Journal of Organometallic Chemistry, 248 (1983) C9–C12
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

BIS- AND TRIS-ACETONITRILE COMPLEXES OF IRON(II)

DANIEL CATHELINE and DIDIER ASTRUC
Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France)

(Received March 2nd, 1983)

Summary

Photolysis of $[CpFe(CO)_3]^+ PF_6^-$ in CH_3CN in the presence of 2-, 4- or 6-electron ligands gives $[CpFeL_n(NCCH_3)_{3-n}]^+ PF_6^-$ (n = 1: L = CO, PPh_3, cyclohexene, dimethylthiophene; n = 2 : L_2 = dppe or n = 3 : L_3 = cyclooctatetraene, or three phospholes), whereas in the absence of added ligand a thermally stable purple tris(acetonitrile) complex is isolable only using permethylated Cp. The synthetic potential of the acetonitrile complexes is illustrated by the stepwise replacement of the acetonitrile ligands.

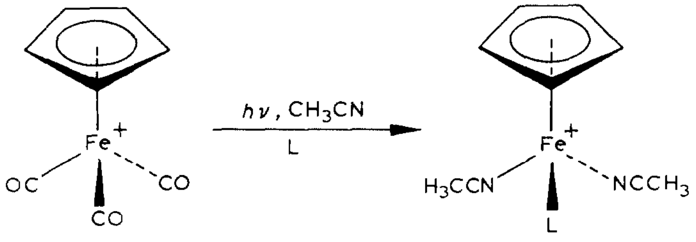
Polyacetonitrile complexes, known for many transition metals [1], have proved useful intermediates in organometallic synthesis and catalysis. Although it is possibly the most developed organometallic family, $CpFe^{II}$ forms only mono(acetonitrile) complexes $[CpFe^{II}(L_1)(L_2)(NCCH_3)]^+ X^-$ [2]. We describe here straight-forward routes to the bis(acetonitrile) complexes $[CpFe^{II}(L)(NCCH_3)_2]^+ PF_6^-$ and to the tris(acetonitrile) complex $[C_5Me_5Fe^{II}(NCCH_3)_3]^+ PF_6^-$, and the reactions of these complexes.

Some time ago we described convenient syntheses of $[CpFe^{II}(CO)_3]^+ PF_6^-$, 1 [3] (from Cp_2Fe, CO and $AlCl_3$) and of $[C_5Me_5Fe^{II}(CO)_3]^+ PF_6^-$, 2 [4] (from $C_5Me_5Fe(CO)_2Br$, CO and $AlCl_3$). The synthesis of bis- and tris-(acetonitrile) complexes of iron(II) is based on the photolysis of 1 and 2 in CH_3CN.

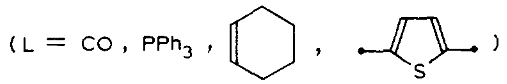
The photolysis of 1 (Hanovia lamp, 250 nm) in CH_3CN produces only ferrocene and inorganic Fe^{II} (when the cell is degassed with N_2). The same result is obtained starting from $(CpFe\text{-}\eta^6\text{-toluene})^+ PF_6^-$, 3 [5,6]. However, when the photolysis of 1 is carried out without degassing, thermally stable, air-sensitive $[CpFe(CO)(NCMe)_2]^+ PF_6^-$, 4, can be isolated in 65% crude yield upon concentration in vacuo and precipitation by ether. Photolysis of 1 or 3 with degassing N_2 in the presence of a stoichiometric amount of PPh_3 gives dark red crystals of thermally stable, air sensitive $[CpFe(PPh_3)(NCMe)_2]^+ PF_6^-$, 5, in 94% yield

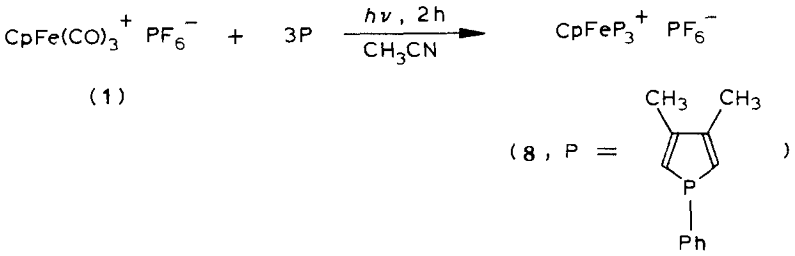
0022-328X/83/$03.00

after concentration of the acetonitrile solution and cooling to −20°C. The coupling (d, 4 Hz) between the Cp hydrogens and phosphorus indicates the presence of one coordinated phosphine. $[CpFe(L)(NCMe)_2]^+ PF_6^-$ (L = cyclohexene, **6**; dimethylthiophene, **7** (eq. 1) were similarly obtained in 54 and 58% crude yields, respectively, but their purification was precluded by their instability in solvents other than CH_3CN. In the presence of one mole 1-phenyl-3,4-dimethylphosphole (P) photolysis of **1** produced exclusively the air stable orange complex $(CpFeP_3)^+ PF_6^-$, **8**, in 94% yield based on P (note that no $[CpFe(P)(NCMe)_2^-]^+ PF_6^-$ is obtained in contrast to other cases above). The presence of three coordinated phosphorus ligands in **8** is shown by the quartet (2 Hz) for the Cp signal in the 200 MHz ^1H NMR spectrum, and confirmed by elemental analysis.



(1)

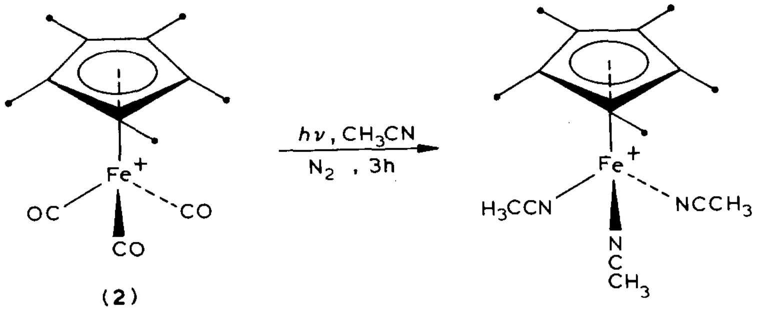




Photolysis of **1** (2 h) with degassing N_2 in the presence of dppe gives the known complex $[CpFe(dppe)(NCMe)]^+ PF_6^-$, **9** [2a] in 93% yield.

The photolysis of **2** in CH_3CN with degassing N_2 leads, after 3 h, to the disappearance of all the metal—carbonyl IR stretches and to a deep purple solution; concentration and cooling to −20°C gives thermally stable, air-sensitive purple crystals of $[C_5Me_5Fe(NCMe)_3]^+ PF_6^-$, **10**; spectroscopic data and elemental analyses establish the molecular structure of **10** (eq. 2).

When photolysis of **2** is carried out without degassing N_2, red $[C_5Me_5Fe(CO)(NCMe)_2]^+ PF_6^-$, **11** is isolated in 62% yield; alternatively **11** can be obtained selectively by bubbling CO into an acetonitrile solution of **10** at 20°C for 30 minutes. Indeed, **10** is a good starting material for Fe^{II} complexes bearing various ligands. For instance, **10** reacts thermally with 1 mol PPh_3 (30 min, 20°C, CH_3CN) to give $[C_5Me_5Fe(PPh_3)(NCMe)_2]^+ PF_6^-$, **12**, as air sensitive red microcrystals in



(2) (10) (2)

88% yield. A chiral iron center is easily obtained by subsequent reactions of **5** with 1 atm CO (1 h, 40—50°C, CH_3CN), which give the known complex $[CpFe(CO)(PPh_3)(NCMe)]^+ PF_6^-$, **13** [2b] in 95% yield. Further examples of the selective removal of one, two or three MeCN ligands from **10** are its thermal reactions with dppe (1 h, 20°C, CH_3CN) and cyclooctatetraene COT (12 h, reflux, CH_3CN) to give $[C_5Me_5Fe(dppe)(NCMe)]^+ PF_6^-$, as a THF solvate, **15** (90%) and $(C_5Me_5Fe\text{-}\eta^6\text{-COT})^+ PF_6^-$ (**16**, 57%, Scheme 1), respectively.

10 → $[C_5Me_5Fe(L)(NCMe)_2]^+ PF_6^-$ (11: L = CO; 12: L = PPh_3)

10 → $[C_5Me_5Fe(dppe)(NCMe)]^+ PF_6^-$ (13)

10 → $[C_5Me_5Fe(\eta^6\text{-COT})]^+ PF_6^-$ (14)

SCHEME 1

It should be noted that photolysis of $[CpFe(\eta^6\text{-}p\text{-xylene})]^+ PF_6^-$ in various solvents was reported to give a series of complexes $[CpFeL_3]^+ PF_6^-$ in the presence of excess ligand (arenes, phosphines, phosphite) [6—8]. However, all our attempts to complex arenes by thermal reactions with **10** have so far failed, despite the fact that such a process is known in the related ruthenium chemistry [1h]; this is possibly due to the extreme unstability of η^4-areneiron intermediates, whereas there are known examples of stable η^4-areneruthenium complexes [9].

^1H and ^{13}C NMR chemical shift are given in ppm from internal TMS. Infrared spectra were recorded with Nujol mulls between KBr plates (ν in cm^{-1}).

4: ^1H NMR (CD_3COCD_3): 5.03 (s, 5H, Cp); 2.43 (s, 6H, MeCN). IR: 2190 (w, ν(CN)); 1980 (s, ν(CO)).

5: ^1H NMR (CD_3COCD_3): 7.40 (m, 15H, Ph); 4.30 (d, 5H, Cp, J(PH) 4 Hz); 2.25 (s, 6H, MeCN). IR: 2300 (w, ν(CN)).

6: ^1H NMR (CD_3CN): 4.70 (m, 2H, complexed CH); 4.43 (s, 5H, Cp); 1.90 (m, 14H, CH_2 and MeCN). IR: 2300 (w, ν(CN)).

7: ^1H NMR (CD_3COCD_3): 6.53 (s, 2H, $SC_4H_2(Me_2)$); 5.10 (s, 5H, Cp); 2.56 (b, 12H, $SC_4H_2(Me)_2$ and MeCN). IR: 2250 (w, ν(CN)).

8: ^1H NMR (200 MHz, CD_3COCD_3): 7.33 (m, 15H, Ph); 6.63 (m, 6H, CH, J(PH) 35 Hz); 5.13 (q, 5H, Cp, J(PH) 2 Hz); 1.75 (s, 18H, Me). ^{13}C NMR

(CD_3CN): 151.28 (dd, $C\beta$); 132.90, 132.13, 131.42, 130.65 (Ph); 129.20 (dd, $C\alpha$); 79.15 (s, Cp); 17.13 (dd, Me).

10: ^{1}H NMR (CD_3COCD_3): 2.42 (s, 9H, MeCN); 1.66 (s, 15H, C_5Me_5). IR: 2290 (w, ν(CN)). Mössbauer IS 0.54 mm s^{-1}/Fe; QS 2.37 mm s^{-1}.

11: ^{1}H NMR (CD_3COCD_3): 2.40 (s, 6H, MeCN); 1.70 (s, 15H, C_5Me_5). ^{13}C NMR (CD_2Cl_2): 216.01 (CO); 132.61 (Me*C*N); 91.68 (C_5Me$_5$); 9.35 (C$_5$*Me*$_5$); 4.43 (*Me*CN). IR: 2300 (w, ν(CN)); 1970 (s, ν(CO)).

12: ^{1}H NMR (CD_3COCD_3): 7.59 (m, 15H, Ph); 2.42 (s, 6H, MeCN); 1.37 (s, 15H, C_5Me_5). ^{13}C NMR (CD_3CN): 165.14 (Me*C*N); 133.10, 132.61, 132.13, 128.49, 127.52, 127.10, 126.67 (Ph); 82.00 (C_5Me$_5$); 6.87 (C$_5$*Me*$_5$); 1.72 (*Me*CN). IR: 2280 (w, ν(CN)).

13: ^{1}H NMR (CD_3COCD_3): 7.73 (m, 15H, Ph); 3.33 (m, 4H, CH_2); 2.06 (s, 3H, CH_3CN); 1.36 (s, 15H, C_5Me_5). ^{13}C NMR (CD_3CN): 134.34, 133.43, 131.76, 131.38, 129.72, 129.64, 129.49 (Ph); 88.37 (C_5Me$_5$); 28.52 (b, CH_2); 9.94 (C$_5$*Me*$_5$); 1.67 (*Me*CN). IR: 2280 (w, ν(CN)).

14: ^{1}H NMR (CD_3COCD_3): 6.60 (m, 2H, Hγ); 5.76 (m, 4H, Hα and Hβ); 4.83 (m, 2H, uncomplexed CH); 1.80 (s, 15H, C_5Me_5). ^{13}C NMR (CD_3CN): 134.14 (uncomplexed CH); 104.67 (Cα); 102.87 (Cβ); 97.10 (C_5Me$_5$); 94.48 (Cγ); 9.22 (C$_5$*Me*$_5$).

Satisfactory analyses for C, H and Fe, and where appropriate P and N, were obtained for complexes **4**, **5**, **8**, **10**, **11**, **13** and **14**.

We thank F. Mathey (CNRS-SNPE, Thiais) for a generous gift of 1-phenyl-3,4-dimethylphosphole and BASF (Ludwigshafen, West Germany) for a generous gift of $Fe(CO)_5$.

References

1 (a) T.A. Manuel, Adv. Organomet. Chem., 3 (1965) 181; (b) R.B. King, J. Organomet. Chem., 8 (1967) 139; (c) W. Strohmeier and G. Hartmann, Z. Naturforsch. B, 19 (1964) 655; (d) A. Von Feltz and P. Sennewald, Z. Anorg. Allg. Chem., 358 (1968) 29; (e) R.B. King and A. Fronzaglia, J. Chem. Soc. Chem. Comm., (1965) 547; ibid., (1966) 274; Inorg. Chem., 5 (1966) 1837; (f) E.W. Abel, M.A. Bennet and G. Wilkinson, J. Chem. Soc., (1959) 3178; (g) K.K. Bhasin, W.G. Balkeen and P.L. Pauson, J. Organomet. Chem., 204 (1981) C25; (h) T.P. Gill and K.R. Mann, Organometallics, 1 (1982) 485.

2 (a) P.M. Treichel and D.C. Molzahn, Synth. React. Met.-Org. Chem., 9 (1979) 21; (b) P.M. Treichel, R.L. Shubkin, K.W. Barnett and D. Reichard, Inorg. Chem., 5 (1966) 1177.

3 E. Román and D. Astruc, Inorg. Chem., 18 (1979) 3284.

4 D. Catheline and D. Astruc, J. Organomet. Chem., 226 (1982) C52.

5 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Tetrahedron Letters, 25 (1963) 1725.

6 (a) A.N. Nesmeyanov, N.A. Vol'kenau and L.S. Shilovtseva, Dokl. Akad. Nauk, SSSR, 190 (1970) 857; (b) The photodecomposition of $CpFe^+(C_6Me_6)OH^-$ in H_2O is discussed in J.-R. Hamon, D. Astruc and P.M. Michaud, J. Amer. Chem. Soc., 103 (1981) 758 (see ref. 57 therein).

7 K.R. Mann and T.P. Gill, Inorg. Chem., 19 (1980) 3007.

8 E.D. Laganis, R.G. Finke and V. Boekelheide, Proc. Natl. Acad. Sci., USA 78, 1981, p. 2657.

9 (a) E.O. Fischer and C. Elschenbroich, Chem. Ber., 103 (1970) 162; (b) G. Huttner and S. Lange, Acta. Crystallogr., Sect. B, 28 (1972) 2049; (c) E.L. Muetterties, J.R. Bleeke, E.W. Wucherer and T.A. Albright, Chem. Rev., 82 (1982) 499.