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Abnormal Reactions of Sterically Bulky Organometallics ArM (Ar=2,4,6-Tri-*t*-butylphenyl, M=Li or MgBr) with Lead Dichloride

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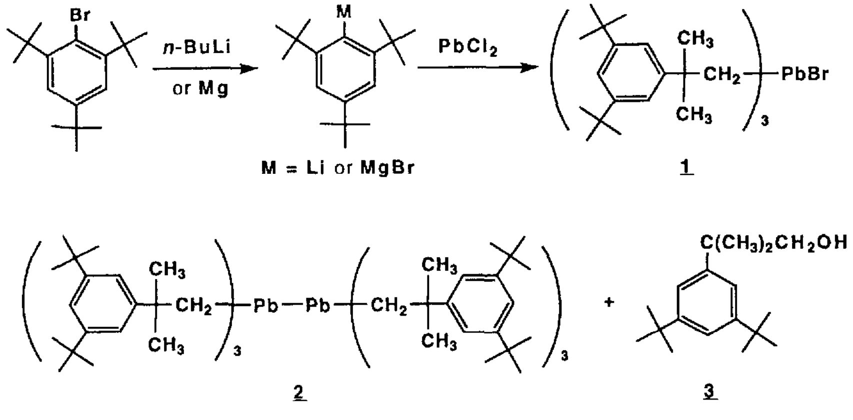
Abstract: *Reaction of **ArLi** (**Ar**: 2,4,6-tri-t-butylphenyl), generated from **ArBr** and n-BuLi, or **ArMgBr** with lead dichloride resulted in the formation of plumbane **Ar'$_3$PbBr**, diplumbane (**Ar'$_3$Pb**)$_2$, and **Ar'OH** having a rearranged group **Ar'** (**Ar'**: 2-(3,5-di-t-butylphenyl)-2-methylpropyl). The structure of **Ar'$_3$PbBr** was established by X-ray crystallographic analysis.*

The chemistry of sterically congested molecules have been of current interest because they not only exhibit interesting chemical properties[1] but also are very useful for kinetic stabilization of highly reactive molecules such as multiple-bond compounds of heavier typical elements.[2] During our study on sterically congested molecules[3] we became interested in the synthesis of organolead compounds having sterically bulky groups. We report here the abnormal reaction of 2,4,6-tri-*t*-butylphenyllithium (**ArLi**; **Ar** denotes 2,4,6-tri-*t*-butylphenyl hereafter) and the corresponding Grignard reagent **ArMgBr** with $PbCl_2$ giving organolead compounds bearing rearranged aralkyl substituents.

Reaction of **ArLi**, prepared from **ArBr** (813 mg, 2.5 mmol) and *n*-BuLi (1.60 *M* hexane solution, 1.72 ml, 2.75 mmol), with $PbCl_2$ (0.5 equiv) in THF at -78 °C afforded plumbane **1** (0.207 mmol, 25%), diplumbane **2** (0.051 mmol, 12%), and alcohol **3** (0.079mmol 3%).[4] When **ArMgBr** was allowed to react with $PbCl_2$ (0.5 equiv) in refluxing THF, **1** (14%), **2** (22%), and **3** (9%) were obtained (Scheme 1).



Scheme 1.

The structures of 1-3 were established by elemental analysis and spectral data.[5] Although the elemental analyses of 1 and 2 indicate the composition of $(Ar_3PbBr)_n$ and $(Ar_3Pb)_n$ respectively, their ^1H and ^{13}C NMR spectra clearly suggest that they contain 2-(3,5-di-*t*-butylphenyl)-2-methylpropyl groups (denoted as Ar' hereafter) of a rearranged skeleton instead of Ar groups. Futhermore, to our surprise, 1 was not a chloride but a bromide in the both reactions.[6] The ^1H NMR of 1 shows methylene protons at δ 1.96 with satellites of $^2J_{PbH}$ (31.4 Hz), two kinds of methyl protons with an 18:6 ratio, and two kinds of aromatic protons with a 2:1 ratio. The ^{13}C NMR of 1 is also consistent with the proposed rearranged structure; the methylene carbon α to Pb appearing at δ 58.6 shows satellites of $^1J_{PbC}$ (144.5 Hz). The patterns of ^1H and ^{13}C NMR spectra of 2 *are very similar to those of 1, suggesting 2 also has the rearranged Ar' group. The structure of 1 was finally* confirmed by X-ray crystallographic analysis as shown in Fig. 1.[7] In 1 the three Ar' groups are arranged like a pinwheel so that the bulky 2-(3,5-di-*t*-butylphenyl)propyl parts of the Ar' groups are separated as far as possible from each other.

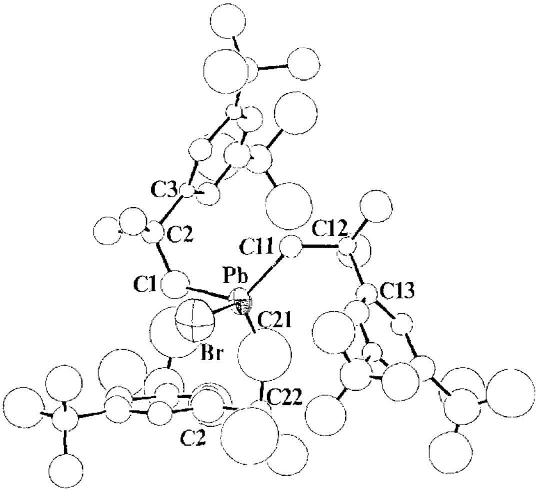
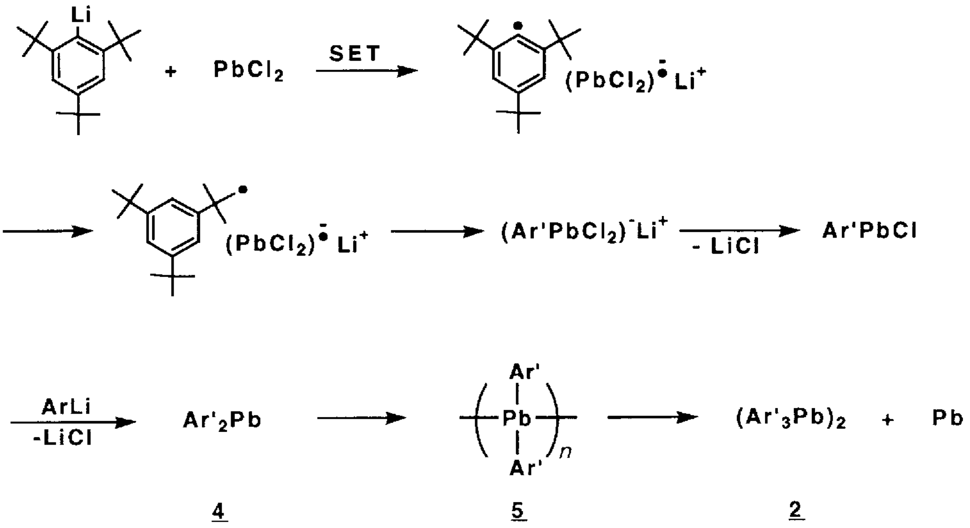


Fig. 1. *ORTEP* drawing of 1 ; Selected bond length (Å) and angles (deg) ; Pb-Br 2.656(7), Pb-C1 2.16(5), Pb-C11 2.15(4), Pb-C21 1.7(1), C1-C2 1.52(6), C11-C12 1.58(6), C21-C22 1.6(1), C2-C3 1.54(6), C12-C13 1.49(5), C22-C23 1.58(6), Br-Pb-C1 100(1), Br-Pb-C11 97(1), Br-Pb-C21 111(3), C1-Pb-C11 124(2), C1-Pb-C21 104(3), C11-Pb-C21 119(3), Pb-C1-C2 120(3), Pb-C11-C12 121(3), Pb-C21-C22 152(7), C1-C2-C3 116(4), C11-C12-C13 103(3), C21-C22-C23 96(5) ; Selected torsion angles (deg) ; Pb-C1-C2-C3 63(5), Pb-C11-C12-C13 -64(5), Pb-C21-C22-C23 49(15).

The reaction of 1 with t-butyllithium in THF resulted in the quantitative formation of 2, thus establishing the diplumbane structure of 2. The molecular weight obtained by vapor pressure osmometry in benzene (1780) is also indicative of the diplumbane structure (calcd *MW* 1884). The reaction of 1 with methyllithium yielded methylplumbane Ar'_3PbCH_3 in 83% yield.

Since 2,4,6-tri-*t*-butylphenyl (Ar) is a very useful group for kinetic stabilization, some attempts to introduce this group onto Group 14 elements have been reported. The reaction of ArLi with tetrafluorosilane gave Ar_2SiF_2,[8] while that with dichlorogermane·dioxane complex afforded an isomerized product resulting from insertion into the *o*-*t*-butyl group.[9] In the reactions with tin halides the products vary depending on the reagents and/or reaction conditions; reaction with $SnCl_2$ gives Ar_2Sn (though not isolated in a pure state but only detected by Mössbauer spectroscopy),[10] while those with SnX_4 (X = Cl, Br, I) afford Ar_2SnX_2, $ArAr'SnX_2$ or $ArAr'_2SnX$ with a rearranged group Ar' in some cases.[11] The reaction with $PbCl_2$ reported in the present study is unique in that all the Ar groups in the products exist as a rearranged form.

Although the mechanism for the skeletal rearrangement is not clear at present, we consider that it probably involves radical Ar• generated by electron transfer from ArLi to $PbCl_2$ since Ar• reportedly rearranges to afford radical Ar'•.[12] A plausible mechanism for the formation of **2** is shown in Scheme 2.



Scheme 2.

The initial intermediates, plumbylene **4**, polymerize to give polyplumbane **5**, which undergoes disproportionation to afford diplumbane **2** and lead metal.[13] Similar polymerization of divalent lead species and subsequent disproportionation of the polymer have been reported.[14]

The mechanism for the formation of **1** and **3** must await further experiments, which are currently in progress.

References and Notes

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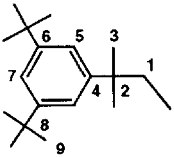
4. In addition to these products, 2,4,6-tri-*t*-butylphenol (1%) and 1,3,5-tri-*t*-butylbenzene (22%) were obtained.
5. Compounds **1** - **3** showed the following ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra in

$CDCl_3$. The following numbering was used for the assignment of ^{13}C NMR.



1: ^1H NMR δ 1.12(s, 18H), 1.33(s, 54H), 1.96(s, 6H; $^2J_{PbH}$ = 32.5 Hz), 7.14(d, J = 1.6 Hz, 6H), 7.28(t, J = 1.6 Hz, 3H); ^{13}C NMR δ 31.5(C9), 33.5(C3, $^3J_{PbC}$ = 76.9 Hz), 35.0(C8), 39.8(C2, $^2J_{PbC}$ = 28.1 Hz), 58.6(C1, $^1J_{PbC}$ = 144.5 Hz), 119.1(C5), 120.3(C7), 148.6(C4, $^3J_{PbC}$ = 32.4 Hz), 150.6 (C6). **2**: ^1H NMR δ 1.28(s, 108H), 1.43(s, 36H), 2.35(s, 12H; $^2J_{PbH}$ = 17.7 Hz), 7.19(t, J = 1.7 Hz, 6H), 7.24(d, J = 1.7 Hz, 12H); ^{13}C NMR δ 31.6 (C9), 33.3(C3, $^3J_{PbC}$ = 30.1 Hz), 35.0(C8), 40.4 (C2, $^2J_{PbC}$ = 27.6 Hz), 46.8(C1, $^1J_{PbC}$ = 51.3 Hz), 119.4(C5, C7), 149.9(C6), 151.5(C4, $^3J_{PbC}$ = 48.7 Hz). **3**: ^1H NMR δ 1.18(t, J = 6.8 Hz, 1H), 1.33(s,18H), 1.35(s,6H), 3.61(d, J = 6.8Hz, 2H), 7.23(d, J = 1.7 Hz, 2H), 7.30(t, J = 1.7 Hz, 1H); ^{13}C NMR δ 25.5(C3), 31.6(C9), 35.0(C8), 40.4 (C2), 73.3(C1), 120.3(C5, C7), 145.1(C4), 150.5(C6).

6. Anal. Calcd for $C_{54}H_{87}PbBr$ C, 63.37; H 8.57; Br 7.81%. Found C, 63.24; H, 8.50; Br 7.78%.
7. *Crystallographic data:* Compound **1**: $C_{54}H_{87}PbBr$, M = 1023.39, monoclinic, a = 9.99(1), b = 37.14(4), c = 15.00(1) Å, β = 102.26(7) °, V = 5437(9) Å^3, Z = 4, space group $P2_1/n$, D_c = 1.250 g cm^{-3}, μ = 38.84 cm^{-1}. The intensity data ($2\theta \leq 50$ °) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the structure was solved by direct methods. Among the non-hydrogen atoms only the lead and bromine atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2549 observed reflections [$I>3.00\sigma(I)$] and 235 variable parameters with R (R_w) = 0.120 (0.135). Although the refinement has not yet been converged with satisfactory agreement factors because of inferiority of the single crystal used, the crystallographic data here described sufficiently support the presupposed molecular structure of **1**. Preparation of a single crystal of good quality and further refinement are now in progress.
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