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**Ruthenium germyl complex [(Ph<sub>3</sub>P)ClRuGeCl<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>-2-(η<sup>6</sup>-Trip)-6-Trip)] (1) is reduced with four electrons to yield the vinyl anion type complex [(Ph<sub>3</sub>P)Ru=GeK(C<sub>6</sub>H<sub>3</sub>-2-(η<sup>6</sup>-Trip)-6-Trip)] (3a) exhibiting a novel coordination mode for a germylidyne ligand. Formation of a gold–germanium bond in reaction with [(Ph<sub>3</sub>P)AuCl] and reaction with monofluorobenzene is presented.**

The higher homologues of the carbyne ligand [C–R] are referred to as tetrylidyne ligands [E–R] (E = Si–Pb), and the first tetrylidyne transition metal complex [Cp(CO)<sub>2</sub>Mo≡GeAr'] was synthesized by Power and coworkers in 1996 [Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-(Mes)<sub>2</sub>, Mes = 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>].<sup>1,2</sup> Filippou *et al.* have further developed the family of tetrylidyne complexes and have presented a broad variety of examples of these low valent Group 14 element compounds.<sup>3–13</sup> Heavy carbyne coordination chemistry has also been investigated by Hadlington, Hashimoto, Jones, Tilley, and Tobita, so that there are now numerous examples in the literature [(M≡E) M = Nb, Cr, Mo, W, Mn, Re, Fe, Co, Rh, Ir, Ni, Pt; E = Si, Ge, Sn, Pb].<sup>14–25</sup> We have recently added the tetrylidyne (E = Ge, Sn, Pb) of Co, Rh and Ir to this family.<sup>23–25</sup>

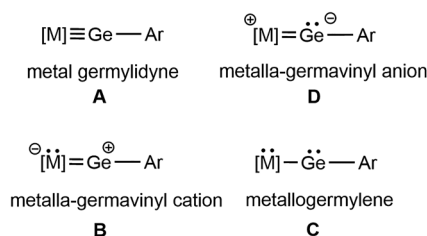
In heavy carbyne transition metal coordination compounds, the transition metal tetrylidyne, the tetrylidyne ligands build a linear triple bond [R–E≡M] with transition metal fragments (Scheme 1A). This bond consists of a σ-bond, which results from donation of the Group 14 element lone pair to the transition metal and two π-bonds derived from transition metal d-orbital donation into empty Group 14 element p-orbitals.<sup>26–31</sup> We have recently shown that after bromide abstraction from the tetrylene complexes [(Me<sub>3</sub>P)<sub>3</sub>HirEBrTbb] (E = Ge, Sn, Tbb = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-(*t*-Bu)C<sub>6</sub>H<sub>2</sub>) heavy metalla vinyl-cations [(Me<sub>3</sub>P)<sub>3</sub>Hir=E–Tbb]<sup>+</sup> (E = Ge, Sn) were obtained (Scheme 1B).<sup>32</sup> In these cations the bonding of the [Sn–Tbb] ligand at the iridium fragment consists of a σ-donor interaction Sn → Ir and only one π-backbond from the iridium atom to the tin. Furthermore, there is an empty p-orbital

# Tetrylidyne coordination modes: vinyl-type germa–ruthena anion [Ru=Ge:]<sup>−</sup> and its reaction with monofluorobenzene

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at the tin atom and the cationic charge is primarily residing at the tin atom.<sup>32</sup> Therefore we consider this bonding situation of the [Sn–Tbb] tetrylidyne ligand at iridium as a heavy metalla vinyl-cation (Scheme 1B).<sup>32</sup> This vinyl-type coordination of [Sn–Tbb] was also observed in the cationic hydride abstraction product [Cp<sub>2</sub>Ti=SnAr\*(SnHAr\*)][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] [(Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-(Trip)<sub>2</sub>, Trip = 2,4,6-C<sub>6</sub>H<sub>2</sub>iPr<sub>3</sub>] and the iron complex [Cp\*(Pr<sub>2</sub>MeP)Fe=SnAr'] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] shows also a comparable electronic situation.<sup>21,33,34</sup> The metallotetrylene bonding mode (Scheme 1C) of the tetrylidyne ligands [E–R] is well known and was presented in the literature for the heavy elements of the Group 14 together with reactivity studies of the [M–E–R] unit (E = Si, Ge, Sn and Pb).<sup>21,18,21,35–42</sup> Pandey, Frenking and coworker discussed in a comparative study the metal–germanium interaction in metallogermynes and metal germylidyne complexes (Scheme 1A and C).<sup>29</sup> We present in this manuscript with the germa–ruthena vinyl anion a hitherto unknown bonding mode for a germylidyne ligand [Ge–Ar\*] (Scheme 1D) and show first reactions of this unprecedented [Ru=Ge:]<sup>−</sup> moiety.

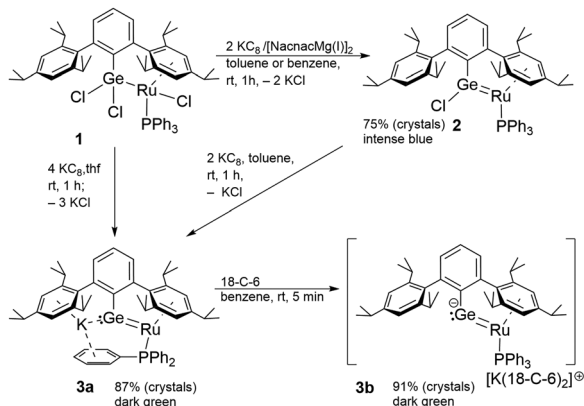
Starting with the ruthenium–germyl complex 1, which is synthesized following a literature procedure, the germylene coordination compound 2 was obtained straightforwardly by two-electron reduction of complex 1 (Scheme 2).<sup>43</sup> The reduction gives a zero valent ruthenium complex coordinated by a chlorogermylene ligand. The ruthenium germylene coordination compound 2 (Fig. 1) shows a Ru–Ge bond length of 2.27500(18) Å, which is a very short bond between these elements



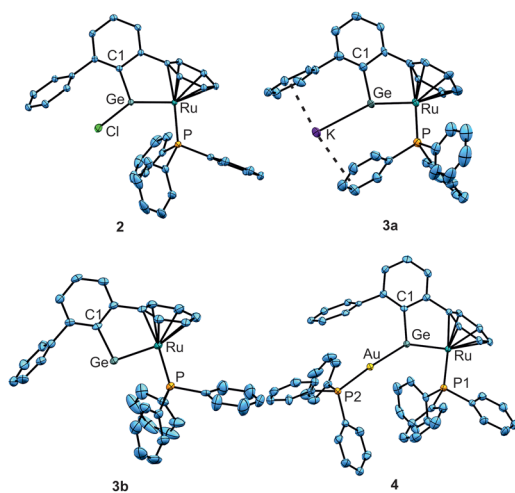
Scheme 1 Bonding modes of the germylidyne ligand.

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**Scheme 2** Reduction of germyl complex **1**, synthesis of chloro germylene complex **2** and germa vinyl anion **3a** and **3b**.



**Fig. 1** ORTEPs of the molecular structures of **2**, **3a**, **3b** and **4**. Thermal ellipsoids are shown at 50% probability. *i*Pr groups, hydrogen atoms and cation  $[K(18-C-6)]^+$  have been omitted. Selected interatomic distances [Å] and angles [°]: **2**: Ge–Ru 2.27500(18), Ru–P 2.2883(3), Ge–C1 1.9766(13), Ge–Cl 2.2123(4), C1–Ge–Ru 108.41(4); **3a**: Ge–Ru 2.3531(10), Ru–P 2.256(2), Ge–C1 2.058(8), Ge–K 3.259(2), K–C<sub>Trip</sub> 3.192(10) – 3.337(8), K–C<sub>PPh</sub> 3.287(10) – 3.357(10), C1–Ge–Ru 97.8(2); **3b**: Ge–Ru 2.3865(9), Ru–P 2.2488(19), Ge–C1 2.055(7), C1–Ge–Ru 97.1(2); **4**: Ge–Ru 2.3215(5), Ge–Au 2.4129(5), Ru–P1 2.2708(11), Au–P2 2.3357(11), Ge–C1 2.017(4), Ge–Au–P2 171.0(1), C1–Ge–Ru 101.8(1).

and can be compared with the so far shortest Ru–Ge bond of 2.2821(6) Å in  $Cp^*Ru(GeHTrip)H(PMe^iPr_2)$ .<sup>44</sup>

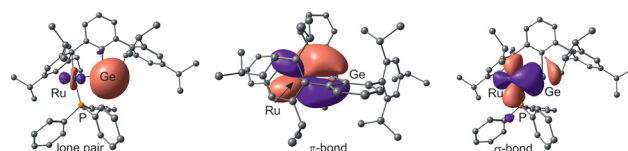
Other comparable Ru–Ge coordination compounds exhibit slightly longer Ru–Ge bond lengths [2.3162(2)–2.3579(3) Å].<sup>45–48</sup> The germylene coordination in complex **2** features a typical  $\sigma$ -donor and  $\pi$ -acceptor interaction with the ruthenium atom.  $\sigma$ -Donation from a germanium *s*-orbital into a ruthenium *d*-orbital results in a  $\sigma$ -bond featuring polarization to the germanium atom (NLMO: atomic contributions Ru–Ge: 37, 58%, Table 1).  $\pi$ -Backdonation from a filled ruthenium *d*-orbital into an empty *p*-orbital of germanium was observed and this interaction is polarized to the ruthenium atom (NLMO: atomic contributions Ru–Ge: 71, 23%, Table 1).

**Table 1** Selected results of DFT<sup>49</sup> calculations [BP86-D3BJ, def2-SVP/TZVP(Ru, Ge, P, Cl, Au)]<sup>49–57</sup> and NBO analyses<sup>58</sup>

	<b>2</b>	<b>3a</b>	<b>3b</b>	<b>4</b>
Ru–Ge [Å]	2.27271	2.34713	2.38133	2.30474
<i>q</i> [e] Ru, Ge	−0.47, 0.96	−0.47, 0.09	−0.51, 0.32	−0.43, 0.31
Wiberg/Löwdin	1.01/1.80	1.09/1.75	0.99/1.88	1.08/1.66
$\sigma$ -bond occ.	1.8056	1.6821	1.3952	1.7537
Ru–Ge% (NLMO)	37, 58	55, 37	71, 23	46, 48
$\pi$ -bond occ.	1.8652	1.8037	1.7936	1.8470
Ru–Ge% (NLMO)	71, 23	66, 24	71, 19	67, 26

Two-electron reduction of the zero valent ruthenium germylene complex **2** or four-electron reduction of germyl complex **1** with  $KC_8$  affords formation of a novel germa–ruthena vinyl anion **3a** as a potassium salt (Scheme 2). After addition of crown ether 18-crown-6 (18-C-6) to compound **3a** salt **3b** was isolated featuring separation of the anion and cation in the solid-state structure. The germa vinyl anions **3a** and **3b** feature a longer Ru–Ge bond [**3a**: 2.3531(10), **3b**: 2.3865(9) Å] (Fig. 1) in comparison to the chloro germylene complex **2**. Solutions of **3a** and **3b** are thermally stable at rt and **3a** was also heated to 100 °C without decomposing.

In Fig. 2 the natural localized molecular orbitals representing the *s*-orbital at germanium and the Ru–Ge interactions of compound **3b** are shown (results for **3a** were placed in the SI). Because of the two-electron reduction, in **3b** a reduced natural charge of the germanium atom in comparison to the germylene complex **2** was observed (Table 1). The steric strain of the chelating ligand, which manifests itself in a small angle at germanium [**3b**: C1–Ge–Ru 97.1(2)°] (Fig. 1), enables the formation of a germanium *s*-orbital lone-pair (Fig. 2 left NLMO). Consequently, both the Ru–Ge  $\sigma$ -bond (Fig. 2 right NLMO) and the  $\pi$ -bond (Fig. 2, middle NLMO) consist of an interaction mainly between a Ge *p*-orbital and a Ru *d*-orbital. These Ru–Ge  $\sigma$ -bond and  $\pi$ -interactions in **3b** feature both polarization of the bonds to the ruthenium atom ( $\sigma$ -bond: atomic contributions Ru–Ge **3b**: 71, 23%), ( $\pi$ -bond atomic contributions Ru–Ge **3b**: 71, 19%, Table 1). Thus, in anion **3b** a germilydine ligand [Ge–Ar\*] coordinates at ruthenium *via*  $\sigma$ - and  $\pi$ -donation from ruthenium *d*-orbitals into empty germanium *p*-orbitals. The analysis of the electronic situation in anion **3b** leads to the rationalization as a Ru=Ge double bond and a lone pair at germanium. We discuss this bonding motif, which is enforced by the steric strain of the chelat-forming ligand, as a novel bonding mode in tetrylidyne coordination chemistry (Scheme 1D). With the formal fragmentation of complex **3** into a  $(\eta^6-C_6H_6)Ru(PR_3)$  fragment being



**Fig. 2** NLMOs representing the Ru–Ge interactions in **3b** [lone pair: Ge 4s (83%) 4p (17%), Ru 5s (92%) 4d (7%),  $\pi$ -bond: Ge 4p (100%), Ru 4d (100%),  $\sigma$ -bond: Ge 4s (11%) 4p (88%), Ru 5s (3%) 4d (97%) orbital].<sup>59</sup>



isolobal with :CH<sub>2</sub> we propose that the tetryldyne coordination complex **3** be designated as a heavy vinyl anion [Ru=Ge:]<sup>-</sup>.

This type of heavy metalla vinyl anion structural motif can be compared with carbene-CH-deprotonated carbene complexes [Li(dmp)][(Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Ta=C(CMe<sub>3</sub>)] (dmp = *N,N'*-dimethylpiperazine).<sup>60</sup>

The chemical properties of the germa-ruthena vinyl anion **3a** were evaluated in reaction with the gold electrophile [(Ph<sub>3</sub>P)AuCl] and fluorinated benzene derivatives. The [Ru=Ge:]<sup>-</sup> anion reacts as a nucleophile and substitutes the chloride ligand at the gold atom to give a [Ru=Ge-Au]-unit (Scheme 3). The Ge-Au bond length observed in the molecular structure of **4** (Fig. 1) of 2.4129(5) Å lies in the range of published interatomic distances between these elements [2.7587(7)–2.345(1) Å].<sup>61–64</sup> The gold coordination compound **4** shows a longer Ru-Ge bond in comparison to the germylene complex **2** and the bond length can be compared with distances observed in germylene ruthenium coordination compounds [2.3162(2)–2.3579(3) Å].<sup>45–48</sup> The germylene-gold coordination features a σ-bond and the Ru-Ge interaction consists of a σ- and π-bond. This type of germanium-gold coordination was previously reported treating a borylated silagermenide [K][(Me<sub>3</sub>Si)(NHB)Si=GeAr\*] with two equivalents of gold electrophile [(Me<sub>2</sub>IPr)AuCl] at 80 °C to yield trans-[(Me<sub>2</sub>IPr)Au-(NHB)Si=GeAr\*Au(Me<sub>2</sub>IPr)] exhibiting an Au-Ge bond of 2.3919(4) Å [NHB = B(NMes)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>, Me<sub>2</sub>IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene].<sup>64</sup>

Optimization of the conditions for crystallization of potassium salts **3a** and **3b** prompted us to test *o*-difluorobenzene as solvent. Surprisingly, we observed the reaction of a C-F bond of the *o*-difluorobenzene solvent and formation of a Ge-C bond (Scheme 3). To evaluate the scope of this reaction we investigated the reaction of hexafluoro- and monofluorobenzene (Scheme 3). The halides were treated with the salt **3a** at rt in benzene and the substitution reaction was monitored by NMR spectroscopy. Furthermore, addition of crown ether 18-C-6 to the mixture leads to shorter reaction times, which is probably due to complexation of the potassium cation resulting in separation of cation and anion of the germa-ruthena vinyl salt **3b**.

In the case of *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and C<sub>6</sub>F<sub>6</sub> we isolated the substitution products, and the molecular structures are shown in Fig. 3. Compounds **5** and **6** are diaryl germylene coordination compounds featuring a trigonal planar coordinated germanium atom and a short Ru-Ge bond of **5**: 2.2855(3) and **6**: 2.28155(18) Å, respectively. These Ru-Ge bonds are slightly longer than the Ru-Ge bond in **2**. Reactivity studies of very

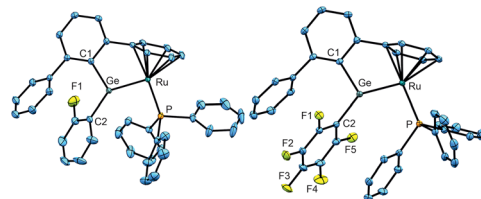
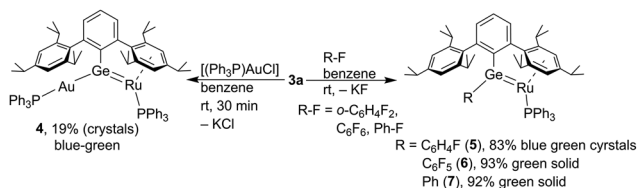


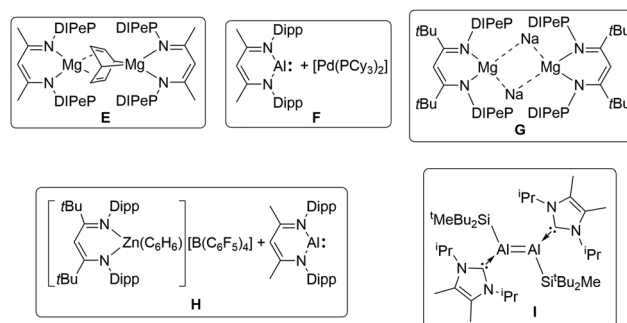
Fig. 3 ORTEPs of the molecular structures of **5** and **6**. Thermal ellipsoids are shown at 50% probability. *i*Pr groups and hydrogen atoms have been omitted. Selected interatomic distances [Å] and angles [°]: **5**: Ge–Ru 2.2855(3), Ru–P 2.2893(6), Ge–C1 1.992(2), Ge–C2 1.957(2), C1–Ge–C2 115.6(1), C1–Ge–Ru 106.1(1), C2–Ge–Ru 138.0(1); **6**: Ge–Ru 2.28155(18), Ru–P 2.2872(3), Ge–C1 1.9972(13), Ge–C2 1.9772(13), C1–Ge–C2 110.1(1), C1–Ge–Ru 106.4(1), C2–Ge–Ru 142.2(1).

stable C–F bonds<sup>65–67</sup> is a research topic of high interest (C<sub>6</sub>H<sub>5</sub>F: C–F *DH*<sub>298</sub> 127.2 ± 0.7 kcal mol<sup>-1</sup>).<sup>65–73</sup> In addition to the reactions of C–F bonds mediated by transition metals, it was also previously reported that compounds of main-group elements react with C–F bonds of fluorobenzenes. Low valent compounds of magnesium,<sup>74–76</sup> boron,<sup>77,78</sup> aluminium,<sup>79–84</sup> gallium,<sup>85</sup> silicon,<sup>86,87</sup> germanium,<sup>88,89</sup> tin,<sup>88</sup> phosphorus<sup>90,91</sup> and bismuth<sup>92</sup> exhibit reactions with C–F units. The reaction of monofluorobenzene however was observed in comparison to the presented germa-ruthena vinyl anion **3b** with examples of more electropositive elements shown in Scheme 4 E–I.<sup>74–76,83,84</sup> Furthermore, C–F bond reactivity of monofluorobenzene was also observed by calcium and strontium hydrides and a magnesium dinitrogen complex.<sup>93–96</sup>

To conclude, upon two electron reduction of an arylchloro-germylene ruthenium complex an anionic coordination compound [(Ph<sub>3</sub>P)Ru=Ge(C<sub>6</sub>H<sub>3</sub>-2-{η<sup>6</sup>-Trip}-6-Trip)]<sup>-</sup> featuring a hitherto unknown coordination mode in heavy carbyne, tetryldyne coordination chemistry was observed. This bonding mode expands in a systematic way the tetryldyne ligand-transition metal interactions described in the literature so far. Because of the chelating terphenyl ligand enforcing a small C–Ge–Ru angle at germanium a vinyl anion type coordination compound [Ru=Ge:]<sup>-</sup> comprising a Ge *s*-orbital lone pair is isolated. In addition, both σ- and π-interactions are established in the Ru=Ge double bond from orthogonal germanium *p*-orbitals and ruthenium *d*-orbitals. With the monofluorobenzene reaction



Scheme 3 Synthesis of gold complex **4** and reactions with fluorobenzenes.



Scheme 4 Monofluorobenzene C–F reaction with **E** (DIPeP = 2,6-(3-pentyl)phenyl),<sup>76</sup> **F** (Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>84</sup> **G**,<sup>74</sup> **H**<sup>75</sup> and **I**.<sup>83</sup>



of this germa–ruthena vinyl anion we are expanding the exclusive family of main-group element compounds that react with monofluorobenzene to include the least electropositive example. Furthermore, an example of the coordination chemistry of the vinyl anion leading to the formation of an [Au–Ge=–Ru] unit was characterized based on the reaction with a gold electrophile.

F. S. experiments, writing of manuscript, crystallographic investigations and SI, L. R. synthesis of **3a**, L. W. supervision, funding acquisition, manuscript writing and review.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Full experimental details are provided as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6cc01226d>.

CCDC 2512263–2512268 contain the supplementary crystallographic data for this paper.<sup>†</sup>

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