Reactions of Mesityl Azide with Ferrocene-Based N-Heterocyclic Germynes, Stannynes and Plumbynes, Including PPh₂-Functionalised Congeners

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Dedicated to Prof. Joachim W. Heinicke on the occasion of his 75th birthday

Abstract: The reactivity of ferrocene-based N-heterocyclic tetrerylenes [[Fe(n)²−C₅H₅−NSiBuMe₂]₂E] (E = Ge, Sn, Pb) towards mesityl azide (MesN₂) is compared with that of PPh₂-functionalised congeners exhibiting two possible reaction sites, namely the E° and E³⁺ atom. For E = Ge and Sn the reaction occurs at the E° atom, leading to the formation of N₂ and an E₂⁻NMes unit. The germanimines are sufficiently stable for isolation. The stannanimines furnish follow-up products, either by [2 + 3] cycloaddition with MesN₂ or, in the PPh₂-substituted case, by NMes transfer from the Sn⁹⁺ to the P⁷⁺ atom. Whereas [[Fe(n)²−C₅H₅−NSiBuMe₂]₂Pb] and other dianionplumbynes studied are inert even without forcing conditions, the PPh₂-substituted congener forms an addition product with MesN₂, thus showing a behaviour similar to that of frustrated Lewis pairs. The germynes of this study afford copper(I) complexes with CuCl, including the first structurally characterised linear dicoordinate halogenido complex [CuX(L)] with a heavier tetrylene ligand L.

Introduction

Since more than a century,[1] the Staudinger reaction of organic azides RN₃ with phosphines R=P (R, R' = alkyl or aryl) has provided access to iminophosphoranes RN=P⃗N, which are generally unstable, but could be isolated in certain cases.[2] A significant kinetic stabilisation of phosphazides by intramolecular coordination of the P-bonded nitrogen atom to a Lewis acid was suggested by Grützmacher in 1999.[3] In view of the well-known analogy between phosphines and N-heterocyclic carbenes (NHCs),[4] it is not surprising that organic azides can react with NHCs in a similar manner to afford cyclic guanidine derivatives NH–⃗N, as was shown by Bielawski in 2005.[5] The intermediate triazenes NH–N–NH are thermally much more robust towards N₂ extrusion than the analogous phosphazides RN–N–PR₃.⁷⁻⁸ We note in this context that the synthesis of imines of the type RN=C=X (i.e. isocyanide dichlorides)[5] by reaction of organic azides with the transient singlet carbene Cl₂C= has been reported by Baldwin already in 1968; N₂ extrusion occurs even below room temperature in this case.[6] The heavier carbene analogues can react with organic azides in a similar fashion, giving rise to imine analogues with formal E=N (E = SI–Pb) double bonds.[7] This was first shown by Satgé in 1978, who reported the formation of the transient germanimine (Me₃Si)₂Ge=NPh together with N₂ in the reaction of the dianiongermylene (Me₃Si)₂Ge with PhN=.[8] In 1991 Meller described the first structurally characterised stable germanimines [(Si₅Me₃)ArN]₂Ge=NAr (obtained from the reaction of ArN with [(Me₅Si)ArN]₂Ge, Ar = mesityl (Mes) or 2,6-diisopropylphenyl (Dipp)).[9] This was followed in 1993 by the first structurally characterised stable stannanimine [(Me₃Si)₂SnN]₄NDipp (obtained from DippN₂ and [(Me₃Si)₂Sn]₄N at ~30 °C).[10] The only other stable stannanimine known to date, [(Me₃Si)₂CH₃]₂SnN–[SiBu₃(NDipp)] (obtained from [(Me₃Si)₂CH₃]₂Sn and SiBu₃(NDipp)], was reported one year later by Ando.[11] The paucity of isolable stannanimines is due to the fact that, owing to their reactive polar Sn–N bond, stannanimines readily form their head-to-tail dimers (viz. 1,3,2,4-diazadiastetetinodides) or give [2 + 3] cycloadducts with the organic azide to furnish stannatetrazoles, as was shown by Pinchuk and by Neumann already in the 1980s.[12] The publication of the N-heterocyclic silylene (CHN–Bu₃)Si, the first stable compound containing dicoordinate Si³⁺ by Denk and West in 1994[13] was followed in the same year by their report of its reaction with trietyl azide, which furnished the THF complex of the silanimine (CHN–Bu₃)Si–NCP₃.[14] Since then, numerous reactions of organic azides with free or base-stabilised silylenes furnishing free or base-stabilised silanimines have been described.[15] Among the reactions of organic azides with heavier carbene analogues, plumbynes have apparently been investigated least extensively. We are aware of only three studies in this context.
The first study was published in 2002 by Klinkhammer, who described the reaction of [(MeSi)2Si]2Pb (1) with 1-adamantyl azide in toluene at −30 °C, which furnished the triazenido Pb4 complex 2 with a four-membered PbN2 heterocycle due to migration of a (Me, Si)2Si group from Pb to N (Scheme 1, top). In 2017 Song reported the reaction of the N-heterocyclic plumbylene o-C6H4(NDipp)Pb (3) with mesityl azide under harsh conditions (110 °C, toluene). N2 was liberated, but no plumbylamine was observed. The reaction resulted in a donor-functionalised plumbylene 4 with tricoordinate Pb4 due to a chelating secondary amino group, which was plausibly formed by insertion of an NMes unit into a benzylic C–H bond, thus affording a Me2C=NH–Mes moiety (Scheme 1, bottom).

Of particular interest for the present work is Wesemann’s study of the reaction of organic azides with intramolecular Lewis pairs composed of a tetrylene and a phosphane unit, which included also the plumbylene Ar*Pb[CHPh(PPh2)3] (5).

\[
\text{Ar}^* = 2,6-(2,4,6-iPr)}_3\text{C}_6\text{H}_3\text{C}_2\text{H}_6, \text{Ad = 1-adamantyl, Mes = mesityl.}
\]

\[
\text{Ar}^* = 2,6-(2,4,6-iPr)}_3\text{C}_6\text{H}_3\text{C}_2\text{H}_6, \text{Ad = 1-adamantyl, Mes = mesityl.}
\]

The Pb4 atom of 5 is dicoordinate. In contrast, the corresponding stannylene 6 and germylene 9 exhibit tricoordinate tetrel atoms due to intramolecular coordination of the P atom, thus resembling our recently reported ferrocene-based N-heterocyclic plumbylene 12, stannylene 13 and germylene 14 functionalised with a PPh2 group (Figure 1, top).

Compounds 5, 6, 9 and 12–14 contain two different sites suitable for reaction with an organic azide, viz. the P atom and the tetrel atom. Wesemann observed that plumbylene 5 and stannylene 6 react with AdN3 in the same fashion, affording addition products 7 and 8 featuring a four-membered EMPC heterocycle (E = Sn, Pb; N denotes the terminal AdN3 nitrogen atom; Scheme 2, top). An analogous reaction had previously been reported by Ionkin for the stannylene \([\text{Bu}_3\text{PCH}_2\text{C}(\text{CF}_3)_2\text{O}]\text{Sn}\), which contains a tetracoordinate Sn4 atom due to intramolecular P coordination; only one equivalent of AdN3 was consumed even under forcing conditions. From a formal point of view, the products of these reactions can be described as phosphazides which are engaged in an intramolecular coordination of their P-bonded nitrogen atom to the divalent tetrel atom. A completely different behaviour was found for germylene 9, where formation of N3 and of the corresponding germanimin 10 (kinetic product) was observed, followed by slow isomerisation of the latter to the iminophosphorane-functionalised germylene 11 (thermodynamic product; Scheme 2, bottom). The reactions of the Lewis pairs 5 and 6 with 1-adamantyl azide are reminiscent of reactions reported for several borane-phosphane (B/P) frustrated Lewis pairs (FLPs) with organic azides, where FLP addition to the terminal nitrogen atom of the azide (N) occurred, resulting in four- or five-membered heterocycles with a BNP subunit. Wesemann’s results inspired us to investigate the behaviour of plumbylene...
12, stannylene 13 and germylene 14 towards an organic azide. We selected MesN₂, which is a readily available aryl azide considered particularly safe for use (C/N atom number ratio not lower than 3).²⁶ We were interested in the influence of the Lewis pair nature of the donor-functionalised N-heterocyclic tetrylenes 12–14 in this context and therefore included the unfunctionalised congeners \([\text{Fe}(\eta^5\text{C}_3\text{H}_5\text{N}5\text{SiMe}_3)_2]\) [E = Pb (15)],²⁶ \([\text{Sn}(\eta^5\text{C}_3\text{H}_5\text{NSiBuMe}_3)_2]\) [E = Ge (17); Figure 1, bottom] in our study. The SiBuMe group was chosen instead of the SiMe₃ substituent present in 12–14, because all three unfunctionalised tetrylenes are stable and can be isolated in pure form, whereas the trimethylsilyl-substituted plumbylene \([\text{Fe}-(\eta^5\text{C}_3\text{H}_5\text{N}5\text{SiMe}_3)_2\text{Pb}]\) is unstable.²⁷ Furthermore, the bulkier nature of SiBuMe₂ in comparison with SiMe₃ is expected to compensate for part of the reduced steric encumbrance of the tetræl atom due to the absence of the PPh₃ substituent.

**Results and Discussion**

The N-heterocyclic germylene \([\text{Fe}(\eta^5\text{C}_3\text{H}_5\text{N}5\text{SiBuMe}_3)_2]\) Ge (17) was conveniently prepared analogous to the stannylene \([\text{Fe}(\eta^5\text{C}_3\text{H}_5\text{N}5\text{SiBuMe}_3)_2]\) Sn (16)²⁸ by reacting LiN(SiMe₃)₂, \([\text{GeCl}_2(1,4\text{dioxane})]\) and \([\text{Fe}(\eta^5\text{C}_3\text{H}_5\text{N}5\text{HSiBuMe}_3)_2]\) in a 2:1:1 molar ratio in THF. The product was obtained in 92% yield and was structurally characterised by single-crystal X-ray diffraction (XRD). Pertinent metric parameters of germylene 17 and of the products of the reactions with MesN₂ obtained in this study are collected in Table 1. Data for known N-heterocyclic tetrylenes which served as starting materials for the new compounds contained in Table 1 have been included in this Table for comparison. The molecular structure of 17 is shown in Figure 2. The molecule exhibits approximate C₂ symmetry about the Fe–Ge axis. The germanium bond lengths and angles are very similar to the values published for the N-trimethylsilyl homologue.²⁹ The germanium bond angle of 107.22(7)° determined for 17 is essentially identical to the value reported by Lappert for the emblematic acyclic dianorganomercury \([\text{Me}_2\text{Si}(\eta^5\text{C}_3\text{H}_5\text{N})\text{Ge}]\) viz. 107.1(2)°.²⁹ This is in line with previous observations that the 1,1’-ferrocenylene backbone of N-heterocyclic carbenes and their heavier analogues \([\text{Fe}(\eta^5\text{C}_3\text{H}_5\text{N}5\text{R})_2]\)

![Figure 2. Molecular structure of germylene 17 in the crystal (ORTEP with ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity, alkyl groups drawn as capped sticks).](image)

**Table 1. Pertinent metric parameters for the N-heterocyclic tetrylenes of this study and the products of their reactions with mesityl azide.**

| E–N₁, E–N₂ [Å] | E–N/P [Å] | N₁–E–N₂ [°] | Tilt angle [°][b] | N–C₁₉₆₅–C₁₅₆₇–N [°] |
|-----------------|-----------|-------------|-------------------|------------------|
| \(12\) (E = Pb) | 2.260(2), 2.132(2) | 2.8624(8) | 95.32(9) | 6.3 | 26.2 | ref. [23] |
| \(13\) (E = Sn) | 2.126(3), 2.084(3) | 2.7526(8) | 98.11(10) | 6.1 | 23.1 | ref. [23] |
| \(14\) (E = Ge) | 1.9530(18), 1.9160(18) | 2.6497(6) | 100.69(7) | 8.9 | 22.2 | ref. [23] |
| \(16\) (E = Sn) | 2.098(2), 2.066(2) | 105.09(10) | 2.8 | 8.2 | ref. [28] |
| \(17\) (E = Ge) | 1.8669(17), 1.8685(18) | 107.22(7) | 7.8 | 12.0 | this work |
| \(18\) (E = Sn)³⁰ | 2.035(5), 2.027(5) | 2.063(5) | 115.60(19) | 1.0 | 0.9 | this work |
| \(19\) (E = Ge)³⁰ | 1.830(5), 1.827(5) | 1.714(5) | 114.6(2) | 5.7 | 4.5 | this work |
| \(20\) (E = Pb) | 2.308(3), 2.241(3) | 2.386(3) | 91.19(11) | 3.4 | 0.7 | this work |
| \(21\) (E = Sn) | 2.174(3), 2.136(3) | 2.285(2) | 94.05(10) | 5.1 | 10.0 | this work |
| \(22\) (E = Ge) | 1.8909(16), 1.8625(16) | 1.7268(17) | 108.06(7) | 9.8 | 26.4 | this work |
| \(23\) (E = Ge) | 1.976(3), 1.943(3) | 2.110(3) | 98.24(13) | 7.7 | 11.1 | this work |

[a] Dihedral angle formed by the best planes of the cyclopentadienyl rings. [b] Two independent molecules with very similar bond parameters; data arbitrarily given for molecule 1. [c] Two independent molecules, one of them showing disorder; data given for the non-disordered molecule.

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(E = C–Pb) gives rise to large bond angles at the divalent tetrel atom close to those of corresponding acyclic congeners.\textsuperscript{27–29,31,32} The Sn–N bonds of stannylene 16 are longer than the Ge–N bonds of germylene 17 by ca. 0.2 Å, which is in accord with the difference of the covalent radii of tin (1.39 Å) and germanium (1.20 Å).\textsuperscript{33} In turn, the Ge\textsuperscript{I} bond angle of 17 is slightly wider (by 2°) than the Sn\textsuperscript{I} bond angle of 16, which is in agreement with Bent’s rule.\textsuperscript{34,35}

With the complete series of donor-functionalised heavier N-heterocyclic tetrylenes 12–14 and the unfunctionalised congeners 15–17 in hand, we next studied the reactivity of these six compounds towards mesityl azide (Scheme 3). Reactions

\begin{scheme}
\textbf{Scheme 3.} The ferrocene-based N-heterocyclic tetrylenes 15–17 and the Ph\textsubscript{5}P-functionalised congeners 12–14 (used as racemic compounds, only one enantiomer is shown) and their reactions with mesityl azide (isolated yield given in brackets).
\end{scheme}
were observed for all compounds except \([\{\text{Fe-(\(\eta^5\)-C}_5\text{H}_5\_N_SiBuMe}_3\_C\}_3\text{Pb}\}] (15). Since plumbelyne 15 was inert even under rather forcing conditions (105 °C, toluene) almost identical to those used by Song for \(\sigma\text-C_6\text{H}_4\text-(NDipp)}\text{Pb} (3; Scheme 1, bottom), we tested three additional dianionplumbelynes in this context, viz. the acyclic congener \([\{\text{Me}_2\text{Si}}\text{N}_2\text{Pb}\}] (38) as well as our recently reported five- and six-membered \(\eta^3\)-heterocyclic plumbelynes \(\sigma\text-C_6\text{H}_4\text{(NSiMe}_3\_Pb} and \(\text{nap(NSiMe}_3\_Pb} (\text{nap} = \text{naphthalene-1,8-diyli}) [31] all containing \text{Me}_2\text{Si} instead of SiBuMe substituteds to decrease steric congestion. However, these compounds proved to be equally inert. The stannelyne \([\{\text{Fe-(\(\eta^5\)-C}_5\text{H}_5\_N_SiBuMe}_3\_C\}_3\text{Sn}\}] (16) showed a smooth and swift reaction with \text{MesN}_3 (2 equiv.) at room temperature, furnishing the stannatetrazole 18 (structurally characterised by XRD, Figure 3) in 83 % yield. The use of 1 equiv. of the azide resulted in an equimolar mixture of 18 and unreacted 16. This is in line with previous reports that an initially formed stannamine is prone to form a \(2+3\) cycloadduct with an organic azide. [13][13][13][13]

Stannatetrazole 18 is a spiro compound with a five- and a six-membered heterocycle connected by the Sn atom. Schulz recently confirmed computationally that closely related compounds obtained from the acyclic dianionstannylene \([\{\text{Me}_2\text{Si}}\text{N}_2\text{Sn} and \text{aryl azides contain a tin(IV) atom with four highly polar Sn–N single bonds} and\text{ an} \text{infrared} \text{atom} \text{chelated by a tetraazabutadiene ligand.} [37][37][37][37] A comparison of the Sn–N bond lengths of stannelyne 16 (average value 2.06 Å, dicoordinate Sn) and stannatetrazole 18 (average value 2.05 Å, tetracoordinate Sn) shows that obviously the increase in coordination number from two to four is compensated by the decrease in the covalent radius on going from Sn to Sn. This behaviour is not unusual. For example, a comparison of the cyclic dianionstannylene \(\text{Me}_2\text{Si}+(\text{NDipp})\text{Sn} [38] and the corre-

Figure 3. Molecular structure of stannatetrazole 18 in the crystal (ORTEP with ellipsoids drawn at the 50 % probability level, hydrogen atoms omitted for clarity, alkyl and aryl groups drawn as capped sticks). Selected bond lengths (Å) and angle (°): N3–N4 1.390(7), N4–N5 1.267(8), N5–N6 1.396(7); N3–Sn1–N6 106.9(2).

Figure 4. Molecular structure of the non-disordered molecule of germani-
mine 19 in the crystal (ORTEP with ellipsoids drawn at the 50 % probability level, hydrogen atoms omitted for clarity, alkyl and aryl groups drawn as capped sticks).
In contrast to \([\text{[Fe}(\eta^1\text{C}_2\text{H}_4\eta\text{-NSiBuMe}_2)_2]\text{Pb]}\) (15), which was inert towards MesN\(_2\) even under forcing conditions (see above), the donor-functionalised N-heterocyclic plumbylene 12 reacted with this azide already under fairly mild conditions (60°C, toluene), affording the addition product 20 (structurally characterised by XRD, Figure 5) with a six-membered PbNPCNCN heterocycle (\(N\) denotes the terminal MesN\(_2\) nitrogen atom). 20 may be viewed as a phosphazide stabilised by intramolecular coordination of the P-bonded nitrogen atom to the Lewis acidic Pb\(^2\) atom, which is in a trigonal pyramidal bonding environment (sum of angles 274°).

The Pb–NP bond is considerably longer (2.39 Å) than the two other Pb–N bonds (average value 2.27 Å). These values may be compared with the Pb–N distances of the 4-dimethylaminopyridine (DMAP) adduct of plumbylene 15\(^{[27]}\) which exhibits two similarly short Pb–N bonds to the amino substituents (average value 2.27 Å), while the coordinative Pb–N\(_{pyridine}\) bond (2.50 Å) of \([15\text{(DMAP)}]\) is ca. 11 Å longer than the Pb–NP bond of 20, pointing to a significant ylidic character of the phosphazide unit (\(R\text{'},P\text{'},\text{N}^\text{-}\text{N}^\text{-}\text{N}\text{-N}\text{-NR}\) present in the latter. The Pb–NP bond length of Wesemann’s plumbylene-azide addition compound 7 has a value of 2.43 Å and is thus slightly longer (by 4 Å) than the corresponding bond of 20, while their P–N bond lengths are essentially identical (1.64 Å)\(^{[21]}\).

Whereas the reaction of \([\text{[Fe}(\eta^1\text{C}_2\text{H}_4\eta\text{-NSiBuMe}_2)_2]\text{Sn]}\) (16) with MesN\(_2\) afforded a \([2+3]\) cycloadduct (stannatetrazole 18, see above), the donor-functionalised congener 13 furnished the iminophosphorane-functionalised stannylene 21 under the same mild conditions (structurally characterised by XRD, Figure 6).

The Sn\(^2\) atom of 21 is in a trigonal pyramidal bonding environment (sum of angles 289°). The Sn–NP bond is considerably longer (2.29 Å) than the two other Sn–N bonds (average value 2.16 Å) and essentially identical with the Sn–NP bond of the iminophosphorane-functionalised diarylstannylene Ar*Sn\([\text{C}_6\text{H}_6\{\text{P(NAd)Ph}_2\}]\) reported by Wesemann; in the same vein, the P–N bond lengths of both compounds are indistinguishable within experimental error, viz. 1.619(3) Å for 21 and 1.613(5) Å for Wesemann’s compound.\(^{[20]}\) A comparison of the tetrel-nitrogen bonds present in 20 and 21 reveals that the bonds of stannylene 21 are shorter by ca. 0.1 Å than the corresponding bonds of plumbylene 20, which is in line with the difference of the covalent radii of Sn (1.39 Å) and Pb (1.46 Å).\(^{[33]}\)

In comparison to 12 and 13, which contain tricoordinate P,N,N-bonded tetrel atoms, the \(^{207}\)Pb NMR signal of 20 and the \(^{119}\)Sn NMR signal of 21 are moderately high-field shifted in C\(_6\)D\(_6\) solution \([\delta^{(207}\text{Pb})=2493 \text{ vs. 3050 ppm for 20 and 12, respectively}; \delta^{(119}\text{Sn})=-1 \text{ vs. 187 ppm for 21 and 13, respectively},\) in line with a tricoordinate N,N,N-bonded nature of the respective tetrel atom.\(^{[40]}\) For comparison, a substantially low-field shifted signal indicative of dicoordinate Pb\(^+\) and Sn\(^+\), respectively, was observed for \([\text{[Fe}(\eta^1\text{C}_2\text{H}_4\eta\text{-NSiMe}_2)_2]\text{Pb]}\) \([\delta^{(207}\text{Pb})=4333 \text{ ppm}]^{[20]}\) and \([\text{[Fe}(\eta^1\text{C}_2\text{H}_4\eta\text{-NSiMe}_2)_2]\text{Sn]}\) \([\delta^{(119}\text{Sn})=589 \text{ ppm}]^{[29]}\) which do not contain a donor substituent.

Finally, the reaction of mesityl azide with the donor-functionalised germylene 14 at room temperature afforded the germanimine 22, which was found to undergo a slow isomerisation to the corresponding iminophosphorane-functionalised
germylene 23. Both isomers were structurally characterised by XRD.

The PhP₂-functionalised germanimine 22 contains a tetra-coordinate Ge⁹⁺ atom due to an intramolecular coordinative Ge–P bond (Figure 7), which is ca. 0.2 Å shorter than that of germylene 14. Analogous to germanimine 19, the Ge⁹⁺ atom is involved in a short (1.73 Å) and two long Ge–N bonds (average value 1.88 Å). These bonds are slightly elongated with respect to 19 (1.71 and 1.83 Å, see above) due to the higher coordination number of the Ge⁹⁺ atom of 22, viz. four vs. three in 19. Similar to 19, Wesemann’s germanimine 10, which was obtained as the kinetic product from germylene 9 and AdN₃, also contains a tricoordinate Ge⁹⁺ atom and exhibits a Ge–N bond length of 1.71 Å; however, no coordination of the PPh₂ unit was observed in this case. [21]

The iminophosphorane-functionalised germylene 23 (Figure 8), which is formed as thermodynamic product from the PPh₂-functionalised germanimine 22 by rearrangement, contains a Ge⁹⁺ atom in a trigonal pyramidal bonding environment (sum of angles 300°). The molecular structure is analogous to that of the corresponding stannylene 21. The Ge–NP bond is considerably longer (2.11 Å) than the two other Ge–N bonds (average value 1.96 Å), in accord with the corresponding bond lengths determined for 21, when the difference of the covalent radii of Sn (1.39 Å) and Ge (1.20 Å) is taken into account. [33] The P–N bond lengths of both compounds are essentially identical, viz. 1.625(3) Å for 23 and 1.619(3) Å for 21; they also compare well with the value of 1.608(2) Å reported by Wesemann for the iminophosphorane-functionalised germylene 11. [21]

When compared with the reactions of Wesemann’s plumbylene 5 and germylene 9 with AdN₃ (Scheme 2), [21] the respective behaviour of plumbylene 12 and germylene 14 towards MesN₃ is completely analogous. However, while Wesemann’s PPh₂-functionalised stannylene 6 afforded an addition product (8), an iminophosphorane (21) was obtained from our PPh₂-functionalised stannylene 13. The primary interaction of organic azides with main-group element Lewis acids has been shown to involve the C-bonded N atom. [14] In contrast, the Staudinger reaction begins with a nucleophilic attack of the phosphane PR₃ on the terminal nitrogen atom (N) of the organic azide RN₃. [23, 46] Slootweg recently addressed the mechanism of the reaction of RN₃ with the B/P FLP tBuPCH₂BPh₃ and found that the initial nucleophilic attack typical of a Staudinger reaction is kinetically less favourable than adduct formation of the Lewis acidic B atom with the Lewis basic C-bonded N atom. [23a] With MesN₃ and tBuN₃, the reaction afforded the respective addition product containing a four-membered BNPC heterocycle via a six-membered ring (BNNNPC) intermediate. The inertness of the unfunctionalised plumbylenes of our study towards MesN₃ strongly indicates that the reaction of the azide occurs at the PPh₂ unit of the donor-functionalised plumbylenes 5 and 12. The fact that 5 reacts already at room temperature, while elevated temperatures are needed in the case of 12 is perfectly plausible in view of the fact that the P atom of 12 is engaged in an intramolecular coordinative bond to the Pb atom, while no such bond is present in 5, whose P atom is therefore readily available for reaction with the azide. In both cases, however, the resulting phosphazide is efficiently stabilised in this scenario by intramolecular adduct formation with the respective Lewis acidic Pb⁺ atom. Our results obtained with the lighter congeners, viz. stannylene pair 13 and 16 and germylene pair 14 and 17, suggest that in these cases the reaction with the azide occurs at the divalent tetrel atom, leading to an E=N double bond, which is highly reactive in the case of E=Sn so that only follow-up products (18, 21) were observed.

Inspired in part by Breher’s study of the ligand properties of the N-mesityl homologue of 17 in transition metal chemistry [46] as well as the recent report by Jambor and Herres-Pawlis on copper(I) germylene complexes in the context of lactide polymerisation, [47] we also addressed the coordination behaviour of the unfunctionalised germylene 17 and the donor-functionalised congeners 14 and 23 towards CuCl (Scheme 4). [46]
Me₃Si(NtBu)₂Ge appears to be the only cyclic diaminogermylene investigated in terms of CuCl coordination to date. The complex obtained resulted from the reaction of six equivalents of this germylene with four equivalents of CuCl, thus exhibiting a 3:2 stoichiometric ratio of these components. In contrast to this, the reaction of 17 with CuCl furnished a product (24) with a composition corresponding to a 1:1 complex [(17)CuCl]. Although an NMR spectroscopic analysis of a C₆D₆ solution of this product revealed no significant coordination-induced signal shifts in comparison to free 17, an XRD study clearly showed that formation of a germylene-copper(I) complex had taken place and confirmed the 1:1 ratio already inferred from microanalytical data. While the composition of product 24 corresponds to a simple 1:1 complex [(17)CuCl], the solid state structure is not that simple. The Lewis structure of 24 given in Scheme 4 corresponds to the molecular structure in the crystal, which is shown in Figure 9. Pertinent metric parameters of 24 and of the other copper(I) complexes of this study are collected in Table 2.

The crystal structure of 24 exhibits four CuⅠ-bonded germylene moieties in the asymmetric unit. Two of them form a chlorido-bridged dimeric complex [(17)Cu(μ-Cl)]₂ containing two tricoordinate GeⅡ atoms (Ge₁ and Ge₂) as part of a diamond-shaped Cu₂Cl₂ core. The other two moieties form a less symmetric dimer, which contains one tricoordinate (Ge⁴) and one tetracoordinate GeⅡ atom (Ge₃). Only one of the two Cl atoms (Cl₃) adopts a bridging position between the two CuⅠ atoms of this dimer. The second Cl atom (Cl₄) is in a bridging

Scheme 4. Reactions of the N-heterocyclic germynes 17, 14 and 23 with CuCl (isolated yields given in brackets). The Lewis structures of the copper(I) complexes 24, 25 and 26 reflect the results obtained for the solid state by XRD.
position between the tetracoordinate Ge\textsuperscript{II} atom Ge3 and the Cu\textsuperscript{I} atom Cu4 bonded to the tricoordinate Ge\textsuperscript{II} atom Ge4 of this less symmetric dimer. Instead of the diamond-shaped Cu\textsubscript{I}Cl\textsubscript{2} core of the other dimer, a five-membered heterocyclic GeCu\textsubscript{II}Cl core is present in the less symmetric dimer. All four Cu\textsuperscript{I} atoms are in a trigonal planar coordination environment with two chlorine atoms and one germanium atom as bonding partners. The Cu\textsuperscript{I} atom Cu3 bonded to the tetracoordinate Ge\textsuperscript{II} atom Ge3 in the less symmetric dimer is connected to one of the Cl atoms (Cl1) of the Cu\textsubscript{II}Cl\textsubscript{2} core of the symmetric dimer, thus joining the two dimeric units together and making this particular Cl atom μ\textsuperscript{1}-tricoordinate. The Cu–Cl distances of this tricoordinate Cl atom range from ca. 2.31 to 2.38 Å, while the other three Cl atoms exhibit shorter Cu–Cl bonds (2.23–2.30 Å) due to their coordi-
nate nature. The Cu–Ge bond lengths of 24 lie in the small range from 2.25 to 2.30 Å, which compares well with other germylene complexes of tricoordinate Cu\textsuperscript{II}.\textsuperscript{[47,48a,b]}

The fact that Cl4 is bridging a Cu\textsuperscript{I} atom and a Ge\textsuperscript{II} atom, instead of two Cu\textsuperscript{I} atoms, suggests that the Cu–Cl and the Ge–Cl interactions in our system are of similar strength. Note that a chloride transfer to the germanium atom upon coordination of transition metal chlorides (MCl\textsubscript{2}, M = Fe, Co, Ni, Zn; CuCl), corresponding to the formation of a chlorogermylene containing tetravalent germanium by Ge\textsuperscript{II} insertion into the M–Cl bond, was recently described by Cabeza for a donor-stabilised N-heterocyclic germylene with tricoordinate Ge\textsuperscript{II} due to intramolecular coordination of a P(Pr\textsubscript{2})\textsubscript{2} unit.\textsuperscript{[48d,e]}

The germanium atom of Cabeza’s chlorogermyl copper complex is in a distorted pseudotetrahedral bonding environment, showing a distance of 0.75 Å to the plane formed by its two nitrogen atoms and the copper atom (sum of angles with respect to these three atoms: 321°).\textsuperscript{[48d]}

The situation is quite different in the present case. Ge3 has a distance of only 0.23 Å from its CuN\textsubscript{2} plane, close to a trigonal planar arrangement (sum of angles: 356°). The bond vector formed with its additional bonding partner, Cl4, is almost perpendicular to the CuN\textsubscript{2} plane, in accord with a donor-acceptor interaction of the chlorido ligand with the vacant p-type orbital at the Ge\textsuperscript{II} atom. This notion is further supported by the Ge3–Cl4 distance of 2.60 Å. This bond is much longer than the Ge–Cl bonds of Cu\textsuperscript{I} complexes obtained from chlorogermylenes with tricoordinate Ge\textsuperscript{II} due to chelating β-diketiminato or aminotropiminato units,\textsuperscript{[48h,k]} which are typically 2.30 Å and thus close to the sum of the covalent radii of Ge (1.20 Å) and Cl (1.02 Å).\textsuperscript{[13]} In the same vein, the Cl–Ge–Cu angles in these chlorogermylene complexes are ca. 120°, while the Cl4–Ge3–Cu3 angle of 24 is 94°, reflecting the approximately perpendicular orientation of the Cl4–Ge3 bond vector with respect to the CuN\textsubscript{2} plane as described above.

### Table 2. Pertinent metric parameters for the copper complexes of this study.

|     | Ge–N\textsuperscript{II} [Å] | Ge–N/P [Å] | N–Ge–N\textsuperscript{II} [°] | Cu–Ge [Å] | Cu–Cl [Å] |
|-----|-----------------------------|-------------|---------------------------------|------------|----------|
| 24  | 1.824(5), 1.832(5), 1.834(5), 1.852(5), 1.861(5), 1.836(6) | 111.2(2) | 2.2561(9) | 2.3459(16),\textsuperscript{[30]} 2.2417(15),\textsuperscript{[30]} 2.3838(16),\textsuperscript{[30]} 2.2523(17),\textsuperscript{[30]} 2.3078(14),\textsuperscript{[30]} 2.2972(14),\textsuperscript{[30]} 2.2693(9) | 2.2504(9) | 2.2972(14) |
| 25  | 1.911(10), 1.945(10), 1.946(8), 1.849(11), 1.889(3), 1.878(3) | 102.0(4) | 2.3817(19) | 2.3817(19) | 2.3530(19) |
| 26  | 1.979(3) | 96.55(13) | 2.2522(6) | 2.1026(11) |

\[a\] Cyclopentadienyl-bonded N atoms. \[b\] Bond to tricoordinate Cl1. \[c\] Two independent molecules; data refer to the non-disordered one.

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The reaction of 14 with CuCl afforded a product (25) with a composition corresponding to a 2:1 complex [(14),CuCl] according to microanalytical data, which, however, were not in accord with an analytically pure sample of such composition. The product gave rise to rather complicated NMR spectra, which were not suitable to provide conclusive evidence for the nature of the species in solution. A structural investigation by XRD revealed a trigonal-planar coordination environment of the Cu atom, which is bonded to a P atom and two different Ge atoms, one of them carrying the Cl atom. The Lewis structure of 25 given in Scheme 4 corresponds to the molecular structure in the crystal (Figure 10). The NMR spectra obtained for 25 are compatible with such a structure also in solution. Note that the tetravalent Ge atom Ge1 is a centre of chirality. Consequently, in combination with the two different planar-chiral ferrocene moieties, four diastereomers may result. We have isolated only a single diastereomer, which was obtained as a racemic compound. Figure 10 arbitrarily shows the \( \text{P} \text{R} \text{S} \text{S} \) enantiomer. The NMR spectra of the crude product do not indicate the presence of other diastereomers. In particular, the \( ^{11} \text{P} \text{[H]} \) NMR spectrum (Figure S26 in the Supporting Information) exhibits only two signals, as expected for 25 with its two different phosphorus atoms. 25 was obtained in only 26% yield. We cannot exclude, therefore, that other diastereomers were also formed in the reaction of 14 with CuCl, but remained unnoticed due to low solubility.

The quality of the crystals obtained was poor (very small crystal size and weak scattering ability), thus compromising the presence of other diastereomers. In particular, the NMR spectra of the crude product do not indicate the presence of other diastereomers. In particular, the \( ^{11} \text{P} \text{[H]} \) NMR spectrum (Figure S26 in the Supporting Information) exhibits only two signals, as expected for 25 with its two different phosphorus atoms. 25 was obtained in only 26% yield. We cannot exclude, therefore, that other diastereomers were also formed in the reaction of 14 with CuCl, but remained unnoticed due to low solubility.

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The quality of the crystals obtained was poor (very small crystal size and weak scattering ability), thus compromising the result of the XRD analysis performed for 25. Nevertheless, a meaningful discussion of metric parameters is possible at least for the heavy atoms. The Cu atom is in a trigonal planar bonding environment, being coordinated by two germanium atoms and one phosphorus atom. The Cu–P distance of 2.27 Å lies in the region typical for tricoordinate Cu’ triarylpolysiloxane complexes, comparing well with, for example, \([\text{CuX}_2\text{PPh}_3]\) \(\text{NR}_2\) (2.21 Å for \( X = \text{Cl}, R = \text{Et} \); 2.24 Å for \( X = \text{Br}, R = \text{nBu} \); 2.23 Å for \( X = I, R = \text{tBu} \)) \(^{40}\), \([\text{CuX}\text{PPh}_3]\text{J} \) (2.27, 2.28 and 2.27 Å for \( X = \text{Cl}, \text{Br}, \text{I} \), respectively) \(^{30}\), \([\text{CuPPh}_3]\text{J}\) \(\text{BPPh}_3\) \(\text{J}\) (2.26–2.29 Å) \(^{31}\) and \([\text{Cu}-(\text{CF}_3)\text{J}\text{J}\text{PPh}_3]\text{J}\) (2.27 Å) \(^{32}\), the latter germyl complex apparently being the only structurally characterised tricoordinate Cu’ phosphosline complex with a copper-germanium bond (Cu–Ge 2.38 Å). Both germanium atoms of 25 are tetracoordinate and reside in a distorted pseudotetrahedral bonding environment. Their shared bonding partner is the Cu atom, the Cu–Ge bond length being 2.38 and 2.35 Å for Ge1 and Ge2, respectively. The intramolecular coordination of the P atom present in gemylene 14 has remained intact for Ge2, but not for Ge1. Ge1 is tetravalent. The Cu–Ge1 (2.38 Å), Cu1–Cl (2.26 Å) and Ge1–N distances (average value 1.93 Å) are similar to those reported for Cabeza’s chlorogermyl copper complex (see above; Cu–Ge 2.36 Å, Ge–Cl 2.26 Å, Ge–N 1.93 Å) \(^{33}\). The same holds true for the distance of the Ge atom to the CuN plane, which is 0.61 Å for Ge1 in 25 and 0.75 Å for Cabeza’s compound (see above). However, the corresponding distance of Ge2 is only 0.29 Å. Ge2 is part of still intact gemylene 14 acting as a ligand for the chlorogermyl-bonded Cu atom. The loss of electron density at Ge2 by copper(I) complexation obviously leads to a stronger coordination of the PPh3 moiety, as is reflected by a Ge2–P distance of 2.43 Å as opposed to 2.65 Å determined for the Ge–P bond of gemylene F; a much smaller, but still significant, contraction is observed for the corresponding Ge–N bonds (average value 1.93 Å in 14 vs. 1.90 Å for Ge2 in 25). A similar effect, albeit less pronounced, has been observed by Baceiredo for a donor-stabilised gemylene with tricoordinate Ge’ due to intramolecular coordination of a PPh3 unit, whose Ge–P distance shortens from 2.43 to 2.39 Å upon complexation by a \([\text{RhCl(COD)}]\) fragment \(^{34}\). To summarise, compound 25 contains a tetravalent germanium atom (Ge1, chlorogermyl ligand) and a divalent germanium atom (Ge2, donor-stabilised gemylene ligand). To a first approximation, bonding in this complex may be rationalised, and symbolised, in the following simplified way: \( \text{P} \rightarrow \text{Ge} \rightarrow \text{Cl} \rightarrow \text{Cu} \rightarrow \text{Ge} \). Finally, the reaction of the iminophosphorane-functionalised gemylene 23 with CuCl cleanly afforded the gemylene-copper(I) complex [(23)CuCl] \(\text{[26, Scheme 4]}\). In view of the substantial number of Cu’ iminophosphorane complexes, \(^{35}\) it has not been obvious a priori that this reaction leads to a Cu’ gemylene complex. Solution NMR spectra are in accord with the structure found in the solid state, which is shown in Figure 11. The coordination environment of the Cu atom of 26 is linear dicoordinate (bond angle 176°). The Cu–Cl bond length of 2.10 Å is typical for this arrangement and several structurally characterised examples of complexes \([\text{CuCl} \text{L}]\) with \( L = \text{carbene (CAAC, NHC)} \) or donor-stabilised silylene, but not with \( L = \text{germylene or heavier analogues, have been reported}^{36}\). The Cu–Ge distance of 2.25 Å corresponds to the shortest Cu–Ge bond lengths determined for 24 (see above), where we have a combination of tricoordinate Ge and tricoordinate Cu. In the case of 26, we have a combination of dicoordinate Cu’ and tetracoordinate Ge’, since the intramolecular coordination of
the iniminophosphorane N atom found for germylene 23 is also present in its copper complex 26. Cu coordination leads to a substantial shortening of all three Ge–N bonds. Analogous to 25 (see above), the effect is largest (0.13 Å) for the coordinative bond, which is contracted from 2.11 Å in 23 to 1.98 Å in 26, while the two other Ge–N bonds experience a less pronounced contraction (0.08 Å on average).

Conclusion

We have compared the reactivity of the ferrocene-based N-heterocyclic tetrylenes [Fe(η5–C5H5–NSiBuMe3)2]E [E = Pb (15), Sn (16),Ge (17)] towards mesityl azide with that of the PPh3-functionalised congeners 12–14, whose phosphorus(III) atom constitutes a second possible reaction site in addition to the respective tetr(II) atom. Our results indicate that the reaction of this azide with the stannylenes and germanyles 13 and 16 and germylenes 14 and 17 invariably occurs at the divalent tetrel atom, leading to an E=N double bond. The resulting germanimines 19 and 22 could be isolated. However, the latter isomerised readily to iniminophosphorane 23 by NMes transfer from the Ge5 to the PIII atom due the reactive Ge=N bond. In line with previous observations (see above), the reactivity of the Sn=N bond is even higher, so that only follow-up products were observed in the reactions of the stannylenes 13 and 16, namely, iniminophosphorane 21 (most likely formed by NMes transfer from the SnIV to the PIII atom of the transient stannanimine) and stannate-trazol 18 (formed by [2 + 3] cycloaddition of the transient stannanimine with mesityl azide). All four unfunctionalised dianiomoplumbylene of our study, viz. the N-heterocyclic compounds o-C6H4(NSiMe3)2Pb, nap(NSiMe3)2Pb and [Fe–(η5-C5H5–NSiBuMe3)2]Pb (15) as well as the acyclic congener [[Me5Si2]N]Pb, proved to be inert towards MesN3 even under forcing conditions. In contrast, the behaviour of the PPh3-functionalised dianiomoplumbylene 12 towards mesityl azide is analogous to that of Wesemann’s PPh3-functionalised (alkyl)(aryl)plumbylene 5, being strongly reminiscent of B/P FLPs in both cases. While 5 reacts already at room temperature, moderately higher temperatures are needed in the case of 12. This may be ascribed to the fact that the P atom of 12, in contrast to that of 5, is engaged in an intramolecular coordinative bond to the Pb atom. Consequently, plumbylene 12 exhibits a reduced frustration in comparison to 5 and thus belongs to the so-called active Lewis pairs (ALPs), which can show FLP-like behaviour due to the weakness of their coordinative bond.[26] Investigations addressing the activation of fundamentally important small molecules with 12 and closely related ALPs are underway in our laboratory. In addition, our study has demonstrated the ability of the unfunctionalised N-heterocyclic germylene 17 and its donor-functionalised relatives 14 and 23 to act as ligands for copper(II), thus underlining the potential of such ferrocene-based, and hence redox-functionalised, N-heterocyclic germylenes in coordination chemistry.[56] Notably, compound 26 is the first structurally characterised linear dicoordinate copper(I) halogenido complex [CuX(L)] with a heavier tetrylene ligand L.

Experimental Section

All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. [Fe(η5–C5H5–NH5SiBuMe3)2]30, [GeCl4(1,4-dioxane)]32, 12–14,35 15,36 1637 and MesN338 were synthesised by adapted versions of the published procedures. NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for 1H. Elemental analyses were carried out with a Herauratech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany.

Synthesis of 17: Li[N(SiMe3)2] (395 mg, 2.36 mmol) was added to a stirred solution of [Fe(η5–C5H5–NH5SiBuMe3)2] (500 mg, 1.12 mmol) in THF (6 mL). After 30 minutes [GeCl4(1,4-dioxane)] (260 mg, 1.12 mmol) was added and stirring was continued for 2 h. Volatile components were removed under reduced pressure. n-Hexane (6 mL) was added to the residue. Insoluble material was removed by filtration through a small pad of celite. The solvent was removed from the filtrate under reduced pressure, leaving the product as a brownish-yellow viscous oil. Yield 534 mg (92%). Crystallisation of the product was initiated in a concentrated n-hexane solution by scratching with a glass rod. After the first crystals appeared, the flask was stored at ~40°C. The mother liquor was separated from the orange product, which was finally dried under reduced pressure. 1H NMR (400 MHz, C2D2): δ = 3.87, 3.78 (2 m, 2 × 4 H, cyclopentadienyli), 1.00 (s, 18 H, CMe3), 0.29 (s, 12 H, SiMe3) ppm. 13C(1H) NMR (101 MHz, C2D2): δ = 110.1 (Cmes), 68.9, 66.7 (2 × CH), 27.6 (Cmes), 18.9 (Cmes), −1.0 ppm (SiMe3). Anal. calc. for C12H16N2FeGeSi5: C 51.20, H 7.43, N 5.44%; found C 50.74, H 7.56, N 5.19%.

Synthesis of 18: Mesityl azide (77 mg, 0.24 mmol) was added to a stirred solution of 16 (132 mg, 0.24 mmol) in n-hexane (3 mL). Stirring was discontinued after 30 min. The solution was stored at −40°C for crystallisation. The mother liquor was separated from the
yellow crystals, which were subsequently dried under reduced pressure. Yield 168 mg (83%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)); \(\delta = 6.93\) (s, 4 H, Mes CH), 7.05–6.98 (m, 2 x 2 H, Ph o-H), 6.98–6.87 (m, 4 H, Ph m-H), 6.72 (s, 2 H, Mes CH), 4.29, 3.97 (2 m, 2 x 2 H, cyclopentadienyl H), 3.93, 3.65, 3.59 (3 m, 3 x 1 H, cyclopentadienyl CH), 2.25 (s, 6 H, Mes CH-o), 2.09 (s, 3 H, Mes CH-p), 0.48, 0.25 ppm (2 s, 2 x 9 H, SiMe\(_3\)). \(^{13}\)C\((\text{H})\) NMR (101 MHz, CD\(_2\)Cl\(_2\)); \(\delta = 149.7\) (Mes C\(\text{C}_2\)), 129.1 (Mes C\(\text{C}_2\)), 94.7 (cyclopentadienyl C\(\text{C}_2\)), 69.3, 68.5 (2 x cyclopentadienyl CH), 27.5 (C\(\text{M}_{\text{e}}\)), 21.4 (Mes C\(\text{C}_2\)), 21.1 (C\(\text{M}_{\text{e}}\)), 20.1 (Mes C\(\text{C}_2\)), 2.8 ppm (Si\(\text{Me}_3\)); Mes C\(\text{C}_2\) not detected. Anal. calc. for \(\text{C}_2\text{H}_9\text{N}_2\text{FeP}_{\text{Si}}\text{S}_{\text{Si}}\) (684.39): C 57.42, H 7.62, N 6.48%; found C 58.40, H 6.86, N 6.44%.

Synthesis of 19: A solution of mesityl azide (52 mg, 0.32 mmol) in \(n\)-hexane (1 mL) was added to a stirred solution of 17 (165 mg, 0.32 mmol) in \(n\)-hexane (5 mL). After 10 minutes the volume of the solution was reduced to ca. 3 mL. The solution was stored at \(-40^\circ\text{C}\) for crystallisation. The orange product was separated from the mother liquor and subsequently dried under reduced pressure. Yield 149 mg (72%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)); \(\delta = 7.01\) (s, 2 H, Mes CH), 3.91, 3.82 (2 m, 2 x 4 H, cyclopentadienyl H), 2.55 (s, 6 H, Mes CH), 2.30 (s, 3 H, Mes CH-p), 0.94 (s, 18 H, C\(\text{M}_{\text{e}}\)), 0.26 ppm (12 H, Si\(\text{Me}_3\)). \(^{13}\)C\((\text{H})\) NMR (101 MHz, CD\(_2\)Cl\(_2\)); \(\delta = 142.7\) (Mes C\(\text{C}_2\)), 131.9 (Mes CH), 128.8, 127.4 (2 x Mes C\(\text{C}_2\)), 100.2 (cyclopentadienyl C\(\text{C}_2\)), 70.3, 67.7 (2 x cyclopentadienyl CH), 27.2 (C\(\text{M}_{\text{e}}\)), 24.5 (Mes C\(\text{C}_2\)), 20.6 (Mes C\(\text{C}_2\)), 20.5 (C\(\text{M}_{\text{e}}\)), –2.6 ppm (Si\(\text{Me}_3\)). \(^{31}\)P\((\text{H})\) NMR (186 MHz, CD\(_2\)Cl\(_2\)); \(\delta = -217.7\) ppm. Anal. calc. for \(\text{C}_2\text{H}_9\text{N}_2\text{FeP}_{\text{Si}}\text{S}_{\text{Si}}\) (855.67): C 56.15, H 7.07, N 9.82%; found C 56.34, H 7.01, N 8.88%.

Synthesis of 19: A solution of mesityl azide (52 mg, 0.32 mmol) in \(n\)-hexane (1 mL) was added to a stirred solution of 17 (165 mg, 0.32 mmol) in \(n\)-hexane (5 mL). After 10 minutes the volume of the solution was reduced to ca. 3 mL. The solution was stored at \(-40^\circ\text{C}\) for crystallisation. The orange product was separated from the mother liquor and subsequently dried under reduced pressure. Yield 149 mg (72%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)); \(\delta = 7.01\) (s, 2 H, Mes CH). The solution was stored at \(-40^\circ\text{C}\) for crystallisation. The orange product was separated from the mother liquor and subsequently dried under reduced pressure. Yield 149 mg (72%).

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Synthesis of 19: A solution of mesityl azide (52 mg, 0.32 mmol) in \(n\)-hexane (1 mL) was added to a stirred solution of 17 (165 mg, 0.32 mmol) in \(n\)-hexane (5 mL). After 10 minutes the volume of the solution was reduced to ca. 3 mL. The solution was stored at \(-40^\circ\text{C}\) for crystallisation. The orange product was separated from the mother liquor and subsequently dried under reduced pressure. Yield 149 mg (72%).
Synthesis of 24: CuCl (30 mg, 0.30 mmol) was added to a stirred solution of 17 (120 mg, 0.23 mmol) in toluene (5 mL). After 18 h insoluble material was removed by filtration through a short pad of celite, followed by washing with toluene (1.5 mL). Volatile components were removed from the combined filtrate and washing solution. The product was extracted from the residue with n-hexane (3 × 2 mL). After filtration of the extract to remove trace amounts of insoluble material, the volume was reduced to ca. 0.5 mL. Yellow crystals were obtained after several days, which were separated from the mother liquor and subsequently dried under reduced pressure. Yield 61 mg (42%). 1H NMR (400 MHz, CD2Cl2): δ = 3.84, 3.75 (2 m, 2 × 4 H, cyclopentadienyl H), 1.10 (s, 18 H, Bn), 0.54 ppm (s, 12 H, SiMe3). 13C(1H) NMR (101 MHz, CD2Cl2): δ = 106.9 (Cipso), 69.3, 67.3, 65.8 (2 × cyclopentadienyl CH), 27.9 (CMes), 19.2 (CMes), −0.1 ppm (SiMe3). Anal. calcld for C12H14ClCuFeGeN2Si3: C 43.02; H 4.56; found C 43.11; H 4.64; N 4.72%.

Synthesis of 25: CuCl (25 mg, 0.21 mmol) was added to a stirred solution of 14 (90 mg, 0.15 mmol) in toluene (5 mL). After 72 h insoluble material was removed by filtration through a short pad of celite, followed by washing with toluene (1 mL). The volume of the combined filtrate and washing solution was reduced to ca. 0.5 mL. n-Hexane (0.5 mL) was added. The solvent was slowly evaporated under ambient conditions, affording the crude product as a dark brownish red microcrystalline solid, which was washed with n-hexane (2 × 0.2 mL) and subsequently dried under reduced pressure. Yield 25 mg (26%). 1H NMR (400 MHz, CD2Cl2): δ = 7.95, 7.47 (2 br, 2 × 2 H, Ph), 7.31–7.29 (2 × 7 H, 5 m, 5 Ph), 7.20–7.18 (1 m, 1 Ph), 7.10–7.05 (m, 4 H, Ph), 6.99–6.95 (m, 5 H, Ph), 6.87 (m, 1 H, Ph), 4.60, 4.22, 4.11, 3.88 (4 m, 4 × 1 H, cyclopentadienyl H), 3.89, 3.74 (2 m, 2 × 2 H, cyclopentadienyl H), 3.66–3.62 (m, 4 H, cyclopentadienyl H), 3.30, 3.02 (2 m, 2 × 1 H, cyclopentadienyl H), 0.53 (s, 18 H, SiMe3), 0.50, 0.24 ppm (2 s, 2 × 9 H, SiMe3). 13C(1H) NMR (101 MHz, CD2Cl2): δ = 135.7 (d, J = 10.8 Hz), 134.4 (d, J = 14.5 Hz), 134.2, 133.9, 133.7 (d, J = 14.3 Hz), 132.7, 132.2, 132.1, 130.9, 129.9 (d, J = 11.0 Hz), 129.7, 129.7, 129.4 (d, J = 9.6 Hz), 128.6, 128.5, 128.2 (16 × Ph), 109.3 (d, J = 17.5 Hz), 105.1, 104.0 (3 × cyclopentadienyl CH), Cipso one of the expected four Cipso signals and Cipso signals not detected), 76.4 (d, J = 5–6 Hz, Ph), 74.5, 72.4, 71.9 (d, J = 5.7 Hz), 70.4, 69.3, 69.3, 68.3 (d, J = 5.4 Hz), 67.5, 67.4, 66.7 (d, J = 4.2 Hz), 66.3, 66.1, 65.1 (14 × cyclopentadienyl CH), 5.1 (two isochronous signals, SiMe3), 3.6, 3.1 ppm (2 × SiMe3). 31P(1H) NMR (202 MHz, CD2Cl2): δ = −7.5, −17.5 ppm. Satisfactory microanalytical data could not be obtained.

Synthesis of 26: CuCl (10 mg, 0.10 mmol) was added to a stirred solution of 23 (67 mg, 0.09 mmol) in toluene (1 mL). After 24 h insoluble material was removed by filtration through a short pad of celite, followed by washing with toluene (1 mL). The volume of the combined filtrate and washing solution was reduced to ca. 0.5 mL. The solution was placed in a 5 mm NMR tube and was subsequently layered with n-hexane (ca. 3 mL). After two weeks yellow crystals had formed, which were separated from the mother liquor and subsequently dried under reduced pressure. Yield 51 mg (67%). 1H NMR (400 MHz, CD2Cl2): δ = 7.76–7.72, 7.54–7.49 (2 m, 2 × 2 H, Ph), 7.10–7.06 (m, 1 m, 1 Ph), 6.93–6.89 (m, 3 m, 3 Ph), 6.84 (s, 1 H, Mes CH3), 6.83–6.79 (m, 2 H, Ph CH3), 6.70 (s, 1 H, Mes CH3), 4.43, 4.20, 4.05, 4.03, 3.82, 3.68, 3.65 (7 m, 7 × 1 H, cyclopentadienyl H), 2.11, 2.06, 1.97 (3 s, 3 × 3 H, Mes CH3), 0.62, 0.41 ppm (2 s, 2 × 9 H, SiMe3).

X-ray crystallography: For each data collection a single crystal was mounted on a micro-mount and all geometric and intensity data were taken from this sample at 100(2) K, except for 23, which was measured at 253(2) K due to a phase transition below this temperature. Data collections were carried out either on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector on a Stoe StadiVario diffractometer equipped with a 4-circle goniometer and a Dectris Pilatus 200 K detector. The data sets were correct for absorption, Lorentz and polarization effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against F2 (SHELXL2014/7).221 C-bonded H atoms were included in the models in calculated positions, heteroatom-bonded H atoms have been found in the difference Fourier maps. All H atoms were treated with the 1.2-fold or 1.5-fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table S1 in the Supporting Information.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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