Journal of Organometallic Chemistry, 272 (1984) 417–426
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE USE OF FERROCENE IN ORGANOMETALLIC SYNTHESIS: A TWO-STEP PREPARATION OF CYCLOPENTADIENYLIRON ACETONITRILE AND PHOSPHINE CATIONS VIA PHOTOLYSIS OF CYCLOPENTADIENYLIRON TRICARBONYL OR ARENE CATIONS

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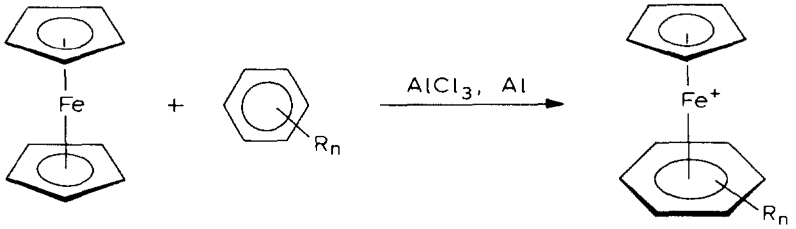
(Received January 30th, 1984)

Summary

UV photolysis of $\{CpFe^{II}(CO)_3\}^+\ PF_6^-$ (I) or $\{CpFe^{II}(\eta^6\text{-toluene})\}^+\ PF_6^-$ (II) in CH_3CN in the presence of 1 mole of a ligand L gives the new air sensitive, red complexes $\{CpFe^{II}(NCCH_3)_2L\}^+PF_6^-$ (III, $L = PPh_3$; IV; $L = CO$; VIII, $L =$ cyclohexene; IX, $L =$ dimethylthiophene) and the known air stable complex $\{CpFe^{II}(PMe_3)_2(NCMe)\}^+PF_6^-$ (V). The last product is also obtained by photolysis in the presence of 2 or 3 moles of PMe_3. In the presence of dppe, the known complex $\{CpFe^{II}\ (dppe)(NCCH_3)\}^+$ (XI) is obtained. Complex III reacts with CO under mild conditions to give the known complex $\{CpFe(NCCH_3)(PPh_3)CO\}^+PF_6^-$ (X). UV photolysis of I in CH_3CN in the presence of 1-phenyl-3,4-dimethylphosphole (P) gives $\{CpFe^{II}P_3\}^+\ PF_6^-$ (XII); UV photolysis of II in CH_2Cl_2 in the presence of 3 moles of PMe_3 or 1 mole of tripod $(CH_3C(CH_2Ph_2)_3)$ provides an easy synthesis of the known complexes $\{CpFe^{II}(PMe_3)_3\}^+\ PF_6^-$ (VII) or $\{CpFe^{II}\text{-}\eta^3\text{-tripod}\}^+\ PF_6^-$ (XIII). Since I and II are easily accessible from ferrocene, these photolytic syntheses provide access to a wide range of piano-stool cyclopentadienyliron(II) cations in a 2-step process from ferrocene.

Introduction

While ferrocene has a rich organic chemistry [1], its conversion into other organometallic derivatives has been relatively little explored [2]. The most general ligand exchange reaction is that with arenes (eq. 1) discovered by Nesmeyanov's group in the early 60's [3], which has proved useful for the activation of arenes [4]. In 1979 we reported an efficent synthesis of $\{CpFe(CO)_3\}^+\ PF_6^-$ from ferrocene and CO [5] (eq. 2). This was the first entry into piano-stool organoiron chemistry from ferrocene.



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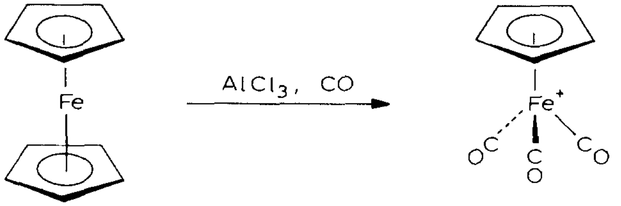

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(I)

In a preliminary communication [6], we described the photolytic replacement of the three carbonyl groups of I by 2 acetonitriles and one other ligand when a stoichiometric amount of the ligand was added to an acetonitrile solution of I. We noted that the same complexes are accessible via photolysis of $\{CpFe^{II}\text{-}\eta^6\text{-toluene}\}^+$ PF_6^- (II). We also demonstrated the synthetic potential of these reactions by further selective replacement of the acetonitrile ligands. These results are described in detail below. A recent paper on the photolysis of $\{CpFe(\eta^6\text{-}p\text{-xylene})\}^+$ PF_6^- in CH_3CN, presents evidence for the formation of $\{CpFe(NCMe)_3\}^+$ at low temperature, and the syntheses of related phosphite and isocyanide derivatives were also reported in 1983 [7]. Some of the products described here were previously known but the photolytic reaction provides easy, high yield routes to them.

In our preliminary communication, we also reported the thermally stable complex $\{C_5Me_5Fe(NCMe)_3\}^+$ PF_6^- and its substitution chemistry. Full details of that aspect will be given later. There have been several reports in the recent literature [9] concerning the photolytic exchange of arenes in the cations $\{CpFe(\eta^6\text{-arene})\}^+$ (eq. 3).

$$\{CpFe(\text{arene 1})\}^+ + \text{arene 2} \rightarrow \{CpFe(\text{arene 2})\}^+ + \text{arene I} \qquad (3)$$

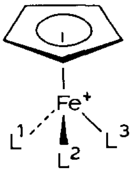
Although only relatively uninteresting $\{CpFe(\eta^6\text{-arene})\}^+$ complexes and a few interesting $\{CpFe(\text{cyclophane})\}^+$ complexes have been made in this way, the method could be of value if complexes not accessible via the direct ligand exchange route (eq. 1) could be made. In fact the approach gave $\{CpFe(\text{phosphite})_3\}^+$ cations [7,9], which are also accessible thermally from $\{CpFe(\eta^6\text{-arene})\}^+$ cations (arene = nitrobenzene, isomeric nitrotoluene, aniline) [10].

$$\{CpFe(\text{arene})\}^+ + 3P(OR)_3 \rightarrow \{CpFe[P(OR)_3]\}^+ + \text{arene} \qquad (4)$$

The method proves to be quite general. In addition to the new acetonitrile complexes, we describe below the straightforward preparation of the known complexes $\{CpFe(PMe_3)_3\}^+$ [16] and $\{CpFe(\text{tripod})\}^+$ [17] and the photolytic synthesis of the new cation $\{CpFe(\text{phosphole})_3\}^+$. These piano-stool complexes are listed in Table 1.

TABLE 1

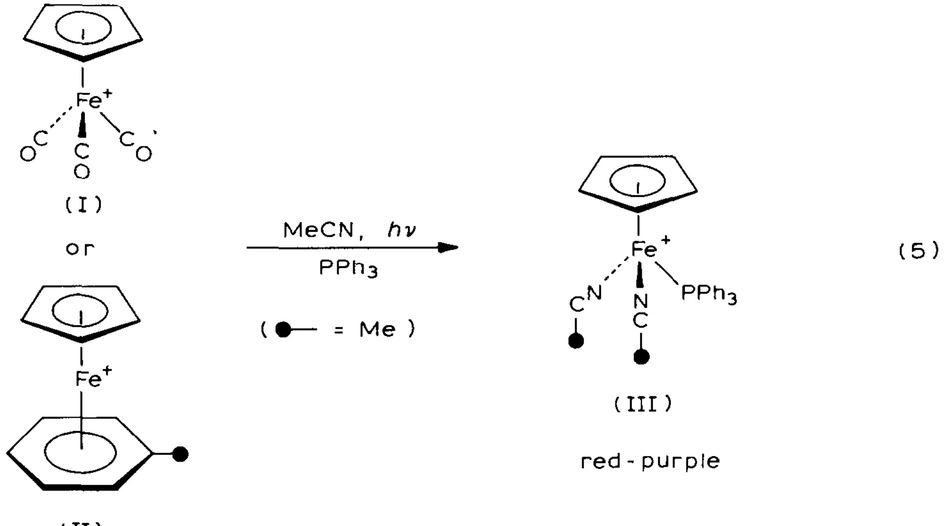
PIANO-STOOL COMPLEXES



	L^1	L^2	L^3
I	CO	CO	CO
III	PPh_3	NCMe	NCMe
IV	CO	NCMe	NCMe
V	PMe_3	PMe_3	NCMe
VII	PMe_3	PMe_3	PMe_3
VIII	C_6H_{10}	NCMe	NCMe
IX	$S(CMe)(CH)_2(CMe)$	NCMe	NCMe
X	PPh_3	CO	NCMe
XI	$Ph_2PCH_2CH_2PPh_2$		NCMe
XII	$PhP(CH)(CMe)_2CH$	$PhP(CH)(CMe)_2CH$	$PhP(CH)(CMe)_2CH$
XIII	$(Ph_2PCH_2)_3CMe$		

Results and discussion

In the course of our work [11] on $\{CpFe(\eta^6\text{-}C_6Me_6)\}^+ PF_6^-$ we noted that room temperature photolysis of this complex in a degassed CH_3CN solution gave a transient intense purple color. The purple photoproduct persisted at −40 °C as previously reported [7]. Similar experiments with $\{CpFe(CO)_3\}^+ PF_6^-$ gave the same results. Thus, we were led to think that a common unstable purple acetonitrile complex $\{CpFe(NCMe)_3\}^+$ was formed upon photolysis of either I or II. We also



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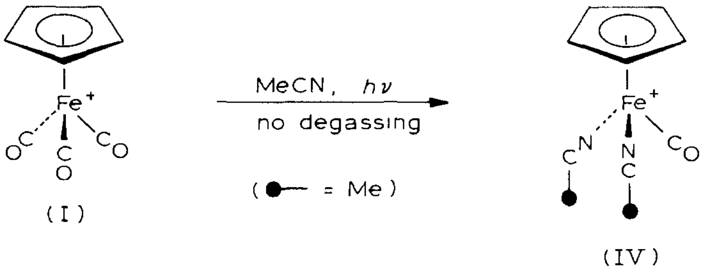
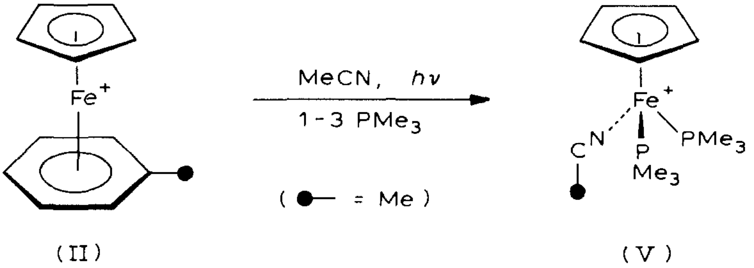
knew that photolysis of $\{CpFe(\eta^6\text{-}C_6H_6)\}^+ BF_4^-$ in CH_3CN or THF [12] and of $\{CpFe(\eta^6\text{-}C_6Me_6)\}^+ OH^-$ in H_2O rapidly gives Fe^{2+}, ferrocene, and the arene. Subsequently we attempted to trap $\{CpFe(NCMe)_3\}^+$ using a stoichiometric amount of a stabilizing ligand L. Photolysis of I or II in a degassed acetonitrile solution in the presence of 1 mole of PPh_3 gave a stable red-purple solution from which the air sensitive, thermally stable new complex $\{CpFe(NCMe)_2(PPh_3)\}^+ PF_6^-$ (III) was isolated in 94% yield as red-purple crystals after concentration of the acetonitrile solution and cooling to −20 °C (eq. 5).

The red carbonyl complex $\{CpFe(NCMe)_2CO\}^+ PF_6^-$ (IV) was prepared in 65% yield, as the sole product, by photolysis of I in CH_3CN without degassing, so that a CO atmosphere remained in the photolysis cell (eq. 6).



(6)

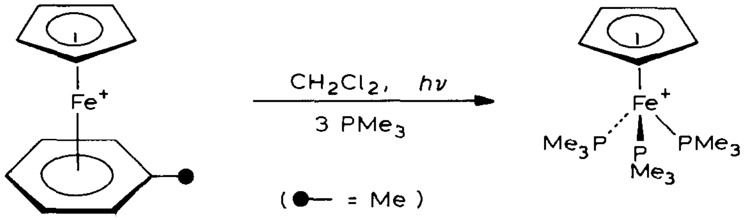
The photolysis of $(CpFe\text{-}\eta^6\text{-toluene})^+$ in the presence of PMe_3 follows a peculiar course; the known orange complex $\{CpFe(NCMe)(PMe_3)_2\}^+ PF_6^-$ [16], is formed selectively, no matter what Fe/PMe_3 ratio is used. When only 1 mole of PMe_3 is used the reaction of PMe_3 with the intermediate complex $\{CpFe(NCMe)_2(PMe_3)\}^+PF_6^-$ (VI) is faster than the formation of this complex (eq. 7); thus all the PMe_3 is consumed before the end of the photodecomplexation of II, which explains the formation of ferrocene and $\{Fe(NCMe)_6\}^{2+}(PF_6^-)_2$ as by-products.



(7)

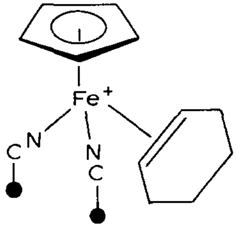
On the other hand, if the photolysis of II in CH_3CN is effected in the presence of three moles of PMe_3, the last mole of PMe_3 does not react with V under ambient conditions in acetonitrile and so the known complex V is readily available; the synthesis reported by Treichel in 1981 [16] involves the photolysis of the less easily accessible starting material $\{CpFe(PMe_3)_2(CO)\}^+ PF_6^-$.

The known yellow tris(trimethylphosphine) complex $\{CpFe(PMe_3)_3\}^+ PF_6^-$, (VII) [16] is obtained by using CH_2Cl_2 as the solvent for the photolysis of II (eq. 8). Thus, a single carbonyl or phosphorus ligand stabilizes the piano-stool cationic complex $\{CpFe(NCMe)_2L\}^+$.



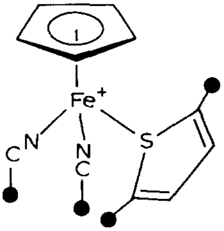
(II) (VII) (8)

We also attempted to synthesize analogous complexes using other ligands such as cyclohexene and dimethylthiophene. {CpFe(NCMe)$_2$(η^2-cyclohexene)}$^+$ PF$_6$$^-$ (VIII) and {CpFe(NCMe)$_2$(η^1-dimethylthiophene)}$^+$ PF$_6$$^-$ (IX) were made from I by the reaction shown in eq. 5, and their structures were confirmed by ^{1}H NMR and IR spectra. However, the two complexes, which were obtained from concentrated acetonitrile solution by precipitation with ether could not be recrystallized and subjected to elemental analysis because of their thermal unstability.



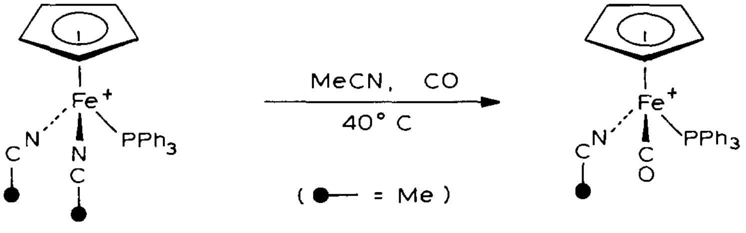
(VIII)

(●— = Me)



(IX)

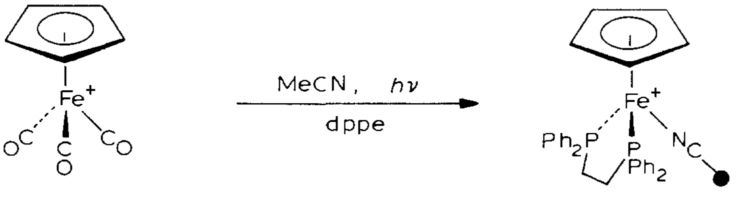
The methods give piano-stool complexes bearing two labile acetonitrile ligand, accessible in two high-yield steps from ferrocene and the synthetic potential of these complexes is obvious. For instance III reacts with CO under mild conditions (eq. 9) in CH$_3$CN to give {CpFe(CO)(PPh$_3$)NCMe)}$^+$ PF$_6$$^-$ (X) in 95% yield.



(III) (X) (9)

Complex X was previously made by Treichel in 9% yield by a tedious route [13]. The ease and selectivity of the reaction are remarkable, no dicarbonyl compound being isolated. Our synthesis of X represented the first application of the photolytic route to preparation of chiral piano-stool complexes; other examples have since been reported independently [7].

The reaction of eq. 5 can also be used to introduce directly two identical L ligands or a chelating diphos ligand. When photolysis of I or II is performed in a degassed acetonitrile solution containing 1 mol dppe, the red crystalline complex $\{CpFe(dppe)(NCMe)\}^+ PF_6^-$ (XI) reported by Treichel in 1979 [8], is obtained in 93% yield (eq. 10). It should be noted that King [14] prepared many CpFe(dppe) derivatives in the late 60's [14] and that Green reported CpFe(dppe)I in 1971 [15].



(10)

(I (or II)) (XI)

(dppe = $Ph_2P(CH_2)_2PPh_2$)

The stable orange complex $\{CpFe(phosphole)_3\}^+ PF_6^-$ (XII) can be made directly from I in a degassed acetonitrile solution photolysis even if only one equivalent of phosphole is added (eq. 11), whereas under these conditions PPh_3 and PMe_3 give the mono- and bis-phosphine complexes, respectively (eq. 5, 7).

The ^1H NMR spectrum of XII (Fig. 1) exhibits a quartet at δ 5.13 ppm for the Cp ligand due to coupling with the three phosphorus bound to iron (J(PH) 1.59 Hz). The $\{^1H\}$ ^{13}C spectrum shows a splitting of the phosphole ring carbons, in addition

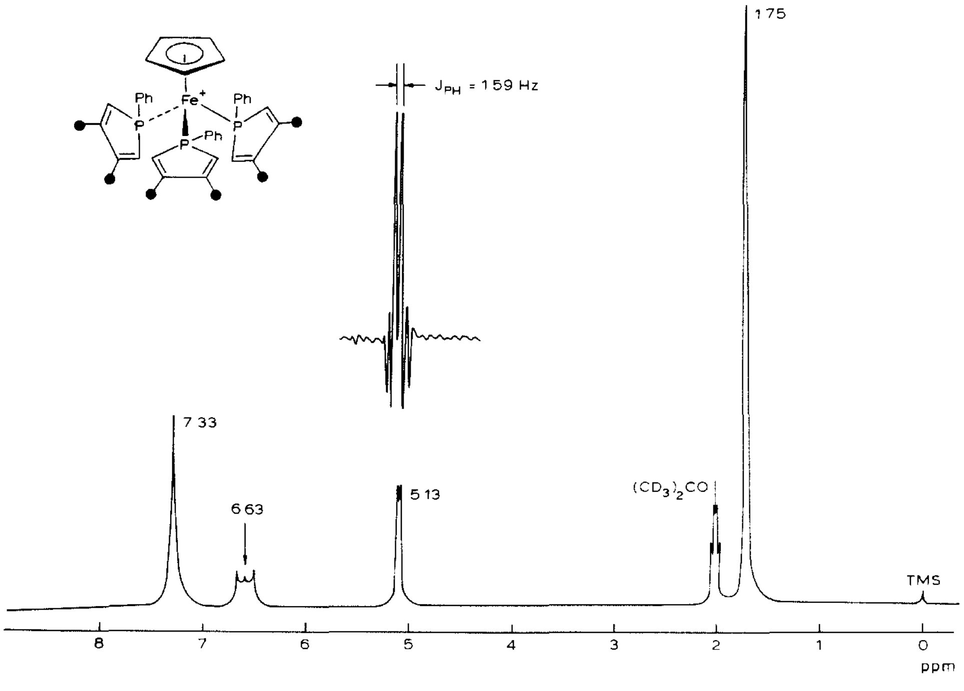
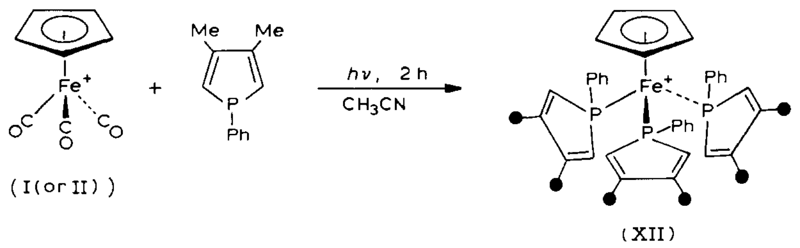


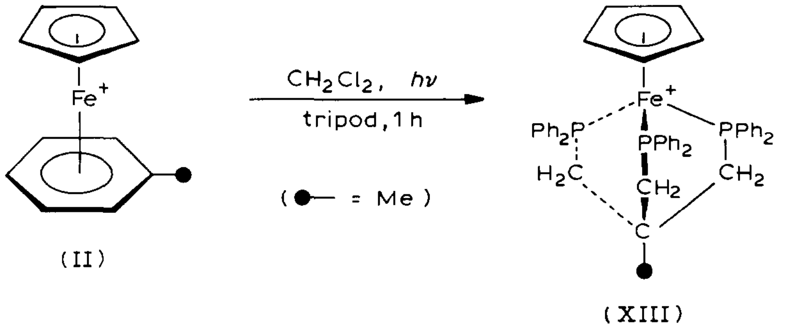
Fig. 1. 200 MHz ^1H spectrum of $\{CpFe[Ph\overline{PCH=C(CH_3)C(CH_3)=CH}]_3\}^+ PF_6^-$ (XII) in CD_3COCD_3 solution.



(11)

to coupling with phosphorus. We again assume that formation of XII under these photolytic conditions implies that replacement of all three acetonitriles by phosphole ligands is faster than photocleavage of the carbonyls in I.

The photolysis of II in a degassed CH_2Cl_2 solution containing 1 mole of tripod $\{CH_3C(CH_2PPh_2)_3\}$ rapidly gives the known complex $\{CpFe(\eta^3\text{-tripod})\}^+ PF_6^-$ (XIII) (eq. 12); an alternative, recently reported, route to XIII is more complicated and time consuming [17]. The reaction shown in eq. 13 gives yellow crystals of XIII in 85% yield from II and the tripod ligand. The redox chemistry of XIII is al present under scrutiny.



(12)

Experimental

Reagent grade CH_2Cl_2 and CH_3CN were distilled from P_2O_5 under nitrogen; diethyl ether was distilled from sodium benzophenone ketyl; acetone was distilled from B_2O_3. All other chemicals were used as received. All manipulations carried out using Schlenk techniques under argon or in a nitrogen filled Vacuum Atmospheres glove-box. Photolyses were performed with a Hanovia lamp, 250 nm, 450 W. Infrared spectra were recorded on a Pye Unicam SP 1100 infrared spectrometer, either in Nujol mulls between KBr disks or in solution using 0.1 mm cells with KBr windows. Absorptions are given in cm^{-1} polystyrene being used for standardization. ^1H NMR spectra were recorded with a Varian EM 360 instrument (60 MHz). ^{13}C NMR spectra are recorded with a Brücker WH 90 instrument (20.115 MHz, F.T. mode). Chemical shifts are reported in ppm with reference to internal tetramethylsilane (TMS) for ^1H and ^{13}C NMR. Elemental analysis were performed by the Center for Microanalyses of the CNRS at Lyon-Villeurbanne.

1. Synthesis of $\{CpFe(NCMe)_2L\}^+ PF_6^-$, (III, L = PPh$_3$; VIII, L = cyclohexene; IX, L = dimethylthiophene)

$\{CpFe(CO)_3\}^+ PF_6^-$ (I) (1 g, 3 mmol) is photolysed in 200 ml of CH_3CN with 3 mmole of L for 3 h at room temperature while a stream of argon is passed through the cell. Concentration to 5 ml in vacuo and addition of 100 ml of diethyl ether precipitates $\{CpFe(NCMe)2L\}^+ PF_6^-$ as a red powder.

III, L = PPh_3, yield: 94%. ^1H NMR (CD_3CN): 7.40 (m, 15H, Ph), 4.30 (d, 5H, Cp, *J*(PH) 4Hz), 2.25 ppm (s, 6H, MeCN). IR: 2300 cm^{-1} (ν(CN)). Anal. Found: C, 53.54; H, 4.38; P, 9.78; N, 4.42; Fe, 9.20. $C_{27}H_{26}P_2N_2FeF_6$ calcd.: C, 53.15; H, 4.29; P, 10.15; N, 4.58; Fe, 9.15%.

VIII, L = cyclohexene, yield: 58%. ^1H NMR (CD_3CN): 4.70 (m, 2H, complexed CH), 4.43 (s, 5H, Cp), 1.90 ppm (m, 14H, CH_α, CH_β, MeCN). IR: 2300 cm^{-1} (ν(CN)).

IX, L = dimethylthiophene, yield: 54%. ^1H NMR (CD_3CN): 6.53 (s, 2H, $SC_4H_2(Me_2)$), 5.10 (s, 5H, Cp), 2.56 ppm (b, 12H, $SC_4H_2(Me)_2$, *Me*CN). IR: 2250 cm^{-1} (ν(CN)).

2. *Synthesis of* $\{CpFe(NCMe)_2(CO)\}^+ PF_6^-$ *(IV)*

1 g (3 mmol) of $\{CpFe(CO)_3\}^+ PF_6^-$ is photolysed in 200 ml of MeCN without degassing of the cell, so that free CO is continuously present. After 3 h the initially yellow solution turns red. The solvent is evaporated under vacuum to 20 ml and 150 ml of diethyl ether is added to precipitate $\{CpFe(CO)(NCMe)_2\}^+ PF_6^-$ as a red powder (65% yield). ^1H NMR (CD_3COCD_3): 5.03 (s, 5H, Cp), 2.43 ppm (s, 6H, MeCN). IR: 2190 (ν(CN)), 1980 cm^{-1} (ν(CO)). Anal. Found: C, 31.47; H, 3.19; N, 7.64. $C_{10}H_{11}N_2OFePF_6$ calcd.: C, 31.94; H, 2.95; N, 7.45%.

3. *Synthesis of* $\{CpFe(NCMe)(PPh_3)(CO)\}^+ PF_6^-$ *(X)*

610 mg (1 mmol) of $\{CpFe^+(PPh_3)(NCMe)_2\}^+ PF_6^-$ (III) is stirred in 50 ml of MeCN at 40 °C for 2 h under 1 atm of CO. After concentration of the solvent in vacuo, addition of diethyl ether precipitates $\{CpFe(NCMe)(PPh_3)(CO)\}^+ PF_6^-$ as an orange powder (84%); this is shown to be pure by comparison of its ^1H NMR and infrared spectra with those of an authentic sample [13].

4. *Synthesis of* $\{CpFe(\eta^2\text{-dppe})(NCMe)\}^+ PF_6^-$ *(XI)*

1 g (3 mmol) of $\{CpFe(CO)_3\}^+ PF_6^-$ (I) is photolysed under a stream of nitrogen in 200 ml of MeCN with 1.2 g (3 mmol) of 1,2-bis(diphenylphosphino)ethane (dppe) [20]. After 2.5 h the solvent is evaporated under vacuum to 10 ml and addition of diethyl ether (100 ml) precipitates $\{CpFe(\eta^2\text{-dppe})(NCMe)\}^+ PF_6^-$ (XI) as a red powder (93%), this is shown to be pure by comparison of its NMR and infrared spectra with those of an authentic sample [8].

5. *Synthesis of* $\{CpFe^+(PMe_3)_2(NCMe)\}^+ PF_6^-$ *(V)*

716 mg (2 mmol) of $\{CpFe^+(\eta^6\text{-}C_6H_5CH_3)\}^+ PF_6^-$ (II) is photolysed in 200 ml of MeCN in presence of 1 to 3 equivalent of PMe_3. After 2 h the solvent is concentrated in vacuo to 10 ml and of diethyl ether (150 ml) is added to precipitate $\{CpFe^+(NCMe)(PMe_3)_2\}^+ PF_6^-$ (V) (with 3 eq. of PMe_3: yield 74%). ^1H NMR (CD_3CN): 4.21 (t, 5H, Cp, J(PH) ≃ 2 Hz), 1.95 (s, 3H, NCMe), 1.48 ppm (m, 18H, PMe_3). IR: 2380 cm^{-1} (ν(CN)).

6. *Synthesis of* $\{CpFe(1\text{-Phenyl-}3,4\text{-dimethylphosphole})_3\}^+ PF_6^-$ *(XII)*

1.1 g (3.3 mmol) of $\{CpFe^+(CO)_3\}^+ PF_6^-$ (II) and 600 mg (3.3 mmol) of

1-phenyl-3,4-dimethylphosphole are photolysed in 200 ml of MeCN under a stream of nitrogen. After 2.5 h the solvent is concentrated under vacuum to 10 ml and diethyl ether (200 ml) is added to precipitate $\{CpFe(Phosphole)_3\}^+$ PF_6^- (XII) as an orange powder (94% yield calculated vs. phosphole).

^1H NMR (CD_3COCD_3) (200 MHz): 7.33(m, 15H, Ph), 6.63(m, 6H, CH), 5.13 (q, 5H, Cp J(PH) 1.59 Hz), 1.75 ppm (s, 18H, Me). ^{13}C NMR (CD_3CN): 151.3 (dd, C), 132.9, 132.1, 131.4, 130.6 (Ph), 129.90 (dd, C_β), 79.1 (Cp), 17.1 ppm (dd, CH_3). Anal. Found: C, 59.25; H, 5.32; Fe, 7.00; P, 15.55. $C_{41}H_{14}P_4FeF_6$ calcd.: C, 59.29; H, 5.34; Fe, 6.72; P, 14.92%.

7. *Synthesis of* $\{CpFe(tripod)\}^+$ PF_6^- *(XIII)*

716 mg (2 mmol) of $\{CpFe(\eta^6\text{-}C_6H_5CH_3)\}^+$ PF_6^- (II) and 1.24 g (2 mmol) of $CH_3C(CH_2PPh_2)_3$ (tripod) [20] are photolysed in 200 ml of CH_3COCH_3 for 2 h. After concentration of the solution in vacuum to 10 ml, diethyl ether (150 ml) is added to precipitate $CpFe\{(tripod)\}^+$ PF_6^- (XIII) as an orange powder (85%) this is shown to be pure by comparison of its ^1H NMR parameters with literature data [17].

8. *Synthesis of* $\{CpFe(PMe_3)_3\}^+$ PF_6^- *(VII)*

716 mg (2 mmol) of $\{CpFe(\eta^6\text{-}C_6H_5CH_3)\}^+$ PF_6^- (II) is photolysed in 200 ml of CH_2Cl_2 with 456 mg (6 mmol) of PMe_3. After 2 h, evaporation of the solvent in vacuum to 10 ml and addition of diethyl ether precipitate crude $\{CpFe(PMe_3)_3\}^+$ PF_6^- (VII), this is recrystallized from acetonitrile ether to give pure $\{CpFe(PMe_3)_3\}^+$ PF_6^- (75% yield). ^1H NMR (CD_3CN): 4.30 (q, 5H, Cp, J(PH) 2 Hz), 1.45 ppm (m, 27H, PMe_3).

Acknowledgments

We thank BASF (Ludwigshafen, West Germany) for a generous gift of iron carbonyl, Dr. F. Mathey (CNRS-SNPE, Thiais) for a generous gift of 1-phenyl-3,4-dimethylphosphole, Dr. L. Szilagyi (University of Debrecan, Hungary) and S. Sindbankit (Centre for Physical Measurements, University of Rennes) for valuable NMR assistance.

References

1 M. Rosenblum, The Chemistry of the Iron Group Metallocenes, John Wiley, New-York, 1965.

2 K. Jonas, Advan. Organomet. Chem., 19 (1981) 97.

3 (a) A.N. Nesmeyanov, Intern. Union Pure Applied Chemistry, Butterworths, London, 1968, p. 221; (b) A.N. Nesmeyanov, Advan. Organomet. Chem., 10 (1972) 1; (c) D.W. Slocum, ibid., 10 (1962) 79; (d) W.E. Silverthorn, ibid., 12 (1975) 47; (e) R.G. Sutherland, J. Organomet. Chem. Library, 3 (1977) 311.

4 D. Astruc, Tetrahedron Report No. 157, Tetrahedron, (1983) 4027.

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

6 D. Catheline and D. Astruc, J. Organomet. Chem., 248 (1983) C9.

7 T.P. Gill and K.R. Mann, Inorg. Chem., 22 (1983) 1986.

8 P.M. Treichel, D.C. Molzahn, Synth. React. Inorg. Met. Org. Chem., 1979, 9, 21.

9 (a) T.P. Gill, and K.R. Mann, Inorg. Chem., 19 (1980) 3008; (b) T.P. Gill and K.R. Mann, J. Organomet. Chem., 216 (1981) 65; (c) R.T. Swann and V. Boekelheide, ibid., 231 (1982) 143; (d) E.D. Laganis, R.G. Finke and V. Boekelheide, Proc. Nat. Acad. Sci., USA, 78 (1981) 2657.

10 C.C. Lee, U.S. Gill, M. Iqbal, C.I. Azogu and R.G. Sutherland, J. Organomet. Chem., 231 (1982) 151.

11 J.-R. Hamon, D. Astruc and P. Michaud, J. Am. Chem. Soc., 103 (1981) 758.

12 A.N. Nesmeyanov, N.A. Vol'kenau and L.S. Shilovtseva, Dokl. Akad. Nauk. SSSR, 190 (1970) 857.

13 P.M. Treichel, R.L. Shubkin, K.W. Barnett and D. Reichard, Inorg. Chem., 5 (1966) 1177.

14 (a) R.B. King and K.H. Pannell, Inorg. Chem., 7 (1968) 1510; (b) R.B. King, L.H. Houk and K.H. Pannel, Inorg. Chem., 8 (1969) 1047; (c) R.B. King, R.N. Kapoor and K.H. Pannel, J. Organomet Chem., 20 (1969) 187.

15 M.L.H. Green and R.N. Whiteley, J. Chem. Soc. A, (1971) 1943

16 P.M. Treichel and D.A. Komar, J. Organomet. Chem., 206 (1981) 77.

17 S.G. Davies, S.J. Simpson, H. Felkin, F. Tadj and G. Watts, J. Chem. Soc. Dalton Trans., (1983) 981.

18 T.P. Gill and K.R. Mann, Organometallics 1 (1982) 485.

19 B.N. Stornhoff, Coord. Chem. Rev., 23 (1977) 1.

20 H. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.