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Communications

Bis(germyl)-Substituted Niobocenes

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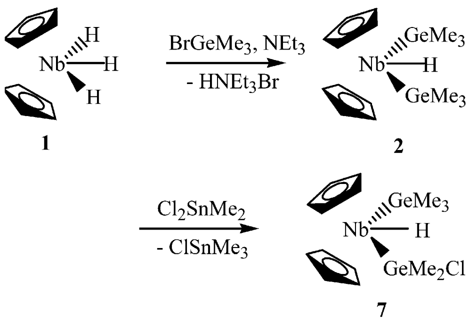
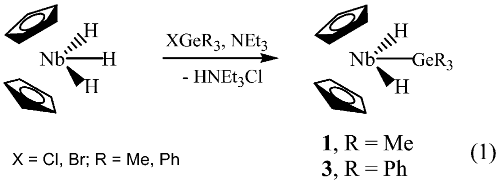
Summary: Reactions of niobocene hydrides with halogermanes present a new effective method for the synthesis of mono(germyl)- and bis(germyl)niobocenes. Chlorodemethylation of $Cp_2NbH(GeMe_3)_2$ *under the action of* Cl_2SnMe_2 *is very facile and leads to the first asymmetric niobocene having two different germanium centers.*

We have recently reported that mono(halosilyl)- and bis(halosilyl)niobocene hydrides have nonclassical interligand hypervalent interactions (IHI) between the hydride and halosilyl ligands.[1] Corresponding tin-substituted complexes lack this sort of interligand interaction because the M−Sn bonds are too long to allow any significant overlap between the (Sn−Cl)* antibonding orbital and the bonding orbital of the short M−H bond.[2] Taking into account the similarity of covalent radii of silicon and germanium, it is of interest to investigate the possible occurrence of IHI in the mono- and bis(halogermyl) systems.

Scheme 1



The mono(germyl)-substituted niobocenes $Cp'_2NbH_2(GeCl_mR_n)$ ($Cp' = C_5H_4SiMe_3$)[3] have been recently prepared by oxidative addition of H_xGeR_y ($x = 1, 2; x + y = 4$, R = alkyl) and $HGeCl(C_6H_{13})_2$ to $[Cp'_2NbH]$, generated in situ by thermolysis of Cp'_2NbH_3. However, mixed hydridohalogermanes $H_xGeX_yR_z$ (X = Cl, Br), needed for the study of IHI, are much less accessible than the simple organogermanes H_zGeR_x and halogermanes X_yGeR_x. We have been developing an alternative approach to main-group-element-substituted complexes based on direct interaction of basic metal−hydride bonds with Lewis acidic E−X bonds (E = group 4 or 5 element, X = halogens and other good leaving groups). In particular, facile preparation of mono(stannyl)[2] and mono(plumbyl)[4] dihydrides $Cp_2NbH_2(EMe_3)$ (E = Sn, Pb) was achieved. Here we report an extension of this approach to the synthesis of new mono(germyl)- and the first bis(germyl)-substituted niobocenes, including a compound bearing two different germyl groups, one of which has an interligand hypervalent interaction[1] with the central hydride.



1, R = Me
3, R = Ph (1)

Trimethylgermanes Me_3GeX (X = Cl, Br) readily react with Cp_2NbH_3 in the presence of NEt_3 as the HCl sponge, affording the mono(germyl) derivative $Cp_2NbH_2(GeMe_3)$ (**1**) in moderate to good yields (eq 1). Using an excess of Me_3GeCl does not lead to further reactions, whereas with 2 equiv of Me_3GeBr the first bis(germyl)niobocene hydride, $Cp_2NbH(GeMe_3)_2$ (**2**), was obtained (Scheme 1). Analogously, **2** is formed in high yield when **1** is treated with 1 equiv of Me_3GeBr in the presence of NEt_3. Using excess Me_3GeBr does not cause a bromodemethylation reaction and formation of bromogermyl complexes $Cp_2NbH_2(GeMe_2Br)$ or $Cp_2NbH(GeMe_2Br)_2$,

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a type of reactivity observed in the corresponding tin chemistry. The mono(germyl) complex $Cp_2NbH_2(GePh_3)$ (**3**) was obtained in 70% yield by a similar reaction of Ph_3GeX with Cp_2NbH_3. Compound **3** does not react with an excess of Me_3GeBr, most likely for steric reasons. The complexes **1**−**3** are air- and light-sensitive, dark-colored (green, blue, or brown) substances.[5]

With the aim of synthesizing chlorogermyl derivatives, the interaction of Cp_2NbH_3 with Me_2GeCl_2 was studied. In contrast to the easy preparation of $Cp_2NbH_2(SnClMe_2)$,[2] this reaction results in a mixture and low yields of the germyl complexes. The main product was inevitably a dark material of unknown composition, insoluble in nonpolar solvent. When strictly 1 equiv of Me_2GeCl_2 is used, the soluble part consists of an equimolar mixture of $Cp_2NbH(GeClMe_2)_2$ (**4**) and $Cp_2NbH_2(GeClMe_2)$ (**5**); the latter compound is present in the form of two isomers, one with the germyl group in the central position (**5a**) and the other one with a lateral germyl (**5b**). We have previously argued that formation of the lateral isomer, disfavored by steric factors, manifests the presence of stabilizing interligand hypervalent interactions (IHI) between the hydride and main-group-element substituent.[1c] To elucidate whether **5b** is a kinetic or thermodynamic product, thermolysis of a C_6D_6 solution of the mixture of **5a** and **5b** was monitored by ^1H NMR spectroscopy. The initial ratio **5a**:**5b** = 1:1 does not change after heating for 90 min at 50 °C, but after 2 h at 100 °C both of the the monogermyl complexes disappear and signals due to the bis(germyl) species **4** grow, strongly resembling chemistry observed for silicon analogues.[1c] Therefore, the formation of **5b** suggests that an interaction between the hydride and chlorogermyl group is possible (vide infra).

Overnight reaction of **2** with Me_2SnCl_2 in ether in an exact 1:1 stoichiometry gives a mixture of **2** and the new product **6**, having nonequivalent germyl groups in the ^1H NMR spectrum. A crystal of **6** suitable for X-ray study was obtained by cooling the mother liquor to −16 °C. X-ray diffraction study[6] revealed that **6** is an unusual adduct between the asymmetric bis(germyl) hydride derivative $Cp_2Nb(GeClMe_2)(H)(GeMe_3)$ (**7**) and Me_2SnCl_2 (Figure 1). Complex **6** is unstable in solution, cleanly transforming into the symmetrical compound $Cp_2Nb(GeClMe_2)_2(H)$, characterized by NMR spectra.[7]

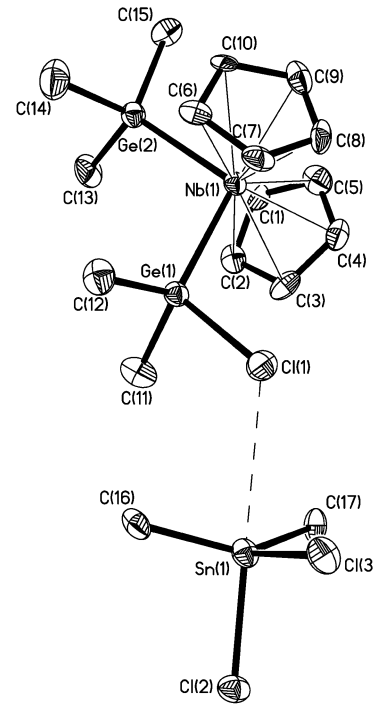

Figure 1. Molecular structure of adduct **6**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

	Bond Lengths		
Nb(1)−Ge(1)	2.608(1)	Ge(1)−C(12)	1.96(1)
Nb(1)−Ge(2)	2.702(1)	Ge(1)−C(11)	1.96(1)
Sn(1)−C(16)	2.081(9)	Ge(1)−Cl(1)	2.358(3)
Sn(1)−C(17)	2.109(9)	Ge(2)−C(14)	1.95(1)
Sn(1)−Cl(3)	2.364(3)	Ge(2)−C(13)	1.97(1)
Sn(1)−Cl(2)	2.400(3)	Ge(2)−C(15)	2.01(1)
	Bond Angles		
Ge(1)−Nb(1)−Ge(2)	108.31(4)	C(12)−Ge(1)−C(11)	104.8(5)
C(12)−Ge(1)−Nb(1)	118.7(3)	C(12)−Ge(1)−Cl(1)	97.8(3)
C(11)−Ge(1)−Nb(1)	120.2(3)	C(11)−Ge(1)−Cl(1)	97.9(4)
Cl(1)−Ge(1)−Nb(1)	113.32(8)	C(14)−Ge(2)−C(13)	103.4(5)
C(14)−Ge(2)−Nb(1)	113.1(4)	C(14)−Ge(2)−C(15)	104.9(5)
C(13)−Ge(2)−Nb(1)	114.7(4)	C(13)−Ge(2)−C(15)	105.4(5)
C(15)−Ge(2)−Nb(1)	114.3(3)	C(16)−Sn(1)−Cl(2)	101.6(3)
C(16)−Sn(1)−C(17)	140.1(4)	C(17)−Sn(1)−Cl(2)	101.6(3)
C(16)−Sn(1)−Cl(3)	101.7(3)	Cl(3)−Sn(1)−Cl(2)	97.06(9)
C(17)−Sn(1)−Cl(3)	107.1(3)		

It also chlorinates **2** in solutions, most likely via dissociation into tin-free $Cp_2Nb(GeClMe_2)(H)(GeMe_3)$ (**7**) so that reaction of **2** with Me_2SnCl_2 (1:1) after 24 h affords **7** in 69% isolated yield (Scheme 1). Complex **7** is the first well-defined example of a group 5 trisubstituted metallocene having three different substituents in the metallocene bisectral plane. The ^1H NMR spectrum of **7** shows signals due to the Cp ring and hydride at 4.57 and −3.55 ppm, respectively. Two nonequivalent germyl ligands give rise to singlets at 0.94 ppm (integrated as 6) and 0.33 (integrated as 9) for the $GeClMe_2$ and $GeMe_3$ groups, respectively.

The molecular structure of **6** is presented in Figure 1, and selected bond lengths and angles are listed in Table 1. A relatively long contact of 3.310 Å between the germanium-bound chlorine Cl(1) and the tin atom was found, signifying a weak intermolecular donor−acceptor interaction. This results in a distorted TBP

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(5) Surprisingly, these colored compounds show pure NMR spectra and correct analyses. Moreover, different colors for the same compound obtained from similar preparations can be observed. It appears, therefore, that these dark colors are not intrinsic but, rather, are due to a small amount of highly colored impurities, apparently caused by light-induced decomposition. Very pure recrystallized materials are almost colorless.

(6) X-ray analysis of **6**: $C_{17}H_{32}Cl_3Ge_2NbSn$, $M_r = 699.56$, monoclinic, space group $C2/c$, $a = 28.763(4)$ Å, $b = 8.217(1)$ Å, $c = 23.765(3)$ Å, $\beta = 119.357(6)°$, $V = 4895.8(11)$ Å^3, $Z = 8$, $F(000) = 2720$, $\mu = 4.224$ mm^{-1} (Mo Kα, $\lambda = 0.710\ 73$ Å), $D_c = 1.898$ g cm^{-3}. R1 = 0.0685, wR2 = 0.1556 for 3009 reflections with $I > 2\sigma(I)$ and 224 parameters. GOF = 0.952, residuals $\Delta\rho_{min}$, $\Delta\rho_{max} = -1.941$, 4.035 e Å^{-3} (near Sn atom). A selected crystal of dimensions 0.40 × 0.20 × 0.04 mm was mounted on the top of a glass fiber using perfluoropolyether oil and cooled to 110 K. A total of 14 256 reflections ($1.62 < \theta < 27.00°$) were collected on a Bruker SMART CCD diffractometer (ω scan, 0.3°/frame), yielding 5297 unique data ($R_{int} = 0.1216$). The structure was solved by direct methods and refined by full-matrix least squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using SHELXTL software. All H atoms were placed in calculated positions and refined using a riding model. The hydride atom was not revealed.

(7) The preparation, characterization, and reactivity of $Cp_2Nb(GeClMe_2)_2(H)$ will be reported in a follow-up paper.

geometry around the tin atom, characterized by two different Sn−Cl bond lengths and by small bond angles between the apical chlorine Cl(2) and equatorial groups (Cl(2)−Sn−Cl(3) bond angle of 97.06(9)° and Cl(2)−Sn−C(17) and Cl(2)−Sn−C(16) both equal to 101.6(3)°). The chlorine atom Cl(2) lies trans to the germanium-bound chlorine Cl(1) and has a longer (2.400(3) Å) Sn−Cl(2) bond than does the chlorine Cl(3) (2.364(3) Å) resting in the distorted equatorial plane. Apart from this, the structure of **6** is similar to those of the lateral monosilyl complex $Cp_2Nb(SiClMe_2)H_2$ and bis(silyl) complex $Cp_2Nb(SiClMe_2)_2H$, both having M−H···Si−Cl interligand hypervalent interactions (IHI),[1c] provoking the question whether an analogous interaction is possible for the chlorogermyl ligand. As is typical for a compound with IHI, the chlorine atom Cl(1) lies in the niobocene bisectral plane trans to the hydride, making an overlap between the Ge−Cl(1) antibonding orbital and the Nb−H bonding orbital possible. The $Nb-GeMe_2Cl$ bond (2.608(1) Å) is shorter than the $Nb-GeMe_3$ bond (2.702(1) Å), which can be due to the cooperative effect of Bent's rule[8] and IHI.[1c] Accordingly, the Ge−Cl bond of 2.358(3) Å is very long, compared to those of other L_nM-GeR_2Cl derivatives[9] (2.215−2.270(3) Å, R = alkyl, aryl), and is comparable in length to the Ge−Cl bond of $Cp_2W(SiMe_3)(GeMe_2Cl)$ (2.3541(4) Å), which is already elongated due to the conjugation of the (Ge−Cl)* antibonding orbital with the tungsten lone pair.[10] Short M−E and long E−Cl bonds are characteristic for IHI.[1c] Because the bis(silyl)niobocenes $Cp_2NbH(SiMe_2X)_2$ having IHIs of *both the silyls* with the central hydride exhibit diminished Si−Nb−Si bond angles of 105° compared to classical bis(silyl)niobocenes (about 110°),[1c] the average value of 107.5° is a good estimate for the angle between the lateral ligands in $Cp_2Nb(E'R_3)H(ER_2Cl)$, in which there is the IHI between the central hydride and *only one lateral group* ER_2Cl. The Ge(1)−Nb-Ge(2) bond angle of 108.31(4)° in **6** is close to this value, which suggests that the strength of the Nb−H···Ge−Cl interaction is comparable with the strength of the IHI Nb−H···Si−Cl.

Presumably, coordination of Cl_2SnMe_2 to the $GeClMe_2$ group of **6**, although weak, increases to some extent the electron deficiency of the germanium center, thus making it more prone to interaction with the hydride. The question, whether significant IHI between germyl and hydride ligands is possible in the absence of an external Lewis acid, is under current investigation.

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Supporting Information Available: Text giving experimental details and tables giving crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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