

## Preliminary communication

# PREPARATION AND HYDRIDE REDUCTION OF THE ELECTRON-RICH CATIONS $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_2\text{L}]^+$ ( $\text{L} = \text{CO}$ , $\text{PPh}_3$ , $\text{PMe}_3$ ) AND $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^+$

STEPHEN G. DAVIES\*, STEPHEN J. SIMPSON and SUSAN E. THOMAS

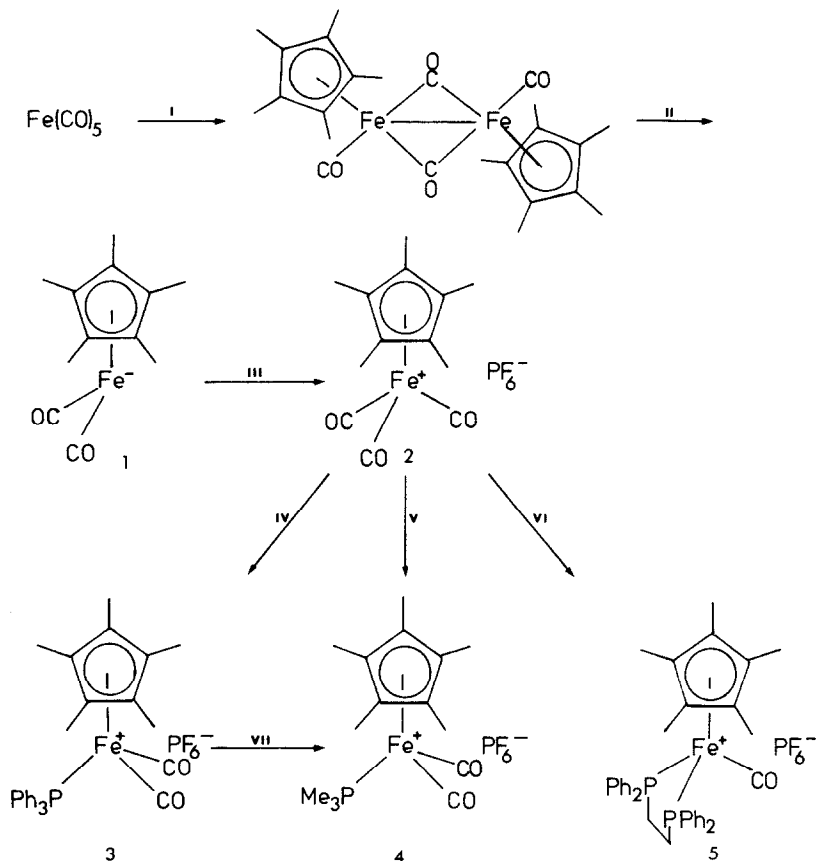
*The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY  
 (Great Britain)*

(Received July 5th, 1983)

## Summary

The cations  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_2\text{L}]^+$  (3,  $\text{L} = \text{PPh}_3$ ; 4,  $\text{L} = \text{PMe}_3$ ) and  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^+$  (5) have been prepared from  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_3]^+$  (2) by controlled decarbonylation reactions. Hydride reduction of these cations occurs at CO to give  $(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_2\text{H}$  from 2 and 3, and  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})\text{H}]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  from 5, while complete reduction of carbon monoxide to the methyl complex  $(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})-(\text{PMe}_3)\text{Me}$  is observed for cation 4.

One mechanism for the homogeneous reduction of carbon monoxide in the presence of transition metal catalysts is believed to proceed sequentially via metal carbonyl hydride in equilibrium with formylmetal hydroxy-methylmetal and then methylmetal complexes [1]. We have recently developed models for the reduction of metal carbonyl ligands to methylmetals based on the electron-rich  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L}_2)\text{CO}]^+$  cations ( $\text{L} =$  phosphine ligand) [2]. The two electron-donating phosphine ligands are essential to make these complexes electron-rich and thus disfavour attack by hydride at the cyclopentadienyl ligand and favour attack on the metal carbonyl. In order to extend our studies to similar cations containing two carbon monoxide ligands and hence only one phosphine ligand we reasoned that it would be necessary to permethylate the cyclopentadienyl ring. Nucleophilic addition to the pentamethylcyclopentadienyl ligand would be disfavoured for electronic and steric reasons. We describe here the synthesis of the cations  $[(\eta^5\text{-Me}_5\text{C}_5)\text{Fe}(\text{CO})_3]^+$  (2),  $[(\eta^6\text{-Me}_5\text{C}_5)\text{Fe}(\text{L})(\text{CO})_2]^+$  (3,  $\text{L} = \text{PPh}_3$ ; 4,  $\text{L} = \text{PMe}_3$ ) and  $[(\eta^5\text{-Me}_5\text{C}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CO}]^+$  (5) and their reductions

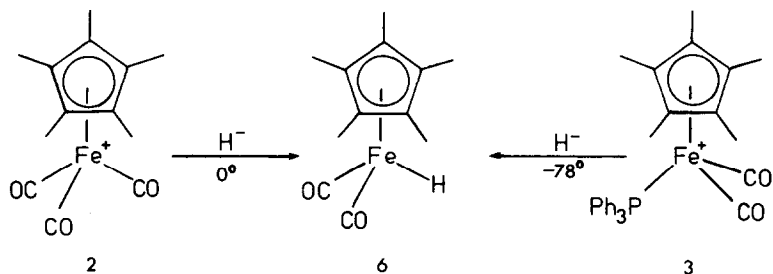


(i)  $\text{Me}_5\text{C}_5\text{H}$ ; (ii) lithium naphthalenide; (iii)  $\text{ClCO}_2\text{Et}$  then  $\text{HCl}$  then  $\text{NH}_4\text{PF}_6$ ; (iv)  $\text{PPh}_3$ ,  $\text{DMSO}$ ; (v)  $\text{PMe}_3$ ,  $\text{DMSO}$ ; (vi)  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ , acetone,  $\text{Me}_3\text{NO}$ ; (vii)  $\text{PMe}_3$ , acetone.

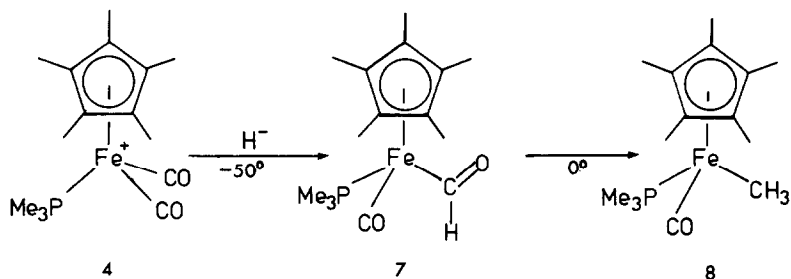
with lithium aluminium hydride. The reduction of cation 2 with sodium borohydride has been recently reported [3].

Thermolysis of iron pentacarbonyl with pentamethylcyclopentadiene [4] generates  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_2]_2$  [5]. In our hands the best conditions for the reduction of this dimer to the anion 1 employ lithium naphthalenide. Treatment of solutions of anion 1 with ethyl chloroformate followed by hydrogen chloride gas generates after anion exchange the cation  $[(\text{Me}_5\text{C}_5)\text{Fe}(\text{CO})_3]^+ \text{PF}_6^-$  (2). We have previously demonstrated that controlled replacement of one or two carbon monoxide ligands can be achieved for this type of cation in the presence of dimethylsulphoxide or trimethylamine *N*-oxide respectively [6]. Thus treatment of the tricarbonyl cation 2 with triphenylphosphine or trimethylphosphine in dimethyl sulphoxide produces the corresponding dicarbonyl monophosphine complexes 3 and 4, respectively. Treatment of cation 3 with trimethylphosphine generates cation 4 by phosphine exchange.

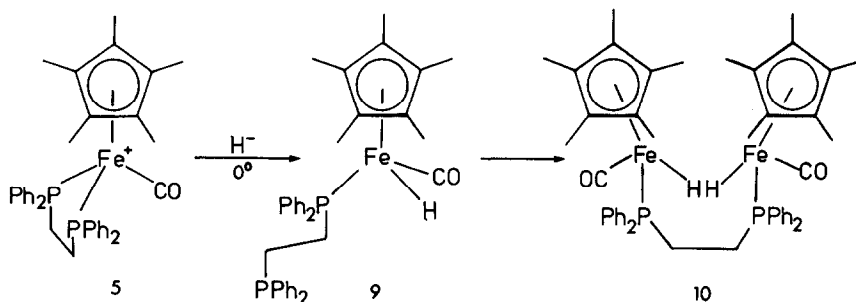
The bisphosphine monocarbonyl cation 5 is formed in the reaction of cation 2 with trimethylamine *N*-oxide in the presence of 1,2-bis(diphenylphosphino)-ethane.



Lithium aluminium hydride reduction of cations **2** and **3** produced in each case the dicarbonyl hydride complex **6**. The reactions presumably proceed via initial attack onto a carbonyl ligand to generate unstable formyl intermediates followed by dissociation of carbon monoxide or triphenylphosphine and rearrangement of formyl to carbonyl hydride. In contrast, reduction of cation **4** leads exclusively to the methyl complex **8**. Monitoring this reduction



by  $^1\text{H}$  NMR spectroscopy allowed the observation of the intermediate formyl complex **7** ( $\delta$  14.19 ppm). In this case ligand dissociation is less likely to occur allowing observation of the formyl species **7** which exists long enough to be reduced further or disproportionate [2] to methyl. Hydride reduction of the bisphosphine cation **5** resulted in the formation of the diiron dihydride complex **10**. By analogy with our work on the equivalent cyclopentadienyl complex this product would be expected to result from disproportionation of the monomeric carbonyl hydride **9** [7].



We thank the British Petroleum Company Ltd., for a Fellowship (to S.J.S.) and Laporte Industries Ltd., for a studentship (to S.E.T.).

## References

- 1 W.A. Herrmann, *Angew. Chem. Int. Edn. Engl.*, 21 (1982) 117, and ref. therein.
- 2 S.G. Davies, J. Hibberd and S.J. Simpson, *J. Chem. Soc. Chem. Commun.*, (1982) 1404; S.G. Davies and S.J. Simpson, *J. Organomet. Chem.*, 240 (1982) C48.
- 3 C. Lapinte and D. Astruc, *J. Chem. Soc. Chem. Commun.*, (1983) 430.
- 4 F.X. Kohl and P. Jutzi, *J. Organomet. Chem.*, 243 (1983) 119.
- 5 R.B. King and M.B. Bisnette, *J. Organomet. Chem.*, 8 (1967) 287.
- 6 S.G. Davies, *J. Organomet. Chem.*, 179 (1979) C5.
- 7 S.G. Davies, J. Hibberd, S.J. Simpson and O. Watts, *J. Organomet. Chem.*, 241 (1983) C31.

---

**JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 254, No. 2**


---

**AUTHOR INDEX**

- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Avakyan, V.G., 173</p> <p>Baskar, A.J., 149</p> <p>Beletskaya, I.P., 189</p> <p>Belsky, V.K., 189</p> <p>Bock, H., 219</p> <p>Bolesławski, M., 159</p> <p>Borisova, I.V., 189</p> <p>Bulychev, B.M., 167</p> <p>Cano, F.H., 249</p> <p>Carmona, D., 249</p> <p>Ceccon, A., 199, 207</p> <p>Dammel, R., 219</p> <p>Davies, S.G., C29</p> <p>Erofeev, A.B., 167</p> <p>Esteruelas, M.A., 249</p> <p>Fañanás, F.J., 267</p> <p>Foces-Foces, C., 249</p> <p>Gambaro, A., 199, 207</p> <p>Garcia-Blanco, S., 249</p> <p>Gusel'nikov, L.E., 173</p> <p>Gusev, A.I., 167</p> <p>Herberich, G.E., 143</p> <p>Herrmann, W.A., 219</p> <p>Hoberg, H., 267</p> <p>Hooker, R.H., C25</p> <p>Kerber, R.C., 131</p> <p>Kirillova, N.I., 167</p> <p>Kirpichenko, S.V., 173</p> <p>Kolosova, N.D., 189</p> <p>Krapivin, A.M., 243</p> <p>Kriechbaum, G.W., 219</p> | <p>Lal, K., 193</p> <p>Leckey, N.T., 193</p> <p>Lobkovsky, E.B., 167</p> <p>Lukehart, C.M., 149</p> <p>McPherson, H.D., 261</p> <p>Mahmoud, K.A., C25</p> <p>Nametkin, N.S., 173, 243</p> <p>Oro, L.A., 249</p> <p>Pfisterer, H., 219</p> <p>Rest, A.J., C25</p> <p>Riegel, H.J., 267</p> <p>Romanin, A.M., 199, 207</p> <p>Serwatowski, J., 159</p> <p>Simpson, S.J., C29</p> <p>Söhnne, D., 143</p> <p>Soloveychik, G.L., 167</p> <p>Suslova, E.N., 173</p> <p>Thomas, S.E., C29</p> <p>Trusov, V.V., 243</p> <p>Tyurin, V.D., 243</p> <p>Usón, R., 249</p> <p>Venzo, A., 199, 207</p> <p>Volkova, V.V., 173</p> <p>Voronkov, M.G., 173</p> <p>Wardell, J.L., 261</p> <p>Watts, W.E., 193</p> <p>Zemlyansky, N.N., 189</p> <p>Ziegler, M.L., 219</p> |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|