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.

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.

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Contribution from the Departments of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4,
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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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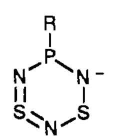
Johan C. van de Grampel,[‡] and Jan L. de Boer[‡]

Received February 16, 1989

The reaction of $(CO)_5Cr(RPCl_2)$ (R = ${}^tBu$, ${}^iPr_2N$) 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 $(CO)_5Cr[\overline{P(Me_3SiNH)NSNSN}H]$ (**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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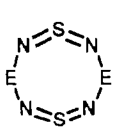

2

$S_3N_3^-$ 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] ${}^tBuAs$[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 = ${}^tBu$, Ph) with

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(1) Chivers, T. *Chem. Rev.* **1985**, *85*, 341.

(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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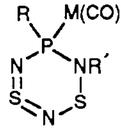
K_2SN_2 in acetonitrile produces **3a** and **3b**, respectively, as the major products.[10,11] An X-ray analysis of **3a** showed that the six-membered PN_3S_2 ring adopts a boat conformation with localized –N=S=N– and >N—S—N< units.[11] In contrast, the corresponding reaction with $Cr(CO)_5(AsBu^tCl_2)$ gives predominantly a mononuclear complex of **2** (E = $AsBu^t$) and only minor amounts of $Cr(CO)_5[\overline{As(Bu^t)NSNSNH}]$.[6]


3a (M = Cr, R = ^{t}Bu, R′ = H)
b (M = Cr, R = Ph, R′ = H)
c (M = Cr, R = NH_2, R′ = H)
d (M = W, R = NH_2, R′ = H)
e (M = Cr, R = $N(SiMe_3)_2$, R′ = $SiMe_3$)
f (M = Cr, R = $NH(SiMe_3)$, R′ = H)

In a preliminary communication,[12] we reported the formation of *trans*-$(CO)_5Cr[^iPr_2NP(NSN)_2PNPr_2^i]Cr(CO)_5$ (**5**), which contains an almost planar $P_2N_4S_2$ ring, from the reaction of $(CO)_5Cr(Pr_2^iNPCl_2)$ with $(Me_2N)_3S^+NSO^-$ in acetonitrile. We now describe the preparation of *cis*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ (**4**) in a similar manner and a structural comparison of the cis and trans isomers of binuclear $Cr(CO)_5$ complexes of **2** (E = PR). A rational approach to the synthesis of the ring system **1**, stabilized by coordination to an $M(CO)_5$ unit, is also reported.

Experimental Section

Reagents and General Procedures. All experimental procedures involving air- or moisture-sensitive compounds were performed under an atmosphere of dry nitrogen. Solvents were dried by heating them under reflux with the appropriate drying agent and were distilled before use. The following chemicals were prepared by published methods: KNSO,[13,14] TAS^+NSO^- [TAS^+ = $(Me_2N)_3S^+$],[9,15] $^tBuPCl_2$,[16] $^iPr_2NPCl_2$,[17] $(Me_3Si)_2NPNSiMe_3$,[18] $(CO)_5Cr(^tBuPCl_2)$,[19] $(CO)_5Cr(^iPr_2NPCl_2)$.[20] Chromatographic separations were performed by use of flash chromatography.[21]

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr windows) or solutions on a Nicolet DX-5 FTIR spectrometer. ^{31}P NMR spectra were obtained by use of a Varian XL-200 spectrometer, and ^{31}P chemical shifts are reported relative to external 85% H_3PO_4. ^1H NMR spectra were recorded by use of a Bruker 200 spectrometer. Chemical shifts are reported relative to external Me_4Si. Mass spectra were obtained on a Kratos MS80RFA instrument (EI/70 eV). Chemical analyses were performed by the Analytical Services Division of the Department of Chemistry, The University of Calgary.

Preparation of $(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$. A solution of $Cr(CO)_5(^tBuPCl_2)$ (1.8 g, 5.0 mmol) in acetonitrile (20 mL) was added dropwise to a stirred suspension of KNSO (1.01 g, 10 mmol) in acetonitrile (30 mL) at −20 °C. The reaction mixture was stirred at 23 °C for 60 h. Solvent was removed in vacuo and the residue was extracted with methylene dichloride (25 mL). The extract was passed through anhydrous Na_2SO_4, and the volume of the filtrate was reduced to 2 mL. Chromatography on a silica-60 column (2 × 20 cm) using a pentane/methylene dichloride (9:1) mixture as eluant gave two orange-red fractions. After removal of solvent, these products were recrystallized from hexane to give orange-red crystals of *cis*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ (0.37 g, 0.54 mmol) and orange-red crystals of *trans*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ (0.28 g, 0.41 mmol). The structure of the cis isomer was determined by X-ray crystallography. Anal. Calcd for $C_{18}H_{18}Cr_2N_4O_{10}P_2S_2$: C, 31.76; H, 2.67; N, 8.23. Found: C, 31.02; H, 2.87; N, 7.93. IR (Nujol): 1287 s, 1154 m, 1012 w cm^{-1}. IR (CCl_4): 2071 w, 2063 m, 1994 w, 1960 s, 1944 s cm^{-1}. ^1H NMR: $\delta[(CH_3)_3C]$ +1.22 (d), $^3J_{P-H}$ = 18.0 Hz. Spectroscopic data for the trans isomer. IR (Nujol): 1292 s, 1150 m, 1012 w cm^{-1}. IR (CCl_4): 2061 m, 2004 w, 1958 s, 1944 s cm^{-1}. ^1H NMR: $\delta[(CH_3)_3C]$ +1.33 (d, $^3J_{P-H}$ = 17.4 Hz).

Preparation of $(CO)_5Cr[^iPr_2NP(NSN)_2PN^iPr_2]Cr(CO_5)$. A solution of $(Me_2N)_3S^+NSO^-$ (0.90 g, 4.0 mmol) in acetonitrile (20 mL) was added dropwise to a solution of $(CO)_5Cr(^iPr_2NPCl_2)$ (0.79 g, 2.0 mmol) in acetonitrile (10 mL) at −20 °C. The reaction mixture was stirred at 23 °C for 16 h. Solvent was removed in vacuo, and the crude reaction mixture was extracted with methylene dichloride. Chromatography on a silica-60 (230–400 mesh) column (2 × 15 cm) with a mixture of hexane/methylene dichloride (2:1) as eluant gave an orange-red fraction. Solvent was removed from this fraction in vacuo, and the residue was recrystallized from hexane/methylene dichloride (4:1) to give orange-red crystals of $(CO)_5Cr[^iPr_2NP(NSN)_2PN^iPr_2]Cr(CO)_5$ (23 mg, 0.03 mmol). IR (Nujol): 1284 s, 1193 w, 1171 m, 1151 m, 1137 w, 1114 w, 1066 m, 174 s cm^{-1}. IR (CCl_4): 2060 m, 1990 w, 1948 s. ^{31}P NMR: $\delta(^{31}P)$ +112.6 ppm. The structure of this product was established by X-ray crystallography (vide infra).

Preparation of $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$.[22] A solution of $Cr(CO)_6$ (3.0 g, 13.6 mmol) in THF (250 mL) was irradiated (450-W Hanovia lamp) for 24 h at 20 °C. The orange solution was transferred to a 500-mL three-necked flask, and then $(Me_3Si)_2NPNSiMe_3$ (3.6 g, 12.9 mmol) was added by syringe. The reaction mixture was stirred at 23 °C for 16 h, and then solvent was removed in vacuo to give a viscous green liquid, which was dissolved in pentane/diethyl ether (50 mL, 10:1) to remove unreacted $Cr(CO)_6$ (60 mg) by filtration. Removal of solvent in vacuo gave $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$ (5.4 g, 11.5 mmol) as a thick green liquid, but numerous attempts at crystallization from various solvents were unsuccessful. This product exhibits a singlet at +298.0 ppm and no other signals were observed in the ^{31}P NMR spectrum. Consequently, the material so obtained was used without further purification in subsequent reactions.

Preparation of $Cr(CO)_5[\overline{P(Me_3SiNR)NSNSNR'}]$, (3e, R = R′ = $SiMe_3$; 3f, R = R′ = H). A mixture of solid S_4N_4 (0.61 g, 3.3 mmol) and $Cr(CO)_5[P(NSiMe_3)N(SiMe_3)_2]$ (3.0 g, 6.5 mmol) in methylene dichloride (150 mL) was stirred at 23 °C for 4 days. The solvent was removed under vacuum and the residue was extracted with *n*-pentane (150 mL) to give 0.42 g of insoluble material. Removal of the pentane from the filtrate under vacuum gave a very viscous dark yellow oil (3.0 g), which exhibited only one signal in the ^{31}P NMR spectrum (in $CDCl_3$) at +151.0 ppm. Attempts to crystallize this product were unsuccessful, but sublimation occurred very slowly at 55 °C (0.1 Torr) to give **3e** (0.70 g, 0.12 mmol) as yellow moisture-sensitive needles. MS: *m/e* 489 ($M^+ - SiMe_3$). Satisfactory analytical data could not be obtained for **3e** so the crude product was converted to the more easily crystallized derivative **3f** by the following procedure.

The reaction mixture obtained as described above was treated with 2-propanol (10 mL) and stirred for 1 more day. Solvents were removed in vacuo, and the residue was dissolved in methylene dichloride and passed through a silica-60 column using methylene dichloride as eluant. A dark orange fraction, which yielded a mixture of S_4N_4 and the product, was collected. This mixture was dissolved in pentane (to remove S_4N_4) and passed through a silica-60 column using pentane as eluant. Recrystallization of the product from pentane gave dark orange crystals of **3f** (0.13 g, 0.31 mmol), mp 89–90 °C. Anal. Calcd for $C_8H_{11}CrN_3O_5PS_2Si$: C, 22.96; H, 2.65; N, 13.39. Found: C, 22.77; H, 2.64; N, 13.21. IR (Nujol): 3363 w, 3292 w, 1252 s, 1098 s, 939 m, 840 m, 677 s, 651 s cm^{-1}. IR (CCl_4): 2069 s, 1967 m, 1959 s, 1942 vs cm^{-1}. ^1H NMR ($CDCl_3$): 4.06 (s, br, 1 H), 2.79 (d, $^2J_{P-H}$ = 12.0 Hz, 1 H), 0.37 (s, 9 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +110.9 ppm.

X-ray Analyses. A suitable bright red block-shaped crystal, 0.16 × 0.19 × 0.25 mm, of *cis*-$(CO)_5Cr[^tBuP(NSN)_2PBu^t]Cr(CO)_5$ (**4**) and a suitable bright red block-shaped crystal, 0.11 × 0.075 × 0.17 mm, of *trans*-$(CO)_5Cr[^iPr_2NP(NSN)_2PNPr^i_2]Cr(CO)_5$ (**5**) were glued on the

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Table I. Crystallographic Data for *cis*-(CO)$_5$Cr[^{t}BuP(NSN)PBu^t]-Cr(CO)$_5$ (**4**) and *trans*-(CO)$_5$Cr[^{i}Pr$_2$NP(NSN)$_2$PPr$_2^i$]Cr(CO)$_5$ (**5**)

	4	**5**
formula	$C_{18}H_{18}Cr_2N_4O_{10}P_2S_2$	$C_{22}H_{28}Cr_2N_6O_{10}P_2S_2$
fw	680.42	766.56
space group; no.	$P2_1/n$; 14	$P2_1/c$; 14
a, Å	15.2435 (9)	13.389 (3)
b, Å	12.456 (1)	13.280 (4)
c, Å	16.087 (2)	18.431 (3)
β, deg	109.180 (7)	104.12 (2)
V, Å^3	2883.3 (5)	3178 (5)
Z	4	4
T, K	298	110
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.567	1.602
μ, cm^{-1}	10.4	9.5
R, R_w^{a}	0.031, 0.031	0.062, 0.052

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

top of a glass fiber and mounted on an Enraf-Nonius CAD-4F diffractometer. Unit cell dimensions and their standard deviations were determined from the setting angles of 17 reflections in the range 16.94° < θ < 17.41° for **4** and of 22 reflections in the range 6.29° < θ < 10.38° for **5** in four alternate settings,[23] respectively. Reduced cell calculations did not indicate any higher lattice symmetry.[24] Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 2 h of X-ray exposure time; there was no indication of crystal decomposition. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects; correction for absorption was judged to be not necessary in view of the observed small intensity variation for a 360° Ψ-scan of the reflections (301) close to axial for **4** and (060) for **5**, respectively. Variance, $\sigma^2(I)$, was calculated on the basis of counting statistics and the term (P^2I^2), where P (=0.006 and 0.022, respectively) is the instability constant as derived from the excess variance in the reference reflections.[25] Pertinent numerical data on the structure determinations are given in Table I.

The structure of **4** was solved by direct methods using the program SHELXS86.[26] Refinement on F was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located on a difference Fourier map. In the final calculation H atoms were refined with one overall temperature factor. Convergence was reached at $R = 0.031$.

One Cr atom of **5** could be located by Patterson techniques (SHELXS86[26]). Extension of the model was accomplished by direct methods applied to difference factors using the program DIRDIF.[27] Refinement on F was carried out by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. At this stage of the refinement, 21 (of 28) hydrogen atoms could be located on a difference Fourier map. The positions of the remaining H atoms were calculated from an sp^3 hybridization at C. Due to the low observation (no. of observations = 2551) to parameter (no. of refined parameters = 398) ratio (=6.4), in the final calculation, H atoms were refined in the riding mode with fixed C–H bond lengths of 1.0 Å and one overall temperature factor. Convergence was reached at $R = 0.062$. The temperature factors of N(3) and C(18) were nonpositive definite and some atoms showed unrealistic temperature factors, suggesting some degree of disorder, which is in line with the weak scattering power of the crystals investigated.

Final difference Fourier maps for both structures did not show any significant residual features. For both structures neutral-atom scattering factors[28] were used with anomalous dispersion corrections[29] being applied to the non-hydrogen atoms. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program XTAL[30] and the EUCLID[31] package.

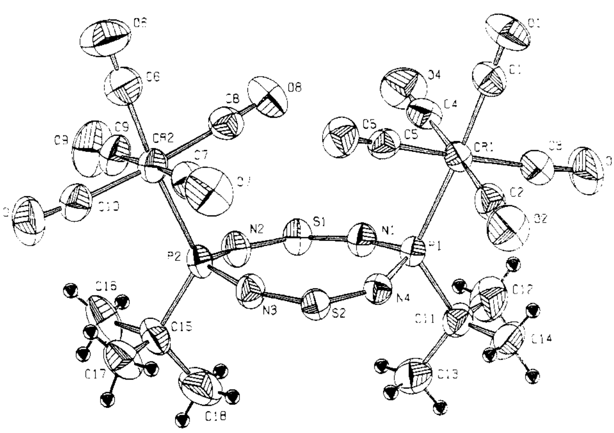

Figure 1. ORTEP drawing and the atomic numbering scheme for *cis*-(CO)$_5$Cr[^{t}BuP(NSN)$_2$PBu^t]Cr(CO)$_5$ (**4**).

Results and Discussion

Preparation of Binuclear Cr(CO)$_5$ Complexes of the R$_2$P$^{III}{}_2$N$_4$S$_2$ Ring. Metal carbonyl complexes of R$_2$PNSO ligands are readily obtained in good yields from the corresponding R$_2$PCl complexes via metathetical reactions with the NSO$^-$ ion.[13] The treatment of these complexes with potassium *tert*-butoxide promotes condensation to give binuclear complexes of acyclic sulfur diimides.[13]

$$2ML_n(R_2PNSO) \xrightarrow[-SO_2]{KO^tBu} L_nMP(R)_2NSN(R)_2PML_n \quad (1)$$

The attempted extension of this synthetic method to metal carbonyl complexes of RP(NSO)$_2$ results in the direct formation of binuclear complexes of the eight-membered ring R$_2$P$^{III}{}_2$N$_4$S$_2$ (**2** (E = PR)).

$$2Cr(CO)_5(RPCl_2) + 4KNSO \xrightarrow{-2SO_2} (CO)_5Cr[RP(NSN)_2PR]Cr(CO)_5 + 4KCl \quad (2)$$

The reaction of Cr(CO)$_5$(RPCl$_2$) (R = ^{t}Bu, ^{i}Pr$_2$N) with KNSO in a 1:2 molar ratio in acetonitrile at −20 °C gave soluble products that could be isolated as orange-red, air-stable crystals after chromatography on silica. When R = ^{t}Bu, the major product was shown by X-ray crystallography to be *cis*-(CO)$_5$Cr[^{t}BuP(NSN)$_2$PBu^t]Cr(CO)$_5$ (**4**). In the IR spectrum, compound **4** shows bands at 1287 s and 1154 m cm^{-1} attributed to ν_{as}(NSN) and ν_s(NSN), respectively,[33] and the typical pattern of bands in the 1900–2100-cm^{-1} region for a Cr(CO)$_5$ group.[9] The ^{1}H NMR spectrum shows a doublet ($^3J_{P-H}$ = 18.0 Hz) at δ +1.22. A second product, which has spectroscopic characteristics similar to those of **4**, was isolated. In the IR spectrum, bands characteristic of the NSN group were observed at 1292 and 1150 cm^{-1}, in addition to the distinctive group of bands in the 1900–2100-cm^{-1} region for a Cr(CO)$_5$ moiety, and the ^{1}H NMR spectrum exhibits a doublet ($^3J_{P-H}$ = 17.4 Hz) at δ +1.33. In view of the close correspondence between the spectra of the minor product and those of **4**, we propose that it is *trans*-(CO)$_5$Cr[^{t}BuP(NSN)$_2$PBu^t]-Cr(CO)$_5$. Crystals suitable for an X-ray structural determination could not be obtained. However, in the case of R = ^{i}Pr$_2$N, the product that was isolated from reaction 2 by chromatography was shown by X-ray crystallography to be *trans*-(CO)$_5$Cr[^{i}Pr$_2$NP-(NSN)$_2$PNPr$_2^i$]Cr(CO)$_5$ (**5**) although the yield was low. When R = Ph, reaction 2 produced a black insoluble powder, which could not be identified.

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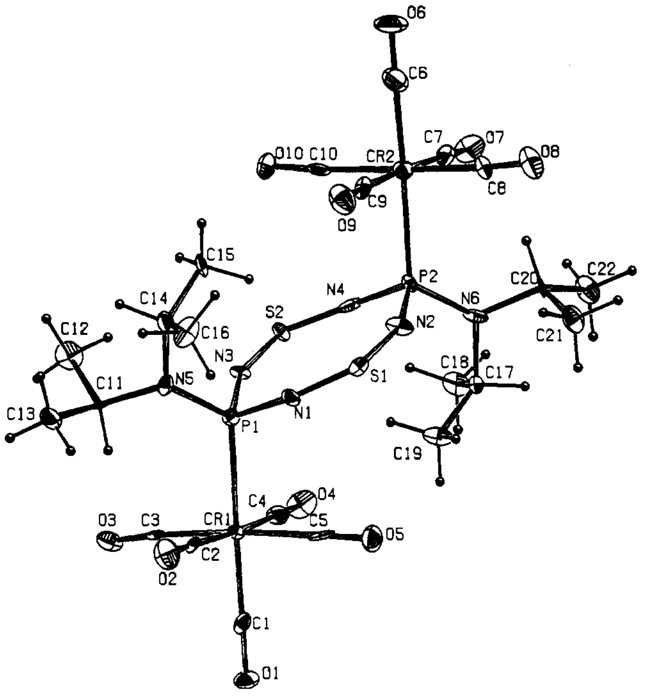

Figure 2. ORTEP drawing and the atomic numbering scheme for *trans*-(CO)$_5$Cr[Pr$^i_2$NP(NSN)$_2$PNPr$^i_2$]Cr(CO)$_5$ (**5**).

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for *cis*-(CO)$_5$Cr[^{t}BuP(NSN)$_2$PBu^t]Cr(CO)$_5$ (**4**) and *trans*-(CO)$_5$Cr[Pr$_2{}^i$NP(NSN)$_2$PNPr$_2{}^i$]Cr(CO)$_5$ (**5**)

4		**5**	
P(2)–N(3)	1.671 (3)	P(1)–N(1)	1.668 (8)
P(2)–N(2)	1.680 (4)	P(1)–N(3)	1.690 (8)
P(1)–N(4)	1.687 (4)	P(2)–N(2)	1.705 (8)
P(1)–N(1)	1.673 (3)	P(2)–N(4)	1.679 (8)
S(2)–N(3)	1.498 (3)	S(1)–N(1)	1.522 (2)
S(2)–N(4)	1.511 (4)	S(1)–N(2)	1.502 (8)
S(1)–N(2)	1.504 (4)	S(2)–N(3)	1.522 (8)
S(1)–N(1)	1.501 (3)	S(2)–N(4)	1.512 (8)
N(3)–P(2)–N(2)	111.6 (2)	N(1)–P(1)–N(3)	110.0 (4)
N(1)–P(1)–N(4)	111.7 (2)	N(2)–P(2)–N(4)	109.4 (4)
P(2)–N(3)–S(2)	154.2 (3)	P(1)–N(1)–S(1)	150.2 (6)
P(2)–N(2)–S(1)	147.0 (2)	P(1)–N(3)–S(2)	152.8 (6)
P(1)–N(4)–S(2)	146.3 (2)	P(2)–N(2)–S(1)	152.7 (6)
P(1)–N(1)–S(1)	155.0 (3)	P(2)–N(4)–S(2)	150.1 (6)
N(3)–S(2)–N(4)	124.7 (2)	N(1)–S(1)–N(2)	125.4 (5)
N(2)–S(1)–N(1)	123.9 (2)	N(3)–S(2)–N(4)	124.4 (5)

The difference in the identities of the isolated products obtained from reaction 2 and that observed by Herberhold et al.[10,11] for the reaction of Cr(CO)$_5$(^{t}BuPCl$_2$) with SN$_2{}^{2-}$ deserves further comment. The initial product of the latter reaction is probably a binuclear acyclic sulfur diimide,[34] by analogy with the reactions of M(CO)$_5$(R$_2$PCl) with SN$_2{}^{2-}$.[34,35] A subsequent [1,3] sigmatropic rearrangement of a chlorine atom from phosphorus to sulfur would give an intermediate, which, upon reaction with SN$_2{}^{2-}$, could generate (after hydrolysis) the observed six-membered ring, **3a**. In the case of the NSO$^-$ reaction it seems reasonable to propose the formation of Cr(CO)$_5$[RP(NSO)$_2$],[36] which undergoes condensation with the loss of SO$_2$ in the presence of KNSO to give the observed products **4** and **5**.

Scheme I. 1,4-Cycloaddition Reaction of (CO)$_5$Cr[P(NSiMe$_3$)N(SiMe$_3$)$_2$] with S$_4$N$_4$

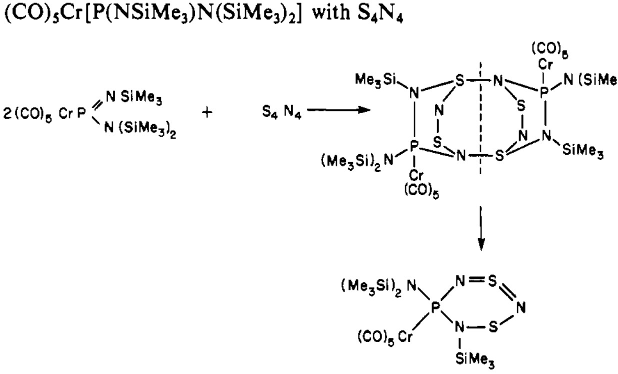

Table III. IR (cm^{-1}) and NMR Data for Compounds **3a**, **3b**, **3c**, and **3f**

	3a[a]	**3b**[a]	**3c**[a]	**3f**[b]
ν(CO)	2068 m 1956 s 1940 vs	2071 m 1971 s 1955 vs	2076 m 1952 vs	2069 s 1967 m 1959 s 1942 vs
ν_{as}(NSN)	1107 s	1099 s	1085 s	1098 s
ν(NHR)[c]			3433 m 3315 m	3363 w
ν(NH)[d]	3247 m	3323 m	3227 m	3292 w
δ(^{31}P)[e]	131.7	115.2	105.6	110.9
δ(NHR)[c,f]			3.50 d	2.79
$^2J_{P-H}$[g]			5.7	12.0
δ(NH)[d,f]	4.26 br	4.50 d	4.26 d, br	4.06 br
$^2J_{P-H}$[g]		8.2	5.4	

[a] Data taken from ref 11. [b] This work. [c] Exocyclic group: **3c** (R = H); **3f** (R = SiMe$_3$). [d] Endocyclic group. [e] In ppm (reference external 85% H$_3$PO$_4$). [f] d = doublet. [g] In Hz.

X-ray Crystal Structures of *cis*-(CO)$_5$Cr[^{t}BuP(NSN)$_2$PBu^t]Cr(CO)$_5$ (4) and *trans*-(CO)$_5$Cr[^{i}Pr$_2$NP(NSN)$_2$PNPr$^i_2$]Cr(CO)$_5$ (5).

ORTEP 32 drawings of **4** and **5** with the atomic numbering schemes are displayed in Figures 1 and 2, respectively, and the pertinent bond lengths and bond angles are compared in Table II. The trans derivative, **5**, possesses a noncrystallographic inversion center inside the ring, which is essentially planar with small distortions toward a chair conformation. The phosphorus atoms are 0.08 (1) Å out of and on opposite sides of the best P$^{III}{}_2$N$_4$S$_2$ plane. In contrast, the cis derivative **4** is distorted from planarity toward a boat conformation with P(1) and P(2) above the plane by 0.188 (7) and 0.204 (6) Å, respectively. The bond angles at nitrogen of 146–155° for **4** and 150–153° for **5** are unusually large compared to the values found for **2** (E = RAs)[4,5] and metal complexes of **2** (E = RAs),[6,8] presumably as a consequence of the near planarity of the rings in **4** and **5** (cf. N$_4$P$_4$F$_8$, ∠PNP = 147.2°).[37] Nevertheless, the values of the S–N bond lengths of 1.50–1.52 Å and the bond angles of 124–125° at sulfur in **4** and **5** are of the same order as those in metal carbonyl complexes of **2** (E = AsR)[6-8] and indicate sulfur diimide (–N=S=N–) character. The endocyclic P–N bond lengths in **4** and **5** are in the ranges 1.67–1.69 and 1.67–1.71 Å, respectively; cf. d(P–N) = 1.70–1.73 Å for metal complexes of R$_2$PNSNPR$_2$,[34,35,38,39] consistent with an increase in the s character of the nitrogen bonding orbitals. The exocyclic P–N bond lengths of ca. 1.66 Å in **5** and the almost planar geometry at these nitrogen atoms [sum of angles at N(5) of 356 (1)°, at N(6) of 357 (1)°] indicate strong N(pπ)–P(dπ) contributions; cf. (Pr$_2{}^i$NPO)$_3$[40] and (CO)$_5$Cr(Pr$_2{}^i$NPO).[41] The structural parameters involving the Cr(CO)$_5$

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(34) Structural studies of binuclear metal carbonyl complexes of R$_2$PNSNPR$_2$ show that the ligand adopts a cis, trans geometry. (a) Chivers, T.; Lensink, C.; Richardson, J. F. *Organometallics* **1986**, *5*, 819. (b) Hübner, T.; Gieren, A. *Z. Kristallogr.* **1986**, *174*, 95.

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groups in **4** and **5** are unremarkable. In summary, the overall structures of **4** and **5** appear to be those of cyclic sulfur diimides with almost planar conformations enforced by the bulky groups on phosphorus.

Preparation and Spectroscopic Characterization of $Cr(CO)_5$-$[\overline{P(Me_3SiNR)NSNSNR'}]$ (3e, R = R' = $SiMe_3$; 3f, R = R' = H). Recently, we reported a high yield synthesis of the $P^VN_3S_2$ ring,[42] which exploited an earlier discovery by Appel and Halstenberg[43] of the double 1,4-cycloaddition reaction of a P=N bond in a λ^5-iminophosphine with S_4N_4. In this investigation, we have used this synthetic approach for the preparation of metal carbonyl complexes of the $P^{III}N_3S_2$ ring **1** in its protonated form. The $Cr(CO)_5$ complex of $Me_3SiN{=}P{-}N(SiMe_3)_2$ is obtained as a viscous green liquid by treatment of $Cr(CO)_5(THF)$ with the λ^3-iminophosphine.[22] The 1,4-cycloaddition reaction of the complex so obtained with S_4N_4 in a 2:1 molar ratio proceeds slowly at 23 °C in methylene dichloride and is complete after 4 days to give one major phosphorus-containing product (Scheme I). The crude product **3e** was obtained in ca. 80% yield as a viscous yellow oil, which could be purified by sublimation only with great difficulty. Treatment of this product with Pr^iOH produced orange crystals of **3f**. The IR and spectroscopic data for **3f**, which are compared with the corresponding data for **3a-c** in Table III, indicate the presence of nonequivalent N-H groups, one endocyclic and one exocyclic. This conclusion was confirmed by the X-ray structural determination of **3f**.[44]

A variety of λ^3-iminophosphines, RP=NR', are available,[45] and we have investigated briefly the extension of the synthetic approach illustrated in Scheme I to the preparation of the free ligand, **1**, as its N-protonated or N-alkylated derivative. The reactions of S_4N_4 with RP = NR' (R = $(Me_3Si)_2N$, R' = $SiMe_3$; R = $Pr^i{}_2N$, R = ${}^tBu$) in toluene at 0 °C give dark red solutions containing a mixture of at least five products (^{31}P NMR spectra). In view of the ambident reactivity of RP = NR', it is likely that nucleophilic degradation of S_4N_4 by the phosphorus(III) reagent[46] competes with the 1,4-cycloaddition reaction. Thus the success of this route to **1** is dependent on the prevention of nucleophilic degradation by coordination of the phosphorus lone pair to a metal center.

Conclusions. The reaction of $Cr(CO)_5(RPCl_2)$ with 2 mol of NSO^- produces binuclear complexes of the novel ligand, **2** (E = PR). Both cis (R = ${}^tBu$) and trans (R = $Pr^i{}_2N$) isomers of these complexes have been structurally characterized. The eight-membered $P^{III}{}_2N_4S_2$ rings in these complexes adopt almost planar conformations as a result of the bulky groups on phosphorus. A rational synthesis of the protonated form of the $P^{III}N_3S_2$ ring, as a complex with $Cr(CO)_5$, has been discovered. This new approach is not suitable for the preparation of the free ligand **1**, as an N-protonated or N-alkylated derivative, but it can probably be extended to other complexes of type **3**. The structural parameters for $Cr(CO)_5$ complexes of the ligands **1**, in its protonated form, and **2** (E = PR) are indicative of localized -N=S=N- units in the cyclophospha(III)thiazene rings.

Acknowledgment. We thank the NSERC (Canada) for financial support and Mark Edwards for carrying out the reactions of λ^3-phosphinimines with S_4N_4. We are also grateful to Professor M. Herberhold (Universität Bayreuth) for helpful correspondence and a preprint of ref 11.

Supplementary Material Available: Tables listing crystal data, atom coordinates, thermal parameters, bond distances, bond angles, and torsion angles for **4** and **5** (22 pages); tables of calculated and observed structure factors for **4** and **5** (36 pages). Ordering information is given on any current masthead page.

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[44] The structure of **3f** is very similar to that reported for **3a**.[11] The $P^{III}N_3S_2$ ring in **3f** adopts a half-boat conformation with two short (1.560 (6) and 1.571 (7) Å) and two long (1.654 (7) and 1.684 (6) Å) S-N bond lengths and bond angles of 119.4 (4) and 107.6 (3)° at the two sulfur atoms. Chivers, T.; Fait, J. F.; Lensink, C. *Acta Crystallogr.*, in press.

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Syntheses and Characterization of Trigonal-Bipyramidal Rhodium(I) Complexes of Tris(2-(diphenylphosphino)ethyl)phosphine and Determination of a Spectroscopic Trans-Influence Series by $^{31}P\{^1H\}$ NMR Spectroscopy[1]

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Received August 19, 1988

A series of low-spin, five-coordinate rhodium(I) complexes of the tripod ligand tris(2-(diphenylphosphino)ethyl)phosphine, PP_3, were synthesized and characterized by elemental analyses, infrared spectra, and $^{31}P\{^1H\}$ NMR spectra. The complexes have trigonal-bipyramidal geometries in which the PP_3 ligand occupies four of the five sites of C_{3v} symmetry and the variable fifth ligand is monodentate. The ^{31}P NMR spectral patterns are consistent with AMX_3 and $AKMX_3$ spin systems. The NMR spectra permit a determination of the trans influence of the fifth ligand on the rhodium-phosphorus apical coupling constant and the chemical shifts of the apical and equatorial phosphorus atoms of PP_3.

Introduction

The synthesis and characterization of new five-coordinate complexes and the coordination properties of chelating polydentate ligands such as tris(2-(diphenylphosphino)ethyl)phosphine, $P(CH_2CH_2PPh_2)_3$ (PP_3), continue to be active areas of research.[3-9] The chelating tetradentate ligand PP_3 is ideally suited for synthesis of low-spin, trigonal-bipyramidal complexes with C_{3v} symmetry; $^{31}P\{^1H\}$ NMR studies on those resultant complexes should permit an evaluation of the electronic and steric properties of the variable

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[1] Presented at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, 1985; see Abstract INOR 208. Abstracted from the M.S. thesis of J.J.G., The Ohio State University, 1985.

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