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Haloalkyl complexes of the transition metals

VI *. A study of the reactions of halomethyldicarbonylcyclopentadienyliron complexes with some tertiary phosphine, amine and sulphur ligands

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Abstract

The reactions of [CpFe(CO)$_2$CH$_2$X] with a series of tertiary phosphines, amines, and SMe$_2$ have been investigated in both CH$_3$CN and THF ($Cp = \eta^5$-C_5H_5 and $X = Cl$, Br or I). Two types of cationic products, namely the ylide complexes [CpFe(CO)$_2$CH$_2$L]$^+$ or the disubstituted complexes [CpFe(CO)L$_2$]$^+$, were obtained, depending on the halide (X), the ligand (L) and the solvent used. The reactions of [CpFe(CO)$_2$CH$_2$L]Br with L in CH$_3$CN gave [CpFe(CO)L$_2$]Br for L = PMe$_3$ and PMe$_2$Ph, suggesting that [CpFe(CO)$_2$CH$_2$L]$^+$ is an intermediate in the formation of [CpFe(CO)L$_2$]$^+$ from [CpFe(CO)$_2$CH$_2$X] on reaction with L. The relative rates of reaction of [CpFe(CO)$_2$CH$_2$Br] with L were determined by ^{1}H NMR spectroscopy, and the rate found to increase with increasing pK_a and decreasing cone angle of L. PBu$^t_3$ was found not to react with [CpFe(CO)$_2$CH$_2$Cl] under any of the conditions used, although it readily reacts with [CpFe(CO)$_2$CH$_2$Br] to form the cationic ylide complex. In general, the rate of reaction of [CpFe(CO)$_2$CH$_2$X] with L increases in the sequence $Cl < Br < I$. The reaction of [CpFe(CO)$_2$CH$_2$Br] with bis(diphenylphosphino)ethane yields a bridged dicationic ylide complex [Cp(CO)$_2$FeCH$_2$P(Ph)$_2$(CH$_2$)$_2$P(Ph)$_2$CH$_2$Fe(CO)$_2$Cp]$^{2+}$.

Introduction

Complexes of the type [L$_n$MCH$_2$X] (L$_n$M = transition metal and its associated ligands, X = halogen) have been known for many years [1–3]. Also, well known is the susceptibility of the halomethyl carbon to nucleophilic attack [1]. Previous work

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in these laboratories has shown that the products of reactions of certain cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) halomethyl complexes with neutral nucleophiles depend on a number of factors, including the metal and its associated ligands, the nucleophile and the solvent used [4–6]. Hence, for example, $[CpFe(CO)_2CH_2Cl]$ reacts with PPh_3 in methanol to give $[CpFe(CO)_2CH_2PPh_3]Cl$, whereas $[CpRu(CO)_2CH_2Cl]$ does not react with PPh_3 under identical conditions. Similarly, $[CpW(CO)_3CH_2Cl]$ will react with PPh_3 in acetonitrile to give $[CpW(CO)_3CH_2PPh_3]Cl$, whereas $[CpMo(CO)_3CH_2Cl]$ under identical conditions, gives $[CpMo(CO)_2(PPh_3)Cl]$ [4]. We have previously reported that the reaction of $[CpFe(CO)_2CH_2Cl]$ (**1a**) with tertiary phosphines can give two types of product, namely $[CpFe(CO)_2CH_2L]^+$ (**2**) (where L is a tertiary phosphine) or $[CpFe(CO)L_2]^+$ (**3**) depending on the solvent used and the size and pK_a of the ligand involved in the reaction [4,5]. Thus the reaction of **1a** with PPh_3 gave **2g** in both acetonitrile and methanol, whereas the corresponding reactions of **1a** with PMe_2Ph yielded **2b** in methanol and **3b** in acetonitrile. In the light of the above, we decided to carry out a more detailed study of these reactions using a wider range of ligands L, and determine the effect of changing the halogen in $[CpFe(CO)_2CH_2X]$ on the reactivity of the system and also the effect the solvent has on the type of product formed. We hoped to obtain further information on the mechanism of these reactions.

Results and discussion

Both $[CpFe(CO)_2CH_2Cl]$ (**1a**) and $[CpFe(CO)_2CH_2Br]$ (**1b**) are well-known and were made by published literature methods [1]. The complex $[CpFe(CO)_2CH_2I]$ (**1c**) has been reported in the literature [2], but it was not fully characterized, being said to be too unstable to permit this. We succeeded in synthesizing the compound by two routes. The first route is similar to that used by Green et al. [1], i.e. reaction of $[CpFe(CO)_2CH_2OCH_3]$ with dry HI gas followed by purification of the product by chromatography (eqns. 1 and 2)

$$\mathrm{Na[CpFe(CO)_2] + ClCH_2OCH_3 \xrightarrow{THF} [CpFe(CO)_2CH_2OCH_3] + NaCl} \qquad (1)$$

$$\mathrm{[CpFe(CO)_2CH_2OCH_3] + HI \xrightarrow{hexane} [CpFe(CO)_2CH_2I] + [CpFe(CO)_2I] + CH_3OH} \qquad (2)$$

The second, and more convenient, method involves treating $[CpFe(CO)_2CH_2Br]$ with NaI, a route commonly used for converting alkyl bromides into alkyl iodides [7].

$$\mathrm{[CpFe(CO)_2CH_2Br] \xrightarrow[acetone,\ RT]{excess\ NaI} [CpFe(CO)_2CH_2I] + NaBr} \qquad (3)$$

We have isolated $[CpFe(CO)_2CH_2I]$ as lustrous yellow crystals, melting at 28 ° C, and fully characterised it by IR, ^1H and ^{13}C NMR, micro-analysis, and mass spectrometry (see Experimental section and Table 1). Pure **1c** was found to be stable to air and light for short periods of time. A sample was kept at -15 ° C for two years with only very minor degradation. Compound **1c**, like **1a** and **1b**, loses a methylene group to form $[CpFe(CO)_2X]$ on decomposition at room temperature in both solution or as the solid.

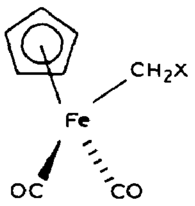
Table 1

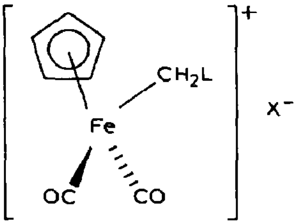
Melting points and spectral data for $[CpFe(CO)_2CH_2X]$

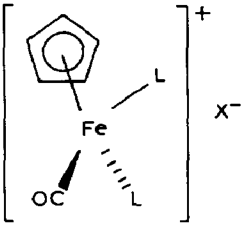
Compound	X	m.p. (°C)	ν(CO) [a] (cm^{-1})	^{13}C NMR [b,c] (δ)	^{1}H NMR [b] (δ)	Most abundant molecular ion
1a	Cl	65–68	2026 1974	214.40(CO) 86.24(Cp) 33.70(CH_2)	4.90s(5H) 4.24s(2H)	226 [d]
1b	Br	54–58	2027 1975	214.43(CO) 86.81(Cp) 25.67(CH_2)	4.89s(5H) 3.94s(2H)	270/272 [d]
1c	I	28	2027 1977	214.99(CO) 87.75(Cp) −6.51(CH_2)	4.86s(5H) 3.02s(2H)	318 [d]

[a] In hexane solution, all bands strong. [b] In $CDCl_3$ relative to TMS. [c] In presence of $Cr(acac)_3$, 0.08 *M* [22]. [d] The isotope patterns were in close agreement with a computer simulated isotope pattern of this formula.

The ^{1}H NMR signal for the CH_2X group shows the large expected shift due to the varying electron-withdrawing effect of the halogens, whilst the Cp resonance shows only a very minor upfield shift as X varies from Cl to I (see Table 1). The ^{13}C NMR shifts for the carbon atom of the CH_2X group are as follows: X = Cl, $\delta = 33.7$; X = Br, $\delta = 25.7$; X = I, $\delta = -6.5$ ppm. The change in the shifts on going from X = Cl to X = Br of 8 ppm, and on going from X = Br and X = I of 19 ppm, reflect the electronegativity different between the halogens. Also of interest is that







1	X
1a	Cl
1b	Br
1c	I

2	L
2a	PMe_3
2b	PMe_2Ph
2c	$PMePh_2$
2d	PEt_2Ph
2e	$PEtPh_2$
2f	PBu^t_3
2g	PPh_3
2h	NMe_3
2i	Py
2j	SMe_2
2k	$AsPh_3$

3	L
3a	PMe_3
3b	PMe_2Ph
3c	$PMePh_2$

Table 2

Products of the reaction of **1b** with L in THF

Compound	React. time (d)	Yield (%)	m.p. (°C)	ν(CO) (cm^{-1}) [a]	^{1}H NMR (δ ppm) [b]	Elemental analysis [c]	
[CpFe(CO)$_2$CH$_2$PMe$_3$]Br (**2a**)	4	83	185(dec)	2021s 1964s	1.27[d, 2H, ^1J(PH) 13.0 Hz] 2.03[d, 9H, ^2J(PH) 13.0 Hz] 5.70[s, 5H]	C H	38.05(37.93) 4.60(4.60)
[CpFe(CO)$_2$CH$_2$PMe$_2$Ph]Br (**2b**)	10	82	165(dec)	2023s 1968s	[d] 1.32[d, 2H, ^2J(PH) 13.0 Hz] 2.11[d, 6H, ^2J(PH) 13.0 Hz] 5.11[s, 5H]; 7.43–8.13[m, 5H]	C H	47.05(46.94) 4.40(4.50)
[CpFe(CO)$_2$CH$_2$PBu$^t_3$]BPh$_4$ (**2f**)	30	17	168–182(dec)	2027s 1976s	1.40[d, 2H, ^2J(PH) 13.0 Hz] 1.38[d, 27H, ^2J(PH) 12.6 Hz] 4.55[s, 5H], 7.0–7.42[m, 20H]	C H	74.10(74.14) 7.75(7.58)
[{CpFe(CO)$_2$CH$_2$}$_2$diphos]Br$_2$ (**4**)	11	33	200–210(dec)	2027s 1973s	1.83[tp, 4H, ^2J(PH)+^2J(PH) 13.0 Hz] 2.90[d, 4H, ^2J(PH) 5.0 Hz] 5.10[s, 10H]; 7.57–8.40[m, 20H]	C H	53.30(53.50) 4.03(4.20)
[CpFe(CO)$_2$CH$_2$NMe$_3$]Br (**2h**)	5	76	193–200(dec)	2023 1964	[e] 3.10[s, 9H]; 4.03[s, 2H] 5.30[s, 5H]	C H N	39.95(39.88) 4.90(4.83) 4.20(4.23)
[CpFe(CO)$_2$CH$_2$C$_5$H$_5$N]Br (**2i**)	10	14	162–174(dec)	2022s 1967s	2.33[s, 2H]; 5.30[s, 5H] 5.43[s, 2H]; 7.77–8.73[m, 3H]; 9.50[d, 2H, ^2J(α-H) 6.0 Hz]	[f] C H N	42.60(44.44) 2.85(3.42) 3.85(4.00)
[CpFe(CO)$_2$CH$_2$SMe$_2$]Br (**2j**)	9	35	147–148	2030s 1975s	2.87[s, 2H]; 3.15[s, 6H]; 5.30[s, 5H]	C H	35.80(36.04) 3.95(3.90)

[a] Measured in CH$_2$Cl$_2$. [b] In CDCl$_3$ unless otherwise stated; s = singlet, d = doublet, tp = pseudo triplet, m = multiplet. [c] Calculated values in parenthesis. [d] CD$_3$CN. [e] CD$_3$OD. [f] The monohydrate requires C, 42.28; H, 3.79; N, 3.79.

the ^{13}C resonances of the Cp rings shift marginally downfield as X varies from Cl to Br to I (see Table 1), a trend opposite to that observed for the [CpFe(CO)$_2$X] complexes, whilst the CO resonances of both complex types move downfield as X varies from Cl to I [8]. The observed effect of varying X on the Cp resonances of [CpFe(CO)$_2$CH$_2$X] is likely to be due to electronic effects, probably relating to the varying electronegativities and π-donor abilities of the halides. Possibly a canonical form of type $^{\delta+}\mathrm{Fe}\overset{\cdots}{-}\mathrm{CH_2}\cdots\mathrm{X}^{\delta-}$ exists in solution. This would result in withdrawal of electrons from the cyclopentadienyl group, reducing the ring current and hence causing an upfield shift of the Cp resonance. This effect would be greater for X = Cl, as observed.

The reactions of **1a**, **1b** and **1c** with L in THF and acetonitrile are summarised in eqs. 4 and 5. Characterisation data for compounds **2a**, **b**, **f**, **h**–**j** and **4** are in Table 2.

$$\underset{\textbf{(1)}}{[\mathrm{CpFe(CO)_2CH_2X}]} + \mathrm{L} \rightarrow \underset{\textbf{(2)}}{[\mathrm{CpFe(CO)_2CH_2L}]^+\mathrm{X}^-} \qquad (4)$$

Reaction 4 in acetonitrile was successfully used in the following cases:

X = Cl; L = PEtPh (**2d**), PEtPh$_2$ (**2e**), PPh$_3$ (**2g**), AsPh$_3$ (**2k**)
X = Br; L = PMe$_2$Ph (**2b**), PMePh$_2$ (**2c**), PBu$^t_3$ (**2f**), PPh$_3$ (**2g**), NMe$_3$ (**2h**), pyridine (**2i**) and SMe$_2$ (**2j**)
X = I; L = PPh$_3$ (**2g**)

Reaction 4 in THF was successfully used for the following cases

X = Cl; L = PMe$_2$Ph (**2b**)
X = Br; L = PMe$_3$ (**2a**), PMe$_2$Ph (**2b**), PMePh$_2$ (**2c**), PBu$^t_3$ (**2f**), NMe$_3$ (**2h**), pyridine (**2i**) and SMe$_2$ (**2j**)

$$\underset{\textbf{(1)}}{[\mathrm{CpFe(CO)_2CH_2X}]} + 2\mathrm{L} \rightarrow \underset{\textbf{(3)}}{[\mathrm{CpFe(CO)(L)_2}]^+\mathrm{X}^-} + \ldots \qquad (5)$$

Reaction 5 was carried out for X = Cl; L = PMe$_3$ (**3a**), PMe$_2$Ph (**3b**), PMePh$_2$ (**3c**) in acetonitrile and for L = PMe$_3$ (**3a**) in THF.

The products of reaction 4 are analogous to those obtained on the quaternisation of tertiary phosphines, amines, and sulphides with an alkyl halide by an S_N2 mechanism [9]. In contrast to the reactions of tertiary phosphines with **1b**, the reaction of tertiary amines with **1b** is not a general process, and only NMe$_3$ and pyridine gave isolable products. In the case of the reaction of NEt$_3$ with **1b** in THF, only the amine salt [Et$_3$NH]Br could be isolated. From reaction in methanol, however, [CpFe(CO)$_2$CH$_2$OCH$_3$] was also isolated, and identified from its spectral data. A similar reaction was observed previously upon heating **1a** in methanol, to give [CpFe(CO)$_2$CH$_2$OCH$_3$] [4]. The isolation of the amine salt indicates that MeOH is a better nucleophile than NEt$_3$. The isolation of the amine salt from the THF reaction is difficult to rationalise unless the carbene [CpFe(CO)$_2$(CH$_2$)]$^+$ is generated in situ.

The nature of the phosphine clearly influences the type of product formed. Hence the reaction of **1b** with PMe$_3$, a ligand with a high pK_a and small cone angle, gave a product of type **3** in CH$_3$CN. In contrast, the reaction of (**1b**) with PPh$_3$, a ligand with a low pK_a and large cone angle, gave a product of type **2** in the same solvent.

The formation of **2g** from the reaction of **1b** with PBu^t_3, a ligand with a high pK_a and large cone angle, therefore implies that the steric size of the phosphine rather than its pK_a determines the product type formed.

The reactivity of complex **1a** contrasts with that of **1b**. Thus PBu^t_3 does not react with **1a** in either THF, CH_3CN or methanol at either room temperature or reflux. But like **1b**, **1a** reacts with PMe_2Ph in THF to yield the ylide type product $[CpFe(CO)_2CH_2PMe_2Ph]Cl$ (**2b**), which was isolated as the BPh_4^- salt. Unlike **1b** though, **1a** reacts with PMe_3, which has a larger pK_a and smaller cone angle than PMe_2Ph, to form the disubstituted cationic product $[CpFe(CO)(PMe_3)_2]Cl$ (**3a**). These results indicate that the halogen has a considerable effect on the reactivity of the complex $[CpFe(CO)_2CH_2X]$.

The effect that the solvent has on the course of the reaction is demonstrated by the fact that neither **1a** nor **1b** react with PPh_3 in THF, though **1a–1c** all readily react with PPh_3 in CH_3CN or CH_3OH to form the ylide type product **2g**. The solvent effect is further demonstrated by the fact that $[CpFe(CO)_2CH_2Cl]$ (**1a**) reacts with PMe_2Ph in CH_3CN to form a product of type **3**, whereas in THF these reactants yield a product of type **2**. A third example is the reaction of **1b** with PBu^t_3; the reaction in THF yielded a product of type **2** in 17% yield after 30 d at room temperature, whereas the reaction in CH_3CN yielded **2f** in 65% yield after 11 d at room temperature.

The reactions of **1b** with PMe_2Ph, $PMePh_2$, PPh_3, pyridine, NMe_3 and SMe_2 in a 1/2 molar ratio in CH_2CN were monitored by ^1H NMR spectroscopy, the relative intensities of the Cp peaks of starting material and product at room temperature being determined. The rate of the reactions followed the sequence $PMe_2Ph > PMePh_2 > PPh_3 > SMe_2 >$ pyridine, with $t_{1/2}$ values estimated as < 4 min, 4 min, 23 min, 30 min, and 35 min respectively (± 1 min) (where $t_{1/2}$ is the time taken for half-completion of the reaction). For the phosphines, the cone angles increase and the pK_a's decrease in the following order $PMe_2Ph < PMePh_2 < PPh_3$ [10–15]. (The cone angles are 122, 136 and 145°, and the pK_a values are 6.49, 4.59 and 2.73 respectively.) Hence the ligands with smaller cone angles and larger pK_a values react more quickly, probably because of their greater nucleophilicity and lower steric hindrance.

Similarly, monitoring the intensities in the ^1H NMR spectra of the Cp peaks of starting material and product at room temperature showed that the rate of the reaction of **1a–1c** with PPh_3 under identical conditions follows the order (Cl < Br < I),with a reactivity ratio for Cl/Br of 1/640, the rate for X = I being too high to be determined at room temperature by the techniques used. The reaction of CH_3X with neutral nucleophiles shows a similar trend in rate, i.e. Cl < Br < I (1/ca. 40/ca. 80) [9]. Thus the metal has a significant effect on the rate of reaction of the halomethyl complex relative to that of the corresponding methyl halide.

The reaction of **2b** with an excess of PMe_2Ph in CH_3CN gave, after work up involving treatment with $NaBPh_4$, $[CpFe(CO)(PMe_2Ph)_2]BPh_4$ in 55% yield along with $[PMe_3Ph]Br$ in 30% yield.

$$[CpFe(CO)_2CH_2PMe_2Ph]Br + \text{xs. } PMe_2Ph \rightarrow [CpFe(CO)(PMe_2Ph)_2]^+ + [PMe_3Ph]Br \quad (6)$$

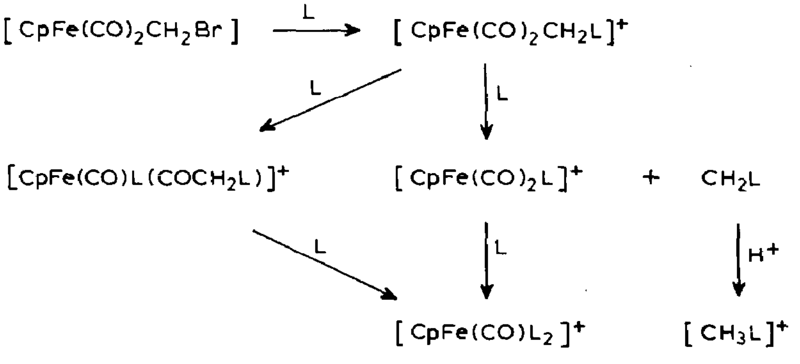
$$[CpFe(CO)(PMe_2Ph)_2]Br + NaBPh_4 \rightarrow [CpFe(CO)(PMe_2Ph)_2]BPh_4 + NaBr \quad (7)$$

Similarly **2a** reacted with excess PMe_3 to give, on work-up with $NaBPh_4$, $[CpFe(CO)(PMe_3)_2]BPh_4$ in 35% yield; ^1H NMR evidence indicated that $[PMe_4]BPh_4$ is also formed in this reaction.

These results imply that in the reactions of $[CpFe(CO)_2CH_2X]$ with an excess of a tertiary phosphine with a sufficiently small cone angle and large pK_a, $[CpFe(CO)_2CH_2L]^+X^-$ is an intermediate, and that further reaction displaces CO and "CH_2–L" to give $[CpFe(CO)L_2]X$. Since $[CpFe(CO)_2CH_2NMe_3]Br$ does not react with PMe_3, it appears that the nature of the CH_2–L bond is a determining factor in whether or not $CH_2{=}L$ is eliminated. Other workers have shown that $[CpFe(CO)_2(PMe_3)]I$ readily reacts with PMe_3 under reflux in CH_3CN to give $[CpFe(CO)(PMe_3)_2]I$ [16]. Similarly, we have shown that $[CpFe(CO)_2(PMe_2Ph)]I$ reacts with PMe_2Ph to give $[CpFe(CO)(PMe_2Ph)_2]I$. Of two proposed mechanisms for the reaction described in eq. 6 [4], the formation of $[PMe_3Ph]Br$ and $[PMe_4]Br$ is consistent with the elimination of the ylide $CH_2{=}PR_3$ and its subsequent protonation to give $[PR_3CH_3]^+$. Monitoring the reaction of **1b** with PMe_2Ph by IR and ^1H NMR spectroscopy showed that at least three intermediate species could be seen during formation of **3b**. Two of these intermediates were identified as $[CpFe(CO)_2CH_2PMe_2Ph]Br$ (**2b**) and $[CpFe(CO)_2(PMe_2Ph)]Br$. A third intermediate, with $\nu(CO)$ at 1996 and 1771 cm^{-1} and a Cp peak in the ^1H NMR at $\delta = 4.96$, could be $[CpFe(CO)(PMe_2Ph)(COCH_2PMe_2Ph)]^+$ formed by alkyl migration in **2b** and subsequent reaction with PMe_2Ph. Alkyl migration has been observed for transition metal ylide complexes [19]. $[PMe_3Ph]Br$ was also obtained from the above reaction in 38% yield.

The spectroscopic evidence suggests that the ylide species **2** form rapidly on reaction of **1** with L, and that this is followed by a slower reaction to give **3**; the rate of this latter reaction depends greatly on the phosphine concentration. A suggested scheme for these reactions is shown in Scheme 1. The reaction of **1b** with diphos gave the di-cation $[\{CpFe(CO)_2CH_2\}_2(PPh_2CH_2)_2]^{2+}$ (**4**) as the only product; no evidence for $[CpFe(CO)(CH_2diphos)]^+$ was obtained.

Products analogous to **2h** and **2j**, namely $[CpFe(CO)_2CH_2NMe_3]I$ (**5**) and $[CpFe(CO)_2CH_2SMe_2]BH_4$ (**6**) have been prepared previously [17,18], though by different routes. The sulphonium salt **6** has been shown to have organic synthetic utility as a cyclopropanation reagent [18]. We hoped that the phosphonium salts **2a** and **2g** would display synthetic potential in Wittig type reactions. However, the



Scheme 1

ylides $[CpFe(CO)_2CH{=}PR_3]$ could not be readily synthesised by simple deprotonation of the parent quarternary salts (**2a** and **2g**) by use of NaOMe/MeOH in the presence of benzophenone or butyllithium in THF as base. Phosphonium ylide complexes $[LM{-}CH{=}PR_3]$ e.g. $[(CO)_5ReCH{=}PPh_3]$ are known with other metal systems [19], but these were not synthesized by direct deprotonation of the parent complex.

Experimental

All reactions were carried out under nitrogen by use of standard Schlenk-tube techniques. Tetrahydrofuran (THF) and hexane were distilled from $LiAlH_4$ or sodium, methanol was distilled from $CaCl_2$, and acetonitrile was distilled from P_2O_5. Tertiary phosphines (Strem Chemicals Inc. excluding PPh_3which was obtained from Merck), tertiary amines and dimethylsulphide (Merck) were used without further purification. PMe_3 was synthesized by the method described by Mann and Wells [20]. $[CpFe(CO)_2CH_2Cl]$ and $[CpFe(CO)_2CH_2Br]$ were prepared by a published method [1] as was dry HI gas [21]. All other reagents were obtained commercially. Melting points were recorded on a Kofler Hot stage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin–Elmer 983 spectrophotometer. ^1H NMR spectra were recorded on a Varian XL100, Varian EM360, Bruker WH90 or a Varian XR200 spectrometer. ^{13}C NMR were recorded on a Varian XR200 spectrometer. Mass spectra were obtained with a VG Micromass 16F spectrometer, operated at 70 eV ionising voltage. The source temperature was initially 50–60 °C, and was raised to ca. 150 °C during the runs. The *m/e* values quoted refer to those peaks in a peak cluster which correspond to the ions containing the metal isotope of the highest natural abundance. Calculated mass spectra were obtained by use of a computer program. Where the isotope pattern for any particular parent ion is in close agreement with a particular combination of isotopes, this is noted.

Preparation of $[CpFe(CO)_2CH_2I]$

Method (i). A solution of $Na[CpFe(CO)_2]$ (14.18 mmol) in THF (20 ml) was added to a stirred solution of $ClCH_2OCH_3$ (1.25 ml, 15.50 mmol) in THF (4 ml) at −78 °C. The solution was allowed to warm to room temperature. After 2.5 h the solvent was removed under reduced pressure and the product, $[CpFe(CO)_2(CH_2OCH_3)]$, extracted with hexane. The extract was filtered, and dry HI gas was vigorously bubbled through it for 70 min, after which, infrared monitoring of the carbonyl bands of both starting material and products showed the reaction to be complete. The solvent was removed under reduced pressure, the product dissolved in a minimum of hexane, and the solution transferred to a silica gel column. Upon elution with 20/1 hexane/ether, a yellow band was collected and the solution evaporated in vacuo. The dark yellow solid was then recrystallised from hexane at −78 °C, yielding 1.32 g (59%) of $[CpFe(CO)_2CH_2I]$ as a yellow crystalline solid. Found: C, 30.40; H, 2.30 $C_8H_7FeIO_2$ calc.: C, 30.20; H, 2.20%.

Method (ii). Dry NaI (0.154 g, 1.027 mmol) was added to a solution of $[CpFe(CO)_2CH_2Br]$ (0.196 g, 0.72 mmol) in acetone (5 ml). The solution was stirred for 60 min and the solvent was then removed under reduced pressure and the product extracted with hexane. The extract was filtered, concentrated, and transferred to a silica gel column. On eluting with 20/1 hexane/ether a yellow band was collected, and the solution was concentrated under reduced pressure, filtered, and cooled at −78 °C to give a yellow crystalline precipitate of **1c** (0.138 g, 60%).

*Reactions of [CpFe(CO)$_2$CH$_2$Br] (**1b**) with PMe$_3$, PMe$_2$Ph, PBu$^t_3$, PPh$_2$CH$_2$CH$_2$PPh$_2$, NMe$_3$, C$_5$H$_5$N, and SMe$_2$ in tetrahydrofuran. Synthesis of compounds **2a**, **2b**, **2f**, **2h**, **2i**, **2j**, **4***

General procedure. Compound **1b** (1 mmol) was dissolved in THF (20 ml) and the ligand (1 mmol) was added. An excess of the ligand was added in the cases of NMe_3 and SMe_2. The mixture was kept at room temperature in the dark for several days. For reaction times, see Table 2. The crystalline products were collected by vacuum filtration, washed with tetrahydrofuran or diethyl ether (2 × 10 ml), and recrystallised from dichloromethane/diethylether or methanol/diethyl ether to give the products **2a**, **2b**, **2f**, **2h**, **2i**, **2j**, **4**, $X = Br^-$ as yellow, air-stable crystalline solids. (**2f** isolated as BPh_4^- salt). For yields and characterisation data for the products see Table 2.

*Reaction of **1b** with PPh$_2$CH$_2$CH$_2$PPh$_2$ in acetonitrile*

A mixture of **1b** (0.38 g, 1.4 mmol) and the diphos (0.56 g, 1.4 mmol) in acetonitrile (20 ml) was stirred and heated under reflux for 1.5 h. The product **4** came out of solution after 10 min. The mixture was cooled (−15 °C) and the product **4** then collected by vacuum filtration, washed with diethyl ether (2 × 10 ml), and dried in vacuo. Yield 0.07 g (7.5%). The solid was shown by its spectral data to be identical in all respects to the product **4** obtained from the reaction of **1b** with diphos in tetrahydrofuran. The acetonitrile mother filtrate was evaporated in vacuo and the residue washed with diethyl ether (3 × 50 ml) to remove unchanged diphos. Drying in vacuo then gave an orange solid. IR (CH_2Cl_2) ν(CO) 2021s, 1967s cm^{-1}. The ^{1}H NMR (CD_3OD) suggested that it was an impure sample of **4**. The product resisted attempts at further purification.

*Reaction of **1b** with pyridine in acetonitrile*

A mixture of **1b** (0.33 g, 1.22 mmol) and dry pyridine (distilled from KOH) (0.15 ml, 0.1 g, 1.2 mmol) in acetonitrile (10 ml) was stirred and heated under reflux for 1.25 h. Evaporation in vacuo gave a yellow solid, which was recrystallised from MeOH/Et_2O to give 0.30 g (67%) of orange/yellow polyhedra, m.p. 168–174 °C/dec. IR and NMR spectra were identical to those of product **2i** obtained by use the tetrahydrofuran as solvent. The product appeared to be the monohydrate.

*Reaction of **1b** with PBu$^t_3$ in CH$_3$CN*

[CpFe(CO)$_2$CH$_2$Br] (0.62 g, 2.28 mmol) was dissolved in CH_3CN (12 ml) and PBu$^t_3$ (0.46 g, 2.28 mmol) added. The solution was kept at room temperature for 11 d, and the solvent then removed in vacuo to leave a red-brown oily solid. This was taken up in methanol and a solution of $NaBPh_4$ (0.78 g, 2.28 mmol) in methanol was added. The precipitate was filtered off, and recrystallised from CH_2Cl_2/ether, to give the yellow air stable solid [CpFe(CO)$_2$CH$_2$PBu$^t_3$]BPh$_4$, in 68% yield.

Reaction of 1b with PPh_3, PMe_2Ph, $PMePh_2$, pyridine and SMe_2 in CH_3CN

Complex **1b** (0.035 g, 0.131 mmol) was dissolved along with the ligand (0.262 mmol) in CH_3CN (1.5 ml) in an NMR tube, which was sealed under N_2. The reactions were followed by ^1H NMR (observing the Cp peaks) and the products **2b**, **2c**, **2g**, **2i** and **2j** isolated as their BPh_4^- salts as described before.

Reaction of 1b with triethylamine

Use of the general procedure with tetrahydrofuran as solvent gave a 40% yield of a colourless solid, which was identified by its ^1H NMR spectrum as $[Et_3NH]Br$. No organometallic product was isolated. When the reaction was carried out in refluxing acetonitrile there was extensive decomposition. The IR spectrum of the reaction mixture showed bands attributable to $[CpFe(CO)_2]_2$. With methanol as solvent $[Et_3NH]Br$ was isolated in 62% yield, and the formation $[CpFe(CO)_2(CH_2OMe)]$ inferred from ^1H NMR and IR data.

Reaction of $[CpFe(CO)_2(CH_2PMe_2Ph)]Br$ (2b) with excess PMe_2Ph

A mixture of **2b** (0.20 g, 0.50 mmol) and dimethylphenylphosphine (0.2 ml, 0.19 g, 1.5 mmol) in acetonitrile (10 ml) was kept at room temperature in the dark for 2 d. Colourless cuboid crystals were present in the reaction mixing along with some decomposition product. The decomposition product was discarded and the colourless solid dried in vacuo. Yield 0.02 g (30%), ^1H NMR (CD_3OD): $\delta = 2.62$ [d, 9H, ^2J(PH) 14.6 Hz], $\delta = 7.86$–8.66 (m, 5H); ^{13}C NMR (CD_3OD): $\delta = 9.78$ [d, ^1J(PC) 56.5 Hz]; 123.35 [d, ^1J(PC) 87.6 Hz]; 130.98 [d, ^2J(PC) 12.5 Hz]; 132.16 [d, ^3J(PC) 10.4 Hz]; 135.38 [d, ^4J(PC) 2.8 Hz]. These data support the structure $[(CH_3)_3PPh]Br$. The clear filtrate was evaporated in vacuo giving a brown oil, which was washed with diethyl ether (3 × 20 ml) and dried in vacuo. To a solution of sodium tetraphenylborate (0.342 g, 1 mmol) in methanol (1 ml) was added a solution of the oil in the same solvent (2 ml). The precipitate formed was collected by vacuum filtration, washed with methanol (2 × 10 ml), and dried. It was recrystallised from CH_2Cl_2/Et_2O to give $[CpFe(CO)(PMe_2Ph)_2]BPh_4$, 0.20 g (55%). The spectral data were fully consistent with those in the literature [5]. The methanolic filtrate and washings were evaporated in vacuo, and dried to give a colourless solid, 0.06 g; the ^1H NMR ($CDCl_3$/DMSO-d_6) spectrum indicated that it was impure $[(CH_3)_3PPh]BPh_4$.

Reaction of $[CpFe(CO)_2(CH_2PMe_3)]Br$ (2a) with excess PMe_3

A mixture of **2a** (0.174 g, 0.5 mmol) and trimethylphosphine (3.12 mmol) in acetonitrile (10 ml) was left at room temperature in the dark for 2 d. It was then filtered to remove products of decomposition and the clear filtrate was evaporated in vacuo. The resulting orange oil was dissolved in methanol (5 ml) and the solution added to one of sodium tetraphenylborate (0.17 g, 0.50 mmol) in the same solvent (2 ml). The precipitate that formed was washed with methanol (2 × 2 ml) and recrystallised from CH_2Cl_2/Et_2O to give a yellow solid. Yield 0.10 g (35%). ^1H NMR and IR data were fully consistent with its being $[CpFe(CO)(PMe_3)_2]BPh_4$ [5]. The methanolic filtrate and washings were concentrated in vacuo and diluted with diethyl ether to give a colourless solid 0.120 g. The ^1H NMR spectrum suggested that this product was $[(CH_3)_4P]BPh_4$, but the data were not definitive.

Reaction of [CpFe(CO)$_2$CH$_2$NMe$_3$]Br (2h) with excess PMe$_3$

The compound **2h** (0.165 g, 0.50 mmol) was dissolved in acetonitrile (20 ml) and PMe$_3$ (6.2 mmol) added. The mixture was heated under reflux for 6 h. Work up gave a 73% recovery of starting material along with products of decomposition.

Attempted reaction of NMe$_3$ with (2a)

A mixture of **2a** and excess NMe$_3$ in acetonitrile were allowed to stand at room temperature in the dark for 7 d. Work-up gave a 60% recovery of starting material, the remainder being products of decomposition.

Reaction of 1a with PMe$_3$ in THF

[CpFe(CO)$_2$CH$_2$Cl] (0.297 g, 1.311 mmol) was dissolved in THF (10 ml) and PMe$_3$ (1.311 mmol) was added. The solution was kept at room temperature in the dark for 6 d, after which a large quantity of yellow crystals had separated. These were filtered off to give (0.29 g, 39%) [CpFe(CO)(PMe$_3$)$_2$]Cl. IR (CH$_2$Cl$_2$) ν(CO): 1962 cm^{-1} ^{1}H NMR (CDCl$_3$): $\delta = 5.04$ t (5H, ^3J 4.1 Hz), $\delta = 1.67$ d (18H, ^2J 10.4 Hz). The product was very hygroscopic, becoming a yellow oil in air. The elemental analysis (C, 40.45; H, 6.65%) suggested that the product was in the monohydrate form once exposed to air (C$_{12}$H$_{25}$ClFeO$_3$P$_2$ requires C, 40.63; H, 7.05%). Treatment of the product with NaBPh$_4$ in methanol yielded [CpFe(CO)(PMe$_3$)$_2$]BPh$_4$ [5].

Reaction of 1a with PMe$_2$Ph in THF

Complex **1a** (0.24 g, 1.06 mmol) was dissolved in THF (10 ml), PMe$_2$Ph (0.15 ml, 1.06 mmol) was added, and the solution was kept in the dark for 10 d at room temperature. The solvent was removed under reduced pressure and the product extracted with MeOH. To the extract was added a solution of NaBPh$_4$ (0.36 g, 1.06 mmol) in methanol. The yellow precipitate of [CpFe(CO)$_2$CH$_2$PMe$_2$Ph]BPh$_4$ was filtered off (0.49 g, 72%).

The reaction of 1c with PPh$_3$ in CH$_3$CN

Complex **1c** (0.042 g, 0.131 mmol) was dissolved along with PPh$_3$ (0.069 g, 0.262 mmol) in CH$_3$CN (1.5 ml) in an NMR tube which was sealed under N$_2$. The reaction was monitored by NMR spectroscopy, and found to be complete in 12 min. Work-up as described above, yielded [CpFe(CO)$_2$CH$_2$PPh$_2$]I (0.045 g, 59%).

Reaction of 1a with PMePh$_2$ or PPh$_3$ in CH$_3$CN

Complex **1a** (0.030 g, 0.131 mmol) was dissolved along with the phosphine (0.131 mmol) in CH$_3$CN (1.5 ml) in an NMR tube and the tube sealed under N$_2$. The reaction was monitored by NMR spectroscopy. The products **2c** or **2g** were isolated as their BPh$_4^-$ salts, as described previously [5].

Preparation of [CpFe(CO)$_2$(CH$_2$PPh$_3$)]Br (2g)

The reaction of **1b** with triphenylphosphine in methanol under reflux gave **2g** in 71% yield, m.p. 119–121°C, IR (CH$_2$Cl$_2$) ν(CO) 2022s, 1969s cm^{-1}. The spectroscopic properties of this compound are similar to those reported for the corresponding iodide [5].

Attempted formation of [$CpFe(CO)_2(CHPR_3)$]

Use of **2g** as the starting material and NaOMe/MeOH as a base in the presence of benzophenone gave no new products, as indicated by IR spectroscopy and TLC examination. The use of tetrahydrofuran as the solvent and butyllithium as base also gave no isolable products. In the absence of any ketonic trapping agents, attempted preformation of the ylide **9** did not lead to any isolable products.

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