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Synthesis of $[W(\eta^5\text{-}C_5H_5)_2H(L)]^+$ and $[W(\eta^5\text{-}C_5H_5)_2L_2]^{2+}$ cations ($L = NCMe, NCPh, C_4H_8O$ or $CNBu^t$). Crystal and molecular structures of $[W(\eta^5\text{-}C_5H_5)_2H(C_4H_8O)][CF_3SO_3]$ and $[W(\eta^5\text{-}C_5H_5)_2(NCMe)_2][CF_3SO_3]_2$‡

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The cationic hydride complexes $[W(\eta\text{-}C_5H_5)_2H(L)][CF_3SO_3]$ [L = NCMe, NCPh, tetrahydrofuran (thf) or $CNBu^t$] have been synthesized by reaction of $[W(\eta\text{-}C_5H_5)_2H_2]$ and methyl trifluoromethanesulfonate in the presence of the σ-donor ligand L. Kinetic measurements on ligand-substitution reactions in CD_3CN solution indicate that L is labile in solution; $[W(\eta\text{-}C_5H_5)_2H(L)]^+$ cations have half-lives of 315(10), 122(6) and 6.68(5) h (L = NCMe, NCPh or thf respectively) at 44 °C. The activation energy E_a for tetrahydrofuran substitution in $[W(\eta\text{-}C_5H_5)_2H(thf)]^+$ is 132 ± 1 kJ mol^{-1}. An X-ray crystallographic determination of the structure of $[W(\eta\text{-}C_5H_5)_2H(thf)][CF_3SO_3]$ demonstrates that the tetrahydrofuran ligand is oriented 'in-plane' with the centroid–W–centroid plane, indicating that the thf acts as a simple σ-donor ligand. Reaction of $[W(\eta\text{-}C_5H_5)_2H_2]$ with an excess of CF_3SO_3Me yields the dicationic tungstenocene complex $[W(\eta\text{-}C_5H_5)_2(NCMe)_2][CF_3SO_3]_2$ as demonstrated by IR and NMR spectroscopy and X-ray crystallography.

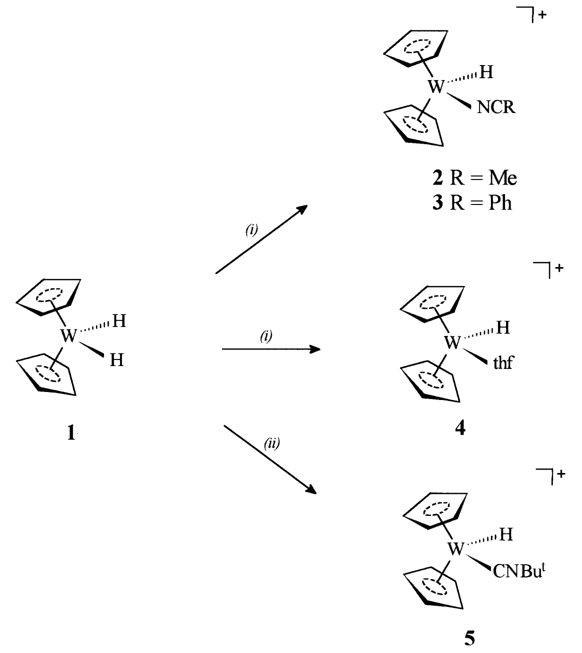
Early transition-metal organometallic hydride complexes are of importance in a wide range of processes including hydrogenation reactions,[1] C–H activation reactions,[2] the dehydrocoupling of silanes[3] and hydrocarbon desulfurisation reactions.[4] The reaction of the cationic zirconium complex $[Zr(\eta\text{-}C_5H_5)_2Me(thf)][BPh_4]$ (thf = tetrahydrofuran) with hydrogen leads to the terminal hydride complex $[Zr(\eta\text{-}C_5H_5)_2H(thf)][BPh_4]$, which is susceptible to a wide range of insertion reactions including alkene polymerisation.[5] It is in the nature of such highly reactive complexes that characterisation of the organometallic species involved in these reactions is awkward. Frequently, compounds are structurally characterised as dimers or clusters containing bridging hydrides and the nuclearity of the active metal hydride remains unknown. In this context we recently reported the photochemical synthesis and characterisation of the terminal hydride complex $[W(\eta\text{-}C_5H_5)_2H(NCMe)][PF_6]$, equation (1).[6] The quantities of $[W(\eta\text{-}C_5H_5)_2H(NCMe)][PF_6]$

$$[W(\eta\text{-}C_5H_5)_2H(C_2H_4)]^+ + MeCN \xrightarrow{h\nu} [W(\eta\text{-}C_5H_5)_2H(NCMe)]^+ + C_2H_4 \quad (1)$$

available through this route are somewhat limited. In the course of our studies we have discovered a new, high-yielding route to such weakly solvated $[W(\eta\text{-}C_5H_5)_2H]^+$ cations. In this paper we describe the synthesis and spectroscopic characterisation of several new $[W(\eta\text{-}C_5H_5)_2H(L)][CF_3SO_3]$ complexes, together with the crystal structures of $[W(\eta\text{-}C_5H_5)_2H(thf)][CF_3SO_3]$ and $[W(\eta\text{-}C_5H_5)_2(NCMe)_2][CF_3SO_3]_2$.

Results and Discussion

The strong basicity of $[W(\eta\text{-}C_5H_5)_2Me_2]$ may be used in reaction with certain proton sources to generate alkyltungstenocene cations.[6–8] In a related way, we have used methyl trifluoromethanesulfonate, CF_3SO_3Me, as an organometallic methylating agent, in reaction with $[W(\eta\text{-}C_5H_5)_2H_2]$ **1** to prepare a range of cationic bis(cyclopentadienyl)tungsten hydride complexes, as shown in Scheme 1. Thus, reaction of **1** with 1 mol equivalent of CF_3SO_3Me in acetonitrile solution leads to the rapid formation of $[W(\eta\text{-}C_5H_5)_2H(NCMe)][CF_3SO_3]$ **2** in essentially quantitative yield. The ^1H NMR spectrum shows a singlet at δ −12.53, assigned to the hydride ligand. The presence of ^{183}W satellites [14.4% natural abundance, $J(^{183}WH) = 63.5$ Hz] unequivocally demonstrates that **2** is a mononuclear complex containing a terminal hydride ligand. Consistent with this, the IR spectrum shows an intense band at 1923 cm^{-1}, assigned to the ν(WH) stretching mode.[9] In a similar fashion, $[W(\eta\text{-}C_5H_5)_2H(NCPh)][CF_3SO_3]$ **3**, $[W(\eta\text{-}C_5H_5)_2H(thf)][CF_3SO_3]$ **4** and $[W(\eta\text{-}C_5H_5)_2H(CNBu^t)][CF_3SO_3]$ **5** may be prepared. Their spectroscopic data similarly indicate the compounds to be mononuclear metal hydrides. The NMR and IR spectral and analytical data for compounds **2**–**5** are summarised in Table 1.



Scheme 1 Synthesis of cationic hydride complexes **2**–**5**. (*i*) 1 mol equivalent CF_3SO_3Me, L (L = MeCN, PhCN or thf), 0 °C; (*ii*) 1 mol equivalent CF_3SO_3Me, $CNBu^t$, thf, 0 °C

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‡ This paper is dedicated to the late Dr. Andrew McCamley.

Table 1 Analytical and spectroscopic data

Complex	Analysis[a] (%)	IR[b] (cm^{-1})	^1H NMR[c]	^{13}C NMR
2	C 30.45 (30.9) H 2.75 (2.80) N 2.50 (2.80)	2323 [ν(CC) + δ(CH_3)] 2271 [ν(CN)] 1923 [ν(WH)]	5.36 (10 H, s, η-C_5H_5) 2.60 (3 H, s, CH_3) −12.53 [1 H, s, hydride, $J(^{183}WH) = 63.5$]	85.65 (η-C_5H_5) 4.84 (CH_3)
3	C 37.5 (38.1) H 2.80 (2.85) N 2.50 (2.50)	2224 [ν(CN)] 1933 [ν(WH)]	7.80 (2 H, m, C_6H_5) 7.73 (1 H, m, C_6H_5) 7.62 (2 H, m, C_6H_5) 5.52 (10 H, s, η-C_5H_5) −12.03 [1 H, s, hydride, $J(^{183}WH) = 62.9$]	137.55 (C_{ipso}, C_6H_5) 135.23 (CH, C_6H_5) 133.89 (CH, C_6H_5) 130.10 (CH, C_6H_5) 111.00 (CN) 86.47 (η-C_5H_5)
4	C 33.75 (33.6) H 3.65 (3.60)	1933 [ν(WH)]	5.45 (10 H, s, η-C_5H_5) 3.66 (4 H, m, CH_2O) 1.71 (4 H, m, CH_2) −12.43 [1 H, s, hydride, $J(^{183}WH) = 69.0$]	87.03 (η-C_5H_5)[d] 28.10 (CH_2O)
5	C 35.15 (35.1) H 3.70 (3.70) N 2.60 (2.60)	2138 [ν(CN)] 1925 [ν(WH)]	5.44 (10 H, s, η-C_5H_5) 1.51 (9 H, s, CH_3) −11.40 [1 H, s, hydride, $J(^{183}WH) = 67.8$]	147.85 (WCN) 83.76 (η-C_5H_5) 60.77 ($CNBu^t$) 30.14 (CH_3)
6	C 27.7 (27.7) H 2.40 (2.30) N 4.15 (4.05)	2325 [ν_{sym}(CN)] 2301 [ν_{asym}(CN)]	6.35 (10 H, s, η-C_5H_5) 2.92 (6 H, s, CH_3)	139.70 (CN) 98.56 (η-C_5H_5) 5.55 (CH_3)

[a] Given as found (required). [b] Nujol mull. Complexes also show strong bands at 1222, 1166, 1064, 1027 and 638 cm^{-1}, assigned to the $CF_3SO_3^-$ counter ion. [c] In $(CD_3)_2CO$ solution (295 K), data given as: chemical shift (δ) (relative intensity, multiplicity, J/Hz, assignment). [d] One resonance of thf ligand too broad to be observed, indicating relatively slow rotation about W−O bond.

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

W−O(1)	2.141(9)	C(12)−C(13)	1.59(3)
O(1)−C(11)	1.47(2)	C(13)−C(14)	1.43(3)
O(1)−C(14)	1.42(2)	W−Cp(ave.)	1.95
C(11)−C(12)	1.42(3)		
W−O(1)−C(11)	125.9(11)	C(11)−O(1)−C(14)	107.9(11)
W−O(1)−C(14)	126.1(12)	Cp−W−Cp	143.5

Cp = C_5H_5 ring centroid.

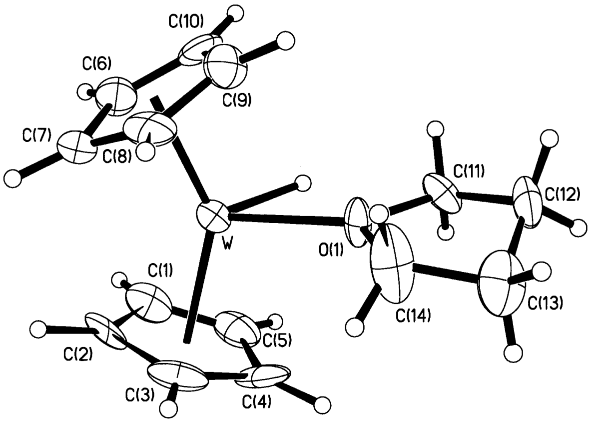
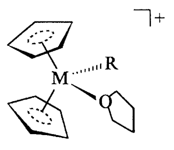
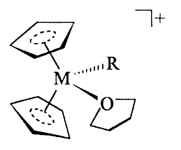


Fig. 1 Molecular structure of the cation of complex **4**

The related compound $[W(\eta\text{-}C_5H_5)_2H(NCMe)][BF_4]$ may be prepared analogously, using trimethyloxonium tetrafluoroborate as the source of CH_3^+.

The molecular structure of compound **4**, as determined by X-ray diffraction, is illustrated in Fig. 1. Selected bond lengths and angles are given in Table 2. The tungsten centre adopts the bent-ring structure typical of metallocene species containing additional ligands, with rings eclipsed. The tungsten–cyclopentadienyl centroid distances, at 1.960 and 1.934 Å, and intraring C−C distances (average 1.42 Å) are unsurprising.[8]





There are no other related (tetrahydrofuran) tungsten complexes reported to date; some mononuclear complexes are presented in Table 3 for comparison, together with data concerning related cationic $[M(\eta\text{-}C_5H_5)_2X(thf)]^+$ complexes. It is noteworthy that the W−O bond length, at 2.141(9) Å, is somewhat shorter than in other (tetrahydrofuran) tungsten complexes. Jordan[11] has previously invoked O→Zr π bonding to account for the short Zr−O bond length and the 'in-plane' orientation **A** of the thf ligand in $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$ (where 'in-plane' describes the relative orientations of the centroid−Zr−centroid and thf ligand planes).

In contrast to this d^0 zirconium complex, the d^2 tungsten centre in complex **4** has no energetically available empty orbital into which the thf ligand might π-donate. As a consequence, the sterically preferred 'out-of-plane' geometry **B** is observed. The structural parameter Δ [= (M−O) − average(M−centroid)] may be used as an indicator of the bonding; the Zr−O bond length in $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$ is shorter than the zirconium–centroid distance by 0.05 Å, whereas the W−O bond length in complex **4** is longer than the tungsten–centroid distance by 0.19 Å. Forcing d^0 metallocene thf complexes to adopt an 'out-of-plane' geometry by steric constraints *e.g.* $[Ti(\eta\text{-}C_5Me_5)_2Me(thf)]^+$ or by providing other donor ligands *e.g.* $[Zr(\eta\text{-}C_5H_5)_2(CH_2CH_2SiMe_3)(thf)]^+$ shifts the Δ value towards that observed for **4**. We conclude that the short W−O bond length indicates strong σ bonding between the cationic tungstenocene centre and the thf ligand rather than any W−O π bonding.

We presume that complexes **2**–**4** are formed *via* an unstable $[W(\eta\text{-}C_5H_5)_2H_2Me]^+$ cation, which undergoes rapid reductive elimination of methane as shown in Scheme 2. Subsequent co-

Table 3 Selected bond lengths and angles for complex **4** and related complexes

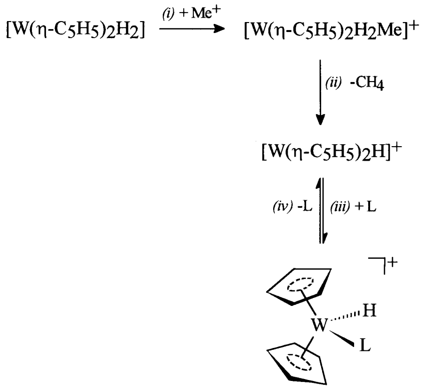
Complex	M–O/Å	Orientation of thf ligand[a]	Δ/Å	Ref.
$[Zr(\eta\text{-}C_5H_5)_2Me(thf)]^+$	2.12(1)	In plane	−0.05	10(*a*)
$[Ti(\eta\text{-}C_5Me_5)_2Me(thf)]^+$	2.154(6)	Out of plane	0.03	10(*b*)
$[Yb(\eta\text{-}C_5H_5)_2Me(thf)]^+$	2.311(6)	Out of plane	0.06	10(*c*)
$[Zr(\eta\text{-}C_5H_5)_2(CH_2CH_2SiMe_3)(thf)]^+$	2.32(1)	Out of plane	0.11	5
4	2.141(9)	Out of plane	0.19	This work
$[WCl_3(OR)_2(thf)]$[b]	2.154(4)			10(*d*)
$[\{WCl_3(thf)_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCCH)]$	2.226(9)			10(*e*)
$[WCl_4(NR)(thf)]$[c]	2.237(3)			10(*f*)
$[WCl_4(\eta^2\text{-}MeCCMe)(thf)]$	2.242(4)			10(*e*)

[a] Orientation with respect to the centroid–M–centroid plane. [b] R = 2,6-Diphenylphenoxy. [c] R = *p*-Tolyl.

Table 4 Kinetic data for σ-donor ligand substitution in complexes **2**–**4** measured at 44 °C

Complex	$10^{-7}k_1/s^{-1}$	$t_{\frac{1}{2}}$/h
2	6.1(2)	315(10)
3	15.7(7)	122(6)
4*	288(0)	6.68(5)
$[W(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OR^*)\text{-}Me(NCMe)]^+$	1170(20)	1.65(3)

* k_1 values at 54, 64 and 74 °C are 1.25(8) × 10^{-4}, 5.40(8) × 10^{-4} and 2.16(0) × 10^{-3} s^{-1} respectively.



Scheme 2 Proposed mechanism for the formation of $[W(\eta\text{-}C_5H_5)_2H(L)][CF_3SO_3]$ (L = MeCN, PhCN or thf)

ordination of donor ligand L (NCR, thf or Bu^tNC) leads to the electronically saturated product $[W(\eta\text{-}C_5H_5)_2H(L)][CF_3SO_3]$. The extent to which co-ordination is reversible is governed, to a large extent, by the donor strength of L. In this context the lability of the MeCN ligand in **2** was previously noted.[6] Complexes **2**–**4** undergo relatively slow ligand-exchange reactions in deuteriated acetonitrile, forming $[W(\eta\text{-}C_5H_5)_2H(NCCD_3)]^+$. McNally and Cooper[12] have shown that acetonitrile exchange in the complex $[W(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OR^*)Me(NCMe)]^+$ $[OR^* = OCHPh(Pr^i)]$ occurs *via* a dissociative mechanism (Scheme 2). We assume that reactions of complexes **2**–**4** proceed similarly. Pertinent kinetic data concerning the rate of σ-donor ligand substitution by $NCCD_3$ in **2**–**4** at 44 °C are presented in Table 4; the substitution reactions follow first-order kinetics in tungsten concentration, as expected. Acetonitrile exchange in **2** is relatively slow at 44 °C ($t_{\frac{1}{2}}$ = 13.1 d). The benzonitrile ligand in **3** is somewhat more labile ($t_{\frac{1}{2}}$ = 5.1 d), which is presumably a reflection of the poorer σ-donor character of PhCN.[13] The rates of nitrile substitution in the hydride complexes **2** and **3** are substantially slower than that of the related complex $[W(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OR^*)Me(NCMe)]^+$ ($t_{\frac{1}{2}}$ = 1.65 h). This lability may be interpreted in terms of an α interaction (either an agostic bond or methylene hydride complex) stabilising the formally unsaturated $[W(\eta\text{-}C_5H_5)_2Me]^+$. Such an interaction has been used to account for the stereochemical stability of $[W(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OR^*)Me]^+$.[12]

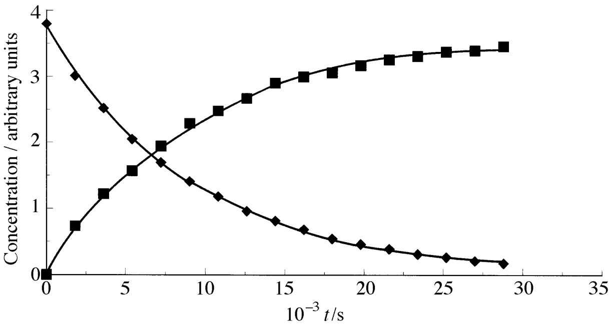
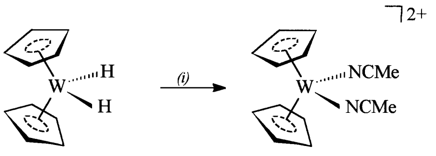


Fig. 2 Consumption of $[W(C_5H_5)_2H(thf)]^+$ (◆) and production of $[W(C_5H_5)_2H(NCCD_3)]^+$ (■) in acetonitrile solution at 44 °C



6

Scheme 3 Synthesis of the dicationic complex **6**. (*i*) Excess of CF_3SO_3Me, MeCN, 0 °C

The tetrahydrofuran ligand in complex **4** is markedly more labile than the nitrile ligands in **2** and **3**, with half-life $t_{\frac{1}{2}}$ = 6.7 h rather than several days (Fig. 2). Tetrahydrofuran is a worse σ-donor ligand than acetonitrile, and the absence of any π-bonding character between tungsten and tetrahydrofuran (see earlier) in complex **4** leads to a relatively weak bond, susceptible to dissociation. The rather shorter half-life of **4** in CD_3CN solution is convenient for measurement of activation parameters; kinetic data measured at four different temperatures yield an activation energy $E_a = 132 \pm 1$ kJ mol^{-1}.

In contrast to the nitrile and tetrahydrofuran ligands in complexes **2**–**4**, the isocyanide ligand in **5** is inert to substitution by acetonitrile. The kinetic data measured for **2**–**4** indicate that the order of half-life for ligand displacement Bu^tNC > MeCN > PhCN > thf is appropriate.

Reaction of complex **1** with an excess of CF_3SO_3Me leads to the replacement of both hydride ligands and the formation of the dicationic bis(cyclopentadienyl)tungsten complex $[W(\eta\text{-}C_5H_5)_2(NCMe)_2][CF_3SO_3]_2$ **6**, as shown in Scheme 3. Complex **6** may be crystallised from acetonitrile–diethyl ether mixtures in good yield. The low-temperature crystal structure confirms its identity, and shows that the crystals contain one further molecule of free MeCN solvent held within the unit cell. The molecular structure of the cation of **6** is shown in Fig. 3, and selected bond lengths and angles are presented in Table 5. Refinement was hampered by disorder problems in both

Table 5 Selected bond lengths (Å) and angles (°) for complex **6**

W−N(1)	2.084(15)	C(1)−C(2)	1.42(3)
W−N(2)	2.091(14)	C(3)−C(4)	1.47(3)
N(1)−C(1)	1.16(2)	W−Cp	1.97
N(2)−C(3)	1.11(2)		
N(1)−W−N(2)	80.0(6)	W−N(2)−C(3)	176(2)
W−N(1)−C(1)	177(2)	N(2)−C(3)−C(4)	180(2)
N(1)−C(1)−C(2)	178(2)	Cp−W−Cp	135.6

Cp = C_5H_5 ring centroid.

Table 6 Selected bond lengths for complex **6** and related complexes

Complex	W−N/Å	N≡C/Å	Ref.
fac-$[W(CO)_3(NCMe)_3]$	2.21(1)	1.12(1)	14(*a*)
$[WI_2(NCMe)_2(CO)_3]$	2.17(2)	1.20(2)	14(*b*)
$[WI_2(NCMe)(CO)(\eta^2\text{-}MeCCMe)_2]$	2.13(1)	1.09(2)	14(*c*)
$[W(\eta\text{-}C_5H_5)(NCMe)(NO)\{\eta^2\text{-}CH_2CPh_2(C_6H_4)\}]$	2.15(1)	1.14(1)	14(*d*)
$[W(\eta\text{-}C_7H_8)(\eta\text{-}C_3H_5)(NCMe)_2]^+$	2.12(2)	1.13(3)	14(*e*)
$[W(\eta\text{-}C_5H_5)_2Et(NCMe)]^+$	2.11(1)	1.12(1)	6
$[\{W(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(NCMe)\}_2]^{2+}$	2.10(2)	1.19(3)	6
6	2.09(1)	1.13(2)	This work

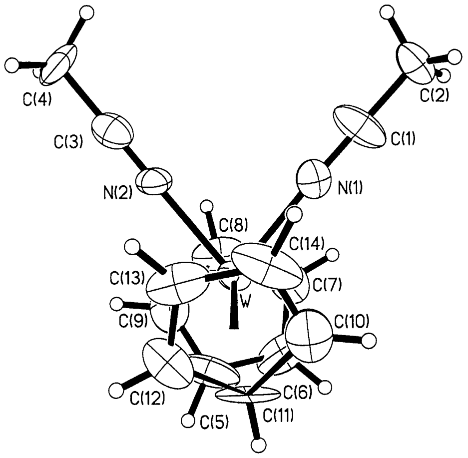


Fig. 3 Molecular structure of the cation of complex **6**

$CF_3SO_3^-$ anions, which limit the precision of the bond lengths and angles reported. Nevertheless, the structure clearly shows a pseudo-tetrahedrally co-ordinated tungsten centre containing two cyclopentadienyl ligands and two acetonitrile ligands. The N(1)−W−N(2) bond angle, at 80.0(6)°, is typical of a d^2 bis(cyclopentadienyl)metal centre. The angles at the nitrogen, C(1) and C(3) atoms (*ca.* 176–179°) show that the acetonitrile ligands are essentially linear and η^1-bound. The W−N bond lengths [average 2.088(15) Å] are shorter than those seen in neutral tungsten–acetonitrile complexes (Table 6), presumably as a result of the cationic charge of the complex. They are rather more similar to those of related cationic bis(cyclopentadienyl)tungsten(IV) complexes reported previously. The N≡C bond lengths [average 1.13(2) Å] are not distinguishable from the value determined for free MeCN (1.155 Å).[15] While low precision precludes a more thorough discussion, the cationic cyclopentadienyl complexes presented in Table 6 all appear to show relatively short W−N bond lengths, with N≡C bond lengths essentially unchanged. This is in accord with the co-ordinated acetonitrile acting as a simple σ-donor ligand, with little π-acceptor character shown. The presence of IR bands at 2325 and 2301 cm^{-1}, to higher wavenumber compared with that of free MeCN (2293 cm^{-1}), provides supporting evidence for this behaviour.

The structure of complex **6**, with only two nitrile ligands, contrasts with that of the related hafnocene dication $[Hf(\eta\text{-}C_5H_5)_2(NCMe)_3]^{2+}$.[16] This is in keeping with its formal 18-electron nature. Such strong Lewis acids are finding increasing use in synthesis,[17] and to this end our work is continuing in this area.

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. 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 °C) 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 compound $[W(\eta\text{-}C_5H_5)_2H_2]$ was prepared according to literature methods.[18]

Nuclear magnetic resonance spectra were recorded using Bruker AS-250 and WH-400 spectrometers, and referenced using the resonances of residual protons in the deuteriated solvents. The variable-temperature unit was calibrated from a second thermocouple inserted in a dummy sample. Temperatures were accurate to ±2 K. Infrared spectra were recorded using a Perkin-Elmer 1720X FTIR spectrometer. Microanalyses were obtained using a Leeman Labs CE440 analyser. Kinetic runs were carried out in NMR tubes placed in a thermostatted water-bath for complexes **2** and **3**, and in the spectrometer for **4**, using the integrated cyclopentadienyl resonances to monitor the reaction. Samples included tetramethylsilane as an integration standard. For **2** and **3** spectra were acquired using 32 scans with a relaxation delay of 1 s between pulses, and acquired for **4** at 44, 54, 64 and 74 °C using 16, 8, 2 and 1 scan respectively with a relaxation delay of 60 s between pulses.

Preparation

$[W(\eta\text{-}C_5H_5)_2H(NCMe)][CF_3SO_3]$ 2. A typical preparation was as follows. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.1 g, 0.32 mmol) in MeCN (30 cm^3) at 0 °C was added CF_3SO_3Me in diethyl ether (0.4 mmol). The mixture was stirred for 1 h at 0 °C before warming to room temperature and stirring overnight. The solvent was removed under reduced pressure and the residue recrystallised from acetonitrile–diethyl ether to yield *ca.* 0.14 g (80%) of yellow crystals of complex **2**. A similar procedure was used for the preparation of **3** and **4**, which were isolated as orange crystalline solids in similar yields.

$[W(\eta\text{-}C_5H_5)_2H(CNBu^t)][CF_3SO_3]$ 5. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.1 g, 0.32 mmol) in thf (30 cm^3) containing a few drops of $CNBu^t$ at 0 °C was added CF_3SO_3Me in diethyl ether (0.4 mmol). The mixture was stirred for 1 h and allowed to warm to room temperature. Work-up as described above gave *ca.* 0.15 g (85%) of a yellow powder of complex **5**.

$[W(\eta\text{-}C_5H_5)_2(NCMe)_2][CF_3SO_3]_2$ 6. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.1 g, 0.32 mmol) in MeCN (30 cm^3) at 0 °C was added an excess of CF_3SO_3Me (0.2 cm^3). The mixture was stirred for 1 h and allowed to warm to room temperature to give a dark orange solution. Work-up as described above gave *ca.* 0.29 g (90%) of orange crystals of complex **6**.

Crystallography

Crystallographic data for complexes **4** and **6** are summarised in Table 7. Suitable single crystals were quickly glued to quartz fibres, coated in Nujol and cooled in the cold nitrogen

Table 7 Crystal data for complexes **4** and **6**[a]

	4	**6**
(*a*) Crystal parameters		
Formula	$C_{15}H_{19}F_3O_4SW$	$C_{18}H_{29}F_6N_3O_6S_2W$
M	536.21	735.33
Crystal system	Monoclinic	Monoclinic
Space group[b]	$P2_1$	$P2_1/n$
a/Å	7.578(8)	7.708(5)
b/Å	10.072(10)	13.925(12)
c/Å	11.004(10)	23.221(18)
β/°	100.62(7)	90.97(8)
U/Å^3	826	2492
Z	2	4
Crystal dimensions/mm	0.13 × 0.25 × 0.32	0.27 × 0.27 × 0.31
Colour	Yellow	Red
D_c/g cm^{-3}	2.157	1.960
μ(Mo-Kα)/mm^{-1}	7.17	4.89
(*b*) Data collection		
Data collected (h, k, l)	±9, 12, 13	8, 16, ±27
Reflections collected	1661	4727
Independent reflections	1542	4361
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	1451	3080
Variation in standards (%)	6	<1
(*c*) Refinement		
R[c]	0.038	0.088
$wR2$[d]	0.100	0.294
Δ/σ_{max}	0.000	0.004
ρ[e]/e Å^{-3}	0.95	4.10
N_o/N_v[f]	7.0	14.0
S	1.089	1.040
Weighting scheme, w^{-1}[g]	$\sigma^2(F_o^2) + 0.077P^2$	$\sigma^2(F_o^2) + 0.197P^2 + 48.95P$

[a] Data collected at 200 K on a Siemens R3m diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); $2\theta_{max} = 50°$; three standards every 197 reflections; data corrected for absorption (Gaussian). 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] Absolute configuration of complex **4** confirmed by refinement of Flack parameter 0.00(3). [c] $R = \Sigma|F_o - F_c|/\Sigma F_o$ for $F_o \geqslant 4\sigma(F_o)$. [d] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data. [e] The structure of complex **4** shows peaks of residual electron density within 1.3 Å of the tungsten atom, but none greater than 0.97 Å remained elsewhere; the structure of **6** shows significant peaks of residual electron density around the disordered anions. [f] N_o = number of observations, N_v = number of variables. [g] $P = [\max(F_o^2, 0) + 2F_c^2]/3$, where $\max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken.

gas stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection. The structure solutions were carried out using SHELXTL PLUS[19] software on a DEC Microvax-II computer. The tungsten atom positions were determined by the Patterson method. Subsequent Fourier-difference syntheses revealed the positions of the other non-hydrogen atoms. Refinements were carried out with SHELXL 93[20] software on an Elonex 486DX computer, minimising the weighted R factor $wR2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined, with fixed isotropic thermal parameters, riding on the supporting carbon atom. The hydride ligand in **4** was constrained to be 1.6 Å from the tungsten[21] and equidistant from the cyclopentadienyl centroids. There was evidence of disorder in the trifluoromethanesulfonate anions of **6**, and a similarity restraint applied to the S–O, S–C and C–F bond lengths was required for satisfactory refinement. There was also rotational disorder in the cyclopentadienyl ligands (as indicated by the anisotropic displacement parameters of the carbon atoms). The cyclopentadienyl ligands were constrained to be regular pentagons, with the C–C bond length refined. Recrystallisation of samples of **6** and recollection of the diffraction data did not provide improved results.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/274.

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References

1 C. J. Schaverien, *Organometallics*, 1994, **13**, 69; P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623; R. Choukroun, B. Douziech and F. Soleil, *J. Chem. Soc., Chem. Commun.*, 1995, 2107; A. Antinolo, F. G. Carrillo, S. Garciayuste and A. Otero, *Organometallics*, 1994, **13**, 2761.

2 B. J. Deelman, W. M. Stevels, J. H. Teuben, M. T. Lakin and A. L. Spek, *Organometallics*, 1994, **13**, 3881; E. Quignard, A. Choplin and J. M. Basset, *J. Chem. Soc., Dalton Trans.*, 1994, 2411; R. M. Bullock, C. E. L. Headford, K. M. Hennessy, S. E. Kegley and J. R. Norton, *J. Am. Chem. Soc.*, 1989, **111**, 3897; H. G. Alt, J. S. Han and R. D. Rogers, *J Organomet. Chem.*, 1993, **445**, 115.

3 H. G. Woo, F. Harrod, J. Henique and E. Samuel, *Organometallics*, 1992, **11**, 1095; J. Y. Corey, J. L. Huhmann and X. H. Zhu, *Organometallics*, 1993, **12**, 1121; S. Bourg, R. J. P. Corriu, M. Enders and J. J. E. Moreau, *Organometallics*, 1995, **14**, 564; L. K. Figge, P. J. Carroll and D. H. Berry, *Organometallics*, 1996, **15**, 209.

4 J. Wachter and M. L. Ziegler, *Organometallics*, 1992, **11**, 1403; T. E. Burrow, D. L. Hughes, A. J. Lough, M. J. Maguire,

R. H. Morris and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1995, 2583; A. Antinolo, F. G. Carrillo, M. Fajardo, S. Garciayuste and A. Otero, *J. Organomet. Chem.*, 1994, **482**, 93.

5 Y. W. Alelyunas, N. C. Baenziger, P. K. Bradley and R. F. Jordan, *Organometallics*, 1994, **13**, 148.

6 A. J. Carmichael and A. McCamley, *J. Chem. Soc., Dalton Trans.*, 1995, 3125.

7 N. J. Cooper, M. L. H. Green and R. Mahtab, *J. Chem. Soc., Dalton Trans.*, 1979, 1557.

8 P. Jernakoff, J. R. Fox, J. C. Hayes, S. Lee, B. M. Foxman and N. J. Cooper, *Organometallics*, 1995, **14**, 4504.

9 R. B. Girling, P. Grebenik and R. N. Perutz, *Inorg. Chem.*, 1986, **25**, 31.

10 (*a*) A. S. Guram, Z. Y. Guo and R. F. Jordan, *J. Am. Chem. Soc.*, 1993, **115**, 4902; (*b*) M. Bochmann, A. J. Jaggar, L. M. Wilson, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1989, **8**, 1838; (*c*) W. J. Evans, R. Dominguez and T. P. Hanusa, *Organometallics*, 1986, **5**, 263; (*d*) L. K. Johnson, S. C. Virgil, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1990, **112**, 5384; (*e*) S. G. Bott, D. L. Clark, M. L. H. Green and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1991, 471; (*f*) D. C. Bradley, R. J. Errington, M. B. Hursthouse, R. L. Short, B. R. Ashcroft, G. R. Clark, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.*, 1987, 2067.

11 R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.

12 J. P. McNally and N. J. Cooper, *J. Am. Chem. Soc.*, 1989, **111**, 4500.

13 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1.

14 (*a*) E. J. M. Hamilton, D. E. Smith and A. J. Welch, *Acta Crystallogr., Sect. C*, 1987, **43**, 1214; (*b*) M. G. B. Drew, P. K. Baker, E. M. Armstrong and S. G. Fraser, *Polyhedron*, 1988, **7**, 245; (*c*) E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics*, 1988, **7**, 319; (*d*) N. Brunet, J. D. Debad, P. Legzdins, J. Trotter, J. E. Veltheer and V. C. Yee, *Organometallics*, 1993, **12**, 4572; (*e*) K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F. M. Miao and J. Woolcock, *Acta Crystallogr., Sect. B*, 1982, **38**, 456.

15 B. Swanson, D. F. Shriver and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 2182.

16 P. N. Billinger, P. P. K. Claire, H. Collins and G. R. Willey, *Inorg. Chim. Acta*, 1988, **149**, 63.

17 K. Suzuki, *Pure Appl. Chem.*, 1994, **66**, 1557.

18 R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1967, 1155.

19 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1990.

20 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

21 R. J. Klingler, J. C. Huffman and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 208.

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