Group 6 Metallocene(IV)–Main Group Metal Complexes: Synthesis and Structures of a Mo–B–Li Compound and of $[W(\eta\text{-}C_5H_5)_2H\{SnCl_2CH(SiMe_3)_2\}]$ *

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The reaction between $[\{Mo(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)\}_4]$ **Ia**, $B(C_6H_2Bu^t{}_3\text{-}2,4,6)Cl_2$ and $Me_2NCH_2CH_2NMe_2$ (tmen) afforded the crystalline complex $[Mo(\eta\text{-}C_5H_5)H_2\{(C_5H_4)BH(C_6H_2Bu^t{}_2\text{-}4,6\text{-}CMe_2CH_2\text{-}2)\}\text{-}\{Li(tmen)\}]$ **1**, having single hydrido bridges between Li and Mo (H_a) and Li and B (H_c). A single-crystal structure analysis gave the bond distances Mo–H_a 1.66(5), Mo–H_b 1.44(6), Li–H_a 1.67(6), Li–H_c 1.90(6), B–H_c 1.21(5), Mo···Li 3.08(1) and Li···B 2.63(1) Å. Detailed multinuclear NMR spectroscopic data for **1** showed that the same structure was retained in $[^2H_8]$toluene solution. From **Ib** (the tungsten equivalent of **Ia**) and $SnX_2R'_2$ [$R' = CH(SiMe_3)_2$, X = F or Cl] or $SnCl_3R'$ (prepared from $SnCl_4$ and LiR′) the new W–Sn complexes $[W(\eta\text{-}C_5H_5)H(Y)]$ [Y = $SnCl_2R'$ **2**, $SnCl(Me)R'$, $SnFR'_2$ or $SnClR'_2$] were prepared and characterised. A single-crystal structure determination of **2** gave W–Sn 2.706(1), Sn–C 2.180(8) and average Sn–Cl 2.423(3) Å.

The preparation of the kinetically stable aryl- and alkylphosphinidinemetal complexes $[M(\eta\text{-}C_5H_5)_2(=PR)]$ ($R = C_6H_2Bu^t{}_3\text{-}2,4,6$; M = Mo[1] or W[2]) and $[Mo(\eta\text{-}C_5H_5)_2(=PR')]$ [$R' = CH(SiMe_3)_2$][1] from the appropriate compound $[\{M(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)\}_4]$ **I** and $PRCl_2$, equation (1), or $PR'Cl_2$ has led

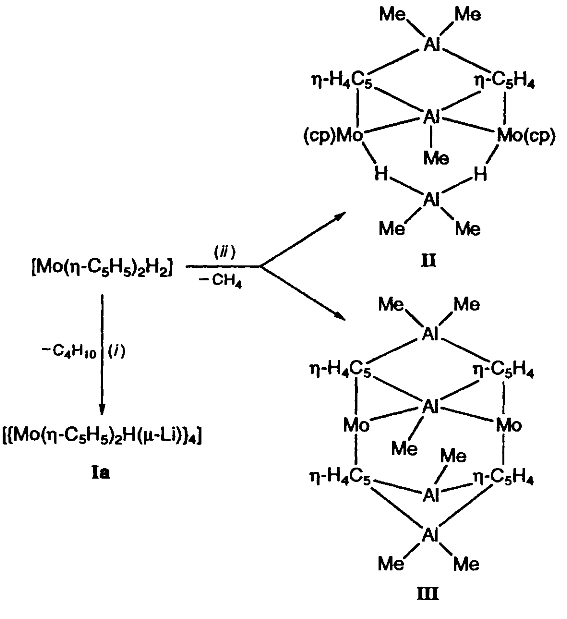
$$\tfrac{1}{4}[\{M(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)\}_4] + PRCl_2 \longrightarrow [M(\eta\text{-}C_5H_5)_2(=PR)] + LiCl + HCl \quad (1)$$

us to investigate corresponding systems containing boron or tin(IV) rather than phosphorus; the results are described in this paper (some brief reference to the tin work was made in ref. 2).

Accordingly, we now report on the $[\{M(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)\}_4]\text{-}BRCl_2$ (M = Mo), $\text{-}SnX_2R'_2$ (X = F or Cl, M = Mo) and $\text{-}SnCl_3R$ (M = W) systems. The aryldichloroborane $BRCl_2$ had previously been prepared from boron trichloride and LiR,[3] while the hydridomolybdenocene(IV)–lithium complex **Ia**, like the tungsten analogue **Ib**, had been obtained from $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo for **Ia**, W for **Ib**) and *n*-butyllithium, Scheme 1.[4]

Metal bonding between a molybdenocene(IV) moiety and an electron-deficient main-group metal (M′) centre has been demonstrated by Green and co-workers for M′ = Li (**Ia** in Scheme 1)[4] and M′ = Al (**II** and **III** in Scheme 1).[5] Hydrido-bridging between boron and lithium has been observed in $[(2,4,6\text{-}Me_3C_6H_2)_2B(\mu\text{-}H)_2Li(dme)]$ **IV**[6] (dme = 1,2-dimethoxyethane) and between boron and molybdenum was found *inter alia* in $[N(PPh_3)_2][Mo(CO)_4\{(\mu\text{-}H)_2BH_2\}]$ **V**[7] and $[MoH\{(\mu\text{-}H)_2BH_2\}(PMe_3)_4]$ **VI**.[8] The crystal structures of **I**,[9] **II**,[10] **III**,[10] **IV**,[6] **V**,[7] **VI**,[8] and $[Mo(\eta\text{-}C_5H_5)_2H_2]$[11] have been established, although without certainty regarding the hydrido positions in **I** and **II**.

The supermesityl $C_6H_2Bu^t{}_3\text{-}2,4,6$ ($\equiv \bar{R}$) has extensively been used in recent years; it originally gained prominence with the



Scheme 1 Synthesis of molybdenocene(IV)-lithium[4] and -aluminium[5] compounds. cp = $\eta\text{-}C_5H_5$. (*i*) $LiBu^n$; (*ii*) Al_2Me_6

discovery of RP=PR.[12] No doubt because of its steric bulk, activation of a *tert*-butyl C–H bond by cyclometallation has frequently been found,[13] as in the formation of the bicyclic compound **VII** [from $PR(Cl)R' + LiBu^n$][14] or **VIII** {from $2LiOR'' + [W(CBu^t)Cl_3(dme)]$ ($R'' = C_6H_3Bu^t{}_2\text{-}2,6$)}.[15]

Our initial objective in the organotin work was to obtain a stannylene-molybdenocene or -tungstenocene complex $[M(\eta\text{-}C_5H_5)_2(=SnR'_2)]$, related to $[M(\eta\text{-}C_5H_5)_2(=PR')]$. Numerous dialkylstannylene complexes $[M''L_n(=SnR'_2)]$ are known for a wide range of later transition metals M″.[16] We have provided some evidence for $[Mo(\eta\text{-}C_5H_5)_2(=SnR'_2)]$ **IX**, from **Ia** *via* $[Mo(\eta\text{-}C_5H_5)_2H(SnFR'_2)]$ (by reaction with $SnF_2R'_2$) and its dehydrofluorination using $LiBu^t$.[2] The only other early transition-metal stannylene complex is the crystallographically

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* No reprints available.

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

Non-SI unit employed: Torr ≈ 133 Pa.

characterised $[Zr(\eta-C_5H_4Me)_2(=SnR'_2)_2]$.[17] Owing to our failure to obtain X-ray-quality crystals of **IX**, we report herein on early steps of our alternative strategy aimed at the tungsten analogue.

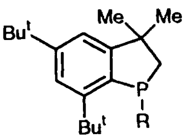
Results and Discussion

Preparation of $[Mo(\eta-C_5H_5)H_2\{(C_5H_4)\text{-}BH(C_6H_2Bu^t_2\text{-}4,6\text{-}CMe_2CH_2\text{-}2)\}\{Li(tmen)\}]$ **1**.—Treatment of $[\{Mo(\eta-C_5H_5)_2H(\mu-Li)\}_4]$ **Ia** with dichloro(2,4,6-tri-*tert*-butylphenyl)borane and 1,2-bis(dimethylamino)ethane (tmen) in refluxing toluene afforded the yellow-green compound **1**, albeit in modest yield, equation (2), which was soluble in

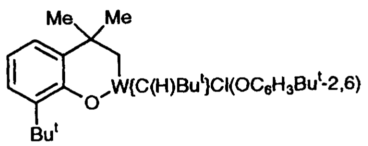
$$\tfrac{1}{4}\underset{\textbf{Ia}}{[\{Mo(\eta-C_5H_5)_2H(\mu-Li)\}_4]} + BRCl_2 + tmen \longrightarrow \textbf{1} \qquad (2)$$

hexane, benzene or toluene. No attempts were made to vary the relative proportions of the reagents in order to optimise the yield of **1**, nor to identify the coproducts from the reaction.

The use of a base such as tmen to increase the nucleophilicity of a lithium alkyl or amide reagent is well documented.[18] Its role, at least in part, is to lower the degree of aggregation of the neutral ligand-free molecule, and to increase the electron density of the incipient anion. It may be that the tetramer **Ia** with tmen yields the monomer $[Mo(\eta-C_5H_5)_2H\{Li(tmen)\}]$ **X**.



VII

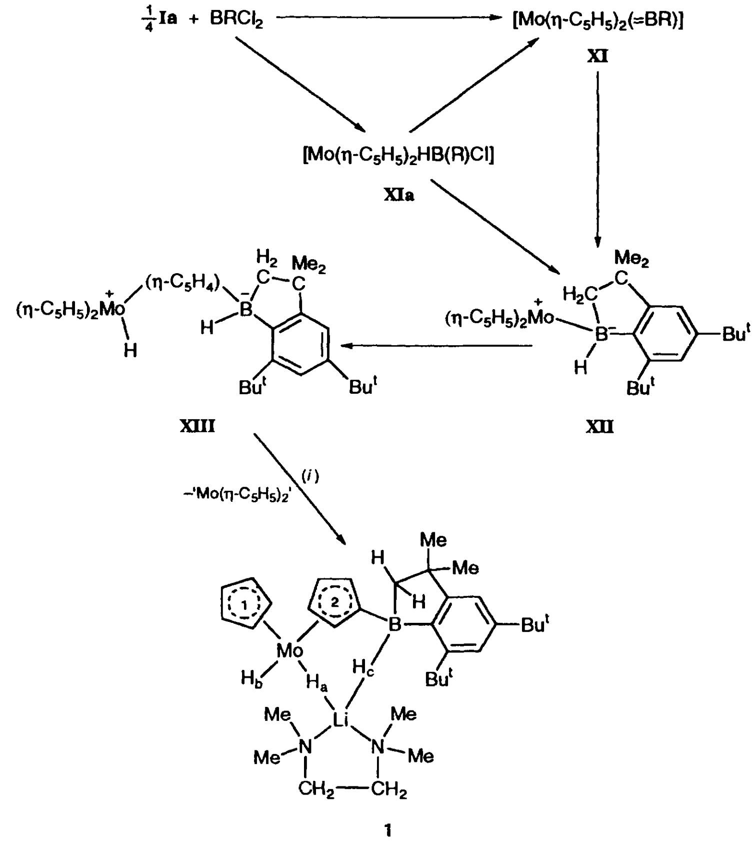


VIII

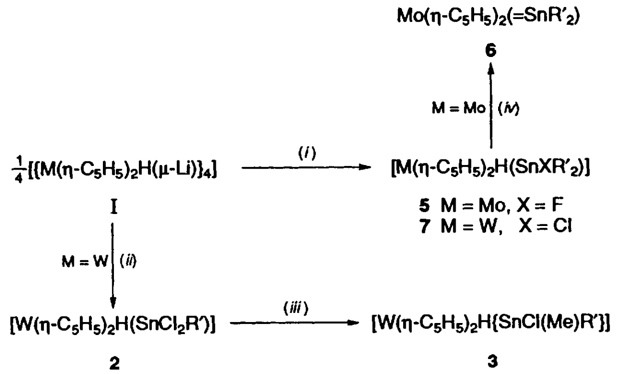
While the molecular structure of crystalline **1** has been established by a single-crystal X-ray diffraction study (see below), and its integrity in hydrocarbon solution (by NMR spectroscopy) has been shown to be unchanged, the mode of its formation is open to speculation. A possible pathway is shown in Scheme 2. It is proposed that a borinidine **XI** is the initial transient intermediate, which undergoes oxidative cyclometallation to afford **XII**, the Lewis-acid boron centre of which deprotonates one of the Mo-bound cyclopentadienyl ligands to yield **XIII** which in turn with **X** yields **1**. Alternatively, as pointed out by a referee, the initial product may have been $[Mo(\eta-C_5H_5)_2H\{B(R)Cl\}]$ **XIa**, which with HCl elimination yielded **XII**, either directly or *via* **XI**.

Preparation of $[W(\eta-C_5H_5)_2H\{SnCl(X)R'\}]$ $[R' = CH(SiMe_3)_2$; X = Cl **2** *or* Me **3**].—The route to complexes **2** and **3** from $[\{W(\eta-C_5H_5)_2H(\mu-Li)\}_4]$ **Ib** and $SnCl_3R'$ **4** is shown in Scheme 3. The formation of **4** from $SnCl_4$ and LiR is unexceptional as is the reaction between **Ib** and **4** yielding **2**, although its dehydrochlorination was a possibility. The reaction of **2** with methyllithium [(*iii*) in Scheme 3] might have been expected to result in its dehydrochlorination yielding $[W(\eta-C_5H_5)_2(=SnClR')]$, by analogy with the LiBu^t-triggered dehydrofluorination of $[Mo(\eta-C_5H_5)_2H(SnFR'_2)]$ **5** yielding the compound tentatively formulated as $Mo(\eta-C_5H_5)_2(=SnR'_2)$ **6**; attempts to obtain X-ray-quality crystals were unsuccessful. In the event, reaction (*iii*) led to **3**. Compound **2** is an unusual stannyltungsten complex, and hence its single-crystal molecular structure was determined (see below).

NMR Spectroscopic Identification of the Structure of Complex **1** *in* $[^2H_8]$*Toluene Solution*.—Various NMR spectroscopic techniques, including $^1H,^1H\text{-}\{^{11}B\}$, ^{11}B, ^{13}C DEPT



Scheme 2 Proposed reaction pathway to complex **1** from **Ia** + $BRCl_2$ + tmen. (*i*) $[Mo(\eta-C_5H_5)_2H\{Li(tmen)\}]$ **X**



Scheme 3 Synthesis of the stannyl–Group 6 metal complexes **2**, **3** and **5**–**7**. (*i*) $SnF_2R'_2$ or $SnCl_2R'_2$; (*ii*) $SnCl_3R'$ **4**, C_6H_5Me; (*iii*) LiMe, Et_2O; (*iv*) $LiBu^t$, C_6H_{14}

(distortionless enhancements by polarisation transfer) and various two-dimensional methods were employed to establish the structure of complex **1** in $[^2H_8]$toluene solution. In the low-frequency region of the ^1H NMR spectrum, two signals at δ −10.71 and −10.52 were assigned to be the terminal Mo–H_b and bridging Mo–H_a (see **1** in Scheme 2), based on ^1H–^1H COSY (correlation spectroscopy) and NOESY (nuclear Overhauser effect spectroscopy) experiments. The two metal hydrido signals form an AB pattern with coupling constant $^2J(^1H_a–^1H_b) = 11.3$ Hz. No coupling between the $^{95,97}Mo$ nuclei with ^1H_a or ^1H_b was observed. However, the fine structure of these two signals is assigned to the coupling $^1J(^1H_a–^7Li) = 6.05$ and $^2J(^1H_b–^7Li) = 3.95$ Hz. The experimental and the simulated ^1H NMR spectra of these regions are shown in Fig. 1.

Coupling due to ^{14}N ($I = 1$, 99.63%) is possible, and this was considered in the simulation. In the cyclopentadienyl region the singlet at δ 4.24 is assigned to the cp^1 protons, and the signals at δ 4.08, 4.61, 4.68 and 4.78 to the cp^2 protons (see **1** in Scheme 2). The AB quartet at δ 1.04 is assigned to the BCH_2 protons, based on the ^1H-^{13}C COSY experiment. By comparing the ^1H and ^1H-$\{^{11}B\}$ NMR spectra recorded at 500 MHz, we conclude that the BH_c signal is obscured by the signal in the δ 1.0–2.5 region. The presence of the B–H_c bond was confirmed by the ^{11}B and ^{11}B-$\{^1H\}$ spectra, the former showing a doublet centred at δ −19.0, $^1J(^{11}B–^1H_c) = 71 \pm 20$ Hz.

The CH_2 group attached to boron is identified (COSY and DEPT) as having $\delta(^{13}C)$ 57.86, the protons being an AB doublet, $\delta(^1H)$ 1.04. The broad ($w_{\frac{1}{2}} = 800$ Hz) signal at δ 46.13 (at 11.744 T) is assigned to the CH_2 groups of the tmen ligand, with $\delta(^1H)$ 2.1.

In summary, we conclude that the structure of complex **1** in toluene solution is identical to that found in the crystal.

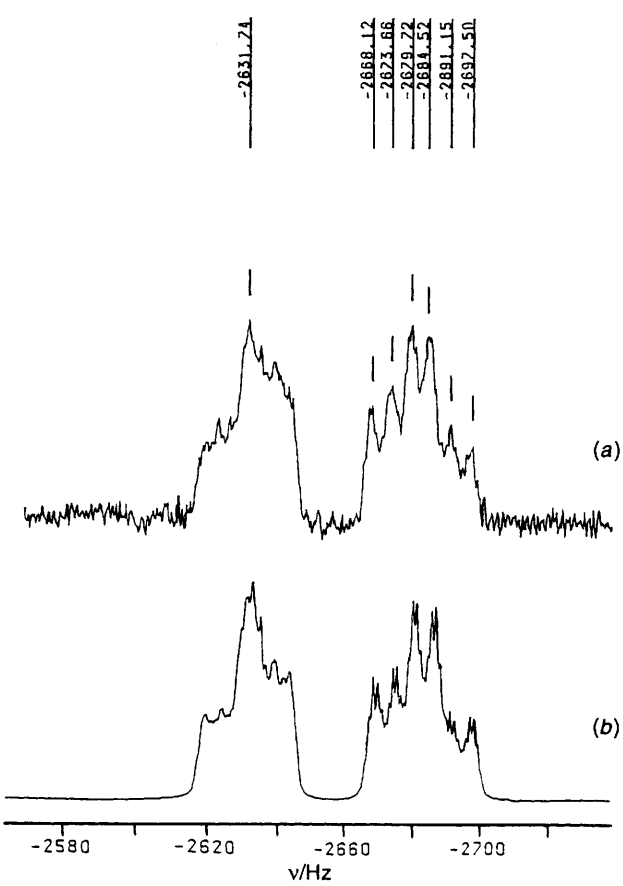


Fig. 1 Experimental (*a*) and simulated (*b*) ^1H NMR spectra at 500 MHz of complex **1** in $[^2H_8]$toluene in the region δ −10 to −11

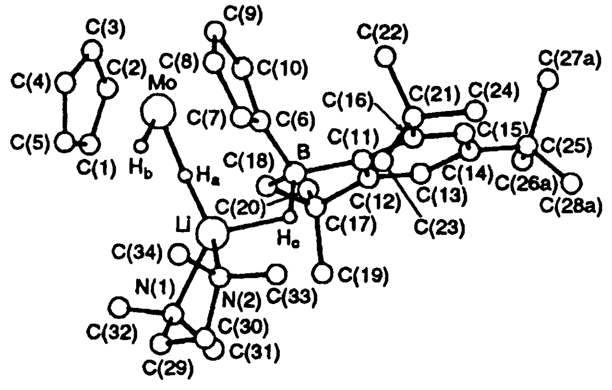


Fig. 2 Molecular structure of complex **1** and atom labelling

Crystal Structure of Crystalline Complex **1**.—The molecular structure of complex **1** with the atom numbering scheme is shown in Fig. 2, with selected bond lengths and angles in Table 1 and atomic coordinates in Table 4. The hydrido H-atom positions, although of low accuracy, were successfully refined by least squares and are structurally sensible. The hydride ligand H_c completes an approximately tetrahedral geometry at B and together with H_a provides a similar environment around Li. For Mo, the H_a–Mo–H_b angle of 80(3)° and the dihedral angle of 34° between the two cyclopentadienyl planes are in good agreement with the corresponding angles of 75.5(3) and 34.2° in $[Mo(\eta\text{-}C_5H_5)_2H_2]$.[11] The Mo···Li distance of 3.08(1) Å is significantly longer than the directly bonded Mo–Li distances of 2.61(4)–2.77(4) Å in $[\{Mo(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)\}_4]$ **Ia**.[9] Since Al and Li have similar covalent radii (1.30 and 1.34 Å), comparison may also be made with **II** (see Scheme 1),[10] containing both direct Al–Mo (average length 2.65 Å) and Al–H–Mo [Al···Mo (average) 2.97 Å] bonds. The Li···B distance of 2.63(1) Å is comparable to the corresponding distance of 2.50(1) Å in $[(2,4,6\text{-}Me_3C_6H_2)_2B(\mu\text{-}H)_2Li(dme)]$ **IV**.[6] The average C–C distances of 1.38 Å in the C_5H_5 ring are significantly shorter than in the C_5H_4 ring, 1.42 Å. The B–H_c (Li) distance of 1.21(5) Å is comparable to the bridging B–H distances of 1.14(3) Å in **IV**, 1.14(9) and 1.26(11) Å in $[N(PPh_3)_2][Mo(CO)_4\{(\mu\text{-}H)_2BH_2\}]$ **V**[7] and 1.12 Å in $[MoH\{(\mu\text{-}H)_2BH_2\}(PMe_3)_4]$ **VI**.[8] The bridging Mo–H_a (Li) distance of 1.66(5) Å is shorter than the corresponding values in **V** [1.99(9) and 2.04(8) Å][7] and **VI**, 1.96 Å. The terminal Mo–H_b bond distance of 1.44(6) Å is shorter than that in **VI**, 1.63 Å.[8] The Li–H distances of 1.67(6) (H_a) and 1.90(6) (H_c) Å compare with 2.06(4) Å in **IV**.[6]

Crystal Structure of Crystalline Complex **2**.—The molecular structure of complex **2** with the atom numbering scheme is

Table 1 Intramolecular bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Mo–H$_a$	1.66(5)	Mo–H$_b$	1.44(6)	C(11)–C(12)	1.387(8)	C(11)–C(16)	1.429(8)
Mo–cp(1)	1.948	Mo–cp(2)	1.951	C(12)–C(13)	1.404(9)	C(12)–C(17)	1.532(8)
Mo···Li	3.08(1)	Li···B	2.63(1)	C(13)–C(14)	1.385(9)	C(14)–C(15)	1.356(9)
H$_a$–Li	1.67(6)	H$_c$–B	1.21(5)	C(14)–C(25)	1.543(9)	C(15)–C(16)	1.396(8)
H$_c$–Li	1.90(6)	B–C(6)	1.634(9)	C(16)–C(21)	1.526(8)	C(17)–C(18)	1.522(9)
B–C(11)	1.652(9)	B–C(18)	1.682(11)	C(17)–C(19)	1.534(8)	C(17)–C(20)	1.529(9)
Li–N(1)	2.169(11)	Li–N(2)	2.173(12)	C(21)–C(22)	1.535(8)	C(21)–C(23)	1.517(10)
N(1)–C(29)	1.448(10)	N(1)–C(31)	1.448(10)	C(21)–C(24)	1.558(10)	C(25)–C(26a)	1.54(2)
N(1)–C(32)	1.454(11)	N(2)–C(30)	1.461(10)	C(25)–C(27a)	1.579(13)	C(25)–C(28a)	1.501(14)
N(2)–C(33)	1.470(12)	N(2)–C(34)	1.453(11)	C(25)–C(26b)	1.53(2)	C(25)–C(27b)	1.51(2)
C(1)–C(2)	1.401(11)	C(1)–C(5)	1.350(12)	C(25)–C(28b)	1.59(2)	C(29)–C(30)	1.476(13)
C(2)–C(3)	1.362(11)	C(3)–C(4)	1.383(12)	C(35)–C(36)	1.331(15)	C(35)–C(40)	1.547(15)
C(4)–C(5)	1.414(9)	C(6)–C(7)	1.422(10)	C(35)–C(41)	1.19(2)	C(36)–C(37)	1.406(15)
C(6)–C(10)	1.416(8)	C(7)–C(8)	1.419(8)	C(37)–C(38)	1.12(2)	C(38)–C(39)	1.63(2)
C(8)–C(9)	1.408(10)	C(9)–C(10)	1.424(9)	C(39)–C(40)	1.25(2)		
H$_a$–Mo–H$_b$	80(3)	cp(1)–Mo–cp(2)	149.9	C(11)–C(12)–C(17)	116.4(5)	C(13)–C(12)–C(17)	120.5(5)
H$_a$–Mo–cp(1)	108	H$_a$–Mo–cp(2)	92	C(12)–C(13)–C(14)	120.4(6)	C(13)–C(14)–C(15)	117.2(6)
H$_b$–Mo–cp(1)	99	H$_b$–Mo–cp(2)	106	C(13)–C(14)–C(25)	120.4(6)	C(15)–C(14)–C(25)	122.4(6)
Mo–H$_a$–Li	135(4)	B–H$_c$–Li	113(4)	C(14)–C(15)–C(16)	124.2(6)	C(11)–C(16)–C(15)	119.3(5)
H$_c$–B–C(6)	106(3)	H$_c$–B–C(11)	113(3)	C(11)–C(16)–C(21)	122.0(5)	C(15)–C(16)–C(21)	118.8(5)
H$_c$–B–C(18)	110(3)	C(6)–B–C(11)	118.0(5)	C(12)–C(17)–C(18)	102.9(5)	C(12)–C(17)–C(19)	107.7(5)
C(6)–B–C(18)	110.2(5)	C(11)–B–C(18)	99.3(5)	C(12)–C(17)–C(20)	113.3(5)	C(18)–C(17)–C(19)	110.3(5)
H$_a$–Li–H$_c$	95(3)	H$_a$–Li–N(1)	111(2)	C(18)–C(17)–C(20)	113.7(5)	C(19)–C(17)–C(20)	108.7(5)
H$_a$–Li–N(2)	145(2)	H$_c$–Li–N(1)	119(2)	B–C(18)–C(17)	106.8(5)	C(16)–C(21)–C(22)	109.7(5)
H$_c$–Li–N(2)	104(2)	N(1)–Li–N(2)	85.2(4)	C(16)–C(21)–C(23)	111.1(5)	C(16)–C(21)–C(24)	113.2(5)
Li–N(1)–C(29)	102.0(5)	Li–N(1)–C(31)	111.0(5)	C(22)–C(21)–C(23)	110.5(5)	C(22)–C(21)–C(24)	107.0(5)
Li–N(1)–C(32)	115.5(5)	C(29)–N(1)–C(31)	109.9(6)	C(23)–C(21)–C(24)	105.2(5)	C(14)–C(25)–C(26a)	114.0(7)
C(29)–N(1)–C(32)	108.9(6)	C(31)–N(1)–C(32)	109.2(7)	C(14)–C(25)–C(27a)	108.2(7)	C(14)–C(25)–C(28a)	108.4(7)
Li–N(2)–C(30)	103.9(6)	Li–N(2)–C(33)	115.7(6)	C(14)–C(25)–C(26b)	107(1)	C(14)–C(25)–C(27b)	111(1)
Li–N(2)–C(34)	111.6(5)	C(30)–N(2)–C(33)	109.6(6)	C(14)–C(25)–C(28b)	108.3(9)	C(26a)–C(25)–C(27a)	103.7(8)
C(30)–N(2)–C(34)	109.5(6)	C(33)–N(2)–C(34)	106.5(7)	C(26a)–C(25)–C(28a)	112.5(8)	C(27a)–C(25)–C(28a)	109.9(9)
C(2)–C(1)–C(5)	109.3(7)	C(1)–C(2)–C(3)	107.0(7)	C(26b)–C(25)–C(27b)	122(1)	C(26b)–C(25)–C(28b)	100(1)
C(2)–C(3)–C(4)	109.3(6)	C(3)–C(4)–C(5)	106.8(7)	C(27b)–C(25)–C(28b)	108(1)	N(1)–C(29)–C(30)	115.9(7)
C(1)–C(5)–C(4)	107.6(7)	B–C(6)–C(7)	129.8(5)	N(2)–C(30)–C(29)	112.7(7)	C(35)–C(40)–C(39)	107(1)
B–C(6)–C(10)	124.7(6)	C(7)–C(6)–C(10)	105.5(5)	C(36)–C(35)–C(40)	116.4(9)	C(36)–C(35)–C(41)	136(1)
C(6)–C(7)–C(8)	110.4(5)	C(7)–C(8)–C(9)	106.6(6)	C(40)–C(35)–C(41)	107(1)	C(35)–C(36)–C(37)	121(1)
C(8)–C(9)–C(10)	108.3(5)	C(6)–C(10)–C(9)	109.2(6)	C(36)–C(37)–C(38)	138(2)	C(37)–C(38)–C(39)	99(1)
B–C(11)–C(12)	107.5(5)	B–C(11)–C(16)	136.7(5)	C(38)–C(39)–C(40)	138(1)		
C(12)–C(11)–C(16)	115.8(5)	C(11)–C(12)–C(13)	123.0(5)				

cp(1) and cp(2) are the centroids of the C(1)–C(5) and C(6)–C(10) rings.

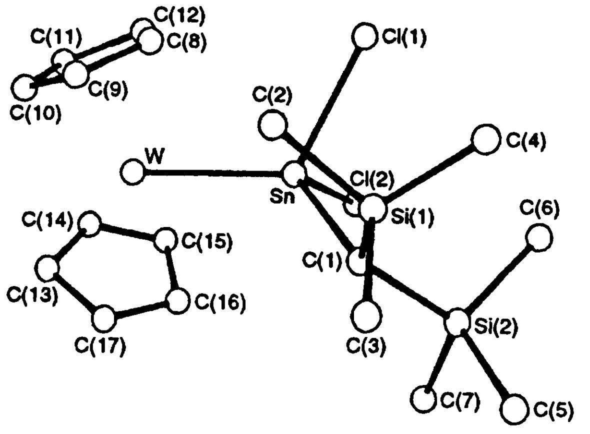


Fig. 3 Molecular structure of complex **2** and atom labelling

shown in Fig. 3, with selected bond lengths and angles in Table 2 and atomic coordinates in Table 5.

For complex **2** the hydride H atom could not be located but its presence can be inferred crystallographically from the non-planarity of the two cyclopentadienyl ring centroids, W and Sn, with the sum of angles at W being 351°. This is similar to that found in [W(cp)$_2$H{NN(H)C$_6$H$_4$F-4}][PF$_6$] (356.1°)[19] and within the range 351–356° reported in that reference for other [W(cp)$_2$H(X)] molecules. In **2** the cp–W–cp angle of 145° is larger and the Cp–W–Sn angles of 102 and 104° are smaller than the comparable angles in [W(cp)$_2$H{NN(H)-C$_6$H$_4$F-4}]$^+$ presumably due to the large bulk of the SnCl$_2$R′ group.

The W–Sn bond length of 2.706(1) Å is shorter than that in triaryltin–tungsten bonds, *e.g.* 2.837(1) Å in [W-(CO)$_2$(cp){=C(H)C$_6$H$_4$Me-4}(SnPh$_3$)],[20] but closer to that of 2.756(7) Å in the chloro-substituted Sn–W compound [{W(CO)$_3$(cp)}(SnCl$_2$)Os$_3$(CO)$_{12}$Cl].[21]

Experimental

General Procedures.—All manipulations were carried out under an argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from CaH$_2$ (hexane) or Na [tetrahydrofuran (thf), OEt$_2$]. Melting points are uncorrected. The ^{1}H, ^{13}C, ^{119}Sn and ^{19}F NMR spectra were recorded using a Bruker 80, 360 or 500 MHz spectrometer. The chemical shifts (δ) recorded were relative to SiMe$_4$ (^{1}H and ^{13}C), BF$_3$(OEt$_2$) (^{11}B), SnMe$_4$ (^{119}Sn) and CFCl$_3$ (^{19}F). The compounds [{M(η-C$_5$H$_5$)$_2$H(μ-Li)}$_4$][4] (M = Mo or W) and SnR$_2$X$_2$ (X = Cl[22] or F[23]) were prepared according to literature methods.

X-Ray Data Collection Structure Solution and Refinement for Complexes **1** *and* **2**.—Data were collected using a crystal, sealed in a capillary under argon, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ scan mode with Mo-Kα X-radiation

(λ = 0.710 73 Å). Intensities were measured for $+h + k \pm l$ reflections with $2 < \theta < 25°$. Corrections were made for Lorentz and polarisation effects and for compound **2** a correction was made for absorption using DIFABS[24] (maximum 1.40, minimum 0.81).

Both structures were solved by the automated heavy-atom routines of SHELXS 86[25] and refined by full-matrix least squares with all non-H atoms anisotropic using the SDP-PLUS package.[26] For complex **1** the hydride H atoms were located on a difference map and refined with U_{iso} fixed at 0.038 Å^2; other H atoms were fixed at calculated positions. Also for **1** both the C(25) Bu^t group and a molecule of toluene solvate are disordered over two orientations. For **2**, the hydrogen atoms were omitted. Further details are given in Table 3, final atomic coordinates in Tables 4 and 5.

Table 2 Intramolecular bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

W–Sn	2.706(1)	W–C(8)	2.293(12)
W–C(9)	2.317(14)	W–C(10)	2.276(13)
W–C(11)	2.244(14)	W–C(12)	2.285(12)
W–C(13)	2.27(2)	W–C(14)	2.228(14)
W–C(15)	2.277(14)	W–C(16)	2.320(13)
W–C(17)	2.325(14)	Sn–Cl(1)	2.405(3)
Sn–Cl(2)	2.442(3)	Sn–C(1)	2.180(8)
Si(1)–C(1)	1.870(9)	Si(1)–C(2)	1.880(12)
Si(1)–C(3)	1.868(12)	Si(1)–C(4)	1.866(12)
Si(2)–C(1)	1.889(9)	Si(2)–C(5)	1.905(11)
Si(2)–C(6)	1.873(11)	Si(2)–C(7)	1.906(12)
C(8)–C(9)	1.37(2)	C(8)–C(12)	1.43(2)
C(9)–C(10)	1.36(2)	C(10)–C(11)	1.39(2)
C(11)–C(12)	1.45(2)	C(13)–C(14)	1.45(2)
C(13)–C(17)	1.41(2)	C(14)–C(15)	1.38(2)
C(15)–C(16)	1.45(2)	C(16)–C(17)	1.41(2)
W–cp(1)	1.948	W–cp(2)	1.938
Cl(1)–Sn–Cl(2)	93.5(1)	Cl(1)–Sn–C(1)	102.8(2)
Cl(2)–Sn–C(1)	104.9(2)	C(1)–Si(1)–C(2)	111.7(4)
C(1)–Si(1)–C(3)	108.7(5)	C(1)–Si(1)–C(4)	114.1(5)
C(2)–Si(1)–C(3)	105.4(6)	C(2)–Si(1)–C(4)	108.5(5)
C(3)–Si(1)–C(4)	108.1(5)	C(1)–Si(2)–C(5)	110.1(4)
C(1)–Si(2)–C(6)	111.7(4)	C(1)–Si(2)–C(7)	111.9(5)
C(5)–Si(2)–C(6)	108.0(5)	C(5)–Si(2)–C(7)	103.6(5)
C(6)–Si(2)–C(7)	111.2(5)	Sn–C(1)–Si(1)	112.6(4)
Sn–C(1)–Si(2)	116.5(4)	Si(1)–C(1)–Si(2)	116.5(4)
C(9)–C(8)–C(12)	110(1)	C(8)–C(9)–C(10)	110(1)
C(9)–C(10)–C(11)	109(1)	C(10)–C(11)–C(12)	109(1)
C(8)–C(12)–C(11)	103(1)	C(14)–C(13)–C(17)	106(1)
C(13)–C(14)–C(15)	111(1)	C(14)–C(15)–C(16)	105(1)
C(15)–C(16)–C(17)	109(1)	C(13)–C(17)–C(16)	108(1)
W–Sn–C(1)	123.7(2)	cp(1)–W–cp(2)	144.7
cp(1)–W–Sn	102.2	cp(2)–W–Sn	103.8
W–Sn–Cl(1)	117.64(8)	W–Sn–Cl(2)	109.57(8)

cp(1) is the centroid of ring C(8)–C(12), cp(2) that of C(13)–C(17).

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

Preparations.—Complex **1**. Dichloro(2,4,6-tri-*tert*-butylphenyl)borane (1.90 g, 5.65 mmol) in toluene (50 cm^3) was added to a suspension of [{Mo(η-C$_5$H$_5$)$_2$H(μ-Li)}$_4$] **Ia** (1.36 g, 1.45 mmol) and tmen (0.90 cm^3, 5.96 mmol) in toluene (50 cm^3) at ambient temperature. The mixture was heated under reflux for 5 h, turning green-brown with a grey precipitate. The filtrate was concentrated and cooled yielding a green-brown solid, which was filtered off. Recrystallisation from hexane–toluene yielded the green-yellow complex **1** (1.10 g), m.p. 126–128 °C. NMR (C$_6$D$_6$): ^{1}H (250 MHz), δ −10.71 (m, 1 H), −10.52 (m, 1 H), −8.82 (s, 1 H), 0.28 (s, 3 H), 1.04 (m, 2 H), 1.49 (s, 3 H), 1.50 (s, 9 H), 1.76 (s, 9 H), 1.90 (s, 3 H), 1.96 (br s, 12 H), 2.10 (br s, 4 H), 4.08 (br s, 1 H), 4.24 (s, 5 H), 4.61 (br s, 1 H), 4.68 (br s, 1 H), 4.78 (br s, 1 H), 7.46 (d, 1 H, J = 1.7), and 7.60 (d, 1 H, J = 1.70 Hz); ^{13}C-{^{1}H} (125.5 MHz), δ 1.84, 32.76, 33.93, 34.25, 34.91, 35.38, 38.34, 44.24, 46.13, 47.16, 57.86, 73.06, 77.13, 77.85, 85.03, 89.29, 81.12, 117.11, 119.94, 138.36, 147.14, 153.08 and 163.28; ^{11}B (160.5 MHz), δ −19.0 [d, J(B–H) = 71 Hz].

SnCl$_3$R′ **4** [R′ = CH(SiMe$_3$)$_2$]. A solution of LiR′ (1.71 g, 10.3 mmol) in diethyl ether (50 cm^3) was added to a stirring solution of SnCl$_4$ (2.68 g, 10.3 mmol) in diethyl ether (30 cm^3) at 0 °C. The mixture was refluxed for 1 h and the white precipitate filtered off. The solvent from the colourless filtrate was evaporated *in vacuo* and the colourless oily residue was distilled. Compound **4** (1.53 g, 39%) was collected as the fraction having b.p. 93–98 °C (0.1 Torr).

[W(η-C$_5$H$_5$)$_2$H(SnCl$_2$R′)] **2** [R′ = CH(SiMe$_3$)$_2$]. The complex [{W(η-C$_5$H$_5$)$_2$H(μ-Li)}$_4$] **Ia** (0.42 g, 1.3 mmol) in toluene (100 cm^3) was added to a stirring suspension of SnCl$_3$R′ **4** (0.50 g, 1.3 mmol) in toluene (20 cm^3) at *ca.* 20 °C. The mixture was stirred for 2 h and the precipitate formed was filtered off. The reddish orange filtrate was concentrated and cooled to yield the orange crystalline compound **2** (0.72 g, 75%), m.p. 115–117 °C. NMR (C$_6$D$_6$): ^{1}H (80 MHz), δ 0.60 (s, 18 H), 4.70 [s, 10 H, satellite peaks J(^{1}H–^{183}W) = 11], and −13.43 (s, 1 H); ^{13}C-{^{1}H}, δ 4.0, [^1J(C–H) = 119], 24.6, [^1J(C–H) = 105 Hz], and 76.5, [^1J(C–H) = 183]; ^{119}Sn (134.3 MHz), δ 57.9 [J(^{119}Sn–^{183}W) = 1680.5 Hz].

Table 3 Crystal structure details for compounds **1** and **2** *

	1	**2**
Formula	$C_{34}H_{56}LiMoN_2$	$C_{17}H_{30}Cl_2Si_2SnW$
Crystal dimensions/mm	0.4 × 0.2 × 0.2	2.0 × 0.15 × 0.15
M	698.7	664.0
a/Å	9.966(6)	10.181(9)
b/Å	20.110(4)	17.858(9)
c/Å	20.319(8)	12.566(9)
β/°	100.72(4)	92.46(5)
U/Å^3	4001.3	2282.4
D_c/g cm^{-3}	1.16	1.93
F(000)	1276	1272
μ(Mo-Kα)/cm^{-1}	3.5	65.8
Unique reflections measured	7257	4371
Significant reflections, $I > n\sigma(I)$	3124 (n = 3)	2784 (n = 1)
No. of variables	457	208
R	0.044	0.039
R′	0.055	0.048
$(\Delta\rho)_{max}$/e Å^{-3}	0.52	0.75

* Details in common: monoclinic, space group $P2_1/c$; Z = 4; T 293 K; $w = 1/\sigma^2(F)$.

Table 4 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	1548.0(5)	1718.7(3)	1201.7(3)	C(19)	−3892(6)	152(4)	762(3)
H$_a$	31(57)	1488(30)	772(29)	C(20)	−2264(8)	−626(4)	1451(4)
H$_b$	1254(55)	2280(31)	759(29)	C(21)	−2831(5)	2120(3)	2819(3)
H$_c$	−2408(54)	1651(30)	1076(28)	C(22)	−1354(7)	2173(4)	3201(3)
B	−1774(7)	1305(4)	1516(4)	C(23)	−3043(7)	2564(4)	2204(4)
Li	−1384(10)	1893(6)	413(5)	C(24)	−3765(7)	2417(4)	3281(4)
N(1)	−2069(5)	1556(3)	−608(3)	C(25)	−5213(6)	7(3)	3292(3)
N(2)	−2232(5)	2848(3)	48(3)	C(26a)	−5365(11)	−741(7)	3125(6)
C(1)	2141(9)	983(4)	438(4)	C(27a)	−4456(15)	18(7)	4047(6)
C(2)	2783(8)	795(4)	1084(4)	C(28a)	−6566(11)	353(8)	3225(7)
C(3)	3659(7)	1294(4)	1329(4)	C(26b)	−4460(21)	−641(12)	3526(12)
C(4)	3580(6)	1793(5)	855(4)	C(27b)	−5736(23)	464(12)	3775(9)
C(5)	2605(7)	1587(4)	295(3)	C(28b)	−6497(17)	−287(12)	2798(9)
C(6)	−316(5)	1678(3)	1777(3)	C(29)	−2352(9)	2178(5)	−966(4)
C(7)	67(6)	2349(3)	1693(3)	C(30)	−3001(9)	2699(5)	−621(4)
C(8)	1432(6)	2461(4)	2024(3)	C(31)	−3311(9)	1169(5)	−667(4)
C(9)	1916(6)	1851(4)	2316(3)	C(32)	−1070(9)	1185(6)	−898(4)
C(10)	855(6)	1370(4)	2156(3)	C(33)	−3135(9)	3165(5)	450(5)
C(11)	−2688(5)	1086(3)	2081(3)	C(34)	−1166(9)	3327(4)	−4(5)
C(12)	−3083(5)	430(3)	1956(3)	C(35)	3495(10)	4140(5)	611(6)
C(13)	−3895(6)	83(3)	2337(3)	C(36)	3847(8)	4770(5)	537(5)
C(14)	−4326(5)	389(3)	2871(3)	C(37)	4739(9)	5106(9)	1046(5)
C(15)	−3947(5)	1031(3)	3000(3)	C(38)	5351(10)	4990(9)	1552(6)
C(16)	−3162(5)	1397(3)	2627(3)	C(39)	4853(14)	4227(7)	1631(6)
C(17)	−2668(6)	105(3)	1342(3)	C(40)	4125(12)	3804(6)	1283(5)
C(18)	−1511(6)	549(4)	1209(3)	C(41)	2802(12)	3737(7)	279(9)

Atoms C(26a)–C(28a) have occupancy 0.6, C(26b)–C(28b) have occupancy 0.4.

Table 5 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for complex **2**

Atom	*x*	*y*	*z*
W	1372.4(4)	897.8(2)	1959.9(3)
Sn	2373.3(6)	−503.6(3)	2116.1(5)
Cl(1)	3107(4)	−1079(2)	516(2)
Cl(2)	589(3)	−1402(2)	2308(3)
Si(1)	5583(3)	−645(2)	2877(2)
Si(2)	3615(3)	−1760(2)	4003(2)
C(1)	388(1)	−84(0)	331(1)
C(2)	562(1)	18(1)	196(1)
C(3)	663(1)	−38(1)	407(1)
C(4)	638(1)	−146(1)	222(1)
C(5)	501(1)	−194(1)	503(1)
C(6)	356(1)	−256(1)	304(1)
C(7)	209(1)	−174(1)	483(1)
C(8)	266(1)	85(1)	51(1)
C(9)	285(1)	155(1)	95(1)
C(10)	169(1)	193(1)	93(1)
C(11)	73(1)	148(1)	44(1)
C(12)	131(2)	77(1)	15(1)
C(13)	17(2)	162(1)	305(1)
C(14)	−68(1)	113(1)	241(1)
C(15)	−45(1)	38(1)	266(1)
C(16)	57(1)	39(1)	350(1)
C(17)	93(2)	114(1)	373(1)

[W(η-$C_5H_5)_2$H(SnClR$'_2$)] **7** [R$'$ = CH(SiMe$_3)_2$]. As for the preparation of complex **2**, but using SnCl$_2$R$'_2$ in place of SnCl$_3$R$'$. Compound **7** (0.60 g, 72%), m.p. 88–90 °C, was obtained from SnCl$_2$R$'_2$ (0.54 g) and **Ib** (0.34 g). NMR (C_6D_6): ^{1}H (80 MHz), δ 0.35 (s, 18 H), 0.49 (s, 18 H), 4.21 [s, 10 H, *J*(C–H) = 11], and −12.98 (s, 1 H); ^{13}C-{^{1}H} δ 5.18, 14.67 and 75.9; ^{119}Sn, δ 86.75 [*J*(^{119}Sn–^{183}W) = 1296.6 Hz].

[Mo(η-$C_5H_5)_2$H(SnFR$'_2$)] **5** [R$'$ = CH(SiMe$_3)_2$]. As for the preparation of complex **2**, except that hexane was used as solvent. The complex [{Mo(η-$C_5H_5)_2$H(μ-Li}$_4$] **Ia** (0.38 g, 1.62 mmol) and SnF$_2$R$'_2$ (0.77 g, 1.62 mmol) afforded compound **5** (0.83 g, 75%), m.p. 200–203 °C. NMR (C_6D_6): ^{1}H (80 MHz), δ 0.34 (s, 18 H), 0.46 (s, 18 H), 4.27 (s, 10 H), and −9.38 [s, 1 H, *J*(H–F) = 4.4]; ^{13}C-{^{1}H}, δ 4.82, 4.97, 19.04, 19.14 [*J*(^{13}C–^{119}Sn) = 42.6] and 78.59; ^{119}Sn (134.3 MHz), δ 353.3 [d, *J*(^{119}Sn–^{19}F) = 2314]; ^{19}F (75.28 MHz), δ −161.5 [s, satellite peaks, *J*(^{119}Sn–^{19}F) = 2319 Hz].

[W(η-$C_5H_5)_2$H{SnCl(Me)R$'$}] **3** [R$'$ = CH(SiMe$_3)_2$]. A hexane solution of LiMe (0.65 cm^3, 1.4 mol dm^{-3}, 0.91 mmol) in diethyl ether (50 cm^3) was added to a stirring solution of [W(η-$C_5H_5)_2$H(SnCl$_2$R$'$)] **2** (0.60 g, 0.90 mmol) in diethyl ether (100 cm^3). The mixture was stirred for 2 h; the precipitate which had formed was filtered off. Diethyl ether was removed *in vacuo* from the filtrate and the residue was extracted into pentane (2 × 50 cm^3). Concentration and cooling of the extract afforded the yellow crystalline compound **3** (0.51 g, 88%) (Found: C, 33.6; H, 5.15. $C_{18}H_{33}ClSi_2SnW$ requires C, 35.2; H, 5.35%), m.p. 146–148 °C. ^{1}H NMR (C_6D_6, 80 MHz): δ 0.21 (s, 18 H), 0.48 (s, 18 H), 0.83 (s, 3 H), 4.0 (s, 5 H), 4.2 (s, 5 H) and −13.07 [s, 1 H, satellite peaks, *J*(H–W) = 73.4, ^{2}*J*(H–Sn) = 164.3 Hz].

Reaction of [{Mo(η-$C_5H_5)_2$H(SnFR$'_2$)] **5** *with* LiBu^t.—A hexane solution of LiBu^t (0.35 cm^3, 1.7 mol dm^{-3}, 5.95 mmol) was added to complex **5** (0.40 g, 0.59 mmol) in hexane (125 cm^3). The red mixture was stirred at 20 °C for 3 h. Filtration, concentration and cooling of the filtrate afforded a deep red solid compound believed to be **6** (0.68 g, 59%). NMR (C_6D_6): ^{1}H (360 MHz), δ 0.51 (s, 36 H) and 4.30 (s, 5 H); ^{13}C-{^{1}H}, δ 5.32, 15.75 and 78.48; ^{119}Sn (134.3 MHz), δ 256.8 (s). The chemical ionisation (ammonia) mass spectral peak at *m*/*z* = 665 is assigned to [Mo(η-$C_5H_5)_2$(SnR$'_2$)]$^+$.

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References

1 P. B. Hitchcock, M. F. Lappert and W.-P. Leung, *J. Chem. Soc., Chem. Commun.*, 1987, 1282.

2 R. Bohra, P. B. Hitchcock, M. F. Lappert and W.-P. Leung, *Polyhedron*, 1989, **8**, 1884.

3 A. G. Avent, M. F. Lappert, B. W. Skelton, C. L. Raston, L. M. Engelhardt, S. Harvey and A. H. White, in *Heteroatom Chemistry*, ed. E. Block, VCH, New York, 1990, ch. 15.

4 B. R. Francis, M. L. H. Green, T. Luong-Thi and G. A. Moser, *J. Chem. Soc., Dalton Trans.*, 1976, 1339.

5 M. L. H. Green, R. E. MacKenzie and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1976, 1993.

6 J. Hooz, S. Akiyama, F. J. Cedar, M. J. Bennett and R. M. Tuggle, *J. Am. Chem. Soc.*, 1974, **96**, 274.

7 S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkewich, T. J. Marks, D. L. Tipton and B. R. Whittlesey, *J. Am. Chem. Soc.*, 1977, **99**, 7154.

8 J. L. Atwood, W. E. Hunter, E. Carmona-Guzman and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 467.

9 R. A. Forder and K Prout, *Acta Crystallogr., Sect. B*, 1974, **30**, 2318.

10 R. A. Forder, M. L. H. Green, R. E. MacKenzie, J. S. Poland and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1973, 426.

11 A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink and G. D. Stucky, *Inorg. Chem.*, 1977, **16**, 3303.

12 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587.

13 I. P. Rothwell, *Polyhedron*, 1985, **4**, 177.

14 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 691.

15 M. R. Churchill, J. W. Ziller, J. H. Freudenberger and R. R. Schrock, *Organometallics*, 1984, **3**, 1554.

16 M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267.

17 R. M. Whittal, G. Ferguson, J. F. Gallagher and W. E. Piers, *J. Am. Chem. Soc.*, 1991, **113**, 9867.

18 P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47 and refs. therein.

19 F. W. B. Einstein, T. Jones, A. J. L. Hanlan and D. Sutton, *Inorg. Chem.*, 1982, **21**, 2585.

20 D. Hodgson, J. A. K. Howard, F. G. A. Stone and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1985, 1331.

21 D. B. Firfiray, A. Irving and J. R. Moss, *J. Chem. Soc., Chem. Commun.*, 1990, 377.

22 T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551.

23 C. Couret, J. Escudié, J. Satgé, A. Raharinirina and J. D. Andriamizaka, *J. Am. Chem. Soc.*, 1985, **107**, 8280.

24 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 159.

25 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.

26 SDP-PLUS, Enraf-Nonius, Delft, 1985.

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