Triazidogermyl complexes of tungsten: synthesis, crystal structure and hydrolysis to a metallocyclotrigermoxane

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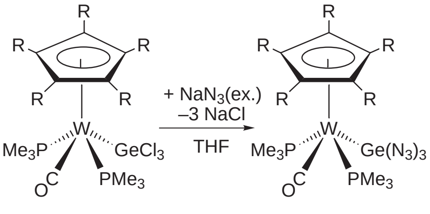
The synthesis and full characterization of the triazidogermyl complexes *trans*-(η^5-C_5R_5)W(CO)$_n$(PMe$_3$)$_{3-n}$Ge(N$_3$)$_3$ (2a: R = H, *n* = 1; 2b: R = Me, *n* = 1; 5b: R = Me, *n* = 2) is reported; the crystal structures of 2a and of the metallocyclotrigermoxane [Cp*W(CO)$_2$(PMe$_3$)Ge(N$_3$)(μ_2-O)]$_3$·C_6H_6 (6b·C_6H_6), the product of partial hydrolysis of 5b, are described.

Polyazidogermanes belong to a class of potentially explosive Ge(IV) compounds due to their propensity to decompose exothermally eliminating dinitrogen.[1] Studies of these compounds are very rare, and include some synthetic and spectroscopic work on GeMe$_n$(N$_3$)$_{4-n}$ (*n* = 0–3).[2] An approach for the kinetic stabilisation of triazidogermanes is presented here involving the use of 'electron-rich' organometal fragments. This is demonstrated by the synthesis and full characterization of the tungsten triazidogermyl complexes *trans*-(η^5-C_5R_5)W(CO)$_n$(PMe$_3$)$_{3-n}$Ge(N$_3$)$_3$ (**2a**: R = H, *n* = 1; **2b**: R = Me, *n* = 1; **5b**: R = Me, *n* = 2).

Treatment of **1a**[3] with an excess of NaN$_3$ in THF at ambient temperature resulted in the formation of **2a**. Similarly, prolonged heating of **1b**[3] with NaN$_3$ in refluxing THF afforded **2b** (eqn. (1)).† Monitoring of the reaction of **1b** with NaN$_3$ revealed the intermediate formation of the mixed azido(chloro)germyl complexes *trans*-Cp*W(CO)(PMe$_3$)$_2$[GeCl$_{3-m}$(N$_3$)$_m$] (Cp* = C_5Me_5; **1b-1**: *m* = 1; **1b-2**: *m* = 2).‡ A byproduct was also formed in this reaction, which was easily separated from **2b** by taking advantage of its high solubility in pentane; this byproduct was identified by IR and NMR spectroscopy to be the chloro complex *trans*-Cp*W(CO)(PMe$_3$)$_2$Cl (**3b**).[3]§ We suggest an associative mechanism for the nucleophilic substitution reactions in eqn. (1). In the first step, slow addition of the azide anion to the germanium atom of **1a** and **1b** occurs to give a five-coordinate metallogermanate intermediate. It is followed by a rapid displacement of chloride to afford the substitution product *trans*-(η^5-C_5R_5)W(CO)(PMe$_3$)$_2$[GeCl$_2$(N$_3$)], this sequence of steps being repeated consecutively to afford **2a** and **2b**. Increased steric congestion at the germanium center of **1b** is assumed to cause the five-coordinate germanate intermediates, formed after azide addition to **1b**, **1b-1** and **1b-2**, to follow a parallel decomposition pathway, which involves α-elimination of the chloro complex **3b**.§



(1)

a: R = H; b: R = Me

Complexes **2a** and **2b** were isolated as yellow, thermally robust solids, which begin to decompose upon slow heating at 150 and 177 °C. Both compounds are soluble in CH$_2$Cl$_2$ and in THF but insoluble in pentane, and were fully characterized.† Thus, the IR spectra of **2a** and **2b** display two ν_{asym}(N$_3$) absorptions, which appear at similar wavenumbers to those of germanium(IV) azides [Me$_3$GeN$_3$: ν_{asym}(N$_3$) = 2103 cm^{-1}; Ph$_3$GeN$_3$: ν_{asym}(N$_3$) = 2107 cm^{-1}][4] and higher than those of germanium(II) azides [Tp′GeN$_3$: ν_{asym}(N$_3$) = 2043 cm^{-1}].[5] The NMR spectroscopic data of **2a** and **2b** are similar to those of **1a** and **1b** and indicate the presence of only the *trans* stereoisomer in solution, which in the case of **2a** was also confirmed by a single-crystal X-ray diffraction study (Fig. 1).¶ Single crystals were obtained upon diffusion of pentane into a THF solution of **2a** at −30 °C. **2a** has similar bonding parameters to **1a** indicating the presence of an electron-rich metal center.[3] The tetrahedral environment of the germanium atom is strongly distorted as shown by the mean N–Ge–N and W–Ge–N bond angles of 96.2(4)° and 120.6(3)°, respectively. The W–Ge bond [2.5099 (9) Å] is short and the mean Ge–N bond length of 1.931(7) Å is larger than that of H$_3$GeN$_3$ (g) [1.845(6) Å][6] and that calculated for a Ge–N single bond (1.84 Å).[7] All these structural data can be rationalized using either the atom rehybridization model of Bent[8] or suggesting the presence of tungsten–triazidogermyl π back-bonding.[3] As observed for other covalent azides of main-group elements,[9] the azide groups in **2a** adopt a slightly bent configuration with a mean N–N–N bond angle of 172.9(13)° and two significantly different N–N bond lengths [(N$_\alpha$–N$_\beta$)$_{av.}$ = 1.225(11) Å; (N$_\beta$–N$_\gamma$)$_{av.}$ = 1.113(12) Å], which are close to the experimental values of a N–N double [1.20 Å] and a N–N triple bond [1.10 Å], respectively.[10]

Less electron-rich metal fragments can also be used for the kinetic stabilisation of triazidogermanes as shown by the high-

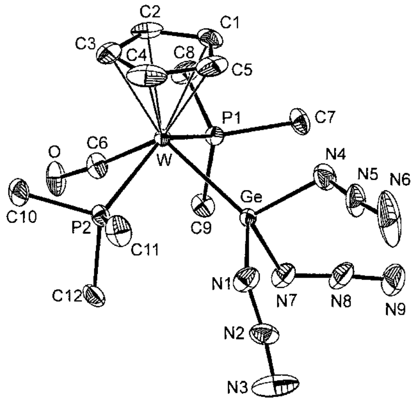


Fig. 1 ZORTEP plot of the molecular structure of **2a** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W–Ge 2.5099(9), W–P(1) 2.4818(18), W–P(2) 2.4796(19), W–C(6) 1.939(8), Ge–N(1) 1.942(7), Ge–N(4) 1.926(7), Ge–N(7) 1.925(7), N(1)–N(2) 1.221(11), N(2)–N(3), 1.110(11), N(4)–N(5) 1.207(11), N(5)–N(6) 1.104(13), N(7)–N(8) 1.247(11), N(8)–N(9) 1.124(12), W–Ge–N(1) 123.4(3), W–Ge–N(4) 111.4(3), W–Ge–N(7) 126.9(2), N(1)–Ge–N(4) 95.9(4), N(1)–Ge–N(7) 94.7(3), N(4)–Ge–N(7) 98.0(4), Ge–N(1)–N(2) 121.1(6), Ge–N(4)–N(5) 119.4(7), Ge–N(7)–N(8) 118.0(7), N(1)–N(2)–N(3) 171.6(16), N(4)–N(5)–N(6) 172.4(11), N(7)–N(8)–N(9) 174.6(11).

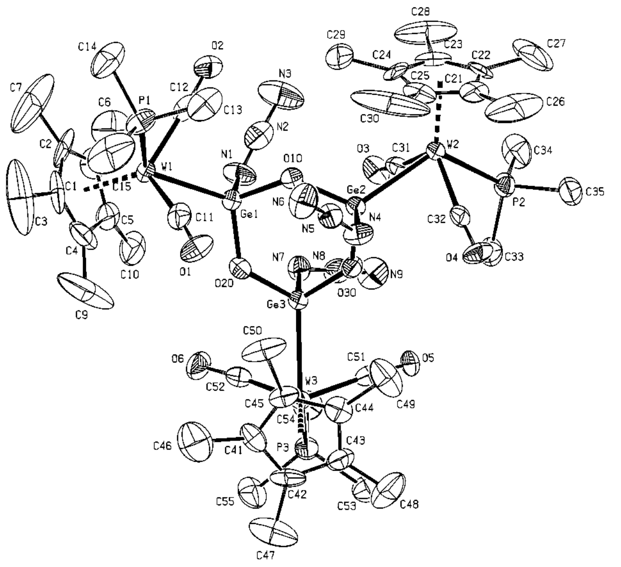


Fig. 2 ORTEP plot of a molecule of **6b** in the crystal lattice of **6b**·C_6H_6 with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)–Ge(1) 2.5240(13), W(2)–Ge(2) 2.5365(12), W(3)–Ge(3) 2.5287(12), W(1)–P(1) 2.441(4), W(2)–P(2) 2.446(3), W(3)–P(3) 2.457(3), Ge(1)–N(1) 1.896(12), Ge(2)–N(4) 1.971(11), Ge(3)–N(7) 1.934(11), Ge(1)–O(10) 1.778(9), Ge(1)–O(20) 1.767(8), Ge(2)–O(10) 1.763(9), Ge(2)–O(30) 1.755(8), Ge(3)–O(20) 1.790(8), Ge(3)–O(30) 1.791(8), W(1)–Ge(1)–N(1) 113.0(5), W(2)–Ge(2)–N(4) 113.5(3), W(3)–Ge(3)–N(7) 112.4(4), O(10)–Ge(1)–O(20) 105.2(4), O(10)–Ge(2)–O(30) 107.9(4), O(20)–Ge(3)–O(30) 104.1(4), Ge(1)–O(10)–Ge(2) 130.8(5), Ge(1)–O(20)–Ge(3) 126.4(5), Ge(2)–O(30)–Ge(3) 131.8(4).

yield synthesis of *trans*-Cp*W(CO)$_2$(PMe$_3$)Ge(N$_3$)$_3$ (**5b**) from *trans*-Cp*W(CO)$_2$(PMe$_3$)GeCl$_3$ (**4b**)[11] and NaN$_3$.† Single crystals of the metallocyclotrigermoxane **6b** resulting from partial hydrolysis of **5b** were obtained upon slow evaporation of a solution of **5b** in benzene at 20 °C. Complex **6b** crystallizes with one benzene molecule in the asymmetric unit. The crystal structure of **6b** (Fig. 2), displays a non-planar six-membered Ge_3O_3 ring with similar Ge–O bond lengths [$(\text{Ge–O})_{\text{av.}} = 1.774(8)$ Å] and Ge–O–Ge bond angles [$(\text{Ge–O–Ge})_{\text{av.}} = 129.7(5)°$] to those of $(Ph_2GeO)_3$ [$(\text{Ge–O})_{\text{av.}} = 1.769(4)$ Å; $(\text{Ge–O–Ge})_{\text{av.}} = 128.6(2)°$] and $(^tBu_2GeO)_3$ [Ge–O = 1.781(1) Å; (Ge–O–Ge) = 133.0(1)°].[12] The cyclotrigermoxane ring in **6b** adopts an unusual conformation, the O(20) atom residing outside the plane formed by the other ring atoms. Each germanium atom bears an azide group and a Cp*W(CO)$_2$PMe$_3$ fragment in a distorted tetrahedral environment. In order to minimize the steric repulsion between these substituents, the azide groups on Ge(1) and Ge(3) occupy the axial positions of the six-membered ring, the transition-metal fragments the equatorial positions, and are *trans* arranged with respect to the corresponding substituents at the Ge(2) atom. Preliminary studies show that hydrolysis of the triazidogermyl complexes offers a general route to ring structures.

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Notes and references

† Spectroscopic data: For **2a**: IR (THF, cm^{-1}): 2108 (vs), 2085 (s) [$\nu_{\text{asym}}(N_3)$], 1833 (s) [ν(CO)]. IR (CH$_2$Cl$_2$, cm^{-1}): 2110 (vs), 2087 (s) [$\nu_{\text{asym}}(N_3)$], 1834 (s) [ν(CO)]. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 1.78 (m, ^2J(PH) + ^4J(PH) 8.7 Hz, 18H, P*Me$_3$*), 5.18 (t, ^3J(PH) 1.4 Hz, 5H, C$_5$*H$_5$*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 20 °C): δ 23.6 (m, ^1J(PC) + ^3J(PC) 34.9 Hz, P*Me$_3$*), 85.4 (*C$_5$*H$_5$), 238.4 (t, ^2J(PC) 24.7 Hz, *C*O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ −23.2 (^1J(WP) 209.3 Hz). EI-MS (70 eV): *m/z* 629 [M]$^+$, 587 [M − N$_3$]$^+$, 559 [M − N$_3$ − CO]$^+$, 471 [M − GeN$_6$]$^+$, 429 [M − GeN$_9$]$^+$, 415 [M − GeN$_6$ − CO − N$_2$]$^+$, 401 [M − GeN$_9$ − CO]$^+$, 277 [M − GeN$_9$ − 2 PMe$_3$]$^+$. For **2b**: IR (THF, cm^{-1}): 2110 (vs), 2084 (s) [$\nu_{\text{asym}}(N_3)$], 1822 (s) [ν(CO)]. IR (CH$_2$Cl$_2$, cm^{-1}): 2112 (vs), 2087 (s) [$\nu_{\text{asym}}(N_3)$], 1822 (s) [ν(CO)]. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 1.66 (m, ^2J(PH) + ^4J(PH) 8.9 Hz, 18H, P*Me$_3$*), 2.00 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 20 °C): δ 12.3 (C$_5$*Me$_5$*), 23.5 (m, ^1J(PC) + ^3J(PC) 33.4 Hz, P*Me$_3$*), 101.0 (*C$_5$*Me$_5$), 248.6 (t, ^2J(PC) 28.7 Hz, *C*O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ −26.5 (^1J(WP) 237.9 Hz). For **5b**: IR (THF, cm^{-1}): 2114 (s), 2094 (s) [$\nu_{\text{asym}}(N_3)$], 1935 m, 1861 (vs) [ν(CO)]. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 20 °C): δ 1.09 (d, ^2J(PH) 9.4 Hz, 9H, P*Me$_3$*), 1.64 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 20 °C): δ 10.9 (C$_5$*Me$_5$*), 18.5 (d, ^1J(PC) 37.8 Hz, P*Me$_3$*), 103.0 (*C$_5$*Me$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz, 20 °C): δ −21.3 (^1J(WP) 235.4 Hz). EI-MS (70 eV): *m/z* 651 [M]$^+$, 609 [M − N$_3$]$^+$, 437 [M − GeN$_6$ − CO − N$_2$]$^+$, 409 [M − GeN$_6$ − 2 CO − N$_2$]$^+$.

‡ Several runs of the reactions of **1b** with NaN$_3$ were carried out and stopped at different times leading, after separation of **3b**, to mixtures of the germyl complexes **1b-1**, **1b-2** and **2b** in variable ratios. These were studied by NMR spectroscopy allowing an unequivocal assignment of the resonances of **1b-1** and **1b-2**. Selected spectroscopic data: **1b-1**: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 1.69 (m, ^2J(PH) + ^4J(PH) 8.8 Hz, 18H, P*Me$_3$*), 1.99 (s, 15H, C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ −28.6 (^1J(WP) 242.5 Hz). **1b-2**: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 1.67 (m, ^2J(PH) + ^4J(PH) 8.9 Hz, 18H, P*Me$_3$*), 1.98 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 20 °C): δ 12.1 (C$_5$*Me$_5$*), 23.2 (m, ^1J(PC) + ^3J(PC) 33.4 Hz, P*Me$_3$*), 100.8 (*C$_5$*Me$_5$), 249.2 (t, ^2J(PC) = 29.0 Hz, *C*O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ −27.5 (^1J(WP) 236.8 Hz). In addition, IR monitoring of the reaction of **1b** with NaN$_3$ revealed the initial increase in intensity of an absorption at 2096 cm^{-1}, which is assigned to the $\nu_{\text{asym}}(N_3)$ vibration of **1b-1**. This absorption was gradually replaced by the two $\nu_{\text{asym}}(N_3)$ absorptions of **1b-2** at 2106 and 2081 cm^{-1}, the latter overlapping with the absorptions of **2b** at 2110 and 2084 cm^{-1}. In comparison, the ν(CO) absorption was only slightly shifted with increasing reaction time from 1819 cm^{-1} (**1b**) to 1822 cm^{-1} (**2b**).

§ Formation of the azido complex *trans*-Cp*W(CO)(PMe$_3$)$_2$N$_3$ was also observed to a much smaller extent and indicated in the IR spectra of the reaction solutions by a weak $\nu_{\text{asym}}(N_3)$ absorption at 2160 cm^{-1}. Evidence for an associative mechanism is given by the fact, that reaction of **1b** with NaN$_3$ is considerably slower than those of **1a** and **4b** with NaN$_3$, and takes weeks to achieve completion.

¶ Data for both structures were collected on a Stoe IPDS area detector. *Crystal data:* for **2a**: $C_{12}H_{23}GeN_9OP_2W$, $M = 627.79$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 13.292(3)$, $b = 17.976(5)$, $c = 8.9106(17)$ Å, $V = 2129.1(8)$ Å^3, $Z = 4$, $D_c = 1.959$ g cm^{-3}, μ(Mo-Kα) = 6.715 mm^{-1}, $F(000) = 1208$, $T = 170$ K. Data collection in the range $4.5° \le 2\theta \le 52.4°$. 17712 Total reflections, 4171 unique ($R(\text{int}) = 0.0787$) with $I > 2\sigma(I)$. Residual electron density, min./max. −0.907/0.932 e Å^{-3}. Refinement of the 235 parameters resulted in $R_1 = 0.0327$, $wR_2(F^2) = 0.0829$, GOF = 1.065. For **6b**: $C_{51}H_{78}Ge_3N_9O_9P_3W_3$, $M = 1823.51$, tetragonal, space group $P\bar{4}2_1c$ (no. 114), $a = b = 28.444(4)$, $c = 15.907(3)$ Å, $V = 12870(4)$ Å^3, $Z = 8$, $D_c = 1.882$ g cm^{-3}, μ(Mo-Kα) = 6.590 mm^{-1}, $F(000) = 7055$, $T = 180$ K. Data collection in the range $4.5° \le 2\theta \le 52.3°$. 111058 Total reflections, 12724 unique ($R(\text{int}) = 0.0927$) with $I > 2\sigma(I)$. Residual electron density, min./max. −1.165/1.525 e Å^{-3}. Refinement of the 704 parameters resulted in $R_1 = 0.0462$, $wR_2(F^2) = 0.1047$, GOF = 1.059.

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