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Triple bonds of niobium with silicon, germaniun and tin: the tetrylidyne complexes [(κ^3-tmps)(CO)$_2$Nb≡E–R] (E = Si, Ge, Sn; tmps = MeSi(CH$_2$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 (NMe$_4$)[Nb(CO)$_4$(κ^2-tmps)] (**1**) (tmps = MeSi(CH$_2$PMe$_2$)$_3$) with a suitable organotetrel(II)halide. Compound **1** was obtained from (NMe$_4$)[Nb(CO)$_6$] and the triphosphane tmps by photodecarbonylation. Reaction of **1** with the disilene *E*-Tbb(Br)Si=Si(Br)Tbb in the presence of 4-dimethylaminopyridine afforded selectively the red-brown silylidyne complex [(κ^3-tmps)(CO)$_2$Nb≡Si–Tbb] (**2-Si**, Tbb = 4-*tert*-butyl-2,6-bis(bis(trimethylsilyl)methyl)phenyl). Similarly, treatment of **1** with E(Ar^{Mes})Cl (E = Ge, Sn; Ar^{Mes} = 2,6-mesitylphenyl) afforded after elimination of (NMe$_4$)Cl and two CO ligands the deep magenta colored germylidyne complex [(κ^3-tmps)(CO)$_2$Nb≡Ge–Ar^{Mes}] (**3-Ge**), and the deep violet, light-sensitive stannylidyne complex [(κ^3-tmps)(CO)$_2$Nb≡Sn–Ar^{Mes}] (**3-Sn**), respectively. Formation of **3-Sn** proceeds *via* the niobiastannylene [(κ^3-tmps)(CO)$_3$Nb–SnAr^{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(Nb–Si) = 232.7(2) pm; d(Nb–Ge) = 235.79(4) pm; d(Nb–Sn) = 253.3(1) pm) reported to date. Reaction of **3-Ge** with a large excess of H$_2$O afforded upon cleavage of the Nb–Ge triple bond the hydridogermanediol Ge(Ar^{Mes})H(OH)$_2$. Photodecarbonylation of [CpNb(CO)$_4$] (Cp = η^5-C$_5$H$_5$) in the presence of Ge(Ar^{Mes})Cl afforded the red-orange chlorogermylidene complex [Cp(CO)$_3$Nb=Ge(Ar^{Mes})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.

Introduction

Complexes of the general formula [L$_n$M≡E–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 M≡E bond.[1–4] Isolation of these compounds is very challenging and requires specific stereo-electronic properties of the metal fragment L$_n$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 cyclodimerisation or unintentional intra- or intermolecular σ-bond activations destroying the M≡E–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. 1*c* and 5) and even group 10 metals[6] 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

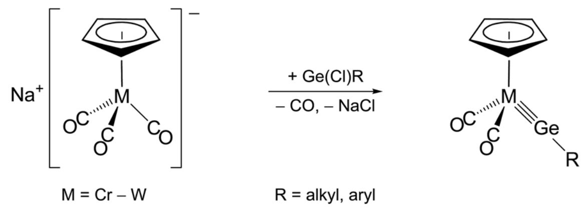
M≡E functionality. Group 5 metal complexes featuring a triple bond to the heavier tetrels (E = Si–Pb) are presently not known, and even compounds with a M═E double bond are very scarce and poorly characterized illustrating the challenge to make such compounds.[7] We decided to address this issue, and present herein a systematic, efficient approach to the first complexes containing Nb≡E (E = Si–Sn) triple bonds.

Results and discussion

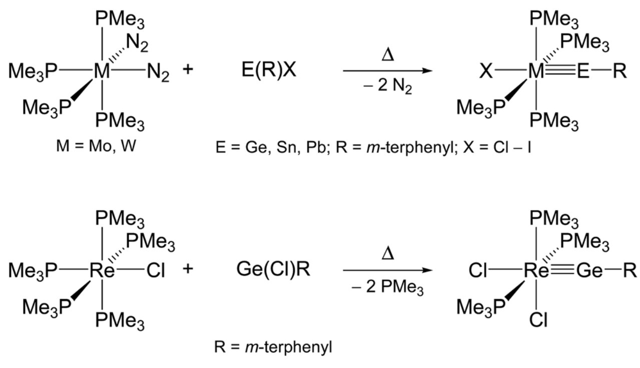
Two methods have been employed so far for the formation of transition metal-tetrel (Si–Pb) triple bonds. The first method, abbreviated as the "salt elimination method", involves a substitution reaction of a suitable anionic 18 VE metal complex with an organotetrel(II) halide, as exemplified by the synthesis of Cp-substituted group 6 metal tetrylidyne complexes (Scheme 1).[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 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).[2f,2g,2l,3a,4a,4b]

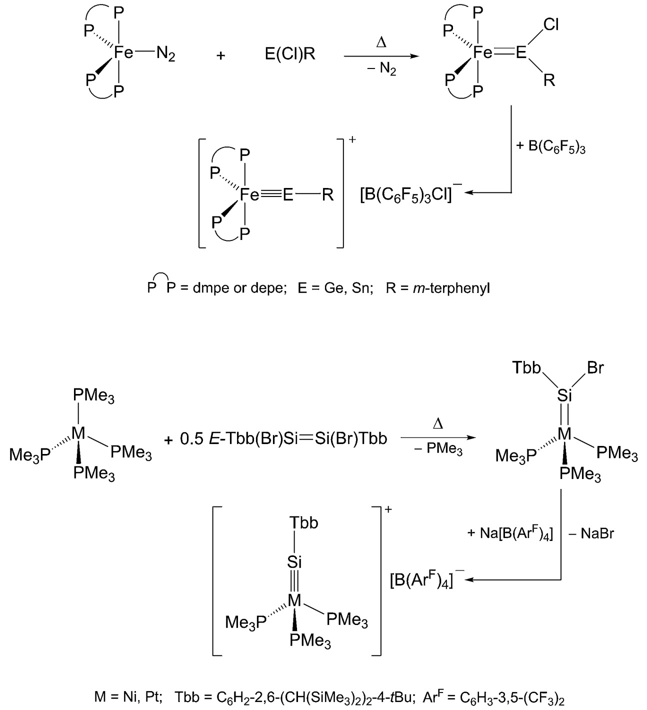
Alternatively, haloylidene complexes are initially obtained by this method, which are subsequently converted to cationic ylidyne complexes by halide abstraction. Examples demonstrating this reaction path include the preparation of group 8 and 10 ylidyne complexes (Scheme 3).[5,6]



Scheme 1 Preparation of half-sandwich group 6 metal germylidyne 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 $[Nb(CO)_6]^-$ was chosen. For this purpose the canary yellow salts $(NR_4)[Nb(CO)_6]$ (R = Me, Et) were prepared, following the method developed by J. E. Ellis *et al.*[9] However, these compounds proved to be unreactive towards the *m*-terphenyltetrel(II)halides $E(Ar^{Mes})Cl$ (E = Ge, Sn; Ar^{Mes} = 2,6-mesitylphenyl; mesityl (Mes) = 2,4,6-trimethylphenyl).[10] For example, IR monitoring of the reaction of $(NEt_4)[Nb(CO)_6]$ with $Ge(Ar^{Mes})Cl$ 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 $[Nb(CO)_6]^-$. 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 $[Nb(CO)_4L_2]^-$ (L_2 = bidentate di- or oligo-arylphosphane ligand) have been accessed from $[Nb(CO)_6]^-$ 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 $MeSi(CH_2PMe_2)_3$ (tmps).[12]

Photolysis of $(NMe_4)[Nb(CO)_6]$ was carried out in the presence of one equivalent of tmps in THF at room temperature. A high-power blue light LED (λ = 465 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 $[Nb(CO)_6]^-$ (λ_{max} = 440 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 $[\mathrm{Nb(CO)_4}(\kappa^2\text{-tmps})]^-$ proceeding *via* the pentacarbonyl intermediate $[\mathrm{Nb(CO)_5}(\kappa^1\text{-tmps})]^-$ (ν(CO) in THF: 1966 (m), 1821 (vs) cm^{-1}). After work-up the salt $(\mathrm{NMe_4})[\mathrm{Nb(CO)_4}(\kappa^2\text{-tmps})]$ (**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 tetrahydrofurane (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}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. The IR spectrum of **1** in THF displays four ν(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 M(CO)$_4$ fragment.[14] All ν(CO) bands of **1** are shifted to lower frequencies than those of $[\mathrm{Nb(CO)_4(Ph_2PCH_2CH_2PPh_2)}]^-$ (ν(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 Nb(dπ) → CO(π*) 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}P{^{1}H} NMR spectrum of **1** displays a sharp singlet for the ^{31}P nucleus of the pendant CH$_2$PMe$_2$ arm, which appears at almost the same position ($\delta(\mathrm{P_A}) = -55.8$ ppm in benzene-d_6) as that of the non-coordinated ("free") tmps (δ(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 ($\delta(\mathrm{P_B}) = -11.6$ 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 ($Q = -0.32 \times 10^{-28}$ m^2; $I = 9/2$, 100% natural abundance) and its effect on the relaxation time.[15] Further structural information was provided by the ^{29}Si{^{1}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 ($^2J(\mathrm{Si,P_A}) = 14.7$ Hz, $^2J(\mathrm{Si,P_B}) = 8.2$ 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.

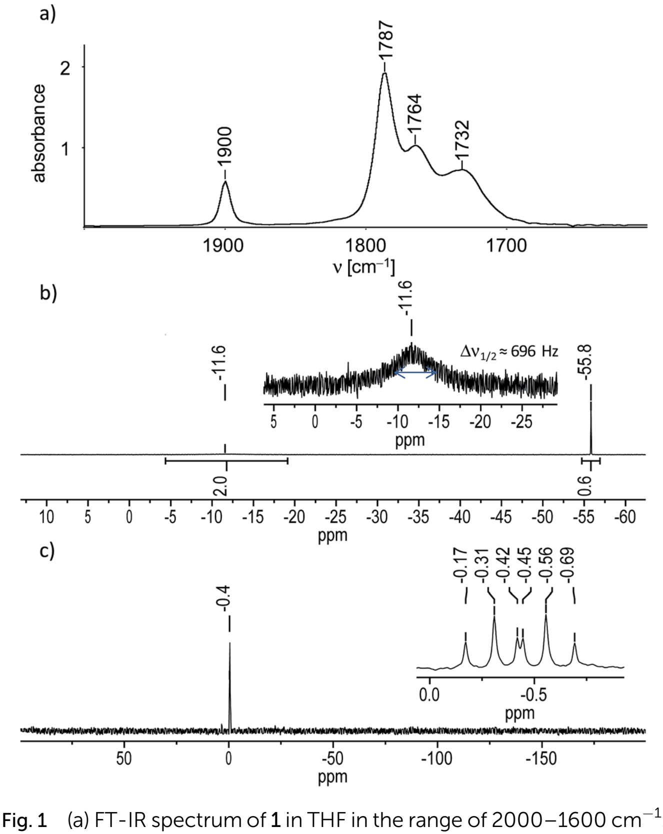
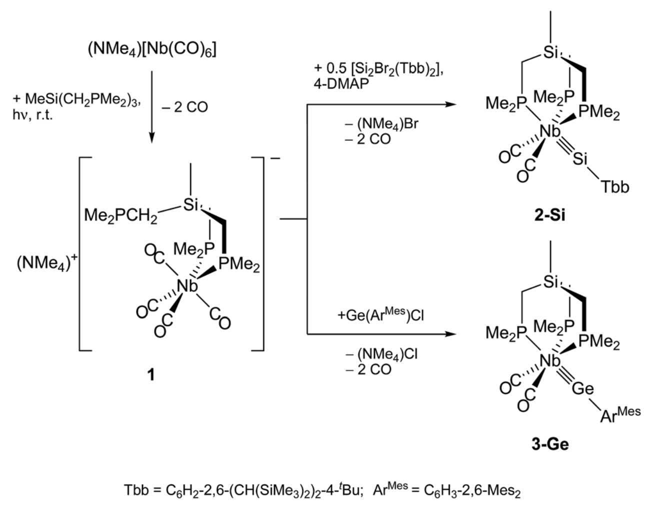


Fig. 1 (a) FT-IR spectrum of **1** in THF in the range of 2000–1600 cm^{-1}. (b) ^{31}P{^{1}H} NMR spectrum of **1** in benzene-d_6; an enlarged excerpt with the broad signal at $\delta = -11.6$ ppm is shown in the inset. (c) ^{29}Si{^{1}H} NMR spectrum of **1** in THF-d_8; an enlarged excerpt with the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

Complex **1** was found to be a very suitable nucleophile for the formation of Nb≡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)Tbb[16] 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 ((NMe$_4$)Br). IR monitoring revealed a complete and selective conversion to the silylidyne complex $[(\kappa^3\text{-tmps})(\mathrm{CO})_2\mathrm{Nb{\equiv}Si{-}Tbb}]$ (**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



Tbb = C$_6$H$_2$-2,6-(CH(SiMe$_3$)$_2$)$_2$-4-^{t}Bu; Ar^{Mes} = C$_6$H$_3$-2,6-Mes$_2$

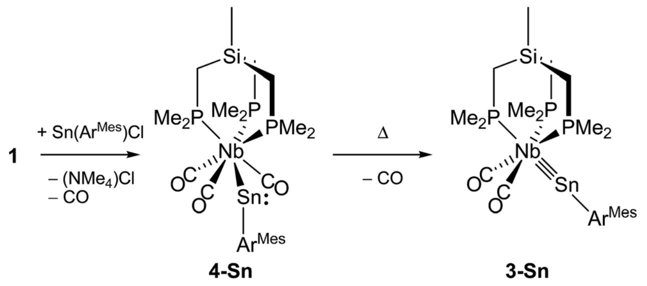
Scheme 4 Synthesis of the niobium silylidyne complex **2-Si** and the germylidyne complex **3-Ge**.

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 Ge(Ar^{Mes})Cl in toluene at −40 °C followed by warming to room temperature afforded rapidly and selectively the germylidyne complex [(κ^3-tmps)$(CO)_2$Nb≡Ge–Ar^{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 [(κ^3-tmps)$(CO)_3$Nb–GeAr^{Mes}] could be obtained during IR monitoring of the reaction of **1** with Ge(Ar^{Mes})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 Sn(Ar^{Mes})Cl with **1** in toluene afforded after stirring at ambient temperature the brick-red metallostannylene [(κ^3-tmps)$(CO)_3$Nb–SnAr^{Mes}] (**4-Sn**) with a small amount of the stannylidyne complex [(κ^3-tmps)$(CO)_2$Nb≡SnAr^{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}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 metallostannylenes. In fact previous attempts to transform the metallostannylenes [Cp$(CO)_3$M–SnR] (M = Cr, Mo, W; R = Ar^{Mes}, Ar^{Trip}; Ar^{Trip} = C_6H_3-2,6-$Trip_2$, Trip = C_6H_2-2,4,6-iPr_3),[17] [Cp$(CO)_2$Fe–SnR] (R = Ar^{Dipp}, Ar^{Trip}; Ar^{Dipp} = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-iPr_2)[18] or [Cp*$(CO)_3$W–Sn(IDipp)]$^+$ (Idipp = C[N(Dipp)CH]$_2$, Dipp = C_6H_3-2,6-iPr_2)[2n] 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 Nb≡Sn triple bond resulting from the higher energy and larger radial extension of the d orbitals, which are engaged in the Nb(dπ) → SnR(π*) back bonding, may be also a driving force for the reaction.



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

The tetrylidyne complexes **2-Si**, **3-Ge** and **3-Sn** were characterized by elemental analyses, IR spectroscopy and ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{29}Si{^{1}H} and ^{119}Sn{^{1}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 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(Nb–Si)$_{mean}$ 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(Nb–Ge)$_{mean}$ = 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(Nb–Sn)$_{mean}$ 282.9 pm).[21]

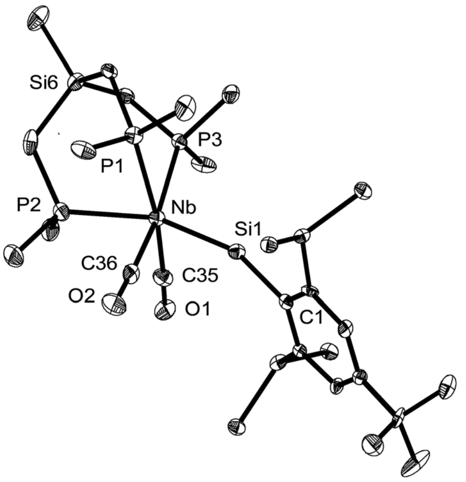


Fig. 2 DIAMOND plot of the molecular structure of the silylidyne complex **2-Si** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and the methyl groups of the $C^{2,6}$–CH$(SiMe_3)_2$ substituents were omitted for clarity. Selected bond lengths [pm] 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).

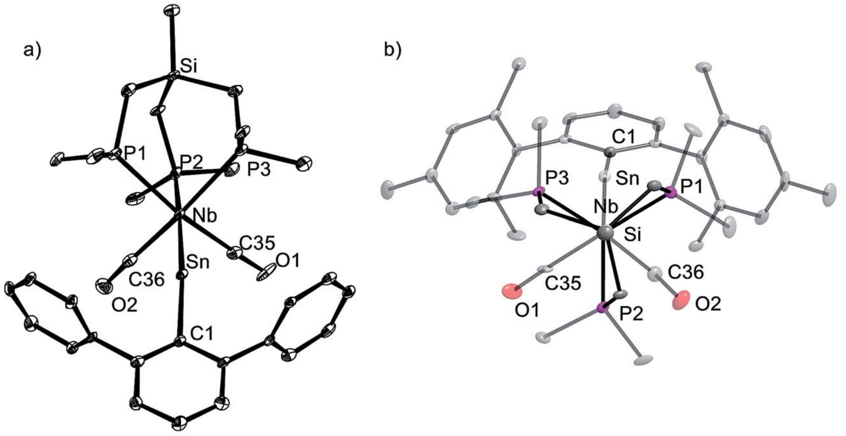


Fig. 3 (a) DIAMOND plot of the molecular structure of the stannylidyne complex **3-Sn** (toluene) in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K. Hydrogen atoms and methyl groups of the Ar^{Mes} substituent were omitted for clarity. Selected bond lengths [pm] and 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 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 tetrylidyne complexes (*e.g.* $d(\text{Mo}{\equiv}\text{Si})$ in $[\text{Cp(CO)}_2\text{Mo}{\equiv}\text{Si–Ar}^{\text{Trip}}]$ = 222.41(7) pm;[1a] $d(\text{Mo}{\equiv}\text{Ge})$ in $[\text{Cp(CO)}_2\text{Mo}{\equiv}\text{Ge–R}]$ (R = $C(SiMe_3)_3$, Ar^{Mes}, Ar^{Trip}) = 227–228 pm;[2a,2b,2i,2m] $d(\text{Mo}{\equiv}\text{Sn})$ in *trans*-$[\text{X(PMe}_4)\text{Mo}{\equiv}\text{Sn–Ar}^{\text{Mes}}]$ (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 ($d(\text{Nb}{\equiv}\text{E})_{\text{calc}}$ = Si: 218 pm, Ge: 230 pm, Sn: 248 pm).

In all complexes the tetrylidyne ligand is slightly bent at the tetrel 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 tmps ligand and the $SiMe_3$ 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).[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 tetrylidyne complexes. The IR spectra of **2-Si**, **3-Ge** and **3-Sn** display two ν(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 $M(CO)_2$ fragment (Fig. 4a). The ν(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 stannylidyne ligand $SnAr^{Mes}$ has a higher σ-donor/π-acceptor ratio than the germylidyne ligand $GeAr^{Mes}$. Notably, the ν(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

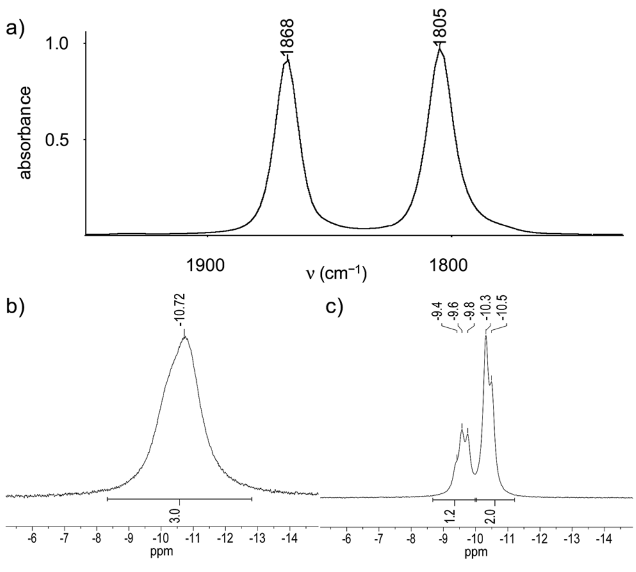


Fig. 4 (a) IR ν(CO) absorption bands of the germylidyne complex **3-Ge** in toluene. (b) $^{31}P\{^1H\}$ NMR signal of the germylidyne complex **3-Ge** in THF-d_8 at 283 K. (c) $^{31}P\{^1H\}$ NMR signals of the germylidyne complex **3-Ge** in THF-d_8 at 193 K.

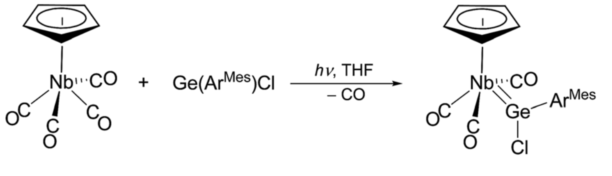
rationalized with the stronger +I effect of the Tbb substituent, leading to a higher σ-donor/π-acceptor ratio of the silylidyne ligand SiTbb than that of the germylidyne ligand GeAr^{Mes}. The low-frequency position of the ν(CO) bands of **2-Si**, **3-Ge** and **3-Sn** suggests the presence of an electron-rich Nb center that is engaged in strong Nb(dπ) → CO(π*) backbonding. Additional evidence for a strong Nb(dπ) → CO(π*) backbonding is provided by the $^{13}C\{^1H\}$ NMR spectra, which all display a broad CO signal at even lower field ($\delta_{CO} = 238.7$ ppm (**2-Si**), 239.2 ppm (**3-Ge**), 238.9 ppm (**3-Sn**)) than that of **1** ($\delta_{CO} = 226.5$ ppm).[27] 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$_{aryl}$ 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 $^{29}Si\{^1H\}$ NMR spectrum of **2-Si** displays at 298 K a very broad signal ($\Delta\nu_{1/2}$ = 130 Hz) for the Nb≡Si nucleus at $\delta = 267.8$ ppm, for which the $^2J(^{29}Si,^{31}P)$ coupling could not be resolved. In comparison, the remote positioned bridgehead Si atom of the tmps ligand and the 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}P nuclei ($^2J(^{29}Si,^{31}P) = 9.7$ Hz) (Fig. S16 and S17 (ESI†)). Similarly, the $^{31}P\{^1H\}$ 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 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.[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(P,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 germylidyne complex **3-Ge** and the related molybdenum germylidyne complexes [Cp(CO)$_2$Mo≡Ge–R] (R = C(SiMe$_3$)$_3$, Ar^{Mes}, Ar^{Trip}). Thus treatment of [Cp(CO)$_2$Mo≡Ge–R] with H$_2$O 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(OR′)R] (R′ = H, Me), which were fully characterized.[2m] In contrast, no reaction of **3-Ge** with H$_2$O (one equiv.) was observed in THF even at 60 °C. The inertness of **3-Ge** can be rationalized with the stronger metal-germylidyne Nb(dπ) → 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 H$_2$O addition at the Nb≡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 H$_2$O addition products. Instead, a continuous decrease in intensity of the two ν(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 hydridogermanediol[29] was isolated as a pale yellow solid and characterized by IR and ^{1}H NMR spectroscopy. Its IR spectrum displays two ν(OH) bands at 3600 and 3398 cm^{-1} and a characteristic ν(Ge–H) band at 2104 cm^{-1}, the latter one appearing at a close position to that of GeBr$_2$HMes (ν(Ge–H) = 2105 cm^{-1}).[30] In the ^{1}H 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(H,H) = 3.5 Hz) in the integral ratio of 2 : 1. Notably, the Ge–OH protons of the germanetriol Ge(Ar^{Trip})(OH)$_3$ have a similar chemical shift ($\delta = 0.77$ ppm in CDCl$_3$).[29k]

Attempts were also undertaken to access cationic tetrylidyne complexes. For this purpose, [CpNb(CO)$_4$][31] was prepared using a slightly modified procedure[32] 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 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 [Cp(CO)$_3$Nb≡GeAr^{Mes}]$^+$ were not successful so far. For example, no reaction of **5-Ge** with Na[B(Ar^F)$_4$] (Ar^F = C$_6$H$_3$-3,5-(CF$_3$)$_2$) was observed in C$_6$H$_5$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°). 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



5-Ge

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

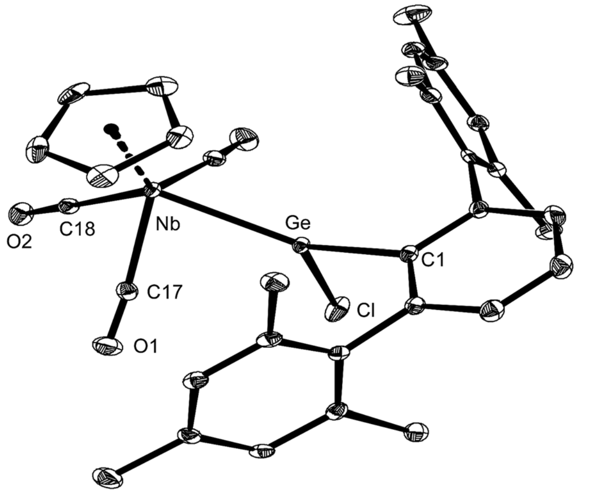


Fig. 5 DIAMOND plot of the molecular structure of **5-Ge** in the solid state. Thermal ellipsoids were set at 30% electronic probability at 100 K, and hydrogen atoms were omitted for clarity. Selected bond lengths [pm] and angles [°]: Nb–Ge 251.78(6), Ge–C1 196.2(4), Ge–Cl 219.1(1), Nb–C17 207.4(3), 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*(Nb–Ge) = 267.3 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,2l,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*(Ge–Cl) = 232.2(1) pm),[5] [$(PMe_3)_3Ni{=}Ge(Ar^{Mes})Cl$] (*d*(Ge–Cl) = 230.03(8) pm)[6] or [$(PMe_3)_3Pd{=}Ge(Ar^{Mes})Cl$] (*d*(Ge–Cl) = 227.3(1) 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 ν(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 ν(CO) absorption bands of **5-Ge** are high-frequency shifted compared to those of [$CpNb(CO)_3THF$] (ν(CO) in THF = 1961, 1840 cm^{-1})[31] or [$CpNb(CO)_3PEt_3$] (ν(CO) in THF = 1953, 1850 cm^{-1}),[28b] but appear at roughly the same position as those of [$CpNb(CO)_3N_2$] (ν(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 N_2 ligand. The ^1H and $^{13}C\{^1H\}$ 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 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.

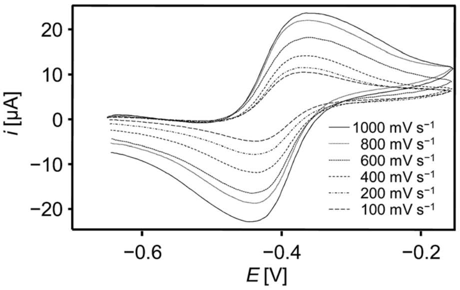


Fig. 6 Single-scan cyclic voltammograms of the reversible one-electron oxidation of **3-Ge** at different scan rates in THF at −11 °C (supporting electrolyte: $[NBu_4][PF_6]$ (0.1 M); reference electrode: 0.004 M $[Fe(C_5Me_5)_2]^{+1/0}$/0.1 M $[NBu_4][PF_6]$/THF).

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 germylidyne 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:** $E_{pa} + E_{pc}/2 = -468$ mV, **3-Sn:** $E_{pa} + E_{pc}/2 = -435$ mV (scan rate = 100 mV s^{-1})). Evidence that the redox process at $E_{1/2} = -405$ 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 $CoCp_2$ in DME = −740 mV) was observed in fluorobenzene even at 70 °C, whereas an instantaneous oxidation of **3-Ge** occurred upon treatment with one equivalent of [$Fe(\eta^5\text{-}C_5Me_5)_2$][$B(Ar^F)_4$] in fluorobenzene solution at −30 °C. Unfortunately, attempts to isolate the putative germylidyne complex radical cation [$(\kappa^3\text{-tmps})(CO)_2Nb(GeAr^{Mes})$]$^+$ 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*-[$ClMo(PMe_3)_4{\equiv}E{-}Ar^{Mes}$] (E = Ge: $E_{1/2}$ in $C_6H_5F = -340$ 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 (NMe_4) [$Nb(CO)_4(\kappa^2\text{-tmps})$] 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 [CpNb(CO)$_4$] (Cp = η^5-C_5H_5) by Ge(Ar^{Mes})Cl afforded also the novel chlorogermylidene complex [Cp(CO)$_3$Nb=Ge(Ar^{Mes})Cl]. The structural, spectroscopic and electrochemical data of the tetrylidyne complexes [(κ^3-tmps)(CO)$_2$Nb≡Si–Tbb] (**2-Si**), [(κ^3-tmps)(CO)$_2$Nb≡Ge–Ar^{Mes}] (**3-Ge**) and [(κ^3-tmps)(CO)$_2$-Nb≡Sn–Ar^{Mes}] (**3-Sn**) suggest the presence of an electron-rich metal center that is engaged into strong metal (dπ) → ER(π*) and metal (dπ) → CO(π*) back bonding. Remarkably, one-electron oxidation and reduction of the germylidyne complex **3-Ge** are electrochemically reversible.

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36 Rapid oxidation of **3-Ge** was evidenced by the immediate disappearance of the green color of the fluorobenzene solution of $[Fe(\eta^5\text{-}C_5Me_5)_2][B(Ar^F)_4]$ at the dropping site and the change of the color of the reaction solution to brown-red. After evaporation of the solvent and washing of the residue with *n*-pentane to remove $[Fe(\eta^5\text{-}C_5Me_5)_2]$, a brown oil was obtained, which displayed in the IR spectrum in THF mainly two intense, broad ν(CO) bands at 1954 and 1889 cm^{-1}. The brown oil contained according to ^{31}P NMR spectroscopy diamagnetic impurities and could not be crystallized.