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Formation, X-ray Structure, and Deprotonation of an *S,S'*-Methylene-Bridged $P_2N_4S_2$ Ring

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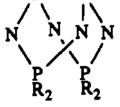
There is an extensive chemistry of binary sulfur–nitrogen (S–N) anions,[1] several of which are known only in coordination complexes with metals.[2,3] Although there is polarographic evidence for the formation of $S_4N_4^{2-}$ at low temperatures,[4] this dianion has only been characterized in Ir[5a] and Pt[5b] complexes as a tridentate (N,S,S′) ligand formed by insertion of the metal into an S–N bond of S_4N_4. Anions of diphosphadithiatetrazocines **1** are unknown, but Pt^0 or Pd^0 compounds readily undergo oxidative addition with these inorganic heterocycles to give η^2-*S,S′*-metal complexes.[6]



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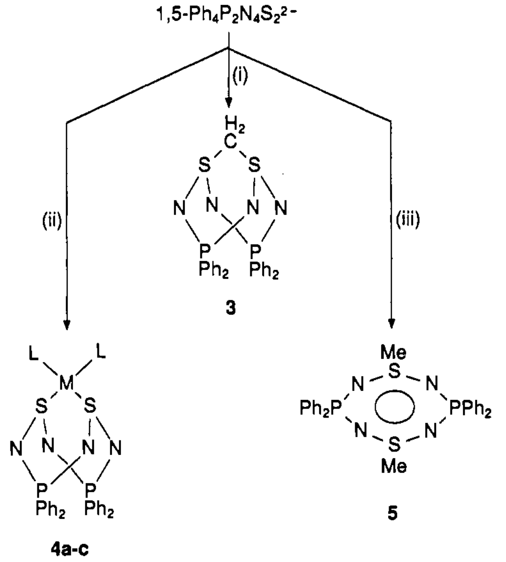
We report here the preparation of the thermally stable dianion of **1** (R = Ph), which reacts with diiodomethane to give the novel bicyclic compound **3** in which a methylene group bridges the sulfur atoms of a $P_2N_4S_2$ ring (see Scheme I). The methylene bridge in **3** is readily deprotonated to give the carbanion $Ph_4P_2N_4S_2CHLi$. The dianion of **1** (R = Ph) may also be used to prepare η^2-S,S′ complexes of Ni and Pt (**4a–c**) and the *S,S′*-dimethyl derivative **5**.

The reduction of **1** (R = Ph) with 2 molar equiv of Super-Hydride gives very good yields of the corresponding dianion as its dilithium salt. A solution of Li[BEt_3H] in THF (1.22 mmol) was added dropwise to a colorless solution of 1,5-$Ph_4P_2N_4S_2$ (0.61 mmol) in THF (15 mL) at −78 °C. The solution became yellow with the evolution of H_2 gas and, upon warming to room temperature, the deposition of a yellow precipitate of $Li_2[Ph_4P_2N_4S_2]$ (**2**) (0.46 mmol). This product is very slightly soluble in THF and insoluble in diethyl ether or toluene and decomposes in acetonitrile or dichloromethane. It is extremely moisture-sensitive but can be stored under a nitrogen atmosphere for several days at 23 °C without decomposition. It was shown to contain **2**[7] by the preparation of several derivatives (Scheme I).

Scheme I. Reactions of 1,5-$Ph_4P_2N_4S_2^{2-}$ [a]



[a] Key: (i) CH_2I_2; (ii) $PtCl_2(PPh_3)_2$, $PtCl_2(PEt_3)_2$, or $NiCl_2$(diphos); (iii) $2CH_3I$; (**4a**) M = [$Pt(PPh_3)_2$]; (**4b**) M = [$Pt(PEt_3)_2$]; (**4c**) M = Ni(diphos).

The new bicyclic derivative **3** was obtained by the treatment of $Li_2[Ph_4P_2N_4S_2]$ with diiodomethane. An excess of CH_2I_2 (1.20 mmol) in THF was added to a slurry of $Li_2[Ph_4P_2N_4S_2]$ (0.61 mmol) in THF at −78 °C. Reaction occurred at room temperature and, after 62 h, workup produced air-stable white crystals of $Ph_4P_2N_4S_2CH_2$ (**3**) in 23% yield after recrystallization from CH_2Cl_2–hexanes (1:2).[9] The NMR data for **3** are consistent with a structure in which a methylene group bridges the two sulfur atoms of a $P_2N_4S_2$ ring symmetrically and this conclusion was confirmed by an X-ray structural determination.[10]

The molecular geometry and atomic numbering scheme for **3** are shown in Figure 1. The introduction of the CH_2 bridge expands

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[5] (a) Edelmann, F.; Roesky, H. W.; Spang, C.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 931. (b) Hursthouse, M. B.; Motevalli, M.; Kelly, P. F.; Woollins, J. D. *Polyhedron* **1989**, *8*, 997.

[6] (a) Chivers, T.; Dhathathreyan, K. S.; Ziegler, T. *J. Chem. Soc., Chem. Commun.* **1989**, 86. (b) Chivers, T.; Edwards, M.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1992**, *31*, 2156.

[7] Satisfactory C, H, and S analyses were obtained for **2**, but N values were consistently low. Elemental analysis also revealed the absence of boron in **2**. The ^{31}P NMR spectrum of a slurry of **2** in THF shows a broad signal at ca. 0 ppm, but we cannot rule out the possibility that this is due to a small amount of decomposition product. Although the dilithium compound **2** is represented as a monomer, it is recognized that, by analogy with structurally characterized lithium derivatives of sulfur diimides,[8] the structure of **2** may involve the association of monomer units, which would account for its insolubility.

[8] (a) Pauer, F.; Rocha, J.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1477. (b) Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127.

[9] The $^{31}P\{^1H\}$ NMR spectrum of the crude product indicated the formation of two minor products, and several crystallizations were necessary to obtain an analytically pure sample of **3**. Anal. Calcd for $C_{25}H_{22}N_4P_2S_2$ (**3**): C, 59.51; H, 4.39; N, 11.10. Found: C, 59.12; H, 4.27; N, 11.30. $^{31}P\{^1H\}$ NMR (in CH_2Cl_2): δ −19.4 ppm. ^1H NMR (in $CDCl_3$): δ 6.9–7.9 ppm (m, C_6H_5, 20 H), 2.96 ppm (t, CH_2, 2 H), $^4J(^1H–^{31}P)$ = 0.7 Hz. $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 127.5–132.0 ppm (C_6H_5), 33.1 ppm (t, CH_2), $^3J(^{13}C–^{31}P)$ = 43.1 Hz. MS (EI, 70 eV): *m/z* 504 (M^+, 100%).

[10] Crystal data for $C_{25}H_{22}N_4P_2S_2$ (**3**): $M = 504.6$; triclinic space group $P\bar{1}$, $a = 10.340\ (1)$, $b = 12.964\ (2)$, $c = 10.175\ (2)$ Å, $\alpha = 109.96\ (1)°$, $\gamma = 73.89\ (1)°$, $V = 1195.0\ (6)$ Å^3, $Z = 2$, $D_c = 1.40$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\ 69$ Å), μ(Mo Kα) = 1.72 cm^{-1}, $T = 293$ K, $R = 0.050$ ($R_w = 0.060$) for 2448 unique observations with $I/\sigma(I) \geq 3.0$. Data were collected at 293 K on an Enraf-Nonius CAD4F diffractometer in the $\theta/2\theta$ mode. All non-hydrogen atoms except phenyl carbons were refined anisotropically. Hydrogen atom thermal parameters were fixed at 20% higher than those of the attached carbon atoms. Hydrogen positions were idealized on the basis of the geometries of the attached atoms. Final refinement was on *F*, by least-squares methods, refining 178 parameters and utilizing the weighting scheme of the form $w = 4F^2/\sigma^2(F^2)$.

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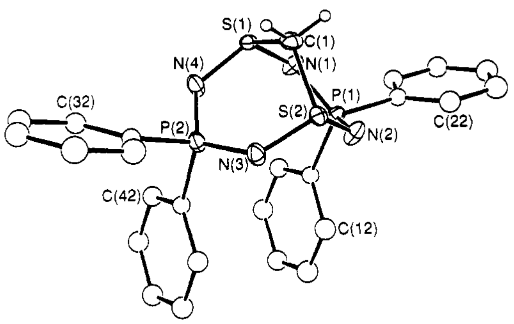

Figure 1. ORTEP plot for $Ph_4P_2N_4S_2CH_2$ (**3**). Selected bond lengths (Å) and bond angles (deg): S(1)–N(1) 1.592 (3), S(1)–N(4) 1.595 (3), S(2)–N(2) 1.594 (3), S(2)–N(3) 1.597 (3), S(1)–C(1) 1.827 (4), S(2)–C(1) 1.812 (4), P(1)–N(1) 1.620 (3), P(1)–N(2) 1.609 (3), P(2)–N(3) 1.610 (3), P(2)–N(4) 1.607 (3), N(1)–S(1)–N(4) 115.6 (2), N(1)–S(1)–C(1) 102.5 (2), N(4)–S(1)–C(1) 102.4 (2), N(2)–S(2)–N(3) 115.0 (2), N(2)–S(2)–C(1) 103.4 (2), N(3)–S(2)–C(1) 103.3 (2), N(1)–P(1)–N(2) 118.2 (2), N(3)–P(2)–N(4) 119.1 (2), S(1)–N(1)–P(1) 123.4 (2), S(2)–N(2)–P(1) 124.6 (2), S(2)–N(3)–P(2) 123.8 (2), S(1)–N(4)–P(2) 126.0 (2), S(1)–C(1)–S(2) 113.0 (2).

the S–S separation from 2.528 (1) Å in (**1**) (R = Ph)[11] to 3.033 (1) Å in (**3**), accompanied by a wide S(1)–C(1)–S(2) angle of 113.0 (2)° at the methylene carbon. In addition, the methylene bridge enforces larger endocyclic bond angles at phosphorus and nitrogen, resulting in mean N–P–N and S–N–P angles of 118.6 (2) and 124.5 (2)°, respectively [cf. 110.8 (1) and 120.9 (2)°, respectively for **1** (R = Ph)]. The mean S–N and P–N bond lengths in **3** are not significantly different from those found for **1**.[11]

The new reagent **2** may also be used to prepare η^2-S,S′ complexes of **1** with platinum or nickel (see Scheme I). The latter cannot be prepared by the oxidative addition of **1** with nickel(0) complexes.[12] The known compound $Pt(PPh_3)_2(Ph_4P_2N_4S_2)$ (**4a**) and the new derivative $Pt(PEt_3)_2(Ph_4P_2N_4S_2)$ (**4b**) were produced by the reactions of a slurry of **2** with *cis*-$PtCl_2(PR_3)_2$ (R = Ph or Et, respectively) at −78 °C.[13] The nickel complex $Ni(diphos)(Ph_4P_2N_4S_2)$ (**4c**) was obtained in a similar manner from $NiCl_2(diphos)$. The ^{31}P NMR spectrum of **4c** in CH_2Cl_2 consists of two 1:2:1 triplets at δ 45.5 and 44.1 ppm with $^4J(P–P)$ = 9.3 Hz.

The *S*,*S*′-dimethyl derivative, **5**, was isolated as air-stable white crystals in ca. 30% yield after the treatment of a slurry of **2** in THF at 23 °C with 2 molar equiv of iodomethane.[14] This synthesis of **5** represents a considerable improvement over the existing procedure, which involves the use of the explosive reagent $Me_2S(NBr)_2$ in a three-step process.[15] *S*,*S*′-Dialkyl derivatives of **2**, as exemplified by **5**, are potential precursors (via thermolysis) for polymers based on alternating PN/SN backbones with three-coordinate sulfur,[16] but they cannot be prepared by the cyclocondensation reaction of $Ph_2PN_2(SiMe_3)_3$ with either $RSCl_3$[17] or 3 molar equiv of RSCl (R = alkyl).[19]

Although the natures of the S–S bonds in **1** and $(\mu\text{-}S_2)Fe_2(CO)_6$ are quite different,[20] the formation and subsequent reactions of the dianion of **1** described above resemble the behavior of the dianion of $(\mu\text{-}S_2)Fe_2(CO)_6$.[23] Further investigations of the incorporation of bridging units into the $P_2N_4S_2$ ring by treatment of the dianion of **1** with metal or non-metal halides are in progress.

Finally, we note that the bridging CH_2 group in **3** is readily deprotonated by ^nBuLi in THF at −78 °C.[24] The carbanion $Ph_4P_2N_4S_2CHLi$ so formed reacts with iodomethane to give $Ph_4P_2N_4S_2CH(CH_3)$, which exhibits signals at δ −18.4 and −20.4 ppm in the ^{31}P NMR spectrum for the inequivalent Ph_2P groups (cf. δ −19.4 ppm for **3**). By analogy with related organosulfur carbanions, e.g. those derived from 1,3-dithianes,[24] the chemistry of this new carbanion is likely to be extensive.

Acknowledgment. Financial support from the NSERC (Canada) is gratefully acknowledged.

Supplementary Material Available: Tables listing atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances, bond angles, anisotropic thermal parameters, parameters for hydrogen atoms, and least-squares planes (8 pages). Ordering information is given on any current masthead page.

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(12) Chivers, T.; Edwards, M. Unpublished results.

(13) $^{31}P\{^1H\}$ NMR data for **4a** (in CH_2Cl_2): δ 18.3 (t, Ph_3P, $^4J(P–P)$ = 4.6 Hz, $^1J(P–Pt)$ = 2861 Hz), 39.3 ppm (t, Ph_2P, $^4J(P–P)$ = 4.2 Hz, $^3J(P–Pt)$ = 562 Hz), in good agreement with the literature values.[6] $^{31}P\{^1H\}$ NMR data for **4b** (in CH_2Cl_2): δ 4.5 (t, Et_3P, $^4J(P–P)$ = 3.6 Hz, $^1J(P–Pt)$ = 2733 Hz), 35.9 ppm (t, Ph_2P, $^4J(P–P)$ = 3.6 Hz, $^3J(P–Pt)$ = 536 Hz).

(14) The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated that **5** is the only phosphorus-containing product, but several recrystallizations were necessary to obtain a pure sample (free from lithium iodide). $^{31}P\{^1H\}$ NMR data for **5** (in CH_2Cl_2): δ 27.0 ppm. ^1H NMR (in $CDCl_3$): δ 7.3–8.0 ppm (m, C_6H_5, 20 H), 2.84 ppm (t, CH_3, 6 H), $^4J(H–P)$ = 1.2 Hz [cf. lit. δ 2.86, $^4J(H–P)$ = 1.4 Hz].[16] $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 45.7 ppm (t, CH_3), $^3J(C–P)$ = 21.0 Hz. MS (EI, 70 eV): *m/z* 520 (M^+, 7%), 505 ($M^+ - CH_3$, 100%), 490 ($M^+ - 2CH_3$, 39%).

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(20) The S–S bond in $(\mu\text{-}S_2)Fe_2(CO)_6$ has been compared to that in organic disulfides[21] whereas the S–S interaction in dithiatetrazocines may be viewed as an intramolecular $\pi^*–\pi^*$ interaction.[22]

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(23) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(24) The facile formation of carbanions, via deprotonation, is a well-established feature of organosulfur chemistry. Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; Chapter 2, p 36.