Trimeric [α-(1,1,3,3-Tetramethyl-2-indanylidene)benzyl]lithium: Structural Example of an Unsolvated Vinyllithium Derivative[1]

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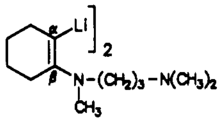
The X-ray structure of [α-(1,1,3,3-tetramethyl-2-indanylidene)benzyl]lithium discloses the stabilization of a vinylic carbanion by two lithium cations in a hydrocarbon milieu. Each lithium cation is in turn coordinated to two carbanion centers and additionally to one aromatic CC bond as well as to one CH bond of a methyl group. These bonding interactions result in an unsolvated trimer with pseudo-C_3 symmetry. Moderate strain along the CC double bond can be discerned for the phenyl substituent in front of the rigid 1,1,3,3-tetramethyl-2-indanylidene moiety within each one of the monomeric subunits. $(C_{20}H_{21}Li)_3$ crystallizes triclinic with $Z = 2$, space group $P\bar{1}$ (No. 2), $a = 12.854$ (4) Å, $b = 13.010$ (4) Å, $c = 16.011$ (5) Å, $\alpha = 109.21$ (2)°, $\beta = 94.73$ (3)°, $\gamma = 92.52$ (3)°.

Introduction

The structure of vinyllithium (ethenyllithium) is not known, and only very few of its derivatives have been structurally characterized. The first X-ray analysis[2] of a genuine 1-alkenyl monolithium compound (1) revealed the aggregation of two monomeric subunits, held together by two lithium cations each of which was coordinated with two α-carbon atoms and with two nitrogen atoms of the chelating β-substituent. Tetracoordination of the two sp^2-hybridized carbanionic centers was achieved by contacts to the two lithium cations (C–Li = 2.16 and 2.20 Å) above and below the plane of the CC double bond. A similar bonding situation was recently described[3] for dimeric 2-lithiobenzofuran (2) and the corresponding 2-lithiobenzothiophene, both with the bidentate donor *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and with their dimeric structures conserved in toluene solution. Additional examples with formally sp^2-hybridized carbanionic centers could be cited[4] by extending the scope to aryllithium derivatives and lithiated cumulenes. The bis(vinyllithium) derivative 3 turned out to be a tetrameric tetraetherate in both the solid[5] and dissolved[6] (THF) states. Tetracoordination of a vinyl–carbanion center was also made possible in the monomeric dilithio compound 4 (solid or in THF)[7] by sharing the two lithium cations with the second (aryl) carbanionic atom. All of these examples were stabilized by intra- (1) or intermolecular (2–4) lithium coordination to the lone electron pairs of heteroatoms (O or N) in the donor groups. In the absence of such "solvation" by donor functions, organolithium compounds tend to higher aggregation states, as found in the crystal structures of tetrameric ethyllithium[8] and methyllithium[9] or of hexameric cyclohexyllithium[10] and [(2,2,3,3-tetramethylcyclopropyl)methyl]lithium.[11] Some of these compounds constitute early recognized examples[8a,10] of agostic[12] interactions which can also help to improve the coordinative saturation of lithium by ligation of CH bonds. We now describe the solid-state structure of the unsolvated (by heteroatoms) vinyllithium derivative 5, showing how a sterically shielded sp^2-carbanionic center can be stabilized in a hydrocarbon milieu.



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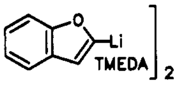

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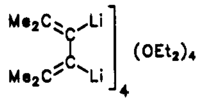

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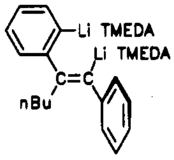

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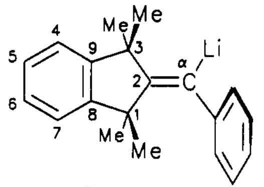

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Results and Discussion

[α-(1,1,3,3-Tetramethyl-2-indanylidene)benzyl]lithium (5) was formed by bromine/lithium exchange in pentane

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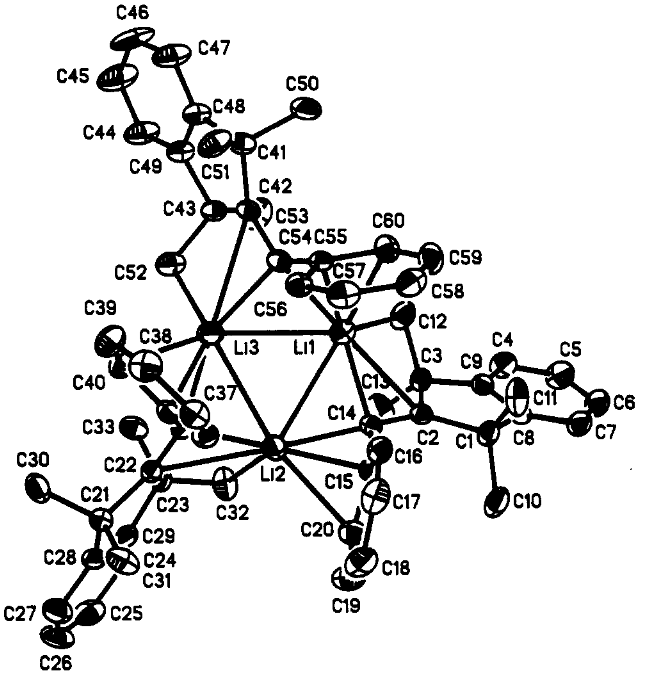


Figure 1. Top view of the trimeric unit of $(5)_3$ with crystallographic numbering of the non-hydrogen atoms and thermal ellipsoids at the 30% probability level.

solution. Although the crude product could not be recrystallized, it contained single crystals suitable for X-ray analysis at −80 °C which revealed the trimeric molecular unit $(5)_3$ shown in the ORTEP plot of Figure 1. The edges of an almost equilateral Li_3 triangle are bridged by three carbanionic α-carbon atoms, C(14), C(34), and C(54). Most of the corresponding interatomic distances and angles of the three monomeric subunits, as calculated from the atomic coordinates in Table I, conform to effective C_3 symmetry within the uncertainty limits. We have therefore listed only the averaged geometrical parameters in Tables II and III. For example, the Li(2)–C(15) distance in Table II is equivalent by pseudo-C_3 symmetry with the Li(1)–C(55) distance (compare Figures 1 and 2).

Structure of the Monomeric Subunits of $(5)_3$. Figure 2 depicts one of the monomeric subunits **5** and some essential features of its incorporation into the trimer $(5)_3$. The C(2)–C(14) double bond has the normal length of 1.336 (5) Å and almost coplanar carbon ligands with a torsional angle C(1)–C(2)–C(14)–C(15) = −6.6°. Although the exocyclic anionic atom C(14) is coordinated to Li(1) and Li(2) with equal and rather short distances of 2.13 Å, these two lithium cations maintain quite different relations with the C(2)–C(14) double bond. The position of Li(2) is somewhat below this ethylene double bond with a torsional angle C(1)–C(2)–C(14)–Li(2) of 134.7°, which allows additional coordination to the aromatic C(15)–C(20) bond. The same contacts (within pseudo-C_3 symmetry) are observed for Li(1) with the ipso- and *o*-carbon atoms C(55) and C(60) and with the carbanionic C(54) of the adjacent monomeric subunit. However, Li(1) occupies an almost perpendicular position (Table III) with respect to the C(14)–Li(2) and C(2)–C(3) bonds and thus coordinates also with the C(2)–C(14) π-system. If all of these contacts are counted as the formal ligation of three pairs of electrons to Li(1), a fourth electron pair may be considered as disposable by the lateral coordination of one CH bond of the C(12) methyl group, qualifying[8a,9a] as an "agostic" interaction by the short averaged Li(1)–C(12) distance of 2.511 (8) Å and the angle Li(1)–H–C(12) of ca. 107 (8)°.

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $(5)_3$ at −80 °C, Including the "Agostic" Hydrogen Atoms (Coordinates × 10³)

	x	*y*	*z*	*U*(eq)[a]
Li(1)	6294 (5)	2490 (6)	8332 (4)	52 (3)
Li(2)	7209 (5)	562 (5)	7231 (4)	52 (3)
Li(3)	7847 (5)	1489 (5)	9124 (4)	53 (3)
C(1)	4930 (3)	2583 (3)	6080 (3)	47 (2)
C(2)	5270 (3)	1968 (3)	6727 (2)	38 (1)
C(3)	4281 (3)	1669 (3)	7128 (2)	42 (2)
C(4)	2329 (3)	1901 (4)	6716 (3)	63 (2)
C(5)	1628 (4)	2271 (5)	6184 (3)	77 (3)
C(6)	1975 (4)	2750 (4)	5604 (3)	71 (2)
C(7)	3036 (3)	2886 (4)	5531 (3)	60 (2)
C(8)	3743 (3)	2515 (3)	6057 93)	44 (2)
C(9)	3399 (3)	2031 (3)	6643 (2)	42 (2)
C(10)	5261 (4)	2074 (6)	5147 (3)	79 (3)
C(11)	5341 (4)	3803 (4)	6457 (4)	72 (3)
C(12)	4301 (4)	2247 (5)	8134 (3)	65 (2)
C(13)	4127 (4)	427 (4)	6916 (4)	74 (3)
C(14)	6221 (3)	1692 (3)	6930 (2)	38 (1)
C(15)	7123 (3)	1835 (3)	6437 (2)	39 (2)
C(16)	7800 (3)	2787 (3)	6700 (3)	47 (2)
C(17)	8648 (3)	2848 (5)	6231 (3)	63 (2)
C(18)	8854 (4)	1987 (5)	5503 (3)	72 (3)
C(19)	8229 (4)	1025 (5)	5262 (3)	70 (2)
C(20)	7381 (3)	947 (3)	5725 (3)	51 (2)
C(21)	9523 (3)	−1406 (3)	7396 (2)	46 (2)
C(22)	8536 (3)	−794 (3)	7689 (2)	39 (2)
C(23)	7577 (3)	−1642 (3)	7471 (3)	44 (2)
C(24)	7449 (4)	−3702 (3)	6495 (3)	60 (2)
C(25)	8009 (5)	−4573 (4)	6040 (3)	75 (3)
C(26)	9068 (6)	−4445 (4)	5991 (3)	81 (3)
C(27)	9620 (4)	−3443 (4)	6416 (3)	66 (2)
C(28)	9069 (3)	−2558 (3)	6878 (2)	50 (2)
C(29)	8004 (3)	−2690 (3)	6916 (2)	45 (2)
C(30)	10275 (4)	−1407 (4)	8201 (3)	67 (2)
C(31)	10129 (4)	−935 (4)	6795 (4)	70 (2)
C(32)	6639 (4)	−1352 (4)	6972 (4)	66 (2)
C(33)	7230 (4)	−1776 (4)	8331 (3)	55 (2)
C(34)	8454 (3)	272 (3)	8082 (2)	39 (2)
C(35)	9383 (3)	1086 (3)	8398 (2)	38 (2)
C(36)	9722 (3)	1735 (3)	7911 (3)	47 (2)
C(37)	10522 (3)	2549 (3)	8257 (3)	51 (2)
C(38)	11010 (3)	2767 (4)	9105 (3)	61 (2)
C(39)	10665 (3)	2166 (4)	9606 (3)	64 (2)
C(40)	9864 (3)	1326 (3)	9262 (3)	49 (2)
C(41)	7265 (3)	3981 (3)	11355 (3)	47 (2)
C(42)	6959 (3)	3006 (3)	10484 (2)	37 (1)
C(43)	6491 (3)	2041 (3)	10733 (2)	43 (2)
C(44)	6506 (4)	1834 (4)	12292 (3)	71 (2)
C(45)	6723 (5)	2328 (5)	13201 (3)	98 (3)
C(46)	7119 (5)	3421 (5)	13535 (3)	102 (3)
C(47)	7311 (4)	4003 (4)	12987 (3)	77 (2)
C(48)	7095 (3)	3496 (3)	12074 (3)	49 (2)
C(49)	6697 (3)	2418 (3)	11735 (2)	47 (2)
C(50)	6562 (5)	4935 (4)	11427 (3)	76 (2)
C(51)	8424 (4)	4409 (4)	11442 (3)	63 (2)
C(52)	6983 (4)	971 (4)	10309 (3)	60 (2)
C(53)	5306 (4)	1851 (5)	10456 (4)	72 (3)
C(54)	7053 (3)	2941 (3)	9641 (2)	39 (2)
C(55)	7416 (3)	3889 (3)	9376 (2)	38 (1)
C(56)	8460 (3)	4046 (3)	9209 (3)	44 (2)
C(57)	8741 (4)	4828 (3)	8841 (3)	53 (2)
C(58)	8022 (4)	5456 (3)	8598 (3)	59 (2)
C(59)	6994 (4)	5316 (4)	8761 (3)	61 (2)
C(60)	6697 (3)	4548 (3)	9139 (3)	49 (2)
H(12A)	453 (3)	306 (4)	832 (3)	78
H(12B)	349 (3)	215 (3)	835 (3)	78
H(12C)	483 (3)	194 (3)	842 (3)	78
H(32A)	686 (3)	−121 (3)	641 (3)	79
H(32B)	631 (3)	−68 (4)	741 (3)	79
H(32C)	613 (3)	−194 (4)	681 (3)	79
H(52A)	675 (3)	41 (3)	1055 (3)	72
H(52B)	773 (3)	105 (3)	1043 (3)	72
H(52C)	679 (3)	71 (3)	963 (3)	72

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

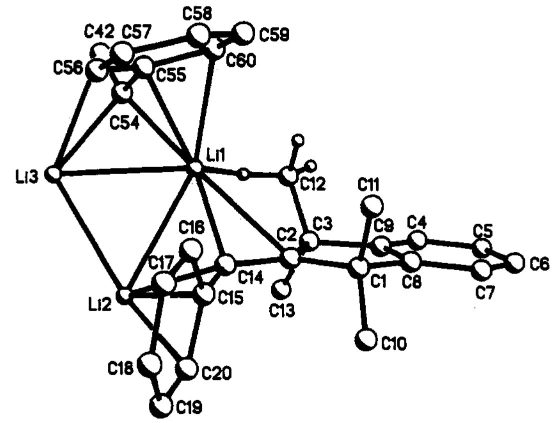


Figure 2. Partial structure of $(5)_3$, showing one monomeric subunit 5 with the agostic interaction of one methyl hydrogen atom at C(12) and displaying the quasi-benzyl anion of the next subunit.

Table II. Averaged Experimental Bond Lengths (Å) for $(5)_3$

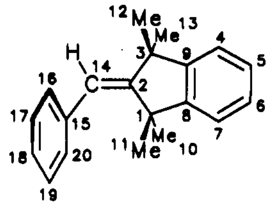
Li–Li	2.891 (9)	Li(1)–C(2)	2.719 (7)
Li(1)–C(12)	2.511 (8)	Li(1)–C(14)	2.138 (8)
Li(2)–C(14)	2.122 (8)	Li(2)–C(15)	2.373 (8)
Li(2)–C(20)	2.606 (6)	C(1)–C(2)	1.552 (5)
C(1)–C(8)	1.516 (5)	C(1)–C(10)	1.540 (7)
C(1)–C(11)	1.547 (7)	C(2)–C(3)	1.554 (5)
C(2)–C(14)	1.336 (5)	C(3)–C(9)	1.509 (5)
C(3)–C(12)	1.527 (6)	C(3)–C(13)	1.538 (7)
C(4)–C(5)	1.391 (7)	C(4)–C(9)	1.390 (6)
C(5)–C(6)	1.382 (9)	C(6)–C(7)	1.379 (8)
C(7)–C(8)	1.397 (6)	C(8)–C(9)	1.381 (6)
C(14)–C(15)	1.496 (5)	C(15)–C(16)	1.405 (6)
C(15)–C(20)	1.401 (5)	C(16)–C(17)	1.384 (6)
C(17)–C(18)	1.378 (7)	C(18)–C(19)	1.380 (8)
C(19)–C(20)	1.391 (7)		

Table III. Averaged Experimental Angles (deg) for $(5)_3$

Li–Li–Li	60.0 (2)	C(2)–Li(1)–C(12)	58.9 (2)
C(12)–Li(1)–C(14)	84.1 (3)	C(14)–Li(1)–C(54)	151.2 (4)
C(2)–C(1)–C(8)	103.1 (3)	C(2)–C(1)–C(10)	112.5 (3)
C(8)–C(1)–C(10)	110.5 (4)	C(2)–C(1)–C(11)	112.0 (3)
C(8)–C(1)–C(11)	109.5 (3)	C(10)–C(1)–C(11)	109.2 (4)
Li(1)–C(2)–C(3)	87.6 (3)	C(1)–C(2)–C(3)	108.5 (3)
Li(1)–C(2)–C(14)	50.6 (2)	C(1)–C(2)–C(14)	129.1 (4)
C(3)–C(2)–C(14)	122.4 (3)	C(2)–C(3)–C(9)	103.5 (3)
C(2)–C(3)–C(12)	113.6 (3)	C(9)–C(3)–C(12)	110.9 (3)
C(2)–C(3)–C(13)	110.5 (3)	C(9)–C(3)–C(13)	109.5 (4)
C(12)–C(3)–C(13)	108.7 (4)	C(1)–C(8)–C(7)	127.0 (4)
C(1)–C(8)–C(9)	112.4 (3)	C(3)–C(9)–C(4)	127.5 (4)
C(3)–C(9)–C(8)	111.9 (3)	Li(1)–C(14)–Li(2)	85.5 (3)
Li(2)–C(14)–C(2)	147.5 (3)	Li(2)–C(14)–C(15)	80.0 (3)
C(2)–C(14)–C(15)	122.6 (3)	Li(2)–C(15)–C(14)	61.7 (3)
Li(2)–C(15)–C(16)	120.0 (3)	Li(2)–C(15)–C(20)	83.1 (3)
C(16)–C(15)–C(20)	116.9 (4)	Li(2)–C(20)–C(15)	64.7 (3)

The phenyl substituent C(15–20) is slightly buckled and almost orthogonal to the plane C(2)–C(14)–C(15) with torsional angles of ca. 90–94°, not much different from the corresponding value[7] of 100.8° in 4. The formally sp^2-hybridized anionic electron pair at C(14) can thus interact with the phenyl π-system, forming a quasi-benzyl anion; indeed, the bonding relations of Li(2) with C(14), C(15) and C(20) are quite similar to those of solid benzyllithium[13] and of lithiated pinacolone anil.[14] The delocalization of negative charge into the phenyl ring should be less than in benzyllithium, however, and is clearly recognized only in donor solvents by NMR spectroscopy. A shrinked angle C(16)–C(15)–C(20) = 116.9 (4)° is expected at the *ipso*-carbon atom C(15) due[15] to the σ-donor character of C(14).

In the crystal structure[16] of 2-benzylidene-1,1,3,3-tetramethylindan (6) as the parent olefin of 5, the phenyl group C(15–20) is almost orthogonal (86.5°) to the slightly twisted (3°) double bond C(2)–C(14). Formal substitution of the proton at C(14) of 6 by two lithium cations has produced the single strong structural change in $(5)_3$ of shrinking the angle C(2)–C(14)–C(15) from 129.0 (2)° in 6 to 122.6 (3)°. Probably as a consequence, all of the three CC bonds emanating from C(2) are a little more than 0.01 Å longer in $(5)_3$ than in 6, whereas the angle C(1)–C(2)–C(14) grows by 1.4° and C(1)–C(2)–C(3) becomes smaller by 1.6°. All structural parameters other than the angle at C(14) are not significantly different for $(5)_3$ and 6. The averaged short nonbonding distances C(10)/C(15) = 3.32 Å, C(11)/C(15) = 3.35 Å, and C(11)/C(16) = 3.47 Å appear to cause rather moderate strain effects, because the four methyl groups of $(5)_3$ show almost no back-bending[17] of their H_3C–C(quaternary)–C(aromatic) angles (global average 110.1 (4)° in Table III) toward the C_6H_4 moiety. The 1,1,3,3,-tetramethyl-2-indanylidene fragment of $(5)_3$ is planar at C(2), C(8), and C(9) but slightly bent at C(1) and C(3); as a whole, it is geometrically quite similar to that in 7 where stronger front strain along the CC double bond was expressed mainly by distortions outside of this fragment.[17]



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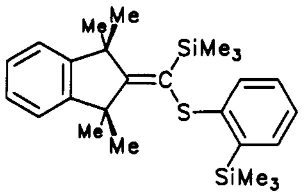

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Structure of the Central Li_3C_3 Core. The central core, Li(1)–C(14)–Li(2)–C(34)–Li(3)–C(54) as shown in Figure 1, consists of a very flat and angularly distorted 1,3,5-trilithiacyclohexane ring compressed to an averaged height of only 0.23 Å, which carries all three phenyl substituents in quasi-axial and the 2-indanylidene groups (junctions C(2), C(22), and C(42)) in quasi-equatorial positions. However, as may be gleaned from the side-on view in Figure 3, all of these six substituents are tilted by approximately 60° from the mean Li_3C_3 ring plane and thus conducive to the auxiliary coordination modes (i.e., CH(52) to Li(3) and CH(32) to Li(2)). They are still sterically shielding in a sufficiently high degree such as to prevent the stacking of two trimers to give a hexamer like cyclohexyllithium.[10] The Li_3C_3 ring is separated from the next Li_3 triangle by 7.20 Å. Its dimensions are comparable with those of the open faces[10] of cyclohexyllithium and also of the first trimeric carbon–lithium compound,[18] [2,6-bis(dimethylamino)phenyl]lithium, especially with regard to the Li–C–Li and C–Li–C angles, but exhibit a general

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Table IV. Crystallographic Data for $(5)_3$

mol formula	$(C_{20}H_{21}Li)_3$	space group	$P\bar{1}$ (No. 2)
mol wt	$(268.3)_3$	cryst system	triclinic
a, Å	12.854 (4)	cryst size, mm	0.3 × 0.17 × 0.57
b, Å	13.010 (4)	temp, °C	−80
c, Å	16.011 (5)	diffractometer	Nicolet R3m
α, deg	109.21 (2)	radiation	Mo Kα
β, deg	94.73 (3)	λ, Å	0.71069
γ, deg	92.52 (3)	monochromator	graphite
V, Å^3	2512.6 (8)	μ, cm^{-1}	0.5
D_{calc}, g cm^{-3}	1.064	scan method	ω
Z	2	scan width, deg	1.1
refl measrd at index range	$h,\pm k,\pm l$	speed, deg min^{-1}	1.8–29.3
no. of refl collected	7211	2θ range, deg	2–45
no. of unique refl	6426	background, deg	0.5
no. of refl observd	4444	intens stdds	2 after every 48
F	$>3\sigma(F)$	$F(000)$	864
variables	757	GOF	1.36
final R	0.0654	final R_w	0.0744
		w^{-1}	$\sigma^2(F) + 0.0012F^2$
largest Δ/σ	0.073	max resid e-dens, e Å^{-3}	0.20

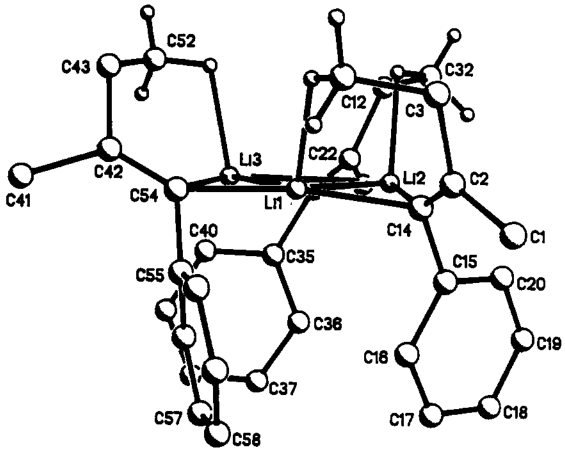

Figure 3. Side view of the central Li_3 triangle of $(5)_3$ with selected atoms from the hydrocarbon parts.

trend to shorter Li(1)–C(14) and Li–Li bonds (Table II) and to a slightly closer distance of 4.13 (2) Å between the carbanionic centers.

The trimeric nature of the last-mentioned compound[18] had been ascribed to its larger (and therefore energetically more favorable) separation of the carbanionic centers, as compared to a hypothetical dimer. This argument is probably not valid in the case of $(5)_3$ because model calculations on possible alternatives $(5)_2$ indicate separations in the range of 3.5 Å, which would be tolerable. However, such a dimer $(5)_2$ would suffer from additional repulsive interactions between methyl and phenyl groups of any two different subunits **5**, whereas such *inter*subunit repulsions are absent in $(5)_3$ due to distances above 4 Å.

In terms of the point-charge model,[19] the central Li_3C_3 core of $(5)_3$ might appear from Figure 1 to deviate grossly from the predicted[20] regular hexagonal arrangement. However, a closer inspection of the left-hand side of Figure 3 suggests that the doubly-occupied "anionic" sp^2-orbital at C(54) should protrude into the Li_3C_3 plane, placing a region of high electron density closer to Li(1) and Li(3). Due to pseudo-C_3 symmetry, the same argument applies to C(14) and C(34) such that a regular hexagon is approximated by the six charge centers. For the present case, this supports the point-charge model which is of course an oversimplification and may not always be able to explain finer details.[21]

Conclusion

Without solvation, the vinyllithium derivative **5** avoids being monomeric in the crystalline state despite the steric shielding of its carbanion part. The trimeric structure $(5)_3$ is compatible with the ionic CLi bonding model and appears to be the smallest aggregate which is devoid of strain other than some front strain along the ethylene double bond within each monomeric subunit.

The triangular array of lithium cations in $(5)_3$ is embedded in a belt of hydrocarbon moieties and stabilized by close contacts to the electron-rich parts of these. Disorder phenomena were not observed in the present structure which exemplifies the benefits of using the rigid[17] 1,1,3,3-tetramethyl-2-indanylidene substituent in order to generate a simple and straightforward geometrical situation.

Experimental Part

General Comments. The experiments were performed in 5- or 10-mm NMR tubes under a stream of dried and deoxygenated argon or nitrogen gas. Pentane and diethyl ether solvents were dried over sodium wire.

Synthesis and Characterization. The best crystals were obtained in a 5-mm ^{1}H NMR tube charged with 108 mg (0.32 mmol) of 2-(α-bromobenzylidene)-1,1,3,3-tetramethylindan[22] and 1.0 mL of dry pentane. After the major part of the bromo olefin had dissolved, *n*-butyllithium (0.18 mL, 0.40 mmol) in pentane was added by syringe under argon within 1 min at ambient temperature. A clear solution was formed by cautious shaking for a short time. Transparent, colorless plates began to grow within less than 1 h, followed by a colorless powder which, after 2 h, was removed by repeated ablution with dry pentane (at least five times; see below). Residual pentane was swept off in a stream of argon, yielding 39 mg (46%) of trimeric **5**.

A correct combustion analysis was not obtained because this very reactive[23] organolithium compound could not be recrystallized. Carboxylation of the crude material gave the same carboxylic acid which had previously been obtained from the Grignard analogue.[22] For spectroscopic characterization, we report here the NMR spectra in ether at 25 °C which confirm the C_s symmetry of **5** under these conditions.

^{1}H NMR (ether): $\delta = 6.27$ (t, $^3J = 7$ Hz, *p*-H), 6.50 (d, $^3J = 7.5$ Hz, 2 *o*-H), 6.80 (partially hidden t, $^3J = 7.5$ Hz, 2 *m*-H), 6.93

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(s, C_6H_4). ^{13}C NMR (ether): δ = 32.9 and 34.7 (2 CH_3), 47.1 and 50.5 (C(1,3)), 115.9 (*p*-C), 121.8 (2 *o*-C), 122.7 and 123.1 (C(4,7)), 126.0 and 126.4 (C(5,6)), 127.9 (2 *m*-C), 149.2 (ipso-C), 152.3 and 154.6 (C(8,9)), 160.3 (C(2)), 184.1 (C_α).

The colorless powder, as collected above, contained the "dimerization" product previously[22] isolated from the Grignard analogue of **5**. It was detected under the present conditions even though we had earlier[22] reported that it was not observed by bromine/lithium exchange.

Crystal Structure Determination. The sample was sealed under argon in a glass capillary. Cell constants were determined by a least-squares fit of the setting angles of 25 centered reflections between 2θ = 18–25°. Lorentz and polarization corrections were applied in data collection (see Table IV).

Structure Solution and Refinement. It was difficult to obtain a good model by direct methods (SHELXS-86,[24] PC version), and a very high number (1200) of possible solutions had to be calculated in order to get starting positions for a model refining well with isotropic thermal parameters. This model showed the tetramethylindan fragments. The remaining non-hydrogen atoms were found from a difference-Fourier map. The position of the Li atom emerged after assigning part of the carbon anisotropic thermal parameters. All hydrogen atoms were located and their positions refined with fixed $U_i = 1.2U$(eq) from U(eq) of the hydrogen-bearing carbon atoms. The structure was refined using the SHELXTL-PLUS[25] program package with full matrix least-squares procedures. The solution converged slowly but steadily.

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Supplementary Material Available: Tables of crystal data, fractional coordinates, bond distances, bond angles, anisotropic thermal parameters, and fractional coordinates of hydrogen atoms (12 pages). Ordering information is given on any current masthead page. Structure factor amplitudes are available on request from the author.

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Synthesis, Structure, Dynamic Behavior, and Reactivity of Chiral Rhenium Primary Phosphine and Phosphido Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRH_2)]^+X^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}RH)$

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Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (X = OTs ($OSO_2\text{-}p\text{-}C_6H_4CH_3$), OTf ($OSO_2CF_3$)) with PRH_2 (**a**, R = Ph; **b**, R = Me; **c**, *t*-Bu) give the primary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRH_2)]^+X^-$ (**2a**$^+$TsO$^-$, **2b**$^+$TfO$^-$, **2c**$^+$TfO$^-$; 89–96%). Reactions of **2a–c**$^+$X$^-$ with *t*-BuO$^-$K$^+$ give the phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}RH)$ (**4a–c**; 63–98%). Reactions of **4c** with TfOH and HCl gas give **2c**$^+$TfO$^-$ and **2c**$^+$Cl$^-$ (62–89%). NMR data show that **2c**$^+$TfO$^-$ preferentially adopts a solution $RePRH_2$ conformation that places the *tert*-butyl group in the interstice between the cyclopentadienyl and small nitrosyl ligands. An analogous conformation is found in crystalline **2c**$^+$Cl$^-\cdot(CH_2Cl_2)_{0.5}$ (orthorhombic, *Pbca*, a = 15.265 (3) Å, b = 18.698 (5) Å, c = 19.796 (5) Å, Z = 8), which also exhibits a P··H··Cl hydrogen bond (H··Cl 2.90 Å). NMR, IR, and conductance properties indicate an identical interaction in solution. NMR data show that **4a,b** exist as 50:50 and 89:11 mixtures of Re,P configurational diastereomers that interconvert with $\Delta G^\ddagger$ of 11.5 (**4a**) and 13.5 (**4b**, minor → major) kcal/mol. Reaction of **4c** and MeOTf gives (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(P(t\text{-}Bu)MeH)]^+TfO^-$ (95%) in >98% diastereomeric excess (monoclinic, $P2_1/c$, a = 11.499 (1) Å, b = 9.227 (1) Å, c = 30.399 (1) Å, β = 100.53 (1)°, Z = 4).

The synthesis, structure, and dynamic and chemical properties of transition-metal terminal phosphido complexes have continued to attract the attention of numerous researchers.[1-3] In particular, we have been conducting an extensive study of chiral, coordinatively saturated, pyramidal, rhenium phosphido complexes of the general formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}XX')$.[4-8] These com-

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