

**PREPARATION AND ^{31}P DNMR STUDIES OF HOMODINUCLEAR
 AND *cis*-MONONUCLEAR COMPLEXES OF $\text{Ph}_2\text{PNSNPPH}_2$:
 CRYSTAL STRUCTURE OF *cis*- $\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PNSNPPH}_2) \cdot 0.5\text{C}_6\text{H}_6$ ***

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Summary

The reaction of K_2SN_2 with $\text{ML}_n(\text{Ph}_2\text{PCl})$ ($\text{ML}_n = \text{Cr}(\text{CO})_5$, $\text{Mo}(\text{CO})_5$, $\text{MnCp}'(\text{CO})_2$ ($\text{Cp}' = \text{methylcyclopentadienyl}$)) yields complexes of the type $\text{L}_n\text{MP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PML}_n$ in which the bridging ligand adopts a *cis,trans* conformation and is coordinated through the phosphorus atoms to the two metal centres. In solution these complexes undergo a *cis,trans* \rightarrow *trans,cis* interconversion, and a ^{31}P DNMR study has provided the activation energies for this process ($E_a = 10.1$ (M = Cr), 9.8 (M = Mo) and 13.4 (M = Mn) ± 0.2 kcal mol $^{-1}$). The ^{31}P chemical shifts, infrared frequencies (ν_{as} and $\nu_s(\text{NSN})$) and visible absorption maxima for this series of complexes are discussed in terms of the observed activation energies. The reaction of K_2SN_2 with *cis*- $\text{ML}_n(\text{Ph}_2\text{PCl})_2$ ($\text{ML}_n = \text{Cr}(\text{CO})_4$ or $\text{Mo}(\text{CO})_4$) gives complexes of the type *cis*- $\text{ML}_n(\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P})$ in which the chelating *cis,cis* ligand is coordinated to the metal via both phosphorus atoms. The structure of *cis*- $\text{Cr}(\text{CO})_4(\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P}) \cdot 0.5\text{C}_6\text{H}_6$ has been determined by X-ray crystallography. Crystal data: triclinic, space group $P\bar{1}$, a 9.878(1), b 12.240(1), c 12.610(2) Å, α 87.795(9), β 77.018(10), γ 81.027(9)°, V 1467.6(6) Å 3 , $Z = 2$. The structure was solved by direct methods and refined by least-squares techniques to give a final $R = 0.034$ and $R_w = 0.036$. The geometry around the chromium atom is approximately octahedral, but the planar, chelating PNSNP ligand is tilted at an angle of 126.7° with respect to the plane containing the C_2CrP_2 unit. The P–N bond distances are both 1.727(2) Å; the S–N distances are 1.525(2) and 1.523(2) Å; the angles at the nitrogen atoms are 129.4(1) and 128.8(1)° and the angle at sulphur is 123.0(1)°.

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday and in appreciation of an inspiring teacher.

Introduction

The free ligand $R_2PNSNPR_2$ is known only for $R = t\text{-Bu}$ [1]. Other derivatives ($R = \text{Et, Cy, Ph}$) are unstable [2]. Recently we described the preparation of $(\text{CO})_5\text{MoP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PMo}(\text{CO})_5$, the first stable homodinuclear complex of a ligand of this type [3]. An X-ray structural determination showed that the ligand $\text{Ph}_2\text{PNSNPPh}_2$ adopts a *cis,trans* conformation in this complex and ^{31}P DNMR studies provided evidence for a *cis,trans* \rightarrow *trans,cis* conversion in solution (Fig. 1) [3]. Subsequently, Herberhold and co-workers [4,5] reported the preparation of the related complex $(\text{CO})_5\text{CrP}(\text{Bu-t})_2\text{PNSN}(\text{Bu-t})_2\text{PCr}(\text{CO})_5$. As a result of these studies, three methods are now potentially available for the preparation of such complexes. (a) Treatment of complexes of the type $L_n\text{M}(\text{Ph}_2\text{PNSO})$ with a base, e.g. potassium *t*-butoxide [3,6].

(b) The reaction of complexes of the type $L_n\text{M}(\text{Ph}_2\text{PCl})$ with K_2SN_2 [3].

(c) Direct reaction of $t\text{-Bu}_2\text{PNSNP-t-Bu}_2$ with metal carbonyl complexes containing easily displaced ligands, e.g. $\text{M}(\text{CO})_5(\text{THF})$ ($\text{M} = \text{Cr, Mo, W}$), $\text{CpMn}(\text{CO})_2(\text{THF})$ or $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ [4,5].

The main purpose of this investigation was to evaluate the effect of changing the metal fragments in complexes of the type $L_n\text{MP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PML}_n$ on the activation energy for the *cis,trans* \rightarrow *trans,cis* isomerization. To this end we have employed method (b) as a general route for the preparation of homodinuclear complexes of $\text{Ph}_2\text{PNSNPPh}_2$. We have also used this synthetic approach to prepare complexes of the type *cis*- $\text{M}(\text{CO})_4(\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P})$ ($\text{M} = \text{Cr, Mo}$) and determined the X-ray crystal structure of the mononuclear chromium complex.

Experimental

All experimental procedures were performed under dry nitrogen or argon. Solvents were dried by heating under reflux with the appropriate drying agent, distilled, and stored in bottles fitted with a teflon stopcock with two nitrogen inlets. Solvents were transferred under nitrogen through a rubber septum fitted to one of the outlets by use of a double-tipped stainless steel needle. The following chemicals were prepared by published methods: K_2SN_2 [7], $\text{Cr}(\text{CO})_5(\text{Ph}_2\text{PCl})$ [8], $\text{Mn}(\text{CO})_2\text{Cp}'(\text{Ph}_2\text{PCl})$ [9], *cis*- $\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCl})_2$ [10] and *cis*- $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCl})_2$ [10]. The preparation of $(\text{CO})_5\text{MoP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PMo}(\text{CO})_5$ (**1b**) was described in a communication [3]. Infrared spectra were recorded as Nujol mulls (KBr windows)

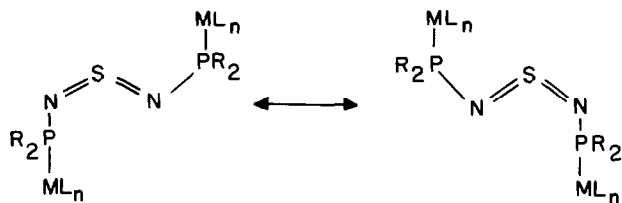


Fig. 1. The interconversion of the *cis,trans*- and *trans,cis*-isomers of $L_n\text{MP}(\text{R})_2\text{NSN}(\text{R})_2\text{PML}_n$.

or hexane solutions on a Nicolet DX-5 FTIR spectrometer. Raman spectra were obtained on a Jarrell-Ash Model 25-100 double monochromator calibrated with carbon tetrachloride. A Coherent Radiation CR4 Argon ion laser fitted with an Innova plasma tube was used to obtain exciting radiation at 514 and 600 nm. Solid samples were made up as KBr discs (ca. 10 mm diameter) placed in a glass vial, which was rotated at 1000 rpm to prevent thermal decomposition. UV-VIS spectra were measured by use of a Cary 219 spectrophotometer. ^{31}P NMR spectra were recorded with use of a Varian XL-200 spectrometer. Chemical shifts are reported in ppm downfield from 85% H_3PO_4 in D_2O . Melting points were obtained on samples in open capillary tubes and are uncorrected. Chemical analyses were performed by the Analytical Services division of the Department of Chemistry, University of Calgary.

*Preparation of $(\text{CO})_5\text{CrP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PCr}(\text{CO})_5$ (**1a**)*

A solution of $\text{Cr}(\text{CO})_5(\text{Ph}_2\text{PCl})_2$ (0.80 g, 1.94 mmol) in acetonitrile (15 ml) was added dropwise over a period of 30 min to a stirred suspension of K_2SN_2 (0.12 g, 0.90 mmol) in acetonitrile (15 ml) cooled to -40°C . The reaction mixture, which turned dark red during the addition, was allowed to warm to room temperature. Solvent was removed in vacuo and the residue was treated with methylene dichloride (5 ml) and purified by chromatography on a silica-60 (230–430 mesh) column (10×2.5 cm) using pentane/methylene dichloride (3/1) as eluant. The dark orange-red fraction was collected. After removal of the solvent, the residue was recrystallized from n-hexane to give black crystals of $(\text{CO})_5\text{CrP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PCr}(\text{CO})_5$ (0.22 g, 0.27 mmol, 30% yield) m.p. $118\text{--}120^\circ\text{C}$. Anal. Found: C, 49.66; H, 2.38; N, 3.00. $\text{C}_{34}\text{H}_{20}\text{Cr}_2\text{N}_2\text{O}_{10}\text{P}_2\text{S}$ calc: C, 50.13; H, 2.48; N, 3.44%. Spectroscopic data are summarized in Table 1.

*Preparation of $(\text{CO})_2\text{Cp}'\text{MnP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PMnCp}'(\text{CO})_2$ (**1c**) ($\text{Cp}' = \text{CH}_3\text{C}_5\text{H}_4$)*

A solution of $\text{Mn}(\text{CO})_2\text{Cp}'(\text{Ph}_2\text{PCl})$ (1.02 g, 2.40 mmol) in acetonitrile (20 ml) was added dropwise to a stirred suspension of K_2SN_2 (0.14 g, 1.01 mmol) in acetonitrile (20 ml) cooled to -40°C . The mixture was allowed to warm to room temperature then stirred for 16 h. Solvent was removed in vacuo and the residue was purified by chromatography on a silica-60 (230–400 mesh) column (10×2.5 cm)

TABLE 1

^{31}P NMR, IR AND UV-VIS SPECTROSCOPIC DATA FOR **1a–c**, **2a** AND **2b**

Compound	$\delta(^{31}\text{P})^a$	$\Delta(^{31}\text{P})^b$	$\nu_{as}(\text{NSN})^c$ (cm^{-1})	$\nu_s(\text{NSN})^c$ (cm^{-1})	$\nu(\text{CO})^e$ (cm^{-1})	λ_{max}^f (nm)
1a	116.4	40.0	1189	1081 ^d	2065msh, 1988w, 1951sbr	470
1b	93.7	29.6	1193	1067	2075msh, 1994w, 1955sbr	430
1c	147.2	44.4	1176	1058	1938s, 1873s	525
2a	95.3	74.1	1158	1105	2015msh, 1938w, 1909sbr	525
2b	73.0	51.8	1166	1106	2028msh, 1938w, 1909sbr	482

^a In acetone- d_6 at 20°C ; chemical shifts are in ppm relative to external 85% H_3PO_4 in D_2O .

^b Difference between the chemical shifts of **1a**, **1b** etc. and those of the corresponding chlorodiphenylphosphine complexes, e.g. $\text{Cr}(\text{CO})_5(\text{Ph}_2\text{PCl})$. ^c Nujol mulls. ^d In the Raman spectrum this band appeared as a strong peak which exhibited resonance enhancement when 600 nm exciting radiation was used. ^e In hexane (**1a–c**) or CCl_4 (**2a** and **2b**). ^f In CH_2Cl_2 .

using pentane/methylene dichloride (1/1) as eluant. The purple fraction was collected. After removal of the solvent, the residue was recrystallized from n-hexane to give black crystals of $(\text{CO})_2\text{Cp}'\text{MnP}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{PMnCp}'(\text{CO})_2$ (0.04 g, 0.05 mmol, 5%). Anal. Found: C, 59.88; H, 4.19; N, 3.01. $\text{C}_{40}\text{H}_{34}\text{Mn}_2\text{N}_2\text{O}_4\text{P}_2\text{S}$ calc: C, 59.26; H, 4.24; N, 3.46%. Spectroscopic data are summarized in Table 1.

Preparation of cis-Cr(CO)₄(P(Ph)₂NSN(Ph)₂P) (2a)

A solution of $\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCl})_2$ (0.59 g, 0.97 mmol) in methylene dichloride (10 ml) was added dropwise to a stirred suspension of K_2SN_2 (0.17 g, 1.23 mmol) in acetonitrile (10 ml) cooled to -40°C . The mixture was allowed to warm to room temperature then stirred for 16 h. Solvent was removed in vacuo and the residue extracted with a hexane/methylene dichloride mixture (10/1). Recrystallization from hexane/methylene dichloride (2/1) yielded *cis*- $\text{Cr}(\text{CO})_4(\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P})$ (0.13 g, 0.22 mmol, 23%) as a dark purple solid, m.p. 160°C (dec.). Anal. Found: C, 56.40; H, 3.37; N, 4.71. $\text{C}_{28}\text{H}_{20}\text{CrN}_2\text{O}_4\text{P}_2\text{S}$ calc: C, 56.57; H, 3.40; N, 4.71%. Spectroscopic data are summarized in Table 1.

Preparation of cis-Mo(CO)₄(P(Ph)₂NSN(Ph)₂P) (2b)

A solution of *cis*- $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCl})_2$ (1.10 g, 1.69 mmol) in a mixture of acetonitrile (5 ml) and methylene dichloride (5 ml) was added dropwise to a stirred suspension of K_2SN_2 (0.23 g, 1.69 mmol) in acetonitrile (20 ml) at -40°C . The mixture was allowed to warm to room temperature then stirred for 16 h. Solvent was removed in vacuo and the product was purified by chromatography on a silica-60 (230–400 mesh) column (10 × 2.5 cm) using pentane/methylene dichloride (2/1) as eluant. An orange-brown fraction was collected. Removal of solvent yielded *cis*- $\text{Mo}(\text{CO})_4(\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P})$ (0.28 g, 0.44 mmol, 26%). An analytically pure sample was obtained by recrystallization from hexane/methylene dichloride, m.p. 155°C (dec.). Anal. Found: C, 52.91; H, 3.10; N, 4.27. $\text{C}_{28}\text{H}_{20}\text{MoN}_2\text{O}_4\text{P}_2\text{S}$ calc: C, 52.67; H, 3.16; N, 4.39%. Spectroscopic data are summarized in Table 1.

X-Ray analysis

Crystals of *cis*- $\text{Cr}(\text{CO})_4\text{P}(\text{Ph})_2\text{NSN}(\text{Ph})_2\text{P} \cdot 0.5\text{C}_6\text{H}_6$ suitable for an X-ray structural determination were obtained by recrystallization from benzene/hexane. A purple crystal (0.5 × 0.3 × 0.2 mm) was mounted in a glass capillary under an atmosphere of dry nitrogen. The complex crystallizes in the space group $P\bar{1}$ with cell dimensions of a 9.878(1), b 12.240(1), c 12.610(2) Å, α 87.795(9), β 77.017(10), γ 81.027(9)°, and V 1467.6(6) Å³ as determined by least-squares refinement of 25 accurately centered reflections with $8.9^\circ < \theta < 16^\circ$. The final choice of space group was based on the centric distribution of E values (K curve) [11] and the successful solution of the structure. For the formula $\text{C}_{28}\text{H}_{20}\text{CrN}_2\text{O}_4\text{P}_2\text{S} \cdot 0.5\text{C}_6\text{H}_6$, $Z = 2$, D 1.434 g cm⁻³, $\mu(\text{Mo}-K_\alpha)$ 6.26 cm⁻¹ and $F(000) = 650$. The data were collected at 21(1)°C on an Enraf–Nonius CAD4F automated diffractometer using the ω -2 θ scan technique (scan speed of 0.5 to 3.3° min⁻¹, scan range 1.5 (0.74 + 0.347tan θ)) and Mo – K_α radiation (graphite monochromator). The data were corrected for background, Lorentz, and polarization effects as well as crystal decay (average of 15% drop in intensity standards). 5150 unique reflections were collected to a maximum $\theta = 25^\circ$, of which 3684 were considered observed ($I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics). An absorption correction was applied using

an empirical method (difabs) [12] in order to account for the capillary and grease used in the mounting of the crystal. The minimum and maximum absorption corrections were 0.87 and 1.06, respectively.

Atomic scattering factors for non-H atoms were those of Cromer and Mann [13], the H scattering factors were taken from ref. 14 and real and anomalous dispersion corrections were applied to all non-H atoms [15]. The structure was solved by direct

TABLE 2

POSITIONAL PARAMETERS ($\times 10^4$) AND VALUES OF B_{eq} ($\times 10$) FOR THE NON-HYDROGEN ATOMS OF *cis*-Cr(CO)₄(P(Ph)₂NSN(Ph)₂P)·0.5C₆H₆

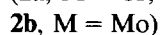
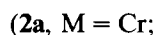
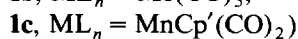
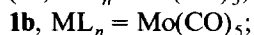
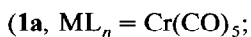
Atom	x	y	z	B_{eq}
Cr	2494.2(5)	7029.6(4)	9130.0(3)	26.3(2)
S	3201.4(9)	10040.7(6)	9390.6(6)	32.9(4)
P(1)	3624.0(8)	8213.2(6)	7845.2(6)	26.8(3)
P(2)	3148.6(8)	7904.7(6)	10522.2(6)	26.6(3)
N(1)	3478(3)	9567(2)	8248(2)	33(1)
N(2)	3098(3)	9321(2)	10409(2)	31(1)
O(1)	-120(2)	8748(2)	9474(2)	49(1)
O(2)	4996(2)	5186(2)	8669(2)	48(1)
O(3)	947(3)	5551(2)	10774(2)	56(1)
O(4)	1292(3)	5863(2)	7581(2)	57(1)
C(1)	884(3)	8102(2)	9353(2)	32(1)
C(2)	4086(3)	5901(2)	8853(2)	31(1)
C(3)	1561(3)	6123(2)	10169(2)	35(1)
C(4)	1784(3)	6333(3)	8142(2)	35(1)
C(11)	3079(3)	8520(2)	6551(2)	28(1)
C(12)	3998(3)	8847(3)	5639(2)	41(2)
C(13)	3532(4)	9144(3)	4693(3)	49(2)
C(14)	2171(4)	9099(3)	4644(2)	47(2)
C(15)	1262(3)	8765(3)	5540(3)	48(2)
C(16)	1717(3)	8469(3)	6490(2)	38(2)
C(21)	5527(3)	7887(2)	7397(2)	30(1)
C(22)	6059(3)	6933(3)	6787(3)	41(2)
C(23)	7503(4)	6590(3)	6491(3)	52(2)
C(24)	8401(4)	7197(4)	6817(3)	64(2)
C(25)	7881(4)	8135(4)	7402(3)	63(2)
C(26)	6444(3)	8484(3)	7698(3)	44(2)
C(31)	1855(3)	7849(2)	11803(2)	30(1)
C(32)	1917(3)	6923(3)	12462(2)	38(2)
C(33)	837(4)	6808(3)	13347(3)	48(2)
C(34)	-324(4)	7608(3)	13576(3)	48(2)
C(35)	-402(3)	8540(3)	12941(3)	43(2)
C(36)	686(3)	8670(2)	12055(2)	35(1)
C(41)	4838(3)	7568(2)	10908(2)	28(1)
C(42)	6020(3)	7084(2)	10169(2)	35(1)
C(43)	7326(3)	6871(3)	10434(3)	42(2)
C(44)	7462(4)	7148(3)	11456(3)	45(2)
C(45)	6293(4)	7642(3)	12198(3)	44(2)
C(46)	4995(3)	7859(2)	11928(2)	35(1)
C(5)	6374(5)	4492(3)	4744(3)	60(2)
C(6)	5930(5)	5366(3)	4139(3)	62(2)
C(7)	4562(6)	5884(3)	4396(3)	62(2)

methods (MULTAN 78) [16], which clearly revealed the positions of the atoms of the CrPNSNP ring, and difference Fourier syntheses. Refinement was carried out by full-matrix least-squares techniques based on F , minimizing the function $\Sigma w(|F_0| - |F_c|)^2$, where $w = [\sigma^2(F) + 0.0001F^2]^{-1}$. H atoms were located on a difference Fourier map and included in idealized positions with an isotropic thermal parameter set to $1.1 \times B_{\text{eq}}$ of the bonded atom. In the final cycles all non-H atoms were refined anisotropically and a value of $0.87(11) \times 10^{-5}$ was determined for the isotropic extinction correction. The model converged for 3684 reflections and 371 variables with $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0| = 0.034$, $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma W|F_0|^2]^{1/2} = 0.036$ and $GOF = 1.14$. The final atomic coordinates for the non-H atoms are given in Table 2. Lists of thermal parameters, hydrogen atom coordinates, complete bond lengths and angles, and structure factors are available from the authors.

Results and discussion

Reactions of the complexes $ML_n(\text{Ph}_2\text{PCL})_x$ ($x = 1$ or 2) with $K_2\text{SN}_2$

The metathetical reaction of $K_2\text{SN}_2$ with complexes of the type $ML_n(\text{Ph}_2\text{PCL})_x$ ($x = 1, 2$) in acetonitrile provides a convenient and general synthesis of complexes of the $\text{Ph}_2\text{PNSNPPH}_2$ ligand. Both homodinuclear and mononuclear complexes have been prepared in this way.



The complexes **1a–c** and **2b** are dark orange or red and **2a** is purple. In the solid state they are stable towards air or moisture, but hydrolysis occurs slowly in solution to give $M(\text{CO})_5(\text{Ph}_2\text{PNH}_2)$ identified by ^{31}P NMR spectroscopy [17]. The structure of **1b** has been determined previously by X-ray crystallography [3] and spectroscopic data (Table 1) indicate that the other homodinuclear complexes, **1a** and **1c**, adopt a similar *cis,trans* conformation of the ligand. An X-ray structural analysis of **2a** is described below.

Although ligands of the type RNSNR ($R = \text{alkyl, aryl}$) form a variety of complexes with organometallic substrates, in which M–N, M–S or M– π -N=S bonding may be involved [18], the major products of these metathetical reactions are complexes of $\text{Ph}_2\text{PNSNPPH}_2$ with only the phosphorus atoms coordinated to the metal. We have, however, detected by TLC very small amounts of an additional product in these reactions, but preparative scale chromatography gave insufficient material for spectroscopic identification. It is possible that these products involve a different mode of coordination of the $\text{Ph}_2\text{PNSNPPH}_2$ ligand to the metal centres.

Crystal and molecular structures of cis-Cr(CO)₄(P(Ph)₂NSN(Ph)₂P) · 0.5C₆H₆

The crystal structure of **2a** consists of discrete molecular units with no unusual intermolecular contacts. Half a molecule of benzene per molecule of **2a** is present as solvent of crystallization. The benzene molecule sits on a crystallographically imposed centre of symmetry. Figure 2 shows an ORTEP drawing with the atomic numbering scheme for the molecule. Selected bond lengths and bond angles are given in Table 3. The complex **2a** has approximately octahedral symmetry about the Cr atom and the P₂N₂S ligand, which is planar to within 0.02 Å, is tilted at an angle of 126.7° with respect to the C₂CrP₂ unit, which is planar to within 0.04 Å. The conformation of the Ph₂PNSNPh₂ ligand in this mononuclear, chelate complex is, of necessity, *cis,cis* in contrast to the *cis,trans* conformation of the homodinuclear complexes. The *cis* and *trans* designations refer to the geometry of substituents relative to individual S=N bonds. The values of the angles at the nitrogen atoms in **2a** (128.8(1) and 129.4(1) Å) are close to that found for the nitrogen atom in the *cis*-S=N unit of **1b** (130.8(2)°), but substantially larger than the angle at the nitrogen atom of the *trans*-S=N bond of **1b** (117.9(2)°) [3]. The angle at the sulphur atom in **2a** of 123.0(1)° is also significantly larger than the corresponding angles in **1b** (116.0(2)°) or other *cis,trans*-sulphur diimides, ca. 117° [19–21], but it is similar

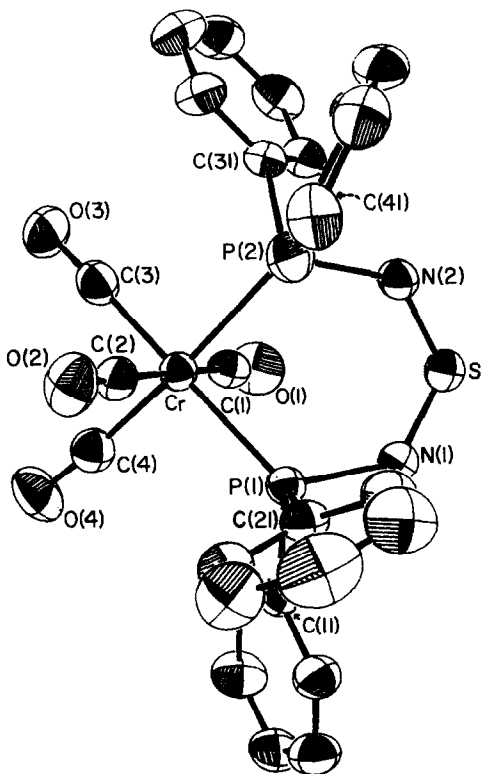


Fig. 2. ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for *cis*-Cr(CO)₄(P(Ph)₂NSN(Ph)₂P) (**2a**). Half a molecule of C₆H₆ per molecule of **2a** is present in the crystal as solvent of crystallization.

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR *cis*-Cr(CO)₄(P(Ph)₂NSN(Ph)₂P)·0.5C₆H₆

Cr–P(1)	2.341(1)	N(2)–P(2)	1.727(2)
Cr–P(2)	2.349(1)	P(1)–C(11)	1.839(3)
Cr–C(1)	1.873(3)	P(1)–C(21)	1.822(3)
Cr–C(2)	1.901(3)	P(2)–C(31)	1.826(3)
Cr–C(3)	1.861(3)	P(2)–C(41)	1.823(3)
Cr–C(4)	1.853(4)	C(1)–O(1)	1.152(4)
P(1)–N(1)	1.727(2)	C(2)–O(2)	1.142(4)
N(1)–S	1.525(2)	C(3)–O(3)	1.150(4)
S–N(2)	1.523(2)	C(4)–O(4)	1.158(4)
P(1)–Cr–P(2)	90.0(0)	N(1)–S–N(2)	123.0(1)
P(1)–Cr–C(1)	88.4(1)	S–N(2)–P(2)	128.8(1)
P(1)–Cr–C(2)	92.0(1)	Cr–P(2)–N(2)	116.5(1)
P(1)–Cr–C(3)	178.4(1)	Cr–P(1)–C(11)	120.8(1)
P(1)–Cr–C(4)	95.0(1)	Cr–P(1)–C(21)	117.3(1)
P(2)–Cr–C(1)	86.7(1)	N(1)–P(1)–C(11)	96.9(1)
P(2)–Cr–C(2)	96.3(1)	N(1)–P(1)–C(21)	99.8(1)
P(2)–Cr–C(3)	89.3(1)	C(11)–P(1)–C(21)	102.1(1)
P(2)–Cr–C(4)	173.5(1)	Cr–P(2)–C(31)	110.6(1)
C(1)–Cr–C(2)	176.9(1)	Cr–P(2)–C(41)	124.9(1)
C(1)–Cr–C(3)	90.1(1)	N(2)–P(2)–C(31)	99.1(1)
C(1)–Cr–C(4)	89.3(1)	N(2)–P(2)–C(41)	98.0(1)
C(2)–Cr–C(3)	89.5(1)	C(31)–P(2)–C(41)	104.2(1)
C(2)–Cr–C(4)	87.6(1)	Cr–C(1)–O(1)	178.3(3)
C(3)–Cr–C(4)	85.6(1)	Cr–C(2)–O(2)	176.1(3)
Cr–P(1)–N(1)	116.1(1)	Cr–C(3)–O(3)	176.6(3)
P(1)–N(1)–S	129.4(1)	Cr–C(4)–O(4)	175.6(3)

to the values found for other *cis,cis*-sulphur diimides, RNSNR (R = ClC₆H₄S (124°) [22], R = Ph₂As (125.7°) [23]). The S–N bond lengths of 1.523(2) and 1.525(2) Å in **2a** are not significantly different from either the *cis*- or *trans*-S=N bonds in **1b** (1.515(3) and 1.529(4) Å), respectively [3]). The P–N bond lengths of 1.727(2) Å are, however, slightly longer than the *cis*-P–N bond in **1b** (1.706(3) Å) and are comparable to the value of 1.732(3) Å found for the *trans*-P–N bond in **1b** [3]. All these P–N bonds are significantly shorter than the value of 1.77 Å usually quoted for a P–N single bond [24]. This may indicate some N(*pπ*) → P(*dπ*) contribution to these bonds (vide infra).

The tilting of the P₂N₂S ring towards C(2) appears to be reflected in a longer Cr–C(2) bond length of 1.901(3), cf. 1.873(3) Å for Cr–C(1). Possibly as a consequence of the elongation of the Cr–C(2) bond the shortest C=O bond, 1.142(4) Å, also involves C(2), cf. an average value of 1.153(4) Å for the other three C=O bonds.

Fluxional behaviour of the homodinuclear complexes, **1a–c**

In a preliminary study [3] we described the variable temperature ³¹P{¹H} NMR spectra of **1b** in acetone-*d*₆. At –90 °C two equally intense singlets were observed at +96.0 and +90.5 ppm consistent with the existence of the *cis,trans* isomer in solution at that temperature. When the temperature of the solution was gradually

TABLE 4
VARIABLE TEMPERATURE ^{31}P NMR DATA FOR **1a-c**

	$\delta(^{31}\text{P}_{cis})^a$	$\delta(^{31}\text{P}_{trans})^a$	$\delta(^{31}\text{P})^b$	Coalescence temp. ($^{\circ}\text{C}$)	E_a^c (kcal mol $^{-1}$)
1a	114.2	117.8	116.4	-64	10.1
1b	90.5	96.0	93.7	-60	9.8
1c	143.5	149.1	147.2	-59	13.4

^a In acetone- d_6 at -90°C ; chemical shifts are in ppm relative to external 85% H_3PO_4 in D_2O . The assignments for the non-equivalent phosphorus atoms are tentative (see text). ^b In acetone- d_6 at 20°C .

^c Activation energies (± 0.2) for the *cis,trans* \leftrightarrow *trans,cis* interconversion [25].

raised, these two signals broadened and collapsed until at $+20^{\circ}\text{C}$ a single, sharp singlet was observed at $+93.7$ ppm. The reverse of these changes was observed when the solution was cooled again to -90°C . These observations were interpreted in terms of a rapid *cis,trans* to *trans,cis* interconversion (Fig. 1). The coalescence temperature was -60°C corresponding to an interconversion barrier of 9.4 ± 0.2 kcal mol $^{-1}$ for this process [25]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1a** and **1c** in acetone- d_6 exhibit changes as a function of temperature similar to those described for **1b**. These similarities and the frequencies of the ν_{as} and ν_s (NSN) bands in the vibrational spectra (Table 1) are good evidence for a *cis,trans* structure for **1a** and **1c**. The ^{31}P NMR chemical shifts, coalescence temperatures, and activation energies for the *cis,trans* \rightarrow *trans,cis* interconversion of **1a-c** are given in Table 4.

It is not possible to make an unambiguous assignment of the two signals observed in the low temperature ^{31}P NMR spectra of **1a-c** from the present data. A comparison of the $\delta(^{31}\text{P})$ values for **1a-1c**, **2a** and **2b** with those for the corresponding Ph_2PCl complexes, e.g. $\text{M}(\text{CO})_5(\text{Ph}_2\text{PCl})$ ($\text{M} = \text{Cr}$ or Mo), is, however, suggestive. To a first approximation, the subtraction of the latter values from the former eliminates the effect of the metal fragment on the $\delta(^{31}\text{P})$ values. Consequently, these differences can be taken as an indication of the influence of the sulphur diimide unit on ^{31}P chemical shifts. The ^{31}P NMR signals for **1a-c**, **2a** and **2b** are all shifted to high field relative to those of the corresponding Ph_2PCl complexes, but the upfield shifts for **2a** and **2b** are larger (Table 1). It is reasonable to assume that the *cis,cis*-conformation of the chelating ligand in **2a** and **2b** is rigid and will be retained in solution. Thus the higher upfield shifts of **2a** and **2b** are associated with phosphorus atoms that are in *cis*-conformations relative to the other substituent attached to the $\text{N}=\text{S}$ bond in these complexes. On this basis, we tentatively conclude that the upfield signal in the low temperature ^{31}P NMR spectra of **1a-c** can be assigned to the phosphorus atom in a *cis*-conformation and the lower field signal belongs to the phosphorus atom in the *trans*-conformation. The shorter P-N distance found for the *cis* compared to the *trans* phosphorus atom in **1b** has been attributed to stronger $\text{N}(p\pi) \rightarrow \text{P}(d\pi)$ bonding to the *cis*-phosphorus atom consistent with the assignment of this phosphorus environment to the upfield signal.

Ab initio molecular orbital calculations for the model sulphur diimide MeNSNMe provide a value of 16.0 kcal mol $^{-1}$ for the *cis,trans* \rightarrow *trans,cis* interconversion barrier and predict lower values with increasing bulk of the substituents attached to nitrogen [26]. The E_a values of 10.1 , 9.8 and 13.4 ± 0.2 kcal mol $^{-1}$ found for **1a**, **1b**, and **1c**, respectively, are consistent with these theoretical predictions. A possible

explanation of the higher E_a value for **1c** compared to the essentially identical values for **1a** and **1b** can be surmised from an inspection of the spectroscopic data in Table 1. The manganese complex, **1c**, shows a higher upfield ^{31}P NMR chemical shift relative to the corresponding Ph_2PCl complex, lower NSN stretching frequencies, and lower transition energies for the visible absorption band when compared to the corresponding data for **1a** and **1b**. As a result of the formal +1 charge on the metal, the $\text{Cp}'\text{Mn}(\text{CO})_2$ substituent is expected to be a weaker π -donor to phosphorus than $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}$ or W). Consequently, $\text{N}(p\pi) \rightarrow \text{P}(d\pi)$ bonding will be stronger for **1c** than **1a** or **1b** and this will be reflected in a higher upfield ^{31}P chemical shift for **1c**. Concomitantly, the stronger involvement of nitrogen in π -bonding to phosphorus will result in weaker S–N π -bonding in the sulphur diimide unit of **1c** consistent with the observation of lower NSN stretching frequencies. The lower transition energy for the visible absorption band of **1c** may also be a reflection of weaker π -bonding in the $\text{N}=\text{S}=\text{N}$ unit if this band involves a transition from a π -type orbital. However, the assignment of the absorption spectra of sulphur diimides to the appropriate electronic transitions is not well established [27,28]. Nevertheless, the stronger $\text{N}(p\pi) \rightarrow \text{P}(d\pi)$ bonding in **1c** is expected to make inversion at nitrogen more difficult and, hence, lead to a higher activation energy for the *cis,trans* \rightarrow *trans,cis* interconversion.

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