

Bis- η -cyclopentadienyl complexes of niobium and tungsten with silyl and stannyl ligands

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Received 23 March 1995

Abstract

The thermal reaction of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ with SiMe_3H gives $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$, which readily loses SiMe_3H to give the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}]$ fragment, which can be trapped by PMe_3 to give $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SiMe}_3)(\text{PMe}_3)]$. The reaction of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta\text{-H}_2\text{C}=\text{CHPh})]$ with SiMe_3H yields the bis-silyl $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$, which also readily loses SiMe_3H ; thus reaction of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$ with PMe_3 gives $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SiMe}_3)(\text{PMe}_3)]$. The reaction of $[\{\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{HLi}\}_4]$ with SnMe_3Cl gives $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$, which is deprotonated by ${}^n\text{BuLi}$ to give the weakly nucleophilic anion $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)]^-$. The reaction of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ with SnMe_2Cl_2 in the presence of Et_3N gives $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_2\text{Cl})_2]$, which is readily methylated to yield the tungsten bis-stannyl $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2]$.

Keywords: Niobium; Tungsten; Silicon; Tin

1. Introduction

There has been recent interest in bis(η -cyclopentadienyl)transition metal complexes containing silyl and stannyl ligands [1–3]. Tilley and coworkers have studied the synthesis and reactivity of Group 4 [4] and Group 5 [5] metallocene silyl complexes, and recently the disilene ($\text{Me}_2\text{Si}=\text{SiMe}_2$) and silene ($\text{Me}_2\text{Si}=\text{CH}_2$) ligands have been stabilized on metallocene centres [6]. Berry and coworkers have reported trialkylsilyl derivatives of tantalum [7], molybdenum and tungsten [8]. Compounds with bonds between lanthanide metals and Si, Ge or Sn have also been reported [9].

We previously described the preparation and chemistry of the bent-metallocene $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SnMe}_3)]$ [10] and noted that the Nb–Sn bond was quite unreactive. Here we describe the synthesis of closely related complexes containing Nb–Si and W–Sn bonds.

2. Results and discussion

The reaction between an excess of SiMe_3H and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ at 35°C gives the mono-silyl complex $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ (**1**) (Scheme 1). The reaction may proceed via reductive elimination of H_2 to give $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}]$ and subsequent oxidative addition of SiMe_3H . The tantalum analogues $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiR}_3)]$ ($\text{SiR}_3 = \text{SiH}_3, \text{SiMeH}_2, \text{SiMe}_2\text{H}, \text{SiMe}_3, \text{SiMe}_2\text{Cl}$ or $\text{Si}(\text{OMe})_3$) were prepared in a similar manner from $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ but higher temperatures were required [7]. Previously we prepared the analogous niobium–tin complex $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SnMe}_3)]$ by reaction of $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\text{Li}\}_x]$ with SnMe_3Cl [10a]; however, the addition of SiMe_3Cl to $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\text{Li}]_x$ resulted in a very slow reaction and after several days yielded a mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$, $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$. This slower nucleophilic substitution at Si by $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]^-$ compared with Sn may reflect both the smaller size of Si and the greater strength of the Si–Cl bond.

The spectroscopic data for **1** and other compounds described in this report are presented in Table 1. The ^1H NMR spectrum of a freshly prepared sample of **1** shows

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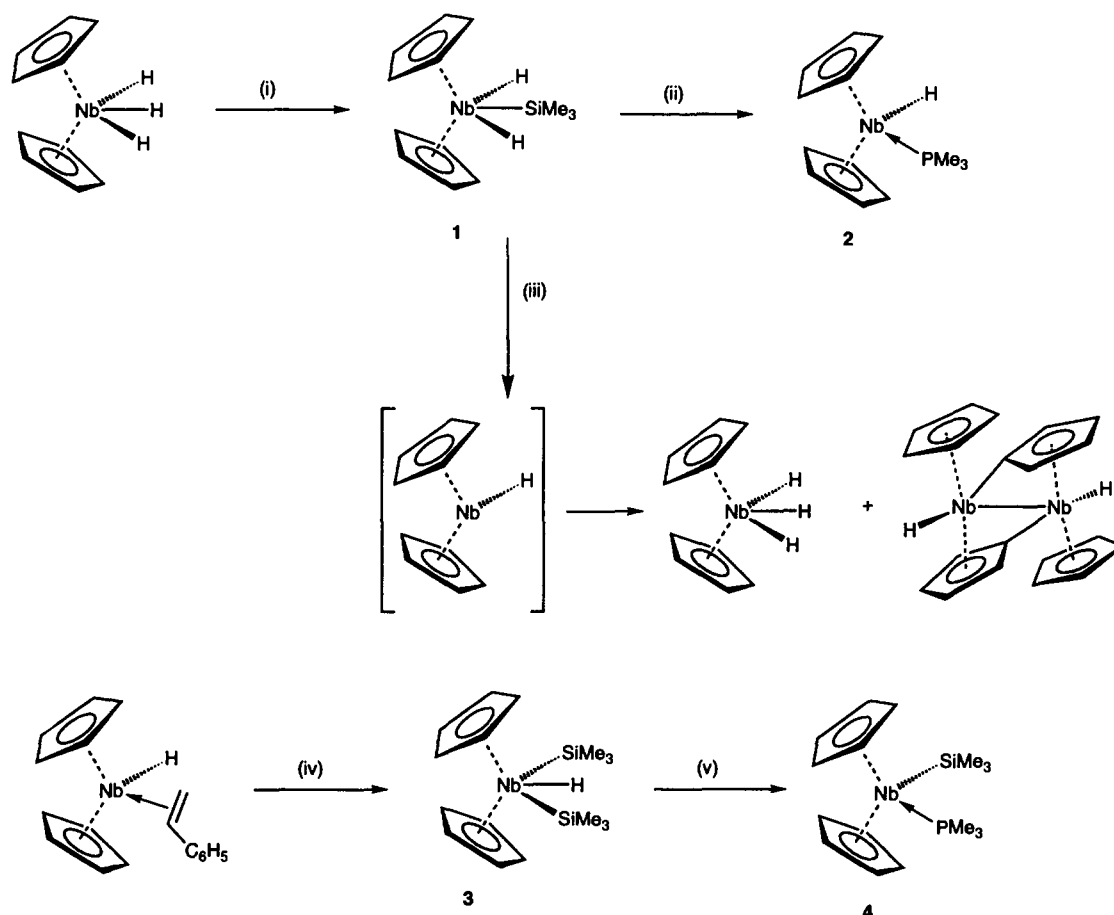
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resonances assigned to $(\eta\text{-C}_5\text{H}_5)$ and SiMe_3 with a broad ($\Delta\nu_{1/2} = 100$ Hz) signal at $\delta = -4.9$ ppm assigned to Nb–H. The low abundance of the spin-active silicon isotope (^{29}Si ; $I = \frac{1}{2}$; 4.7%), together with the relatively small $^2J(^{29}\text{Si}\text{-H})$ coupling constants, means that ^{29}Si satellites are not observed. The quadrupolar ^{93}Nb nucleus (100%; $I = \frac{9}{2}$) means that NMR spectra of nuclei which are σ bound to Nb are broad and frequently unobservable at room temperature. We have not obtained ^{29}Si spectra for any of the compounds reported here. The NMR data suggest that only the symmetrical isomer of **1** is present in solution, behaviour which is in contrast with the formation of both symmetrical and asymmetrical isomers in the case of $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiR}_3)]$.

The silyl complex **1** might have the non-classical structure $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-H-SiMe}_3)]$ [11]. The best method for characterizing such structures in solution involves measurement of the hydride–silicon coupling constant. Values typical of a classical structure have $0 \text{ Hz} < ^2J_{\text{H-}^{29}\text{Si}} < 7 \text{ Hz}$, whilst larger values (up to 70 Hz) are associated with the one-bond coupling of a “molecular silane” structure. Given the broadness of the hydride resonance of **1** we are unable to distinguish be-

tween a classical or “molecular silane” structure. The analogous niobocene silyl complexes $[\text{Nb}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{H})_2(\text{SiR}_3)]$ with $\text{SiR}_3 = \text{SiMe}_2\text{Ph}$, SiMePh_2 , SiPhH_2 , SiPh_2H or SiPh_3 were recently reported by Otero and coworkers; the spectroscopic data for these compounds are consistent with a classical structure. The structure of $[\text{Nb}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{H})_2(\text{SiHPh}_2)]$ has been determined by single-crystal X-ray diffraction and shows an classical undistorted Cp_2MX_3 structure with no short H–Si contacts [12]. In contrast, the molecular structure of $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_2\text{H})_2]$ determined by X-ray diffraction shows an asymmetric structure with an inconclusively short H–Si contact [7].

Solutions of **1** are unstable and decompose slowly at room temperature. After 30 min at room temperature the ^1H NMR spectrum shows new resonances at $\delta = -2.0$ ppm and $\delta = -3.6$ ppm owing to $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ and a broad hydride signal at $\delta = -2.5$ ppm that can be assigned to “niobocene” $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-}\sigma\text{-C}_5\text{H}_4\text{H})_2\}]$ [13]. An additional doublet near 0.0 ppm may be assigned to SiMe_3H . The intensity of these additional resonances increases with time. These observations indicate a facile reductive elimination of SiMe_3H from **1** to give the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}]$ fragment,



Scheme 1. The synthesis and reactions of niobium silyl complexes. Reagents and conditions: (i) excess Me_3SiH , 35°C , 7 days, 50%; (ii) PMe_3 , 60°C , 8 days, 39%; (iii) C_6D_6 solution; (iv) excess Me_3SiH , 20°C , 7 days, 55%; (v) excess PMe_3 , 55°C , 7 days, 65%.

which is known to give $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ and the $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-}\sigma\text{-C}_5\text{H}_4)\text{H}\}_2]$ dimer (Scheme 1) [13]. Clearly this elimination of SiMe_3H is an equilibrium process, and the formation of **1** from $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ and an excess of SiMe_3H involves displacement of this equilibrium towards the product by the excess of silane. The facile elimination of SiMe_3H from **1** and **3** meant that satisfactory microanalytical data could not be obtained.

The facile reductive elimination of SiMe_3H from **1** to give the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}]$ fragment is also indicated by the reaction of **1** with PMe_3 , which yields the previously reported complex $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)\text{H}]$ (**2**) [13].

The previously described [14] complex $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-H}_2\text{C}=\text{CHPh})\text{H}]$ reacts with SiMe_3H under mild conditions to give the bis-silyl compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$ (**3**). This reaction is analogous to that used for the preparation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)_2]$, and the mechanism of that reaction has been discussed [10a]. The ^1H NMR spectrum of **3** shows resonances assigned to the $(\eta\text{-C}_5\text{H}_5)$ and SiMe_3 moieties, with the expected integrals; a broad resonance at $\delta = -3.6$ ppm is assigned to Nb-H ; again no ^{29}Si satellites were observed. Berry and coworkers [7] have prepared a number of tantalum analogues of **3** by reaction of $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2(\text{L})(\text{Me})]$ ($\text{L} = \text{PMe}_3$ or $\text{CH}_2=\text{CH}_2$) with silanes. The spectroscopic data sug-

Table 1
Spectroscopic and analytical data ^a

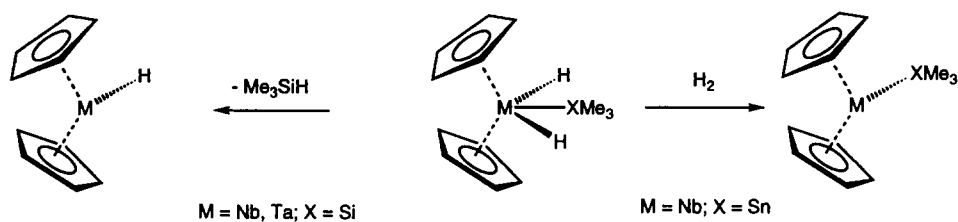
Compound and analysis ^b given as found (%) (required%)	δ (ppm)	
	^1H NMR data	$^{119}\text{Sn}(^1\text{H})$ and other NMR data
$[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ (1) Green C, 44.5 (52.3); H, 5.1 (6.7)	4.59 (s, 10H, $(\eta\text{-C}_5\text{H}_5)$) 0.55 (s, 9H, SiMe_3) -4.9 (br s, 2H, $\Delta\nu_{1/2} = 45$ Hz, Nb-H)	
$[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$ (3) Pale green C, 52.4 (51.9); H, 8.7 (7.9)	4.37 (s, 10H, $(\eta\text{-C}_5\text{H}_5)$) 0.40 (s, 18H, SiMe_3) -3.6 (br s, 1H, $\Delta\nu_{1/2} = 35$ Hz, Nb-H)	
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$ (5) ^c Yellow	4.02 (s, 10H, $(\eta\text{-C}_5\text{H}_5)$) 0.39 (s, 9H, $J(\text{H-Sn}) = 36$ Hz, SnMe_3) -12.34 (s, 1H, $J(\text{H-}^{183}\text{W}) = 77$ Hz, $J(\text{H-Sn}) = 140$ Hz, W-H)	$^{119}\text{Sn}(^1\text{H})$: -38.0 ($J(^{119}\text{Sn-}^{183}\text{W}) = 859$ Hz)
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{D}(\text{SnMe}_3)]$ (5-d ₁)		$^2\text{H}(^1\text{H})$: -12.3 (s, $J(^2\text{H-}^{183}\text{W}) = 12$ Hz, $J(^2\text{H-Sn}) = 21$ Hz, W-D) $^{119}\text{Sn}(^1\text{H})$: -37.65 ($J(^{119}\text{Sn-}^{183}\text{W}) = 858$ Hz, $J(^{119}\text{Sn-}^2\text{H}) = 22$ Hz)
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_2\text{Cl})_2]$ (7) Bright yellow C, 26.2 (24.6); H 3.5 (3.2); Cl, 11.3 (10.4) Mass spectrum (electron impact (EI)): m/e 647 $[\text{P} - \text{Cl}]^+$	5.00 (s, 10H, $J(\text{H-Sn}) = 8$ Hz, $(\eta\text{-C}_5\text{H}_5)$) 0.58 (s, 12H, $J(\text{H-Sn}) = 36$ Hz, SnMe_2)	$^{119}\text{Sn}(^1\text{H})$: 240.3 ($J(^{119}\text{Sn-}^{183}\text{W}) = 1142$ Hz, $J(^{119}\text{Sn-}^{117}\text{Sn}) = 1323$ Hz)
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2]$ (8) Bright orange C, 30.6 (29.9); H, 4.6 (4.4)	3.83 (s, 10H, $J(\text{H-Sn}) = 7$ Hz, $(\eta\text{-C}_5\text{H}_5)$) 0.30 (s, 18H, $J(\text{H-Sn}) = 36$ Hz, SnMe_3)	$^{119}\text{Sn}(^1\text{H})$: -26.1 ($J(^{119}\text{Sn-}^{183}\text{W}) = 912$ Hz, $J(^{119}\text{Sn-}^{117}\text{Sn}) = 1058$ Hz)
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_2\text{Cl})]$ (9) ^d Yellow C, 29.7 (28.8); H 3.5 (3.4); Cl 7.4 (7.1) Mass spectrum (EI): m/e 463 $[\text{P} - \text{Cl}]^+$	4.76 (s, 10H, $J(\text{H-Sn}) = 6$ Hz, $(\eta\text{-C}_5\text{H}_5)$) 0.52 (s, 6H, $J(\text{H-Sn}) = 33$ Hz, SnMe_2Cl) -13.00 (s, 1H, $J(\text{H-}^{183}\text{W}) = 72$ Hz, $J(\text{H-Sn}) = 159$ Hz, W-H)	$^{119}\text{Sn}(^1\text{H})$: 224.5 ($J(^{119}\text{Sn-}^{183}\text{W}) = 1230$ Hz)

^a Unless otherwise stated, all NMR data is at room temperature in benzene-*d*₆, at 300 MHz (^1H), 46.07 MHz (^2H) or 111.87 MHz (^{119}Sn). In the case of coupling constants the use of ^{119}Sn or ^{117}Sn indicates that coupling to the individual isotopes was resolved; the use of Sn indicates that coupling to the two isotopes was not separately resolved.

^b Microanalytical data is given as the best results from at least two independent determinations.

^c This known compound is characterized spectroscopically; no analytical data are available.

^d IR (KBr pellet): $\nu(\text{W-H})$ 1901(s) cm^{-1} .



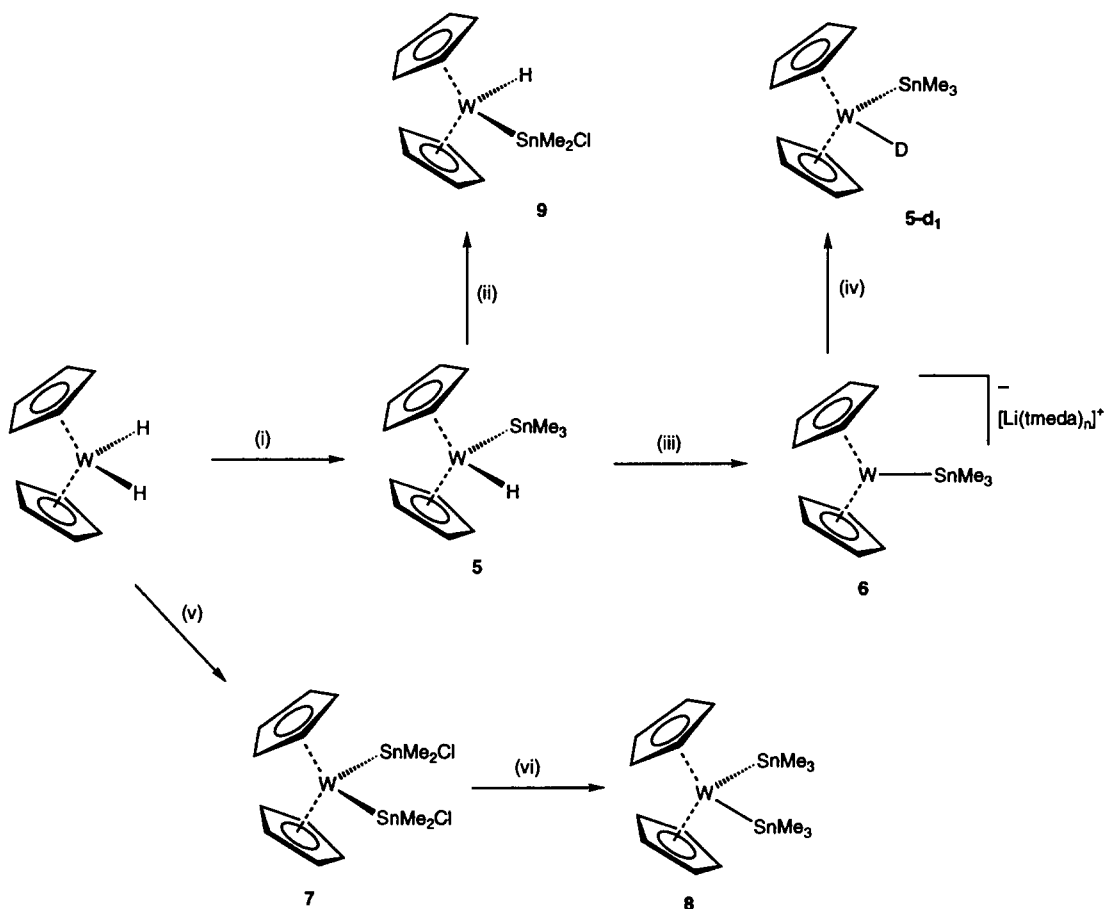
Scheme 2. The elimination of H_2 from $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SnMe}_3)]$ and of SiMe_3H from $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$.

gest the formation of only the symmetrical isomer of **3** in contrast with the observation of the unsymmetrical isomer of $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMeH}_2)_2]$, although asymmetrical isomers of the other tantalum bis-silyls are not formed.

The compound **3** appears to be stable at room temperature and NMR spectra do not reveal any elimination of SiMe_3H in the absence of other reagents. However, heating a toluene solution of **3** with PMe_3 slowly produced a red solution from which deep-red feathery polycrystallites of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)(\text{SiMe}_3)]$ (**4**) were isolated. Compound **4** was characterized by comparison of its spectroscopic data with those reported by Tilley and coworkers [5]. This reaction appears to pro-

ceed by elimination of SiMe_3H to give the $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SiMe}_3)]$ fragment, which is trapped by PMe_3 . Berry and coworkers [7] have observed that $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiR}_3)_2]$ complexes also react reversibly with PMe_3 to give $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)(\text{SiR}_3)]$ and HSiR_3 .

It appears from this and previously reported work [7,10] that certain trends may be identifiable in the reactivities of the dihydrides $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{XMe}_3)]$ and the monohydrides $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{XMe}_3)_2]$ ($\text{M} = \text{Nb}; \text{X} = \text{Sn or Si}$) ($\text{M} = \text{Ta}; \text{X} = \text{Si}$). Thus the complexes containing Nb–Sn bonds display a wide range of reactions in which the Nb–Sn bond is inert; for example the reactions of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SnMe}_3)]$ with L ($\text{L} = \text{styrene, PMe}_3, \text{isoprene or butadiene}$) result in elimina-



Scheme 3. The synthesis and reactions of tungsten stannyl complexes. Reagents and conditions: (i) $n\text{-BuLi}$, toluene, and then Me_3SnCl , 65%; (ii) Me_2SnCl_2 , Et_3N , toluene, 70%; (iii) $n\text{-BuLi}$, petroleum ether; (iv) D_2O , THF; (v) Me_2SnCl_2 , Et_3N , toluene, 70%; (vi) MeMgI , Et_2O , 70%.

tion of H_2 and formation of $[Nb(\eta-C_5H_5)_2(L)(SnMe_3)]$. The corresponding tantalum compounds $[Ta(\eta-C_5H_5)_2H_2(SnMe_3)]$ and $[Ta(\eta-C_5H_5)_2H(SnMe_3)_2]$ are less reactive and elimination of H_2 is difficult to achieve; this may reflect the higher bond strengths of third-row elements. We note that the spectroscopic data show a symmetrical structure for $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$, but the elimination of H_2 may proceed via the formation of an asymmetric intermediate with *cis*-hydride ligands, and this would be analogous to the ground state *cis*-dihydride structures observed for the asymmetric isomers of $[Ta(\eta-C_5H_5)_2H_2(SiR_3)]$.

As noted, the Nb–Si complex $[Nb(\eta-C_5H_5)_2H_2(SiMe_3)]$ readily loses Me_3SiH at room temperature, whilst symmetric and asymmetric $[Ta(\eta-C_5H_5)_2H_2(SiR_3)]$ complexes isomerize at 80°C and lose SiR_3H at 110°C [7].

The elimination of either XMe_3H or H_2 from $[M(\eta-C_5H_5)_2H_2(XMe_3)]$ ($X = Si$ or Sn ; $M = Nb$ or Ta) is depicted in Scheme 2. The results indicate that, whereas stannyl complexes lose H_2 , the corresponding silyl complexes preferentially lose SiR_3H . The observed reversibility of the addition of $SiMe_3H$ to the $[Nb(\eta-C_5H_5)_2H]$ fragment suggests that these reactions proceed under thermodynamic control and thus that the reaction products are those dictated by bond dissociation energies (BDEs). The following BDEs are taken from [15]: Si–H, 378 kJ mol⁻¹; Sn–H, 308 kJ mol⁻¹; H–H, 436 kJ mol⁻¹. We note that for the Sn–H and Si–H data the BDE values from other sources can vary by as much as 50 kJ mol⁻¹.

The reactions of the niobium stannyl $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$ proceed by elimination of H_2 to give H–H and Nb–Sn bonds, which suggests that the reaction is driven by the strength of the H–H bond in H_2 .

The niobium silyl complex $[Nb(\eta-C_5H_5)_2H_2(SiMe_3)]$ readily undergoes elimination of $SiMe_3H$ (giving Si–H and Nb–H bonds) and does not lose H_2 (which would give H–H and Nb–Si bonds). Since the Si–H bond is almost as strong as the H–H bond, the deciding factor is the relative strengths of the Nb–Si and Nb–H bonds and, since $SiMe_3H$ is eliminated, it appears that the Nb–H bond is stronger than the Nb–Si bond in these compounds.

In 1974, Lappert and coworkers [16] prepared the complex $[W(\eta-C_5H_5)_2H(SnMe_3)]$ (5) by the reaction between $[W(\eta-C_5H_5)_2H_2]$ and $[Me_3SnNMe_2]$. Here we report that $W(\eta-C_5H_5)_2HSnMe_3$ (5) can also be prepared by the reaction between the structurally characterised [17] tetrameric lithium complex $[(W(\eta-C_5H_5)_2HLi)_4]$ and $SnMe_3Cl$ (Scheme 3). The ¹¹⁹Sn chemical shift which we have determined by direct observation is in close agreement with that obtained by the ¹H{¹¹⁹Sn} internuclear double resonance technique [18].

The reaction of $[W(\eta-C_5H_5)_2H(SnMe_3)]$ with ⁿBuLi–*N,N,N',N'*-tetramethylethylenediamine (tmeda) gave a yellow solid, which we tentatively suggest to be $[W(\eta-C_5H_5)_2(SnMe_3)][Li(tmeda)_x]$ (6) by analogy with $[Nb(\eta-C_5H_5)_2H(SnMe_3)][Li(12-crown-4)]$ [10b] and $[(W(\eta-C_5H_5)_2HLi)_4]$ [17]. Addition of D_2O to 6 produced a yellow solution, from which $[W(\eta-C_5H_5)_2D(SnMe_3)]$ (5–*d*₁) was isolated with about 75% yield. Addition of $SnMe_3Cl$ to 6 produced a clear colourless solution, from which no tractable product could be isolated, and there was no evidence for the formation of the bis-stannyl $[W(\eta-C_5H_5)_2(SnMe_3)_2]$.

Bulychev and coworkers [19] have observed that $[Mo(\eta-C_5H_5)_2H_2]$ reacts with alkyltin halides in the presence of triethylamine to give Mo–Sn complexes, including the structurally characterized $[Mo(\eta-C_5H_5)_2HSnMe_3]$ [19]. The same synthetic approach has been applied to $[Re(\eta-C_5H_5)_2H]$ [20]. We have shown that the reaction between $[W(\eta-C_5H_5)_2H_2]$ and two equivalents of $SnMe_2Cl_2$ in the presence of an excess of triethylamine gives the distannane derivative $[W(\eta-C_5H_5)_2(SnMe_2Cl)_2]$ (7) together with $[Et_3NH]Cl$. The ¹¹⁹Sn{¹H} NMR spectrum of 7 shows a singlet ($\delta = 240.3$ ppm) with satellites due to coupling to ¹⁸³W (¹*J*(¹¹⁹Sn–¹⁸³W) = 1142 Hz), as well as a further set of satellites due to coupling to ¹¹⁷Sn (²*J*(¹¹⁹Sn–¹¹⁷Sn) = 1323 Hz); this second set of satellites arise from the isotopomer $[W(\eta-C_5H_5)_2(^{119}SnMe_2Cl)(^{117}SnMe_2Cl)]$. The low intensity signals due to the isotopomer $[^{183}W(\eta-C_5H_5)_2(^{119}SnMe_2Cl)(^{117}SnMe_2Cl)]$ were not observed, nor were signals due to isotopomers containing ¹¹⁵Sn ($I = \frac{1}{2}$; 0.35% abundance).

Treatment of $[W(\eta-C_5H_5)_2(SnMe_2Cl)_2]$ (7) with $MeMgI$ brought about replacement of the two chlorine groups to give the bis-stannyl complex $[W(\eta-C_5H_5)_2(SnMe_3)_2]$ (8) with a good yield. The ¹¹⁹Sn{¹H} NMR spectrum of 8 shows a singlet ($\delta = -26.1$ ppm) with satellites due to coupling to ¹⁸³W (¹*J*(¹¹⁹Sn–¹⁸³W) = 912 Hz), as well as a further set of satellites due to coupling to ¹¹⁷Sn (²*J*(¹¹⁹Sn–¹¹⁷Sn) = 1058 Hz) in the isotopomer $[W(\eta-C_5H_5)_2(^{119}SnMe_3)(^{117}SnMe_3)]$.

The reaction between $SnMe_2Cl_2$, Et_3N and $[W(\eta-C_5H_5)_2H(SnMe_3)]$ gave a good yield of yellow needles. These were identified as the unexpected product $[W(\eta-C_5H_5)_2H(SnMe_2Cl)]$ (9) in which the W– $SnMe_3$ has been replaced by W– $SnMe_2Cl$. The ¹H NMR spectrum of 9 shows a singlet ($\delta = -13.00$ ppm; ¹*J*(¹H–¹⁸³W) = 72 Hz; ²*J*(¹H–¹¹⁹Sn) \approx ²*J*(¹H–¹¹⁷Sn) = 159 Hz) assigned to W–H which integrates for one proton relative to the $(\eta-C_5H_5)_2$ and $SnMe_3$ resonances. The mechanism of this reaction has not been investigated, although we note that the silicon complexes $[W(\eta-C_5H_5)_2(SiMe_3)(SiR_2Cl)]$ ($R = ^iPr$ or CD_3), which are analogues of our expected product, undergo rapid intramolecular methyl exchange and intermolecular scrambling of Cl^- .

The new compounds and reactions described in this work are shown in Schemes 1 and 3.

3. Experimental details

All preparations, manipulations and reactions were carried out using standard techniques for handling air-sensitive materials (Schlenk line and glove-box). Solvents were pre-dried over molecular sieves (4A or 5A) and then distilled from appropriate drying agents. Deuterated solvents were stored over activated molecular sieves or sodium–potassium alloy. The compounds $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ [21], $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta\text{-H}_2\text{C}=\text{CH-Ph})]$ [14] and $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ [22] were synthesized by published methods. NMR spectra were obtained with a Bruker AM-300 instrument. ^1H NMR spectra were referenced to the residual protiosolvent (benzene- d_6 , $\delta = 7.10$ ppm; toluene- d_8 , $\delta = 2.05$ ppm). In the case of ^{119}Sn and ^{31}P NMR, spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software, with respect the following standards: SnMe_4 (^{119}Sn) and 85% $\text{H}_3\text{PO}_4\text{-D}_2\text{O}$ (^{31}P). Elemental analysis was performed by the Analysis Department of the Inorganic Chemistry Laboratory, University of Oxford.

3.1. Preparation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ (1)

The pressure above a solution of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ (4.25 g, 18.8 mmol) in toluene (100 cm^3) in a large Young's ampoule was reduced and SiMe_3H (3 cm^3) was vacuum distilled. The mixture was stirred at 35°C for 7 days. The volatiles were removed under reduced pressure and the residue was extracted with pentane: diethyl ether (2:1; 300 cm^3). The extract was cooled to -80°C to give a green-yellow polycrystalline product. (yield, about 50%).

3.2. Reaction of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ with PMe_3

A solution of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SiMe}_3)]$ (0.6 g, 2 mmol) in toluene (60 cm^3) was treated with an excess of PMe_3 (about 1 cm^3) and the mixture was kept at 60°C for 8 days to give a red solution. The volatiles were removed under reduced pressure and the red residue extracted with diethyl ether (150 cm^3). The extracts were filtered and cooled to -80°C to give red crystals of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)\text{H}]$ (2) (yield, 230 mg (39%)).

3.3. Preparation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$ (3)

A solution of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-H}_2\text{C}=\text{CHPh})\text{H}]$ (prepared from $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ (1.85 g, 8.2 mmol) and an excess of styrene) in toluene (70 cm^3) was treated

with an excess of SiMe_3H (about 1.5 cm^3) and the mixture was stirred at 20°C for 7 days, during which there was little colour change. The volatiles were removed under reduced pressure and the residue extracted with pentane (60 cm^3). Cooling of the extract to -80°C gave a green powder (yield, 1.67 g (55%)).

3.4. Preparation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)(\text{SiMe}_3)]$ (4)

A solution of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SiMe}_3)_2]$ (0.3 g, 0.8 mmol) in toluene (30 cm^3) was treated with an excess of PMe_3 (0.75 cm^3) and the mixture was kept at 55°C for 7 days to give a red solution. The volatiles were removed under reduced pressure and the residue was extracted into pentane (30 cm^3). The solution was filtered and the filtrate was cooled to -80°C to give feathery red polycrystallites (yield, 190 mg (65%)).

3.5. Preparation of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$ (5)

A solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ (1.88 g, 5.95 mmol) in toluene (80 cm^3) was treated with an excess of $^n\text{BuLi}$ (5 cm^3 of 2.5 M solution in hexane, 12.5 mmol) with stirring. Addition of 1,2-dimethoxyethane (about 1 cm^3) gave a yellow precipitate. The suspension was stirred for 30 min and the solid was allowed to settle. The liquid was decanted and the solid was washed with light petroleum (60 cm^3). The solid was suspended in light petroleum (80 cm^3) and a solution of Me_3SnCl (1.19 g, 5.93 mmol) in light petroleum (50 cm^3) was added during 30 min to give a yellow solution over a red-brown solid. Filtration followed by cooling the filtrate to -80°C gave $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$ (yield, 1.83 g (65%)).

3.6. Preparation of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{D}(\text{SnMe}_3)]$ (5- d_1)

A solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$ (200 mg, 0.4 mmol) in light petroleum (60 cm^3) was treated dropwise with $^n\text{BuLi}:\text{tmeda}$ (1:1 mixture, excess) in light petroleum to give an orange-yellow precipitate. Stirring was continued for 15 min and the solid was allowed to settle. The supernatant liquid was discarded and the solid washed with light petroleum (40 cm^3). The solid was suspended in light petroleum (80 cm^3) and a solution of D_2O (1 cm^3) and tetrahydrofuran (THF) (10 cm^3) was added rapidly, giving an emulsion. The solvents were removed under reduced pressure and the residue dried in vacuo for 1 h. Extraction with pentane (20 cm^3) gave a yellow solution, which was cooled to -25°C and then to -80°C , giving yellow crystals (yield, 150 mg (75%)).

3.7. Preparation of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_2\text{Cl})_2]$ (7)

A stirred solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ (0.55 g, 1.74 mmol) in toluene (50 cm^3) containing an excess of

Et_3N (about 2 cm^3) was treated with a solution of SnMe_2Cl_2 (0.76 g, 3.48 mmol) in toluene (40 cm^3). A heavy white precipitate was formed. After 30 min the yellow solution was filtered and the solvent removed under reduced pressure to give a yellow solid. This was extracted with toluene (50 cm^3), the extract was filtered, and pentane (10 cm^3) was added. Cooling to -80°C gave light-yellow crystals (yield, less than 30%). The insoluble material from the first filtration was dissolved in technical-grade acetone (60 cm^3) and a further quantity of product (contaminated by some Et_3NHCl) was obtained by cooling this solution to -80°C (total yield, 0.83 g (70%)).

Work-up of the product from this reaction must be performed carefully in order to avoid contamination of the product with $[\text{Et}_3\text{NH}]\text{Cl}$; the best conditions appear to be to carry out the reaction at room temperature in toluene, to filter the yellow solution to remove the white ammonium salt, then to cool it to precipitate the product. Heating the reaction mixture causes significant amount of $[\text{Et}_3\text{NH}]\text{Cl}$ to dissolve and subsequently to co-crystallize with **7**. Even after careful isolation the product contains traces of $[\text{Et}_3\text{NH}]\text{Cl}$.

3.8. Preparation of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2]$ (**8**)

A solution of MeMgI (from MeI , 0.3 ml, 4 mmol) in diethyl ether (40 cm^3) was added to $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_2\text{Cl})_2]$ (0.382 g, 0.56 mmol) and the solution was stirred for 3 days. No noticeable colour change occurred. The solvent was removed under reduced pressure and the residue extracted with THF (20 cm^3). The extract was treated with THF (20 cm^3) containing H_2O (1 cm^3) to decompose the excess of the Grignard reagent. The volatiles were removed under reduced pressure and the residue dried in vacuo for 1 h. Extraction of the residue with pentane (10 cm^3) gave an orange solution which failed to deposit crystals at -80°C . The solvent was removed under reduced pressure to give an oily orange solid (yield, 250 mg (70%)).

3.9. Preparation of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_2\text{Cl})]$ (**9**)

A stirred solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{SnMe}_3)]$ (1.835 g, 3.83 mmol) in toluene (60 cm^3) containing an excess of Et_3N (5 cm^3) was treated with SnMe_2Cl_2 (0.838 g, 3.83 mmol) in toluene (20 cm^3). After 2–3 min a precipitate appeared. Stirring was continued for 14 h to give a white solid in a yellow solution. The solid was filtered off and discarded. The solvent was removed under reduced pressure and the residue taken up in toluene:diethyl ether (1:1; 120 cm^3). The solution was cooled to -25°C and then to -80°C to give yellow needles (yield, 1.35 g (70%)).

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