Chem. Ber.*, 89 (1956) 2397; (b) J.-F. Helling, D.M. Braitsch and T.J. Meyer, *J. Chem. Soc. Chem. Commun.*, (1971) 920; (c) E.L. Muetterties and J.-R. Bleeke, *Acc. Chem; Res.*, 12 (1979) 234; (d) M. Brookhart, W. Lamanna and M.B. Humphrey, *J. Am. Chem. Soc.*,