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Relative Stabilities and Interconversion of *exo*- and *endo*-Trithiatetrazocines. Preparation and Structure of *exo*-$Ph_2PN_4S_3NPPh_3$

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The effect of steric bulk at the 7-position of 1,3,5,2,4,6,8-trithiatetrazocines on the relative stabilities of exo and endo isomers has been probed by analysis of the isomer distribution in the sterically hindered derivative $Ph_2PN_4S_3NPPh_3$. ^{31}P NMR spectroscopy reveals that the exo isomer is favored, slightly, in solution. The exo isomer crystallizes preferentially; X-ray crystallographic analysis confirms the exo disposition of the exocyclic $-NPPh_3$ ligand. Interconversion of the two isomers, by means of a 1,3-nitrogen shift, is rapid at room temperature.

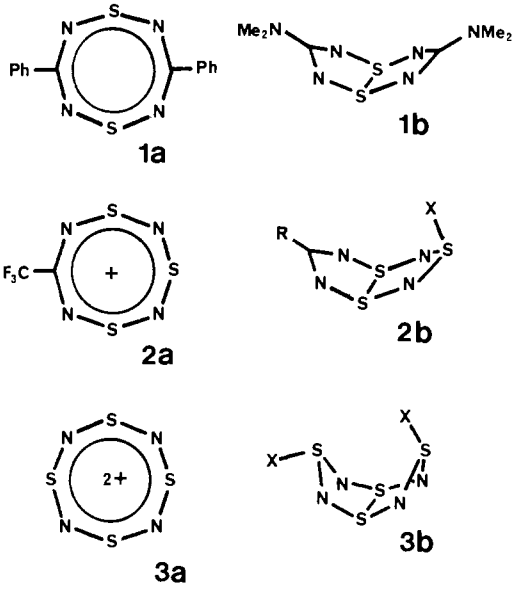
Introduction

Di-, tri- and tetrathiatetrazocines exist in one of two conformational motifs (Chart I). The 3,5-diphenyldithiatetrazocine (**1a**),[2] the trithiatetrazocinium cation $CF_3CN_4S_3^+$ (**2a**),[3] and the tetrathiatetrazocinium cation $S_4N_4^{2+}$ (**3a**)[4] all possess essentially planar structures, while the 3,5-dimethylaminodithiatetrazocine (**1b**),[2] all structurally characterized 3-substituted trithiatetrazocines (**2b**),[5] and 1,5-substituted tetrathiatetrazocines $S_4N_4X_2$ (**3b**)[6] are characterized by sharply puckered boatlike rings. The electronic origins for this dichotomy arise from the weakening of the cyclic π-system occasioned by the presence of (i) π-donor ligands at the heteroatom (as in **1b**) or (ii) the covalently bound substituents at sulfur (as in **2b** and **3b**).[7] Both perturbations induce an electronic instability that drives a second-order Jahn–Teller distortion of the cyclic framework into the folded conformation.[8]

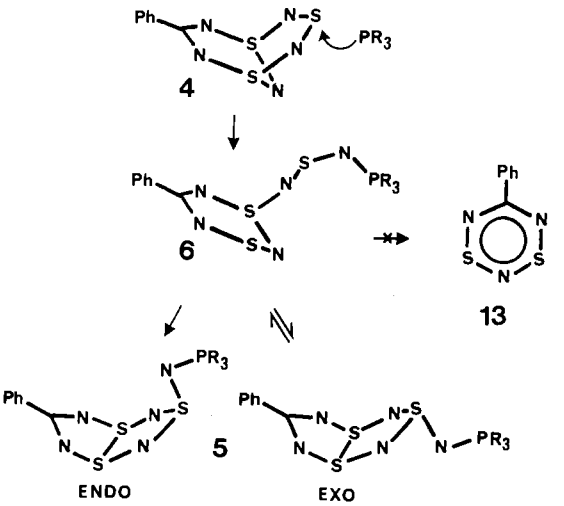
Our concerns in the present paper, however, stem not from this conformational isomerism, but from the configurational isomerism (exo and endo) possible for compounds such as **2b**. Although most structurally characterized derivatives of this type possess the endo geometry,[5] a recent study of the reactions of the bicyclic heterocycle $PhCN_5S_3$ (**4**) with tertiary phosphines established the existence of both the exo- and endo-trithiatetrazocines (**5**) (Scheme I).[9] The reactions were observed to proceed via the intermediate dithiatriazine (**6**), affording the exo isomer of **5** as the kinetically favored product. Indeed, in one case, the reaction involving triphenylarsine rather than triphenylphosphine, the exo isomer could be isolated and structurally characterized.[10] In all cases, however, this isomer completely converted, upon standing in solution for several minutes, into the thermodynamically preferred endo product. The proposed mechanism for the interconversion involved a series of 1,3-nitrogen shifts and the intermediacy of **6** (Scheme I).

In order to explore the exo/endo equilibrium, in particular the possibility that the subtle electronic factors which influence the balance between the two isomers can be offset by steric effects, we prepared the phosphatrithiatetrazocine system **7** (Scheme II). Our hope was that the large effective cone angle of the Ph_2P unit

Chart I



Scheme I



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Scheme II

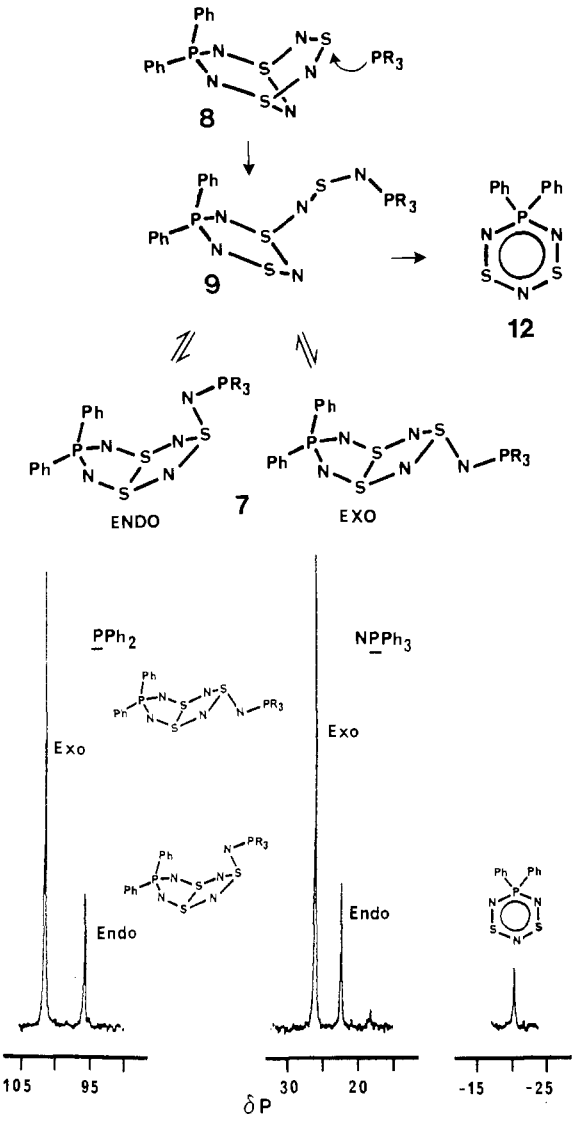


Figure 1. ^{31}P NMR spectrum of **7**.

might block the inside of the trithiatetrazocine "basket", thereby rendering the endo isomer less stable than its exo analogue. The results of this study are provided below.

Results and Discussion

Preparation of $Ph_2PN_4S_3NPPh_3$ (7). The preparative route to the phosphatrithiatetrazocines **7** was based on that already described for **5**. The required starting material, the bicyclic structure **8**, was prepared by the reaction of $Ph_2P(NSiMe_3)N(SiMe_3)_2$ with $S_3N_3Cl_3$. Subsequent treatment of **8** with triphenylphosphine then afforded **7**. The course of this reaction was conveniently monitored by ^{31}P NMR spectroscopy. As in our previous work[9] the resonance of the $-NPPh_3$ group provided a very reliable indicator of both structure and stereochemistry. The reaction of **8** with triphenylphosphine is relatively slow; mixing equimolar quantities of the two reagents at room temperature in chloroform did not lead to the rapid and specific generation of the expected intermediate **9** (Scheme II). Instead the ^{31}P signals of the two reagents slowly diminished over several minutes, to be replaced by two sets of signals corresponding to the *endo*- and *exo*-phosphatrithiatetrazocines (**7**). Several, much weaker signals were also observed, none of which could be assigned unequivocally. After several hours, the spectrum reflected the presence of the two trithiatetrazocines in an approximately 3:1 (exo:endo) ratio.

When the reaction of **8** with Ph_3P was performed in acetonitrile instead of chloroform, the exo isomer of **7** precipitated from solution in 76% yield. This material could be recrystallized from CH_2Cl_2/CH_3CN as pale yellow blocks, whose identity was confirmed by X-ray diffraction (vide infra) and also by redissolving the crystals in chloroform and checking the resultant ^{31}P NMR spectrum (Figure 1). At −40 °C only the signals of the *exo* isomer were observed, but when the solution was warmed to room temperature, the endo isomer rapidly grew in at the expense of the exo isomer. At equilibrium at room temperature the exo:endo ratio was approximately 3:1 (Figure 1), as in the crude reaction mixtures.

Table I. Partial Listing of Atomic Coordinates and Isotropic Thermal Temperature Factors (B_{eq}, Å^2) in *exo*-**7** with Esd's in Parentheses

atom	*x*	*y*	*z*	B_{eq}
S(1)	0.1872 (2)	0.1915 (1)	0.6578 (1)	4.09 (5)
S(2)	0.0604 (2)	0.17961 (9)	0.8001 (1)	3.19 (4)
S(3)	0.0998 (2)	0.0724 (1)	0.6857 (1)	3.86 (5)
P(1)	0.3555 (2)	0.10188 (9)	0.7729 (1)	3.17 (4)
P(2)	−0.0820 (2)	0.2462 (1)	0.90861 (1)	3.09 (4)
N(1)	0.3329 (5)	0.1698 (3)	0.7082 (3)	3.6 (1)
N(2)	0.0969 (5)	0.2265 (3)	0.7161 (3)	3.9 (1)
N(3)	0.0067 (4)	0.1063 (3)	0.7443 (4)	3.6 (1)
N(4)	0.2402 (5)	0.0453 (3)	0.7395 (4)	3.4 (1)
N(5)	−0.0732 (5)	0.2162 (3)	0.8109 (3)	3.5 (1)
C(1)	0.5043 (6)	0.0611 (4)	0.7634 (4)	3.5 (2)
C(2)	0.6214 (6)	0.0813 (3)	0.8186 (4)	3.5 (2)
C(3)	0.7370 (6)	0.0525 (4)	0.8070 (5)	4.1 (2)
C(4)	0.7371 (7)	0.0024 (4)	0.7438 (5)	5.3 (2)
C(5)	0.6220 (7)	−0.0185 (4)	0.6885 (6)	7.6 (2)
C(6)	0.5073 (7)	0.0112 (4)	0.6989 (5)	6.0 (2)
C(7)	0.3752 (6)	0.1246 (3)	0.8910 (4)	2.9 (2)
C(8)	0.3742 (7)	0.0744 (4)	0.9559 (5)	4.6 (2)
C(9)	0.3864 (7)	0.0913 (4)	1.0474 (5)	5.6 (2)
C(10)	0.4016 (7)	0.1591 (4)	1.0737 (5)	5.4 (2)
C(11)	0.4035 (7)	0.2097 (4)	1.0113 (5)	5.4 (2)
C(12)	0.3904 (6)	0.1931 (4)	0.9189 (5)	3.9 (2)

Table II. Selected Bond Distances (Å) and Angles (deg) in *exo*-**7** with Esd's in Parentheses

S(1)–S(2)	2.532 (3)	P(1)–N(1)	1.611 (5)
S(1)–N(1)	1.610 (5)	P(1)–N(4)	1.624 (5)
S(1)–N(2)	1.580 (5)	P(1)–C(1)	1.788 (7)
S(2)–N(2)	1.662 (5)	P(1)–C(7)	1.792 (7)
S(2)–N(3)	1.669 (5)	P(2)–N(5)	1.597 (5)
S(2)–N(5)	1.614 (5)	P(2)–C(13)	1.787 (7)
S(3)–N(3)	1.596 (5)	P(2)–C(19)	1.788 (7)
S(3)–N(4)	1.608 (5)	P(2)–C(25)	1.809 (7)
N(1)–S(1)–N(2)	118.7 (3)	N(5)–P(2)–C(13)	104.5 (3)
N(2)–S(2)–N(3)	100.7 (3)	N(5)–P(2)–C(19)	113.7 (3)
N(2)–S(2)–N(5)	101.3 (3)	N(5)–P(2)–C(25)	114.0 (3)
N(3)–S(2)–N(5)	102.1 (3)	C(13)–P(2)–C(19)	108.1 (3)
N(3)–S(3)–N(4)	117.8 (3)	C(13)–P(2)–C(25)	109.0 (3)
N(1)–P(1)–N(4)	110.7 (3)	C(19)–P(2)–C(25)	107.3 (3)
N(1)–P(1)–C(1)	108.7 (3)	S(1)–N(1)–P(1)	119.4 (3)
N(1)–P(1)–C(7)	111.6 (3)	S(1)–N(2)–S(2)	117.4 (3)
N(4)–P(1)–C(1)	107.1 (3)	S(2)–N(3)–S(3)	116.0 (3)
N(4)–P(1)–C(7)	112.5 (3)	S(3)–N(4)–P(1)	118.9 (3)
C(1)–P(1)–C(7)	106.0 (3)	S(2)–N(5)–P(2)	118.7(3)

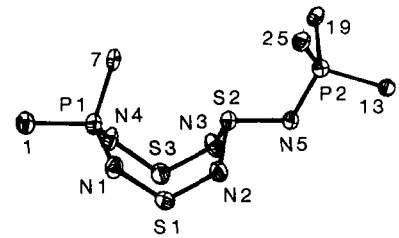


Figure 2. ORTEP drawing of the structure of *exo*-**7**.

Crystal and Molecular Structure of *exo*-$Ph_2PN_4S_3NPPh_3$. Atomic coordinates for the structure, which consists of discrete molecules of *exo*-**7** are provided in Table I; pertinent structural data are compiled in Table II. The ORTEP drawing in Figure 2 illustrates the structure and indicates the exo disposition of the exocyclic $-NPPh_3$ group. The endocyclic structural parameters

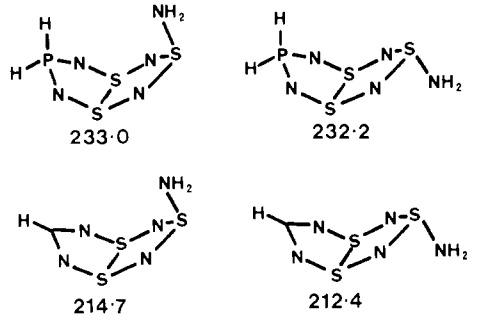
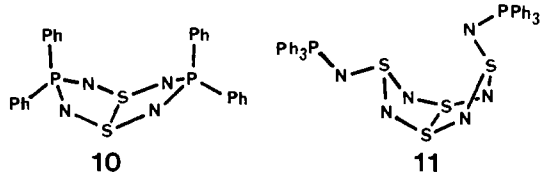


Figure 3. Heats of formation (kcal/mol) for model compounds.

of the eight-membered PN_4S_3 ring suggests, not surprisingly, that it can be considered as a composite of the two structures $(Ph_2P)_2N_4S_2$ (**10**)[11] and $(Ph_3PN)_2S_4N_4$ (**11**).[6c]



The Exo/Endo Balance in Trithiatetrazocines. The formation of *endo*-**5** (R = Ph) as the preferred isomer indicates a subtle but distinct thermodynamic preference for this configuration.

In order to probe the possibility that the switchover in relative exo/endo stabilities between **5** and **7** is electronic in origin, we performed a series of MNDO molecular orbital calculations on model structures related to **5** and **7**. In both model systems, the $-NPPh_3$ group was replaced by an NH_2 group, and the CPh and PPh_2 units of **5** and **7** were replaced respectively by CH and PH_2 units. The MNDO calculations were performed with full geometry optimization within C_s symmetry, and with the additional restriction that the transannular S---S contact was fixed at 2.6 Å for both exo and endo forms.[12] The predicted heats of formation of these models are summarized in Figure 3. The results suggest very little energetic difference between the exo and endo forms for either model (the predicted preference for the exo simply reflects the limit of reliability of the computational method when applied to molecules of this size). The conclusion that we draw is that the electronic energy balance for both model systems is much the same;[13] the reversal in the stabilities of the exo and endo isomers of **5** and **7** stems from a steric effect (not simulated by our calculations) rather than from any differences in their electronic structures.

The 1,3-Shift Reaction in 5 and 7. In our earlier study of the interconversion of the exo and endo isomers of **5** we proposed a mechanism involving the intermediacy of the dithiatriazine **6**, i.e. a ring contraction/expansion sequence facilitated by a series of 1,3-nitrogen shift steps.[9] As indicated above, the equilibrium for the reaction strongly favored the endo form. We suggest that the equilibrium of the exo and endo isomers of **7** proceeds via a similar mechanism. The absence of any spectroscopic evidence for the intermediacy of a six-membered species, i.e. **9**, suggests that, within the context of the 1,3-shift mechanism, **9** lies close to the transition state for the isomerization process. Attempts to perform a kinetic analysis of the exo–endo equilibration process were thwarted by the thermal lability of the phosphatrithiatetrazocine structure (a feature that is in marked contrast to the thermally robust carbon-based framework of **5**). Upon standing at or above room temperature in solution, **7** slowly degrades, changing color from orange to purple. ^{31}P NMR analysis (see Figure 1) reveals the gradual formation of the phosphadithiatriazine $Ph_2PN_3S_2$ (**12**) ($\delta(P) = -21.2$). Evidently loss of the $NSNPPh_3$ "tail" from the six-membered structure **9** to produce **12** (Scheme II) competes more successfully with the ring expansion/contraction sequence than it does in **6** to produce **13** (Scheme I). This observation is certainly in keeping with other elimination reactions leading to **12** and **13**.[14]

Table III. Crystallographic Data for *exo*-**7**

formula	$P_2S_3N_5C_{30}H_{25}$
fw	613.7
cryst size, mm	0.18 × 0.18 × 0.40
a, Å	10.552 (2)
b, Å	19.177 (3)
c, Å	15.008 (2)
β, deg	102.86 (1)
V, Å^3	2961 (2)
Z	4
space group	$P2_1/n$
D_{calc}, g cm^{-3}	1.38
linear abs coeff, cm^{-1}	3.7
scan technique	$\theta/2\theta$
scan speed, deg min^{-1}	4–16
scan width, deg	1.0 ± 0.3 tan θ
transm factors	0.93–0.95
R_i for data merge	0.03
h,*k*,*l* ranges	0 to 10, 0 to 18, −14 to +14 reflcns
no. of reflcns measd	3072
no. of unique data	2754
no. of dta with $F_o^2 > 3\sigma(F_o^2)$	1558
refined params	361
$R(F^2)$	0.037
$R_w(F^2)$	0.040
GOF	1.1
ext cor	none

Experimental Section

Starting Materials and General Procedures. *N*,*N*,*N*′-Tris(trimethylsilyl)diphenylphosphoramidine $Ph_2P(NSiMe_3)N(SiMe_3)_2$ was prepared, as described previously, from the reaction of Me_3SiN_3 (Aldrich) with $Ph_2PN(SiMe_3)_2$ (itself prepared from Ph_2PCl (Aldrich) with $LiN(SiMe_3)_2 \cdot Et_2O$).[15] $S_3N_3Cl_3$[16] was prepared by the oxidation of S_4N_4[17] with SO_2Cl_2 (Aldrich). The bicyclic compound **8** was prepared by the reaction of $Ph_2P(NSiMe_3)N(SiMe_3)_2$ with $S_3N_3Cl_3$.[18] All reactions and sample manipulations were carried out under an atmosphere of nitrogen or argon. ^{31}P NMR spectra were recorded on a Bruker WH-400 MHz spectrometer, using 10-mm tubes; chemical shifts are cited with reference to external H_3PO_4. Infrared spectra (CsI plates, Nujol mulls) were recorded on a Nicolet 20SX/C FTIR spectrometer. All melting points are uncorrected. Chemical analyses were performed by MHW Laboratories, Phoenix, AZ. The MNDO calculations were performed by using the MOPAC suite of programs.[19]

Preparation of *exo*-$Ph_2PN_4S_3NPPh_3$ (*exo*-7). A mixture of $Ph_2PN_5S_3$ (**8**) (0.52 g, 1.5 mmol) and triphenylphosphine (0.39 g, 1.5 mmol) was stirred in 20 mL of CH_3CN under nitrogen for 16 h. The resulting buff solid, *exo*-**7** (0.70 g, 76%), was filtered off and recrystallized from CH_2Cl_2/CH_3CN as pale yellow blocks, dec pt >160 °C. Anal. Calcd for $C_{30}H_{25}N_5P_2S_3$: C, 58.72; H, 4.11; N, 11.41. Found: C, 58.56; H, 4.21; N, 11.46. IR (Nujol mull): 1436 (m), 1116 (m), 1089 (w), 1037 (s), 1021 (s), 996 (m), 976 (m), 952 (s, br), 794 (m), 755 (m), 747 (m), 735 (m), 722 (s), 691 (s), 566 (s), 544 (w), 528 (s), 506 (m), 479 (m) cm^{-1}. δP ($CDCl_3$, external H_3PO_4 reference): 101.7 (Ph_2P), 26.2 ($NPPh_3$). $\delta(P)$ for the corresponding endo isomer: 95.9 (Ph_2P), 22.7 ($NPPh_3$).

Crystal Structure Analysis. Crystals of *exo*-**7** were obtained as yellow air-stable blocks by crystallization from CH_2Cl_2/CH_3CN. All X-ray data were collected on an Enraf-Nonius CAD-4 instrument at 293 K with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The data

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(12) Failure to invoke this restriction caused the trithiatetrazocine framework to unfold to a nearly planar form.
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crystal was mounted with epoxy on a glass fiber. Unit cell dimensions were obtained from a least-squares analysis of the diffractometer positions for 24 reflections with $18° < 2\theta < 20°$. Table III gives the cell dimensions and some of the details for and the results of data collection and structure refinement. The structure was solved by using MULTAN and refined by full-matrix least-squares methods that minimized $\sum w(\Delta F)^2$. All non-H atoms were refined anisotropically; H atoms were constrained to idealized positions (d(C-H) = 0.95 Å) with isotropic B values equal to 1.2B of the attached carbon atom.

Atomic scattering factors and anomalous dispersion corrections were taken from ref 20. All programs used were those provided by the Enraf-Nonius Structure Determination Package.

(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV, Tables 2.2B and 2.3.1.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERCC), the National Science Foundation (EPSCOR program), and the State of Arkansas for financial support. We also thank the NSERCC for a postdoctoral fellowship to S.W.L.

Registry No. 7, 122594-36-9; 8, 90498-60-5; $Ph_2P(NSiMe_3)N(SiMe_3)_2$, 61500-31-0; S_3N_3Cl, 5964-00-1; S_4N_4, 28950-34-7; triphenylphosphine, 603-35-0.

Supplementary Material Available: Tables of hydrogen atom coordinates (Table S1), distances and angles within the phenyl rings (Table S2), and thermal parameters (Table S3) for *exo*-7 (4 pages); a listing of observed and calculated structures factors for *exo*-7 (19 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4, and University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Cyclophospha(III)thiazenes: Preparation and Structural Comparison of *cis*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ and *trans*-$(CO)_5Cr[^iPr_2NP(NSN)_2PNPr^i_2]Cr(CO)_5$ and a Rational Synthesis of the $P^{III}N_3S_2$ Ring

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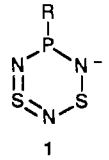
The reaction of $(CO)_5Cr(RPCl_2)$ (R = ^{t}Bu, $^iPr_2N$) with $(Me_2N)_3S^+NSO^-$ in acetonitrile produces the complexes *cis*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ (**4**) and *trans*-$(CO)_5Cr[^iPr_2NP(NSN)_2NPPr^i_2]Cr(CO)_5$ (**5**), which have been structurally characterized by X-ray crystallography. The crystals of **4** are monoclinic, space group $P2_1/n$, with a = 15.2435 (9) Å, b = 12.456 (1) Å, c = 16.078 (2) Å, β = 109.180 (7)°, V = 2883.3 (5) Å^3, and Z = 4. The final R and R_w values were 0.031 and 0.031, respectively. The crystals of **5** are monoclinic, space group $P2_1/c$, with a = 13.389 (3) Å, b = 13.280 (4) Å, c = 18.431 (3) Å, β = 104.12 (2)°, V = 3178 (1) Å^3, and Z = 4. The final R and R_w values were 0.062 and 0.052, respectively. The eight-membered $P^{III}_2N_4S_2$ ring in **4** is distorted from planarity toward a boat conformation with the phosphorus atoms ca. 0.20 Å above and the sulfur atoms ca. 0.12 Å below the plane of the ring. The trans derivative **5** possesses a noncrystallographic inversion center inside the $P^{III}_2N_4S_2$ ring, which is essentially planar with small distortions toward a chair conformation. The S-N bond lengths in **4** and **5** are in the range 1.50-1.52 Å, and the bond angles at sulfur are 124-125°. The bond angles at nitrogen are in the ranges 146-155 and 150-153°, respectively. The 1,4-cycloaddition reaction of $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$ with S_4N_4 in methylene dichloride, followed by treatment of the product with 2-propanol, yields the complex $(CO)_5Cr[P(Me_3SiNH)NSNSNH]$ (**3f**), which contains the six-membered $P^{III}N_3S_2$ ring system.

Introduction

The RP^{III} group is isoelectronic with a two-coordinate sulfur atom as a substituent in a sulfur-nitrogen ring system. Thus it is reasonable to propose the possibility of heterocycles such as **1** and **2** as phosphorus(III) analogues of the π-electron-rich systems



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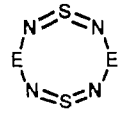

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$S_3N_3^-$ and S_4N_4, respectively.[1] In addition to the versatile ligand properties of these cyclic compounds, their molecular and electronic structures are of interest.[2]

Eight-membered rings of type **2** (E = PR) are unknown, although the first example of an As^{III} analogue (E = AsMe) was reported in 1971.[3] Subsequently, X-ray structural studies of **2** (E = PhAs,[4] MesAs,[4] ^{t}BuAs[5]) revealed a boat conformation for the ring with d(S-N) = 1.51-1.52 Å and ∠AsNS = 128-132°. The ligand **2** (E = AsR) can be incorporated into metal carbonyl complexes either as a monodentate or as a bidentate chelating ligand in which the As(III) atom(s) are bonded to one or two metal centers, respectively.[6-9] Neither the structural parameters nor the conformation of the ring is changed significantly upon coordination.[6-8] The arsenic compounds are obtained from the reaction of $RAsCl_2$ with either $Me_3SiNSNSiMe_3$ (E = AsMe,[3] AsPh,[4] AsMes[4]) or K_2NS_2 (E = AsBu^t)[5]. Metathetical reactions of these reagents with $RPCl_2$ do not give **2** (E = PR) even when R is a very bulky group.[9] However, Herberhold et al. have recently reported that the reaction of $(CO)_5Cr(RPCl_2)$ (R = ^{t}Bu, Ph) with

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(2) Structures **1** and **2** have been represented by use of localized sulfur diimide units, -N=S=N-, although it is possible that the lone pairs of electrons on phosphorus are involved in a delocalized π-system in these rings.
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