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

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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 $(\text{NMe}_4)[\text{Nb}(\text{CO})_4(\kappa^2\text{-tmps})]$ (**1**) ($\text{tmps} = \text{MeSi}(\text{CH}_2\text{PMe}_2)_3$) with a suitable organotetrel(II)halide. Compound **1** was obtained from $(\text{NMe}_4)[\text{Nb}(\text{CO})_6]$ and the triphosphane tmps 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 $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Si}-\text{Tbb}]$ (**2-Si**, $\text{Tbb} = 4\text{-tert-butyl-2,6-bis}(\text{bis}(\text{trimethylsilyl})\text{methyl})\text{phenyl}$). Similarly, treatment of **1** with $\text{E}(\text{Ar}^{\text{Mes}})\text{Cl}$ (E = Ge, Sn; $\text{Ar}^{\text{Mes}} = 2,6\text{-mesitylphenyl}$) afforded after elimination of $(\text{NMe}_4)\text{Cl}$ and two CO ligands the deep magenta colored germylidyne complex $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Ge}-\text{Ar}^{\text{Mes}}]$ (**3-Ge**), and the deep violet, light-sensitive stannylidyne complex $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Sn}-\text{Ar}^{\text{Mes}}]$ (**3-Sn**), respectively. Formation of **3-Sn** proceeds via the niobiastannylene $[(\kappa^3\text{-tmps})(\text{CO})_3\text{Nb}-\text{SnAr}^{\text{Mes}}]$ (**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 ($d(\text{Nb}-\text{Si}) = 232.7(2)$ pm; $d(\text{Nb}-\text{Ge}) = 235.79(4)$ pm; $d(\text{Nb}-\text{Sn}) = 253.3(1)$ pm) reported to date. Reaction of **3-Ge** with a large excess of H_2O afforded upon cleavage of the Nb–Ge triple bond the hydridogermanediol $\text{Ge}(\text{Ar}^{\text{Mes}})\text{H}(\text{OH})_2$. Photodecarbonylation of $[\text{CpNb}(\text{CO})_4]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) 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 $[\text{L}_n\text{M}\equiv\text{E}-\text{R}]$ (M = d-block metal; E = Si–Pb; R = singly bonded group (e.g. alkyl, aryl); 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.^{1–4} Isolation of these compounds is very challenging and requires specific stereo-electronic properties of the metal fragment L_nM 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 σ -bond activations destroying the $\text{M}\equiv\text{E}-\text{R}$ functionality. Whereas earlier work concentrated exclusively on group 6 metals, recent studies have shown that also group 7,^{2l,3d,4d} group 8 (ref. 1c and 5) and even group 10 metals⁶ 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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[†] 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



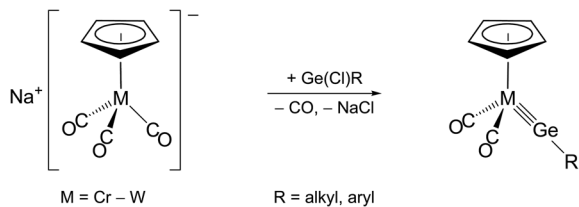
$M\equiv E$ functionality. Group 5 metal complexes featuring a triple bond to the heavier tetrrels ($E = \text{Si-Pb}$) are presently not known, and even compounds with a $M=E$ double bond are very scarce and poorly characterized illustrating the challenge to make such compounds.⁷ We decided to address 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

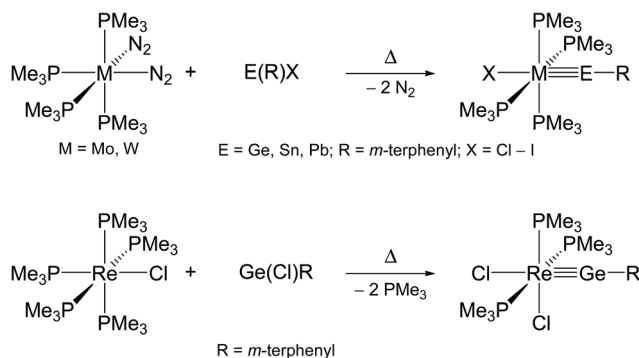
Two methods have been employed so far for the formation of transition metal-tetrrel (Si-Pb) triple bonds. The first method, abbreviated as the “salt elimination method”, involves a substitution reaction of a suitable anionic 18 VE metal complex with an organotetrrel(II) halide, as exemplified by the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

The second method, commonly termed “ N_2/PMe_3 elimination method”, takes advantage of the exchange of labile ligands (mostly N_2 or PMe_3) in neutral 18 VE metal complexes by suitable organotetrrel(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).^{2f,2g,2l,3a,4a,4b}

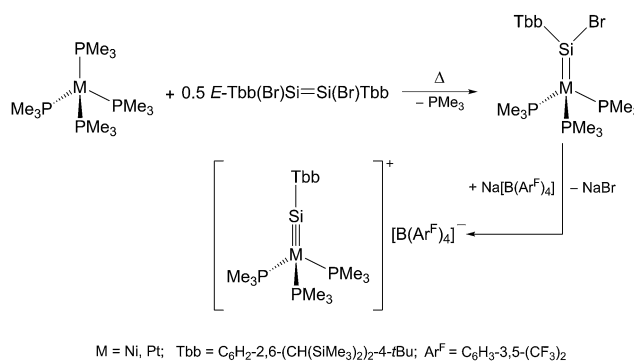
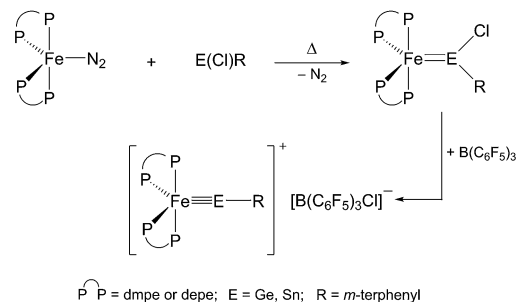
Alternatively, haloylidene complexes are initially obtained by this method, which are subsequently converted to cationic ylidyne complexes by halide abstraction. Examples demonstrating this reaction path include the preparation of group 8 and 10 ylidyne complexes (Scheme 3).^{5,6}



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 N_2/PMe_3 elimination method.



Scheme 3 Preparation of group 8 and 10 metal tetrylidyne complexes via haloylidene complexes using the N_2/PMe_3 elimination method.

We decided to apply the first method, given the availability of anionic niobium carbonyl complexes.⁸ At first, the homoleptic carbonyl niobate $[\text{Nb}(\text{CO})_6]^-$ was chosen. For this purpose the canary yellow salts $(\text{NR}_4)[\text{Nb}(\text{CO})_6]$ ($\text{R} = \text{Me}, \text{Et}$) were prepared, following the method developed by J. E. Ellis *et al.*⁹ However, these compounds proved to be unreactive towards the *m*-terphenyltetrrel(II)halides $\text{E}(\text{Ar}^{\text{Mes}})\text{Cl}$ ($\text{E} = \text{Ge}, \text{Sn}$; $\text{Ar}^{\text{Mes}} = 2,6$ -mesitylphenyl; mesityl (Mes) = 2,4,6-trimethylphenyl).¹⁰ 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 σ -donor/ π -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.¹¹ 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).¹²

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 CH_2Cl_2)¹³ was conceived to be advantageous preventing the formation of insoluble brown decomposition



products formed during the photolysis using a high-pressure mercury-lamp.^{11a}

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) 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 ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ 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 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.¹⁴ 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 cm^{-1}) or related disubstituted arylphosphane-carbonyl niobates.^{11b} 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}P nucleus of the pendant CH_2PMe_2 arm, which appears at almost the same position ($\delta(\text{P}_A) = -55.8$ 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}P nuclei at considerably lower field ($\delta(\text{P}_B) = -11.6$ 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}Nb nucleus ($Q = -0.32 \times 10^{-28} \text{ m}^2$; $I = 9/2$, 100% natural abundance) and its effect on the relaxation time.¹⁵ 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}P nuclei in the integral ratio 1 : 2 ($^2J(\text{Si}, \text{P}_A) = 14.7$ Hz, $^2J(\text{Si}, \text{P}_B) = 8.2$ 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 (E = Si–Sn). Thus addition of a freshly prepared, orange-colored solution of a mixture of the 1,2-dibromodisilene *E*-Tbb(Br)Si=Si(Br)Tbb¹⁶ 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 silyldiyne complex $[(\kappa^3\text{-tmps})(\text{CO})_2\text{Nb}\equiv\text{Si-Tbb}]$ (**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

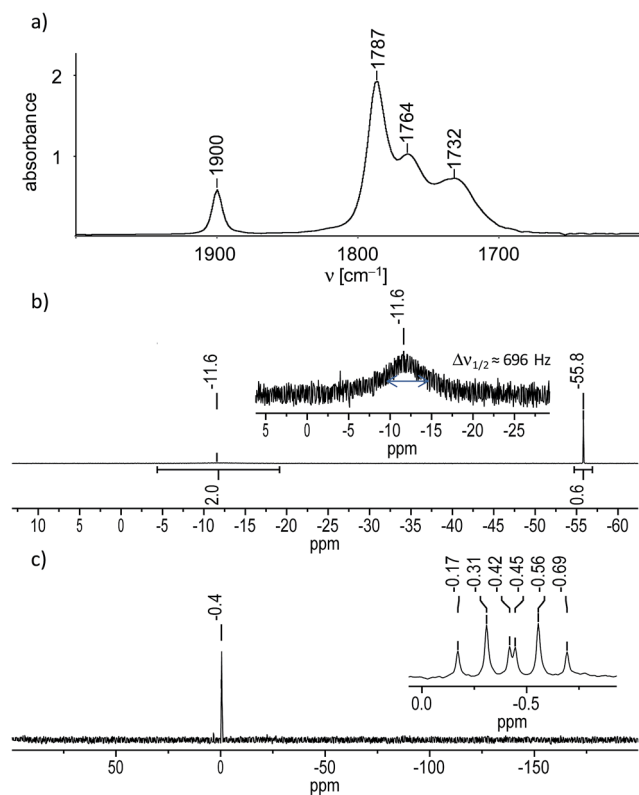
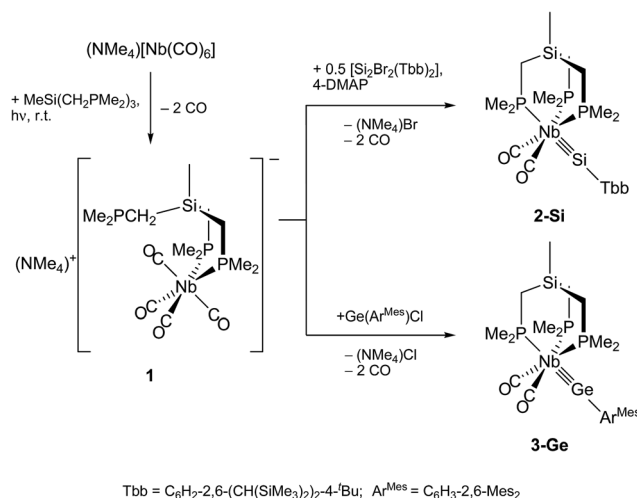


Fig. 1 (a) FT-IR spectrum of **1** in THF in the range of 2000–1600 cm^{-1} . (b) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in benzene- d_6 ; an enlarged excerpt with the broad signal at $\delta = -11.6$ ppm is shown in the inset. (c) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** in 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 silyldiyne complex **2-Si** and the germyldiyne 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 germylydine 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 metallogermylene 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 stannylydine 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 stannylydine 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 ^1H 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 $[\text{Cp}(\text{CO})_3\text{M}-\text{SnR}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{Ar}^{\text{Mes}}, \text{Ar}^{\text{Trip}}, \text{Ar}^{\text{Triip}} = \text{C}_6\text{H}_3-2,6\text{-Trip}_2, \text{Trip} = \text{C}_6\text{H}_2-2,4,6\text{-iPr}_3$),¹⁷ $[\text{Cp}(\text{CO})_2\text{Fe}-\text{SnR}]$ ($\text{R} = \text{Ar}^{\text{Dipp}}, \text{Ar}^{\text{Triip}}, \text{Ar}^{\text{Dipp}} = \text{C}_6\text{H}_3-2,6\text{-Dipp}_2, \text{Dipp} = \text{C}_6\text{H}_3-2,6\text{-iPr}_2$)¹⁸ or $[\text{Cp}^*(\text{CO})_3\text{W}-\text{Sn}(\text{IDipp})]^+$ ($\text{IDipp} = \text{C}[\text{N}(\text{Dipp})\text{CH}]_2, \text{Dipp} = \text{C}_6\text{H}_3-2,6\text{-iPr}_2$)²⁰ into terminal stannylydine 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 Nb≡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 tetrylydine complexes **2-Si**, **3-Ge** and **3-Sn** were characterized by elemental analyses, IR spectroscopy and ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ 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 (κ^3 -bonded) tmps ligand, which spans three facial coordination sites with the P–Nb–P bite angles varying in a small range (85.3–87.9°). A view along the Si⋯Nb vector reveals that the CH₂ groups connecting the bridgehead Si atom with the P donors are twisted out creating a local C₃ 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 tetrylydine 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),¹⁹ 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).²⁰ 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).²¹

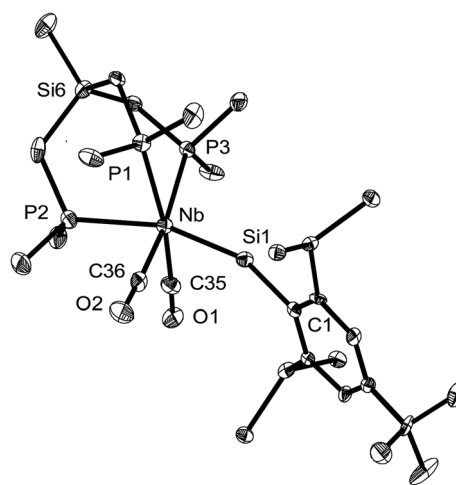
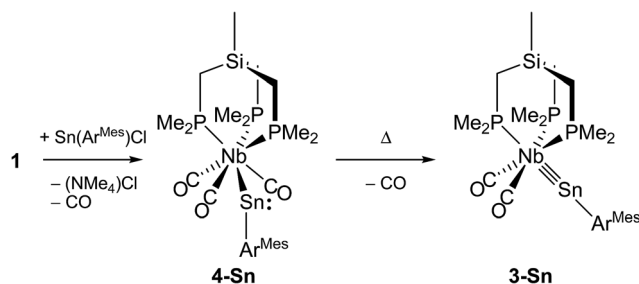


Fig. 2 DIAMOND plot of the molecular structure of the silylydine complex **2-Si** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and the methyl groups of the C^{2,6}-CH(SiMe₃)₂ substituents were omitted for clarity. Selected bond lengths [pm] and 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 stannylydine complex **3-Sn** via the niobiastannylene **4-Sn**.



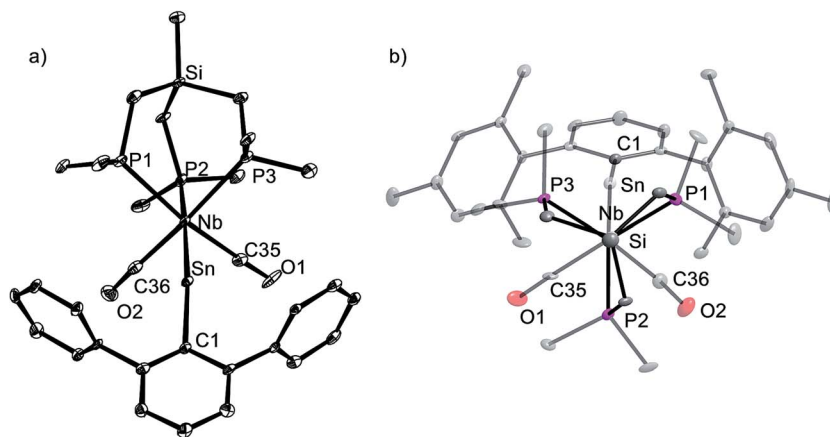


Fig. 3 (a) DIAMOND plot of the molecular structure of the stannylydne complex **3-Sn** (toluene) in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and methyl groups of the Ar^{Mes} substituent were omitted for clarity. Selected bond lengths [pm] and angles [$^\circ$] 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 tmps ligand.

Notably, a comparison of the Nb–E triple bond lengths of **2-Si**, **3-Ge** and **3-Sn** with those of related molybdenum tetrylydne 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;^{1a} $d(\text{Mo}\equiv\text{Ge})$ in $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Ge}-\text{R}]$ (R = C(SiMe₃)₃, Ar^{Mes}, Ar^{Trip}) = 227–228 pm;^{2a,2b,2i,2m} $d(\text{Mo}\equiv\text{Sn})$ in $\text{trans}-[\text{X}(\text{PMe}_2)_2\text{Mo}\equiv\text{Sn}-\text{Ar}^{\text{Mes}}]$ (X = Cl, Br, I) = 248–249 pm)²² reveals that the differences in the M≡E triple bond lengths (E = Si: 10 pm; E = Ge: 8–9 pm; E = 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).²³ A series of additive triple bond radii for most elements of the periodic table have been predicted by P. Pyykkö *et al.*²⁴ 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 tetrylydne ligand is slightly bent at the tetrel center as evidenced by the bonding angle Nb–E–C1 (**2-Si**: 159.2(2) $^\circ$, **3-Ge**: 164.0(1) $^\circ$, **3-Sn**: 160.9(3) $^\circ$). 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 ylydne 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 tmps ligand and the SiMe₃ 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).²⁵ It should be also taken into consideration, that deviation of the M≡E–R atom sequence from linearity does not require a lot of energy, indicating that subtle electronic effects may cause such a bending.²⁶

Further structural information was obtained from the IR and NMR spectra of the tetrylydne 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 cm^{-1} in toluene) than those of **3-Ge** (1868 and 1805 cm^{-1} in toluene), which suggests that the stannylydne ligand SnAr^{Mes} has a higher σ -donor/ π -acceptor ratio than the germylydne ligand GeAr^{Mes} . Notably, the $\nu(\text{CO})$ bands of **2-Si** appear also at lower wavenumbers (1855 and 1790 cm^{-1} in toluene) than those of **3-Ge**. This shift can be

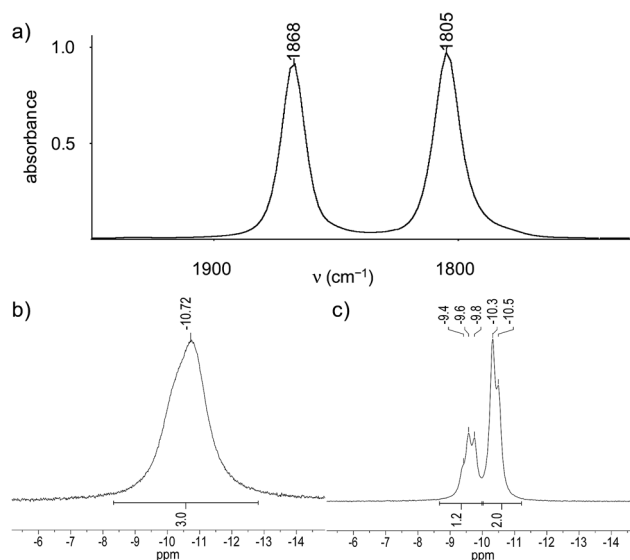


Fig. 4 (a) IR $\nu(\text{CO})$ absorption bands of the germylydne complex **3-Ge** in toluene. (b) $^{31}\text{P}\{^1\text{H}\}$ NMR signal of the germylydne complex **3-Ge** in $\text{THF}-d_8$ at 283 K. (c) $^{31}\text{P}\{^1\text{H}\}$ NMR signals of the germylydne complex **3-Ge** in $\text{THF}-d_8$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



rationalized with the stronger +I effect of the Tbb substituent, leading to a higher σ -donor/ π -acceptor ratio of the silyldiylidene ligand SiTbb than that of the germyldiylidene ligand GeAr^{Mes}. 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 Nb($d\pi$) \rightarrow CO(π^*) backbonding. Additional evidence for a strong Nb($d\pi$) \rightarrow CO(π^*) 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).²⁷ The number and relative intensity of the NMR signals indicate an averaged C_s symmetry of the tetryldiylidene complexes in solution and a rapid rotation of the tetrel-bonded aryl group about the E-C_{aryl} bond. The signals of all nuclei directly attached to the quadrupolar ^{93}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 Nb \equiv 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 SiMe₃ 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}P nuclei ($^2J(^{29}\text{Si}, ^{31}\text{P}) = 9.7$ Hz) (Fig. S16 and S17 (ESI[†])). 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}P NMR signals expected for an AX₂ 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.²⁸ In fact, lowering of the temperature lead to a “decoupling” of the Nb nucleus and allowed to resolve the two ^{31}P NMR signals and their $^2J(\text{P}, \text{P})$ coupling of 20.9 Hz as illustrated by the ^{31}P NMR spectrum of **3-Ge** at 193 K (Fig. 4c). Taking advantage of the same effect, also the ^{119}Sn resonance of **3-Sn**, that was not observable in 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[†])).

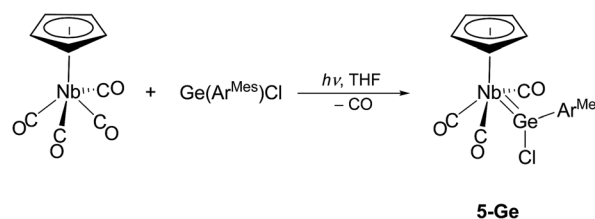
First studies reveal a marked difference in the reactivity of the niobium germyldiylidene complex **3-Ge** and the related molybdenum germyldiylidene complexes [Cp(CO)₂Mo \equiv Ge-R] (R = C(SiMe₃)₃, Ar^{Mes}, Ar^{Triip}). Thus treatment of [Cp(CO)₂Mo \equiv Ge-R] with H₂O or MeOH (one equiv.) in diethyl ether at 0 °C followed by warming to ambient temperature afforded within one hour selectively the brown hydroxy/methoxygermylidene complexes [Cp(CO)₂(H)Mo=Ge(O'R)] (R' = H, Me), which were fully characterized.^{2m} In contrast, no reaction of **3-Ge** with H₂O (one equiv.) was observed in THF even at 60 °C. The inertness of **3-Ge** can be rationalized with the stronger metal-germyldiylidene Nb($d\pi$) \rightarrow GeR(π^*) 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 H₂O addition at the Nb \equiv 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 H₂O 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 Ge(Ar^{Mes})H(OH)₂, as well as a benzene-insoluble brownish part. The unprecedented hydridogermanediol²⁹ was isolated as a pale yellow solid and characterized by IR and ^1H NMR spectroscopy. Its IR spectrum displays two $\nu(\text{OH})$ bands at 3600 and 3398 cm⁻¹ and a characteristic $\nu(\text{Ge-H})$ band at 2104 cm⁻¹, the latter one appearing at a close position to that of GeBr₂HMe₃ ($\nu(\text{Ge-H}) = 2105$ cm⁻¹).³⁰ In the ^1H NMR spectrum a distinctive doublet signal is observed for the Ge(OH)₂ protons at $\delta = 0.91$ ppm and a triplet signal for the Ge-H functionality at $\delta = 5.61$ ppm ($^2J(\text{H}, \text{H}) = 3.5$ Hz) in the integral ratio of 2 : 1. Notably, the Ge-OH protons of the germanetriol Ge(Ar^{Triip})(OH)₃ have a similar chemical shift ($\delta = 0.77$ ppm in CDCl₃).^{29k}

Attempts were also undertaken to access cationic tetryldiylidene complexes. For this purpose, [CpNb(CO)₄]³¹ was prepared using a slightly modified procedure³² and irradiated in THF with a high-power blue light LED ($\lambda = 465$ nm) in the presence of one equivalent of Ge(Ar^{Mes})Cl. IR monitoring of the reaction revealed a quite selective decarbonylation leading to the chlorogermlylidene 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 germyldiylidene complex cation [Cp(CO)₃Nb \equiv GeAr^{Mes}]⁺ were not successful so far. For example, no reaction of **5-Ge** with Na[B(Ar^F)₄] (Ar^F = C₆H₃-3,5-(CF₃)₂) was observed in C₆H₅F 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°). The symmetry plane passes through the atoms Nb, Ge, C1 and Cl, and bisects the CpNb(CO)₃ fragment and the central ring of the *m*-terphenyl substituent.

The germylidene ligand adopts an upright conformation, with the Ar^{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 chlorogermlylidene complex **5-Ge**.



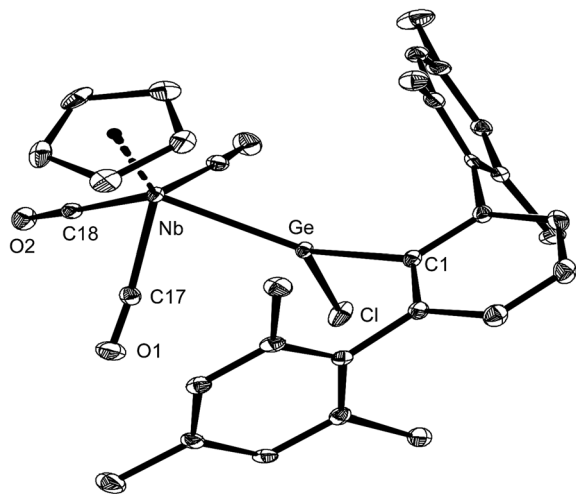


Fig. 5 DIAMOND plot of the molecular structure of **5-Ge** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K, and hydrogen atoms were omitted for clarity. Selected bond lengths [pm] and angles [°]: Nb–Ge 251.78(6), Ge–C1 196.2(4), Ge–Cl 219.1(1), Nb–C17 207.4(3),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

($d(\text{Nb-Ge}) = 267.3 \text{ pm}$)²⁰ 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_{aryl} angle (141.4(1)°) being much larger than the C_{aryl}–Ge–Cl angle (99.8(1)°). This distortion can be attributed to the large steric demand of the Ar^{Mes} substituent and the low tendency of germanium for isovalent hybridization.^{1a,1b,2f,3d} The Ge–Cl bond of **5-Ge** (219.1(1) pm) compares well with that of Ge(Ar^{TRIP})Cl (220.3(2) pm),³³ but is considerably shorter than those of chlorogermylidene complexes containing electron-rich metal centers, such as [(dmpe)₂Fe=Ge(Ar^{Mes})Cl] ($d(\text{Ge-Cl}) = 232.2(1) \text{ pm}$),⁵ [(PMe₃)₃Ni=Ge(Ar^{Mes})Cl] ($d(\text{Ge-Cl}) = 230.03(8) \text{ pm}$)⁶ or [(PMe₃)₃Pd=Ge(Ar^{Mes})Cl] ($d(\text{Ge-Cl}) = 227.3(1) \text{ pm}$),⁶ 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 cm⁻¹, as expected for a Nb(CO)₃ fragment with local C_s symmetry, which are assigned to the A' (all three CO modes in phase), A' (two CO_{lat} modes in phase; CO_{diag} mode out-of-phase) and A'' symmetric (two CO_{lat} 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)₃THF] ($\nu(\text{CO})$ in THF = 1961, 1840 cm⁻¹)³¹ or [CpNb(CO)₃PEt₃] ($\nu(\text{CO})$ in THF = 1953, 1850 cm⁻¹),^{28b} but appear at roughly the same position as those of [CpNb(CO)₃N₂] ($\nu(\text{CO})$ in *n*-heptane = 1991, 1905 cm⁻¹)³⁴ suggesting a similar σ -donor/ π -acceptor ratio of the germylidene GeAr^{Mes}Cl and the N₂ ligand. The ¹H and ¹³C{¹H} NMR spectra also confirm the C_s symmetry of **5-Ge** in solution. Rotation of the *m*-terphenyl substituent about the Ge–C_{aryl} bond occurs fast on the NMR

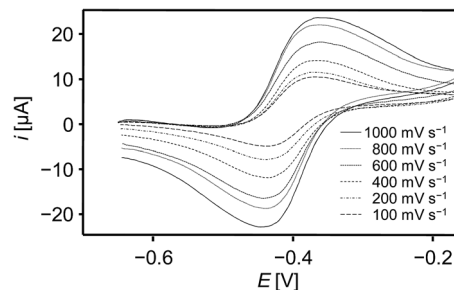


Fig. 6 Single-scan cyclic voltammograms of the reversible one-electron oxidation of **3-Ge** at different scan rates in THF at $-11 \text{ }^\circ\text{C}$ (supporting electrolyte: [NBu₄][PF₆] (0.1 M); reference electrode: 0.004 M [Fe(C₅Me₅)₂]^{+1/0}/0.1 M [NBu₄][PF₆]/THF).

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

Electrochemical studies

Electrochemical studies of the tetrylidyne 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 germylidene complex **3-Ge** are electrochemically reversible occurring at a half wave potential ($E_{1/2}$) of -2.612 mV and -405 mV vs. the dmfc^{+1/0} redox couple (dmfc = decamethylferrocene), respectively (Fig. 6).³⁵

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** ($2: E_{\text{pa}} + E_{\text{pc}}/2 = -468 \text{ mV}$, **3-Sn**: $E_{\text{pa}} + E_{\text{pc}}/2 = -435 \text{ mV}$ (scan rate = 100 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 CoCp₂ in DME = -740 mV) was observed in fluorobenzene even at $70 \text{ }^\circ\text{C}$, whereas an instantaneous oxidation of **3-Ge** occurred upon treatment with one equivalent of [Fe(η⁵-C₅Me₅)₂][B(Ar^F)₄] in fluorobenzene solution at $-30 \text{ }^\circ\text{C}$. Unfortunately, attempts to isolate the putative germylidene complex radical cation [(κ³-tmpe)(CO)₂-Nb(GeAr^{Mes})⁺] failed so far.³⁶ Notably, the redox potential for the one-electron oxidation of **3-Ge** is slightly lower than that of the molybdenum tetrylidyne complexes *trans*-[ClMo(PMe₃)₄≡E-Ar^{Mes}] (E = Ge: $E_{1/2}$ in C₆H₅F = -340 mV ; E = Sn: $E_{1/2}$ in THF = -350 mV ; E = Pb: $E_{1/2}$ in THF = -358 mV) verifying the presence of an electron-rich Nb center in **3-Ge**.

Conclusion

The synthesis of the tailor-made carbonyl-niobate (NMe₄) [Nb(CO)₄(κ²-tmpe)] 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(π^*) and metal ($d\pi$) \rightarrow CO(π^*) back bonding. Remarkably, one-electron oxidation and reduction of the germlydene complex **3-Ge** are electrochemically reversible.

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