Solid State and Solution Structures of Dimeric Organolithium Derivatives of a $P_2N_4S_2$ Ring

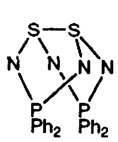
Tristram Chivers,* Mark Edwards, Robert W. Hilts, Masood Parvez and Rainer Vollmerhaus

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

An X-ray structural determination of the dimer $[Li(Ph_4P_2N_4S_2Ph)\cdot THF]_2$ (THF = tetrahydrofuran) reveals a step-shaped structure; ^7Li and ^{31}P NMR investigations of $[Li(Ph_4P_2N_4S_2R)\cdot THF]_2$ (R = Me, Bu^t, Ph), as a function of temperature and concentration, in THF solution show that this dimer is fluxional and indicate the presence of a second dimeric species.

The $P_2N_4S_2$ ring in **1** is an informative model for investigating reactions of sulfur–nitrogen heterocycles since, in contrast to the behaviour of S_4N_4, the integrity of the eight-membered ring is invariably retained.[1–5] Furthermore, ^{31}P NMR spectroscopy provides a revealing probe of solution structures[3–5] and fluxional processes.[4b,6] For example, the reaction of **1** with alkyllithiums generates the organolithium derivatives **2a** and **2b**, which have been used to prepare fluxional σ-*S* bonded complexes of the type **3**.[7] In contrast, the reaction of S_4N_4 with an alkyllithium results in ring contraction to give $S_3N_3^-$.[8] The structural characterization of **2a**, **2b** or a related organolithium derivative is crucial to the development of the potentially extensive coordination chemistry of the novel anionic ligands $Ph_4P_2N_4S_2R^-$. We report here the X-ray structure of (**2c**·THF)$_2$ and variable temperature ^7Li and ^{31}P NMR evidence for the fluxional behaviour of this dimer in solution.

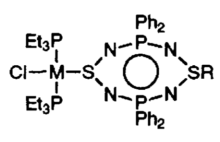
Colourless blocks of (**2c**·THF)$_2$, prepared by addition of a slight excess of phenyllithium to **1** in THF at −78 °C, were



1

$Li[Ph_4P_2N_4S_2R]$

2a; R = Me
2b; R = Bu^t
2c; R = Ph



3 (Me = Pt, Pd; R = Me)

obtained from THF–diethyl ether at 23 °C.† The molecular geometry and atomic numbering scheme are shown in Fig. 1. The reaction of **1** with phenyllithium results in the attachment of the phenyl group to sulfur and the opening up of the S–S separation from 2.528(1) Å in **1**[9] to 3.31(1) Å in (**2c**·THF)$_2$. In contrast to the structure of 1,5-$Ph_4P_2N_4S_2Ph_2$,[10] in which the heterocyclic ring adopts a chair conformation, the $P_2N_4S_2$ ring in (**2c**·THF)$_2$ is boat-shaped with sulfur atoms on the same side of the ring. The molecule is a centrosymmetric dimer with a step-shaped (ladder) structure reminiscent of that found for some organolithium derivatives of bis(trimethylsilyl)sulfur diimide[11,12] and a variety of organonitogen-lithium compounds.[13] Each lithium atom is coordinated to two nitrogen atoms, N(1) and N(2) or N(1)* and N(2)*, of one of the $P_2N_4S_2$ rings almost symmetrically [*d*(Li–N) = 2.03(2) and 2.08(2) Å] and to one nitrogen atom, N(2)* or N(2), of the other $P_2N_4S_2$ ring [*d*(Li–N) = 2.10(2) Å]. In this respect the structure of (**2c**·THF)$_2$ differs significantly from that of [$(Me_3SiN)_2S(Ph)Li$·THF]$_2$ in which the lithium atoms are bonded asymmetrically to NSN units [*d*(Li–N) = 2.022(5) and 2.393(5) Å].[12] A single THF molecule completes the coordination sphere of the lithium atoms. Coordination to lithium has a pronounced effect on the S–N bond lengths, which increase from 1.62 Å in **1** to 1.72(1) and 1.755(9) Å in (**2c**·THF)$_2$.

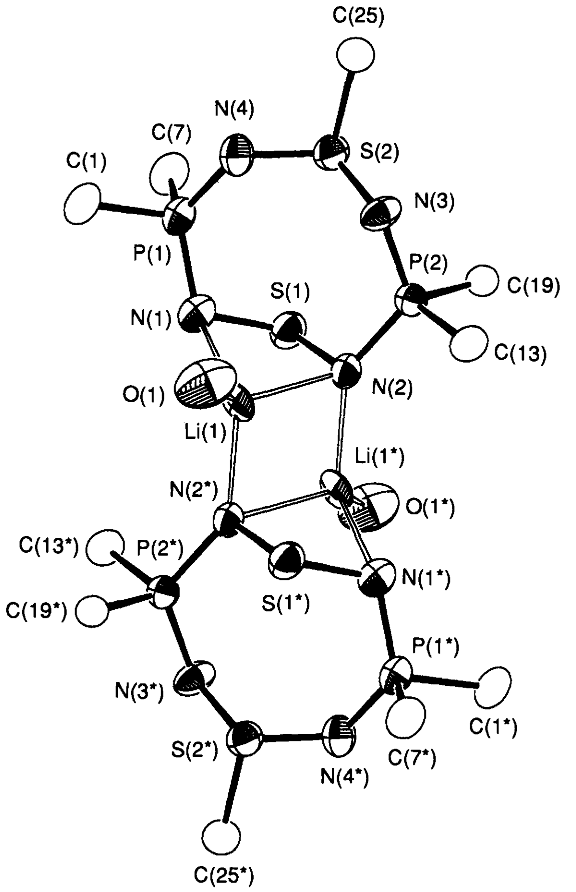


Fig. 1 ORTEP diagram (50% probability ellipsoids) for [Li($Ph_4P_2N_4S_2Ph$)·THF]$_2$; selected bond lengths (Å) and bond angles (°): S(1)–N(1) 1.72(1), S(1)-N(2) 1.755(9), S(2)–N(3) 1.608(9), S(2)–N(4) 1.60(1), P(1)–N(1) 1.618(10), P(1)–N(4) 1.619(10), P(2)–N(2) 1.649(9), P(2)–N(3) 1.608(9), Li(1)–N(1) 2.08(2), Li(1)–N(2) 2.03(2), Li(1)–N(2)* 2.10(2), Li(1)–O 2.01(2); N(1)–S(1)–N(2) 101.7(5), N(3)–S(2)–N(4) 111.5(6), N(1)–P(1)–N(4) 121.1(5), N(2)–P(2)–N(3) 121.1(5), P(1)–N(1)–S(1) 110.4(6), S(1)–N(2)–P(2) 107.3(5) P(2)–N(3)–S(2) 119.2(6), S(2)–N(4)–P(1) 118.7(6), S(1)–N(1)–Li(1) 84.2(7), S(1)–N(2)–Li(1) 84.5(7), N(1)–Li(1)–N(2) 81.9(8), N(2)–Li(1)–N(2)* 98(1). * Indicates symmetry-related atoms. For clarity, only the O atoms of THF molecules and the α-C atoms of *P*- and *S*-bound phenyl groups are shown.

The nitrogen atoms N(1) and N(1)* are three-coordinate in (**2c**·THF)$_2$ whereas N(2) and N(2)* are four-coordinate. Consequently, the phosphorus atoms of each $P_2N_4S_2$ ring are inequivalent so that the combination of ^{31}P NMR with ^{7}Li NMR spectroscopy provides important insights into the solution structures of **2a–c**. As indicated in Fig. 2 the ^{31}P NMR spectrum of a 58 mmol dm^{-3} solution of **2c** in THF at 333 K exhibits a broad resonance at δ 22.0, which is resolved at 190 K into two resonances of equal intensity at δ 24.5 and 21.6, and a third resonance at δ 19.5. When the temperature of the solution is raised gradually from 190 to 235 K the two signals at high frequency broaden simultaneously and eventually collapse to give one averaged resonance at δ 23.1. The reverse of these changes occurs upon cooling. The same pattern of behaviour is observed for the THF solutions of **2a** and **2b** in this temperature range. We attribute these observations to the presence of a dimer, with a structure similar to that of (**2c**·THF)$_2$, which undergoes a rapid fluxional process above 235 K. Coalescence for the two site exchange in the unsymmetrical dimer occurs at 223 K which corresponds to an activation energy of 41 kJ mol^{-1}.[14] This two-site exchange process could occur *via* an eight-membered $Li_2N_4S_2$ ring (see Fig. 3) of the type that has been established in the solid state for [{$Me_3SiNS(Bu^t)NBu^t$}Li]$_2$.[11] The third resonance ob-

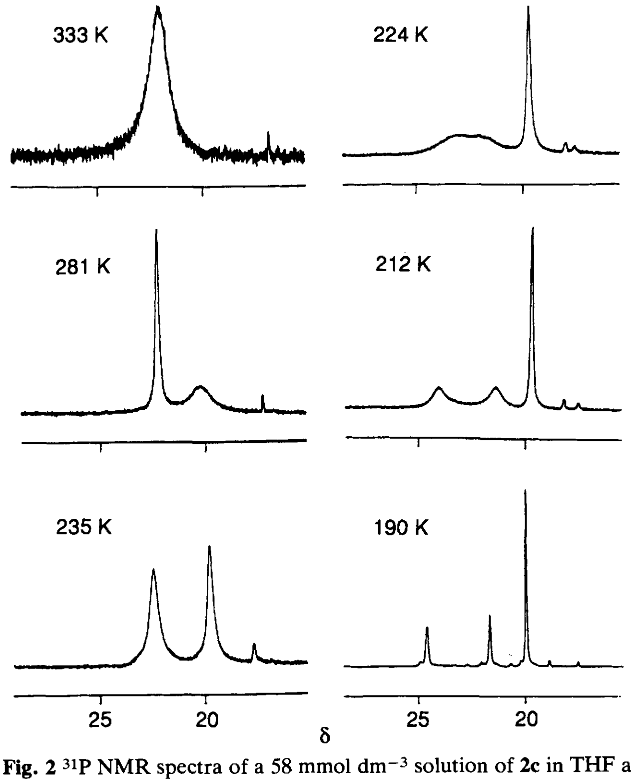


Fig. 2 ^{31}P NMR spectra of a 58 mmol dm^{-3} solution of **2c** in THF at various temperatures obtained on a Bruker AM 400 instrument operating at 161.978 MHz with 85% H_3PO_4 as the external reference

---

† *Crystal data* for $C_{34}H_{33}LiN_4OP_2S_2$: M = 646.67, triclinic, space group, $P\bar{1}$ (No. 2); at 293 K, a = 13.189(10), b = 13.335(8), c = 11.760(5) Å, α = 90.67(4), β = 114.15(4), γ = 114.05(5)°, V = 1683(2) Å^3, Z = 2, μ(Mo-Kα) = 0.286 mm^{-1}, F(000) = 676, D_c = 1.276 g cm^{-3}. Intensity were collected on a Rigaku AFC6S diffractometer operating in the ω-2θ mode and using the Mo-Kα radiation (λ = 0.71069 Å, graphite monochromator) and were corrected for absorption. Total number of unique reflections 5950, of which 2287 had $I > 3\sigma(I)$. Crystal dimensions 0.70 × 0.35 × 0.20 mm. The structure was solved by Fourier techniques and was refined by full-matrix least-squares calculations to R = 0.072 and R_w = 0.060.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

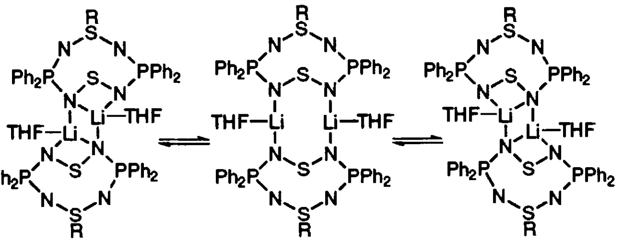


Fig. 3 Proposed two-site exchange process for $[Li(Ph_4P_2N_4S_2R)]_2$ (R = Me, Bu^t, Ph)

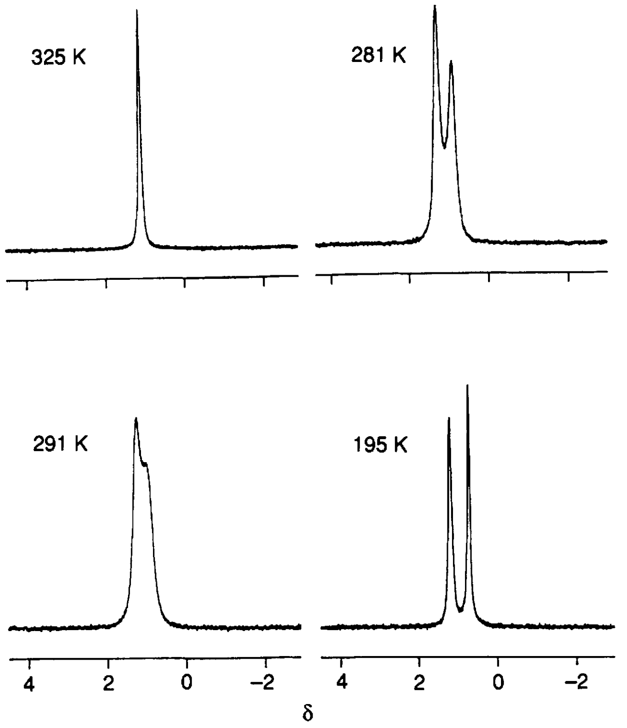


Fig. 4 ^7Li NMR spectra of a 58 mmol dm^{-3} solution of **2c** in THF at various temperatures obtained on a Bruker AM 400 instrument operating at 155.508 MHz with $LiClO_4$ (4.0 mol dm^{-3}) in D_2O as the external reference

served as a singlet (^{31}P = δ 18–20) at 190 K for **2a–c** is attributed to a species with equivalent phosphorus atoms. The intensity of the ^{31}P NMR resonances of the dimer $(\mathbf{2c}\cdot THF)_2$ decreases relative to that of the resonance at δ 18–20 with dilution of the THF solution, and at 13 mmol dm^{-3} only the latter resonance is observed at 185 K. This suggests that the symmetrical species is either a monomer or a more highly solvated dimer with equivalent phosphorus atoms.

The ^7Li NMR spectrum of a 58 mmol dm^{-3} solution of **2c** in THF at 205 K exhibits two resonances at δ 0.98 and 0.35 (*vs.* external 4.0 mol dm^{-3} $LiClO_4$ in D_2O) indicating the presence of two species [the lithium sites in the dimer $(\mathbf{2c}\cdot THF)_2$ are equivalent]. Upon dilution of the solution to 33 mmol dm^{-3}, the relative intensity of the resonance at δ 0.98 decreases and at 13 mmol dm^{-3} this resonance is no longer observed. This suggests that the ^7Li NMR resonance at δ 0.98 can be attributed to the unsymmetrical dimer of **2c**. The ^7Li NMR spectra of **2a** in THF exhibit similar changes with concentration.

Finally, we note that a second process, as manifested by the collapse of the resonance for the symmetrical species in both the ^{31}P NMR (see Fig. 2) and ^7Li NMR spectra (see Fig. 4), occurs in the temperature range 235–335 K. The temperature-dependent spectra are inconsistent with a monomeric structure for the symmetrical species, since dissociation to a monomer should be favoured by an increase in temperature. Consequently, we propose that this species is a dimer involving an eight-membered $Li_2N_4S_2$ ring (see Fig. 3), but with each lithium atom coordinated to two THF molecues. The increase in the relative intensities of the ^7Li and ^{31}P NMR resonances of this species upon dilution is consistent with this suggestion while the disappearance of these resonances with an increase in temperature is ascribed to the dissociation of one THF molecule (per lithium atom) to give the unsymmetrical dimer. Variation in the degree of solvation of dimeric structures is a well-established feature of the solution structures of organonitrogen–lithium compounds.[13,15]

The NMR and X-ray structural evidence presented here show that the organic group of an organolithium reagent becomes attached exclusively to a sulfur atom of the $P_2N_4S_2$ ring in **1**. The possibility that the fluxional unsymmetrical species is an *N*-alkylated (arylated) isomer[1,7] can be excluded. The η^2-*N*,*N′* mode of coordination of the lithium atom to the $P_2N_4S_2$ ring in the dimer of **2c** suggests that the ligand behaviour of the $Ph_4P_2N_4S_2R^-$ will not be limited to the η^1-*S* coordination mode reported heretofore.[7] Other possibilities including η^1-N, η^2-*N*,*N′* (*cf.* lithium sulfinimidamides),[16] and η^2-*N*,*S* are under investigation.

We thank the NSERC (Canada) for financial support.

Received, 5th May 1993; Com. 3/02580B

References

1 T. Chivers, D. D. Doxsee, M. Edwards and R. W. Hilts, in *The Chemistry of Inorganic Ring Systems*, ed. R. Steudel, Elsevier, New York, 1992, ch. 15, p. 271.
2 N. Burford, T. Chivers, M. N. S. Rao and J. F. Richardson, *Inorg. Chem.*, 1984, **23**, 1946.
3 T. Chivers, G. Y. Dénès, S. W. Liblong and J. F. Richardson, *Inorg. Chem.*, 1989, **28**, 3683.
4 (*a*) T. Chivers, K. S. Dhathathreyan and T. Ziegler, *J. Chem. Soc., Chem. Commun.*, 1989, 86; (*b*) T. Chivers, M. Edwards, A. Meetsma, J. C. van de Grampel and J. van der Lee, *Inorg. Chem.*, 1992, **31**, 2156.
5 T. Chivers and R. W. Hilts, *Inorg. Chem.*, 1992, **31**, 5272.
6 T. Chivers, M. Edwards, P. N. Kapoor, A. Meetsma, J. C. van de Grampel and A. van der Lee, *Inorg. Chem.*, 1990, **29**, 3068.
7 T. Chivers, M. Edwards, R. W. Hilts, A. Meetsma and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1992, 3053.
8 R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *Polyhedron*, 1987, **6**, 1541.
9 N. Burford, T. Chivers and J. F. Richardson, *Inorg. Chem.*, 1983, **22**, 1482.
10 T. Chivers, S. S. Kumaravel, A. Meetsma, J. C. van de Grampel and A. van der Lee, *Inorg. Chem.*, 1990, **29**, 4591.
11 F. Pauer and D. Stalke, *J. Organomet. Chem.*, 1991, **418**, 127.
12 F. T. Edelmann, F. Knösel, F. Pauer, D. Stalke and W. Bauer, *J. Organomet. Chem.*, 1992, **438**, 1.
13 K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.
14 J. Sandstrom, *Dynamic NMR Spectroscopy*, Academic, New York, 1982.
15 L. M. Jackman and L. M. Scarmoutzos, *J. Am. Chem. Soc.*, 1987, **109**, 5348.
16 K. Vrieze and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 145.