Preparation and *X*-Ray Crystal Structure of *trans*-$\mathrm{(CO)_5Cr[Pr^i_2NP(NSN)_2PNPr^i_2]Cr(CO)_5}$, a Binuclear Complex of a Planar $\mathrm{P^{III}_2N_4S_2}$ Ring

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The reaction of $\mathrm{(CO)_5Cr(Pr^i_2NPCl_2)}$ with $\mathrm{(Me_2N)_3S^+NSO^-}$ in acetonitrile produces, in low yield, *trans*-$\mathrm{(CO)_5Cr[Pr^i_2NP(NSN)_2PNPr^i_2]Cr(CO)_5}$ shown by *X*-ray crystallography to contain an almost planar $\mathrm{P_2N_4S_2}$ ring.

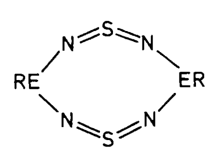
Eight-membered rings of the type (**1**) (E = As) are readily obtained from the reaction of $\mathrm{RAsCl_2}$ with either $\mathrm{Me_3SiNSNSiMe_3}$ (R = Me,[1] Ph,[2] mesityl[2]) or $\mathrm{K_2NS_2}$ (R = $\mathrm{Bu^t}$).[3] Metathetical reactions of these reagents with $\mathrm{RPCl_2}$ do not give (**1**) (E = P),[4] however, and Herberhold *et al.* have recently reported that treatment of $\mathrm{Cr(CO)_5(PBu^tCl_2)}$ with $\mathrm{K_2SN_2}$ in acetonitrile produces $\mathrm{Cr(CO)_5[\overline{P(Bu^t)NSNSN}H]}$, a complex of a six-membered ring.[5] We now describe the first example of a $\mathrm{P^{III}_2N_4S_2}$ ring system, (**1**) (E = P, R = $\mathrm{Pr^i_2N}$), which was isolated as a bis-$\mathrm{Cr(CO)_5}$ complex. Surprisingly, the heterocyclc ring in this complex adopts an almost planar structure.

The synthesis of complexes of (**1**) (E = P) is based on our finding that a co-ordinated $\mathrm{R_2PNSO}$ ligand is converted to an acylic sulphur diimide $\mathrm{R_2PNSNPR_2}$ in high yields upon treatment with potassium t-butoxide.[6] The application of this method to $\mathrm{RP(NSO)_2}$ complexes is shown here to provide a source of the co-ordinated ligand (**1**) (E = P, R = $\mathrm{Pr^i_2N}$).

$$\mathrm{2ML_{\mathit{x}}[R_{3\text{-}\mathit{n}}P(NSO)_{\mathit{n}}]} \xrightarrow{-n\mathrm{SO_2}} \mathrm{L_{\mathit{x}}M[R_{3\text{-}\mathit{n}}P(NSN)_{\mathit{n}}PR_{3\text{-}\mathit{n}}]ML_{\mathit{x}}} \quad (1)$$

Orange-red crystals of $\mathrm{(CO)_5Cr[Pr^i_2NP(NSN)_2PNPr^i_2]Cr(CO)_5}$ (**2**) were obtained in low yield (3%) from the reaction of $\mathrm{(Me_2N)_3S^+NSO^-}$[7] with $\mathrm{Cr(CO)_5(Pr^i_2NPCl_2)}$[8] in a 2:1 molar ratio in acetonitrile at 23 °C followed by chromatography on silica using hexane/$\mathrm{CH_2Cl_2}$ (2:1) as eluant: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. (in $\mathrm{CDCl_3}$) + 112.5 p.p.m.; i.r. (Nujol): 1284s, 1193w, 1171m, 1151m, 1137w, 1114m, 1006m, 974s, 653vs, 560m, 458m $\mathrm{cm^{-1}}$; (in $\mathrm{CCl_4}$): 2060m,sh, 1990w, 1948s, $\mathrm{cm^{-1}}$.

The structure of (**2**) was determined by *X*-ray crystallography.† The molecular geometry and atomic numbering scheme are shown in Figure 1. The $\mathrm{As_2N_4S_2}$ in (**1**) (E = As, R = Ph,[2] mesityl,[2] $\mathrm{Bu^t}$[3]) adopts a boat conformation and the ring geometry and structural parameters do not change substantially in the complex, $\mathrm{Os_3(CO)_{10}[Bu^tAs(NSN)_2AsBu^t]}$.[9] By contrast the geometry of the $\mathrm{P_2N_4S_2}$ ring in (**2**) approaches planarity with the bulky $\mathrm{Pr^i_2N}$ and $\mathrm{Cr(CO)_5}$ substituents in *trans*-positions. The molecule possesses a non-crystallographic inversion centre inside the ring, which is distorted towards a chair conformation with the following deviations from the best plane, P(1) +0.08, N(1) −0.05, S(1) −0.02, N(2) +0.04, P(2) −0.08, N(4) +0.09, S(2) −0.03, N(3) −0.09 Å. The bond angles of 150—153° at nitrogen in (**2**) are unusually large compared to the values of 128—135° found for (**1**) (E = As)[2,3] and the metal complex $\mathrm{Os_3(CO)_{10}[Bu^tAs(NSN)_2AsBu^t]}$,[9] presumably as a consequence of the planarity of the ring, *cf.* $\mathrm{(NPF_2)_4}$, <PNP 147°.[10] The endocyclic P–N bond lengths are in the range 1.67—1.71 Å, *cf.* *d*(P–N) 1.70—1.73 Å for complexes of $\mathrm{R_2PNSNPR_2}$ (R = Ph,[11,12] $\mathrm{Bu^t}$[13]), consistent with an increase in s character of the nitrogen bonding orbitals. The exocyclic P–N bond lengths of



(1)

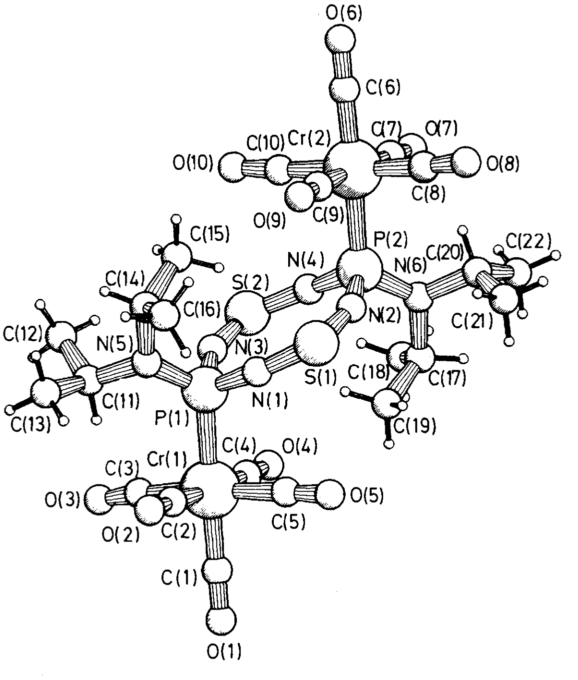


Figure 1. A PLUTO drawing of $\mathrm{(CO)_5Cr[Pr^i_2NP(NSN)_2PNPr^i_2]Cr(CO)_5}$ (**2**). Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.668(8), P(1)–N(3) 1.690 (8), P(1)–N(5) 1.663(7), P(2)–N(2) 1.705(8), P(2)–N(4) 1.679(8), P(2)–N(6) 1.653(7); S(1)–N(1) 1.522(8), S(1)–N(2) 1.502(8), S(2)–N(3) 1.522(8), S(2)–N(4) 1.512(8); N(1)–P(1)–N(3) 110.0(4), N(2)–P(2)–N(4) 109.5(4), P(1)–N(1)–S(1) 150.2(6), P(1)–N(3)–S(2) 152.8(6), P(2)–N(2)–S(1) 152.7(6), P(2)–N(4)–S(2) 150.1(6), N(1)–S(1)–N(2) 125.4(5), N(3)–S(2)–N(4) 124.4(5).

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† *Crystal data*: $\mathrm{C_{22}H_{28}Cr_2N_6O_{10}P_2S_2}$ (**2**), M = 766.6, monoclinic, space group $P2_1/c$ (No. 14); at 110 K a = 13.389(3), b = 13.280(4), c = 18.431(3) Å, β = 104.12(2)°, U = 3178 Å^3, Z = 4, μ(Mo-K_α) = 9.5 $\mathrm{cm^{-1}}$, $F(000)$ = 1568, D_c = 1.602 g $\mathrm{cm^{-3}}$. Intensity data were collected at 110 K on an Enraf-Nonius CAD-4F diffractometer operating in the ω–2θ mode and using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). Total number unique reflections 5580, of which 2551 had $I > 2.5\,\sigma(I)$. Crystal dimensions 0.075 × 0.11 × 0.17 mm. The structure was solved by Patterson techniques (SHELXS86) and direct methods (DIRDIF) and was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms to R 0.062 and R_w 0.052.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ca. 1.66 Å and the almost planar geometry at these nitrogen atoms [sum of angles at N(5) 356.2°, at N(6) 356.7°] indicate strong N(pπ)–P(dπ) contributions, *cf.* $(Pr^i_2NPO)_3$[14] and $(CO)_5Cr(Pr^i_2NPO)$.[15] The values of S–N bond lengths of 1.50—1.52 Å and the bond angles of 124—125° at sulphur are typical for cyclic sulphur diimides.[2,3,9,16] Thus the overall structure appears to be that of a cyclic sulphur diimide with an almost planar ring conformation imposed by the bulky groups on phosphorus.

We propose that (**2**) is formed *via* a condensation reaction [equation (1), $n = 2$] in which $(Me_2N)_3S^+NSO^-$ serves as the base to promote SO_2 elimination. However, the reactions of the bifunctional complexes $L_xM(RPCl_2)$ with NSO^- are more complicated than the corresponding reactions of $L_xM(R_2PCl)$,[6] as indicated by ^{31}P n.m.r. spectra of reaction mixtures. Further investigations of these reactions are in progress in an effort to identify other products that decompose on a variety of chromatography columns. Finally we note that attempts to prepare arsenic analogues of the binuclear complex (**2**) from (**1**) (E = As, R = Ph, Bu^t) and $Cr(CO)_5$(tetrahydrofuran) have produced only the mononuclear complexes, *cis*-$Cr(CO)_4[RAs(NSN)_2AsR]$.[17]

Note added in proof: The preparation of *cis*-$M(CO)_4[PhAs(NSN)_2AsPh]$ (M = Cr, Mo) and the *X*-ray crystal structure of the Mo derivative have also recently been reported.[18]

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