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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 $[\mathrm{Pd(PPh_3)_4}]$ and $[\mathrm{Pt(PPh_3)_4}]$ gave the complexes $[\mathrm{M(NHPb)(PPh_3)_3}]$ (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 π 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.[1] Contrary to their lighter analogues, the N-heterocyclic carbenes,[2] silylenes,[3,4] germylenes,[4,5] and stannylenes,[4,6] 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[7] in addition to few reports on compounds featuring bonds between lead and palladium or platinum.[8−10]

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.[2] They normally form complexes in which the $\mathrm{C_{NHC}}$−M bond is oriented in a coplanar fashion relative to the plane of the N-heterocycle, leading to planar units of the type $\mathrm{M{-}C(NRR')_2}$. 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.[11] We initiated the present study to investigate whether this geometric situation would persist for complexes of the heavier analogues of NHCs, in which the $\mathrm{sp^2}$-σ orbital becomes less nucleophilic and the unoccupied p-π orbital becomes more Lewis acidic. We selected the N-heterocyclic plumbylene **1** (Scheme 1) and studied its coordination chemistry with $\mathrm{Pd^0}$ and $\mathrm{Pt^0}$ complexes.

The preparation of **1** has been described previously.[1a] The NHPb complexes $[\mathrm{Pd}(\mathbf{1})(\mathrm{PPh_3})_3]$ [**2**] and $[\mathrm{Pt}(\mathbf{1})(\mathrm{PPh_3})_3]$ [**3**] were prepared by reacting 1 equiv of **1** with $[\mathrm{Pd(PPh_3)_4}]$ and $[\mathrm{Pd(PPh_3)_4}]$, 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 $\mathrm{Pd^0}$ or $\mathrm{Pt^0}$. 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 $[\mathrm{Pd(PPh_3)_4}]$ or $[\mathrm{Pt(PPh_3)_4}]$.

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

Crystals of $[\mathbf{2}]\cdot 2\mathrm{C_7H_8}$ and $[\mathbf{3}]\cdot 2\mathrm{C_7H_8}$ 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 $[\mathbf{2}]\cdot 2\mathrm{C_7H_8}$ and $[\mathbf{3}]\cdot 2\mathrm{C_7H_8}$ 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.[1a] 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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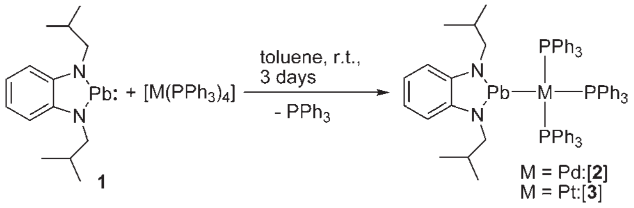
Scheme 1. Synthesis of Complexes [2] and [3]



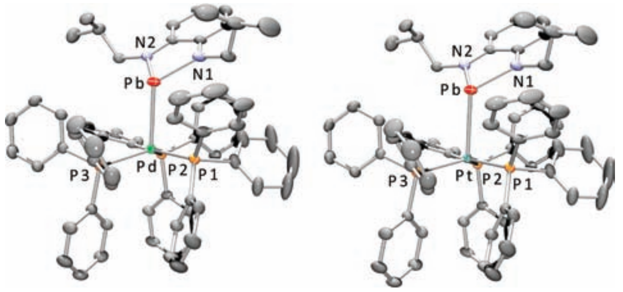


Figure 1. Molecular structures of (left) [2] and (right) [3]. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for [2] [[3]]: M−Pb, 2.8214(3) [2.8558(2)]; Pb−N1, 2.190(3) [2.198(4)]; Pb−N2, 2.185(3) [2.192(3)]; M−P1, 2.3352(8) [2.2920(10)]; 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 NN → Pb (where "NN" represents the midpoint between the two nitrogen atoms of the plumbylene ligand) and Pb → M (M = Pd, Pt) measure 125.5° in [2] and 124.5° in [3].

For the lighter carbene, silylene, germylene, and stannylene analogues of 1, sp^2 hybridization of the subvalent group-14 atom (E^{II}) is normally assumed, leading to a singlet state with a filled sp^2 hybrid orbital and an empty p orbital. Coordination of these N-heterocyclic ligands to transition metals occurs via interaction of the filled sp^2 orbital with an empty orbital on the transition metal, leading to a coplanar arrangement of the four atoms in the $N_2E^{II}\rightarrow M$ moiety. The geometrical parameters found for [2] and [3], in particular the small angle between the NN−Pb and Pb−M vectors, indicate a different mode of bonding in which the transition metal (Pd^0 or Pt^0) acts as a d-electron donor and the empty p orbital at the Pb^{II} atom functions as an acceptor. The unshared electron pair in the Pb 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[12] and an N-heterocyclic stannylene,[13] 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.[14] 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;[15] for technical details, see 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.[16] 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).

Table 1. Experimental and Calculated (DFT-TPSS[a]) Bond Parameters for Complexes [2] and [3][b]

	X-ray data	TPSS-D3(BJ)	TPSS
	Complex [2]		
Pb−Pd	2.8214(3)	2.823	2.905
Pb−N[c]	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[d]	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[c]	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[d]	124.5	117.3	126.9
D_e		38.9	3.5

[a] Basis sets: def2-TZVP (−f for C, N); def2-QZVP for Pd/Pt and Pb. [b] Bond lengths are given in Å, bond angles in deg, and dissociation energies (D_e) in kcal/mol. [c] Average of the two values. [d] NN = midpoint between the two nitrogen atoms of the plumbylene.

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(*N*,*N*′-dimethylamido)benzene]E^{II} (E = C, Si, Ge, Sn, Pb) bound to $\{(H_3P)_3Pd\}$ and $\{(H_3P)_3Pt\}$ complex fragments. These results indicated a continuous change from an $sp^2(E^{II})\rightarrow d(M)$ to a $d(M)\rightarrow p(E^{II})$ donor−acceptor orbital interaction bonding mode for the series of divalent group-14 ligands coordinated to Pd^0 and Pt^0. The NN−E^{II}−Pd angle changed from practically linear for the carbene and silylene ligands to ~141° for the germylene ligand and ~101° for the stannylene ligand. An almost perpendicular arrangement of the plane of the heterocycle relative to the Pd−Pb bond (NN−Pb−Pd angle = 91°) was calculated for the plumbylene derivative (Figure 2). The angle calculated for the model compound is 34.5° 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 Pd^0 and 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 NN−Pb−M angles to values of ~125°. DFT calculations on a sterically less congested Pd^0 model compound showed an even greater decrease in the NN−Pb−Pd^0 angle to

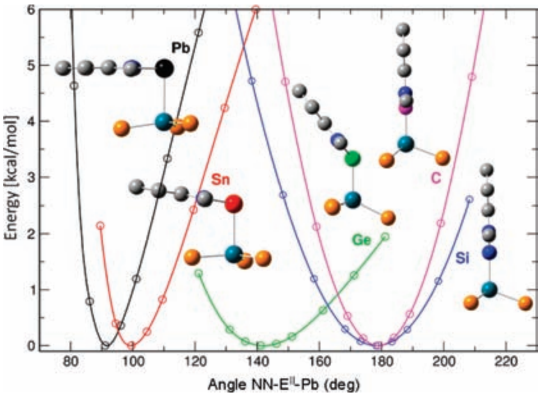


Figure 2. Energy as a function of NN−E^{II}−Pd bending angle for N-heterocyclic plumbylene, stannylene, germylene, silylene, and carbene ligands bonded to Pd^0.

~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^{II} compounds (carbenes and silylenes) bind to Pd^0 via the filled sp^2 hybrid orbital, leading to a planar arrangement of the four atoms of the N$_2$E^{II}→Pd^0 moiety. Intramolecular dispersion interactions substantially influence the computed structures and should be included in accurate treatments of large molecular systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details for the synthesis, characterization data for all compounds, DFT data, and crystallographic data (CIF) for compounds [**2**]·2C$_7$H$_8$ and [**3**]·2C$_7$H$_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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