Synthesis and Characterisation of Cationic Bis(cyclopentadienyl)tungsten(IV) Complexes containing Alkyl, Chloride and Hydride Ligands†

Adrian J. Carmichael and Andrew McCamley*
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

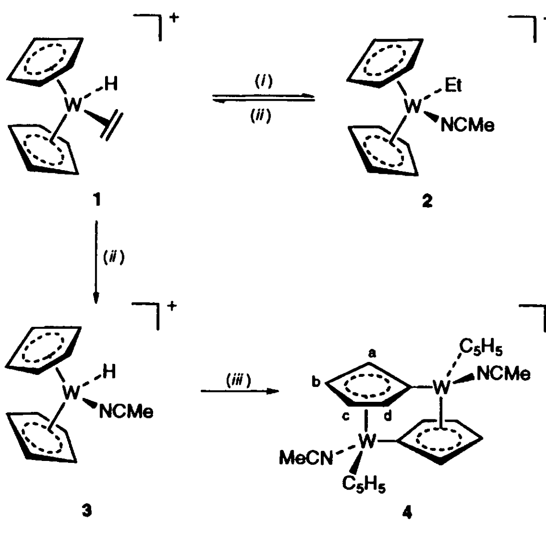
The cationic complexes $[W(\eta-C_5H_5)_2R(NCMe)][PF_6]$ (R = Et or H), $[W(\eta-C_5H_5)_2Me(NCR')][BF_4]$ and $[W(\eta-C_5H_5)_2Cl(NCR')][BF_4]$ (R' = Me or Ph) have been prepared and characterised by ^1H and ^{13}C NMR and IR spectroscopy, and by X-ray crystallography in the case of $[W(\eta-C_5H_5)_2Et(NCMe)][PF_6]$. The complex $[W(\eta-C_5H_5)_2H(NCMe)][PF_6]$ is unstable in solution at room temperature, decomposing slowly to yield the dinuclear C–H activation product $[\{W(\eta-C_5H_5)(\mu-\eta^1:\eta^5-C_5H_4)(NCMe)\}_2][PF_6]_2$ as demonstrated by NMR spectroscopy and X-ray crystallography.

The synthesis and characterisation of cationic organometallic compounds containing metal–alkyl groups is an area of current interest. Such compounds show a high degree of reactivity in organic and polymer synthesis. For example, the ruthenium cation $[Ru(\eta-C_5Me_5)Me(NO)(H_2O)]^+$ contains a labile water ligand easily displaced by olefins such as methyl acrylate, with subsequent insertion into the Ru–Me bond leading to C–C bond formation.[1] Paramagnetic, electron-deficient alkylchromium cations such as $[Cr(\eta-C_5Me_5)Me(thf)_2]^+$ (thf = tetrahydrofuran) have been characterised and shown to be active catalysts for ethene polymerisation.[2] In a similar fashion, bis(cyclopentadienyl)zirconium alkyl complexes, of which $[Zr(\eta-C_5H_5)_2Me(thf)]^+$ is the archetypal example, are extremely efficient catalysts for olefin polymerisation.[3,4] Zirconocene cations are also susceptible to CO and alkyne insertion, leading ultimately to the formation of unsaturated organic carbonyl complexes.[5,6] The tungsten(V) cation $[W(\eta-C_5Me_5)Me_3(O_3SCF_3)]^+$ has been used to effect the N–N cleavage of hydrazine.[7] The reactivity shown by these and other complexes exemplifies the value of organometallic cations in a range of important processes, and new routes to their preparation are being sought.

The groups of Cooper and Green have described the synthesis of a range of bis(cyclopentadienyl)tungsten compounds over the past decade or more. Their preparations of $[W(\eta-C_5H_5)_2H_2]$ and $[W(\eta-C_5H_5)_2Cl_2]$ remain the most convenient entries to this area of chemistry.[8] Such compounds have been used as probes in a wide range of mechanistic studies including α- and β-elimination reactions,[9–13] nucleophilic attack at a cyclopentadienyl ligand,[14] C–H activation studies[15,16] and methyl-migration reactions.[17] Recently a range of *ansa*-metallocene complexes of molybdenum and tungsten has been reported.[18] As part of a programme directed towards homogeneous small-molecule activation we have sought new methods for the preparation of cationic $[W(\eta-C_5H_5)_2]$-based compounds. We now report new and high-yielding routes to some novel tungsten(IV) organometallic cations, together with the crystal structures of two of the derivatives.

Results and Discussion

The synthesis of a range of cationic bis(cyclopentadienyl)tungsten complexes is summarised in Scheme 1. We have found that stirring $[W(\eta-C_5H_5)_2(C_2H_4)H][PF_6]$ **1** in acetonitrile solution at room temperature leads to the formation of $[W(\eta-C_5H_5)_2Et(NCMe)][PF_6]$ **2** in greater than 90% yield. The reaction is relatively slow, taking several days at room temperature. The insertion of the ethene ligand in **1** into the tungsten–hydride bond has been observed previously, and a related product $[W(\eta-C_5H_5)_2(PPh_3)H][PF_6]$ was isolated.[19] In contrast to this thermal reaction, irradiation of **1** in acetonitrile using a broad-band UV/VIS source induces the liberation of free ethene (as observed in the solution NMR spectra of the reaction mixture) and $[W(\eta-C_5H_5)_2H(NCMe)][PF_6]$ **3** is formed. While **3** is stable in the crystalline state, and reasonably so in acetonitrile solution, it reacts upon dilution with diethyl ether or in acetone solution with loss of hydrogen to yield the dinuclear compound $[\{W(\eta-C_5H_5)(\mu-\eta^1:\eta^5-C_5H_4)(NCMe)\}_2][PF_6]_2$ **4**. Compounds **2**–**4** have been characterised by their NMR and IR spectra and by combustion analysis (Table 1).



Scheme 1 Synthesis of complexes **2**–**4**. (*i*) 20 °C, MeCN; (*ii*) *hν*, 20 °C, MeCN; (*iii*) 20 °C, Me_2CO

The molecular structure of compound **2** has been determined by single-crystal X-ray diffraction, and shows a pseudo-tetrahedral tungsten centre with ethyl and acetonitrile ligands (Fig. 1). The fractional atomic coordinates are given in Table 2

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data

Complex	Analysis[a] (%)	IR[b] (cm^{-1})	^{1}H NMR[c]	^{13}C NMR
2	C, 31.70 (31.80) H, 3.25 (3.45) N, 3.10 (2.70)	2321 [ν(CC) + δ(CH$_3$)] 2284 [ν(CN)]	5.37 (10 H, s, η-C_5H_5) 2.78 (3 H, s, CH_3CN) 1.38 [3 H, t, *J*(HH) = 7.3, CH_3CH_2] 0.90 [2 H, q, *J*(HH) = 7.3, CH_3CH_2, *J*(^{183}WH) = 7.2]	92.09 (η-C_5H_5) 22.34 (CH_3CH_2) 4.87 (CH_3CN) −14.63 [CH_3CH_2, *J*(^{183}WC) = 53.9]
3	C, 28.85 (28.70) H, 2.70 (2.80) N, 2.80 (2.80)		5.35 (10 H, s, η-C_5H_5) 2.59 (3 H, s, CH_3CN) −12.51 [1 H, s, hydride, *J*(^{183}WH) = 64.0]	85.64 (η-C_5H_5) 4.68 (CH_3CN)
4[d]			6.04 (1 H, m, H_c)[e] 5.72 (5 H, s, η-C_5H_5) 5.52 (1 H, m, H_b)[e] 4.88 (1 H, m, H_d)[e] 4.76 (1 H, m, H_a)[e] 2.74 (3 H, s, CH_3CN)	
6	C, 34.35 (34.15) H, 3.20 (3.50) N, 3.40 (3.10)	2342 [ν(CC) + δ(CH$_3$)] 2273 [ν(CN)]	5.38 (10 H, s, η-C_5H_5) 2.84 (3 H, s, CH_3CN) 0.31 [3 H, s, CH_3, *J*(^{183}WH) = 5.5]	91.58 (η-C_5H_5) 4.01 (CH_3CN) −30.79 [CH_3, *J*(^{183}WC) = 59.4]
7	C, 41.65 (41.35) H, 3.45 (3.50) N, 2.65 (2.70)	2224 [ν(CN)]	7.91 (2 H, m, C_6H_5) 7.77 (1 H, m, C_6H_5) 7.66 (2 H, m, C_6H_5) 5.53 (10 H, s, η-C_5H_5) 0.46 [3 H, s, CH_3, *J*(^{183}WH) = 5.5]	137.90 (C_q, C_6H_5)[f] 135.45 (CH, C_6H_5) 134.41 (CH, C_6H_5) 130.16 (CH, C_6H_5) 118.18 (CN) 93.16 (η-C_5H_5) −28.92 (CH_3)
9	C, 29.95 (30.20) H, 2.80 (2.75) N, 2.90 (2.90)	2324 [ν(CC) + δ(CH$_3$)] 2292 [ν(CN)]	5.96 (10 H, s, η-C_5H_5) 2.96 (3 H, s, CH_3CN)	136.23 (CN) 98.04 (η-C_5H_5) 4.78 (CH_3CN)
10	C, 36.90 (37.85) H, 2.90 (2.80) N, 2.25 (2.60)	2251 [ν(CN)]	7.99 (2 H, m, C_6H_5) 7.82 (1 H, m, C_6H_5) 7.71 (2 H, m, C_6H_5) 6.09 (10 H, s, η-C_5H_5)	136.51 (C_q, C_6H_5)[f] 136.20 (CH, C_6H_5) 135.31 (CH, C_6H_5) 130.18 (CH, C_6H_5) 110.42 (CN) 98.53 (η-C_5H_5)

[a] Given as found (required). [b] Nujol mull. Complex **2** also shows strong bands at 851 and 558 cm^{-1}, assigned as ν(P–F) of the PF_6^- counter ion; **6, 7, 9** and **10** also show a strong band at 1033 cm^{-1}, assigned as ν(B–F) of the BF_4^- counter ion. [c] In $(CD_3)_2CO$ solution (295 K), data given as: chemical shift (δ) (relative intensity, multiplicity, *J*/Hz, assignment). [d] Characterisation by NMR and X-ray diffraction data only. [e] Assignments made using nuclear Overhäuser effect (NOE) spectroscopy; labels refer to Scheme 1. [f] Cq refers to the quaternary carbon of the phenyl group.

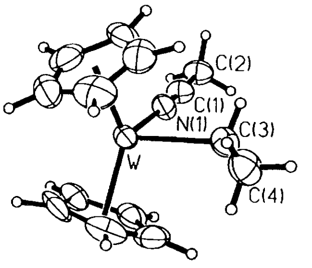


Fig. 1 Molecular structure of the cation of compound **2** (50% thermal ellipsoids)

Table 2 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	2462.9(3)	900.3(2)	2288.7(2)
P	2987(2)	7133.1(12)	170.7(13)
F(1)	2841(7)	7038(5)	1271(4)
F(2)	1357(6)	6534(4)	3(5)
F(3)	4099(6)	6221(3)	123(5)
F(4)	1864(8)	8028(4)	203(4)
F(5)	4642(7)	7729(4)	322(4)
F(6)	3143(7)	7245(4)	−931(3)
N	2174(7)	737(4)	3750(4)
C(1)	2107(8)	678(4)	4532(5)
C(2)	2045(9)	621(5)	5561(5)
C(3)	68(8)	75(5)	2308(5)
C(4)	−742(9)	−190(6)	1384(6)
C(5)	1460(12)	1947(6)	1222(7)
C(6)	2998(10)	2270(5)	1617(8)
C(7)	2798(11)	2427(5)	2585(7)
C(8)	1065(10)	2246(5)	2749(7)
C(9)	317(10)	1969(5)	1913(7)
C(10)	4824(9)	626(6)	1503(6)
C(11)	3599(10)	5(6)	1139(6)
C(12)	3231(10)	−616(5)	1849(7)
C(13)	4137(8)	−374(5)	2653(5)
C(14)	5145(8)	415(5)	2453(6)

and selected bond lengths and angles in Table 3. The W–C(3) bond length of 2.252(7) Å and W–C(3)–C(4) angle of 118.5(5)° are consistent with a conventional tungsten–carbon σ bond, while the W–N bond length, at 2.112(6) Å, is somewhat shorter than those found in other tungsten-(0) and -(II) acetonitrile complexes {*e.g.* $[W(CO)_3(NCMe)_3]$, $[W(CO)_3(NCMe)(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] and $[WI_2(CO)_3(NCMe)_2]$ have average W–N bond lengths of 2.209, 2.190 and 2.167 Å respectively}[20–22] and reflects the strong bonding between the acetonitrile ligand and the cationic tungsten(IV) centre in **2**. It is rather more similar to the W–N bond lengths found in $[W(\eta^6\text{-}C_7H_8)(\eta^3\text{-}C_3H_5)(NCMe)_2][PF_6]$.[23] The W–N≡C(1)–C(2) linkage in **2**, with angles at N and C(1) of 175.9(6) and 178.6(7)°, is essentially linear. The mean tungsten–cyclopentadienyl carbon bond length is 2.296 Å, and the ring centroid–tungsten–ring centroid angle is 140.2°. The IR spectrum of **2** shows bands at 2321 and 2284 cm^{-1}, assigned to ν(CC) + δ(CH$_3$) combination and ν(CN) stretching modes respectively.[24] These are shifted *ca.* 30 cm^{-1} to higher frequencies compared with free MeCN (2293 and 2255 cm^{-1}), as is common for terminal nitrile complexes.

In a slow thermal reaction, compound **3** reacts to form the C–H activation product **4**, the structure of which is illustrated in Fig. 2. The fractional atomic coordinates are given in Table 4 and selected bond lengths and angles in Table 5. The dinuclear tungsten cation lies on a crystallographic centre of inversion located at the centroid of the two tungsten and two metallated cyclopentadienyl carbon atoms. As described for **2**, the W–N(1) bond length of 2.10(2) Å is extremely short, as a consequence of the dicationic nature of the tungsten complex. The C(5')–W–N(1) angle, at 83.5(6)° is slightly more open than the corresponding C(3)–W–N(1) angle in **2** [80.0(2)°], presumably due to the larger steric requirements of the 'alkyl' group in **4** compared with the ethyl group in **2**. The acetonitrile ligands are close to linear, given the precision of the structure determination. The W ··· W separation of 3.836 Å is comparable to that in the related neutral complex *trans*-[{W(η-C_5H_5)(μ-η^1:η^5-C_5H_4)H}$_2$] (3.811 Å)[25] and much too long to signify any tungsten–tungsten interaction.[26] We envisage that the reaction occurs by dissociation of the nitrile ligand of **3** to form a transient 16-electron intermediate which rapidly inserts into the C–H bond of a second molecule of **3**, as shown in Scheme 2. Reductive elimination of 2 mol equivalents of hydrogen results in the formation of **4**. The reversible reaction in step (*i*) has been demonstrated by dissolving **3** in CD_3CN; complete exchange of co-ordinated MeCN occurs over a period of 24 h.

In an effort to expand the number of routes available for the preparation of compounds **2**–**4** and their analogues, we have investigated the reactions of [W(η-C_5H_5)$_2$]-based compounds with certain proton sources and oxidising agents. These results are summarised in Scheme 3. Dialkyl complexes such as **5** offer a non-photochemical route to 16-electron [W(η-C_5H_5)$_2$R]$^+$ intermediates. Protonation of **5** with the strong acid HBF_4 in acetonitrile solution leads to the formation of [W(η-C_5H_5)$_2$Me(NCMe)][BF_4] **6** in essentially quantitative yield. We presume this reaction occurs *via* an unstable [W(η-C_5H_5)$_2$Me$_2$H]$^+$ cation, which reductively eliminates methane and co-ordinates acetonitrile to form **6**. The strong basicity of [W(η-C_5H_5)$_2$H$_2$] is well known, with the trihydride [W(η-C_5H_5)$_2$H$_3$]$^+$ a stable entity.[27] The benzonitrile analogue [W(η-C_5H_5)$_2$Me(NCPh)][BF_4] **7** may be prepared in a similar manner. The IR spectrum of **7** shows an intense peak at 2224 cm^{-1}, shifted to lower frequency relative to free benzonitrile (2250 cm^{-1}). This is in contrast to the acetonitrile complexes described earlier and is indicative of the stronger π-accepting nature of PhCN compared with MeCN.[24] We have observed no spectroscopic features consistent with a tungsten hydride complex of the type [W(η-C_5H_5)$_2$H(CH_2PR_3)]$^+$, observed in the α-elimination studies of Green *et al.*[10]

Upon reaction of [W(η-C_5H_5)$_2$(H)Cl] **8** with $AgBF_4$ in

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

W–N	2.112(6)	N–C(1)	1.120(9)
W–C(3)	2.252(7)	C(1)–C(2)	1.471(9)
C(3)–C(4)	1.511(10)	W–Cp	1.96
N–W–C(3)	80.0(2)	W–C(3)–C(4)	118.5(5)
W–N–C(1)	175.9(6)	Cp–W–Cp	140.2
N–C(1)–C(2)	178.6(7)		

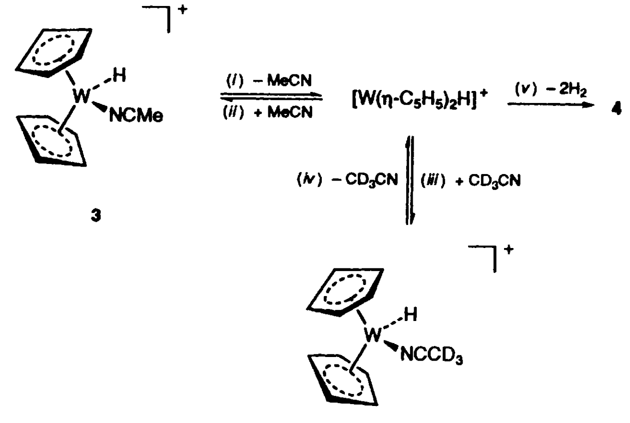
Cp = Centroid of cyclopentadienyl ring.

Table 4 Fractional atomic coordinates (× 10^4) for complex **4**

Atom	*X/a*	*Y/b*	*Z/c*
W	394.2(9)	2026.4(6)	982.4(7)
P	6627(9)	7241(7)	3343(6)
F(1)	5083(29)	7986(22)	3035(21)
F(2)	8200(29)	8364(20)	3047(18)
F(3)	4999(29)	6110(20)	3654(19)
F(4)	7215(25)	8350(17)	4919(14)
F(5)	5961(29)	6122(19)	1734(17)
F(6)	8121(28)	6500(20)	3677(24)
N(1)	−1019(22)	1722(18)	2496(18)
C(1)	−1670(33)	1613(20)	3438(21)
C(2)	−2537(39)	1509(27)	4515(25)
C(3)	3266(30)	2335(23)	2413(20)
C(4)	2001(28)	808(21)	1891(21)
C(5)	1729(25)	179(20)	400(20)
C(6)	2637(29)	1239(24)	−11(21)
C(7)	3570(29)	2567(23)	1203(23)
C(8)	1113(35)	3946(23)	399(25)
C(9)	−526(32)	2895(24)	−590(24)
C(10)	−2143(35)	2603(24)	−115(26)
C(11)	−1406(34)	3636(26)	1344(29)
C(12)	535(36)	4404(24)	1588(30)

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

W–N(1)	2.10(2)	C(1)–C(2)	1.41(3)
W–C(5)	2.32(2)	W–Cp (C_5H_5)	1.92
W–C(5')	2.22(2)	W–Cp (C_5H_4)	1.97
N(1)–C(1)	1.19(3)		
		W–C(5')–C(4')	122.6(13)
N(1)–W–C(5')	83.5(6)	W–C(5')–C(6')	127.0(14)
W–N(1)–C(1)	174(2)	Cp–W–Cp	141.1
N(1)–C(1)–C(2)	176(3)		



Scheme 2

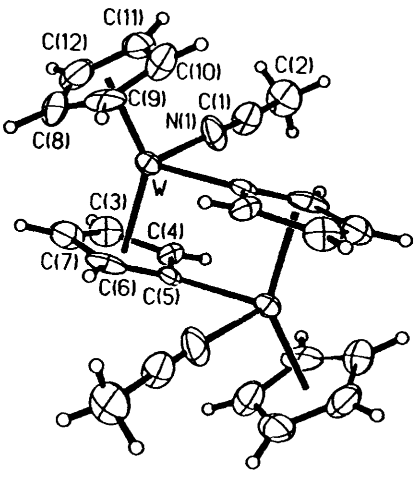
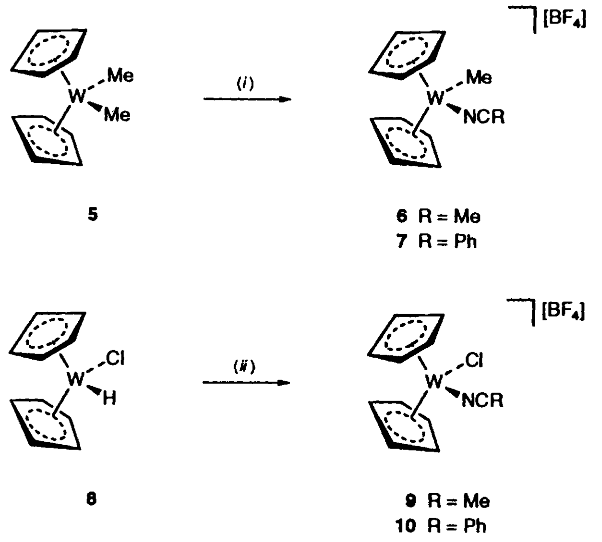


Fig. 2 Molecular structure of the cation of compound **4** (50% thermal ellipsoids)

Table 6 Crystal data for complexes **2** and **4**[a]

	2	**4**
Formula	$C_{14}H_{18}F_6NPW$	$C_{24}H_{24}F_{12}N_2P_2W_2$
M	529.11	998.09
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	7.977(5)	7.362(12)
b/Å	14.440(9)	10.373(14)
c/Å	14.260(9)	10.517(19)
α/°		109.97(12)
β/°	90.66(5)	99.11(14)
γ/°		105.08(12)
U/Å^3	1642	701
Z	4	1
Crystal dimensions/mm	0.12 × 0.16 × 0.26	0.16 × 0.23 × 0.27
Colour	Orange	Orange
D_c/g cm^{-3}	2.140	2.363
F(000)	1008	468
μ(Mo-Kα)/mm^{-1}	7.19	8.41
T/K	240	250
Data collected (h,k,l)	±10, 18, 18	7, ±11, ±11
Reflections collected	3941	2020
Independent reflections	3794	1846
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	3221	1691
Variation in standards	<0.01	<0.02
R[b]	0.039	0.087
$wR2$[c]	0.112	0.226
Δ/σ_{max}	0.000	0.007
ρ/e Å^{-3}[d]	2.40	3.81
N_o/N_v[e]	18.2	9.6
S	1.065	1.028
Weighting scheme, w^{-1}[f]	$\sigma^2(F_o^2) + 0.075P^2 + 1.061P$	$\sigma^2(F_o^2) + 0.204P^2 + 0.158P$

[a] Data collected on a Siemens R3m diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); $2\theta_{max}$ = 55 (**2**) or 45° (**4**); three standards every 197 reflections; data corrected for absorption (Gaussian) and extinction in the case of complex **2**. Refinements were carried out on F^2. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters U = 0.08 Å^3. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o \geqslant 4\sigma(F_o)$]. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ for all data. [d] The structures show residual peaks of electron density within 1.3 Å of the tungsten atom; no peaks greater than 0.97 (**2**) or 1.55 e Å^{-3} (**4**) remained elsewhere. [e] N_o = Number of observations, N_v = number of variables. [f] $P = [\max(F_o^2,0) + 2F_c^2]/3$, where $\max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken.



Scheme 3 Synthesis of complexes **6**, **7**, **9** and **10**. (*i*) HBF_4·OEt_2, RCN, 20 °C; (*ii*) $AgBF_4$, OEt_2, RCN, 20 °C

acetonitrile metallic silver is deposited and [W(η-C_5H_5)$_2$Cl(NCMe)][BF_4] **9** is formed. In a similar fashion, [W(η-C_5H_5)$_2$Cl(NCPh)][BF_4] **10** may be prepared. This reactivity is in contrast to the report that treatment of [W(η-C_5H_5)$_2$(H)I] with other silver salts such as silver acetate results in decomposition.[28] A related complex may be prepared indirectly from [W(η-C_5H_5)$_2$Me(Ph)]; upon oxidation, the 17-electron cation [W(η-C_5H_5)$_2$Me(Ph)]$^+$ is formed, which may be reduced by the trityl radical in acetonitrile to [W(η-C_5H_5)$_2$(CH$_2$Ph)(NCMe)]$^+$.[29] It seems likely that oxidation of **8** yields [W(η-C_5H_5)$_2$(H)Cl]$^+$ as a transient intermediate which, in the presence of donor nitrile ligands, eliminates hydrogen and leads to [W(η-C_5H_5)$_2$Cl(NCR)]$^+$ cations. We have not been able to effect the abstraction of chloride ion from **8** using silver salts.

In conclusion, we have described here simple and versatile methods for the preparation of tungstenocene cations. We are currently exploring their reactivity.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of argon, or in a dry-box under an atmosphere of nitrogen. All solvents were purified and dried by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, light petroleum (b.p. 40–60°) and diethyl ether over sodium–potassium alloy ($NaK_{2.2}$), tetrahydrofuran over molten potassium, acetonitrile over calcium hydride and acetone over anhydrous magnesium sulfate.

The compounds [W(η-C_5H_5)$_2$H$_2$],[8] [W(η-C_5H_5)$_2$Cl$_2$],[8] [W(η-C_5H_5)$_2$(C$_2$H$_4$)H][PF$_6$],[19] [W(η-C_5H_5)$_2$Me$_2$][20] and [W(η-C_5H_5)$_2$(H)Cl][30] were prepared according to literature methods. Photochemical reactions were carried out using a water-cooled 150 W medium-pressure mercury lamp irradiating stirred solutions in Youngs ampoules or Youngs NMR tubes.

Nuclear magnetic resonance spectra were recorded using Bruker AC-250 and WH-400 spectrometers and referenced using the resonances of residual protons in the deuteriated solvents, infrared spectra using a Perkin-Elmer 1720X FTIR spectrometer. Microanalyses were obtained using a Leeman Labs CE440 analyser.

Preparations.—$[W(\eta\text{-}C_5H_5)_2Et(NCMe)][PF_6]$ **2**. A colourless solution of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H][PF_6]$ (0.1 g, 0.2 mmol) in MeCN (20 cm^3) was stirred in the dark at room temperature for 1 week to give an orange solution. Removal of solvent under reduced pressure followed by recrystallisation from acetonitrile–diethyl ether yielded *ca.* 95 mg (90%) of orange crystals of compound **2**.

$[W(\eta\text{-}C_5H_5)_2H(NCMe)][PF_6]$ **3**. A stirred solution of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H][PF_6]$ (0.1 g, 0.2 mmol) in MeCN (20 cm^3) was irradiated for 5 h, during which time the solution became yellow. Addition of diethyl ether (40 cm^3) precipitated *ca.* 95 mg (95%) of a yellow powder of compound **3**, which was washed with ether (15 cm^3) and dried *in vacuo*.

$[\{W(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(NCMe)\}_2][PF_6]_2$ **4**. A solution of compound **3** in MeCN (5 cm^3) was layered with diethyl ether (5 cm^3) and cooled to 0 °C. On standing, orange crystals of **4** slowly grew. Yield $\approx$ 50%.

$[W(\eta\text{-}C_5H_5)_2Me(NCR)][BF_4]$ (R = Me **6** or Ph **7**). A typical preparation of compound **6** is as follows. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2Me_2]$ (0.1 g, 0.3 mmol) in MeCN (5 cm^3) at 0 °C was added $HBF_4\cdot OEt_2$ (0.6 mmol). The mixture was stirred for 1 h at 0 °C. Addition of diethyl ether (30 cm^3) precipitated *ca.* 0.13 g (95%) of an orange-brown powder of **6**, which was washed with ether (15 cm^3) and dried *in vacuo*. A similar procedure was used for the preparation of **7**, isolated as an orange-brown powder. Yield 95%.

$[W(\eta\text{-}C_5H_5)_2Cl(NCR)][BF_4]$ (R = Me **9** or Ph **10**). A typical preparation of compound **9** is as follows. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2(H)Cl]$ (0.075 g, 0.21 mmol) in MeCN (5 cm^3) was added $AgBF_4$ (0.055 g, 0.28 mmol) in MeCN (10 cm^3). The mixture was stirred overnight giving a grey-red suspension. The solvent was removed under reduced pressure and the residue extracted with acetone (30 cm^3), producing a dark red solution which was filtered, concentrated and layered with diethyl ether. On standing, purple microcrystals of **9** slowly grew. Yield *ca.* 75 mg, 75%. A similar procedure was used for the preparation of **10**, isolated as a dark red powder in a similar yield.

Crystal Structure Determinations.—Crystallographic data for complexes **2** and **4** are summarised in Table 6. Suitable single crystals were quickly glued to quartz fibres, coated in Nujol and cooled in the cold nitrogen gas stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection. The tungsten atom positions were determined by the Patterson method. Subsequent Fourier-difference syntheses revealed the positions of the other non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined, with fixed isotropic thermal parameters, riding on the supporting carbon atom. The structure solutions were carried out using SHELXTL PLUS[31] software on a DEC MicroVax-II computer. Refinements were carried out with SHELXL 93[32] software on an Elonex 486DX computer, minimising the weighted R factor $wR2$. Final non-H atomic coordinates are given in Tables 2 and 4, with selected bond lengths and angles in Tables 3 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Dr. J. J. Hastings (Warwick) for his help in running some of the NMR spectra. We acknowledge the EPSRC for providing an Earmarked studentship (to A. J. C.)

References

1 E. Hauptmann, M. Brookhart, P. J. Fagan and J. C. Calabrese, *Organometallics*, 1994, **13**, 774.
2 B. J. Thomas, S. K. Noh, G. K. Schulte, S. C. Sendlinger and K. H. Theopold, *J. Am. Chem. Soc.*, 1991, **113**, 893.
3 R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.
4 M. Bochmann and S. J. Lancaster, *Organometallics*, 1993, **12**, 633.
5 A. S. Guram, Z. Guo and R. F. Jordan, *J. Am. Chem. Soc.*, 1993, **115**, 4902.
6 Y. W. Alelyunas, N. C. Baenziger, P. K. Bradley and R. F. Jordan, *Organometallics*, 1994, **13**, 148.
7 R. R. Schrock, T. E. Glassma, M. G. Vale and M. Kol, *J. Am. Chem. Soc.*, 1993, **115**, 1760.
8 R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1967, 1155.
9 N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1121.
10 J. C. Green, M. L. H. Green and C. P. Morley, *Organometallics*, 1985, **4**, 1302.
11 J. P. McNally, D. Glueck and N. J. Cooper, *J. Am. Chem. Soc.*, 1988, **110**, 4838.
12 J. P. McNally and N. J. Cooper, *J. Am. Chem. Soc.*, 1989, **111**, 4500.
13 J. P. McNally and N. J. Cooper, *Organometallics*, 1988, **7**, 1704.
14 T. C. Forshner, J. A. Corella II and N. J. Cooper, *Organometallics*, 1990, **9**, 2478.
15 K. L. Tang Wong, J. L. Thomas and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1974, **96**, 3694.
16 M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27.
17 D. C. Pestana, T. S. Koloski and D. H. Berry, *Organometallics*, 1994, **13**, 4173.
18 L. Labella, A. Chernega and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1995, 395.
19 F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324.
20 E. J. M. Hamilton, D. E. Smith and A. J. Welch, *Acta Crystallogr., Sect. C*, 1987, **43**, 1214.
21 D. J. Darensbourg, D. J. Zalewski, C. Plepys and C. Campana, *Inorg. Chem.*, 1987, **26**, 3727.
22 M. G. B. Drew, P. K. Baker, E. M. Armstrong and S. G. Frazer, *Polyhedron*, 1988, **7**, 245.
23 K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F. M. Miao and J. Woolcock, *Acta Crystallogr., Sect. B*, 1982, **38**, 456.
24 H. Endres in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 13.7, pp. 261–266.
25 C. Couldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1979, **35**, 335.
26 A. Bino, F. A. Cotton, Z. Dori and J. C. Sekutowski, *Inorg. Chem.*, 1978, **10**, 2946.
27 R. B. Girling, P. Grebenik and R. N. Perutz, *Inorg. Chem.*, 1986, **25**, 31.
28 M. A. Bennett and H. P. Schwemlein, *Aust. J. Chem.*, 1989, **42**, 587.
29 P. Jernakoff and N. J. Cooper, *Organometallics*, 1986, **5**, 747.
30 A. R. Dias and C. C. Romão, *J. Organomet. Chem.*, 1982, **233**, 223.
31 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1990.
32 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Received 11*th May* 1995; *Paper* 5/03002A