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## Palladium and Platinum Complexes of a Benzannulated N-Heterocyclic Plumbylene with an Unusual Bonding Mode

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Supporting Information

**ABSTRACT:** Reaction of the *N,N'*-diisobutyl-substituted benzannulated N-heterocyclic plumbylene (NHPb) **1** with [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] gave the complexes [M(NHPb)(PPh<sub>3</sub>)<sub>3</sub>] (M = Pd [**2**], Pt [**3**]). X-ray diffraction studies of both complexes showed an angle of ~125° between the plumbylene plane and the transition-metal–Pb axis, indicating coordination of the transition metal to the empty  $\pi$  orbital of the plumbylene Pb atom. The experimentally determined metric parameters of complexes [**2**] and [**3**] are discussed on the basis of DFT calculations.

The synthesis and characterization of a few N-heterocyclic plumbylenes (NHPbs) has been described.<sup>1</sup> Contrary to their lighter analogues, the N-heterocyclic carbenes,<sup>2</sup> silylenes,<sup>3,4</sup> germynes,<sup>4,5</sup> and stannylens,<sup>4,6</sup> the coordination chemistry of the potentially monodentate NHPbs has not been explored to date. The literature contains only one report describing an adduct of a benzannulated NHPb<sup>7</sup> in addition to few reports on compounds featuring bonds between lead and palladium or platinum.<sup>8–10</sup>

In general, the lighter analogues of N-heterocyclic plumbylenes, in particular the N-heterocyclic carbenes (NHCs), are known to be excellent ligands for various transition metals.<sup>2</sup> They normally form complexes in which the C<sub>NHC</sub>–M bond is oriented in a coplanar fashion relative to the plane of the N-heterocycle, leading to planar units of the type M–C(NRR')<sub>2</sub>. Only a few exceptions to this rule are known, most of which result from steric crowding at the metal center or the presence of very bulky *N,N'*-substituents on the NHC ligand.<sup>11</sup> We initiated the present study to investigate whether this geometric situation would persist for complexes of the heavier analogues of NHCs, in which the sp<sup>2</sup>– $\sigma$  orbital becomes less nucleophilic and the unoccupied p– $\pi$  orbital becomes more Lewis acidic. We selected the N-heterocyclic plumbylene **1** (Scheme 1) and studied its coordination chemistry with Pd<sup>0</sup> and Pt<sup>0</sup> complexes.

The preparation of **1** has been described previously.<sup>1a</sup> The NHPb complexes [Pd(**1**)(PPh<sub>3</sub>)<sub>3</sub>] [**2**] and [Pt(**1**)(PPh<sub>3</sub>)<sub>3</sub>] [**3**] were prepared by reacting 1 equiv of **1** with [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>], respectively, over 3 days in toluene at ambient temperature (Scheme 1). Initiation of the reaction could be detected visually by a color change of the reaction mixture from red to dark-purple in the case of the palladium complex and to

blue-green in the platinum case. Concentration of the reaction solution and cooling to –20 °C allowed the isolation of complexes [**2**] and [**3**] as dark-purple and dark-blue-green solids, respectively [see the Supporting Information (SI)]. Like plumbylene **1**, the plumbylene complexes [**2**] and [**3**] are very sensitive toward oxygen and moisture. The complexes are soluble in toluene and benzene.

The benzannulated NHPb can substitute one triphenylphosphine ligand in the coordination sphere of Pd<sup>0</sup> or Pt<sup>0</sup>. Complexes with more than one plumbylene ligand could not be obtained even when an excess of up to 4 equiv of **1** was reacted with [Pd(PPh<sub>3</sub>)<sub>4</sub>] or [Pt(PPh<sub>3</sub>)<sub>4</sub>].

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for both complexes exhibited the features expected for the plumbylene and phosphine ligands. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectra, broad signals were found at 11.5 ppm for [**2**] and 42.8 ppm (with <sup>195</sup>Pt satellites, <sup>1</sup>J<sub>P,Pt</sub> = 4422 Hz) for [**3**]. The <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum of [**3**] showed a broad resonance at –1016 ppm.

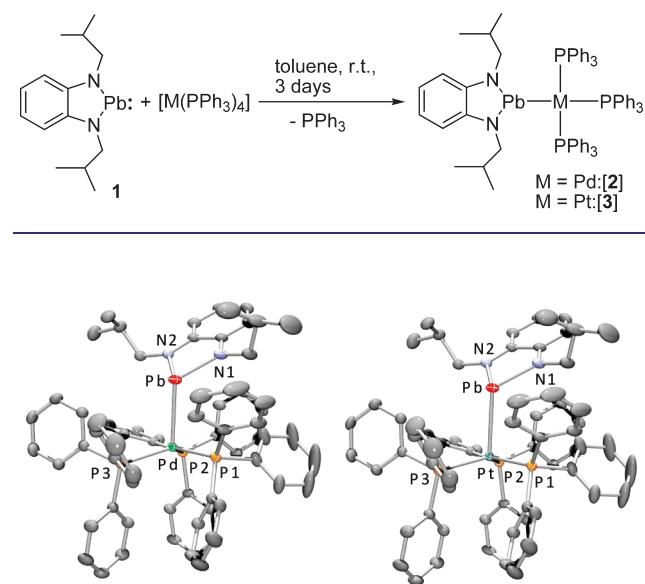
Crystals of [**2**]·2C<sub>7</sub>H<sub>8</sub> and [**3**]·2C<sub>7</sub>H<sub>8</sub> suitable for X-ray diffraction analyses (see the SI) were obtained by cooling saturated toluene solutions of the complexes to –20 °C. The molecular structures of the complexes are depicted in Figure 1. The crystal structures of [**2**]·2C<sub>7</sub>H<sub>8</sub> and [**3**]·2C<sub>7</sub>H<sub>8</sub> are essentially isostructural. The transition-metal atom in each complex is surrounded in a strongly distorted tetrahedral fashion by the plumbylene and three triphenylphosphine ligands. The Pd–Pb separation in [**2**] [2.8214(3) Å] is shorter than the Pt–Pb separation in [**3**] [2.8558(2) Å], while all three Pd–P distances in [**2**] [2.3352(8)–2.2773(8) Å] are longer than the Pt–P distances in [**3**] [2.2920(10)–2.3210(10) Å]. The important metric parameters of the plumbylene ligands (Pb–N distances, N–Pb–N angle) in the two complexes are identical within experimental error, and the Pb–N distances in the coordinated plumbylene ligand are slightly elongated relative to the free plumbylene.<sup>1a</sup> The five-membered heterocycles of the plumbylene ligands in both complexes are essentially planar.

The most striking features of the molecular structures of [**2**] and [**3**] are the range of the angles at the transition metal and the orientation of the plumbylene ligands in the complexes. Apparently because of steric crowding, all of the P–M–P angles in [**2**] and [**3**] [110.61(3)–121.53(3)°] are larger than the tetrahedral angle, while the Pb–M–P angles [92.08(3)–105.11(2)°] are

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Scheme 1. Synthesis of Complexes [2] and [3]



**Figure 1.** Molecular structures of (left) [2] and (right) [3]. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for [2] [[3]]: M–Pb, 2.8214(3) [2.8558(2)]; Pb–N1, 2.190(3) [2.198(4)]; Pb–N2, 2.185(3) [2.192(3)]; M–P1, 2.3352(8) [2.2920(10)]; M–P2, 2.3451(8) [2.2960(10)]; M–P3, 2.3773(8) [2.3210(10)]; Pb–M–P1, 92.51(2) [92.08(3)]; Pb–M–P2, 103.97(2) [103.75(2)]; Pb–M–P3, 105.11(2) [103.06(2)]; P1–M–P2, 118.27(3) [118.58(4)]; P1–M–P3, 110.61(3) [111.20(4)]; P2–M–P3, 120.83(3) [121.53(3)]; N1–Pb–N2, 75.15(11) [74.78(13)].

significantly smaller. The angles between the two vectors  $\text{NN} \rightarrow \text{Pb}$  (where “NN” represents the midpoint between the two nitrogen atoms of the plumbylene ligand) and  $\text{Pb} \rightarrow \text{M}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) measure  $125.5^\circ$  in [2] and  $124.5^\circ$  in [3].

For the lighter carbene, silylene, germylene, and stannylene analogues of **1**,  $\text{sp}^2$  hybridization of the subvalent group-14 atom ( $\text{E}^{\text{II}}$ ) is normally assumed, leading to a singlet state with a filled  $\text{sp}^2$  hybrid orbital and an empty p orbital. Coordination of these N-heterocyclic ligands to transition metals occurs via interaction of the filled  $\text{sp}^2$  orbital with an empty orbital on the transition metal, leading to a coplanar arrangement of the four atoms in the  $\text{N}_2\text{E}^{\text{II}} \rightarrow \text{M}$  moiety. The geometrical parameters found for [2] and [3], in particular the small angle between the  $\text{NN}-\text{Pb}$  and  $\text{Pb}-\text{M}$  vectors, indicate a different mode of bonding in which the transition metal ( $\text{Pd}^0$  or  $\text{Pt}^0$ ) acts as a d-electron donor and the empty p orbital at the  $\text{Pb}^{\text{II}}$  atom functions as an acceptor. The unshared electron pair in the  $\text{Pb}$   $\text{sp}^2$  hybrid orbital remains unaffected by this type of bonding.

A related bonding situation has been observed in the NHC adducts of a dialkylplumbylene<sup>12</sup> and an N-heterocyclic stannylene,<sup>13</sup> where the NHC acts as base toward the Lewis acidic p orbital of the plumbylene and stannylene, respectively. The empty p orbital also acts as an acceptor orbital in dimeric plumbylenes.<sup>14</sup> To the best of our knowledge, donor interactions of electron-rich transition metals with Lewis acidic plumbylenes like those observed here in [2] and [3] have not been described to date.

To obtain a better understanding of the unusual mode of bonding between the plumbylene and the transition metal, we studied complexes [2] and [3] using state-of-the-art dispersion-corrected density functional theory (DFT-D3;<sup>15</sup> for technical details, see

**Table 1.** Experimental and Calculated (DFT-TPSS<sup>d</sup>) Bond Parameters for Complexes [2] and [3]<sup>b</sup>

	X-ray data	TPSS-D3(BJ)	TPSS
Complex [2]			
Pb–Pd	2.8214(3)	2.823	2.905
Pb–N <sup>c</sup>	2.187	2.237	2.226
P–Pd	2.3352(8)–2.3773(8)	2.313–2.332	2.376–2.411
Pd–Pb–NN <sup>d</sup>	125.5	117.0	128.9
$D_e$		37.4	4.0
Complex [3]			
Pb–Pt	2.8558(2)	2.856	2.969
Pb–N <sup>c</sup>	2.195	2.223	2.231
P–Pt	2.2920(10)–2.3210(10)	2.292–2.308	2.336–2.337
Pt–Pb–NN <sup>d</sup>	124.5	117.3	126.9
$D_e$		38.9	3.5

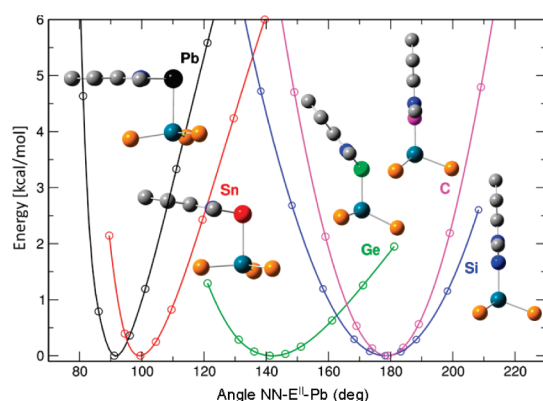
<sup>a</sup>Basis sets: def2-TZVP (–f for C, N); def2-QZVP for Pd/Pt and Pb.

<sup>b</sup>Bond lengths are given in Å, bond angles in deg, and dissociation energies ( $D_e$ ) in kcal/mol. <sup>c</sup>Average of the two values. <sup>d</sup>NN = midpoint between the two nitrogen atoms of the plumbylene.

the SI). Our experimental structural data nicely agree with those obtained from the DFT calculations. The calculated Pb–Pd and Pb–Pt bond lengths agree with the experimentally determined values only when the intramolecular dispersion corrections are taken into account (Table 1, TPSS-D3(BJ) vs TPSS). This supports previous findings of the importance of intramolecular dispersion effects in (transition) metal complexes with large and bulky groups.<sup>16</sup> The seemingly better agreement for the Pd–Pb–NN bending angle in the uncorrected TPSS calculation is attributed to missing neighbor molecules, which were absent in our single-molecule treatment and would “open” the structure in a periodic DFT-D3 calculation on the crystal (for a recent example, see ref 17).

To provide further illustration and explanation of the bonding situation in compounds [2] and [3] and to investigate the trend in the bonding mode of group-14 carbene analogues, we performed calculations on the model compounds [1,2-bis( $\text{N},\text{N}'$ -dimethylamido)benzene] $\text{E}^{\text{II}}$  ( $\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) bound to  $\{(\text{H}_3\text{P})_3\text{Pd}\}$  and  $\{(\text{H}_3\text{P})_3\text{Pt}\}$  complex fragments. These results indicated a continuous change from an  $\text{sp}^2(\text{E}^{\text{II}}) \rightarrow \text{d}(\text{M})$  to a  $\text{d}(\text{M}) \rightarrow \text{p}(\text{E}^{\text{II}})$  donor–acceptor orbital interaction bonding mode for the series of divalent group-14 ligands coordinated to  $\text{Pd}^0$  and  $\text{Pt}^0$ . The  $\text{NN}-\text{E}^{\text{II}}-\text{Pd}$  angle changed from practically linear for the carbene and silylene ligands to  $\sim 141^\circ$  for the germylene ligand and  $\sim 101^\circ$  for the stannylene ligand. An almost perpendicular arrangement of the plane of the heterocycle relative to the Pd–Pb bond ( $\text{NN}-\text{Pb}-\text{Pd}$  angle =  $91^\circ$ ) was calculated for the plumbylene derivative (Figure 2). The angle calculated for the model compound is  $34.5^\circ$  smaller than the value observed for [2], which can be attributed to steric repulsion between the plumbylene and phosphine ligands in the real system. Details of an orbital-based bonding analysis are given in the SI.

In summary, we have prepared and characterized N-heterocyclic plumbylene  $\text{Pd}^0$  and  $\text{Pt}^0$  complexes and established an unusual bonding mode in these derivatives that is apparently caused by the interaction of filled orbitals of the transition-metal center with the empty p orbital of the plumbylene. This type of interaction leads to a decrease in the  $\text{NN}-\text{Pb}-\text{M}$  angles to values of  $\sim 125^\circ$ . DFT calculations on a sterically less congested  $\text{Pd}^0$  model compound showed an even greater decrease in the  $\text{NN}-\text{Pb}-\text{Pd}^0$  angle to



**Figure 2.** Energy as a function of NN-E<sup>II</sup>–Pd bending angle for N-heterocyclic plumblylene, stannylene, germylene, silylene, and carbene ligands bonded to Pd<sup>0</sup>.

~90°, which also supports the proposed new d–p-type interaction. The DFT calculations also confirmed the experimental observation that the lighter N-heterocyclic E<sup>II</sup> compounds (carbenes and silylenes) bind to Pd<sup>0</sup> via the filled sp<sup>2</sup> hybrid orbital, leading to a planar arrangement of the four atoms of the N<sub>2</sub>E<sup>II</sup>–Pd<sup>0</sup> moiety. Intramolecular dispersion interactions substantially influence the computed structures and should be included in accurate treatments of large molecular systems.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental details for the synthesis, characterization data for all compounds, DFT data, and crystallographic data (CIF) for compounds [2]·2C<sub>7</sub>H<sub>8</sub> and [3]·2C<sub>7</sub>H<sub>8</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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