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# Triple bonds of niobium with silicon, germanium and tin: the tetrylidyne complexes $[(\kappa^3\text{-tmpts})(\text{CO})_2\text{Nb}\equiv\text{E}-\text{R}]$ (E = Si, Ge, Sn; tmpts = $\text{MeSi}(\text{CH}_2\text{PMe}_2)_3$ ; R = aryl) $^\dagger$

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A systematic, efficient approach to first complexes containing a triple bond between niobium and the elements silicon, germanium or tin is reported. The approach involves a metathetical exchange of the niobium-centered nucleophile  $(\text{NMe}_4)[\text{Nb}(\text{CO})_4(\kappa^2\text{-tmpts})]$  (**1**) (tmpts =  $\text{MeSi}(\text{CH}_2\text{PMe}_2)_3$ ) with a suitable organotetrel(ii)halide. Compound **1** was obtained from  $(\text{NMe}_4)[\text{Nb}(\text{CO})_6]$  and the triphosphane tmpts by photodecarbonylation. Reaction of **1** with the disilene  $E\text{-Tbb}(\text{Br})\text{Si}=\text{Si}(\text{Br})\text{Tbb}$  in the presence of 4-dimethylaminopyridine afforded selectively the red-brown silylidyne complex  $[(\kappa^3\text{-tmpts})(\text{CO})_2\text{Nb}\equiv\text{Si-Tbb}]$  (**2-Si**, Tbb = 4-*tert*-butyl-2,6-bis(bis(trimethylsilyl)methyl)phenyl). Similarly, treatment of **1** with  $\text{E}(\text{Ar}^{\text{Mes}})\text{Cl}$  (E = Ge, Sn;  $\text{Ar}^{\text{Mes}}$  = 2,6-mesitylphenyl) afforded after elimination of  $(\text{NMe}_4)\text{Cl}$  and two CO ligands the deep magenta colored germylidyne complex  $[(\kappa^3\text{-tmpts})(\text{CO})_2\text{Nb}\equiv\text{Ge-Ar}^{\text{Mes}}]$  (**3-Ge**), and the deep violet, light-sensitive stannylidyne complex  $[(\kappa^3\text{-tmpts})(\text{CO})_2\text{Nb}\equiv\text{Sn-Ar}^{\text{Mes}}]$  (**3-Sn**), respectively. Formation of **3-Sn** proceeds via the niobiastannylene  $[(\kappa^3\text{-tmpts})(\text{CO})_3\text{Nb-SnAr}^{\text{Mes}}]$  (**4-Sn**), which was detected by IR and NMR spectroscopy. The niobium tetrylidyne complexes **2-Si**, **3-Ge** and **3-Sn** were fully characterized and their solid-state structures determined by single-crystal X-ray diffraction studies. All complexes feature an almost linear tetrel coordination and the shortest Nb–E bond lengths ( $d(\text{Nb-Si}) = 232.7(2)$  pm;  $d(\text{Nb-Ge}) = 235.79(4)$  pm;  $d(\text{Nb-Sn}) = 253.3(1)$  pm) reported to date. Reaction of **3-Ge** with a large excess of  $\text{H}_2\text{O}$  afforded upon cleavage of the Nb–Ge triple bond the hydridogermanediol  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{H}(\text{OH})_2$ . Photodecarbonylation of  $[\text{CpNb}(\text{CO})_4]$  (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) in the presence of  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$  afforded the red-orange chlorogermylidene complex  $[\text{Cp}(\text{CO})_3\text{Nb}=\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}]$  (**5-Ge**). The molecular structure of **5-Ge** features an upright conformation of the germylidene ligand, a trigonal-planar coordinated Ge atom, and a Nb–Ge double bond length of 251.78(6) pm, which lies in-between the Nb–Ge triple bond length of **3-Ge** (235.79(4) pm) and a Nb–Ge single bond length (267.3 pm). Cyclic voltammetric studies of **2-Si**, **3-Ge**, and **3-Sn** reveal several electron-transfer steps. One-electron oxidation and reduction of the germylidyne complex of **3-Ge** in THF are electrochemically reversible suggesting that both the radical cation and radical anion of **3-Ge** are accessible species in solution.

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## Introduction

Complexes of the general formula  $[\text{L}_n\text{M}\equiv\text{E-R}]$  (M = d-block metal; E = Si–Pb; R = singly bonded group (e.g. alkyl, aryl);  $\text{L}_n$  = ligand sphere) featuring a triple bond between a d-block metal and the tetrels Si/Ge/Sn/Pb are an intriguing class of

compounds with an auspicious synthetic potential originating from the highly reactive, polar  $\text{M}\equiv\text{E}$  bond.<sup>1–4</sup> Isolation of these compounds is very challenging and requires specific stereo-electronic properties of the metal fragment  $\text{L}_n\text{M}$  as well as a steric protection of the electrophilic tetrel center by a tailor-made, bulky substituent R to circumvent a head-to-tail cyclo-dimerisation or unintentional intra- or intermolecular  $\sigma$ -bond activations destroying the  $\text{M}\equiv\text{E-R}$  functionality. Whereas earlier work concentrated exclusively on group 6 metals, recent studies have shown that also group 7,<sup>2l,3d,4d</sup> group 8 (ref. 1c and 5) and even group 10 metals<sup>6</sup> can be incorporated into triple bonding with the tetrels Si–Pb. Extension of this chemistry to the group 5 elements V–Ta seemed attractive to investigate whether the lower electronegativity and larger metallic radii of these elements compared to Cr–W would have an effect on the

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$^\dagger$  Electronic supplementary information (ESI) available: Syntheses and analytical data of **1**, **2-Si**, **3-Ge**, **3-Sn** and **5-Ge**, illustrations of the IR and heteronuclear magnetic resonance spectra of **1**, **2-Si**, **3-Ge**, **3-Sn** and **5-Ge**, details of the cyclic voltammetric studies of **2-Si**, **3-Ge** and **3-Sn**, and crystal structure determination of **2-Si**, **3-Ge** (THF), **3-Sn** (toluene) and **5-Ge**. CCDC 1553387–1553389 and 1555671. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc02708g

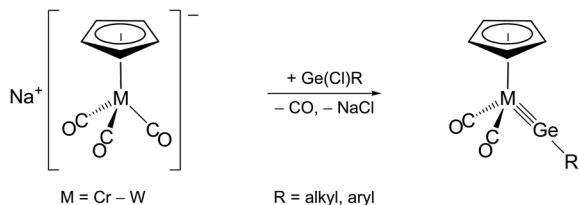
$M\equiv E$  functionality. Group 5 metal complexes featuring a triple bond to the heavier tetrrels ( $E = \text{Si-Pb}$ ) are presently not known, and even compounds with a  $M=E$  double bond are very scarce and poorly characterized illustrating the challenge to make such compounds.<sup>7</sup> We decided to address this issue, and present herein a systematic, efficient approach to the first complexes containing  $\text{Nb}\equiv E$  ( $E = \text{Si-Sn}$ ) triple bonds.

## Results and discussion

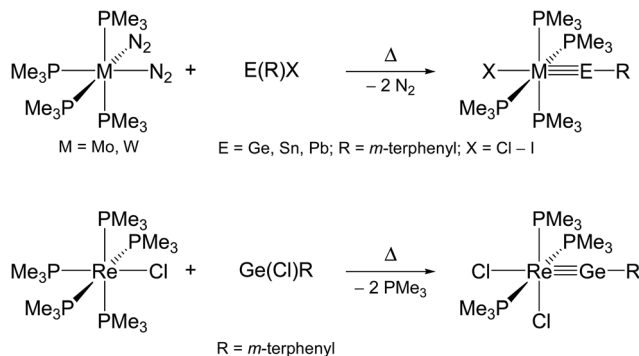
Two methods have been employed so far for the formation of transition metal-tetrel ( $\text{Si-Pb}$ ) triple bonds. The first method, abbreviated as the “salt elimination method”, involves a substitution reaction of a suitable anionic 18 VE metal complex with an organotetrel(II) halide, as exemplified by the synthesis of Cp-substituted group 6 metal tetrylidyne complexes (Scheme 1).<sup>2a,2b,2i,2j,2m</sup>

The second method, commonly termed “ $\text{N}_2/\text{PMe}_3$  elimination method”, takes advantage of the exchange of labile ligands (mostly  $\text{N}_2$  or  $\text{PMe}_3$ ) in neutral 18 VE metal complexes by suitable organotetrel(II) halides. This approach may afford directly neutral ylidyne complexes, as demonstrated by the syntheses of phosphane-substituted group 6 and 7 metal tetrylidyne complexes (Scheme 2).<sup>2f,2g,2l,3a,4a,4b</sup>

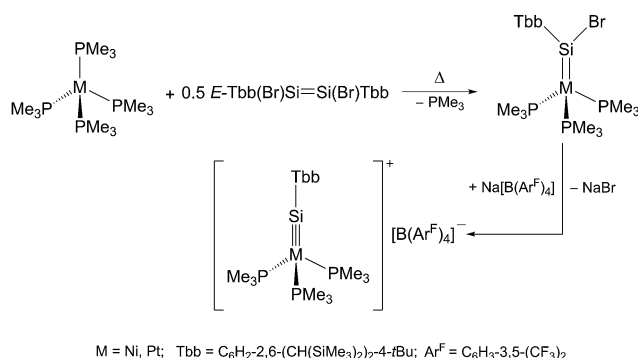
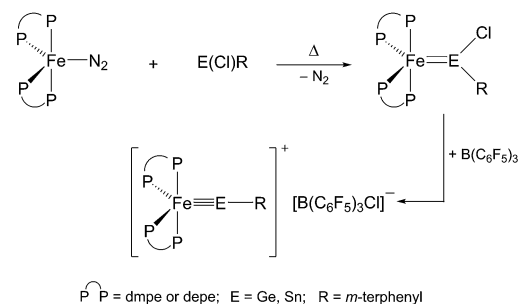
Alternatively, haloylidyne complexes are initially obtained by this method, which are subsequently converted to cationic ylidyne complexes by halide abstraction. Examples demonstrating this reaction path include the preparation of group 8 and 10 metal tetrylidyne complexes (Scheme 3).<sup>5,6</sup>



Scheme 1 Preparation of half-sandwich group 6 metal germlylidyne complexes by the salt elimination method.



Scheme 2 Preparation of neutral group 6 and 7 metal tetrylidyne complexes by the  $\text{N}_2/\text{PMe}_3$  elimination method.



Scheme 3 Preparation of group 8 and 10 metal tetrylidyne complexes via haloylidyne complexes using the  $\text{N}_2/\text{PMe}_3$  elimination method.

We decided to apply the first method, given the availability of anionic niobium carbonyl complexes.<sup>8</sup> At first, the homoleptic carbonyl niobate  $[\text{Nb}(\text{CO})_6]^-$  was chosen. For this purpose the canary yellow salts  $(\text{NR}_4)[\text{Nb}(\text{CO})_6]$  ( $\text{R} = \text{Me, Et}$ ) were prepared, following the method developed by J. E. Ellis *et al.*<sup>9</sup> However, these compounds proved to be unreactive towards the *m*-terphenyltetrel(II)halides  $\text{E}(\text{Ar}^{\text{Mes}})\text{Cl}$  ( $\text{E} = \text{Ge, Sn}; \text{Ar}^{\text{Mes}} = 2,6\text{-mesitylphenyl}; \text{mesityl (Mes)} = 2,4,6\text{-trimethylphenyl}$ ).<sup>10</sup> For example, IR monitoring of the reaction of  $(\text{NEt}_4)[\text{Nb}(\text{CO})_6]$  with  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$  in refluxing toluene did not provide any evidence for a conversion of the niobate even after prolonged heating, probably due to the poor nucleophilicity of  $[\text{Nb}(\text{CO})_6]^-$ . Therefore, as next we turned our attention to niobates containing ligands with a higher  $\sigma$ -donor/ $\pi$ -acceptor ratio than CO, such as trialkyl- or triarylphosphanes. Various carbonyl(phosphane) niobates of the general formula  $[\text{Nb}(\text{CO})_4\text{L}_2]^-$  ( $\text{L}_2 =$  bidentate di- or oligo-arylphosphane ligand) have been accessed from  $[\text{Nb}(\text{CO})_6]^-$  upon photolytic CO substitution.<sup>11</sup> In order to increase the electron density at the metal centre, we decided to use the highly basic, albeit, very oxygen-sensitive, tripodal alkylphosphane  $\text{MeSi}(\text{CH}_2\text{PMe}_2)_3$  (tmps).<sup>12</sup>

Photolysis of  $(\text{NMe}_4)[\text{Nb}(\text{CO})_6]$  was carried out in the presence of one equivalent of tmps in THF at room temperature. A high-power blue light LED ( $\lambda = 465 \text{ nm}$ ) was used instead of a high-pressure mercury UV-lamp. The use of a nearly monochromatic source with an exciting wavelength close to the longest-wavelength absorption maximum of  $[\text{Nb}(\text{CO})_6]^-$  ( $\lambda_{\text{max}} = 440 \text{ nm}$  in  $\text{CH}_2\text{Cl}_2$ )<sup>13</sup> was conceived to be advantageous preventing the formation of insoluble brown decomposition

products formed during the photolysis using a high-pressure mercury-lamp.<sup>11a</sup>

In fact, IR-monitoring of the reaction revealed a slow, but very selective conversion into the tetracarbonyl niobate  $[\text{Nb}(\text{CO})_4(\kappa^2\text{-tmps})]^-$  proceeding *via* the pentacarbonyl intermediate  $[\text{Nb}(\text{CO})_5(\kappa^1\text{-tmps})]^-$  ( $\nu(\text{CO})$  in THF: 1966 (m), 1821 (vs)  $\text{cm}^{-1}$ ). After work-up the salt  $(\text{NMe}_4)[\text{Nb}(\text{CO})_4(\kappa^2\text{-tmps})]$  (**1**) was isolated in nearly quantitative yield (97%) as an orange, analytically pure, very air-sensitive powder, which decolorizes immediately upon exposure to air. The salt decomposes upon heating at 142 °C to a dark brown mass, and is well soluble in acetonitrile and tetrahydrofuran (THF), but only moderately soluble in benzene, toluene, and diethyl ether. Attempts to grow suitable single crystals of **1** for an X-ray diffraction study failed, however unambiguous proof for the composition and structure of **1** was provided by elemental analysis, IR spectroscopy and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectroscopy. The IR spectrum of **1** in THF displays four  $\nu(\text{CO})$  absorption bands at 1900, 1787, 1764 and 1732  $\text{cm}^{-1}$  (Fig. 1a), the band pattern being typical for octahedral *cis*-disubstituted metal tetracarbonyl complexes with a local  $C_{2v}$  symmetry of the  $\text{M}(\text{CO})_4$  fragment.<sup>14</sup> All  $\nu(\text{CO})$  bands of **1** are shifted to lower frequencies than those of  $[\text{Nb}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^-$  ( $\nu(\text{CO})$  in THF = 1908, 1806, 1782 and 1746  $\text{cm}^{-1}$ ) or related disubstituted arylphosphane-carbonyl niobates.<sup>11b</sup> This shift to lower

frequencies evinces the stronger +I effect of the P-bonded alkyl substituents in **1**, which enhances the electron density at the metal center and leads to a stronger  $\text{Nb}(\text{d}\pi) \rightarrow \text{CO}(\pi^*)$  back-bonding and softening of the CO bonds in **1**. The NMR spectra of **1** corroborate the presence of an overall  $C_s$  symmetric complex, in which one of the arms of the tripodal ligand tmps is pendant and the other two arms are bonded to the niobium center. For example, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** displays a sharp singlet for the  $^{31}\text{P}$  nucleus of the pendant  $\text{CH}_2\text{PMe}_2$  arm, which appears at almost the same position ( $\delta(\text{P}_\text{A}) = -55.8$  ppm in benzene- $d_6$ ) as that of the non-coordinated ("free") tmps ( $\delta(\text{P}) = -55.1$  ppm in benzene- $d_6$ ), and a very broad signal for the two symmetry-equivalent Nb-bonded  $^{31}\text{P}$  nuclei at considerably lower field ( $\delta(\text{P}_\text{B}) = -11.6$  ppm in benzene- $d_6$ ) (Fig. 1b). The broadness of the second signal ( $\Delta\nu_{1/2}$  (full width at half maximum) = 696 Hz) is caused by the quadrupole moment of the  $^{93}\text{Nb}$  nucleus ( $Q = -0.32 \times 10^{-28} \text{ m}^2$ ;  $I = 9/2$ , 100% natural abundance) and its effect on the relaxation time.<sup>15</sup> Further structural information was provided by the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **1**, which shows a sharp signal for the bridgehead Si atom, that is split to a doublet of triplets (Fig. 1c) due to coupling with the two chemically different types of  $^{31}\text{P}$  nuclei in the integral ratio 1 : 2 ( $^2J(\text{Si}, \text{P}_\text{A}) = 14.7 \text{ Hz}$ ,  $^2J(\text{Si}, \text{P}_\text{B}) = 8.2 \text{ Hz}$ ). A positional exchange of the pendant and the Nb-bonded arms of the tmps ligand in **1** was not observed in solution at 298 K.

Complex **1** was found to be a very suitable nucleophile for the formation of  $\text{Nb} \equiv \text{E}$  triple bonds ( $\text{E} = \text{Si}-\text{Sn}$ ). Thus addition of a freshly prepared, orange-colored solution of a mixture of the 1,2-dibromodisilene  $E\text{-Tbb}(\text{Br})\text{Si}=\text{Si}(\text{Br})\text{Tbb}$ <sup>16</sup> and 4-dimethylamino pyridine (4-DMAP) (molar ratio 1 : 4), to a solution of one equiv. of **1** in toluene at ambient temperature was accompanied by an immediate color change to red-brown, and precipitation of a white solid  $(\text{NMe}_4)\text{Br}$ . IR monitoring revealed a complete and selective conversion to the silyldiynide complex  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb} \equiv \text{Si}-\text{Tbb}]$  (**2-Si**, Scheme 4). After work-up, complex **2-Si** was isolated in 59% yield as a red-brown, extremely air-sensitive, microcrystalline solid, which

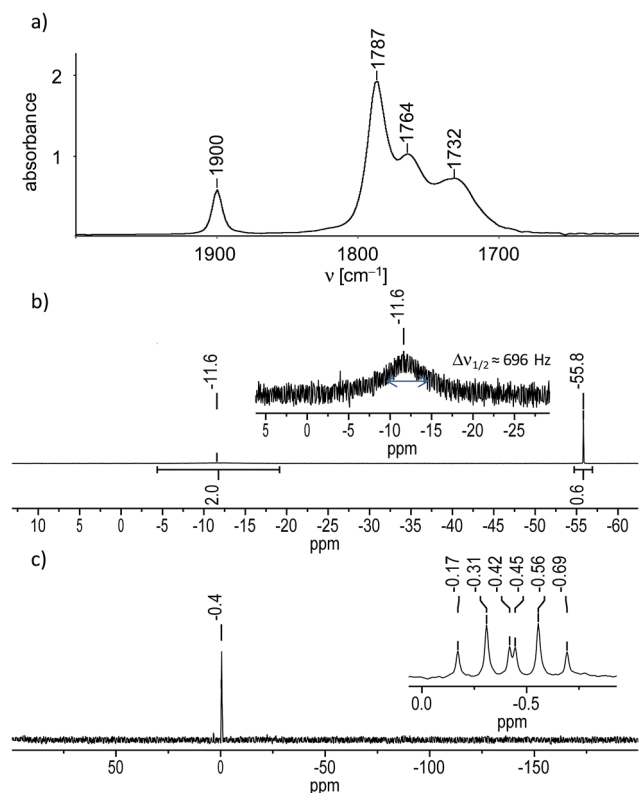
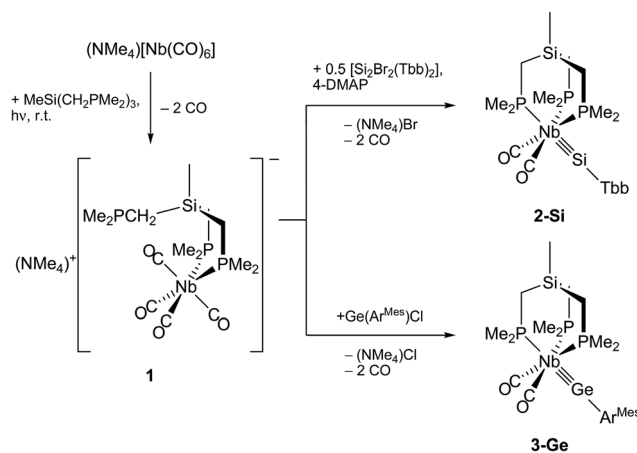


Fig. 1 (a) FT-IR spectrum of **1** in THF in the range of 2000–1600  $\text{cm}^{-1}$ . (b)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in benzene- $d_6$ ; an enlarged excerpt with the broad signal at  $\delta = -11.6$  ppm is shown in the inset. (c)  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **1** in THF- $d_8$ ; an enlarged excerpt with the signal at  $\delta = -0.44$  ppm is depicted in the inset.



Scheme 4 Synthesis of the niobium silyldiynide complex **2-Si** and the germyldiynide complex **3-Ge**.

decolorizes immediately upon exposure to air. Compound **2-Si** is remarkably thermostable, and decomposes to a dark brown mass at 258 °C. It is moderately soluble in *n*-pentane, but readily soluble in benzene, toluene and THF.

Similarly, treatment of complex **1** with the *m*-terphenylgermanium(II) chloride  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$  in toluene at  $-40$  °C followed by warming to room temperature afforded rapidly and selectively the germylidyne complex  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Ge}-\text{Ar}^{\text{Mes}}]$  (**3-Ge**) (Scheme 4). Compound **3-Ge** was isolated as a deep-magenta, very air-sensitive, thermally stable powder (dec. at 284 °C), that is moderately soluble in benzene and toluene, and well soluble in THF. No evidence for the formation of the putative metallocermylene intermediate  $[(\kappa^3\text{-tmps})(\text{CO})_3\text{Nb}-\text{GeAr}^{\text{Mes}}]$  could be obtained during IR monitoring of the reaction of **1** with  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$  in toluene, the reaction starting at  $-35$  °C and proceeding rapidly with CO evolution below  $0$  °C.

In comparison, reaction of the analogous *m*-terphenyltin(II) chloride  $\text{Sn}(\text{Ar}^{\text{Mes}})\text{Cl}$  with **1** in toluene afforded after stirring at ambient temperature the brick-red metallostanlylene  $[(\kappa^3\text{-tmps})(\text{CO})_3\text{Nb}-\text{SnAr}^{\text{Mes}}]$  (**4-Sn**) with a small amount of the stannylidyne complex  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{SnAr}^{\text{Mes}}]$  (**3-Sn**) (Scheme 5). Prolonged heating at  $80$  °C and periodic evacuation of the reaction tube was necessary to remove the released CO and to convert **4-Sn** almost quantitatively into the stannylidyne complex **3-Sn**, which after work-up was isolated as a dark violet, very air-sensitive powder in 70% yield. Complex **3-Sn** is as **3-Ge** thermally stable and decomposes upon heating at  $266$  °C. However, unlike **3-Ge**, complex **3-Sn** was found to be extremely light sensitive. Thus exposure of the deep-violet solutions of **3-Sn** to fluorescent, ambient light or sun light lead to deposition of a tin mirror and formation of tmps and 1,3-dimesitylbenzene as evidenced by  $^1\text{H}$  NMR spectroscopy. Therefore, all operations during the synthesis, isolation and characterization of **3-Sn** had to be carried out under exclusion of light.

Decarbonylation of **4-Sn** to afford **3-Sn** is a remarkable, new type of reaction in the chemistry of metallostanlylenes. In fact previous attempts to transform the metallostanlylenes  $[\text{Cp}(\text{CO})_3\text{M}-\text{SnR}]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{R} = \text{Ar}^{\text{Mes}}, \text{Ar}^{\text{Trip}}, \text{Ar}^{\text{Dipp}}$ ;  $\text{Ar}^{\text{Trip}} = \text{C}_6\text{H}_3-2,6\text{-Trip}_2$ ,  $\text{Trip} = \text{C}_6\text{H}_2-2,4,6\text{-iPr}_3$ ),<sup>17</sup>  $[\text{Cp}(\text{CO})_2\text{Fe}-\text{SnR}]$  ( $\text{R} = \text{Ar}^{\text{Dipp}}, \text{Ar}^{\text{Trip}}, \text{Ar}^{\text{Dipp}} = \text{C}_6\text{H}_3-2,6\text{-Dipp}_2$ ,  $\text{Dipp} = \text{C}_6\text{H}_3-2,6\text{-iPr}_2$ )<sup>18</sup> or  $[\text{Cp}^*(\text{CO})_3\text{W}-\text{Sn}(\text{IDipp})]^+$  ( $\text{IDipp} = \text{C}[\text{N}(\text{Dipp})\text{CH}]_2$ ,  $\text{Dipp} = \text{C}_6\text{H}_3-2,6\text{-iPr}_2$ )<sup>20</sup> into terminal stannylidyne complexes failed. We assume, that the increased steric pressure imposed by the

tripodal ligand at the metal center weakens the Nb–CO bonds in the seven-coordinate complex **4-Sn** and decreases thereby the barrier for a CO dissociation. In addition, formation of a strong  $\text{Nb}\equiv\text{Sn}$  triple bond resulting from the higher energy and larger radial extension of the d orbitals, which are engaged in the  $\text{Nb}(\text{d}\pi) \rightarrow \text{SnR}(\pi^*)$  back bonding, may be also a driving force for the reaction.

The tetrylidyne complexes **2-Si**, **3-Ge** and **3-Sn** were characterized by elemental analyses, IR spectroscopy and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{29}\text{Si}\{^1\text{H}\}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectroscopy. In addition their molecular structures were determined by single-crystal X-ray crystallography (Fig. 2 and 3). All complexes are distorted octahedral and feature a tridentate ( $\kappa^3$ -bonded) tmps ligand, which spans three facial coordination sites with the P–Nb–P bite angles varying in a small range ( $85.3\text{--}87.9^\circ$ ). A view along the  $\text{Si}\cdots\text{Nb}$  vector reveals that the  $\text{CH}_2$  groups connecting the bridgehead Si atom with the P donors are twisted out creating a local  $C_3$  symmetric, right or left-handed conformation, which reduces the bite of the chelating triphosphane ligand and optimizes the bonding with the niobium center (Fig. 3b). In solution, however, a rapid interchange of the two conformational enantiomers occurs according to NMR spectroscopy leading to averaged  $C_s$  symmetric structures.

The tetrylidyne complexes **2-Si**, **3-Ge** and **3-Sn** feature the shortest Nb–Si, Nb–Ge and Nb–Sn bonds reported to date. In practice, the Nb–Si bond of **2-Si** ( $232.7(2)$  pm) is *ca.* 28 pm shorter than the Nb–Si single bonds of silyl complexes ( $d(\text{Nb}-\text{Si})_{\text{mean}}$  of 28 structurally characterized complexes =  $261.3$  pm),<sup>19</sup> and the Nb–Ge bond of **3-Ge** ( $235.79(4)$  pm) *ca.* 31 pm shorter than a Nb–Ge single bond ( $d(\text{Nb}-\text{Ge})_{\text{mean}} = 267.3$  pm).<sup>20</sup> Similarly, the Nb–Sn bond of **3-Sn** ( $253.3(1)$  pm) is *ca.* 30 pm shorter than a Nb–Sn single bond ( $d(\text{Nb}-\text{Sn})_{\text{mean}} = 282.9$  pm).<sup>21</sup>

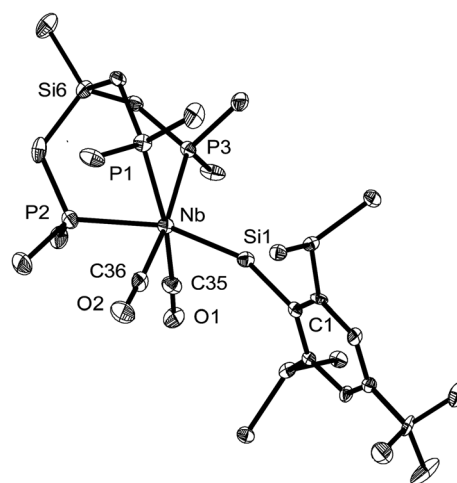
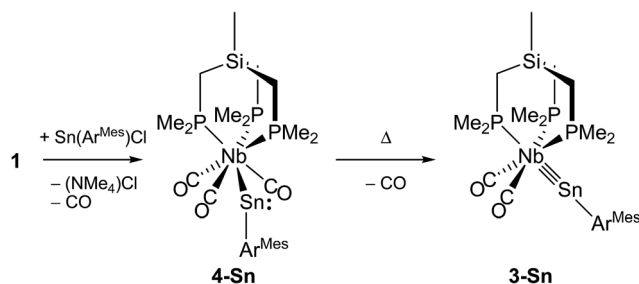


Fig. 2 DIAMOND plot of the molecular structure of the silylidyne complex **2-Si** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and the methyl groups of the  $\text{C}^{2,6}\text{-CH}(\text{SiMe}_3)_2$  substituents were omitted for clarity. Selected bond lengths [pm] and angles [°]: Nb–Si1  $232.7(2)$ , Nb–P1  $259.9(2)$ , Nb–P2  $258.4(2)$ , Nb–P3  $259.3(2)$ , Nb–C35  $206.8(9)$ , Nb–C36  $206.3(7)$ , Si1–C1  $189.0(7)$ , C35–O1  $117.6(8)$ , C36–O2  $117.9(7)$ ; Nb–Si1–C1  $159.2(2)$ , P1–Nb–P2  $85.61(7)$ , P1–Nb–P3  $85.31(6)$ , P2–Nb–P3  $87.92(6)$ , C35–Nb–C36  $93.3(3)$ .



Scheme 5 Synthesis of the niobium stannylidyne complex **3-Sn** via the niobiastannylene **4-Sn**.





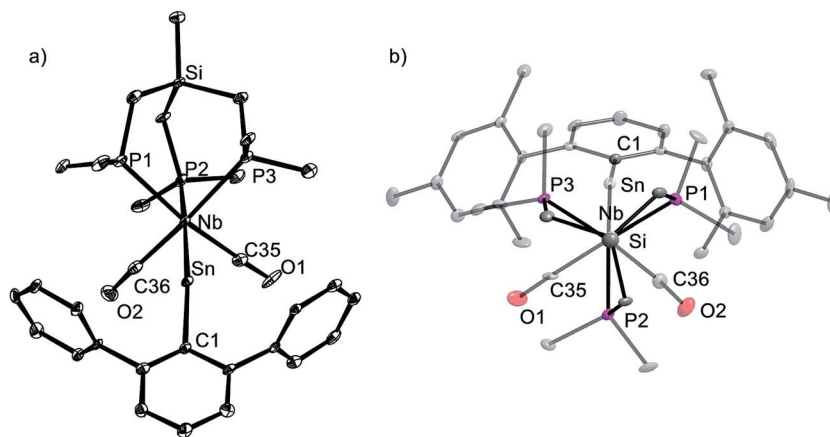


Fig. 3 (a) DIAMOND plot of the molecular structure of the stannylidyne complex **3-Sn** (toluene) in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and methyl groups of the  $\text{Ar}^{\text{Mes}}$  substituent were omitted for clarity. Selected bond lengths [pm] and angles [°] of **3-Sn** (toluene) (bond lengths and angles for **3-Ge** (THF) are given in brackets): Nb–Sn 253.3(1) [235.79(4)], Nb–P1 260.6(4) [259.5(1)], Nb–P2 255.1(3) [258.0(1)], Nb–P3 258.6(4) [261.2(1)], Nb–C35 205.7(14) [206.0(5)], Nb–C36 207.1(16) [206.5(5)], Sn–C1 214.2(1) [196.3(4)], C35–O1 116.8(18) [116.8(6)], C36–O2 115.4(18) [115.5(6)]; Nb–Sn–C1 160.9(3) [164.0(1)], P1–Nb–P2 87.7(1) [86.30(4)], P1–Nb–P3 85.9(1) [86.08(4)], P2–Nb–P3 87.4(1) [87.82(4)], C35–Nb–C36 90.9(5) [92.5(2)]. (b) Top view of **3-Sn** along the Si...Nb vector illustrating the  $C_3$ -symmetric twist of the tamps ligand.

Notably, a comparison of the Nb–E triple bond lengths of **2-Si**, **3-Ge** and **3-Sn** with those of related molybdenum tetrylidyne complexes (e.g.  $d(\text{Mo}\equiv\text{Si})$  in  $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Si}-\text{Ar}^{\text{Trip}}] = 222.41(7)$  pm;<sup>1a</sup>  $d(\text{Mo}\equiv\text{Ge})$  in  $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Ge}-\text{R}]$  ( $\text{R} = \text{C}(\text{SiMe}_3)_3$ ,  $\text{Ar}^{\text{Mes}}$ ,  $\text{Ar}^{\text{Trip}} = 227\text{--}228$  pm;<sup>2a,2b,2i,2m</sup>  $d(\text{Mo}\equiv\text{Sn})$  in  $\text{trans-}[\text{X}(\text{PMe}_4)\text{Mo}\equiv\text{Sn}-\text{Ar}^{\text{Mes}}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I} = 248\text{--}249$  pm)<sup>22</sup>) reveals that the differences in the  $\text{M}\equiv\text{E}$  triple bond lengths ( $\text{E} = \text{Si}$ : 10 pm;  $\text{E} = \text{Ge}$ : 8–9 pm;  $\text{E} = \text{Sn}$ : 5–6 pm) compare reasonably well with the difference (7 pm) of the metallic radii of the two elements ( $r_{\text{Nb}} = 147$  pm,  $r_{\text{Mo}} = 140$  pm; radii for a coordination number of 12).<sup>23</sup> A series of additive triple bond radii for most elements of the periodic table have been predicted by P. Pyykkö *et al.*<sup>24</sup> The experimental Nb–E triple bond lengths **2-Si**, **3-Ge** and **3-Sn**, are however, longer than the sum of the theoretically predicted triple bond radii ( $d(\text{Nb}\equiv\text{E})_{\text{calc}} = \text{Si}$ : 218 pm, Ge: 230 pm, Sn: 248 pm).

In all complexes the tetrylidyne ligand is slightly bent at the tetrrel center as evidenced by the bonding angle Nb–E–C1 (**2-Si**: 159.2(2)°, **3-Ge**: 164.0(1)°, **3-Sn**: 160.9(3)°). Bending occurs in all cases towards the CO ligands. It is presently unclear, whether this phenomenon, which is also observed in a series of group 6 metal dicarbonyl ylidyne complexes, is of steric or electronic origin or both. No clear evidence for steric congestion is at least provided by the molecular structures of **2-Si**, **3-Ge** and **3-Sn**. For example, the closest van der Waals contacts were found in **2-Si** between the methyl groups of the tamps ligand and the  $\text{SiMe}_3$  methyl groups of the Tbb substituent ( $d(\text{H}\cdots\text{H}) = 244$  pm). These contacts are longer than twice the van der Waals radius of hydrogen ( $r_{\text{vdW}}(\text{H}) = 110$  pm).<sup>25</sup> It should be also taken into consideration, that deviation of the  $\text{M}\equiv\text{E}-\text{R}$  atom sequence from linearity does not require a lot of energy, indicating that subtle electronic effects may cause such a bending.<sup>26</sup>

Further structural information was obtained from the IR and NMR spectra of the tetrylidyne complexes. The IR spectra of

**2-Si**, **3-Ge** and **3-Sn** display two  $\nu(\text{CO})$  bands of almost equal intensity, which are typical for *cis*-dicarbonyl complexes and can be assigned to the in-phase ( $A'$  symmetric) and out-of-phase ( $A''$  symmetric) CO stretching modes assuming local  $C_s$  symmetry of the  $\text{M}(\text{CO})_2$  fragment (Fig. 4a). The  $\nu(\text{CO})$  bands of **3-Sn** appear at lower frequencies (1851 and 1791  $\text{cm}^{-1}$  in toluene) than those of **3-Ge** (1868 and 1805  $\text{cm}^{-1}$  in toluene), which suggests that the stannylidyne ligand  $\text{SnAr}^{\text{Mes}}$  has a higher  $\sigma$ -donor/ $\pi$ -acceptor ratio than the germylidyne ligand  $\text{GeAr}^{\text{Mes}}$ . Notably, the  $\nu(\text{CO})$  bands of **2-Si** appear also at lower wavenumbers (1855 and 1790  $\text{cm}^{-1}$  in toluene) than those of **3-Ge**. This shift can be

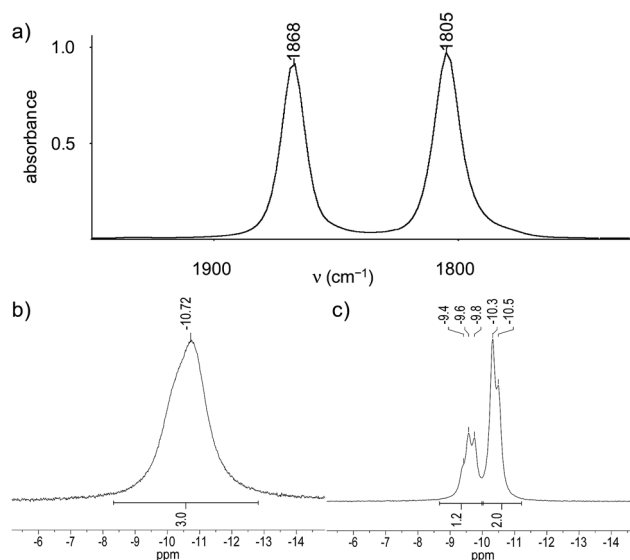


Fig. 4 (a) IR  $\nu(\text{CO})$  absorption bands of the germylidyne complex **3-Ge** in toluene. (b)  $^{31}\text{P}\{^1\text{H}\}$  NMR signal of the germylidyne complex **3-Ge** in  $\text{THF}-d_8$  at 283 K. (c)  $^{31}\text{P}\{^1\text{H}\}$  NMR signals of the germylidyne complex **3-Ge** in  $\text{THF}-d_8$  at 193 K.



rationalized with the stronger +I effect of the Tbb substituent, leading to a higher  $\sigma$ -donor/ $\pi$ -acceptor ratio of the silylidyne ligand SiTbb than that of the germylidyne ligand GeAr<sup>Mes</sup>. The low-frequency position of the  $\nu(\text{CO})$  bands of **2-Si**, **3-Ge** and **3-Sn** suggests the presence of an electron-rich Nb center that is engaged in strong  $\text{Nb}(\text{d}\pi) \rightarrow \text{CO}(\pi^*)$  backbonding. Additional evidence for a strong  $\text{Nb}(\text{d}\pi) \rightarrow \text{CO}(\pi^*)$  backbonding is provided by the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, which all display a broad CO signal at even lower field ( $\delta_{\text{CO}} = 238.7$  ppm (**2-Si**), 239.2 ppm (**3-Ge**), 238.9 ppm (**3-Sn**)) than that of **1** ( $\delta_{\text{CO}} = 226.5$  ppm).<sup>27</sup> The number and relative intensity of the NMR signals indicate an averaged  $C_s$  symmetry of the tetrylidyne complexes in solution and a rapid rotation of the tetrel-bonded aryl group about the E- $C_{\text{aryl}}$  bond. The signals of all nuclei directly attached to the quadrupolar  $^{93}\text{Nb}$  nucleus are significantly broadened due to fast relaxation (*vide supra*). For example, the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **2-Si** displays at 298 K a very broad signal ( $\Delta\nu_{1/2} = 130$  Hz) for the  $\text{Nb}\equiv\text{Si}$  nucleus at  $\delta = 267.8$  ppm, for which the  $^2J(^{29}\text{Si}, ^{31}\text{P})$  coupling could not be resolved. In comparison, the remote positioned bridgehead Si atom of the tmps ligand and the  $\text{SiMe}_3$  groups of the Tbb substituent give rise to sharp signals at  $\delta = -0.7$  ppm and  $+1.5$  ppm, respectively, with the first of these signals being split into a quartet due to coupling to the three  $^{31}\text{P}$  nuclei ( $^2J(^{29}\text{Si}, ^{31}\text{P}) = 9.7$  Hz) (Fig. S16 and S17 (ESI<sup>†</sup>)). Similarly, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2-Si** and **3-Ge** show only one broad signal at  $\delta = -13.0$  ppm ( $\Delta\nu_{1/2} \approx 182$  Hz at 298 K) and  $-10.7$  ppm ( $\Delta\nu_{1/2} \approx 187$  Hz at 283 K), respectively, instead of two  $^{31}\text{P}$  NMR signals expected for an  $\text{AX}_2$  spin system (Fig. 4b). Broadness of the signals can be influenced by the temperature given the well known relationship between the quadrupole-coupled nuclear relaxation time and the temperature dependent molecular correlation time.<sup>28</sup> In fact, lowering of the temperature lead to a “decoupling” of the Nb nucleus and allowed to resolve the two  $^{31}\text{P}$  NMR signals and their  $^2J(\text{P}, \text{P})$  coupling of 20.9 Hz as illustrated by the  $^{31}\text{P}$  NMR spectrum of **3-Ge** at 193 K (Fig. 4c). Taking advantage of the same effect, also the  $^{119}\text{Sn}$  resonance of **3-Sn**, that was not observable in  $\text{THF}-d_8$  at room temperature, could be detected at 243 K as a very broad signal ( $\Delta\nu_{1/2} \approx 1297$  Hz) at  $\delta = 829.7$  ppm (Fig. S36 (ESI<sup>†</sup>)).

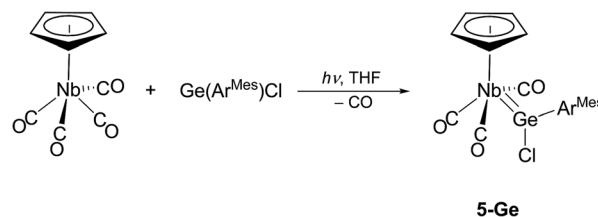
First studies reveal a marked difference in the reactivity of the niobium germylidyne complex **3-Ge** and the related molybdenum germylidyne complexes  $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Ge}-\text{R}]$  ( $\text{R} = \text{C}(\text{SiMe}_3)_3$ ,  $\text{Ar}^{\text{Mes}}$ ,  $\text{Ar}^{\text{Trip}}$ ). Thus treatment of  $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Ge}-\text{R}]$  with  $\text{H}_2\text{O}$  or  $\text{MeOH}$  (one equiv.) in diethyl ether at  $0^\circ\text{C}$  followed by warming to ambient temperature afforded within one hour selectively the brown hydroxy/methoxygermylidene complexes  $[\text{Cp}(\text{CO})_2(\text{H})\text{Mo}=\text{Ge}(\text{OR}')\text{R}]$  ( $\text{R}' = \text{H}, \text{Me}$ ), which were fully characterized.<sup>2m</sup> In contrast, no reaction of **3-Ge** with  $\text{H}_2\text{O}$  (one equiv.) was observed in THF even at  $60^\circ\text{C}$ . The inertness of **3-Ge** can be rationalized with the stronger metal-germylidyne  $\text{Nb}(\text{d}\pi) \rightarrow \text{GeR}(\pi^*)$  back bonding, which reduces the electrophilicity of the Ge center in **3-Ge**, and increases in combination with the steric protection of the metal center by the tridentate tmps ligand the activation barrier for the  $\text{H}_2\text{O}$  addition at the  $\text{Nb}\equiv\text{Ge}$  bond. In fact, a large excess of water (925 equiv.) and prolonged heating (3 h) was necessary to effectuate a full conversion of **3-Ge** accompanied by a color change of the reaction solution

from magenta to orange. IR monitoring of the reaction did not provide any evidence for the formation of the anticipated  $\text{H}_2\text{O}$  addition products. Instead, a continuous decrease in intensity of the two  $\nu(\text{CO})$  bands of **3-Ge** was observed suggesting the formation of mainly CO-free products. Benzene extraction of the orange-brown solid obtained after solvent evaporation afforded a benzene soluble, pale-orange part containing mainly the germanediol  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{H}(\text{OH})_2$ , as well as a benzene-insoluble brownish part. The unprecedented hydridogermanediol<sup>29</sup> was isolated as a pale yellow solid and characterized by IR and  $^1\text{H}$  NMR spectroscopy. Its IR spectrum displays two  $\nu(\text{OH})$  bands at 3600 and 3398  $\text{cm}^{-1}$  and a characteristic  $\nu(\text{Ge}-\text{H})$  band at 2104  $\text{cm}^{-1}$ , the latter one appearing at a close position to that of  $\text{GeBr}_2\text{HMes}$  ( $\nu(\text{Ge}-\text{H}) = 2105$   $\text{cm}^{-1}$ ).<sup>30</sup> In the  $^1\text{H}$  NMR spectrum a distinctive doublet signal is observed for the  $\text{Ge}(\text{OH})_2$  protons at  $\delta = 0.91$  ppm and a triplet signal for the  $\text{Ge}-\text{H}$  functionality at  $\delta = 5.61$  ppm ( $^2J(\text{H}, \text{H}) = 3.5$  Hz) in the integral ratio of 2 : 1. Notably, the  $\text{Ge}-\text{OH}$  protons of the germanetriol  $\text{Ge}(\text{Ar}^{\text{Trip}})(\text{OH})_3$  have a similar chemical shift ( $\delta = 0.77$  ppm in  $\text{CDCl}_3$ ).<sup>29k</sup>

Attempts were also undertaken to access cationic tetrylidyne complexes. For this purpose,  $[\text{CpNb}(\text{CO})_4]^+$ <sup>31</sup> was prepared using a slightly modified procedure<sup>32</sup> and irradiated in THF with a high-power blue light LED ( $\lambda = 465$  nm) in the presence of one equivalent of  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$ . IR monitoring of the reaction revealed a quite selective decarbonylation leading to the chlorogermylidene complex **5-Ge**, which after work-up was isolated as red-orange, air-sensitive crystals in 25% yield (Scheme 6). Remarkably attempts to abstract the chloride from **5-Ge** and to form the putative germylidyne complex cation  $[\text{Cp}(\text{CO})_3\text{Nb}\equiv\text{GeAr}^{\text{Mes}}]^+$  were not successful so far. For example, no reaction of **5-Ge** with  $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$  ( $\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2$ ) was observed in  $\text{C}_6\text{H}_5\text{F}$  at room temperature.

Complex **5-Ge** is the first niobium germylidene complex to be reported. Its solid-state molecular structure was determined by single-crystal X-ray crystallography (Fig. 5). The four-legged piano stool complex is  $C_s$  symmetric and features a trigonal-planar coordinated Ge-atom (sum of angles at the Ge atom =  $360.0^\circ$ ). The symmetry plane passes through the atoms Nb, Ge, C1 and Cl, and bisects the  $\text{CpNb}(\text{CO})_3$  fragment and the central ring of the *m*-terphenyl substituent.

The germylidene ligand adopts an upright conformation, with the  $\text{Ar}^{\text{Mes}}$  substituent pointing towards the cyclopentadienyl ring. The Nb–Ge distance (251.78(6) pm) of **5-Ge** lies in-between that found for the Nb–Ge triple bond of **3-Ge** (235.79(4) pm) (*vide supra*) and that of a Nb–Ge single bond



Scheme 6 Synthesis of the niobium chlorogermylidene complex **5-Ge**.



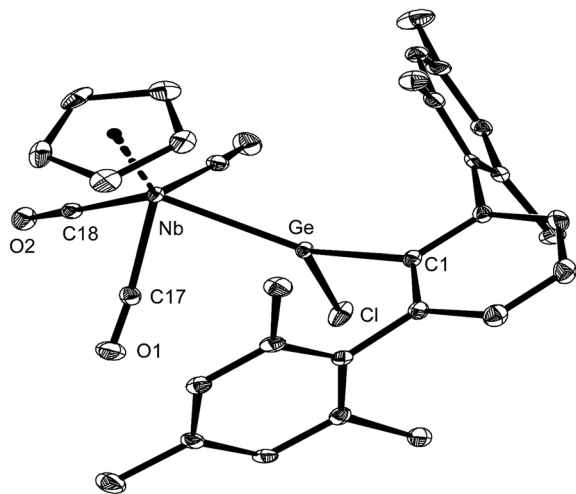


Fig. 5 DIAMOND plot of the molecular structure of **5-Ge** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K, and hydrogen atoms were omitted for clarity. Selected bond lengths [pm] and angles [°]: Nb–Ge 251.78(6), Ge–C1 196.2(4), Ge–C1 219.1(1), Nb–C17 207.4(3), Nb–C18 206.1(4), C17–O1 115.2(4), C18–O2 114.5(5); Nb–Ge–C1 141.4(1), Nb–Ge–Cl 118.75(4), Cl–Ge–C1 99.8(1).

( $d(\text{Nb-Ge}) = 267.3 \text{ pm}$ )<sup>20</sup> indicating the presence of a Nb–Ge double bond in **5-Ge**. The angles at the Ge atom differ markedly with the Nb–Ge–C<sub>aryl</sub> angle ( $141.4(1)^\circ$ ) being much larger than the C<sub>aryl</sub>–Ge–Cl angle ( $99.8(1)^\circ$ ). This distortion can be attributed to the large steric demand of the Ar<sup>Mes</sup> substituent and the low tendency of germanium for isovalent hybridization.<sup>1a,1b,2f,3d</sup> The Ge–Cl bond of **5-Ge** (219.1(1) pm) compares well with that of Ge(Ar<sup>TriP</sup>)Cl (220.3(2) pm),<sup>33</sup> but is considerably shorter than those of chlorogermaylidene complexes containing electron-rich metal centers, such as [(dmpe)<sub>2</sub>Fe=Ge(Ar<sup>Mes</sup>)Cl] ( $d(\text{Ge-Cl}) = 232.2(1) \text{ pm}$ ),<sup>5</sup> [(PMe<sub>3</sub>)<sub>3</sub>Ni=Ge(Ar<sup>Mes</sup>)Cl] ( $d(\text{Ge-Cl}) = 230.03(8) \text{ pm}$ )<sup>6</sup> or [(PMe<sub>3</sub>)<sub>3</sub>Pd=Ge(Ar<sup>Mes</sup>)Cl] ( $d(\text{Ge-Cl}) = 227.3(1) \text{ pm}$ ),<sup>6</sup> in which a strong M(dπ) → Ge(pπ) back bonding is presumed to cause a strong polarization of Ge–Cl bond leading to a facile chloride abstraction by Lewis acids. The reduced polarization of the Ge–Cl bond of **5-Ge** provides a rationale for its inertness towards mild chloride abstraction reagents.

The solution IR and NMR spectra of **5-Ge** are fully consistent with its solid-state molecular structure. Thus, the IR spectrum of **5-Ge** in THF displays three intense  $\nu(\text{CO})$  absorption bands at 1980, 1910 and 1899  $\text{cm}^{-1}$ , as expected for a Nb(CO)<sub>3</sub> fragment with local C<sub>s</sub> symmetry, which are assigned to the A' (all three CO modes in phase), A' (two CO<sub>lat</sub> modes in phase; CO<sub>diag</sub> mode out-of-phase) and A'' symmetric (two CO<sub>lat</sub> modes out-of-phase) CO stretching modes, respectively. The  $\nu(\text{CO})$  absorption bands of **5-Ge** are high-frequency shifted compared to those of [CpNb(CO)<sub>3</sub>THF] ( $\nu(\text{CO})$  in THF = 1961, 1840  $\text{cm}^{-1}$ )<sup>31</sup> or [CpNb(CO)<sub>3</sub>PEt<sub>3</sub>] ( $\nu(\text{CO})$  in THF = 1953, 1850  $\text{cm}^{-1}$ ),<sup>28b</sup> but appear at roughly the same position as those of [CpNb(CO)<sub>3</sub>N<sub>2</sub>] ( $\nu(\text{CO})$  in *n*-heptane = 1991, 1905  $\text{cm}^{-1}$ )<sup>34</sup> suggesting a similar  $\sigma$ -donor/ $\pi$ -acceptor ratio of the germaylidene GeAr<sup>Mes</sup>Cl and the N<sub>2</sub> ligand. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra also confirm the C<sub>s</sub> symmetry of **5-Ge** in solution. Rotation of the *m*-terphenyl substituent about the Ge–C<sub>aryl</sub> bond occurs fast on the NMR

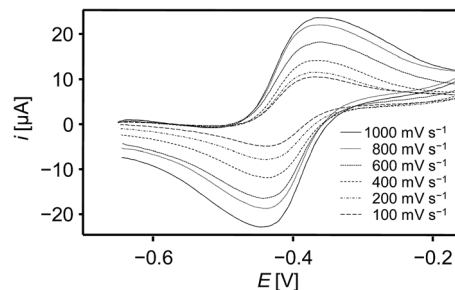


Fig. 6 Single-scan cyclic voltammograms of the reversible one-electron oxidation of **3-Ge** at different scan rates in THF at  $-11^\circ\text{C}$  (supporting electrolyte: [NBu<sub>4</sub>][PF<sub>6</sub>] (0.1 M); reference electrode: 0.004 M [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+1/0</sup>/0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]/THF).

time-scale at ambient temperature leading to an exchange of the two diastereotopic *ortho* (C<sup>2,6</sup>) and *meta* (C<sup>3,5</sup>) positions of the enantiotopic mesityl substituents. Therefore, only one singlet signal is observed in the <sup>1</sup>H NMR spectrum of **5-Ge** for the C<sup>2,6</sup>-bonded methyl groups and C<sup>3,5</sup>-bonded protons of the mesityl substituents, respectively.

## Electrochemical studies

Electrochemical studies of the tetraylidene complexes **2-Si**, **3-Ge** and **3-Sn** were carried out using cyclic voltammetry to elucidate the redox properties of these compounds. All complexes display a rich electrochemistry involving several electron-transfer steps (see ESI, chapter 3†). Remarkably, both the one-electron reduction and oxidation of the germaylidene complex **3-Ge** are electrochemically reversible occurring at a half wave potential ( $E_{1/2}$ ) of  $-2.612 \text{ mV}$  and  $-405 \text{ mV}$  vs. the dmfc<sup>1+/0</sup> redox couple (dmfc = decamethylferrocene), respectively (Fig. 6).<sup>35</sup>

In comparison, the corresponding redox steps of **2-Si** and **3-Sn** are irreversible (ESI, chapter 3†), but one-electron oxidation **2-Si** and **3-Sn** occurs at similar potentials as that of **3-Ge** ( $E_{\text{pa}} + E_{\text{pc}}/2 = -468 \text{ mV}$ , **3-Sn**:  $E_{\text{pa}} + E_{\text{pc}}/2 = -435 \text{ mV}$  (scan rate =  $100 \text{ mV s}^{-1}$ )). Evidence that the redox process at  $E_{1/2} = -405 \text{ mV}$  involves a one electron oxidation of **3-Ge** was provided by chemical means. Thus, no reaction of **3-Ge** with the one-electron reducing agent cobaltocene ( $E_{1/2}$  of CoCp<sub>2</sub> in DME =  $-740 \text{ mV}$ ) was observed in fluorobenzene even at  $70^\circ\text{C}$ , whereas an instantaneous oxidation of **3-Ge** occurred upon treatment with one equivalent of [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>][B(Ar<sup>F</sup>)<sub>4</sub>] in fluorobenzene solution at  $-30^\circ\text{C}$ . Unfortunately, attempts to isolate the putative germaylidene complex radical cation [(κ<sup>3</sup>-tmpr)(CO)<sub>2</sub>-Nb(GeAr<sup>Mes</sup>)<sup>+</sup>] failed so far.<sup>36</sup> Notably, the redox potential for the one-electron oxidation of **3-Ge** is slightly lower than that of the molybdenum tetraylidene complexes *trans*-[ClMo(PMe<sub>3</sub>)<sub>4</sub>≡E-Ar<sup>Mes</sup>] (E = Ge:  $E_{1/2}$  in C<sub>6</sub>H<sub>5</sub>F =  $-340 \text{ mV}$ ; E = Sn:  $E_{1/2}$  in THF =  $-350 \text{ mV}$ ; E = Pb:  $E_{1/2}$  in THF =  $-358 \text{ mV}$ ) verifying the presence of an electron-rich Nb center in **3-Ge**.

## Conclusion

The synthesis of the tailor-made carbonyl-niobate (NMe<sub>4</sub>) [Nb(CO)<sub>4</sub>(κ<sup>2</sup>-tmpr)] allowed to explore its reactivity towards



a series of organotetrel(II) halides, which lead to the isolation of the first niobium complexes featuring triple bonds with the elements Si, Ge and Sn. Photochemical CO substitution in  $[\text{CpNb}(\text{CO})_4]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) by  $\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}$  afforded also the novel chlorogermlydene complex  $[\text{Cp}(\text{CO})_3\text{Nb}=\text{Ge}(\text{Ar}^{\text{Mes}})\text{Cl}]$ . The structural, spectroscopic and electrochemical data of the tetrylidyne complexes  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Si-Tbb}]$  (**2-Si**),  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Ge-Ar}^{\text{Mes}}]$  (**3-Ge**) and  $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Sn-Ar}^{\text{Mes}}]$  (**3-Sn**) suggest the presence of an electron-rich metal center that is engaged into strong metal ( $d\pi$ )  $\rightarrow$  ER( $\pi^*$ ) and metal ( $d\pi$ )  $\rightarrow$  CO( $\pi^*$ ) back bonding. Remarkably, one-electron oxidation and reduction of the germlydine complex **3-Ge** are electrochemically reversible.

## Acknowledgements

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