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Activation of Aryl Germanium(II) Chlorides by $[Mo(PMe_3)_6]$ and $[W(\eta^2\text{-}CH_2PMe_2)H(PMe_3)_4]$: A New Route to Metal–Germanium Triple Bonds[**]

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Homoleptic trimethylphosphane complexes of transition metals, such as $[Mo(PMe_3)_6]$ (**2**-Mo)[1] and $[W(PMe_3)_6]$ (**2**-W),[2] form a class of rare and very reactive compounds.[3–5] The high reactivity of these complexes originates from the combination of strong σ-donor and weak π-acceptor properties of the PMe_3 ligand, which leads to very electron-rich metal centers[6] that are capable of activating σ bonds. A consequence of the high reactivity of the metal centers and the steric pressure caused by the PMe_3 ligands in the complexes $[M(PMe_3)_6]$ (M = Mo, W) is the facile dissociation of one PMe_3 ligand to afford, through an intramolecular C–H bond activation, the cyclometalated products $[M(\eta^2\text{-}CH_2PMe_2)H(PMe_3)_4]$.[1,2] The complexes $[M(PMe_3)_6]$ and their cyclometalation products are subject to various ligand displacement and oxidative addition reactions.[7] We report here a new reaction type of these electron-rich metal complexes that involves a Ge–Cl bond heterolysis of an aryl germanium(II) chloride to form metal–germanium triple bonds.

A new method was developed for the synthesis of the starting materials $[Mo(PMe_3)_6]$ (**2**-Mo) and $[W(\eta^2\text{-}CH_2PMe_2)H(PMe_3)_4]$ (**2**-W-c) involving the reduction of *trans*-$[MCl_2(PMe_3)_4]$ (**1**-M; M = Mo, W)[8,9] with sodium

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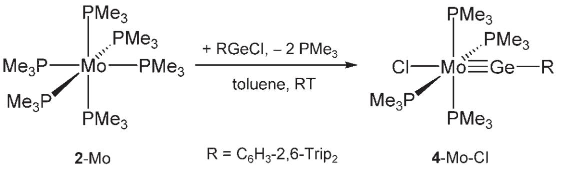
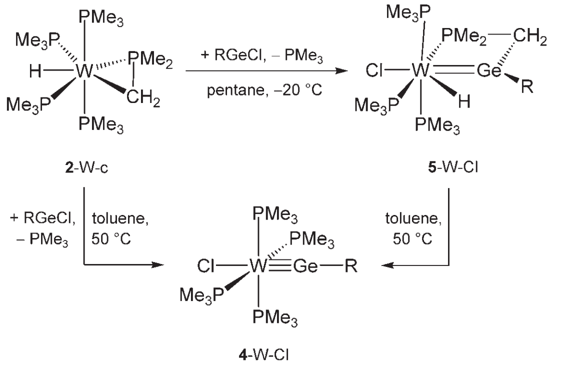
powder in THF in the presence of excess PMe_3.[10] This method offers several advantages compared to the published methods.[1,7a,b,11] Complex **2**-Mo was thereby obtained as a beige solid in about 60% yield,[12] and complex **2**-W-c as a bright yellow, very air-sensitive solid in 93% yield. Complex **2**-Mo reacts with one equivalent of the aryl germanium(II) chloride $Ge(C_6H_3\text{-}2,6\text{-}Trip_2)Cl$ (**3**; Trip = $C_6H_2\text{-}2,4,6\text{-}iPr_3$)[13] in toluene to give selectively upon elimination of two PMe_3 ligands the germylidyne complex **4**-Mo-Cl, which was isolated as a brown, air-sensitive, crystalline solid in 67% yield [Eq. (1)].[10] No intermediates were observed in this reaction, which is complete within two hours at room temperature.[14]



(1)

In contrast, treatment of **2**-W-c with one equivalent of **3** in pentane at −20 °C afforded selectively a thermolabile, very air-sensitive, green product, which was identified by X-ray crystallography and NMR spectroscopy to be the tungsten(II) hydrido–germylidene complex **5**-W-Cl (Scheme 1).[10] Conversion of **2**-W-c into **5**-W-Cl is probably initiated by an insertion of **3** into the W−C bond of **2**-W-c.[15] Heating of complex **5**-W-Cl in toluene at 50 °C gave selectively the brown, air-sensitive germylidyne complex **4**-W-Cl in an unprecedented 1,2-elimination reaction, in which a Ge−C bond is cleaved by a W−H functionality (Scheme 1).[10] This rearrangement reaction occurs also in the solid state when samples of **5**-W-Cl are heated slowly in vacuum to 125 °C. Alternatively, the germylidyne complex **4**-W-Cl can be directly obtained in 64% yield upon heating an equimolar mixture of **2**-W-c and **3** in toluene at 50 °C (Scheme 1).



Scheme 1. Stepwise transformation of **2**-W-c into the germylidyne complex **4**-W-Cl. R = $C_6H_3\text{-}2,6\text{-}Trip_2$.

Complexes **4**-M-Cl (M = Mo, W) and **5**-W-Cl were fully characterized.[10] Both germylidyne complexes are thermally stable solids which are very soluble in pentane and decompose upon melting at 142 °C (**4**-Mo-Cl) and 184 °C (**4**-W-Cl). The hydrido–germylidene complex **5**-W-Cl can be stored for a few hours at room temperature. However, its green solutions in toluene or pentane turn gradually brown at ambient temperature as a result of formation of **4**-W-Cl. The molecular structure of **4**-W-Cl was determined by single-crystal X-ray diffraction and exhibits an octahedral complex of roughly C_{2v} symmetry in which the germylidyne and the chlorido ligands are in a *trans* arrangement (Ge-W-Cl 179.3(1)°, Figure 1).[10,16]

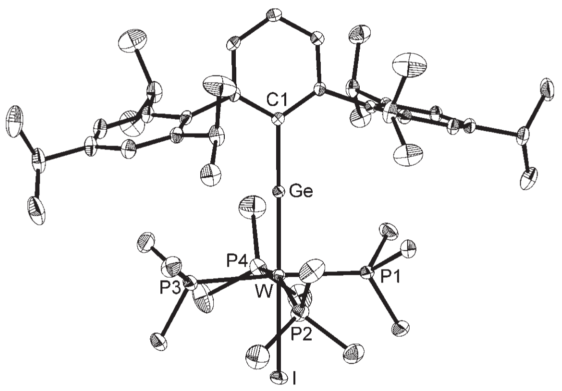


Figure 1. DIAMOND plot of the molecular structure of **4**-W-I in the solid state. Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] of **4**-W-I [values for **4**-W-Cl are given in square brackets]: W-Ge 2.3206(4) [2.338(1)], W-I 2.8797(5) [W-Cl 2.540(3)], W-P1 2.4711(8) [2.473(4)], W-P2 2.4967(8) [2.498(4)], W-P3 2.4888(8) [2.473(3)], W-P4 2.4883(8) [2.477(4)], Ge-C1 2.004(2) [1.982(10)]; W-Ge-C1 175.79(7) [177.9(3)], Ge-W-I 177.592(9) [Ge-W-Cl 179.3(1)], Ge-W-P1 90.81(2) [92.55(9)], Ge-W-P2 102.36(2) [101.69(9)], Ge-W-P3 91.96(2) [91.73(8)], Ge-W-P4 97.39(2) [99.30(8)].

Complex **4**-W-Cl features a nearly linear coordinated germanium atom (W-Ge-C1 177.9(3)°) and a W≡Ge triple-bond length of 2.338(1) Å, which compares well with those of *trans*-$[X(PMe_3)_4W{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Trip_2]$ (X = I, W−Ge 2.3206(4) Å, Figure 1; X = H, W−Ge 2.324(1) Å, Figure 2), but is slightly

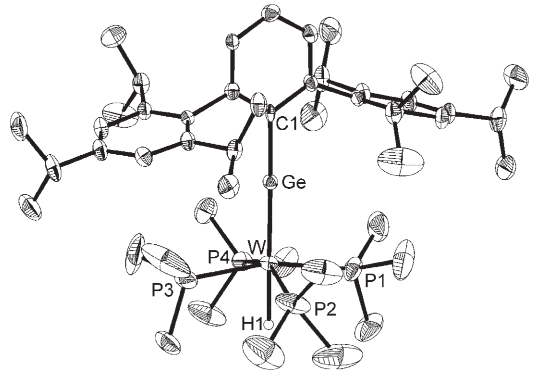


Figure 2. DIAMOND plot of the molecular structure of **4**-W-H in the solid state. Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: W-Ge 2.324(1), W-H1 1.78(9), W-P1 2.457(3), W-P2 2.442(2), W-P3 2.429(3), W-P4 2.443(2), Ge-C1 1.977(6); W-Ge-C1 178.9(2), Ge-W-H1 179(3), Ge-W-P1 97.31(7), Ge-W-P2 102.53(7), Ge-W-P3 97.24(7), Ge-W-P4 103.49(6).

larger than those of the germylidyne complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-C$_5$Me$_5$)] (X = Cl, Br, I, NCO, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, W−Ge 2.293(1)–2.3060(9) Å)[17] and [Cp(CO)$_2$W≡Ge-C$_6$H$_3$-2,6-Mes$_2$] (W−Ge 2.277(1) Å).[18]

Consistent with the molecular structure shown in Figure 1, the ^{31}P{^{1}H} NMR spectra of the germylidyne complexes **4**-Mo-Cl and **4**-W-Cl display a singlet resonance at $\delta = -2.7$ and -31.0 ppm (^1J(W,P) = 262 Hz), respectively, and their ^{1}H NMR spectra show the expected number and multiplicity of signals for the *m*-terphenyl substituent and the PMe$_3$ ligands of *trans*-configured, C_{2v}-symmetric complexes.[10] Compound **5**-W-Cl is the first example of a tungsten hydrido–germylidene complex to be characterized by X-ray crystallography.[10,19] Its molecular structure shows a pentagonal bipyramidal, roughly C_s-symmetric complex, with two PMe$_3$ ligands (P2 and P4) occupying the apical positions (P2-W-P4 173.46(3)°). The other tungsten-bonded atoms (Ge, P1, Cl, P3, and H54) lie in the equatorial plane of the bipyramid (Figure 3).[20] Complex **5**-W-Cl features a planar four-membered metallacycle (W-Ge-C37-P1 torsion angle: 0.6(2)°) that incorporates a germanium atom in trigonal-planar coordination (sum of interligand angles: 360°). The steric pressure exerted by the *m*-terphenyl substituent increases significantly one of the external bond angles at germanium (W-Ge-C1 159.8(1)°), which in turn leads to a small endocyclic bond angle at germanium (W-Ge-C37 97.8(1)°), thus increasing the ring strain. The W−Ge bond length of **5**-W-Cl (2.4543(4) Å) is one of the smallest to be reported so far for a tungsten–germanium double bond,[21] and lies between those reported for W−Ge triple bonds (2.277(1)–2.338(1) Å, see above) and W−Ge single bonds (2.493(2)–2.681(3) Å).[15f,g,18] The hydrido ligand could be located in the difference Fourier map and lies in the equatorial plane (W−H54 1.73(4) Å). This bond length lies in the range found for W−H bonds by neutron diffraction (1.715(4)–1.778(3) Å).[22] The orientation of the W−H54 vector and the Ge−H54 separation of 2.36(4) Å, which is considerably larger than that expected for a Ge−H single bond (1.53–1.62 Å),[23] do not indicate any bonding interaction between the hydrido ligand and the unsaturated germanium center.

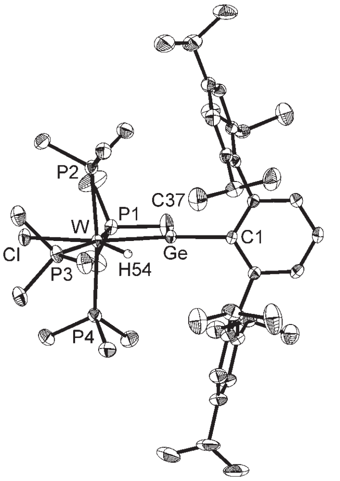
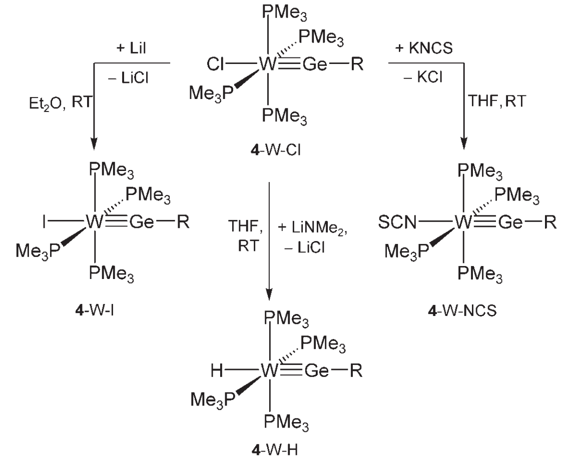


Figure 3. DIAMOND plot of the molecular structure of **5**-W-Cl in the solid state. Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms except H54 are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: W-Ge 2.4543(4), W-Cl 2.5217(9), W-H54 1.73(4), W-P1 2.4806(9), W-P2 2.480(1), W-P3 2.507(1), W-P4 2.470(1), Ge-C1 2.022(3), Ge-C37 2.034(4), P1-C37 1.818(4); W-Ge-C1 159.8(1), W-Ge-C37 97.8(1), C1-Ge-C37 102.4(2), Ge-W-H54 66(1), Ge-W-Cl 148.48(2), Ge-W-P1 67.86(2), Ge-W-P2 93.22(2), Ge-W-P3 133.46(2), Ge-W-P4 93.28(3), Cl-W-P1 80.62(3), Cl-W-P2 87.12(3), Cl-W-P3 78.06(3), Cl-W-P4 87.73(3), P1-W-P2 91.77(3), P1-W-P4 91.36(3), P2-W-P3 87.36(3), P2-W-P4 173.46(3), W-P1-C37 103.2(1), Ge-C37-P1 91.1(2).

The NMR and IR spectra corroborate the solid-state structure of **5**-W-Cl.[10] The ^{31}P{^{1}H} NMR spectrum displays three resonance signals at $\delta = -36.2$ (PMe$_2$, ^1J(W,P$_X$) = 214 Hz), -34.4 (2 × PMe$_3$, ^1J(W,P$_M$) = 243 Hz), and -32.7 ppm (1 × PMe$_3$, ^1J(W,P$_A$) = 163 Hz) with the multiplicity pattern of an AM$_2$X spin system (^2J(P$_A$,P$_M$) = 28 Hz, ^2J(P$_A$,P$_X$) = 111 Hz, ^2J(P$_M$,P$_X$) = 20 Hz). The hydrido signal appears in the ^{1}H NMR spectrum at $\delta = 0.49$ ppm as a doublet of doublets of triplets (^2J(P,H) = 70.8 Hz, ^2J(P,H) = 17.6 Hz, ^2J(P$_M$,H) = 15.1 Hz, ^1J(W,H) = 14.9 Hz), and the IR spectrum of **5**-W-Cl exhibits one ν(W−H) absorption band at 1812 cm^{-1}, which lies in the frequency range of W−H stretching modes of terminal hydrido ligands.[17c,24]

Complex **4**-W-Cl is a useful starting material for the preparation of other tungsten germylidyne complexes. Thus, treatment of **4**-W-Cl with an excess of KNCS in THF at ambient temperature afforded the isothiocyanato complex **4**-W-NCS, which was isolated as a dark brown solid in 88% yield (Scheme 2). Complex **4**-W-NCS can also be prepared in 55% yield from **5**-W-Cl and KNCS in THF at ambient temperature. Similarly, the reaction of **4**-W-Cl with an excess of LiI in diethyl ether gave selectively the iodido derivative **4**-W-I (Scheme 2). Complex **4**-W-I was isolated in 79% yield as a red-brown, microcrystalline solid, which melts at 194 °C and starts decomposing at 198 °C. Unexpectedly, treatment of **4**-W-Cl with LiNMe$_2$ afforded selectively the hydrido–germylidyne complex **4**-W-H (Scheme 2). Two equivalents of LiNMe$_2$ were required according to NMR spectroscopy for the quantitative consumption of **4**-W-Cl, which probably proceeds via a dimethylamido complex intermediate that undergoes β-hydride elimination. Complex **4**-W-H was isolated as a crystalline, red-brown, very air-sensitive solid,



Scheme 2. Chloride substitution reactions of the germylidyne complex **4**-W-Cl. R = C$_6$H$_3$-2,6-Trip$_2$.

which decomposes upon melting at 189 °C. Complexes **4**-W-X (X = NCS, I, H) were fully characterized.[10] The molecular structures of **4**-W-I and **4**-W-H (Figures 1 and 2, respectively) reveal the same bonding features of the germylidyne ligand as **4**-W-Cl, including the almost-linear coordination geometry at germanium (W-Ge-C_{aryl}: 175.79(7)° (**4**-W-I), 178.9(2)° (**4**-W-H)) and the very short W−Ge bonds (2.3206(4) Å (**4**-W-I), 2.324(1) Å (**4**-W-H)).[25] The solid-state Raman spectrum of **4**-W-H displays a ν(W−H) band at 1658 cm^{-1},[26] which appears at higher energy than that of *trans*-[H(dmpe)$_2$W≡CMes] (ν(W−H) 1600 cm^{-1}; dmpe = $Me_2PCH_2CH_2PMe_2$).[27] This observation suggests that the germylidyne ligand exerts a weaker *trans* influence than the carbyne ligand.[17c] In the ^{1}H NMR spectrum of **4**-W-H the hydrido ligand gives rise to a quintet signal at $\delta = -5.56$ ppm (^2J(P,H) = 30.6 Hz, ^1J(W,H) = 61.2 Hz). The ^{31}P{^{1}H} NMR spectra of the germylidyne complexes display one singlet resonance for the PMe_3 ligands at $\delta = -28.2$ (**4**-W-NCS), −46.8 (**4**-W-I), and −30.6 ppm (**4**-W-H), thus confirming the *trans* configuration of the complexes. The ^{31}P NMR signal is in all cases flanked by a pair of tungsten satellites, and the ^1J(W,P) coupling constants have similar values (**4**-W-NCS 257 Hz, **4**-W-I 256 Hz, **4**-W-H 252 Hz) compared to that of **4**-W-Cl (262 Hz). Finally, the ^{13}C{^{1}H} NMR spectra of all germylidyne complexes exhibit a characteristic low-field signal for the germanium-bonded C_{aryl} atom at $\delta = 177.1$ (**4**-W-Cl), 176.6 (**4**-W-NCS), 174.4 (**4**-W-I), and 178.1 ppm (**4**-W-H), which appears at slightly lower field than that of **3** ($\delta = 164.6$ ppm).

This work demonstrates that reactions of organogermanium(II) chlorides with electron-rich metal complexes can follow unprecedented pathways, finally leading to compounds with metal–germanium triple bonds. This work complements our recent studies on the activation of organotetrel(II) halides by d^6 metal centers, which have culminated in the isolation of compounds featuring triple bonds to linear-coordinated germanium, tin, and lead centers.[17,28] Extension of the methodology presented here to Group 8 metals is quite appealing, and should lead to ylidyne complexes of metals with a different d-electron configuration and coordination sphere. Efforts in this direction are in progress.

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[10] The Supporting Information contains detailed experimental procedures for the preparation and the analytical and spectroscopic characterization of the starting materials **2**-Mo and **2**-W-c and of all products. It also contains the NMR spectroscopic data of **3**. CCDC-608272 (**4**-W-Cl·*n*-C_5H_{12}), CCDC-608273 (**4**-W-I·0.5*n*-C_5H_{12}), CCDC-608274 (**4**-W-H), and CCDC-608275 (**5**-W-Cl·*n*-C_5H_{12}) 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.

[11] The advantages of the new method are the following: a) the use of PMe_3 as solvent is avoided, and b) the starting materials **1**-Mo and **1**-W can be readily obtained in good overall yields starting from $MoCl_5$ and WCl_6, respectively.

[12] Depending on the work-up conditions, either pure **2**-Mo or a mixture of **2**-Mo and its cyclometalation product [Mo(η^2-CH_2PMe_2)H(PMe_3)$_4$] (**2**-Mo-c) was isolated (see the Supporting Information).

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metalation product [Mo(η^2-CH_2PMe_2)H(PMe_3)$_4$] (**2**-Mo-c); see the Supporting Information).

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[16] The *m*-terphenyl substituent adopts in all germylidyne complexes an eclipsed conformation with respect to the {WX(PMe_3)$_4$} fragment (X = Cl, I, H), as evidenced by the interplane angle (**4**-W-Cl 1.8(3)°, **4**-W-I 3.60(7)°, **4**-W-H 7.9(2)°) between the least-square plane through the tungsten atom, germanium atom, and the central aryl ring carbon atoms, and the least-square plane of the atoms Ge, W, P1, and P3. It should be also noted that all germylidyne complexes show a similar geometric deviation of the WP_4 core from planarity. The two *trans*-located PMe_3 ligands which are oriented perpendicular to the germanium-bonded phenyl ring (P2 and P4 in Figure 1 and Figure 3) are bent more strongly away from the germylidyne ligand than the other two PMe_3 ligands (P1 and P3).

[17] a) A. C. Filippou, A. I. Philippopoulos, P. Portius, D. U. Neumann, *Angew. Chem.* **2000**, *112*, 2881; *Angew. Chem. Int. Ed.* **2000**, *39*, 2778; b) A. C. Filippou, P. Portius, A. I. Philippopoulos, *Organometallics* **2002**, *21*, 653; c) A. C. Filippou, A. I. Philippopoulos, P. Portius, G. Schnakenburg, *Organometallics* **2004**, *23*, 4503.

[18] 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.

[19] Only one hydrido–germylidene complex, [{PhB(CH_2PPh_2)$_3$}(H)$_2$Ir=$GeMes_2$], has been reported so far: J. D. Feldman, J. C. Peters, T. Don Tilley, *Organometallics* **2002**, *21*, 4065.

[20] The maximum deviation of the atoms W, Ge, P1, Cl, P3, and H54 from the least-square plane is less than 10 pm.

[21] The W–Ge bond length of **5**-W-Cl compares well with that of the germylidene complex [(η^5-C_5Me_4Et)W(CO)$_2$(=$GeMe_2$)$GeMe_3$] (W–Ge 2.459(2) Å: K. Ueno, K. Yamaguchi, H. Ogino, *Organometallics* **1999**, *18*, 4468), but is smaller than those of other tungsten germylidene complexes (W–Ge 2.505(2)–2.632(2) Å): a) G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang, L. Zsolnai, *J. Organomet. Chem.* **1985**, *282*, 331; b) P. Jutzi, B. Hampel, K. Stroppel, C. Krüger, K. Angermund, P. Hofmann, *Chem. Ber.* **1985**, *118*, 2789; c) P. Jutzi, B. Hampel, M. B. Hursthouse, A. J. Howes, *J. Organomet. Chem.* **1986**, *299*, 19; d) W.-W. du Mont, L. Lange, S. Pohl, W. Saak, *Organometallics* **1990**, *9*, 1395; e) N. Tokitoh, K. Manmaru, R. Okazaki, *Organometallics* **1994**, *13*, 167.

[22] R. Bau, M. H. Drabnis, *Inorg. Chim. Acta* **1997**, *259*, 27.

[23] The experimental value for the Ge–H bond length of GeH_4 is 1.5251(5) Å: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, C. S. Pote, *Structure Data of Free Polyatomic Molecules*, Landolt-Börnstein, New Series II, Vol. 7 (Eds. K.-H. Hellwege, A. M. Hellwege), Springer, Berlin, **1976**. The calculated value for the Ge–H bond length of GeH_2 ranges from 1.584 to 1.617 Å: Q.-S. Li, R.-H. Lü, Y. Xie, H. F. Schaefer III, *J. Comput. Chem.* **2002**, *23*, 1642.

[24] M-H-E three-center interactions (M = Mo, E = Ge; M = W, E = Si) give rise to ν(M-H-E) absorption bands at considerably lower wave numbers: a) J. L. Vincent, S. Luo, B. L. Scott, R. Butcher, C. J. Unkefer, C. J. Burns, G. J. Kubas, A. Lledós, F. Maseras, J. Tomàs, *Organometallics* **2003**, *22*, 5307; b) T. Watanabe, H. Hashimoto, H. Tobita, *Angew. Chem.* **2004**, *116*, 220; *Angew. Chem. Int. Ed.* **2004**, *43*, 218.

[25] It is noticeable that the W–Ge triple-bond length of **4**-W-H does not differ from those of **4**-W-X (X = Cl, I), despite the presence of a hydrido ligand which exerts a strong *trans* influence. This finding suggests that the σ-bonding part of the W–Ge bond, which is expected to be weakened in **4**-W-H by the hydrido ligand, has a minor influence on the W–Ge triple-bond length.

[26] The W–H stretching mode of **4**-W-H was also observed in the IR spectrum at 1654 cm^{-1} (Supporting Information).

[27] F. Furno, T. Fox, H. W. Schmalle, H. Berke, *Organometallics* **2000**, *19*, 3620.

[28] a) A. C. Filippou, P. Portius, A. I. Philippopoulos, H. Rohde, *Angew. Chem.* **2003**, *115*, 461; *Angew. Chem. Int. Ed.* **2003**, *42*, 445; b) A. C. Filippou, A. I. Philippopoulos, G. Schnakenburg, *Organometallics* **2003**, *22*, 3339; c) A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293; *Angew. Chem. Int. Ed.* **2004**, *43*, 2243; d) A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem.* **2004**, *116*, 6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6512; e) A. C. Filippou, G. Schnakenburg, A. I. Philippopoulos, N. Weidemann, *Angew. Chem.* **2005**, *117*, 6133; *Angew. Chem. Int. Ed.* **2005**, *44*, 5979.