

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

Alexander C. Filippou,\* Ragnar Steck and Gabriele Kociok-Köhn

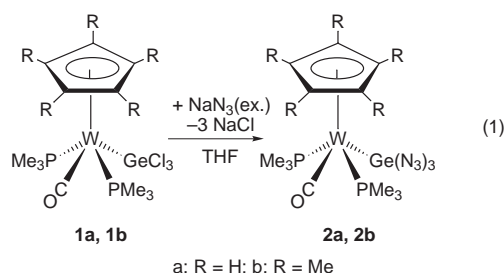
Fachinstitut für Anorganische und Allgemeine Chemie, Humboldt-Universität zu Berlin, Hessische Str. 1-2, D-10115 Berlin, Germany. E-mail: filippou@chemie.hu-berlin.de

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The synthesis and full characterization of the triazidogermyl complexes *trans*-( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)W(CO)<sub>n</sub>(PMe<sub>3</sub>)<sub>3-n</sub>Ge(N<sub>3</sub>)<sub>3</sub> (**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)<sub>2</sub>(PMe<sub>3</sub>)Ge(N<sub>3</sub>)<sub>3</sub>( $\mu_2$ -O)]<sub>3</sub>·C<sub>6</sub>H<sub>6</sub> (**6b**·C<sub>6</sub>H<sub>6</sub>), the product of partial hydrolysis of **5b**, are described.

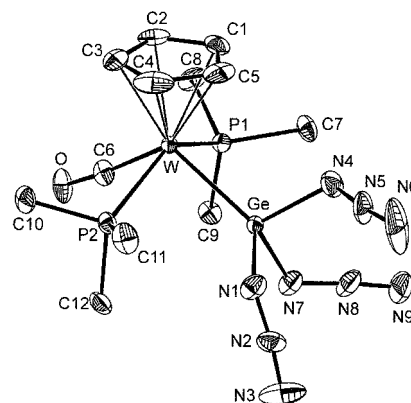
Polyazidogermans belong to a class of potentially explosive Ge(IV) compounds due to their propensity to decompose exothermally eliminating dinitrogen.<sup>1</sup> Studies of these compounds are very rare, and include some synthetic and spectroscopic work on GeMe<sub>n</sub>(N<sub>3</sub>)<sub>4-n</sub> (*n* = 0–3).<sup>2</sup> An approach for the kinetic stabilisation of triazidogermans 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*-( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)W(CO)<sub>n</sub>(PMe<sub>3</sub>)<sub>3-n</sub>Ge(N<sub>3</sub>)<sub>3</sub> (**2a**: R = H, *n* = 1; **2b**: R = Me, *n* = 1; **5b**: R = Me, *n* = 2).

Treatment of **1a**<sup>3</sup> with an excess of NaN<sub>3</sub> in THF at ambient temperature resulted in the formation of **2a**. Similarly, prolonged heating of **1b**<sup>3</sup> with NaN<sub>3</sub> in refluxing THF afforded **2b** (eqn. (1)).<sup>†</sup> Monitoring of the reaction of **1b** with NaN<sub>3</sub>



revealed the intermediate formation of the mixed azido-(chloro)germyl complexes *trans*-Cp\*W(CO)(PMe<sub>3</sub>)<sub>2</sub>[GeCl<sub>3-m</sub>(N<sub>3</sub>)<sub>m</sub>] (Cp\* = C<sub>5</sub>Me<sub>5</sub>; **1b-1**: *m* = 1; **1b-2**: *m* = 2).<sup>‡</sup> 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<sub>3</sub>)<sub>2</sub>Cl (**3b**).<sup>§</sup> 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 metalgermanate intermediate. It is followed by a rapid displacement of chloride to afford the substitution product *trans*-( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)W(CO)(PMe<sub>3</sub>)<sub>2</sub>[GeCl<sub>2</sub>(N<sub>3</sub>)], 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  $\alpha$ -elimination of the chloro complex **3b**.<sup>§</sup>

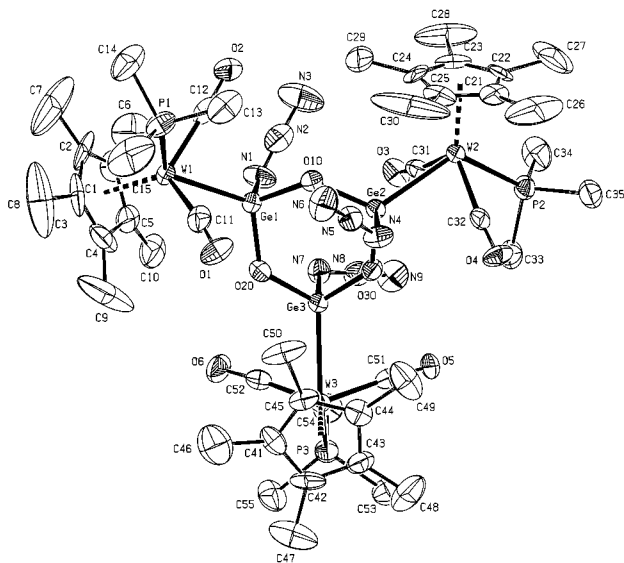
Complexes **2a** and **2b** were isolated as yellow, thermally robust solids, which begin to decompose upon slow heating at 150 and 177 °C. Both compounds are soluble in CH<sub>2</sub>Cl<sub>2</sub> and in



**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).

THF but insoluble in pentane, and were fully characterized.<sup>†</sup> Thus, the IR spectra of **2a** and **2b** display two  $\nu_{\text{asym}}(\text{N}_3)$  absorptions, which appear at similar wavenumbers to those of germanium(IV) azides [Me<sub>3</sub>GeN<sub>3</sub>:  $\nu_{\text{asym}}(\text{N}_3) = 2103 \text{ cm}^{-1}$ ; Ph<sub>3</sub>GeN<sub>3</sub>:  $\nu_{\text{asym}}(\text{N}_3) = 2107 \text{ cm}^{-1}$ ]<sup>4</sup> and higher than those of germanium(II) azides [Tp'GeN<sub>3</sub>:  $\nu_{\text{asym}}(\text{N}_3) = 2043 \text{ cm}^{-1}$ ].<sup>5</sup> 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).<sup>¶</sup> 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.<sup>3</sup> 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<sub>3</sub>GeN<sub>3</sub> (g) [1.845(6) Å]<sup>6</sup> and that calculated for a Ge–N single bond (1.84 Å).<sup>7</sup> All these structural data can be rationalized using either the atom rehybridization model of Bent<sup>8</sup> or suggesting the presence of tungsten–triazidogermyl  $\pi$  back-bonding.<sup>3</sup> As observed for other covalent azides of main-group elements,<sup>9</sup> 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 <sub>$\alpha$</sub> –N <sub>$\beta$</sub> )<sub>av.</sub> = 1.225(11) Å; (N <sub>$\beta$</sub> –N <sub>$\gamma$</sub> )<sub>av.</sub> = 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.<sup>10</sup>

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



**Fig. 2** ORTEP plot of a molecule of **6b** in the crystal lattice of **6b**·C<sub>6</sub>H<sub>6</sub> 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)<sub>2</sub>(PMe<sub>3</sub>)Ge(N<sub>3</sub>)<sub>3</sub> (**5b**) from *trans*-Cp\*W(CO)<sub>2</sub>(PMe<sub>3</sub>)GeCl<sub>3</sub> (**4b**)<sup>11</sup> and NaN<sub>3</sub>.† Single crystals of the metallocyclotrioxane **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<sub>3</sub>O<sub>3</sub> ring with similar Ge–O bond lengths [(Ge–O)<sub>av.</sub> = 1.774(8) Å] and Ge–O–Ge bond angles [(Ge–O–Ge)<sub>av.</sub> = 129.7(5)°] to those of (Ph<sub>2</sub>GeO)<sub>3</sub> [(Ge–O)<sub>av.</sub> = 1.769(4) Å; (Ge–O–Ge)<sub>av.</sub> = 128.6(2)°] and (tBu<sub>2</sub>GeO)<sub>3</sub> [Ge–O = 1.781(1) Å; (Ge–O–Ge) = 133.0(1)°].<sup>12</sup> The cyclotrioxane 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)<sub>2</sub>PMe<sub>3</sub> 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<sup>-1</sup>): 2108 (vs), 2085 (s) [ν<sub>asym</sub>(N<sub>3</sub>)], 1833 (s) [ν(CO)], IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2110 (vs), 2087 (s) [ν<sub>asym</sub>(N<sub>3</sub>)], 1834 (s) [ν(CO)]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 20 °C): δ 1.78 (m, <sup>2</sup>J(PH) + <sup>4</sup>J(PH) 8.7 Hz, 18H, PMe<sub>3</sub>), 5.18 (t, <sup>3</sup>J(PH) 1.4 Hz, 5H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz, 20 °C): δ 23.6 (m, <sup>1</sup>J(PC) + <sup>3</sup>J(PC) 34.9 Hz, PMe<sub>3</sub>), 85.4 (C<sub>5</sub>H<sub>5</sub>), 238.4 (t, <sup>2</sup>J(PC) 24.7 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz, 20 °C): δ -23.2 (<sup>1</sup>J(WP) 209.3 Hz). EI-MS (70 eV): *m/z* 629 [M]<sup>+</sup>, 587 [M – N<sub>3</sub>]<sup>+</sup>, 559 [M – N<sub>3</sub> – CO]<sup>+</sup>, 471 [M – GeN<sub>6</sub>]<sup>+</sup>, 429 [M – GeN<sub>5</sub>]<sup>+</sup>, 415 [M – GeN<sub>6</sub> – CO – N<sub>3</sub>]<sup>+</sup>, 401 [M – GeN<sub>6</sub> – CO]<sup>+</sup>, 277 [M – GeN<sub>6</sub> – 2 PMe<sub>3</sub>]<sup>+</sup>. For **2b**: IR (THF, cm<sup>-1</sup>): 2110 (vs), 2084 (s) [ν<sub>asym</sub>(N<sub>3</sub>)], 1822 (s) [ν(CO)]. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2112 (vs), 2087 (s) [ν<sub>asym</sub>(N<sub>3</sub>)], 1822 (s)

[ν(CO)]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 20 °C): δ 1.66 (m, <sup>2</sup>J(PH) + <sup>4</sup>J(PH) 8.9 Hz, 18H, PMe<sub>3</sub>), 2.00 (s, 15H, C<sub>5</sub>Me<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz, 20 °C): δ 12.3 (C<sub>5</sub>Me<sub>3</sub>), 23.5 (m, <sup>1</sup>J(PC) + <sup>3</sup>J(PC) 33.4 Hz, PMe<sub>3</sub>), 101.0 (C<sub>5</sub>Me<sub>3</sub>), 248.6 (t, <sup>2</sup>J(PC) 28.7 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz, 20 °C): δ -26.5 (<sup>1</sup>J(WP) 237.9 Hz). For **5b**: IR (THF, cm<sup>-1</sup>): 2114 (s), 2094 (s) [ν<sub>asym</sub>(N<sub>3</sub>)], 1935 (m, 1861 (vs) [ν(CO)]). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 1.09 (d, <sup>2</sup>J(PH) 9.4 Hz, 9H, PMe<sub>3</sub>), 1.64 (s, 15H, C<sub>5</sub>Me<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75.5 MHz, 20 °C): δ 10.9 (C<sub>5</sub>Me<sub>3</sub>), 18.5 (d, <sup>1</sup>J(PC) 37.8 Hz, PMe<sub>3</sub>), 103.0 (C<sub>5</sub>Me<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ -21.3 (<sup>1</sup>J(WP) 235.4 Hz). EI-MS (70 eV): *m/z* 651 [M]<sup>+</sup>, 609 [M – N<sub>3</sub>]<sup>+</sup>, 437 [M – GeN<sub>6</sub> – CO – N<sub>3</sub>]<sup>+</sup>, 409 [M – GeN<sub>6</sub> – 2 CO – N<sub>3</sub>]<sup>+</sup>.

‡ Several runs of the reactions of **1b** with NaN<sub>3</sub> 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**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 20 °C): δ 1.69 (m, <sup>2</sup>J(PH) + <sup>4</sup>J(PH) 8.8 Hz, 18H, PMe<sub>3</sub>), 1.99 (s, 15H, C<sub>5</sub>Me<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz, 20 °C): δ -28.6 (<sup>1</sup>J(WP) 242.5 Hz). **1b-2**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 20 °C): δ 1.67 (m, <sup>2</sup>J(PH) + <sup>4</sup>J(PH) 8.9 Hz, 18H, PMe<sub>3</sub>), 1.98 (s, 15H, C<sub>5</sub>Me<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz, 20 °C): δ 12.1 (C<sub>5</sub>Me<sub>3</sub>), 23.2 (m, <sup>1</sup>J(PC) + <sup>3</sup>J(PC) 33.4 Hz, PMe<sub>3</sub>), 100.8 (C<sub>5</sub>Me<sub>3</sub>), 249.2 (t, <sup>2</sup>J(PC) = 29.0 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz, 20 °C): δ -27.5 (<sup>1</sup>J(WP) 236.8 Hz). In addition, IR monitoring of the reaction of **1b** with NaN<sub>3</sub> revealed the initial increase in intensity of an absorption at 2096 cm<sup>-1</sup>, which is assigned to the ν<sub>asym</sub>(N<sub>3</sub>) vibration of **1b-1**. This absorption was gradually replaced by the two ν<sub>asym</sub>(N<sub>3</sub>) absorptions of **1b-2** at 2106 and 2081 cm<sup>-1</sup>, the latter overlapping with the absorptions of **2b** at 2110 and 2084 cm<sup>-1</sup>. In comparison, the ν(CO) absorption was only slightly shifted with increasing reaction time from 1819 cm<sup>-1</sup> (**1b**) to 1822 cm<sup>-1</sup> (**2b**).

§ Formation of the azido complex *trans*-Cp\*W(CO)(PMe<sub>3</sub>)<sub>2</sub>N<sub>3</sub> was also observed to a much smaller extent and indicated in the IR spectra of the reaction solutions by a weak ν<sub>asym</sub>(N<sub>3</sub>) absorption at 2160 cm<sup>-1</sup>. Evidence for an associative mechanism is given by the fact, that reaction of **1b** with NaN<sub>3</sub> is considerably slower than those of **1a** and **4b** with NaN<sub>3</sub>, and takes weeks to achieve completion.

¶ Data for both structures were collected on a Stoe IPDS area detector. *Crystal data*: for **2a**: C<sub>12</sub>H<sub>23</sub>GeN<sub>9</sub>O<sub>2</sub>P<sub>2</sub>W, *M* = 627.79, orthorhombic, space group *Pna*2<sub>1</sub> (no. 33), *a* = 13.292(3), *b* = 17.976(5), *c* = 8.9106(17) Å, *V* = 2129.1(8) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.959 g cm<sup>-3</sup>, μ(Mo-Kα) = 6.715 mm<sup>-1</sup>, *F*(000) = 1208, *T* = 170 K. Data collection in the range 4.5° ≤ 2θ ≤ 52.4°. 17712 Total reflections, 4171 unique (*R*(int) = 0.0787) with *I* > 2σ(*I*). Residual electron density, min./max. -0.907/0.932 e Å<sup>-3</sup>. Refinement of the 235 parameters resulted in *R*<sub>1</sub> = 0.0327, *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.0829, GOF = 1.065. For **6b**: C<sub>51</sub>H<sub>78</sub>Ge<sub>3</sub>N<sub>9</sub>O<sub>3</sub>P<sub>3</sub>W<sub>3</sub>, *M* = 1823.51, tetragonal, space group *P4̄21c* (no. 114), *a* = *b* = 28.444(4), *c* = 15.907(3) Å, *V* = 12870(4) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.882 g cm<sup>-3</sup>, μ(Mo-Kα) = 6.590 mm<sup>-1</sup>, *F*(000) = 7055, *T* = 180 K. Data collection in the range 4.5° ≤ 2θ ≤ 52.3°. 111058 Total reflections, 12724 unique (*R*(int) = 0.0927) with *I* > 2σ(*I*). Residual electron density, min./max. -1.165/1.525 e Å<sup>-3</sup>. Refinement of the 704 parameters resulted in *R*<sub>1</sub> = 0.0462, *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.1047, GOF = 1.059.

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- G. Bertrand, J.-P. Majoral and A. Bacciredo, *Acc. Chem. Res.*, 1986, **19**, 17.
- (a) I. Ruidisch and M. Schmidt, *J. Organomet. Chem.*, 1964, **1**, 493; (b) J. E. Drake and R. T. Hemmings, *Can. J. Chem.*, 1973, **51**, 302.
- A. C. Filippou, J. G. Winter, G. Kociok-Köhn, C. Troll and I. Hinz, *Organometallics*, in press and references therein.
- (a) J. S. Thayer and R. West, *Inorg. Chem.*, 1964, **3**, 889; (b) W. T. Reichle, *Inorg. Chem.*, 1964, **3**, 402.
- A. C. Filippou, P. Portius and G. Kociok-Köhn, *Chem. Commun.*, 1998, 2327.
- J. D. Murdoch and D. W. H. Rankin, *J. Chem. Soc., Chem. Commun.*, 1972, 748.
- R. Blom and A. Haaland, *J. Mol. Struct.*, 1985, **128**, 21.
- H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.
- (a) T. M. Klapötke and A. Schulz, *Inorg. Chem.*, 1996, **35**, 4995; (b) T. M. Klapötke, *Chem. Ber.*, 1997, **130**, 443.
- Holleman-Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter Verlag, Berlin, Germany, 1995.
- A. C. Filippou, J. G. Winter, M. Feist, G. Kociok-Köhn and I. Hinz, *Polyhedron*, 1998, **17**, 1103.
- (a) L. Roß and M. Dräger, *Chem. Ber.*, 1982, **115**, 615; (b) H. Puff, S. Franken, W. Schuh and W. Schwab, *J. Organomet. Chem.*, 1983, **254**, 33.

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