Journal of Organometallic Chemistry, 254 (1983) C29—C32
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PREPARATION AND HYDRIDE REDUCTION OF THE ELECTRON-RICH CATIONS $[(Me_5C_5)Fe(CO)_2L]^+$ ($L = CO, PPh_3, PMe_3$) AND $[(Me_5C_5)Fe(CO)(Ph_2PCH_2CH_2PPh_2)]^+$

STEPHEN G. DAVIES*, STEPHEN J. SIMPSON and SUSAN E. THOMAS
The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY (Great Britain)

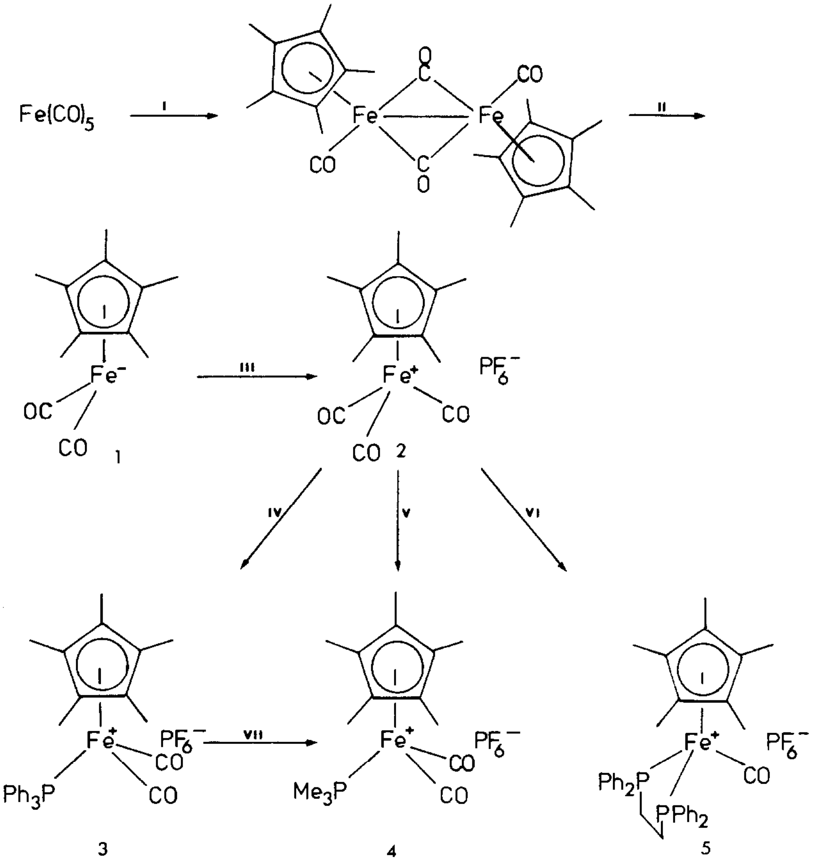
(Received July 5th, 1983)

Summary

The cations $[(Me_5C_5)Fe(CO)_2L]^+$ (3, $L = PPh_3$; 4, $L = PMe_3$) and $[(Me_5C_5)Fe(CO)(Ph_2PCH_2CH_2PPh_2)]^+$ (5) have been prepared from $[(Me_5C_5)Fe(CO)_3]^+$ (2) by controlled decarbonylation reactions. Hydride reduction of these cations occurs at CO to give $(Me_5C_5)Fe(CO)_2H$ from 2 and 3, and $[(Me_5C_5)Fe(CO)H]_2(Ph_2PCH_2CH_2PPh_2)$ from 5, while complete reduction of carbon monoxide to the methyl complex $(Me_5C_5)Fe(CO)(PMe_3)Me$ 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 hydroxymethylmetal and then methylmetal complexes [1]. We have recently developed models for the reduction of metal carbonyl ligands to methylmetals based on the electron-rich $[(\eta^5\text{-}C_5H_5)Fe(L_2)CO]^+$ cations (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 $[(\eta^5\text{-}Me_5C_5)Fe(CO)_3]^+$ (2), $[(\eta^6\text{-}Me_5C_5)Fe(L)(CO)_2]^+$ (3, $L = PPh_3$; 4, $L = PMe_3$) and $[(\eta^5\text{-}Me_5C_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]^+$ (5) and their reductions

0022-328X/83/$03.00

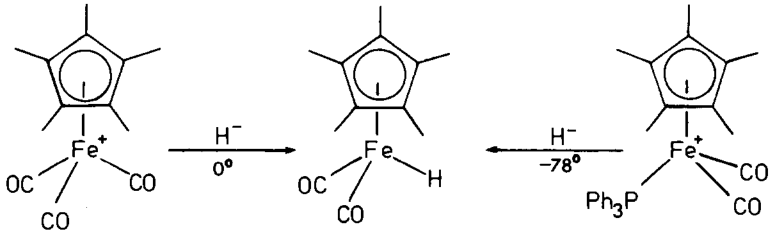


(i) Me_5C_5H; (ii) lithium naphthalenide; (iii) $ClCO_2Et$ then HCl then NH_4PF_6; (iv) PPh_3, DMSO; (v) PMe_3, DMSO; (vi) $Ph_2PCH_2CH_2PPh_2$, acetone, Me_3NO; (vii) PMe_3, acetone.

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

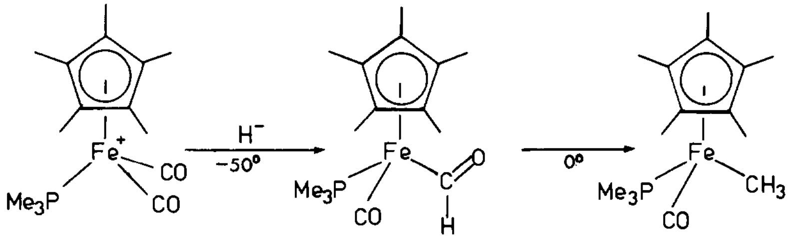
Thermolysis of iron pentacarbonyl with pentamethylcyclopentadiene [4] generates $[(Me_5C_5)Fe(CO)_2]_2$ [5]. In our hands the best conditions for the reduction of this dimer to the anion 1 employ lithium naphthalenide. Treatment of solutions of anion 1 with ethyl chloroformate followed by hydrogen chloride gas generates after anion exchange the cation $[(Me_5C_5)Fe(CO)_3]^+ PF_6^-$ (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.

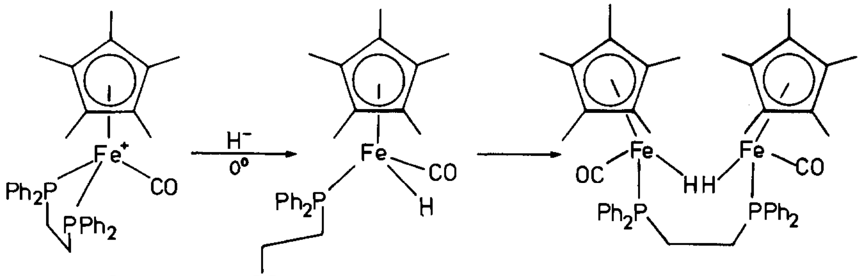


2 6 3

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}H NMR spectroscopy allowed the observation of the intermediate formyl complex 7 (δ 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].



4 7 8



5 9 10

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

Avakyan, V.G., 173

Baskar, A.J., 149
Beletskaya, I.P., 189
Belsky, V.K., 189
Bock, H., 219
Bolesławski, M., 159
Borisova, I.V., 189
Bulychev, B.M., 167

Cano, F.H., 249
Carmona, D., 249
Ceccon, A., 199, 207

Dammel, R., 219
Davies, S.G., C29

Erofeev, A.B., 167
Esteruelas, M.A., 249

Fañanás, F.J., 267
Foces-Foces, C., 249

Gambaro, A., 199, 207
Garcia-Blanco, S., 249
Gusel'nikov, L.E., 173
Gusev, A.I., 167

Herberich, G.E., 143
Herrmann, W.A., 219
Hoberg, H., 267
Hooker, R.H., C25

Kerber, R.C., 131
Kirillova, N.I., 167
Kirpichenko, S.V., 173
Kolosova, N.D., 189
Krapivin, A.M., 243
Kriechbaum, G.W., 219

Lal, K., 193
Leckey, N.T., 193
Lobkovsky, E.B., 167
Lukehart, C.M., 149

McPherson, H.D., 261
Mahmoud, K.A., C25

Nametkin, N.S., 173, 243

Oro, L.A., 249

Pfisterer, H., 219

Rest, A.J., C25
Riegel, H.J., 267
Romanin, A.M., 199, 207

Serwatowski, J., 159
Simpson, S.J., C29
Söhnen, D., 143
Soloveychik, G.L., 167
Suslova, E.N., 173

Thomas, S.E., C29
Trusov, V.V., 243
Tyurin, V.D., 243

Usón, R., 249

Venzo, A., 199, 207
Volkova, V.V., 173
Voronkov, M.G., 173

Wardell, J.L., 261
Watts, W.E., 193

Zemlyansky, N.N., 189
Ziegler, M.L., 219