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Germylidyne Complexes

Open-Shell Complexes Containing Metal–Germanium Triple Bonds**

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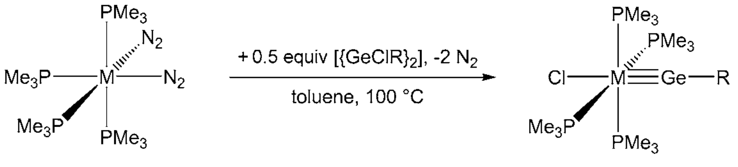
The chemistry of compounds featuring triple bonds of the Group 14 elements Si–Pb with transition metals is a research area combining modern molecular main-group-element with transition-metal chemistry. Following the first report of a molybdenum germylidyne complex by Power et al.,[1] a series of uncommon complexes of the general formula *trans*-[$XL_4M{\equiv}E{-}R$] (M = Mo, W; E = Ge–Pb; X = halogen; L = phosphane; R = bulky alkyl or aryl group), have become accessible in our group by taking advantage of a very efficient N_2/PMe_3 elimination method.[2] Recently, also the first silylidyne complex, [$Cp(CO)_2Mo{\equiv}Si{-}R$] (Cp = C_5H_5; R = C_6H_3-2,6-$Trip_2$; Trip = 2,4,6-triisopropylphenyl), has been isolated.[3] All these compounds are closed-shell 18 valence electron (VE) complexes, which contain linear-coordinated, triply bonded Si–Pb atoms. In comparison, open-shell congeners of these intriguing compounds are presently unknown. This situation is not surprising as even open-shell alkylidyne complexes are very rare and quite reactive species.[4] Quantum-chemical calculations of the germylidyne, stannylidyne, and plumbylidyne complexes *trans*-[$XL_4M{\equiv}E{-}R$] revealed that these compounds have a similar electronic structure with Fischer-type alkylidyne complexes,[5] and contain a d^6 configured metal center and a metal-centered HOMO, that is non-bonding with respect to the metal–tetrel triple bond.[2a,-d,e,f,6] The theoretical results implied that the compounds *trans*-[$XL_4M{\equiv}E{-}R$] should be prone to one-electron oxidation providing access to unprecedented Si–Pb analogues of open-shell alkylidyne complexes. Experimental verification of this prediction is presented herein with the synthesis and full characterization of the first open-shell 17 VE germylidyne complexes *trans*-[$Cl(PMe_3)_4M{\equiv}Ge{-}C_6H_3$-2,6-$Mes_2$][$B(C_6F_5)_4$] (M = Mo, W; Mes = 2,4,6-trimethylphenyl).

The entry into this chemistry provided the 18 VE germylidyne complexes *trans*-[$Cl(PMe_3)_4M{\equiv}Ge{-}C_6H_3$-2,6-$Mes_2$] (**1**-Mo: M = Mo; **1**-W: M = W), which were obtained selectively upon heating the dinitrogen complexes *cis*-[$M(N_2)_2(PMe_3)_4$][7] (M = Mo, W) with 0.5 equivalents of the organogermanium(II) chloride [{$GeCl(C_6H_3$-2,6-$Mes_2)$}$_2$][8] in toluene at 100 °C [Eq. (1)]. The products were isolated as air-sensitive, wine-red (**1**-Mo) and dark brown-red (**1**-W) solids in good yields.[9] Both germylidyne complexes are very soluble in pentane and are thermally robust solids, which decompose upon melting at 229 °C (**1**-Mo) and 230 °C (**1**-W).



M = Mo, W; R = C_6H_3-2,6-Mes_2

1-M

(1)

The molecular structures of **1**-Mo and **1**-W were determined by single-crystal X-ray diffraction.[9] The isostructural, *trans*-configured, distorted octahedral complexes display nearly linear coordinated germanium atoms (**1**-Mo, Mo-Ge-C1 176.27(8)°; **1**-W, W-Ge-C1 176.3(1)°) and very short M–Ge distances (**1**-Mo, 2.3041(3) Å; **1**-W, 2.3106(4) Å) (Figure 1), which compare well with those of other 18 VE germylidyne complexes.[2b,g,i]

The most distinctive NMR spectroscopic features of **1**-Mo and **1**-W are the two ^{1}H NMR singlet signals found for the methyl groups of the *m*-terphenyl substituent in a 6:12 integral ratio, and the singlet ^{31}P NMR signal of the four chemically equivalent PMe_3 ligands (**1**-Mo: $\delta = -1.3$ ppm; **1**-W: $\delta = -29.5$ ppm, $^1J(^{183}W,^{31}P) = 261$ Hz), both of which confirm the *trans*-configuration and an overall C_{2v} symmetry of the complexes in solution. Furthermore, a downfield shifted ^{13}C NMR signal is observed for the germanium-bonded C_{aryl} atom (**1**-Mo, $\delta = 168.7$ ppm; **1**-W, $\delta = 174.1$ ppm), which appears slightly downfield of that of [$GeCl(C_6H_3$-2,6-$Mes_2)$]$_2$ ($\delta = 154.6$ ppm) and is characteristic of arylgermanium compounds in low-oxidation states.[9]

The electrochemical behavior of **1**-Mo and **1**-W was studied by cyclic voltammetry.[9] The 18 VE germylidyne

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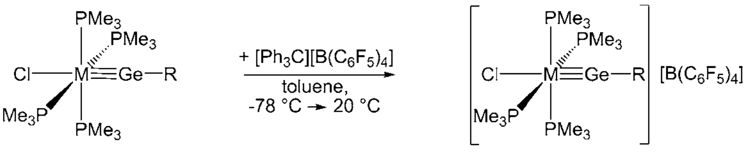
complexes undergo in C_6H_5F at room temperature a reversible one-electron oxidation at a half-wave potential $E_{1/2}$ of -0.35 V and -0.39 V vs. the $[Fe(C_5Me_5)_2]^{+1/0}$ redox couple, respectively (Figure 2).[10–12] The $E_{1/2}$ of **1**-W (-0.91 V vs. the $[Fe(C_5H_5)_2]^{+1/0}$ redox couple)[12] compares well with that of the methylidyne complex *trans*-$[Cl(PMe_3)_4W{\equiv}C\text{-}H]$ ($E_{1/2}$ (THF) $= -0.88$ V vs. the $[Fe(C_5H_5)_2]^{+1/0}$ redox couple),[4d] reflecting the electronic analogy of **1**-Mo and **1**-W with Fischer-type alkylidyne complexes.

The CV studies suggested, that open-shell germylidyne complexes might be accessible upon one-electron oxidation of **1**-Mo and **1**-W using suitable oxidants.[13] In fact, treatment of **1**-Mo and **1**-W with one equivalent of $(Ph_3C)[B(C_6F_5)_4]$[14] in toluene afforded selectively the 17 VE germylidyne complexes *trans*-$[Cl(PMe_3)_4M{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2][B(C_6F_5)_4]$ (**2**-Mo: M = Mo; **2**-W: M = W), which were isolated as persimmon-red, extremely sensitive, microcrystalline solids in 70–76 % yield [Eq. (2)].[9] Both compounds decompose rapidly in THF and CH_2Cl_2 and are much less thermally stable solids (**2**-Mo: 96 °C (decomp.); **2**-W: 92 °C (decomp.)) than their 18 VE congeners.



1-M M = Mo, W; R = C_6H_3-2,6-Mes_2 **2**-M (2)

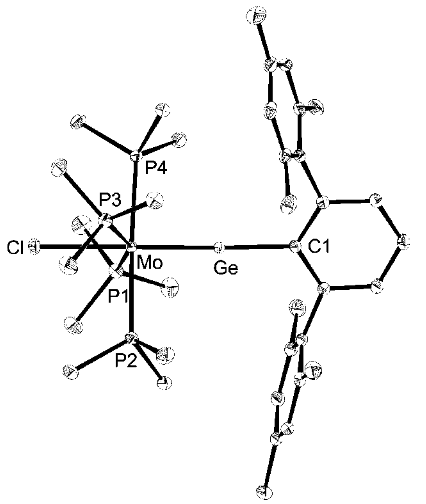


Figure 1. ORTEP plot of the molecular structure of **1**-Mo in the solid state. Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **1**-Mo (bond angles and lengths of **1**-W are given in square brackets): M–Ge 2.3041(3) [2.3106(4)], M–Cl 2.5380(7) [2.529(1)], M–P1 2.4837(7) [2.481(1)], M–P2 2.4732(7) [2.463(1)], M–P3 2.4917(7) [2.474(1)], M–P4 2.4595(7) [2.450(1)], Ge–C1 1.994(3) [1.995(4)]; M-Ge-C1 176.27(8) [176.3(1)], Ge-M-Cl 178.25(2) [178.35(3)], Ge-M-P1 100.92(2) [104.10(3)], Ge-M-P2 88.86(2) [88.80(3)], Ge-M-P3 104.10(2) [101.14(3)], Ge-M-P4 87.96(2) [87.97(3)], P1-M-Cl 77.34(2) [77.55(4)], P2-M-Cl 91.32(2) [91.27(4)], P3-M-Cl 77.64(2) [77.20(3)], P4-M-Cl 91.87(2) [91.97(4)].

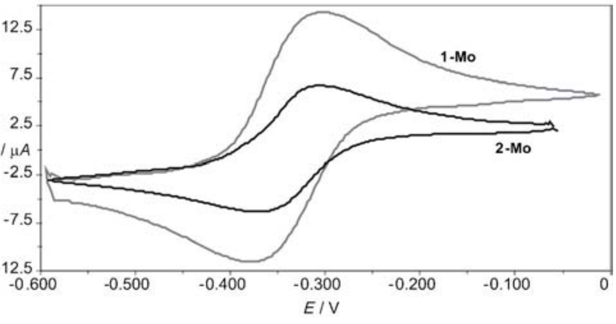


Figure 2. Single-scan cyclic voltammograms of complexes **1**-Mo (gray) and **2**-Mo (black) in fluorobenzene at room temperature ($\nu = 100$ mV s^{-1}; supporting electrolyte: $(NBu_4)PF_6$ (10^{-1} M); reference: 0.004 M $[Fe(C_5Me_5)_2]^{+1/0}$/0.1 M $(NBu_4)PF_6/C_6H_5F$).

The cyclic voltammograms of **2**-Mo and **2**-W in C_6H_5F at ambient temperature show that the 17 VE germylidyne complexes are reversibly reduced at the same half-wave potential (**2**-Mo: $E_{1/2} = -0.35$ V; **2**-W: $E_{1/2} = -0.39$ V vs. the $[Fe(C_5Me_5)_2]^{+1/0}$ redox couple) found for the one-electron oxidation of **1**-Mo and **1**-W, respectively (Figure 2).[9,11,12]

The crystal structures of **2**-Mo·$(C_6H_6)(C_6H_5F)$ and **2**-W·2 C_6H_6 were determined by single-crystal X-ray diffraction (Figure 3). The two salts are essentially isotypic and are composed of well separated cations and anions.[9,15] The *trans*-configured, distorted-octahedral 17 VE germylidyne complex cations[16] feature nearly linear-coordinated germanium atoms (**2**-Mo, Mo-Ge-C1 175.3(1)°; **2**-W, W-Ge-

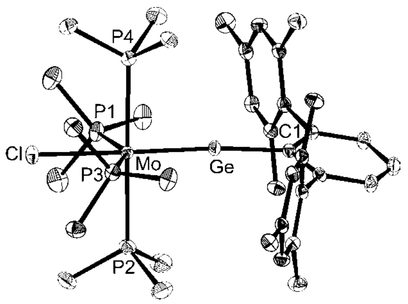


Figure 3. ORTEP plot of the structure of the complex cation of **2**-Mo in the solid state. The thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **2**-Mo (bond angles and lengths of **2**-W are given in square brackets): M–Ge 2.3023(4) [2.321(2)], M–Cl 2.4878(9) [2.499(4)], M–P1 2.537(1) [2.531(4)], M–P2 2.539(1) [2.526(4)], M–P3 2.532(1) [2.518(4)], M–P4 2.536(1) [2.523(4)], Ge–C1 1.962(3) [1.931(15)]; M-Ge-C1 175.3(1) [172.9(4)], Ge-M-Cl 177.75(3) [175.7(1)], Ge-M-P1 101.82(3) [101.4(1)], Ge-M-P2 91.12(3) [92.9(1)], Ge-M-P3 105.01(3) [106.9(1)], Ge-M-P4 87.76(3) [87.1(1)], Cl-M-P1 76.13(3) [75.1(1)], Cl-M-P2 89.81(3) [89.5(2)], Cl-M-P3 77.02(3) [76.6(1)], Cl-M-P4 91.35(3) [90.6(1)]

C1 172.9(4)°). and have nearly identical M–Ge bond lengths (**2**-Mo, 2.3023(4) Å; **2**-W 2.321(2) Å) to those of the closed-shell, parent complexes **1**-M, indicating the presence of metal–germanium triple bonds. In contrast, the M–P bonds of **2**-M (average: d(Mo-P) = 2.536(1) Å; d(W-P) = 2.525(3) Å),[17] are longer than those of **1**-M (d(Mo-P) = 2.475(9) Å; d(W-P) = 2.467(7) Å), whereas the M–Cl bonds (**2**-Mo, 2.4878(9) Å; **2**-W, 2.499(4) Å) are shorter than those of **1**-M (**1**-Mo, 2.5380(7) Å; **1**-W, 2.529(1) Å; Figure 1 and Figure 3).

These structural trends can be explained upon comparing the electronic structures of **1**-M and **2**-M obtained by DFT calculations.[9] Orbital analysis reveals that the HOMO of **1**-M is oriented perpendicular to the Cl-M-Ge axis, has mainly metal d_{xy} character and is non-bonding with respect to the germylidyne and chloro ligand. The HOMO of **1**-M is, however, bonding with respect to the phosphane ligands; the π-bonding involves back-donation from the filled metal d_{xy} orbital into the π-acceptor orbitals of the PMe_3 ligands (mainly σ*(P-C) in character).[18] Oxidation of **1**-M results in a depopulation of this orbital (metal-based oxidation), which is filled with only one electron in **2**-M (SOMO, Figure 4). Therefore, oxidation of **1**-M eliminates the M–P π-back-bonding leading to an elongation of the M–P bonds. In comparison, the M–Cl distances decrease upon oxidation due to the decreasing ionic radius of the metal, whereas the M–Ge distances are not affected.[19]

Additional information on the electronic structure of **2**-Mo and **2**-W was provided by the continuous-wave (cw) X-band EPR spectra (Figure 5). The EPR spectrum of **2**-Mo is characterized by g values, which show significant anisotropy ($g_{xx} = 2.090$, $g_{yy} = 2.060$ and $g_{zz} = 1.970$). Complex **2**-W shows an even larger g tensor anisotropy with $g_{xx} = 2.194$, $g_{yy} = 2.160$, $g_{zz} = 1.900$.

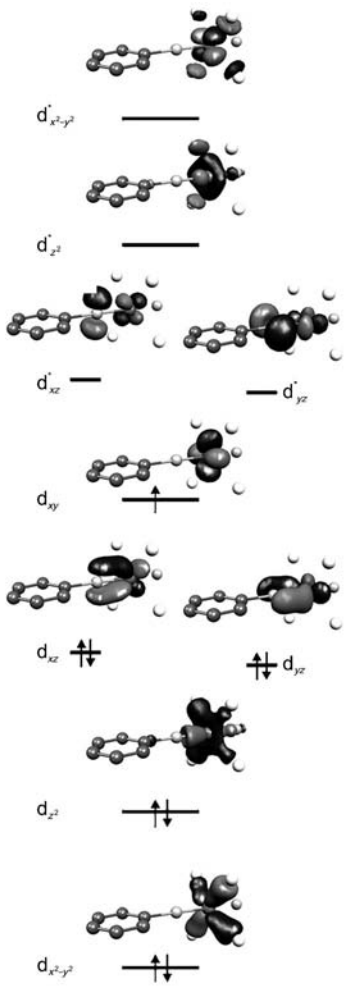


Figure 4. Calculated natural orbitals with metal d character of complex **2**-Mo (isosurface value 0.06 electron $Å^{-3/2}$). The mesityl substituents have been omitted for clarity.

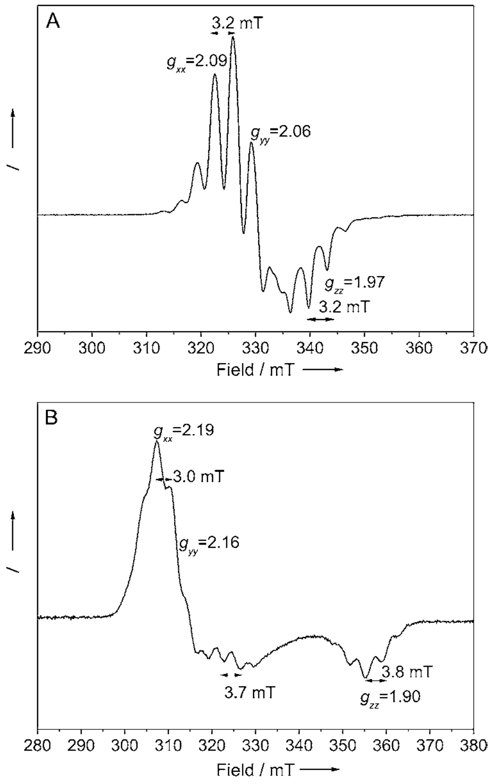


Figure 5. cw-EPR spectra of frozen C_6H_5F solutions of A) **2**-Mo and B) **2**-W recorded at $\nu_{mw} = 9.470$ GHz, $T = 30$ K.

The g shifts of **2**-W are a factor of 2–3 larger than those of the **2**-Mo (Table 1). This difference is caused by the spin-orbit coupling interaction, which is about a factor of 3 larger for W than for Mo.[20]

The observation of only three g values near the free-electron g value ($g_e = 2.0023$) and no additional signals indicates that complexes **2**-Mo and **2**-W have a low spin, d^5

Table 1: g values and g shifts of the germylidyne complexes **2**-Mo and **2**-W.[a]

Compd	g_{xx}	g_{yy}	g_{zz}	Δg_{xx}	Δg_{yy}	Δg_{zz}
2-Mo	2.090	2.060	1.970	+0.088	+0.058	−0.032
2-W	2.194	2.160	1.900	+0.192	+0.158	−0.102

[a] The g shifts Δg_{xx}, Δg_{yy}, and Δg_{zz} are given by the following equations: $\Delta g_{xx} = g_{xx} - g_e$, $\Delta g_{yy} = g_{yy} - g_e$, $\Delta g_{zz} = g_{zz} - g_e$ (g_e is the free-electron g value).

metal configuration ($S = {}^1\!/_2$),[21] resulting from the strong ligand field of the germylidyne and the phosphane ligands. Furthermore, the experimental observation of two approximately equal g values larger than g_e and one value smaller than g_e indicate that both complexes have a $(d_{xz},d_{yz})^4(d_{xy})^1$ ground-state configuration. Metal π-back donation to the π-acceptor germylidyne ligand, stabilizes apparently the metal d_{xz} and d_{yz} orbitals relative to the d_{xy} orbital, which becomes the SOMO of the complex in full agreement with the results of the DFT calculations (Figure 4). For this configuration the components of the g matrix are given by the following equations, where ζ is the spin-orbit coupling constant, E_{xy}, E_{xz}, E_{yz} and $E_{x^2-y^2}$ are the energies of the bonding orbitals with metal d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$ character, and $E^*_{x^2-y^2}$ is the energy of the anti-bonding orbital with metal $d_{x^2-y^2}$ character [Eq. (3); Figure 4].[22]

$$\begin{aligned} g_{xx} &= g_e + \frac{2\zeta}{E_{xy} - E_{xz}} > g_e \\ g_{yy} &= g_e + \frac{2\zeta}{E_{xy} - E_{yz}} > g_e \\ g_{zz} &= g_e - \frac{8\zeta}{E_{xy} - E_{x^2-y^2}} - \frac{8\zeta}{E^*_{x^2-y^2} - E_{xy}} < g_e \end{aligned} \tag{3}$$

As a result the g_{xx} and g_{yy} values should be larger than g_e, while g_{zz} should be smaller than g_e as observed. The bulk spin density is found on the metal. A significant negative spin density of −17% (**2**-Mo) and −12% (**2**-W) is present on the Ge atom, which stems from spin polarization[23] of the bonding orbitals, involving the metal d_{xz}, d_{yz}, and d_{z^2} atomic orbitals. Spin density at the Cl atom has been observed experimentally using advanced pulsed EPR techniques (see supplementary information).

Finally, each component of the g matrix is in both spectra split into a quintet with a 1:4:6:4:1 intensity pattern, which results from the hyperfine interaction with the four equivalent ^{31}P atoms ($I = {}^1\!/_2$). The observed hyperfine coupling constants (**2**-Mo: $A_x = 3.2$ mT, $A_y = 3.2$ mT, $A_z = 3.2$ mT; **2**-W: $A_x = 3.0$ mT, $A_y = 3.7$ mT, and $A_z = 3.8$ mT) compare well with the calculated values, which are negative and range from −2.8 mT to −3.9 mT.

In conclusion, the first open-shell complexes containing metal–germanium triple bonds were prepared and their properties and structures studied by a combination of experimental and theoretical methods. Studies reveal that the electron-transfer approach can be extended to a variety of other heavier Group 14 analogues of metal alkylidyne complexes leading to new open-shell compounds at the interface of main-group and transition-metal chemistry.

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Keywords: germanium · molybdenum · redox chemistry · triple bonds · tungsten

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[9] The Supporting Information contains the syntheses, the analytical and spectroscopic data of complexes **1**-Mo – **2**-W, and the electrochemical studies of these compounds, including the cyclic voltammograms and Tables of the CV results. It also contains the crystallographic data of **1**-Mo – **2**-W, additional information of the EPR studies of **2**-Mo and **2**-W, and of the DFT calculations (BP86/TZV-ZORA basis set) including selected calculated bond lengths and angles and the cartesian atomic coordinates of the geometry-optimized minimum structures. CCDC 847001 (**1**-Mo·(*n*-C_5H_{12})), 847002 (**1**-W·0.5(*n*-C_6H_{14})), 847003 (**2**-Mo·(C_6H_6)(C_6H_5F)) and 847004 (**2**-W·2C_6H_6) 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.

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[15] No intra- or interionic contacts with the electrophilic germanium centers were found in **2**-Mo and **2**-W. The closest interionic contacts exist in **2**-Mo and **2**-W between a methyl hydrogen atom of the *m*-terphenyl substituent and a fluorine atom of the borate anion (**2**-Mo: H···F 2.368 Å; **2**-W: H···F: 2.447 Å). These contacts are shorter than the sum of the van der Waals radii of fluorine and hydrogen (2.67 Å): a) K. Reichenbächer, H. I. Süss, J. Hulliger, *Chem. Soc. Rev.* **2005**, *34*, 22; b) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[16] One-electron oxidation has a minor influence on the coordination geometry of the complexes. Both redox couples *trans*-$[Cl(PMe_3)_4M{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2]^{+1/0}$ display the same geometric distortion of the MP_4 core, in which two *trans*-located PMe_3 ligands (P2 and P4) are orthogonal to the M–Ge bond axis, whereas the other two *trans*-arranged PMe_3 ligands (P1 and P3) are bent away from the germylidyne ligand towards the chloro ligand. This geometric distortion is of steric origin and results from the steric demand of the methyl groups of the PMe_3 ligands. Therefore, the model complexes *trans*-$[Cl(PH_3)_4M{\equiv}Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2]^{+1/0}$ do not display such a distortion.

[17] The unweighted mean value x_u of the four M−P bond lengths of **1**-Mo–**2**-W is given, respectively. The standard deviation σ of x_u (value in parenthesis) was calculated using the equation $\sigma^2 = \Sigma(x_i - x_u)^2/(n^2 - n)$, where x_i is the individual value and $n = 4$.

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[19] A closer analysis of the M–Ge triple bonds reveals that two counterbalancing effects are operative upon oxidation, as the σ-component of the M–Ge bond is strengthened, while the two π-components are weakened.

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[21] Analogous alkylidyne complexes have been described as d^1 (M(V) systems (Ref. [4d]). However, the high metal d-orbital contribution to the SOMO (d_{xy}) and the HOMO and HOMO-1 molecular orbitals (d_{xz}, d_{yz}) suggests that a description of the germylidyne complexes **2**-Mo and **2**-W as d^5 M(I) systems is more appropriate.

[22] Owing to the covalent character of the M−P σ bonds, both the bonding and antibonding orbitals $d_{x^2-y^2}$ and $d_{x^2-y^2}*$ have a considerable metal d character (Figure 4) and contribute to the shift of the g_{zz} value. This situation differs from the classical, idealized description by crystal field theory, where the metal–ligand bonds are considered as ionic: P. H. Rieger, *Coord. Chem. Rev.* **1994**, *135–136*, 203.

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