JOM 23411

Haloalkyl complexes of the transition metals

VIII *. The synthesis and properties of $[CpW(CO)_3CH_2X]$ ($X = OCH_3$, Cl, Br, I) and their reactivity with neutral donor ligands

Holger B. Friedrich and John R. Moss

Department of Chemistry, University of Cape Town, Rondebosch, 7700 (South Africa)

(Received October 27, 1992)

Abstract

The complexes $[CpW(CO)_3CH_2X]$ ($Cp = \eta^5\text{-}C_5H_5$, X = Cl, Br, I) have been prepared. Their reactions with a series of tertiary phosphines, amines, SMe_2 and $AsPh_3$ in THF, CH_3CN, CH_2Cl_2 and MeOH have been investigated. Two types of cationic products, namely the ylide complexes $[CpW(CO)_3CH_2L]^+$ and the disubstituted complexes $[CpWL_2(CO)_2]^+$, were obtained, the outcome depending on the halide (X), the pK_a, cone angle and concentration of the ligand (L), and the solvent used. These variables were also found to have significant influence on the reaction rates. The reactions of $[CpW(CO)_3CH_2X]$ with L were found to be significantly slower than those of the analogous $[CpFe(CO)_2CH_2X]$ complexes with the same ligands.

1. Introduction

Monohalomethyl complexes of the transition metals are of much current interest [1,2], because they can be precursors of a wide range of useful compounds such as methylene complexes [3], hydroxymethyl complexes [4] and methylene-bridged complexes [5], all of which have been shown to play a part in catalytic processes [6]. The methylene complexes are also promising reagents for electrophilic cyclopropanations [7] and for alkene metathesis [8]. Halomethyl complexes can also act as precursors of transition metal stabilized ylide complexes [9] that can be used for further synthetic manipulations [10].

As was described previously, the reactions of halomethyl transition metal complexes depend on a number of factors [11]. Thus the solvent used, the cone angle and pK_a of the reacting ligand (L), the ligand concentration (the ratio of ligand to metal) and the nature of the carbon-bonded halogen of the halomethyl complex determine both the rate of the reaction and the products formed. Another factor affecting the reactivity of $[CpM(CO)_nCH_2X]$ systems is the nature of the metal, M. For example, $[CpW(CO)_3CH_2Cl]$ reacts with PPh_3 in acetonitrile to give $[CpW(CO)_3CH_2PPh_3]Cl$, but, under identical conditions $[CpMo(CO)_3CH_2Cl]$ gives $[CpMo(PPh_3)(CO)_2Cl]$ [11a,b]. These results indicate that the reaction of $[CpW(CO)_3CH_2X]$ (X = Cl, Br, I) with ligands, L, may give products similar to those obtained from the reactions of $[CpFe(CO)_2CH_2X]$ with L. We were therefore interested to see how the reactivity of the $[CpW(CO)_3CH_2X]$ system would compare with that of the $[CpFe(CO)_2CH_2X]$ system, and specifically in studying the effect of a change of metal (from iron to tungsten) on these halomethyl systems.

2. Results and discussion

2.1. Preparation and properties of $[CpW(CO)_3CH_2X]$

The complexes $[CpW(CO)_3CH_2X]$ {$X = OCH_3$ (**1**), Cl (**2a**), Br (**2b**)} were prepared in good yield by the method described by Green *et al.* [12], as shown in eqns. (1) and (2). (Note: $ClCH_2OCH_3$ is a potent carcinogen.)

$$Na[CpW(CO)_3] + ClCH_2OCH_3 \longrightarrow [CpW(CO)_3CH_2OCH_3] + NaCl \quad (1)$$

Correspondence to: Professor J.R. Moss.

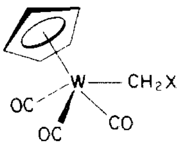
* For Part VII, see ref. 32.

$$[\mathrm{CpW(CO)_3CH_2OCH_3}] + \mathrm{HX\ (gas)} \longrightarrow [\mathrm{CpW(CO)_3CH_2X}] + \mathrm{CH_3OH} \quad (2)$$
$$(\mathrm{X = Cl, Br})$$

The complex [CpW(CO)$_3$CH$_2$I] (**2c**) was prepared by treating [CpW(CO)$_3$CH$_2$Br] with NaI, a route commonly used for converting alkyl bromides into alkyl iodides [13] and employed previously to convert [CpFe(CO)$_2$CH$_2$Br] into [CpFe(CO)$_2$CH$_2$I] [11c], eqn. (3).

$$[\mathrm{CpW(CO)_3CH_2Br}] + \mathrm{NaI} \longrightarrow [\mathrm{CpW(CO)_3CH_2I}] + \mathrm{NaBr} \quad (3)$$

Complex **2c** was obtained previously by a different method, in low yield, but was only partially characterised [14,15]. We obtained the complex [CpW(CO)$_3$-CH$_2$I] as yellow crystals in good yield by the route shown in eqn. (3), and found it to be stable to air and light for short periods (contrary to the previous report). A sample of **2c** has been kept under nitrogen at −15°C for over five years with only minor degradation. Complexes **2a** and **2b** were found to be more stable than **2c** under all conditions, with a stability order for [CpW(CO)$_3$CH$_2$X] of X = Cl ≫ Br > I. Complexes **1**–**2c** were also found to be less stable than their Cp* analogues, [Cp*W(CO)$_3$CH$_2$X] (X = OCH$_3$, Cl, Br, I) [16], in all respects. Compounds **2a**–**2c** decompose to form [CpW(CO)$_3$X] at room temperature both in solution and in the solid state. Data for complexes **1**–**2c** are listed in Tables 1 and 2. Neither the melting points, ^{13}C NMR spectra nor mass spectra of these functionalized methyl complexes have been reported previously. The complexes **2a**–**2c** are depicted in Fig. 1.



X	compound
OCH$_3$	1
Cl	2a
Br	2b
I	2c

Fig. 1. Molecular formula for complexes **1**, **2a**–**2c**.

The data for the [CpW(CO)$_3$CH$_2$X] systems show interesting differences from those for the [CpFe(CO)$_2$-CH$_2$X] system. For example, whereas the complexes [CpFe(CO)$_2$CH$_2$X] (X = Cl, Br, I) show a decrease in melting point as X changes from Cl to Br to I (*ca.* 65°C, *ca.* 54°C, and 28°C respectively) [11c], the melting points of the [CpW(CO)$_3$CH$_2$X] complexes in that sequence. The tungsten halomethyl complexes generally have higher melting points than their iron analogues, and appear to be more stable in air in the absence of light.

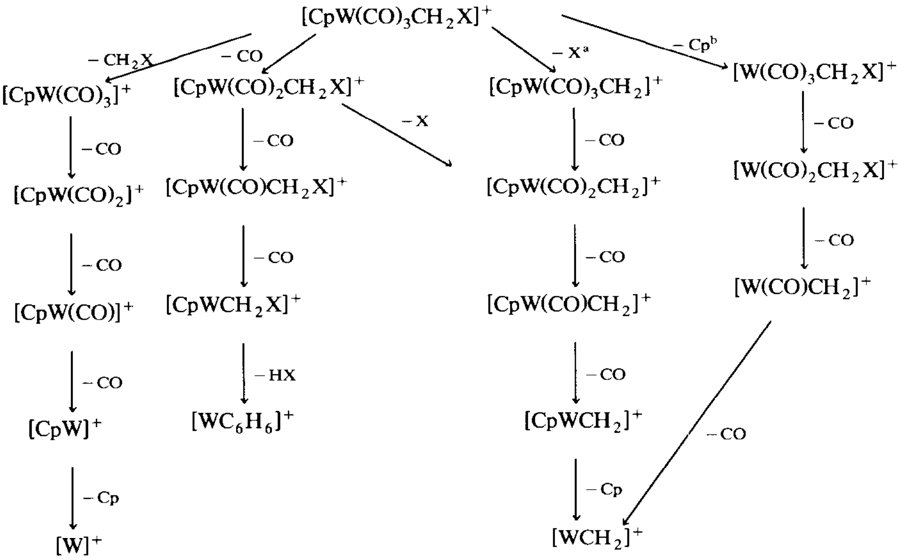
The carbonyl stretching frequencies for the tungsten complexes show a very slight shift to higher wave numbers as X changes from Cl to Br to I and are at higher wave numbers than those for their [CpMo (CO)$_3$CH$_2$X] analogues [12]. Also, the carbonyl stretching frequencies are 12–15 cm^{-1} higher than those observed for their Cp* analogues [16], as would be expected [17].

The ^{1}H NMR spectra show the expected trend for the chemical shifts for the CH$_2$X protons, *i.e.*

TABLE 1. Data for [CpW(CO)$_3$CH$_2$X]

Compound	X	m.p. (°C)	IR (ν(CO)) [a] (cm^{-1})	^{1}H NMR [b] (δ)	^{13}C NMR [b] (δ)	molecular [c] ion
1	OCH$_3$	44–45	2025 1940 1926	5.45 [s, 5H] 4.60 [s, 2H] 3.27 [s, 3H]	228.5 (*cis*-CO) 216.3 (*trans*-CO) 91.5(Cp), 63.6 CH$_3$) 47.8(CH$_2$)	
2a	Cl	> 78 (dec)	2031 1950 1934	5.57 [s, 5H] 4.30 [s, 2H]	227.1 (*cis*-CO) 215.5 (*trans*-CO) 92.6(Cp), 9.9(CH$_2$)	382
2b	Br	80–85	2031 1950 1935	5.59 [s, 5H] 3.98 [s, 2H]	226.9 (*cis*-CO) 215.5 (*trans*-CO) 93.0(Cp), −2.03(CH$_2$)	426/428
2c	I	99–102	2031 1951 1938	5.56 [s, 5H] 3.16 [s, 2H]	227.2 (*cis*-CO) 216.0 (*trans*-CO) 93.8(Cp), −36.9(CH$_2$)	474

[a] Measured in hexane, all bands strong. [b] Measured in CDCl$_3$ relative to TMS (δ = 0.00 ppm), s = singlet. [c] Mass of most abundant isotope combination.



[a] This pathway is only observed for X = Br and I (compounds (**2b**) and (**2c**)).

[b] This pathway is only observed for X = Cl and Br (compounds (**2a**) and (**2b**)).

Scheme 1. An illustration of possible mass spectral fragmentations giving rise to the major ions observed for complexes **2**.

$CH_2OCH_3 > CH_2Cl > CH_2Br > CH_2I$, whilst the Cp resonance shows little or no variation with changing X. The change in the ^{13}C NMR shifts of 11.9 ppm on going from X = Cl to X = Br and of 34.9 ppm on going from X = Br to X = I reflect the electronegativity differences between the halogens. The difference between the shifts for X = Br and X = I is however significantly greater for the W complex than for the Fe complex (34.9 ppm *vs.* 19 ppm). The ^{13}C resonances for the Cp rings shift marginally downfield as X is varied from Cl to Br to I. This is as observed for the iron complexes and the observed chemical shifts can be rationalized in terms of the contribution in solution of the canonical form $^{\delta+}W \doteq CH_2 \cdots X^{\delta-}$. This would result in the withdrawal of electrons from the cyclopentadienyl group, reducing the ring current and hence causing an upfield shift of the Cp resonance. Such an effect would be greatest for X = Cl, as is observed.

The ^{13}C NMR assignments for complex **1** were made with the aid of an APT NMR experiment. The assignments for the CH_2 and CH_3 carbons agree well with those for [CpFe(CO)$_2$CH$_2$OCH$_3$] [18*] and with other ^{13}C NMR data obtained for methoxymethyl complexes [19].

Low resolution electron impact (EI) mass spectra were obtained for complexes **2a**–**2c** and all show molecular ions of low intensity (3–5%). The intensities of the major peaks of these complexes are listed in Table 2, with probable assignments. The probable fragmentation pathways are shown in Scheme 1. Most interesting is the apparent formation of the carbene (methylene) species under EI. Similarly, the [CpFe(CO)$_2$CH$_2$X] (X = Cl, Br, I) complexes appear to form Fe = CH$_2$ carbene species readily under EI [20]. As observed for [CpFe(CO)$_2$CH$_2$X] [20], the relative abundance of the proposed tungsten carbene species appears to depend on the relative abilities of the halogens as leaving groups ($I \gg Br > Cl$). Steven and Beauchamp [21] have shown that [CpFe(CO)$_2$CH$_2$]$^+$ is observed in the EI mass spectrum of [CpFe(CO)$_2$CH$_2$OCH$_3$] if protonation agents are present. The probable presence of carbene species in the EI spectra of complexes **2a**–**2c** in the absence of protonation agents thus suggests that the W = CH$_2$ carbene species are formed more easily from [CpW(CO)$_3$CH$_2$X] under electron impact conditions.

2.2. *Reactions of [CpW(CO)$_3$CH$_2$X] (X = Cl, Br, I) with neutral nucleophiles*

[CpW(CO)$_3$CH$_2$Cl] reacts with PPh$_3$ in THF to give a cationic ylide-type product [CpW(CO)$_3$CH$_2$PPh$_3$]$^+$, that was isolated as its BPh$_4^-$ salt. This product has been reported before [11b]. In contrast, [CpW(CO)$_3$CH$_2$Cl] reacts with PMe$_2$Ph in refluxing THF to give the disubstituted product [CpW(PMe$_2$Ph)$_2$(CO)$_2$]$^+$, that was isolated as its PF$_6^-$ salt.

---

* Reference number with asterisk indicates a note in the list of references.

TABLE 2. Some mass spectral data for $[CpW(CO)_3CH_2X]$

Ion [a]		Relative peak intensities (%) [b]		
		X = Cl	X = Br	X = I
M		5	3	3
M-CO		6	18	61
M-2CO		11	36	48
M-3CO		100	100	100
M-3CO-HX		11	37	17
M-2CO-HX-Cp		0	3	2
$M-CH_2X$	$\{=CpW(CO)_3\}$	4	7	4
$M-CH_2X-CO$	$\{=CpW(CO)_2\}$	10	13	11
$M-CH_2X-2CO$	$\{=CpW(CO)\}$	12	13	10
$M-CH_2X-3CO$	$\{=CpW\}$	24	22	20
M-X		0	6	6
M-CO-X		6	18	25
M-2CO-X		8	21	43
M-3CO-X		16	35	79
M-3CO-X-Cp		3	0	0
M-Cp		5	0	0
M-Cp-CO		7	2	0
M-Cp-2CO		10	13	0
M-Cp-3CO		14	18	0
$M-CH_2X-Cp$		20	0	3
$M-CH_2X-Cp-CO$		0	0	6
$M-CH_2X-Cp-2CO$		3	6	11
WX		24	20	0
C_3H_3W		20	12	3
C_3H_2W		10	10	1
W		4	5	4
HX		1	0	21
X		0	0	9
C_3H_3		6	12	5
C_3H_2		3	3	2
CH_2X		4	0	0
C_2H_2		0	5	5
Cp_2W		0	15	2

[a] $M=[CpW(CO)_3CH_2X]$; all ions have a single positive charge; ion refers to probable assignment. [b] Peak intensities are relative to the base peak at m/z 298 (X = Cl); m/z 342/344 (X = Br); m/z 390 (X = I).

$[CpW(CO)_3CH_2Br]$ reacts with excess L (L = PMe_3, $PEtPh_2$) to give the ylide-type products $[CpW(CO)_3CH_2L]^+$, isolated as their BPh_4^- salts (see Tables 3 and 4 for data). The reaction of $[CpW(CO)_3CH_2Br]$ with bis(diphenylphosphino)ethane (dppe) gives the bridged dicationic ylide complex $[CpW(CO)_3CH_2P(Ph)_2(CH_2)_2P(Ph)_2CH_2W(CO)_3Cp]^{2+}$. This latter complex is unstable in solution and was characterised by IR spectroscopy and elemental analysis, and partially by ^1H NMR spectroscopy (see Table 5).

Complex (**2a**) reacted with L (L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, $AsPh_3$) in refluxing methanol to give the ylide-type complexes $[CpW(CO)_3CH_2L]^+$ in low to moderate yields. Similarly, complex (**2b**) reacted with $AsPh_3$ in MeOH to give the cationic ylide complex $[CpW(CO)_3CH_2AsPh_3]^+Br^-$, which was treated with $[N^nBu_4]PF_6$ to give $[CpW(CO)_3CH_2AsPh_3]PF_6$.

To gain a greater insight into the reactions of the halomethyl tungsten complexes with ligands, L, the reaction of complex **2a** with $AsPh_3$ in methanol was studied in more detail. We found that the reaction of $[CpW(CO)_3CH_2Cl]$ with $AsPh_3$ in refluxing methanol gives a mixture of two products, $[CpW(CO)_3H]$ (about 49% yield), as identified by ^1H NMR, IR and mass spectrometry [22], in addition to the ylide complex $[CpW(CO)_3CH_2AsPh_3]Cl$, which was isolated as its PF_6^- salt in 22% (recrystallized) yield. Similarly, the reaction of $[CpW(CO)_3CH_2Br]$ with $AsPh_3$ in refluxing methanol gives $[CpW(CO)_3H]$ and $[CpW(CO)_3CH_2AsPh_3]^+$ in 57% and 32% yields respectively.

Dissolution of $[CpW(CO)_3CH_2Cl]$ (**2a**) in methanol results in almost quantitative formation of $[CpW(CO)_3CH_2OCH_3]$ (**1**), as judged by IR spectroscopy, after *ca.* 3 h at room temperature. However, work-up of the solution gave a mixture of complexes **1** and **2a**, with the former slightly predominating. A possible explanation for this partial reversal of the above reaction is that HCl is formed in solution and reacts with **1** upon concentration of the methanol to give complex **2a**. Dissolving complex **2a** in methanol, allowing it to react completely to give complex **1**, then adding $AsPh_3$ and refluxing the solution results in no change in the types or ratios of products formed. However, when $[CpW(CO)_3CH_2OCH_3]$ is dissolved in methanol and the solution refluxed in the presence of $AsPh_3$, no reaction takes place. It thus seems clear that in the reaction of $[CpW(CO)_3CH_2Cl]$ with $AsPh_3$ in methanol, it is the small equilibrium concentration of the chloromethyl complex **2a** that reacts with $AsPh_3$ to form the ylide complex.

Refluxing of a solution of **1** in MeOH or CH_3CN does not give any $[CpW(CO)_3H]$. Refluxing of a solution $[CpW(CO)_3CH_2Cl]$ in MeOH or MeOD, however, gave the hydride complex $[CpW(CO)_3H]$ after 3 h, as shown by IR and ^1H NMR spectroscopy. This suggests that the hydride may be formed by an α-migration of hydrogen from the CH_2 carbon atom of **2a** to the metal. Such an α-migration (1,2 shift) of hydride has been previously observed for a cyclopentadienyl tungsten methyl complex [23], and 1,2 shifts are also known for other haloalkyl metal systems [24].

No transition metal ylide-type product is formed in the reaction of **2a** with PCy_3 (Cy = cyclohexyl) in MeOH; instead only **1** and $[HPCy_3]^+$ are obtained.

Like those of the iron $[CpFe(CO)_2CH_2X]$ system [11c], the reactions of $[CpW(CO)_3CH_2X]$ (X = Cl, Br) with ligands, L, in acetonitrile can give two types of ligand product, namely a ylide-type product $[CpW(CO)_3CH_2L]X$ (**3**) and a disubstituted product $[CpWL_2(CO)_2]X$ (**4**). The reactions of complexes **2a**, **2b** and **2c** with neutral nucleophiles, L, in acetonitrile are

TABLE 3. Data for complexes **3a**–**3l**

Compound	No.	m.p. (°C)	IR ν(CO) [a] (cm^{-1})	Elemental [b] Analysis
[CpW(CO)$_3$CH$_2$PMe$_3$]BPh$_4$	**3a**	> 272(dec)	2033s, 1953sh, 1925s	C: 58.20 (58.21) H: 4.85 (4.85)
[CpW(CO)$_3$CH$_2$PMe$_2$Ph]BPh$_4$	**3b**	176–180	3034s, 1951sh, 1928s	C: 61.16 (61.17) H: 4.85 (4.72)
[CpW(CO)$_3$CH$_2$PMePh$_2$]BPh$_4$	**3c**	82–84	2035s, 1950sh, 1931s	C: 63.70 (63.71) H: 4.60 (4.62)
[CpW(CO)$_3$CH$_2$PEt$_3$]BPh$_4$	**3d**	154–158	2027s, 1940sh 1916s	C: 60.20 (59.67) H: 5.20 (5.35)
[CpW(CO)$_3$CH$_2$PEtPh$_2$]BPh$_4$	**3e**	180–190	2035s, 1953sh, 1929s	C: 63.55 (64.06) H: 5.00 (4.77)
[CpW(CO)$_3$CH$_2$PPh$_3$]BPh$_4$	**3f**	192–198 [c]	2035s, 1953sh, 1933s	[d] [d]
[CpW(CO)$_3$CH$_2$PCy$_3$]BPh$_4$	**3g**	125–134	2031s, 1950m, 1921vs	C: 65.20 (64.72) H: 6.40 (6.34)
[CpW(CO)$_3$CH$_2$AsPh$_3$]BPh$_4$	**3h**	175–177	2036s, 1955sh, 1933s	C: 62.90 (62.90) H: 4.60 (4.31)
[CpW(CO)$_3$CH$_2$NMe$_3$]BPh$_4$	**3i**	182–184	2034s, 1957m, 1923s	C: 59.10 (59.57) H: 4.95 (4.96) N: 1.95 (1.93)
[CpW(CO)$_3$CH$_2$NC$_5$H$_5$]BPh$_4$	**3k**	161–163	2033s, 1953m, 1927s	C: 61.20 (61.19) H: 4.40 (4.29) N: 1.95 (1.88)
[CpW(CO)$_3$CH$_2$SMe$_2$]BPh$_4$	**3l**	168–176(dec)	2037s, 1954sh, 1935s	C: 57.25 (57.57) H: 4.60 (4.53)

[a] In CH$_2$Cl$_2$ solution; [b] calculated values in parentheses; [c] data from ref. [11b]; [d] not obtained.

depicted in eqns. (4)–(6).

$$[\mathrm{CpW(CO)_3CH_2X}] + \mathrm{L} \longrightarrow [\mathrm{CpW(CO)_3CH_2L}]\mathrm{X} \qquad (4)$$

X = Cl: L = PMe$_3$(**3a**), PMePh$_2$ (**3c**), PEtPh$_2$ (**3e**), PPh$_3$ (**3f**), AsPh$_3$ (**3h**) and NMe$_3$ (**3i**); no reaction for P^{t}Bu$_3$, SMe$_2$;

X = Br: L = PMe$_3$ (**3a**), PMe$_2$Ph (**3b**), PMePh$_2$ (**3c**), PEtPh$_2$ (**3e**), PPh$_3$ (**3f**), PCy$_3$ (**3g**), AsPh$_3$ (**3h**), NMe$_3$ (**3i**), Py (**3k**) and SMe$_2$ (**3l**); no reaction for P^{t}Bu$_3$, P(OMe)$_3$, NEt$_3$;

X = I: L = PEt$_3$ (**3d**), PPh$_3$ (**3f**).

$$[\mathrm{CpW(CO)_3CH_2X}] + 2\mathrm{L} \longrightarrow [\mathrm{CpW(L)_2(CO)_2}]\mathrm{X} + \text{other products} \qquad (5)$$

X = Cl: L = PMe$_3$ (**4a**), PMe$_2$Ph (**4b**).

$$2[\mathrm{CpW(CO)_3CH_2Br}] + \mathrm{dppe} \longrightarrow [\{\mathrm{CpW(CO)_3CH_2}\}_2(\mu\text{-dppe})]\mathrm{Br_2} \qquad (6)$$

As can be seen from eqns. (4)–(6), the ylide product is formed in nearly all cases in the reaction of complex **2a** with neutral nucleophiles, L. The ligand PMe$_2$Ph, however, reacts with **2a** to form only the disubstituted product (even when used in a 1 : 1 ratio with complex **2a**), whilst a 1 : 1 ratio of PMe$_3$ to **2a** reacts to give a mixture of [CpW(CO)$_3$CH$_2$PMe$_3$]$^+$ and [CpW(PMe$_3$)$_2$(CO)$_2$]$^+$. This result is interesting because PMe$_3$ has a higher pK_a and smaller cone angle than PMe$_2$Ph, and thus might have been expected to form only the disubstituted product for both electronic and steric reasons. The IR and NMR data indicate that the carbonyl groups are *trans* to each other in complexes **4a** and **4b** [25]. The complexes of types **3** and **4** are represented in Fig. 2.

No evidence for alkyl migrations to given complexes of the type [CpWL(CO)$_2${C(O)CH$_2$X}] was obtained in any of the reactions. Complexes of the type [CpW(CO)$_3${C(O)CH$_2$X}] are known, but were obtained by a different route [26].

Whereas 2 mol of PMePh$_2$ react with 1 mol of [CpFe(CO)$_2$CH$_2$Cl] to give a disubstituted ligand product, the same reaction of PMePh$_2$ with **2a** gives only a ylide-type product. A further difference between the iron and tungsten systems is that, whereas the iron bromomethyl complex reacts with P^{t}Bu$_3$ to give a ylide-type product, the tungsten analogue **2b** does not react with this phosphine. In contrast, [CpFe(CO)$_2$-CH$_2$Cl] does not react with PPh$_3$ in THF, whereas [CpW(CO)$_3$CH$_2$Cl] does react to form the ylide complex. Like the iron system, however, neither complex

TABLE 4. ^1H NMR data for complexes **3a–3k** [a]

Compound	CH_2L	Cp	Ph	Alkyl
$[CpW(CO)_3CH_2PMe_3]BPh_4$	1.38 (d, $^2J = 16.0$)	5.78 (s)	7.82, 7.04 (m, 20H)	1.76 (d, 9H, $^2J = 14.0$)
$[CpW(CO)_3CH_2PMe_2Ph]BPh_4$	1.66 (d, $^2J = 17.0$)	5.70 (s)	7.72, 7.29, 6.94 (m, 25H)	2.07 (d, 6H, $^2J = 13.8$)
$[CpW(CO)_3CH_2PMePh_2]BPh_4$	2.00 (d, $^2J = 16.4$)	5.73 (s)	7.68, 7.30 (m, 30H)	2.38 (d, 6H, $^2J = 13.2$)
$[CpW(CO)_3CH_2PEt_3]BPh_4$	1.26 (d, $^2J = 15.9$)	5.79 (s)	7.33, 7.00, 6.84 (m, 20H)	2.08 (dq, 6H, $^3J(HH) = 7.6$, $^2J(PH) = 12.2$); 1.22 (dt 9H, $^3J(HH) = 7.6$, $^3J(PH) = 17.5$)
$[CpW(CO)_3CH_2PEtPh_2]BPh_4$	1.92 (d, $^2J = 16.0$)	5.66 (s)	7.66, 7.30, 6.89 (m, 30H)	3.42 (m, 1H); 2.70 (m, 1H); 1.23 (m, 3H)
$[CpW(CO)_3CH_2PPh_3]BPh_4$	2.28 (d, $^2J = 16.5$)	5.68 (s)	7.64, 7.27, 6.91 (m, 35H)	
$[CpW(CO)_3CH_2PCy_3]BPh_4$	1.21 d, $^2J = 16.6$)	5.83 (s)	7.33, 6.99, 6.72 (m, 20H)	1.10 (m, 33H)
$[CpW(CO)_3CH_2NC_5H_5]BPh_4$	4.58 (s)	5.38 (s)	7.33, 7.00, 6.92 (m, 20H)	7.93, 7.59 (m, 5H)
$[CpW(CO)_3CH_2NMe_3]BPh_4$	3.08 (s)	5.77 (s)	7.33, 6.95 (m, 20H)	3.08 (s, 9H)
$[CpW(CO)_3CH_2SMe_2]BPh_4$	3.02 (s)	5.92 (s)	7.34, 6.87 (m, 20H)	2.94 (s, 6H)
$[CpW(CO)_3CH_2AsPh_3]BPh_4$	2.30 (s)	5.69 (s)	7.70, 7.30, 7.00 (m, 35 H)	

[a] In CD_3NO_2 relative to TMS ($\delta = 0.00$ ppm); J values in Hz, ^2J represents PH coupling unless otherwise stated, s = singlet, d = doublet, m = multiplet, dq = doublet of quartets, dt = doublet of triplets.

2a nor **2b** react with NEt_3 or $P(OMe)_3$ under these conditions.

There are differences between the behaviour of complex **2b** and that of complex **2a**. Thus, **2a** does not react with SMe_2 in CH_3CN or THF, whereas **2b** does react in CH_3CN to form complex **3l**. Also, unlike complex **2b**, complex **2a** reacts with PMe_2Ph to give the disubstituted product **4b**. In contrast, complex **2b** reacts with PMe_2Ph to give the ylide-type product **3b**. These results clearly demonstrate that the halogen affects the reactivity of $[CpW(CO)_3CH_2X]$ and the products formed.

The solvent can clearly affect the course of the reaction. Thus, complex **2a** reacts with PMe_2Ph in CH_3CN to give the disubstituted product **4b**, whereas in methanol the reaction of complex **2a** with PMe_2Ph gives the ylide-type product **3b**. The solvent effect is further illustrated by the fact that complex **2a** reacts with $PMePh_2$ in CH_3CN or CH_3OH to give the ylide product **3c**, whereas no reaction takes place between these reagents in THF.

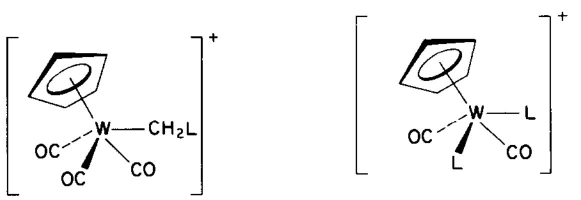
As was observed for the reactions of $[CpFe(CO)_2CH_2Cl]$ and $[CpMo(CO)_3CH_2Cl]$ with neutral nucleophiles [27], complex **2a** reacts with PCy_3 in CH_2Cl_2 in the presence of $TlPF_6$ to give (**3g**). Complex **2c** reacts with NEt_3 under similar conditions to give **3j**.

The data for the new cationic ylide complexes reported in eqn. (4) and for complex **4b** are listed in Tables 3–5. Of interest are the ^1H NMR resonances of the CH_2L protons, which correlate linearly with the

TABLE 5. Data for further products obtained from the reactions of complexes **2** with ligands L

Compound	m.p. (°C)	IR (ν(CO)) [a] (cm^{-1})	^1H NMR [b] (δ)	Elemental analysis [c]
$[CpW(CO)_3CH_2NMe_3]Br$	[d]	2030s, 1955m, 1915s	5.86(s, Cp), 4.17(s, CH_2), 3.16(s, Me_3)	C: 59.10 (59.57) H: 4.95 (4.96) N: 1.95 (1.93)
$[CpW(CO)_3CH_2NEt_3]PF_6$	141–142	2029s, 1942sh, 1917s	5.80(s, Cp), 3.73(s, CH_2) 3.22(q, $(N(CH_2CH_3)_3$, $^3J = 7.2$); 1.30(t, $(-Me)_3$, $^3J = 6.3$)	C: 29.90 (30.36) H: 3.80 (3.71) N: 2.60 (2.36)
$[CpW(CO)_3CH_2AsPh_3]PF_6$	193–195	2031s, 1944sh 1928s	5.68(s, Cp), 2.60(s, CH_2), 7.68(s, Ph_3)	C: 40.58 (40.60) H: 2.76 (2.80)
$[CpW(PMe_2Ph)_2(CO)_2]PF_6$	218–220	1955m 1872vs	5.32(t, Cp, $^3J(PH) = 2.4$); 7.54(m, Ph_2); 2.18(d, $2Me_2$, $^2J(PH) = 9.7$)	C: 37.75 (38.01) H: 3.70 (3.72)
$[CpW(PMe_3)_2(CO)_2]BPh_4$	[e]	1956m 1875vs	5.78(t, Cp, $^3J(PH) = 1.5$); 7.34, 6.84(m, Ph_4) [f]	[e]
$[\{CpW(CO)_3CH_2\}_2\{\mu\text{-dppe}\}][BPh_4]_2$	[d]	2034s 1955m 1926s	5.59(s, Cp), 7.60, 7.30, 6.90(m, Ph_6) [g]	C: 63.60 (63.79) H: 4.80 (4.51)

[a] In CH_2Cl_2; [b] in CD_3NO_2 unless otherwise stated, relative to TMS ($\delta = 0.00$ ppm), J values in Hz; [c] calculated values in parentheses; [d] not obtained; [e] compound impure; [f] in acetone-d_6, PMe_3 peak obscured by solvent; [g] compound unstable in solution.



compound	L
3a	PMe$_3$
3b	PMe$_2$Ph
3c	PMePh$_2$
3d	PEt$_3$
3e	PEtPh$_2$
3f	PPh$_3$
3g	PCy$_3$
3h	AsPh$_3$
3i	NMe$_3$
3j	NEt$_3$
3k	py
3l	SMe$_2$

compound	L
4a	PMe$_3$
4b	PMe$_2$Ph

Fig. 2. Molecular formulae for complexes **3** and **4**.

pK_a of the bonded ligand, L (Fig. 3), the least squares correlation line showing a very close fit to the experimental points; the correlation coefficient for the least squares plot is 0.99. It may thus be possible to obtain an accurate estimate of the pK_a value of a tertiary phosphine of unknown pK_a with this graph provided a ylide-type product can be made with such a ligand. As would be expected, the δ values of the CH_2 peaks rise as the pK_a of the ligand falls.

The reactions of **2b** with PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, py, NMe$_3$ and SMe$_2$ in a 1:2 molar ratio in CH$_3$CN were monitored by ^{1}H NMR spectroscopy, by measuring the relative intensities of the Cp peaks of the starting material and product at room temperature (23°C). The rate of the reactions followed the sequence: NMe$_3$ $\approx$ PMe$_2$Ph > PMe$_3$ > PMePh$_2$ > SMe$_2$ > PPh$_3$ > py, with half-life values of 26, 36, 47, 85, 203, 300 and 445 min respectively ($\pm$ 1 min.). For the phosphines, the cone angles increase and the pK_a values decrease in the order [28]: PMe$_3$ < PMe$_2$Ph < PMePh$_2$ < PPh$_3$. Thus, in the case of the [CpFe(CO)$_2$-CH$_2$X] complexes, the ligands with smaller cone angles and larger pK_a values react more rapidly The exception to this sequence is PMe$_2$Ph, which reacts more rapidly than PMe$_3$, in spite of its greater steric bulk and lower nucleophilicity. The difference (in pK_a and bulk) between these ligands is however very small, and the [CpW(CO)$_3$CH$_2$X] complexes seem to be particularly reactive towards PMe$_2$Ph, as noted earlier. Since P^{t}Bu$_3$, a ligand with a large pK_a and a large cone angle, does not react with complex **2b**, the cone angle of the ligands appears to be the most important factor in these reactions.

Comparison of the rates of the reaction of the ligands PMe$_2$Ph, PMePh$_2$, PPh$_3$, SMe$_2$ and py with [CpFe(CO)$_2$CH$_2$Br] [11c] and [CpW(CO)$_3$CH$_2$Br] shows that the reactions of the iron bromomethyl complex are between seven times and 21 times as fast as those of its tungsten analogue. Thus the metal has a significant effect on the rate of reactions of L$_n$MCH$_2$Br complexes.

Monitoring the intensities of the Cp peaks in the ^{1}H NMR spectra at room temperature showed that the rates of the reactions of **2a–2c** with 2 mol PPh$_3$ under identical conditions follow the order Cl $\ll$ Br < I, with a reactivity ratio for Br : I of 1 : 13. The rate for X = Cl is extremely slow, with $t_{1/2}$ > 3 months at room temperature.

The reactions of **2b** with several concentrations of PMePh$_2$ in CH$_3$CN were also monitored similarly by ^{1}H NMR spectroscopy. The rate of reaction was found to increase significantly with increasing ligand concen-

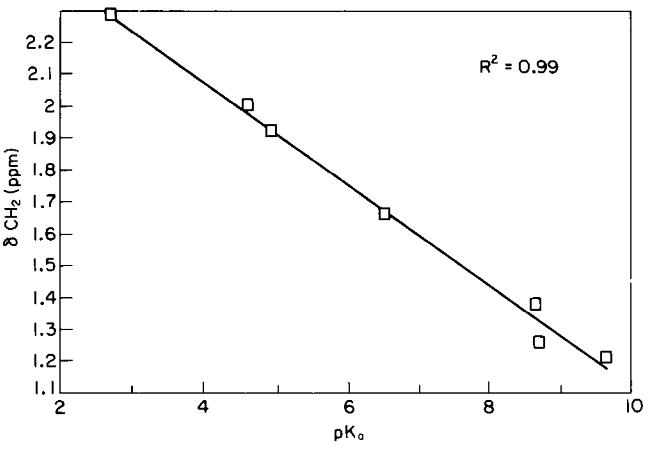


Fig. 3. A plot of the pK_a of tertiary phosphines *vs.* δCH$_2$ for complexes **3a–3g**.

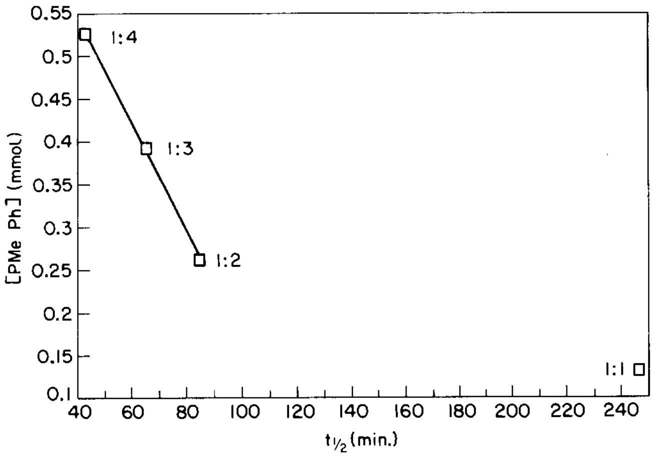
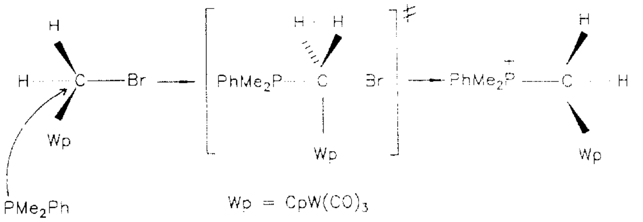


Fig. 4. A plot of $t_{1/2}$ *vs.* concentration of PMe$_2$Ph in the reaction of **2b** with PMePh$_2$.



Scheme 2. A possible mechanism for the reaction of **2b** with PMe$_2$Ph to form the ylide **3**.

tration. In fact, with exclusion of the reaction involving a 1 : 1 ratio of **2b**: PMePh$_2$, the $t_{1/2}$ values correlate linearly ($R^2 = 1.00$) with the PMePh$_2$ concentration for ratios of (**2b**): PMePh$_2$ of 1 : 2, 1 : 3 and 1 : 4 (Fig. 4).

The qualitative kinetic data obtained indicates that the reaction of **2b** with PMePh$_2$ appears to proceed by a concerted (S$_N$2) mechanism (Scheme 2). This is in contrast to the mechanism proposed for the reactions of [CpFe(CO)$_2$CH$_2$X] with L [11b,c]. Complexes **3a**–**3g** can be regarded as metal-substituted quaternary phosphonium salts and a general synthesis of phosphonium salts is by the reaction of a tertiary phosphine with an alkyl halide [29]. The mechanism proposed to explain the kinetic data (Scheme 2) is also supported by the observation that: (a) complex **2b** can be regarded as a metal-substituted primary alkyl halide, and (b) primary alkyl halides usually react with tertiary phosphines by a S$_N$2 reaction [30]. The rate equation: rate = k[CpW(CO)$_3$CH$_2$Br][PMePh$_2$] appears to hold up to 70–75% completion of the reaction, with $k = 0.59\ (\pm 0.02)\ \mathrm{s}^{-1}$. A similar rate equation appears to hold for the reaction of **2b** with L (L = PMe$_3$, $k = 0.87\ (\pm 0.03)\ \mathrm{s}^{-1}$; L = PMe$_2$Ph, $k = 2.08\ (\pm 0.07)\ \mathrm{s}^{-1}$; L = PPh$_3$, $k = 0.26\ (\pm 0.02)\ \mathrm{s}^{-1}$). No corresponding data for the reactions of other halomethyl transition metal complexes with PR$_3$ are available [1].

3. Experimental details

Methanol was distilled over CaCl$_2$ or Mg/I$_2$, and CH$_2$Cl$_2$ was dried over CaCl$_2$ and distilled from CaH$_2$. The complexes [CpW(CO)$_3$]$_2$ [31], [CpW(CO)$_3$CH$_2$OCH$_3$], [CpW(CO)$_3$CH$_2$Cl], [CpW(CO)$_3$CH$_2$Br] [12], and [CpW(CO)$_3$H] [22] were prepared by published procedures. ^{1}H NMR spectra were recorded on a Varian XL100, Varian EM60, Brücker WH90 or a Varian XR200 spectrometer. ^{13}C NMR spectra, as well as COSY, HETCOR and APT experiments, were recorded on a Varian XR200 spectrometer. Chemical shifts are reported relative to TMS ($\delta = 0.00$ ppm) as internal (XL100, EM60, WH90) or external (VXR200) reference. The qualitative kinetic studies were carried out on the Varian EM60 spectrometer at 23°C. All other details were as reported previously [11c].

3.1. Preparation of [CpW(CO)$_3$CH$_2$I] (2c)

Dry NaI (0.059 g, 0.394 mmol) was added to a solution of [CpW(CO)$_3$CH$_2$Br] (0.102 g, 0.267 mmol) in acetone (5 ml). The solution was stirred for 90 min and the solvent was then removed under reduced pressure. The product was extracted with hexane (9 ml), and the solution filtered and cooled to −78°C. A yellow–orange crystalline precipitate of **2c** was separated (0.11 g, 87%).

3.2. Reaction of [CpW(CO)$_3$CH$_2$Cl] (2a) with PPh$_3$ in THF

Complex **2a** (0.148 g, 0.387 mmol) was dissolved in THF (7 ml) and PPh$_3$ (0.203 g, 0.778 mmol) was added. The solution was refluxed overnight and the solvent removed under reduced pressure. The residue was dissolved in a minimum of MeOH and the solution filtered into a solution of NaBPh$_4$ (0.130 g, 0.387 mmol) in a minimum of MeOH. The resulting yellow precipitate of [CpW(CO)$_3$CH$_2$PPh$_3$]BPh$_4$ was filtered off and recrystallised from CH$_2$Cl$_2$–hexane (0.025 g, 11%).

3.3. Reaction of 2a with PMe$_2$Ph in THF

Complex **2a** (0.10 g, 0.26 mmol) was dissolved in THF (3 ml) and PMe$_2$Ph (0.28 g, 2.03 mmol) was added. The solution was refluxed for 26 h and the solvent then removed under reduced pressure. The product was dissolved in a minimum of MeOH and the solution filtered into a solution of ^{n}Bu$_4$NPF$_6$ (0.10 g, 0.26 mmol) in MeOH (2.5 ml). A yellow precipitate formed gradually. The product, [CpW(PMe$_2$Ph)$_2$(CO)$_2$]PF$_6$, was filtered off and recrystallised from CH$_2$Cl$_2$–ether (0.044 g, 23%).

3.4. Reaction of [CpW(CO)$_3$CH$_2$Br] (2b) with PMe$_3$ in THF

Complex **2b** (0.15 g, 0.36 mmol) was dissolved in THF (3 ml) and PMe$_3$ (0.36 mmol) was added. The mixture was allowed to stand in the dark for six days by which time yellow needles of [CpW(CO)$_3$CH$_2$PMe$_3$]Br had separated. The mother liquor was decanted and the residue recrystallised from CH$_2$Cl$_2$–hexane (0.007 g, 4%). IR ν(CO) (CH$_2$Cl$_2$): 2029s, 1940sh, 1918vs cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.86 (s, 5H); 1.95 (d, 9H); 2.25 (d, 2H, $^2J = 16.2$ Hz). The mother liquor from the decantation was found to contain only starting material.

3.5. Reaction of 2b with L (L = PEtPh$_2$, dppe) in THF

Complex **2b** (0.50 mmol) was dissolved in THF (1 ml). The ligand (PEtPh$_2$ or dppe) (0.50 mmol) was added along with THF (2 ml). The solution was kept at room temperature in the dark for 140 days or 24 days.

The products were isolated as yellow BPh_4^- salts as described before: [CpW(CO)$_3$CH$_2$PEtPh$_2$]BPh$_4$ (44%). [CpW(CO)$_3$CH$_2$PPh$_2$(CH$_2$)$_2$PPh$_2$CH$_2$(CO)$_3$WCp]]-(BPh$_4$)$_2$ (26%).

3.6. Reactions of 2a with PPh$_3$, PMePh$_2$, PMe$_2$Ph, PEtPh$_2$ and AsPh$_3$ in MeOH

General procedure: Compound **2a** (0.60 mmol) was dissolved in MeOH and the ligand (0.60 mmol) was added. The solutions were then refluxed for between 3–24 h (see below) and the solvent was then removed *in vacuo* to leave an oily solid. The products were isolated as their BPh_4^- salts (for L = PPh$_3$, PMePh$_2$, PMe$_2$Ph and PEtPh$_2$) or PF_6^- salts (0.70 mmol) (for L = AsPh$_3$). Reaction times and yields for the various ligand reactions are in parentheses. (PPh$_3$: 3.25 h, 35%; PMePh$_2$: 3.5 h, 47%; PMe$_2$Ph: 16 h, 8%; PEtPh$_2$: 21 h, 51%; AsPh$_3$: 23.5 h, 36%).

An attempt was made to isolate the chloride salt of [CpW(CO)$_3$CH$_2$AsPh$_3$]$^+$ (**3h**). The crude oily solid was triturated with hexane to give a yellow solid. This was recrystallised from CH$_2$Cl$_2$–hexane to give yellow platelets of [CpW(CO)$_3$CH$_2$AsPh$_3$]Cl in 6% yield. IR (CH$_2$Cl$_2$): ν(CO)2028s, 1924vs cm^{-1}; m.p. 103–115°C. The elemental analysis suggested that the product might be a dihydrate after exposure to air. Anal. Found: C, 44.15; H, 3.25. $C_{27}H_{26}AsO_5W$ calc.: C, 44.74; H, 3.60%.

3.7. Reaction of 2a with PCy$_3$

Complex **2a** (0.20 g, 0.51 mmol) and PCy$_3$ (0.15 g, 0.53 mmol) were refluxed in MeOH (8 ml) for 5.5 h. The solution was concentrated and filtered into a solution of NaBPh$_4$ (0.51 mmol) in a minimum of MeOH. A white precipitate formed instantly, and was identified as [HPCy$_3$]BPh$_4$ (0.24 g, 77%). ^{1}H NMR (CDCl$_3$): δ = 1.21, 1.78 (m, 29H); 6.98, 7.34 (20H). The yellow supernatant liquid was concentrated under reduced pressure and cooled to −15°C, to give yellow crystals of **1** (0.09 g, 47%).

3.8. Reactions of 2a and 2b with AsPh$_3$ in MeOH

(a) Complex **2b** (0.134 g, 0.314 mmol) was dissolved in MeOH (7 ml) and AsPh$_3$ (0.097 g, 0.317 mmol) was added. The mixture was refluxed for 2.5 h, and the solvent then evaporated *in vacuo*. The dark oily residue was washed with hexane (3 × 10 ml). The washings were concentrated under reduced pressure and cooled to −78°C. A yellow precipitate of [CpW(CO)$_3$H] (0.060 g, 57%) was separated, and was identified from its IR, ^{1}H NMR and mass spectra, which were identical to those of an authentic sample. The hexane-insoluble residue was taken up in MeOH and the solution filtered into a solution of ^{n}Bu$_4$NPF$_6$ (0.122 g, 0.314 mmol) in MeOH. (This procedure was performed using dry N$_2$-saturated MeOH under an atmosphere of N$_2$.) The solution was allowed to stand overnight, during which fine yellow needles of [CpW(CO)$_3$CH$_2$AsPh$_3$]PF$_6$ separated. The product was recrystallized from CH$_2$Cl$_2$–hexane (0.034 g, 32%).

(b) Complex **2a** (0.235 g, 0.614 mmol) was dissolved in MeOH (12 ml) and AsPh$_3$ (0.188 g, 0.614 mmol) was added. The mixture was refluxed for 3 h. Work-up as described above gave CpW(CO)$_3$H (49%) and [CpW-(CO)$_3$CH$_2$AsPh$_3$]PF$_6$ (22%).

(c) Complex **2a** (0.101 g, 0.264 mmol) was dissolved in MeOH (12 ml) and the solution kept for 3 h in the dark. IR monitoring of the ν(CO) region showed only bands from [CpW(CO)$_3$CH$_2$OCH$_3$]. AsPh$_3$ (0.081 g, 0.264 mmol) was then added and the mixture allowed to stand in the dark for nine months. The solvent was removed under reduced pressure. The products were worked up as described above, to afford [CpW(CO)$_3$H] (0.030 g, 34%) and complex **3h**, isolated as its BPh_4^- salt (0.057 g, 22%).

3.9. Reaction of 2a with refluxing MeOH or MeOD

Complex **2a** (0.09 g, 0.23 mmol) was dissolved in MeOH (12 ml) or MeOD (3 ml) and the solution refluxed for 3.25 h. IR monitoring of the ν(CO) region showed the initial appearance of bands from [CpW(CO)$_3$CH$_2$OCH$_3$], followed by the appearance of bands from [CpW(CO)$_3$H]. The hydride was worked up as described earlier and identified by IR, ^{1}H NMR and mass spectroscopy.

3.10. Reactions of 2a with L (L = PMe$_3$, PMePh$_2$, PEtPh$_2$, PPh$_3$, AsPh$_3$ and NMe$_3$) in CH$_3$CN

General procedure: Complex (**2a**) (0.50 mmol) was dissolved in CH$_3$CN (10 ml) and the ligand (0.50–1.00 mmol) was added. The mixture was kept in the dark. (For reaction times and percentage yields see values in parentheses). The product was then worked up with NaBPh$_4$ as described before, to give yellow crystals of [CpW(CO)$_3$CH$_2$L]BPh$_4$: L = PMePh$_2$ (**3c**) (5.5d, 21%), PEtPh$_2$ (**3e**) (23 days, 10%), PPh$_3$ (**3f**) (8 days, 10%), AsPh$_3$ (**3h**) (24 days, 18%) and NMe$_3$ (**3i**) (34 days, 20%).

Reaction of **2a** with PMe$_3$ (1:1 and 1:2 molar ratios) in CH$_3$CN afforded a mixture of complexes [CpW(CO)$_3$CH$_2$PMe$_3$]$^+$ (**3a**) and [CpW(PMe$_3$)$_2$-(CO)$_2$]$^+$ (**4a**), as shown by IR and ^{1}H NMR spectroscopy, after six to seven days in the dark.

3.11. Reaction of 2a with PMe$_2$Ph in CH$_3$CN

Complex **2a** (0.133 g, 0.348 mmol) was dissolved in CH$_3$CN (1.5 ml) in an NMR tube and PMe$_2$Ph (0.049 g, 0.355 mmol) was added. The tube was sealed under

N_2 and kept at 57°C. The reaction was monitored by ^1H NMR spectroscopy. After 45.5 h, the reaction was judged to be complete, and yellow crystals had formed in the NMR tube. Working up the product with $^tBuNPF_6$ (0.136 g, 0.351 mmol) as described above gave yellow crystals of $[CpW(PMe_2Ph)_2(CO)_2]PF_6$ (**4b**) in 40% yield.

*3.12. Reactions of **2b** with L (L = PMe_3, PMe_2Ph, $PMePh_2$, $PEtPh_2$, PPh_3, $AsPh_3$ and NMe_3, py and SMe_2) in CH_3CN*

General procedure: Complex **2b** (0.056 g, 0.131 mmol) was dissolved along with the ligand (0.131 mmol) in CH_3CN (1.5 ml) in an NMR tube, that was sealed under N_2. The reactions were monitored by ^1H NMR (by observing the Cp peaks) and the products **3a–3f**, **3h**, **3i**, **3k** and **3l** were isolated as their BPh_4^- salts as described before. Reaction times, yields and deviations from the general procedure are noted in parentheses. L = PMe_3 (22 h, 68%), PMe_2Ph (4.75 h, 68%), $PMePh_2$ (11.5 h, 63%), $PEtPh_2$ (27.5 h, 74%), PPh_3 (51 h, 62%), $AsPh_3$ (123 h, 42%), NMe_3 (2.5 h, 72%, 0.29 mmol NMe_3), py (48.75 h, 51%) and SMe_2 (24 h, 49%).

*3.13. Reaction of **2b** with dppe in CH_3CN*

Complex **2b** (0.093 g, 0.218 mmol) and dppe (0.173 g, 0.439 mmol) were dissolved in CH_3CN (4.5 ml). The mixture was stirred in the dark at room temperature for four days. The solvent was then evaporated *in vacuo*. The residue was taken up in MeOH, and the solution was filtered to remove unchanged dppe, then concentrated. Addition of ether gave a very low yield of a yellow compound believed to be $[\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})]Br_2$. IR : ($CH_2Cl_2$) ν(CO): 2034s, 1955m, 1928s cm^{-1}.

The solvent was then evaporated *in vacuo* and the product isolated as its BPh_4^- salt, $[\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})](BPh_4)_2$ (0.161 g, 43%). This salt was found to be very unstable in solution.

*3.14. Reaction of **2b** with PCy_3 in CH_3CN*

Complex **2b** (0.08 g, 0.19 mmol) was dissolved in CH_3CN (7 ml). PCy_3 (0.073 g, 0.262 mmol) was added and the suspension was kept in the dark for seven days. The oily yellow product was worked up with $NaBPh_4$ as described above to give complex (**3g**) (0.030 g, 17%).

*3.15. Reactions of [$CpW(CO)_3CH_2I$] (**2c**) with PEt_3 or PPh_3*

Complex **2c** (0.062 g, 0.131 mmol) was dissolved in CH_3CN or CD_3CN (1.5 ml) in an NMR tube. The phosphine (0.262 mmol) was added and the tube sealed under N_2. The reactions were monitored by ^1H NMR spectroscopy (by observing the Cp peaks). The half-life for the reaction of (**2c**) with PEt_3 was too short to be determined. The products (**3d**) and (**3f**) were isolated as their BPh_4^- salts as described previously. Reaction times and yields are in parentheses: L = PEt_3 (15 min, 40%) and L = PPh_3 (10 h, 70%).

*3.16. Reaction of **2a** and **2c** with L (L = PCy_3 and NEt_3 respectively) in CH_2Cl_2*

The complex **2a** or **2c** (0.3 mmol) was dissolved in CH_2Cl_2 (2 ml), and $TlPF_6$ (0.45 mmol) and L (0.6 mmol) were added along with CH_2Cl_2 (4 ml). The solutions was stirred at room temperature (for reaction times and yields see below), then filtered, and the product was precipitated by addition of hexane. $[CpW(CO)_3CH_2PCy_3]PF_6$ (**3g**): 6 days; 60%; IR: (CH_2Cl_2) ν(CO): 2029s, 1945m, 1920s cm^{-1}; m.p.: 112–114°C. This complex was treated with more $NaBPh_4$ to give the BPh_4^- salt. $[CpW(CO)_3CH_2NEt_3]PF_6$ (**3j**): 3 days, 67%.

Acknowledgments

We thank the FRD and University of Cape Town for financial support of this research and Prof. G.E. Jackson for useful discussions on the rate studies.

References and notes

1 H.B. Friedrich and J.R. Moss, *Adv. Organomet. Chem., 33* (1991) 235.

2 (a) S.K. Mandal, D.M. Ho and M. Orchin, *J. Organomet. Chem., 397* (1990) 313; (b) R. McCrindle, G. Ferguson and A.J. McAlees, *J. Chem. Soc., Chem. Commun.*, (1990) 1524; (c) R. McCrindle, G.J. Arsenault, A. Gupta, M.J. Hampden-Smith, R.E. Rice and A.J. McAlees, *J. Chem. Soc. Dalton Trans.*, (1991) 949; (d) D.M. Hester and G.K. Yang, *Organometallics, 10* (1991) 369; (e) T.A. Annan, D.G. Tuck, M.A. Khan and C. Peppe, *Organometallics, 10* (1991) 2159; (f) H. Nishiyama, M. Horihata, T. Hirai, S. Wakamatsu and K. Itoh, *Organometallics, 10* (1991) 2706.

3 D.L. Thorn, *Organometallics, 1* (1982) 879, and references therein.

4 V. Guerchais and C. Lapinte, *J. Chem. Soc. Chem. Commun.*, (1986) 663, and references therein.

5 Y.C. Lin, J.C. Calabrese and S.S. Wreford, *J. Am. Chem. Soc., 105* (1983) 1679.

6 (a) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl., 15* (1976) 136; (b) C.P. Casey, M.A. Andrews, D.R. McAllister and J.E. Rinz, *J. Am. Chem. Soc., 102* (1980) 1927; (c) J.C. Calabrese, D.C. Roe, D.L. Thorn and T.H. Tulip, *Organometallics, 3* (1984) 1223.

7 (a) C.P. Casey, W.H. Miles, H. Tukada and J.M. O'Connor, *J. Am. Chem. Soc., 104* (1982) 3761; (b) C.P. Casey, in M. Jones and R.A. Moss (eds.) *Reactive Intermediates*, John Wiley, New York, 1981, vol. 2, ch. 4.

8 E.J. O'Connor and P. Helquist, *J. Am. Chem. Soc., 104* (1982) 1869.

9 H. Werner, W. Paul, R. Feser, R. Zolk and P. Thometzek, *Chem. Ber., 118* (1985) 261.

10 J.F. Hoover and J.M. Stryker, *Organometallics, 7* (1988) 2028, and references therein.

11 (a) C. Botha, J.R. Moss and S. Pelling, *J. Organomet. Chem., 220* (1981) C21; (b) S. Pelling, C. Botha and J.R. Moss, *J. Chem. Soc. Dalton Trans.,* (1983) 1495; (c) G.C.A. Bellinger, H.B. Friedrich and J.R. Moss, *J. Organomet. Chem., 366* (1989) 175.

12 M.L.H. Green, M. Ishaq and R.N. Whiteley, *J. Chem. Soc., (A)* (1967) 1508.

13 A.I. Vogel, *A Textbook of Practical Organic Chemistry*, 4th edn. Longman Ltd. London, 1978, p. 399.

14 R.B. King and D.M. Braitsch, *J. Organomet. Chem., 54* (1973) 9.

15 P.M. Stretch, *M.Sc. Thesis*, University of Cape Town, 1984, p. 43.

16 J.R. Moss, M.L. Niven and P.M. Stretch, *Inorg. Chim. Acta, 119* (1986) 117.

17 J.T. Malito, R. Shakir and J.L. Atwood, *J. Chem. Soc. Dalton Trans.,* (1980) 1253.

18 ^{13}C NMR data for [CpFe(CO)$_2$CH$_2$OCH$_3$] in CDCl$_3$ relative to TMS: 216.6 (CO), 85.9 (Cp), 65.3 (CH$_2$), 60.3 (CH$_3$) ppm.

19 (a) G. Erker, R. Schlund and C. Krüger, *J. Organomet. Chem., 338* (1988) C4; (b) G. Erker, R. Schlund, M. Albrecht and C. Sarter, *J. Organomet. Chem., 353* (1988) C27.

20 H.B. Friedrich, *Ph.D. Thesis*, University of Cape Town, 1990.

21 A.E. Steven and J.L. Beauchamp, *J. Am. Chem. Soc., 100* (1978) 2584.

22 R.B. King and J.J. Eisch, *Organometallic Synthesis,* vol. 1, Academic Press, London, 1965 pp. 155–156.

23 N.J. Cooper and M.L.H. Green, *J. Chem. Soc. Dalton Trans.,* (1979) 1121.

24 D. Seyferth, *Acc. Chem. Res., 5* (1972) 65.

25 (a) F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., John Wiley, New York, 1988, p. 1037; (b) K.W. Barnett, D.L. Beach, S.P. Gaydus and T.G. Pollmann, *J. Organomet. Chem., 69* (1974) 121.

26 F. Tafesse and M. Dilgassa, *Bull. Chem. Soc. Ethiop., 1* (1987) 83.

27 E.K. Barefield, P. McCarten and M.C. Hillhouse, *Organometallics, 4* (1985) 1682.

28 (a) C.A. Tollman, *Chem. Revs., 77* (1977) 313; (b) W.A. Henderson and C.A. Streuli, *J. Am. Chem. Soc., 82* (1960) 5791; (c) M.N. Golovin, M.D. Matiur Rahman, J.E. Belmonte and W.P. Giering, *Organometallics, 4* (1985) 1981; (d) T. Allman and R.G. Goel, *Can. J. Chem., 60* (1981) 716; (e) C.A. Tollman, *J. Am. Chem. Soc., 92* (1970) 2956; (f) R.P. Stewart and P.M. Treichel, *Inorg. Chem., 7* (1968) 1942; (g) R.J. Dennenberg and D.J. Darensbourg, *Inorg. Chem., 11* (1972) 72.

29 J. Emsley and D. Hall, *The Chemistry of Phosphorus*, Harper and Row, London, 1976, p. 255.

30 J. Emsley and D. Hall, *The Chemistry of Phosphorus*, Harper and Row, London, 1976, p. 114.

31 (a) R. Birdwhistell, P. Hackett and A.R. Manning, *J. Organomet. Chem., 157* (1978) 239; (b) M.A. El-Hinnawi and A.K. El-Qaseer, *J. Organomet. Chem., 281* (1985) 119.

32 H.B. Friedrich, J.R. Moss and B.K. Williamson, *J. Organomet. Chem., 384* (1990) 325.