

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

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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 $\text{Pb}(\text{NR}^1\text{R}^2)_2$ ($\text{R}^1 = \text{R}^2 = \text{SiMe}_3$; $\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = t\text{Bu}$)^[1] and $[\text{Pb}(\text{NR}-\kappa\text{N})_2(\mu\text{-EMe}_2)]_n$ ($\text{R} = t\text{Bu}$, $\text{E} = \text{Si}$, Sn , $n = 1$; $\text{R} = i\text{Pr}$, $\text{E} = \text{Si}$, $n = 2$)^[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 $\text{Pb}(\text{NR}^1)_2(\text{R}^2)$ are very scarce, and the only known example is $\{\text{Pb}(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{NH}_2\}_2$ ($\text{Trip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_3$).^[4,5] The chemistry of Pb^{II} amides has been little explored. In fact, only a few reactions of the diamides $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Pb}(\text{N}t\text{Bu}-\kappa\text{N})_2(\mu\text{-SiMe}_2)$ 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 $\{\text{Pb}(\text{R})\text{Br}\}_2$ (**1a**, $\text{R} = 2,6\text{-Trip}_2\text{C}_6\text{H}_3$)^[11] with LiNMe_2 in diethyl ether afforded selectively aryl lead(II) amide $\{\text{Pb}(\text{R})\text{NMe}_2\}_2$ (**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 $\{\text{Pb}(\text{NMe}_2)_2\}_2$, 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

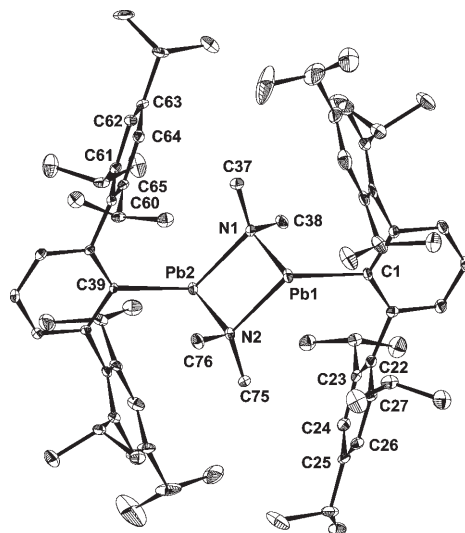


Figure 1. DIAMOND plot of the molecular structure of **1b** in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1–N1 2.329(3), Pb1–N2 2.426(3), Pb1–C1 2.399(4), Pb2–N1 2.427(3), Pb2–N2 2.321(3), Pb2–C39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

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 $\{\text{Pb}(\text{R})\text{X}\}_2$ ($\text{X} = \text{Br}$ (**1a**): 4.257(8) Å; $\text{X} = \text{I}$ (**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

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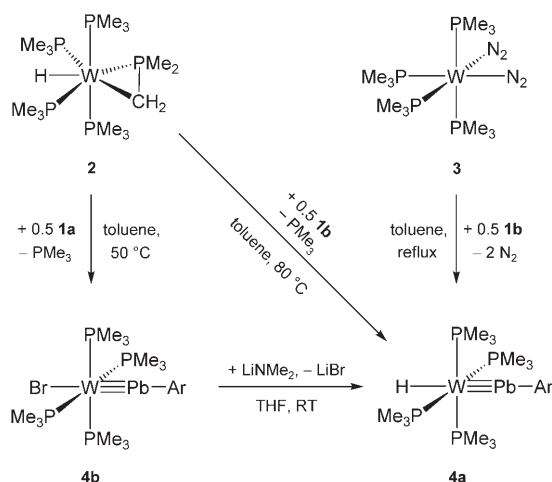
[**] We thank the Deutsche Forschungsgemeinschaft (project FI 445/6-1) for the generous financial support of this work. We also thank U. Kätel, W.-D. Bloedorn, and A. Thiesies at the Humboldt University of Berlin for the elemental analyses and the 2D NMR spectra.

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 ¹H NMR spectrum (C₆D₆, 298 K) for the methyl protons of the NMe₂ groups (δ = 1.70 and 4.17 ppm),^[19] that is, the dimeric structure of **1b** is retained in solution.^[20] The ¹³C{¹H} NMR spectrum of **1b** displays a characteristic low-field signal for the lead-bonded C_{aryl} atom at δ = 244.8 ppm, which appears at higher field than the corresponding signals of the aryl lead(II) halides **1a** (δ _C = 287.9 ppm) and **1c** (δ _C = 276.7 ppm).^[10b,11]

Treatment of lead(II) amide **1b** with two equivalents of [W(η^2 -CH₂PMe₂)(H)(PMe₃)₄] (**2**)^[21] in toluene at 80 °C afforded the hydrido plumbilydine complex *trans*-[H-(PMe₃)₄W=Pb(2,6-Trip₂C₆H₃)] (**4a**, Scheme 1). The same



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

complex was selectively formed on heating of **1b** and two equivalents of *cis*-[W(N₂)₂(PMe₃)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, plumbilydine 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 plumbilydine complex *trans*-[Br(PMe₃)₄W=Pb(2,6-Trip₂C₆H₃)] (**4b**), which is then treated with an excess of LiNMe₂ in THF at ambient temperature to afford the desired product (Scheme 1). Hydrido plumbilydine 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] plumbilydine complexes *trans*-[X(PMe₃)₄W=

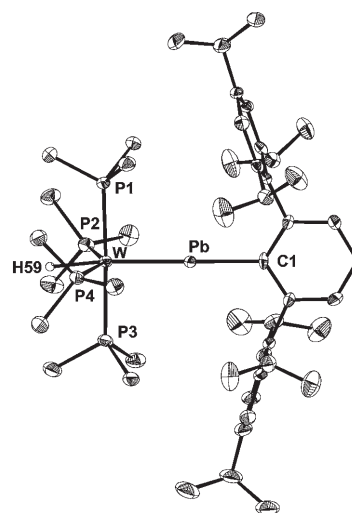


Figure 2. DIAMOND plot of the molecular structure of **4a**·2 (*n*-C₅H₁₂) in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms except H59 and those of the solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: W–Pb 2.5525(3), W–H59 1.71(2), W–P1 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).

PbC₆H₃(2,6-Trip₂C₆H₃)] (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 plumbilydine 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.

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(PMe₃)₄W=Ge(2,6-Trip₂C₆H₃)] (ν (W–H) = 1658 cm^{−1})^[21c] and *trans*-[H-(dmpe)₂W=CMe₃] (ν (W–H) = 1600 cm^{−1}; dmpe = Me₂PCH₂CH₂PMe₂).^[27] This observation suggests that the *trans* influence of the ylidene ligand decreases in the series CR > GeR > PbR. In the ¹H NMR spectrum of **4a** a distinctive quintet signal is observed for the hydride ligand at δ = −6.52 ppm (²*J*(P,H) = 30.7 Hz, ¹*J*(W,H) = 63 Hz). The ³¹P{¹H} NMR spectrum of **4a** shows one singlet resonance for the PMe₃ ligands at δ = −34.5 ppm, which appears at lower field than those of **4b** (δ _P = −43.6 ppm) and **4c** (δ _P = −53.9 ppm),^[10b] and confirms the *trans* configuration of the complex. The ³¹P NMR signal is flanked by a pair of tungsten satellites,^[28] for which the ¹*J*(W,P) coupling constant of 258 Hz compares well with those of plumbilydine complexes **4b** (¹*J*(W,P) = 257 Hz) and **4c** (¹*J*(W,P) = 258 Hz).^[10b] Finally, the ¹³C{¹H} NMR spectrum of **4a** features a low-field-shifted signal for the lead-bonded C_{aryl} atom at δ = 267.2 ppm, which has a similar chemical shift to those of complexes **4b** (δ _C = 270.2 ppm) and **4c** (δ _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

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product. The latter intermediate is probably also formed in the reaction of **4b** with LiNMe₂ 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 WP₄ core to **4b** and **4c**, such that two *trans*-disposed PMe₃ ligands (P2 and P4 in Figure 2) are pushed further away from the plumbidyne 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(PMe₃)₄W≡Ge(2,6-Trip₂C₆H₃)] (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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