

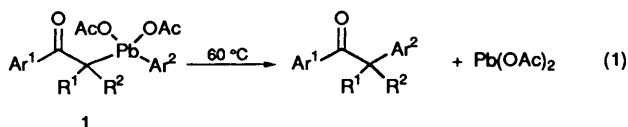
## Preparation of Diorganolead Dicarboxylates from Aryllead Triacetates: an Investigation of Ligand Coupling in some Diorganolead(IV) Compounds

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Aryllead triacetates have been found to react with arylboronic acids and vinylboronic acids to give diaryllead and aryl(vinyl)lead diacetates, respectively, in high yield. Symmetrical divinyllead diacetates are also readily accessed by reaction between vinylboronic acids and lead tetraacetate. It has been shown that diaryllead, aryl(vinyl)lead, and divinyllead diacetates produced in this way undergo a copper(I)-catalysed coupling to yield biaryls, vinylaromatics and buta-1,3-dienes, respectively, in high yield. With unsymmetrical diorganolead diacetates, it has been found that the coupling is not intramolecular, and thus the three possible products are produced.

The C-arylation of  $\beta$ -dicarbonyl compounds and other soft nucleophiles by aryllead(IV) triacetates has been investigated in considerable detail during the last 15 years.<sup>1</sup> More recently, attention has been focused on the mechanism of this reaction, and there is now ample proof that aryl free radicals are not involved.<sup>2-4</sup> Although there is only indirect evidence,<sup>5</sup> it would appear that they probably belong to that growing group of reactions of hypervalent species known as ligand-coupling reactions,<sup>6</sup> a suggestion first made by Sir Derek Barton.<sup>2</sup>

The indirect evidence for ligand-coupling came from our study of the thermal reactions of a group of aryl(phenacyl)lead diacetates of type **1**. For compounds where  $R^1, R^2 \neq H$ , these diorganolead(IV) compounds were thermally unstable, giving modest yields of deoxybenzoin derivatives and lead(II) acetate when heated in chloroform at *ca.* 60 °C [reaction (1)]. The least



stable of these compounds was an  $\alpha, \alpha$ -dimethyl derivative (*i.e.* **1** in which  $R^1 = R^2 = \text{Me}$ ), while the most stable was an unsubstituted compound (where  $R^1 = R^2 = \text{H}$ ). Since our study excluded the possibility that the C-C bond-forming reaction depicted in reaction (1) involved aryl radical formation, and since symmetrical products resulting from intermolecular reactions were not formed, we concluded that the deoxybenzoin derivatives were produced in a ligand coupling process.

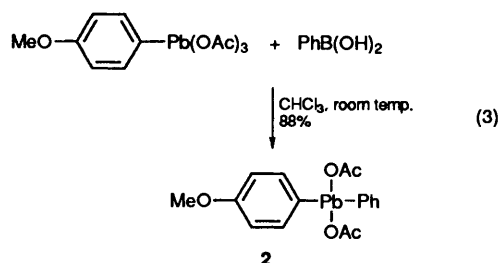
Attempts to observe intermediates such as **1** in reactions between  $\beta$ -dicarbonyl compounds and aryllead triacetates have so far been unsuccessful and, therefore, if formed, must be highly unstable; this would be expected in view of the destabilising effect of substitution on the  $\alpha$ -carbon in compounds of type **1**.

In this paper we examine the possibility of ligand coupling in diaryllead diacetates, aryl(vinyl)lead diacetates, and divinyllead diacetates. Although such diorganolead diacetates are known,<sup>7,8</sup> the reported methods of synthesis are only useful for obtaining symmetrical compounds. In seeking a more flexible route to such compounds we turned to the boron-lead exchange method we had employed to prepare aryllead triacetates [reaction (2)].<sup>9</sup> During that work, it was found that treatment

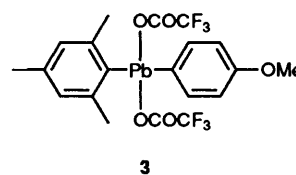


of phenylboronic acid with lead tetraacetate, in the absence of a catalytic amount of mercury(II) acetate, gave a mixture of phenyllead triacetate and diphenyllead diacetate. The absence

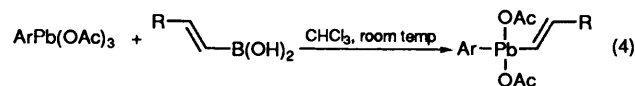
of any other products suggested that treatment of an aryllead triacetate with an arylboronic acid may provide a simple route to diaryllead diacetates. This proved to be the case with the reaction between *p*-methoxyphenyllead triacetate and phenylboronic acid in chloroform at room temperature producing the diaryllead diacetate **2** in high yield [reaction (3)]. In a similar



way, reaction of *p*-methoxyphenyllead triacetate with mesitylboronic acid followed by treatment with trifluoroacetic acid gave an almost quantitative yield of the diaryllead bis(trifluoroacetate) **3**.

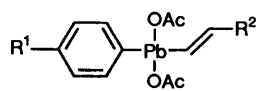


The above route to diaryllead diacetates was readily adapted to the synthesis of aryl(vinyl)lead diacetates; this involved reaction of an aryllead triacetate with a vinylboronic acid as shown in reaction (4). The four compounds, phenyl[(*E*)-



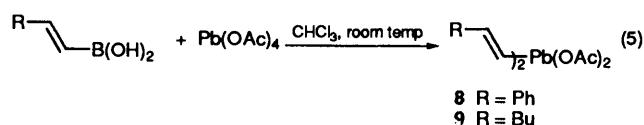
styryl]lead diacetate **4**, (*E*)-hex-1-enyl(phenyl)lead diacetate **5**, *p*-methoxyphenyl[(*E*)-styryl]lead diacetate **6**, and (*E*)-hex-1-enyl(*p*-methoxyphenyl)lead diacetate **7**, produced in this way were all obtained in good yield and there was no evidence for the introduction of more than one vinyl group to lead.

This behaviour of vinylboronic acids with lead(IV) acetates makes it possible to access, very simply, a wide range of divinyllead diacetates. Thus, treatment of 2 equiv. of (*E*)-styrylboronic acid with lead tetraacetate gave bis[(*E*)-styryl]-

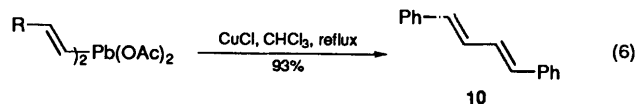


- 4 R<sup>1</sup> = H, R<sup>2</sup> = Ph  
 5 R<sup>1</sup> = H, R<sup>2</sup> = Bu  
 6 R<sup>1</sup> = MeO, R<sup>2</sup> = Ph  
 7 R<sup>1</sup> = MeO, R<sup>2</sup> = Bu

lead diacetate **8** in high yield [reaction (5)]. Bis[*(E)*-hex-1-enyl]lead diacetate **9**, a relatively unstable compound, was also obtained in this way.

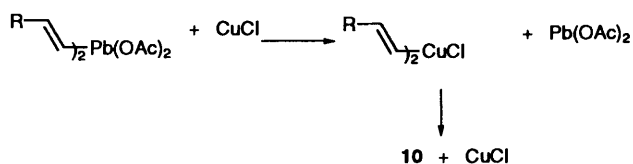


**Examination of Ligand Coupling.**—Our initial investigation of possible ligand coupling in the above diorganolead compounds was carried out with distyryllead diacetate **8**. Unlike the aryl(phenacyl)lead diacetates,<sup>5</sup> compound **8** was quite stable in refluxing chloroform and chloroform–pyridine. However, it was eventually found that the required carbon–carbon coupling could be brought about by copper catalysis. For example, compound **8** when heated with copper(II) acetate (1 equiv.) in chloroform gave a moderate yield (61%) of (*E,E*)-1,4-diphenylbuta-1,3-diene **10**. It appeared likely that copper(I) was the effective species since a similar reaction with copper(I) chloride in place of copper(II) led to faster formation of the diene **10** in almost quantitative yield [reaction (6)]. Small quantities (3–5%



by NMR spectroscopy) of styryl acetate were also produced in this reaction.

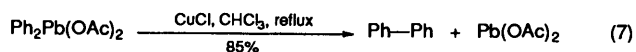
It seemed likely that the major reaction pathway involved oxidative addition of the two vinyl residues to copper(I), followed by a ligand coupling in the copper(III) species thus generated (Scheme 1), as has been proposed for other coupling



Scheme 1

reactions involving copper reagents.<sup>6,10</sup> In support of such a mechanism, the reaction proved to be catalytic in copper(I); the diene **10** could be isolated in 73% yield when the reaction was carried out with 0.1 equiv. of copper(I).

The reaction could also be extended to diaryllead diacetates, as demonstrated by the isolation of biphenyl in high yield when diphenyllead diacetate was refluxed in chloroform with 1.0 equiv. of copper(I) chloride [reaction (7)]. However, the

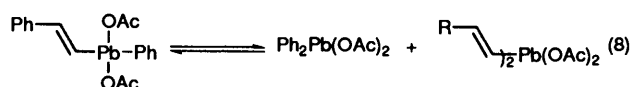


potentially more useful specific intramolecular coupling in unsymmetrical diorganolead diacetates proved to be not achievable. As can be seen from Table 1, reactions of the

diorganolead compounds **2**, **4** and **6** under the conditions employed in reaction (7) gave the three possible coupled products, in each case in ratios which were not very different from those expected for non-specific coupling.

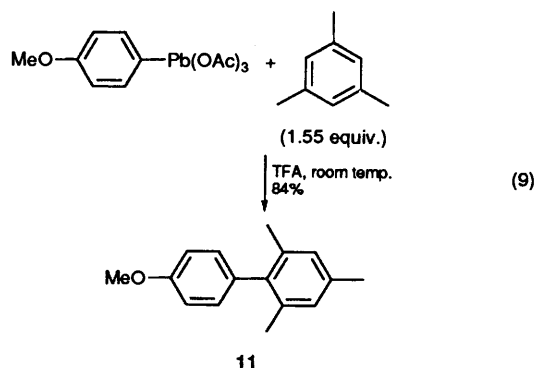
In a final attempt to achieve the desired reaction, *p*-methoxyphenyl(phenyl)lead diacetate **2** was heated with degassed Raney Ni in chloroform. These conditions had been found useful in producing biaryls in good yields from diaryltellurium dichlorides; however, only symmetrical compounds had been examined in that study.<sup>11</sup> Although the percentage of the unsymmetrical biaryl, 4-methoxybiphenyl, was enhanced (75%) the total yield (42%) of biaryls was poor.

With regard to the mechanism which we tentatively propose for the copper(I)-catalysed coupling, it should be pointed out that the results could also be accommodated by an intramolecular coupling following a fast exchange of the ligands on lead(IV) as shown in reaction (8) for compound **4**. Similar



exchanges have been observed for tellurium(IV) compounds<sup>11</sup> and for arylidiodine(III) compounds.<sup>12</sup> Possible support for such a proposal comes from the failure of *p*-methoxyphenyllead triacetate to yield any 4,4'-dimethoxybiphenyl when heated with copper(I) chloride in chloroform.

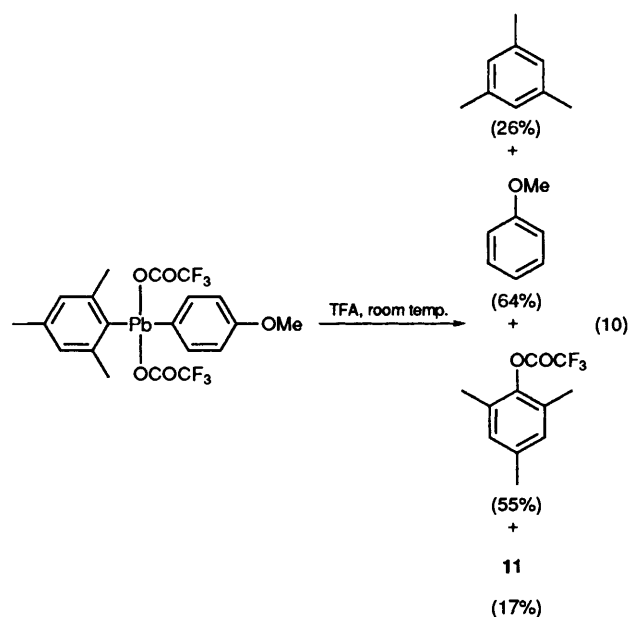
During the course of this work a question arose concerning the mechanism of the high-yielding biaryl-forming reaction we reported early in our study of the chemistry of aryllead(IV) triacetates.<sup>13</sup> An example of this biaryl synthesis is shown in reaction (9), and from our detailed investigation of the reaction



we came to the conclusion that it was cationic in nature with the rate-determining step being formation of a  $\pi$ -complex between the arene and the aryllead(IV) diacetate cation. The possibility that, for the reaction shown [reaction (9)] the diaryllead(IV) bistrifluoroacetate **3** was on the reaction pathway and collapsed in trifluoroacetic acid to the biaryl **11** was not considered at that time. We have now addressed this question with an examination of the effect of trifluoroacetic acid on the diaryllead compound **3** [reaction (10)]. Although some of the biaryl **11** was produced, the low yield (17%) excludes the lead(IV) compound **3** as an intermediate in reaction (9) and reinforces our view that the reaction proceeds by the previously proposed cationic mechanism.<sup>13</sup> The products formed in reaction (10) can all be explained in terms of the two possible protodemetalations of the starting material, and subsequent reaction of the two aryllead trifluoroacetates produced with either trifluoroacetic acid alone or with mesitylene or anisole in the presence of trifluoroacetic acid.<sup>13</sup>

**Table 1** Copper(I) catalysed C–C coupling in diorganolead diacetates

R <sup>1</sup> R <sup>2</sup> Pb(OAc) <sub>2</sub>		Products (ratio %)			
R <sup>1</sup>	R <sup>2</sup>	R <sup>1</sup> –R <sup>1</sup>	R <sup>1</sup> –R <sup>2</sup>	R <sup>2</sup> –R <sup>2</sup>	Total yield (%)
Ph	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	15	54	31	74
Ph	( <i>E</i> )-PhCH=CH	18	55	27	77
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	( <i>E</i> )-PhCH=CH	21	62	17	66



### Experimental

For general experimental procedures see our earlier paper.<sup>14</sup> Phenylboronic acid was purchased from Aldrich Chemical Company. *p*-Methoxyphenylboronic acid,<sup>9</sup> mesitylboronic acid,<sup>9</sup> (*E*)-styrylboronic acid,<sup>15</sup> (*E*)-hex-1-enylboronic acid,<sup>15</sup> *p*-methoxyphenyllead triacetate<sup>16</sup> and phenyllead triacetate<sup>17</sup> were prepared by previously reported methods.

**Synthesis of *p*-Methoxyphenyl(phenyl)lead Diacetate 2.**—The cyclic anhydride of phenylboronic acid (0.344 g, 1.105 mmol) was added to *p*-methoxyphenyllead triacetate (1.628 g, 3.316 mmol) in chloroform (20 cm<sup>3</sup>) and the mixture was stirred at room temperature for 30 h. The resulting solution was then filtered through Celite and concentrated to ca. 3 cm<sup>3</sup>. The concentrate was treated with light petroleum (40 cm<sup>3</sup>) and kept at 4 °C overnight to yield the *title compound 2* (1.49 g, 88%) as needles, m.p. 172–175 °C (decomp.) (Found: C, 39.0; H, 3.4. C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>Pb·H<sub>2</sub>O requires C, 38.7; H, 3.8%); δ<sub>H</sub>(CDCl<sub>3</sub>) 2.04 (6 H, s, 2 × OCOMe), 3.83 (3 H, s, OMe), 6.96 and 7.64 (4 H, AA'BB', <sup>207</sup>Pb satellites gave *J*<sub>Pb,ortho</sub> 174, 3-H and 5-H, 2-H and 6-H respectively), 7.39 (1 H, m, 4'-H), 7.47 (2 H, m, 3'-H and 5'-H) and 7.73 (2 H, m, <sup>207</sup>Pb satellites gave *J*<sub>Pb,ortho</sub> 189, 2'-H and 6'-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 22.7 (2 × OCOMe), 55.3 (OMe), 116.0 (C-3 and C-5), 130.7 (C-2' and C-6' or C-3' and C-5'), 130.8 (C-4'), 134.1 (C-2' and C-6' or C-3' and C-5'), 135.4 (C-2 and C-6), 161.3 (C-1'), 161.4 (C-4), 162.1 (C-1) and 181.7 (2 × C=O); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1491, 1433, 1395, 1341 and 1160.

**Synthesis of *p*-Methoxyphenyl(2,4,6-trimethylphenyl)lead Bis(trifluoroacetate) 3.**—2,4,6-Trimethylphenylboronic acid (0.861 g, 5.25 mmol) was added to a stirred solution of *p*-methoxyphenyllead triacetate (2.455 g, 5.0 mmol) in dry chloroform (30 cm<sup>3</sup>) and the mixture was stirred at room temperature for 24 h. The mixture was washed with water (20 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and evaporated at 40 °C, and

finally at reduced pressure (1 mmHg). The crude diaryllead diacetate was dissolved in dry chloroform (5 cm<sup>3</sup>) and trifluoroacetic acid (0.85 cm<sup>3</sup>) and then pumped at 1 mmHg to remove acetic acid and solvent. This treatment was repeated until the <sup>1</sup>H NMR spectrum showed no residual acetate ligands. The yellow crystalline solid was dissolved in dry chloroform (20 cm<sup>3</sup>), filtered through Celite, washed with chloroform (2 × 10 cm<sup>3</sup>) and the solvent evaporated at 50 °C to give the *title compound 3* (3.120 g, 94.5%) as pale yellow crystals, m.p. 163–165 °C (Found: C, 36.8; H, 3.0. C<sub>20</sub>H<sub>18</sub>F<sub>6</sub>O<sub>5</sub>Pb requires C, 36.4; H, 2.8%); δ<sub>H</sub>(CDCl<sub>3</sub>) 2.33 (3 H, s, Me, <sup>207</sup>Pb satellites gave *J*<sub>Me,Pb</sub> 8.9), 2.58 (6 H, s, 2 × Me, <sup>207</sup>Pb satellites gave *J*<sub>Me,Pb</sub> 19.5), 3.86 (3 H, s, OMe), 7.16 (2 H, s, 2 × mesityl ArH, <sup>207</sup>Pb satellites gave *J*<sub>3,Pb</sub> 98), 7.20 and 7.70 (4 H, AA'BB', <sup>207</sup>Pb satellites gave *J*<sub>3,Pb</sub> 57 and *J*<sub>2,Pb</sub> 160, 3-H and 5-H, 2-H and 6-H, respectively); δ<sub>C</sub>(CDCl<sub>3</sub>) 21.1 (4-Me, <sup>207</sup>Pb satellites gave *J*<sub>Me,Pb</sub> 22), 23.1 (2-Me and 6-Me, <sup>207</sup>Pb satellites gave *J*<sub>Me,Pb</sub> 113), 55.6 (OMe), 117.2 (ArH *ortho* to OMe, <sup>207</sup>Pb satellites gave *J*<sub>CH,Pb</sub> 171), 117.6 (q, CF<sub>3</sub>, *J*<sub>C,F</sub> 287), 131.3 (ArH, <sup>207</sup>Pb satellites gave *J*<sub>CH,Pb</sub> 165), 134.4 (ArH, <sup>207</sup>Pb satellites gave *J*<sub>CH,Pb</sub> 154), 140.8 (C–CH<sub>3</sub> *ortho* to Pb, <sup>207</sup>Pb satellites gave *J*<sub>C,Pb</sub> 127), 142.7 (C–CH<sub>3</sub> *para* to Pb, <sup>207</sup>Pb satellites gave *J*<sub>C,Pb</sub> ca. 31), 156.3 (C–Pb), 161.8 (C–Pb), 162.4 (C–OCH<sub>3</sub>, <sup>207</sup>Pb satellites gave *J*<sub>C,Pb</sub> ca. 33) and 165.6 (q, C–CF<sub>3</sub>, *J*<sub>C,CF</sub> 40).

**Synthesis of Phenyl[(*E*)-styryl]lead Diacetate 4.**—(*E*)-Styrylboronic acid (359 mg, 2.43 mmol) was added to a solution of phenyllead triacetate (1.018 g, 2.21 mmol) in chloroform (30 cm<sup>3</sup>), and the mixture was stirred at room temperature for 18 h. After filtration through Celite, the solution was concentrated to ca. 5 cm<sup>3</sup> and light petroleum (50 cm<sup>3</sup>) was added. The solution was cooled at 0 °C for 24 h to yield the *title compound 4* as colourless crystals, m.p. 183–185.5 °C (Found: C, 43.0; H, 3.7. C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>Pb requires C, 42.8; H, 3.6%); δ<sub>H</sub>(CDCl<sub>3</sub>) 2.05 (6 H, s, 2 × OCOMe), 7.30–7.41 (6 H, m, 4'-H and C<sub>6</sub>H<sub>5</sub>CH), 7.45 (2 H, m, 3'-H and 5'-H), 7.46 (1 H, d, *J* 16.2, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 380, CH=CHPb), 7.55 (1 H, d, *J* 16.2, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 428, CH=CHPb) and 7.72 (2 H, d, *J* 7.0, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 180, 2'-H and 6'-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 22.8 (Me), 127.4 (*ortho*-styryl or *meta*-styryl), 128.6 (*ortho*-styryl or *meta*-styryl), 129.7 (CH=CHPb), 130.7 (C-2' and C-6' or C-3' and C-5'), 130.8 (C-2' and C-6' or C-3' and C-5'), 133.8 (styryl quaternary), 135.8 (C-4'), 146.9 (*para*-styryl), 148.7 (CH=CHPb), 161.7 (C-1') and 181.9 (2 × C=O); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1574, 1556, 1490 and 1427.

**Synthesis of (*E*)-Hex-1-enyl(phenyl)lead Diacetate 5.**—(*E*)-Hex-1-enylboronic acid (0.52 g, 4.1 mmol) was added to a solution of phenyllead triacetate (1.70 g, 3.7 mmol) in chloroform (12 cm<sup>3</sup>). The mixture was stirred for 24 h at 40 °C and then filtered through Celite. The filtrate was concentrated to ca. 4 cm<sup>3</sup> and diluted with light petroleum (60 cm<sup>3</sup>) to precipitate the *title compound 5* (0.96 g, 54%) as an unstable waxy solid, m.p. 97–102 °C (decomp.); δ<sub>H</sub>(CDCl<sub>3</sub>) 0.88 (3 H, t, *J* 6.8, Me), 1.20–1.49 (4 H, m, 2 × CH<sub>2</sub>), 1.95 (6 H, s, 2 × Me), 2.09 (2 H, m, CH<sub>2</sub>), 6.49 (1 H, dt, *J* 15.4, 6.7, CH=CHPb), 6.67 (1 H, d, *J* 15.4, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 511, CH=CHPb), 7.29–7.49 (3 H, m, ArH) and 7.70 (2 H, br d, *J*<sub>ortho</sub> 8.4, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 168, 2'-H and 6'-H); δ<sub>C</sub>(CDCl<sub>3</sub>) 13.4 (Me),

21.8 (CH<sub>2</sub>), 22.8 (2 × Me), 29.9 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 131.1 (C-3' and C-5'), 134.0 (C-2', C-4', C-6'), 148.7 (vinylic C), 150.1 (vinylic C), 163.5 (C-1') and 182.5 (2 × C=O);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1568, 1435 and 1394.

**Synthesis of *p*-Methoxyphenyl[(*E*)-styryl]lead Diacetate 6.**—(*E*)-Styrylboronic acid (400 mg, 2.68 mmol) was added to a solution of *p*-methoxyphenyllead triacetate (120 g, 2.44 mmol) in chloroform (12 cm<sup>3</sup>) and the mixture was stirred at room temperature for 4 h. After this it was filtered through Celite and the filtrate was concentrated to ca. 2 cm<sup>3</sup>. It was then diluted with light petroleum (50 cm<sup>3</sup>) and kept at 0 °C for 40 h to yield the *title compound* **6** (1.13 g, 87%) as colourless crystals, m.p. 205–208 °C (decomp.) (Found: C, 42.3; H, 3.7. C<sub>19</sub>H<sub>20</sub>O<sub>5</sub>Pb requires C, 42.6; H, 3.8%);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.98 (6 H, s, 2 × Me), 3.82 (3 H, s, OMe), 7.04 (2 H, m, *J*<sub>ortho</sub> 8.0, 3'-H and 5'-H), 7.31–7.48 (5 H, m, Ph), 7.44 (1 H, d, *J* 16.0, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 340, CH=CHPb), 7.66 (1 H, d, *J* 16.0, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 430, CH=CHPb) and 7.78 (2 H, m, *J*<sub>ortho</sub> 8.0, 2'-H and 6'-H);  $\delta_{\text{C}}(\text{CDCl}_3)$  23.0 (2 × Me), 55.1 (OMe), 115.2 (C-3' and C-5'), 127.0 (*ortho*-phenyl or *meta*-phenyl), 128.6 (*ortho*-phenyl or *meta*-phenyl), 129.0 (CH=CHPb), 135.9 (quaternary phenyl), 143.3 (*para*-phenyl), 153.1 (CH=CHPb), 156.2 (C-4'), 160.7 (C-1') and 181.0 (2 × C=O);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1572, 1533, 1491 and 1398.

**Synthesis of (*E*)-Hex-1-enyl(*p*-methoxyphenyl)lead Diacetate 7.**—(*E*)-Hex-1-enylboronic acid (0.486 g, 3.80 mmol) was added to a solution of *p*-methoxyphenyllead triacetate (1.70 g, 3.46 mmol) in chloroform (15 cm<sup>3</sup>), and the mixture was stirred at room temperature for 24 h. The solution was then filtered through Celite and the filtrate was concentrated to ca. 3 cm<sup>3</sup>. It was then diluted with light petroleum (60 cm<sup>3</sup>) and kept at –20 °C for 24 h to yield the *title compound* **7** (1.31 g, 74%), a slightly unstable colourless solid, m.p. 127–129 °C (decomp.) (Found: C, 39.6; H, 4.7. C<sub>17</sub>H<sub>24</sub>O<sub>5</sub>Pb requires C, 39.6; H, 4.7%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.90 (3 H, t, *J* 6.8, Me), 1.34 (2 H, tq, *J* 7.2 and 6.8, CH<sub>2</sub>), 1.43 (2 H, tt, *J* 7.6 and 7.2, CH<sub>2</sub>), 2.02 (6 H, s, 2 × Me), 2.22 (2 H, ddt, *J* 6.9, 7.6 and 1.5, CH<sub>2</sub>), 3.80 (OMe), 6.59 (1 H, dt, *J* 15.8 and 6.9, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 320, CH=CHPb), 6.82 (1 H, dt, *J* 15.8 and 1.5, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 500, CH=CHPb), 7.02 and 7.63 (4 H, AA'BB', <sup>207</sup>Pb satellites gave *J*<sub>Pb,ortho</sub> 166 and *J*<sub>Pb,meta</sub> 52.0, 2'-H and 6'-H, 3'-H and 5'-H, respectively);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.7 (Me), 22.1 (CH<sub>2</sub>), 22.7 (2 × Me), 30.2 (CH<sub>2</sub>), 35.3 (CH<sub>2</sub>), 55.3 (OMe), 116.0 (C-3' and C-5'), 135.4 (C-2' and C-6'), 148.4 (CH=CHPb), 151.2 (CH=CHPb), 152.8 (C-4'), 161.5 (C-1') and 181.9 (2 × C=O);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1572, 1552, 1491, 1425 and 1398.

**Synthesis of Bis[(*E*)-styryl]lead Diacetate 8.**—(*E*)-Styrylboronic acid (591 mg, 4.00 mmol) was added to a solution of lead tetraacetate (887 mg, 2.00 mmol) in chloroform (8 cm<sup>3</sup>), and the mixture was stirred at room temperature for 1 h. The solution was filtered through Celite and the filtrate was concentrated to ca. 2 cm<sup>3</sup>. It was then diluted with light petroleum (50 cm<sup>3</sup>) and kept overnight at 0 °C to yield the *title compound* **8** (0.828 g, 78%) as colourless crystals, m.p. 196–198 °C (decomp.) (Found: C, 44.9; H, 3.7. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub>Pb requires C, 45.2; H, 3.8%);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.08 (6 H, s, 2 × Me), 7.18 (4 H, m, *meta*-styryl), 7.22–7.29 (6 H, m, *ortho* and *para*-styryl), 7.43 (2 H, d, *J* 16.2, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 330, CH=CHPb) and 7.59 (2 H, d, *J* 16.2, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 435, CH=CHPb);  $\delta_{\text{C}}(\text{CDCl}_3)$  23.0 (2 × Me), 127.3 (*ortho* or *meta*-styryl), 128.7 (*ortho* or *meta*-styryl), 129.7 (<sup>207</sup>Pb satellites gave *J*<sub>Pb,C</sub> 5280, CH=CHPb), 135.4 (<sup>207</sup>Pb satellites gave *J*<sub>Pb,C</sub> 296 Hz, quaternary styryl), 146.4 (*para*-styryl), 148.6 (<sup>207</sup>Pb satellites gave *J*<sub>Pb,C</sub> 1287, CH=CHPb) and 181.9 (2 × C=O);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1570, 1548, 1504 and 1427.

**Synthesis of Bis[(*E*)-hex-1-enyl]lead Diacetate 9.**—(*E*)-Hex-1-enylboronic acid (0.268 g, 2.10 mmol) was added to a solution of lead tetraacetate (0.443 g, 1.00 mmol) in chloroform (5 cm<sup>3</sup>) at room temperature and the mixture was stirred for 1 h at room temperature. The solution was then filtered through Celite and the filtrate was concentrated to ca. 1 cm<sup>3</sup>. It was then diluted with light petroleum (50 cm<sup>3</sup>) and kept for 24 h at 0 °C to yield the *title compound* **9** (0.280 g, 57%) as an unstable solid, m.p. 157–160 °C (decomp.);  $\delta_{\text{H}}(\text{CDCl}_3 + (\text{CD}_3)_2\text{SO})$  0.92 (6 H, t, *J* 7.5, 2 × Me), 1.26–1.40 (4 H, m, 2 × CH<sub>2</sub>), 1.40–1.50 (4 H, m, 2 × CH<sub>2</sub>), 1.96 (6 H, s, 2 × OMe), 2.24 (4 H, dt, *J* 6.7 and 5.5, 2 × allylic CH<sub>2</sub>), 6.55 (2 H, dt, *J* 15.8 and 6.7, CH=CHPb) and 6.92 (2 H, d, *J* 15.8, <sup>207</sup>Pb satellites gave *J*<sub>Pb,H</sub> 460, CH=CHPb).

**Reaction of Bis[(*E*)-styryl]lead Diacetate 8 with Copper(i) Chloride.**—A mixture of the lead compound **8** (0.220 g, 0.415 mmol) and copper(i) chloride (41 mg, 0.415 mmol) in chloroform (20 cm<sup>3</sup>) was heated at reflux under nitrogen for 15 h. The mixture was cooled, filtered, and the filtrate was washed with water (2 × 20 cm<sup>3</sup>) and saturated brine (20 cm<sup>3</sup>) and evaporated. The residue was fractionated by flash chromatography on silica gel in light petroleum–ether (40:1) to yield (*E,E*)-1,4-diphenylbuta-1,3-diene **10** (70 mg, 93%) as colourless needles, m.p. 151–152 °C (lit.,<sup>18</sup> 152.5 °C).

**Reaction of Diphenyllead Diacetate with Copper(i) Chloride.**—Diphenyllead diacetate (0.655 g, 1.37 mmol) and copper(i) chloride (0.135 g, 1.37 mmol) were heated at reflux in chloroform (20 cm<sup>3</sup>) under nitrogen for 15 h. The reaction was worked up as for the reaction of compound **8** above and the residue was filtered through silica gel in ether to yield biphenyl (0.179 g, 85%), m.p. 69.5–70.5 °C (lit.,<sup>19</sup> 71 °C).

**Reaction of *p*-Methoxyphenyl(phenyl)lead Diacetate 2 with Copper(i) Chloride.**—The diaryllead diacetate **2** (1.32 g, 2.59 mmol) and copper(i) chloride were heated at reflux in chloroform (40 cm<sup>3</sup>) under nitrogen for 24 h. The reaction mixture was worked up as for the reaction of compound **8** above, and the crude product was fractionated by radial chromatography on silica gel in light petroleum–ether (99:1) to produce biphenyl (43 mg, 0.279 mmol), m.p. 70–71 °C (lit.,<sup>19</sup> 71 °C), 4-methoxybiphenyl (186 mg, 1.01 mmol), m.p. 87–89 °C (lit.,<sup>20</sup> 90 °C) and 4,4'-dimethoxybiphenyl (128 mg, 0.596 mmol), m.p. 174–176 °C (lit.,<sup>21</sup> 175 °C).

**Reaction of Phenyl[(*E*)-styryl]lead Diacetate 4 with Copper(i) Chloride.**—The aryl(vinyl)lead diacetate **4** (619 mg, 1.22 mmol) and copper(i) chloride (121 mg, 1.22 mmol) were heated at reflux in chloroform (25 cm<sup>3</sup>) under nitrogen for 18 h. The reaction mixture was worked up as for the reaction of compound **8** above, and the product was analysed by gas chromatography (SGE BPI column) to show the presence of biphenyl (14%), (*E*)-stilbene (21%) and (*E,E*)-1,4-diphenylbuta-1,3-diene (42%).

**Reaction of *p*-Methoxyphenyl[(*E*)-styryl]lead Diacetate 6 with Copper(i) Chloride.**—The aryl(vinyl)lead diacetate **6** (1.36 g, 2.54 mmol) and copper(i) chloride (252 mg, 2.54 mmol) were heated at reflux in chloroform (40 cm<sup>3</sup>) under nitrogen for 18 h. The reaction was worked up as for the reaction of compound **8** above, and the crude product was fractionated by radial chromatography on silica gel in light petroleum–ether (99:1) to yield (*E,E*)-1,4-diphenylbuta-1,3-diene (58 mg, 0.282 mmol), (*E*)-4-methoxystilbene (219 mg, 1.04 mmol), m.p. 132.5–134 °C (lit.,<sup>22</sup> 135–136 °C) and 4,4'-dimethoxybiphenyl (75 mg, 0.350 mmol).

Reaction of *p*-Methoxyphenyl(2,4,6-trimethylphenyl)lead Bis(trifluoroacetate) **3** in Trifluoroacetic Acid.—The diaryllead compound **3** (0.330 g, 0.50 mmol) was stirred in trifluoroacetic acid (2.0 cm<sup>3</sup>) under anhydrous conditions for 2.5 h, with monitoring at 2.0 h by <sup>1</sup>H NMR spectroscopy indicating complete reaction of the starting material. The mixture was diluted with ether (25 cm<sup>3</sup>), washed with saturated aqueous sodium hydrogen carbonate (3 × 15 cm<sup>3</sup>) and saturated brine (15 cm<sup>3</sup>) and dried (Na<sub>2</sub>SO<sub>4</sub>). The mixture was analysed by gas chromatography on an SGE 25QC3/BP20 capillary column (25 m × 0.33 mm) programmed from 60 to 200 °C to show the presence of mesitylene (0.132 mmol), anisole (0.315 mmol), mesityl trifluoroacetate (0.274 mmol) and 4-methoxy-2',4',6'-trimethylbiphenyl (0.084 mmol).

### Acknowledgements

This work was supported by a grant from the Australian Research Council. C. J. P. gratefully acknowledges receipt of an Australian Postgraduate Research Award.

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Paper 4/04975F

Received 18th August 1994

Accepted 30th August 1994