DOI: 10.1002/anie.200801331

Plumbylidyne Complexes

Tungsten-Mediated Activation of a Pb^{II}–N bond: A New Route to Tungsten–Lead Triple Bonds**

Alexander C. Filippou, Nils Weidemann, and Gregor Schnakenburg*

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Lead(II) amides are a rare class of reactive compounds which have the profound tendency to undergo disproportionation in the absence of sterically demanding substituents at the lead or nitrogen atoms. The lead diamides $Pb(NR^1R^2)_2$ ($R^1 = R^2 = SiMe_3$; $R^1 = SiMe_3$, $R^2 = t$Bu)[1] and $[Pb(NR\text{-}\kappa N)_2(\mu\text{-}EMe_2)]_n$ ($R = t$Bu, E = Si, Sn, $n = 1$; $R = i$Pr, E = Si, $n = 2$),[2] and Pb^{II} porphyrins and phthalocyanines are the most familiar members of this class of compounds.[3] In comparison, organolead(II) amides of the general formula $Pb(NR^1_2)(R^2)$ are very scarce, and the only known example is $\{Pb(2,6\text{-}Trip_2C_6H_3)NH_2\}_2$ (Trip = 2,4,6-iPr$_3$C$_6$H$_2$).[4,5] The chemistry of Pb^{II} amides has been little explored. In fact, only a few reactions of the diamides $Pb\{N(SiMe_3)_2\}_2$ and $Pb(N$*t*$Bu\text{-}\kappa N)_2(\mu\text{-}SiMe_2)$ have been reported to date, including coordination to a metal center,[1c] insertion into a metal–halogen bond,[1c] Pb–N bond protolysis,[6] nucleophilic displacement of the amide ligands by silyl groups,[7] amide/chloride exchange with Lewis acids,[8] and reduction to elemental lead.[9]

We report herein the first structural characterization of an organolead(II) amide and its unprecedented tungsten-mediated Pb^{II}–N bond-cleavage reactions to form tungsten–lead triple bonds.[10]

Treatment of $\{Pb(R)Br\}_2$ (**1a**, R = 2,6-Trip$_2$C$_6$H$_3$)[11] with $LiNMe_2$ in diethyl ether afforded selectively aryl lead(II) amide $\{Pb(R)NMe_2\}_2$ (**1b**), which was isolated as a pale yellow, very air sensitive,[12] microcrystalline solid in 77% yield.[13] Compound **1b** decomposes on heating at 135 °C and is photolabile; its yellow solutions in pentane or toluene slowly deposit elemental lead on prolonged exposure to daylight. The thermal stability of **1b** is remarkable given the thermal lability of $\{Pb(NMe_2)_2\}_2$, which decomposes below room temperature.[14]

Compound **1b** is the first organolead(II) amide to be structurally characterized (Figure 1).[13,15] In the solid state it forms nearly centrosymmetric dimers in which the NMe_2 groups bridge the lead atoms to form a planar[16] Pb_2N_2 parallelogram with two pairs of quite different Pb–N bond lengths (Pb1–N1 2.329(3), Pb2–N2 2.321(3); Pb1–N2 2.426(3), Pb2–N1 2.427(3) Å). The endocyclic bond angles at the lead atoms are considerably more acute (78.7(1) and 78.9(1)°) than those at the nitrogen atoms (101.1(1) and 101.3(1)°; Figure 1). Expectedly, the bridging Pb^{II}–N_{amide} bonds of **1b** (2.32–2.43 Å) are longer than terminal Pb^{II}–N_{amide} bonds (2.23–2.28 Å).[1c,5] This leads to a transannular Pb···Pb distance of 3.6723(7) Å that is considerably shorter than that in $\{Pb(R)X\}_2$ (X = Br (**1a**): 4.257(8) Å; X = I (**1c**): 4.603(1) Å).[10b,11] However, the separation of the lead centers in **1b** is longer than the interatomic distance in elemental lead (3.494 Å),[17] and lies outside the range of distances attributed to direct Pb–Pb bonding (2.84–3.53 Å).[18] The three-coordinate lead centers have trigonal-pyramidal coordination, as evidenced by the sum of angles at Pb1 (292.6°) and Pb2 (291.5°), which are similar to those of **1a** (292.3 and 293.0°) and **1c** (297.2°).[10b,11] Both the NMe_2 groups and the *trans*-arranged aryl substituents are tilted with respect to the Pb_2N_2 core.[19] The Pb–C_{aryl} bonds (2.399(4) and 2.395(3) Å) are longer than those of **1a** (2.33(1) and 2.31(1) Å) and **1c** (2.326(6) Å), and suggest increased intramolecular steric

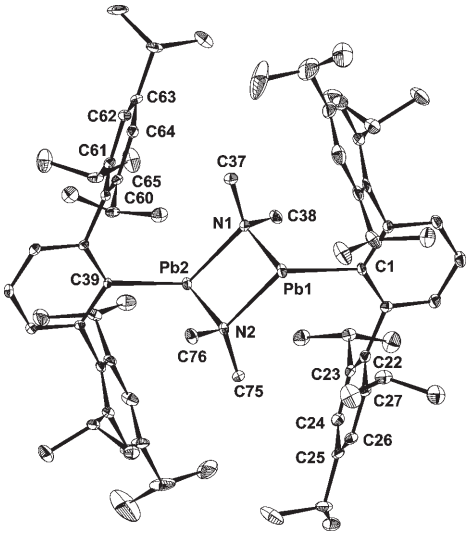


Figure 1. DIAMOND plot of the molecular structure of **1b** in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-N1 2.329(3), Pb1-N2 2.426(3), Pb1-C1 2.399(4), Pb2-N1 2.427(3), Pb2-N2 2.321(3), Pb2-C39 2.395(3); C1-Pb1-N1 95.7(1), C1-Pb1-N2 118.2(1), N1-Pb1-N2 78.7(1), N1-Pb2-N2 78.9(1), N1-Pb2-C39 116.5(1), N2-Pb2-C39 96.1(1), Pb1-N1-Pb2 101.1(1), Pb1-N2-Pb2 101.3(1).

[*] Prof. Dr. A. C. Filippou, N. Weidemann, G. Schnakenburg
Institut für Anorganische Chemie
Universität Bonn
Gerhard-Domagk Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 30-735-327
E-mail: filippou@uni-bonn.de

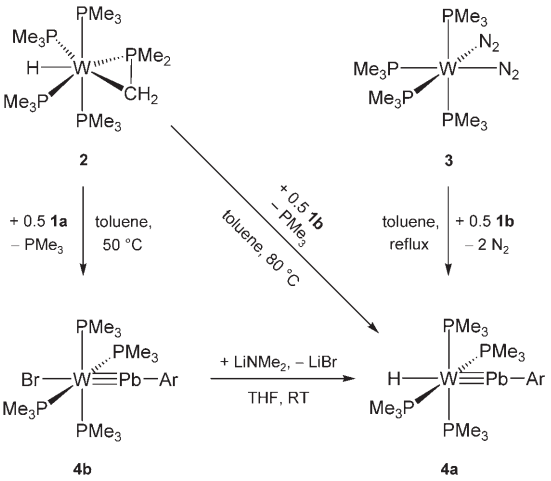
[**] We thank the Deutsche Forschungsgemeinschaft (project FI 445/6-1) for the generous financial support of this work. We also thank U. Kätel, W.-D. Bloedorn, and A. Thiesies at the Humboldt University of Berlin for the elemental analyses and the 2D NMR spectra.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801331.

repulsion of the substituents in **1b** resulting from the shorter Pb···Pb distance.

The NMR spectra of **1b** corroborate the solid-state structure.[13] Thus, two singlet resonance signals of equal intensity are observed in the ^{1}H NMR spectrum (C_6D_6, 298 K) for the methyl protons of the NMe_2 groups ($\delta = 1.70$ and 4.17 ppm),[19] that is, the dimeric structure of **1b** is retained in solution.[20] The $^{13}C\{^1H\}$ NMR spectrum of **1b** displays a characteristic low-field signal for the lead-bonded C_{aryl} atom at $\delta = 244.8$ ppm, which appears at higher field than the corresponding signals of the aryl lead(II) halides **1a** ($\delta_C =$ 287.9 ppm) and **1c** ($\delta_C = 276.7$ ppm).[10b,11]

Treatment of lead(II) amide **1b** with two equivalents of $[W(\eta^2\text{-}CH_2PMe_2)(H)(PMe_3)_4]$ (**2**)[21] in toluene at 80 °C afforded the hydrido plumbylidyne complex *trans*-$[H(PMe_3)_4W{\equiv}Pb(2,6\text{-}Trip_2C_6H_3)]$ (**4a**, Scheme 1). The same



Scheme 1. Syntheses of hydrido plumbylidyne complex **4a**.

complex was selectively formed on heating of **1b** and two equivalents of *cis*-$[W(N_2)_2(PMe_3)_4]$ (**3**)[22] in refluxing toluene (Scheme 1). No intermediates were observed in these unprecedented reactions, which probably involve tungsten-mediated Pb^{II}–N_{amide} bond heterolysis.[23] Alternatively, plumbylidyne complex **4a** can be selectively obtained in two steps starting from **2**. The first step involves thermal activation of the lead(II) bromide **1a** by complex **2** to yield selectively plumbylidyne complex *trans*-$[Br(PMe_3)_4W{\equiv}Pb(2,6\text{-}Trip_2C_6H_3)]$ (**4b**), which is then treated with an excess of $LiNMe_2$ in THF at ambient temperature to afford the desired product (Scheme 1). Hydrido plumbylidyne complex **4a** was isolated as a brown, extremely air-sensitive solid, which decomposes on melting at 186 °C and is very soluble in pentane.

The molecular structure of **4a** was determined by single-crystal X-ray diffraction (Figure 2).[13] The *trans*-configured octahedral complex features a nearly linearly coordinated lead atom (W-Pb-C1 178.7(2)°) and a W–Pb triple bond length of 2.5525(3) Å, which compares well with those of the isostructural[24] plumbylidyne complexes *trans*-$[X(PMe_3)_4W{\equiv}PbC_6H_3(2,6\text{-}Trip_2C_6H_3)]$ (X = Br (**4b**), W–Pb 2.5464(5) Å; X = I (**4c**), W–Pb 2.5477(3) Å).[10b,25] The hydride ligand could be localized in the difference Fourier map at a distance of 1.71(2) Å from the tungsten center, and is *trans*-arranged to the plumbylidyne ligand (Pb-W-H59 173(2)°; Figure 2).[26] The W–P bonds (average length 2.43 Å) and Pb–C_{aryl} bond (2.229(6) Å) of **4a** are shorter than those of **4b** (W–P 2.48 Å, Pb–C_{aryl} 2.254(6) Å) and **4c** (W–P 2.48 Å, Pb–C_{aryl} 2.258(3) Å), probably due to the reduced steric demand of the hydride ligand.

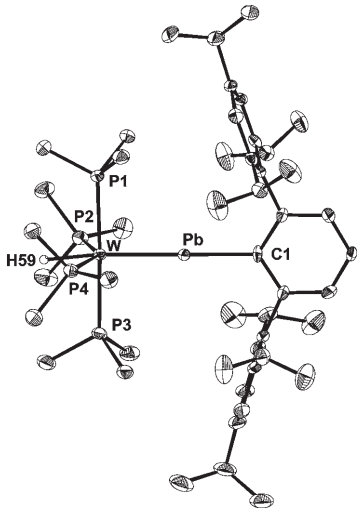


Figure 2. DIAMOND plot of the molecular structure of **4a**·2 (*n*-C_5H_{12}) in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms except H59 and those of the solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-Pb 2.5525(3), W-H59 1.71(2), W-P1 2.436(2), W-P2 2.421(2), W-P3 2.451(2), W-P4 2.424(2), Pb-C1 2.229(6); W-Pb-C1 178.7(2), Pb-W-H59 173(2), Pb-W-P1 91.27(4), Pb-W-P2 107.11(5), Pb-W-P3 90.77(5), Pb-W-P4 108.30(5).

Composition and structure of **4a** were confirmed by the spectroscopic data. Thus, the IR spectrum of **4a** displays a characteristic ν(W–H) band at 1678 cm^{-1}, which appears at higher energy than that of *trans*-$[H(PMe_3)_4W{\equiv}Ge(2,6\text{-}Trip_2C_6H_3)]$ (ν(W–H) = 1658 cm^{-1})[21c] and *trans*-$[H(dmpe)_2W{\equiv}CMes]$ (ν(W–H) = 1600 cm^{-1}; dmpe = $Me_2PCH_2CH_2PMe_2$).[27] This observation suggests that the *trans* influence of the ylidyne ligand decreases in the series CR > GeR > PbR. In the ^{1}H NMR spectrum of **4a** a distinctive quintet signal is observed for the hydride ligand at $\delta = -6.52$ ppm ($^2J(P,H) = 30.7$ Hz, $^1J(W,H) = 63$ Hz). The $^{31}P\{^1H\}$ NMR spectrum of **4a** shows one singlet resonance for the PMe_3 ligands at $\delta = -34.5$ ppm, which appears at lower field than those of **4b** ($\delta_P = -43.6$ ppm) and **4c** ($\delta_P = -53.9$ ppm),[10b] and confirms the *trans* configuration of the complex. The ^{31}P NMR signal is flanked by a pair of tungsten satellites,[28] for which the $^1J(W,P)$ coupling constant of 258 Hz compares well with those of plumbylidyne complexes **4b** ($^1J(W,P) = 257$ Hz) and **4c** ($^1J(W,P) = 258$ Hz).[10b] Finally, the $^{13}C\{^1H\}$ NMR spectrum of **4a** features a low-field-shifted signal for the lead-bonded C_{aryl} atom at $\delta = 267.2$ ppm, which has a similar chemical shift to those of complexes **4b** ($\delta_C =$ 270.2 ppm) and **4c** ($\delta_C = 267.9$ ppm).[10b]

Compounds featuring a triple bond to lead are of immense significance for the understanding of chemical bonding.[10,29] The unprecedented Pb–N bond heterolysis of organolead(II) amide **1b** reported herein suggests that other lead–element σ bonds also could be activated by electron-rich metal centers to provide access to a plethora of exciting compounds featuring triply bonded lead.

Received: March 19, 2008
Published online: June 23, 2008

Keywords: amides · hydride ligands · lead · Pb–N activation · tungsten

[1] a) D. H. Harris, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1974**, 895; b) M. S. J. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc. Dalton Trans.* **1977**, 2004; c) T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power, A. J. Thorne, *J. Chem. Soc. Chem. Commun.* **1983**, 639; d) M. F. Lappert, P. P. Power, *J. Chem. Soc. Dalton Trans.* **1985**, 51.

[2] a) M. Veith, M. Grosser, *Z. Naturforsch. B* **1982**, *37*, 1375; b) B. Wrackmeyer, K. Horchler, H. Zhou, M. Veith, *Z. Naturforsch. B* **1989**, *44*, 288; c) B. Wrackmeyer, C. Stader, K. Horchler, *J. Magn. Reson.* **1989**, *83*, 601.

[3] a) K. M. Barkigia, J. Fajer, A. D. Adler, G. J. B. Williams, *Inorg. Chem.* **1980**, *19*, 2057; b) M. J. Plater, S. Aiken, T. Gelbrich, M. B. Hursthouse, G. Bourhill, *Polyhedron* **2001**, *20*, 3219; c) P. M. Burnham, M. J. Cook, L. A. Gerrard, M. J. Heeney, D. L. Hughes, *Chem. Commun.* **2003**, 2064; d) Y. Bian, L. Li, J. Dou, D. Y. Y. Cheng, R. Li, C. Ma, D. K. P. Ng, N. Kobayashi, J. Jiang, *Inorg. Chem.* **2004**, *43*, 7539.

[4] C. Stanciu, S. S. Hino, M. Stender, A. F. Richards, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **2005**, *44*, 2774.

[5] For a few recent examples of heteroleptic lead(II) amides bearing a pendant donor atom, see: a) A. Murso, M. Straka, M. Kaupp, R. Bertermann, D. Stalke, *Organometallics* **2005**, *24*, 3576; b) M. Chen, J. R. Fulton, P. B. Hitchcock, N. C. Johnstone, M. F. Lappert, A. V. Protchenko, *Dalton Trans.* **2007**, 2770.

[6] a) B. Cetinkaya, I. Gümrükcü, M. F. Lappert, J. L. Atwood, R. D. Rogers, M. J. Zaworotko, *J. Am. Chem. Soc.* **1980**, *102*, 2088; b) P. B. Hitchcock, M. F. Lappert, B. J. Samways, E. L. Weinberg, *J. Chem. Soc. Chem. Commun.* **1983**, 1492; c) S. Suh, D. M. Hoffman, *Inorg. Chem.* **1996**, *35*, 6164; d) R. Papiernik, L. G. Hubert-Pfalzgraf, M. Veith, V. Huch, *Chem. Ber./Recl.* **1997**, *130*, 1361.

[7] a) K. W. Klinkhammer, W. Schwarz, *Angew. Chem.* **1995**, *107*, 1448; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1334; b) C. Förster, K. W. Klinkhammer, B. Tumanskii, H. Krüger, H. Kelm, *Angew. Chem.* **2007**, *119*, 1174; *Angew. Chem. Int. Ed.* **2007**, *46*, 1156.

[8] a) M. Veith, M. Grosser, V. Huch, *Z. Anorg. Allg. Chem.* **1984**, *513*, 89; b) B. Wrackmeyer, J. Weidinger, W. Milius, *Z. Anorg. Allg. Chem.* **1998**, *624*, 98; c) B. Wrackmeyer, A. Pedall, J. Weidinger, *Z. Naturforsch. B* **2001**, *56*, 1009.

[9] M. Veith, J. Frères, P. König, O. Schütt, V. Huch, J. Blin, *Eur. J. Inorg. Chem.* **2005**, 3699.

[10] For compounds featuring triple bonds to lead, see: a) A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293; *Angew. Chem. Int. Ed.* **2004**, *43*, 2243; b) A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem.* **2004**, *116*, 6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6512.

[11] L. Pu, B. Twamley, P. P. Power, *Organometallics* **2000**, *19*, 2874.

[12] Yellow solutions of **1b** in pentane or diethyl ether turn immediately cloudy and colorless upon exposure to air.

[13] All syntheses and analytical and spectroscopic data are included in the Supporting Information. Suitable yellow prismatic single crystals of **1b** were grown by slow evaporation of a concentrated pentane solution at ambient temperature in a glove box, and dark brown single crystals of **4a**·2(n-C_5H_{12}) were obtained by slow cooling of a concentrated pentane solution from ambient temperature to −30 °C. CCDC 681781 (**1b**) and 681780 (**4a**·2(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.

[14] $\{Pb(NMe_2)_2\}_2$ is the only other lead(II) dimethylamide presently known: M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1984**, *23*, 413.

[15] Only two base-stabilized organolead(II) amides have been structurally characterized so far: a) W. Leung, Q. W. Ip, S. Yong, T. C. W. Mak, *Organometallics* **2003**, *22*, 4604; b) W. Leung, K. Wong, Z. Wang, T. C. W. Mak, *Organometallics* **2006**, *25*, 2037.

[16] The maximum deviation of the atoms N1, N2, Pb1, and Pb2 from the least-squares plane is 0.003(3) Å.

[17] a) H. P. Klug, *J. Am. Chem. Soc.* **1946**, *68*, 1493; b) A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford, **1984**, p. 1288.

[18] a) H. Preut, F. Huber, *Z. Anorg. Allg. Chem.* **1976**, *419*, 92; b) K. W. Klinkhammer, T. F. Fässler, H. Grützmacher, *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem. Int. Ed.* **1998**, *37*, 124; c) M. Stürmann, M. Weidenbruch, K. W. Klinkhammer, F. Lissner, H. Marsmann, *Organometallics* **1998**, *17*, 4425; d) M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem.* **1999**, *111*, 145; *Angew. Chem. Int. Ed.* **1999**, *38*, 187; e) M. Stürmann, W. Saak, M. Weidenbruch, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 579; f) L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524; g) F. Stabenow, W. Saak, H. Marsmann, M. Weidenbruch, *J. Am. Chem. Soc.* **2003**, *125*, 10172.

[19] The interplane angles between the amino groups (C37/N1/C38 and C75/N2/C76) and the Pb_2N_2 core of 80.1(4) and 81.9(3)°, respectively, lead to two different pairs of Pb-N-C angles (Pb1-N1-C37 107.3(3), Pb2-N2-C75 109.5(2)°; Pb1-N1-C38 113.4(2), Pb2-N2-C76 112.1(2)°). Thereby, short contacts result between the methyl hydrogen atoms at C37 and C75 and the center of gravity (C_g) of the peripheral phenyl rings C60–C65 and C22–C27, respectively (H(C37/C75)···C_g 2.64/2.65 Å), which may explain the considerable upfield ^{1}H NMR shift of one of the signals of the N-bonded methyl groups (C(37/75)H_3: δ = 1.70 ppm, C(38/76)H_3: δ = 4.17 ppm). Similarly, the terphenyl substituents are tilted, as evidenced by the dihedral angles of 71.9 and 73.6° between the Pb_2N_2 ring plane and the plane defined by the atoms Pb1/Pb2/C1 and Pb1/Pb2/C39, respectively.

[20] Dissociation of **1b** in solution to form monomers should lead to exchange of the methyl positions through rapid rotation about the Pb–N bond.

[21] a) V. C. Gibson, C. E. Graimann, P. M. Hare, M. L. H. Green, J. A. Bandy, P. D. Grebenik, K. Prout, *J. Chem. Soc. Dalton Trans.* **1985**, 2025; b) M. L. H. Green, G. Parkin, M. Chen, K. Prout, *J. Chem. Soc. Dalton Trans.* **1986**, 2227; c) A. C. Filippou, N. Weidemann, A. I. Philippopoulos, G. Schnakenburg, *Angew. Chem.* **2006**, *118*, 6133; *Angew. Chem. Int. Ed.* **2006**, *45*, 5987.

[22] E. Carmona, A. Galindo, M. L. Poveda, R. D. Rogers, *Inorg. Chem.* **1985**, *24*, 4033.

[23] The reaction pathways leading from **2** or **3** to complex **4a** are presently unknown. A possible sequence of reaction steps involves metal coordination of **1b** to give the aminoplumbylidene complex intermediate [WL(PMe_3)$_4$(Pb(R)NMe_2)] (L = PMe_3, N_2), followed by rapid ligand dissociation and migration of the NMe_2 group to the tungsten center to give the plumbylidyne complex intermediate [W(NMe_2)(PMe_3)$_4$(PbR)], which finally undergoes β-hydride elimination to give the final

product. The latter intermediate is probably also formed in the reaction of **4b** with $LiNMe_2$ to give **4a**.

[24] Complexes **4a–c** have very similar structures. Thus, the *m*-terphenyl substituents always adopt an eclipsed conformation, as indicated by respective angles of 0.7(2), 5.4(2), and 6.3(1)° between the central aryl ring plane and the least-squares plane passing through the atoms Pb, W, P1, and P3. In addition, complex **4a** shows a similar geometric distortion of the WP_4 core to **4b** and **4c**, such that two *trans*-disposed PMe_3 ligands (P2 and P4 in Figure 2) are pushed further away from the plumbylidyne ligand than the other two (P1 and P3).

[25] The W–Pb triple bond length of **4a** does not differ from those of **4b** and **4c**, despite the presence of a hydride ligand exerting a strong *trans* influence. The same effect was observed in the case of the germylidyne complexes *trans*-$[X(PMe_3)_4W{\equiv}Ge(2,6\text{-}Trip_2C_6H_3)]$ (X = H, Cl, I) and suggests that the strong π-bonding part of the W–E bond (E = Ge, Pb), which is not expected to be distinctly effected by the *trans*-disposed ligand X, has a major influence on the W–E triple bond length.

[26] The W–H distance of **4a** lies in the range of W–H bond lengths determined by neutron diffraction (1.71–1.78 Å): R. Bau, M. H. Drabnis, *Inorg. Chim. Acta* **1997**, *259*, 27.

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

[28] No ^{207}Pb satellites were observed in the $^{31}P\{^1H\}$ NMR spectrum of **4a** at room temperature.

[29] a) G. Balázs, L. J. Gregoriades, M. Scheer, *Organometallics* **2007**, *26*, 3058; b) P. P. Power, *Organometallics* **2007**, *26*, 4362.

