Germanium Complexes

DOI: 10.1002/ange.200501968

Ge_2 Trapped by Triple Bonds between Two Metal Centers: The Germylidyne Complexes *trans,trans*-[Cl(depe)$_2$M≡Ge−Ge≡M(depe)$_2$Cl] (M = Mo, W) and Bonding Analyses of the M≡Ge−Ge≡M Chain[**]

Alexander C. Filippou, Gregor Schnakenburg,*
Athanassios I. Philippopoulos, and Nils Weidemann

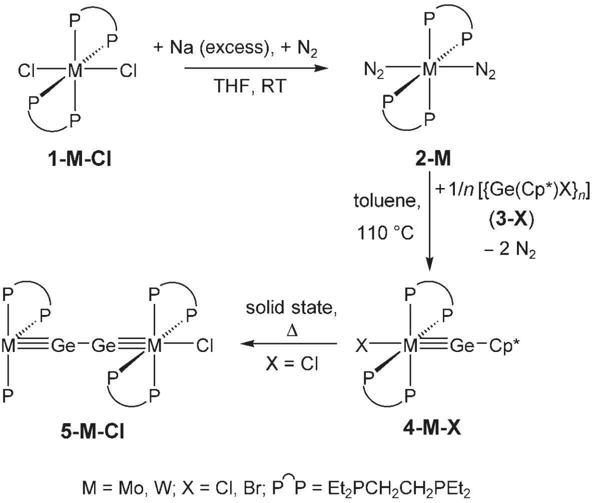
Complexes, in which sp-hybridized carbon chains span two transition-metal centers, $[L_nMC_xM'L'_n]^{y+}$, (L_n, L'_n = ligand sphere; x,y = integer) have attracted particular attention in recent years.[1] These compounds form an important class of carbon-based molecular wires,[2] which are appealing for studies of the electronic communication between redox-active metal termini,[3] and are of potential practical importance in molecular electronics[4] and in nonlinear optics.[5] Moreover, these compounds can be viewed, at large carbon-chain lengths, as polymeric sp-hybridized carbon allotropes, revealing a conceptual relationship to the classical polymeric sp^2- and sp^3-hybridized carbon allotropes, graphite and diamond.[6] For $x = 2$, three classes of metal complexes have been reported to date (**Ia**–**Ic**, Scheme 1). The ethynediyl complexes **Ia** are by far the most prevalent.[1a,b,d,f,7] In contrast, analogous compounds of the heavier Group 14 elements Si–Pb are not known to date.[8] This situation is not surprising given the reluctance of these elements to form triple bonds.[9,10] A rich elimination and substitution chemistry of main-group elements was elaborated in recent years using the heterolytic or homolytic cleavage of Cp*–element bonds (Cp* = C_5Me_5).[11] A successful implementation of this method in the synthesis of the first transition-metal complexes with triply bonded Ge_2 chains is presented herein.

$[L_nM{-}C{\equiv}C{-}M'L'_n]$ $[L_nM{=}C{=}C{=}M'L'_n]$ $[L_nM{\equiv}C{-}C{\equiv}M'L'_n]$

Ia **Ib** **Ic**

Scheme 1. Valence bond structures of C_2 bridged complexes.

For the synthesis, the dichloro complexes *trans*-[MCl$_2$(depe)$_2$] (depe = $Et_2PCH_2CH_2PEt_2$; M = Mo (**1-Mo-Cl**), M = W (**1-W-Cl**)) were employed. Complex **1-Mo-Cl** was obtained upon reduction of *mer*-[MoCl$_3$(thf)$_3$][12] with zinc in THF in the presence of 2.1 equivalents of depe, and **1-W-Cl** upon heating of *trans*-[WCl$_2$(PMe$_3$)$_4$][13] with 2.1 equivalents of depe in toluene at reflux. Both compounds were isolated as slightly air-sensitive, orange-yellow solids in 90 % yield and decompose upon melting at 211 and 205 °C, respectively.[14] Reduction of **1-M-Cl** with sodium powder in THF under N_2 atmosphere afforded selectively the dinitrogen complexes *trans*-[M(depe)$_2$(N$_2$)$_2$] (M = Mo (**2-Mo**), M = W (**2-W**)), which were isolated as air-sensitive, orange (**2-Mo**) and bright red (**2-W**) solids in 98 and 72 % yields, respectively (Scheme 2).[14,15]



Scheme 2. Stepwise synthesis of the germylidyne complexes **4-M-X** and **5-M-Cl** starting from the dichlorides **1-M-Cl**.

Treatment of **2-Mo** with a stoichiometric amount of the germanium(II) halides [{Ge(Cp*)X}$_n$] (X = Cl, $n = 1$ (**3-Cl**); X = Br, $n = 2$ (**3-Br**))[16] in toluene at reflux gave the brown-orange, air-sensitive molybdenum germylidyne complexes **4-Mo-Cl** and **4-Mo-Br** in 32 % and 44 % yields, respectively (Scheme 2).[14,17] Both compounds are very soluble in pentane and melt in sealed capillaries under vacuum at 152 and 155 °C, respectively. Simultaneous thermal analysis (thermogravimetry/differential thermal analysis/mass spectrometry (TG-DTA-MS)) of **4-Mo-Cl** revealed that the germylidyne complex melts at the extrapolated onset temperature $T_{on}^{ex} = 144$ °C (peak temperature, $T_p = 149$ °C) and then decomposes at 181 °C releasing C_5Me_5H.[14,18] These results prompted us to study the thermolysis of **4-Mo-Cl** on a preparative scale. Upon heating the germylidyne complex **4-Mo-Cl** at 180–185 °C under static vacuum, the brown-orange sample of **4-Mo-Cl** melted and then turned progressively to a red-brown mass. Analysis of the molten mass by ^1H and $^{31}P\{^1H\}$ NMR

---

[*] Prof. Dr. A. C. Filippou, Dipl.-Chem. G. Schnakenburg,
Dipl.-Chem. N. Weidemann
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: filippou@chemie.hu-berlin.de
Dr. A. I. Philippopoulos
Institute of Physical Chemistry
NCSR Demokritos
Ag. Paraskevi Attikis, 15310 Athens (Greece)

[**] We are grateful to the Humboldt-Universität zu Berlin, the Deutsche Forschungsgemeinschaft (project FI 445/6-1), and the IKYDA program (D/03/40387) for the generous financial support of this work, Dipl. Ing. I. Hinz for assistance in the experimental work, Dr. U. Hartmann and U. Kätel for the elemental analyses and Dr. M. Feist for the STA analysis. N. Weidemann thanks the Fonds der Chemischen Industrie for a fellowship. depe = $Et_2PCH_2CH_2PEt_2$.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

spectroscopy revealed a gradual conversion of **4-Mo-Cl** into the digermanium complex **5-Mo-Cl**, which after completion of the reaction and work-up was obtained as an air-sensitive, brown solid in 27% yield (Scheme 2).[14] During the thermolysis of **4-Mo-Cl**, a yellow volatile material deposited on the cold top part of the reaction tube and was identified by NMR spectroscopy to be a mixture of depe, Cp*H,[19] 1,2,3,4-tetramethylpentafulvene,[20] and some $[\mathrm{GeCp}^*_2]$.[21] These results suggest that homolysis of the Ge–Cp* bond occurs upon thermal activation of **4-Mo-Cl** to generate [MoCl(Ge)(depe)$_2$] and Cp* radicals. The [MoCl(Ge)(depe)$_2$] radicals dimerize to form **5-Mo-Cl**, whereas the Cp* radicals disproportionate under the reaction conditions to give Cp*H and 1,2,3,4-tetramethylpentafulvene.[22] Heating of an equimolar mixture of complex **2-W** and **3-Cl** in toluene at reflux afforded a 7.7:1 mixture of the tungsten germylidyne complexes **4-W-Cl** and **5-W-Cl** (Scheme 2). Thermolysis of this mixture at 190 °C under static vacuum transformed **4-W-Cl** into the digermanium complex **5-W-Cl**, which was isolated as a very air-sensitive, green-brown solid in 30% overall yield. Complex **5-W-Cl** decomposes upon melting at 240 °C.[14] The molecular structures of **4-Mo-Br** and **5-W-Cl** were determined by single-crystal X-ray diffraction (Figures 1 and 2). The *trans*-configured octahedral complex **4-Mo-Br** has a very short Mo–Ge triple bond (2.2798(5) Å) and an almost linear coordinated germanium atom (Mo-Ge-C_{Cp*} 177.46(8)°) which has an η^1-bonded Cp* substituent as shown by the Ge–C1/C5 distances, the alternating $(C–C)_{ring}$ bond lengths, and the bond angles at the C1 atom (Figure 1).[23] The Mo–Ge bond of **4-Mo-Br** is even shorter than those of the dppe complexes *trans*-[X(dppe)$_2$Mo$\equiv$Ge-(η^1-Cp*)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, X = Cl, 2.3185(6) Å; X = Br, 2.3103(6) Å).[9c] This situation suggests that sterically less-demanding phosphine ligands of higher σ-basicity strengthen the metal–germanium triple bonds. Complex **5-W-Cl** features a crystallographically imposed center of symmetry at the midpoint of the Ge–Ge bond, an almost linear Ge$_2$ chain spanning the two *trans*-configured, octahedral tungsten centers (W-Ge-Ge# 175.13(3)°), and two W–Ge triple bonds (2.3087(5) Å) that are linked by a short Ge–Ge single bond (2.362(1) Å) (Figure 2). The W–Ge bonds of **5-W-Cl** compare well with those of the germylidyne complexes *trans*-[X(dppe)$_2$W$\equiv$Ge-(η^1-Cp*)] (X = H, Cl, Br, I, NCO, CN; W-Ge 2.293(1)–2.3184(6) Å).[9c,g] The Ge–Ge distance (2.362(1) Å) is the shortest known for a Ge–Ge single bond.[24,25] This distance can be rationalized with the increased s character of the σ hybrid orbitals forming the Ge–Ge bond and the π conjugation of the W$\equiv$Ge bonds (see below). Note the Ge–Ge bond length of **5-W-Cl** lies close to the range of lengths calculated for Ge$_2$ (2.36–2.46 Å).[26] The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra corroborate the structures of complexes **4-M-X** and **5-M-Cl** (X = Cl, Br; M = Mo, W). Thus, the ^{1}H and ^{13}C{^{1}H} NMR spectra display a double set of resonances for the diastereotopic ethyl groups and methylene protons of the depe ligands, as expected for diamagnetic complexes of the general formula *trans*-[M(depe)$_2$(L)(L′)].[14] In addition, the NMR spectra of **4-M-X** reveal a fast haptotropic shift of the Cp* substituent. This shift gives rise to one singlet signal for the methyl protons in the ^{1}H NMR spectra, and two singlet resonances in the ^{13}C{^{1}H} NMR spectra, one for the methyl carbon and one for the ring carbon nuclei of the Cp* group.[14] The ^{31}P{^{1}H} NMR spectra display a singlet resonance confirming the *trans*-configuration of **4-M-X** and **5-M-Cl**. The ^{31}P NMR signals of the Ge$_2$-bridged complexes (**5-Mo-Cl**, $\delta = 56.3$ ppm; **5-W-Cl**, $\delta = 38.2$ ppm) appear slightly upfield of those of the mononuclear complexes (**4-Mo-Cl**, $\delta = 57.2$ ppm; **4-W-Cl**, $\delta = 39.2$ ppm), and for the tungsten compounds are flanked by a pair of satellites arising from coupling with the ^{183}W nucleus (**4-W-Cl**, ^1J(W,P) = 259 Hz; **5-W-Cl**, ^1J(W,P) = 249 Hz).[14]

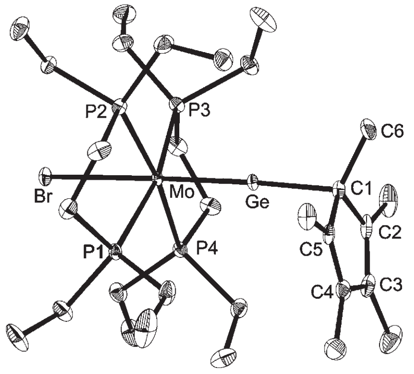


Figure 1. DIAMOND plot of the molecular structure of **4-Mo-Br**, thermal ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mo-Ge 2.2798(5), Ge-C1 2.046(3), Mo-Br 2.6899(5), Mo-P1 2.479(1), Mo-P2 2.498(1), Mo-P3 2.465(1), Mo-P4 2.4812(9), C1-C2 1.504(4), C2-C3 1.356(5), C3-C4 1.466(5), C4-C5 1.353(4), C1-C5 1.485(4); Mo-Ge-C1 177.46(8), Ge-Mo-Br 177.94(2), Ge-Mo-P1 95.38(2), Ge-Mo-P2 95.30(2), Ge-Mo-P3 96.86(2), Ge-Mo-P4 92.80(2), Ge-C1-C2 99.8(2), Ge-C1-C5 99.9(2), Ge-C1-C6 114.0(2).

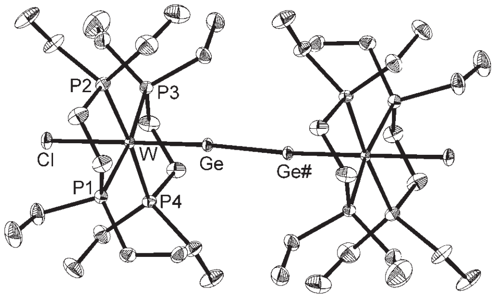
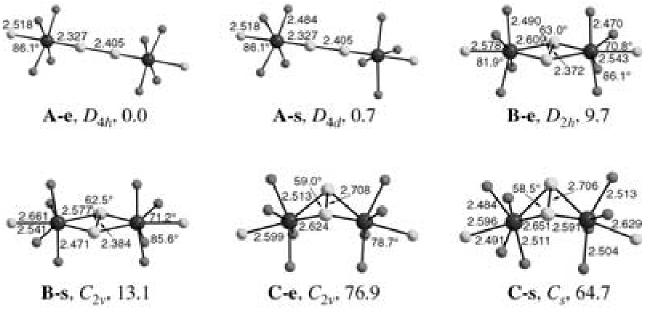


Figure 2. DIAMOND plot of the molecular structure of **5-W-Cl**, thermal ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: W-Ge 2.3087(5), Ge-Ge# 2.362(1), W-Cl 2.518(1), W-P1 2.455(1), W-P2 2.459(1), W-P3 2.470(1), W-P4 2.461(1); W-Ge-Ge# 175.13(3), Ge-W-Cl 176.66(3), Ge-W-P1 92.96(3), Ge-W-P2 94.47(3), Ge-W-P3 95.59(3), Ge-W-P4 90.28(3).

Density functional theoretical (DFT) calculations of the model complex *trans,trans*-[Cl(PH$_3$)$_4$WGe$_2$W(PH$_3$)$_4$Cl] (**5-PH$_3$-W-Cl**) were performed without symmetry restraints using the exchange correlation functionals B3LYP and BP86 and various basis sets.[14,27] Geometry optimization of the model compound at the B3LYP/IIa level of theory led to six minimum structures on the ground-state singlet potential-energy surface, which can be classified into one pair of isomers featuring an end-on coordinated Ge_2 ligand (**A**), and two pairs of isomers displaying a side-on bonded Ge_2 ligand (**B**, **C**; Figure 3). Each pair consists further of an eclipsed (**e**) and a staggered conformer (**s**) differing in the orientation of the $[WCl(PH_3)_4]$ fragments. The eclipsed isomer **A-e** of D_{4h} symmetry and the corresponding D_{4d} symmetric staggered isomer **A-s**, which feature a linear end-on bonded Ge_2 chain, are the most stable compounds and differ in energy by less than 1 kJ mol^{-1}. The isomers **B** displaying a planar W_2Ge_2 bicyclic ring lie at slightly higher energy than **A** (10–13 kJ mol^{-1}), whereas the species **C** with a W_2Ge_2 butterfly structure are considerably less stable than **A** (Figure 3). The calculated bond lengths and angles of the eclipsed isomer **A-e** compare well with the experimental values of **5-W-Cl** (Table 1).



A-e, D_{4h}, 0.0 **A-s**, D_{4d}, 0.7 **B-e**, D_{2h}, 9.7

B-s, C_{2v}, 13.1 **C-e**, C_{2v}, 76.9 **C-s**, C_s, 64.7

Figure 3. Selected bond lengths [Å] and bond angles [°], symmetries, and relative energies [kJ mol^{-1}, ZPVE corrected] of the minimum structures of **5-PH$_3$-W-Cl** (B3LYP/IIa). Hydrogen atoms are omitted for clarity.

Table 1: Comparison of selected bonding parameters of **5-PH$_3$-W-Cl** (**A-e** isomer) with those of **5-W-Cl**.

Method/basis set	W–Ge [Å]	Ge–Ge [Å]	W–Cl [Å]	P-W-Cl [°]	P-W-P_{cis} [°]
B3LYP/IIa	2.327	2.405	2.518	86.1	89.7
RI-BP86/I	2.357	2.453	2.541	86.9	89.8
BP86/IIb	2.328	2.389	2.456	86.2	89.7
X-ray (**5-W-Cl**)	2.3087(5)	2.362(1)	2.518(1)	86.7[a]	89.8[a]

[a] Mean value.

Analysis of the electronic charge distribution of **A-e** using the natural bond orbital (NBO) partitioning scheme[28] gives an optimal Lewis structure with two W–Ge triple bonds connected by a Ge–Ge single bond. Both W–Ge triple bonds are composed of one σ component, which is polarized towards germanium (64.8 %), and two degenerate π bonds, which result from the overlap of pure tungsten d orbitals and germanium p orbitals and are polarized towards tungsten (71.6 %) (Table 2). The polarity of the W–Ge bonds is reflected in the partial charges of the W and Ge atoms (−1.25 and +0.30, respectively) and the Wiberg bond index of 1.71.[29] Further evidence for the considerable ionic character of the W–Ge triple bonds of **A-e** was provided by the energy-partitioning analysis of the interaction between the closed-shell fragments *trans*-$[WCl(\eta^1\text{-}Ge_2)(PH_3)_4]^+$ and $[WCl(PH_3)_4]^-$ using the energy decomposition analysis (EDA) method,[30] which revealed a considerable contribution of the electrostatic term ΔE_{elstat} (−622.6 kJ mol^{-1}) to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} = -1374.4$ kJ mol^{-1}), leading to a 55 % covalent character of the W–Ge triple bonds (Table 2). The EDA analysis also showed that the degenerate W–Ge π bonds make the largest contribution (78 %) to the orbital interaction energy ΔE_{orb} indicating the same high π-bonding character of the W–Ge bonds in **A-e** as in *trans*-$[Cl(CO)_4W{\equiv}GeH]$.[31] Taking into account the polarization of the W–Ge σ and π bonds, an extreme view of isomer **A-e** is that of a Ge_2^{2+} ion, which is embedded in an $\eta^1{:}\eta^1$ bonding mode between two d^6 $[WCl(PH_3)_4]^-$ fragments by two σ ($[Ge_2]^{2+} \rightarrow [WCl(PH_3)_4]^-$) and four π $[WCl(PH_3)_4]^- \rightarrow [Ge_2]^{2+}$) donor–acceptor bonds. Ge_2^{2+} has a singlet ground state with a very weak and long Ge–Ge bond (3.099 Å) owing to Coulomb repulsion.[32] Metal complexation is accompanied by a considerable electron drift from the metal fragments to Ge_2^{2+}, which decreases the partial charges on the germanium atoms from +1 to +0.3, reduces thereby the Coulomb repulsion, and shortens the Ge–Ge bond by 0.694 Å (B3LYP/IIa, Table 1).

The π bonding and π* antibonding orbitals of the W-Ge-Ge-W chain form four doubly degenerate levels (HOMO−3, HOMO,

Table 2: Results of the W–Ge and Ge–Ge bonding analyses of the isomer **A-e** (B3LYP/IIa).

Bond		NBO analysis[a]						EDA[b] [kJ mol^{-1}]			
A–B	occ.	% (A)	hyb.	% (B)	hyb.	q(A)	WBI	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{int}
W–Ge	σ: 1.90	35.2	$sd^{2.1}$	64.8	$sp^{0.5}$	−1.25	1.71	507.4	−622.6	−751.8 (55 %)	−866.5
	π_1: 1.85	71.6	d	28.4	p					$\Delta E_\sigma(a_1)$: −144.1	
	π_2: 1.85	71.6	d	28.4	p					$\Delta E_\pi(e)$: −588.4	
Ge–Ge	1.96	50.0	$sp^{1.9}$	50.0	$sp^{1.9}$	+0.30	1.10	909.4	−398.4	−795.3 (67 %)	−283.8
										$\Delta E_\sigma(a_1)$: −730.1	
										$\Delta E_\pi(e)$: −65.0	

[a] NBO analysis of the W–Ge and Ge–Ge bonds: NBO occupancies, bond polarization in % (W) and % (Ge), orbital hybridization, NPA partial charges q(A) and Wiberg bond index (WBI). [b] Energy decomposition analysis of the W–Ge and Ge–Ge bonds (BP86/IIb): Pauli repulsion (ΔE_{Pauli}), electrostatic interaction (ΔE_{elstat}), orbital interaction ($\Delta E_{orb} = \Delta E_\sigma(a_1) + \Delta E_\pi(e) + \Delta E_{rest}(b_1+b_2)$), and total interaction energy (ΔE_{int}) between the closed-shell C_{4v}-symmetric fragments *trans*-$[WCl(\eta^1\text{-}Ge_2)(PH_3)_4]^+$ and $[WCl(PH_3)_4]^-$ (W–Ge bond) and the C_{4v}-symmetric doublet fragments *trans*-$[WCl(Ge)(PH_3)_4]$ (Ge–Ge bond) in the frozen geometry of **A-e**; the percentage of ΔE_{orb} in the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$) reflects the covalent character of the bonds and is given in parenthesis; $\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb}$.

LUMO, and LUMO + 3; Figure 4) resulting from the in-phase or out-of-phase combination of the tungsten $d_{xz}(d_{yz})$ orbitals and the germanium $p_x(p_y)$ orbitals (the z axis of the Cartesian coordinate system and the C_4 symmetry axis of **A-e** are collinear).[33] Four electrons occupy the lowest energy e_{1u} symmetric pair of molecular orbitals (HOMO−3), which are bonding with respect to the W–Ge and Ge–Ge linkages, and four electrons occupy the e_{1g} symmetric pair of orbitals (HOMO), which are bonding with respect to the W–Ge linkages but antibonding with respect to the Ge–Ge linkage (Figure 4).[33,34] This molecular orbital picture corresponds in valence bond terms to the digermanehexayl formula [L$_n$W≡Ge–Ge≡WL$_n$] and suggests some π conjugation of the W–Ge triple bonds.[35] This proposal is supported by the NBO and EDA analyses, which indicate the presence of a Ge–Ge σ bond with low π-bonding character (WBI (Ge–Ge) = 1.10; ΔE_π is 8.2 % of ΔE_{orb}; Table 2), and the natural resonance theoretical (NRT) analysis of **A-e**,[36] which provides 21 different resonance structures with a resonance weight greater than 1 % leading to a natural bond order of 2.76 for the W–Ge bonds and 1.06 for the Ge–Ge bond.[37]

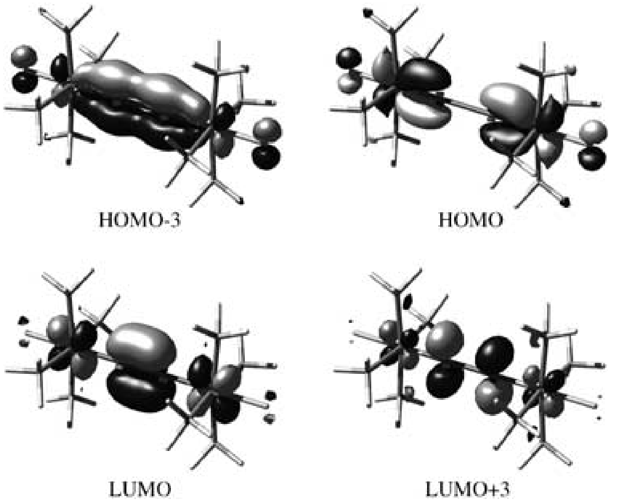


Figure 4. π and π* Kohn–Sham orbitals of the W-Ge-Ge-W chain in **A-e**. Only one of the doubly degenerate π and π* levels is depicted.

Analysis of the wave function using the electron localization function (ELF)[38] at the B3LYP/IIa level of theory shows, that the density of localized electrons between tungsten and germanium has a toroidal shape typical for triple bonds.[9f,14,39] Volume integration of the electron density over the valence disynaptic basins connecting the W with the Ge nuclei and linking the two Ge nuclei, leads to a population of 5.7 electrons in the W–Ge bonding region and 2.6 electrons in the Ge–Ge bonding region, which supports the bonding picture of two conjugated W–Ge triple bonds in **A-e**.[40] This result is further confirmed by the quantification of conjugation in **A-e** using the anisotropy of the induced current density (AICD) of the Ge–Ge bond.[41] The AICD isosurface plot of **A-e** at an isosurface value of 0.015 displays strong delocalization over the atoms (Figure 5). The continuous boundary surface enclosing the conjugating Ge atoms breaks at an isosurface value of 0.041 (Figure 5), which suggests that the extent of conjugation in **A-e** is lower that in benzene (0.08) or butadiene (0.069), but higher than in 1,3-butadiyne (0.013) at the same level of theory.[42] Conjugation in **A-e** might be caused by the small HOMO–LUMO gap of 2.7 eV which leads to an excitation energy of 2.67 eV ($\lambda = 464$ nm) for the allowed one-electron transition (TD-RIDFT/TZVPP).[43]

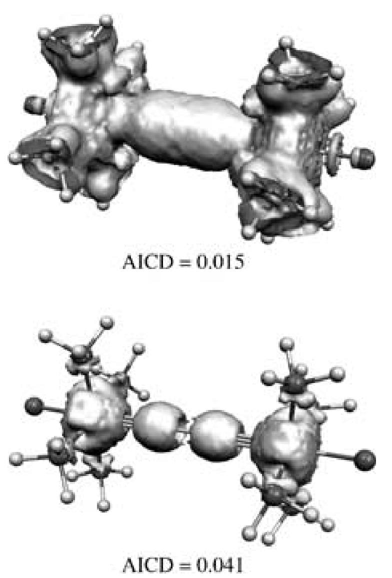


Figure 5. Isosurface plots of the AICD in **A-e** at 0.015 (top) and the critical value of 0.041 (bottom), at which the topology of the AICD boundary surface changes.

The Ge–Ge bond fragmentation energy of **A-e** (ΔE_{frag} = 221.0 kJ mol^{-1}) is lower than that of Ge_2H_6 (288.5 kJ mol^{-1}) calculated at the same level of theory (B3LYP/IIa, Table 3).[44] Inclusion of relaxation and zero-point vibrational effects (ZPVE) leads to a theoretical value of 217.1 kJ mol^{-1} for the Ge–Ge bond dissociation energy of **A-e** ($D°_0$), which is also lower than that of Ge_2H_6 ($D°_0$ = 270.4 kJ mol^{-1}; Table 3),[44] the latter value comparing well with the experimental value ($D°$ = 276 kJ mol^{-1}).[45] In comparison, the Ge–Ge bond length of **A-e** (2.405 Å) is shorter than that of Ge_2H_6 (2.439 Å, Table 3) leading to an opposite bond length/dissociation energy correlation to that usually observed. This result suggests that the radicals *trans*-[WCl(Ge)(PH$_3$)$_4$] formed upon Ge–Ge bond homolysis are stabilized by delocalization of the unpaired electron in the electronic ground state ($^2A_1$).[46] This electronic stabilization provides a rationale for the preferred formation of the radicals *trans*-[WCl(Ge)(depe)$_2$] during thermolysis of **4-W-Cl**. The energy (ZPVE corrected) required to cleave the W≡Ge bond of **A-e** into the fragments *trans*-[WCl(η^1-Ge$_2$)(PH$_3$)$_4$][47] and [WCl(PH$_3$)$_4$] in the respective $^2A_1$ and ^4A electronic ground states and minimum geometries, was calculated to be slightly lower (333.9 kJ mol^{-1}) than that of the germylidyne complex *trans*-[Cl(PH$_3$)$_4$W≡Ge-Me] (354.8 kJ mol^{-1}) (Table 3). The species *trans*-[WCl(η^1-Ge$_2$)(PH$_3$)$_4$] is a local minimum on the energy potential surface and relaxes to a C_{2v} symmetric species featuring a side-on bonded Ge$_2$ ligand.[47] The released relaxation energy of −52.2 kJ mol^{-1} reduces the W–Ge bond dissociation energy of **A-e** to 281.7 kJ mol^{-1} (Table 3).

Table 3: Fragmentation, bond dissociation, and Gibbs free dissociation energies [kJ mol^{-1}] of the Ge–Ge and W–Ge bonds of **5-PH$_3$-W-Cl** (**A-e** isomer), Ge_2H_6, and *trans*-[Cl(PH$_3$)$_4$W≡Ge-Me] (B3LYP/IIa).

Compound	Bond	Length [Å]	ΔE_{frag}[a]	ΔE_{relax}[b]	ΔE_{ZPVE}[c]	$D°_0$[d]	ΔE_{therm}[e]	$\Delta G°$[f]
5-PH$_3$-W-Cl (A-e)	Ge–Ge	2.405	+221.0	−0.2	−3.7	+217.1	−55.4	+161.7
Ge_2H_6	Ge–Ge	2.439	+288.5	−2.3	−15.8	+270.4	−45.8	+224.6
5-PH$_3$-W-Cl (A-e)	W–Ge	2.327	+476.6	−133.1	−9.6	+333.9	−74.3	+259.6
						+281.7[g]	−69.6[g]	+212.1[g]
[Cl(PH$_3$)$_4$W≡Ge-Me]	W–Ge	2.304	+622.3	−251.9	−15.6	+354.8	−56.4	+298.4

[a] Homolytic fragmentation energy to the fragments in the geometry adopted by the molecule prior to fragmentation and in the electronic state, in which the number of unpaired electrons corresponds to the number of broken bonds. [b] Relaxation energy of both fragments to their minimum geometry and electronic ground state. [c] Zero point vibrational energy correction to the bond dissociation energy. [d] Bond dissociation energy at 0 K; $D°_0 = \Delta E_{frag} + \Delta E_{relax} + \Delta E_{ZPVE}$. [e] Thermal and entropic corrections to the dissociation energy (298.15 K, 1 atm). [f] Gibbs free homolytic bond dissociation energy at standard conditions; $\Delta G° = D°_0 + \Delta E_{therm}$. [g] See text and ref. [47].

Several experimental and theoretical studies have been carried out on the diatomic molecule Ge_2.[48] Ge_2 can be regarded as the lightest member in the family of germanium clusters Ge_n, which are of importance owing to their potential applications in nanoelectronics.[48] Encapsulation of this very reactive species in the complexes **5-M-Cl** provides a new example for the ability of stereoelectronically well-defined transition-metal fragments to stabilize high temperature molecules in unprecedented bonding patterns.

Received: June 7, 2005

Keywords: density functional calculations · germanium · molybdenum · triple bonds · tungsten

---

[1] Reviews and accounts on metal-bonded sp-hybridized carbon chains: a) W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923; b) H. Lang, *Angew. Chem.* **1994**, *106*, 569; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 547; c) M. Akita, Y. Moro-oka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420; d) U. Bunz, *Angew. Chem.* **1996**, *108*, 1047; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 969; e) M. I. Bruce, *Coord. Chem. Rev.* **1997**, *166*, 91; f) F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, *178–180*, 431; g) S. Szafert, J. A. Gladysz, *Chem. Rev.* **2003**, *103*, 4175; h) M. Akita, A. Sakurai, M.-C. Chung, Y. Moro-oka, *J. Organomet. Chem.* **2003**, *670*, 2; i) M. I. Bruce, P. J. Low, *Adv. Organomet. Chem.* **2004**, *50*, 179.

[2] a) M. D. Ward, *Chem. Soc. Rev.* **1995**, *24*, 121; b) A. Harriman, R. Ziessel, *Chem. Commun.* **1996**, 1707.

[3] Selected references on the electronic coupling between C_x-bridged metal centers: a) M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Böhme, G. Frenking, J. A. Gladysz, *J. Am. Chem. Soc.* **1997**, *119*, 775; b) F. Coat, M.-A. Guillevic, L. Toupet, F. Paul, C. Lapinte, *Organometallics* **1997**, *16*, 5988; c) M. Guillemot, L. Toupet, C. Lapinte, *Organometallics* **1998**, *17*, 1928; d) P. Belanzoni, N. Re, A. Sgamellotti, C. Floriani, *J. Chem. Soc. Dalton Trans.* **1998**, 1825; e) S. Kheradmandan, K. Heinze, H. W. Schmalle, H. Berke, *Angew. Chem.* **1999**, *111*, 2412; *Angew. Chem. Int. Ed.* **1999**, *38*, 2270; f) M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best, G. A. Heath, *J. Am. Chem. Soc.* **2000**, *122*, 1949; g) F. Paul, W. E. Meyer, L. Toupet, H. Jiao, J. A. Gladysz, C. Lapinte, *J. Am. Chem. Soc.* **2000**, *122*, 9405; h) H. Jiao, J. A. Gladysz, *New J. Chem.* **2001**, *25*, 551.

[4] a) *An Introduction to Molecular Electronics* (Eds.: M. C. Petty, M. R. Bryce, D. Bloor), Oxford University Press, New York, **1995**; b) D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383; c) S. Creager, C. J. Yu, C. Bamdad, S. O'Connor, T. Maclean, E. Lam, Y. Chong, G. T. Olsen, J. Luo, M. Gozin, J. F. Kayyem, *J. Am. Chem. Soc.* **1999**, *121*, 1059, and references therein.

[5] a) N. J. Long, *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21; b) I. R. Whittall, A. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *43*, 349.

[6] For sp carbon allotropes see: a) F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101; b) R. J. Lagow, J. J. Kampa, H.-C. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw, E. Munson, *Science* **1995**, *267*, 362; c) T. Gibtner, F. Hampel, J.-P. Gisselbrecht, A. Hirsch, *Chem. Eur. J.* **2002**, *8*, 408.

[7] C_2-bridged transition-metal complexes having the valence formulae **Ib** and **Ic** are very rare: a) M. L. Listemann, R. R. Schrock, *Organometallics* **1985**, *4*, 74; b) D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne, P. T. Wolczanski, *J. Am. Chem. Soc.* **1989**, *111*, 9056; c) K. G. Caulton, R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky, Z. Xue, *Organometallics* **1992**, *11*, 321; d) B. E. Woodworth, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1998**, *120*, 9028.

[8] The dimetallaheterocumulenes $[\mathrm{Cp^R(CO)_2Mn{=}E{=}Mn(CO)_2Cp^R}]$ (E = Ge, Sn, Pb; $\mathrm{Cp^R} = \eta^5$-C_5H_5, η^5-C_5H_4Me, η^5-C_5Me_5) are the only members of the complex series $[L_nME_xM'L'_n]^{y+}$ (E = Si–Pb) known. Their syntheses and reactions are described in: a) W. Gäde, E. Weiss, *J. Organomet. Chem.* **1981**, *213*, 451; b) N. M. Kostic, R. F. Fenske, *J. Organomet. Chem.* **1982**, *233*, 337; c) D. Melzer, E. Weiss, *J. Organomet. Chem.* **1984**, *263*, 67; d) J. D. Korp, I. Bernal, R. Hörlein, R. Serrano, W. A. Herrmann, *Chem. Ber.* **1985**, *118*, 340; e) W. A. Herrmann, H.-J. Kneuper, E. Herdtweck, *Angew. Chem.* **1985**, *97*, 1060; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1062; f) W. A. Herrmann, *Angew. Chem.* **1986**, *98*, 57; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 56; g) H.-J. Kneuper, E. Herdtweck, W. A. Herrmann, *J. Am. Chem. Soc.* **1987**, *109*, 2508; h) F. Ettel, G. Huttner, L. Zsolnai, *Angew. Chem.* **1989**, *101*, 1525; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1496; i) W. A. Herrmann, H.-J. Kneuper, E. Herdtweck, *Chem. Ber.* **1989**, *122*, 437; j) F. Ettel, G. Huttner, W. Imhof, *J. Organomet. Chem.* **1990**, *397*, 299; k) F. Ettel, G. Huttner, L. Zsolnai, C. Emmerich, *J. Organomet. Chem.* **1991**, *414*, 71; l) B. Schiemenz, F. Ettel, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1993**, *458*, 159; m) F. Ettel, M. Schollenberger, B. Schiemenz, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1994**, *476*, 153.

[9] For transition-metal complexes featuring triple bonds to germanium, tin, or lead see: a) L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 650; b) A. C. Filippou, A. I. Philippopoulos, P. Portius, D. U. Neumann, *Angew. Chem.* **2000**, *112*, 2881; *Angew. Chem. Int. Ed.* **2000**, *39*, 2778; c) A. C. Filippou, P. Portius, A. I. Philippopoulos, *Organometallics* **2002**, *21*, 653; d) A. C. Filippou, P. Portius, A. I. Philippopoulos, H. Rohde,

Angew. Chem. **2003**, *115*, 461; *Angew. Chem. Int. Ed.* **2003**, *42*, 445; e) A. C. Filippou, A. I. Philippopoulos, G. Schnakenburg, *Organometallics* **2003**, *22*, 3339; f) A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293; *Angew. Chem. Int. Ed.* **2004**, *43*, 2243; g) A. C. Filippou, A. I. Philippopoulos, P. Portius, G. Schnakenburg, *Organometallics* **2004**, *23*, 4503; h) A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem.* **2004**, *116*, 6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6512.

[10] For experimental studies on heavier Group 14 element analogues of alkynes see: a) A. Sekiguchi, S. S. Zigler, R. West, J. Michl, *J. Am. Chem. Soc.* **1986**, *108*, 4241; b) M. Bogey, H. Bolvin, C. Demuynck, J.-L. Destombes, *Phys. Rev. Lett.* **1991**, *66*, 413; c) M. Cordonnier, M. Bogey, C. Demuynck, J.-L. Destombes, *J. Chem. Phys.* **1992**, *97*, 7984; d) N. Wiberg, C. M. M. Finger, K. Polborn, *Angew. Chem.* **1993**, *105*, 1140; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1054; e) L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524; f) R. Pietschnig, R. West, D. R. Powell, *Organometallics* **2000**, *19*, 2724; g) C. Bibal, S. Mazieres, H. Gornitzka, C. Couret, *Angew. Chem.* **2001**, *113*, 980; *Angew. Chem. Int. Ed.* **2001**, *40*, 952; h) A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930; i) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785; j) N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* **2002**, 1066; k) P. P. Power, *Chem. Commun.* **2003**, 2091; l) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626; m) A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755.

[11] P. Jutzi, G. Reumann, *J. Chem. Soc. Dalton Trans.* **2000**, 2237.

[12] a) R. Poli, H. D. Mui, *J. Am. Chem. Soc.* **1990**, *112*, 2446; b) F. Stoffelbach, D. Saurenz, R. Poli, *Eur. J. Inorg. Chem.* **2001**, 2699.

[13] a) P. R. Sharp, *Organometallics* **1984**, *3*, 1217; b) P. R. Sharp, J. C. Bryan, J. M. Mayer, *Inorg. Synth.* **1990**, *28*, 326.

[14] The Supporting Information contains the Experimental Section including the syntheses, analytical, and spectroscopic data of the complexes **1-M-Cl**, **2-M**, **4-Mo-X** and **5-M-Cl** (M = Mo, W; X = Cl, Br). It also contains the crystallographic data of the germylidyne complexes **4-Mo-Br** and **5-W-Cl** and details of the simultaneous thermal analysis of **4-Mo-Cl** and of the electronic structure calculations of **5-PH$_3$-W-Cl**. CCDC-259718 (**4-Mo-Br**) and CCDC-259719 (**5-W-Cl**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] Alternative methods for the synthesis of **2-Mo** and **2-W** are described in: a) J. Chatt, G. A. Heath, R. L. Richards, *J. Chem. Soc. Dalton Trans.* **1974**, 2074; b) W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, D. A. Rankin, *J. Chem. Soc. Dalton Trans.* **1984**, 1703; c) T. A. George, M. E. Noble, *Inorg. Chem.* **1978**, *17*, 1678; d) G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson, O. Eisenstein, *J. Am. Chem. Soc.* **1993**, *115*, 569.

[16] a) J. G. Winter, P. Portius, G. Kociok-Köhn, R. Steck, A. C. Filippou, *Organometallics* **1998**, *17*, 4176; b) ref. [9c].

[17] ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude products isolated after completion of the reactions, revealed the concomitant formation of **1-Mo-X**, [GeCp*$_2$], and **5-Mo-X**. Several recrystallizations from pentane were necessary to separate the complexes **4-Mo-X** from the by-products decreasing the overall yields (see Supporting Information).

[18] Signals for the ions $[\mathrm{C_5Me_5H}]^+$ (m/z 136) and $[\mathrm{C_7H_7}]^+$ (m/z 91) appeared in the EI mass spectra of the gases evolved with the beginning of decomposition. The intensity of these signals increased rapidly above 181 °C (see Supporting Information).

[19] a) R. S. Threlkel, J. Bercaw, *J. Organomet. Chem.* **1977**, *136*, 1; b) J. M. Manriquez, P. J. Fagan, L. D. Schertz, T. J. Marks, *Inorg. Synth.* **1982**, *21*, 181; c) F. X. Kohl, P. Jutzi, *J. Organomet. Chem.* **1983**, *243*, 119.

[20] a) J. C. Pando, E. A. Mintz, *Tetrahedron Lett.* **1989**, *30*, 4811; b) P. Jutzi, A. Mix, *Chem. Ber.* **1992**, *125*, 951; c) P. Jutzi, T. Heidemann, B. Neumann, H. G. Stammler, *Synthesis* **1992**, 1096; d) S. Döring, G. Erker, *Synthesis* **2001**, 43.

[21] P. Jutzi, F. Kohl, P. Hofmann, C. Krüger, Y.-H. Tsay, *Chem. Ber.* **1980**, *113*, 757.

[22] a) A. G. Davies, J. Lusztyk, *J. Chem. Soc. Chem. Commun.* **1980**, 554; b) A. G. Davies, J. Lusztyk, *J. Chem. Soc. Perkin Trans. 2* **1981**, 692; c) P. N. Culshaw, J. C. Walton, L. Hughes, K. U. Ingold, *J. Chem. Soc. Perkin Trans. 2* **1993**, 879; d) W. R. Roth, F. Hunold, *Liebigs Ann.* **1995**, 1119.

[23] For a detailed discussion of the bonding parameters of η^1-bonded Cp* substituents in germylidyne complexes see ref [9c].

[24] The Ge–Ge distance in elemental germanium is 2.44 Å: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford, **1984**, p. 1279.

[25] For Ge–Ge single bonds connecting unsaturated germanium centers see: a) A. Sekiguchi, H. Yamazaki, C. Kabuto, H. Sakurai, S. Nagase, *J. Am. Chem. Soc.* **1995**, *117*, 8025; b) H. Schäfer, W. Saak, M. Weidenbruch, *Angew. Chem.* **2000**, *112*, 3847; *Angew. Chem. Int. Ed.* **2000**, *39*, 3703; c) A. Sekiguchi, Y. Ishida, N. Fukaya, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 1158; d) G. Ramaker, A. Schäfer, W. Saak, M. Weidenbruch, *Organometallics* **2003**, *22*, 1302; e) G. Ramaker, W. Saak, D. Haase, M. Weidenbruch, *Organometallics* **2003**, *22*, 5212.

[26] W. Xu, Y. Zhao, Q. Li, Y. Xie, H. F. Schäfer III, *Mol. Phys.* **2004**, *102*, 579, and references therein.

[27] Basis set I is of valence double-ζ quality (LANL2DZ) and includes the quasi-relativistic effective core potentials LANL2. The auxiliary basis sets for the density fitting were generated automatically. Basis set IIa is of valence triple-ζ quality (6-311G* for C, H, Cl, P; TZVPP for Ge and W [ECP{MEFIT, WB}]), and IIb is a triple-ζ slater-type basis set with two sets of polarization functions. More details can be found in the Supporting Information.

[28] A. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[29] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

[30] a) K. Morokuma, *Acc. Chem. Res.* **1977**, *10*, 294; b) T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1.

[31] M. Lein, A. Szabó, A. Kovács, G. Frenking, *Faraday Discuss.* **2003**, *124*, 365.

[32] $\mathrm{Ge_2}^{2+}$ is suggested to be metastable with respect to dissociation to Ge^+ ions: W. A. Saunders, *Phys. Rev. B* **1989**, *40*, 1400.

[33] As in linear polyynes, the parity of the π-bonding orbitals of the W-Ge-Ge-W chain alternates with respect to the mirror plane bisecting the Ge–Ge bond of **A-e** (σ_h plane of the molecule). The lowest energy orbital (HOMO−3) has zero nodes, the number of nodes increases by one on going from one orbital to the one next highest in energy, and the nodes are symmetrically located with respect to the σ_h plane of **A-e**.

[34] HOMO−2 and HOMO−1 are molecular orbitals of δ symmetry resulting, respectively, from the in-phase and out-of-phase combination of the tungsten d_{xy} orbitals (see Supporting Information).

[35] The coefficients of the germanium $p_x(p_y)$ atomic orbitals are larger in the HOMO−3 than in the HOMO suggesting some Ge–Ge π overlap. Since the W–Ge π bonds are polarized towards the tungsten, the occupancies of the corresponding natural atomic orbitals at germanium are quite low (occ. p_x and $p_y = 0.64\,e^-$) depleting the π overlap of the germanium $p_x(p_y)$ functions.

[36] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593.

[37] 13 of these resonances structures have W−Ge triple bonds and eight have W−Ge double bonds. The combined weight of resonance structures featuring W−Ge triple bonds is 76%.

[38] a) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683; b) A. Savin, B. Silvi, F. Colonna, *Can. J. Chem.* **1996**, *74*, 1088.

[39] a) H. Grützmacher, T. F. Fässler, *Chem. Eur. J.* **2000**, *6*, 2317; b) N. O. J. Malcolm, R. J. Gillespie, P. L. A. Popelier, *J. Chem. Soc. Dalton Trans.* **2002**, 3333.

[40] The high population of the W−Ge disynaptic basins justifies the denotation of the W−Ge bonds as triple bonds, for which six electrons would be needed. The disynaptic basin of the Ge−Ge bond has a population of 2.6 electrons, which suggests the Ge−Ge bond to be slightly more than a classical single bond, reflecting the effect of π conjugation.

[41] R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214.

[42] For the recent dispute on the conjugative stabilization of 1,3-butadiyne see: a) D. W. Rogers, N. Matsunaga, A. A. Zavitsas, F. J. McLafferty, J. F. Liebman, *Org. Lett.* **2003**, *5*, 2373; b) P. D. Jarowski, M. D. Wodrich, C. S. Wannere, P. v. R. Schleyer, K. N. Houk, *J. Am. Chem. Soc.* **2004**, *126*, 15036; c) D. Cappel, S. Tüllmann, A. Krapp, G. Frenking, *Angew. Chem.* **2005**, *117*, 3683; *Angew. Chem. Int. Ed.* **2005**, *44*, 3617.

[43] This excitation gives the strongest absorption band in the calculated UV/Vis spectrum of **A-e** and may rationalize the green-brown color of complex **5-W-Cl** (see Supporting Information).

[44] The calculated Ge−Ge fragmentation energy of Ge_2H_6 compares well with that reported by H.-J. Himmel, H. Schnöckel, *Chem. Eur. J.* **2003**, *9*, 748. Our calculations show, however, that the GeH_3 radicals have a pyramidal C_{3v} symmetric minimum geometry (Ge−H 1.544 Å; H-Ge-H 110.8°) in the doublet ground state, which differs marginally from the geometry adopted by the GeH_3 fragments (Ge−H 1.540 Å; H-Ge-H 108.5°) in the D_{3d} symmetric minimum structure of Ge_2H_6. Our results lead to a very low relaxation energy of the two GeH_3 fragments (-2.3 kJ mol^{-1}) and differ from those of H.-J. Himmel and Schnöckel, according to which the GeH_3 radicals have a trigonal-planar minimum geometry.

[45] M. J. Almond, A. M. Doncaster, P. N. Noble, R. Walsh, *J. Am. Chem. Soc.* **1982**, *104*, 4717.

[46] Selected bond lengths [Å] and bond angles [°] of the radicals *trans*-$[WCl(Ge)(PH_3)_4]$ in their C_{4v} symmetric minimum structure and doublet ground state: W-Ge 2.329, W-Cl 2.528, W-P 2.483; P-W-Cl 85.9, P-W-P_{cis} 89.7. Additional evidence for the delocalization of the unpaired electron in *trans*-$[WCl(Ge)(PH_3)_4]$ was provided by NBO and ELF analyses.

[47] Two minimum structures were found for the fragment *trans*-$[WCl(Ge_2)(PH_3)_4]$ on the potential energy surface, a C_{4v} symmetric structure featuring an end-on bonded Ge_2 ligand, and a C_{2v} symmetric isomer featuring a side-on bonded Ge_2 ligand, which is 52.5 kJ mol^{-1} lower in energy than the end-on bonded species (see Supporting Information). Preference of the side-on coordination mode was also found in $[W(CO)_5(Ge_2)]^{2-}$ by calculations: C. Esterhuysen, G. Frenking, *Chem. Eur. J.* **2003**, *9*, 3518.

[48] a) A. Kant, B. H. Strauss, *J. Chem. Phys.* **1966**, *45*, 822; b) J. Harris, R. O. Jones, *Phys. Rev. A* **1978**, *18*, 2159; c) J. E. Kingcade, Jr., U. V. Choudary, K. A. Gingerich, *Inorg. Chem.* **1979**, *18*, 3094; d) J. E. Northrup, M. L. Cohen, *Chem. Phys. Lett.* **1983**, *102*, 440; e) G. Pacchioni, *Chem. Phys. Lett.* **1984**, *107*, 70; f) J. E. Kingcade, H. M. Nagarathna-Naik, I. Shim, K. A. Gingerich, *J. Phys. Chem.* **1986**, *90*, 2830; g) P. W. Deutsch, L. A. Curtiss, J. P. Blaudeau, *Chem. Phys. Lett.* **1997**, *270*, 413; h) J. Wang, G. Wang, J. Zhao, *Phys. Rev. B* **2001**, *64*, 205411.