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Preliminary communication

OXIDATIVE CLEAVAGE OF THE Fe—Fe BOND IN $[C_5Me_5Fe(CO)_2]_2$ USING FERROCINIUM ION: A FACILE ROUTE TO THE SYNTHETICALLY USEFUL COMPLEXES $[C_5Me_5Fe(CO)_2(\text{solvent})]^+$

DANIEL CATHELINE and DIDIER ASTRUC

Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex (France)

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Summary

Complexes of the type $\{Fp'(\text{solvent})\}^+ PF_6^-$, **3a—3d**, ($Fp' = (\eta^5\text{-}C_5Me_5)\text{-}Fe(CO)_2$, solvent = THF, CH_3COCH_3, CH_3CN, or pyridine) are conveniently prepared by the reaction between Fp'_2 and $Cp_2Fe^+ PF_6^-$ ($Cp = \eta^5\text{-}C_5H_5$) in the solvent under ambient conditions. The complexes $\{Fp'L\}^+ PF_6^-$, **3e—3g**, ($L = CO, PPh_3, P(OPh)_3$) are readily prepared from $\{Fp'THF\}^+$. Fp'H is formed by treatment of **3a** with $NaBH_4$. $Fp'SC(S)NMe_2$ can be prepared from **3a** or **3e** and $NaSC(S)NMe_2$.

The derivatives of $CpFe(CO)_2R$* are one of the most useful and widely studied groups of transition metal organometallic complexes [1]. Access to the piano-stool pentamethylcyclopentadienyliron [2] complexes (A) allows for the stabilization of unstable C_5H_5 analogues, including those formed by CO reduction [3], methylene complexes [4], 17-electron iron carbonyls [5], and complexes bearing labile ligands [6].

The methods of synthesis often differ from those for the parent C_5H_5 series, as exemplified by the routes to $Cp'(\eta^6\text{-arene})Fe^+$ [7], $Fp'CO^+$ [8], $Cp'Fe(CO)(\eta^2\text{-}S_2CNR_2)$ [9] and $Cp'Fe(NCMe)(\eta^2\text{-dppe})^+$ [6]; two modes of cleavage of the Fe—Fe bond in the readily available dimer Fp'_2 (**1**) [2], are particularly attractive: the first is reduction by monoelectronic reducing agents which should lead to Fp'^- (eq. 1).

$$Fp'_2 \xrightarrow{+e^-} [Fp'_2]^- \xrightarrow{+e^-} 2Fp'^- \tag{1}$$

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*$Cp = C_5H_5$; $Cp' = C_5Me_5$; $Fp = CpFe(CO)_2$; $Fp' = Cp'Fe(CO)_2$

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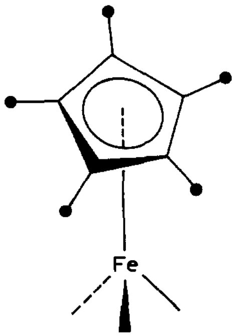


(A)

Reduction by Na/Hg, satisfactory in the parent C_5H_5 series, does not work, and reduction on a K mirror is necessary [7]. We report here preliminary results on the syntheses of complexes 3 using the other mode of cleavage, viz. oxidation by the one-electron oxidizing agent ferrocinium [10] (eq. 2).

$$\mathrm{Fp}'_2 \xrightarrow{-e^-} [\mathrm{Fp}'_2]^+ \xrightarrow[\mathrm{S}]{-e^-} \mathrm{Fp}'\mathrm{S}^+ \qquad (2)$$

(1)

(S = Solvent)

(3a, THF;
3b, acetone;
3c, acetonitrile;
3d, pyridine)

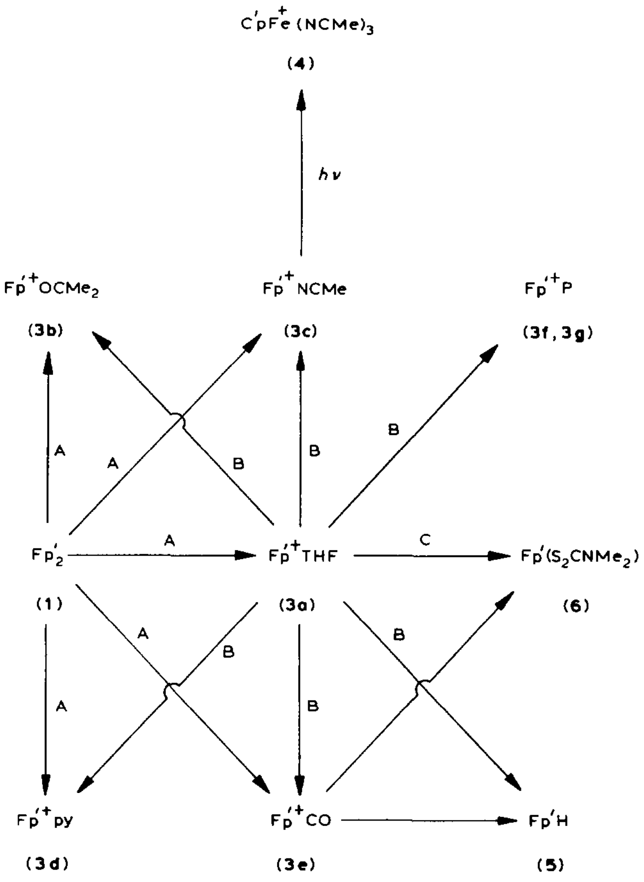
There are precedents for the oxidative cleavage of $\{C_5H_5Fe(CO)_2\}_2$, using $AgBF_4$ [11], $FeCl_3$ [12], O_2/HBF_4 [13], Ph_3C^+ [14], or electrochemical methods [15], to generate $\{CpFe(CO)_2L\}^+$ (2) [11—15] but ferrocinium salts have not been used. We find that the ferrocinium salt, $Cp_2Fe^+ PF_6^-$, is the cleanest and most convenient oxidizing agent for the syntheses of the useful stable complexes $\{Fp'(solvent)\}^+ PF_6^-$ (3), and the key role of these cationic intermediates is illustrated below. Irreversible two-electron oxidation of 1 (Pt anode, DMF, $NaBF_4$ 0.1 *M*) occurs at 0.5 V vs. SCE and indicates that ferrocinium ion is a good candidate for effecting this oxidation chemically $\{Cp_2Fe/Cp_2Fe^+, + 0.5$ V vs. SCE$\}$. Reaction of 1 with 2 mol of $Cp_2Fe^+ PF_6^-$ at ambient temperature overnight in a mixture of CH_2Cl_2 and a coordinating solvent (THF, acetone, acetonitrile, pyridine) gives a quantitative yield of crude [Fp'(solvent)] [PF_6] after evaporation of the solvents in vacuo, removal of ferrocene with ether, extraction with acetone and precipitation from ether. Recrystallization from acetone gives high yields of 3a—3d. The acetone, acetonitrile and pyridine adducts 3b—3d can also be prepared from the THF adduct 3a by addition of the free ligand to the CH_2Cl_2/THF solution used for the preparation of 3a. $[Fp'(NCMe)]^+ PF_6^-$ (3c), can be photolyzed (Hanovia lamp, 240 nm, 3 h) under ambient conditions to give the useful known complex $[Cp'Fe(NCMe)_3]^+ PF_6^-$ (4) in 80% yield [6]. Other $[Fp'L]^+$ complexes are prepared similarly from 3a under ambient conditions (Scheme 1, Table 1).

TABLE 1

PREPARATION OF COMPLEXES 3a—3g, 5 AND 6

	Product	Mode of synthesis [a]	Reaction conditions [b]	Yield [c] from Fp'_2
$Fp'L^+$; L = THF	3a	A	CH_2Cl_2/THF (2/1); 12 h	65
$Fp'L^+$; L = acetone	3b	A,B	A: Me_2CO (excess 10/1); 3 h	60
$Fp'L^+$; L = acetonitrile	3c	A,B	B: $NCCH_3$ (excess 10/1); 30 min	60
$Fp'L^+$; L = pyridine	3d	A,B	B: Pyridine (excess 10/1); 30 min	65
$Fp'L^+$; L = CO	3e	A,B	A: CH_2Cl_2/THF (2/1); 3 atm CO; 12 h	75
$Fp'L^+$; L = PPh_3	3f	C	CH_2Cl_2; PPh_3 (excess 3/1); 12 h	70
$Fp'L^+$; L = $P(OPh)_3$	3g	C	CH_2Cl_2, $P(OPh)_3$ (excess 3/1); 12 h	70
$Fp'R$; R = H	5	B	CH_2Cl_2; $NaBH_4$ (excess 5/1); 3 h	60
$Fp'R$; R = $SC(S)NMe_2$	6	C	CH_2Cl_2; $Na^+\ {}^-S_2CNMe_2$ (excess 5/1); 1 h	15

[a] A: direct oxidation of 1 with $Cp_2Fe^+PF_6^-$ in solvent/CH_2Cl_2 2/1; B: addition of ligand in situ to 3a; C: isolation of 3a prior to reaction. [b] Room temperature. [c] After recrystallization from acetone or ethanol (except 5,6 from n-pentane).



SCHEME 1

This route is the most convenient one for the synthesis of the complex $Fp'(CO)^+ PF_6^-$ (3e), [8] which is obtained quantitatively by replacement of THF in 3a by CO under 3 atm CO in CH_2Cl_2/THF. The phosphine and phosphite adducts 3f and 3g are best prepared from 3a in pure CH_2Cl_2. Olefins fail to react with 3a under various conditions, whereas they form $\{CpFe(CO)_2(olefin)\}^+$ from $\{CpFe(CO)_2THF\}^+$ (2a) [16]. Anionic ligands also displace THF from 3a. Reaction between 3a and $NaBH_4$ in CH_2Cl_2 gives a 60% yield of Fp'H (5) [3a], whereas NaS_2CNMe_2 gives only a 15% yield of $Fp'\eta^1$-SC(S)NMe_2 (6). However a 90% yield of 6 can be obtained from 3e and NaS_2CNMe_2 in Me_2CO. These routes are the only ones available for the new monodentate complex 6.

Complex 2a was previously prepared from $CpFe(CO)_2I$ and $AgBF_4$ in THF [16]. Reaction between Fp_2 and ferrocinium ion in THF overnight gives crude 2a in quantitative yield. The latter route is facile and avoids the use of a silver salt and the difficult separation of colloidal AgI from 2a. A THF solution of 2a reacts with CO (1 atm) at ambient temperature to give $[FpCO]^+$ PF_6^- [17] in 75% yield from Fp_2. Thus the new route is of general interest for the preparation of both the parent and permethylated families of complexes 2 and 3, and presumably could be used for many other bimetallic species.

The new complexes reported gave satisfactory analyses, and the ^1H and ^{13}C NMR and IR spectra were as expected.

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