<sup>1</sup>H NMR spectrum of the reaction mixture after five min revealed

new resonances corresponding to 1:1 mixture of lead-bound

## The synthesis of monomeric terminal lead aryloxides: dependence on reagents and conditions<sup>†</sup>‡

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The successful synthesis of terminal lead aryloxides is shown to be dependent upon reaction conditions, including choice of solvent and alkali metal aryloxide precursor.

There is a large literature base detailing the coordination chemistry of lead(II) and trying to address its bonding properties, with an emphasis on how divalent lead might interact with biological molecules.<sup>1,2</sup> In addition, there has been considerable interest in the lead(II) lone pair with regards to both its stability and its purported stereochemical activity.<sup>3-6</sup> However, the chemistry of the ligands bonded to lead, especially in mimicking the reactivity of transition metal counterparts, has been widely ignored. This is partially due to the instability of lead complexes and their tendency to form insoluble precipitates which are difficult to characterize and use in further transformations. For instance, only a handful of terminal lead alkoxide and aryloxides have been reported to date,<sup>7-10</sup> and only one of these is monometallic.<sup>7</sup> This is in sharp contrast with the vast array of transition metal counterparts.<sup>11-13</sup>

We have recently reported the synthesis of a series of  $\beta$ -diketiminate lead(II) halide complexes in which we employed the bulky  $\beta$ -diketiminate anion, [{N(2,6-'Pr\_2C\_6H\_3)C(Me)}\_2CH], (BDI) to support monomeric, 3-coordinate lead centres.<sup>14</sup> These ligands have been previously utilised to stabilise low-coordinate transition metal complexes as the isopropyl groups on the ligand aryl group limit the number of coordinated ligands around the metal center.<sup>15-17</sup> Both the BDI–lead chloride and bromide complexes are relatively thermally and photolytically stable and the [(BDI)PbCI] (1) can be generated in sufficient quantities for use as a starting reagent for the development of the chemistry of low-coordinate lead.

To minimize the risk of forming aggregates in solution, our initial focus was on generating bulky lead-aryloxide complexes. Synthesis of a lead-aryloxide containing the 2,6-di-*tert*-butyl-4-methylphenoxide (BHT) group was attempted by treatment of chloride 1 with LiBHT in THF. An insoluble white precipitate was formed, however, the major species remaining in solution was neutral BDI-H. Interestingly, when a solution of chloride 1 was added to a suspension of unsolvated LiBHT in toluene or benzene, the mixture became homogeneous, and formation of a yellow crystalline solid was observed upon standing for 30 min. The

β-diketiminate ligand and BHT. However, no precipitate other than the slow forming yellow crystalline solid was observed, even upon addition of pentane or other non-polar solvents. Confused as to the identity of this new complex, an X-ray diffraction study was performed on the crystalline solid, which has crystallized about an inversion centre.<sup>18</sup> The molecular structure revealed that a lead-aryloxide complex had not formed, but instead heterotetrametallic adduct,  $[{(BDI)PbCl}{LiO(2,6-di-'Bu-4-MeC_6H_2)}]_2$ (2) had been generated in which a lithium-aryloxide  $[Li(OAr)]_2$ dimer is coordinated by two [(BDI)PbCl] moieties via a chloridelithium interaction (Fig. 1, Scheme 1). A pyramidal geometry is observed around the lead metal centre, with the sum of the bond angles around the metal centre equal to 272.3°, or a degree of pyramidalization (DP) of 98%.14,19 This is similar to the parent chloride complex 1 (DP = 103%); however, as would be expected by such a complex, both the Pb-Cl and Pb-N bond distances are elongated by 0.073 Å and 0.035 Å, respectively.<sup>14</sup> The  $Li_2O_2$ dimer is a common binding motif for bulky lithium-aryloxide complexes, with the THF adduct of LiBHT crystallographically characterized.20



**Fig. 1** ORTEP diagram of compound **2** with H atoms omitted and C atoms minimized for clarity. Ellipsoid probably shown at 30%. Atoms with a prime (') in the atoms labels are at equivalent position (-x, -y, -z). Selected bond lengths (Å) and angles (°): Pb–N(1), 2.315(3); Pb–N(2), 2.315(3); Pb–Cl, 2.6381(10); Li–O', 1.849(7); Li–O, 1.885(7); Li–Cl, 2.358(7); O–C(30), 1.337(4); O'–Li, 1.849(7); N(1)–Pb–N(2), 82.86(11); N(1)–Pb–Cl, 94.14(3); N(2)–Pb–Cl, 94.33(8); O'–Li–O, 96.8(3); O'–Li–Cl, 140.1(4); O–Li–Cl, 123.2(3); Li–Cl–Pb, 102.19(17); C(30)–O–Li', 145.3(3); C(30)–O–Li, 131.0(3); Li'–O–Li, 83.2(3).

Heterotetrametallic complex 2 is both light and temperature sensitive and will decompose to a black insoluble precipitate over the course of a day at ambient temperatures. We were unable to force complex 2 to eliminate lithium chloride by heating, sonicating, or addition of N, N, N', N'-tetramethylethylenediamine or AgOTf, the latter of which resulted in the immediate

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<sup>‡</sup> Electronic supplementary information (ESI) available: Fig. S1. Temperature dependent NMR spectra of **3** showing the change in resonances corresponding to the (2,6-di-tBu-4-MeC<sub>6</sub>H<sub>2</sub>) protons ( $T_c = 278$  K) and the N-(2,6-di-iPrC<sub>6</sub>H<sub>3</sub>) protons ( $T_c = 248$  K). See DOI: 10.1039/b707984b



Scheme 1 Reactivity of 1 with Li- and NaBHT (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide).

decomposition of the complex. The inability to convert 2 to our desired lead aryloxide was initially attributed to the bulky aryl substituent, that is, we postulated the desired lead-BHT complex (3) would be destabilized by interaction between the *tert*-butyl groups on the aryloxide and the isopropyl groups on the  $\beta$ diketiminate ligand. We reasoned that decreasing the steric bulk around the aryloxide ligand would make the synthesis of a leadaryloxide viable, indeed, treatment of complex 1 with lithio-2,4-ditert-butylphenoxide resulted in the formation of the lead aryloxide 4 after 30 min at room temperature (eqn (1)). This compound is stable indefinitely in the solid state, but will slowly decompose in solution. The X-ray crystal structure (Fig 2) revealed that the angles between the ligands around the metal centre to be even more acute than the chloride 1 (sum of the bond angles  $= 254.6^{\circ}$ , DP = 118%). The Pb–N bond lengths are similar to other BDI– Pb complexes and the Pb–O bond length of 2.182(4) Å is slightly shorter than Van Zandt's lead aryloxide dimer  $[Pb(OAr')_2]_2$  (Ar' = 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) of 2.229–2.257 Å.<sup>9</sup>



The viability of a [(BDI)Pb(BHT)] complex **3** appeared feasible from the structural data of **4**. The 2-*tert*-butyl group on the aryloxide ligand of **4** lies directly below the BDI-plane, leaving a void in front of the Pb–O bond that is potentially large enough to accommodate another tertiary butyl group. Space filling models of the postulated BHT complex **3** revealed that this species, although sterically crowded, is potentially viable. Lithium-chloride adducts of transition metals are not unusual, and, in a few notable examples, lithium chloride adducts have been isolated as apparent intermediates in salt metathesis reactions in which the lithium ion is bound to both the leaving group, such as an amido or alkoxide functional group, as well as the transition-metal



**Fig. 2** ORTEP diagram of compound **4** with H atoms omitted and C atoms minimized for clarity. Ellipsoid probably shown at 30%. Selected bond lengths (Å) and angles (°): Pb–N(1), 2.270(5); Pb–N(2), 2.288(5); Pb–O, 2.182(4); O–C(30), 1.345(8); N(1)–Pb–N(2), 82.34(19); N(1)–Pb–O, 83.32(18); N(2)–Pb–O, 88.97(18); Pb–O–C(30), 127.3(4).

bound chloride.<sup>21–24</sup> As there are significantly fewer examples of sodium-chloride adducts of transition metals potentially due to the weaker Na–Cl bond,<sup>25</sup> the BHT–aryloxide reagent was changed to NaBHT. This route was indeed successful as treatment of a toluene solution of chloride 1 with NaBHT resulted in clean formation of the aryloxide 3 after stirring overnight (Scheme 1). This complex is stable in the solid state but, similar to aryloxide 4, slowly decomposes in solution.

The X-ray crystal structure of **3** revealed slightly longer Pb– O (2.212(2) Å) and Pb–N bond lengths compared to **4** (Fig 3); however, the geometry around both the metal centre as well as the aryloxide ligand are considerably distorted as compared to complex **4**. For instance, in the latter, the bond angles around the lead metal centre ranged from  $82-89^{\circ}$ . In contrast, one of the N–Pb–O bond angles of the BHT complex **3** is significantly more obtuse ( $103.00(7)^{\circ}$ ), leading to a larger sum of bond angles ( $273.4^{\circ}$ ) and a 96.2% DP. In addition, the *ipso* carbon atom of the BHT ligand lies 0.198 Å out of the plane generated by the other ring carbons (note, in the solid state structure of **4**, this distance is only 0.073 Å). The solid-state structure also revealed the BHT aryloxide ligand to be canted towards one of the 2,6-isopropyl aryl rings of the BHT ligand. Although factors governing all of these distortions are unclear, some can be



**Fig. 3** ORTEP diagram of compound **3** with H atoms omitted and C atoms minimized for clarity. Ellipsoid probably shown at 30%. Selected bond lengths (Å) and angles (°): Pb–N(1), 2.309(2); Pb–N(2), 2.302(2); Pb–O, 2.212(2); O–C(30), 1.352(3); N(1)–Pb–N(2), 83.06(8); N(1)–Pb–O, 87.32(7); N(2)–Pb–O, 103.00(7); C(30)–O–Pb, 125.91(16).

attributed to solid-state packing forces. The canting of the BHT ligand was not observed in the solution phase as only two different environments were detected for the isopropyl groups, even at -78 °C. However, broadening of the resonances corresponding to the BHT ligand was observed at room temperature, indicative of hindered rotation around the Pb–O bond ( $\Delta G^{\ddagger} = 13 \text{ kcal mol}^{-1}$ ), similar to that observed in the [(BDI)Pb–N(SiMe<sub>3</sub>)<sub>2</sub>] system.<sup>14</sup> In addition, broadening of the *N*-aryl resonances was observed at RT, indicating a hindered rotation of the  $N_{aryl}$ -C bond ( $\Delta G^{\ddagger} = 16 \text{ kcal mol}^{-1}$ ). This restricted rotation has not been observed in other BDI–Pb systems and may be a function of the bulky aryloxide substituent.<sup>14</sup>

In conclusion, we have developed a reliable synthetic route towards the synthesis of rare terminal lead aryloxide complexes *via* salt metathesis from lead chloride complex **1**. We have isolated a lithium-lead heterotetrametallic complex, which initially appeared to be an intermediate in the salt metathesis pathway. However, as we were unable to force this complex to lose LiCl and form the desired BHT-aryloxide **3** and instead generated **3** from an alternative pathway, the validity of the complex as an actual intermediate in the salt metathesis pathway is in question. Reasons behind the solvent effect on the reaction outcome as well as factors governing the relative stability of the heterotetrametallic complex **2** compared to the lead-aryloxide complexes **3** and **4**, including DFT investigations, are currently in progress.

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