33. Low-Temperature X-Ray Crystal-Structure Analysis of the Thermally Unstable Lithiated 2-Butenyl *tert*-Butyl Sulfide: A Comparison with Model *ab initio* MO Calculations[1]

by **Dieter Seebach*** and **Thomas Maetzke**

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum,
Universitätstr. 16, CH-8092 Zürich

and **Richard K. Haynes**

Department of Organic Chemistry,
University of Sydney, Sydney, New South Wales 2006, Australia

and **Michael N. Paddon-Row** and **Stephen S. Wong**

Department of Organic Chemistry, University of New South Wales,
P.O. Box 1, Kensington, New South Wales 2033, Australia

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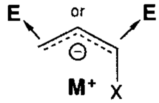
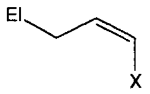
Single crystals of the *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex **6** of the title compound have been isolated. Compound **6** decomposes in the crystalline state above –20°. From the bond lengths and angles obtained by X-ray crystal-structure analysis (data collected at –70°), compound **6** is best described as a (*E*)-1-(*tert*-butylthio)-1-lithio-2-butene with the double bond acting as an additional ligand on lithium (unsymmetrical allylic group). The S-atom is in a *cisoid*-arrangement in a common plane with the four C-atoms of the butenyl system. The *t*-Bu group and the Li-atom are located above and below this plane. The structure is discussed with respect to the reactivity of **6** (α/γ reactivity). The gross structure is reproduced surprisingly well by an *ab initio* SCF MO calculation of the model lithiopropene-1-thiol **7** (HS instead of *t*-BuS, CH_2 instead of $CHCH_3$, no solvation of Li). The prominent difference is the symmetry of the allylic moiety in the calculated structure.

1. Introduction. – Nucleophilic organometallic derivatives **A** of heterosubstituted allylic anions are most useful reagents in organic syntheses, because they can give



A



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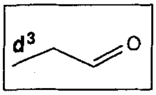

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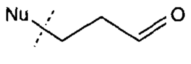

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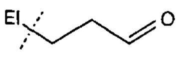

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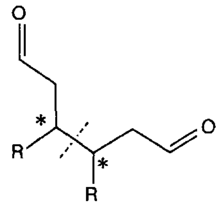

F

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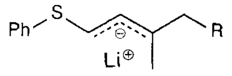
[1] Part of the projected Dissertation of *Th. M.*, ETH Zürich.

products **B** *via* γ-attack by electrophiles, and thus correspond to d^3-synthons **C** (reactivity 'Umpolung' [1–3] of a *Michael* acceptor, compare **D** with **E**).

This becomes most useful in the combination of an a^3- with a d^3-synthon, see **F**, since C–C bond formation occurs between remote functional groups; this becomes especially valuable, if such coupling between two trigonal centers diastereoselectively generates two new stereogenic centers [4]. There is a wealth of information in the literature on ways to achieve the desired remote reactivity in such cases. The choice of the heteroatom and metal in **A**, addition of chelating ligands, use of cosolvents, type of electrophile, kinetic *vs.* thermodynamic control (reaction time, reaction temperature) *etc.* can be decisive in determining whether the α- or γ-products are formed. The most extensive review article on this subject, covering the literature up to the end of the seventies, has been published in *Organic Reactions* (630 references! [5]).



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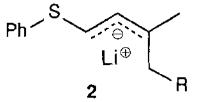

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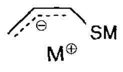

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Of the numerous d^3-reagents [2] [3] of type **A** known, those containing at least one S-substituent (X = S) were among the first to be described [6–9] [16][2–5]). Yet, very little is known about their structures. The following evidence typically rests upon *product* structure determinations: **A** $\geqslant$ 19.5 kcal/mol rotational barrier for interconversion between

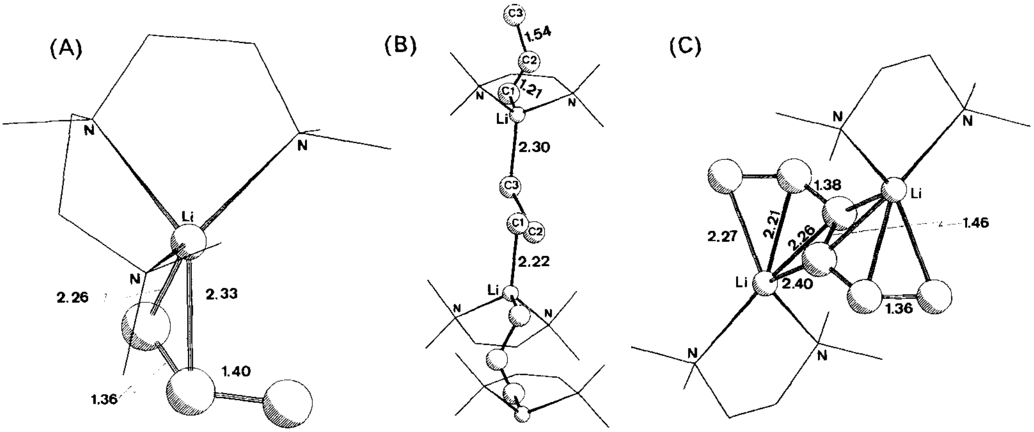

Fig. 1. *X-Ray crystal structures of three allyllithium derivatives.* (A) Monomeric allyllithium with a chelating triamino ligand on Li [47b]; we agree with *Weiss et al.* [47b] and do not consider the Li–C distance of 2.7 Å as bonding, see *Footnotes 8* and *13*. (B) Section of polymeric allyllithium with TMEDA ligands on Li [47a]. (C) Doubly lithiated hexadiene (or dilithium hexatrienediide) containing two allyllithium units with η^4 bonding of the π-system and TMEDA ligands on the Li's [49]. The views (A), (B), and (C) are reconstructed from the published coordinates.

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[2]) For our reviews in which the S-based d^3-reagents are emphasized, see [2] [10–15], original papers [17–25].

[3]) For other reviews covering S-substituted allylic-anion derivatives, see [3] [26–32].

[4]) A review dealing with hydrocarbon allylic-anion derivatives has just appeared [33]. For an article on metallated allylic carbamates, see [34].

[5]) For some recent papers describing the use of allylic S-substituted organometallic reagent in synthesis, see [4] [35–37] and ref. cit. therein.

the two geometrical isomers **1** and **2** [38] and a *cis*-configuration⁶) of the doubly metallated propenethiol **3** which gives *cis*-vinyl thioethers **4** with electrophiles [19] [24]; see also the discussions in [4b] and [36b]. While the structures of simple⁷) allyllithium and allylmagnesium compounds have been determined [47–49], see *Fig. 1*, no crystal structure⁸⁻¹⁰) of any hetero-substituted derivative has been published until now. This is probably due to the limited thermal stability of these compounds, even in the solid state. Thus, during our experimentation with lithiated allylic thioethers, the object of the investigation to be described here, foul-smelling decomposition products were formed when the temperature of the samples rose too high (above *ca.* −20°)¹¹). It is not surprising, therefore, that it took many months to mount a suitable crystal on the diffractometer. It also appeared reasonable to do independent theoretical studies of the structure. The results are reported in the following sections.

2. Isolation and Crystal Structure of [(*E*)-1-(*tert*-Butylthio)-2-butenyl](*N,N,N′,N′*-tetramethylethylenediamine)lithium. – Deprotonation of (*E*)-2-buten-1-yl *tert*-butyl thioether (**5**) [55] with *sec*-BuLi in hexane containing an equivalent amount of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) at −50° and two crystallizations from hexane/TMEDA at −78° gave colorless crystals of **6** which were not allowed to warm above −40° at any time. The purification and selection of suitable single crystals was done in an apparatus similar to that described by us previously [56]. The X-ray measurement was carried out at −70°. The results are depicted in the *Scheme, Figs. 2* and *3*, and *Tables 1* and *2*.

In the *Scheme* are shown some distances and angles. *Fig. 2* is a ORTEP stereoplot of one of the molecules¹²), and *Fig. 3* presents two views of one molecule in the structure which we think are especially instructive (PLUTO [58] plots).

The Li-atom is in bonding distance (< 2.4 Å) to the TMEDA N-atoms and the three C-atoms of the allylic system, with the two N-atoms and the terminal C-atoms of the allyl group (C(1) and C(3)) forming a pseudo-tetrahedral ligand sphere around the metal.

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⁶) The preference for *cisoid*-arrangement is generally observed in systems which can be considered as having 6π-electrons on 4 atoms. For leading references, see [39], the reviews [40–43] and the most recent calculations on metalated oxime derivatives [44].

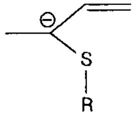
⁷) Systems stabilized by aryl groups have been studied extensively [33] [45] [46].

⁸) In the crystal structures of an azaallyllithium (enaminate) [50] and of an oxapentadienyllithium (dienolate) [51] the metal, while being close to the heteroatom, is also coordinated by a C-atom of the π-system.

⁹) For general discussions of structures of organolithium compounds, see [45] [52] [53].

¹⁰) For an excellent collection of recent literature on structure, preparation, and reactions of polar organometallic compounds, with emphasis on π-systems, see [54].

¹¹) We did not investigate the debris; they could arise from α-elimination of RS$^-$ (**i**→**ii**), from 1,2- (→**iii**), or from 1,4-sigmatropic shift (→**iv**) of R, *i.e. Wittig* rearrangement. For a discussion and examples of these various reactions, see [5].



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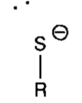

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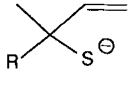

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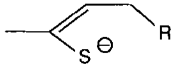

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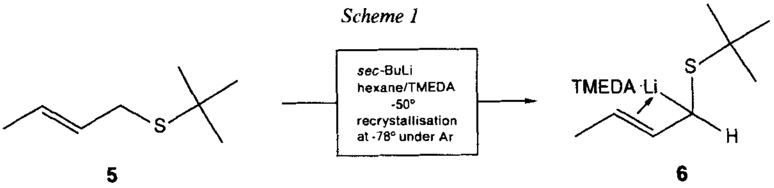
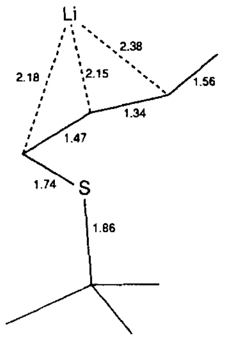
¹²) From here on, average bond lengths and angles of the two molecules in the asymmetric unit cell are given.

Scheme 1





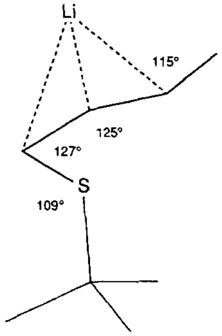


Table 1. *Crystal-Structure Analysis of* **6**

Formula	$C_{14}H_{31}N_2SLi$	d_x [g·cm^{-3}]	0.97
Crystal dimension	0.3 × 0.4 × 0.4 mm		
Crystal system	monoclinic	Radiation	MoK_α (graphite monochromator)
Space group	$P2_1/c$		
a [Å]	22.303(9)	Temp. [°C]	– 70
b [Å]	10.103(3)	$(\sin\theta/\lambda)_{max}$	0.53
c [Å]	24.181(5)	Reflections recorded	4461
β [°]	137.90(2)	Reflections [$I > 3\sigma(I)$]	1720
V [Å^3]	3653	R	0.063
Z	8	$R_w(w = {}^1/\sigma^2(F_0))$	0.063

Table 2. *Bond Distances, Angles, and Torsional Angles of* **6**[a]
(standard deviations in units of the last significant figure in parentheses)

Distances [Å]		Angles [°]		Torsional angles [°]	
S(1)–C(1)	1.74(1)	S(1)–C(1)–C(2)	127(1)	S(1)–C(1)–C(2)–C(3)	– 15.8
S(1)–C(5)	1.86(1)	C(1)–S(1)–C(5)	109.0(5)	C(5)–S(1)–C(1)–C(2)	– 84.5
C(1)–C(2)	1.47(1)	C(1)–C(2)–C(3)	125(1)	C(1)–C(2)–C(3)–C(4)	– 174.9
C(1)–Li(1)	2.18(1)	C(1)–Li(1)–C(3)	66.0(6)		
C(2)–C(3)	1.34(1)	C(2)–C(1)–Li(1)	69.1(8)		
C(2)–Li(1)	2.15(1)	C(2)–C(3)–Li(1)	63.6(7)		
C(3)–C(4)	1.56(1)	C(2)–C(3)–C(4)	115(1)		
C(3)–Li(1)	2.38(1)	N(1)–Li(1)–N(2)	88.6(7)		
N(1)–Li(1)	2.09(1)	Li(1)–C(1)–S(1)	95.0(7)		
N(2)–Li(1)	2.08(1)				

[a] Mean values of the two monomeric units in the asymmetric unit cell.

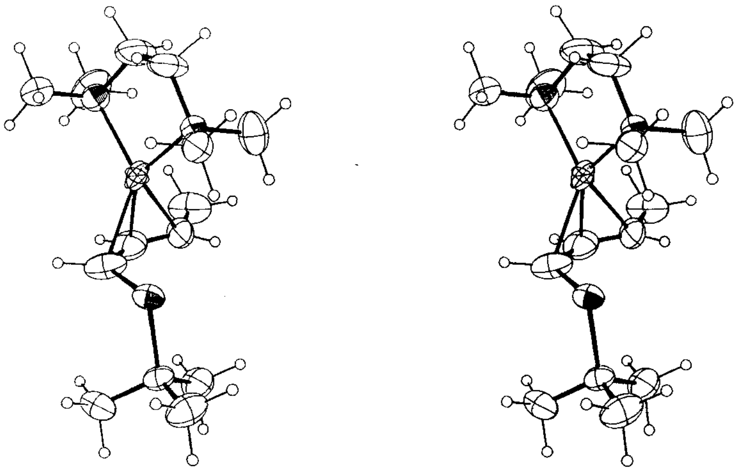


Fig. 2. *ORTEP* [66] *stereoview of one monomeric structural unit in the asymmetric unit cell of* **6**. Vibrational ellipsoids are drawn at the 30% level, all H-atoms are calculated.

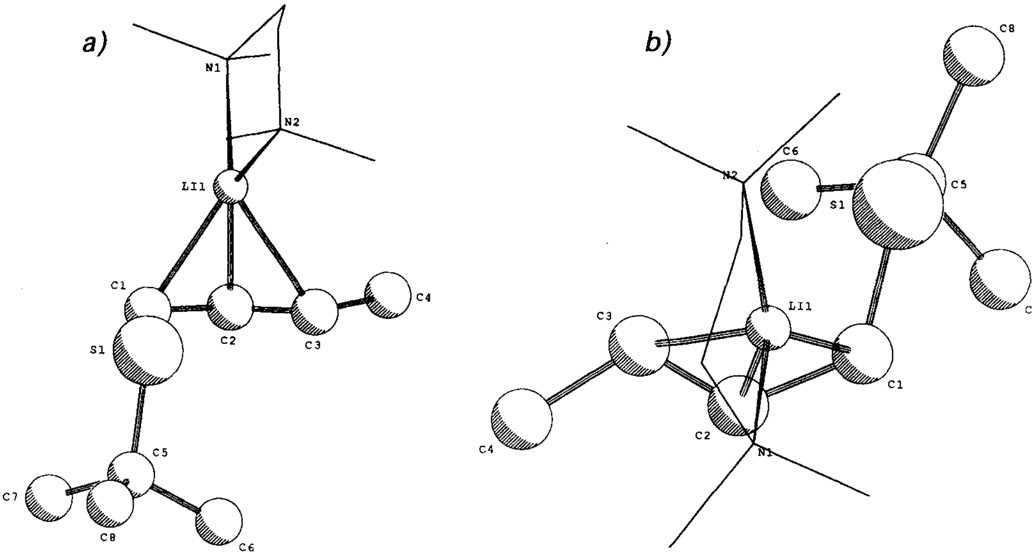


Fig. 3. a) *View parallel to plane C(1)–C(2)–C(3)*; b) *view down normal to plane C(1)–C(2)–C(3)*. Arbitrary numbering.

The S–Li distance (2.9 Å) does not indicate any interaction between these atoms, see the comparison with other RS-C-Li derivatives in *Fig. 4* below, with $[Li_2(Thf)_4\{SCH(SiMe_3)_2\}_2]$ (2.50 Å) [69] and with polymeric $LiSCH_3$ (2.4 Å) [45]. The allyl moiety is an η^3-ligand, the C-atom in α-position to S (C(1)) of which is closer to the metal than the C(γ) (C(3)): 2.2 *vs.* 2.4 Å. (The typical[13]) Li–C distances in crystal structures are

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[13]) See also Scheme 3 in [57] and the data collected in [45]. There is remarkably little variation of the 2.2-Å value on going from such diverse structures as tetrameric alkyllithium, to dimeric phenyllithium, to monomeric benzyllithium, to trityllithium, and to α-S-substituted Li compounds!

all around 2.2 Å, also in those with lithium/π-interactions [45], see *Figs. 1* and *4*.) As is clearly evident from the presentations in *Fig. 2* and *3*, the *cisoid*-S-atom and the four C-atoms of the butenyl group of **6** lie approximately in a plane, with Li and the *t*-Bu group located above and below this plane, respectively. The *t*-Bu–S bond is very long (1.86 Å)[14]) with the tertiary C-atom placed almost exactly perpendicular above the S-atom: angle C(1)–S(1)–C(5) 109.9°, dihedral angle C(5)–S(1)–C(1)–C(2) –84.5°. The bond length of the allylthio moiety in the lithiated compound **6** are *very* similar to those in comparable allyl thioethers (average of 15 structures in the *Cambridge* file [58]): the C,C double bond character of the C(2)–C(3) bond is fully retained (1.34 Å), and the C(1)–C(2) bond is only slightly shortened upon lithiation (1.49 [58] *vs.* 1.47 Å). The bond lengths and angles in the TMEDA part of the structure deviate somewhat from the standard geometry [59] which may be due to some disorder[15]).

3. Crystal Structure and Reactivity? – The structure of **6** confirms the *cisoid*-arrangement of the heteroatom with respect to the allyl moiety, concluded earlier from the product configuration. The long *t*-Bu–S bond can be interpreted as the result of an n-σ^* interaction[16]), found in all other structures of α-S-substituted organolithium compounds[17]) [59a] [62] [63] (see *Fig. 4*) and also concluded from NMR studies of these species [57]. A comparison of the two S–C bonds would indicate that the mode of decomposition might be a *Wittig* rearrangement, rather than α-elimination (**iii** and **iv** *vs.* **ii** in *Footnote 11*). If the crystal structure resembles the species which gives rise to product formation with electrophiles in solution, it is clear that the Li-atom, located essentially in the middle of the allyl moiety, does not lend itself for directing reagents selectively to one or the other end (α- or γ-attack)[18]). This is compatible with the delicate effects influencing the outcome of such reactions (see discussion and references in the *Introduction*).

4. Computational Studies. – Model *ab initio* SCF MO calculations on the lithiated allylic thiol system **7** were carried out in order to gain further insight into the effect (if any) of a neighbouring S-atom on the geometry of the allyl moiety. Owing to limitations in computation resources, it was not possible to carry out optimizations on **6** itself. It was, therefore, necessary to select a smaller system, **7**, which is expected to retain the important structural features found in **6**.

Full geometry optimizations were carried out at the *Hartree-Fock* (HF) level using the 3-21G basis set [70] and the GAUSSIAN 82 suite of programs [71]. Optimized structures were determined from analytically computed forces using the *Schlegel* algorithm [72]. Single-point calculations were carried out on the optimized geometries using the 3-

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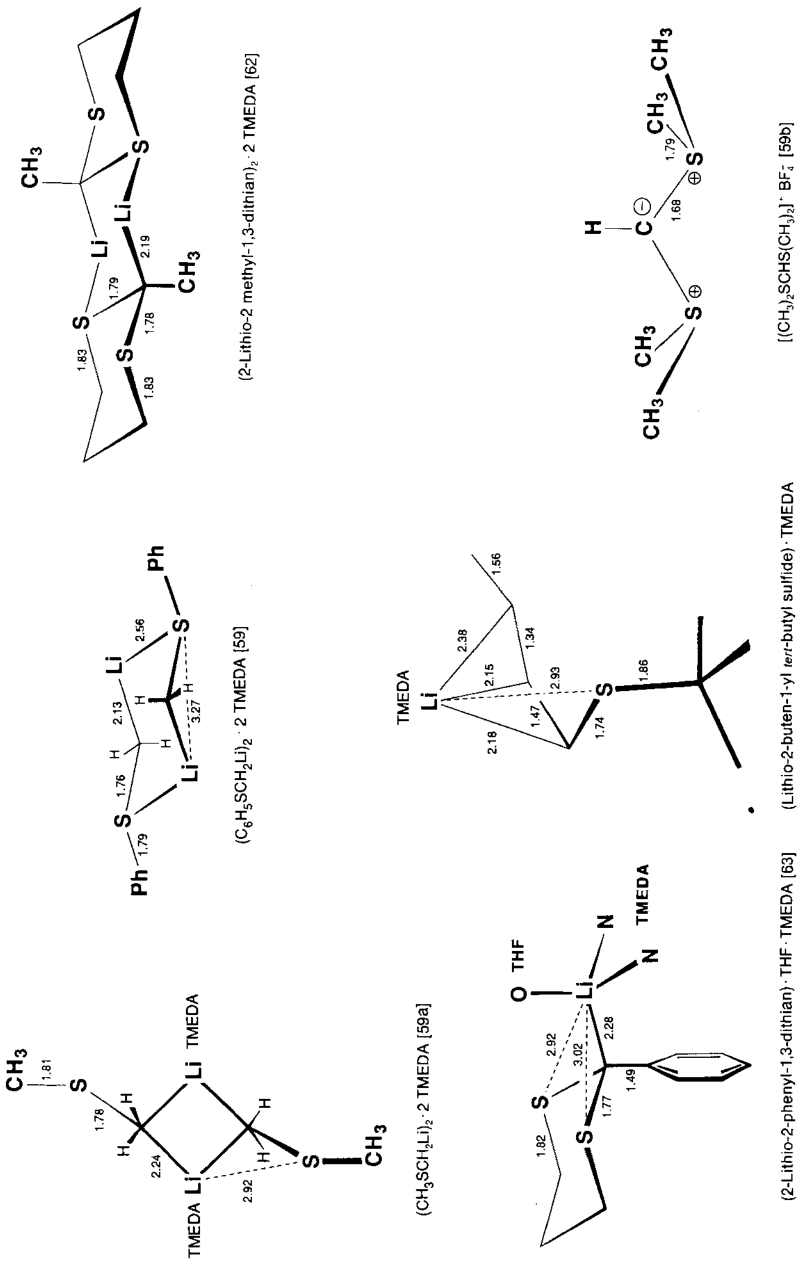
[14]) In fact, the longest S–C bond in the *Cambridge Crystallographic Data Base* [58] is 1.868 Å (version of 7/1987).

[15]) The short CH_2–CH_2 bond length (1.35 Å) and the short Li–N distances (2.08 Å) could be a consequence of disorder, and thus the correlation between anion stability and Li–N distance may not hold here [49] [60] [61]. Disorder is also indicated by the unusually low density of the crystal of **6** (0.97 g · cm^{-3}), *cf.* the other allyllithium structures obtained with low density crystals (0.92 [47a], 0.88 [47b], 0.95 g · cm^{-3} [49]).

[16]) In this terminology, a Li–C bond is considered equal to a non-bonding pair of electrons (*cf.* [57]).

[17]) In α-sulfinyl- [64] and α-sulfonyl-carbanion derivatives [65], the Li is located on one of the O-atoms with a trigonal carbanionic C-atom. Thus, these intriguing structures can not be compared with C-lithiated species.

[18]) It is generally assumed that the Li first captures the electrophile on one of its ligand sites occupied by solvent or TMEDA by a replacement, followed by insertion of the electrophile into the Li–C bond. See the discussions in [52] [59c].



$(CH_3SCH_2Li)_2 \cdot 2$ TMEDA [59a]

$(C_6H_5SCH_2Li)_2 \cdot 2$ TMEDA [59]

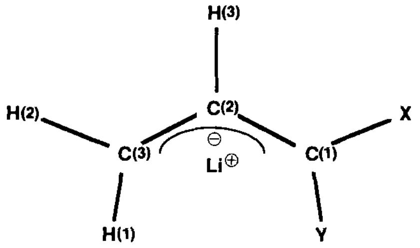
(2-Lithio-2 methyl-1,3-dithian)$_2$ · 2 TMEDA [62]

(2-Lithio-2-phenyl-1,3-dithian) · THF · TMEDA [63]

(Lithio-2-buten-1-yl *tert*-butyl sulfide) · TMEDA

$[(CH_3)_2SCHS(CH_3)_2]^+ BF_4^-$ [59b]

Fig. 4. *Comparison of bond distances in S-substituted carbanion derivatives known until now*



7a X = H, Y = SH
b X = SH, Y = H

21 + G basis set [73], *i.e.* 3-21 + G//3-21G, which differs from the 3-21G basis set in that it is augmented by diffuse s and p functions on the non-H-atoms.

Two stable configurations were located, corresponding to the *cisoid-* and *transoid-*structures, *i.e.*, **7a** and **7b**, respectively. Structural details for these molecules are given in *Fig. 5*[19]). Preliminary calculations revealed that both **7a** and **7b** have two stable conformations, that differ in the value of the H(5)–S–C(1)–C(2) dihedral angle. Only the more stable (and fully optimized) conformations of **7a** and **7b** are dealt with here.

The *cisoid-*structure **7a** is calculated to be 28.3 kJ/mol more stable than the *transoid-*configuration **7b** at the 3-21G level. This stabilization is slightly reduced to 27.1 kJ/mol at the 3-21 + G//3-21G level, which is consistent with previous experience that diffuse functions have little effect on the relative energies of neutral organometallic species [74]. The calculated strong energetic preferences for **7** to adopt the *cisoid-*configuration **7a** is fully consistent with the observed crystal structure of **6**, which likewise displays a *cisoid-*disposition of the heteroatom relative to the allyl moiety.

The C(1)–C(2)–C(3)–Li subunits in **7a** and **7b** *(Fig. 5)* are structurally very similar to that calculated for allyllithium [75] *(Fig. 6)*. Thus, these subunits correspond to near symmetrical bridged structures in which the C_3 allyl group may be regarded as a η^3-ligand. Therefore, as in the case of allyllithium, the bonding between the allyl moiety and lithium in **7a** and **7b** is almost exclusively ionic [75]. This conclusion is supported by the results of natural population (NP) analysis [76] on **7a** which give a total NP of Li of 2.11 electrons, which reveals its essentially complete cationic character.

The Li–S distance is 2.50 Å in **7a** and 3.53 Å in **7b**. Interestingly, the geometry of the C(1)–C(2)–C(3)–Li unit is barely affected upon moving the S-atom from the *cisoid-*position to the *transoid-*position. It is, therefore, unlikely that any covalent bonding exists between Li and S in **7a**, although electrostatic interaction between these atoms could be present[20]).

A remarkable feature of the calculated optimized structure of allyllithium is the deviation of the H-atoms from the C(1)–C(2)–C(3) plane [75] [77], with the inner

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[19]) Total and relative energies in hartrees (= 2625 kJ/mol)

	7a	**7b**
3-21G//3-21G	– 518.79999 (0.0)	– 518.78920 (28.3)
3-21 + G//3-21G	– 518.81345 (0.0)	– 518.80313 (27.1)

[20]) Note that the Li–S distance in **7a** is comparable to that (2.44 Å) calculated for the complex Li^+SH_2 at the 3-21G level [74]. The latter has a 3-21G binding energy of 75 kJ/mol, which is probably largely electrostatic in origin [74].

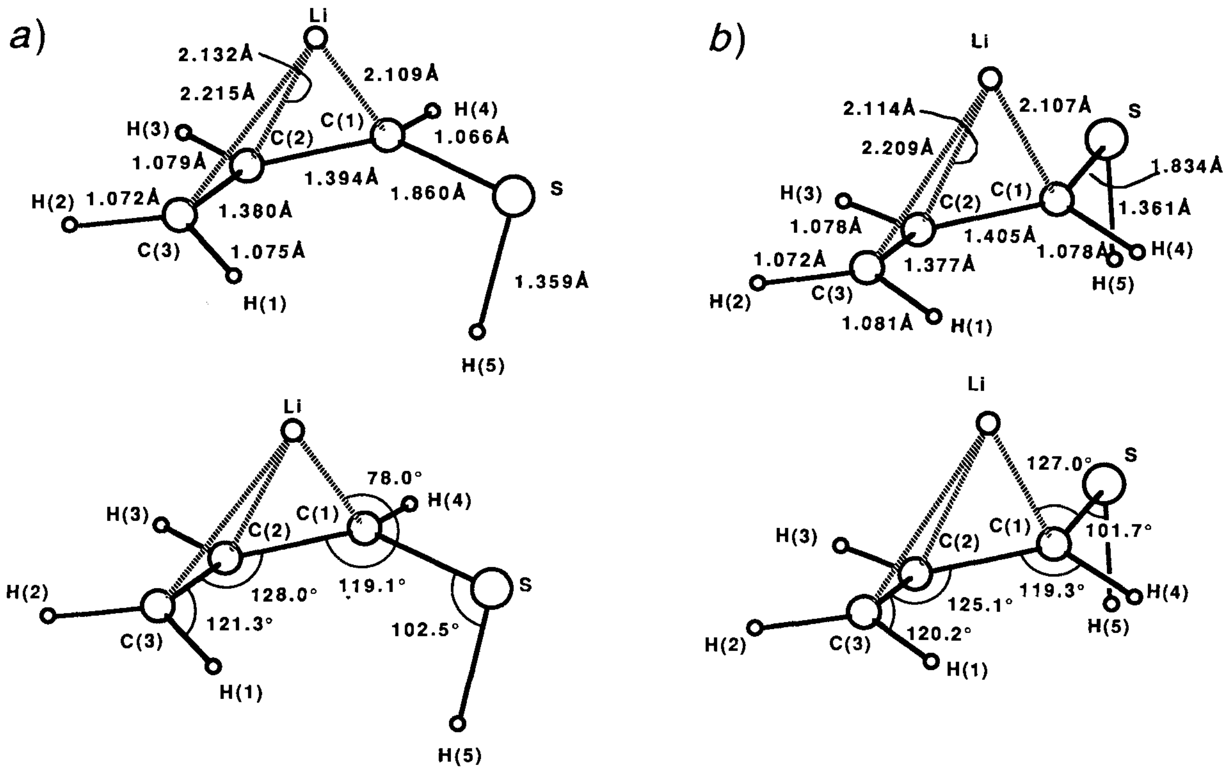

Fig. 5. *3-21G optimized structures for lithiated allylic thiol complexes,* a) cisoid-*configuration* **7a**; b) transoid-*configuration* **7b**. For further details, see *Table 3.*

Table 3. *Cartesian Coordinates* [Å] *of HF/3-21G Optimized Geometries of* **7a**, **7b**, *and Allyllithium*

	Atom	*X*	*Y*	*Z*
7a[a])	C(3)	0.0000	0.0000	0.0000
	C(2)	0.0000	0.0000	1.3802
	C(1)	1.0984	0.0000	2.2389
	S	2.7817	0.3944	1.5541
	Li	1.3668	– 1.5379	0.8214
	H(1)	0.8181	0.4172	– 0.5594
	H(2)	– 0.9268	– 0.1013	– 0.5284
	H(3)	– 0.9447	– 0.1689	1.8728
	H(4)	1.0040	0.1392	3.2917
	H(5)	2.5505	1.5294	0.8432
7b[b])	C(3)	0.0000	0.0000	0.0000
	C(2)	0.0000	0.0000	1.3766
	C(1)	1.1491	0.0000	2.1857
	S	0.9898	– 0.0924	4.0106
	Li	1.2516	– 1.6161	0.8382
	H(1)	0.8536	0.3806	– 0.5439
	H(2)	– 0.9225	– 0.0504	– 0.5430
	H(3)	– 0.9345	– 0.2065	1.8734
	H(4)	2.0409	0.4949	1.8361
	H(5)	0.7182	1.2027	4.3295
Allyllithium complex[c])	C(1)	– 0.4213	– 0.3705	0.0000
	H(m)	– 1.4697	– 0.6294	0.0000
	C(2)	0.1530	– 0.1028	1.2413
	C(2)	0.1530	– 0.1028	– 1.2413
	Li	0.1530	1.6472	0.0000
	H(o)	– 0.3806	– 0.3373	2.1412
	H(o)	– 0.3806	– 0.3373	– 2.1412
	H(i)	1.2321	– 0.0903	1.3276
	H(i)	1.2321	– 0.0903	– 1.3276

[a]) See *Fig. 5a*. [b]) See *Fig. 5b*. [c]) See *Fig. 6*.

H-atoms, H_i, bending away from the metal, and the outer H-atoms, H_o, remaining essentially in the plane, and the middle H-atoms, H_m, bending towards the metal (see *Fig. 6*).

This feature is also retained in **7a** and **7b**. Thus, inspection of the appropriate dihedral angles reveals that the inner S- and H-atom, H(1), of the *cisoid*-structure **7a** are bent away from the Li, whereas the middle H-atom H(3) is bent towards the Li. For **7b** the S, now

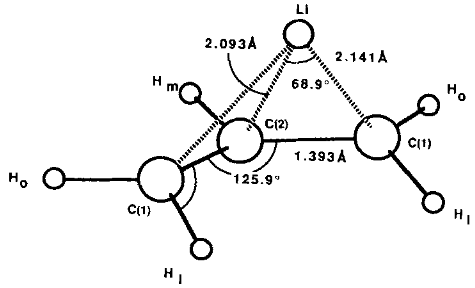

Fig. 6. *3-21G optimized structure for allyllithium* (C_s symmetry). Geometrical details from [75]. See also *Table 3*.

being in the outside position, is nearly coplanar with the three C-atoms. However, the two inner H-atoms H(1) and H(4) are bent away from the metal with the middle H-atom H(3) bent towards the metal.

It is gratifying that the salient structural features for **7a** described above are also present in the observed crystal structure for **6**, notwithstanding the fact that **7a** refers to a vibrationless unsolvated species in the gas phase, whereas **6** is obviously solvated and is part of a crystal lattice.

For example, the S-atom in **6** is bent away from the metal with an S–C(1)–C(2)–C(3) dihedral angle of 16° *(Table 2)*, which is almost identical to the value calculated (14°) for **7a**. The C(1)–C(2)–C(3) angles in **6** (125°) and **7a** (128°) are comparable, but the S–C(1)–C(2) angle is substantially larger (by 8°) in **6** compared to **7a**. The S–H bond in **7a** makes a dihedral angle with the C(1)–C(2) bond of only 49° which is in contrast to the value of 83° for the dihedral angle made by the *t*-Bu group in **6** (C(5)–S–C(1)–C(2)). This result suggests that the dihedral angle made by the *t*-Bu group in **6** is determined more by steric factors than by 'negative hyperconjugation' [78].

The Li-bridge is less symmetrical in **6** compared to **7a**, the difference between the C(1)–Li and C(3)–Li distances in **6** (0.2 Å) being twice as large as that in **7a** (0.1 Å). This enhanced asymmetry in the Li-bridge of **6** is also reflected by the C–C bond lengths of the allyl moiety. Whereas in **6** C(1)–C(2) (1.47 Å) and C(2)–C(3) (1.34 Å) show strong single and double bond character, respectively, the bonds in **7a** have almost identical lengths (they differ by only 0.014 Å). This effect is also observed for allyllithium; the unsolvated species is predicted to be symmetrical *(Fig. 6)*, whereas the crystal structure of the solvated species reveals strongly unequal C–C bond lengths *(Fig. 1a)* [47b].

Several factors could be responsible for the enhanced asymmetry of the Li-bridge found for **6** compared to that calculated for **7**, such as solvation effects and substituent effects in **6**, or basis set deficiencies in the calculations of **7a**. These factors are being assessed by more substantial calculations. The results of that study, together with a detailed energetic picture of the conformational and rotational barriers in **7a** and **7b** and in the non-lithiated allylic thiol anions will be the subject of a forthcoming publication [79].

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5. Experimental. – The compound **6** is air- and temp.-sensitive. All manipulations on the crystals were, therefore, performed below –40° under Ar. For the X-ray measurements, a single crystal was mounted in a thin-walled glass capillary with octane as adhesive. Measurements were made with an *Enraf-Nonius CAD-4* diffractometer equipped with a cooling device. The calculations were made with program suites SHELX 86, SHELX 76 [67], and XRAY [68].

*{(*E*)-1-[(*tert*-Butyl)thio]-2-butenyl}(*N,N,N',N'*-tetramethylethylenediamine)lithium* (**6**). To a soln. of 1.033 g (7.16 mmol) of (*E*)-1-[(*tert*-butyl)thio]but-2-ene in 100 ml of hexane and 1 ml (7.16 mmol) of TMEDA were added 6.83 ml (7.52 mmol) of *sec*-BuLi at –50°. After stirring for 1 h at –50°, the soln. was allowed to warm up to –30° and filtered (under Ar) into an apparatus similar to the one described in [56] for mounting temp.-sensitive crystals in an inert atmosphere. The slightly yellowish soln. was then cooled to –75°. After removing the mother liquor, the white crystalline solid was washed twice with hexane and then dissolved at –20° in 25 ml of hexane and 1 ml of TMEDA. At –78°, clear colorless crystals separated out. After the supernatant soln. had been removed with a syringe, the dry crystals were handled and mounted under the microscope in a second part of the apparatus mentioned above.

REFERENCES

[1] E. J. Corey, *Pure Appl. Chem.* **1967,** *14,* 19.

[2] D. Seebach, *Angew. Chem.* **1979,** *91,* 259; *ibid. Int. Ed.* **1979,** *18,* 239.

[3] T. A. Hase, 'Umpoled Synthons', Wiley, New York, 1987.

[4] a) M. R. Binns, R. K. Haynes, A. A. Katsifis, P. A. Schober, S. C. Vonwiller, *Tetrahedron Lett.* **1985,** *26,* 1565; M. R. Binns, R. K. Haynes, D. E. Lambert, P. A. Schober, *ibid.* **1985,** *26,* 3385; b) M. R. Binns, R. K. Haynes, *Aust. J. Chem.* **1987,** *40,* 937.

[5] J.-F. Biellmann, J.-B. Ducep, *Org. React.* **1982,** *27,* 1.

[6] B. W. Erickson, Ph. D. Thesis, Harvard University, 1970.

[7] J.-F. Biellmann, J.-B. Ducep, *Tetrahedron Lett.* **1968,** 5629.

[8] E. J. Corey, R. Noyori, *Tetrahedron Lett.* **1970,** 311.

[9] E. J. Corey, B. W. Erickson, R. Noyori, *J. Am. Chem. Soc.* **1971,** *93,* 1724.

[10] D. Seebach, *Angew. Chem.* **1969,** *81,* 690; *ibid. Int. Ed.* **1969,** *8,* 639.

[11] D. Seebach, *Synthesis* **1969,** 17.

[12] D. Seebach, M. Kolb, *Chem. Ind. London* **1974,** 687.

[13] D. Seebach, K.-H. Geiss, in 'New Applications of Organometallic Reagents in Organic Synthesis', Ed. D. Seyferth, Elsevier, Amsterdam, 1976.

[14] D. Seebach, in 'Modern Synthetic Methods', Ed. R. Scheffold, Salle + Sauerländer, Aarau–Frankfurt am Main, 1976.

[15] B.-T. Gröbel, R. Bürstinghaus, D. Seebach, *Synthesis* **1976,** 121.

[16] E. J. Corey, D. Seebach, Harvard University 1965/66, see ref. [11], p. 28.

[17] D. Seebach, M. Kolb, B.-T. Gröbel, *Angew. Chem.* **1973,** *85,* 42; *ibid. Int. Ed.* **1973,** *12,* 69.

[18] D. Seebach, M. Kolb, B.-T. Gröbel, *Tetrahedron Lett.* **1974,** 3171.

[19] K. H. Geiss, B. Seuring, R. Pieter, D. Seebach, *Angew. Chem.* **1974,** *86,* 484; *ibid. Int. Ed.* **1974,** *13,* 479.

[20] D. Seebach, K.-H. Geiss, M. Pohmakotr, *Angew. Chem.* **1976,** *88,* 449; *ibid. Int. Ed.* **1976,** *15,* 437.

[21] D. Seebach, M. Kolb, *Liebigs Ann. Chem.* **1977,** 811.

[22] D. Seebach, R. Bürstinghaus, B.-T. Gröbel, M. Kolb, *Liebigs Ann. Chem.* **1977,** 830.

[23] K.-H. Geiss, D. Seebach, B. Seuring, *Chem. Ber.* **1977,** *110,* 1833.

[24] M. Pohmakotr, K.-H. Geiss, D. Seebach, *Chem. Ber.* **1979,** *112,* 1420.

[25] L. Widler, Th. Weber, D. Seebach, *Chem. Ber.* **1985,** *118,* 1329.

[26] D. A. Evans, G. C. Andrews, *Acc. Chem. Res.* **1974,** *7,* 147.

[27] M. Schlosser, *Angew. Chem.* **1974,** *86,* 751; *ibid. Int. Ed.* **1974,** *13,* 701.

[28] S. Warren, *Acc. Chem. Res.* **1978,** *11,* 401.

[29] E. Block, *Org. Chem.* **1978,** *37,* 1; 'Reactions of Organosulfur Compounds', Academic Press, New York, 1978.

[30] H. J. Reich, *Acc. Chem. Res.* **1979,** *12,* 22.

[31] M. Kolb in 'The Chemistry of Ketenes, Allenes and Related Compounds', Ed. S. Patai, Wiley, New York, 1980, Part 2.

[32] T. Hayashi, *J. Synth. Org. Chem. Jpn.* **1986,** *44,* 245.

[33] K. Müllen, *Angew. Chem.* **1987,** *99,* 192; *ibid. Int. Ed.* **1987,** *26,* 204.

[34] D. Hoppe, *Angew. Chem.* **1984,** *96,* 930; *ibid. Int. Ed.* **1984,** *23,* 932; D. Hoppe, T. Krämer, *Angew. Chem.* **1986,** *98,* 171; *ibid. Int. Ed.* **1986,** *25,* 160 and ref. cit. therein.

[35] E. Dziadulewicz, T. Gallagher, *Tetrahedron Lett.* **1985,** *26,* 4547; E. Dziadulewicz, Ph. D. Thesis, Bath University, U.K., 1987.

[36] a) J.-M. Fang, L.-F. Liao, B.-C. Hong, *J. Org. Chem.* **1986,** *51,* 2828; b) J.-M. Fang, B.-C. Hong, L.-F. Liao, *ibid.* **1987,** *52,* 855; c) B.-S. Guo, W. Doubleday, T. Cohen, *J. Am. Chem. Soc.* **1987,** *109,* 4710.

[37] T. Fujisawa, K. Umezu, M. Suzuki, T. Sato, *Chem. Lett.* **1986,** 1675.

[38] J. F. Biellmann, J. B. Ducep, *Tetrahedron* **1971,** *27,* 5861.

[39] R. Schlecker, D. Seebach, *Helv. Chim. Acta* **1977,** *60,* 1459.

[40] D. Seebach, D. Enders, *Angew. Chem.* **1975,** *87,* 1; *ibid. Int. Ed.* **1975,** *14,* 15.

[41] P. Beak, D. B. Reitz, *Chem. Rev.* **1978,** *78,* 275; P. Beak, W. J. Zajdel, *ibid.* **1984,** *84,* 471.

[42] R. R. Fraser, in 'Comprehensive Carbanion Chemistry', Ed. E. Buncel and T. Durst, Elsevier, Amsterdam, 1984, Part B.

[43] H. Ahlbrecht, *Chimia* **1977,** *31,* 391.

[44] R. Glaser, A. Streitwieser, *J. Am. Chem. Soc.* **1987,** *109,* 1258.

[45] W.N. Setzer, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1985,** *24,* 353.

[46] G. Boche, H. Etzrotd, M. Marsch, W. Massa, G. Baum, H. Dietrich, W. Mahdi, *Angew. Chem.* **1986,** *98,* 84; *ibid. Int. Ed.* **1986,** *25,* 104.

[47] a) H. Köster, E. Weiss, *Chem. Ber.* **1982,** *115,* 3422; b) U. Schürmann, E. Weiss, *J. Organomet. Chem.* **1987,** *322,* 299.

[48] M. Marsch, K. Harms, W. Massa, G. Boche, *Angew. Chem.* **1987,** *99,* 706; *ibid. Int. Ed.* **1987,** *26,* 696.

[49] S.K. Arora, R.B. Bates, W.A. Beavers, R.S. Cutler, *J. Am. Chem. Soc.* **1975,** *97,* 6271; R.B. Bates, in 'Comprehensive Carbanion Chemistry', Ed. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, Part A.

[50] D.B. Collum, D. Kahne, S.A. Gut, R.T. DePue, F. Mohamadi, R.A. Wanat, J. Clardy, G. Van Duyne, *J. Am. Chem. Soc.* **1984,** *106,* 4865; H. Dietrich, R. Knorr, *ibid.* **1986,** *108,* 2462.

[51] R. Amstutz, J.D. Dunitz, T. Laube, W.B. Schweizer, D. Seebach, *Chem. Ber.* **1986,** *119,* 434.

[52] M. Schlosser, 'Struktur und Reaktivität polarer Organometalle', Springer Verlag, Berlin, 1973; B.J. Wakefield, 'The Chemistry of Organolithium Compounds', Pergamon Press, Oxford–New York, 1974.

[53] D. Seebach, in 'The R. A. Welch Foundation Conferences on Chemical Research', Houston, Texas, 1984.

[54] R.B. Bates, C.A. Ogle, 'Carbanion Chemistry', Springer Verlag, Berlin, 1983.

[55] R.K. Haynes, unpublished results.

[56] D. Seebach, R. Amstutz, T. Laube, W.B. Schweizer, J.D. Dunitz, *J. Am. Chem. Soc.* **1985,** *107,* 5403.

[57] D. Seebach, R. Hässig, J. Gabriel, *Helv. Chim. Acta* **1983,** *66,* 308.

[58] Cambridge Crystallographic Database, version of 7/1987; Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

[59] a) R. Amstutz, T. Laube, W.B. Schweizer, D. Seebach, J.D. Dunitz, *Helv. Chim. Acta* **1984,** *67,* 224; b) R. Amstutz, Ph.D. Thesis Nr. 7210, ETH Zürich, 1983; c) D. Seebach, J. Hansen, P. Seiler, J.M. Gromek, *J. Organomet. Chem.* **1985,** *285,* 1.

[60] J.J. Brooks, G.D. Stucky, *J. Am. Chem. Soc.* **1972,** *94,* 7333.

[61] J.J. Brooks, W. Rhine, G.D. Stucky, *ibid.* **1972,** *94,* 7346.

[62] R. Amstutz, D. Seebach, P. Seiler, W.B. Schweizer, J.D. Dunitz, *Angew. Chem.* **1980,** *92,* 59; *ibid. Int. Ed.* **1980,** *19,* 53.

[63] R. Amstutz, J.D. Dunitz, D. Seebach, *Angew. Chem.* **1981,** *93,* 487; *ibid. Int. Ed.* **1981,** *20,* 465.

[64] H.-J. Gais, I. Edelmeier, H.J. Lindner, J. Vollhardt, *Angew. Chem.* **1986,** *98,* 916; *ibid. Int. Ed.* **1986,** *25,* 939; H.J. Gais, H.J. Lindner, J. Vollhardt, *Angew. Chem.* **1985,** *97,* 865; *ibid. Int. Ed.* **1985,** *24,* 859.

[65] G. Boche, M. Marsch, K. Harms, G.M. Sheldrick, *Angew. Chem.* **1985,** *97,* 577; *ibid. Int. Ed.* **1985,** *24,* 573.

[66] C.K. Johnson, 'ORTEP-III. Report ORNL-5138', Oak Ridge National Laboratory, Tennessee, USA, 1976.

[67] G. Sheldrick, 'SHELX-76, SHELX-86. Program for Crystal Structure Determination', University Chemical Laboratory, GB-Cambridge, England, 1986.

[68] J.M. Stewart, G.J. Kruger, H.L. Ammon, C.D. Dickerson, S.R. Hall, 'The X-Ray System. Version of June 1972. Technical Report TR-192', Computer Science Centre, University of Maryland, College Park MD, USA, 1972.

[69] M. Aslam, R.A. Bartlett, E. Block, M.M. Olmstead, P.P. Power, G.E. Sigel, *J. Chem. Soc., Chem. Commun.* **1985,** 1674.

[70] J.S. Binkley, J.A. Pople, W.J. Hehre, *J. Am. Chem. Soc.* **1980,** *102,* 939.

[71] J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder, R. Seeger, J.A. Pople, GAUSSIAN 82, Carnegie–Mellon University, Pittsburgh, PA 15213, U.S.A.

[72] H.B. Schlegel, *J. Comput. Chem.* **1982,** *3,* 214.

[73] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.v.R. Schleyer, *J. Comput. Chem.* **1983,** *4,* 294.

[74] P.v.R. Schleyer, T. Clark, A.J. Kos, G.W. Spitznagel, C. Rhode, D. Arad, K.N. Houk, N.G. Rondan, *J. Am. Chem. Soc.* **1984,** *106,* 6467.

[75] T. Clark, C. Rhode, P. v. R. Schleyer, *Organometallics* **1983,** *2,* 1344.

[76] a) A.E. Reed, F. Weinhold, *J. Am. Chem. Soc.* **1985,** *107,* 1919; b) A.E. Reed, P.B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985,** *83,* 735; c) A.E. Reed, F. Weinhold, *QCPE* **1985,** *5,* 504.

[77] P. v. R. Schleyer, *Pure Appl. Chem.* **1984,** *56,* 151.

[78] P. v. R. Schleyer, A.J. Kos, *Tetrahedron* **1983,** *39,* 1141.

[79] M.N. Paddon-Row, S.S. Wong, manuscript to be published.