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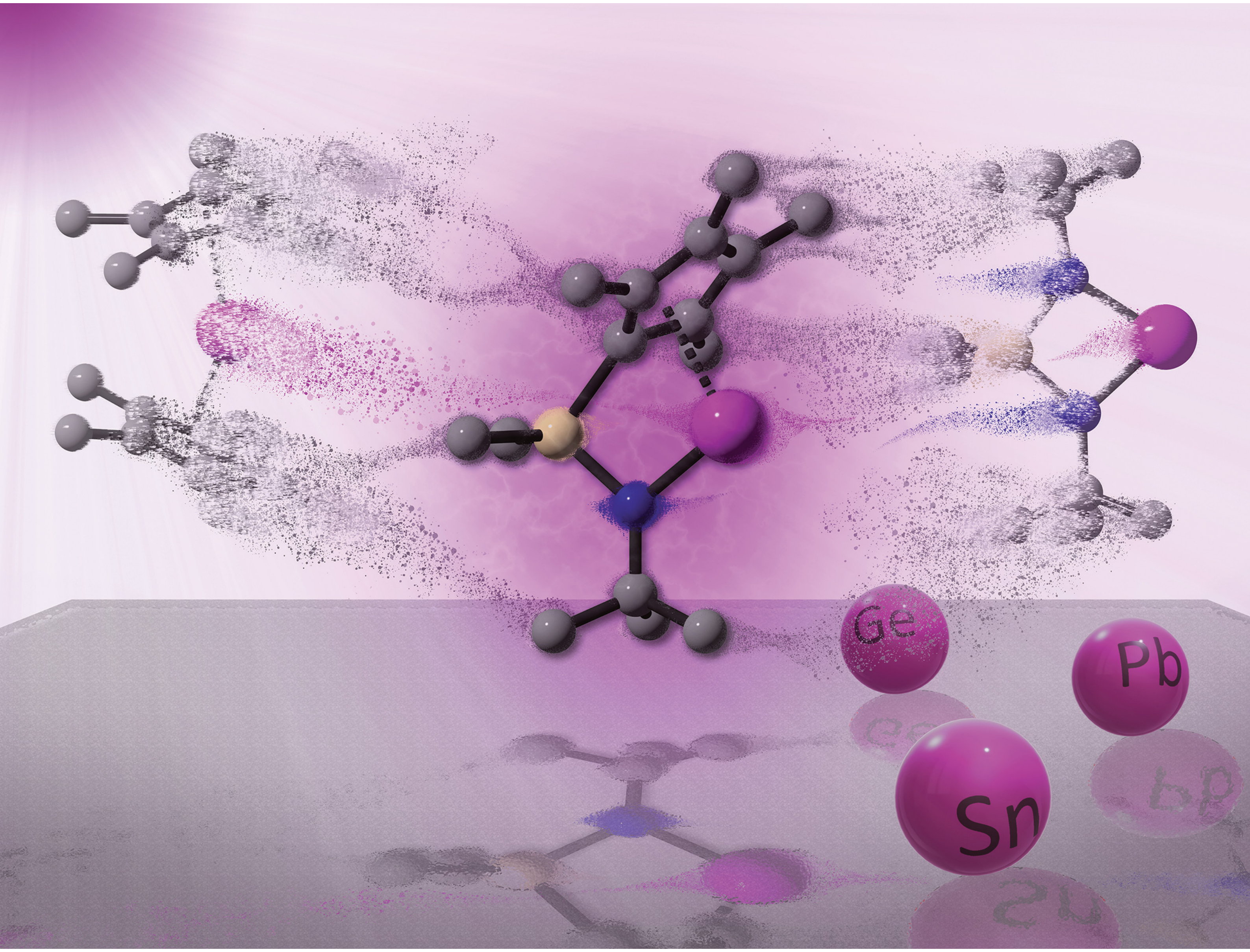

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Heavier N-heterocyclic half-sandwich tetrylenes†

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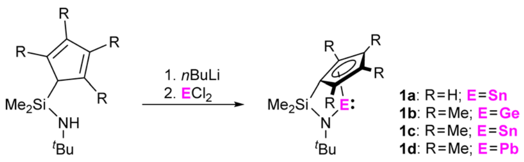
ansa-Half-sandwich complexes of the group 14 elements germanium, tin and lead are reported, which represent a new class of Lewis amphiphilic tetrylenes and bridge the gap between classical N-heterocyclic systems and group 14 metallocenes. These compounds can form complexes both with carbenes and transition metal fragments.

Divalent group 14 compounds with the tetrel element in the oxidation state +II, commonly referred to as tetrylenes, have attracted significant attention for several decades.[1] Among other things, persistent examples of these species have been applied in bond activation processes and as ligands for various metal fragments.[2] The discovery of the first stable singlet carbene dates back to the early work of Wanzlick *et al.* and was later complemented by the first structural authentications of such species by Bertrand *et al.* and Arduengo *et al.*[3] The history of the discovery of the heavier diorgano congeners is a bit more convoluted, as reports of an N-heterocyclic silylene by Denk and West *et al.* in 1994, as well as Lappert *et al.*'s descriptions of bis(trimethylsilyl)methyl and bis(trimethylsilyl)-amido germylenes, stannylenes and plumbylenes in 1973/1974, and Veith's note of an N-heterocyclic stannylene in 1975 are often regarded as the first examples.[4] However, it is worth noting that the description of heavier group 14 metallocenes (tetrelocenes) pre-date those reports in all cases (Cp^*_2Si: Jutzi *et al.*, 1986;[5] Cp_2Ge: Scibelli *et al.*, 1973;[6] Cp_2Sn: Fischer *et al.*, 1956;[7] Cp_2Pb: Fischer *et al.*, 1956[8]), and there can be no doubt that tetrelocenes of the type Cp_2E are also divalent diorgano tetrel(II) species, although their reactivities differ from that of "typical" tetrylenes in some cases.[2b,9] Due to the frontier orbital configuration in singlet tetrylenes, with a lone pair and a vacant orbital of *p* symmetry at the low-valent tetrel atom, tetrylenes can exhibit Lewis amphiphilic character, although the Lewis acidity is sometimes quenched by donor ligands and/or substituents. Tetrelocenes on the other hand, do not exhibit significant σ donor character, but can act as electron acceptors, as highlighted by amine, bipyridine and NHC complexes of stannocenes and plumbocene.[9,10] With the aim to merge the two fields of tetrelocenes and heavier bis(amido)tetrylenes, we investigated the possibility of applying *ansa*-half-sandwich ligands to Ge(II), Sn(II) and Pb(II). These ligands are already quite common in transition metal chemistry, for instance in group 4 complexes,[11] but have not seen much application in main-group chemistry so far.[12] Herein, we report the first heavier N-heterocyclic half-sandwich tetrylenes and reactivity studies of their donor and acceptor behaviour.

Reaction of the dilithiated ligands, bearing a (tetramethyl)-cyclopentadienide and a *tert*-butyl amido substituent, with $GeCl_2$, $SnCl_2$, and $PbCl_2$ resulted in the formation of the corresponding *ansa*-half-sandwich tetrylenes **1a-d** (Scheme 1). Whereas compounds **1b,c** were obtained as orange to red oils, **1a** was isolated in form of yellow crystals and **1d** in form of dark red crystals. **1a-d** were examined by multinuclear NMR spectroscopy, which in case of the tin and lead species, **1a,c,d**, allows for comparison with related di-N-heterocyclic systems and tetrelocenes. In the $^{119}Sn\{^1H\}$ NMR spectrum a signal is observed at −296 ppm for **1a**, and at −315 ppm for **1c**. Quite interestingly, these shifts are positioned between the typical low-field shifted resonances usually observed for di-N-heterocyclic stannylenes, as for instance reported for the structurally closely related Veith stannylene, and related stannocenes, which typically exhibit very upfield-shifted resonances.

This clearly reflects the electronic influence of both substituent sides, as the deshielding of the tetrel atom in tetrylenes is usually associated with a large paramagnetic component to the NMR chemical shift, which relates to the energy gap



Scheme 1 Synthesis of *ansa*-half-sandwich tetrylenes **1a-d**.

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between the lone pair and the vacant p orbital. This contribution is much smaller in tetrelocenes, as the lone pair is quite low in energy due to its high s character. The same phenomenon is observable for plumbylene **1d**, for which a signal in the ^{207}Pb{^{1}H} NMR spectrum is observed at +1562 ppm, which is also located in-between the typical low-field shift range of diamido plumbylenes and high-field shifted resonances of plumbocenes (Fig. 1).

Structural characterization of **1a**,**d** in the solid state by single crystal X-ray diffraction confirms the molecular structures of the compounds and reveals interesting intermolecular interactions (Fig. 2 and Fig. S51, S52, ESI†).[13,14] In both structures, the tetrel atom is bound to the cyclopentadienide group in what might best be perceived as a strongly distorted η^3 to η^5 mode with unequal Sn/Pb–C$^{\mathrm{Cp}}$ bond distances (Sn–C: 249.54(16) to 338.86(18) pm; Pb–C: 249.37(23) to 339.50(21) pm) although the C–C distances within the cyclopentadienyl ring do not display isolated single and double bonds, but are rather relatively uniform, indicating a certain degree of aromaticity (**1a**: 139.71(20) to 143.22(21) pm; **1d**: 139.60(33) to 146.82(28) pm). When interpreting these bonding situations, it must be taken into consideration that the Sn/Pb–Cp interaction is relatively ionic in nature[10c] and that there are significant intermolecular interactions in the solid state (Fig. S51–S52, ESI†). Thus, we believe drawing a circle within the Cp ring is justified. Furthermore, the shorter Sn/Pb–C$^{\mathrm{Cp}}$ contacts are in the same range as the bond lengths found in stannocene, $\mathrm{Cp_2Sn}$, (255.54(7) to 283.79(10) pm)[9] and a related plumbocene, $\mathrm{((Me_2{}^tBuSi)\text{-}Me_4C_5)_2Pb}$, (270.71(44) to 277.30(48) pm).[16] The Sn–N bond length in **1a** is 210.64(12) pm, which is similar to Veith's stannylene (209.1(8) pm),[17] and the Pb–N bond length in **1d** is 221.47(19) to 222.74(23) pm, which is elongated compared to other N-heterocyclic plumbylenes, possessing Pb–N bond lengths between 208.7(5) and 213.6(5) pm.[18] These elongations may result from the formation of polymeric chains in the solid state (Fig. S52, ESI†). Interestingly, such intermolecular interactions in the solid state are common for unsubstituted plumbocenes, but not for decamethylplumbocene or stannocenes.[19]

The C$^{\mathrm{Cp}}$–E–N angle around the tetrel, is 71.1° for **1a** and 70.6° for **1d**, which is similar to other four-membered N-heterocyclic stannylenes[17] and plumbylenes.[20]

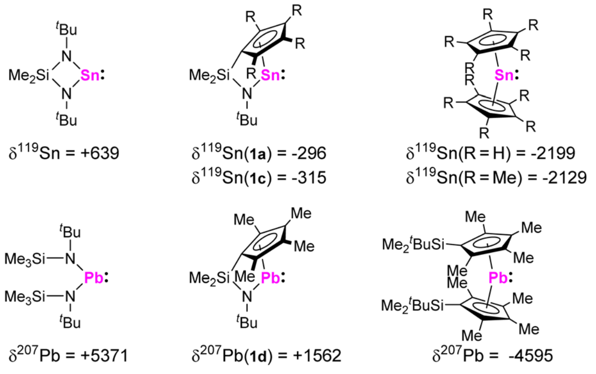

Fig. 1 ^{119}Sn and ^{207}Pb NMR chemical shifts of stannylenes **1a** and **1c**, plumbylene **1d**, and related literature-known compounds.[15]

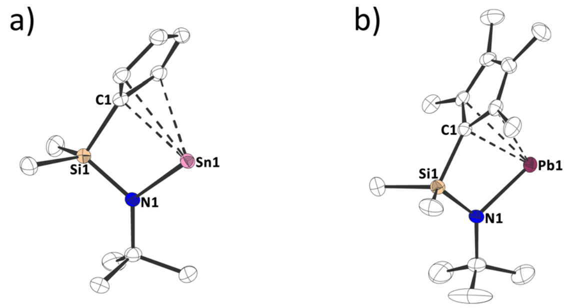

Fig. 2 Molecular structure of (a) **1a** and (b) **1d** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity).

Following the NMR and structural characterizations, we inspected the molecular orbitals of **1a-d** by DFT calculations[14] (PBE0-D3/def2-TZVPP//PBE0-D3/def2-TZVP), which reveals that the orbital configuration is qualitatively identical in all four cases and that the LUMO corresponds to a vacant p orbital with a large coefficient at the central tetrel atom. This is typical for tetrelocenes as well as for "classical" tetrylenes. However, while in many tetrylenes the lone pair at the tetrel atom corresponds to the HOMO, it is energetically located significantly lower in tetrelocenes, due to higher s character. In **1a-d**, the lone pair at the tetrel atom has a comparable shape to that in other N-heterocyclic tetrylenes and corresponds to the HOMO-2/3 (Fig. 3 and Table S1, ESI†).

To study the reactivities of this new class of heavier N-heterocyclic tetrylenes and compare them with "classical" tetrylenes and tetrelocenes, three different reaction types were examined: oxidative additions, electron acceptor behavior (Lewis acidity) and electron donor behavior (Lewis basicity). To investigate oxidative addition reactions, **1a-d** were treated with triethylsilane in toluene-D$_8$, but no reactions were observed even after stirring for 4 h at 333 K. However, **1a**,**c** were found to undergo rapid oxidative addition reactions with diphenyl diselenide, as indicated by ^{119}Sn and ^{77}Se NMR spectroscopy. When solutions of **1a**,**c** in benzene-D$_6$ were treated with equimolar amounts of diphenyl diselenide at ambient conditions, the ^{119}Sn{^{1}H} NMR spectra displayed new signals at −88.6 ppm[21] (**1a**/**2a**) and at −70.5 ppm (**1c**/**2b**). Furthermore, in the ^{77}Se{^{1}H} NMR spectra, signals at 137.8 ppm[21] (**1a**/**2a**) and 120.9 ppm (**1c**/**2b**) were observed, which displayed tin satellites corresponding to $^{1}J_{^{77}\mathrm{Se-Sn}}$ coupling constants of 1627 Hz (**1a**/**2a**) and 1631 Hz (**1c**/**2b**).

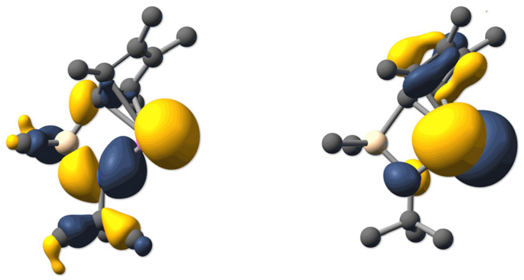

Fig. 3 Kohn–Sham molecular orbital contours of the HOMO-3 (left) and LUMO (right) of germylene **1b** (PBE0-D3/def2-TZVPP//PBE0-D3 def2-TZVP; isovalue 0.04).

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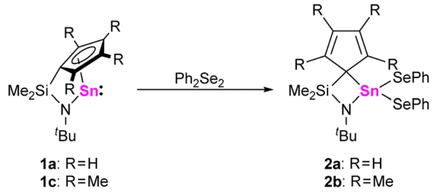
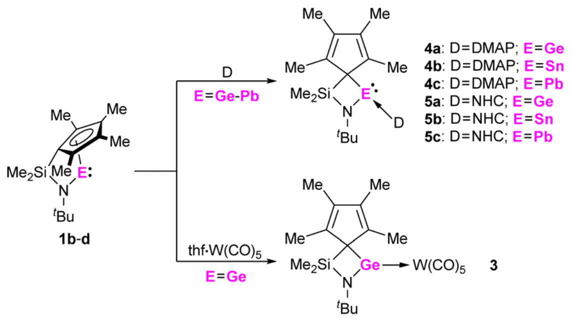


Scheme 2 Reactions of **1a,c** with diphenyl diselenide.

By comparison with related literature known compounds, we tentatively assign these signals to the corresponding bis(phenylseleniumyl)stannanes **2a,b** (Scheme 2). These findings are in line with other N-heterocyclic stannylenes, which give the analogous oxidative addition products.[22,23]

To investigate the Lewis acidity of half-sandwich tetrylenes **1b-d**, we reacted them with 4-(dimethylamino)-pyridine (DMAP) and 1,3-diisopropyl-4,5-dimethyl-imidazolin-2-ylidene (NHC). When mixtures of **1b-d** and DMAP or NHC in benzene-D$_6$ were inspected by multinuclear NMR spectroscopy, the formation of the corresponding adducts **4a-c** and **5a-c** was observed (Scheme 3). Most significantly, the carbene carbon atoms in **5a-c** give rise to resonances at 179.4 ppm (**5a**), 182.9 ppm (**5b**) and 204.9 ppm (**5c**) in the ^{13}C{^{1}H} NMR spectra, clearly indicating a carbene metal coordination. Furthermore, crystals of **5a-c**, suitable for single crystal X-ray diffraction could be obtained, allowing for solid-state structural characterization of these complexes (Fig. 4 and Fig. S54–S56, ESI†). Interestingly, the carbene coordination results in a change of bonding mode of the cyclopentadienyl substituent, as it adopts a σ bond to the central tetrel atom in all cases, **5a-c**. Thus, a four-membered ring moiety consisting of the Si, N, C^{Cp} and Ge/Sn/Pb atoms is observed. This is remarkable, since such a change in bonding mode was not observed in stannocene and plumbocene NHC complexes, which we reported previously,[9,10c] and DFT calculations (PBE0-D3/def2-TZVP) suggest that the corresponding uncoordinated tetrylene with a σ bonded Cp ring is not a minimum on the potential energy surface.[14]

The Ge–C1^{Cp} bond length in **5a** is 215.02(13) pm, the Sn–C1^{Cp} bond length in **5b** is 233.95(29) pm and the Pb–C1^{Cp} bond length in **5c** is 243.72(37) pm, which is slightly longer than typical Ge/Sn/Pb–C single bonds, although it must be mentioned that it is difficult to find structurally closely related examples,[24–27] and the elongation might be related to steric reasons to some degree. The Ge/Sn/Pb–C^{NHC} bond lengths are Ge–C2^{NHC} (**5a**): 214.19(14) pm; Sn–C2^{NHC} (**5b**): 237.23(28) pm and Pb–C2^{NHC} (**5c**): 251.17(36) pm, which is comparable to diamino germylene NHC adducts (*e.g.* 214.9(3) to 219.2(3) pm),[28] diamino stannylene NHC adducts (*e.g.* 239.9(4) pm),[29] and diamino plumbylene NHC adducts (*e.g.* 258.6(7) pm).[30] In contrast, these bonds are shorter than what was observed in related stannocene NHC complexes (245.06(10) ppm to 250.6 ppm) and a plumbocene NHC complex (272.5 pm), indicating a stronger binding of the NHC to the tetrel atom in **5a-c**. This is also reflected by calculated (PBE0-D3/def2-TZVP) bond dissociation energies (BDEs), which are +110.4 kJ mol^{-1} (**5a**), +105.1 kJ mol^{-1} (**5b**) and +101.6 kJ mol^{-1} (**5c**).[14] The increasingly stronger binding from **5c** over **5b** to **5a** is presumably due to the elevated Lewis acidity. Noteworthy, comparable stannocene NHC complexes exhibit smaller BDEs (65.9 to 96.6 kJ mol^{-1}),[9] indicating a more pronounced Lewis acidity in **5a-c** compared to their tetrelocene relatives, which may very well be related to the bonding flexibility of the ligand, with the Cp group being able to adopt different bonding modes, from η$^{3-5}$ π complexation to σ bonding.



Scheme 3 Reactions of **1b-d** with 4-(dimethylamino)-pyridine (DMAP), 1,3-diisopropyl-4,5-dimethyl-imidazolin-2-ylidene (NHC) and thf·W(CO)$_5$.

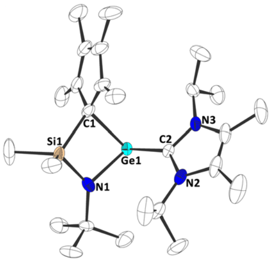


Fig. 4 Molecular structure of **5a** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity).

Finally, the Lewis basicity of germylene **1b** and its concomitant ability to bind to a transition metal fragment was investigated. While complexation to a transition metal fragment is quite common for many di-N-heterocyclic tetrylenes,[1] such complexes are unknown for tetrelocene, due to the almost non-existing σ donor abilities of the central atom in these systems.[9] Two routes were found to yield the germylene–tungsten complex **3**. Irradiation (365 nm) of a mixture of **1b** and W(CO)$_6$ in thf (Scheme 3), or treatment of Cl$_2$Ge·W(CO)$_5$[31] with the corresponding dilithiated ligand in thf gave **3**. Orange crystals, suitable for single crystal X-ray diffraction, allowed for a structural characterization of this germylene tungsten complex (Fig. 5 and Fig. S53, ESI†). Interestingly, as in carbene complexes **5a-c**, the Cp group adopts a σ bonding mode to the germanium atom. The Ge–W bond length is 252.92(5) pm, which is shorter than in a Cp*(Cl)Ge·W(CO)$_5$ complex (257.1(1) pm),[32] and in related NHGe·W(CO)$_5$ complexes,[33] which may indicate some π backbonding. This is in-line with the previously shown acceptor properties of **1b** and with the discussion of π backbonding in a (RSe)$_2$Ge·W(CO)$_5$ complex with a similar Ge–W bond length (252.8(1) pm).[34]

In Summary, our work bridges the gap between tetrelocenes and ''classical'' N-heterocyclic tetrylenes, and shows that the applied *ansa*-half-sandwich ligands are also suitable ligand

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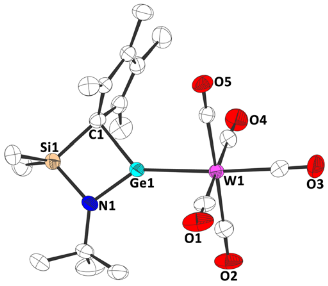

Fig. 5 Molecular structure of **3** in the crystal (displacement ellipsoids at 50% probability level, hydrogen atoms omitted for clarity).

systems for stabilizing low valent tetrel(II) atoms. Additionally, we found that a key feature of these ligands in tetrylene chemistry is their ability to switch between different bonding types, as the Cp group can adopt both σ bonding and π complexation modes, depending on the electronic and steric situation at the tetrel atom. Furthermore, we could show that these N-heterocyclic half-sandwich tetrylenes possess Lewis amphiphilic character, as they can form complexes both with donor molecules such as DMAP or NHCs, and – in case of germylene **1b** – with the transition metal fragment $W(CO)_5$.

In the future, these compounds might be of interest as monomers in ring-opening polymerization or for applications in bond activation processes.

Conflicts of interest

There are no conflicts to declare.

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