Generation of Bis[2,6-di(4-methoxy-phenyl)phenyl]plumbylene and its Insertion into n-Butyliodide to Give a Tetrahedral Triorganolead(IV) Iodide

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Dedicated to Professor H. Schumann on the occasion of his 65th birthday
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Introduction

There is currently widespread interest in the chemistry of carbenes and their heavy atom analogues ER₂, the silylenes, germylenes, stannylenes, and plumbylenes (E = C, Si, Ge, Sn, Pb). A recent review reflects the activities in these areas of Organometallic Chemistry in the last decade [1].

While diorganocarbenes R₂C are mostly unstable, transient species, the derivatives of the heavier congeners of carbon gain in stability on descending Group IV of the Periodic Table. Stable carbene analogues, mainly with bulky alkyl and aryl groups, have been isolated and structurally characterized. While the stability of ER₂ compounds increases with the mass of the central atom E, the reactivity of these species is greatly reduced. Relativistic effects (the “inert pair effect”) make R₂Sn and in particular R₂Pb compounds much poorer nucleophiles and electrophiles. The knowledge about the reactivity pattern of plumbylenes is therefore rather limited [1].

Following related studies in the chemistry of diarylgermylenes [2] we have recently also investigated the preparation and reactivity of some new diarylplumbylenes. There are several reports on stable monomeric Ar₂Pb compounds in the literature, which all feature extremely bulky aryl groups Ar with branched substituents in the ortho-positions of the ipso-arene carbon atom [3 - 5]. Sterically less crowded groups Ar lead to reduced shielding of the lead centers and hence to dimerization to give tetrapyridiplumbylenes R₂Pb=PbR₂ [6, 7].

In the present study a new ligand was designed, which can sufficiently stabilize the plumbylene Ar₂Pb, but also allows for a certain reactivity, e. g. towards insertion substrates. 2,6-Diphenyl-phenyl (“terphenyl”) substituents have proved to be suitable ligands for Ar₂E molecules in the past because of their wing-like shielding of the metal atom E. The nucleophilic character of E in such bis(“terphenyl”)plumbylenes can be enhanced by electron-donating substituents in the periphery of the Ar group where they are not able to interfere with the chemistry at the lead atom. Substituents in the ortho-positions are less suitable because of the resulting excessive crowding and/or the danger of direct interaction with the metal atom.

2,6-Bis(4-methoxy-phenyl)phenyl (“Bipap”) groups were therefore chosen as the target substituents for Ar₂E molecules and the ArLi reagents.
Preparative Results

2,6-Bis(4-methoxy-phenyl)-1-iodo-benzene (Bipapl) was prepared in a Grignard reaction between 2,6-dibromo-1-iodo-benzene and 4-bromoanisol in tetrahydrofuran at reflux temperature in 61% yield. The colourless crystalline product was metallated using equivalent quantities of n-butyllithium in hexane/diethylether at room temperature to give BipapLi. Pale yellow crystals were obtained in 83% yield and shown to be the dietherate by spectroscopic and X-ray techniques (below and Exp. Part) (eq. (1) and (2)).

Addition of anhydrous PbCl₂ to the reaction mixture obtained from Bipapl and n-BuLi in the molar ratio 1:2 at -60°C and slow warming to room temperature gave a dark precipitate which slowly dissolved upon continued stirring at 20 °C. From the resulting green solution a yellow crystalline product could be isolated in 73% yield and identified as the triorganolead iodide (n-Bu)(Bipap)₂PbI. It is the insertion product of the plumbylene (Bipap)₂Pb into the n-BuI by-product of the primary reaction (eqs (2), (3)).

(n-Bu)(Bipap)₂PbI was identified by its analytical, spectroscopic and structural data. The NMR spectra are proof of the equivalence of the two Bipap ligands in the molecule. Only one set of ¹H and ¹³C signals is observed. The intensity ratio for the Bipap and Bu resonances is in agreement with the proposed composition. In the mass spectrum (CI) the plumbylene cation (Bipap)₂Pb⁺ is detected as the ion of highest mass. It appears that under the conditions of this experiment the retro-insertion (eq. (4)) takes place.

Structural Results

BipapLi

The structure of BipapLi dietherate has been determined by single crystal X-ray diffraction methods. Pale yellow crystals obtained from n-hexane/diethylether at -35 °C are monoclinic, space group C2/c with Z = 4 formula units and eight molecules of diethylether in the unit cell. The lattice contains discrete molecules of the 1:2 adduct (Bipap)Li · (OEt₂)₂ with no unusual sub-van der Waals contacts. The molecule has crystallographical C₂-symmetry with the twofold axis passing through the atoms C3, C4 and Li (Fig. 1).

The lithium atom is three-coordinate with the carbon atom C4 and the oxygen atoms O/O' as nearest neighbours. The configuration of the metal atom is planar by symmetry, but the angle O-Li-O [116.1(2)°] is smaller and the angles O-Li-C4 [121.9(1)°] are larger than 120°. The distance Li-
C4 = 2.128(4) Å is surprisingly long and indicates a largely polar interaction between these two atoms. The Li-O distances [1.954(2) Å] are in the expected range.

In the literature there are several reports on structures of related aryllithium compounds which show close similarities to the findings for BipapLi • (OEt2)2. The parent “terphenyl” compound, 2,6-diphenyl-phenyl-lithium, 2,6-P2C6H3Li, was investigated (as the dietherate) by Robinson et al., who also found a C2-symmetrical molecular skeleton [Li-C 2.106(9) Å] [8]. Among the “tetraphenyl” analogues, 2,4,6-triphenyl-phenyl-lithium 2,4,6-P3C6H3Li • (OEt2)2 was investigated both by Power and Olmstead [9] (at –130 K) as well as by Girolami, Suslick et al. [10] (at 299 K). The two forms have slightly different molecular geometries (with and without C2-symmetry). The Li-C distances are 2.074(2) and 2.08(2) Å, respectively, both significantly shorter than in BipapLi • dietherate. 2,6-Bis[2,4,6-triisopropyl-phenyl]phenyl-lithium crystallizes with only one Et2O molecule [11]. The adduct has two-coordinate lithium atoms with a C-Li distance of 2.017(7) Å. The unsolvated compound forms dimeric molecules [12], as do other donor-free aryllithiums [13].

(n-Bu)(Bipap)2Pbl

The yellow crystals of this compound (from toluene at –35 °C) are monoclinic, space group P21/n with Z = 4 formula units in the unit cell. The lattice contains no solvent and there are no unusual contacts between the monomeric units. The lead atom is strictly four-coordinate with one Pb-I, one Pb-C(alkyl) and two Pb-C(aryl) bonds: Pb-I 2.8490(8), Pb-C3 2.288(10), Pb-C1 2.278(8) and Pb-C2 2.240(10) Å.

This new triorganolead(IV) iodide therefore appears to be the first compound of this type which is strictly monomeric in the solid state and has no iodine bridging between lead atoms and no auxiliary donor ligand [14]. The Pb-I distance in (n-Bu)(Bipap)2Pbl [2.8490(8) Å] can thus be taken as an important benchmark value for an unperturbed lead(IV)-iodine bond.

This value is to be compared with Pb-I-Pb bridge bonds of 3.038 and 3.360 Å [Pb-I-Pb 108.1°] in Me3PbI [15] or with the terminal Pb-I bond in (4-MeO-C6H4)(4-Me-C6H4)[2-Me2NCH2-C6H4]PbI with penta-coordinated lead atoms, which is 2.956 Å long [16, 17].

Discussion

It has been shown in the past that plumbynes Ar2Pb with extremely bulky groups Ar can be isolated as metastable species. However, these heavy carbene analogues show strongly reduced nucleophilic and electrophilic character and react only very sluggishly in substitution or oxidative addition reactions. In the present work it has been demonstrated that diarylplumbynes with suitably designed aryl substituents (reduced steric bulk, electron-donating substituents in the periphery of the ligands) can be easily subjected to nucleo/elecrophilic insertion reactions with alkyl halide substrates. The products are stable triorganolead halides which are not associated in the solid state.

Experimental Part

General methods: The experiments were carried out under an atmosphere of dry nitrogen using Schlenk tech-
2,6-Dibromoiodobenzene was prepared and purified according to published procedures [18]. Solvents were appropriately dried, distilled, and saturated with dry nitrogen. All NMR spectra were recorded at 20 °C on a Jeol JNM-LA 400 spectrometer (1H at 400.05, 13C at 100.50 MHz) in sealed tubes with predried C6D6 as solvent. The numbering of H and C atoms for assignment of NMR data (Fig. 3) is different from the scheme used for X-ray data. Mass spectra were recorded with a Finnigan MAT 90 spectrometer (chemical ionisation, isobutane) and with an analytical gas-liquid chromatography unit Hewlett-Packard 5890, Series II (column HP1, cross-linked methylsilicon gum 12 m/0.2 mm, film thickness 0.33 μm) with a mass selective detector HP MS 5971 A (electron impact ionisation, 70 eV). Microanalyses were performed in-house by combustion.

BipapLi: A suspension of magnesium chips (7.25 g, 0.3 mol) in 300 ml of tetrahydrofuran was activated with a few drops of 1,2-dibromoethane with stirring. Ten percent of a solution of 4-bromoanisol (50.7 g, 0.27 mol) in 300 ml of tetrahydrofuran was added and stirring continued until a mildly exothermic reaction commenced. The addition was slowly continued to maintain reflux of the solvent. After completion of the addition, reflux was maintained for another 2 h. A solution of 2,6-dibromoiodobenzene (28.0 g, 77.4 mmol) in 100 ml of tetrahydrofuran was then added dropwise at room temperature over a period of 1 h, and the reaction mixture stirred for another 3 h. Iodine (33.4 g, 0.13 mol) was added to -35 °C and stirring continued over night. A solution of Na2SO3 (16.6 g) in water (400 ml) was used to destroy the excess iodine in a separatory funnel. The aqueous layer was separated and washed twice with 100 ml of toluene. The combined organic layers were washed with 200 ml of water, followed by 250 ml of a saturated aqueous NaCl solution. MgSO4 was then used to dry the organic phase and the solvents were evaporated after filtration. Most of the iodoanisol by-product was removed by vacuum distillation at 66 °C/22 mbar. Recrystallization of the crude product from isopropanol/toluene (3:1, v/v) gave colourless needle-like crystals (19.4 g, 61%). NMR, 1H: δ 3.30 (s, 6H, OMe), 6.80 (d, J 8.4 Hz, 4H, H1/4), 7.03 (t, J 7.3 Hz, 1H, H3), 7.12 (d, J 7.3 Hz, 2H, H3/5), 7.27 (d, J 8.4 Hz, 4H, H2/6); 13C: δ 55.0 (OMe), 106.0 (C1), 113.9 (C3/5), 127.8 (C4), 129.2 (C3/5), 131.2 (C2/6), 139.0 (C2/6), 159.8 (C4). MS (El): m/z 416.3 [M]+, 289.4 [M]-1, 274.3 [M+-I-Me], 258.3 [M+-2C6H4OMe]. C20H17O2I (416.25): calcd. C 57.23, H 4.12; found: C 57.23; H 4.08.

Bipap[PbBu+]2: To a slurry of BipapI (1.8 g, 4.3 mol) in a mixture of 2 ml of hexane and 10 ml of diethyl ether was added at 20 °C. 2.8 ml of a 1.6 M solution of n-BuLi in hexane (4.5 mol) and the reaction mixture stirred for 30 min. The resulting clear yellow solution was reduced in volume to incipient crystallization. Subsequent cooling to -35 °C gave pale yellow crystals (1.59 g, 83 %). NMR, 1H: 1.09 (t, J 7.3 Hz, 12H, MeC), 3.30 (s, 6H, MeO), 3.34 (q, J 7.3 Hz, 8H, CH2), 6.79 (d, J 8.0 Hz, 4H, H3/5), 7.12 (t, J 7.3 Hz, 1H, H3), 7.43 (d, J 7.3 Hz, 2H, H3/5), 7.45 (d, J 8.0 Hz 4H, H2/6). 13C: 15.3 (MeC), 58.9 (MeO), 65.8 (CH2), 113.4 (C3/5), 126.6 (C3/5), 128.3 (C2/6), 130.7 (C4), 135.7 (C7), 143.2 (C2/6), 159.2 (C4), 176.9 (C1).

(n-BuBipap)2PbI: 2.25 ml of a 1.6 M solution of n-BuLi in hexane (3.92 mmol) was added with stirring at -60 °C to a slurry of BipapI (1.48 g, 3.56 mmol) in 10 ml of diethyl ether. Stirring was continued for 1 h and PbCl2 (0.50 g, 1.78 mmol) was added. The reaction mixture was allowed to warm to room temperature within 1 h, during which time a dark precipitate formed. After stirring for another hour at room temperature the precipitate dissolved and the solution turned green. The volatile components were evaporated in vacuo. Extraction of the residue with 20 ml of toluene and cooling of the solution to -35 °C gave yellow crystals (1.02 g, 73%). NMR, 1H: 0.86 (t, J 7.3 Hz, 3H, MeC), 1.22 (tq, J 7.2 and 7.3 Hz, 2H, MeCH2), 1.50 (t, J 8.8 Hz, 2H, CH2Pb), 1.93 (tt, J 8.8 and 7.2 Hz, 2H, CH2Pb), 3.41 (s, 12H, MeO), 6.77 (d, J 8.2 Hz, 8H, H3/5), 6.92 (t, J 7.1 Hz, 2H, H4), 7.07 (d, J 7.1 Hz, 4H, H3/5), 7.30 (d, J 8.2 Hz, 8H, H2/6). 13C: 13.5 (MeC), 27.1 (CH2Pb), 33.1 (CH2Pb), 46.1 (MeCH2), 54.9 (MeO), 114.2 (C3/5), 125.8 (C3/5), 129.2 (C2/6), 131.1 (C4), 136.6 (C1), 142.0 (C2/6), 149.6 (C4), 159.3 (C4). MS(Cl): m/z 785.9 [(Bipap)2Pb]+, 553.7 [BipapBuPb]+, 290.4 [Bipap]+. C44H43I04Pb (969.92): calcd. C 57.23, H 4.12; found: C 56.65, H 4.73.

Crystal structure determinations

The data for (Bipap)2PbI · 2 Et2O and (n-Bu)(Bipap)2PbI were collected on a Nonius DIP2020 image plate system and an Enraf Nonius CAD4 diffractometer, respectively, using graphite-monochromated Mo-Kα radiation. Data of (n-Bu)(Bipap)2PbI were corrected for absorption effects (μMo-Kα = 48.9 cm-1); psi-scans, Tmin/Tmax = 0.527/0.641). The structures were solved by a combi-
nation of direct methods and difference-Fourier syntheses and refined by full matrix least-squares calculations on $F^2$. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their corresponding C atoms with fixed isotropic contributions. Crystal data for (Bipap)Li $\cdot 2$ Et$_2$O, $C_{28}H_{37}LiO_4$. $M_t = 444.52$, pale yellow crystal, monoclinic, $a = 14.998(1)$, $b = 14.474(1)$, $c = 12.289(1)$, $\alpha = 105.249(4)^\circ$, space group $C2/c$, $Z = 4$, $V = 2573.8(3)$ $\text{Å}^3$, $\rho_{\text{calc}} = 1.147$ g cm$^{-3}$, F(000) = 960; $T = -130^\circ$C. 5389 measured and 2826 unique reflections [$R_{\text{int}} = 0.019$]; 153 refined parameters, $wR2 = 0.1386$, $R = 0.0590$ for 2290 reflections $[F_o \geq 2\sigma(F_o)]$ used for refinement. Residual electron densities: +0.16 / -0.14 e Å$^{-3}$. The function minimized was: $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.1197$, $b = 8.47$. Important interatomic distances and angles are given in the figure captions. Anisotropic thermal parameters and complete lists of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC 149198 and 149199.

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