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COMMUNICATION

Tetrylidyne Coordination Modes: Vinyl-Type Germa-Ruthena Anion [Ru=Ge:]$^-$ and its Reaction with Monofluorobenzene

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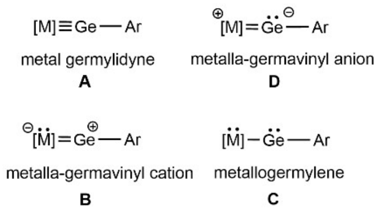
Ruthenium germyl complex [(Ph$_3$P)ClRuGeCl$_2$(C$_6$H$_3$-2-{η^6-Trip}-6-Trip)] (1) is reduced with four electrons to yield the vinyl anion type complex [(Ph$_3$P)Ru=GeK(C$_6$H$_3$-2-{η^6-Trip}-6-Trip)] (3a) exhibiting a novel coordination mode for a germylidyne ligand. Formation of a gold-germanium bond in reaction with [(Ph$_3$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)$_2$Mo≡GeAr'] was synthesized by Power and coworkers in 1996 [Ar' = C$_6$H$_3$-2,6-(Mes)$_2$, Mes = 2,4,6-C$_6$H$_2$Me$_3$].[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 tetrylidynes (E = Ge, Sn, Pb) of Co, Rh and Ir to this family.[23-25]



Scheme 1. Bonding modes of the germylidyne ligand.

In heavy carbyne transition metal coordination compounds, the transition metal tetrylidynes, the tetrylidyne ligands build a linear triple bond [R–E≡M] with transition metal fragments (Scheme 1, **A**). 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 [(Me$_3$P)$_3$HIrEBrTbb] (E = Ge, Sn, Tbb = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-(t-Bu)C$_6$H$_2$) heavy metalla vinyl-cations [(Me$_3$P)$_3$HIr=E–Tbb]$^+$ (E = Ge, Sn) were obtained (Scheme 1, **B**).[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 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 1, **B**).[32] This vinyl-type coordination of [Sn-Tbb] was also observed in the cationic hydride abstraction product [Cp$_2$Ti=SnAr*(SnHAr*)][HB(C$_6$F$_5$)$_3$] [Ar* = C$_6$H$_3$-2,6-(Trip)$_2$), Trip = 2,4,6-C$_6$H$_2$$iPr_3$] and the iron complex [Cp*(^{i}Pr$_2$MeP)Fe=SnAr'][B(C$_6$F$_5$)$_4$] shows also a comparable electronic situation.[21, 33, 34] The metallotetrylene bonding mode (Scheme 1, **C**) of the tetrylidyne ligands [E–R] is well known and was presented in the literature for the heavy elements of the Group 14 together with reactivity studies of the [M–Ë–R] unit (E = Si, Ge, Sn and Pb).[2, 18, 21, 35-42] Pandey, Frenking and coworker discussed in a comparative study the metal-germanium interaction in metallogermylenes and metal germylidyne complexes (Scheme 1, **A**, **C**).[29] We present in this manuscript with the germa-ruthena vinyl anion a hitherto unknown bonding mode for a germylidyne ligand [Ge–Ar*] (Scheme 1, **D**) and show first reactions of this unprecedented [Ru=Ge:]$^-$ 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** (Figure 1) shows a Ru–Ge bond length of 2.27500(18) Å, which is a very short bond between these

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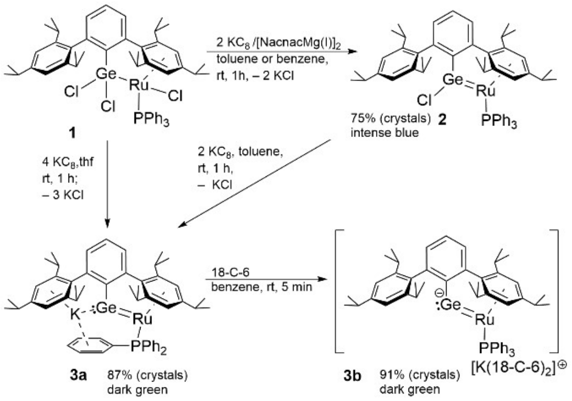
elements and can be compared with the so far shortest Ru–Ge bond of 2.2821(6) Å in Cp*Ru(GeHTrip)H(PMe^{i}Pr$_2$).[44]



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

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).

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] (Figure 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.

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

	2	3a	3b	4
Ru–Ge [Å]	2.27271	2.34713	2.38133	2.30474
q [*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

In Figure 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)°] (Figure 1), enables the formation of a germanium s-orbital lone-pair (Figure 2 left NLMO). Consequently, both the Ru–Ge σ-bond (Figure 2 right NLMO) and the π-bond (Figure 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 germylidyne 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 1, **D**). With the formal fragmentation of complex **3** into a (η^6-C$_6$H$_6$)Ru(PR$_3$) fragment being isolobal with :CH$_2$ we propose that the tetrylidyne coordination complex **3** be designated as a heavy vinyl anion [Ru=Ge:]$^-$.

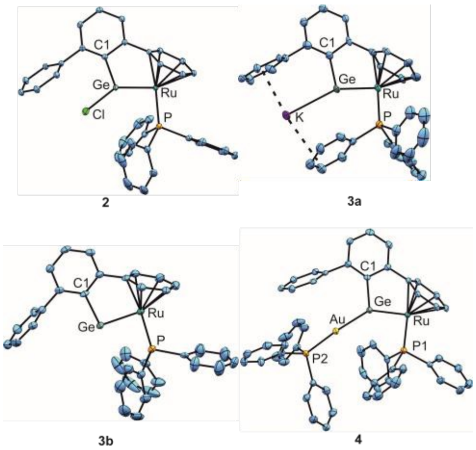


Fig. 1 ORTEPs of the molecular structures of **2**, **3a**, **3b** and **4**. Thermal ellipsoids are shown at 50% probability. *i*Pr groups, hydrogen atoms and cation [K(18-C-6)$_2$]$^+$ have been omitted. Selected interatomic distances [Å] and angles [°]: **2**: Ge-Ru 2.27500(18), Ru-P 2.2883(3), Ge-C1 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).

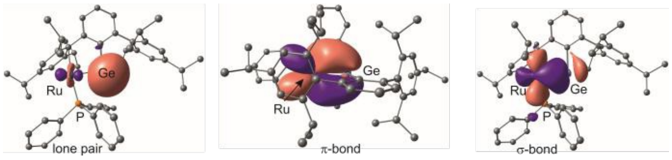


Fig. 2 NLMOs representing the Ru-Ge interactions in **3b** [lone pair: Ge 4s (83%) 4p (17%), Ru 5s (92%) 4d (7%), π-bond: Ge 4p (100%), Ru 4d (100%), σ-bond: Ge 4s (11%) 4p (88%), Ru 5s (3%) 4d (97%) orbital] .[59]

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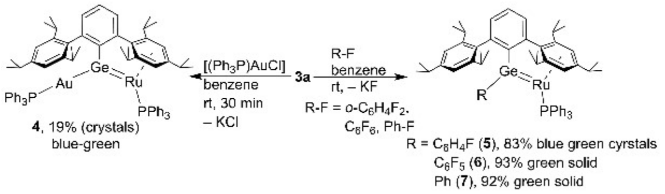
This type of heavy metalla vinyl anion structural motif can be compared with carbene-CH-deprotonated carbene complexes $[Li(dmp)][(Me_3CCH_2)_3Ta{=}C(CMe_3)]$ (dmp = *N,N'*-dimethylpiperazine).[60]

The chemical properties of the germa-ruthena vinyl anion **3a** were evaluated in reaction with the gold electrophile $[(Ph_3P)AuCl]$ 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** (Figure 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 $[K(18\text{-}C\text{-}6)][(Me_3Si)(NHB)Si{=}GeAr^*]$ with two equivalents of gold electrophile $[(Me_2IPr)AuCl]$ at 80°C to yield trans-$[(Me_2IPr)Au\text{-}(NHB)Si{=}GeAr^*Au(Me_2IPr]$ exhibiting an Au–Ge bond of 2.3919(4) Å [NHB = $B(NMes)_2(CH_2)_2$, Me_2IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene].[64]



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

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**.

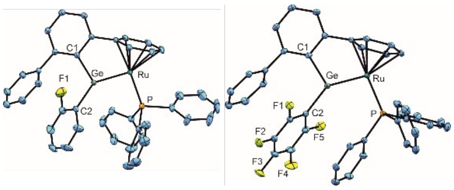
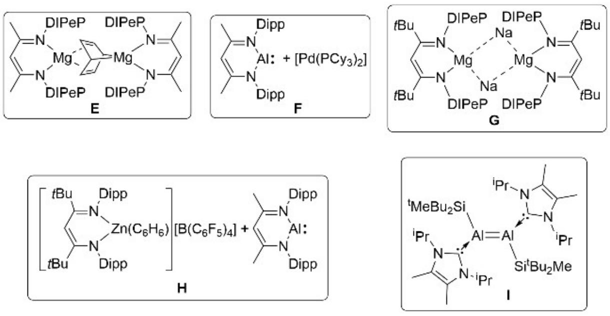


Fig. 3 ORTEPs of the molecular structures of **5** and **6**. Thermal ellipsoids are shown at 50% probability. *i*Pr groups and hydrogen atoms have been omitted. Selected interatomic distances [Å] and angles [°]: **5**: Ge-Ru 2.2855(3), Ru-P 2.2893(6), Ge-C1 1.992(2), Ge-C2 1.957(2), C1-Ge-C2 115.6(1), 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).

In the case of $o\text{-}C_6H_4F_2$ and C_6F_6 we isolated the substitution products, and the molecular structures are shown in Figure 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), respectively. These Ru–Ge bonds are slightly longer than the Ru-Ge bond in **2**. Reactivity studies of very stable C–F bonds[65-67] is a research topic of high interest (C_6H_5F: 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 bismuth[92] 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]



Scheme 4. Monofluorobenzene C-F reaction with **E** (DIPeP = 2,6-(3-pentyl)phenyl),[76] **F** (Dipp = 2,6-$iPr_2C_6H_3$),[84] **G**,[74] **H**[75] and **I**.[83]

To conclude, upon two electron reduction of an arylchlorogermylene ruthenium complex an anionic coordination compound $[(Ph_3P)Ru{=}\ddot{G}e(C_6H_3\text{-}2\text{-}\{\eta^6\text{-}Trip\}\text{-}6\text{-}Trip)]^-$ 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 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

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leading to the formation of an [Au-Ge=Ru] unit was characterized based on the reaction with a gold electrophile.

Author contributions

F. S. experiments, writing of manuscript, crystallographic investigations and ESI, 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 ESI.

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Data availability

Full experimental details are provided as part of the ESI.