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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

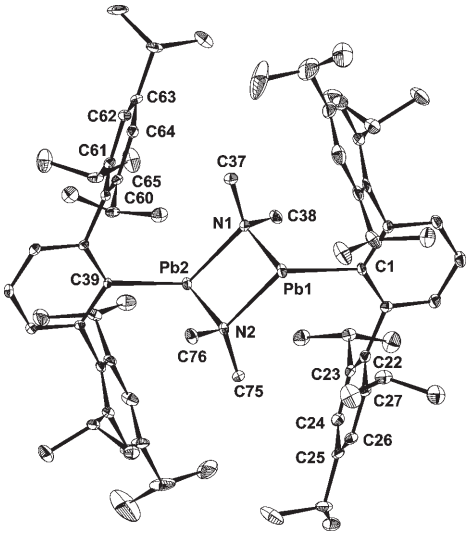

Figure 1. DIAMOND plot of the molecular structure of **1b** in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1-N1 2.329(3), Pb1-N2 2.426(3), Pb1-C1 2.399(4), Pb2-N1 2.427(3), Pb2-N2 2.321(3), Pb2-C39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

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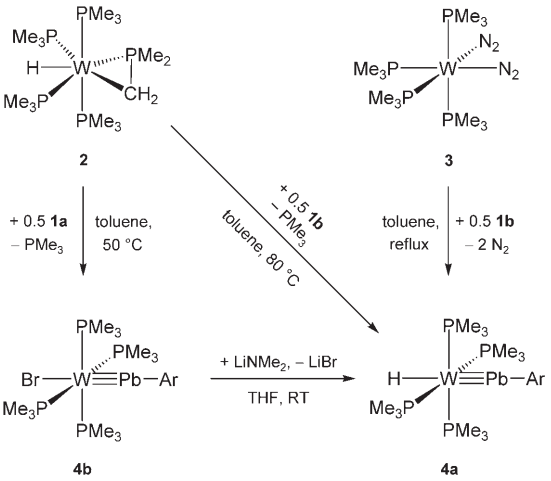
repulsion of the substituents in **1b** resulting from the shorter Pb···Pb distance.

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.

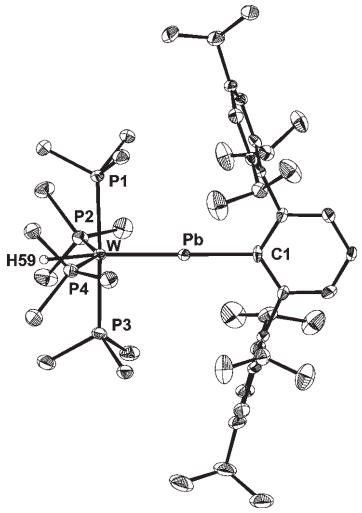


Figure 2. DIAMOND plot of the molecular structure of **4a**·2 (*n*-C_5H_{12}) in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms except H59 and those of the solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-Pb 2.5525(3), W-H59 1.71(2), 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.

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[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.

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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.

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