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

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Synthesis of 4,6-di-*tert*-butyl-*N*-(dipp)-*o*-aminophenol 1b. Hydrazine hydrate (0.512 g, 16 mmol) was added dropwise to the suspension of 4,6-di-*tert*-butyl-*N*-(dipp)-*o*-iminoquinone[S1] (3 g, 8 mmol) in MeOH (50 ml). The solution became colorless and gaseous nitrogen was released during this process. Addition of distilled water (50 ml) resulted in a formation of the white precipitate of corresponding *o*-aminophenol. The crystalline product was collected by filtration and air-dried.

Yield 2.5 g (84 %). ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 1.10 (d, 6H, CH$_3$(Pr^i), *J* 6.7 Hz); 1.11 (s, 9H, (Bu^t)); 1.13 (d, 6H, CH$_3$(Pr^i), *J* 6.7 Hz); 1.47 (s, 9H, (Bu^t)); 3.03 (septet, 2H, CH(Pr^i); *J* 6.7 Hz); 6.29 (d, 1H, H$_{AP}$, *J* 2.2 Hz), 6.89 (d, 1H, H$_{AP}$, *J* 2.2 Hz); 7.18 (s, 3H, H$_{ar}$). Found (%): C, 81.98; H, 10.43. Calculated (%): C, 81.84; H, 10.30.

General procedure for the synthesis of plumbylenes 3a and 3b. The equimolar quantity of LiN(SiMe$_3$)$_2$ solution in hexane was added to the corresponding 4,6-di-*tert*-butyl-*N*-(substituted)-*o*-aminophenol (0.3 g of **1a** or 0.41 g of **1b**; 1.08 mmol) in THF (10 ml). Reaction mixture was stirred for 1h at room temperature. The color of reaction mixture became light orange one. The resulting solution was added to the suspension of PbCl$_2$ (0.3 g, 1.08 mmol) in THF (5 ml). The solution was vigorously stirred under heating on a water bath at 60°C for 1.5 h. The color of reaction mixture turned to deep brown one and the fine powdered LiCl was precipitated. All volatiles were evaporated under reduced pressure. The residue was dissolved in hexane (15 ml) and filtered. Complexes **1** and **2** were isolated as yellow crystalline solids from the corresponding concentrated hexane solutions.

4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*o*-amidophenolatolead(II) 3a: Yield 0.35 g (67 %). ^{1}H NMR (C$_6$D$_6$, 400 MHz), δ: 1.01 (s, 9H, (Bu^t)); 1.33 (s, 9H, (Bu^t)); 1.58 (s, 9H, N(Bu^t)); 6.64 (d, 1H, H$_{AP}$, *J* 2.2 Hz); 7.22 (d, 1H, H$_{AP}$, *J* 2.2 Hz). Found (%): C, 44.91; H 6.14. Calculated (%): C, 44.80; H, 6.06.

4,6-di-*tert*-butyl-*N*-(dipp)-*o*-amidophenolatolead(II) 3b: Yield 0.32 g (70 %). ^{1}H NMR (C_6D_6, 400 MHz), δ: 1.01 (d, 6H, CH_3(Pr^i), *J* 6.7 Hz); 1.04 (d, 6H, CH_3(Pr^i), *J* 6.7 Hz); 1.22 (s, 9H, (Bu^t)); 1.55 (s, 9H, (Bu^t)); 3.40 (septet, 2H, CH(Pr^i), *J* 6.7 Hz); 6.65 (d, 1H, H_{AP}, *J* 2.2 Hz), 7.1 (m, 3H, H_{ar}); 7.35 (d, 1H, H_{AP}, *J* 2.2 Hz). Found (%): C, 53.57; H, 6.20. Calculated (%): C, 53.40; H, 6.03.

^{1}H-NMR spectra were recorded on either Bruker Avance III (400 MHz) or Bruker DPX-200 (200 MHz) instruments.

References:

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