Facile Preparation of Mono- and Bis(tin)-Substituted Niobocenes with Functionalized Stannyl Ligands: The Search for Non-Classical Interligand Interactions

Georgii I. Nikonov,*[a] Lyudmila G. Kuzmina,[b] Jörg Lorberth,[c] and Judith A. K. Howard[d]

Keywords: Niobium / Tin / Hydrides / Group 5 / Group 14

The reaction of niobocene trihydride [Cp_2NbH_3] with one equivalent of an alkyl- or aryltin halide X_nSnR_{4-n} (n = 1, 2) leads to products of the displacement of hydride by tin, i.e. [$Cp_2NbH_2(SnX_{3-n}R_n)$] [R = Me, n = 3 (**1**); R = Me, X = Cl, n = 2 (**3**); R = Ph, n = 3 (**4**); R = Ph, X = Cl, n = 2 (**5**); R = Et, X = Br, n = 2 (**6**)]. Use of an excess of the tin reagent results in a halodealkylation exchange reaction at the tin atom bound to the metal center. Reaction of the mono(silyl) complexes [$Cp_2NbH_2(SiXMe_2)$] (X = Cl, Ph) with organotin halides X_nSnR_{4-n} gives products of the displacement of silicon by tin, whereas the bis(silyl) complex [$Cp_2NbH(SiPhMe_2)_2$] does not undergo this reaction. The bis(tin)-substituted niobocene [$Cp_2NbH(SnMe_3)_2$] has been prepared by the reaction of [$Cp_2NbH_2(SnMe_3)$] with the tin amide Me_3SnNMe_2 under thermal conditions, as well as by the literature method of thermolysis of [$Cp_2NbH(\eta^2\text{-}C_2H_3Ph)$] in the presence of Me_3SnH. Reaction of [$Cp_2NbH(SnMe_3)_2$] with two equivalents of Cl_2SnMe_2 affords the bis(tin)-substituted complex [$Cp_2NbH(SnClMe_2)_2$] (**9**). The possible presence of non-classical hypervalent H···Sn–Cl interactions in this compound has been assessed by means of X-ray structure analysis. The structural data for **9** are in accord with an essentially classical description as a tin-substituted dihydride complex without significant Sn···H interactions.

Introduction

We have been studying the chemistry of trisubstituted Group-5 metallocene complexes bearing hydride and main-group element ligands in the bisecting plane of the metallocene moiety.[1−3] Initially, we focused on the development of convenient synthetic approaches to compounds of this class. These efforts resulted in the introduction of the insertion/deprotonation method based on the interaction of metallocene trihydrides [Cp_2MH_3] (M = Nb, Ta) with Group-15 halides XER_2 (E = P, As, Sb, Bi; X = Cl, Br).[1] This method provides easy access to dihydrides of the general formula [$Cp_2MH_2(ER_2)$]. A very similar approach, namely main-group element displacement of hydride, has recently been used by ourselves in the preparation of a plumbio-substituted niobocene,[2] and previously by Bulychev et al. in the preparation of a tin-substituted tantalocene.[4]

In this paper, we report an extension of these studies to the syntheses of mono- and bis(tin)-substituted niobocenes. Our interest in compounds of this type was intensified following our recent discovery of non-classical H···Si−Cl interligand interactions in the related silicon-substituted niobocene complexes [$Cp_2NbYH(SiR_2X)$] (Y = H, SiR_2X) bearing functionalized silyl ligands SiR_2X.[2] Thus, we were interested in finding analogous H···Sn−Cl interactions in the present systems. The main-group element displacement of hydride and halodealkylation exchange approaches reported herein provide a convenient entry to the chemistry of tin-substituted metallocenes bearing functionalized stannyl substituents SnX_nR_{3-n} (X = Cl, Br; R = Et, Me; n = 1, 2).

Results and Discussion

Mono(tin)-Substituted Complexes

The first tin-substituted niobocene hydrides [$Cp_2NbH_2(SnMe_3)$] (**1**) and [$Cp_2NbH(SnMe_3)_2$] (**2**), were prepared by Green et al. by means of oxidative addition of $HSnMe_3$ to the 16-electron intermediates [Cp_2NbH] and [$Cp_2NbCH_2CH_2Ph$], which were generated in situ from [Cp_2NbH_3] and the styrene complex [$Cp_2NbH(\eta^2\text{-}C_2H_3Ph)$], respectively.[5] This approach cannot, however, be applied to the syntheses of complexes bearing functionalized stannyl ligands since the parent compounds $XSnR_2H$ are not easily accessible. Green et al. also reported a metathetical reaction leading to **1**, between the anionic complex [Cp_2NbH_2]Li and $ClSnMe_3$, although this reaction proceeds under reducing conditions, thus restricting the use of functionalized tin reagents.[5] In 1986, Bulychev et al. showed that Cl_3SnMe and Cl_2SnMe_2 react with the d^0 complex [Cp_2TaH_3] to give [$Cp_2TaH_2(Cl_nSnMe_{3-n})$] ($n$ = 1, 2), whereas $ClSnMe_3$ does not undergo such a reaction.[4] The highest yields were observed when these reactions were carried out in the presence of an amine, which served to consume the generated HCl. These findings prompted this study of the analogous niobocene chemistry.

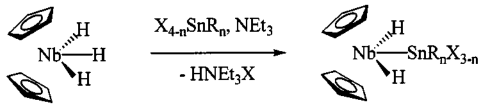
[Cp_2NbH_3] reacts readily with one equivalent of a tin halide X_nSnR_{4-n} (n = 1, 2) in diethyl ether in the presence of

---

[a] Chemistry Department, Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russia
Fax: (internat.) + 7-095/932-8846
E-mail: nikonov@org.chem.msu.su
[b] Institute of General and Inorganic Chemistry,
RAS, Leninsky Prosp. 31, 117907 Moscow, Russia
[c] Fachbereich Chemie, Philipps-Universität Marburg,
Hans-Meerwein-Strasse, D-35032 Marburg, Germany
[d] Chemistry Department, University of Durham,
South Road, Durham DH1 3LE, U.K.

1434−1948/99/0505−0825 $ 17.50+.50/0

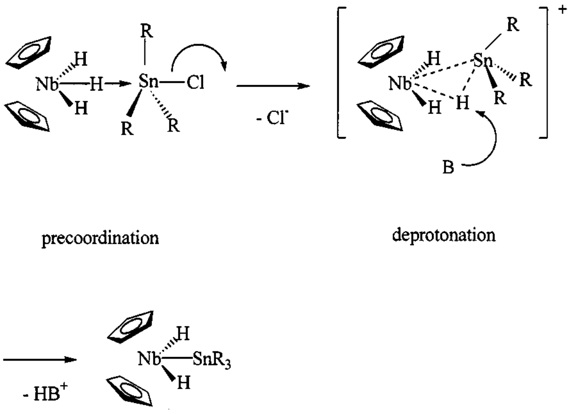
NEt_3, to give the mono(tin)-substituted complexes $[Cp_2NbH_2(SnX_{3-n}R_n)]$ [R = Me, n = 3 (**1**); R = Me, X = Cl, n = 2 (**3**); R = Ph, n = 3 (**4**); R = Ph, X = Cl, n = 2 (**5**); R = Et, X = Br, n = 2 (**6**)] (Equation 1). The reactions commence immediately after the reactants are mixed and result in the formation of a flocculent precipitate of $ClH{\cdot}NEt_3$. The mixtures were left to stir overnight to ensure completion of the reactions. Complexes **1**, **3−6** could easily be isolated (after filtration and removal of the solvent) and were obtained as pale-yellow, air-sensitive, crystalline materials. The products seemingly showed indefinite thermal stability, as is also the case for the related plumbyl-substituted complex $[Cp_2NbH_2(PbMe_3)]$.[2] In contrast, the related Group-15 substituted complexes $[Cp_2NbH_2(EPh_2)]$ (E = Sb, Bi) exhibit little thermal stability and $Cp_2NbH_2(BiPh_2)$ is also very light-sensitive. Complexes **1**, **3−6** were characterized by NMR and IR spectroscopy. Their ^1H-NMR spectra are in accord with the formation of only one isomer, specifically that having a centrally positioned tin substituent and lateral hydride ligands. In contrast, the mono(silyl) complex $[Cp_2NbH_2(SiClMe_2)]$ exists in two isomeric forms, one of which, with a lateral silyl group, exhibits non-classical bonding between the hydride and silicon ligands.[3]



(1)

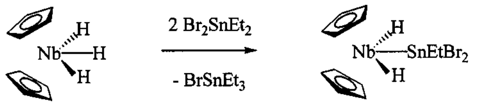
X	Cl	Cl	Cl	Cl	Br
R	Me	Me	Ph	Ph	Et
n	3	2	3	2	2
	1	**3**	**4**	**5**	**6**

The mechanism of the reaction according to Equation 1 is intriguing. The d^0 complex $[Cp_2NbH_3]$ lacks a metal-centered lone pair of electrons, hence conventional nucleophilic substitution of halide at the tin center is not possible. Although the reaction is carried out in the presence of an amine to consume the HCl released, the amine cannot effect deprotonation of $[Cp_2NbH_3]$ to give a metallocene anion $[Cp_2NbH_2]^-$ amenable to a substitution reaction. It has long been shown by Tebbe that $[Cp_2NbH_3]$ is a basic, rather than an acidic hydride compound.[6] In fact, it can only be deprotonated by bases as strong as BuLi. Moreover, it has been shown that alkyltin halides react with $[Cp_2TaH_3]$ even in the absence of an amine, the yield being decreased as a result of subsequent reactions of the product with the generated HCl.[7] The absence of intermediate $[Cp_2NbH_2]^-$ in the reaction of Equation 1 was further supported by the results of an attempted reaction of $[Cp_2NbH_3]$ with D_2O in the presence of NEt_3. No deuterium incorporation was observed by NMR spectroscopy after stirring the mixture overnight. Therefore, the reaction of $[Cp_2NbH_3]$ with an alkyltin halide must occur through a direct interaction of a basic Nb−H bond with the tin reagent. The most likely mechanism is similar to that proposed by Pasynskii et al. for the reaction of $[Cp_2NbH(CO)]$ with tin halides.[8] It involves coordination of the Sn−Cl bond along the M−H polar bond forming a hydride-bridged bimetallic adduct and a five-coordinated tin center. Proton abstraction and halide dissociation complete the reaction (Scheme 1). At present, it is not clear as to whether dissociation of a halide precedes (this possibility is shown in Scheme 1) or follows the proton abstraction. More detailed studies are required to elucidate this matter.



Scheme 1

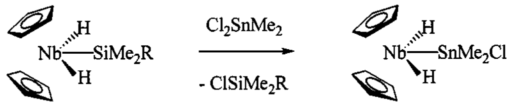
Preparation of compound **1** according to Equation 1 has apparent advantages over the reported procedures[5] since it allows for easy isolation of the product and requires only one step rather than two, starting from $[Cp_2NbH_3]$. Moreover, it provides an easy access to complexes with functionalized tin ligands. In order to carry out this reaction successfully, it is necessary to use strictly one equivalent of the tin halide, since excess X_nSnR_{4-n} effects a facile halodealkylation exchange reaction. For example, reaction of Cp_2NbH_3 with two equivalents of $ClSnMe_3$ gives a mixture of **1** and **3**. Similarly, addition of $ClSnMe_3$ to **1** results in the slow replacement of Me by Cl in **1** to give **3**, a process that could be monitored by NMR spectroscopy over a period of several days. In contrast, reaction of **1** with the more electrophilic Cl_2SnMe_2, leading to complex **3** and $ClSnMe_3$, reached completion in the course of overnight monitoring. Analogously, reaction of $[Cp_2NbH_3]$ with two equivalents of Br_2SnEt_2 furnished the dibrominated complex $Cp_2NbH_2(SnBr_2Et)$ (**7**) in high yield (Equation 2). Halodealkylation exchange reactions between transition metal tin complexes and tin halides have previously been observed in some tin-substituted molybdenocenes[9] and tungstenocenes.[10] Moreover, some silyl-substituted molybdenocene compounds have been shown to undergo intramolecular halodealkylation exchange between their coordinated silyl groups.[11] In comparison, in the non-transition metal chemistry of tin, and even more so in the case of silicon, analogous group interchange requires elevated temperatures. Apparently, it is coordination to the transition metal center that facilitates the exchange reaction, probably as a result of weakening of the Sn−C bond of the coordinated stannyl moiety. Bulychev showed that coordination of a stannyl group to a transition metal center effects rehybridization of the tin center,[9][12] in accordance with Bent's rule.[13] Thus, more tin s-orbital character contributes to bonding with the metal center and consequently more tin p-orbital character is left for bonding with the alkyl substituents. This also means that the Sn−C bonds become more polar. The increase in p-orbital character also causes lengthening of the Sn−C bonds, which should decrease steric strain in the transition state for exchange. The observation that treatment of [$Cp_2Nb(CO)(SnPh_3)$] with HCl leads to the formation of [$Cp_2Nb(CO)(SnCl_3)$][8] rather than to cleavage of the Sn−Nb bond is a further manifestation of the rehybridization effect.



(2)

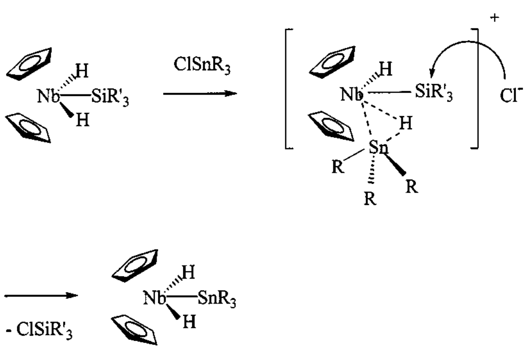
Tin-for-Silicon Exchange

We were interested in employing the hydride by tin displacement reaction for the preparation of mixed silicon/tin-substituted niobocenes of the formula [$Cp_2NbH(SiR'_3)(SnR_3)$]. No compounds of this type have hitherto been prepared. However, we found that the action of $X_{4-n}SnR_n$ on the mono(silyl) complexes [$Cp_2NbH_2(SiPhMe_2)$] and [$Cp_2NbH_2(SiClMe_2)$] led to quantitative yields of the corresponding mono(tin) compounds [$Cp_2NbH_2(SnX_{3-n}R_n)$] (Equation 3). Addition of Cl_2SnMe_2 to the bis(silyl) complex [$Cp_2NbH(SiPhMe_2)_2$] resulted in no reaction. In the latter case, the central hydride ligand is seemingly sterically too hindered by the silyl ligands to allow interaction with the tin halide. Two mechanisms can, in principle, be invoked to account for the above tin-for-silicon exchange. One implies a direct attack of the tin halide on the metal−silicon bond, while the second involves interaction of X_nSnR_{4-n} with the lateral hydride ligand as discussed above, with subsequent attack of the released halide anion X^- on the silicon substituent, as shown in Scheme 2. We favour the latter possibility, since it necessitates a less hindered transition state. The driving force for this exchange reaction seems to be the formation of a stable Si−Cl bond.



(3)

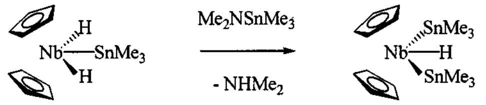
R = Ph, Cl



Scheme 2

Bis(tin)-Substituted Complexes

The bis(tin)-substituted niobocene [$Cp_2NbH(SnMe_3)_2$] (**2**) has been prepared by Green et al. by oxidative addition of $HSnMe_3$ to the olefin hydride complex [$Cp_2NbH(\eta^2\text{-}C_2H_3Ph)$].[5] Reaction of [$Cp_2NbH(SnMe_3)$]K · (18-crown-6) with $ClSnMe_3$ has also been reported to give **2**.[14] In contrast, we have found the anionic mono(tin)-substituted complex [$Cp_2NbH(SnMe_3)$]Li · (15-crown-5) (**8**) to be incapable of serving as a precursor for bis(tin) derivatives. Attempted reaction of Cl_2SnMe_2 with **8** resulted in a complex mixture of products. The potassium salt appears to have a weakly bound cation and therefore a more nucleophilic metallocene anion, whereas the lack of selectivity in the latter reaction can be explained in terms of effective competition between the metathetical reaction and the facile halodealkylation. This presumably leads to a mixture of mono- and bis(tin)-substituted complexes with variable numbers of alkyl and halogen groups on each tin atom. Also, as mentioned above, due to the facile halodealkylation at the tin center, the hydride-by-tin displacement reaction cannot be employed for the synthesis of bis(tin) derivatives starting from the mono(tin)-substituted compounds. As an alternative approach to complex **2**, we studied Lappert's amine elimination reaction.[15] This method involves interaction of a metal hydride with a tin amide $R_2NSnR'_3$ and requires elevated temperatures (ca. 80−100°C). Lappert et al. used this reaction to prepare [$Cp_2TaH_2(SnMe_3)$] from [Cp_2TaH_3] and Me_2NSnMe_3, whereas an analogous reaction with [Cp_2NbH_3] led to bis(niobocene) owing to the low thermal stability of niobocene trihydride.[5] By heating a mixture of complex **1** with Me_2NSnMe_3 at 85°C for 8 h, we obtained **2** as the main reaction product (Equation 4).

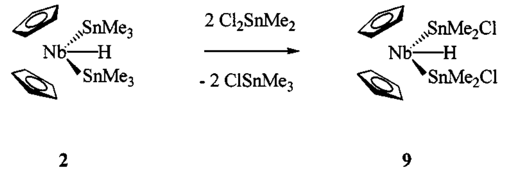


(4)

1 **2**

Complex **2** was used as a starting material for the synthesis of the functionalized bis(tin)-substituted complex [$Cp_2NbH(SnClMe_2)_2$] (**9**) by the chlorodemethylation exchange reaction. Thus, overnight stirring of a mixture of two equivalents of Cl_2SnMe_2 with one equivalent of **2** led to complex **9** in high yield (Equation 5). The product was characterized by spectroscopic methods and X-ray diffraction analysis.

As the mono(tin)-substituted niobocenes have centrally positioned tin ligands, they were considered unlikely to show any significant interligand Sn−H interactions.[3c] In contrast, the bis(tin) complex **9** is a structural analogue of the non-classical bis(silyl) complex [Cp_2NbH-



(5)

$(SiClMe_2)_2]$,[3a] and therefore might be expected to show analogous non-classical bonding between Sn and the hydride ligands. To clarify this matter, an X-ray structural investigation of **9** was undertaken. Structures of four tin-substituted niobocenes[5][8] and of one tin-substituted tantalocene[7] have previously been reported, but only one of these, namely the anionic complex $[Cp_2Nb(SnMe_3)_2]^-$, has two tin ligands bound at the metal center.[5a] Crystals of **9** suitable for X-ray analysis were grown from diethyl ether solution. The crystal structure was found to contain two independent molecules of **9** per unit cell. The molecular structure of one of these is shown in Figure 1. Selected bond lengths and angles are given in Table 1. It is noteworthy that in both independent molecules the hydride ligands could be localized from the difference map and refined to the realistic Nb−H distances of 1.76(6) and 1.80(5) Å, in spite of the presence of three heavy atoms. In a neutron diffraction study of $[Cp_2NbH(SiClMe_2)_2]$, the hydride was found at a distance of 1.813 Å from the niobium,[16] while the Nb−H bond lengths in $[Cp_2NbH_3]$, determined by accurate NMR relaxation studies, were found to fall in the range 1.78−1.80 Å.[17] However, the two molecules of **9** are different in that in one of them the hydride is symmetrically positioned in the bisecting plane of the niobocene moiety, while in the second it is shifted closer to one of the tin centers resulting in a short contact of 2.13 Å. An analogous short Sn−H contact of 2.16(4) Å found in the compound $[Cp'Mn(CO)_2HSnPh_3]$ was taken as an indication of complexation of the $H-SnR_3$ bond.[18] Apart from this, the geometries of the four tin centers in the two molecules of **9** are very similar, which rules out any speculation about Sn−H non-classical bonding in the asymmetric structure of **9**. Thus, the observed Nb−Sn σ-bond lengths lie in the range 2.8015−2.8114(6) Å, while the Sn−Cl bonds fall in the range 2.448−2.479(1) Å, but no systematic trends in these parameters are in evidence. Both the Nb−Sn and Sn−Cl bonds are somewhat shorter in the second molecule than the corresponding bonds in the first, which can be attributed to crystal packing effects. This observation suggests that the coordination environments about the tin atoms are very soft. In comparison, the Nb−Sn bond lengths in other tin derivatives of niobocene, bearing SnR_3 (R = alkyl, aryl) ligands, are found in the range 2.817−2.862(1) Å,[5][8] whereas in the trichlorotin derivative $[Cp_2Nb(CO)(SnCl_3)]$[8] a shorter Nb−Sn bond length of 2.764(1) Å is observed due to the electron-withdrawing effect of the chloro substituents. The most compelling evidence in favour of a classical description of **9** and the absence of significant Sn−H interaction is provided by the large values of 109.7(2)° and 108.87(2)° for the Sn−Nb−Sn bond angles in the two independent molecules. In the non-classical complex $[Cp_2NbH(SiClMe_2)_2]$, a noticeably smaller Si−Nb−Si bond angle of 105.57(4)° is found, which reflects the attraction of the lateral Si atoms to the central hydride.[3a] The former values are close to the Si−M−Si bond angles of 110.81(5)° and 109.90(7)° found in the classical complexes $[Cp_2NbH(SiPhMe_2)_2]$[3c] and $[Cp_2TaH(SiHMe_2)_2]$,[19] respectively.

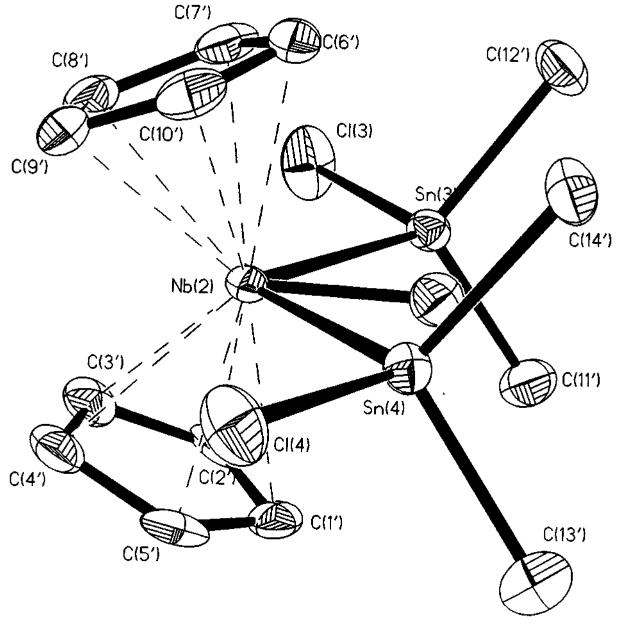


Figure 1. Molecular structure of **9**; hydrogen atoms other than hydride are omitted for the sake of clarity

Conclusions

We have shown herein that reaction of niobocene trihydride with alkyltin halides gives the products of direct displacement of hydride by tin, and thus represents an effective method for the synthesis of niobocene dihydride complexes substituted by functionalized tin ligands. Moreover, we have found that the use of an excess of the tin halide effects a halodealkylation exchange reaction at the coordinated tin center, thus giving products with a larger number of halide substituents at the tin atom. In comparison with the corresponding chemistry in uncoordinated-to-metal tin compounds, this reaction is remarkably facile. This approach has been exploited synthetically in the preparation of the bis(tin)-substituted complex $[Cp_2NbH(SnClMe_2)_2]$ (**9**) from $[Cp_2NbH(SnMe_3)_2]$. At present, it would seem that this halodealkylation exchange reaction represents the only feasible route for preparing compound **9**. Reaction of tin halides with silyl hydride derivatives of niobocene proceeds only for the mono(silyl) dihydride substituted compounds and affords the products of displacement of silicon by tin. Thus, a synthetic approach to the elusive mixed tin/silicon complexes of the formula $[Cp_2NbH(SnR_3)(SiR'_3)]$ has still to be developed. Finally, an X-ray structure determination of compound **9** did not reveal any significant non-classical Sn−H interligand interaction. The reason for this appears

Table 1. Selected bond lengths [Å] and angles [°] for **9**

lengths			
Nb(1)−Sn(1)	2.8062(5)	Nb(2)−Sn(4)	2.8015(5)
Nb(1)−Sn(2)	2.8114(6)	Nb(2)−Sn(3)	2.8072(5)
Nb(1)−H(1)	1.76(6)	Nb(2)−H(2)	1.80(5)
Sn(1)−C(11)	2.143(6)	Sn(3)−C(11′)	2.144(6)
Sn(1)−C(12)	2.156(6)	Sn(3)−C(12′)	2.151(6)
Sn(1)−Cl(1)	2.4787(14)	Sn(3)−Cl(3)	2.4475(14)
Sn(2)−C(14)	2.141(7)	Sn(4)−C(13′)	2.149(6)
Sn(2)−C(13)	2.146(7)	Sn(4)−C(14′)	2.157(5)
Sn(2)−Cl(2)	2.4781(14)	Sn(4)−Cl(4)	2.4704(13)
Sn(2)−H(1)	2.13(6)		
angles			
Sn(1)−Nb(1)−Sn(2)	109.675(17)	Sn(4)−Nb(2)−Sn(3)	108.865(17)
Sn(1)−Nb(1)−H(1)	60.5(18)	Sn(4)−Nb(2)−H(2)	54.6(15)
Sn(2)−Nb(1)−H(1)	49.1(18)	Sn(3)−Nb(2)−H(2)	54.3(15)
C(11)−Sn(1)−C(12)	106.8(3)	C(11′)−Sn(3)−C(12′)	106.9(3)
C(11)−Sn(1)−Cl(1)	96.4(2)	C(11′)−Sn(3)−Cl(3)	100.4(2)
C(12)−Sn(1)−Cl(1)	96.89(19)	C(12′)−Sn(3)−Cl(3)	97.2(2)
C(11)−Sn(1)−Nb(1)	122.5(2)	C(11′)−Sn(3)−Nb(2)	118.96(19)
C(12)−Sn(1)−Nb(1)	119.92(16)	C(12′)−Sn(3)−Nb(2)	120.45(19)
Cl(1)−Sn(1)−Nb(1)	108.49(4)	Cl(3)−Sn(3)−Nb(2)	108.77(4)
C(14)−Sn(2)−C(13)	108.1(3)	C(13′)−Sn(4)−C(14′)	105.7(3)
C(14)−Sn(2)−Cl(2)	96.8(2)	C(13′)−Sn(4)−Cl(4)	98.22(19)
C(13)−Sn(2)−Cl(2)	100.8(2)	C(14′)−Sn(4)−Cl(4)	98.65(17)
C(14)−Sn(2)−Nb(1)	121.5(2)	C(13′)−Sn(4)−Nb(2)	120.66(19)
C(13)−Sn(2)−Nb(1)	118.6(2)	C(14′)−Sn(4)−Nb(2)	116.42(18)
Cl(2)−Sn(2)−Nb(1)	106.37(4)	Cl(4)−Sn(4)−Nb(2)	113.62(4)
Cl(2)−Sn(2)−H(1)	145.0(15)		

to be the long Nb−Sn bond length, which leads to only minor overlap between the Nb−H bonding and Sn−Cl antibonding orbitals, and therefore precludes the transfer of electron density from the former to the latter.

Experimental Section

General: All manipulations were carried out using conventional Schlenk techniques. − Solvents were dried with sodium or sodium benzophenone ketyl. − NMR: Varian VXR-400 spectrometer (^{1}H: 400 MHz; ^{13}C: 100.4 MHz). − IR: Perkin-Elmer 1600 FT-IR spectrometer. − Tin halides were purchased from Merck. − [Cp_2NbH_3] was prepared by the modified procedure reported in an earlier publication.[1a] Compounds **1** and **2** have been reported previously.[5]

Preparation of $Cp_2NbH_2(SnMe_3)$ (1): 0.502 g (2.22 mmol) of [Cp_2NbH_3] and 0.442 g (2.22 mmol) of Me_3SnCl were mixed in 70 mL of diethyl ether, and then 3 mL of NEt_3 was added. The mixture was stirred overnight, then filtered, and the residue was washed with 50 mL of diethyl ether. All volatiles were then removed in vacuo from the combined filtrate and washings to leave a light-beige powder. Yield: 0.730 g (1.88 mmol, 85%). NMR data are as reported in the literature.[5b]

Preparation of Cp_2NbH_2(SnMe$_2$Cl) (3). − Method a: The preparation was carried out analogously to that of **1**, to afford **3** in 80% yield.

Method b: [$Cp_2NbH_2SnMe_3$] (0.502 g, 1.72 mmol) and Me_2SnCl_2 (0.386 g, 1.72 mmol) were mixed in 20 mL of diethyl ether, and then 2 mL of NEt_3 was added. The resulting mixture was stirred for 2 d. The solvent was then removed in vacuo and the residue was extracted with toluene. The solution was filtered and all volatiles were removed in vacuo to leave rose-pink crystals. Yield: 0.233 g (0.54 mmol, 32%).

Method c: 0.142 g (1.34 mmol) of [$Cp_2NbH_2SiMe_3$] was added to a solution of 0.098 g (0.45 mmol) of Me_2SnCl_2 in 2 mL of NEt_3 and 10 mL of diethyl ether. The resulting mixture was left overnight, then filtered, and the residue was extracted with 10 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions, to leave a pale-pink substance. Yield: 0.184 g (0.45 mmol, 100%).

Method d: 0.483 g (0.45 mmol) of [$Cp_2NbH_2SiMe_2Ph$] was added to 0.295 g (1.34 mmol) of Me_2SnCl_2 and 3 mL of NEt_3 in 40 mL of diethyl ether. A bright-red colour soon developed. The mixture was left overnight, whereupon a light-lilac solution was obtained. This solution was filtered, and the residue was extracted with 4× 40 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions to leave a lilac-coloured substance. Yield: 0.540 g. NMR spectra showed the product to be a mixture of $Cp_2NbH_2SnMe_2Cl$ and $ClSiMe_2Ph$.

Analytically pure material, prepared by Method b, was obtained by recrystallization from diethyl ether. − ^{1}H NMR ([D$_6$]benzene): δ = 4.82 (s, 10 H, Cp), 1.05 [s + d, ^2J(Sn−H) = 31.6 Hz, 6 H, CH$_3$], −4.79 [s + 2d, ^2J(Sn−H) = 254.5 and 239.2 Hz, 2 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 87.4 (s, Cp), 18.0 (s, Me). − $C_{12}H_{18}ClNbSn$ (409.34): calcd. C 35.21, H 4.43; found C 34.95, H 4.01.

Preparation of $Cp_2NbH_2(SnPh_3)$ (4): 0.335 g (1.48 mmol) of [Cp_2NbH_3] and 0.571 g (1.48 mmol) of Ph_3SnCl were mixed in 15 mL of toluene, and then 1 mL of NEt_3 was added. The resulting mixture was stirred overnight, then filtered, and the residue was washed with 15 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions to leave a white powder. Yield: 0.800 g (1.33 mmol, 90%). − IR (Nujol): $\tilde{\nu}$ = 1682 cm^{-1} (Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = 7.98 [d, J(H−H) = 7.6 Hz, 6 H, Ph], 7.32 [t, J(H−H) = 7.4 Hz, 6 H, Ph], 7.22 [t, J(H−H) = 7.4 Hz, 3 H, Ph], 4.48 (s, 10 H, Cp), −4.28 [s + d, ^2J(Sn−H) = 180.8

Hz, 2 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 137.3 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 127.4 (s, Ph), 86.8 (s, Cp). − $C_{28}H_{27}NbSn$ (575.14): calcd. C 58.47, H 4.73; found C 58.58, H 4.96.

Preparation of $Cp_2NbH_2(SnClPh_2)$ (5): 0.448 g (1.98 mmol) of [Cp_2NbH_3] and 0.681 g (1.48 mmol) of Ph_2SnCl_2 were mixed in 15 mL of diethyl ether, and then 1 mL of NEt_3 was added. The resulting mixture was stirred overnight. The supernatant solution was then decanted and the residue was extracted with 5 × 10 mL of toluene. All volatiles were removed in vacuo from the combined toluene fractions to leave a white crystalline material. Yield: 0.388 g (0.727 mmol, 37%). − IR (Nujol): $\tilde{\nu}$ = 1682 cm^{-1} (Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = 8.60 [d, J(H−H) = 6.8 Hz, 4 H, Ph], 7.32 [t, J(H−H) = 7.6 Hz, 4 H, Ph], 7.18 (t, J_{H-H} = 7.2 Hz, 2 H, Ph), 4.52 (s, 10 H, Cp), −4.18 [s + 2d, J(Sn−H) = 131 Hz and ^{2}J(Sn−H) = 125 Hz, 2 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 152.8, 135.5, 128.6, 128.3 (s, Ph), 87.7 (s, Cp). − $C_{22}H_{22}ClNbSn$ (533.49): calcd. C 49.53, H 4.16; found C 49.51, H 4.88.

Preparation of $Cp_2NbH_2(SnEt_2Br)$ (6): 3 mL of NEt_3 was added to 0.730 g (3.23 mmol) of [Cp_2NbH_3] in 40 mL of diethyl ether. Then, 1.087 g (3.23 mmol) of Et_2SnBr_2 in 10 mL of diethyl ether was added, resulting in the immediate deposition of white flakes. The mixture was stirred overnight, then filtered, and the residue was washed with 10 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions to leave a light-yellow powder. Yield: 1.148 g (2.38 mmol, 74%). − IR (Nujol): $\tilde{\nu}$ = 1682 cm^{-1} (Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = 4.57 (s, 10 H, Cp), 1.56 [t, ^{3}J(H−H) = 7.8 Hz, 6 H, CH_3], 1.35 (m, 4 H, CH_2), −4.61 [s + d, ^{2}J(Sn−H) = 247.7 Hz, 2 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 87.2 (s, Cp), 17.3 (s, CH_3), 11.8 (s, CH_2). − $C_{14}H_{22}BrNbSn$ (481.85): calcd. C 34.90, H 4.60; found C 34.54, H 4.37.

Preparation of $Cp_2NbH_2(SnEtBr_2)$ (7): 4 mL of NEt_3 was added to 0.292 g (0.606 mmol) of $Cp_2NbH_2(SnEt_2Br)$ in 25 mL of diethyl ether. Then, 0.204 g (0.606 mmol) of Et_2SnBr_2 was added, resulting in the immediate deposition of white flakes. The mixture was stirred overnight, then filtered, and the residue was washed with 25 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions to leave a light-yellow powder, which was recrystallized from cold diethyl ether. NMR spectra revealed the product to be **7** contaminated by a minor impurity; complete removal of this impurity could not be achieved. Yield: 0.210 g. − IR (Nujol): $\tilde{\nu}$ = 1728.2 cm^{-1} (Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = 4.67 (s, 10 H, Cp), 1.52 [t, ^{3}J(H−H) = 7.8 Hz, 6 H, CH_3], 1.38 (m, 4 H, CH_2), −4.60 [s + d, ^{2}J(Sn−H) = 247.4 Hz, 2 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 87.33 (s, Cp), 17.46 (s, CH_3), 11.74 (s, CH_2).

Preparation of $Cp_2NbH(SnMe_3)_2$ (2). − Method a: Preparation from [$Cp_2NbH(C_2H_3Ph)$] in 82% yield according to the literature method.[5b]

Method b: A mixture of 0.381 g (0.98 mmol) of [$Cp_2NbH_2(SnMe_3)$] and 0.204 g (0.98 mmol) of Me_3SnNMe_2 in 10 mL of toluene was heated at 85°C for 8 h. All volatiles were then removed in vacuo and the residue was extracted with 20 mL of diethyl ether. Removal of the solvent left 0.250 g (0.45 mmol, 46%) of a brown substance. The obtained product was found to be contaminated by minor amounts of impurities. NMR data are as reported in the literature.[5b]

Preparation of $Cp_2NbH(SnClMe_2)_2$ (8): 0.652 g (2.97 mmol) of Me_2SnCl_2 was added to a suspension of 0.819 g (1.48 mmol) of [$Cp_2NbH(SnMe_3)_2$] in 50 mL of diethyl ether and the resulting mixture was stirred overnight. The supernatant solution was then decanted and the residue was extracted with 30 mL of diethyl ether. All volatiles were removed in vacuo from the combined fractions to leave 0.777 g of a white crystalline substance. This material was washed with 15 mL of petroleum ether to ensure complete removal of Me_3SnCl and then recrystallized from diethyl ether. Yield: 0.547 g (0.92 mmol, 62%). − IR (Nujol): $\tilde{\nu}$ = 1664 cm^{-1} (Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = 4.58 [s + d, J(Sn−H) = 4.5 Hz, 10 H, Cp], 0.52 [s + d, ^{2}J(Sn−H) = 35.8 Hz, 12 H, Me], −4.78 [s + d, ^{2}J(Sn−H) = 280.0 Hz, 1 H, Nb−H]. − ^{13}C NMR ([D$_6$]benzene): δ = 88.0 (s, Cp), 5.2 (s, Me). − $C_{14}H_{23}Cl_2NbSn_2$ (592.77): calcd. C 28.38, H 3.91; found C 28.01, H 3.77.

Crystal Structure Determination of 9: Colourless crystals of **9** were grown from diethyl ether solution. A crystal of **9** of dimensions 0.22 × 0.16 × 0.12 mm was covered with oil and mounted at 150(2) K on a Siemens three-circle diffractometer equipped with an area CCD detector (SMART system). Crystal data: M_r = 592.77; monoclinic, space group $P2(1)/n$; a = 17.0123(3) Å, b = 8.31860(10) Å, c = 27.76540(10), β = 96.82°, Z = 8, V = 3901.48(8) Å^3, $d_{calcd.}$ = 2.018 gcm^{-3}. Data collection: 2θ range from 1.34° to 26.50°, *hkl* range −19 to 21, −10 to 8, −34 to 31; 25550 measured reflections, of which 8085 were considered as unique [R(int) = 0.0527]; analytical absorbtion correction based on Ψ scans (μ = 3.380 mm^{-1}, T_{max} = 0.6872, T_{min} = 0.5235). The structure amplitudes for the 8085 independent reflections were obtained after the usual Lorentz and polarization corrections. The structure was solved by direct methods[20] and refined by full-matrix least-squares procedures[21] against F^2. Only the reflections with $F_o^2 > 2\sigma F_o^2$ were used in the refinements (6371). Hydrogen atoms were found from the difference map and were refined isotropically. In the final cycles of the refinement, all non-hydrogen atoms were refined with anisotropic temperature parameters. $R1$ = 0.0351 and $wR2$ = 0.0553 (only observed reflections), and $R1$ = 0.0574 and $wR2$ = 0.0598 (all data); 528 parameters, *GooF* = 1.121. The largest peak in the final difference Fourier map had an electron density of 0.704 e·Å^{-3}, while the lowest hole had a value of −0.764 e·Å^{-3}. The location and magnitude of the residual electron density was of no chemical significance. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository number (CCDC-105593), the names of the authors, and the full journal citation.

Acknowledgments

Support of this research by the Russian Fund for Basic Research is gratefully acknowledged.

---

[1] [1a] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Organometallics* **1994**, *13*, 3127. − [1b] G. I. Nikonov, L. G. Kuzmina, P. Mountford, D. A. Lemenovskii, *Organometallics* **1995**, *14*, 3588. − [1c] G. I. Nikonov, L. G. Kuzmina, Yu. K. Grishin, D. A. Lemenovskii, N. B. Kazennova, *J. Organomet. Chem.* **1997**, *547*, 183. − [1d] G. I. Nikonov, K. Harms, J. Lorberth, D. A. Lemenovskii, *Inorg. Chem.* **1995**, *34*, 2461. − [1e] G. I. Nikonov, A. J. Blake, J. Lorberth, D. A. Lemenovskii, S. Wocadlo, *J. Organomet. Chem.* **1997**, *547*, 235. − [1f] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Polyhedron* **1996**, *15*, 1565. − [1g] G. I. Nikonov, L. G. Kuzmina, J. A. K. Howard, *Organometallics* **1997**, *16*, 3723.

[2] G. I. Nikonov, E. V. Avtomonov, W. Massa, *Chem. Ber.* **1997**, *130*, 1629.

[3] [3a] G. I. Nikonov, L. G. Kuzmina, D. A. Lemenovskii, V. V. Kotov, *J. Am. Chem. Soc.* **1995**, *117*, 10133. − [3b] G. I. Nikonov, L. G. Kuzmina, D. A. Lemenovskii, V. V. Kotov, *J. Am. Chem. Soc.* **1996**, *118*, 6333 [corr.]. − [3c] G. I. Nikonov, S. F.

Vyboishchikov, L. G. Kuzmina, D. A. Lemenovskii, J. A. K. Howard, *Chem. Eur. J.*, accepted.

[4] T. M. Arkhireeva, B. M. Bulychev, A. N. Protsky, G . L. Soloveichik, V. K. Bel′sky, *J. Organomet. Chem*. **1986**, *317*, 33.

[5] [5a] M. L. H. Green, A. K. Hughes, P. Mountford, *J. Chem. Soc., Dalton Trans.* **1991**, 1699. – [5b] M. L. H. Green, A. K. Hughes, P. Mountford, *J. Chem. Soc., Dalton Trans.* **1991**, 1407.

[6] F. N. Tebbe, *J. Am. Chem. Soc.* **1973**, *96*, 5412.

[7] T. M. Arkhireeva, B. M. Bulychev, A. N. Protsky, G. L. Soloveichik, V. K. Bel′sky, *Koord. Khimiia* **1987**, *13*, 986.

[8] V. V. Skripkin, O. G. Volkov, A. A. Pasynskii, A. S. Antyshkina, L. M. Dikareva, V. N. Ostikova, M. A. Porai-Koshits, S. L. Davydova, S. G. Sakharov, *J. Organomet.Chem*. **1984**, *263*, 345.

[9] A. N. Protsky, B. M. Bulychev, G. L. Soloveichik, V. K. Bel′sky, *Inorg. Chim. Acta* **1986**, *115*, 121.

[10] M. L. H. Green, A. K. J. Hughes, *J. Organomet. Chem*. **1996**, *506*, 221.

[11] [11a] D. C. Pestana, T. S. Koloski, D. H. Berry, *Organometallics* **1994**, *13*, 4173. – [11b] L. K. Figge, P. J. Carroll, D.H. Berry, *Organometallics* **1996**, *15*, 209.

[12] V. K. Bel′sky, A. N. Protsky, B. M. Bulychev, G. L. Soloveichik, *Doklady AN SSSR, Chem.* **1986**, *287*, 857; *Chem. Abstr.* **1987**, *106*, 50365a.

[13] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

[14] A. K. Hughes, Ph. D. Thesis, Oxford University, **1990**.

[15] D. H. Harris, S. A. Keppie, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1973**, 1653.

[16] M. Leech, J. A. K. Howard, L. G. Kuzmina, G. I. Nikonov, manuscript in preparation.

[17] V. I. Bakhmutov, E. V. Vorontsov, G. I. Nikonov, D. A. Lemenovskii, *Inorg. Chem.* **1998**, *37*, 279.

[18] U. Schubert, E. Kunz, B. Harkers, J. Willnecker, J. Meyer, *J. Am. Chem. Soc.* **1989**, *111*, 2572.

[19] Q. Jiang, P. J. Carroll, D. H. Berry, *Organometallics* **1991**, *10*, 3648.

[20] G. M. Sheldrick, “SHELXS-86, Program for Crystal Structure Solution”, *Acta Crystallogr.* **1990**, *146*, 467.

[21] G. M. Sheldrick, *SHELXTL-96, Program for Crystal Structure Refinement*, Universität Göttingen, **1996**.

Received November 3, 1998
[I98377]