Isolation, Structural Characterization, and Photochemical Study of an Acylplumbane, Mes_3PbCOR, R = Me, Ph

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Summary: The reaction between (trimesitylplumbyl)lithium, Mes_3PbLi, and acyl chlorides, RCOCl, R = Ph, Me, led to the high yield formation of the first isolable, stable acylplumbanes, Mes_3PbCOR, R = Me (1), Ph (2). Single crystal X-ray analysis of 2, which crystallized in space group $P\bar{1}$, $a = 9.1530(10)$ Å, $b = 12.378(3)$ Å, $c = 14.197(3)$ Å, $\alpha = 75.25(2)°$, $\beta = 75.530(10)°$, $\gamma = 82.16(2)°$, confirmed the structure. Ultraviolet irradiation of 2 in methanol resulted in the unusual formation of methyl benzoate, a result also observed upon thermal decomposition of 2 in methanol.

Subsequent to the initial report by Brook on the synthesis of an acylsilane,[1a] the chemistry[1b,c] and photochemistry[1b,d] of acylsilanes, -germanes, and -stannanes have been well-studied and documented. However, there exists only a single report concerning the transient observation of an analogous acylplumbane, R_3PbCOR.[2] In 1971 Willemsens reported that a yellow solution observed at −30 °C in THF contained acetyltriphenyllead, $Ph_3PbCOMe$, as determined by infrared and ^1H NMR spectroscopy. An infrared stretching frequency at 1694 cm^{-1} and a methyl resonance at 2.69 ppm indicated the presence of the acetyl compound, but attempts to isolate this material resulted in recovery of only acetophenone, hexaphenyldilead, and metallic lead.

A methodology for stabilization of organometallic compounds containing bonding patterns that normally evade isolation involves the use of the mesityl group, Mes. This may be exemplified by the isolation of a silicon–silicon double bonded compound, i.e. tetramesityldisilene.[3] We report the use of the mesityl group to synthesize the first stable, characterizable, acylplumbanes, Mes_3PbCOR, R = Me, Ph, eq 1.[4]

Both acylplumbanes are air-stable yellow crystalline compounds. The acetyl compound, 1, exhibited the onset

$$\mathrm{Mes_3Pb{-}PbMes_3 + Li} \rightarrow 2[\mathrm{Mes_3Pb}]^{-}\mathrm{Li}^{+} \xrightarrow{\mathrm{RCOCl}} \mathrm{Mes_3PbCOR} \quad (1)$$

of decomposition at 140 °C whereas the benzoyl derivative, 2, exhibited a melting point at 155–7 °C. These data illustrate the stability engendered by the mesityl groups. An infrared study (hexane) exhibited ν(CO) for the new compounds, 1 = 1688.3 cm^{-1}, 2 = 1649.7 cm^{-1}, in the anticipated region on the basis of the reported ν(CO) for the triphenylacetyl compounds of C (1710 cm^{-1}), Si (1644 cm^{-1}), Ge (1669 cm^{-1}), and Sn (1670 cm^{-1}).[6] It has been established that substituents on the different group 14 elements do not appreciably alter these stretching frequencies, thus the comparison between the triphenylmethyl, -silyl, -germyl, and -stannyl compounds and the trimesityllead compounds is appropriate. The value for the Pb acetyl compound more closely resembles the C analogs, indicating the effect of the metal is significantly less than that exerted by Si, Ge, or Sn. Both 1 and 2 exhibit a visible spectrum (hexane) (1, $\lambda_{max} = 382$ ($\epsilon = 700$); 2, $\lambda_{max} = 448$ ($\epsilon = 400$)) in the region expected for the n–π^* transition of the acyl group 14 metalloids and metals.[1] The acetyl compound exhibits a degree of fine structure to this band whereas the benzoyl compound exhibits a broad featureless absorption. In the Si, Ge, and Sn compounds the n–π^* bands are weak with extinction coefficients in the 200–300 range, thus the values for the acyl lead compounds are somewhat greater.

Further characterization was possible using NMR spectroscopy. Compounds 1 and 2 exhibited ^{207}Pb resonances ($CDCl_3$) at −431.7 and −429.5 ppm and ^{13}C acyl carbon resonances at 249.9 and 245.3 ppm, respectively, in accord with expectation.

We have performed a single crystal X-ray structural analysis on 2. The structure is illustrated in Figure 1.[7] The carbonyl C=O bond length of 1.200(11) Å is marginally shorter than those reported for various Si and Ge acyl compounds,[8] which cluster around 1.23 and 1.22 Å, respectively, and is essentially similar to normal ketone

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[1] (a) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373. (b) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *17*, 95. (c) Mitchell, T. N. *J. Organomet. Chem.* **1992**, *439*, 127. (d) Dalton, J. C. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, p 149.

[2] Willemsens, L. C. *J. Organomet. Chem.* **1971**, *27*, 45.

[3] Fink, M. J.; Michalczyk, K.; Haller, R.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

[4] In a typical experimental procedure 1.0 g (0.89 mmol) of hexamesityldillead[5] in 30 mL of THF was stirred overnight with 0.1 g of Li (14.3 mmol) in a 100-mL round-bottomed flask under argon and the yellow solution became a charcoal-gray slurry of $[Mes_3Pb]^-Li^+$. This slurry was cannulated into a 100-mL three-necked flask and was treated with a 30-mL THF solution of benzoyl chloride (0.3 g, 2.14 mmol) at −78 °C over 30 min. Subsequent to complete addition the mixture was stirred at the low temperature for 2 h and then permitted to warm to room temperature and the solvent removed under vacuum to yield a yellow solid residue. This was recrystallized from hexane to form 0.31 g (0.46 mmol, 26%) of benzoyltrimesityllead, **2**. The acetyl derivative, 1, was synthesized in a similar manner in 35% yield. The spectroscopic data and elemental analyses for 1 and 2 are in accord with expectations. **1** (mp 140 °C dec): ^1H NMR ($CDCl_3$, ppm) 2.21 (s, Me), 2.23 (s, Me), 2.48 (s, MeCO, ^3J(Pb–H = 22 Hz), 6.9 (bd, Ph); ^{13}C NMR ($CDCl_3$, ppm) 20.9 (Me), 25.8 (Me), 41.8 (MeCO), 128.8, 137.8, 143.9, 158.9 (Ar), 249.9 (CO); ^{207}Pb NMR ($CDCl_3$, ppm) −431.7; IR (hexane) ν(CO) 1688.3 cm^{-1}. Anal. Calcd (found): C, 56.7 (57.3); H, 6.22 (5.92). **2** (mp 155–157 °C): ^1H NMR ($CDCl_3$, ppm) 2.47 (s, Me), 2.53 (s, Me), 7.04, 7.14–8.4 (Ar); ^{13}C NMR ($CDCl_3$, ppm) 21.7 (Me), 26.5 (Me), 128.9, 130.8, 133.6, 134.8, 137.9, 144.2, 159.5, 162.7 (Ar), 245.3 (CO); ^{207}Pb NMR ($CDCl_3$, ppm) −429.5; IR ν(CO) 1649.7 cm^{-1}. Anal. Calcd (found): C, 60.9 (61.0); H, 5.72 (5.72).

[5] (a) Lesbre, M.; Satgé, J.; Voigt, D. *Comput. Rend.* **1958**, *246*, 594. (b) Sebald, A.; Harris, R. K. *Organometallics* **1990**, *9*, 2096.

[6] Peddle, G. J. D. *J. Organomet. Chem.* **1966**, *5*, 486.

[7] Crystallographic data for **2**: triclinic, space group $P\bar{1}$, $a = 9.1530(10)$ Å, $b = 12.378(3)$ Å, $c = 14.197(3)$ Å, $\alpha = 75.25(2)°$, $\beta = 75.530(10)°$, $\gamma = 82.16(2)°$, $V = 1501.6(5)$ Å^3, $Z = 2$, $d_{calcd} = 1.48$ Mg/m^3. A total of 4248 reflections were measured at 298 °C (2θ range 3.5–45.0° using Mo Kα radiation, $\lambda = 71.073$ pm) on a Siemens R3m/V diffractometer. The structure was solved by direct methods (SHELXTL PLUS) using 3266 absorption corrected reflections ($I > 4\sigma_I$; $R = 0.032$, $R_w = 0.035$).

[8] (a) Chieh, P. C.; Trotter, J. *J. Chem. Soc. A* **1969**, 1778. (b) Harrison, R. W.; Trotter, J. *J. Chem. Soc. A* **1968**, 258. (c) Sharma, H. K.; Vincenti, S. P.; Vicari, R.; Cervantes, F.; Pannell, K. H. *Organometallics* **1990**, *9*, 2109. (d) Sharma, H. K.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1991**, *409*, 321.

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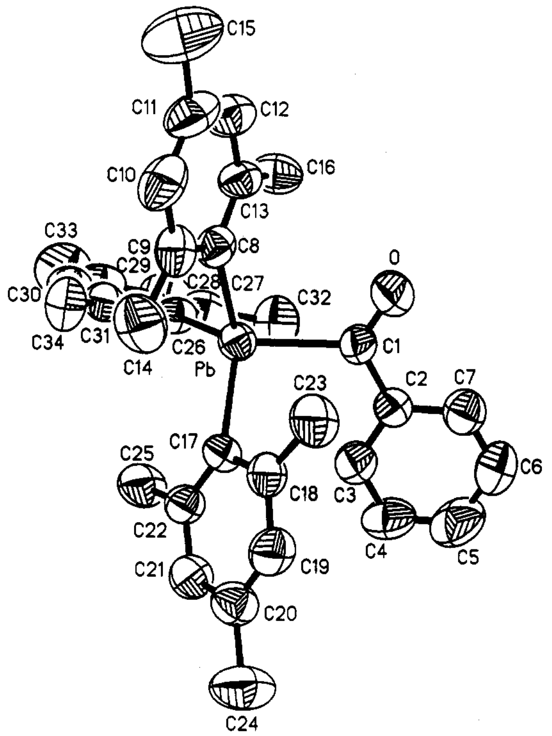

Figure 1. Molecular structure of $(Mes)_3PbCOPh$, **2**. Bond lengths (Å): Pb–C(1) = 2.329(8); Pb–C(8) = 2.250(7); Pb–C(17) = 2.242(8); Pb–C(26) = 2.250(6); C(1)–O = 1.200(11); C(1)–C(2) = 1.487(10). Bond angles (deg): C(1)–Pb–C(8) = 104.9(3); C(1)–Pb–C(17) = 98.3(3); C(1)–Pb–C(26) = 116.9(3); Pb–C(1)–C(2) = 121.4(6); O–C(1)–Pb = 117.6(5); O–C(1)–C(2) = 120.8(7).

bond lengths. This feature of the lead acyls correlates with their higher CO stretching frequencies. The angles about acyl—carbon are normal; however, there is a significant deviation from the tetrahedral angles around Pb (i.e. the C—Pb—C angles (deg) are 117.4(3), 116.9(3), 116.2(3), 103.2(2), 104.9(3), and 98.3(3)).

We have made a preliminary study of the photochemical behavior of **2** in methanol with, and without, added base. In the former case a range of organic products were obtained as analyzed via IR, GC/mass spectrometry, and HPLC, eq 2.

$$\mathrm{Mes_3PbCOPh + MeOH \rightarrow \underset{57\%}{PhC(O)OMe} + \underset{38\%}{MesH} + \underset{5\%}{PhCHO}} \qquad (2)$$

The formation of small amounts of benzaldehyde suggests a Norrish type II cleavage occurred similar to that reported in the case of photolysis of acylsilanes in base-free methanol.[9] However, the formation of high yields of methyl benzoate, an unexpected product, indicates that the photochemistry is more complex. We suggest that, together with the Norrish type II cleavage of the lead–acyl carbon bond, a competitive photochemical solvolysis of the lead–mesitylene carbon bond occurs, leading to transient formation of $Mes_2PbCOPh(OMe)$ which undergoes a reductive elimination of methyl benzoate and formation of Mes_2Pb, eq 3.

$$\mathrm{Mes_3PbCOR + MeOH \rightarrow Mes_2PbCOPh(OMe) + MesH}$$

$$\mathrm{Mes_2PbCOPh(OMe) \rightarrow [Mes_2Pb] + PhC(O)OMe} \qquad (3)$$

The fate of the lead containing products suggested is presently unclear. Normally, diaryllead(II) species further disproportionate to hexaaryldilead, tetraaryllead, and metallic Pb. Trapping by methanol to form $Mes_2Pb(OMe)H$ and subsequent formation of dilead compounds are possible, and sparingly soluble lead containing compounds are formed in conjunction with the organic products described; however to date they have defied complete characterization.

Photochemistry of **2** in the presence of pyridine (catalytic amount as per the Brook rearrangement conditions for acylsilanes) yields only mesitylene and methyl benzoate. It appears that the base interacts with the acyl group and eliminates the Norrish II photochemistry. Thermal treatment of **2** in MeOH also leads to formation of mesitylene and methyl benzoate (no benzaldehyde), indicating that the process taking place is both thermal and photochemical. This is reminiscent of the observation by Bassindale, Brook, and Harris that thermal treatment of acylsilanes led to formation of siloxycarbene intermediates, thus paralleling their photochemistry.[10] It is noteworthy that we observed no decomposition, neither photochemical nor thermal, that led to elimination of mesitylphenyl ketone, as might be expected from the data reported for the transiently observed $Ph_3PbCOMe$.[2] We continue detailed studies on the acyllead compounds and general utility of the trimesityllead group.

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Supplementary Material Available: Tables of crystal data, data collection, and refinement, complete bond lengths and bond angles, torsion angles, anisotropic thermal parameters, atomic coordinates, and H atom positional parameters (10 pages). Ordering information is given on any current masthead page.

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(9) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 454.

(10) Bassindale, A. R.; Brook, A. G.; Harris, R. *J. Organomet. Chem.* **1975**, *90*, C6.