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Formation and Reactions of a Kinetically Stabilized Diarylplumbylene

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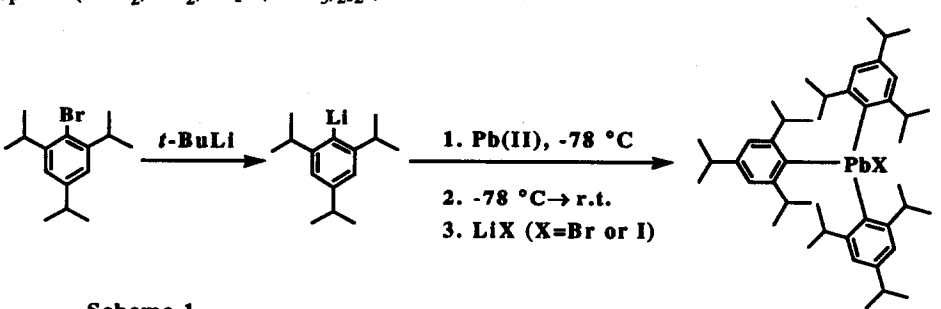
Abstract: Reaction of TipLi (Tip=triisopropylphenyl) with Pb(II) electrophiles resulted in the formation of a plumbylene stable in solution, which was trapped by MeI, $(PhS)_2$ or $(PhSe)_2$ giving the corresponding insertion products. In the absence of the trapping reagents the reaction afforded Tip_3PbX (X=Br or I).

We recently reported unexpected reactions of ArM (Ar=2,4,6-tri-*t*-butylphenyl, M=Li or MgBr) with lead dichloride.[1] This result led us to investigate reactions between other sterically crowded organolithium reagents and lead-containing electrophiles. Now we here describe novel formation and reactions of a kinetically stabilized plumbylene Tip_2Pb, which is obtained in the reaction of TipLi (Tip=2,4,6-triisopropylphenyl) with Pb(II) electrophiles ($PbCl_2$, PbI_2, $Pb[N(SiMe_3)_2]_2$[2]).



Scheme 1

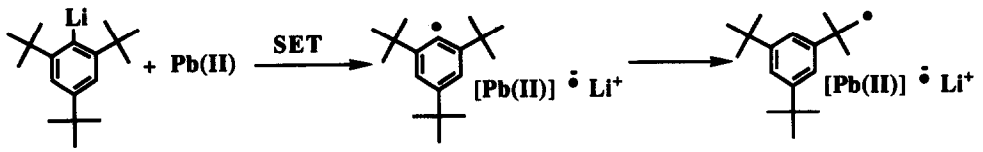
1 : X = Br

2 : X = I

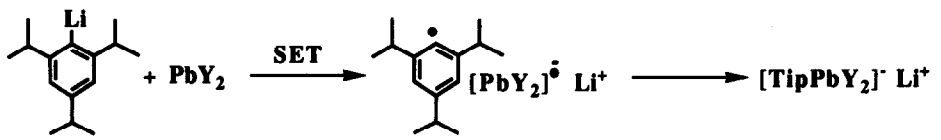
Table 1. Reactions of TipLi with Pb(II) electrophiles

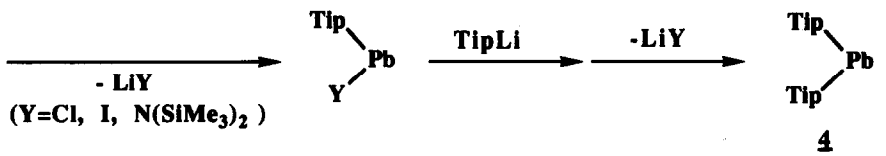
entry	electrophile	solvent	LiX	products (%)	
1	$PbCl_2$	THF	LiBr	**1** (10)	**3** (64)
2	PbI_2	THF	LiI	**2** (4)	**3** (75)
3	$Pb[N(SiMe_3)_2]_2$	ether	LiBr	**1** (20)	**3** (68)

Reactions of TipLi, generated from TipBr (253 μl, 1.0 mmol) and *t*-BuLi (n-pentane solution, 2.05 mmol), with Pb(II) electrophiles (0.5 mmol) in THF or ether at -78 °C afforded halotris(2,4,6-triisopropylphenyl)plumbanes 1, 2[3,4] and TipH 3 (Scheme 1, Table 1).



Scheme 2

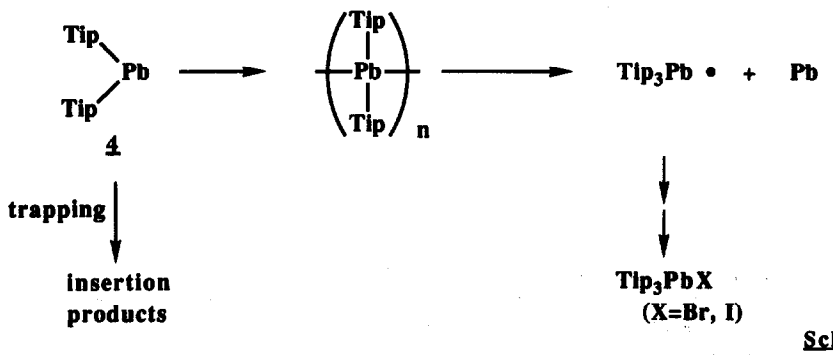




Scheme 3

Production of the trisubstituted plumbane, in which the lead atom is directly connected to the benzene ring in Tip group, was in remarkable contrast with the skeletal rearrangement in the reaction of ArM with lead dichloride (Scheme 2).[1] A plausible mechanism for the formation of 1 or 2 is illustrated in Schemes 3 and 4. Formation of a plumbylene 4 (Scheme 3) and its polymerization followed by disproportionation[5] (Scheme 4) were probably involved, since deposition of lead metal was observed in any cases.

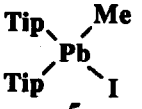
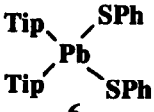
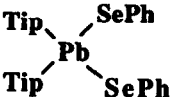
In order to clarify the intermediacy of the plumbylene 4, several trapping experiments were performed. Addition of TipLi (2 equiv.) in ether to an ether solution of $Pb[N(SiMe_3)_2]_2$ (1 equiv.) at -40 °C result-



Scheme 4

ed in a purple colored solution suggesting the formation of the plumbylene 4 (Scheme 3). To this solution were added trapping reagents (MeI, PhSSPh, PhSeSePh) and the reaction mixture was warmed slowly to room temperature. After the work up, the corresponding insertion products 5-7[6] were obtaind as shown in Table 2.

Table 2. Trapping of Plumbylene

entry	reagent	products	yield /%
1	MeI	 5	9
2	PhSSPh	 6	33
3	PhSeSePh	 7	30

Lappert et al. reported the preparation of the sole example of a kinetically stabilized plumbylene, $Pb[CH(SiMe_3)_2]_2$ in 3% yield,[7] which was trapped by $Mo(CO)_6$ to afford $[(Me_3Si)_2CH]_2PbMo(CO)_5$ in 4% yield.[8] It is most difficult to trap a plumbylene among bivalent species of group 14 elements, since it easily polymerizes to undergo disproportionation. The attempted reaction of $Pb[CH(SiMe_3)_2]_2$ with MeI resulted in the formation of PbI_2, and no addition product was isolated.[8] The successful isolation of the insertion product of 4 to C-I bond, *i.e.* $Tip_2Pb(Me)I$ (5), is in sharp contrast with the Lappert's result.

Seyferth et al.[9] described oxidative addition of dimethylstannylene into S-S bond of $(\mu\text{-}S_2)Fe(CO)_6$. We have demonstrated that effective trapping with PhSSPh and PhSeSePh also proceeds for a plumbylene. These are the first examples of insertion reactions of a plumbylene.

Direct observation of Tip_2Pb (4) by NMR and UV spectroscopy is under current investigation.

References and Notes

1. R. Okazaki, K. Shibata, and N. Tokitoh, *Tetrahedron Lett.*, **1991**, *32*, 6601.
2. D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, **1974**, 895.
3. Products were obtained as an inseparable mixture of Tip_3PbX (X = Cl, Br, I). Treatment of the mixture with excess amount of LiBr or LiI in THF at room temperature, afforded pure Tip_3PbBr or Tip_3PbI respectively.
4. Bromotris[2,4,6-(1-methylethyl)phenyl]plumbane 1: m.p. 176-178 °C; Anal. Calcd for $C_{45}H_{69}BrPb$: C, 60.25; H, 7.75; Br, 8.91%. Found: C, 59.97; H, 7.61; Br, 9.19%; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.04 (brd, 36H, J = 6.0 Hz), 1.20 (d, 18H, J = 6.9 Hz), 2.83 (sept, 3H, J = 6.9 Hz), 3.20 (brs, 6H), 7.08(s, 6H, $^4J_{PbH}$ = 50.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.9 (CH_3 in para *i*-Pr), 25.5 (CH_3 in ortho *i*-Pr), 34.1 (CH in para *i*-Pr), 37.4 (CH in ortho *i*-Pr, $^3J_{PbC}$ = 73.0 Hz), 124.3 (meta arom., broad), 149.9 (para arom.), 154.1 (ortho arom.), 163.4 (ipso arom., $^1J_{PbC}$ = 487.5 Hz); ^{207}Pb NMR ($CDCl_3$, 18.7 MHz) δ -126.3. For 2: ^1H NMR ($CDCl_3$, 500 MHz) δ 1.03 (brd, 36H, J = 6.4 Hz), 1.20

(d, 18H, 6.9 Hz), 2.81 (sept, 3H, 6.9 Hz), 3.28 (brs, 6H), 7.05 (s, 6H, $^4J_{PbH}$ = 58.8 Hz).

5. P. G. Harrison, In *Comprehensive Organometallic Chemistry*; G. Wilkinson; F.G.Stone; E.W.Abel, Eds.; Pergamon Press: Oxford, Engrand, **1982**; p.670.
6. Spectral data for 5: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.10 (d, 12H, *J* = 6.7 Hz), 1.11 (d, 12H, *J* = 6.7 Hz),1.19 (d, 12H, *J* = 6.9 Hz), 2.18 (s, 3H, $^2J_{PbH}$ = 59.7 Hz), 2.82 (sept, 2H, *J* = 6.9 Hz), 3.16 (sept, 4H, *J* = 6.7 Hz), 7.03 (s, 4H, $^4J_{PbH}$ = 48.6 Hz); Spectral data for 6: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.97 (d, 24H, *J* = 6.7 Hz), 1.19 (d, 12H, *J* = 7.0 Hz), 2.80 (sept, 4H, *J* = 6.7 Hz), 2.81 (sept, 2H, *J* = 6.7 Hz), 6.98(s, 4H,$^4J_{PbH}$ = 57.7 Hz), 7.03 (m, 6H), 7.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.0 (CH_3 in para *i*-Pr), 24.4 (CH_3 in ortho *i*-Pr), 34.1 (CH in para *i*-Pr), 37.6 (CH in ortho *i*-Pr, $^3J_{PbC}$ = 70.3 Hz), 123.2 (meta in Tip, $^3J_{PbC}$ = 96.1 Hz), 126.7 (para in SPh), 127.9 (meta in SPh), 135.6 (ipso in SPh, $^2J_{PbC}$ = 35.8 Hz), 135.9 (ortho in SPh), 150.4 (para in Tip, $^4J_{PbC}$ = 21.4 Hz), 153.4 (ortho in Tip, $^2J_{PbC}$ = 91.3 Hz), 161.2 (ipso in Tip, $^1J_{PbC}$ = 502.5 Hz). Spectral data for 7: ^{1}H NMR ($CDCl_3$, 500 MHz) 0.95 (d, 24H, *J* = 6.8 Hz), 1.19 (d, 12H, *J* = 6.8 Hz), 2.82 (sept, 6H, *J* = 6.8 Hz), 6.94 (s, 4H, $^4J_{PbH}$ = 56.8 Hz), 7.01 (dd, 4H, *J* = 7, 7 Hz), 7.07 (tt, 2H, *J* = 7, 1 Hz), 7.40 (dd, 4H, *J* = 7, 1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.0 (CH_3 in para *i*-Pr), 24.4 (CH_3 in ortho *i*-Pr), 34.4 (CH in para *i*-Pr), 37.8 (CH in ortho *i*-Pr, $^3J_{PbC}$ = 70.3 Hz), 123.0 (meta in Tip, $^3J_{PbC}$ = 86.2 Hz), 127.1 (para in SePh), 128.1 (meta in SePh), 128.7 (ipso in SePh), 137.3 (ortho in SePh), 150.1 (para in Tip, $^4J_{PbC}$ = 19.8 Hz), 153.3(ortho in Tip, $^2J_{PbC}$ = 84.8 Hz), 159.0 (ipso, $^1J_{PbC}$ = 430.6 Hz); ^{77}Se NMR ($CDCl_3$, 17.0 MHz) δ 931.4; ^{207}Pb NMR ($CDCl_3$, 18.7 MHz) δ -268.6.
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9. D. Seyferth, R. S. Henderson, and M. K. Gallagher, *J. Organomet. Chem.*, **1980**, *193*, C75.

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