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Preparation and ^{31}P NMR Characterization of Structural Isomers of 1,5-Diphosphadithiatetrazocines: X-ray Structures of 1,5-[(*exo*-CCl_3,*endo*-Cl)P]$_2N_4S_2$ and 1,5-$Et_4P_2N_4S_2$

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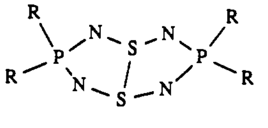
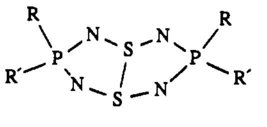
The reaction of $RR'PN_2(SiMe_3)_3$ with $SOCl_2$ (R = Me, R′ = Ph) or SCl_2 (R = Cl, R′ = CCl_3; R = I, R′ = Et) is shown by ^{31}P NMR spectroscopy to produce all three structural isomers of the folded eight-membered rings, 1,5-$R_2R'_2P_2N_4S_2$, in which different groups R and R′ are attached to the same phosphorus atom. The major isomer has one R group and one R′ group in *endo* positions and this isomer has been isolated for R = Me, R′ = Ph. In the case of R = Cl, R′ = CCl_3, the isomer with both Cl substituents in *endo* positions, **2b**, has been isolated and the structure was shown by X-ray crystallography to consist of a folded eight-membered ring with a cross-ring S–S bond [d(S–S) = 2.525 (3) Å]. The crystals of **2b** are monoclinic, space group $P2_1/n$, with $a = 10.944$ (3) Å, $b = 5.859$ (2) Å, $c = 23.831$ (4) Å, $\beta = 100.13$ (2)°, $V = 1504.2$ Å^3, and $Z = 4$. The final R and R_w values were 0.060 and 0.064, respectively. The X-ray structure of 1,5-$Et_4P_2N_4S_2$, **1c**, was also determined. The crystals of **1c** are monoclinic, space group $P2_1/a$, with $a = 9.972$ (2) Å, $b = 10.517$ (3) Å, $c = 10.968$ (3) Å, $\beta = 102.51$ (1)°, $V = 1442.6$ Å^3, and $Z = 4$. The final R and R_w values were 0.055 and 0.057, respectively.

Introduction

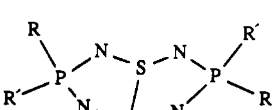
1,5-Diphosphadithiatetrazocines are hybrids of the well-known cyclophosphazenes and cyclothiazenes in which P–N and S–N units alternate in the cyclic framework. The first syntheses of these interesting heterocycles gave rise to low yields of products, which required tedious purification procedures.[1,2] X-ray structural investigations of two of these derivatives, **1a** and **1b**, established the existence of an eight-membered ring folded about a cross-ring S–S bond.[1,2] The ^{1}H NMR and ^{13}C spectra of **1a** revealed the expected inequivalence of the *endo*- and *exo*-methyl groups attached to phosphorus,[1,3] and this inequivalence is retained in solution up to at least 110 °C,[4] implying that the folded structure is rigid. Consequently, three structural isomers **2** (*endo*-R, *endo*-R), **3** (*endo*-R, *exo*-R), and **4** (*exo*-R, *exo*-R) can be anticipated for 1,5-diphosphadithiatetrazocines in which different exocyclic groups are attached to the same phosphorus atom.



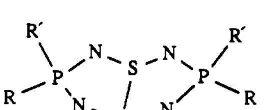
1a (R = Me)
1b (R = Ph)
1c (R = Et)



2a (R = Me, R′ = Ph)
2b (R = Cl, R′ = CCl_3)
2c (R = I, R′ = Et)



3a (R = Me, R = Ph)
3b (R = Cl, R′ = CCl_3)
3c (R = I, R′ = Et)



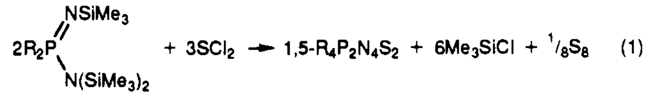
4a (R = Me, R′ = Ph)
4b (R = Cl, R′ = CCl_3)
4c (R = I, R′ = Et)

Recently we have briefly described an improved synthesis of **1a** and **1b** that makes use of the readily prepared reagents $R_2PN_2(SiMe_3)_3$[5,6] in a cyclocondensation reaction with SCl_2[7] (eq 1), and this procedure has facilitated investigations of the reactions of these ring systems.[8–10]

Table I. ^{31}P NMR Chemical Shifts for $RR'PN_2(SiMe_3)_3$

compd[a]	$\delta(^{31}P)$[b]
$Et_2PN_2(SiMe_3)_3$	29.2
$Ph_2PN_2(SiMe_3)$	9.2 (7.3)[7]
$Me(Ph)PN_2(SiMe_3)_3$	12.8
$Cl_3C(Cl)PN_2(SiMe_3)_3$	2.8
$Et(I)PN_2(SiMe_3)_3$	−10.9 (−10.7)[11]

[a] In CH_2Cl_2 (D_2O insert). [b] Reference: external 85% H_3PO_4. Literature values are given in parentheses (all in $CDCl_3$).



$$2R_2P(=NSiMe_3)N(SiMe_3)_2 + 3SCl_2 \rightarrow 1,5\text{-}R_4P_2N_4S_2 + 6Me_3SiCl + {}^1/_8S_8 \qquad (1)$$

The objective of this investigation was to prepare and characterize structural isomers of the type **2–4** by using this new synthetic approach. These isomers were characterized by ^{31}P NMR spectroscopy, and the structure of **2b** was confirmed by X-ray crystallography. The crystal structure of **1c** was also determined for comparison with those of **1a** and **1b**.

Experimental Section

Reagents and General Procedures. All solvents were dried and distilled before use: toluene (Na), dichloromethane (P_4O_{10}), hexanes and pentane (Na), acetonitrile (CaH_2 and P_2O_5), and carbon tetrachloride (P_4O_{10}). All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of nitrogen (99.99% purity) passed through silica gel and P_4O_{10}.

Sulfur dichloride and PCl_3 (Aldrich) were distilled before use. All other reagents were used as received: $SnCl_4$, Bu^{n}Li, EtMgBr, MeMgBr, $PhPCl_2$, Ph_2PCl, and $(Me_3Si)_2NH$ (Aldrich), $SOCl_2$ and EtI (Fisher), and Me_3SiN_3 (Petrarch). Preparative TLC plates (20 cm × 20 cm) were coated with silica gel (2 mm) (Macherey-Nagel).

Literature procedures were used for the preparation of $Me_2PN_2(SiMe_3)_3$,[5] $Me(Ph)PN_2(SiMe_3)_3$,[6] $Et(I)PN_2(SiMe_3)_3$,[11] and $CCl_3(Cl)PN_2(SiMe_3)_3$;[12] $Et_2PN_2(SiMe_3)_3$ and $Ph_2PN_2(SiMe_3)_3$ were prepared from Me_3SiN_3 and $Et_2PN(SiMe_3)_2$[13] or $Ph_2PN(SiMe_3)_2$, respectively, by

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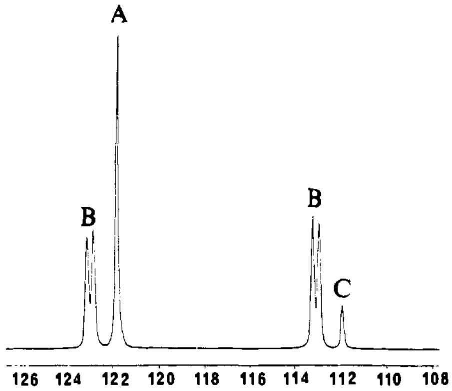

Figure 1. ^{31}P NMR spectrum and assignments of a mixture of the 1,5-[Me(Ph)P]$_2$N$_4$S$_2$ isomers. The assignments are as follows: A (**2a**), B (**3a**), C (**4a**).

using the procedure described for Me(Ph)PN$_2$(SiMe$_3$)$_3$.[6] The ^{31}P NMR chemical shifts for all of these reagents are given in Table I.

Instrumentation. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls (KBr windows) on a Nicolet 50X-FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ACE 200-MHz spectrometer. ^{31}P NMR spectra were obtained by using Varian XL 200-MHz or Bruker AM 400-MHz instruments with 85% H$_3$PO$_4$ as an external reference. Mass spectra were recorded on a Kratos MS 80 RFA spectrometer operating at 70 eV. Chemical analyses were performed by the Analytical Services laboratory of the Department of Chemistry, The University of Calgary.

Preparation and Separation of 1,5-[Me(Ph)P]$_2$N$_4$S$_2$ Isomers 2a, 3a, and 4a. A solution of SOCl$_2$ (1.81 g, 15.2 mmol) in CH$_2$Cl$_2$ (70 mL) was added dropwise (45 min), by transfer needle, to a stirred solution of Me(Ph)PN$_2$(SiMe$_3$)$_3$ (5.63 g, 15.2 mmol) in CH$_2$Cl$_2$ (150 mL) at 0 °C. After 12 h the ^{31}P NMR spectrum of the reaction mixture revealed the presence of all three isomers **2a**, **3a**, and **4a** (Figure 1). The orange-red solution was stirred at room temperature for a total of 18 h, after which the solvent and volatile products were removed under vacuum to give a viscous purple oil. This oil was dissolved in a minimum of CH$_2$Cl$_2$ and transferred dropwise to rapidly stirred pentane (150 mL) at −78 °C. Removal of the solvents under vacuum afforded a pale orange solid (3.00 g), which was extracted once with CH$_2$Cl$_2$ (50 mL). Pentane (40 mL) was added to the CH$_2$Cl$_2$ extract, and after 24 h at −25 °C, a red viscous oil separated out of solution. The solution was decanted from the oil, and solvents were removed under vacuum. The residue was then redissolved in CH$_2$Cl$_2$ (10 mL) and pentane (40 mL) and, after a further 24 h at −25 °C, the solution was decanted from the resulting oil. Solvent was removed under vacuum, leaving 0.36 g of a gummy purple material, which was shown by ^{31}P NMR to be a mixture of all three isomers (no other phosphorus-containing products were present). This residue was separated by TLC on silica gel (developed with CHCl$_3$) to give a purple sample of **3a** (0.15 g, 0.41 mmol) and a mixture of all three isomers almost completely depleted in **3a** (0.07 g, 0.19 mmol). Anal. Calcd for C$_{14}$H$_{16}$N$_4$P$_2$S$_2$: C, 45.90; H, 4.40; N, 15.29. Found for **3a**: C, 46.12; H, 4.36; N, 13.72. Analytical data obtained for several different samples of **3a** gave consistently low N values, but the samples were pure according to the ^{31}P NMR spectra. Found for a mixture of isomers depleted in **3a**: C, 44.99; H, 4.09; N, 14.21. ^{1}H NMR (CDCl$_3$) for **3a**: 0.60 ppm (d, ^2J(H–P) = 13.9 Hz, 3 H, CH_3), 1.80 ppm (d, ^2J(H–P) = 14.3 Hz, 3 H, CH_3), 7.3–7.9 ppm (m, 10 H, C_6H_5). The ^{1}H NMR parameters for the methyl groups of **2a** and **4a** were obtained from the spectrum of the mixture of isomers by comparison with the relative abundance of these isomers as indicated by the ^{31}P NMR spectrum. ^{1}H NMR (CDCl$_3$) for **2a**: 1.54 ppm (d, ^2J(H–P) = 14.2 Hz), 6.8–7.3 ppm (m, C_6H_5). ^{1}H NMR (CDCl$_3$) for **4a**: 1.58 ppm (d, ^2J(H–P) = 15.9 Hz), 6.8–7.3 ppm (m, C_6H_5). The ^{31}P NMR data for **2a**, **3a**, and **4a** are given in Table II.

Preparation and Separation of 1,5-[Cl$_3$C(Cl)P]$_2$N$_4$S$_2$ Isomers 2b, 3b, and 4b. A solution of SCl$_2$ (2.38 g, 23.1 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise (15 min) by transfer needle to a stirred solution of Cl$_3$C(Cl)PN$_2$(SiMe$_3$)$_3$ (6.66 g, 15.4 mmol) in CH$_2$Cl$_2$ (150 mL) at 0 °C. After 24 h a yellow precipitate (*cyclo*-S$_8$) was removed by use of a filter needle and then solvent and volatile products were removed under vacuum to give a mixture of yellow and pale purple solids, which was treated with CH$_2$Cl$_2$ (30 mL). After filtration to remove the insoluble yellow solid, the removal of solvent in vacuo followed by recrystallization from toluene/pentane (50 mL, 1:1) at −25 °C produced **2b** (100 mg). Anal. Calcd for C$_2$Cl$_8$N$_4$P$_2$S$_2$: C, 4.91; N, 11.44. Found: C, 5.08; N, 11.39. IR (Nujol, cm^{-1}): 1116 s, 1100 s, 1067 s, 1033 m, 971 m, 777 m, 747 vs, 723 s, 591 s, 568 m, 546 m, 511 s, 499 s, 432 m. ^{31}P NMR parameters for **2b**, **3b**, and **4b** are given in Table II.

Table II. ^{31}P NMR Chemical Shifts for 1,5-Diphosphadithiatetrazocines

compd[a]	δ(^{31}P)[b]
1,5-Et$_4$P$_2$N$_4$S$_2$ (**1c**)	136.1
1,5-Ph$_4$P$_2$N$_4$S$_2$ (**1b**)	114.1 (113.8)[7]
1,5-[Me(Ph)P]$_2$N$_4$S$_2$ (**2a**)	121.8
1,5-[Me(Ph)P]$_2$N$_4$S$_2$ (**3a**)	113.1, 123.0[c]
1,5-[Me(Ph)P]$_2$N$_4$S$_2$ (**4a**)	111.9
1,5-[Cl$_3$C(Cl)P]$_2$N$_4$S$_2$ (**2b**)	111.0
1,5-[Cl$_3$C(Cl)P]$_2$N$_4$S$_2$ (**3b**)	103.8, 113.8[d]
1,5-[Cl$_3$C(Cl)P]$_2$N$_4$S$_2$ (**4b**)	100.5
1,5-[Et(I)P]$_2$N$_4$S$_2$ (**2c** or **4c**)	125.2
1,5-[Et(I)P]$_2$N$_4$S$_2$ (**3c**)	120.2, 131.8[e]

[a] In CH$_2$Cl$_2$ (D$_2$O insert). [b] Reference: external 85% H$_3$PO$_4$. Literature values are given in parentheses (all in CDCl$_3$). [c] Two doublets; ^4J(^{31}P–^{31}P) = 45.3 Hz. [d] Two doublets; ^4J(^{31}P–^{31}P) = 61.0 Hz. [e] Two doublets; ^4J(^{31}P–^{31}P) = 61.5 Hz.

Preparation of 1,5-[Et(I)P]$_2$N$_4$S$_2$ Isomers. A solution of SCl$_2$ (0.87 g, 8.4 mmol) in CH$_2$Cl$_2$ (15 mL) was added dropwise to a stirred solution of Et(I)PN$_2$(SiMe$_3$)$_3$ (2.44 g, 5.62 mmol) in CH$_2$Cl$_2$ (50 mL) at 23 °C. After 1 h the ^{31}P NMR spectrum revealed a complex mixture of products with chemical shifts in the range −10 to +30 ppm and only a small amount of **2c**, **3c**, and **4c**. It was not possible to isolate pure samples of these isomers. ^{31}P NMR parameters for **3c** and **2c** or **4c** are given in Table II.

Preparation of 1,5-Ph$_4$P$_2$N$_4$S$_2$. A solution of SOCl$_2$ (2.00 g, 16.7 mmol) in CH$_2$Cl$_2$ (30 mL) was added dropwise (25 min), with a transfer needle, to a stirred solution of Ph$_2$PN$_2$(SiMe$_3$)$_3$ (7.23 g, 16.7 mmol) in CH$_2$Cl$_2$ (75 mL) at 23 °C. During the addition the color of the solution became intense yellow and then orange-red. After 3.5 h solvent and volatile products were removed under vacuum to give a pale pink solid, which was recrystallized from acetonitrile at 0 °C to give pale purple crystals of 1,5-Ph$_4$P$_2$N$_4$S$_2$ (2.31 g, 4.71 mmol, 57%) identified by comparison of IR and ^{31}P NMR spectra with those of an authentic sample.[2] The pale purple color of the product is attributed to the presence of trace amounts of Ph$_2$PN$_2$S$_3$ (λ_{max} 550 nm), but this impurity is not detectable by ^{31}P NMR spectroscopy.[7]

Preparation of 1,5-Et$_4$P$_2$N$_4$S$_2$. A solution of SOCl$_2$ (1.09 g, 9.17 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise (20 min), by transfer needle, to a stirred solution of Et$_2$PN$_2$(SiMe$_3$)$_3$ (2.73 g, 9.17 mmol) in CH$_2$Cl$_2$ (50 mL) at 0 °C. After 15 h solvent and volatile products were removed from the red solution under vacuum to give a purple semisolid residue, which was recrystallized twice from hot toluene to give pale yellow crystals of 1,5-Et$_4$P$_2$N$_4$S$_2$ (0.91 g, 3.10 mmol, 67%). Anal. Calcd for C$_8$H$_{20}$N$_4$P$_2$S$_2$: C, 32.31; H, 6.76; N, 18.78. Found: C, 31.90; H, 6.79; N, 18.64. IR (Nujol, cm^{-1}): 1096 s, 1061 vs, 1042 vs, 1028 s, 1005 s, 980 s, 797 m, 780 s, 753 s, 722 m, 662 m, 623 s, 451 s. NMR spectra (δ, ppm) (CDCl$_3$): ^{1}H 0.84 [d of t, ^3J(^{1}H–^{31}P) = 18.6 Hz, ^3J(^{1}H–^{1}H) = 7.6 Hz] (CH$_2$$CH_3$), 1.16 [d of t, ^3J(^{1}H–^{31}P) = 17.9 Hz, ^3J(^{1}H–^{1}H) = 7.5 Hz] (CH$_2$$CH_3$), 1.6–1.8 (m, CH_2CH$_3$); ^{13}C 24.2 [d, ^1J(^{13}C–^{31}P) = 72.0 Hz] (CH_2CH$_3$), 21.2 [d, ^1J(^{13}C–^{31}P) = 85.6 Hz] (CH_2CH$_3$), 7.2 (s, CH$_2$$CH_3$), 4.7 (s, CH$_2$$CH_3$).

X-ray Structural Analyses. Crystals of **1c** and **2b** were obtained by recrystallization from toluene and dichloromethane, respectively. Accurate cell dimensions and crystal orientation matrices were determined on an Enraf-Nonius CAD-4 diffractometer by least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the ω/2θ scan method using variable scan speed (1.25–4.0° min^{-1}), scan width (0.80 + 0.35 tan θ)°, and monochromatized Mo Kα radiation in the range $2 < \theta < 23°$ with h = 0 to 16, k = 0 to 10, and l = −11 to 11 for **1c**. The corresponding values for **2b** were 1.54–6.67° min^{-1}, (1.00 + 0.35 tan θ)°, and $2 < \theta < 25°$ with h = 0 to 13, k = 0 to 6, and l = −28 to 28. Three reflections, monitored every 2 h of exposure time, decreased by 2.1% linearly over the course of data collection for **1c**; this decay was corrected by appropriate scaling. The reflections for **2b** showed insignificant variations. For **1c**, the intensities of 2302 reflections were measured, of which 1437 had $I > 3\sigma(I)$, where $\sigma^2 I = S + 2B + [0.04(S - B)]^2$, with S = scan count, and B = time-averaged background count extended 25% on each side; for **2b**, 3142 reflections were measured, of which 2174 had $I > 3\sigma(I)$. Data were corrected for Lorentz polarization and absorption effects;[14] correction

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Table III. Crystallographic Data for **1c** and **2b**

	1c	**2b**
formula	$C_8H_{20}N_4P_2S_2$	$C_2Cl_8N_4P_2S_2$
fw	298.35	489.75
space group	$P2_1/a$	$P2_1/n$
a, Å	15.244 (3)	10.944 (3)
b, Å	9.494 (3)	5.859 (2)
c, Å	10.210 (2)	23.831 (4)
β, deg	102.51 (1)	100.13 (2)
V, Å^3	1442.6	1504.2
Z	4	4
T, K	295	165
λ, Å	0.71069	0.71069
ρ_{calcd}, g cm^{-1}	1.374	2.163
μ, mm^{-1}	0.512	1.834
R^a	0.055	0.060
$R_w{}^b$	0.057	0.064

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

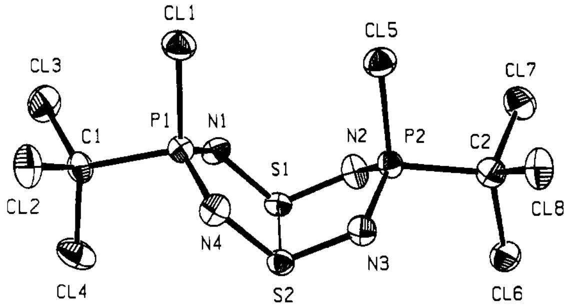

Figure 2. ORTEP plot (50% probability ellipsoids) for 1,5-[*endo*-Cl,*exo*-CCl_3)P]$_2N_4S_2$ (**2b**) showing the atomic numbering scheme.

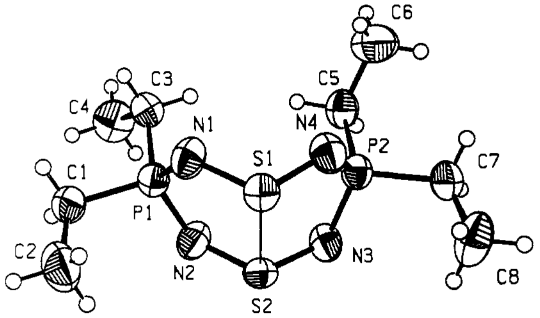

Figure 3. ORTEP plot (50% probability ellipsoids) for 1,5-$Et_4P_2N_4S_2$ (**1c**), showing the atomic numbering scheme.

range was 0.743–1.377 for **1c** and 0.804–1.186 for **2b**. Crystal data are given in Table III.

The structures were solved by direct methods. Refinement of the structures was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic factors for the non-hydrogen atoms. At an intermediate stage in the refinement of **1c**, a difference map revealed all H atoms which were included in the subsequent cycles at geometrically idealized positions (C–H = 0.95 Å) and a fixed overall isotropic temperature factor. Refinement converged with $R = 0.055$ and $R_w = 0.057$ for **1c** and $R = 0.060$ and $R_w = 0.064$ for **2b**. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[15] (**1c** and **2b**) and Stewart, Davidson and Simpson[16] (**1c**) and allowance was made for anomalous dispersion.[17] A difference map calculated at the conclusion of the refinement had no chemically significant features. All computer programs used in this study were part of XTAL2.6[18] and Figures 2 and 3 were plotted using ORTEPII.[19] The atomic coordinates for **2b** and **1c** are given in Tables IV and V, respectively.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters for **2b**

atom	x/a	y/b	z/c	U, Å^2
P(1)	−0.0883 (2)	0.3662 (3)	0.16016 (9)	0.022 (1)
P(2)	0.0534 (2)	0.3710 (3)	0.3184 (1)	0.023 (1)
S(1)	0.1504 (2)	0.3973 (3)	0.22037 (9)	0.023 (1)
S(2)	0.0293 (2)	0.0423 (3)	0.23525 (9)	0.023 (1)
Cl(1)	−0.2320 (2)	0.5585 (4)	0.1694 (1)	0.034 (1)
Cl(2)	−0.2589 (2)	0.1649 (4)	0.0624 (1)	0.040 (1)
Cl(3)	−0.1243 (2)	0.5743 (4)	0.0453 (1)	0.044 (1)
Cl(4)	0.0058 (2)	0.1454 (4)	0.0679 (1)	0.044 (1)
Cl(5)	−0.0982 (2)	0.5579 (3)	0.3173 (1)	0.032 (1)
Cl(6)	0.2631 (2)	0.2139 (4)	0.4026 (1)	0.034 (1)
Cl(7)	0.1514 (2)	0.6518 (4)	0.4187 (1)	0.041 (1)
Cl(8)	0.0175 (2)	0.2344 (4)	0.4330 (1)	0.038 (1)
N(1)	0.0390 (5)	0.504 (1)	0.1750 (3)	0.026 (3)
N(2)	0.1520 (6)	0.485 (1)	0.2841 (3)	0.031 (4)
N(3)	0.0224 (6)	0.108 (1)	0.2991 (3)	0.026 (3)
N(4)	−0.0878 (5)	0.125 (1)	0.1917 (3)	0.026 (3)
C(1)	−0.1181 (7)	0.315 (1)	0.0821 (3)	0.027 (4)
C(2)	0.1233 (7)	0.371 (1)	0.3951 (4)	0.029 (4)

Table V. Atomic Coordinates and Isotropic Thermal Parameters for **1c**

atom	x/a	y/b	z/c	U, Å^2
S(1)	0.1046 (1)	0.0899 (2)	0.5952 (2)	0.047 (1)
S(2)	0.1090 (1)	−0.0229 (2)	0.8172 (2)	0.047 (1)
P(1)	0.2132 (1)	−0.1492 (2)	0.6539 (2)	0.047 (1)
P(2)	0.1964 (1)	0.2349 (2)	0.8224 (2)	0.045 (1)
N(1)	0.1668 (4)	−0.0273 (6)	0.5504 (7)	0.056 (4)
N(2)	0.1775 (4)	−0.1415 (6)	0.7906 (7)	0.057 (4)
N(3)	0.1536 (4)	0.1098 (6)	0.8966 (6)	0.051 (4)
N(4)	0.1559 (4)	0.2253 (6)	0.6631 (7)	0.056 (4)
C(1)	0.1874 (5)	−0.3166 (8)	0.5793 (9)	0.054 (5)
C(2)	0.0867 (6)	−0.3437 (10)	0.5420 (11)	0.089 (7)
C(3)	0.3321 (5)	−0.1379 (8)	0.6785 (9)	0.061 (5)
C(4)	0.3856 (5)	−0.2531 (10)	0.7627 (10)	0.074 (6)
C(5)	0.3170 (5)	0.2324 (8)	0.8651 (9)	0.056 (5)
C(6)	0.3646 (6)	0.3523 (11)	0.8156 (10)	0.086 (7)
C(7)	0.1652 (6)	0.3998 (8)	0.8834 (8)	0.059 (5)
C(8)	0.0644 (6)	0.4203 (10)	0.8640 (10)	0.083 (7)

Results and Discussion

Preparation and ^{31}P NMR Characterization of the Isomers of 1,5-(RR′P)$_2N_4S_2$ (R = Me, R′ = Ph (2a, 3a, 4a); R = Cl, R′ = CCl_3 (2b, 3b, 4b); R = I, R′ = Et (2c, 3c, 4c)). Three isomers with structures of types **2**–**4** are possible for 1,5-diphosphadithiatetrazocines in which different exocyclic groups are attached to a specific phosphorus atom. Isomers **2** and **4** should exhibit a singlet for the two equivalent phosphorus atoms in the ^{31}P NMR spectrum whereas the phosphorus atoms in **3**, which are not related by symmetry, should give rise to two distinct resonances in the region characteristic of 1,5-diphosphadithiatetrazocines (110–140 ppm).[7]

Since $SOCl_2$ was found to be preferable to SCl_2 for the synthesis of 1,5-$R_4P_2N_4S_2$ from $R_2PN_2(SiMe_3)_3$ (R = Et, Ph) (vide infra), this reagent was employed in the initial attempts to prepare the isomers **2**–**4**. The ^{31}P NMR spectrum of the mixture of products that results from the reaction of Me(Ph)$PN_2(SiMe_3)_3$ and $SOCl_2$ (1:1 molar ratio) in methylene dichloride (Figure 1) is consistent with the presence of all three isomers **2a**, **3a**, and **4a**. The singlets at 121.8 and 111.9 ppm are tentatively assigned to **2a** and **4a**, respectively, on steric grounds; i.e., the most abundant of these two isomers has the less bulky substituents in the *endo* positions.[3] The doublets at 123.0 and 113.1 ppm are attributed to the inequivalent phosphorus atoms of the isomer **3a**. The composition of the isomeric mixture is approximately 34% **2a**, 62% **3a**, and 4% **4a** based on the integrated areas of their ^{31}P NMR signals. A pure sample of **3a** was separated by TLC on silica gel plates, but pure specimens of **2a** or **4a** could not be isolated.

The reaction of $Cl_3C(Cl)PN_2(SiMe_3)_3$ with $SOCl_2$ was not successful for the preparation of **2b**, **3b**, and **4b**. However, the use of SCl_2 (2:3 molar ratio, see eq 1) rather than $SOCl_2$ did produce a mixture of these isomers. The ^{31}P NMR data for **2b**,

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Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for **2b**

Bond Distances			
S(1)–S(2)	2.525 (3)	S(1)–N(1)	1.607 (6)
P(1)–N(1)	1.595 (6)	S(2)–N(4)	1.577 (6)
P(1)–N(4)	1.599 (6)	S(2)–N(3)	1.584 (7)
P(1)–C(1)	1.854 (8)	Cl(2)–C(1)	1.766 (8)
P(1)–Cl(1)	1.978 (3)	Cl(3)–C(1)	1.747 (8)
P(2)–N(2)	1.607 (7)	Cl(4)–C(1)	1.764 (8)
P(2)–N(3)	1.626 (6)	Cl(6)–C(2)	1.769 (8)
P(2)–C(2)	1.854 (8)	Cl(7)–C(2)	1.746 (8)
P(2)–Cl(5)	1.985 (3)	Cl(8)–C(2)	1.780 (9)
S(1)–N(2)	1.599 (7)		
Bond Angles			
N(1)–P(1)–N(4)	114.3 (3)	S(1)–N(2)–P(2)	117.0 (4)
N(1)–P(1)–C(1)	107.2 (4)	S(2)–N(3)–P(2)	117.3 (4)
N(1)–P(1)–Cl(1)	111.6 (3)	S(2)–N(4)–P(1)	121.1 (4)
N(4)–P(1)–C(1)	108.4 (4)	Cl(3)–C(1)–Cl(4)	110.9 (5)
N(4)–P(1)–Cl(1)	112.8 (3)	Cl(3)–C(1)–Cl(2)	110.2 (4)
C(1)–P(1)–Cl(1)	101.6 (3)	Cl(3)–C(1)–P(1)	110.4 (4)
N(2)–P(2)–N(3)	112.0 (4)	Cl(4)–C(1)–Cl(2)	109.3 (4)
N(2)–P(2)–C(2)	107.7 (4)	Cl(4)–C(1)–P(1)	106.1 (4)
N(2)–P(2)–Cl(5)	113.5 (3)	Cl(2)–C(1)–P(1)	109.8 (5)
N(3)–P(2)–C(2)	108.0 (3)	Cl(7)–C(2)–Cl(6)	111.0 (4)
N(3)–P(2)–Cl(5)	112.7 (2)	Cl(7)–C(2)–Cl(8)	110.8 (5)
C(2)–P(2)–Cl(5)	102.2 (3)	Cl(7)–C(2)–P(2)	109.7 (4)
N(2)–S(1)–N(1)	113.3 (4)	Cl(6)–C(2)–Cl(8)	110.0 (4)
N(4)–S(2)–N(3)	112.7 (4)	Cl(6)–C(2)–P(2)	107.4 (5)
P(1)–N(1)–S(1)	118.8 (4)	Cl(8)–C(2)–P(2)	107.9 (4)

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for **1c**

Bond Distances			
S(1)–N(1)	1.591 (7)	P(2)–N(4)	1.613 (7)
S(1)–N(4)	1.584 (6)	P(2)–C(5)	1.796 (8)
S(2)–N(2)	1.598 (7)	P(2)–C(7)	1.787 (8)
S(2)–N(3)	1.571 (6)	C(1)–C(2)	1.52 (1)
P(1)–N(1)	1.623 (6)	C(3)–C(4)	1.52 (1)
P(1)–N(2)	1.606 (8)	C(5)–C(6)	1.50 (1)
P(1)–C(1)	1.769 (8)	C(7)–C(8)	1.52 (1)
P(1)–C(3)	1.778 (8)	S(1)–S(2)	2.495 (3)
P(2)–N(3)	1.620 (7)		
Bond Angles			
N(4)–S(1)–N(1)	115.1 (3)	N(3)–P(2)–C(7)	108.3 (4)
N(3)–S(2)–N(2)	115.3 (3)	N(3)–P(2)–C(5)	111.8 (4)
N(2)–P(1)–N(1)	110.6 (4)	C(7)–P(2)–C(5)	105.2 (4)
N(2)–P(1)–C(1)	109.2 (4)	S(1)–N(1)–P(1)	120.9 (4)
N(2)–P(1)–C(3)	113.7 (4)	S(2)–N(2)–P(1)	122.5 (4)
N(1)–P(1)–C(1)	109.6 (3)	S(2)–N(3)–P(2)	121.3 (4)
N(1)–P(1)–C(3)	109.6 (4)	S(1)–N(4)–P(2)	122.2 (4)
C(1)–P(1)–C(3)	103.9 (4)	C(2)–C(1)–P(1)	112.2 (6)
N(4)–P(2)–N(3)	109.0 (3)	C(4)–C(3)–P(1)	116.3 (6)
N(4)–P(2)–C(7)	109.2 (3)	C(6)–C(5)–P(2)	117.0 (6)
N(4)–P(2)–C(5)	113.1 (4)	C(8)–C(7)–P(2)	113.9 (6)

Table VIII. Comparison of Structural Parameters for the Heterocyclic Rings in **1a**, **1b**, **1c**, and **2b**

	1a[a]	**1b**[b]	**1c**[c]	**2b**[c]
d(P–N), Å[d]	1.636 (3)	1.621 (3)	1.616 (8)	1.607 (7)
d(S–N), Å[d]	1.595 (3)	1.590 (3)	1.586 (7)	1.592 (7)
d(S–S), Å	2.551 (2)	2.528 (1)	2.495 (3)	2.525 (3)
∠NPN, deg	110.0 (2) 107.3 (2)	110.8 (1) 110.8 (1)	110.6 (4) 109.0 (3)	114.3 (3) 112.0 (4)
∠PNS, deg[d]	120.7 (2)	120.9 (2)	121.8 (4)	118.6 (4)
angle between the two S_2N_2 planes, deg	114.9	117.3	115.5	113.2
deviation of P atoms from S_2N_2 planes, Å	+0.194 –0.474	–0.214 –0.214	+0.064 +0.238	+0.030 –0.413

[a] Data taken from ref 1. Compound **1b** has a 2-fold axis that passes through the center of the S–S bond and is perpendicular to it. [b] Data taken from ref 2. [c] This work. [d] Mean values.

3b, and **4b** are given in Table II and the integrated areas of the ^{31}P NMR signals revealed a distribution of isomers similar to that found for **2a**, **3a**, and **4a**. In this case a pure sample of **3b** could not be isolated, but crystals of the most abundant symmetrical isomer ($\delta(^{31}P)$ = 111.0 ppm) were obtained by fractional crystallization of the mixture from toluene/pentane (1:1). This isomer was assumed to be **2b**, i.e., the isomer with the less bulky Cl substituent in the *endo* positions (cf. **2a**), and this assumption was confirmed by X-ray crystallography (vide infra).

The ^{31}P NMR spectrum of the reaction of Et(I)PN$_2$(SiMe$_3$)$_3$ with SCl$_2$ (2:3 molar ratio) in CH$_2$Cl$_2$ at 23 °C provides good evidence for the production of **3c** and either **2c** or **4c** (Table II). However, the major phosphorus-containing products from this reaction give rise to signals in the region –10 to +30 ppm, and it was not feasible to isolate pure samples of **2c**, **3c**, or **4c**.

The large four-bond coupling constant (45–61 Hz) between the inequivalent phosphorus atoms of isomers of type **3** is an interesting feature of these ring systems. For comparison, values in the range 16–23 Hz have previously been observed for the corresponding interaction in N-bonded Lewis or Brønsted acid adducts of **1b**.[10] It is not clear whether these high values result from geometrical or electronic factors.

Preparation of 1,5-Diphosphadithiatetrazocines, $R_4P_2N_4S_2$ (R = Et, Ph). Although the preparation of **1b** in ca. 50% yields can be accomplished by the cyclocondensation reaction (eq 1),[7] the attempted synthesis of **1c** by this method was unsuccessful. Consequently, the use of SOCl$_2$ rather than SCl$_2$ for this cyclocondensation was investigated. The reaction of Et$_2$PN$_2$(SiMe$_3$)$_3$ with thionyl chloride (1:1 molar ratio) in dichloromethane at 0 °C produces 1,5-Et$_4$P$_2$N$_4$S$_2$ (**1c**) in 67% yield. This new derivative exhibits a ^{31}P NMR chemical shift at high frequency (+136.1 ppm) characteristic of 1,5-diphosphadithiatetrazocines, a feature that has been attributed to the constraint imposed by the cross-ring S–S interaction in these ring systems.[10] The ^{1}H and ^{13}C NMR spectra of **1c** reveal inequivalent (*exo* and *endo*) ethyl groups attached to phosphorus as expected for a folded structure.

The cyclocondensation reaction of Ph$_2$PN$_2$(SiMe$_3$)$_3$ with SOCl$_2$ rather than SCl$_2$ gave slightly improved yields of **1b** (57% vs 50% for SCl$_2$), but the major advantage of the use of SOCl$_2$ is that sulfur is not formed so that purification of **1b** by recrystallization is more easily achieved.

X-ray Crystal Structures of 1,5-[(*exo*-CCl$_3$,*endo*-Cl)P]$_2$N$_4$S$_2$ (2b) and 1,5-Et$_4$P$_2$N$_4$S$_2$ (1c). The structures of **2b** and **1c** were determined by X-ray crystallography. ORTEP drawings of **2b** and **1c** with the atomic numbering schemes are shown in Figures 2 and 3, respectively, and the pertinent bond lengths and bond angles are given in Tables VI and VII, respectively. The structural parameters for these heterocycles are compared with the corresponding data for **1a** and **1b** in Table VIII.

The X-ray structural determination of **2b** confirms the assumption, based on ^{31}P NMR data, that both Cl substituents are in *endo* positions. The P–Cl distances are 1.978 (3) and 1.985 (3) Å (cf. 2.036–2.045 Å in N$_4$P$_4$Cl$_4$Ph$_4$).[20] The structures of the heterocyclic rings in **1c** and **2b** show the same general features as those of **1a**[1] and **1b**,[2] viz. a bicyclic system in which two five-membered rings share a common S--S bond with *d*(S–S) ~ 2.5 Å. The major difference between the structures of these four heterocycles involves the conformation of the PN$_2$S$_2$ rings (Table VIII). In **1a** the phosphorus atom lies out and on *opposite* sides of the S$_2$N$_2$ planes by 0.194 and 0.474 Å,[1] whereas both phosphorus atoms in **1b** are situated below the S$_2$N$_2$ planes by 0.214 Å. In contrast, one of the phosphorus atoms in **1c** deviates only slightly (0.064 Å) while the other lies 0.238 Å above their respective S$_2$N$_2$ planes. In fact, deviations from planarity found for the phosphorus atoms in **1c** resemble closely those found for the N-methylated derivative of **1b**, i.e., +0.023 and +0.258 Å.[10] In **2b** one PS$_2$N$_2$ ring is essentially planar whereas the other phosphorus atom is 0.413 Å below the S$_2$N$_2$ plane.

The endocyclic bond angles at phosphorus are larger (112.0–114.3° vs 107.3–110.8°) and those at nitrogen in **2b** are somewhat smaller (118.6° vs 120.7–121.8°) compared to the

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corresponding bond angles in **1a–c**.

Conclusion

All three possible structural isomers of 1,5-diphosphadithiatetrazocines are formed in the reaction of reagents of the type $RR'PN_2(SiMe_3)_3$ with $SOCl_2$ or SCl_2. The major product is the unsymmetrical isomer in which one R group and one R′ group occupy *endo* positions. The predominant symmetrical isomer has the least sterically demanding groups in the *endo* positions. The 1,5-diphosphadithiatetrazocines **2b**, **3b**, and **4b** represent the first examples of this ring system with exocyclic P–Cl linkages. As such they provide a unique opportunity to investigate reactions at phosphorus rather than at the sulfur or nitrogen centers of these hybrid ring systems.

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Registry No. **1b**, 80106-10-1; **1c**, 140360-67-4; **2a**, 140360-65-2; **2b**, 140360-66-3; **2c**, 140360-68-5; **3a**, 140461-02-5; **3b**, 140460-06-6; **3c**, 140460-08-8; **4a**, 140460-05-5; **4b**, 140460-07-7; **4c**, 140460-09-9; Me(Ph)$PN_2(SiMe_3)_3$, 69687-06-5; $Cl_3C(Cl)PN_2(SiMe_3)_3$, 50732-23-5; Et(I)$PN_2(SiMe_3)_3$, 58971-96-3; $Ph_2PN_2(SiMe_3)_3$, 61500-31-0; $Et_2PN_2(SiMe_3)_3$, 140360-69-6.

Supplementary Material Available: Tables listing thermal parameters and dihedral angles for **1c** and **2b** and hydrogen coordinates and isotropic thermal parameters for **1c** (6 pages); tables of calculated and observed structure factors for **1c** and **2b** (35 pages). Ordering information is given on any current masthead page.

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Comparison of the Crystalline Adducts of Tetrakis(triphenylacetato)dichromium(II) with Benzene, *p*-Difluorobenzene, and *p*-Xylene

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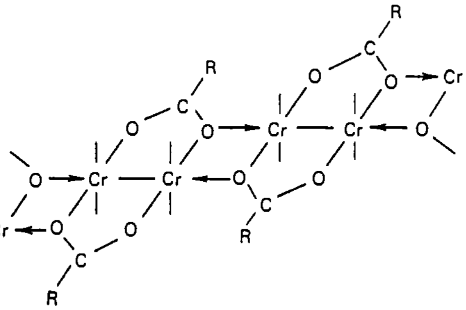
For comparison with the previously described $Cr_2(O_2CCPh_3)_4{\cdot}C_6H_6$ ($1{\cdot}C_6H_6$), we have prepared and structurally characterized analogues with *p*-$C_6H_4F_2$ and *p*-$C_6H_4(CH_3)_2$ in place of benzene. These new compounds are essentially isostructural with $1{\cdot}C_6H_6$ and have the following crystallographic characteristics. $1{\cdot}{}^3/_2C_6H_4F_2$: space group, $P4_2/nnc$, a = 20.698 (6) Å, c = 17.903 (8) Å, V = 7670 (8) Å^3, Z = 4. In addition to the $C_6H_4F_2$ molecules perpendicular to the c axis and stacked alternately with the molecules of **1**, there are two additional and highly disordered $C_6H_4F_2$ molecules in each unit cell. The Cr–Cr and Cr–ring center distances for $1{\cdot}{}^3/_2C_6H_4F_2$ are 2.176 (3) and 3.39 (1) Å, respectively. $1{\cdot}C_6H_4Me_2{\cdot}C_6H_{14}$: space group, $P4_2/ncc$, a = 20.695 (6) Å, b = 17.820 (6) Å, V = 7632 (7) Å^3, Z = 4. In addition to the alternating parallel chains of **1** and $C_6H_4Me_2$ molecules, there are disordered hexane molecules present. The Cr–Cr and Cr–ring center distances are 2.291 (3) and 3.31 (1) Å, respectively. These results, which bracket those (2.256 (4) and 3.30 (1) Å) for $1{\cdot}C_6H_6$, are discussed in terms of the interactions between the molecules of **1** and the π orbitals of the C_6H_6, $C_6H_4F_2$, and $C_6H_4Me_2$ molecules. Attempts to structurally characterize analogous compounds with durenes C_6Me_6, $C_6H_2F_4$, and C_6F_6 were unsuccessful. The short Cr–Cr distance in $1{\cdot}{}^3/_2C_6H_4F_2$ provides indirect support for the correctness of the very short distances in gaseous $Cr_2(O_2CCH_3)_4$. Several factors responsible for the variation in Cr–Cr distances will be discussed.

Introduction

The multiple bonds between chromium atoms[1] are among the more interesting curiosities of contemporary chemistry, but they are common enough and important enough that they are not *mere* curiosities. One of their greatest peculiarities is that in spite of being highly multiple (at least formally), namely, of order six in Cr_2, four in numerous Cr_2^{4+} complexes, or three in $Cr_2(tmtaa)_2$,[2] and among the shortest bonds (relative to the intrinsic size of the atoms) known, they are not very strong. They have also proven extremely troublesome from a theoretical point of view because there is so much electron correlation that extraordinary (and new) approaches have been necessary to obtain reasonable descriptions of them.[3,4]

One particular problem in this area has to do with the influence of axial ligands on the Cr–Cr bond in $Cr_2(LL)_4X_2$ compounds, where LL represents a bridging bidentate ligand (e.g., RCO_2^-) and X is an axially coordinated ligand. Several years ago in an effort to obtain in crystalline form a $Cr_2(O_2CR)_4$-type molecule without axial ligation, we prepared $Cr_2(O_2CCPh_3)_4$ and crystallized it from benzene.[5] The idea here was that the bulky CPh_3 groups would prevent the type of intermolecular association which normally occurs (see I) in $Cr_2(O_2CR)_4$ compounds with R = CH_3,[6] CMe_3,[7] and *o*-PhC_6H_4[8] and no exogenous ligand would be available either. This strategy proved to be only partially effective. The bulk of the CPh_3 groups did lead to a packing arrangement in the crystal such that no intermolecular contacts between an oxygen atom of one molecule and the axial position of a neighbor occurred. However, benzene molecules were incorporated into the crystal in such a way that they served as a very unusual type of axial ligand, as shown schematically in II.



(I)

A theoretical analysis[5] of the nature of the axial interaction of the benzene molecules with the $Cr_2(O_2CCPh_3)_4$ molecules showed that while there are several components, the one that has the greatest effect on the Cr–Cr distance is donation from the

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