estimated as ~2.1 eV.[13] Given these values, $k_{et}^{corr} = 8.3 \times 10^3$ s^{-1} is the rate that would have been observed for the [Co(diAMsar)]-cyt *c* derivative if the driving force and reorganizational energy for the (Ru,Zn)Mb system were applicable. This may be compared to a rate predicted by the observed distance dependence[10] of 2.2×10^4 s^{-1} at $r = 14.5$ Å. The agreement between observed and predicted rates suggests that the simple treatment of driving force and reorganizational energy effects[11] on the rate has validity for a range of modified protein systems.

Acknowledgment. We thank Larry Faulkner for the use of instrumentation, for helpful discussions concerning the electrochemical and photochemical experiments, and for partial financial support from National Science Foundation Grant CHE86-07984. The flash photolysis experiments were carried out in the laboratory of Professor T. L. Brown. D.W.C. acknowledges a graduate fellowship from The Electrochemical Society. This research was supported by a National Science Foundation Presidential Young Investigator Award (CHE87-14889) to R.A.S.

Supplementary Material Available: Experimental details of the preparation and characterization of the [Co(diAMsar)]-cytochrome *c* derivatives (5 pages). Ordering information is given on any current masthead page.

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(13) On the basis of a calculation for $[Co(NH_3)_6]^{2+/3+}$[14] and a Co–N bond length change of 0.174 Å,[8] we estimate λ_{in} = 184 kJ-mol^{-1} for $[Co(diAMsar)]^{2+/3+}$ self-exchange. Assuming λ_{out} = 117 kJ-mol^{-1} as for $[Co(NH_3)_6]^{2+/3+}$[14] and $\lambda \approx$ 100 kJ-mol^{-1} for cytochrome $c^{2+/3+}$ self-exchange[11] gives $\lambda \approx$ 200 kJ-mol^{-1} (2.1 eV) for the [Co(diAMsar)]-cytochrome *c* electron transfer. An alternative calculation using the measured self-exchange rate of $[Co(diAMsar)]^{2+/3+}$ (0.50 M^{-1}s^{-1}) yields λ = 304 kJ-mol^{-1} (3.1 eV) for $[Co(diAMsar)]^{2+/3+}$ self-exchange and also yields λ = 200 kJ-mol^{-1} (2.1 eV) for the [Co(diAMsar)]-cytochrome *c* reaction. (As with the (Ru,Zn)Mb analysis, we have not included the distance-dependent λ_{out} contribution pointed out by Isied et al.[15])

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X-ray Crystal Structure and Hydrocarbon Solution Dynamics of Dimeric 1,1-Bis((dimethylamino)methyl)-2-propyllithium

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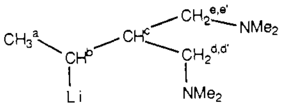
Received September 20, 1988

All dimeric alkyllithiums studied so far were found to be more reactive than their tetrameric counterparts.[1-3] While various reasons have been invoked for this,[2a,3] any sound understanding of the properties of alkyllithium dimers requires detailed knowledge of structure and bonding of these species.[4]

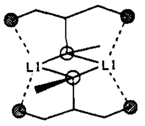
We now report that crystals obtained from pentane solutions of 1,1-bis((dimethylamino)methyl)-2-propyllithium (I) yielded the first X-ray data for a dimeric alkyllithium. Also reported are the dynamics of $(I)_2$ in hydrocarbon solutions.

Table I. Interatomic Distances [Å]

	α-C-Li	α-C-Li′	Li-Li′	Li-N	Li-N′
$(I)_2$	2.19	2.21	2.40	2.09	2.15
III	2.20	2.24	2.39	2.16	2.16
$(IV)_4$ (≡V)	2.27	2.28	2.48, 2.54	2.07	
VI	2.29	2.25, 2.31	2.49, 2.56	2.01	



I



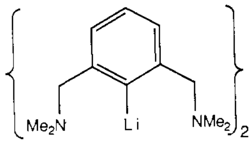
II

○ = CH

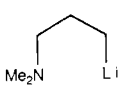
● = NMe_2

I was obtained by treatment of *tert*-butyl[1,1-bis((dimethylamino)methyl)-2-propyl]mercury with 1 equiv of *t*-BuLi in *n*-pentane at −15 °C. After removing volatile materials (pentane, $(t\text{-}Bu)_2Hg$) by bulb-to-bulb distillation (room temperature, 10^{-5} Torr), I was extracted from the residue with pentane and purified by repeated crystallization from pentane to yield colorless crystals subliming (10^{-5} Torr) around 80 °C.[5]

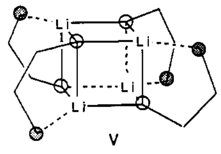
X-ray analysis indicated the crystals to consist of dimeric units II as shown in detail in Figure 1 and located at C_i symmetry sites in the unit cell.[6] In this structure, the two lithium atoms are bridged by the two α-carbons, and their coordination spheres are completed by the intramolecularly coördinated dimethylamino groups. The interatomic distances between Li and α-C and N, respectively, of $(I)_2$ (≡II) and those of III[7] and the related tetramers $(IV)_4$ (≡V)[8] and VI[9] containing only one intramolecularly coordinated dimethylamino group per lithium are given in Table I. The interatomic distances are almost identical in $(I)_2$ and III. It is interesting to notice the larger α-C–Li and Li–Li interatomic distances in the tetramers $(IV)_4$ (≡V) and VI. Although dimers so far were found to be more reactive than tetramers, they may have tighter carbon–lithium bonds, as suggested by the present



III



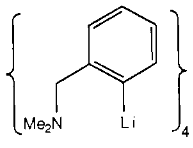
IV



V

○ = CH_2

● = NMe_2



VI

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(6) Crystal data are as follows: $(C_9H_{21}N_2Li)_2$, monoclinic, dimensions: 0.25 × 0.25 × 1.75 mm, space group $P2_1/n$, a = 7.778 (1) Å, b = 15.647 (1) Å, c = 9.367 (3) Å, β = 94.43 (2)°, Z = 2, F_{000} = 368, D_{calcd} = 0.959 g·cm^{-3}, μ(Cu Kα) = 3.9 cm^{-1}. Data collected on an Enraf-Nonius CAD4 [Nickel filtered Cu Kα radiation, λ = 1.5418 Å, sin θ_{max}/λ = 0.609; $\pm h,\pm k,-l$; 4612 reflections; $\omega/2\theta$ scan]. The structure was solved by direct methods (SHELXS 86) and refined on F (SHELX 76) to a final $R(R_w)$ = 0.048 (0.041) for 1560 reflections with $I > 2.5\sigma(I)$; $w = {}^1/\sigma^2(F)$. All positional parameters, anisotropic thermal parameters for the non-H atoms, and isotropic thermal parameters for the H-atoms were refined. A final difference map showed no residual density outside 0.21 and −0.11 e·Å^{-3}.

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Table II. ^{1}H and ^{13}C NMR Spectra[a] [δ (Me_4Si), ppm] of $(I)_2$

						NMe_2 (s) (K)	
^{1}H (K)	H_a (d^b)	H_b (bm^b)	H_d (dd^b) H52	$H_{d'}$ (dd^b)	H_e (dd^b)	183[c]	203
183	1.434 (A)	−0.755	3.312 (A)	1.911 (A)	2.807 (A)	2.365	2.365 (A)
	1.405 (B)		3.015 (B)		2.584 (B)	2.348	2.358 (B)
						2.330	2.350 (A)
						2.316	2.330 (A)
						2.224	2.310 (B)
						2.146	2.224 (B)
							2.174 (A)
							2.151 (B)
294	1.430	−0.745	3.261 (A)	1.991	2.796 (A)	2.366	
			3.052 (B)		2.649 (B)	2.271	

^{13}C (K)	NMe_2 (q^d)		NCH_2 (t^e)	CH (d^f)	CHLi (bd)	CH_3 (q^g)
200	50.36 (A)	50.46 (B)	64.45 (A)	50.83 (A)	19.27 (A)	24.09 (A)
	49.48 (A)	48.88 (B)	62.76 (A)	50.47 (B)	19.86 (B)	
	48.28 (A)	48.55 (B)	65.19 (B)			
	42.99 (A)	44.66 (B)	64.22 (B)			
297	50.93		65.93 (A)	52.04	20.59	24.07
	46.70		64.57 (A)			
			66.52 (B)			
			65.68 (B)			

[a] In *n*-pentane-d_{12}. Signals of H_c, $H_{d'}$(B), and $H_{e'}$ are between 2.43 and 2.05 ppm and are obscured by the NMe_2 signals. [b] J(Hz): ab, 7.4; cd, 11.6; cd′, 4.6; ce, 3.3; dd′, 10.5; ee′, 13.7. [c] At 183 K only six different NMe_2 groups are detected due to broadening of all signals at low temperatures. At 203 K all NMe_2 groups are discernible. Data given were obtained by resolution enhancement. [d] J(C–H) = 132 Hz. [e] J(C–H) = 126 Hz. [f] J(C–H) = 111 Hz. [g] J(C–H) = 125 Hz.

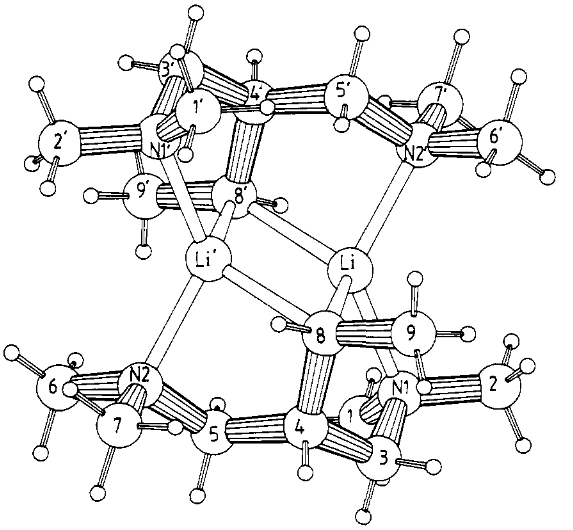


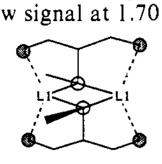
Figure 1. Drawing of the inversion dimer. Selected bond lengths (Å) are as follows: Li–Li′, 2.402 (4); Li–C8, 2.189 (3); Li–C8′, 2.205 (4); Li–N1, 2.092 (3); Li–N2′, 2.154 (3); C8–H81, 1.00 (2); Li–H81′, 2.078 (15).

results. Therefore, their higher reactivity may not to be due to some intrinsic weakness of the R_2Li_2 system but may be caused by more favorable transition states.[2,3] The fact that $(I)_2$ and III have longer lithium–nitrogen bonds than $(IV)_4$ and VI suggests that in the reactions of dimers certain coordinating Lewis bases are more easily displaced by the substrates.[3]

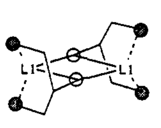
Besides the short C–Li and Li–Li distances in $(I)_2$ the short distance between H52′ and Li (2.59 (2) Å) is also remarkable.

The 62.8 MHz ^{13}C NMR spectra of I in *n*-pentane-d_{12} (Table II) reveal the presence of two species A and B with an intensity ratio (67:33) that is both temperature and concentration independent.[10] The proton decoupled ^{13}C resonance of the α-carbon of **I**-^{6}*Li* consists of two quintets, $J(^{13}C-^6Li) = 7.0$ Hz,[11] indicating A and B to be two dimers.[12] ^{6}Li–^{1}H 2D-HOESY (2D heteronuclear Overhauser spectroscopy)[13] at 248 K exhibited a cross peak for H52′ (H_d) of the major dimer A,[14] revealing a short Li–H52′ distance, which is also found in the crystal structure of $(I)_2$. This indicates that the solution structure is very similar to the crystal structure. Accordingly, dimer A is assigned structure II. The 250 MHz proton spectra (Table II) of the two dimers correspond to such an extent that an analogous structure VII with cis-positioned α-methyl groups is assigned to the minor species B. Up to 230 K all the eight different *N*-methyl groups of II and VII are distinguishable in the ^{1}H and the ^{13}C NMR spectra. Upon warming the *N*-methyl signals broaden and coalesce to give two broad signals (1:1), at 294 K, indicating that exchange of the NMe_2 groups between II and VII environments (vide infra) and, in addition, either loss of diastereotopicity of the NMe_2 groups or exo/endo exchange of methyl within the individual NMe_2 groups of II and VII are fast on the NMR time scales.[16]

At 200 K $(I)_2$ in *n*-pentane-d_{12} shows ^{7}Li NMR[15] resonances at 1.81 and 1.60 ppm with a concentration independent[10] intensity ratio of 84:16. At 245 K the signal at 1.60 ppm and a related signal hidden under the main resonance at 1.81 ppm are coalesced to give a signal at 1.70 ppm. The main signal at 1.81 ppm (II) and the new signal at 1.70 ppm (VII) have a concentration independent intensity ratio of 67:33 and coalesce at 290 K to give one broad signal at 1.75 ppm. The coalescence at 245 K ($\Delta G^{\ddagger}$



VII



VIII

○ = CH

● = NMe_2

○ = $CHCH_3$

● = NMe_2

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(10) Concentration, 0.2–1.0 M; temperature, 183–298 K.

(11) At 240 K the α-^{13}C resonance of the principal dimer A becomes more complicated as the magnetic nonequivalence of the two ^{6}Li nuclei manifests itself [$J(^6Li-^{13}C) = 6.0$ Hz, $J(^6Li'-^{13}C) = 8.0$ Hz]. At higher temperatures this nonequivalence is lifted, probably by fast degenerate rearrangement through VIII (vide infra). In the minor dimer B this process must still be fast at 230 K.

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(14) For dimer B no cross peaks could be observed, probably due to their low intensity.

(15) 97.21 MHz, relative to external 1 M dry LiBr in THF [δ (50% LiBr in H_2O): −1.04 ppm and δ (2-lithiobutane): 0.77 ppm]. Not corrected for volume magnetic susceptibility.

(16) Analysis of the coalescence is impeded by a general downfield shift with increasing temperature mainly of the signals of B.

= 52 ± 1.7 kJ·mol^{-1}) is ascribed to fast degenerate rearrangement of II and VII, respectively, rendering the lithium atoms in VII equivalent. "Chelatomers" of type VIII are likely intermediates in this process and can be formed from II and VII, respectively, by decoordination of two *trans*-NMe$_2$ groups followed by the conformational change and recoordination of the NMe$_2$ groups. At 290 K an exchange between II and VII ($\Delta G^{\ddagger}_{\text{II-VII}}$ = 64 ± 2.1 kJ·mol^{-1}, $\Delta G^{\ddagger}_{\text{VII-II}}$ = 63.5 ± 2.5 kJ·mol^{-1}) becomes apparent, which is possibly initiated by inversion at α-C.[17]

Acknowledgment. The X-ray data were kindly collected by A. J. M. Duisenberg. The investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: An ORTEP plot and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (4 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(17) Such a process would also account for part[16] of the temperature dependence of the NMe$_2$ signals (vide supra). One alternative mode of exchange, proceeding through a tetramer formed from II and VII, is rendered unlikely by the concentration independence of the coalescence temperatures.

An Organometallic Route to Binary Carbon Sulfides. The Structure of C_6S_{12}

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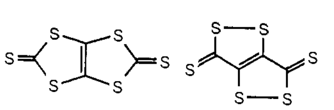
Received December 21, 1988

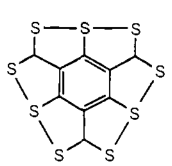
Given the great interest in sulfur nitrides,[1] the corresponding carbon sulfides could be expected to have a rich chemistry. In this report we describe the synthesis of two new carbon sulfides. Prior to our work five molecular carbon sulfides were known to be stable at room temperature: CS_2,[2] C_3S_2,[3] two isomers of C_4S_6,[4,5] and C_9S_9.[6]

$S{=}C{=}S$ $\quad$ $S{=}C{=}C{=}C{=}S$

CS_2 $\quad$ C_3S_2

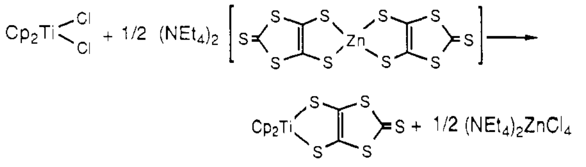


C_4S_6



C_9S_9

Our synthesis of carbon sulfides is predicated on two advances, the recent synthesis of salts of $C_3S_5^{2-}$ [7,8] and the ability of Cp_2Ti^{IV} compounds (Cp = C_5H_5) to serve as group-transfer agents.[9-11] Treatment of Cp_2TiCl_2 with 0.5 equiv of $(Et_4N)_2[Zn(C_3S_5)_2]$[7] in refluxing THF resulted in a color change from red to green. After 3 h the cooled solution was filtered through silica gel, concentrated, and diluted with hexane to afford black green crystals of $Cp_2TiC_3S_5$ (**1**) in 90% yield[12] (eq 1).



(1)

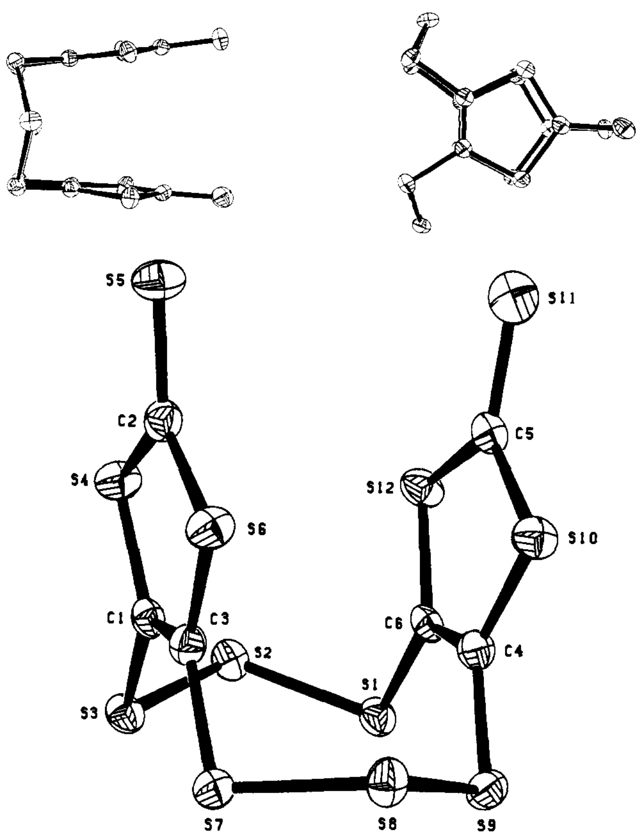


Figure 1. The structure of C_6S_{12} (**2**) with thermal ellipsoids drawn at the 35% level. Side and top views of the C_6S_{12} molecule are shown in the inset.

Solutions of **1** (1 g, 2.67 mmol) and S_2Cl_2 (0.216 mL, 2.67 mmol) each dissolved in 20 mL of CH_2Cl_2 were simultaneously added dropwise into 300 mL of stirred CH_2Cl_2 over a period of 6 h at room temperature. The resulting yellow-orange suspension was filtered, and the yellow solids were washed with CH_2Cl_2. The

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