

bonding region. The p electrons on the halide ligands could function in a similar manner, although apparently to a lesser degree.

The aforementioned overlap effects, while greatly influencing the electronic spectra, particularly the portion associated with the δ orbitals, may not play an important role in determining bond lengths or bond strengths (as measured by force constants or thermodynamic methods). These latter properties are probably set by the much stronger σ and π interactions, which maximize at longer metal-metal distances than δ interactions. A number of examples are apparent in the literature,²³⁻²⁵ where the strength, or even the existence, of the δ orbital has little or no effect on metal-metal bond strength.

In the following series:²⁷

	Mo ₂ - (O ₂ CCH ₃) ₄	Mo ₂ - (O ₂ CCH ₃) ₂ - Cl ₄ ²⁻	Mo ₂ Cl ₈ ⁴⁻
M-M, Å	2.093	2.086	2.14
$\delta \rightarrow \delta^*$, cm ⁻¹	22 700	20 200	19 300
ϵ , M ⁻¹ cm ⁻¹	105	490	1050

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there is no correlation of the $\delta \rightarrow \delta^*$ absorption energy with the bond length. Some previous work²⁸ has emphasized the linear relation between the $\delta \rightarrow \delta^*$ absorption energy and the metal-metal bond length within a restricted series of compounds. This is quite a reasonable hypothesis, and we note a similar excellent linear correlation for the M₂(mhp)₄ systems we have studied. However, the IP of the δ electrons correlates just as well as the metal-metal bond length for the M₂(mhp)₄ systems. Because of chemical periodicity, it is clear that many physical properties will tend to parallel one another. In this paper we have presented what we believe are the fundamental parameters which influence the position and intensity of the $\delta \rightarrow \delta^*$ transition.

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Registry No. Cr₂(mhp)₄, 67634-82-6; Mo₂(mhp)₄, 67634-80-4; W₂(mhp)₄, 67634-84-8; Mo₂(chp)₄, 73274-69-8.

Supplementary Material Available: Tables of spectral data and absorption spectra of Mo₂(chp)₄ and Hchp in tetrahydrofuran, Mo₂(mhp)₄ in an argon matrix at 10 K, Mo₂(mhp)₄ in a nitrogen matrix at 10 K, Mo₂(mhp)₄ in a xenon matrix at 10 K, and W₂(mhp)₄ in an argon matrix at 10 K (8 pages). Ordering information is given on any current masthead page.

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Isolation and Crystal Structures of the Halide-Free and Halide-Rich Phenyllithium Etherate Complexes [(PhLi·Et₂O)₄] and [(PhLi·Et₂O)₃·LiBr][†]

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Abstract: The compounds [(PhLi·Et₂O)₄] and [(PhLi·Et₂O)₃·LiBr] have been isolated, and characterized by single-crystal X-ray studies. The [(PhLi·Et₂O)₄] crystals possess monoclinic symmetry of space group *I2/a*, *Z* = 4, with *a* = 20.043 (18) Å, *b* = 9.707 (8) Å, *c* = 20.498 (16) Å, and β = 96.66 (7)°. The structure consists of two interlocking tetrahedra of four lithium and four phenyl carbon atoms in a distorted cubane framework. Each lithium is further coordinated by oxygen from an ether molecule. The coordination at lithium is approximately tetrahedral. The [(PhLi·Et₂O)₃·LiBr] crystals are also monoclinic of space group *P2₁/c*, *Z* = 4, with *a* = 18.632 (4) Å, *b* = 7.709 (2) Å, *c* = 22.253 (8) Å, and β = 94.63 (3)°. In the case of [(PhLi·Et₂O)₃·LiBr] the framework is further distorted by the presence of Br⁻ instead of a carbon from a phenyl group. The lithium diagonally opposite Br⁻ in the cube is uncoordinated by ether. This is the first structure report for an organolithium halide complex.

The chemical constitution of the lithium alkyls and aryls and the nature of their structure in solution or in the solid phase have been outstanding problems in organometallic chemistry.¹ Much of the published work has concentrated upon the alkyl derivatives, and a number of crystal structures have appeared.² Studies of aryllithium compounds in solution involving both ultraviolet and NMR spectroscopy have been reported.^{3,4} In addition, vapor pressure and ebullioscopic work have established that the degree of association of such compounds in diethyl ether or tetrahydrofuran is two, whereas for the alkyl derivatives it is either four or six.^{5,6} However, the structure of phenyllithium has not

been established with certainty either in solution or in the crystalline state.

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A related problem concerns the complexes of simple⁷ alkyl- or aryllithium compounds with lithium halides, for which no structure has been reported before. Such complexes are typically obtained when an alkyl or aryl halide is treated with lithium metal in diethyl ether solution. Both methyl- and phenyllithium are commercially available as "halide-rich" ether solutions which presumably contain halide incorporated in the complex structure in solution. Cooling these solutions in the case of both MeLi or PhLi affords crystals which contain halide. For example, the composition MeLi·LiBr·2Et₂O has been claimed in the case of methylithium crystals.⁸ Kinetic data suggests that halide complexes of phenyllithium have 1:1 stoichiometry.⁹

A major problem in the X-ray structural investigation of the aryllithiums has been the difficulty in obtaining suitable crystals. We overcame this problem by choosing etherate complexes which crystallize readily from ether solution. This allowed us to obtain suitable crystals in both the case of pure phenyllithium and its lithium bromide complex. These crystals required careful handling because of their air and moisture sensitivity and the fact that the ether of crystallization is not tenaciously held. Attempts to dry these crystals in vacuo resulted in their disintegration; consequently, the crystals were not dried but handled at all times in the presence of small quantities of ether solvent. Only freshly prepared samples were used in structural determinations. The crystals were not more than 1 week old and held at all times at ca. -20 °C so as to avoid attack of the organolithium on the ether solvent.

Experimental Section

Preparation of Compounds. All manipulations were carried out under a purified nitrogen atmosphere in Schlenk apparatus. Solvents were distilled under nitrogen from Na/K benzophenone and degassed several times. Halide-free phenyllithium was prepared by the literature method¹⁰ via the interaction of *n*-BuLi with PhI. The solid PhLi obtained was removed via filtration, washed with hexane, and redissolved in Et₂O. Addition of *n*-hexane and slow cooling afford suitable crystals of the product [(PhLi·Et₂O)₄].

Colorless crystals of [(PhLi·Et₂O)₃·LiBr] were obtained¹¹ by cooling the filtered Et₂O solution from the reaction of excess lithium with bromobenzene.

Collection and Reduction of X-ray Data. X-ray data were collected with a Syntex diffractometer equipped with a locally modified Syntex LT-1 cooling device. The crystal temperature was held near 135 K.

After the crystals had been removed from the crystallization vessel, they were protected from the atmosphere by a layer of silicone oil, while being kept cold with dry ice. Roughly cube shaped specimens (sides about 0.5 mm) were cut and used for data collection. The crystals were attached to mounting fibers with the resin part of epoxy glue and immediately placed in the cold stream of the low-temperature apparatus. Even at the temperature used a relatively rapid decline in diffraction intensity with increasing 2θ was evident for [(PhLi·Et₂O)₃·LiBr]. For this reason the slower than usual scan rate was selected (vide infra).

Crystal data for [(PhLi·Et₂O)₄]: C₄₀H₆₀Li₄O₄; $M_r = 632.67$; colorless prisms; monoclinic; space group $I2/a$ (No. 15); $Z = 4$ (tetramers, twofold symmetry axis required); $a = 20.043$ (18) Å, $b = 9.707$ (8) Å, $c = 20.498$ (16) Å, $\beta = 96.66$ (7)°; $V = 3961$ Å³; $d_{\text{calc}} = 1.06$ Mg m⁻³; $\mu = 1.0$ cm⁻¹ ($T = 135$ K, $\lambda(\text{Mo K}\alpha_1) = 0.70926$ Å). Data collection:¹² Mo K α , graphite monochromator; low temperature; 1° ω scan; 58.6 deg min⁻¹; 0.5 s stationary backgrounds at ω offsets $\pm 1^\circ$; $2\theta_{\text{max}} = 55^\circ$; 4556 unique reflections scanned.

Crystal data for [(PhLi·Et₂O)₃·LiBr]: C₃₀H₄₅BrLi₄O₃; $M_r = 561.35$; colorless prisms; monoclinic; space group $P2_1/c$ (No. 14); $Z = 4$; $a = 18.632$ (4) Å, $b = 7.709$ (2) Å, $c = 22.253$ (8) Å, $\beta = 94.63$ (1)°; $V =$

Table I. Bond Lengths (Å)

a. [(PhLi·Et ₂ O) ₄]			
Li(1)-Li(2)	2.707 (6)	Li(1)-O(1)	2.000 (4)
Li(1)-C(31)	2.317 (4)	Li(1)-Li(1A)	2.505 (8)
Li(1)-Li(2A)	2.661 (6)	Li(1)-C(31A)	2.320 (5)
Li(1)-C(41A)	2.277 (5)	Li(2)-O(2)	2.098 (4)
Li(2)-C(31)	2.348 (5)	Li(2)-C(41)	2.326 (5)
Li(2)-Li(1A)	2.661 (6)	Li(2)-Li(2A)	2.577 (7)
O(1)-C(11)	1.439 (3)	O(1)-C(13)	1.440 (3)
C(11)-C(12)	1.507 (4)	C(13)-C(14)	1.512 (4)
O(2)-C(21)	1.450 (3)	O(2)-C(23)	1.438 (3)
C(21)-C(22)	1.518 (4)	C(23)-C(24)	1.494 (4)
C(31)-C(32)	1.421 (4)	C(31)-C(36)	1.425 (3)
C(31)-Li(1A)	2.320 (5)	C(32)-C(33)	1.394 (3)
C(33)-C(34)	1.391 (4)	C(34)-C(35)	1.383 (4)
C(35)-C(36)	1.395 (3)	C(41)-C(42)	1.422 (3)
C(41)-C(46)	1.422 (3)	C(41)-Li(1A)	2.277 (5)
C(42)-C(43)	1.397 (4)	C(43)-C(44)	1.386 (4)
C(44)-C(45)	1.389 (4)	C(45)-C(46)	1.387 (4)
Li(1A)-Li(2)	2.661 (6)	Li(1A)-C(31)	2.320 (5)
Li(1A)-C(41)	2.277 (5)	Li(1A)-Li(2A)	2.707 (6)
Li(1A)-C(31A)	2.317 (4)	Li(2A)-Li(2)	2.577 (7)
Li(2A)-Li(1A)	2.707 (6)	Li(2A)-C(31A)	2.348 (5)
Li(2A)-C(41A)	2.326 (5)	C(31A)-Li(1A)	2.317 (4)
C(31A)-Li(2A)	2.348 (5)	C(41A)-Li(1)	2.277 (5)
C(41A)-Li(2A)	2.326 (5)		
b. [(PhLi·Et ₂ O) ₃ ·LiBr]			
Br-Li(1)	2.513 (5)	Br-Li(2)	2.537 (5)
Br-Li(3)	2.564 (5)	Li(1)-Li(2)	2.924 (7)
Li(1)-Li(3)	2.968 (6)	Li(1)-Li(4)	2.474 (6)
Li(1)-O(1)	1.959 (5)	Li(1)-C(41)	2.303 (5)
Li(1)-C(51)	2.252 (6)	Li(2)-Li(3)	2.978 (6)
Li(2)-Li(4)	2.497 (7)	Li(2)-O(2)	1.928 (5)
Li(2)-C(51)	2.244 (5)	Li(2)-C(61)	2.329 (5)
Li(3)-Li(4)	2.436 (6)	Li(3)-O(3)	1.956 (5)
Li(3)-C(41)	2.305 (5)	Li(3)-C(61)	2.252 (5)
Li(4)-C(41)	2.140 (6)	Li(4)-C(51)	2.148 (5)
Li(4)-C(61)	2.155 (5)	O(1)-C(11)	1.443 (4)
O(1)-C(13)	1.424 (4)	C(11)-C(12)	1.496 (4)
C(13)-C(14)	1.500 (4)	O(2)-C(21)	1.434 (3)
O(2)-C(23)	1.442 (3)	C(21)-C(22)	1.497 (4)
C(23)-C(24)	1.505 (4)	O(3)-C(31)	1.436 (4)
O(3)-C(33)	1.429 (4)	C(31)-C(32)	1.505 (5)
C(33)-C(34)	1.495 (4)	C(41)-C(42)	1.409 (4)
C(41)-C(46)	1.405 (4)	C(42)-C(43)	1.388 (4)
C(43)-C(44)	1.374 (4)	C(44)-C(45)	1.381 (4)
C(45)-C(46)	1.388 (4)	C(51)-C(52)	1.417 (4)
C(51)-C(56)	1.411 (4)	C(52)-C(53)	1.391 (4)
C(53)-C(54)	1.373 (5)	C(54)-C(55)	1.370 (4)
C(55)-C(56)	1.386 (4)	C(61)-C(62)	1.407 (4)
C(61)-C(66)	1.415 (4)	C(62)-C(63)	1.389 (4)
C(63)-C(64)	1.376 (5)	C(64)-C(65)	1.374 (4)
C(65)-C(66)	1.392 (4)		

3185.9 Å³, $d_{\text{calc}} = 1.17$ Mg m⁻³, $\mu = 14$ cm⁻¹ ($T = 135$ K, $\lambda(\text{MoK}\alpha_1) = 0.70926$ Å). Data collection: Mo K α ; graphite monochromator; low temperature; 1.7° ω scan; 8.37 deg min⁻¹; 6 s stationary backgrounds at ω offsets $\pm 1.2^\circ$, $2\theta_{\text{max}} = 55^\circ$, 7306 unique reflections scanned.

For each compound two monitor reflections remeasured every 200 reflections indicated no decay in intensity. Standard Lorentz and polarization corrections were applied. Extinction and absorption corrections were not applied.

Solution and Refinement of the Structures. The structures were solved by direct methods, [(PhLi·Et₂O)₃·LiBr] with the program SIGNS,¹³ and [(PhLi·Et₂O)₄] with the Nicolet SHELXTL system. Both structures were refined with the block cascade procedure of SHELXTL, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included with fixed C-H geometry and isotropic temperature factors derived from carbon thermal parameters. The least-squares weights were set to give nearly uniform weighted deviations vs. 2θ and F_o . The final R index for [(PhLi·Et₂O)₄] is 0.058 for 2766 "observed" reflections and 217 parameters; the final R index for [(PhLi·Et₂O)₃·LiBr] is 0.041 for 4812 reflections and 344 parameters. For each compound the composition was determined from the X-ray data, and its correctness

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Table II. Bond Angles (deg)

a. [(PhLi-Et ₂ O) ₄]					
Li(2)-Li(1)-O(1)	147.2 (2)	C(42)-C(43)-C(44)	119.8 (2)	Li(1A)-Li(2)-Li(2A)	62.2 (1)
O(1)-Li(1)-C(31)	113.8 (2)	C(44)-C(45)-C(46)	119.7 (2)	Li(1)-O(1)-C(13)	130.0 (2)
O(1)-Li(1)-Li(1A)	144.0 (1)	Li(1)-Li(1A)-Li(2)	63.1 (1)	O(1)-C(11)-C(12)	114.4 (2)
Li(2)-Li(1)-Li(2A)	57.4 (2)	Li(2)-Li(1A)-C(31)	55.7 (1)	Li(2)-O(2)-C(21)	119.3 (2)
C(31)-Li(1)-Li(2A)	104.2 (2)	Li(2)-Li(1A)-C(41)	55.5 (1)	C(21)-O(2)-C(23)	111.6 (2)
Li(2)-Li(1)-C(31A)	102.7 (2)	Li(1)-Li(1A)-Li(2A)	61.3 (1)	O(2)-C(23)-C(24)	109.2 (2)
C(31)-Li(1)-C(31A)	113.0 (2)	C(31)-Li(1A)-Li(2A)	102.7 (2)	Li(1)-C(31)-C(32)	89.6 (2)
Li(2A)-Li(1)-C(31A)	55.7 (1)	Li(1)-Li(1A)-C(31A)	57.4 (2)	Li(1)-C(31)-C(36)	155.9 (2)
O(1)-Li(1)-C(41A)	108.3 (2)	C(31)-Li(1A)-C(31A)	113.0 (2)	C(32)-C(31)-C(36)	111.0 (2)
Li(1A)-Li(1)-C(41A)	107.7 (1)	Li(2A)-Li(1A)-C(31A)	55.1 (1)	Li(2)-C(31)-Li(1A)	69.5 (2)
C(31A)-Li(1)-C(41A)	106.9 (2)	Li(1)-Li(2A)-Li(1A)	55.6 (2)	C(36)-C(31)-Li(1A)	91.5 (2)
Li(1)-Li(2)-C(31)	54.0 (1)	Li(1)-Li(2A)-C(31A)	54.7 (1)	C(32)-C(33)-C(34)	120.3 (2)
Li(1)-Li(2)-C(41)	100.0 (2)	Li(1A)-Li(2A)-C(31A)	54.0 (1)	C(34)-C(35)-C(36)	120.0 (2)
C(31)-Li(2)-C(41)	104.4 (2)	Li(2)-Li(2A)-C(41A)	57.0 (2)	Li(2)-C(41)-C(42)	92.9 (2)
O(2)-Li(2)-Li(1A)	142.4 (2)	C(31A)-Li(2A)-C(41A)	104.4 (2)	C(42)-C(41)-C(46)	111.4 (2)
C(41)-Li(2)-Li(1A)	53.8 (1)	Li(1)-C(31A)-Li(2A)	69.5 (2)	C(42)-C(41)-Li(1A)	111.5 (2)
O(2)-Li(2)-Li(2A)	149.9 (1)	Li(1)-C(41A)-Li(2A)	70.7 (2)	C(41)-C(42)-C(43)	124.9 (2)
C(41)-Li(2)-Li(2A)	57.0 (2)	Li(2)-Li(1)-C(31)	55.1 (1)	C(43)-C(44)-C(45)	118.9 (2)
Li(1)-O(1)-C(11)	114.5 (2)	Li(2)-Li(1)-Li(1A)	61.3 (1)	C(41)-C(46)-C(45)	125.3 (2)
C(11)-O(1)-C(13)	115.5 (2)	C(31)-Li(1)-Li(1A)	57.4 (2)	Li(1)-Li(1A)-C(31)	57.3 (2)
O(1)-C(13)-C(14)	113.5 (2)	O(1)-Li(1)-Li(2A)	141.7 (2)	Li(1)-Li(1A)-C(41)	107.7 (1)
Li(2)-O(2)-C(23)	121.6 (2)	Li(1A)-Li(1)-Li(2A)	63.1 (1)	C(31)-Li(1A)-C(41)	106.9 (2)
O(2)-C(21)-C(22)	113.3 (2)	O(1)-Li(1)-C(31A)	109.7 (2)	Li(2)-Li(1A)-Li(2A)	57.4 (2)
Li(1)-C(31)-Li(2)	70.9 (2)	Li(1A)-Li(1)-C(31A)	57.3 (2)	C(41)-Li(1A)-Li(2A)	55.5 (1)
Li(2)-C(31)-C(32)	115.8 (2)	Li(2)-Li(1)-C(41A)	55.5 (1)	Li(2)-Li(1A)-C(31A)	104.2 (2)
Li(2)-C(31)-C(36)	108.6 (2)	C(31)-Li(1)-C(41A)	104.7 (2)	C(41)-Li(1A)-C(31A)	104.7 (2)
Li(1)-C(31)-Li(1A)	65.4 (2)	Li(2A)-Li(1)-C(41A)	55.5 (1)	Li(1)-Li(2A)-Li(2)	62.2 (1)
C(32)-C(31)-Li(1A)	151.9 (2)	Li(1)-Li(2)-O(2)	141.4 (2)	Li(2)-Li(2A)-Li(1A)	60.4 (1)
C(31)-C(32)-C(33)	125.1 (2)	O(2)-Li(2)-C(31)	104.1 (2)	Li(2)-Li(2A)-C(31A)	105.9 (1)
C(33)-C(34)-C(35)	118.2 (2)	O(2)-Li(2)-C(41)	117.3 (2)	Li(1)-Li(2A)-C(41A)	53.8 (1)
C(31)-C(36)-C(35)	125.4 (2)	Li(1)-Li(2)-Li(1A)	55.6 (2)	Li(1A)-Li(2A)-C(41A)	100.0 (2)
Li(2)-C(41)-C(46)	154.3 (2)	C(31)-Li(2)-Li(1A)	54.7 (1)	Li(1)-C(31A)-Li(1A)	65.4 (2)
Li(2)-C(41)-Li(1A)	70.7 (2)	Li(1)-Li(2)-Li(2A)	60.4 (1)	Li(1A)-C(31A)-Li(2A)	70.9 (2)
C(46)-C(41)-Li(1A)	106.0 (2)	C(31)-Li(2)-Li(2A)	105.9 (1)		
b. [(PhLi-Et ₂ O) ₃ -LiBr]					
Li(1)-Br-Li(2)	70.8 (2)	Li(1)-O(1)-C(13)	124.7 (2)	Li(1)-Li(4)-C(41)	59.3 (2)
Li(2)-Br-Li(3)	71.4 (1)	O(1)-C(11)-C(12)	113.0 (2)	Li(3)-Li(4)-C(41)	60.1 (2)
Br-Li(1)-Li(3)	55.0 (1)	Li(2)-O(2)-C(21)	124.9 (2)	Li(2)-Li(4)-C(51)	57.2 (2)
Br-Li(1)-Li(4)	94.5 (2)	C(21)-O(2)-C(23)	113.1 (2)	C(41)-Li(4)-C(51)	113.1 (2)
Li(3)-Li(1)-Li(4)	52.2 (2)	O(2)-C(23)-C(24)	112.1 (2)	Li(2)-Li(4)-C(61)	59.5 (2)
Li(2)-Li(1)-O(1)	150.6 (2)	Li(3)-O(3)-C(33)	125.9 (2)	C(41)-Li(4)-C(61)	114.9 (2)
Li(4)-Li(1)-O(1)	131.9 (3)	O(3)-C(31)-C(32)	113.2 (3)	Li(1)-O(1)-C(11)	109.4 (2)
Li(2)-Li(1)-C(41)	99.4 (2)	Li(1)-Br-Li(3)	71.5 (1)	C(11)-O(1)-C(13)	113.1 (2)
Li(4)-Li(1)-C(41)	53.1 (2)	Br-Li(1)-Li(2)	55.0 (1)	O(1)-C(13)-C(14)	109.1 (3)
Br-Li(1)-C(51)	102.4 (2)	Li(2)-Li(1)-Li(3)	60.7 (2)	Li(2)-O(2)-C(23)	122.0 (2)
Li(3)-Li(1)-C(51)	97.4 (2)	Li(2)-Li(1)-Li(4)	54.3 (2)	O(2)-C(21)-C(22)	109.5 (2)
O(1)-Li(1)-C(51)	109.1 (2)	Br-Li(1)-O(1)	130.6 (2)	Li(3)-O(3)-C(31)	116.0 (2)
Br-Li(2)-Li(1)	54.2 (1)	Li(3)-Li(1)-O(1)	148.6 (3)	C(31)-O(3)-C(33)	112.7 (2)
Li(1)-Li(2)-Li(3)	60.4 (2)	Br-Li(1)-C(41)	102.4 (2)	O(3)-C(33)-C(34)	109.4 (2)
Li(1)-Li(2)-Li(4)	53.6 (2)	Li(3)-Li(1)-C(41)	49.9 (1)	Li(1)-C(41)-Li(3)	80.2 (2)
Br-Li(2)-O(2)	111.7 (2)	O(1)-Li(1)-C(41)	105.9 (2)	Li(3)-C(41)-Li(4)	66.4 (2)
Li(3)-Li(2)-O(2)	144.0 (2)	Li(2)-Li(1)-C(51)	49.3 (1)	Li(3)-C(41)-C(42)	100.2 (2)
Br-Li(2)-C(51)	101.9 (2)	Li(4)-Li(1)-C(51)	53.8 (2)	Li(1)-C(41)-C(46)	127.5 (2)
Li(3)-Li(2)-C(51)	97.3 (2)	C(41)-Li(1)-C(51)	103.5 (2)	Li(4)-C(41)-C(46)	88.1 (2)
O(2)-Li(2)-C(51)	118.7 (2)	Br-Li(2)-Li(3)	54.7 (1)	C(41)-C(42)-C(43)	124.3 (3)
Li(1)-Li(2)-C(61)	97.9 (2)	Br-Li(2)-Li(4)	93.3 (2)	C(43)-C(44)-C(45)	118.8 (3)
Li(4)-Li(2)-C(61)	52.9 (2)	Li(3)-Li(2)-Li(4)	51.9 (2)	C(41)-C(46)-C(45)	124.6 (3)
C(51)-Li(2)-C(61)	103.4 (2)	Li(1)-Li(2)-O(2)	144.1 (2)	Li(1)-C(51)-Li(4)	68.4 (2)
Br-Li(3)-Li(2)	53.9 (1)	Li(4)-Li(2)-O(2)	154.9 (3)	Li(1)-C(51)-C(52)	91.6 (2)
Br-Li(3)-Li(4)	94.1 (2)	Li(1)-Li(2)-C(51)	49.6 (1)	Li(4)-C(51)-C(52)	158.4 (2)
Li(2)-Li(3)-Li(4)	53.8 (2)	Li(4)-Li(2)-C(51)	53.6 (2)	Li(2)-C(51)-C(56)	130.1 (2)
Li(1)-Li(3)-O(3)	150.7 (2)	Br-Li(2)-C(61)	100.7 (2)	C(52)-C(51)-C(56)	112.6 (2)
Li(4)-Li(3)-O(3)	145.7 (3)	Li(3)-Li(2)-C(61)	48.3 (1)	C(52)-C(53)-C(54)	119.6 (3)
Li(1)-Li(3)-C(41)	49.9 (1)	O(2)-Li(2)-C(61)	117.8 (2)	C(54)-C(55)-C(56)	119.7 (3)
Li(4)-Li(3)-C(41)	53.6 (2)	Br-Li(3)-Li(1)	53.4 (1)	Li(2)-C(61)-Li(3)	81.1 (2)
Br-Li(3)-C(61)	102.0 (2)	Li(1)-Li(3)-Li(2)	58.9 (2)	Li(3)-C(61)-Li(4)	67.1 (2)
Li(2)-Li(3)-C(61)	50.6 (1)	Li(1)-Li(3)-Li(4)	53.4 (2)	Li(3)-C(61)-C(62)	105.2 (2)
O(3)-Li(3)-C(61)	110.7 (2)	Br-Li(3)-O(3)	120.1 (2)	Li(2)-C(61)-C(66)	127.0 (2)
Li(1)-Li(4)-Li(2)	72.1 (2)	Li(2)-Li(3)-O(3)	145.6 (2)	Li(4)-C(61)-C(66)	87.6 (2)
Li(2)-Li(4)-Li(3)	74.2 (2)	Br-Li(3)-C(41)	100.8 (2)	C(61)-C(62)-C(63)	124.5 (3)
Li(2)-Li(4)-C(41)	119.3 (2)	Li(2)-Li(3)-C(41)	97.8 (2)	C(63)-C(64)-C(65)	119.6 (3)
Li(1)-Li(4)-C(51)	57.8 (2)	O(3)-Li(3)-C(41)	116.1 (2)	C(61)-C(66)-C(65)	124.2 (3)
Li(3)-Li(4)-C(51)	118.8 (2)	Li(1)-Li(3)-C(61)	98.5 (2)	Li(1)-C(41)-Li(4)	67.6 (2)
Li(1)-Li(4)-C(61)	118.5 (2)	Li(4)-Li(3)-C(61)	54.6 (2)	Li(1)-C(41)-C(42)	95.1 (2)
Li(3)-Li(4)-C(61)	58.4 (2)	C(41)-Li(3)-C(61)	105.2 (2)	Li(4)-C(41)-C(42)	159.0 (2)
C(51)-Li(4)-C(61)	113.0 (2)	Li(1)-Li(4)-Li(3)	74.4 (2)	Li(3)-C(41)-C(46)	132.5 (2)

Table II (Continued)

C(42)-C(41)-C(46)	112.4 (2)	Li(1)-C(51)-C(56)	131.4 (2)	Li(2)-C(61)-C(62)	88.2 (2)
C(42)-C(43)-C(44)	120.1 (3)	Li(4)-C(51)-C(56)	87.6 (2)	Li(4)-C(61)-C(62)	155.2 (2)
C(44)-C(45)-C(46)	119.8 (3)	C(51)-C(52)-C(53)	123.9 (3)	Li(3)-C(61)-C(66)	132.2 (2)
Li(1)-C(51)-Li(2)	81.1 (2)	C(53)-C(54)-C(55)	119.9 (3)	C(62)-C(61)-C(66)	112.5 (2)
Li(2)-C(51)-Li(4)	69.2 (2)	C(51)-C(56)-C(55)	124.3 (3)	C(62)-C(63)-C(64)	119.6 (3)
Li(2)-C(51)-C(52)	100.6 (2)	Li(2)-C(61)-Li(4)	67.6 (2)	C(64)-C(65)-C(66)	119.5 (3)

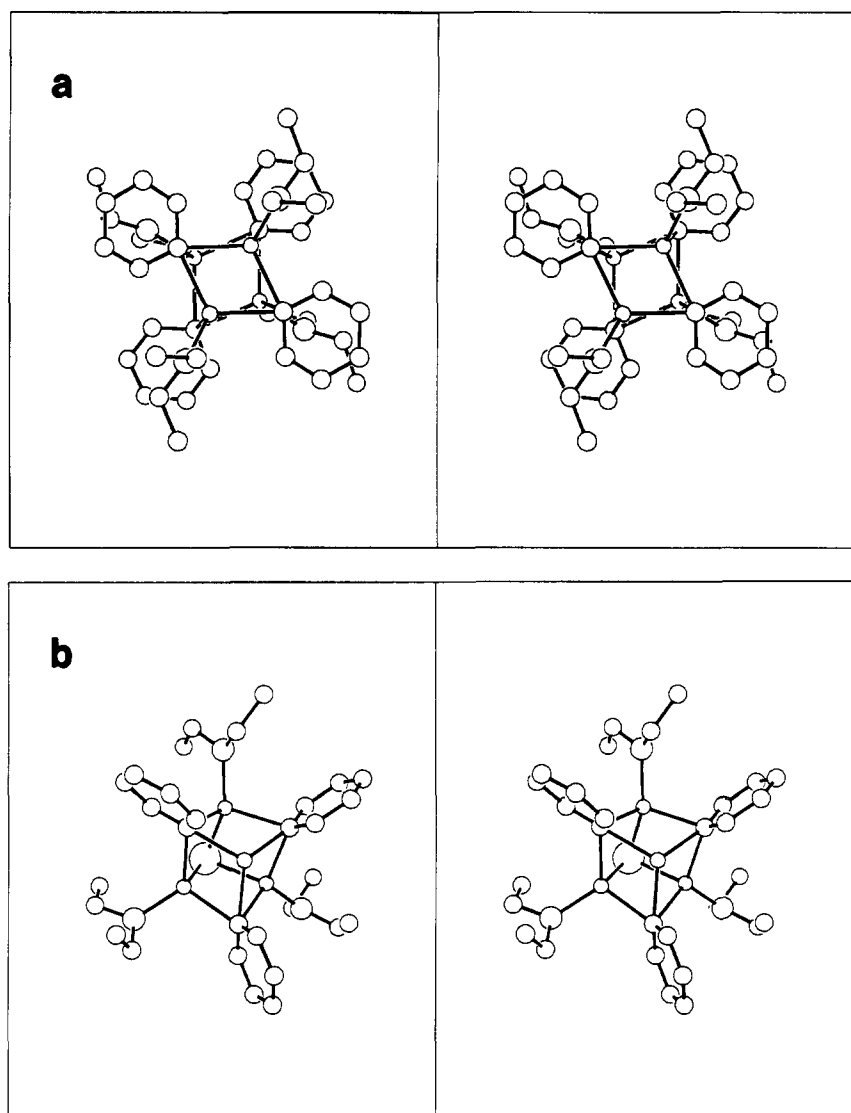


Figure 1. Stereoview of one molecule: (a) [(PhLi·Et₂O)₄] along the crystallographic twofold axis; (b) [(PhLi·Et₂O)₃·LiBr].

was checked by final difference electron density maps, where no features of significance were found.

Bond distances and angles are presented in Tables I and II.¹⁴ Figures 1-4 illustrate geometry and packing for the two compounds. All calculations were performed on a Data General Eclipse S/230 computer.

Results and Discussion

For each compound the crystals are built from discrete clusters, with no readily discernible interaction between units. This is also borne out by the rather high thermal motion found for atoms in the outer regions of the clusters.

The two compounds show the same basic architecture. A core consists of four Li atoms (Li⁺ ions) arranged at the corners of a tetrahedron. Negative ions (phenyl or Br⁻) are situated above each of the faces. In [(PhLi·Et₂O)₄] an ether molecule is attached to each Li corner, whereas in [(PhLi·Et₂O)₃·LiBr] Li opposite Br does not carry ether. The Li-Li distances are in the range 2.5-2.7

Å for [(PhLi·Et₂O)₄] and 2.5-3.0 Å for [(PhLi·Et₂O)₃·LiBr]. Alternatively, the structures can be described as based on a cubane-like arrangement, with Li occupying four nonadjacent corners and phenyl (or Br) the other four.

A similar structural principle is seen in the tetrameric structures of methylithium² and ethyllithium,² where several similar interatomic distances are observed.

Although the main structural motifs are similar for the two compounds under study, there are some differences worth noting. In [(PhLi·Et₂O)₄] the four unique Li-C distances are nearly equal, with an average of 2.33 Å, about 0.1 Å shorter than the sum of van der Waals radii. In [(PhLi·Et₂O)₃·LiBr], on the other hand, there are two groups of Li-C distances; ether-free Li-C is 2.15 Å, and ether-complexed Li-C distances average 2.28 Å (range 2.24-2.33 Å). The Li-O distances are also different in the two molecules. In the Br-free complex they are 2.05 ± 0.05 Å and in the Br complex 1.95 ± 0.02 Å. The more subtle differences in phenyl geometry (Figures 3a,b) probably reflect real effects related to charge differences caused by the presence or absence of Br⁻.

(14) Tables III, IV, and V containing atomic positions, anisotropic thermal parameters, and hydrogen positions are presented as supplementary material. Observed and calculated structure factors are also given.

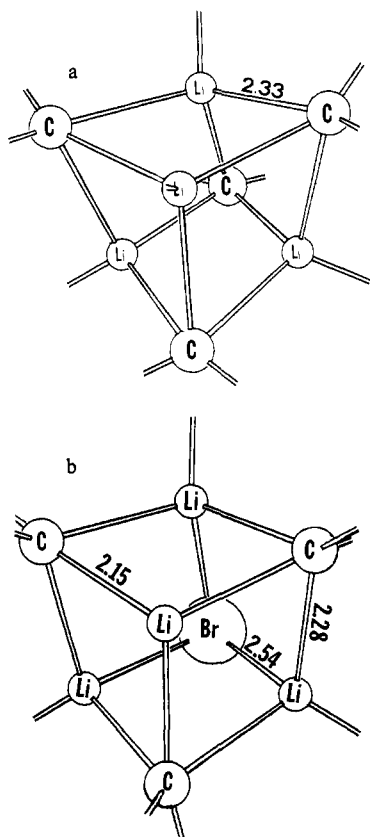


Figure 2. Representation of the central part of the molecules: (a) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_4]$; (b) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}]$.

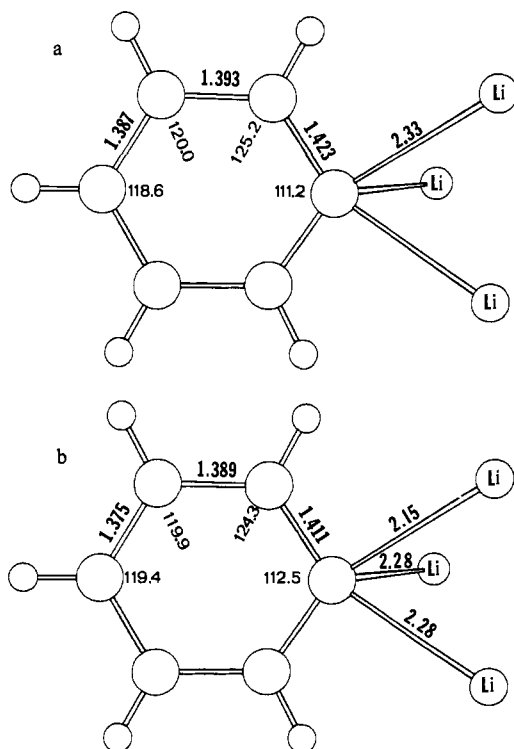


Figure 3. Average geometry for the phenyl Li_3 moiety: (a) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_4]$, Li-C-Li angles range from 65 to 70°; (b) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}]$, Li-C-Li angles range from 66 to 81°.

The orientation of phenyl rings is different in the two compounds. In $[(\text{PhLi}\cdot\text{Et}_2\text{O})_4]$ the plane of the ring is nearly parallel to one edge of the facing Li triangle, while in the other case the ring plane is nearly perpendicular to one edge.

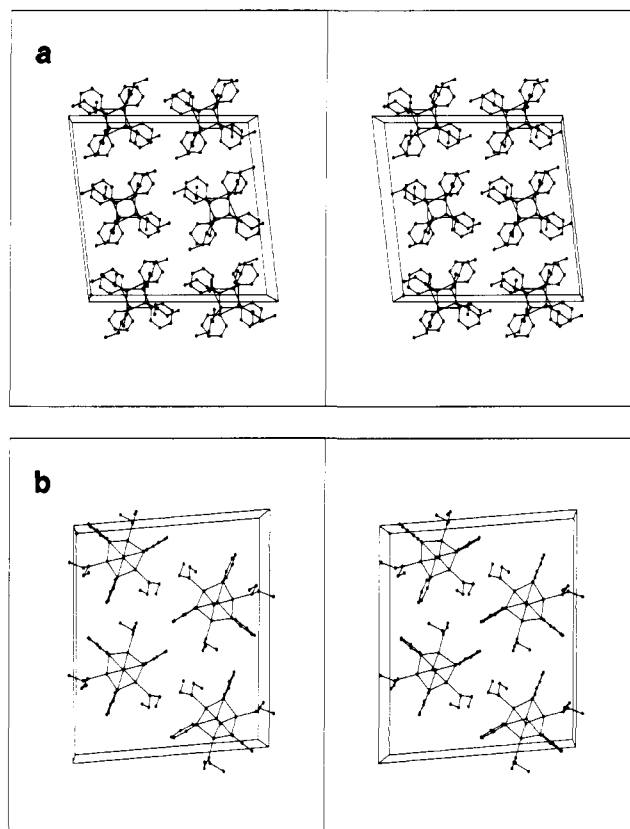


Figure 4. Packing diagrams, viewed along *b*: (a) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_4]$; (b) $[(\text{PhLi}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}]$.

It has been mentioned that the cubane moieties are essentially discrete tetrameric units in the crystal. This raises the question of their structure in solution. The aryllithiums are unique in that they seem to be dimeric in donor solvents. The widely held view that the aryllithium compounds are dimeric has been supported by the crystal structure of $[\{\text{PhLi}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_2\}]_2$.¹⁵ However, TMEDA is a very powerful bidentate donor molecule, which in conjunction with greater steric hindrance may prevent the complex from higher aggregation. Nearly all the alkyl derivatives are tetrameric in solution, even those which are hexameric in the crystal phase; only PhCH_2Li was reported to be monomeric in THF.^{5,6} It appears that the tetrameric units are stable to donor solvents such as Et_2O or THF.¹ Consideration of the Li-C bond distances in $[(\text{PhLi}\cdot\text{Et}_2\text{O})_4]$ shows that they are only slightly (0.05 Å) longer than those in $[(\text{MeLi})_4]$ or $[(\text{EtLi})_4]$. This suggests that these complexes are of similar stability and should have similar structures in solution. Our results seem to indicate that further work in this area is warranted.

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Registry No. $(\text{PhLi}\cdot\text{Et}_2\text{O})_4$, 86129-36-4; $(\text{PhLi}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}$, 86129-37-5.

Supplementary Material Available: Tables containing atomic coordinates, anisotropic thermal parameters, and hydrogen positions (Tables III-V, respectively) as well as observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page. Atomic coordinates will be supplied by the authors upon request.