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Ruthenium germyl complex [(Ph₃P)ClRuGeCl₂(C₆H₃-2-(η⁶-Trip)-6-Trip)] (1) is reduced with four electrons to yield the vinyl anion type complex [(Ph₃P)Ru=GeK(C₆H₃-2-(η⁶-Trip)-6-Trip)] (3a) exhibiting a novel coordination mode for a germylidyne ligand. Formation of a gold–germanium bond in reaction with [(Ph₃P)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)₂Mo≡GeAr'] was synthesized by Power and coworkers in 1996 [Ar' = C₆H₃-2,6-(Mes)₂, Mes = 2,4,6-C₆H₂Me₃].^{1,2} 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.^{3–13} 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].^{14–25} We have recently added the tetrylidyne (E = Ge, Sn, Pb) of Co, Rh and Ir to this family.^{23–25}

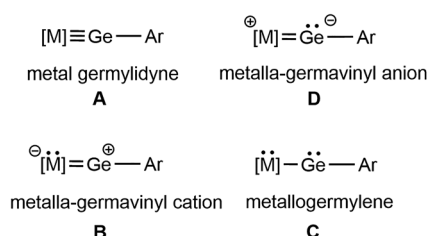
In heavy carbyne transition metal coordination compounds, the transition metal tetrylidyne, the tetrylidyne ligands build a linear triple bond [R–E≡M] with transition metal fragments (Scheme 1A). This bond consists of a σ-bond, which results from donation of the Group 14 element lone pair to the transition metal and two π-bonds derived from transition metal d-orbital donation into empty Group 14 element p-orbitals.^{26–31} We have recently shown that after bromide abstraction from the tetrylene complexes [(Me₃P)₃HirEBrTbb] (E = Ge, Sn, Tbb = 2,6-[CH(SiMe₃)₂]₂-4-(*t*-Bu)C₆H₂) heavy metalla vinyl-cations [(Me₃P)₃Hir=E–Tbb]⁺ (E = Ge, Sn) were obtained (Scheme 1B).³² 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:][−] and its reaction with monofluorobenzene

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at the tin atom and the cationic charge is primarily residing at the tin atom.³² Therefore we consider this bonding situation of the [Sn–Tbb] tetrylidyne ligand at iridium as a heavy metalla vinyl-cation (Scheme 1B).³² This vinyl-type coordination of [Sn–Tbb] was also observed in the cationic hydride abstraction product [Cp₂Ti=SnAr*(SnHAr*)][HB(C₆F₅)₃] [(Ar* = C₆H₃-2,6-(Trip)₂, Trip = 2,4,6-C₆H₂iPr₃] and the iron complex [Cp*(Pr₂MeP)Fe=SnAr'] [B(C₆F₅)₄] shows also a comparable electronic situation.^{21,33,34} 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).^{21,18,21,35–42} Pandey, Frenking and coworker discussed in a comparative study the metal–germanium interaction in metallogermynes and metal germylidyne complexes (Scheme 1A and C).²⁹ 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:][−] moiety.

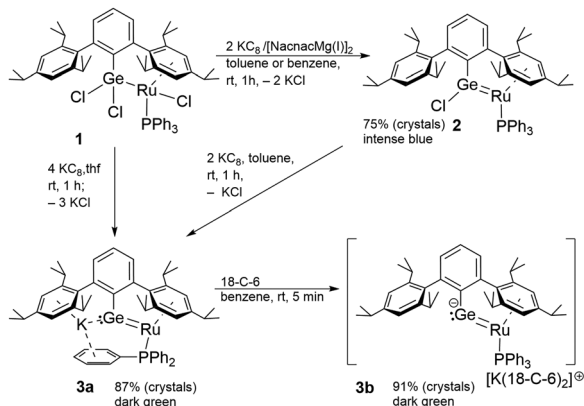
Starting with the ruthenium–germyl complex 1, which is synthesized following a literature procedure, the germylene coordination compound 2 was obtained straightforwardly by two-electron reduction of complex 1 (Scheme 2).⁴³ The reduction gives a zero valent ruthenium complex coordinated by a chlorogermylene 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**.

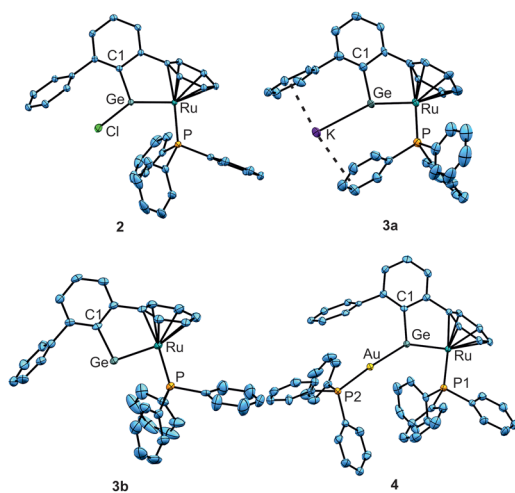


Fig. 1 ORTEPs of the molecular structures of **2**, **3a**, **3b** and **4**. Thermal ellipsoids are shown at 50% probability. *i*Pr groups, hydrogen atoms and cation $[K(18-C-6)]^+$ have been omitted. Selected interatomic distances [Å] and angles [°]: **2**: Ge–Ru 2.27500(18), Ru–P 2.2883(3), Ge–C1 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_{Trip} 3.192(10) – 3.337(8), K–C_{PPh} 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 $Cp^*Ru(GeHTrip)H(PMe^iPr_2)$.⁴⁴

Other comparable Ru–Ge coordination compounds exhibit slightly longer Ru–Ge bond lengths [2.3162(2)–2.3579(3) Å].^{45–48} The germylene coordination in complex **2** features a typical σ -donor and π -acceptor interaction with the ruthenium atom. σ -Donation from a germanium *s*-orbital into a ruthenium *d*-orbital results in a σ -bond featuring polarization to the germanium atom (NLMO: atomic contributions Ru–Ge: 37, 58%, Table 1). π -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 DFT⁴⁹ calculations [BP86-D3BJ, def2-SVP/TZVP(Ru, Ge, P, Cl, Au)]^{49–57} and NBO analyses⁵⁸

	2	3a	3b	4
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
σ -bond occ.	1.8056	1.6821	1.3952	1.7537
Ru–Ge% (NLMO)	37, 58	55, 37	71, 23	46, 48
π -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 σ -bond (Fig. 2 right NLMO) and the π -bond (Fig. 2, middle NLMO) consist of an interaction mainly between a Ge *p*-orbital and a Ru *d*-orbital. These Ru–Ge σ -bond and π -interactions in **3b** feature both polarization of the bonds to the ruthenium atom (σ -bond: atomic contributions Ru–Ge **3b**: 71, 23%), (π -bond atomic contributions Ru–Ge **3b**: 71, 19%, Table 1). Thus, in anion **3b** a germilydyne ligand [Ge–Ar*] coordinates at ruthenium *via* σ - and π -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

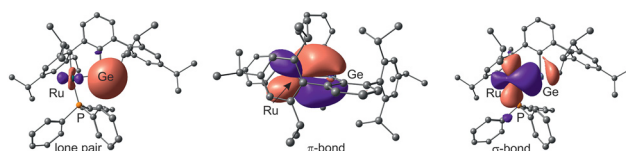


Fig. 2 NLMOs representing the Ru–Ge interactions in **3b** [lone pair: Ge 4s (83%) 4p (17%), Ru 5s (92%) 4d (7%), π -bond: Ge 4p (100%), Ru 4d (100%), σ -bond: Ge 4s (11%) 4p (88%), Ru 5s (3%) 4d (97%) orbital].⁵⁹



isolobal with :CH₂ we propose that the tetrylidyne coordination complex **3** be designated as a heavy vinyl anion [Ru=Ge:]⁻.

This type of heavy metalla vinyl anion structural motif can be compared with carbene-CH-deprotonated carbene complexes [Li(dmp)][(Me₃CCH₂)₃Ta=C(CMe₃)] (dmp = *N,N'*-dimethylpiperazine).⁶⁰

The chemical properties of the germa-ruthena vinyl anion **3a** were evaluated in reaction with the gold electrophile [(Ph₃P)AuCl] and fluorinated benzene derivatives. The [Ru=Ge:]⁻ 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].^{61–64} 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].^{45–48} 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][(Me₃Si)(NHB)Si=GeAr*] with two equivalents of gold electrophile [(Me₂IPr)AuCl] at 80 °C to yield trans-[(Me₂IPr)Au-(NHB)Si=GeAr*Au(Me₂IPr)] exhibiting an Au-Ge bond of 2.3919(4) Å [NHB = B(NMes)₂(CH₂)₂, Me₂IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene].⁶⁴

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*-C₆H₄F₂ and C₆F₆ 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

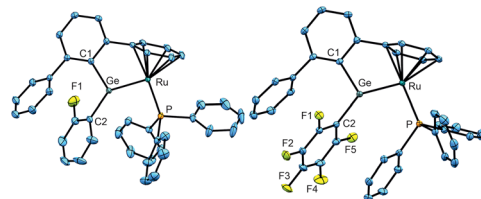
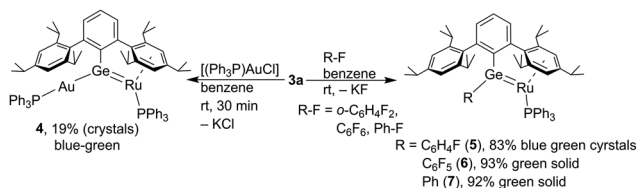


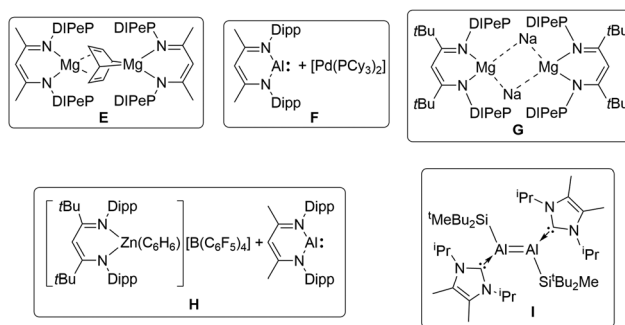
Fig. 3 ORTEPs of the molecular structures of **5** and **6**. Thermal ellipsoids are shown at 50% probability. *iPr* groups and hydrogen atoms have been omitted. Selected interatomic distances [Å] and angles [°]: **5**: Ge–Ru 2.2855(3), Ru–P 2.2893(6), Ge–C1 1.992(2), Ge–C2 1.957(2), C1–Ge–C2 115.6(1), 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^{65–67} is a research topic of high interest (C₆H₅F: C–F *DH*₂₉₈ 127.2 ± 0.7 kcal mol⁻¹).^{65–73} 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,^{74–76} boron,^{77,78} aluminium,^{79–84} gallium,⁸⁵ silicon,^{86,87} germanium,^{88,89} tin,⁸⁸ phosphorus^{90,91} and bismuth⁹² 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.^{74–76,83,84} Furthermore, C–F bond reactivity of monofluorobenzene was also observed by calcium and strontium hydrides and a magnesium dinitrogen complex.^{93–96}

To conclude, upon two electron reduction of an arylchloro-germylene ruthenium complex an anionic coordination compound [(Ph₃P)Ru=Ge(C₆H₃-2-{η⁶-Trip}-6-Trip)]⁻ featuring a hitherto unknown coordination mode in heavy carbyne, tetrylidyne coordination chemistry was observed. This bonding mode expands in a systematic way the tetrylidyne 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:]⁻ 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),⁷⁶ **F** (Dipp = 2,6-*iPr*₂C₆H₃),⁸⁴ **G**,⁷⁴ **H**⁷⁵ and **I**.⁸³



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.[†]

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