Triple bonds of niobium with silicon, germanium and tin: the tetrylidyne complexes [(κ^3-tmps)(CO)_2Nb≡E–R] (E = Si, Ge, Sn; tmps = MeSi(CH_2PMe_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_2PMe_2)_3) with a suitable organotetrel(II)halide. Compound 1 was obtained from (NMe_4)[Nb(CO)_4] and the triphosphine 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 silidyne complex [(κ^3-tmps)(CO)_2Si≡Si–Tbb][2-Si, Tbb = 2-tert-butyl-2,6-bis(bis(trimethylsilyl)methyl)phenyl]. Similarly, treatment of 1 with E(ArMes)Cl (E = Ge, Sn; ArMes = 2,6-mesitylphenyl) afforded after elimination of (NMe_4)Cl and two CO ligands the deep magenta colored germylidene complex [(κ^3-tmps)(CO)_2Nb≡Ge–ArMes] (3-Ge), and the deep violet, light-sensitive stannylidyne complex [(κ^3-tmps)(CO)_2Sn≡SnArMes] (3-Sn), respectively. Formation of 3-Sn proceeds via the niobiastannylene [(κ^3-tmps)(CO)_2Nb≡SnArMes] (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_2O afforded upon cleavage of the Nb–Ge triple bond the hydridogermanediol Ge(ArMes)(H(OH))_2. Photodecarbonylation of [CpNb(CO)_4] (Cp = η^5-C_5H_5) in the presence of Ge(ArMes)Cl afforded the red-orange chlorogermidylenediocarbon complex [Cp(CO)]_2Nb≡Ge(ArMes)Cl (5-Ge). The molecular structure of 5-Ge features an upright conformation of the germidylenediocarbon 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 germidylenediocarbon complex 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_nM≡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 stereochemical properties of the metal fragment L_nM as well as a steric protection of the electrophilic tetrel center by a tailormade, bulky substituent R to circumvent a head-to-tail cyclo-dimerisation 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 7,8,15–16 group 8 (ref. 1c and 5) and even group 10 metals8 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...
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. 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(u) halide, as exemplified by the synthesis of Cp-substituted group 6 metal tetrylidyne complexes (Scheme 1). 1,2a,2b,3j,4a

The second method, commonly termed “N2/PMe3 elimination method”, takes advantage of the exchange of labile ligands (mostly N2 or PMe3) in neutral 18 VE metal complexes by suitable organotetrel(u) 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

We decided to apply the first method, given the availability of anionic niobium carbonyl complexes. At first, the homoleptic carbonyl niobate [Nb(CO)6]− was chosen. For this purpose the canary yellow salts (NR4)[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(u) halides E(ArMes)Cl (E = Ge, Sn; ArMes = 2,6-mesitylphenyl; mesityl (Mes) = 2,4,6-trimethylphenyl).10 For example, IR monitoring of the reaction of (NEt4)[Nb(CO)6] with Ge(ArMes)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)4L2]− (L2 = 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(CH2PMe2)3 (tmps).12

Photolysis of (NMes)2[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]− (λmax = 440 nm in CH2Cl2)13 was conceived to be advantageous preventing the formation of insoluble brown decomposition products.
products formed during the photolysis using a high-pressure mercury-lamp.\textsuperscript{11}\textsuperscript{a}

In fact, IR-monitoring of the reaction revealed a slow, but very selective conversion into the tetracarbonyl niobate [Nb(CO)\textsubscript{4}(\kappa\textsuperscript{2}-tmps)-] proceeding via the pentacarbonyl intermediate [Nb(CO)\textsubscript{5}(\kappa\textsuperscript{2}-tmps)-] (r(CO) in THF: 1966 (m), 1821 (vs) cm\textsuperscript{-1}). After work-up the salt [NMMe\textsubscript{4}][Nb(CO)\textsubscript{4}(\kappa\textsuperscript{2}-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 \textsuperscript{1}H, \textsuperscript{13}C{\textsuperscript{1}H}, \textsuperscript{31}P{\textsuperscript{1}H} and \textsuperscript{29}Si{\textsuperscript{1}H} NMR spectroscopy. The IR spectrum of 1 in THF displays four r(CO) absorption bands at 1900, 1787, 1764 and 1732 cm\textsuperscript{-1} (Fig. 1a), the band pattern being typical for octahedral cis-disubstituted metal tetracarbonyl complexes with a local C\textsubscript{2v} symmetry of the M(CO)\textsubscript{4} fragment.\textsuperscript{14} All r(CO) bands of 1 are shifted to lower frequencies than those of [Nb(CO)\textsubscript{4}(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})]- (r(CO) in THF = 1908, 1806, 1782 and 1746 cm\textsuperscript{-1}) or related disubstituted arylphosphane-carbonyl niobates.\textsuperscript{11}\textsuperscript{a} 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(p*) back-bonding and softening of the CO bonds in 1. The NMR spectra of 1 corroborate the presence of an overall C\textsubscript{4v} 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 \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum of 1 displays a sharp singlet for the \textsuperscript{31}P nucleus of the pendant CH\textsubscript{2}PMe\textsubscript{2} arm, which appears at almost the same position (δ(P\textsubscript{A}) = −55.8 ppm in benzene-d\textsubscript{4}) as that of the non-coordinated (“free”) tmps (δ(P\textsubscript{B}) = −55.1 ppm in benzene-d\textsubscript{4}), and a very broad signal for the two symmetry-equivalent Nb-bonded \textsuperscript{31}P nuclei at considerably lower field (δ(P\textsubscript{e}) = −11.6 ppm in benzene-d\textsubscript{4}) (Fig. 1b). The broadness of the second signal (Δν\textsubscript{1/2} (full width at half maximum) = 696 Hz) is caused by the quadrupole moment of the \textsuperscript{93}Nb nucleus (Q = −0.32 × 10\textsuperscript{-28} m\textsuperscript{2}; I = 9/2, 100% natural abundance) and its effect on the relaxation time.\textsuperscript{15} Further structural information was provided by the \textsuperscript{29}Si{\textsuperscript{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 \textsuperscript{31}P nuclei in the integral ratio 1 : 2 (̧J(Si,P\textsubscript{A}) = 14.7 Hz, ̧J(Si,P\textsubscript{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 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=tSi(=Si(=Br)Tbb\textsuperscript{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 ([NMMe\textsubscript{4}]Br). IR monitoring revealed a complete and selective conversion to the silylidene complex [(k\textsuperscript{2}-tmps)(CO)\textsubscript{2}Nb≡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

![Scheme 4](image_url)
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(n) chloride Ge(ArMes)Cl in toluene at −40 °C followed by warming to room temperature afforded rapidly and selectively the germitylidyne complex [[k^3-tmps](CO)₃Nb=Ge–ArMes] (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 [[k^3-tmps](CO)₃Nb–GeArMes] could be obtained during IR monitoring of the reaction of 1 with Ge(ArMes)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(n) chloride Sn(ArMes)Cl with 1 in toluene afforded after stirring at ambient temperature the brick-red metallasotannylene [[k^3-tmps](CO)₃Nb–SnArMes] (4-Sn) with a small amount of the stannyldiyne complex [[k^3-tmps](CO)₃Nb=SnArMes] (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 stannyldiyne 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 metallostannylenes. In fact previous attempts to transform the metallostannylenes [Cp(CO)₂M–SnR] (M = Cr, Mo, W; R = Ar₃Sn, Ar₃Pₜrip, Ar₃P₂rip = C₆H₅–2,6–TriP₂, TriP = C₆H₅–2,4,6–iPr₃) [Cp(CO)₂Sn–SnR] (R = Ar₃Pₜrip, Ar₃P₂rip; Ar₃P₂rip = C₆H₅–2,6–Dipp₂, Dipp = C₆H₅–2,6–iPr₃) or [Cp⁺[C(CO)₃]W–Sn[I(dipp)]⁺ [I(dipp) = C[N(Dipp)CH₂]₂, Dipp = C₆H₅–2,6–iPr₃] into terminal stannyldiyne 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(drr) → SnR(π*) back bonding, may also be a driving force for the reaction.

The tetryldiyne complexes 2-Si, 3-Ge and 3-Sn were characterized by elemental analyses, IR spectroscopy and ¹H, ¹³C{¹H}, ³¹P{¹H}, ²⁹Si{¹H} and ¹¹⁹Sn{¹H} 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 (k^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 is twisted out creating a local C₅ 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 conformations occurs according to NMR spectroscopy leading to averaged C₅ symmetric structures.

The tetryldiyne 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 = 28 structurally characterized complexes = 261.3 pm), and the Nb–Ge bond of 3-Ge (235.7(4) pm) is ca. 31 pm shorter than a Nb–Ge single bond (d(Nb–Ge)mean = 267.3 pm). 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).

![Fig. 2. DIAMOND plot of the molecular structure of the silyldiyne 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 C₂H₆–CH(SiMe₃)₂ substituents were omitted for clarity. Selected bond lengths (pm) and angles (°): Nb–Si=1 232.7(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), C₅₃–C₁ 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).](Image 343x149 to 513x326)
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 \([\text{Cp(CO)}_2\text{Mo} \equiv \text{Si} \equiv \text{Ar}^{\text{Trip}}]\) = 222.41(7) pm; \(d(\text{Mo} \equiv \text{Ge})\) in \([\text{Cp(CO)}_2\text{Mo} \equiv \text{Ge} \equiv R]\) (R = C(SiMe_3)_3, ArMeso, ArTrip) = 227–228 pm; \(d(\text{Mo} \equiv \text{Sn})\) in \(\text{trans-}[\text{X(PMe_4)}\text{Mo} \equiv \text{Sn} \equiv \text{Ar}^{\text{Meso}}]\) (X = Cl, Br, I) = 248–249 pm) reveals that the differences in the M=E triple bond lengths \(E = \text{Si}: 10\text{ pm}; E = \text{Ge}: 8–9\text{ pm}; E = \text{Sn}: 5–6\text{ pm}\) compare reasonably well with the difference (7 pm) of the metallic radii of the two elements \(r_{\text{Nb}} = 147\text{ pm}, r_{\text{Mo}} = 140\text{ pm}\); radii for a coordination number of 12). A series of additive triple bond radii for most elements of the periodic table have been predicted by P. Pykkö et al. 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 \(d(Nb\equiv E)_{\text{calc}} = \text{Si: 218 pm, Ge: 230 pm, Sn: 248 pm}\).

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 sterical 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 \(d(H \cdots H) = 244\text{ pm}\). These contacts are longer than twice the van der Waals radius of hydrogen \(r_{\text{vdW(H)}} = 110\text{ pm}\). 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.

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 \(r(\text{CO})\) 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 \(C_3\) symmetry of the \(\text{M(CO)}_2\) fragment (Fig. 4a). The \(r(\text{CO})\) 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 stannyldiene ligand SnArMeso has a higher \(\sigma\)-donor/\(\pi\)-acceptor ratio than the germyldiene ligand GeArMeso. Notably, the \(r(\text{CO})\) 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
rationalized with the stronger $\pi$ effect of the Tbb substituent, leading to a higher $\sigma$-donor/$\pi$-acceptor ratio of the silylidene ligand SiTbb than that of the germylidene ligand GeArMes. The low-frequency position of the $\nu$(CO) bands of 3-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($\pi^*$) backbonding. Additional evidence for a strong Nb(d$\pi$) $\rightarrow$ CO($\pi^*$) backbonding is provided by the $^{13}$C($^1$H) 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 $^1$H ($\delta_{CO} = 226.5$ ppm).27 The number and relative intensity of the NMR signals indicate an averaged $C_2$ symmetry of the tetracoordinate complexes in solution and a rapid rotation of the tetracoordinate 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($^1$H) 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 $^J$($^3$Si,$^1$P) coupling could not be resolved. In comparison, the remote positioned bridgehead Si atom of the trims 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 $^1$P nuclei ($^J$(Si,$^1$P) = 9.7 Hz) (Fig. S16 and S17 (ESI†)). Similarly, the $^3$P($^1$H) NMR spectra of 2-Si and 3-Ge show only one broad signal at $\delta = -13.0$ ppm ($\Delta\nu_{1/2} = 182$ Hz at 298 K) and $-10.7$ ppm ($\Delta\nu_{1/2} = 187$ Hz at 283 K), respectively, instead of two $^3$P NMR signals expected for an AX$_2$ spin system (Fig. 4b). Broadening 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 leads to a “decoupling” of the Nb nucleus and allowed to resolve the two $^3$P NMR signals and their $^J$(P,P) coupling of 20.9 Hz as illustrated by the $^3$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 germylidene complex 3-Ge and the related molybdenum germylidene complexes [Cp(CO)$_3$Mo=Ge–R] (R = C(SiMe$_3$)$_3$, Ar$_2$Mes, Ar$_2$Trip). Thus treatment of [Cp(CO)$_3$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=GeOR[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-germylidene Nb(d$\pi$) $\rightarrow$ 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 trimts 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 $\nu$(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$_2$Mes)H(OH)$_2$, as well as a benzene-insoluble brownish part. The unprecedented hydridogermylendiole$^{29}$ was isolated as a pale yellow solid and characterized by IR and $^1$H NMR spectroscopy. Its IR spectrum displays two $\nu$(OH) bands at 3600 and 3398 cm$^{-1}$ and a characteristic $\nu$(Ge–H) band at 2104 cm$^{-1}$, the latter one appearing at a close position to that of GeBr$_3$Mes ( $\nu$(Ge–H) = 2105 cm$^{-1}$).20 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 ($^J$(H,H) = 3.5 Hz) in the integral ratio of 2:1. Notably, the Ge–OH protons of the germanetriol Ge(Ar$_2$Mes)H(OH)$_2$ have a similar chemical shift ($\delta = 0.77$ ppm in CD$_2$Cl$_2$).2m

Attempts were also undertaken to access cationic tetrazylidene complexes. For this purpose, [CpNb(CO)$_3$]$^{13}$ 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$_2$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 germylidene complex cation [Cp(CO)$_3$Nb=GeArMes]$^{3+}$ were not successful so far. For example, no reaction of 5-Ge with Na[B(ArF)$_4$] (ArF = C$_6$H$_3$–3,5-(CF$_3$)$_2$) was observed in C$_6$H$_6$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 CpbNb(CO)$_3$ fragment and the central ring of the m-terphenyl substituent.

The germylidene ligand adopts an upright conformation, with the Ar$_2$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...
The Ge–Cl bond of 5-Ge (219.1(1) pm) compares well with that of Ge(Allen)2Cl (220.3(2) pm), but is considerably shorter than those of chlorogermi[3]dienes containing electron-rich metal centers, such as [(dmpe)2Fe(CO)2Cl] (232.2(1) pm) or [(PMe3)3Pd=Ge(AlEt3)Cl] (230.03(8) pm). This distortion can be attributed to the large steric demand of the ArMes substituent and the low tendency of germanium for isovalent hybridization.

The Ge–Cl bond in 5-Ge is 219.1(1) pm, which is significantly shorter than in other complexes containing Ge–Cl bonds. This distortion is attributed to the large steric demand of the ArMes substituent and the low tendency of germanium for isovalent hybridization.

**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 (E1/2) of −2.612 mV and −405 mV vs. the dmfc+/2 redox couple (dmfc = decamethylferrocene), respectively (Fig. 6).

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: Epa = −468 mV, 3-Sn: Epa = −435 mV (scan rate = 100 mV s−1). This suggests that 3-Ge is electrochemically more active than 2-Si and 3-Sn.

**Conclusion**

The synthesis of the tailor-made carbonyl-niobate (NMe4) [Nb(CO)4(k2-tmps)] allowed to explore its reactivity towards the Nb–Ge double bond in 5-Ge. The angles at the Ge atom differ markedly with the Nb–Ge–Caryl angle (141.4(1)°), which is much larger than the Caryl–Ge–Cl angle (99.8(1)°). This distortion can be attributed to the large steric demand of the ArMes substituent and the low tendency of germanium for isovalent hybridization.

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 Caryl 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) but appear at roughly the same position as those of [CpNb(CO)3N2] (ν(CO) in n-heptane = 1991, 1905 cm−1) suggesting a similar σ-donor/π-acceptor ratio of the germi[3]dienes GeArMesCl and the N2 ligand. The 1H and 13C{1H} NMR spectra also confirm the Caryl symmetry of 5-Ge in solution. Rotation of the m-terphenyl substituent about the Ge–Caryl bond occurs fast on the NMR time-scale at ambient temperature leading to an exchange of the two diastereotopic ortho (C1,2) and meta (C1,3) positions of the entantiotopic mesityl substituents. Therefore, only one singlet signal is observed in the 1H NMR spectrum of 5-Ge for the C1,2-bonded methyl groups and C1,3-bonded protons of the mesityl substituents, respectively.
a series of organotetrel(III) 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)] (Cp = η^5-C_5H_5) by Ge(AMe_3)Cl afforded also the novel chlorogermylidene complex [Cp(CO)NbGe(AMe_3)Cl]. The structural, spectroscopic and electrochemical data of the tetrylidyne complexes [(κ^3-tmps)(CO)NbSn–Si-Tbb] (2-Si), [(κ^3-tmps)(CO)NbGe–AMe_3] (3-Ge) and [(κ^3-tmps)(CO)CpNbSn–Sn–AMe_3] (3-Sn) suggest the presence of an electron-rich metal center that is engaged into strong metal (drπ → ER(π^*) and metal (dπ → CO(π^*)) back bonding. Remarkably, one-electron oxidation and reduction of the germylidene complex 3-Ge are electrochemically reversible.

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References


A CSD survey (13.06.17) revealed that only two niobium germyl complexes have been structurally characterized. The Nb–Ge distances range from 260.8 to 271.0 pm, leading to a mean value of 267.3 pm and a median of 270.2 pm for the Nb–Ge single bond length: (a) A. Antiñolo, F. Carrillo-Hermosilla, A. Castel, M. Fajardo, J. Fernández-Baeza, M. Lanfranchi, A. Otero, M. A. Pellinghelli, G. Rima, J. Satgé and E. Villaseñor, Organometallics, 1998, 17, 1523; (b) G. I. Nikonov, A. V. Churakov and M. Y. Antipin, Organometallics, 2003, 22, 2178.


For example quantum chemical studies on the model compounds \( \text{trans-}[\text{Cl}({\text{PH}_3})_4\text{W}=(\text{E})\text{Pb}] \) at the B3LYP/TZVPP(W,E)//6-311G*(C,H,P,Cl) level of theory reveal that the energy required for bending the tetrylidyne ligand up to 20° is rather small (max. 20 kJ mol\(^{-1}\)) and decreases with increasing atomic number of E.


35 All potentials in the text are given vs. the \([\text{Fe}^\text{II-C}_{5}\text{Me}_{5}]^{1+/0}\) redox couple, which was chosen as the reference standard for the CV experiments due to its favorable properties vs. the \([\text{Fe}^\text{II-C}_{5}\text{H}_{5}]^{1+/0}\) redox couple: (a) I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, *J. Phys. Chem. B*, 1999, 103, 6713; (b) J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, 84, 288. For comparison reasons the half-wave potential of the \([\text{Fe}^\text{II-C}_{5}\text{H}_{5}]^{1+/0}\) redox couple was also determined under the same conditions (THF, –11 °C) and found to be +440 mV vs. the \([\text{Fe}^\text{II-C}_{5}\text{Me}_{5}]^{1+/0}\) redox couple.

36 Rapid oxidation of 3-Ge was evidenced by the immediate disappearance of the green color of the fluoro-benzene solution of \([\text{Fe}^\text{II-C}_{5}\text{Me}_{5}]_{2}\text{B}[\text{ArF}]_{4}\) 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 \([\text{Fe}^\text{II-C}_{5}\text{Me}_{5}]_{3}\), a brown oil was obtained, which displayed in the IR spectrum in THF mainly two intense, broad \([\nu(\text{CO})\text{ bands at } 3189\text{ cm}^{-1}\) bands at 1954 and 1889 cm\(^{-1}\). The brown oil contained according to \(^{31}P\) NMR spectroscopy diamagnetic impurities and could not be crystallized.