

Synthesis and Reactions of Alkali Metal Derivatives of the $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ Dianion: X-ray Structure of $\text{Cp}^*\text{Rh}(\eta^3\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{-N,S,S'})$

Tristram Chivers,* Mark Edwards, Xiaoliang Gao, Robert W. Hiltz, Masood Parvez, and Rainer Vollmerhaus

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

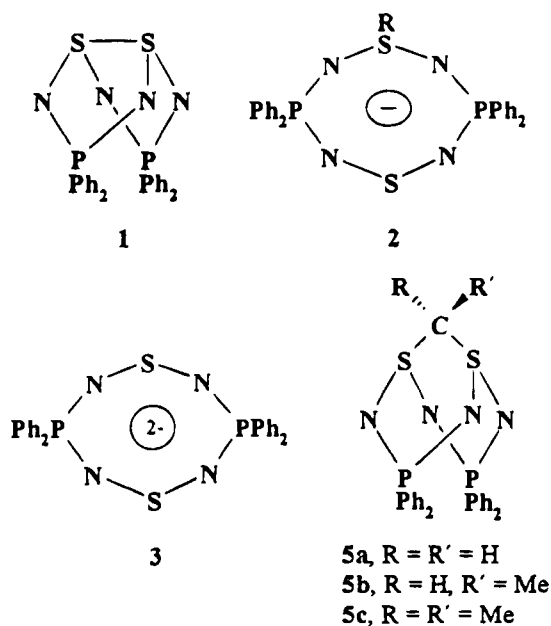
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The reaction of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ with 2 molar equiv of $\text{M}[\text{BEt}_3\text{H}]$ in THF produces $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ (**4a**, $\text{M} = \text{Li}$; **4b**, $\text{M} = \text{Na}$; **4c**, $\text{M} = \text{K}$) in quantitative yields with the concomitant evolution of H_2 gas. The lithium and sodium derivatives are obtained as insoluble, yellow powders, whereas $\{\text{K}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ ($\delta(^{31}\text{P}) = 33.5$ ppm) is soluble in THF when formed initially. The reaction of $\{\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ with CH_2I_2 in THF yields $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{-CH}_2$ (**5a**) in excellent yields. The methylene-bridged compound **5a** is readily deprotonated by $\text{LiN}(\text{SiMe}_3)_2$ in THF, and the subsequent addition of MeI produces $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CHMe}$ (**5b**). In a similar way, **5b** can be deprotonated and methylated to give $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CMe}_2$. The reaction of $\{\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ with $(\text{Cp}^*\text{RhCl}_2)_2$ in THF affords $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$ (**6**), which can also be produced by the oxidative addition of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ to $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2$. The X-ray structure of **6** reveals that the heterocyclic $\text{P}_2\text{N}_4\text{S}_2$ ligand is bonded to Rh in a tridentate ($\eta^3\text{-N,S,S'}$) fashion with $d(\text{Rh-N}) = 2.135(5)$ Å. Crystals of **6** are triclinic, space group $P\bar{1}$ with $a = 10.167(1)$ Å, $b = 17.972(2)$ Å, $c = 9.377(1)$ Å, $\alpha = 100.24(1)^\circ$, $\beta = 93.19(1)^\circ$, $\gamma = 95.35(1)^\circ$, $V = 1674.2(3)$ Å³, and $Z = 2$. The final R and R_w values were 0.045 and 0.058, respectively. The treatment of $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ with a variety of other electrophiles, e.g. $\text{ICH}_2\text{CH}_2\text{I}$, PhCHBr_2 , CHI_3 , CBR_4 , Me_2SiCl_2 , Me_2SnCl_2 , PhPCl_2 , S_2Cl_2 , GeCl_4 , or FeBr_2 , regenerates the folded ring system 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$.

Introduction

Bulky anionic ligands that are adaptable to the variable electronic requirements of transition metals, lanthanides, or actinides have been the subject of numerous investigations.¹ The recently discovered cyclic phosphorus–nitrogen–sulfur (PNS) anions $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R}^-$ (**2**)² and $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ (**3**)³ are of interest in this respect, particularly with regard to the juxtaposition of hard and soft donor sites. These anions are readily generated from the folded ring 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (**1**) by treatment with organolithium reagents or superhydride, respectively. Previous investigations have demonstrated that these novel anionic ligands can readily adjust their bonding modes to satisfy the electronic demands of both early and late transition metals.⁴ For example, the monoanion **2** coordinates in an $\eta^1\text{-S}$ fashion to $\text{Pt}(\text{II})$ or $\text{Pd}(\text{II})$ ^{2a} whereas it may adopt an $\eta^2\text{-N,S}^5$ or an $\eta^4\text{-N,N',S,S'}$ ⁶ bonding mode with group 4 metals.

The first transition metal complexes of the dianion **3** were prepared by the oxidative addition of the neutral ligand 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ to $\text{Pt}(0)$ or $\text{Pd}(0)$ complexes.⁷ More recently we described the synthesis of the highly insoluble dilithium derivative $\{\text{Li}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ and its use in the preparation



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of $\text{Pt}(\text{II})$ and $\text{Pd}(\text{II})$ complexes and the methylene-bridged compound **5a**.³ We have now prepared the sodium and potassium derivatives $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ ($\text{M} = \text{Na}, \text{K}$) in order to compare their properties with those of the lithium derivative. We have also investigated the potential applications of these alkali metal derivatives in the synthesis of organic or nonmetallic derivatives of the $\text{P}_2\text{N}_4\text{S}_2$ ring and metal complexes of the adaptable multidentate ligand **3**. In this paper we report the results of these studies, including the preparation and X-ray structure of $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$, in which the dianion **3** exhibits the novel $\eta^3\text{-N,S,S'}$ bonding mode.

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Experimental Section

Reagents and General Procedures. All solvents were dried, distilled, and purged with nitrogen or argon gas before use. All reactions and the manipulation of air-sensitive products were carried out under an atmosphere of nitrogen by using Schlenk techniques. The compounds 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$,⁸ (Cp^*RhCl_2)₂,⁹ and $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2$ ¹⁰ were prepared by literature methods. Solutions of $\text{M}[\text{BEt}_3\text{H}]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) in THF, iodomethane, and $m\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ were obtained commercially (Aldrich) and used as received. Commercial $\text{LiN}(\text{SiMe}_3)_2$ (Aldrich) was recrystallized from diethyl ether before use. All other reagents were commercial samples used as received.

Instrumentation. ¹H and ¹³C NMR spectra were recorded by using either a Bruker AM-400 or a Bruker AM-200 spectrometer locked to the solvent deuterium resonance. ¹¹B and ³¹P NMR spectra were obtained on the Bruker AM-400 instrument with a D₂O insert. ¹¹B and ³¹P NMR chemical shifts are quoted relative to external $\text{BF}_3\cdot\text{OEt}_2$ in CDCl_3 and 85% H_3PO_4 , respectively. Electron impact mass spectra were recorded by using a Kratos MS80RFA instrument set at 70 eV.

Elemental analyses were performed by the microanalytical service within the Chemistry Department at The University of Calgary and by the Canadian Microanalytical Service Ltd., Vancouver, BC.

Preparation of $\{\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]_2\text{THF}\}_n$ (4b). A solution of $\text{Na}[\text{BEt}_3\text{H}]$ in THF (4.9 mL, 4.9 mmol) was added dropwise to a stirred solution of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (1.10 g, 2.24 mmol) in THF (50 mL) at 23 °C. A yellow precipitate formed instantly, and the evolution of a gas (presumably H_2) was observed. The supernatant was removed by decantation through a cannula, and the remaining yellow solid was washed with THF (2 × 30 mL) and dried under vacuum to give $\{\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]_2\text{THF}\}_n$ in essentially quantitative yield. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_4\text{Na}_2\text{O}_2\text{P}_2\text{S}_2$: C, 56.46; H, 5.33; N, 8.23. Found: C, 55.33; H, 5.02; N, 8.59.

Preparation of $\{\text{K}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ (4c). A solution of $\text{K}[\text{BEt}_3\text{H}]$ (1.0 M in THF) (500 μL , 0.50 mmol) was added by syringe to a solution of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (0.100 g, 0.204 mmol) in THF (5 mL) in a 10 mm o.d. tube under a N_2 atmosphere (glovebox). The solution became yellow immediately, with the evolution of H_2 gas. The ³¹P{¹H} NMR spectrum of this solution exhibited a sharp singlet at 33.5 ppm. After 15 min, a yellow precipitate of $\{\text{K}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]_2\text{THF}\}_n$ was formed and isolated in essentially quantitative yield by filtration. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_4\text{K}_2\text{O}_2\text{P}_2\text{S}_2$: C, 54.04; H, 5.29; N, 8.40. Found (triplicate determinations): C, 53.45, 53.26, 53.06; H, 5.11, 5.04, 5.01; N, 7.70, 7.77, 7.72. A boron analysis indicated <0.3% B.

Preparation of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CH}_2$ (5a). To a stirred solution of $\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]$ (1.20 g, 2.24 mmol) in THF (50 mL) at -78 °C was added CH_2I_2 (0.19 mL, 2.36 mmol) in THF (1 mL). The cold bath was removed, and the reaction mixture was warmed to 23 °C and stirred for 30 min. The solid dissolved, and a clear, pale yellow solution was formed. Solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 (30 mL). The resultant solution was filtered to remove NaI , and the filtrate was pumped to dryness. The residue was crystallized from THF at -20 °C to give $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CH}_2$ (0.803 g, 1.59 mmol, 71%). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_4\text{P}_2\text{S}_2$: C, 59.53; H, 4.39; N, 11.11. Found: C, 59.71; H, 4.40; N, 11.30. ¹H NMR (CDCl_3 , δ): 7.0–7.9 (m, 20H), 2.95 (t, ⁴ $J_{\text{PH}} = 0.7$ Hz, 2H). ³¹P{¹H} NMR (THF, D₂O insert, δ): -19.65 (s).

Preparation of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CHMe}$ (5b). To a stirred THF (30 mL) solution of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CH}_2$ (0.80 g, 1.59 mmol) at -78 °C was added dropwise a THF solution (10 mL) of $\text{LiN}(\text{SiMe}_3)_2\cdot\text{Et}_2\text{O}$ (0.403 g, 1.67 mmol). After the addition, the mixture was allowed to warm slowly to 23 °C in 1 h. The white slurry so formed was stirred at 23 °C for 30 min. The solid was allowed to settle, and the supernatant was removed by decantation through a cannula. THF (30 mL) was added to the solid, and the resultant slurry was cooled to -78 °C. A slight excess of iodomethane (0.11 mL, 253 mg, 1.78 mmol) in THF (1 mL) was added from a syringe. The mixture was warmed to 23 °C slowly and stirred. The solid gradually dissolved, and a clear colorless solution formed. This solution was stirred at 23 °C for an additional 1 h and

Table 1. Crystallographic Data for $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$ (6)

formula	$\text{C}_{34}\text{H}_{35}\text{N}_4\text{P}_2\text{S}_2\text{Rh}$	Z	2
fw	728.65	$V, \text{\AA}^3$	1674.2(3)
crystal system	triclinic	$\rho_{\text{calc}}, \text{g cm}^{-3}$	1.445
space group	$P\bar{1}$ (No. 2)	$F(000)$	748
$a, \text{\AA}$	10.167(1)	μ, mm^{-1}	0.759
$b, \text{\AA}$	17.972(2)	radiation ($\lambda, \text{\AA}$)	Mo $K\alpha$ (0.710 69)
$c, \text{\AA}$	9.377(1)	$T, ^\circ\text{C}$	23.0
α, deg	100.24(1)	R^a	0.045
β, deg	93.19(1)	R_w^b	0.058
γ, deg	95.35(1)		

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

was then pumped to dryness. The residue was dissolved in CH_2Cl_2 (30 mL). The solution was filtered, and solvent was removed from the filtrate under vacuum. The residue was crystallized from THF at -20 °C to give colorless crystals of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CHMe}$ (0.69 g, 1.33 mmol, 84%). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{P}_2\text{S}_2$: C, 60.22; H, 4.66; N, 10.80. Found: C, 60.11; H, 4.76; N, 10.44. ¹H NMR (CDCl_3 , δ): 7.0–7.9 (m, 20H), 2.62 (tq, ⁴ $J_{\text{PH}} = 1.46$ Hz, ³ $J_{\text{HH}} = 6.75$ Hz, 1H), 1.72 (d, ³ $J_{\text{HH}} = 6.75$ Hz, 3H). ³¹P{¹H} NMR (THF, D₂O insert, δ): -18.5 (s), -20.5 (s).

Preparation of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CMe}_2$ (5c). $\text{LiN}(\text{SiMe}_3)_2\cdot\text{Et}_2\text{O}$ (0.048 g, 0.199 mmol) in THF (1 mL) was added dropwise to a stirred solution of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CHMe}$ (0.100 g, 0.193 mmol) in THF (15 mL) at -78 °C. The solution was warmed to 23 °C in 30 min, and a light yellow solution formed. The solution was stirred at 23 °C for 30 min and was then cooled to -78 °C. An excess of MeI (0.40 mmol) in THF (5 mL) was added slowly. The mixture was warmed to 23 °C in 1 h, and a colorless solution formed. After 1 h at 23 °C, the solution was pumped to dryness. The residue was dissolved in CH_2Cl_2 (10 mL), and the solution was filtered. Solvent was removed from the filtrate, and the residue was recrystallized from CH_2Cl_2 /hexanes to give colorless crystals of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{CMe}_2$ (65 mg, 0.122 mmol, 63%). Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{N}_4\text{P}_2\text{S}_2$: C, 60.88; H, 4.92; N, 10.52. Found: C, 60.56; H, 4.75; N, 10.38. ¹H NMR (C_6H_6 , δ): 6.9–7.9 (m, 20H), 1.62 (s, 6H). ³¹P{¹H} NMR (THF, D₂O insert, δ): -19.8 (s).

Preparation of $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$ (6). A slurry of $\{\text{Na}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ (2.43 g, 0.453 mmol) in THF (30 mL) at -30 °C was transferred by cannula to a slurry of (Cp^*RhCl_2)₂ (0.140 g, 0.226 mmol) in THF (30 mL) at -78 °C. The mixture was allowed to reach 23 °C while being vigorously stirred to give an orange-red solution. The solution was stirred for 1 h and filtered through Celite, and solvent was removed from the filtrate under vacuum. The residue was redissolved in CH_2Cl_2 (1 mL), and diethyl ether (10 mL) was added to this solution. A few colorless crystals of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ were formed and isolated by decantation. Solvent was removed from the mother liquor under vacuum, and the residue was dissolved in acetone (1 mL). The solution was then layered with diethyl ether, and after 12 h, dark orange crystals of $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$ (2.41 g, 0.331 mmol, 73% yield) were isolated. The product also crystallizes from a THF–hexane mixture. Anal. Calcd for $\text{C}_{34}\text{H}_{35}\text{N}_4\text{P}_2\text{S}_2\text{Rh}$: C, 56.04; H, 4.84; N, 7.68. Found: C, 55.83; H, 4.67; N, 7.42. ³¹P{¹H} NMR (toluene, δ): 44.7 (d, ⁴ $J_{\text{PP}} = 15.3$ Hz), 43.9 (dd, ⁴ $J_{\text{PP}} = 15.3$ Hz, ³ $J_{\text{RHP}} = 15.3$ Hz). ¹H NMR (CDCl_3 , δ): 7.0–7.6 (m, 20H, C_6H_5), 1.58 (s, 15H, CH_3).

X-ray Structure Determination. Crystallographic data for $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$ (6) are summarized in Table 1. All measurements were made on a Rigaku AFC6S diffractometer with Mo- $K\alpha$ radiation (graphite monochromator).

A dark orange block of 6 obtained by recrystallization from acetone–diethyl ether was mounted on a glass fiber and coated with epoxy. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares fit of the setting angles of 25 reflections in the range $20.0 < 2\theta < 35.0^\circ$. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of $4.0^\circ/\text{min}$, scan width $(1.68 + 0.34 \tan \theta)^\circ$ to a maximum 2θ value of 50.1° . The intensities of 6281 reflections were measured, of which 4752 had $I > 3\sigma(I)$. The structure was solved by the heavy-atom method.^{11,12} The non-hydrogen atoms

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Table 2. Atomic Coordinates and B_{eq} Values for $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
Rh(1)	0.21970(5)	-0.15587(3)	-0.10504(6)	2.71(1)
S(1)	-0.0040(1)	-0.1676(1)	-0.1499(2)	2.65(4)
S(2)	0.2054(1)	-0.2657(1)	-0.0061(2)	2.73(4)
P(1)	-0.0553(2)	-0.2578(1)	0.0719(2)	2.67(4)
P(2)	0.1060(2)	-0.3071(1)	-0.2896(2)	2.58(4)
N(1)	-0.0978(5)	-0.2144(3)	-0.0592(5)	3.2(1)
N(2)	0.0978(5)	-0.2609(3)	0.1176(5)	2.8(1)
N(3)	0.1408(5)	-0.3345(3)	-0.1414(5)	3.1(1)
N(4)	0.0839(5)	-0.2163(3)	-0.2780(5)	2.5(1)
C(1)	0.3786(8)	-0.0949(5)	0.0458(9)	5.2(2)
C(2)	0.2951(7)	-0.0410(4)	0.0118(9)	4.8(2)
C(3)	0.2957(7)	-0.0402(4)	-0.1367(10)	4.8(2)
C(4)	0.3877(8)	-0.0949(5)	-0.1934(9)	5.3(2)
C(5)	0.4374(7)	-0.1256(4)	-0.0784(11)	5.0(2)
C(6)	0.4096(13)	-0.1122(8)	0.1959(13)	12.7(4)
C(7)	0.2162(11)	0.0072(6)	0.1141(15)	12.4(4)
C(8)	0.2215(11)	0.0078(6)	-0.2183(16)	12.4(4)
C(9)	0.4175(14)	-0.1112(7)	-0.3477(12)	13.3(5)
C(10)	0.5384(9)	-0.1834(7)	-0.0821(20)	14.6(5)
C(11)	-0.1181(6)	-0.2094(3)	0.2380(6)	2.7(1)
C(12)	-0.2502(7)	-0.2206(4)	0.2669(7)	3.5(2)
C(13)	-0.2938(7)	-0.1827(4)	0.3936(8)	4.3(2)
C(14)	-0.2098(9)	-0.1348(5)	0.4915(8)	5.3(2)
C(15)	-0.0793(9)	-0.1221(5)	0.4658(8)	5.2(2)
C(16)	-0.0319(7)	-0.1592(4)	0.3391(7)	4.0(2)
C(17)	-0.1500(6)	-0.3507(3)	0.0274(7)	2.9(1)
C(18)	-0.2686(7)	-0.3601(4)	-0.0555(8)	4.5(2)
C(19)	-0.3410(8)	-0.4311(6)	-0.0853(10)	6.6(3)
C(20)	-0.2960(10)	-0.4904(4)	-0.0313(10)	6.1(3)
C(21)	-0.1787(9)	-0.4820(4)	0.0490(9)	5.3(2)
C(22)	-0.1049(7)	-0.4112(4)	0.0805(8)	4.2(2)
C(23)	-0.0363(6)	-0.3652(3)	-0.3816(7)	2.8(1)
C(24)	-0.1077(6)	-0.3433(4)	-0.4934(8)	3.7(2)
C(25)	-0.2133(7)	-0.3900(5)	-0.5706(9)	4.8(2)
C(26)	-0.2488(7)	-0.4584(4)	-0.5336(9)	4.5(2)
C(27)	-0.1825(8)	-0.4804(4)	-0.4211(9)	4.8(2)
C(28)	-0.0748(7)	-0.4365(4)	-0.3474(8)	3.9(2)
C(29)	0.2380(6)	-0.3164(3)	-0.4108(6)	2.5(1)
C(30)	0.3551(7)	-0.3406(4)	-0.3621(7)	3.6(2)
C(31)	0.4570(7)	-0.3513(5)	-0.4524(9)	4.8(2)
C(32)	0.4415(7)	-0.3372(5)	-0.5921(9)	4.9(2)
C(33)	0.3264(7)	-0.3138(4)	-0.6423(7)	4.1(2)
C(34)	0.2269(6)	-0.3025(4)	-0.5512(7)	3.2(2)

were refined anisotropically. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.045$ and $R_w = 0.058$.

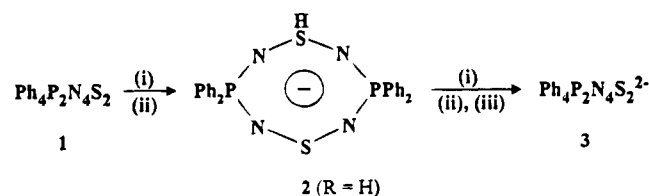
The data were corrected for Lorentz, polarization, and absorption effects, and a correction for secondary extinction was applied. In the refinement cycles, weights were derived from counting statistics. Scattering factors were those of Cromer and Waber,¹³ and allowance was made for anomalous dispersion.^{14,15} All calculations were performed using the teXsan crystallographic software package.¹⁶ The positional parameters for **6** are given in Table 2.

Results and Discussion

Synthesis of $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ (4a, M = Li; 4b, M = Na; 4c, M = K). The addition of 2 molar equiv of a THF solution

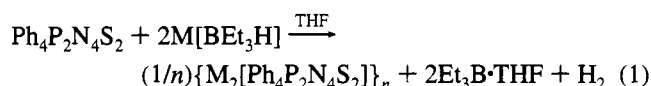
- (11) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATY*. Technical Report; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.
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Scheme 1^a



^a Key: (i) Et_3BH^- ; (ii) $-\text{Et}_3\text{B}$; (iii) $-\text{H}_2$.

of an alkali metal superhydride $\text{M}[\text{BEt}_3\text{H}]$ ($\text{M} = \text{Li}, \text{Na}$) to a solution of $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ in THF at -78°C produces a yellow solution. Evolution of H_2 gas and the formation of a yellow precipitate of $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ occur when this solution is allowed to warm slowly to 23°C . If the reaction is carried out at 23°C , this precipitate is formed immediately. A ^{11}B NMR spectrum of the supernatant ($\text{M} = \text{Li}$) at *ca.* 20°C showed a singlet at δ 71.4 ppm attributable to $\text{Et}_3\text{B}\cdot\text{THF}$ (eq 1).¹⁷



By contrast, the treatment of $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ with $\text{K}[\text{BEt}_3\text{H}]$ in THF at 23°C produces a *clear yellow solution* and H_2 gas is evolved. This solution exhibits a sharp singlet at δ 33.5 ppm in the ^{31}P NMR spectrum and a singlet at δ 4.2 ppm in the ^{11}B NMR spectrum. We tentatively attributed the latter resonance to Et_3B ligands weakly coordinated to the nitrogen atoms of the heterocyclic ring in $\text{K}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]$ and suggest that this coordination complex accounts for the solubility of the potassium derivative in THF. After *ca.* 15 min at 23°C , a yellow precipitate of $\{\text{K}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\cdot 2\text{THF}\}_n$ is deposited. These alkali metal derivatives are extremely oxygen- and moisture-sensitive and have a tendency to lose THF. The analytical data for both the sodium and potassium salts indicate the presence of two molecules of THF. No boron was detected in the potassium salt.

The products $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ formally contain the dianion $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ (**3**), a $12\text{-}\pi$ -electron system isoelectronic with S_4N_4 .¹⁸ Consequently, we have investigated the electrochemical reduction of $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ in acetonitrile (*ca.* 10^{-3} M) containing $0.1\text{ M} [\text{NEt}_4][\text{ClO}_4]$. At a platinum electrode a one-electron reduction occurs at -1.37 V (*vs* SCE). The cyclic voltammograms of this solution at various scan rates showed that the anion radicals so formed were short-lived ($t_{1/2} = 2\text{--}3\text{ s}$) and revealed no evidence for a second reduction step.¹⁹ The eight-membered ring $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ is readily susceptible to nucleophilic attack, e.g. by organolithium reagents.^{2b} Consequently, we surmise that the formation of the dianion **3** involves initial nucleophilic attack via (super)hydride followed by a very fast deprotonation by the second equivalent of (super)hydride (see Scheme 1).¹⁹ Attempts to detect the *S*-hydrido anion **2** ($\text{R} = \text{H}$) by ^1H or ^{31}P NMR monitoring of the reaction of $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ with $\text{M}[\text{BEt}_3\text{H}]$ (1:1 molar ratio) in THF at -90°C were unsuccessful.

The combination of the insolubility of $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ in organic solvents and the extremely air-sensitive nature of these alkali metal derivatives of **3** has thwarted numerous attempts

(17) Wrackmeyer, B. *J. Organomet. Chem.* **1976**, *117*, 313.

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(19) The electrochemical reduction of S_4N_4 produces the anion radical $\text{S}_4\text{N}_4^{\cdot-}$, which is unstable above -25°C . There is also evidence for the formation of the dianion $\text{S}_4\text{N}_4^{2-}$ upon polarographic reduction of S_4N_4 at low temperatures: Chivers, T.; Hojo, M. *Inorg. Chem.* **1984**, *23*, 1526.

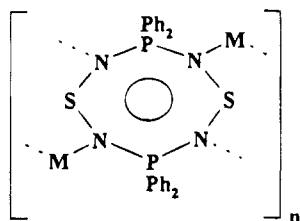


Figure 1. Possible structure of $\{[M]_2[Ph_4P_2N_4S_2]\}_n$ ($M = Li, Na, K$). Coordinated solvent molecules are not shown.

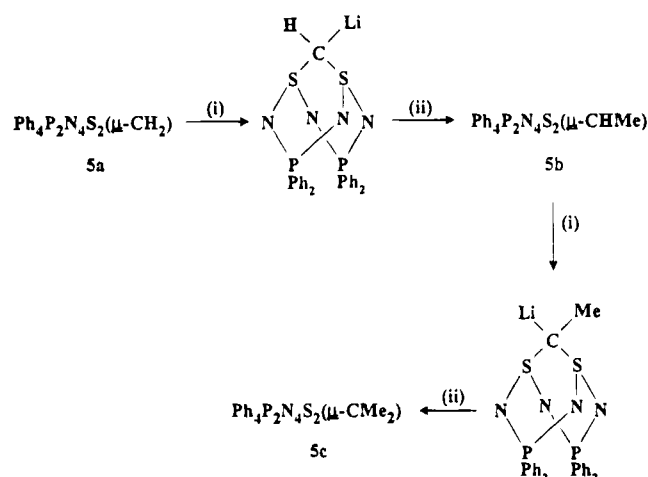
to obtain crystals suitable for an X-ray structural determination.²⁰ We note, however, that the lithium derivatives of the monoanion **2** adopt dimeric ladder-shaped structures in which each Li is coordinated to two nitrogens of one $P_2N_4S_2$ ring and one nitrogen of the other $P_2N_4S_2$ ring.^{2b} The structures of alkali metal derivatives of the diimino- λ^5 -phosphane anion $Ph_2P(NSiMe_3)_2^-$ vary according to the size of the alkali metal, but all exhibit N, N' -coordination.²¹ It seems reasonable, therefore, to propose oligomeric structures for $\{M_2[Ph_4P_2N_4S_2]\}_n$ in which the extent of association may be dependent upon M (see Figure 1). The higher initial solubility of the potassium derivative is attributed to inhibition of the oligomerization process by weakly coordinated BEt_3 molecules.

Preparation of Bridged Derivatives $Ph_4P_2N_4CRR'$. Evidence for the presence of the dianion **3** in $\{M_2[Ph_4P_2N_4S_2]\}_n$ is provided by the preparation of organic derivatives and metal complexes. In a preliminary communication, we reported that the reaction of a slurry of **4a** with diiodomethane in THF produced the methylene-bridged compound **5a** after 62 h at room temperature.³ In this work we found that the use of the sodium derivative **4b** for the reaction with dihalomethanes improved the yield of **5a** substantially, partly because of the easier separation of sodium halides compared to lithium halides, and dramatically reduced the reaction time. Thus the reaction of $\{Na_2[Ph_4P_2N_4S_2]\}_n$ with CH_2I_2 produced **5a** in 71% yield after 30 min.

The reaction of $\{M_2[Ph_4P_2N_4S_2]\}_n$ with organic halides, e.g. MeI, provides a route to S, S' -diorgano derivatives of the type $Ph_4P_2N_4(SR)(SR')$ (where $R = R'$). For example, $Ph_4P_2N_4S_2Me_2$ is obtained in ca. 30% yield from **4a** and 2 molar equiv of iodomethane.³ However, these S, S' -diorgano derivatives (including unsymmetrical examples where $R \neq R'$) are more readily obtained from the reaction of the organolithium derivatives $\{Li[Ph_4P_2N_4S_2R]\}_n$ with organic iodides.²² A careful study of this reaction has shown that the eight-membered rings $Ph_4P_2N_4(SR)(SR')$ are obtained initially in the boat conformation with characteristic ^{31}P NMR chemical shifts in the narrow range 15–17 ppm. Subsequently, the boat conformers slowly isomerize in solution (during workup) to give the corresponding chair isomers ($\delta(^{31}P) = 27$ –28 ppm). In this work the formation of the new potassium derivative **4c** ($\delta(^{31}P) = 33.5$ ppm) was quickly established by the instantaneous reaction with iodomethane in THF to give $Ph_4P_2N_4S_2Me_2$ in the boat conformation ($\delta(^{31}P) = 14.9$ ppm).

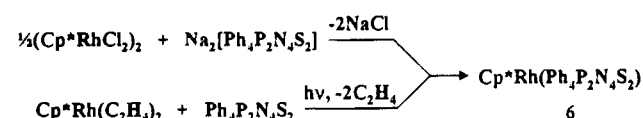
Deprotonation of $Ph_4P_2N_4S_2CH_2$ (5a**).** The ability of sulfur in various oxidation states to enhance the acidity of adjacent C–H bonds is well established.²³ For example, 1,3-dithiane

Scheme 2^a



^a Key: (i) $LiN(SiMe_3)_2 \cdot OEt_2$; (ii) MeI.

Scheme 3



$CH_2CH_2CH_2SCH_2S$ is readily deprotonated by $n-BuLi$.²⁴ We previously reported that **5a** is deprotonated by $n-BuLi$ in THF at -78 °C to give $Ph_4P_2N_4S_2CHLi$, which reacts with iodomethane to give **5b** characterized by singlets at $\delta -18.4$ and 20.4 ppm in the ^{31}P NMR spectrum for the inequivalent PPh_2 groups. We now find that the use of $LiN(SiMe_3)_2 \cdot Et_2O$ as a base results in a much cleaner reaction than the use of $n-BuLi$. Thus the treatment of **5a** with $LiN(SiMe_3)_2 \cdot Et_2O$ at -78 °C, followed by warming to 10 °C, produces $Ph_4P_2N_4S_2CHLi$ quantitatively as determined by ^{31}P NMR ($\delta -12.7$ ppm). The treatment of this lithium reagent with MeI produces **5b** in 84% yield. The C-methyl methylene bridged derivative **5b** is readily characterized by the 1H NMR spectrum, which exhibits resonances for CH, CMe, and PPh_2 protons in the appropriate intensity ratio. The CH resonance appears as a triplet of quartets. The apparent triplet structure is presumably due to the approximate equality of the four-bond couplings [$^4J(HP)$] to the inequivalent phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectrum of **5b** shows two singlets at $\delta -18.5$ and $\delta -20.5$ for the inequivalent phosphorus atoms. As indicated in Scheme 2, the subsequent reaction of **5b** with $LiN(SiMe_3)_2 \cdot Et_2O$ (or $LiN-i-Pr_2$) followed by the addition of MeI yields **5c** (63% yield), which exhibits the expected singlet at -19.8 ppm in the ^{31}P NMR spectrum. The 1H NMR spectrum shows resonances for the CMe_2 and PPh_2 groups in the appropriate intensity ratio.

Preparation and X-ray Structure of $Cp^*Rh(Ph_4P_2N_4S_2)$. The first transition-metal complexes of the dianion **3** were prepared by the oxidative addition of the neutral ligand 1,5- $Ph_4P_2N_4S_2$ to the zerovalent complexes $M(PPh_3)_2L$ ($M = Pt, L = C_2H_4$; $M = Pd, L = 2PPh_3$).⁷ The discovery of the alkali metal derivatives **4a–c** provides an alternative pathway for the synthesis of metal complexes via metathesis with metal halide complexes. For example, the platinum complexes $Pt(PR_3)_2(Ph_4P_2N_4S_2)$ ($R = Et, Ph$) have been prepared from $cis-Pt(PR_3)_2Cl_2$ by this route.³ We now report that the reaction of **4b** with $(Cp^*RhCl_2)_2$ in THF occurs rapidly at room temperature to give $Cp^*Rh(Ph_4P_2N_4S_2)$ (**6**) as dark orange crystals in 73% yield. A

(20) These efforts included carrying out the reaction with superhydride in other solvents, e.g. pyridine or dimethoxyethane, or in the presence of large cations, e.g. NBu_4^+ , $N(PPh_3)_2^+$, or crown ethers.

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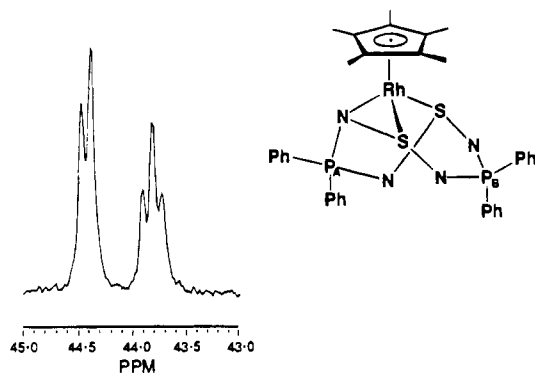


Figure 2. ^{31}P NMR spectrum of $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$.

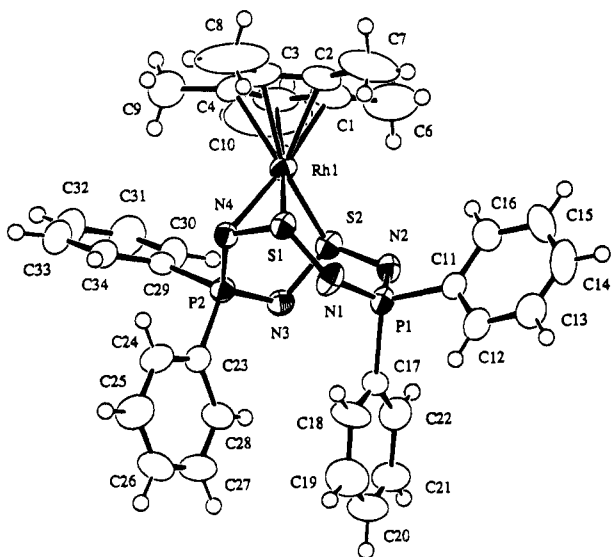


Figure 3. ORTEP drawing of $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$.

small amount of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ (**1**) was also isolated. Complex **6** can also be prepared by the oxidative addition of **1** to $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2$ in THF at room temperature under the influence of UV irradiation for 24 h as determined by the ^{31}P NMR spectrum of the reaction mixture (see Scheme 3), but the yields are lower.

The ^1H NMR spectrum of **6** is consistent with the replacement of the two chloride ligands in $(\text{Cp}^*\text{RhCl}_2)_2$ by the dianion **3**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** consists of two equally intense resonances, a doublet at 44.7 ppm ($J = 15.3$ Hz) and an apparent triplet at 43.8 ppm ($J = 15.3$ Hz) (see Figure 2). The interpretation of this fine structure is not immediately obvious, but it is clear from the appearance of two ^{31}P NMR signals that the $\text{P}_2\text{N}_4\text{S}_2$ ring is asymmetrically bonded to rhodium. The X-ray structure of **6** revealed that the heterocyclic ligand is attached to the metal in a tridentate (N,S,S') fashion. An ORTEP drawing of **6** is shown in Figure 3, and selected bond distances and bond angles are summarized in Table 3. The dianion **3** behaves as a six-electron donor in this Rh(III) complex and forms three metal-containing chelate rings: a three-membered RhNS ring, a five-membered RhNPNS ring, and a six-membered RhSNPNS ring. In the light of this structure, the resonances at 43.8 and 44.7 ppm are tentatively assigned to the inequivalent phosphorus atoms P_A and P_B , respectively, which exhibit a mutual four-bond coupling constant of 15.3 Hz (see Figure 2). Values of $^4J(\text{P}_\text{A}\text{P}_\text{B})$ in the range 16–34 Hz have been previously observed for a variety of adducts of **1** in which the PPH_2 groups are inequivalent.^{25,26} The apparent triplet at

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $\text{Cp}^*\text{Rh}(\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2)$

Bond Distances			
Rh(1)–S(1)	2.273(2)	Rh(1)–S(2)	2.321(2)
Rh(1)–N(4)	2.135(5)	Rh(1)–C(1)	2.162(7)
Rh(1)–C(2)	2.205(7)	Rh(1)–C(3)	2.226(7)
Rh(1)–C(4)	2.221(7)	Rh(1)–C(5)	2.219(7)
S(1)–N(1)	1.593(5)	S(1)–N(4)	1.703(5)
S(2)–N(2)	1.635(5)	S(2)–N(3)	1.664(5)
P(1)–N(1)	1.629(5)	P(1)–N(2)	1.600(5)
P(1)–C(11)	1.822(6)	P(1)–C(17)	1.816(6)
P(2)–N(3)	1.587(5)	P(2)–N(4)	1.652(5)
P(2)–C(23)	1.786(6)	P(2)–C(29)	1.807(6)

Bond Angles			
S(1)–Rh(1)–S(2)	90.70(6)	N(1)–P(1)–N(2)	120.3(2)
S(1)–Rh(1)–N(4)	45.3(1)	N(3)–P(2)–N(4)	116.6(3)
S(2)–Rh(1)–N(4)	87.2(1)	N(1)–S(1)–N(4)	118.6(3)
Rh(1)–S(1)–N(1)	120.7(2)	N(2)–S(2)–N(3)	105.8(3)
Rh(1)–S(1)–N(4)	63.1(2)	S(1)–N(1)–P(1)	128.1(3)
Rh(1)–S(2)–N(2)	110.4(2)	S(2)–N(2)–P(1)	119.7(3)
Rh(1)–S(2)–N(3)	105.1(2)	S(2)–N(3)–P(2)	114.7(3)
Rh(1)–N(4)–S(1)	71.6(2)	S(1)–N(4)–P(2)	123.9(3)
Rh(1)–N(4)–P(2)	106.0(2)		

43.8 ppm is attributed to an overlapping doublet of doublets arising from a two-bond coupling between P_A and Rh (^{103}Rh , $I = 1/2$, 100%) with a value approximately equal to that of $^4J(\text{P}_\text{A}\text{P}_\text{B})$. The P_B –Rh coupling is apparently not observed, presumably because it involves three bonds. The Rh–N bond length in **6** is 2.135(5) Å while the Rh–S bond distances are 2.273(2) and 2.321(2) Å. For comparison, the mean value for Rh–N distances of 16 CpRh complexes is 2.062 Å (with a range of 2.002–2.168 Å) and the mean value for Rh–S bond lengths is 2.306 Å for a range of 2.096–2.380 Å.²⁷

Conclusions. Both soluble ($M = \text{K}$) and insoluble ($M = \text{Li}, \text{Na}$) alkali metal derivatives of the $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ dianion are readily prepared by the reduction of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ with $\text{M}[\text{BEt}_3\text{H}]$ in THF. These highly reactive reagents are useful for the synthesis of both organic derivatives and metal complexes of the $\text{P}_2\text{N}_4\text{S}_2$ ring. There is, however, a delicate balance between redox behavior and nucleophilic displacement when $\{\text{M}_2[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]\}_n$ are treated with organic or inorganic halides. Thus the reactions of the substrates $\text{ICH}_2\text{CH}_2\text{I}$, PhCHBr_2 , CHI_3 , CBr_4 , Me_2SnCl_2 , Me_2SnCl_2 , PhPCl_2 , or SCl_2 all regenerated 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ ($\delta(^{31}\text{P})$ 113.7 ppm). Although the other products of these redox reactions have not been fully characterized, it is apparent that $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ is a very strong reducing agent and further investigations of specific applications of the dianion in this role are warranted.

Acknowledgment. We are grateful to Professor S. Hinman for carrying out the electrochemical experiments and to the NSERC (Canada) for financial support.

Supporting Information Available: Tables giving X-ray experimental details, atomic coordinates and isotropic thermal parameters for hydrogen atoms, bond distances, bond angles, anisotropic thermal parameters, and torsion angles (17 pages). Ordering information is given on any current masthead page.

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(27) Bond length information for Rh–N and Rh–S distances was obtained from the Cambridge database.