

# Free Inorganic, Organic, and Organometallic Ions by Treatment of Their Lithium Salts with 12-Crown-4

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Lithium derivatives of inorganic or organometallic ligands are usually their most common transfer agents.<sup>1,2</sup> As a consequence they are of great synthetic importance, which has led to considerable interest in their structures.<sup>3</sup> These are commonly of an associated, nonclassical, type with bonds that are usually electron deficient as exemplified by the cubane structure of (MeLi)<sub>4</sub>.<sup>4</sup> In fact much of the structural and theoretical interest in lithium compounds has focused on the nature of their association.<sup>3</sup> This has added significantly to our understanding of them and, in a wider context, has contributed to the development of current bonding theories. Frequently, however, the structures of the unassociated anions themselves have been overlooked. This Account describes the synthesis and structure of some of these free anions, which were prepared by the reaction of 12-crown-4 with their lithium salts in ether solution.

Free, unassociated anions are often of significant structural and theoretical interest. This is because the distorting effects of the Li<sup>+</sup> ion, present in the associated species, are absent, allowing the structure of the unperturbed anion to be obtained. In addition, knowledge of the structures of both the free and associated anions allows the changes effected by the Li<sup>+</sup> ion to be accurately measured. The structural information thus obtained often complements the many theoretical studies on these ions. A further effect of separating the anion is that its reactivity is often increased.

Obviously, it is unrealistic to expect that some anions could be obtained as free, unassociated, species in solution and crystallized as part of a lattice with the Li<sup>+</sup> cation coordinated by donor ligands. This is because of the extreme reactivity of certain anions toward the solvent, which is usually an ether of some type.<sup>5</sup> For example, free anions such as CH<sub>3</sub><sup>-</sup> or Ph<sup>-</sup> are far too reactive toward most solvents,<sup>6</sup> under ambient conditions, to enable their ready isolation. However, the reactivity of carbanions can be reduced by changing their steric or electronic properties by using aromatic<sup>3,7</sup> or silyl<sup>8</sup> substituents. In addition, the reactivity of most other common anions such as NR<sub>2</sub><sup>-</sup> (amide), OR<sup>-</sup> (alkoxide/aryl oxide), PR<sub>2</sub><sup>-</sup> (phosphide), and SR<sup>-</sup> (thiolate) is much less than that of the related carbon-centered species. Thus, stabilized carbanions and the various heteroanions mentioned above are, in theory at least, viable candidates for isolation as free ions.

There remains the problem of separating the lithium cation from its associated anion. It is well-known that

the association numbers of lithium reagents can be reduced by adding coordinating agents. For example, the addition of TMEDA (tetramethylethylenediamine)<sup>7</sup> to tetrameric (PhLi·Et<sub>2</sub>O)<sub>4</sub><sup>9</sup> affords the dimeric (PhLi·TMEDA)<sub>2</sub>.<sup>10</sup> The monomer PhLi·PMDETA can be isolated by adding the even stronger coordinating ligand PMDETA (pentamethyldiethylenetriamine).<sup>11</sup> Provided that the reactivity of the anion is compatible with the solvent, it is, in theory, possible to continue this trend and employ a sufficiently powerful coordinating agent for Li<sup>+</sup> to obtain separate ions. The crown ether 12-crown-4 fulfills, within certain limits, the need for a sequestering agent for the Li<sup>+</sup> ion. It is commercially available and easily purified and dried. It was first reported in 1957<sup>12</sup> but received little attention until 10 years later when the seminal work of Pedersen demonstrated the unique properties of crown ethers as a class of compound.<sup>13</sup> The first X-ray structure of a Li<sup>+</sup>/12-crown-4 complex, involving the species LiSCN·12-crown-4 was published in 1981.<sup>14</sup> Since then, a number of structural and binding studies have dealt with inorganic lithium salts complexed to various crowns.<sup>15,16</sup> However, none of these compounds had involved separation of Li<sup>+</sup> from the counteranion.

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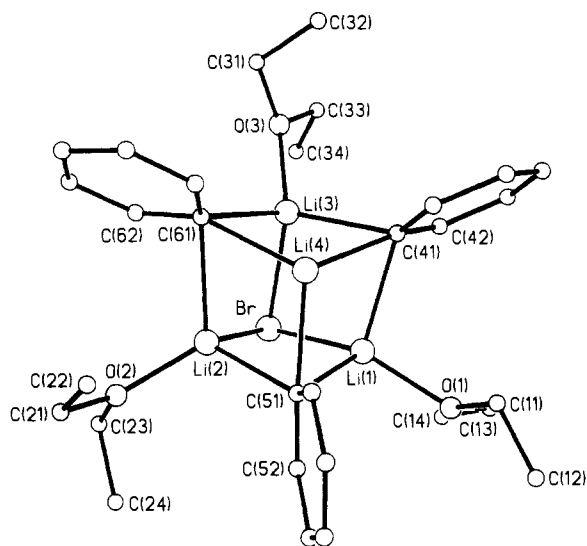
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Philip Power was born in Ireland and received his B.A. (1974) from the University of Dublin and D.Phil. (1977) from the University of Sussex. After postdoctoral work at Stanford University, he joined the faculty at the University of California, Davis, where he is currently an Associate Professor. His research interests lie in the area of unusual bonding coordination numbers and oxidation states throughout the periodic table.



**Figure 1.** Computer-generated plot of  $(\text{PhLi}\cdot\text{Et}_2\text{O})_3\text{LiBr}$ . Selected bond distances (Å) are Br–Li(1) = 2.513 (5), Br–Li(2) = 2.537 (2), Br–Li(3) = 2.564 (5), Li(1)–C(41) = 2.303 (3), Li(1)–C(51) = 2.252 (6), Li(2)–C(51) = 2.244 (5), Li(2)–C(61) = 2.329 (5), Li(3)–C(41) = 2.305 (5), and Li(3)–C(61) = 2.252 (5).

### Initial Work Involving Ether Solvates and 12-Crown-4

Our interest in the structure of lithium reagents began when large crystals were observed growing in an ether solution formed by the reaction of PhBr with Li metal. These were suspected to be a PhLi/LiBr complex of some sort and since the structures of such "halide-rich" complexes were as yet unknown, it was decided to proceed with an X-ray crystal structure determination. The compound proved to have the cubane structure  $(\text{PhLi}\cdot\text{Et}_2\text{O})_3\text{LiBr}$ ,<sup>9</sup> as illustrated in

Figure 1. This and the structure of  $(\text{LiCH}(\text{CH}_2)_2\text{Et}_2\text{O})_2(\text{LiBr})_2\text{Et}_2\text{O}$ ,<sup>17</sup> which was published virtually simultaneously, were the first X-ray structural illustrations of the nature of halide-rich organolithium reagents. The structure of the halide-free species  $(\text{PhLi}\cdot\text{Et}_2\text{O})_4$ <sup>9</sup> (synthesized by the reaction of PhI and *n*-BuLi)<sup>18</sup> was also described, and a comparison of the  $(\text{PhLi}\cdot\text{Et}_2\text{O})_4$  and  $(\text{PhLi}\cdot\text{Et}_2\text{O})_3\text{LiBr}$  showed a more open structure for the latter. This may explain some of the differences in reactivity between halide-rich and halide-free organolithium compounds. Increasing the steric requirements of the aromatic group reduces the degree of association as shown by the structures of the dimers  $[\text{Li}(\text{THF})_2\text{Mes}]_2$ <sup>19</sup> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and  $[\text{Li}(\text{Et}_2\text{O})_2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2]_2$ .<sup>20</sup> On the basis of their increased crowding, it was hoped that the addition of 12-crown-4 to ether or THF solutions of the hindered compound 2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li (R = *i*-Pr or *t*-Bu) would afford a "free" carbanion. However, these reactions did not yield any crystalline material suitable for X-ray analysis.<sup>21</sup>

The first successful application of 12-crown-4, which gave crystalline material, involved ether/THF solutions

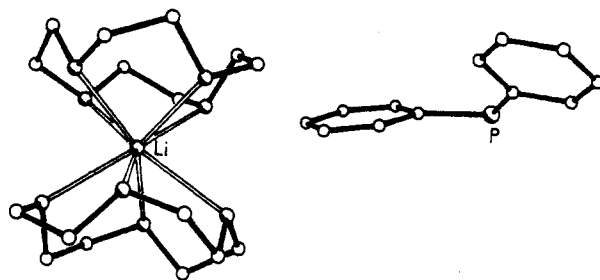
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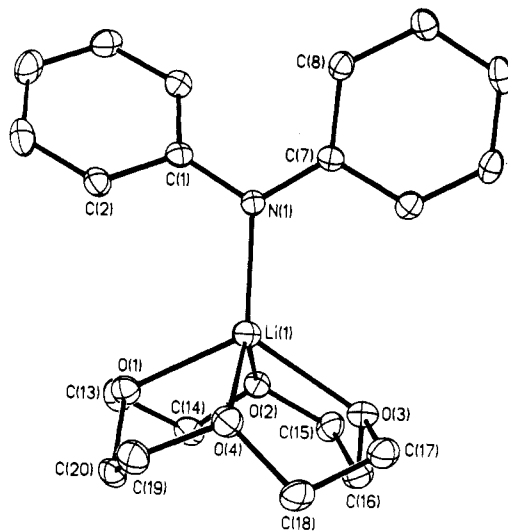
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**Figure 2.** Computer-generated plot of  $[\text{Li}(12\text{-crown-4})_2]^+[\text{PPh}_2]^-$ . Selected bond distances (Å) and the C(1)–P–C(7) angle (deg) are P–C(1) = 1.811 (4), P–C(7) = 1.804 (4), Li–O(av) = 2.374 (8), and C(1)–P–C(7) = 105.2 (2).



**Figure 3.** Computer-generated plot of  $[\text{Li}(12\text{-crown-4})\text{NPh}_2]$ . Each asymmetric unit contains  $1\frac{1}{2}$  molecules with N(2) and Li(2) sitting on a 2-fold axis. Selected bond distances (Å) and angles (deg) with values for the N(2) molecule in braces, are N(1)–Li(1) = 2.007 (5) {2.047 (5)}, N(1)–C(1) = 1.394 (3) {1.387 (2)}, N(1)–C(7) = 1.384 (2), Li(1)–O(1) = 2.106 (3) {2.190 (3)}, Li(1)–O(2) = 2.227 (5) {2.169 (3)}, Li(1)–O(3) = 2.160 (5), Li(1)–O(4) = 2.242 (4), and C(1)–N(1)–C(7) = 118.3 (2) {119.6 (2)}.

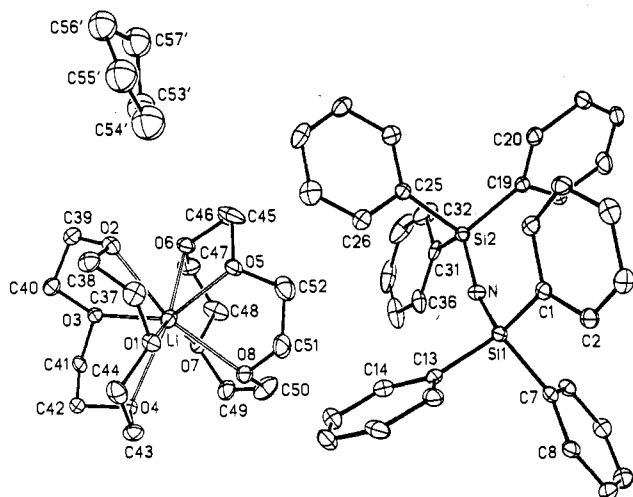
of LiPPh<sub>2</sub> and LiAsPh<sub>2</sub>. Crystals of  $[\text{Li}(12\text{-crown-4})_2]^+[\text{PPh}_2]^-$ <sup>22</sup> and  $[\text{Li}(12\text{-crown-4})_2]^+[\text{AsPh}_2]^- \cdot \text{THF}$ <sup>22</sup> were readily isolated in high yield. The structure of the phosphorus species is illustrated in Figure 2. The structure of the  $[\text{SbPh}_2]^-$ <sup>23</sup> ion was later added to the series. These compounds were the first structurally characterized examples of two-coordinate, diorganonion derivatives of these elements, although prior work involving cyano derivatives of phosphorus, in conjunction with large cations, allowed the structures of  $[\text{P}(\text{CN})\text{Ph}]^-$  and  $[\text{P}(\text{CN})_2]^-$ <sup>24,25</sup> to be determined. An added feature of the separated cation shown in Figure 2 is the unique coordination number of 8 for Li<sup>+</sup>, which had not been hitherto reported. Somewhat later, the structures of the simple Et<sub>2</sub>O and THF solvates of LiPPh<sub>2</sub> and LiP(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub> were obtained, and these proved to have infinite solvated chains of Li<sup>+</sup> and PPh<sub>2</sub><sup>-</sup> or P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anions.<sup>26</sup> Even more recent work in-

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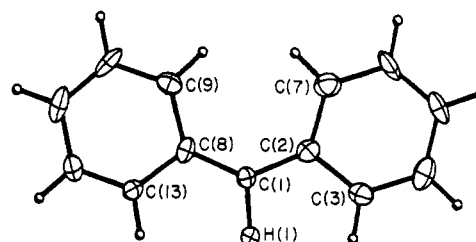


**Figure 4.** Computer-generated plot of  $[\text{Li}(12\text{-crown-4})_2]^+[\text{N}(\text{SiPh}_3)_2]^- \cdot \text{THF}$ . The THF molecule was symmetry generated from refined THF positions to show closest approach of C(54) (refined as an oxygen) to anion and cation (3.4 Å). Important bond distances (Å) and the Si(1)–N–Si(2) angle (deg) are Si(1)–N = 1.633 (4), Si(2)–N = 1.634 (4), and Si(1)–N–Si(2) = 154.9 (3).

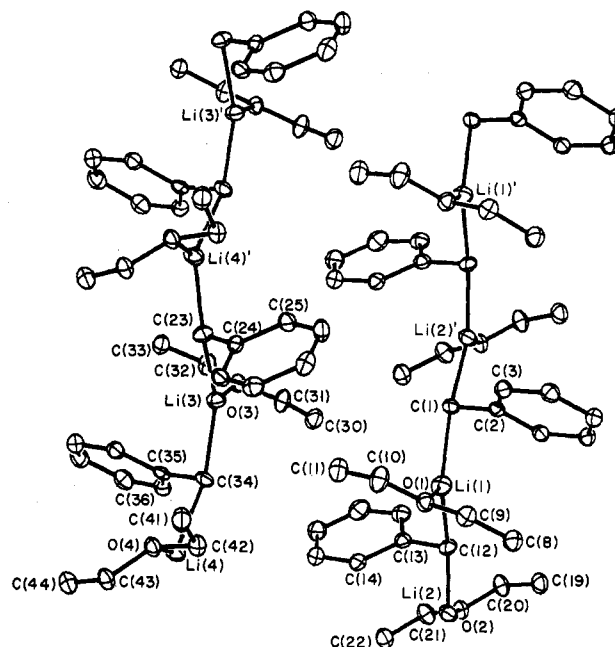
volving  $^{31}\text{P}$  NMR studies has shown that significant structural changes also take place in solution when 12-crown-4 is added.<sup>27</sup> This work also resulted in the structure of the mononuclear lithium phosphide and arsenide<sup>28</sup>  $\text{Li}(\text{THF})_3\text{PHMe}_3$ <sup>27</sup> and  $\text{Li}(1,4\text{-dioxane})_3\text{AsPh}_2$ ,<sup>23</sup> which have pyramidal phosphorus<sup>27–29</sup> or arsenic atoms in contrast to most amides ( $\text{NR}_2^-$ ), which are planar at nitrogen.

### Separate Carbanions and Amide Anions

An attempt to extend the  $[\text{EPh}_2]^-$  (E = P, As, or Sb) series to nitrogen did not result in the isolation of the diphenylamide,  $[\text{NPh}_2]^-$ , ion. Instead the complex  $[\text{Li}(12\text{-crown-4})\text{NPh}_2]^{23}$  (Figure 3) was obtained. Presumably the increased lattice energy obtained upon crystallizing a material with separate  $[\text{NPh}_2]^-$  ions is not sufficient to compensate for rupture of the stronger Li–N bond. A similar structure,  $[\text{Li}(12\text{-crown-4})\text{N}(\text{SiMe}_3)_2]^{30}$  was found in the case of the bis(trimethylsilyl)amide group. Here it was hoped that the multiple p–d  $\pi$ -bonding characteristics of the N–Si bond would reduce the electron density on nitrogen sufficiently to weaken the Li–N bond to the extent that separation of the  $\text{Li}^+$  could be achieved. Despite this lack of success, both these structures were novel in the sense that they were the first for mononuclear lithium amides.<sup>31</sup> Free disilylamide ions were eventually syn-



**Figure 5.** Computer-generated plot of the  $[\text{CHPh}_2]^-$  ion from  $[\text{Li}(12\text{-crown-4})_2][\text{CHPh}_2]$ . Selected bond distances (Å) and the C(2)–C(1)–C(8) angle (deg) are C(1)–C(2) = 1.435 (6), C(1)–C(8) = 1.404 (6), C–C(Ph av) = 1.407 (8), and C(2)–C(1)–C(8) = 132.1 (4).



**Figure 6.** Computer-generated drawing of the unit cell of  $[\text{Li}(\text{Et}_2\text{O})\text{CH}_2\text{Ph}]_n$ . Hydrogen atoms are omitted for clarity. Selected bond distances (Å) are Li(1)–C(1) = 2.218 (8), Li(1)···C(2) = 2.458 (9), Li(1)–C(12) = 2.206 (9), and C(1)–C(2) = 1.426 (5).

thesized by using the  $\text{HN}(\text{SiPh}_3)_2$  precursor, which afforded separation of the  $[\text{N}(\text{SiPh}_3)_2]^-$  ion as shown in Figure 4. The most interesting structural aspects concern the wide  $156.8 (3)^\circ$  Si–N–Si angle and shortened (ca. 1.63 Å) N–Si distances, which probably involve multiple bonding. The ion is isoelectronic with  $[\text{PPN}]^{+33}$  and it is possible that the Si–N–Si angle will be as variable as the P–N–P angle ( $135\text{--}180^\circ$ ), enabling, perhaps, a linear  $[\text{SiNSi}]^-$  species to be characterized eventually.

In spite of the initial failure to isolate crystals involving free carbanions, numerous studies had shown that salts of delocalized carbanions exist in solution as ion pairs. Several of these had been structurally characterized as ligand-complexed metal salts.<sup>3</sup> None, however, had involved separate hydrocarbyl carbanions. When 12-crown-4 was added to a THF solution of  $\text{LiCPh}_3$ , the compound  $[\text{Li}(12\text{-crown-4})_2][\text{CPh}_3] \cdot \text{THF}$ <sup>34</sup> was obtained as red needles. Orange crystals of  $[\text{Li}(12\text{-crown-4})_2][\text{CHPh}_2]$  were similarly obtained. Both compounds involved separate carbanions with  $[\text{Li}(12\text{-crown-4})_2]^+$  counterions.

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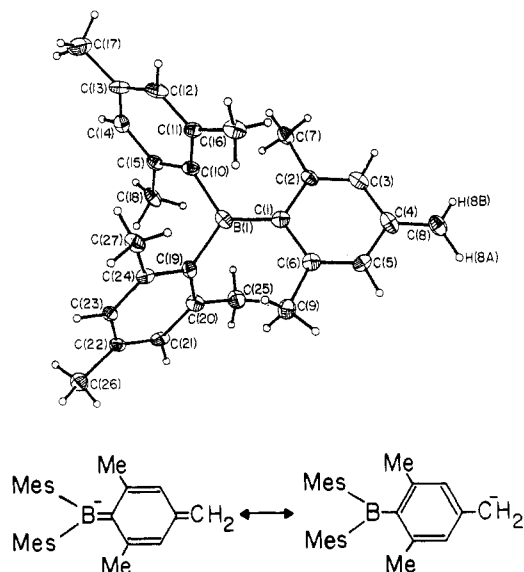
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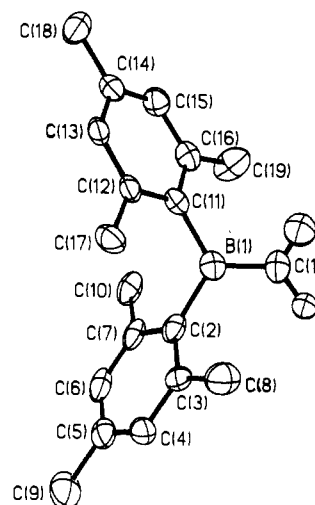


**Figure 7.** Computer-generated plot of the  $[\text{CH}_2\text{C}_6\text{H}_2(3,5\text{-Me}_2)(4\text{-BMes}_2)]^-$  ion. Important bond distances (Å) and angles (deg) are B(1)–C(1) = 1.522 (10), B(1)–C(10) = 1.615 (12), B(1)–C(19) = 1.602 (11), C(1)–C(2) = 1.466 (11), C(2)–C(3) = 1.362 (10), C(3)–C(4) = 1.443 (12), C(4)–C(5) = 1.431 (11), C(5)–C(6) = 1.362 (10), C(1)–C(6) = 1.451 (12), C(4)–C(8) = 1.349 (10), C(1)–B(1)–C(10) = 123.5 (7), C(1)–B(1)–C(19) = 124.9 (8), and C(10)–B(1)–C(19) = 111.6 (6). The two principal, contributing resonance forms of the anion are also shown.

crown-4) $_2$  $^+$  counteranions. The structure of  $[\text{CHPh}_2]^-$  is illustrated in Figure 5. This species is of interest for two reasons. First the ion is planar with a wide C(2)–C(1)–C(8) angle of 132.1 (4) $^\circ$ . The structure, which is in agreement with theoretical calculations, $^{35}$  suggests that delocalization of the negative charge may play a greater role than was previously realized. Also it is notable that the ions  $[\text{NPh}_2]^-$  and  $[\text{CHPh}_2]^-$  are isoelectronic. The Li–anion separation achieved in the case of the latter salt serves to underline the greater strength of the Li–N relative to the Li–C interaction. Attempts to extend the series  $[\text{CPh}_3]^-$  and  $[\text{CHPh}_2]^-$  to the next lower member  $[\text{CH}_2\text{Ph}]^-$  were only partly successful. It was found that benzyl lithium readily crystallized from ether as a chainlike polymer  $[\text{Li}(\text{Et}_2\text{O})\text{CH}_2\text{Ph}]_\infty$  (Figure 6). $^{19}$  The addition of 12-crown-4 afforded a yellow microcrystalline precipitate, which probably involved the free  $[\text{CH}_2\text{Ph}]^-$  ion. However, attempts at recrystallization with THF as solvent resulted in decomposition, presumably due to attack by the very reactive free  $[\text{CH}_2\text{Ph}]^-$  ion on THF.

### Isolation of Anions Having Boron–Carbon Multiple Bonding

Attempts to reduce the powerful nucleophilic character of the benzyl ion to allow its isolation led to some fruitful investigations of boron–carbon multiple bonding. Substitution of the para hydrogen of benzyl with diorganoboryl would be expected to reduce the nucleophilicity of the benzyl  $\text{CH}_2^-$  group to prevent its reaction with ether solvents. The most obvious diorganoboryl candidate was the hindered  $-\text{BMes}_2$  $^{36}$  group, which had already been shown to be capable of this type of stabilization and to display considerable



**Figure 8.** Computer-generated plot of the  $[\text{Mes}_2\text{BCH}_2]^-$  anion from  $[\text{Li}(12\text{-crown-4})_2][\text{Mes}_2\text{BCH}_2]$ . Selected bond distances (Å) and angles (deg) are B(1)–C(1) = 1.450 (7), B(1)–C(2) = 1.627 (7), B(1)–C(11) = 1.610 (8), C(1)–B(1)–C(2) = 121.0 (5), C(1)–B(1)–C(11) = 120.7 (5), and C(2)–B(1)–C(11) = 118.3 (4). Similar values are observed for the other  $[\text{Mes}_2\text{BCH}_2]^-$  anion in the asymmetric unit (i.e., B(2)–C(20) = 1.438 (9) Å).

synthetic utility in carbanion chemistry. $^{37}$  It was decided that, instead of synthesizing and attempting to crystallize a species such as  $\text{LiCH}_2\text{C}_6\text{H}_4\text{-4-BMes}_2$ , the precursor  $\text{BMes}_3$  could be used as it was very similar and was already known $^{38}$  to give  $\text{LiCH}_2\text{C}_6\text{H}_2(3,5\text{-Me}_2)(4\text{-BMes}_2)$  upon treatment with *n*-BuLi. Accordingly, the addition of 12-crown-4 to a THF solution of the latter resulted in the crystallization of the ion shown in Figure 7. $^{39}$  Its structure may be regarded as having approximately equal contributions from the borate and carbanion canonical forms. $^{39}$  There is considerable shortening of the B(1)–C(1) distance, 1.522 (10) Å relative to the other two B–C bonds of  $\sim 1.61$  Å. The methylene C(8)–C(4) distance, 1.349 (10) Å, is also shortened relative to the corresponding length in the  $[\text{Li}(\text{Et}_2\text{O})\text{CH}_2\text{Ph}]_\infty$  structure. The twist angle between the BC(1)–C(10)–C(19) and C(1) ring planes is 25.8 $^\circ$ , which is around half the dihedral angle in  $\text{BMes}_3$ . A fully fledged BC double bond is apparent in the free  $[\text{Mes}_2\text{BCH}_2]^-$  anion $^{40}$  (Figure 8), which was obtained when 12-crown-4 was added to a solution of  $\text{LiCH}_2\text{BMes}_2$ . $^{36,37}$  The  $[\text{C}_2\text{B}=\text{CH}_2]^-$  array is planar and the B=C length is 1.438 (9) Å. This is somewhat longer than the B=C lengths 1.416 (3) Å and 1.391 (4) Å in  $(\text{tmp})\text{B}=(\text{fluorenyl})$  ( $\text{tmp} = 2,2,6,6\text{-tetramethylpiperidine}_2$ ) and  $i\text{-Pr}_2\text{NB}=\text{C}(\text{SiMe}_3)_2$ , $^{41}$  which were published almost simultaneously.

Further work involving the  $\text{BMes}_3$  precursor concerned its treatment with alkali metals to allow the first structural characterization of a boron-centered radical, the radical anion species  $[\text{BMes}_3]^\bullet$ . $^{42}$  When 12-crown-4 was added to a THF solution of  $\text{LiBMes}_3$ , a

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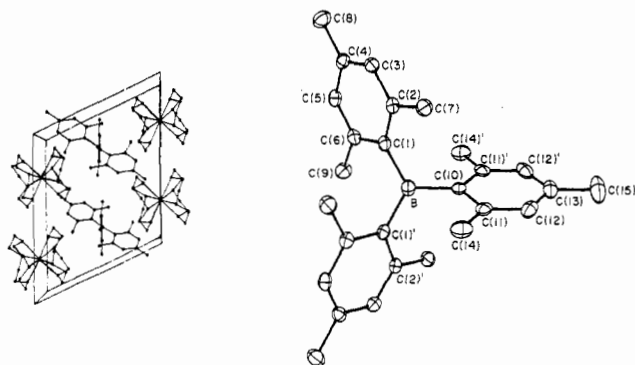
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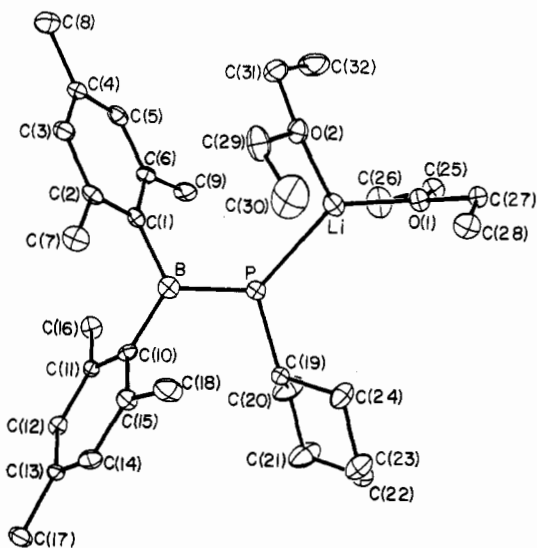
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**Figure 9.** (a) Unit cell view of  $[\text{Li}(12\text{-crown-4})_2]^+[\text{BMe}_3]^-$ . (b) Thermal ellipsoid plot of the  $[\text{BMe}_3]^-$  anion. Selected bond distances (Å) and angles (deg) are B-C(1) = 1.592 (2), B-C(10) = 1.608 (4), C(1)-B-C(1)' = 121.8 (2), and C(1)-B-C(10) = 119.1 (1).

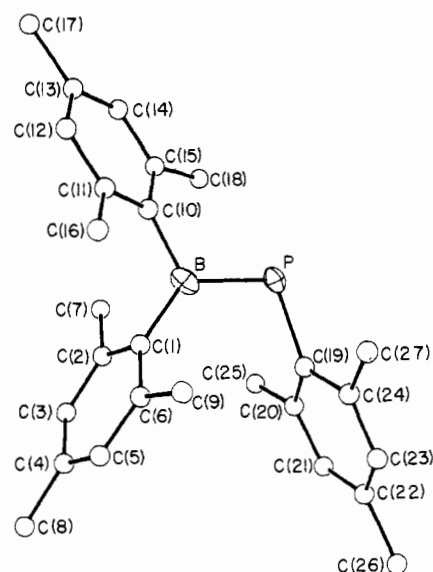


**Figure 10.** Computer-generated drawing of  $\text{Li}(\text{Et}_2\text{O})_2\text{P}(\text{C}_6\text{H}_{11})\text{BMe}_2$ . Important bond distances (Å) and angles (deg) for  $\text{Li}(\text{Et}_2\text{O})_2\text{PRBMe}_2$ , R =  $\text{C}_6\text{H}_{11}$ , and in braces R = Mes are P-B = 1.832 (6) {1.823 (7)}, P-Li = 2.454 (9) {2.451 (14)}; B-P-C(19) = 108.2 (3) {111.7 (4)}, B-P-Li = 127.1 (3) {126.9 (5)}, C(19)-P-Li = 122.4 (3) {121.3 (4)}.

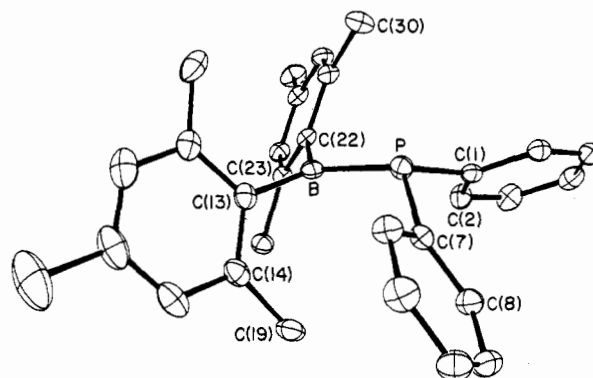
good yield of navy blue crystals of  $[\text{Li}(12\text{-crown-4})_2][\text{BMe}_3]^{+43}$  was obtained. Drawings of the contents of the unit cell and of the radical anion are shown in Figure 9. The  $\text{BC}_3$  radical core is planar and the B-C distances show only a slight lengthening upon reduction. The B-C(1) and B-C(10) distances for the radical are 1.592 (2) and 1.608 (4) Å whereas the corresponding distances for neutral  $\text{BMe}_3$  are 1.579 (2) and 1.580 (3) Å.

### Isolation of Anions Having Boron-Phosphorus Multiple Bonding

These studies led to interest in other boron systems, particularly the poorly investigated boron-phosphorus compounds. Use of the  $-\text{BMe}_2$  group allowed, via sequential reaction of  $\text{Mes}_2\text{BF}$  and  $\text{LiPHR}$  with  $n\text{-BuLi}$ , the isolation<sup>44,45</sup> of the phosphinidene borate complex  $\text{Li}(\text{Et}_2\text{O})_2\text{PRBMe}_2$  (R = Ph,  $\text{C}_6\text{H}_{11}$ , or Mes), an exam-



**Figure 11.** Computer-generated drawing of the  $[\text{MesPBMe}_2]^-$  anion from  $[\text{Li}(12\text{-crown-4})_2][\text{MesPBMe}_2]\cdot\text{THF}$ . Important bond distances (Å) and angles (deg) are P-B = 1.835 (13), B-P-C(19) = 108.2 (5), P-B-C(1) = 126.0 (8), P-B-C(10) = 116.7 (7), and C(1)-B-C(10) = 117.3 (10).



**Figure 12.** Computer-generated thermal ellipsoid plot of  $\text{Mes}_2\text{BPPH}_2$ . Important bond distances (Å) and angles (deg) are B-P = 1.859 (3), C(1)-P-C(7) = 106.9 (1), C(1)-P-B = 116.0 (1), and C(7)-P-B = 116.5 (1).

ple of which is illustrated in Figure 10. The planar nature of this molecule and the short B-P bonds (ca. 1.82–1.83 Å) indicated a considerable amount of multiple B-P bonding. Subsequent treatment of these complexes with 12-crown-4 afforded the anion shown in Figure 11, which had similar B-P bonding characteristics.<sup>44</sup> To establish the length of a B-P bond in a monomeric phosphinoborane, the complex  $\text{Mes}_2\text{BPPH}_2$ <sup>46</sup> was synthesized. Its structure is shown in Figure 12. It has a B-P bond length of 1.859 (3) Å and, in contrast to the planar aminoboranes  $\text{R}_2\text{BNR}'_2$ ,<sup>47</sup> the phosphorus center is pyramidal. The sum of the angles at P is  $\sim 340^\circ$  whereas in normal phosphines, for example,  $\text{PPh}_3$ , it is ca.  $310^\circ$ . In essence, the structure of  $\text{Mes}_2\text{BPPH}_2$  presents a bonding picture intermediate between a planar B-P system with strong  $\text{P} \rightarrow \text{B}$   $\pi$  bonding and the alternative with a much smaller donor interaction and an essentially single B-P bond. The latter situation is exemplified by the structure of

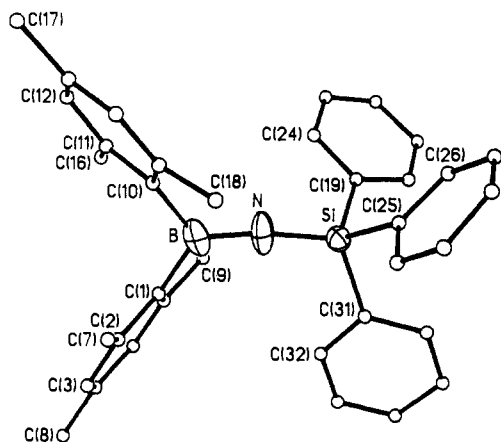
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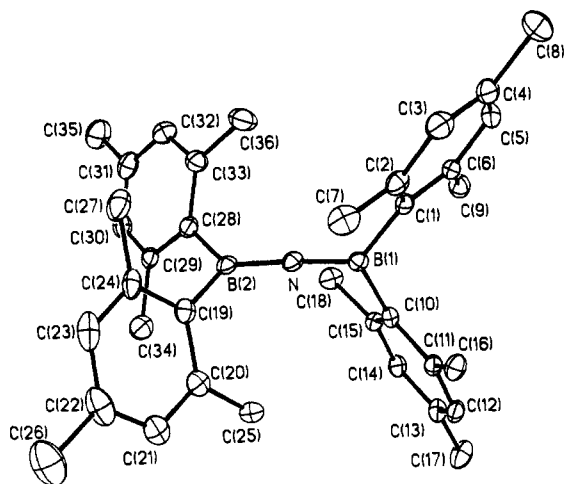
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**Figure 13.** Computer-generated drawing of the  $[\text{Mes}_2\text{BNSiPh}_3]^-$  anion from  $[\text{Li}(12\text{-crown-}4)]_2[\text{Mes}_2\text{BNSiPh}_3]$ . The N-Si and N-B bond distances (Å) are N-Si = 1.639 (8) and N-B = 1.362 (11).



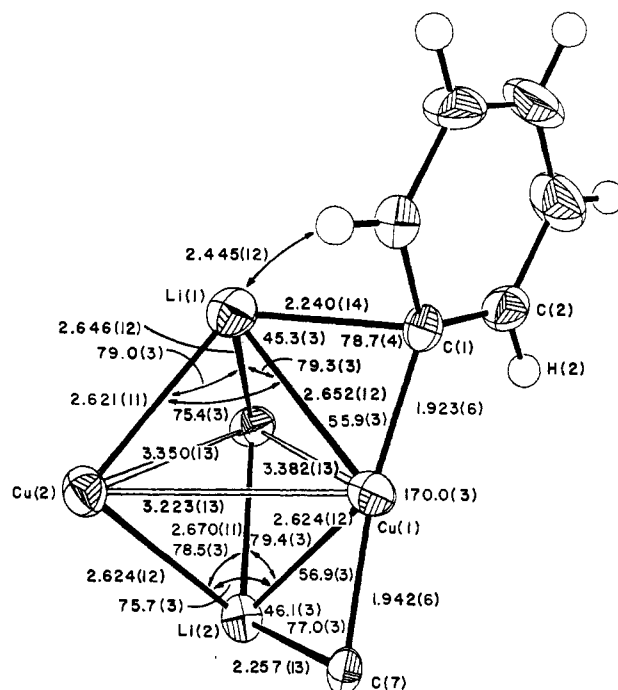
**Figure 14.** Drawing of the  $[\text{Mes}_2\text{BNBMes}_2]^-$  anion from  $[\text{Li}(\text{Et}_2\text{O})_3][\text{Mes}_2\text{BNBMes}_2]$ . Important bond distances (Å) and angles (deg) are N-B(1) = 1.343 (1), N-B(2) = 1.348 (5), B(1)-N-B(2) = 176.2 (3), angle between NB(1)C(1)C(10) and NB(2)-C(19)C(28) planes = 88.1.

$\text{Mes}(\text{H})\text{PB}(\text{Cl})(\text{tmp})$ ,<sup>48</sup> which, because of the competitive  $\text{N} \rightarrow \text{B}$   $\pi$  interaction, has a very pyramidal phosphorus ( $\Sigma \text{P}$  angles =  $307^\circ$ ) and a significantly longer B-P bond of 1.948 (3) Å.

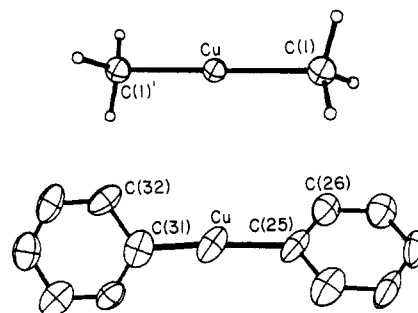
Separation of  $\text{Li}^+$  ions has also been effected in related boron-nitrogen compounds. For example, the addition of 12-crown-4 to ether/THF solutions of  $\text{LiN}(\text{SiPh}_3)\text{BMes}_2$  gives crystals incorporating the anions in Figure 13.<sup>49</sup> In cases involving nitrogen with two boryl substituents, crystals of the linear  $[\text{Mes}_2\text{BNBMes}_2]^-$  with the  $[\text{Li}(\text{Et}_2\text{O})_3]^+$  cation (Figure 14) can be obtained directly from ether solution.<sup>50</sup>

### Organocuprates

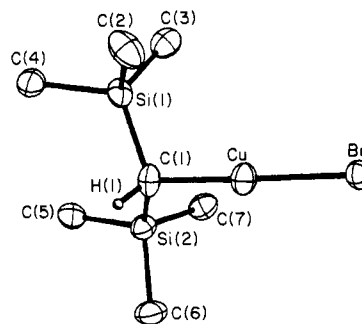
A further application of the 12-crown-4 reagent arose from work on cuprate ( $\text{LiCuR}_2$ ) compounds. In general, these complexes are associated in solution. For example, the species " $\text{LiCuPh}_2$ " is trimeric with three  $\text{CuPh}_2^-$  units bridged by two  $\text{Li}^+$  ions, giving a trigonal-bipy-



**Figure 15.** Thermal ellipsoid plot of the  $[\text{Li}_2\text{Cu}_3\text{Ph}_6]^-$  anion. Five phenyl rings are omitted for clarity in showing the trigonal-bipyramidal framework.



**Figure 16.** Computer-generated drawings of the  $[\text{CuMe}_2]^-$  and  $[\text{CuPh}_2]^-$  anions. Selected bond distances (Å) and angles (deg) are as follows: for  $[\text{CuMe}_2]^-$ , Cu-C(1) = 1.935 (8), C(1)-Cu-C(1') =  $180.0^\circ$ ; for  $[\text{CuPh}_2]^-$ , Cu-C(25) = 1.920 (9), Cu-C(31) = 1.929 (10), C(25)-Cu-C(31) =  $178.5^\circ$  (4), dihedral angle between phenyl rings =  $47.3^\circ$  (9).



**Figure 17.** Computer-generated plot of the  $[\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]^-$  ion. Selected bond distances (Å) and the C(1)-Cu-Br angle (deg) are Cu-Br = 2.267 (2), Cu-C(1) = 1.920 (6), and C(1)-Cu-Br =  $178.7^\circ$  (2).

ramidal framework for the metals as shown in Figure 15. The skeletal arrangement for the  $[\text{Li}_2\text{Cu}_3\text{Ph}_6]^-$ <sup>51</sup> ion is quite persistent and remained unchanged with various cations such as  $[\text{Li}_4\text{Cl}_2(\text{OEt}_2)_{10}]^{2+}$  and  $[\text{Li}$ -

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(THF)<sub>4</sub>]<sup>+</sup>.<sup>52</sup> Related structures had been previously reported by Bau for the [Cu<sub>5</sub>Ph<sub>6</sub>]<sup>-53</sup> and later for the [LiCu<sub>4</sub>Ph<sub>6</sub>]<sup>-54</sup> ions. When 12-crown-4 is added to a solution of LiCuPh<sub>2</sub> or LiCuMe<sub>2</sub>, the lithium is abstracted from the aggregate, and the first mononuclear anions of the type [CuPh<sub>2</sub>]<sup>-</sup> or [CuMe<sub>2</sub>]<sup>-55</sup> (Figure 16) are formed. Other species can also be trapped from the reaction mixtures as illustrated by the structure of the intermediate [Cu(Br)CH(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> ion<sup>53</sup> (Figure 17).

### Conclusion

It is clear that 12-crown-4 is an effective agent for the removal of Li<sup>+</sup> ions from many lithium compounds that are aggregated in solution. The main limitation to its effectiveness arises where lithium is strongly bound to its counteranion as in the case of NR<sub>2</sub><sup>-</sup> and OR<sup>-</sup> species. However, with the proper substituents, such as in [N-(SiPh<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, separation can be achieved in certain cases. It may be that suitable modification of the OR<sup>-</sup> ligand,

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as in [-OBMe<sub>2</sub>]<sup>-56</sup> will also allow separation of a free [OR]<sup>-</sup> anion. However, stronger Li<sup>+</sup> coordinating agents such as the cryptand [211]<sup>57</sup> or spherand ligands<sup>58</sup> will be required to separate the more common NR<sub>2</sub><sup>-</sup> and OR<sup>-</sup> ions. There is also further scope for development in the choice of solvent. For example, use of amine solvents<sup>5</sup> may permit the isolation of carbanions that are far too reactive to isolate in the presence of ethers. Thus, the characterization of a far wider range of reactive ions than is at present known is highly probable in the future.

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## Cyclometalation Chemistry of Aryl Oxide Ligation

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The search for homogeneous transition-metal systems that have the ability to activate normally inert carbon-hydrogen bonds under mild conditions has been the focus of endeavor by many research groups over the past two decades.<sup>1</sup> The significant successes achieved over the past few years have identified two general categories of compound that exhibit this type of reactivity. The first, more thoroughly studied, set involves the activation of carbon-hydrogen bonds by an oxidative-addition pathway to low-valent transition-metal centers.<sup>1-4</sup> This reactivity was initially extensively characterized for the intramolecular activation of the carbon-hydrogen bonds contained in various ligands already coordinated to the metal centers via a heteroatom site.<sup>5-7</sup> However, more recently metal systems able to intermolecularly activate even the most difficult hydrocarbon substrate, methane, have been developed.<sup>8-12</sup> The second, still rapidly developing, area of metal-mediated carbon-hydrogen bond activation involves the use of high-valent, electron-deficient early-d-block,<sup>13</sup> lanthanide,<sup>14</sup> and actinide<sup>15</sup> metal com-

pounds. Again, systems able to activate methane under mild conditions have been devised.<sup>16,17</sup> The absence of an accessible oxidative-addition pathway for these electron-deficient systems has led to the proposal of mechanisms that are electrophilic in nature to account for the observed reactivity.<sup>18,19</sup>

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