

**Lithium Phosphoranylidene Ylides**  
**Mes<sup>\*</sup>-P(=E)=C(H)Li(THF)<sub>3</sub> (E = NMe<sup>\*</sup>,  
 C(SiMe<sub>3</sub>)<sub>2</sub>): Synthesis, Crystal Structure, and  
 Transmetalation**

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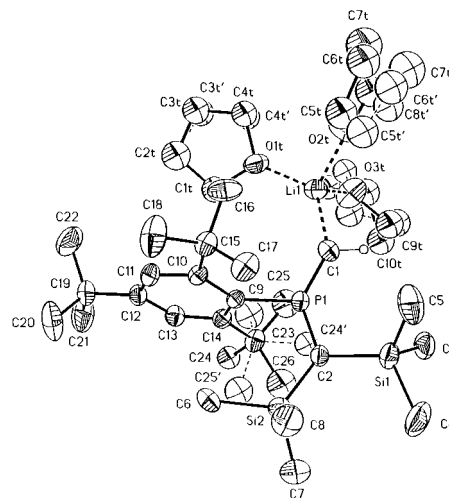
Metalation of phosphonium ylides is a well-known route for the preparation of phosphonium diylides<sup>1</sup> (**I**) and yldiides<sup>2</sup> (**II**) whose nucleophilicity makes them widely used synthetic building blocks in organic chemistry (Scheme 1).<sup>3</sup> While phosphonium diylides (**I**) are well-characterized compounds and their properties and molecular structures have been thoroughly investigated,<sup>4</sup> phosphonium yldiides (**II**) were in most cases postulated as intermediate products whose existence was deduced from their trapping in subsequent chemical reactions.<sup>2</sup>

Having shown in previous reports<sup>5</sup> that phosphoranyl carbenoids are significantly stabilized by incorporation of the carbenoid center in delocalized  $\pi$ -systems, we became interested in metalated methylene-(ylene)-phosphoranes (**III**) which may formally be considered as phosphonium yldiides in a similar manner as (**II**). Here, we report on the first syntheses, crystal structure determinations, and transmetalation reactions of representatives of this type.

Treatment of the phosphalkene **1**<sup>6</sup> or the iminophosphine **2**<sup>7</sup> with dimethylsulfonium methylide<sup>8</sup> cleanly afforded the methylene-(ylene)-phosphoranes **3** and **4**, respectively. Compounds of this type whose phosphorous atoms carry CH<sub>2</sub> fragments were until recently<sup>9</sup> only known as reactive intermediates.<sup>10</sup> Subsequent reactions of **3** and **4** with *n*-butyllithium in THF at 0 °C proceeded via H/Li exchange to give the phosphoranylidene ylides **5** and **6** (Scheme 2) which were isolated as highly air and moisture sensitive, light-yellow crystals.

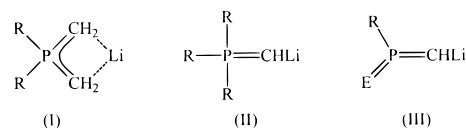
Compounds **3** and **4** exhibit deshielded <sup>31</sup>P NMR resonances characteristic for compounds of this type.<sup>5,11</sup> The <sup>13</sup>C NMR signals of the carbons in the CH<sub>2</sub> fragments ( $\delta^{13}\text{C}$  72.4 (**3**), 73.6 (**4**)) appear as expected at lower fields as compared to simple phosphonium ylides.<sup>4</sup> Lithiation induces a further deshielding of the corresponding resonances in **5** and **6** ( $\Delta\delta^{13}\text{C}$  = 58.4 (**3/5**), 48.7 (**4/6**)) whose magnitude is similar to the metal-induced variation of  $\delta^{13}\text{C}$  in vinyl lithium compounds ( $\Delta\delta$  = 50–65<sup>12</sup>).

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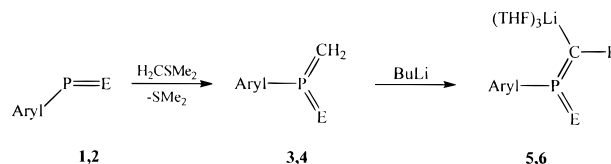


**Figure 1.** ORTEP plot of **5** (40% probability level, H atoms omitted for clarity). Selected bond lengths [pm] and angles [deg] of **5** (**6**): P1–C1 163.2(5) {162.4(5)}, P1–E 170.4(5) {156.4(4)}, P1–C<sub>ipso</sub> 182.6(5) {181.1(6)}, C1–Li1 208.5(11) {208.1(12)}; C1–P1–E 132.7(3) {141.4(3)}, C1–P1–C<sub>ipso</sub> 111.4(3) {110.0(3)}, E–P1–C<sub>ipso</sub> 115.8(2) {108.4(2)}, P1–C1–Li1 140.0(4) {143.3(5)}.

**Scheme 1**



**Scheme 2**



Aryl = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>  
**1,3,5:** E = C(SiMe<sub>3</sub>)<sub>2</sub>  
**2,4,6:** E = NAryl

At the same time, the magnitude of <sup>1</sup>J(P,C) decreases significantly (<sup>1</sup>J(P,C) = 126.6 Hz (**3**), 28.2 Hz (**5**); 148.1 Hz (**4**), 50.0 Hz (**6**)) which may be attributed to a higher p character of the PC-bond and a concomitant increase of s-electron density at the carbon atom.

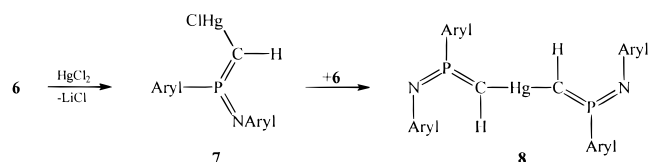
Couplings between lithium and carbon or phosphorus nuclei became visible in <sup>6</sup>Li-doped samples at –70 °C and revealed the presence of isolated AX spin systems (A = <sup>13</sup>C, <sup>31</sup>P; X = <sup>6</sup>Li). The magnitudes of <sup>2</sup>J(P,Li) (5.1 Hz (**5**), 7.5 Hz (**6**)) and <sup>1</sup>J(C,Li) (12.6 Hz (**5**), 13.2 Hz (**6**)) are similar to those in phosphoranylidene carbenoids;<sup>13</sup> the latter also compare to <sup>1</sup>J(C,Li) values of lithiated vinyl compounds.<sup>12</sup>

Both compounds **5** (Figure 1) and **6** were further characterized by single-crystal X-ray diffractometry.<sup>14</sup> As anticipated from the NMR studies, the solids consist of discrete monomeric units. Each monomer contains a tetrahedrally coordinated lithium atom which occupies the sterically more accessible exo-position at the ylidic carbon atom and carries three THF molecules. The phosphorus and carbon atoms in the bis-(ylene)-moieties exhibit

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## Scheme 3

Aryl = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>

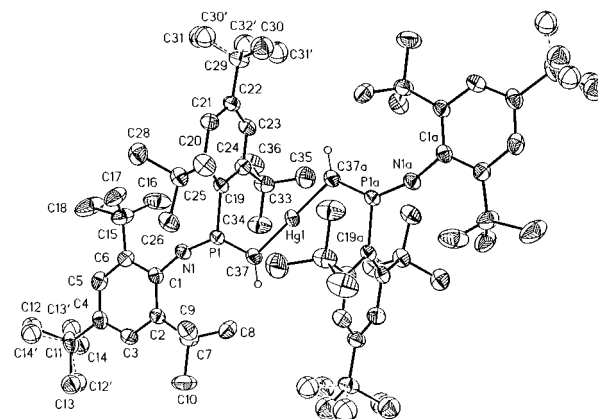
the expected<sup>11</sup> trigonal planar coordination geometries. Interestingly, the central E–P–C bond angles (C1–P1–C2 132.7(3)° (**5**) and N1–P1–C1 141.4(3)° (**6**)) are much wider than in metal-free methylene-(ylene)-phosporanes with otherwise similar substituent patterns.<sup>9,13</sup> Also noticeable are large P–C–Li bond angles (140.0(4)° (**5**), 143.3(5)° (**6**)) and large P1–C2 (P1–N1) distances (170.4(5) pm (**5**), 156.4(4) pm (**6**)) of the adjacent double bonds. In contrast, C–Li distances (208.5–(11) pm (**5**), 208.1(12) pm (**6**)) are significantly shorter than corresponding bond distances in structurally comparable lithium organyls.<sup>12</sup>

The lithium phosphoranylidene ylides **5** and **6** may be easily transformed into new organometallic derivatives with retention of the low-coordinate phosphorus center. Thus, treatment of **6** with 1 equiv of mercurio chloride gave a product which was formulated as the mercurio derivative **7** on the basis of the observed <sup>31</sup>P and <sup>199</sup>Hg NMR data (AX spectrum with δ<sup>31</sup>P 74.7, δ<sup>199</sup>Hg 1430, <sup>2</sup>J(Hg,P) = 972 Hz).<sup>15</sup> Subsequent addition of another equivalent of **6** afforded the diorganomercury compound **8** which was isolated as light-yellow, air and moisture sensitive crystals (Scheme 3). Compound **8** exhibits a slight deshielding of both the metal and phosphorus nuclei (δ<sup>31</sup>P 79.8, δ<sup>199</sup>Hg 1916) and a decrease of <sup>2</sup>J(Hg,P) (512 Hz) as compared to **7**. The values of δ<sup>13</sup>C and <sup>1</sup>J(P,C) for the metalated carbon (δ<sup>13</sup>C 113.0, <sup>1</sup>J(P,C) = 84.7 Hz) are intermediate between the corresponding data for **6** and **4**.

A crystal structure analysis of **8**<sup>14</sup> reveals the presence of centrosymmetric molecules with a linear coordinated Hg atom and a nearly planar, transoid arrangement of the central (N=P=C)<sub>2</sub>Hg moiety (Figure 2). The Hg–C37 distance (205.1(4) pm) closely matches the reported Hg–C distance in the phosphalkene (Mes\*P=CH-)<sub>2</sub>Hg,<sup>16</sup> and the P1–C37 distance (163.0(4) pm) is very similar as in the lithio derivative

(14) Crystal data for **5**: C<sub>38</sub>H<sub>72</sub>LiO<sub>3</sub>PSi<sub>2</sub>, light yellow, monoclinic, space group P2<sub>1</sub>/n (No. 14), *a* = 11.255(4) Å, *b* = 20.644(4) Å, *c* = 18.862(5) Å, β = 98.10(3)°, *V* = 4339(2) Å<sup>3</sup>, *Z* = 4, wR2(*F*<sup>2</sup>) = 0.276. Crystal data for **6**: C<sub>49</sub>H<sub>83</sub>LiO<sub>3</sub>P·C<sub>4</sub>H<sub>8</sub>O, light yellow, triclinic, space group P1 (No. 2), *a* = 10.296(2) Å, *b* = 11.136(2) Å, *c* = 23.633(4) Å, α = 96.52(2)°, β = 98.77(1)°, γ = 95.99(1)°, *V* = 2640(1) Å<sup>3</sup>, *Z* = 2, wR2(*F*<sup>2</sup>) = 0.292. Crystal data for **8**: C<sub>74</sub>H<sub>118</sub>HgN<sub>2</sub>P<sub>2</sub>·2C<sub>4</sub>H<sub>8</sub>O, yellow, monoclinic, space group C2/c (No. 15), *a* = 29.308(4) Å, *b* = 9.957(1) Å, *c* = 29.462(4) Å, β = 108.24(1)°, *V* = 8166(2) Å<sup>3</sup>, *Z* = 4, wR2(*F*<sup>2</sup>) = 0.113.

(15) <sup>199</sup>Hg NMR data were obtained from <sup>31</sup>P-detected <sup>31</sup>P, <sup>199</sup>Hg-HMQC spectra, see: Gudat, D.; Nieger, M.; Schrott, M. *Inorg. Chem.* **1997**, *36*, 1476–1481.



**Figure 2.** ORTEP plot of **8** (40% probability level, H atoms and free solvent omitted for clarity). Selected bond lengths [pm] and angles [deg]: P1–N1 151.1(3), P1–C37 163.0(4), C37–Hg1 205.1(4); N1–P1–C37 136.1(2), N1–P1–C<sub>ipso</sub> 114.52(19), C37–Hg1–C37a 180.000(1), P1–C37–Hg1 116.6(2).

**6**. At the same time, the N1–P1–C37 (136.1(2)°) and P1–C37–Hg1 angles (116.6(2)°) are more acute than in **6**, while the C1–N1–P1 angle (162.1(3)°) becomes wider and the P1–N1 bond concomitantly shorter (151.1(3) pm). Altogether, these effects presumably indicate a different balancing of the mutual interactions between the bulky substituents around the phosphorus atom.

In conclusion, the synthesis and characterization of the metalated bis-(ylene)-phosporanes **5**, **6**, and **8** suggest that incorporation of the metalated carbon atom into a heteroallylic π-electron system indeed adds to the stability of phosphonium ylide systems. The transmetalation **6** → **8** further illustrates the possibility of reactions with retention of the bis-ylene moiety, suggesting that these compounds could serve as valuable synthetic reagents similar to “conventional” phosphonium ylides (**II**). Investigation of further aspects of this chemistry is in progress.

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**Supporting Information Available:** Full experimental procedure for the synthesis of **3–8**, tables of <sup>1</sup>H and <sup>13</sup>C NMR and MS data of **3–6** and **8**, low-temperature <sup>6</sup>Li and <sup>31</sup>P NMR data of **5** and **6**; tables of crystal data, final atomic coordinates, anisotropic thermal parameters, complete positional parameters, and bond distances and angles for **5** and **6** (42 pages). See any current masthead page for ordering and Internet access instructions.

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