Preparation and Characterisation of Anionic Bis(cyclopentadienyl)niobium Complexes: Molecular Structure of $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$†

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The reaction between $[Nb(\eta\text{-}C_5H_5)_2H_3]$ and LiBu,LiBu–1,4,7,10-tetraoxacyclododecane(12-crown-4), NaH–1,4,7,10,13-pentaoxacyclopentadecane(15-crown-5), KH–1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6), or $NaNH_2$ gives $M[Nb(\eta\text{-}C_5H_5)_2H_2]$ (M = Li, **1**; or Na, **5**) and $[M(crown)][Nb(\eta\text{-}C_5H_5)_2H_2]$ [M(crown) = Li(12-crown-4) **2**, Na(15-crown-5) **3** or K(18-crown-6) **4**]. The compound $SnMe_3Cl$ reacts with **1** or **4** to give $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$. The hydrides $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ and $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$ react with LiBu–12-crown-4, $NaNH_2$–15-crown-5 and KH–18-crown-6 to give $[M(crown)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$ [M(crown) = Li(12-crown-4), Na(15-crown-5) **7** or K(18-crown-6) **8**] and $[M(crown)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ [M(crown) = Li(12-crown-4) **9**, Na(15-crown-5) **10** or K(18-crown-6) **11**], respectively. The X-ray crystal structure of **11** shows there to be two separate ions $[Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]^-$ and $[K(18\text{-crown-}6)]^+$ with no close interionic contacts. Structural and spectroscopic evidence is presented for the presence of Nb–H–M interactions, where M = Li, Na or K.

Mononuclear metal carbonyl hydrides $M(CO)_nH_x$ are often acidic and readily lose a proton forming metal carbonylate anions.[1] Similarly, compounds in the class $[M(\eta\text{-}C_5H_5)(CO)_nH_x]$ are well known to form stable anions $[M(\eta\text{-}C_5H_5)(CO)_nH_{x-1}]^-$.[1] The bent bis($\eta$-cyclopentadienyl) hydrides $[M(\eta\text{-}C_5H_5)_2H_x]$ are, however, much less acidic since their metal centres are more electron-rich in the absence of the strongly π-accepting carbonyl ligands.

Nonetheless, it is possible to deprotonate the hydrides $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) using either the alkane-elimination reaction, *e.g.*[2–12] equation (1) or by using the strong base KH or NaH, *e.g.*[13] equation (2) (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). The resulting alkali-metal derivatives show evidence for either M–M′ bonding, or the formation of covalent M–H–M′ systems.

$$[M(\eta\text{-}C_5H_5)_2H_2] + LiR \longrightarrow [\{M(\eta\text{-}C_5H_5)_2HLi\}_4] + RH \quad (1)$$

$$[Mo(\eta\text{-}C_5H_5)_2] + KH + 18\text{-crown-}6 \longrightarrow [K(18\text{-crown-}6)][Mo(\eta\text{-}C_5H_5)_2H] \quad (2)$$

Other examples of closely similar or related systems include the deprotonation of $[Ta(\eta\text{-}C_5H_5)_2H_3]$ by LiBu, although the product was only poorly characterised.[14] The deprotonation of phosphine hydride and cyclopentadienyl phosphine hydride complexes has also been studied.[15–26] We note that the deprotonation of $[M(\eta\text{-}C_5H_5)_2H_3]$ (M = Nb or Ta) by $[Zn(\eta\text{-}C_5H_5)_2]$ or $ZnEt_2$ has also been described.[27–29]

During the progress of this work Struchkov, Lemenovskii and co-workers[30] reported the crystal and molecular structure of $[Na(benzo\text{-}15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2H_2]$. This was prepared by the reaction of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ with NaH at 50 °C followed by addition of benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine). Lemenovskii *et al.*[31] have also described reactions of the complex $[(\eta\text{-}C_5H_5)_2NbH_2Li]$ with $[Ti(\eta\text{-}C_5H_5)_2Cl_n]$ (n = 1 or 2) to give a fulvalene complex, but no characterising data were given for the lithiated complex.

Here we describe studies on anionic $[Nb(\eta\text{-}C_5H_5)_2R_2]^-$ systems where $R_2 = H_2$, $H(SnMe_3)$ or $(SnMe_3)_2$.

Results and Discussion

We set out to investigate the reactions between the trimethyltin-substituted niobium complexes $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ and $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$,[32] and the parent trihydride $[Nb(\eta\text{-}C_5H_5)_2H_3]$, with strong bases.

We had previously shown that addition of LiBu to $[Nb(\eta\text{-}C_5H_5)_2H_3]$ gave a compound which was presumed to be $[\{(\eta\text{-}C_5H_5)_2NbH_2Li\}_n]$ **1**[32] somewhat analogous to the tetramers $[\{(\eta\text{-}C_5H_5)_2MHLi\}_4]$ (M = Mo or W).[5] However, structural characterisation of $[\{(\eta\text{-}C_5H_5)_2NbH_2Li\}_n]$ **1** was precluded by its thermal instability at room temperature and by decomposition in tetrahydrofuran (thf) solutions. Attempts to form X-ray-quality crystals of **1** directly from the reaction of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ with LiBu in various solvent mixtures were unsuccessful. Thus, we decided to attempt to prepare more stable derivatives of **1**.

Addition of a light petroleum solution of LiBu to a toluene solution of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ containing 1 equivalent of 12-crown-4 (1,4,7,10-tetraoxacyclododecane) gave an orange-red powder $[Li(12\text{-crown-}4)][Nb(\eta\text{-}C_5H_5)_2H_2]$ **2** (Scheme 1). This dissolved in thf without decomposition. Similarly, treatment of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ with NaH and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) in thf yielded a red solution from which crystals of $[Na(15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2H_2]$ **3** could be isolated by cooling to −80 °C. Also $[Nb(\eta\text{-}C_5H_5)_2H_3]$ reacted with KH and 18-crown-6 in thf to give red $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2H_2]$ **4**.

Attempts to prepare crown-ether free $Na[Nb(\eta\text{-}C_5H_5)_2H_2]$ using NaH in thf at 50 °C gave the previously described $[\{Nb(\eta\text{-}C_5H_5)(\mu\text{-}\sigma\text{:}\ \eta^5\text{-}C_5H_4)H\}_2]$ in good yields, which is believed to arise from thermal decomposition of $[Nb(\eta\text{-}C_5H_5)_2H_3]$.[33,34] However, treatment of $[Nb(\eta\text{-}C_5H_5)_2H_3]$ with $NaNH_2$ in

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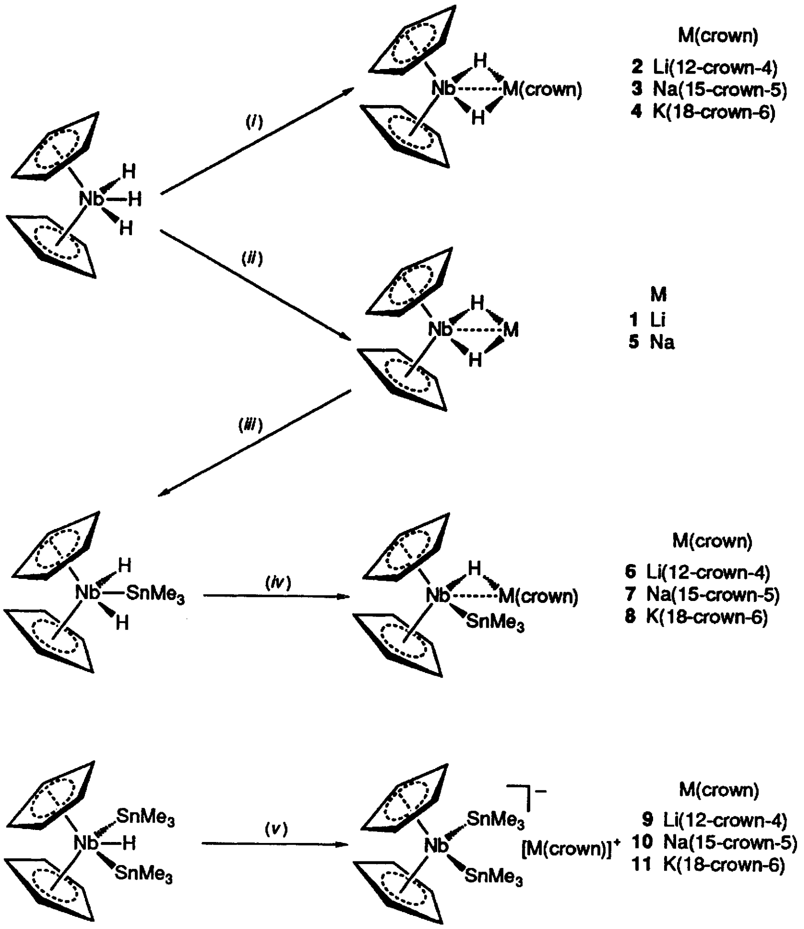
† (1,4,7,10,13,16-Hexaoxacyclooctadecane)potassium bis(η-cyclopentadienyl)bis(trimethylstannyl)niobate(III).

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



Scheme 1 The reactions of [Nb(η-$C_5H_5)_2H_3$], [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-$C_5H_5)_2H(SnMe_3)_2$] with bases. Reagents and conditions: (*i*) LiBu, 12-crown-4, diethyl ether, 15 min, yield 85% of **2**; NaH, 15-crown-5, thf, 6 d, 73% of **3**; or KH, 18-crown-6, thf, 36 h, 70% of **4**; (*ii*) LiBu, toluene, 15 min, **1**; or $NaNH_2$, [$^2H_8$]thf, 3 d, **5**; (*iii*) $SnMe_3Cl$, light petroleum (for M = Li); (*iv*) LiBu, 12-crown-4, light petroleum, 15 min, 82%, **6**; $NaNH_2$, 15-crown-5, [$^2H_8$]thf, 2.5 h, **7**; or KH, 18-crown-6, thf, 14 d, 65%, **8**; (*v*) LiBu, 12-crown-4, pentane, 10 min, **9**; $NaNH_2$, 15-crown-5, [$^2H_8$]thf, 2 h, **10**; or KH, 18-crown-6, thf, 65 °C, 5 d, 50%, **11**

Table 1 Selected ^1H and ^{13}C NMR data for the new compounds *

	^1H NMR (δ)			^{13}C NMR (δ)	
Compound	η-C_5H_5	$SnMe_3$	Hydride	η-C_5H_5	$SnMe_3$
2 [Li(12-crown-4)][Nb(η-$C_5H_5)_2H_2$]	4.20		−10.38	78.6	
3 [Na(15-crown-5)][Nb(η-$C_5H_5)_2H_2$]	4.17		−10.24	75.3	
4 [K(18-crown-6)][Nb(η-$C_5H_5)_2H_2$]	4.14		−9.48	74.6	
5 Na[Nb(η-$C_5H_5)_2H_2$]	4.19		−10.36	75.7	
6 [Li(12-crown-4)][Nb(η-$C_5H_5)_2H(SnMe_3)$]	4.12	−0.31	−10.07	75.4	−3.0
7 [Na(15-crown-5)][Nb(η-$C_5H_5)_2H(SnMe_3)$]	4.10	−0.36	−9.60	75.0	−3.0
8 [K(18-crown-6)][Nb(η-$C_5H_5)_2H(SnMe_3)$]	4.05	−0.38	−9.08	74.8	−2.8
9 [Li(12-crown-4)][Nb(η-$C_5H_5)_2(SnMe_3)_2$]	4.09	−0.27		75.9	−3.2
10 [Na(15-crown-5)][Nb(η-$C_5H_5)_2(SnMe_3)_2$]	4.09	−0.26		not recorded	
11 [K(18-crown-6)][Nb(η-$C_5H_5)_2(SnMe_3)_2$]	4.09	−0.27		75.9	−3.2

* In [$^2H_8$]thf at 300 MHz and 294 K for ^1H, 75.43 MHz and 300 K for ^{13}C. Crown-ether resonances omitted, see text.

[$^2H_8$]thf did provide a route to the crown-ether-free complex Na[Nb(η-$C_5H_5)_2H_2$] **5**.

The reaction of [{(η-$C_5H_5)_2NbH_2Li\}_n$] **1** with $SnMe_3Cl$ to give [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] has already been described.[32] The analogous reaction of **4** with $SnMe_3Cl$ gave a mixture of [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and 18-crown-6 which were identified by ^1H NMR spectroscopy.

Treatment of [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-$C_5H_5)_2H(SnMe_3)_2$] with LiBu and 12-crown-4 gave the orange crystalline lithium complexes [Li(12-crown-4)][Nb(η-$C_5H_5)_2$-H($SnMe_3$)] **6** and [Li(12-crown-4)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **9**, respectively. Similarly, refluxing thf solutions of [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-$C_5H_5)_2H(SnMe_3)_2$] and 18-crown-6 with excess of KH gave red solutions from which the potassium complexes [K(18-crown-6)][Nb(η-$C_5H_5)_2H(SnMe_3)$] **8** and [K(18-crown-6)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **11** could be isolated. Attempts to prepare, and isolate, the corresponding sodium salts using NaH as a base were unsuccessful, even after prolonged reflux in thf; NaH appears to be kinetically less reactive than KH. However, the NMR spectra (Table 1) of the deep red solutions formed by addition of $NaNH_2$ and 15-crown-5 to [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-

Table 2 Selected bond lengths (Å) and angles (°) for compound **11**

Nb–Sn(1)	2.817(1)	Sn(2)–C(3)	2.198(7)
Nb–Sn(2)	2.830(1)	Sn(2)–C(4)	2.187(9)
Sn(1)–C(1)	2.195(9)	K–O$_{av}$	2.763
Sn(1)–C(2)	2.191(7)		
Sn(2)–Nb–Sn(1)	87.18(3)	C(1)–Sn(1)–Nb	113.8(3)

Table 3 Fractional coordinates (× 10^4) for [K(18-crown-6)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **11**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Nb	4078.2(4)	2500	988.1(8)
Sn(1)	2455.8(4)	2500	341.0(6)
Sn(2)	3591.0(4)	2500	3554.2(6)
K	0	0	5000
C(1)	2235(7)	2500	−1709(9)
C(2)	1699(4)	1655(4)	873(8)
C(3)	3992(5)	1678(4)	4778(8)
C(4)	2343(6)	2500	4127(9)
C(11)	5053(6)	1749(5)	403(14)
C(12)	4434(7)	1652(4)	−454(9)
C(13)	3809(6)	1395(3)	180(10)
C(14)	4002(5)	1339(3)	1431(9)
C(15)	4777(6)	1541(4)	1605(10)
C(21)	1552(5)	−19(4)	2686(8)
C(22)	2085(4)	425(4)	4560(8)
C(23)	1858(4)	820(3)	5689(8)
C(24)	1098(5)	796(3)	7546(7)
C(25)	488(5)	406(4)	8251(6)
C(26)	−829(5)	19(4)	8141(6)
O(1)	1397(3)	337(2)	3788(4)
O(2)	1334(3)	448(2)	6432(5)
O(3)	−198(3)	361(2)	7521(4)

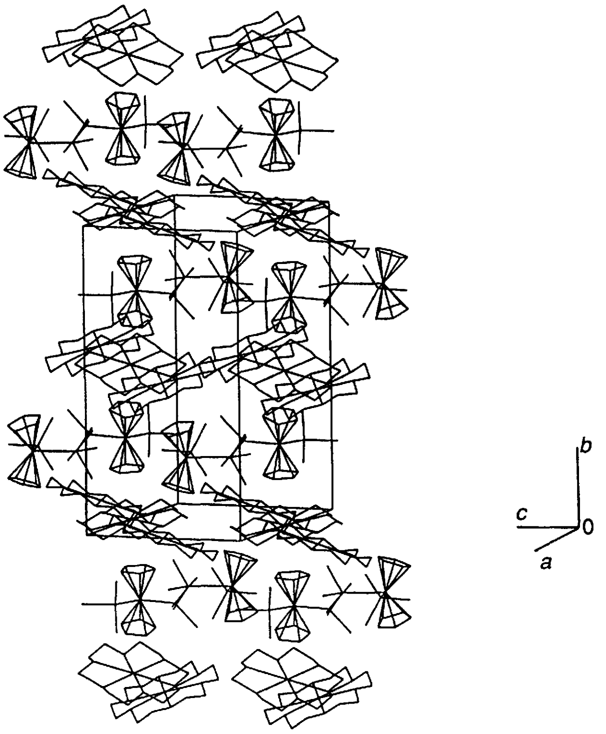


Fig. 1 View of the crystal structure of [K(18-crown-6)] [Nb(η-$C_5H_5)_2(SnMe_3)_2$] **11** showing the packing of the cations and anions. The K atoms lie on the crystallographic inversion centres at (0, 0, $\frac{1}{2}$), (0, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0); the Sn–Nb–Sn linkages are bisected by crystallographic mirror planes at (*x*, $\frac{1}{4}$, *z*), (−*x*, $\frac{3}{4}$, −*z*), ($\frac{1}{2}$ − *x*, $\frac{3}{4}$, $\frac{1}{2}$ + *z*) and ($\frac{1}{2}$ + *x*, $\frac{1}{4}$, $\frac{1}{2}$ − *z*)

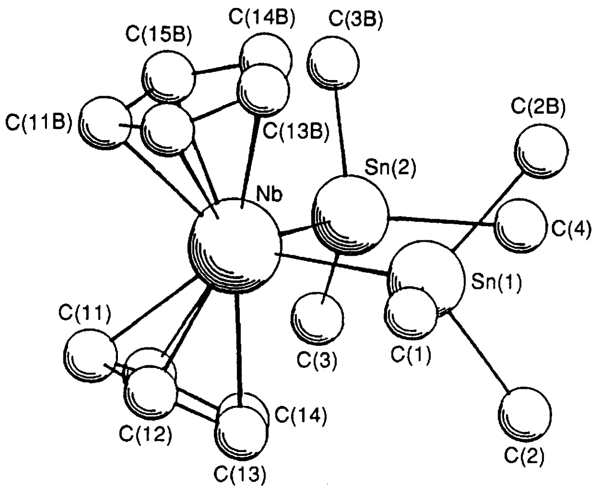


Fig. 2 View of the molecular structure of the [Nb(η-$C_5H_5)_2(SnMe_3)_2]^-$ anion in compound **11**. Hydrogen atoms are omitted for clarity

$C_5H_5)_2H(SnMe_3)_2$] in [$^2H_8$]thf were consistent with the presence of the compounds [Na(15-crown-5)][Nb(η-$C_5H_5)_2H(SnMe_3)$] **7** and [Na(15-crown-5)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **10**. Attempts to isolate these sodium salts by using $NaNH_2$ in thf on a preparative scale were unsuccessful. The poorly crystalline solids thus obtained were found to contain significant amounts of $NaNH_2$ and use of exactly 1 equivalent of $NaNH_2$ invariably led to only partial deprotonation.

The X-ray crystal structure of the salt [K(18-crown-6)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **1** has been determined. Selected bond lengths and angles are presented in Table 2 and the atomic coordinates are given in Table 3. The crystal structure consists of discrete [Nb(η-$C_5H_5)_2(SnMe_3)_2]^-$ anions and [K(18-crown-6)]$^+$ cations and there appear to be no interactions between the ions closer than the appropriate van der Waals radii (Fig. 1). The components of the crystal structure are arranged in alternating sheets of anions and cations, the anion sheets lying at $y = \pm\frac{1}{4}$ and the cation sheets lying at $y = 0$ and $\pm\frac{1}{2}$. The structure of the anion [Nb(η-$C_5H_5)_2(SnMe_3)_2]^-$ is illustrated in Fig. 2. The cation consists of a [K(18-crown-6)]$^+$ cation with the K^+ ion located on a crystallographic inversion centre. The potassium ion lies exactly on the least-squares plane of the oxygen atoms. The oxygen atoms deviate from the least-squares plane by 0.19 Å and on alternating sides of the plane. In the salt [K(18-crown-6)(NCS)] the oxygen atoms also lie 0.19 Å from the least-squares plane.[35] The average K–O distance in compound **11** is 2.763 Å, which may be compared to 2.805 Å for [K(18-crown-6)(NCS)].[35]

The anion [Nb(η-$C_5H_5)_2(SnMe_3)_2]^-$ lies across a crystallographic mirror plane with the Nb, both Sn, C(1) and C(4) atoms in the plane, and the two η-C_5H_5 rings are related by the mirror plane. The Sn–Nb–Sn angle is 87.13(3)° which compares well with the H–Nb–H angle of 86(1)° previously found for the anion [Nb(η-$C_5H_5)_2H_2]^-$.[30] As previously discussed,[30] both of these angles are outside the range previously found for d^2 [M(η-$C_5H_5)_2X_2$] complexes.[36] In the case of the [Nb(η-$C_5H_5)_2(SnMe_3)_2]^-$ anion this may *partly reflect steric factors* due to the bulk of the $SnMe_3$ groups.

The structure of compound **11** clearly shows the absence of any localised interactions between the component ions. This contrasts with the structure of [Na(benzo-15-crown-5)][Nb(η-$C_5H_5)_2H_2$] in which Nb–H–Na interactions are implicated,[30] with ion pairing between the cation and anion. The Na ion is 'pulled' 0.97 Å out of the least-squares plane of the crown ether. Two alternative bonding descriptions may be proposed for this structure. The first, proposed by Struchkov and Lemenovskii, is that the anion possesses a high charge density in the region between the cyclopentadienyl rings, and the cation is electrostatically attracted to this site.[30] Alternatively, we have previously described such interactions as two-electron three-centre covalent bonds between the MH group and the alkali-metal ion.[24–26]

Selected ^1H and ^{13}C NMR data for all the complexes described here are given in Table 1. For all these complexes the chemical shifts of the crown-ether moiety fall in the range δ 3.0–3.6 (^1H) and 68–72 (^{13}C): these data have no diagnostic structural value. The ^1H NMR spectra of the complexes [M(crown)][Nb(η-$C_5H_5)_2H_2$] [M(crown) = Li(12-crown-4) **2**, Na(15-crown-5) **3** or K(18-crown-6) **4**] and Na[Nb(η-$C_5H_5)_2H_2$] **5** display significant high-field shifts of the hydride signal compared to [Nb(η-$C_5H_5)_2H_3$] [δ = −3.1 (broad 'triplet', 1 H) and −3.95 (doublet, 2H) in [$^2H_8$]thf, 300 MHz, 293 K]. These shifts are consistent with there being a greater electron density on the niobium in complexes **2**–**5** as a consequence of their d^2 anionic nature. Similar high-field shifts are observed for the hydride resonances of [M][Nb(η-$C_5H_5)_2H(SnMe_3)$] relative to [Nb(η-$C_5H_5)_2H_2(SnMe_3)$].

The ^1H and ^{13}C NMR chemical shift data for compounds **2**–**11** provide evidence for the existence of an interaction between the cations and anions in solution. Thus the chemical shifts of the hydrido ligands of the salts [M(crown)][Nb(η-$C_5H_5)_2H_2$] **2**–**4** and Na[Nb(η-$C_5H_5)_2H_2$] **5** are dependent on the identity of the cation, the resonance moving to lower fields in the sequence Li < Na < K. This trend presumably reflects a decrease in the covalent character of the H–M interactions in the same order. The ^1H and ^{13}C NMR chemical shifts of the η-C_5H_5 ligand are also cation-dependent.

The NMR data for the monotin-substituted series of salts [M(crown)][Nb(η-$C_5H_5)_2H(SnMe_3)$] **6**–**8** show a trend in the ^1H and ^{13}C chemical shifts that closely resembles that for the dihydride [Nb(η-$C_5H_5)_2H_2]^-$ salts. The hydrido resonance moves by approximately 1 ppm for both series of salts as the cation changes from [Li(12-crown-4)]$^+$ to [K(18-crown-6)]$^+$. The ^1H and ^{13}C NMR chemical shifts of the η-C_5H_5 and $SnMe_3$ ligands are also dependent on the identity of the cation in the [M(crown)][Nb(η-$C_5H_5)_2H(SnMe)$] series of salts. On the basis of these data we conclude that this series of salts contain Nb–H–M interactions in solution. It is unlikely that any interaction between ions can occur through the $SnMe_3$ substituent. Despite repeated attempts we have been unable to obtain suitable single crystals of any of these salts in order to determine the extent of any interaction in the solid state.

The ^1H and ^{13}C NMR chemical shifts of the ditin series of salts [M(crown)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] **9**–**11** are identical within experimental error and we have already demonstrated that there is no interaction between the ions in this series in the solid state. We thus conclude that there is no covalent interaction between the ions in these salts in solution.

No attempt has been made to record ^{119}Sn NMR spectra for any of these salts. We have previously found that, due to interaction with the quadrupolar ^{93}Nb nucleus, the ^{119}Sn spectra of [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-$C_5H_5)_2H(SnMe_3)_2$] are only observed as broad signals at −80 °C.[32]

Conclusion

The reactions and structures proposed for the new compounds **1**–**11** are shown in Scheme 1. The series of salts [M(crown)][Nb(η-$C_5H_5)_2H_2$] [M(crown) = Li(12-crown-4), Na(15-crown-5) or K(18-crown-6)] show NMR behaviour consistent with some degree of interaction between the ions in solution.

The salts [M(crown)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] have discrete ions which display no covalency in solution or in the solid state as evidenced by the X-ray crystal structure of [K(18-crown-6)][Nb(η-$C_5H_5)_2(SnMe_3)_2$] and the ^1H and ^{13}C NMR chemical shifts. On the basis of similar NMR chemical shift arguments, the monotin-substituted series of salts [M(crown)][Nb(η-$C_5H_5)_2H(SnMe_3)$] are proposed to possess some degree of ion pairing in solution, through bridging Nb–H–M groups.

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. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves. Glassware was dried overnight in an oven at 100 °C before use.

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], or calcium hydride (acetonitrile), under an inert atmosphere of dinitrogen before use. NMR samples were prepared in the dry-box; [$^2H_8$]thf was either vacuum transferred from Na/K alloy or pipetted from the same drying agent in the glove-box. Samples of the very moisture sensitive potassium and sodium salts were prepared with an excess of solid KH or NaH respectively in the NMR tube; lithium salts were prepared in rigorously dried tubes. All samples were sealed under vacuum in soda-glass NMR tubes.

Infrared spectra were recorded as CsI or KBr pellets on a Mattson Polaris FT-IR interferometer, samples being prepared in the dry-box. Proton (300 MHz) and ^{13}C (75.43 MHz) NMR spectra were obtained using a Brüker AM-300 spectrometer. Spectra were referenced internally using the residual solvent resonances relative to tetramethylsilane (δ 0). All chemical shifts are quoted in δ, high-field shifts being taken as negative, and coupling constants are in Hz. Elemental analysis was performed by Analytische Laboratorien, Elbach, Germany.

The hydride [Nb(η-$C_5H_5)_2H_3$] was prepared by a literature method,[37] [Nb(η-$C_5H_5)_2H_2(SnMe_3)$] and [Nb(η-$C_5H_5)_2H(SnMe_3)_2$] were prepared as described previously.[32]

Preparations.—[Li(12-crown-4)][Nb(η-$C_5H_5)_2H_2$] **2**. The compound 12-crown-4 (0.6 g, 3.4 mmol) in diethyl ether (250 cm^3) was added to [Nb(η-$C_5H_5)_2H_3$] (0.76 g, 3.4 mmol), and treated with an excess of LiBu (3 cm^3 of a 2.5 mol dm^{-3} solution in hexanes, 7.5 mmol) with stirring. A red precipitate formed instantaneously, and stirring was continued for 15 min. The product was collected by decantation followed by washing with ether (2 × 75 cm^3) and drying *in vacuo*, giving a red-orange powder. Yield 1.2 g, 85% (Found: C, 52.7; H, 6.8. $C_{18}H_{28}LiNbO_4$ requires C, 53.0; H, 6.35%). Selected infrared data: 1568(br) cm^{-1}, ν(Nb–H).

[Na(15-crown-5)][Nb(η-$C_5H_5)_2H_2$] **3**. The compound NaH (3.0 g, 125 mmol), in mineral oil, was washed with light petroleum (2 × 50 cm^3) and dried *in vacuo*. The compound [Nb(η-$C_5H_5)_2H_3$] (1.0 g, 4.4 mmol) in thf (80 cm^3) was added, but no reaction was observed. A solution of 15-crown-5 (1.05 g, 4.7 mmol) in thf (50 cm^3) was added. Stirring soon produced some evolution of gas; the reaction was stirred for 6 d, then allowed to settle. The red solution was decanted and the volume reduced to 65 cm^3. Cooling the solution to −25 °C gave large, red polycrystallites of [Na(15-crown-5)][Nb(η-$C_5H_5)_2H_2$]. Yield 1.50 g, 73% (Found: C, 51.1; H, 6.9. $C_{20}H_{32}NaNbO_5$ requires C, 51.3; H, 6.5%).

[K(18-crown-6)][Nb(η-$C_5H_5)_2H_2$] **4**. The compound KH (2.5 g, 62 mmol), in mineral oil, was washed with light petroleum (2 × 20 cm^3), and then dried *in vacuo*. A solution of [Nb(η-$C_5H_5)_2H_3$] (1.015 g, 4.5 mmol) and 18-crown-6 (1.22 g, 4.6 mmol) in thf (50 cm^3) was added. Effervescence and a crimson-red solution resulted, which was stirred for 36 h. The excess of KH was allowed to settle, the solution was decanted and the volume was reduced to 35 cm^3. Red crystals formed as the solution was slowly cooled to −25 °C. These were washed with light petroleum and dried *in vacuo*. The yield of [K(18-crown-

Table 4 Crystal data for compound **11**

T/K	293
Formula	$C_{28}H_{52}KNbO_6Sn_2$
M	854.09
Crystal symmetry	Orthorhombic
Space group	*Pnma*
a/Å	16.844(7)
b/Å	20.005(4)
c/Å	10.556(3)
U/Å^3	3556.8
Z	4
D_c/g cm^{-3}	1.59
F(000)	1712
Crystal size/mm	0.1 × 0.35 × 0.5
μ/cm^{-1}	18.53
Radiation	Mo-Kα (λ = 0.710 69 Å)
Zone	*hkl*
Scan type	ω–θ
Scan width/°	1.10 + 0.35 tanθ
2θ range/°	3–50
Intensity standards decay (%)	$\approx$22
Reflections collected	3207
Independent reflections	1976 [$I > 3\sigma(I)$]
R_{merge}	0.021
No. of parameters refined	182
R^a	0.027
R'^b	0.028

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, unit weights.

6]$[Nb(\eta\text{-}C_5H_5)_2H_2]$ was 1.67 g, 70% (Found: C, 49.7; H, 6.7. $C_{22}H_{36}KNbO_6$ requires C, 50.0; H, 6.9%).

Reactions between $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2H_2]$ **4** *and* $SnMe_3Cl$. The compound $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2H_2]$ **4** (0.2 g, 0.37 mmol) was dissolved in thf (40 cm^3) and stirred at 20 °C. A solution of $SnMe_3Cl$ in thf was added dropwise until the orange colour was discharged, leaving a faint yellow-brown solution. The solvent was removed under reduced pressure, and the residue extracted with light petroleum (80 cm^3). The yellowish extract was evaporated to dryness. The residue was shown to be a mixture of $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ and 18-crown-6 by the ^{1}H NMR spectrum.

$Na[Nb(\eta\text{-}C_5H_5)_2H_2]$ **5**. The compound $[Nb(\eta\text{-}C_5H_5)_2H_3]$ (0.035 g, 0.16 mmol) was dissolved in [$^2H_8$]thf (0.35 cm^3) in a 5 mm NMR tube containing an excess of $NaNH_2$. The tube was sealed under reduced pressure, allowed to stand at 20 °C and the reaction monitored by ^{1}H NMR spectroscopy. Formation of $Na[Nb(\eta\text{-}C_5H_5)_2H_2]$ was complete after 3 d.

$[Li(12\text{-crown-}4)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$ **6**. A solution of $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ (390 mg, 1 mmol) in light petroleum (100 cm^3) was treated with LiBu (1 cm^3 of a 2.5 mol dm^{-3} solution in hexanes, 2.5 mmol) with stirring. No reaction was observed. The ether 12-crown-4 (176 mg, 1 mmol, 0.19 cm^3) was added by a syringe. A red precipitate formed immediately and stirring was continued for 15 min. The product was collected by decantation of the solvent and dried *in vacuo*, giving a red-orange powder of $[Li(12\text{-crown-}4)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$. Yield 0.47 g, 82% (Found: C, 43.9; H, 6.2. $C_{21}H_{36}LiNbO_4Sn$ requires C, 44.2; H, 6.35%). Selected infrared data: 1620(br) cm^{-1}, ν(Nb–H).

$[Na(15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$ **7**. The compound $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ (63 mg, 0.16 mmol) and $NaNH_2$ (80 mg, 2 mmol) were placed in an NMR tube (diameter 5 mm) and 15-crown-5 (0.35 cm^3, 37 mg, 0.16 mmol) added *via* a syringe. [$^2H_8$]Tetrahydrofuran (0.35 cm^3) was distilled into the tube which was then sealed. After 2.5 h at 20 °C the solution was deep red and an NMR spectrum showed no starting material, but resonances assignable to $[Na(15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$.

$[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$ **8**. The compound KH (2.5 g, 62 mmol), in mineral oil, was washed with light petroleum (2 × 20 cm^3), and dried *in vacuo*. A solution of $[Nb(\eta\text{-}C_5H_5)_2H_2(SnMe_3)]$ (600 mg, 1.57 mmol) and 18-crown-6 (430 mg, 1.63 mmol) in thf (60 cm^3) was added. The solution was stirred and took on a faint red colour over 3 h; stirring was continued at 20 °C for 14 d. The excess of KH was allowed to settle, the solution decanted and the volume reduced to 30 cm^3. Diethyl ether (30 cm^3) was added, and red crystals of $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)]$ deposited over 12 h. Yield 0.45 g, 65% (Found: C, 43.2; H, 6.2. $C_{25}H_{44}KNbO_6Sn$ requires C, 43.4; 6.4%). Selected infrared data: 1635(br) cm^{-1}, ν(Nb–H).

$[Li(12\text{-crown-}4)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ **9**. A pentane (70 cm^3) solution of $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$ (270 mg, 0.5 mmol) and 12-crown-4 (0.12 cm^3, 0.6 mmol, 0.1 g) was treated with LiBu (1 cm^3 of a 2.5 mol dm^{-3} solution in hexanes, 2.5 mmol) with stirring. A red precipitate formed immediately and stirring was continued for 10 min. The product was collected by decantation of the solvent and dried *in vacuo*, giving a red-orange powder. Yield 0.3 g, 80% (Found: C, 39.1; H, 5.9. $C_{24}H_{44}LiNbO_4Sn_2$ requires C, 39.3; H, 6.0%).

$[Na(15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ **10**. The compound $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$ (35 mg, 0.06 mmol) and $NaNH_2$ (50 mg, 0.12 mmol) was placed in an NMR tube (diameter 5 mm) and 15-crown-5 (32 mg, 0.06 mmol) added by syringe. [$^2H_8$]Tetrahydrofuran (0.35 cm^3) was distilled into the tube which was sealed under vacuum. After 2 h at 20 °C the solution was deep red and an NMR spectrum showed no starting material, but resonances assignable to $[Na(15\text{-crown-}5)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$.

$[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ **11**. The compound KH (2.5 g, 62 mmol), in mineral oil, was washed with light petroleum (2 × 20 cm^3), and dried *in vacuo*. A solution of $[Nb(\eta\text{-}C_5H_5)_2H(SnMe_3)_2]$ (460 mg, 0.84 mmol) and 18-crown-6 (340 mg, 0.91 mmol) in thf (20 cm^3) was added. The mixture was stirred at 65 °C for 5 d, giving a bright red solution. The excess of KH was allowed to settle, and the solution decanted. The volume was reduced to 8 cm^3, and ether (20 cm^3) added. This solution was cooled to −80 °C for several days, resulting in the slow precipitation of red single crystals of $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$. Yield 0.36 g, 50% (Found: C, 39.4; H, 6.0. $C_{28}H_{52}KNbO_6Sn_2$ requires C, 39.4; H, 6.1%).

X-Ray Crystal Structure Determination for $[K(18\text{-crown-}6)][Nb(\eta\text{-}C_5H_5)_2(SnMe_3)_2]$ **11**.—The crystal data are listed in Table 4. Crystals of compound **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. 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,[38] and the data were corrected for Lorentz and polarisation effects. 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, Sn and K 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. All calculations were performed using a VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford, using the Oxford CRYSTALS system[39] and plotted using SNOOPI. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[40] The final difference map showed a residual peak of 0.7 e Å^{-3} at 0.8 Å from the Nb atom.

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