ChemComm

COMMUNICATION

Heavier N-heterocyclic half-sandwich tetrylenes†

Inga-Alexandra Bischoff, Bernd Morgenstern and André Schäfer Æ

Cite this: DOI: 10.1039/d2cc03107h

Received 1st June 2022,
Accepted 11th July 2022
DOI: 10.1039/d2cc03107h

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 tetrylene element in the oxidation state +II, commonly referred to as tetrylenes, have attracted significant attention for several decades. Among other things, persistent examples of these species have been applied in bond activation processes and as ligands for various metal fragments. The discovery of the first stable singlet carbone 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. The history of the discovery of the heavier diorganotetrel 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 germynes, stannynes and plumbynes in 1973/1974, and Veith’s note of an N-heterocyclic stannylene in 1975 are often regarded as the first examples. 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; Cp,Ge: Scibelli et al., 1973; Cp2Sn: Fischer et al., 1956; Cp,Sn: Fischer et al., 1956), and there can be no doubt that tetrelocenes of the type Cp,E are also divalent diorganotetrel(n) species, although their reactivities differ from that of “typical” tetrylenes in some cases. Due to the frontier orbital configuration in singlet tetrylenes, with a lone pair and a vacant orbital of p symmetry at the low-valent tetryl 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. 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(n), Sn(n) and Pb(n). These ligands are already quite common in transition metal chemistry, for instance in group 4 complexes, but have not seen much application in main-group chemistry so far. 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 GeCl2, SnCl2, and PbCl2 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, allows for comparison with related di-N-heterocyclic systems and tetrelocenes. In the 119Sn{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 stannynes, 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 tetryl atom in tetrylenes is usually associated with a large paramagnetic component to the NMR chemical shift, which relates to the energy gap...
between the lone pair and the vacant p orbital. This contribution is much smaller in tetrrelencenes, 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$[^1H]$ 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†). In both structures, the tetrrel atom is bound to the cyclopentadienyl group in what might best be perceived as a strongly distorted $\eta^5$ to $\eta^6$ mode with unequal Sn/Pb–C Cp bond distances (Sn–C: 249.54(16) to 338.86(18) pm; Pb–C: 249.37(23) to 339.50(21) pm)9 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 nature10 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–Cp contacts are in the same range as the bond lengths found in stannocene, Cp$_2$Sn, (255.54(7) to 283.79(10) pm)9 and a related plumbocene, [(Me$_2$BuSi)-Me$_2$C$_5$]Pb, (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 $C^5$–E–N angle around the tetrrel, is 71.1° for 1a and 70.6° for 1d, which is similar to other four-membered N-heterocyclic stannylenes17 and plumbylenes.20

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

Following the NMR and structural characterizations, we inspected the molecular orbitals of 1a-d by DFT calculations (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 at the central tetrrel atom. This is typical for tetrrelencenes as well as for “classical” tetrylenes. However, while in many tetrylenes the lone pair at the tetrrel atom corresponds to the HOMO, it is energetically located significantly lower in tetrrelencenes, due to higher s character. In 1a-d, the lone pair at the tetrrel 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 tetrrelencenes, three different reaction types were examined: oxidative additions, electron acceptor behavior (Lewis acidity) and electron donor behavior (Lewis basicity).

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

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).
By comparison with related literature known compounds, we tentatively assign signals to the corresponding bis(phenylethynyl)-titananes 2a,b (Scheme 2). These findings are in line with other N-heterocyclic stannylene, 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-D6 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 13C{1H} 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 previously9,10 indicating a more pronounced Lewis basicity of germylene in 5a-c compared to their tetracoene 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 π-π* to σ bonding.

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 tetracoene, 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)5 in thf (Scheme 3), or treatment of Cl,Ge-W(CO)5 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),12 and in related NHGe-W(CO)3 complexes,13 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 (RSe2)2Ge-W(CO)3 complex with a similar Ge–W bond length (252.8(1) pm).14

In Summary, our work bridges the gap between tetracoene and “classical” N-heterocyclic tetrylenes, and shows that the applied anza-half-sandwich ligands are also suitable ligand...
systems for stabilizing low valent tetrεl(n) atoms. Additionally, we found that a key feature of these ligands in tetrεlene 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 tetrεlenes 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.

Notes and references

1 M. Asay, C. Jones and M. Driess, Chem. Rev., 2011, 111, 354.
2 (a) N. Sen and S. Khan, Chem. – Asian J., 2021, 16, 705; (b) W. P. Neumann, Chem. Rev., 1991, 91, 311.
3 (a) H.-W. Wanzlick and E. Schikora, Angew. Chem., 1960, 72, 494; (b) H.-W. Wanzlick and E. Schikora, Chem. Ber., 1961, 94, 2389; (c) A. Igau, H. Grutzmacher, A. Baceiredo and G. Bertrand, J. Am. Chem. Soc., 1988, 110, 6463; (d) A. J. Arduego III, R. L. Harlow and M. Kline, J. Am. Chem. Soc., 1991, 113, 361.
4 (a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, Z. Anorg. Allg. Chem., 1994, 116, 2691; (b) P. J. Davidson and M. F. Lappert, J. Chem. Soc., Chem. Commun., 1973, 9, 317; (c) D. H. Harris and M. F. Lappert, J. Chem. Soc., Chem. Commun., 1974, 21, 895; (d) M. Veith, Angew. Chem., 1975, 87, 287.
5 P. Jušti, D. Kanne and C. Krüger, Angew. Chem., Int. Ed. Engl., 1986, 25, 164.
6 J. V. Sicbelli and M. D. Curtis, J. Am. Chem. Soc., 1973, 95, 924.
7 E. O. Fischer and H. Grubert, Z. Naturforsch. B, 1956, 11, 423.
8 E. O. Fischer and H. Grubert, Z. Anorg. Allg. Chem., 1956, 286, 237.
9 C. Müller, A. Stahlhich, L. Wirtz, C. Gretsch, V. Huch and A. Schäfer, Inorg. Chem., 2018, 57, 8050.
10 (a) M. A. Beswick, N. L. Cromhout, C. N. Harmer, P. R. Raithby, C. A. Russell, J. S. B. Smith, A. Steiner and D. W. Wright, Chem. Commun., 1996, 1977; (b) D. R. Armstrong, M. A. Beswick, N. L. Cromhout, C. N. Harmer, D. Moncrieff, C. A. Russell, P. R. Raithby, S. Steiner, A. E. H. Wheatley and D. S. Wright, Organometallics, 1996, 17, 3176; (c) S. Danès, C. Müller, L. Wirtz, V. Huch, T. Block, R. Pöttgen, A. Schäfer and D. M. Andrade, Organometallics, 2020, 39, 316.