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Haloalkyl Complexes of the Transition Metals. Part 5*. The Synthesis and Reactions of some New Pentamethylcyclopentadienyl Halomethyl and Methoxymethyl Complexes of Molybdenum(II) and Tungsten(II) and the X-ray Crystal Structure of the Cationic Ylide Complex $[\eta\text{-}C_5Me_5W(CO)_3CH_2PPh_3]I$

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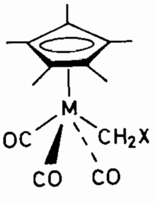
Abstract

Synthetic routes are described for the new halomethyl complexes of the type $[\eta\text{-}C_5Me_5M(CO)_3CH_2X]$. The complexes where M = Mo, X = Cl or OMe and M = W, X = Cl, I, OMe have been fully characterized. Reaction of $[\eta\text{-}C_5Me_5Mo(CO)_3CH_2Cl]$ with PPh_3 in methanol under reflux or acetonitrile at room temperature gives $[\eta\text{-}C_5Me_5Mo(CO)_2(PPh_3)Cl]$, whereas reaction of $[\eta\text{-}C_5Me_5W(CO)_3CH_2I]$ with PPh_3 under similar conditions gives the cationic phosphorus ylide complex $[\eta\text{-}C_5Me_5W(CO)_3CH_2PPh_3]I$. The structure of this ylide complex has been determined by X-ray crystallography. The complex crystallizes with half a molecule of CH_2Cl_2 in the monoclinic space group $P2_1/n$ with $a = 16.616(8)$, $b = 11.738(6)$, $c = 18.126(9)$ Å, $\beta = 101.74(2)°$ and $Z = 4$. The structure was solved and refined to $R = 0.076$. It confirms the formulation of the compound and the presence of the ylide ligand, $W\text{–}C_{ylide}$ 2.34(2) Å, $P\text{–}C_{ylide}$ 1.82(2) Å and the $W\text{–}C_{ylide}\text{–}P$ angle of 119(1)°.

Introduction

Monohalomethyl metal complexes $M\text{–}CH_2X$ may act as precursors for several important classes of compounds including carbene, hydroxymethyl and methylene bridged complexes [1]. These classes of compounds may provide useful models for intermediates proposed in important catalytic reactions such as the Fischer–Tropsch reaction [2]. Investigations into the synthesis, structure and reactivity of halomethyl- and other functionalized alkyl complexes are therefore important. Complexes of the type $M\text{–}CH_2X$ (where X = halogen) have been known for some time [3–5], as has the susceptibility of the halomethyl carbon atom to nucleophilic attack [3]. We have previously reported reactions of certain cyclopentadienyl chloromethyl complexes with tertiary phosphines and found that the products of such reactions are dependent on a number of factors, particularly the metal and its associated ligands [1, 6]. Thus, for example, $[\eta\text{-}C_5H_5Fe(CO)_2CH_2Cl]$ readily reacts with PPh_3 in methanol to give the cationic ylide complex $[\eta\text{-}C_5H_5Fe(CO)_2CH_2PPh_3]^+$, whereas $[\eta\text{-}C_5H_5Ru(CO)_2CH_2Cl]$ gives no ligand product under similar conditions. Also, $[\eta\text{-}C_5H_5W(CO)_3CH_2Cl]$ reacts with PPh_3 to give $[\eta\text{-}C_5H_5W(CO)_3CH_2PPh_3]^+$, whereas under similar conditions the analogous molybdenum complex yields only $[\eta\text{-}C_5H_5Mo(CO)_2(PPh_3)Cl]$ [1]. With a view to finding out more about the factors that affect the course of this type of reaction, we have now investigated the synthesis of some functionalized methyl complexes of molybdenum and tungsten containing the $\eta\text{-}C_5Me_5$ ligand. Pentamethylcyclopentadienyl compounds often show dramatically different chemistry from that shown by their unsubstituted analogues [7]. We now report on the synthesis and



I: M = Mo, X = Cl
II: M = Mo, X = OMe
III: M = Mo, X = Br
IV: M = W, X = Cl
V: M = W, X = OMe
VI: M = W, X = Br
VII: M = W, X = I
VIII: M = W, X = $CH_2PPh_3^+I^-$
IX: $\eta\text{-}C_5Me_5Mo(CO)_2(PPh_3)Cl$

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characterisation of some complexes of the type $[\eta\text{-}C_5Me_5M(CO)_3CH_2X]$ (M = Mo or W, X = Cl, Br, I or OMe) and compare the data and some chemistry with those of their $\eta\text{-}C_5H_5$ analogues. We also report on the reaction of $[\eta\text{-}C_5Me_5W(CO)_3CH_2I]$ with PPh_3, which gives the new cationic ylide complex $[\eta\text{-}C_5Me_5W(CO)_3CH_2PPh_3]I$, and we report the X-ray crystal structure of this complex.

Experimental

All reactions were performed under nitrogen using standard Schlenk tube techniques. Solvents were generally of analytical reagent grade and were further dried where necessary by distillation under nitrogen from a suitable drying reagent. The following compounds were obtained commercially: $[W(CO)_6]$, $[Mo(CO)_6]$ and C_5Me_5H, (Strem Chemicals Inc.); $ClCH_2OCH_3$ (Merck Chemical Company); CH_2ClI (Alpha Products); CH_2I_2 and CH_2Br_2 (BDH Chemicals Ltd.); PPh_3 (Merck Chemical Company); n-butyl lithium in n-hexane (Alpha Products) which was standardized before use. $[\eta\text{-}C_5Me_5M(CO)_3]Li$ (where M = Mo or W) were prepared as previously described [8].

Molecular distillations were performed using a modified Hickman still; column chromatography was carried out using BDH silica gel (40–60 mesh ASTM); melting points were determined using a Kofler hot stage microscope and are uncorrected; microanalyses were performed in the microanalytical laboratory at the University of Cape Town; IR spectra were recorded on Perkin-Elmer 180 and 983 grating spectrophotometers; ^1H NMR spectra were recorded on Varian XL100 (100 MHz) and Bruker WH90 (90 MHz) spectrometers (chemical shifts are relative to tetramethylsilane); mass spectra were recorded on a VG micromass 16F spectrometer operating at 70 eV ionising voltage; samples were introduced as solids, oils or hexane solutions using the direct probe. Characterization data for compounds prepared are given in Table I and mass spectra data in Table II.

Preparation of $[\eta\text{-}C_5Me_5Mo(CO)_3CH_2Cl]$ (I)

(a) A deep red solution of $[\eta\text{-}C_5Me_5Mo(CO)_3]Li$ (7 mmol) in THF (80 cm^3) was added dropwise with stirring to a solution of CH_2ClI (2.40 g, 1.37 mmol) in THF (5 cm^3). This solution turned black on stirring for 3 h at room temperature. The solvent was removed and the residue extracted with hexane. On cooling this solution to 0 °C, $[\eta\text{-}C_5Me_5Mo(CO)_3Cl]$ (0.06 g, 2%) crystallized out. This was filtered off and identified by comparison with previously reported data [8]. The filtrate was cooled to –78 °C when yellow crystals of compound **I** (0.60 g, 24%) were obtained. When a similar reaction to the above was carried out using CH_2ClBr, **I** was obtained in 40% yield.

(b) $[\eta\text{-}C_5Me_5Mo(CO)_3CH_2OMe]$ (0.09 g, 0.25 mmol) was dissolved in hexane (10 cm^3) and dry HCl

TABLE I. Characterization Data for Compounds of the Type $[\eta\text{-}C_5Me_5M(CO)_3CH_2X]$

Compound			Melting point (°C)	Analysis (%)[a]	ν(CO) (cm^{-1})[b]	^1H NMR[c]
M	X	Number				
Mo	Cl	I	87–94 decomp.	C, 45.75(46.11) H, 4.90(4.70)	2024(s) 1946(s) 1929(s)	1.54(s, 15H) 3.91(s, 2H)
	OMe	II	57–65	C, 50.0(50.0) H, 5.61(5.60)	2016(s) 1937(vs) 1921(s)	1.62(s, 15H) 3.24(s, 3H) 4.29(s, 2H)
	Br	III	75–85 decomp.		2023(s) 1947(vs) 1929(s)	1.35(s, 15H) 3.16(s, 2H)
W	Cl	IV	114–122 decomp.	C, 37.7(37.15) H, 4.0(3.79)	2020(s) 1937(vs) 1921(s)	1.64(s, 15H) 4.06(s, 2H)
	OMe	V	71–76	C, 42.05(40.2) H, 4.8(4.50)	2014(s) 1929(vs) 1913(s)	1.72(s, 15H) 3.21(s, 3H) 4.32(s, 2H)
	Br	VI	110–113 decomp.		2020(s) 1935(vs) 1922(s)	1.55(s, 15H) 3.55(s, 2H)
	I	VII	88–92	C, 31.3(30.9) H, 3.3(3.15)	2019(s) 1934(vs) 1922(s)	1.56(s, 15H) 2.84(s, 2H)
	$CH_2PPh_3^+$	VIII[d]	134–140 decomp.	C, 44.4(44.4) H, 3.8(3.84)	2023(s) 1934(s) 1920(sh) $CDCl_3$	1.62[d, 2H, J(P–H) = 14Hz] 2.16(s, 15H) 7.73(m, 15H)

[a] Calculated values in parentheses. [b] Measured in n-hexane except when otherwise stated. [c] Measured in C_6D_6 except when otherwise stated; s = singlet, d = doublet, m = multiplet; δppm. [d] Compound crystallizes with 1 mol CH_2Cl_2.

TABLE II. Mass Spectral Data for some Compounds of Type [η-$C_5Me_5M(CO)_3CH_2X$]

Compound			*m/e* values and suggested assignments[a]
M	X	Number	
Mo	Cl	I	338 (M–CO), 302 (M–CO–Cl), 282 (M–3CO)
	OMe	II	334 (M–CO), 304 (M–2CO–2H), 288 (M–2CO–H_2O), 276 (M–3CO–2H), 259 (M–2CO–CH_2OMe–2H)
	Br	III	382 (M–CO), 368 (M–CO–CH_2), 288 (M–2CO–H_2O), 340 (M–2CO–CH_2), 326 (M–3CO)
W	Cl	IV	452 (M), 424 (M–CO), 396 (M–2CO), 368 (M–3CO)
	OMe	V	420 (M–CO), 403 (M–CO–OH), 390 (M–2CO–2H), 373 (M–2CO–2H–OH), 364 (M–3CO)
	Br	VI	496 (M), 482 (M–CO–CH_2), 468 (M–2CO), 454 (M–2CO–CH_2), 440 (M–3CO)
	I	VII	532 (M–CH_2), 516 (M–CO), 502 (M–CO–CH_2), 488 (M–2CO), 458 (M–3CO–2H), 444 (M–3CO–CH_2–2H), 389 (M–CO–I), 373 (M–CO–I–CH_2–2H), 345 (M–2CO–I–CH_2–2H)

[a]All ions have a single positive charge.

gas bubbled through the solution at room temperature for 15 min. During this time, the yellow solution darkened to orange and a small amount of purple solid formed. The solution was protected from light and allowed to stand for 10 min. This solution was filtered and the solvent removed under reduced pressure from the filtrate to give a residue. This residue was taken up in hexane and cooled to –78 °C to yield yellow–orange crystals of **I** (0.07 g, 78%).

Preparation of [η-$C_5Me_5Mo(CO)_3CH_2OMe$] (II)

A solution of [η-$C_5Me_5Mo(CO)_3$]Li (7 mmol) in THF (80 cm^3) was added dropwise with stirring to a solution of $ClCH_2OMe$ (1.00 cm^3, 1.08 g, 13.4 mmol) in THF (5 cm^3) at 0 °C. The solution was then allowed to warm up to room temperature and stirred for 3 h. The deep red solution went black over this time. The solvent was removed from the reaction solution and the resulting residue extracted with hexane. The yellow–orange hexane extracts were concentrated and chromatographed. Elution with 20% ether/hexane gave compound **II** as yellow crystals (0.47 g, 19%). Elution with dichloromethane then gave [η-$C_5Me_5Mo(CO)_3Cl$] (0.10 g, 5%).

Preparation of [η-$C_5Me_5Mo(CO)_3CH_2Br$] (III)

(a) A solution of [η-$C_5Me_5Mo(CO)_3$]Li (7 mmol) in THF (80 cm^3) was added dropwise to a solution of CH_2Br_2 (1.00 cm^3, 2.50 g, 14.4 mmol) in THF (10 cm^3). The solution was stirred at room temperature for 2 h and the solvent removed under reduced pressure. The residue was extracted with hexane and cooled to –78 °C to give oily orange crystals of **III** (0.43 g, 30%). The product was contaminated with C_5Me_5H, but due to its instability it was not further purified and satisfactory microanalyses were not obtained.

(b) Dry HBr gas was bubbled through a solution of **II** (0.05 g, 0.14 mmol) in hexane (10 cm^3) for 5 min. The solvent and excess HBr were removed under reduced pressure and the residue was taken up in hexane. Cooling to –78 °C gave **III** as yellow–orange crystals (0.033 g, 58%).

Attempted Preparation of [η-$C_5Me_5Mo(CO)_3CH_2I$]

(a) Dry HI gas was bubbled through a solution of **II** (0.30 g, 0.83 mmol) at 0 °C for 12 min. The solution rapidly went a deep orange–red colour. The solvent was removed and the residue extracted with hexane. The hexane extracts were filtered and cooled to –78 °C to give an orange–red crystalline material (0.28 g). An IR spectrum of this orange–red solid showed ν(CO) bands (hexane) at 2027(m), 1949(s) and 1929(m) cm^{-1} which we attributed to [η-$C_5Me_5Mo(CO)_3CH_2I$] as well as ν(CO) bands of [η-$C_5Me_5Mo(CO)_3I$] [8]. Attempts to separate these two compounds were not successful and may be due to the apparently easy decomposition of the iodomethyl compound to the iodide compound.

(b) The reaction of [η-$C_5Me_5Mo(CO)_3$]Li (7 mmol) with CH_2I_2 (12.4 mmol) in THF (80 cm^3) resulted only in the isolation of red [η-$C_5Me_5Mo(CO)_3I$] (0.38 g, 25%).

Preparation of [η-$C_5Me_5W(CO)_3CH_2Cl$] (IV)

Dry HCl gas was bubbled through a solution of [η-$C_5Me_5W(CO)_3CH_2OMe$] (0.14 g, 0.55 mmol) in hexane (15 cm^3) at room temperature for 15 min. The yellow solution paled and a small amount of black residue formed. The solution was protected from light and allowed to stand for 10 min. After this time, the solution was filtered and the solvent and excess HCl removed under reduced pressure. The residue was extracted with hexane, filtered and cooled to –78 °C to give yellow crystalline (**IV**) (0.14 g, 94%).

Preparation of [η-$C_5Me_5W(CO)_3CH_2OMe$] (V)

A deep red solution of [η-$C_5Me_5W(CO)_3$]Li (7 mmol) in THF (80 cm^3) was added dropwise with stirring to a solution of $ClCH_2OMe$ (1.00 cm^3, 1.08 g, 13.4 mmol) in THF (5 cm^3). The solution was stirred at room temperature for 3 h, during which time the solution turned black. The solvent was removed under reduced pressure and the residue extracted with hexane, filtered and the solvent again removed. The resulting orange–yellow oil was chromatographed on a column. Elution with 40% ether/hexane gave a yellow band. Removal of the solvent and recrystallisation of the residue from hexane at −78 °C gave **V** as yellow microcrystals (0.55 g, 18%). Both microanalytical and ^{1}H NMR data suggested that the product was contaminated with some C_5Me_5H.

Preparation of [η-C_5Me_5W(CO)$_3$$CH_2Br$] (VI)

Dry HBr gas was bubbled through a solution of **V** (0.11 g, 0.41 mmol) in hexane (10 cm^3) for 10 min. The solvent was removed and the resulting residue extracted with hexane. The hexane solution was filtered and cooled to −78 °C to give orange–red crystals of **VI** (0.12 g, 93%). The product was contaminated with about 5% of [η-$C_5Me_5W(CO)_3Br$], from which **VI** could not be completely separated.

The reaction of [η-$C_5Me_5W(CO)_3$]Li with CH_2Br_2 resulted in the isolation of yellow crystals in *ca.* 40% yield. IR, ^{1}H NMR, mass spectra and microanalysis suggested that these yellow crystals were [η-$C_5Me_5W(CO)_3CH_3$] by comparison with data reported for this compound [9] and with data obtained on the product of the reaction of [η-$C_5Me_5W(CO)_3$]Li with CH_3I.

Preparation of [η-C_5Me_5W(CO)$_3$$CH_2I$] (VII)

(a) A solution of [η-$C_5Me_5W(CO)_3$]Li (7 mmol) in THF (80 cm^3) was added dropwise to a solution of CH_2ClI (1.00 cm^3, 2.40 g, 13.7 mmol) in THF (5 cm^3) and the solution stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with hexane. This hexane solution was filtered, concentrated and cooled to −78 °C to give bright yellow crystals of **VII** (0.63 g, 17%).

Reaction of [η-$C_5Me_5W(CO)_3$]Li with CH_2I_2 gave [η-$C_5Me_5W(CO)_3CH_3$] in *ca.* 45% yield.

(b) Dry HI gas was bubbled through a solution of **V** (0.12 g, 0.27 mmol) in hexane (10 cm^3) for 30 min. The yellow solution gradually darkened to red–brown. The solvent was removed and the residue extracted with hexane. The resulting solution was filtered and cooled to −78 °C to give a red crystalline solid (0.11 g). This solid was then chromatographed. Elution with 20% CH_2Cl_2/hexane gave a yellow band which after removal of solvent gave **VII** (0.105 g, 73%). Elution with CH_2Cl_2 gave a red band which after removal of solvent yielded [η-$C_5Me_5W(CO)_3I$] (0.03 g, 21%) which was identified by its melting point (m.p.) and IR spectrum [8].

Reaction of [η-C_5Me_5W(CO)$_3$$CH_2I$] with PPh_3

(a) PPh_3 (0.09 g, 0.36 mmol) was added to a solution of **VII** (0.17 g, 0.32 mmol) in acetonitrile (10 cm^3) and the resulting solution allowed to stand in the dark for 20 days. During this time, the solution darkened and a small amount of yellow crystals was deposited. The solvent was removed under reduced pressure and the red oily residue extracted with hexane; this solution contained **VII** and [η-$C_5Me_5W(CO)_3I$]. The hexane-insoluble residue was recrystallized from CH_2Cl_2/hexane to give yellow crystals of [η-$C_5Me_5W(CO)_3CH_2PPh_3$]I·CH_2Cl_2 **VIII** (79%).

(b) A solution of **VII** (0.21 g, 0.39 mmol) and PPh_3 (0.13 g, 0.50 mmol) in methanol (10 cm^3) was heated under reflux for 3 h. The solution darkened from yellow to orange. The solvent was removed under reduced pressure to give an orange oil. This oil was extracted with hexane and shown by IR to be a mixture of **VII** and **V**. The hexane-insoluble residue was recrystallized twice from CH_2Cl_2/hexane to give orange–yellow prisms of **VIII** in 57% yield.

Reaction of [η-C_5Me_5W(CO)$_3$$CH_2Cl$] with PPh_3

PPh_3 (0.18 g, 0.69 mmol) was added to a solution of **IV** in methanol (10 cm^3) and the mixture heated under reflux for 3 h. The solvent was removed under reduced pressure and extraction of the residue with hexane gave **V** (12%), which was identified by its IR spectrum. The hexane-insoluble residue gave [η-$C_5Me_5W(CO)_3CH_2PPh_3$]Cl (29%) which was identified by comparing its IR spectrum with that of **VIII**.

Reaction of [η-C_5Me_5Mo(CO)$_3$$CH_2Cl$] with PPh_3

(a) A solution of **I** (0.25 g, 0.69 mmol) and PPh_3 (0.22 g, 0.82 mmol) in acetonitrile (15 cm^3) was allowed to stand in the dark for 6 days, during which time the solution changed in colour from yellow–orange to deep red. The solvent was removed under reduced pressure and the resulting solid recrystallized from CH_2Cl_2/hexane to give fine orange needles of [η-$C_5Me_5Mo(CO)_2(PPh_3)Cl$] (**IX**) (0.13 g, 53%) m.p. 140–146 °C; IR ν(CO)(CH_2Cl_2) 1948(vs), 1863(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.74(m, C_5Me_5), 7.39(m, PPh_3) ppm. *Anal.* Calc. for $C_{30}H_{30}ClO_2PMo$. C, 61.6; H, 5.17. Found: C, 60.2; H, 5.2%.

(b) A solution of **I** (0.26 g, 0.71 mmol) and PPh_3 (0.24 g, 0.93 mmol) in methanol (30 cm^3) was heated under reflux for 3 h. The solvent was then removed from the resulting red–orange solution and the residue recrystallized from CH_2Cl_2/hexane to give **IX** (0.15 g, 75%). Compound **II** (15%) was extracted from the reaction mixture using hexane.

Crystal and Intensity Data

Crystals of compound **VIII** suitable for X-ray analysis were obtained by recrystallisation from

TABLE III. Crystal Data and Refinement Parameters for [η-$C_5Me_5W(CO)_3CH_2PPh_3$]I·$0.5CH_2Cl_2$ (VIII)

Molecular formula	$C_{32}H_{32}O_3PIW \cdot 0.5CH_2Cl_2$
M_r (g mol^{-1})	848.80
Space group	$P2_1/n$
a (Å)	16.616(8)
b (Å)	11.738(6)
c (Å)	18.126(9)
β (°)	101.74(2)
V (Å^3)	3461(1)
D_m (Mg m^{-3})	1.6
D_c (Mg m^{-3}) (for $Z = 4$)	1.50
F(000)	1644
μ(Mo Kα (cm^{-1})	40.64
Data collection	
Crystal dimensions (mm)	0.28 × 0.18 × 0.10
Scan mode	$\omega - 2\theta$
Scan width (°θ)	1.2
Scan speed (°θ s^{-1})	0.04
Range scanned (2θ) (°)	7–46
Stability of standard reflections (%)	4.8
Number of reflections collected	4647
Number of reflections observed	3310 with $I_{rel} > 2\sigma I_{rel}$
Refinement	
Number of variables	207
$R = \dfrac{\Sigma \lVert F_o\rvert - \lvert F_c \rVert}{\Sigma \lvert F_o \rvert}$	0.076
U_{iso} of hydrogen atoms	
Phenyl hydrogens (Å^2)	0.08(2)
Methyl hydrogens (Å^2)	0.08(2)
Methylene hydrogens (Å^2) (of ylide ligand)	0.10(2)

CH_2Cl_2/hexane. Preliminary photography Cu Kα, λ = 1.5418 Å) established the space group as $P2_1/n$. Accurate cell dimensions were obtained by a least-squares analysis on the setting angles of 25 high order reflections measured on a Philips PW1100 four circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Intensities were collected with an $\omega - 2\theta$ scan technique. The intensities of three reference reflections were monitored every 68 measured reflections throughout the data collection; this ensured instrument stability and monitored any crystal decomposition. The data were corrected for Lorentz polarization effects but not for absorption. Crystal data and experimental details of the data collection are given in Table III.

Solution and Refinement of the Structure

The position of the tungsten atom was located from a Patterson map; subsequent difference syntheses revealed the positions of the remaining non-hydrogen atoms (except for those of the solvent of crystallization). In the final full-matrix refinements, W, I and P atoms were treated anisotropically. The hydrogens on the phenyl rings and the methylene group were modelled with a single temperature factor and placed at 1.00 Å from their parent carbons, their positions being dictated by the geometry of the molecule. The methyls on the cyclopentadienyl ring were treated as rigid groups again with a single temperature factor for all the hydrogens.

Location of the Solvent of Crystallization

A difference map obtained after insertion of the ion pair [η-$C_5Me_5W(CO)_3CH_2PPh_3$]I revealed the solvent of crystallization with peaks of about half the expected electron density and with one of the chlorine atoms apparently disordered, its electron density smeared into two peaks. A ^{1}H NMR spectrum recorded on the crystals at this stage (about 1 month after preparation and original characterization) showed that the relative intensity of the CH_2Cl_2 proton peak had decreased by 50%, concurring with the crystallographic observation of half a solvent molecule per formula unit of salt. The disorder was modelled by placing the one chlorine atom at the midpoint of its smeared electron density peaks, and the entire molecule was inserted at site occupancy factor one half, as per the solvent loss. The chlorine atoms were inserted anisotropically and carbon isotropically.

In the final cycle of refinement, the mean estimated standards deviation (e.s.d.) in the parameters of the non-hydrogen atoms was 100 times greater than the average parameter shift, while the difference map was smooth except next to the tungsten and iodine atoms where the largest residual peaks were <2.0 e Å^{-3}. Further details of the final refinement are shown in Table III. Fractional atomic coordinates and temperature factors are given in Table IV. Scattering factors for all non-hydrogen atoms were taken from Cromer and Mann [10] and from Stewart, Davidson and Simpson [11] for H, with dispersion corrections from Cromer and Liberman [12]. All computations were performed at the Computer Centre of the University of Cape Town on a Sperry 1100/81 using SHELX [13] (data reduction, structure solution and refinement), PLUTO [14] (illustrations) and XANADU [15] (molecular geometry).

Results and Discussion

For the synthesis of the pentamethylcyclopentadienyl molybdenum and tungsten complexes of the type [η-$C_5Me_5M(CO)_3CH_2X$] we followed essentially the same routes as were used for the synthesis of the analogous cyclopentadienyl complex [3, 4]. In some cases, we demonstrated two preparative routes for

TABLE IV. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^4) for Non-hydrogen Atoms for **VIII**

Atoms	x/a	y/b	z/c	U_{iso}
W(1)	2357(1)	1940(1)	−22(1)	482^a
I(1)	1512(1)	5051(1)	7365(1)	720^a
P(1)	924(3)	1275(5)	8265(3)	414^a
Cl(1)	6097(10)	2372(24)	8838(9)	1316^a
Cl(2)	6072(11)	2222(38)	7375(10)	2238^a
O(2)	813(12)	3224(18)	10159(11)	1003(61)
O(3)	2674(12)	−679(20)	9698(12)	1028(65)
O(4)	1894(13)	802(20)	11365(13)	1157(73)
C(1)	1902(11)	1945(19)	8670(11)	476(49)
C(2)	1391(16)	2640(22)	10042(14)	685(69)
C(3)	2515(16)	286(25)	9775(14)	744(75)
C(4)	2068(15)	1221(23)	10809(15)	715(70)
C(5)	5566(29)	1993(46)	7374(27)	687(130)
C(111)	2996(13)	3728(19)	9986(12)	503(53)
C(121)	3105(12)	3280(17)	10769(11)	467(51)
C(131)	3630(12)	2287(17)	10769(11)	443(51)
C(141)	3778(12)	2132(18)	10055(11)	490(52)
C(151)	3397(11)	3025(19)	9568(11)	453(47)
C(112)	2551(14)	4816(21)	9756(13)	648(66)
C(122)	2851(15)	3811(23)	11401(13)	703(69)
C(132)	4004(15)	1640(22)	11446(13)	669(68)
C(142)	4351(16)	1282(23)	9854(15)	775(75)
C(152)	3495(15)	3286(21)	8799(12)	645(65)
C(11)	19(10)	2001(19)	8443(11)	517(52)
C(12)	−712(10)	1468(19)	8432(11)	553(58)
C(13)	−1379(15)	2050(23)	8500(13)	716(68)
C(14)	−1360(17)	3240(25)	8585(15)	830(80)
C(15)	−665(16)	3806(27)	8561(15)	862(83)
C(16)	54(15)	3202(23)	8487(13)	718(69)
C(21)	827(10)	1232(16)	7251(10)	414(47)
C(22)	162(10)	656(16)	6816(10)	549(57)
C(23)	49(14)	704(21)	6032(13)	634(64)
C(24)	540(14)	1303(20)	5708(14)	629(63)
C(25)	1187(15)	1948(24)	6106(14)	717(67)
C(26)	1330(13)	1889(21)	6893(12)	594(57)
C(31)	909(10)	−201(15)	8579(10)	363(45)
C(32)	1292(10)	−999(15)	8179(10)	578(59)
C(33)	1307(16)	−2122(25)	8448(15)	782(75)
C(34)	1007(15)	−2403(24)	9058(14)	755(75)
C(35)	661(15)	−1643(22)	9448(14)	726(72)
C(36)	621(13)	−493(20)	9201(12)	557(58)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U_{ij} values for atoms treated anisotropically with e.s.d.s in parentheses (Å^2 × 10^4)						
W(1)	533(5)	453(5)	405(5)	30(5)	−39(4)	−106(5)
I(1)	902(13)	474(9)	759(11)	54(9)	104(10)	35(9)
P(1)	440(31)	395(3)	363(28)	−30(24)	−24(23)	−4(25)
Cl(1)	709(100)	2716(293)	549(88)	−629(132)	181(75)	−449(136)
Cl(2)	700(114)	5454(607)	626(106)	−173(216)	274(88)	−580(222)

$^a U$ = (1/3)(trace of the orthogonal U_{ij} matrix)

the synthesis of the functionalized alkyl complexes (see 'Experimental'). Thus, the complexes [η-C_5Me_5-$M(CO)_3CH_2OMe$] were prepared by the reactions of Li[η-$C_5Me_5M(CO)_3$] with $ClCH_2OMe$ (where M = Mo or W). The reactions of the resulting methoxymethyl complexes with anhydrous HX gas resulted in the formation of [η-$C_5Me_5M(CO)_3CH_2X$], *i.e.*, following the route of Green *et al.* [3].

$$\mathrm{Li[\eta\text{-}C_5Me_5M(CO)_3] + ClCH_2OMe \longrightarrow [\eta\text{-}C_5Me_5M(CO)_3CH_2OMe]}$$

$$\mathrm{[\eta\text{-}C_5Me_5M(CO)_3CH_2OMe] + HX \longrightarrow [\eta\text{-}C_5Me_5M(CO)_3CH_2X]}$$

(M = Mo or W; X = Cl, Br or I)

We also investigated the reactions of Li[η-C_5Me_5-$M(CO)_3$] with a number of dihalomethanes, *i.e.*, following reactions similar to these reported by King and Braitsch for the cyclopentadienyl complexes [4]. Thus, for example,

$$\mathrm{Li[\eta\text{-}C_5Me_5Mo(CO)_3] + CH_2Br_2 \longrightarrow [\eta\text{-}C_5Me_5Mo(CO)_3CH_2Br]}$$

In most cases, however, the reactions with dihalomethanes did not provide useful routes to the halomethyl complexes and gave unexpected products in some cases. Thus, the reaction of Li[η-C_5Me_5-$W(CO)_3$] with CH_2ClI gave [η-$C_5Me_5W(CO)_3CH_2I$] in 17% yield, instead of the expected chloromethyl complex, and reaction of Li[η-$C_5Me_5W(CO)_3$] with CH_2Br_2 gave [η-$C_5Me_5W(CO)_3CH_3$] in 42% yield. The isolation of this methyl complex may result from the following type of reaction sequence:

$$\mathrm{M{-}CH_2Br \longrightarrow [M{=}CH_2]^+ \longrightarrow M{-}CH_3}$$

Precedents for this type of sequence have been reported [5, 28].

The cyclopentadienyl compounds [η-C_5H_5M-$(CO)_3CH_2X$] where M = Mo or W and X = Cl, Br or I have all been described as unstable, with the order of stability being $-CH_2Cl > CH_2Br > CH_2I$ [3, 4]. We have recently isolated pure samples of the three halomethyl complexes of W and find them to be fairly stable in the absence of light and with a stability order of $CH_2Cl > CH_2Br > CH_2I$ [16]. Also [η-$C_5H_5Mo(CO)_3CH_2Cl$] appears less stable than [η-$C_5H_5W(CO)_3CH_2Cl$]. Similarly with the present η-C_5Me_5 complexes, the tungsten complexes are all stable whereas the Mo complexes are less stable with $Mo{-}CH_2Cl > Mo{-}CH_2Br$; we were unable to isolate $Mo{-}CH_2I$ free from Mo–I. The carbonyl stretching frequencies (see Table I) for the Mo complexes were lower than those for the W complexes, but there was little variation on changing X. Similar results were found for the analogous C_5H_5 compounds [16]. Also the carbonyl stretching frequencies for the C_5Me_5 compounds were found to be approximately 12–15 cm^{-1} lower than those observed for the C_5H_5 analogues [3, 4, 16]. This latter effect has been observed previously and attributed to the greater electron-donating ability of C_5Me_5 ligand as compared to C_5H_5. The ^1H NMR spectra show the expected trend for the chemical shifts (δ ppm) for the CH_2–X protons, *i.e.*, $CH_2OMe > CH_2Cl > CH_2Br > CH_2I$ (see Table I).

The mass spectra were recorded for the compounds **I** to **VII** (see Table II). The three Mo compounds examined did not show parent ions under the conditions used, and in each case the highest m/e ions corresponded to $[M{-}CO]^+$. For the W compounds **V** and **VI**, parent ions were observed with the expected isotope patterns, thus confirming their formulations. The highest m/e ion for **V** corresponded to $[M{-}CO]^+$, whereas for **VII** the highest m/e ion corresponded to $[M{-}CH_2]^+$. Fragmentation data and suggested assignments are given in Table II.

We have previously reported [1] that the reaction of [η-$C_5H_5Mo(CO)_3CH_2Cl$] with PPh_3 gave [η-C_5H_5-$Mo(CO)_2(PPh_3)Cl$], whereas a similar reaction with [η-$C_5H_5W(CO)_3CH_2Cl$] resulted in the formation of the cationic ylide complex [η-$C_5H_5W(CO)_3CH_2$-$PPh_3]^+$. We were therefore interested in investigating reactions of the pentamethylcyclopentadienyl analogues, *i.e.*, [η-$C_5Me_5M(CO)_3CH_2Cl$] (M = Mo or W) with PPh_3, to see if the presence of the C_5Me_5 ligand would affect the course of the reaction. Our results show that the presence of the C_5Me_5 ligand does not appear to alter the course of the reaction since the reaction of [η-$C_5Me_5Mo(CO)_3CH_2Cl$] with PPh_3 gave [η-$C_5Me_5Mo(CO)_2(PPh_3)Cl$] and [η-$C_5Me_5W(CO)_3CH_2Cl$] gave [η-$C_5Me_5W(CO)_3CH_2$-$PPh_3]^+$, *i.e.*, products which are completely analogous to those formed in the reactions of the cyclopentadienyl compounds. Although the reaction of **I** with PPh_3 results in the loss of the methylene group, if a solution of **I** in methanol is allowed to stand overnight in the dark, then the main product isolated is **II**. Similarly, if **III** is refluxed in methanol for 1 h, IR spectroscopy suggested that the products were **II** (90%) and [η-$C_5Me_5Mo(CO)_3Br$] (10%). The reactions of either **I** or **III** that result in formation of **II** presumably involve the retention of the methylene group. We also find that the reaction of [η-$C_5Me_5W(CO)_3CH_2I$] with PPh_3 results in the formation of a higher yield of the cationic ylide complex [η-$C_5Me_5W(CO)_3CH_2PPh_3]^+$ than from **IV**. This might be expected since iodide is a better leaving group than chloride, and we have found this behaviour with other $M{-}CH_2X$ compounds [16]. In order to completely characterize the cationic ylide complex, **VIII** and to find out more information about the bonding of this ligand to metals, we have carried out an X-ray structural investigation of [η-C_5Me_5-$W(CO)_3CH_2PPh_3$]I. Ylides have been found to be useful ligands for transition metals only relatively recently [17–19] and although a number of structural determinations have been carried out on phosphorus ylide complexes [20–24], only one of these reports concerns a tungsten complex [24].

Description of the Structure of [η-C_5Me_5W(CO)$_3$ CH_2PPh_3]I

A view showing the molecular structure of [η-$C_5Me_5W(CO)_3CH_2PPh_3$]I·0.5CH_2Cl_2 with atomic labelling is given in Fig. 1. Bond lengths and angles are shown in Tables V and VI, respectively. The structure consists of discrete ion pairs with no un-

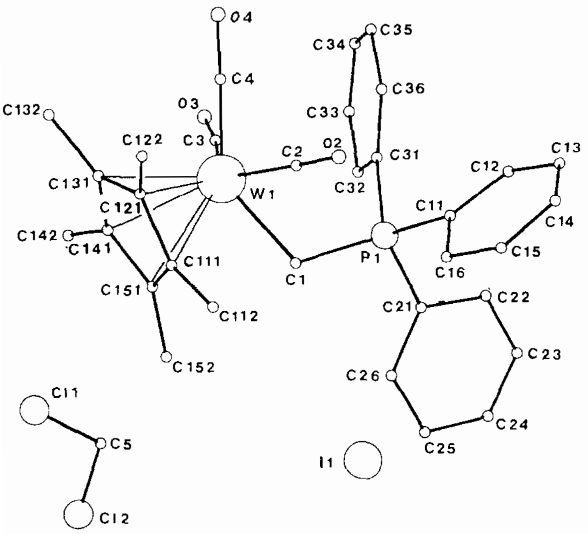

Fig. 1. The molecular structure with atom labelling for [η-$C_5Me_5W(CO)_3CH_2PPh_3$]I·0.5CH_2Cl_2 (VIII).

TABLE V. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses for **VIII**

W–C(1)	2.34(2)
W–C(2)	1.83(3)
W–C(3)	2.00(3)
W–C(4)	1.87(3)
W(1)–C(111)	2.35(2)
W(1)–C(121)	2.31(2)
W(1)–C(131)	2.34(2)
W(1)–C(141)	2.35(2)
W(1)–C(151)	2.38(2)
C(1)–P(1)	1.82(2)
C(2)–O(2)	1.23(3)
C(3)–O(3)	1.18(3)
C(4)–O(4)	1.21(3)
P(1)–C(11)	1.81(2)
P(1)–C(21)	1.81(2)
P(1)–C(31)	1.83(2)
C(111)–C(121)	1.49(3)
C(121)–C(131)	1.46(3)
C(131)–C(141)	1.38(3)
C(141)–C(151)	1.43(3)
C(111)–C(151)	1.38(3)
C(111)–C(112)	1.49(3)
C(121)–C(122)	1.44(3)
C(131)–C(132)	1.47(3)
C(141)–C(142)	1.48(3)
C(151)–C(152)	1.47(3)
C–C phenyl in range	1.33(3)–1.42(3)

TABLE VI. Bond Angles (°) for all Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses for **VIII**

C(2)–W(1)–C(1)	87.5(0.9)
C(3)–W(1)–C(1)	81.0(0.9)
C(3)–W(1)–C(2)	126.6(1.1)
C(4)–W(1)–C(1)	137.2(0.9)
C(4)–W(1)–C(2)	77.2(1.1)
C(4)–W(1)–C(3)	77.0(1.1)
C(111)–W(1)–C(1)	93.2(0.7)
C(111)–W(1)–C(2)	90.0(0.9)
C(111)–W(1)–C(3)	142.3(0.9)
C(111)–W(1)–C(4)	125.9(0.9)
C(121)–W(1)–C(1)	130.5(0.7)
C(121)–W(1)–C(2)	91.3(0.9)
C(121)–W(1)–C(3)	134.4(0.9)
C(121)–W(1)–C(4)	90.1(0.9)
C(121)–W(1)–C(111)	37.3(0.7)
C(131)–W(1)–C(1)	133.4(0.7)
C(131)–W(1)–C(2)	125.4(0.9)
C(131)–W(1)–C(3)	98.4(0.9)
C(131)–W(1)–C(4)	86.2(0.9)
C(131)–W(1)–C(111)	59.3(0.7)
C(131)–W–(1)–C(121)	36.5(0.7)
C(141)–W(1)–C(1)	100.0(0.7)
C(141)–W(1)–C(2)	147.0(1.0)
C(141)–W(1)–C(3)	86.4(0.9)
C(141)–W(1)–C(4)	114.5(0.9)
C(141)–W(1)–C(111)	57.7(0.7)
C(141)–W(1)–C(121)	59.4(0.7)
C(141)–W(1)–C(131)	34.2(0.7)
C(151)–W(1)–C(1)	77.7(0.7)
C(151)–W(1)–C(2)	118.8(0.9)
C(151)–W(1)–C(3)	109.3(0.9)
C(151)–W(1)–C(4)	114.3(0.9)
C(151)–W(1)–C(111)	33.9(0.7)
C(151)–W(1)–C(121)	59.9(0.7)
C(151)–W(1)–C(131)	58.3(0.7)
C(151)–W(1)–C(141)	35.2(0.7)
C(11)–P(1)–C(1)	115.5(0.9)
C(21)–P(1)–C(1)	107.9(0.8)
C(21)–P(1)–C(11)	106.7(0.9)
C(31)–P(1)–C(1)	110.6(0.9)
C(31)–P(1)–C(11)	109.1(0.9)
C(31)–P(1)–C(21)	106.6(0.8)
P(1)–C(1)–W(1)	119.0(1.0)
O(2)–C(2)–W(1)	170.3(2.2)
O(3)–C(3)–W(1)	174.1(2.3)
O(4)–C(4)–W(1)	176.9(2.4)
C(121)–C(111)–W(1)	70.0(1.1)
C(151)–C(111)–W(1)	74.4(1.3)
C(151)–C(111)–C(121)	109.5(1.8)
C(112)–C(111)–W(1)	124.4(1.5)
C(112)–C(111)–C(121)	121.7(1.9)
C(112)–C(111)–C(151)	128.8(2.0)
C(111)–C(121)–W(1)	72.7(1.1)
C(131)–C(121)–W(1)	72.6(1.1)
C(131)–C(121)–C(111)	103.8(1.7)
C(122)–C(121)–W(1)	125.4(1.5)
C(122)–C(121)–C(111)	127.3(2.0)
C(122)–C(121)–C(131)	128.3(1.9)

(continued)

TABLE VI *(continued)*

C(12)–C(131)–W(1)	70.9(1.1)
C(141)–C(131)–W(1)	73.3(1.2)
C(141)–C(131)–C(121)	109.1(1.8)
C(132)–C(131)–W(1)	126.8(1.5)
C(132)–C(131)–C(121)	124.4(1.9)
C(132)–C(131)–C(141)	126.2(2.0)
C(131)–C(141)–W(1)	72.5(1.2)
C(151)–C(141)–W(1)	73.8(1.1)
C(151)–C(141)–C(131)	110.0(1.8)
C(142)–C(141)–W(1)	127.7(1.6)
C(142)–C(141)–C(131)	124.6(2.0)
C(142)–C(141)–C(151)	124.7(2.0)
C(111)–C(151)–W(1)	71.7(1.2)
C(141)–C(151)–W(1)	71.0(1.2)
C(141)–C(151)–C(111)	107.6(1.7)
C(152)–C(151)–W(1)	129.4(1.5)
C(152)–C(151)–C(111)	123.7(2.0)
C(152)–C(151)–C(141)	128.1(1.9)
C(12)–C(11)–P(1)	123.4(0.6)
C(16)–C(11)–P(1)	116.9(1.5)
C(22)–C(21)–P(1)	118.9(0.5)
C(26)–C(21)–P(1)	121.3(1.3)
C(32)–C(31)–P(1)	115.7(0.5)
C(36)–C(31)–P(1)	121.8(1.4)
C–C–C phenyl in range	115.0(1.3)–123.3(2.4)

usually short intermolecular interactions. It confirms the formulation of **VIII** as a cationic complex containing the CH_2PPh_3 ligand. As expected, the C_5Me_5 ring is bonded to the tungsten in a pentahapto fashion with the five W–C_{ring} distances in the range 2.31(2) to 2.38(2) Å. This is the same order as that observed for tungsten complexes containing both the η-C_5H_5 ligand [25, 26] and the η-C_5Me_5 ligand [27]. For the C_5Me_5 ligand, the C_{ring}–C_{ring} distances of 1.38(3) to 1.49(3) Å and the C_{ring}–C_{methyl} distances of 1.44(3) to 1.49(3) Å in **VIII** are also unremarkable. The C_5Me_5 ring is essentially planar; $\Sigma\Delta^2 = 0.0007$ Å^2 for the least squares plane of the five ring carbons, and the maximum deviation of a ring atom from the plane is less than 0.02 Å. All of the methyl substituents on the C_5Me_5 ring are bent away from the tungsten and lie above the plane of the ring. This has been noticed in other structures containing the C_5Me_5 ligand and has been attributed to both steric and electronic effects [27]. W–C distances for the three carbonyl groups in **VIII** are in the range 1.83(3) to 2.00(3) Å, which is similar to that of 1.886(24) to 1.911(26) Å found in [η-$C_5Me_5W(CO)_2NO$] [27], as well as to that in the cyclopentadienyl complexes [η-$C_5H_5W(CO)_3]_2$ of 1.956(5) to 1.996(7) Å [25] and in [η-$C_5H_5W(CO)_3$-Cl] of 1.992(8) to 2.002(12) Å [28]. The C–O distances are also unremarkable, being in the range 1.18(3) to 1.23(3) Å [27]. The W–C–O angles are nearly linear (see Table VI) as is generally found in metal carbonyl complexes of this type.

The final coordination position on the tungsten is taken up by the phosphorus ylide ligand CH_2PPh_3 which is bonded to the metal through the methylene carbon atom with a W–C distance of 2.34(2) Å. This is indicative of a W–C single bond and the value is very close to that found for the W–CH_2-PMe_3 bond length of 2.305(7) Å in the cationic ylide complex [$W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3$] [$CF_3$-$SO_3$] [24]. The W–C–P angle in (**VIII**) is 119(1)° which is smaller than the corresponding angle found in [$W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3$] [$CF_3SO_3$] [24]. A comparison of M–CH_2–PR_3 bond angles and MCH_2–PR_3 bond lengths for several phosphorus ylide complexes is given in Table VII. In these compounds, the range for M–C–P angles is 129 to 115° and the P–C distance is from 1.84 to 1.76 Å. The compounds with the longest P–C_{ylide} distances also tend to have the largest M–C–P angles. Also, the M–C–P angle appears to be dependent on the metal and its associated ligand rather than on the R group in the CH_2PR_3 ligand. In compound **VIII**, the P–C_{ylide} distance of 1.82(2) Å is identical to the P–C_{phenyl} distances (see Table V), all of which correspond to P–C single bonds.

Supplementary Material

Structure factors for compound **VIII** are available from the Editor-in-Chief on request.

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TABLE VII C_{ylide}–P Distances and M–C_{ylide}–P Angles for some Phosphorus Ylide Complexes

Compound	C_{ylide}–P (Å)	M–C_{ylide}–P (°)	Reference
[$Pt_2Cl(CH_2PPh_3)(\mu$-$CH_2)(\mu$-$Ph_2PCH_2PPh_2)_2$] [PF_6]	1.84(2)	129(1)	20
[$W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3$] [$CF_3SO_3$]	1.748(7)	126.4(4)	24
cis-[$Pt(CH_2PPh_3)(PPh_3)_2Cl$]I	1.80(2)	121.8	22, 29
[η-$C_5Me_5W(CO)_3CH_2PPh_3$]I	1.82(2)	119(1)	this work
trans-[$Pt(CH_2PEt_3)(PEt_3)_2I$]I	1.77(3)	118(1)	21
[$Me_3AuCH_2PPh_3$]	1.755(13)	114.9(7)	23

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