Synthesis and Reactivity of Bis(η-cyclopentadienyl) Trimethyltin Derivatives of Niobium: Crystal and Molecular Structure of [{Nb(η-C_5H_5)$_2$($SnMe_3$)}$_2$(μ-O)]†

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The reaction between [Nb(η-C_5H_5)$_2H_3$] and LiBu followed by $SnMe_3Cl$ gives [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] **2**, also produced from [Nb(η-C_5H_5)$_2H_3$] and $SnMe_3H$. Heating **2** with styrene, PMe_3, isoprene or but-2-yne gives [Nb(η-C_5H_5)$_2$L($SnMe_3$)] (L = η-H_2C=CH-C_6H_5, **3**; PMe_3, **4**; η-H_2C=CHCMe=CH_2, **5**; or η-C_2Me_2 **6**). Photolysis of complex **3** in the presence of CO, 2,6-$Me_2C_6H_3NC$, MeCN, or PMe_3 gives [Nb(η-C_5H_5)$_2$L($SnMe_3$)] (L = CO, **7**; 2,6-$Me_2C_6H_3NC$, **8**; η^2-MeCN, **9a** and **9b**; or PMe_3, **4**). Heating **3** with H_2 regenerates **2** and releases styrene. Compound **3**, **5** or **6** reacts with $SnMe_3H$ to give the bis(stannyl) derivative [Nb(η-C_5H_5)$_2$H($SnMe_3$)$_2$] **10**, which is also formed by prolonged heating of [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] with $SnMe_3H$. Photolysis of **3** under CO_2 gives a mixture of **7** and [{Nb(η-C_5H_5)$_2$($SnMe_3$)}$_2$(μ-O)] **11** by cleavage of the CO_2 molecule. Compound **11** crystallises in the orthorhombic space group *Pbca* with a = 8.409(3), b = 21.109(4) and c = 15.582(3) Å. The bridging oxygen atom sits on a crystallographic inversion centre giving a linear Nb–O–Nb group with Nb–O 1.9434(4) and Nb–Sn 2.8619(5) Å.

Many compounds containing bonds between transition metals and the Group 14 elements Si, Ge, Sn and Pb are known.[1–3] Examples where the transition metal is a Group 8 element predominate and there are relatively few compounds containing bonds between early transition metals and the Group 14 elements. Furthermore, there are very few cases where the reaction chemistry of transition metal–Group 14 metal complexes has been studied, the most thorough investigations being by Tilley and co-workers on silyl complexes of Group 4[4–6] and 5.[7] Berry and Jiang have also described some silyl complexes of tantalum.[8,9] We decided to explore the synthesis and properties of early transition metal–tin compounds. Here we report our studies on compounds containing niobium–tin bonds. Previous examples of compounds with Nb–Sn bonds are [Nb(η-C_5H_5)$_2$(CO)(SnR_xCl_{3-x})] (R = Ph, x = 1–3; R = Et, x = 2).[10] The related compounds [M(η-C_5H_5)$_2H_x$($SnMe_3$)] (M = Mo or W, x = 1; M = Ta, x = 2),[11] [Ta(η-C_5H_5)$_2H_2$($SnMe_nCl_{3-n}$)] (n = 0 or 1)[12–14] and [Nb(η-C_5H_5)$_2$($SiMe_3$)X] (X = Cl, CO, PMe_3 and C_2H_4)[15] have been previously described.

Results and Discussion

The compound [Ta(η-C_5H_5)$_2H_2$($SnMe_3$)] was prepared by Lappert from the reaction of the trihydride [Ta(η-C_5H_5)$_2H_3$] with $SnMe_3$(NMe_2).[11] We found that the corresponding reaction using the thermally less stable [Nb(η-C_5H_5)$_2H_3$] gave only the 'niobocene' dimer [{Nb(η-C_5H_5)H(μ-σ,η^5-C_5H_4)}$_2$].[16,17] However, treatment of [Nb(η-C_5H_5)$_2H_3$] with $SnMe_3H$ at room temperature for 14 d gives [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] **2**.

As an alternative approach to [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] we set out to prepare the niobium analogue of [{(η-C_5H_5)$_2TaH_2Li$}$_n$] which we described previously,[18] and to treat this with $SnMe_3Cl$. Addition of LiBu to a toluene solution of [Nb(η-C_5H_5)$_2H_3$] gave an orange powder **1** within 1 min. We presume this orange powder to be [{(η-C_5H_5)$_2NbH_2Li$}$_n$]. Characterisation was prevented since **1** slowly decomposes on standing at room temperature and more rapidly in the presence of tetrahydrofuran. The preparation and characterisation of a series of complexes of stoichiometry [(η-C_5H_5)$_2$NbXYM] (X, Y = H; M = crown ether derivative of Li, Na or K) will be described in a subsequent publication together with some trimethyltin derivatives (X, Y = H or $SnMe_3$; M = same).[19]

Addition of 1 equivalent of $SnMe_3Cl$ to complex **1** led to the isolation of highly crystalline [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] **2** in 70–95% yield. This reaction was typically performed on a scale of 4–5 g and was the most convenient route to **2**. Compound **2** is thermally more stable than [Nb(η-C_5H_5)$_2H_3$]. Thus, C_6D_6 solutions of **2** are unchanged after 1 week at 65 °C whilst solutions of [Nb(η-C_5H_5)$_2H_3$] at 60 °C decompose to the dimer [{Nb(η-C_5H_5)H(μ-σ, η^5-C_5H_4)}$_2$] within hours.[16]

The data characterising **2** and the other new complexes described below are presented in Table 1. They will not be further discussed, except where interpretation is not straightforward. We note, however, that the NMR spectra were frequently broad due to quadrupolar coupling to the ^{93}Nb nucleus ($I = \frac{9}{2}$, natural abundance 100%). This effect has been previously noted and discussed by other workers.[20] In particular, Nb–H resonances were very broad at room temperature, and the ^{119}Sn NMR signals were only observable as very broad resonances under conditions of thermal decoupling of the ^{93}Nb nucleus at −80 °C.

The ^{1}H NMR spectrum of [Nb(η-C_5H_5)$_2H_2$($SnMe_3$)] **2** shows a slightly broad ($\Delta\nu_{\frac{1}{2}}$ = 10 Hz) high-field resonance at δ −5.12 with Sn satellites [^2J(Sn–H) = 168 Hz]. A ^{119}Sn-{^{1}H} NMR spectrum at −80 °C shows a broad singlet at δ 107.6, which is a poorly resolved triplet in the ^{119}Sn-{^{1}H-Me} spectrum [^2J(Sn–H) ≈ 170 Hz]. We propose the symmetrical structure for **2** shown in Scheme 1. This is analogous to [Ta(η-C_5H_5)$_2H_2$($SiMe_2Ph$)][21] and [Ta(η-C_5H_5)$_2H_2$($SnMeCl_2$)][13] whose crystal structures have been determined. The possibility that the two hydrogens in **2** are present as a dihydrogen (η-H_2) ligand[22–24] is ruled out by the preparation of the deuterium-substituted complex [Nb(η-C_5H_5)$_2$H(D)($SnMe_3$)] **2D**, from the reaction of [Nb(η-C_5H_5)$_2H_3$] with $SnMe_3D$. The deuteriated complex shows no resolvable H–D coupling in the rather broad

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† μ-Oxo-bis[bis(η-cyclopentadienyl)(trimethylstannyl)niobium].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: atm = 101 325 Pa.

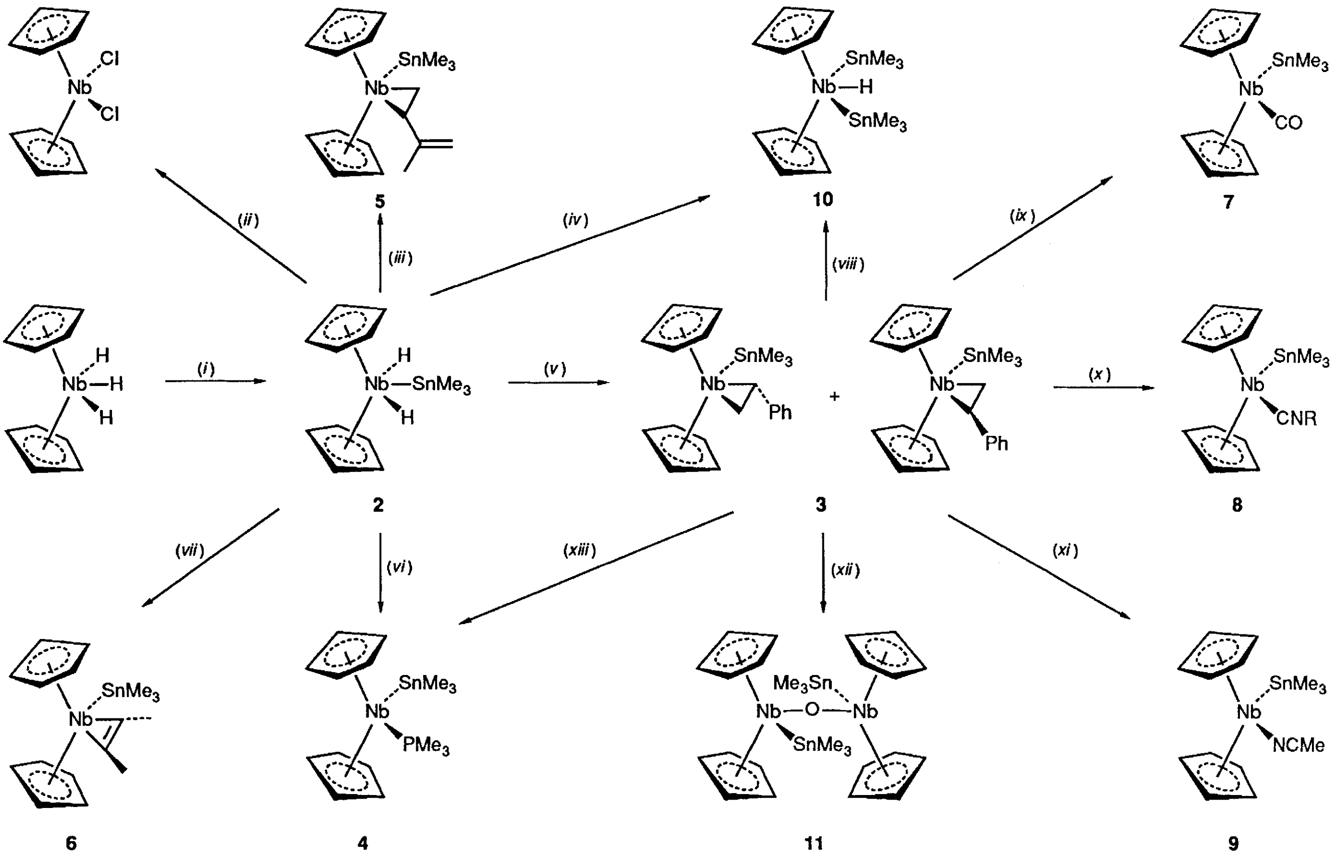
Table 1 Analytical and spectroscopic data

Compound, colour and analysis[a]	NMR data[b] ^{1}H	 ^{13}C
2 [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)][c,d]	4.52 [s, 10 H, *J*(Sn–H) 5, η-C_5H_5]	85.5 [d, *J*(C–H) 177, η-C_5H_5]
Light brown	0.54 [s, 9 H, *J*(Sn–H) 41, $SnMe_3$]	−1.7 [q, *J*(C–H) 126, $SnMe_3$]
C, 40.2 (40.15); H, 5.7 (5.4)	−5.12 [s, 2 H, *J*(Sn–H) 168, Nb–H]	
2D [Nb(η-C_5H_5)$_2$H(D)($SnMe_3$)][c,e]	4.53 (s, 10 H, η-C_5H_5)	85.6 (η-C_5H_5)
	0.53 [s, 9 H, *J*(Sn–H) 38, $SnMe_3$]	−1.7 ($SnMe_3$)
	−5.12 [s, 1 H, *J*(Sn–H) 168, $\Delta\nu_{\frac{1}{2}}$ = 10 Hz, Nb–H]	
3 [Nb(η-C_5H_5)$_2$(η-H_2C=CHPh)($SnMe_3$)][c,f]		
Bright yellow, mixture of two isomers		
C, 51.3 (51.4); H, 5.5 (5.5)		
(*a*) *exo*	4.27 [2, *J*(Sn–H) 6, η-C_5H_5]	152.3 (s, phenyl ring)
	4.02 [s, *J*(Sn–H) 5, η-C_5H_5]	122.9 (partially obscured, phenyl ring)
	2.36 [dd, *J*(H_a–H_b) 12.8, *J*(H_a–H_c) 10.3, H_a]	Two obscured resonances
	1.31 [dd, *J*((H_b–H_a) 12.8, *J*(H_b–H_c) 6.7, H_b]	92.2 [d, *J*(C–H) 176, η-C_5H_5]
	1.02 [dd, *J*(H_c–H_a) 10.3, *J*(H_c–H_b), 6.7, H_c]	90.75 [d, *J*(C–H) 177, η-C_5H_5]
	0.48 [s, *J*(Sn–H) 34, $SnMe_3$]	33.8 [d, *J*(C–H) 147, C–H_a]
		10.7 [dd, *J*(C–H) 146, 148, CH_bH_c]
		−5.9 [q, *J*(C–H) 125, $SnMe_3$]
(*b*) *endo*	4.24 [s, *J*(Sn–H) 5, η-C_5H_5]	Arene resonances obscured
	4.19 [s, *J*(Sn–H) 6, η-C_5H_5]	92.9 [d, *J*(C–H) 176, 2 × η-C_5H_5]
	2.42 [dd, *J*(H_d–H_e) 12.0, *J*(H_d–H_f) 10.8, H_d]	31.9 [d, *J*(C–H) 147, C–H_d]
	1.36 [dd, *J*(H_e–H_d) 12.0, *J*(H_e–H_f) 6.1, H_e]	16.6 [dd, *J*(C–H) 146, 148, CH_eH_f]
		−4.9 [q, *J*(C–H) 126, $SnMe_3$]
	1.01 [dd, *J*(H_f–H_d) 10.8, *J*(H_f–H_e) 6.1, H_f]	
	0.30 [s, *J*(Sn–H) 32, $SnMe_3$]	
4 [Nb(η-C_5H_5)$_2$(PMe_3)($SnMe_3$)][c,g]	4.20 [d, 10 H, *J*(P–H) 2, *J*(Sn–H) 7.5, η-C_5H_5]	83.1 [d, *J*(C–H) 175, η-C_5H_5]
Bright red		
Satisfactory analysis not obtained	0.80 [d, 9 H, *J*(P–H) 7, PMe_3]	23.6 [dq, *J*(C–H) 135, *J*(C–P) 22, PMe_3]
	0.44 [d, 9 H, *J*(Sn–H) 27, $SnMe_3$]	−4.05 [q, *J*(C–H) 130, $SnMe_3$]
5 [Nb(η-C_5H_5)$_2$(η-H_2C=CHCMe=CH_2)($SnMe_3$)][c]	4.36 (s, H_d or H_e)	151.0 (s, quaternary)
Dark green	4.26 (s, H_e or H_d)	98.6 [t, *J*(C–H) 154, CH_dH_e]
C, 47.3 (47.5); H, 5.9 (6.00)	4.21 [s, *J*(Sn–H) 5, η-C_5H_5]	92.6 [d, *J*(C–H) 170, η-C_5H_5]
	4.14 [s, *J*(Sn–H) 5, η-C_5H_5]	90.5 [d, *J*(C–H) 170, η-C_5H_5]
	1.94 (s, H_f, H_g, H_h)	36.1 [d, *J*(C–H) 140, C–H_c]
	1.34 [dd, *J*(H–H), 13, 10, H_c]	25.2 [q, *J*(C–H) 129, $CH_fH_gH_h$]
	0.95 [dd, *J*(H–H) 6.5, 13, H_a or H_b]	9.8 [dd, *J*(C–H) 148, 152, *J*(Sn–C) 70, CH_aH_b]
	0.82 [dd, *J*(H–H) 6.5, 10, H_b or H_a]	−5.8 [q, *J*(C–H) 125, *J*(Sn–C) 147, $SnMe_3$]
	0.41 [s, *J*(Sn–H) 34, $SnMe_3$]	
6 [Nb(η-C_5H_5)$_2$(C_2Me_2)($SnMe_3$)][c,h]	4.53 [s, 10 H, *J*(Sn–H) 6, η-C_5H_5]	142.1 (s, ≡C–)
Pale blue	2.28 (s, 6 H, CH_3)	116.6 (s, ≡C–)
C, 46.1 (46.3); H, 5.6 (5.7)	0.59 [s, 9 H, *J*(Sn–H) 33, $SnMe_3$]	94.7 [d, *J*(C–H) 175, η-C_5H_5]
		19.8 [q, *J*(C–H) 126, Me]
(in [$^2H_8$]toluene at 294 K)	4.48 [s, 10 H, *J*(Sn–H) 6, η-C_5H_5]	17.7 [q, *J*(C–H) 126, Me]
	2.24 [q, 3 H, *J*(H–H) 1, Me]	−3.4 [q, *J*(C–H) 125, *J*(Sn–C) 63, $SnMe_3$]
	2.20 [q, 3 H, *J*(H–H) 1, Me]	
	0.48 [s, 9 H, *J*(Sn–H) 33, $SnMe_3$]	
7 [Nb(η-C_5H_5)$_2$(CO)($SnMe_3$)][c,i]	4.32 [s, 10 H, *J*(Sn–H) 8, η-C_5H_5]	262 [broad, $\Delta\nu_{\frac{1}{2}}$ 200 Hz, CO]
Blue-green	0.42 [s, 9 H, *J*(Sn–H) 33, $SnMe_3$]	85.1 [d, *J*(C–H) 178, η-C_5H_5]
C, 40.2 (40.5); H, 4.8 (4.6)		−5.3 [q, *J*(C–H) 124, *J*(Sn–C) 19, $SnMe_3$]
8 [Nb(η-C_5H_5)$_2$($CNC_6H_3Me_2$-2,6)($SnMe_3$)][c,j]	6.75 (m, 3 H, aryl H)	231.6 (br s, NC)
Red-brown	4.58 [s, 10 H, *J*(Sn–H) 8, η-C_5H_5]	Arene quaternaries obscured
C, 50.85 (51.0); H, 5.4 (5.45)	2.12 (s, 6 H, Me)	128.1 [d, *J*(C–H) 160, 2 × arene *meta*]
		124.6 [d, *J*(C–H) 161, arene *para*]
		86.2 [d, *J*(C–H) 177, η-C_5H_5]
		18.8 [q, *J*(C–H) 128, 2 × Me]
		−5.2 [q, *J*(C–H) 124, $SnMe_3$]
9 [Nb(η-C_5H_5)$_2$(MeCN)($SnMe_3$)][c,k]	4.39 [s, 10 H, *J*(Sn–H) 5.5, η-C_5H_5]	179.8 or 165.1 (s, MeCN)
Pale brown, mixture of two isomers	2.38 (s, 3 H, MeCN)	93.2 [d, *J*(C–H) 177, η-C_5H_5]
C, 41.9 (42.1); H, 5.1 (5.2)	0.65 [s, 9 H, *J*(Sn–H) 36, $SnMe_3$]	23.3 [q, *J*(C–H) 132, MeCN]
Major *exo* (54% by proton integral)		−3.8 [q, *J*(C–H) 125, *J*(Sn–C) 138, $SnMe_3$]
Minor *endo* (46% by proton integral)	4.58 [s, 10 H, *J*(Sn–H) 6.5, η-C_5H_5]	165.1 or 179.8 (s, MeCN)
	2.58 (s, 3 H, MeCN)	96.6 [d, *J*(C–H) 177, η-C_5H_5]
	0.47 [s, 9 H, *J*(Sn–H) 37, $SnMe_3$]	22.5 [q, *J*(C–H) 133, MeCN]
		−5.9 [q, *J*(C–H) 125, *J*(Sn–C) 143, $SnMe_3$]

Table 1 (*continued*)

Compound, colour and analysis[a]	NMR data[b]	
	^{1}H	^{13}C
10 $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$[c,l] Light brown C, 34.65 (34.8); H, 5.3 (5.3)	4.29 [s, 10 H, J(Sn–H) 3, $\eta\text{-}C_5H_5$] 0.31 [s, J(Sn–H) 32, $SnMe_3$] −3.75 [br s, J(Sn–H) 131, $\Delta\nu_{\frac{1}{2}}$ = 25, Nb–H]	84.2 [d, J(C–H) 178, J(Sn–C) 4, $\eta\text{-}C_5H_5$] −3.8 [q, J(C–H) 126, J(Sn–C) 181, $SnMe_3$]
11 $[\{Nb(\eta\text{-}C_5H_5)_2(SnMe_3)\}_2(\mu\text{-}O)]$[c] Blue C, 38.35 (39.5); H, 4.3 (4.85)	4.97 [s, 20 H, J(Sn–H) 8, $\eta\text{-}C_5H_5$] 0.33 [s, 18 H, J(Sn–H) 31, $SnMe_3$]	99.75 ($\eta\text{-}C_5H_5$) −5.3 ($SnMe_3$)

[a] Calculated figures in parentheses. [b] NMR data given as: chemical shift (δ), multiplicity, relative intensity, J in Hz, assignment; all spectra were obtained at room temperature, ^{1}H at 300 MHz and ^{13}C at 75.43 MHz, unless otherwise stated. All ^{13}C spectra were routinely recorded using a gated sequence to give both $^{13}C\text{-}\{^{1}H\}$ and ^{13}C with ^{1}H NOE. Many ^{1}H and ^{13}C NMR resonances display coupling to ^{119}Sn ($I = \frac{1}{2}$, natural abundance 8.58%) and ^{117}Sn ($I = \frac{1}{2}$, natural abundance 7.57%), although in most cases the two couplings cannot be separately resolved [theoretical ratio $J(^{119}Sn/^{117}Sn) = 1.047:1$]. [c] In C_6D_6. [d] ν(Nb–H) 1680s cm^{-1}, $^{119}Sn\{^{1}H\text{-}Me\}$ at 213 K δ 107.6 [br s, J(Sn–H) ≈ 170 Hz], mass spectrum P^+ at m/z 390, highest peak at 387. [e] ν(Nb–H) 1688s, ν(Nb–D) 1213s cm^{-1}; $^{2}D\text{-}\{^{1}H\}$ δ −5.11 [J(D–Sn) 25 Hz, Nb–D]. [f] $^{119}Sn\text{-}\{^{1}H\}$ at 203 K ([$^{2}H_8$]toluene) δ 179.3 (br, s, *exo* isomer) and 170.3 (br s, *endo* isomer). [g] $^{31}P\text{-}\{^{1}H\}$ at 203 K ([$^{2}H_8$]toluene) δ 12.9 (br s, $\Delta\nu_{\frac{1}{2}}$ = 900 Hz), $^{117}Sn\text{-}\{^{1}H\}$ at 193 K ([$^{2}H_8$]toluene) δ 145 (br s, $\Delta\nu_{\frac{1}{2}}$ ~ 400 Hz). [h] ν(C≡C) 1788s cm^{-1}. [i] ν(C≡O) 1909s cm^{-1}. [j] ν(C≡N) 1988(br) cm^{-1}. [k] Carbon-13 NMR assignments based upon C–H shift correlation, nitrile C assignments may be reversed; ν(N≡C) 1756s cm^{-1}. [l] ν(Nb–H) 1634(br) cm^{-1}, $^{119}Sn\text{-}\{^{1}H\}$ at 178 K (Et_2O–[$^{2}H_8$]toluene) δ 180.5 (br s, $\Delta\nu_{\frac{1}{2}}$ = 155 Hz).



Scheme 1 Preparation and reactions of $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$. Reagents: (*i*) either (*a*) LiBu in toluene then $SnMe_3Cl$ in light petroleum, yield 89% or (*b*) $SnMe_3H$ in toluene, 12 d; (*ii*) CH_2Cl_2 in toluene, >60%; (*iii*) isoprene in toluene, 65 °C, 4 d, 63%; (*iv*) $SnMe_3H$ in C_6D_6, 65 °C, 14 d; (*v*) styrene in toluene, 65 °C, 4 d, 60%; (*vi*) PMe_3 in toluene, 65 °C, 14 d, 50%; (*vii*) but-2-yne in toluene, 65 °C, 14 d, 65%; (*viii*) $SnMe_3H$ in toluene, 20 °C, 24 h; (*ix*) 1.5 atm CO in toluene under photolysis, 2 h, 64%; (*x*) $CNC_6H_3Me_2\text{-}2,6$ in toluene in sunlight, 3 d, 87%; (*xi*) MeCN in toluene under photolysis, 2 h, 54%; (*xii*) 1.5 atm CO_2 in toluene under photolysis, 2 h, 30–60%; (*xiii*) PMe_3 in C_6D_6, 25 °C, 3 d

hydride signal ($\Delta\nu_{\frac{1}{2}}$ = 10 Hz) which places an upper limit on J(H–D) of 10 Hz. This may be compared with value for free HD of J(H–D) = 43.2 Hz,[22] and the values typical of molecular hydrogen complexes [$22 < J(H\text{–}D) < 36$ Hz], although values as low as 13 Hz have been observed. The possible existence of a $\eta\text{-}H_2$ ligand is further discounted by measurement of the hydride T_1 relaxation time,[24] this reaches a minimum of 116 ms at 183 K (300 MHz), a value indicative of a classical dihydride structure.[24] A further alternative ground-state structure for complex **2** incorporating a $\eta\text{-}H\text{-}SnMe_3$ ligand[25] appears unlikely from the spectroscopic data. Also, reactions of **2** proceed by reductive elimination of H_2 rather than $SnMe_3H$ (see below).

The IR spectrum of **2D** shows sharp resonances at 1688 and 1213 cm^{-1}, which are assigned to ν(Nb–H) and ν(Nb–D) respectively, the ratio of ν(Nb–H)/ν(Nb–D) being 1.392 (calculated value = 1.406:1).

The complexes [M(η-C_5H_5)H($SnMe_3$)] (M = Mo or W) react with halogenated solvents to give [M(η-C_5H_5)X($SnMe_3$)] (X = Cl, Br or I), or, with excess of solvent, [M(η-C_5H_5)X_2].[11] We have treated **2D** with benzyl bromide and found that even when only 1 equivalent was used the only product was [Nb(η-C_5H_5)$_2$$Br_2$]. Thus, this and other attempts to prepare [Nb(η-C_5H_5)$_2$$X_nH_{2-n}$($SnMe_3$)] ($n$ = 1 or 2) were unsuccessful.

The complex [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)] **2** was treated with a selection of two-electron donor ligands (L = styrene, PMe_3, isoprene or but-2-yne). Generally, smooth reactions occurred resulting in the addition of the ligand L and displacement of H_2 giving [Nb(η-C_5H_5)$_2$L($SnMe_3$)] (L = styrene, **3**; PMe_3, **4**; isoprene, **5**; or but-2-yne, **6**). We assume the reactions proceed *via* an initial reductive elimination of H_2 to give the 16-electron intermediate [Nb(η-C_5H_5)$_2$($SnMe_3$)] followed by addition of L. We note however, that elimination of H_2 from **2** will presumably require initial interchange of position of one hydrogen with the $SnMe_3$ ligand, possibly *via* η^2-H–$SnMe_3$ or η^2-H_2.

These reductive-substitution reactions of complex **2** proceed considerably more slowly than do the analogous reactions of [Nb(η-C_5H_5)$_2$$H_3$]. For example, [Nb($\eta$-$C_5H_5$)$_2$$H_3$] reacts with styrene overnight at room temperature to give [Nb(η-C_5H_5)$_2$(η-CH_2=CHPh)H],[26] whilst for **2** the reaction with styrene requires 4 d at 60 °C.

The ^{1}H NMR spectrum of a freshly prepared C_6D_6 solution of [Nb(η-C_5H_5)$_2$(η-H_2C=CHPh)($SnMe_3$)] **3** shows the presence of only one isomer, namely the *exo* isomer. However, the spectrum slowly changes and after several months at room temperature the spectrum may be assigned to the presence of an equilibrium mixture of *exo* and *endo* isomers in the ratio 60:40. Heating solutions of **3** to 60 °C causes rapid displacement of the equilibrium back to almost pure *exo*. The assignments of the isomers are based upon ^{1}H NMR nuclear Overhauser effect (NOE) difference experiments, as described in the Experimental section. A greater thermodynamic stability for the *exo* isomer would be expected on steric grounds due to the bulk of the $SnMe_3$ ligand. We note that the *exo* and *endo* isomers of [M(η-C_5H_5)$_2$(η-H_2C=CHR)H] (M = Nb or Ta) are known; the interconversion of these complexes is also slow.[27,28]

The ^{13}C NMR data for the ethylenic carbons of the *exo*-styrene ligand of complex **3** [δ(CH_2) 10.7, J(C–H) 146; δ(CH) 33.8, J(C–H) 146 Hz] are suggestive of a high degree of sp^3 rather than sp^2 character for these carbon atoms. Thus the co-ordination of the styrene ligand in complex **3** is close to the 'metallacyclopropane' bonding model.[29,30] This is consistent with the bonding proposed for the analogous [ML_2(H_2C=CHR)H] (L = η-C_5H_5, η-C_5H_4Me or η-C_5Me_5; R = H, Me or Ph; M = Nb or Ta) complexes.[26–28,31–33] These olefin-hydride compounds readily react with donor ligands resulting in insertion of the olefin into the metal–hydrogen bond under thermal conditions;[26,31–33] in contrast, photochemical reactions result in olefin substitution.[31] However treatment of complex **3** with donor ligands resulted in replacement of the styrene rather than its insertion into the Nb–Sn bond (see below); these reactions are also photoinduced, complex **3** appearing to be inert on heating in the dark.

Treatment of complex **2** with 2-methylbutadiene (isoprene) gives the dark green crystalline η-isoprene complex [Nb(η-C_5H_5)$_2$(η^2-H_2C=CHCMe=CH_2)($SnMe_3$)] **5** in which the less-substituted double bond is co-ordinated to the metal. The presence of a Nb–Sn bond in **5** is shown by the presence of tin satellites on the cyclopentadienyl hydrogens [^2J(Sn–H) = 5 Hz]. Furthermore, the ^{13}C NMR spectrum shows two resonances at δ 36.1 and 9.8, which are a doublet and a doublet of doublets respectively in the gated proton-coupled spectrum. The resonance at δ 9.8 also shows a small C–Sn coupling (70 Hz). These are assigned to the co-ordinated isoprene carbons; the remaining isoprene carbon resonances are at δ 25.2 (q), 98.6 (t) and 151 (s), and are respectively assigned as CH_3, unco-ordinated CH_2 and quaternary carbon atoms. This assignment is confirmed by the ^{1}H–^{1}H correlation spectroscopy (COSY)-45 and ^{1}H-^{13}C shift correlation spectra. Thus, in contrast to the reactions between [Nb(η-C_5H_5)$_2$$H_3$] and dienes which give η-allyl derivatives[34–36] there is no insertion of the C=C groups of isoprene into the Nb–Sn bond.

Treatment of complex **2** with but-2-yne at 65 °C over 14 d gives light blue crystalline [Nb(η-C_5H_5)$_2$(η-C_2Me_2)($SnMe_3$)] **6** in 65% yield. The ^{1}H NMR spectrum varies with solvent and temperature. The spectrum in C_6D_6 shows only a singlet at δ 2.28 integrating for six protons, which must be assigned to the two CMe groups. In contrast, in [$^2H_8$]toluene there are two quartets for the but-2-yne methyls [δ 2.24 and 2.20, ^5J(H–H) = 1 Hz]. The separation of these resonances increases with temperature; this is ascribed to a temperature-dependent chemical shift. The ^{13}C NMR spectrum shows four distinct resonances for the co-ordinated but-2-yne ligand. Thus it appears that the ^{1}H NMR spectrum in C_6D_6 is due to accidental equivalence of the chemical shifts. The ^{13}C chemical shifts for the acetylenic carbon atoms are consistent with the but-2-yne acting as a two-electron donor, as required for an 18-electron count for the compound.[37] Variable-temperature NMR measurements on complex **6**, up to 354 K, gave no evidence for rotation of the but-2-yne ligand. We note that the reaction between [M(η-C_5H_5)$_2$$H_3$] (M = Nb or Ta) and alkynes RC_2R has been reported to give the compounds [M(η-C_5H_5)$_2$(η-C_2R_2)H].[27,38–40] More recently, the reactions of alkynes with [Nb(η-C_5H_5)$_2$$H_3$] has been studied in further detail together with the formation of butadienyl complexes [Nb(η-C_5H_5)$_2$($CR^1CR^1CR^2CHR^2$)].[41]

Compound **3** is photosensitive. Thus, photolysis in the presence of donor ligands L = PMe_3, CO, $CNC_6H_3Me_2$-2,6 or MeCN, using either sunlight or, more reliably, a medium-pressure mercury lamp gives the compounds [Nb(η-C_5H_5)$_2$L($SnMe_3$)] (L = PMe_3, **4**; CO, **7**; $CNC_6H_3Me_2$-2,6, **8**; or MeCN, **9**) in good yields. Several reactions were monitored *in situ* by NMR spectroscopy, and were virtually quantitative.

This photochemical route to the compounds [Nb(η-C_5H_5)$_2$L($SnMe_3$)] is to be preferred since it is faster and cleaner than the corresponding thermal reactions of **2**. The bright red phosphine complex [Nb(η-C_5H_5)$_2$(PMe_3)($SnMe_3$)] **4** has also been prepared by heating [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)] in the presence of PMe_3. It is very oxygen sensitive and readily dissociates the PMe_3 ligand. For these reasons satisfactory microanalysis could not be obtained. The ^{31}P NMR spectrum at −80 °C shows a broad singlet at δ 12.9. We were unable to observe a low-temperature ^{119}Sn spectrum due to instrumental limitations. However, the marginally less receptive ^{117}Sn-{^{1}H} NMR spectrum at 193 K shows a very broad ($\Delta\nu_{\frac{1}{2}} \approx$ 400 Hz) singlet at δ 145 with no observable ^{31}P coupling.

The blue-green monocarbonyl [Nb(η-C_5H_5)$_2$(CO)($SnMe_3$)] **7**, is moderately air-stable. The IR spectrum shows a sharp absorption at 1909 cm^{-1} assigned to ν(C≡O). In the ^{13}C NMR spectrum a weak, broad resonance at δ 262 ($\Delta\nu_{\frac{1}{2}}$ = 200 Hz) may be assigned to the carbonyl group. The signal for the analogous carbonyl complex [Nb(η-C_5Me_5)$_2$(^{13}CO)Et] is found at δ 280.2 ($\Delta\nu_{\frac{1}{2}}$ = 88 Hz).[31]

The compounds [Nb(η-C_5H_5)$_2$L($SnMe_3$)] will undergo substitution of one L ligand by another. For example, [Nb(η-C_5H_5)$_2$(CO)($SnMe_3$)] **7** reacts slowly with excess of PMe_3 to give [Nb(η-C_5H_5)$_2$(PMe_3)($SnMe_3$)] **4**. This reaction has been monitored by NMR spectroscopy, and there is no evidence for carbonyl migration to give [Nb(η-C_5H_5)$_2$(PMe_3){C(O)-$SnMe_3$}]. Similarly, methyl migration does not occur for the isoelectronic complex [Nb(η-C_5H_5)$_2$(CO)Me].[42]

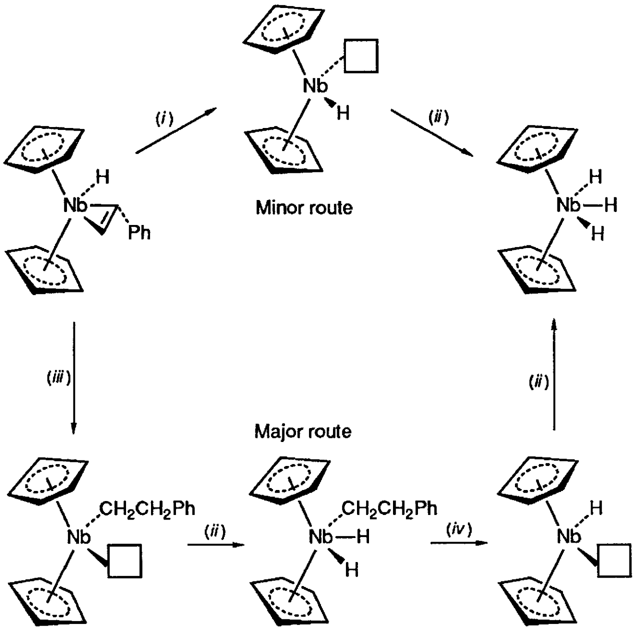
Table 2 Selected ^{13}C NMR data for some structurally characterised acetonitrile complexes

Complex[a]	M–N–C angle (°)	^{13}C chemical shift	Ref.
(*a*) End-on (N-co-ordinated)			
$[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_4Ph_4)(MeCN)][BF_4]$	169.7(2)	211	45
$[Mo(\eta\text{-}C_5H_5)_2I(MeCN)][PF_6]$	179.8(1)	143.3	46 and this work
$[Ru(\eta\text{-}C_5H_4R)(CO)(PPh_3)(MeCN)]^{+b}$	178.5(4)	129.6[c]	47
$[Rh(PPh_3)_3(MeCN)][BF_4]$	169.5(11)	127.8	48
$[Rh_2(O_2CMe_2)(MeCN)_2(py)_2][BF_4]_2$	173.8, 174.8	126 or 127	49
$[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]$	174.7, 176.3, 176.3	118, 126	49
$[Ir_2(\mu\text{-}C_5H_4)_2\{\mu\text{-}(p\text{-}MeC_6H_4N){=}CH(NC_6H_4Me\text{-}p)\}(py)_2(MeCN)_2][BPh_4]$	174(1), 178(1)	113.56	50
$[Mn(\eta\text{-}C_5Me_5)(CO)_2(MeCN)]$	175.3(5)	153.4	51
$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(MeCN)][BF_4]$	179.7(2)	131.3	52
$[Mo_2(\eta\text{-}C_5H_5)_2(CO)_3(MeCN)(\mu\text{-}SPh)_2][BF_4]_2$	175.8(3)	138.9	53
$[MoBr(\eta^3\text{-}C_5H_6Me)(CO)_2(MeCN)_2]$	175.2(9), 173.9(9)	118.2	54
(*b*) Side-on (η^2)			
$[Mo(\eta\text{-}C_5H_5)_2(\eta^2\text{-}MeCN)]$	69.6, 68.9	170.8	55 and this work
$[W(\eta\text{-}C_5H_5)_2(MeCN)]$	No data	174.2	56 and this work
$[MoCl(dmpe)_2(\eta^2\text{-}MeCN)][BF_4]$	73.9	No data	57
$[Nb(\eta\text{-}C_5H_5)_2(MeCN)(SnMe_3)]$	No data	179.8, 165.1	This work

[a] py = Pyridine. [b] X-Ray data for (*R*) isomer of η-neomenthylcyclopentadienyl complex as PF_6 salt. [c] ^{13}C NMR data for (*R*) isomer of menthylcyclopentadienyl complex as BF_4 salt; neomenthyl = 2-isopropyl-5-methylcyclohexyl.

Table 3 Selected bond lengths (Å) and angles (°) for compound **11**, Cp_{cent} is the computed centroid of the η-C_5H_5 ligand

Nb(1)–Sn(1)	2.8619(5)	Sn(1)–C(11)	2.165(6)	O–Nb(1)–Sn(1)	87.52(2)	O–Nb(1)–Cp_{cent}	106
Nb(1)–O	1.9434(4)	Sn(1)–C(12)	2.168(6)	Nb(1)–O–Nb(1)	179.99	Cp_{cent}–Nb(1)–Cp_{cent}	132.12
Nb(1)–Cp_{cent}	2.12	Sn(1)–C(13)	2.191(6)				

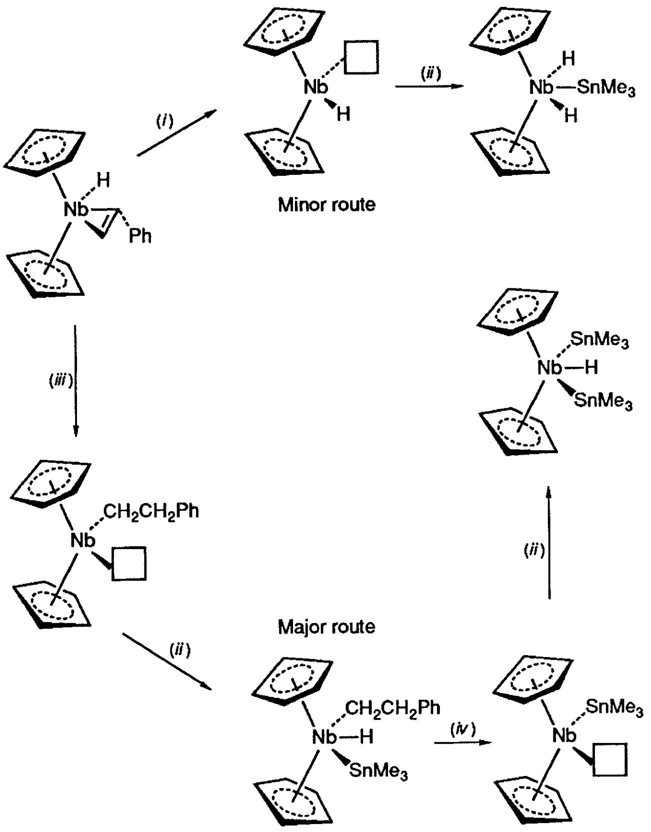


Scheme 2 Mechanism proposed for the reaction of *endo*-$[Nb(\eta\text{-}C_5H_5)_2(\eta\text{-}H_2C{=}CHPh)H]$ with hydrogen. (*i*) Dissociation of styrene; (*ii*) oxidative addition of H_2; (*iii*) olefin insertion into Nb–H bond; (*iv*) reductive elimination of ethylbenzene

The isonitrile complex $[Nb(\eta\text{-}C_5H_5)_2(CNC_6H_3Me_2\text{-}2,6)(SnMe_3)]$ **8** was prepared by photolysis of **3** in the presence of 2,6-dimethylphenylisocyanide. Complex **8** shows a band in the IR spectrum at 1998 cm^{-1} assigned to ν(C≡N). The ^{13}C NMR spectrum shows a broad resonance at δ 231.8 assigned to the isonitrile carbon.

The photolysis of complex **3** with acetonitrile gives a compound of molecular formula $[Nb(\eta\text{-}C_5H_5)_2(MeCN)(SnMe_3)]$ **9**. In solution this compound appears to exist as a mixture of two isomers in the ratio of 54:46, designated **9a** and **9b**, which do not interconvert in solution on the NMR time-scale. Despite repeated efforts, X-ray-quality crystals could not be obtained. The IR spectrum of **9** shows a feature at 1756 cm^{-1} that may be assigned to a side-bound η^2-NCMe. However, the assignment of η^2-NCMe complexes on the basis of IR data has in many cases proven to be erroneous.[43,44] The characterisation of nitrile complexes by ^{13}C NMR spectroscopy has not been widely reported. The ^{13}C chemical shifts for some X-ray structurally characterised N-co-ordinated nitrile complexes (Table 2) fall in the range δ 118–140. The extreme value is δ 153 and the value of δ 211 for $[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_4Ph_4)(MeCN)][BF_4]$ appears to be at exceptionally low field. The value for free acetonitrile is δ 117.7. These data suggest that in these complexes the chemical shift of the nitrile carbon is only slightly shifted to low field by N-co-ordination to the metal. In contrast, no chemical shift data have been reported for either of the structurally characterised η^2-$NCCR_3$ complexes.[41,58] We have prepared $[Mo(\eta\text{-}C_5H_5)_2(\eta^2\text{-}NCMe)]$[58] and recorded the ^{13}C NMR spectrum, the nitrile resonance appearing at δ 170.8; for the tungsten analogue[53] the nitrile resonance appears at δ 174.2. There are no chemical shift data for the other structurally characterised complex $[Mo(dmpe)_2Cl(\eta^2\text{-}MeCN)]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[54]

The two isomers of complex **9** have nitrile resonances at δ 179.8 and 165.1. Thus, we propose that the chemical shift of the nitrile carbon may also be diagnostic of the co-ordination mode of the nitrile ligand. In the case of acetonitrile, resonances with δ >160 are assigned to two-electron side-bound η^2-NCMe ligands. By analogy with the case of two-, three- and four-electron-donor alkyne complexes[55] it is possible that a side-bound nitrile donating four electrons may have a resonance further shifted to lower field. On the basis of these data we propose that **9a** and **9b** are the *exo*- and *endo*-η-MeCN isomers of $[Nb(\eta\text{-}C_5H_5)_2(NCMe)(SnMe_3)]$. Furthermore, a N-co-ordinated complex could not account for the observation of two isomers; only one isomer is observed for the structurally N-co-ordinated complex $[Mo(\eta\text{-}C_5H_5)_2I(MeCN)]^+$.[45]



Scheme 3 Mechanism proposed for the reaction of *endo*-[Nb(η-C_5H_5)$_2$(η-$H_2C{=}CHPh$)H] with $SnMe_3H$. (*i*) Dissociation of styrene; (*ii*) oxidative addition of $SnMe_3H$; (*iii*) olefin insertion into Nb–H bond; (*iv*) reductive elimination of ethylbenzene

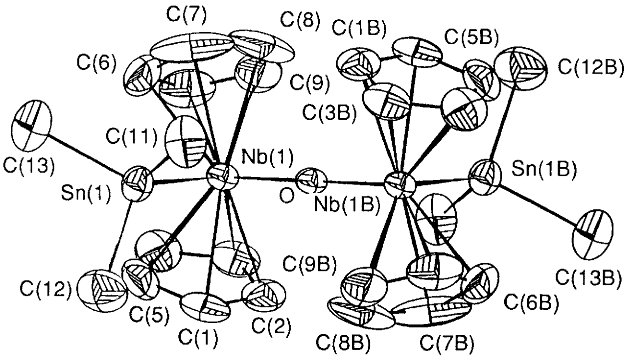


Fig. 1 View of the [{Nb(η-C_5H_5)$_2$($SnMe_3$)}$_2$(μ-O)] molecule showing the atom numbering scheme. The atoms labelled B are related to their counterparts by a crystallographic inversion centre at oxygen. Thermal ellipsoids are drawn at the 50% probability level

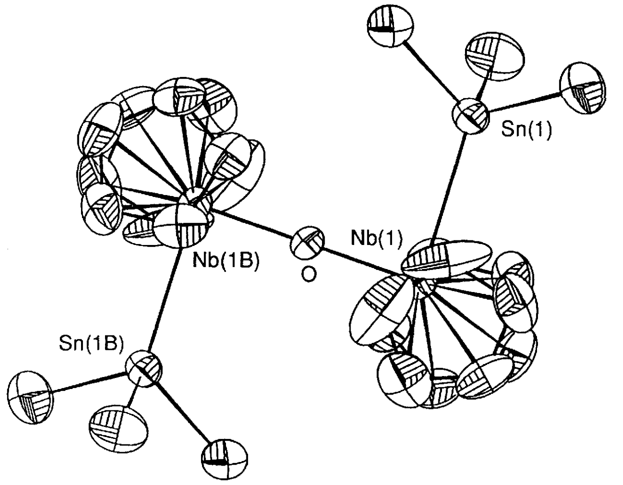


Fig. 2 View of [{Nb(η-C_5H_5)$_2$($SnMe_3$)}$_2$(μ-O)] perpendicular to the Nb–O–Nb plane showing the staggered arrangement of $SnMe_3$ substituents about the Nb–O–Nb fragment. Other details as in Fig. 1

Table 4 Fractional coordinates (× 10^4) for compound **11**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Nb(1)	9 268.3(5)	4 201.0(2)	4 522.5(2)
Sn(1)	10 615.7(4)	3 593.5(2)	5 994.6(2)
O	10 000	5 000	5 000
C(1)	11 862(7)	3 961(3)	3 955(4)
C(2)	11 213(7)	4 419(3)	3 420(4)
C(3)	9 904(7)	4 153(3)	3 015(3)
C(4)	9 795(9)	3 517(3)	3 284(4)
C(5)	10 975(8)	3 405(3)	3 864(4)
C(6)	6 952(7)	3 570(4)	4 797(6)
C(7)	6 999(7)	4 062(7)	5 447(4)
C(8)	6 749(7)	4 619(5)	5 049(8)
C(9)	6 590(7)	4 513(4)	4 214(6)
C(10)	6 673(7)	3 889(4)	4 059(4)
C(11)	10 791(9)	4 128(3)	7 177(4)
C(12)	13 037(8)	3 247(4)	5 905(5)
C(13)	9 425(9)	2 739(3)	6 469(5)

Photolysis of complex **3** in the presence of H_2 (2 atm, 30 h, 65 °C) regenerates [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)] **2**. Similarly photolysis of **3** in the presence of $SnMe_3H$ gives the pale brown crystalline bis(stannyl) derivative [Nb(η-C_5H_5)$_2$H($SnMe_3$)$_2$] **10**. These reactions were monitored by ^1H NMR spectroscpy which showed the only other product to be free styrene. There was no evidence for the formation of ethylbenzene or trimethylstannyl-substituted ethylbenzene. This contrasts with the reaction between [Nb(η-C_5H_5)$_2$(η-$CH_2{=}CHPh$)H] and H_2 which gives [Nb(η-C_5H_5)$_2$$H_3$] and a mixture of ethylbenzene and styrene. The latter products arise from two competing mechanisms, see Scheme 2. The major mechanistic route involves olefin insertion to give the 16-electron intermediate [Nb(η-C_5H_5)$_2$(CH_2CH_2Ph)] and leads to the formation of ethylbenzene as the organic side-product. The minor route involves olefin dissociation to give [Nb(η-C_5H_5)$_2$H] and leads to the formation of styrene as the organic product. The fact that [Nb(η-C_5H_5)$_2$(η-$CH_2{=}CHPh$)($SnMe_3$)] gives only styrene with H_2 reflects the inability of olefins to insert into the Nb–Sn bond. This latter reaction may only proceed by olefin dissociation.

Attempts to prepare the highly sterically crowded molecule [Nb(η-C_5H_5)$_2$($SnMe_3$)$_3$] from the reaction between [Nb(η-C_5H_5)$_2$(η-$CH_2{=}CHPh$)($SnMe_3$)] and Sn_2Me_6 gave only unchanged starting material.

The best route to the bis(stannyl) [Nb(η-C_5H_5)$_2$H($SnMe_3$)$_2$] is *via* [Nb(η-C_5H_5)$_2$(η-$CH_2{=}CHPh$)H]. Thus treatment of [Nb(η-C_5H_5)$_2$(η-$CH_2{=}CHPh$)H] with $SnMe_3H$ gives a mixture of [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)] **2** *ca.* 10% and [Nb(η-C_5H_5)$_2$H($SnMe_3$)$_2$] **10** *ca.* 90%, from which essentially pure **10** may be obtained by careful fractional crystallisation. When this reaction was performed in a sealed NMR tube the spectrum showed the organic products to be ethylbenzene and styrene in about the same ratio (10:1) as found for **10** and **2**. The mechanisms proposed for these reactions are shown in Scheme 3 and are similar to those in Scheme 2. Thus, the major route($\approx$90%) involves olefin insertion followed by oxidative addition of two molecules of $SnMe_3H$ to give the bis(stannyl) complex and ethylbenzene. The minor route involves olefin dissociation followed by oxidative addition of $SnMe_3H$.

As expected, heating [Nb(η-C_5H_5)$_2$$H_2$($SnMe_3$)] with $SnMe_3$ at 60 °C over 14 d gave the bis(stannyl) compound **10**. This reaction proceeds *via* the slow formation of the [Nb(η-$C_5H_5)_2(SnMe_3)$] intermediate.

Photolysis of complex 3 under an atmosphere of CO_2 rapidly produces an intensely blue solution from which very sensitive, dark blue, crystals **11** can be isolated. The ^1H and ^{13}C NMR spectra showed the signals expected for the [Nb(η-$C_5H_5)_2(SnMe_3)$] fragment. When the reaction was carried out using $^{13}CO_2$ the product gave an identical IR spectrum, and there were no additional resonances in the ^{13}C NMR spectrum, even at −90 °C.

The crystal structure of complex **11** has been determined and shows an oxo-bridged dimer [{Nb(η-$C_5H_5)_2(SnMe_3)$}$_2$(μ-O)]. Two views of the molecular structures are provided in Figs. 1 and 2 with selected bond lengths and angles in Table 3 and fractional atomic coordinates in Table 4.

The structure has crystallographically imposed inversion symmetry, and consists of two Nb(η-$C_5H_5)_2(SnMe_3)$ fragments linked by a linear oxygen bridge. Thus the five atoms Sn–Nb–O–Nb–Sn, lie within a perfect plane, with the Sn atoms on opposite sides of the Nb–O–Nb vector. The formal oxidation state of niobium is IV, although the molecule is diamagnetic (NMR spectroscopy). This structure is similar to those reported by Struchkov and co-workers for the dimers [{Nb(η-$C_5H_5)_2$-Bu}$_2$(μ-O)] [Nb–O 1.926(2) Å, Nb–O–Nb 180°][56] and [{Nb(η-$C_5H_4Me)_2Cl$}$_2$(μ-O)] [Nb–O 1.92 Å, Nb–O–Nb 173°].[57,59] The related dication [{Nb(η-$C_5H_5)_2Cl$}$_2$(μ-O)]$^{2+}$ has oxidation states Nb^V–Nb^V and a non-linear [Nb–O–Nb 169.3(8)°] and shorter [1.88(1) Å] Nb=O bond.[60] The geometries of the three neutral dimers, which are diamagnetic although formally Nb^{IV} (d^1), have been rationalised on the basis of a three-centre four-electron bond, utilising one oxygen lone pair and the metal d^1 electrons.[61] The occurrence of such ferromagnetic coupling giving diamagnetic d^1–d^1 dimers is widespread and has been observed for [{Mo(η-$C_5H_5)O(X)$}$_2$(μ-O)] (X = I,[62] SPh[63] or Cl[64]). The recent publication of the molecular structure of [{Mo(η-$C_5H_5)O(Cl)$}$_2$(μ-O)] also contains an analogous description of its electronic structure.[64]

The photolysis of [Nb(η-$C_5H_5)_2$(η-H_2C=CHPh)($SnMe_3$)] under a slight excess of CO_2 was monitored by NMR spectroscopy and showed the products to be a mixture of [Nb(η-$C_5H_5)_2(CO)(SnMe_3)$] and [{Nb(η-$C_5H_5)_2(SnMe_3)$}$_2$(μ-O)] in the ratio *ca.* 1:2.5. It may be presumed that carbonyl complex is formed by the reaction of photogenerated [Nb(η-$C_5H_5)_2$-($SnMe_3$)] with CO produced from the extrusion of oxygen from CO_2 in the formation of the oxo-bridged dimer. It is possible that the reaction of [Nb(η-$C_5H_5)_2$(η-H_2C=CHPh)-($SnMe_3$)] with CO_2 may pass through an initial η^2-CO_2 complex,[65] although no intermediates have been detected by the *in situ* NMR studies.

We investigated the possibility that it might be possible to oxidise [{Nb(η-$C_5H_5)_2(SnMe_3)$}$_2$(μ-O)] to either a paramagnetic monocation or diamagnetic dication. The cyclic voltammogram of complex **11** shows a reversible oxidation at +335 mV (acetonitrile, *vs.* saturated calomel electrode). However, attempts to oxidise **11** with the ferrocenium ion or elemental iodine gave no tractable products.

The complexes [Nb(η-$C_5H_5)_2L(SnMe_3)$] (L = isoprene or but-2-yne) also undergo ligand-substitution and oxidative-addition reactions in the same manner as for [Nb(η-$C_5H_5)_2$-(η-H_2C=CHPh)($SnMe_3$)]. For example, they react with PMe_3 to give [Nb(η-$C_5H_5)_2(PMe_3)(SnMe_3)$] and with $SnMe_3H$ to give [Nb(η-$C_5H_5)_2H(SnMe_3)_2$].

Conclusion

The complex [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] is readily available in multigram quantities and is a useful starting material. Comparison of the reactions of the moieties [Nb(η-$C_5H_5)_2R$], where R = $SnMe_3$, Me or H, show there to be significant differences. The $SnMe_3$ group does not undergo migratory insertion reactions and is less labile than H as ligand.

The complex [Nb(η-$C_5H_5)_2(MeCN)(SnMe_3)$] is observed to exist as two isomers which are proposed to be the *exo*- and *endo*-η^2-MeCN isomers. The nitrile ^{13}C NMR chemical shifts for a number of structurally characterised acetonitrile complexes have been examined, and the data suggest that significantly low-field resonances are attributable to side-on η^2-MeCN ligands. The chemical shifts for terminal N-co-ordinated complexes are little shifted from the value for free acetonitrile.

Experimental

All preparations, manipulations and reactions were carried out under an inert atmosphere of dinitrogen (< 10 ppm oxygen. < 20 ppm water) using standard Schlenk vessels and vacuum-line techniques, or in a dry-box. Dintrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from potassium (tetrahydrofuran, thf), sodium (toluene), sodium–potassium alloy [light petroleum (refers to hydrocarbons with b.p. 40–60 °C unless otherwise stated), diethyl ether, pentane], phosphorus pentaoxide (dichloromethane), or calcium hydride (acetonitrile), under an inert atmosphere of dinitrogen before use. Deuteriated solvents for NMR samples were used as received (Aldrich), or after drying over Na/K alloy, samples being prepared in the dry-box. Celite 545 filtration aid (Koch-Light) was pre-dried in an oven at 80 °C before use. Ultraviolet photolyses were performed with a Hanovia 500 W low-pressure mercury lamp.

Infrared spectra were recorded as CsI or KBr pellets on a Mattson Polaris FT-IR interferometer, ^1H NMR spectra at 300 MHz using a Brüker AM-300 spectrometer, ^{13}C (75.43), ^{31}P (121.44), ^{119}Sn (111.87), ^{117}Sn (106.87) and ^2D (46.07 MHz) spectra using a Brüker AM-300 spectrometer. NMR spectra were referenced internally using the residual solvent (^1H and ^{13}C) resonances relative to tetramethylsilane (δ = 0 ppm), or externally using trimethyl phosphate [$PO(OMe)_3$] in D_2O (^{31}P), tetramethyltin ($SnMe_4$) in C_6D_6 ($^{119}Sn/^{117}Sn$) or with respect to the ^1H shift of the complex (^2D) respectively. All chemical shifts are quoted in δ (ppm), high-field shifts being taken as negative, and coupling constants are in Hz. NMR samples were prepared either under nitrogen in screw-capped tubes (Wilmad), or under vacuum in sealed soda-glass NMR tubes.

Cyclic voltammograms were measured by Dr. G. C. Saunders, whom we thank, using an Oxford Instruments potentiostat and recorded on a Rikadenki X-Y chart recorder. A cell modified for air-sensitive compounds was used, and ferrocene was added after the measurement as an internal reference.

Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services. Elemental analysis was performed by the Analysis Department in this laboratory or, in the cases of very air-sensitive compounds, by Analytische Laboratorien, Elbach.

Literature methods were used for the preparation of the compounds [Nb(η-$C_5H_5)_2Cl_2$],[66] [Nb(η-$C_5H_5)_2H_3$],[67] [Nb-(η-$C_5H_5)_2$(η-H_2C=CHPh)H],[26] tetramethyltin,[68] trimethyltin chloride,[69] trimethyltin hydride, [70] [Mo(η-$C_5H_5)_2$(η-NCMe)][53] and [Mo(η-$C_5H_5)_2$I(MeCN)][BF_4].[46] All other reagents were purchased (Aldrich) and used as received.

Preparations.—[Nb(η-$C_5H_5)_2H_2(SnMe_3)$] **2**. The compound [Nb(η-$C_5H_5)_2H_3$] (4.46 g, 19.9 mmol) in toluene (150 cm^3) was treated dropwise with excess of LiBu (15 cm^3 of 2.5 mol dm^{-3} solution, 37.5 mmol) with vigorous magnetic stirring. Following

Table 5 Crystal data for compound **11**

T/K	293
Formula	$C_{26}H_{38}Nb_2OSn_2$
M	789.78
Crystal symmetry	Orthorhombic
Space group	*Pbca*
a/Å	8.409(3)
b/Å	21.109(4)
c/Å	15.582(3)
U/Å^3	2766.2
Z	4
D_c/g cm^3	1.90
Crystal size/mm	0.4 × 0.5 × 0.05
μ/cm^{-1}	25.82
F[000]	1536
Radiation	Mo-Kα (λ = 0.710 69 Å)
Data collected (h, k, l)	-1 to h, -1 to k, -1 to l
Scan type	ω–2θ
Scan width/°	0.80 + 0.35 tanθ
2θ range/°	3–53
Intensity standards decay	< 10%
Total data collected	4173
Total unique reflections	2869
No. of observations	1964
R_{merge}	0.034
No. of parameters refined	143
R	0.033
R'	0.031
Chebyshev parameters	4.786, −6.319, 3.465, −2.541

a brief induction period (30 s), an orange powder presumed to be $[\{(\eta-C_5H_5)_2NbH_2Li\}_n]$ **1** began to precipitate. After 15 min the precipitate was allowed to settle. The solvent was decanted and the precipitate washed with light petroleum (2 × 150 cm^3). The lithiated material was suspended in light petroleum (200 cm^3) and treated slowly with $SnMe_3Cl$ (3.5 g, 17.6 mmol) in light petroleum (200 cm^3) over 1–1.5 h. The mixture was stirred for 20 min, then filtered through Celite. Cooling the solution to −80 °C yielded large crystals of analytically pure $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$. Yield 6.1 g, 89%.

$[Nb(\eta-C_5H_5)_2H(D)(SnMe_3)]$ **2D**. The compound $SnMe_3H$ (5 mmol) was distilled *via* a calibrated vacuum manifold onto a mixture of KH (500 mg) in Et_2O (40 cm^3). After 3 h at r.t. the resulting yellow solution was decanted and treated with D_2O to give $SnMe_3D$. The volatiles were distilled onto $[Nb(\eta-C_5H_5)_2H_3]$ (350 mg, 1.55 mmol). After 12 d at r.t. the volatiles were removed under reduced pressure to give an off-white solid. This was recrystallised from pentane–toluene at −80 °C giving pale yellow crystals of $[Nb(\eta-C_5H_5)_2H(D)(SnMe_3)]$ **2D**.

$[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$ **3**. The compound $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$ (2.4 g, 6.4 mmol) in toluene (100 cm^3) was treated with excess of styrene (5 cm^3), and heated under vacuum at 65 °C for 4 d to give a yellow solution. The solvent was removed under reduced pressure, and the residue extracted into light petroleum (250 cm^3) containing styrene (1 cm^3). The yellow solution was filtered and cooled to −80 °C yielding bright yellow microcrystals of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$. Yield 1.9 g, 60%.

$[Nb(\eta-C_5H_5)_2(PMe_3)(SnMe_3)]$ **4**. *Method A.* The compound PMe_3 (2 cm^3) was condensed onto a solution of $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$ (0.5 g, 1.3 mmol) in toluene (40 cm^3) and the mixture was heated under reduced pressure at 65 °C for 14 d to give a red solution. The solvent was removed under reduced pressure, and the residue extracted into light petroleum (50 cm^3). The red extract was filtered and cooled to −25 °C yielding powdery red $[Nb(\eta-C_5H_5)_2(PMe_3)(SnMe_3)]$. Yield 300 mg, 50%.

Method B. The compound PMe_3 (0.2 cm^3) was transferred *via* a calibrated vacuum manifold onto a solution of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$ (25 mg, 0.05 mmol) in C_6D_6 and sealed under vacuum. After 3 d at 25 °C the yellow solution had become red, and the NMR spectrum showed the presence of $[Nb(\eta-C_5H_5)_2(PMe_3)(SnMe_3)]$. Similar NMR tube reactions were performed using $[Nb(\eta-C_5H_5)_2(\eta-C_2Me_2)(SnMe_3)]$ **6** and $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHCMe{=}CH_2)(SnMe_3)]$ **5**, giving complete conversion into $[Nb(\eta-C_5H_5)_2(PMe_3)(SnMe_3)]$ after 4 d at 25 °C.

$[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHCMe{=}CH_2)(SnMe_3)]$ **5**. The compound $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$ (480 mg, 1.2 mmol) in toluene (40 cm^3) was treated with excess of isoprene (0.6 cm^3), and heated under vacuum at 65 °C for 4 d to give a light green solution. The solvent was removed under reduced pressure, and the residue extracted into pentane (40 cm^3) containing isoprene (0.5 cm^3). The green solution was filtered and cooled to −25 °C whereupon a slight precipitate was formed. The solution was filtered at −25 °C and cooled to −80 °C giving dark green crystals of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHCMe{=}CH_2)(SnMe_3)]$. Yield 0.35 g, 63%.

$[Nb(\eta-C_5H_5)_2(\eta-C_2Me_2)(SnMe_3)]$ **6**. The compound $[Nb(\eta-C_5H_5)_2H_2(SnMe_3)]$ (400 mg, 1.03 mmol) in toluene (40 cm^3) was treated with excess of but-2-yne (0.75 cm^3, ≈8 mmol), and heated under vacuum at 65 °C for 14 d to give a colourless solution. The volatiles were removed under reduced pressure, and the residue extracted into pentane (45 cm^3). The faint blue extract was filtered and cooled to −80 °C yielding microcrystals of $[Nb(\eta-C_5H_5)_2(\eta-C_2Me_2)(SnMe_3)]$. Yield 300 mg, 65%.

$[Nb(\eta-C_5H_5)_2(CO)(SnMe_3)]$ **7**. A solution of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$ (450 mg, 0.95 mmol) in toluene (30 cm^3) was placed under vacuum in a Young's ampoule and then 1.5 atm CO applied. The solution was subjected to UV radiation for 2 h, giving a faint blue-green solution. The solvent was removed under reduced pressure, and the residue extracted into pentane (40 cm^3). The extract was filtered and cooled to −80 °C yielding analytically pure blue-green crystals of $[Nb(\eta-C_5H_5)_2(CO)(SnMe_3)]$. Yield 250 mg, 64%.

Reaction of $[Nb(\eta-C_5H_5)_2(CO)(SnMe_3)]$ *with* PMe_3. The compound $[Nb(\eta-C_5H_5)_2(CO)(SnMe_3)]$ (20 mg, 0.05 mmol) was dissolved in C_6D_6 in a 5 mm NMR tube and PMe_3 (0.5 mmol) added *via* a calibrated vacuum manifold. The tube was sealed under vacuum and left at room temperature, the NMR spectrum being recorded at intervals. Slow conversion into $[Nb(\eta-C_5H_5)_2(PMe_3)(SnMe_3)]$ was observed over a period of several days, being approximately 80% complete after 10 d. No other products were detected by NMR spectroscopy.

$[Nb(\eta-C_5H_5)_2(CNC_6H_3Me_2\text{-}2,6)(SnMe_3)]$ **8**. The compound $2,6\text{-}Me_2C_6H_3NC$ (100 mg, 0.75 mmol) was added to a solution of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$ (100 mg, 0.2 mmol) in toluene (20 cm^3). The solution was placed in full sunlight for 3 d and a deep red solution resulted. The solvent was removed under reduced pressure, and the excess of isocyanide was removed by sublimation onto a cold-finger (−196 °C). The residue was extracted into pentane (30 cm^3). The extract was filtered and cooled to −80 °C yielding red microcrystalline $[Nb(\eta-C_5H_5)_2(CNC_6H_3Me_2\text{-}2,6)(SnMe_3)]$. Yield 90 mg, 87%.

$[Nb(\eta-C_5H_5)_2(MeCN)(SnMe_3)]$ **9**. Excess of MeCN (2 cm^3) was added to a solution of $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)(SnMe_3)]$ (630 mg, 1.3 mmol) in toluene (40 cm^3). The solution was subjected to UV radiation for 2 h, giving a red-green dichroic solution. The solvent was removed under reduced pressure, and the residue was extracted into pentane (70 cm^3) saturated with MeCN. The dichroic extract was filtered and cooled to −25 °C, whereupon red-brown powdery $[Nb(\eta-C_5H_5)_2(MeCN)(SnMe_3)]$ precipitated and the solvent mixture became two phases. The product was isolated by decanting the solvents and dried *in vacuo*. Yield 300 mg, 54%.

$[Nb(\eta-C_5H_5)_2H(SnMe_3)_2]$ **10**. *Method A.* The compound $[Nb(\eta-C_5H_5)_2(\eta-H_2C{=}CHPh)H]$ (1.05 g, 3 mmol) was dissolved in toluene (50 cm^3) in a Young's ampoule. The solution was cooled to −196 °C under vacuum and $SnMe_3H$ (1.5 cm^3) was distilled in. The solution was warmed to r.t. and left to stand for 5 d. The volatiles were removed under reduced pressure giving a pale brown solid. This was extracted with light petroleum (100 cm^3), and cooled to -80 °C to give thin pale brown plates of [Nb(η-C_5H_5)$_2$H(SnMe$_3$)$_2$]. Yield 0.8 g, 50%.

Method B. The compound [Nb(η-C_5H_5)$_2$(η-H$_2$C=CHPh)(SnMe$_3$)] (0.2 g, 0.4 mmol) was dissolved in toluene (20 cm^3). The compound SnMe$_3$H (0.75 cm^3, an excess) was added by vacuum transfer, and the reaction left to stand at 20 °C. After 24 h the volatiles were removed under reduced pressure leaving a light brown solid. This was extracted with pentane (20 cm^3), filtered and cooled to -80 °C, giving a mixture of fine needles and some very thin plates of [Nb(η-C_5H_5)$_2$H(SnMe$_3$)$_2$].

Method C. The compound [Nb(η-C_5H_5)$_2$H$_2$(SnMe$_3$)] (0.031 g, 0.08 mmol) was dissolved in C_6D_6 in a 5 mm NMR tube. The compound SnMe$_3$H (0.25 mmol) was added *via* a calibrated vacuum manifold, the tube sealed under vacuum, then heated to 65 °C. Monitoring by NMR spectroscopy at periodic intervals showed a slow conversion into [Nb(η-C_5H_5)$_2$H(SnMe$_3$)$_2$], being complete after 14 d.

Method D. The compounds [Nb(η-C_5H_5)$_2$(η-H$_2$C=CHCMe=CH$_2$)(SnMe$_3$)] or [Nb(η-C_5H_5)$_2$(η-C$_2$Me$_2$)(SnMe$_3$)] were treated with SnMe$_3$H in C_6D_6 in NMR tubes as for Method C. Complex **10** was formed after 4 d at 25 °C.

[{Nb(η-C_5H_5)$_2$(SnMe$_3$)}$_2$(μ-O)] **11**. A solution of [Nb(η-C_5H_5)$_2$(η-H$_2$C=CHPh)(SnMe$_3$)] (433 mg, 0.88 mmol) in toluene (30 cm^3) was placed under vacuum in a Young's ampoule and then 2 atm CO$_2$ applied. The solution was subjected to UV radiation for 2 h, giving an intense blue solution. The solvent was removed under reduced pressure, and the residue extracted into diethyl ether (120 cm^3). The extract was filtered, and cooled to -80 °C yielding thin plates of dark blue [{Nb(η-C_5H_5)$_2$(SnMe$_3$)}$_2$(μ-O)]. Yield 100 mg, 30%. A second crop (100 mg) was obtained by reducing the volume of solvent to 30 cm^3 and cooling to -80 °C; this was slightly contaminated by [Nb(η-C_5H_5)$_2$(SnMe$_3$)] ($\approx$10%). Crystals suitable for X-ray structure determination were obtained by slowly cooling a solution in toluene–diethyl ether (1:1).

Difference NOE Experiments.—The two isomers of [Nb(η-C_5H_5)$_2$(η-H$_2$C=CHPh)(SnMe$_3$)] **3** were assigned on the basis of difference ^{1}H NOE experiments performed at 300 MHz and 25 °C. A sample containing *ca.* 30% of the minor isomer was used. The two SnMe$_3$ resonances were irradiated and the resulting spectrum subtracted from the standard spectrum allowing the NOE enhanced peaks to be correlated with the relevant SnMe$_3$ signal. For the minor isomer δ (SnMe$_3$) 0.30, the NOE for the resonance at δ 2.42 was 2.9%, that for the signals at δ 1.36 and 1.01 was <0.5%; this indicates that this isomer is the *endo* isomer. For the major isomer δ (SnMe$_3$) 0.48, the NOE for the resonance at δ 2.36 was <0.1%, whilst for the two resonances at δ 1.02 and 1.31 it was 2.2 and 2.4% respectively, revealing this to be the *exo* isomer.

X-Ray Crystal Structure Determination on [{Nb(η-C_5H_5)$_2$(SnMe$_3$)}$_2$(μ-O)] **11**.—The crystal data are listed in Table 5. Crystals of complex **11** were sealed in glass capillaries under dinitrogen and diffraction data collected using an Enraf–Nonius CAD4F diffractometer. Unit-cell parameters and the orientation matrix were determined from the positions of 25 accurately centred reflections and refined using least-squares procedures. Owing to the shape of the crystal, data were collected using the FLAT mode available in standard Enraf–Nonius software. During data collection three orientation controls were measured every 250 reflections, and three intensity standards were measured every 3600 s of exposure time.

An absorption correction based on azimuthal scan data was applied,[71] and the data were corrected for Lorentz and polarisation effects.[72] Equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in the refinement.

Structure solution and refinement. Heavy-atom techniques were used to determine the position of the Nb and Sn atoms. All other non-hydrogen atoms were located from subsequent Fourier difference syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C–H 0.96 Å) and refined riding on their supporting carbon atoms with a thermal parameter 1.3 times that of the equivalent isotropic thermal parameter of the respective carbon atom. A Chebyshev weighting scheme was applied.[73] All calculations were performed using a VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford, using the Oxford CRYSTALS system[74] and plotted using SNOOPI. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[75] The final difference map showed residual peaks of 0.56 e Å^{-3} situated at 0.86 Å from the Nb atom.

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

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