

# Selective Dehydrocoupling of Phosphines by Lithium Chloride Carbenoids

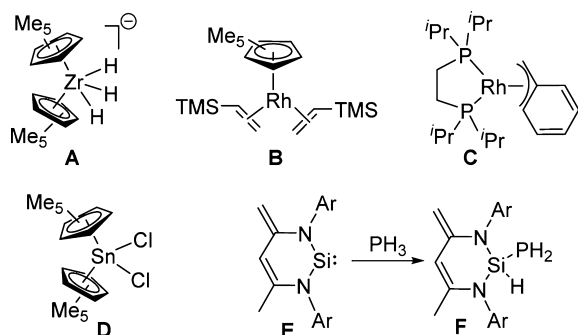
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**S** Supporting Information

**ABSTRACT:** The development of a simple, transition-metal-free approach for the formation of phosphorus–phosphorus bonds through dehydrocoupling of phosphines is presented. The reaction is mediated by electronically stabilized lithium chloride carbenoids and affords a variety of different diphosphines under mild reaction conditions. The developed protocol is simple and highly efficient and allows the isolation of novel functionalized diphosphines in high yields.

Dehydrocoupling has become a powerful synthetic methodology for the formation of a variety of homo- and heteroatomic main-group element bonds. The development of this reaction has particularly been fueled by the synthetic potential and the applicability of the obtained products, e.g., as polymeric and molecular materials.<sup>1</sup> However, the formation of an E–E bond directly from E–H precursors usually requires the use of transition-metal catalysts. One of the first reports goes back to the early 1980s, when Sneddon reported Pt-catalyzed B–B bond formation between borane clusters.<sup>2</sup> Since then, a variety of E–E coupling reactions have been realized using early- and late-transition-metal complexes as catalysts.<sup>3,4</sup> In the case of P–P coupling reactions, the first reports by Stephan's group focused on the use of an anionic zirconocene complex (A in Figure 1).<sup>5,6</sup>



**Figure 1.** Catalysts for the dehydrocoupling of phosphines (A–D) and P–H bond activation by silylene E.

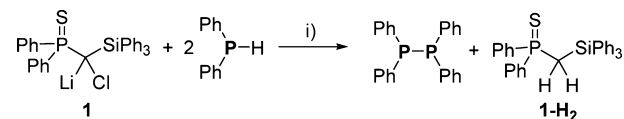
These studies were followed by reports on the use of other group-4 and late-transition-metal complexes (e.g., B and C) by the groups of Tilley, Brookhart, Waterman, and others.<sup>7,8</sup>

Despite the advances in transition-metal catalysis, the past two decades have revealed a series of compounds containing main-group elements that are applicable in bond activation and

formation reactions.<sup>9,10</sup> In the case of P–P coupling reactions, however, only the tin complex Cp\*<sub>2</sub>SnCl<sub>2</sub> (D) reported by Wright and co-workers has been active in P–P bond formation reactions directly from phosphines.<sup>11</sup> Although this bond formation proceeds in a catalytic manner (10 mol %), high reaction temperatures and extended reaction times were necessary to allow for sufficient conversions. To the best of our knowledge, no other practicable or high-yielding synthesis of diphosphines directly from R<sub>2</sub>PH precursors using catalytic or stoichiometric amounts of a main-group metal species has been reported.<sup>12</sup> Instead, 1,1-addition of P–H bonds has been observed for free carbenes<sup>13</sup> and silylenes (e.g., E → F).<sup>14</sup> In this work, we focused on the reactivity of carbenoids toward the P–H bond in phosphines, which led to the development of a highly efficient protocol for the synthesis of diphosphines from the corresponding phosphine precursors.

In previous reports on the ambiphilic nature of carbenoids, we have focused on the influence of stabilization effects on the reactivity.<sup>15,16</sup> Carbenoid **1** was found to be sufficiently stable for controlled handling while keeping its ambiphilic nature.<sup>17</sup> This resulted, for example, in activation of the B–H bond in borane Lewis base adducts.<sup>15</sup> Thus, **1** was chosen as starting point for reactivity studies toward P–H bonds. Treatment of a cooled solution of the carbenoid in tetrahydrofuran (THF) with an excess of diphenylphosphine instantly resulted in decoloration of the yellow solution upon warming to room temperature (Scheme 1). <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy after reaction for 1 h

## Scheme 1. Dehydrocoupling of Ph<sub>2</sub>PH with Carbenoid **1**<sup>a</sup>



<sup>a</sup>Conditions: (i) –78 °C → RT, THF, <1 h, –LiCl.

showed the formation of only two new compounds characterized by singlets at  $\delta_p = 36.6$  and  $-14.8$  ppm (C<sub>6</sub>D<sub>6</sub>). The first signal was assigned to the protonated species **1-H<sub>2</sub>**, while the species resonating at higher field was identified as Ph<sub>4</sub>P<sub>2</sub>. Thus, dehydrocoupling of the phosphine by simultaneous protonation of the carbenoid had taken place. This observation is remarkable not only with respect to the fast and clean conversion but also because it is unprecedented in carbenoid chemistry. Typically, secondary phosphines are lithiated by lithium bases (e.g., Ph<sub>2</sub>PH

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to  $\text{Ph}_2\text{PLi}$ ) and react with alkyl halides to form P–C bonds. In the reaction of **1** with  $\text{Ph}_2\text{PH}$ , however, no comparable reactivity was observed.

We thus turned our attention to an evaluation of the scope of the reaction in terms of applicable carbenoids and phosphine precursors. Thereby, the electronically stabilized carbenoids **1–3**, with the sulfonyl-substituted derivative **3** being a room-temperature-stable representative, as well as the highly reactive compounds **4** and **5** were tested (Figure 2). In a typical

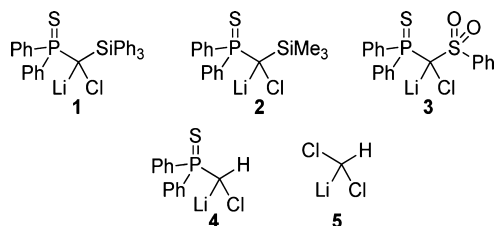


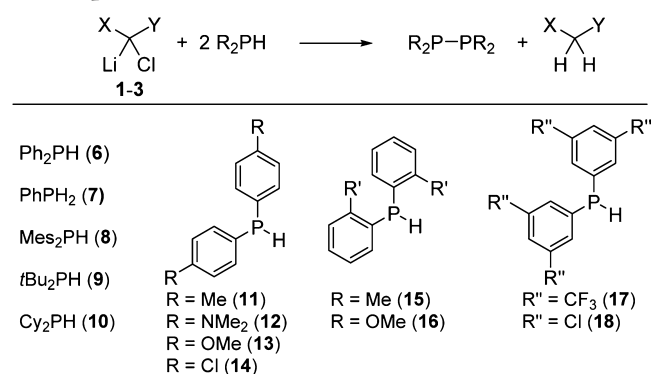
Figure 2. Carbenoids applied in the P–P coupling reaction.

experiment, a cooled solution of the carbenoid was treated with 2 equiv of  $\text{Ph}_2\text{PH}$ , and the obtained reaction mixture was studied by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. While carbenoids **1–3** cleanly formed their corresponding protonated derivatives and diphosphines [see the Supporting Information (SI)], the more reactive carbenoids **4** and **5** delivered complex product mixtures with the diphosphine in less than 10% yield. Hence, electronic stabilization of the carbenoid is required for selective dehydrocoupling (vide infra).

Next, stabilized carbenoids **1–3** were used for evaluation of the substrate scope (Table 1; for experimental details, see the SI). Coupling to the diphosphines was accomplished with a huge variety of different aryl-substituted phosphines. However, no selective conversion to the diphosphines was observed with aliphatic compounds such as  $t\text{Bu}_2\text{PH}$  (**9**) and  $\text{Cy}_2\text{PH}$  (**10**) (entries 9 and 10), suggesting that electronic effects and the P–H polarity might play a role in the reaction mechanism. The reactions were found to be fast, in general being complete within less than 1 h. In most of the cases, decoloring of the yellow carbenoid solution occurred instantly after phosphine addition. Even in the case of room-temperature-stable carbenoid **3**, only a couple of minutes were needed for the reactions to reach completion. Coupling was accomplished using phosphines with electron-rich (entries 5–7 and 13–15) and electron-poor aromatics (entries 16, 17, and 22–24), showing high conversions in all cases. Steric effects were found to influence the efficiency of the coupling reaction. While (*o*-Tol) $_2\text{PH}$  was still efficiently coupled to give (*o*-Tol) $_4\text{P}_2$  (entries 3 and 12), the more bulky mesityl substituent in  $\text{Mes}_2\text{PH}$  limited its dehydrocoupling (entry 4). However, in case of the more reactive and sterically less demanding carbenoid **2**, conversion to the diphosphine was observed in 16% yield (entry 18), suggesting that smaller carbenoids should also efficiently couple more bulky phosphines.

It is interesting to note that the synthetic protocol also allows the presence of functional groups, even chloro and trifluoromethyl groups. This is probably due to the efficient electronic stabilization of the used carbenoids. For example, in the case of the methoxy- or dimethylamino-functionalized systems **12**, **13**, and **16** (Table 1, entries 5–7 and 13–15), no competing side reactions such as ortho metalations were observed. The same was true for chloro-substituted phosphines **14** and **18** (entries 16, 17, 23, and 24), allowing for further functionalizations after the coupling reaction. Besides the secondary phosphines, even the

Table 1. Results of the Carbenoid-Mediated Dehydrocoupling of Phosphines



| entry | $\text{R}_2\text{PH}$ | carbenoid | time [h] | product  | yield [%] <sup>a</sup> |
|-------|-----------------------|-----------|----------|--|------------------------|
| 1     | <b>6</b>              | 1         | 1        | $\text{Ph}_4\text{P}_2$  | 88                     |
| 2     | <b>11</b>             | 1         | 1        | ( <i>p</i> -Tol) $_4\text{P}_2$  | 91                     |
| 3     | <b>15</b>             | 1         | 1        | ( <i>o</i> -Tol) $_4\text{P}_2$  | 69                     |
| 4     | <b>8</b>              | 1         | 24       | $\text{Mes}_4\text{P}_2$   | – <sup>b</sup>         |
| 5     | <b>12</b>             | 1         | 1        | ( <i>p</i> -Me $_2\text{NC}_6\text{H}_4$ ) $_4\text{P}_2$                  | 92                     |
| 6     | <b>13</b>             | 1         | 1        | ( <i>p</i> -MeOC $_6\text{H}_4$ ) $_4\text{P}_2$                           | 91                     |
| 7     | <b>16</b>             | 1         | 1        | ( <i>o</i> -MeOC $_6\text{H}_4$ ) $_4\text{P}_2$                           | 80                     |
| 8     | <b>17</b>             | 1         | 1        | (3,5-(CF $_3$ ) $_2\text{C}_6\text{H}_4$ ) $_4\text{P}_2$                  | 32                     |
| 9     | <b>9</b>              | 1         | 1        | $t\text{Bu}_4\text{P}_2$   | – <sup>b</sup>         |
| 10    | <b>10</b>             | 1         | 1        | $\text{Cy}_4\text{P}_2$  | – <sup>b</sup>         |
| 11    | <b>11</b>             | 2         | <0.5     | ( <i>p</i> -Tol) $_4\text{P}_2$  | 98 [82]                |
| 12    | <b>15</b>             | 2         | <0.5     | ( <i>o</i> -Tol) $_4\text{P}_2$  | 99 [74]                |
| 13    | <b>12</b>             | 2         | <0.5     | ( <i>p</i> -Me $_2\text{NC}_6\text{H}_4$ ) $_4\text{P}_2$                  | 99 [98]                |
| 14    | <b>13</b>             | 2         | <0.5     | ( <i>p</i> -MeOC $_6\text{H}_4$ ) $_4\text{P}_2$                           | 99 [90]                |
| 15    | <b>16</b>             | 2         | <0.5     | ( <i>o</i> -MeOC $_6\text{H}_4$ ) $_4\text{P}_2$                           | 99 [91]                |
| 16    | <b>14</b>             | 2         | <0.5     | (4-ClC $_6\text{H}_5$ ) $_2\text{P}_2$                                     | 67 [61]                |
| 17    | <b>18</b>             | 2         | <0.5     | (3,5-Cl $_2\text{C}_6\text{H}_4$ ) $_4\text{P}_2$                          | 98                     |
| 18    | <b>8</b>              | 2         | 24       | $\text{Mes}_4\text{P}_2$   | 16                     |
| 19    | <b>6</b>              | 3         | 1        | $\text{Ph}_4\text{P}_2$  | 78                     |
| 20    | <b>12</b>             | 3         | <0.5     | ( <i>p</i> -Me $_2\text{NC}_6\text{H}_4$ ) $_4\text{P}_2$                  | 82                     |
| 21    | <b>13</b>             | 3         | <0.5     | ( <i>p</i> -MeOC $_6\text{H}_4$ ) $_4\text{P}_2$                           | 93                     |
| 22    | <b>17</b>             | 3         | <0.5     | (3,5-(CF $_3$ ) $_2\text{C}_6\text{H}_4$ ) $_4\text{P}_2$                  | 93                     |
| 23    | <b>14</b>             | 3         | 24       | (4-ClC $_6\text{H}_5$ ) $_2\text{P}_2$                                     | 95                     |
| 24    | <b>18</b>             | 3         | <0.5     | (3,5-Cl $_2\text{C}_6\text{H}_4$ ) $_4\text{P}_2$                          | 87                     |
| 25    | <b>7</b>              | 1         | 3        | <i>c</i> -Ph $_3\text{P}_5$<br><i>c</i> -Ph $_6\text{P}_6$<br>Ph(H)PP(H)Ph | 70<br>5<br>17          |

<sup>a</sup>Determined by  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy; values in brackets are isolated yields. <sup>b</sup>The reaction was unselective because of decomposition of the carbenoid; multiple products were formed.

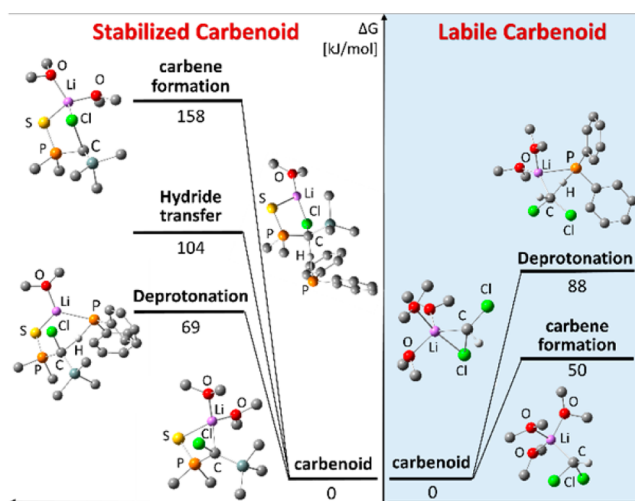
primary phosphine  $\text{PhPH}_2$  was found to undergo P–P bond formation, with a preference for the five-membered cyclophosphane [ $\text{Ph}_5\text{P}_5$ ] (70%) over the six-membered analogue [ $\text{Ph}_6\text{P}_6$ ] (17%) (entry 25).

Overall, the carbenoid-mediated P–P coupling of phosphines offers a facile protocol for the synthesis of a variety of aryl-substituted diphosphines. Contrary to other methods available for the formation of P–P bonds, the “carbenoid route” does not require laborious workup, transition-metal catalysis, long reaction times, elevated temperatures, or different P-containing starting materials.<sup>8</sup> High conversions to the diphosphines were achieved with all three carbenoids **1–3**. However, trimethylsilyl-substituted carbenoid **2** turned out to be the reagent of choice for convenient isolation of the formed diphosphines. Here the protonated species could easily be removed from the reaction

mixture by washing with pentane and recycled for the carbenoid synthesis. Hence, this strategy allowed the clean isolation of the diphosphines in good to excellent yields (Table 1, entries 11–16). Also, novel diphosphines such as the amino- and methoxy-functionalized compounds (*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub>, (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub>, and (*o*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub> could be isolated as colorless solids in high yields of 98, 90, and 91%, respectively. The diphosphines (*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub>, (*p*-Tol)<sub>4</sub>P<sub>2</sub>, and (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub> were additionally characterized by X-ray diffraction analysis, which confirmed the nature of the coupling products (see the SI). The P–P bond lengths in these compounds are 2.214(1), 2.238(1), and 2.252(1) Å, respectively, and are thus comparable to the one in Ph<sub>4</sub>P<sub>2</sub>.<sup>8f</sup>

In view of the efficiency of the P–P bond formation reaction mediated by Li/Cl carbenoids and the broad substrate scope, it was of interest to explore the mechanism of the reaction and the reason for the observed selectivity. At first, the possible involvement of radical species was addressed. In general, no coloring of the reaction mixtures indicative of radical intermediates was observed, except for the reactions with the electron-poor phosphines **14**, **17**, and **18**. In these cases, the mixtures turned to orange (**14**, **18**) and purple (**17**) for a couple of minutes (<5 min) before complete decoloration occurred. However, no radical species could be trapped with the radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). Even in this case, selective formation of the diphosphine was observed. The same holds true when the reaction was performed in the dark. This suggests that no radical mechanism but rather a substitution mechanism including (de)protonation steps is operative. In fact, the observed colors can also be attributed to the corresponding lithium phosphides (Ar<sub>2</sub>PLi),<sup>18</sup> which are formed by a stepwise mechanism in which deprotonation of the phosphine is the initial step. This hypothesis was confirmed by a trapping experiment. Carbenoid **2** was treated with only 1 equiv of **13** at –78 °C, followed by immediate addition of Ph<sub>2</sub>PCL. <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy of the reaction mixture showed the formation of the heterocoupled diphosphine (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P–PPh<sub>2</sub> as the main product ( $\delta_p = -16.6$  and  $-19.1$  ppm;  $^1J_{PP} = 158.4$  Hz) together with (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>P<sub>2</sub> and several compounds arising from Li/Cl exchange reactions (see the SI). Thus, these findings suggest the formation of a phosphide species as an intermediate of the P–P bond formation. The next step of the P–P coupling probably involves hydride–chloride exchange, as found in the case of the B–H bond activation.<sup>15</sup>

The origin of the observed selectivity was finally addressed by computational methods (M06-2X/6-311+g(d); see the SI for details) using a monomeric model system for carbenoid **2** with methyl groups at phosphorus and Me<sub>2</sub>O for completion of the coordination sphere of lithium. Deprotonation of the phosphine as the initial step of the reaction mechanism was found to require only 69 kJ mol<sup>–1</sup>. This activation barrier is lower in energy than those of alternative pathways (Figure 3, left). Hydride transfer ( $\Delta G^\ddagger = 104$  kJ mol<sup>–1</sup>) or carbene formation via LiCl elimination ( $\Delta G^\ddagger = 158$  kJ mol<sup>–1</sup>) require considerably more energy. This confirms the progress of the reaction at low reaction temperatures and the selective formation of the phosphide as a reaction intermediate of the P–P bond formation. A different picture was obtained for the more labile carbenoid CHCl<sub>2</sub>Li (**5**) (Figure 3, right). Here carbene formation possesses a lower activation barrier ( $\Delta G^\ddagger = 50$  kJ mol<sup>–1</sup>) than deprotonation of the phosphine ( $\Delta G^\ddagger = 88$  kJ mol<sup>–1</sup>). The liberated carbene is highly reactive and thus results in the formation of multiple products due to various decomposition reactions, as observed in the



**Figure 3.** Reaction pathways and calculated free energies for the reactions of the carbenoids TMSC(LiCl)P(S)Me<sub>2</sub> and CHCl<sub>2</sub>Li with Ph<sub>2</sub>PH [M06-2X/6-311+g(d)].

experiments. Hence, the electronic stabilization of the carbenoid is necessary to favor the initial deprotonation step over the LiCl elimination and to allow for the selective formation of the diphosphines.<sup>19</sup>

In conclusion, we have shown that Li/Cl carbenoids can be applied for the coupling of phosphines to give the corresponding diphosphines. This observation led to the development of a simple, highly efficient, and versatile synthetic protocol that furnishes the diphosphines in high yields, usually within less than 1 h of reaction. Despite the fast reaction process, the coupling conditions also allow the presence of functional groups (–Cl, –NMe<sub>2</sub>, –OMe) and thus the isolation of novel diphosphines. Electronic stabilization of the Li/Cl carbenoids was found to be necessary for the selective transformation. The presented protocol allows facile access to a variety of diphosphines, which may now give rise to the development of novel applications of this still scarcely explored class of compounds.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental section, spectroscopic and crystallographic data (CIF), and details on the computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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