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Stable O,N-heterocyclic plumbylenes bearing sterically hindered *o*-amidophenolate ligands

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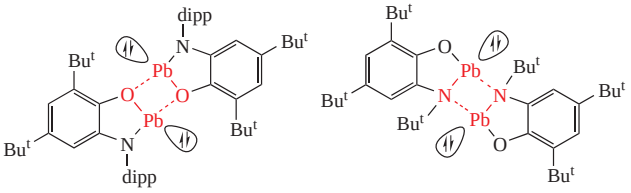
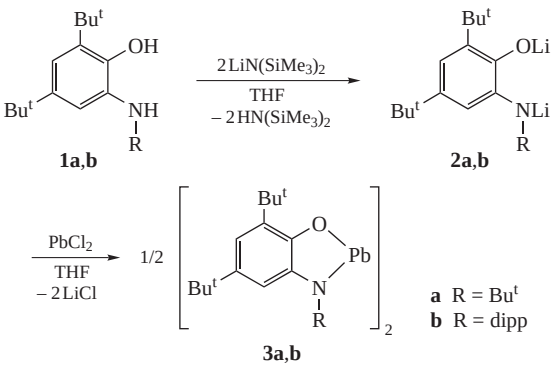
The reaction of dilithium salts of 4,6-di-*tert*-butyl-*N*-(R)-*o*-aminophenols with $PbCl_2$ leads to the formation of new O,N-heterocyclic plumbylenes [R is Bu^t or dipp (2,6-diisopropylphenyl)]. Both compounds possess dimeric structure in crystals according to the X-ray analysis of a single crystal. The formation of unstable paramagnetic plumbylene was detected during an oxidation of 4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*o*-aminophenolatolead(II) with $HgBr_2$.



A great interest towards the chemistry of heavier carbene analogues (known also as tetrylenes) has been initiated by the pioneering works of Lappert, wherein the synthesis and characterization of stable dialkyl and diamido derivatives, $M[CH(SiMe_3)_2]_2$ and $M(NR_2)_2$, respectively, of 14th group elements were studied.[1,2] They were thermally stable, highly reactive and diamagnetic (singlet spin ground state) divalent species. Hereinafter, a big family of Arduengo carbene heavy analogues (Si, Ge, Sn) has been isolated and characterized.[3–5] Moreover, the use of aromatic diamines allowed one to obtain rare examples of benzannulated N-heterocyclic plumbylenes[6] in addition to the well-known compounds of divalent silicon,[7] germanium[8] and tin.[8,9] An exeptional stability was demonstrated by pyridoannulated plumbylenes due to supramolecular aggregation.[10]

Although the chemistry of N-heterocyclic carbenes and their analogues is well developed, there are only few reported examples of the aromatic O,N-heterocyclic tetrylenes comprising amidophenolate dianion. In particular, one germylene[11] and two stannylenes[12,13] bearing sterically hindered redox-active *o*-aminophenols have been isolated. It should be noted that there is no published information about benzannulated O,N-heterocyclic plumbylenes. In this work, we report on the preparation and characterization of two new aromatic O,N-heterocyclic plumbylenes with different substituents at the nitrogen atom of *o*-aminophenol ligand. The introduction of bulk *tert*-butyl substituents into the benzene ring can provide additional stabilization to the radical-anion form of such type of ligands.[13,14]



Scheme 1

It was shown that the direct interaction between $PbCl_2$ and dilithium salts **2a**,**b** [prepared from corresponding 4,6-di-*tert*-butyl-*N*-(R)-*o*-aminophenols **1a**,[14] **1b** and 2 equiv. of $LiN(SiMe_3)_2$ and used *in situ*] in THF provides the diamagnetic compounds of divalent lead **3a**,**b** (Scheme 1).†

The reactions proceeded only under heating (water bath) and vigorous stirring the mixture. The beginning of the process can be monitored visually as a color change of the reaction mixture from yellow-orange to intense red or brown (**3a** or **3b**, respectively) and a precipitation of fine powdered LiCl byproduct. Complexes **3a** and **3b** were isolated as crystalline solids in 70–75% yields. The plumbylenes are extremely sensitive towards oxygen and moisture, but they are quite stable under the anaerobic conditions both in solutions and in the crystalline form up to 100 °C. The single crystal X-ray diffraction analysis revealed that the plumbylene **3a**,**b** molecules are dimerized in the solid state *via* strong intermolecular Pb···N or Pb···O interactions (Figure 1).‡ Note that compound **3a** forms dimers likewise stannylene[13] based on (*N*-phenylamino)phenol, through the two strong donor–acceptor Pb···N interactions [2.422(3) Å], which are longer

† For procedure and characteristics of compounds **3a**,**b**, see Online Supplementary Materials.

‡ *Crystal data for* **3a**: $C_{36}H_{58}N_2O_2Pb_2$, M = 965.22, monoclinic, space group $P2_1/c$, a = 15.5018(5), b = 10.4911(3) and c = 11.7665(4) Å, V = = 1813.88(10) Å^3, Z = 2, d_{calc} = 1.767g cm^{-3}, μ = 9.301 mm^{-1}, $F(000)$ = 936, the final R = 0.0299, wR = 0.0747, and S = 1.060 for 20150 observed reflections with $I > 2\sigma(I)$.

Crystal data for **3b**: $C_{52}H_{74}N_2O_2Pb_2$, M = 1173.51, monoclinic, space group Cc, a = 26.2613(17), b = 8.7465(5) and c = 23.0164(15) Å, V = = 4968.9(5) Å^3, Z = 4, d_{calc} = 1.569 g cm^{-3}, μ = 6.806 mm^{-1}, $F(000)$ = 2320, the final R = 0.0274, wR = 0.0590, and S = 1.030 for 33282 observed reflections with $I > 2\sigma(I)$.

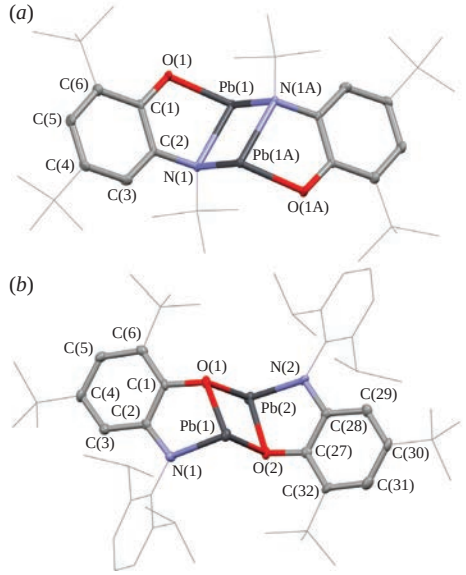
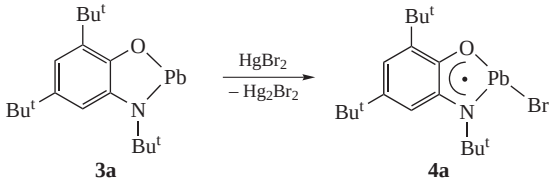


Figure 1 Molecular structures of compounds (*a*) **3a** and (*b*) **3b** represented by thermal ellipsoids at the 50% probability level for the key atoms and wire frame depiction for the peripheral carbon atoms (hydrogen atoms are omitted). Selected bond lengths (Å) and angles (°) for **3a**: Pb(1)–N(1) 2.317(3), Pb(1)–O(1) 2.161(3), Pb(1)–N(1A) 2.422(3), O(1)–C(1) 1.348(5), N(1)–C(2) 1.447(5), O(1)–Pb(1)–N(1) 76.97(11), O(1)–Pb(1)–N(1A) 97.03(11), N(1)–Pb(1)–N(1A) 82.39(12); for **3b**: Pb(1)–N(1) 2.195(6), Pb(1)–O(1) 2.260(4), Pb(1)–O(2) 2.358(4), Pb(2)–N(2) 2.195(6), Pb(2)–O(2) 2.249(4), Pb(2)–O(1) 2.350(4), O(1)–C(1) 1.385(7), N(1)–C(2) 1.397(8), O(2)–C(27) 1.374(8), N(2)–C(28) 1.394(8), N(1)–Pb(1)–O(1) 73.68(18), N(1)–Pb(1)–O(2) 88.5(2), O(1)–Pb(1)–O(2) 82.30(15).

than the covalent Pb(1)–N(1) bonds [2.317(3) Å]. Plumbylene **3b** dimerizes through the donor–acceptor Pb···O interactions [2.350(4)–2.358(4) Å] similar to a stannylene bearing the same ligand.[12] The metal atom in **3a** possess a distorted trigonal pyramidal coordination with O(1), N(1) and N(1A) atoms in the basement and with stereochemically active unshared electron pair at the apical site (see Figure 1). The lead atoms are members of the planar five-membered rings. The amidophenolate ligands establish two parallel planes at a distance of 2.362 Å. The C(1)–O(1) [1.348(5) Å], C(2)–N(1) [1.447(5) Å] and C–C distances in the six-membered carbon ring [1.383(6)–1.417(6) Å] remain in the range typical of the dianion form of *o*-imino-benzoquinone ligand.[15] The Pb(1)–O(1) and Pb(2)–O(2) bond lengths [2.161(3) Å] are shorter than the sum of covalent radii of the relevant elements (2.2 Å),[16] and comparable with related bonds in lead oxyquinolates (2.264–2.299 Å).[17–19] The covalent Pb(1)–N(1) and Pb(2)–N(2) [2.317(3) Å] bonds are slightly longer than the sum of covalent radii of the relevant elements (2.24 Å)[16] and quite close to those [2.338(4) Å] obtained for a similar plumbylene bearing tridentate NNO-ligand.[20]

The O(1), N(1), O(2) and O(2), N(2), O(1) groups of atoms establish the bases of trigonal pyramids for Pb(1) and Pb(2), respectively, in **3b**. The skeletons of amidophenolate ligands are planar while these ligands are practically parallel to the each other. The dihedral angle between these planes is 4.23°. The bending angles along O···N lines in metallocycles have an opposite direction and are 22.93° and 20.68°. The lead atoms are removed from the planes of chelated ligands by 0.625 Å for Pb(2) and 0.649 Å for Pb(1). Such deviation is caused by the repulsion between lead atoms which are separated from each other by 3.4626(3) Å. This distance is quite shorter than the double van der Waals radius for lead (4.6 Å[14]). The Pb(1)–O(1) [2.260(4) Å] and Pb(2)–O(2) [2.249(4) Å] distances are shorter then bonds Pb(2)–O(1) [2.350(4) Å] and Pb(1)–O(2) [2.358(4) Å], which possess the donor–acceptor nature. The Pb–N distances in **3b** [2.195(6) Å] are quite shorter than those in **3a**. These bond lengths lie in the range typical of related benzannulated N-heterocyclic plumbylenes[7] and are close to the sum of covalent radii of nitrogen and lead(II) (2.24 Å) (see Figure 1).[16]

Diamide,[21–26] amidophenolate[13] and catecholate[13,27] tetrylene derivatives are known as capable of reacting with mercury(II) or silver(I) halides and with different stable radicals to give paramagnetic heavier carbene analogues. We have performed oxidation reactions of plumbylenes **3a** and **3b** with $HgHal_2$ (Hal = Cl, Br) in order to observe a formation of the species of paramagnetic compounds **4a** and **4b**, respectively (Scheme 2).



3a **4a**

Scheme 2

We were able to unambiguously detect by EPR spectroscopy only one paramagnetic species **4a** in the reaction of compound **3a** with $HgBr_2$ (see Scheme 2). The EPR spectra of **4a** is well resolved at 290 K (Figure 2). The hyperfine structure appears due to hyperfine splitting (HFS) of an unpaired electron with the following magnetic nuclei: ^{1}H (99.98%, I = 1/2, μ_N = 2.7928), ^{14}N (99.63%, I = 1, μ_N = 0.4037), ^{79}Br (50.69%, I = 3/2, μ_N = 2.1064), ^{81}Br (49.31%, I = 3/2, μ_N = 2.2706), and ^{207}Pb (22.1%, I = 1/2, μ_N = 0.5926). Taking into account the previous results,[19–25] one may assume a similar geometry of a distorted trigonal pyramid with oxygen, nitrogen and bromine atoms at the base and a lead atom at the apex for compound **4a**. The HFS constants due to the proton and nitrogen nuclei are typical of related iminosemiquinonate metal compounds.[28] Compounds of the low-valence lead are usually characterized by the large values of HFS constants a_i(^{207}Pb).[27] In case of Pb^{IV} derivatives, the HFS constants are usually decreased and do not exceed 50 G.[29,30] The value of hyperfine coupling constant a_i(^{207}Pb) observed for paramagnetic derivative **4a** is the highest among the previously

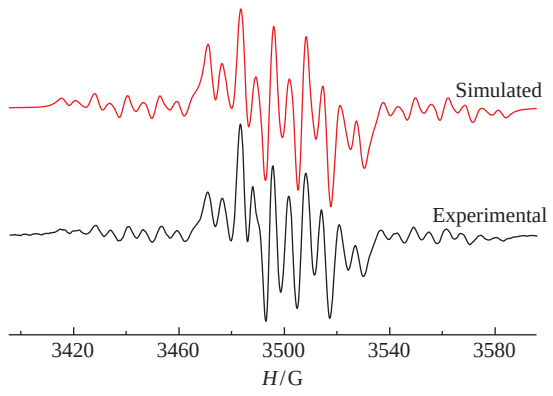


Figure 2 Calculated and experimental EPR spectra of species **4a** in THF solution at 290 K. HFS parameters: a_i(^{1}H) = 4.6 G, a_i(^{14}N) = 7.1 G, a_i(^{79}Br) = 12.0 G, a_i(^{81}Br) = 12.9 G, a_i(^{207}Pb) = 108.5 G, and g_i = 1.9980.

The measurements were performed on a Bruker D8 Quest diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL[33] using full-matrix least-squares procedures based on F^2 values. Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.[34]

CCDC 1831609 and 1831610 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

reported ones for the similar systems and indicates the preservation of a low valence of the metal in the reaction product. At the same time, $a_i(^{207}Pb)$ constant for **4a** is significantly lower than that of known lead-centered radicals (506–1850 G).[31,32] This fact indicates that the spin density in examined paramagnetic specie **4a** is delocalized over the entire chelate ring. The high values of HFS constants due to the bromine magnetic isotopes are evidence of a considerable contribution of $\sigma(\sigma^*)$ orbitals of the Pb–Br bond to the π-MO occupied by the unpaired electron. The complex geometry, wherein the Pb–Br bond is orthogonal to the metallacycle plane, is favourable for this interaction. The isotropic g_i is abnormally low for *o*-iminosemiquinone radical anions. This fact also supports the conclusion concerning a noticeable contribution of lead and bromine AOs to the MO of the unpaired electron. It is necessary to note that the observed paramagnetic plumbylene **4a** was unstable and completely decomposed in the solution within 1 h.

Therefore, this work revealed the two stable O,N-heterocyclic plumbylenes, which were prepared and characterized. The dimerization behavior of these complexes in crystals is caused by the intermolecular Pb–O or Pb–N interactions. The *tert*-butyl-substituted compound **3a** was found to react with mercury bromide providing an unstable paramagnetic plumbylene **4a**, which was confirmed by the EPR spectroscopy.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.026.

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