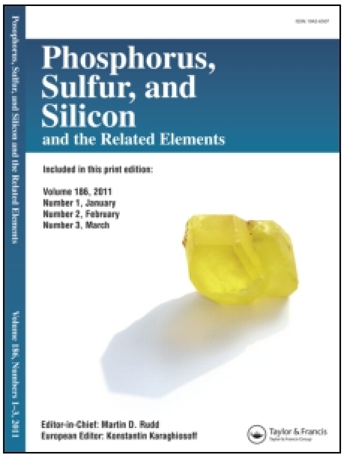

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Phosphorus(III)-Nitrogen-Sulphur Compounds: Synthesis and Metal Complexes

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PHOSPHORUS(III)-NITROGEN-SULPHUR COMPOUNDS: SYNTHESIS AND METAL COMPLEXES

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Abstract The preparation and X-ray structure (M=Mo) of complexes of the type $M(CO)_5(Ph_2PNSO)$ (M=Cr,Mo) are described. These complexes are used in the synthesis of homo- and hetero-dinuclear complexes of $Ph_2PNSNPPh_2$. A ^{31}P DNMR study of these dinuclear complexes indicates a *cis,trans* → *trans, cis* isomerization in solution. The preparation and X-ray structure (M=Cr) of the mononuclear complexes, *cis*-$M(CO)_4(P(Ph)_2NSN(Ph)_2P)$, (M=Cr,Mo) are also described.

INTRODUCTION

Our knowledge of stable phosphorus(III)-nitrogen-sulphur compounds is limited to a single example, **1** (R=t-Bu)[1] and thionylimino derivatives of type **2** are unknown.

$$\underset{\mathbf{1}}{R_2PNSNPR_2} \qquad \underset{\mathbf{2}}{R_2PNSO}$$

This paper describes the synthesis and structural characterization of the first metal complex of the ligand **2** [2] and the application of such complexes in the preparation of both homo- and hetero-dinuclear complexes of **1** (R=Ph). The results of a ^{31}P DNMR study of homodinuclear complexes of **1** (R=Ph) and the synthesis and structural characterization of a chelated, mononuclear complex of **1** (R=Ph) are also reported.

SYNTHESIS

Metal complexes of **2** (R=Ph) are readily prepared by the reaction of the corresponding chlorodiphenylphosphine complexes with KNSO in acetonitrile at -40°C. Treatment of the complexes so obtained with potassium t-butoxide yields homodinuclear complexes of 1 (R=Ph), which are also obtained by the direct reaction of the corresponding chlorodiphenylphosphine complexes with K_2SN_2 in acetonitrile at -40°C.

$$ML_n(Ph_2PCl) + KNSO \longrightarrow ML_n(Ph_2PNSO) + KCl$$
$$(ML_n{=}Cr(CO)_5,\ \mathbf{3a},\ Mo(CO)_5,\ \mathbf{3b})$$
$$\downarrow KOBu\text{-}t$$
$$2ML_n(Ph_2PCl) + K_2SN_2 \longrightarrow L_nMP(Ph)_2NSN(Ph)_2PML_n$$
$$[ML_n{=}Cr(CO)_5,\ \mathbf{4a},\ Mo(CO)_5,\ \mathbf{4b},\ Cp'Mn(CO)_2,\ \mathbf{4c}]$$

The latter route may also be used to prepare chelated, mononuclear complexes of 1 (R=Ph). A related complex of 1 (R=t-Bu) has been obtained recently by the direct reaction of 1 with $Cr(CO)_5(THF)$.[3]

$$ML_n(Ph_2PCl)_2 + K_2SN_2 \longrightarrow ML_nP(Ph)_2NSN(Ph)_2P + 2KCl$$
$$[ML_n{=}Cr(CO)_4,\ \mathbf{5a},\ Mo(CO)_4,\ \mathbf{5b}]$$

The complexes of 2 (R=Ph) can also be used for the synthesis of heterodinuclear complexes of 1 (R=Ph).

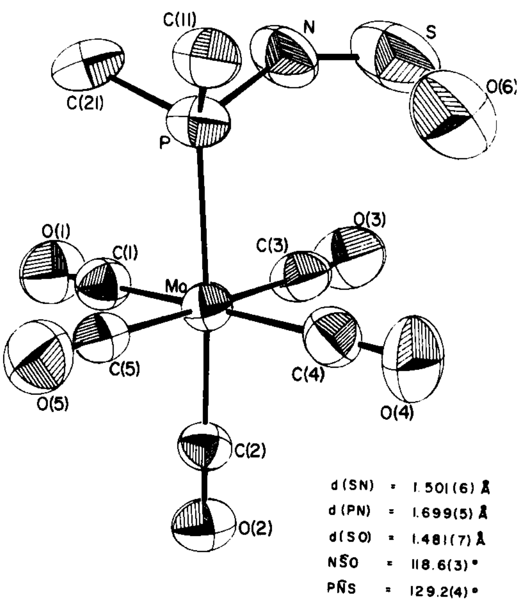
$$\mathbf{3a} \xrightarrow[KOBu\text{-}t]{Mo(CO)_5(Ph_2PNSO)} (CO)_5CrP(Ph)_2NSN(Ph)_2PMo(CO)_5$$

The compounds 3a and 3b are readily hydrolyzed, especially in solution, to give the corresponding complexes of Ph_2PNH_2. The same hydrolysis products are also obtained more slowly from 4a and 4b, but these complexes are air-stable in the solid state.

STRUCTURES

Pertinent structural details for $Mo(CO)_5(Ph_2PNSO)$, 3b, and *cis*-

$Cr(CO)_4(P(Ph)_2NSN(Ph)_2P)$, 5a, are given in Figures 1 and 2.



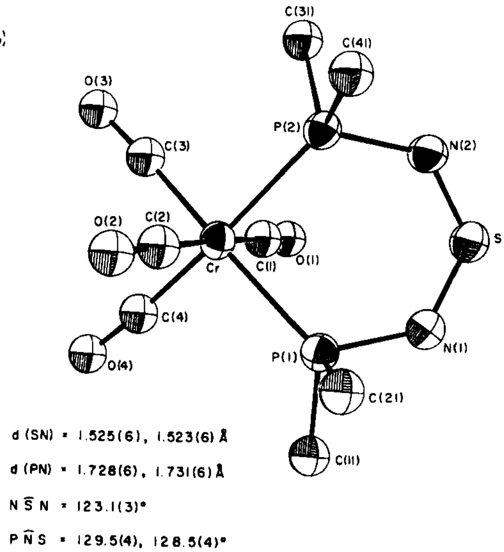


FIGURE 1. Structure of 3b

FIGURE 2. Structure 5a

In 5a the geometry around chromium is approximately octahedral, but the planar cis,cis-PNSNP ligand is tilted at an angle of 126.7° with respect to the plane containing the C_2CrP_2 unit. The structure of 4b has been reported.[2] The planar $Ph_2PNSNPh_2$ ligand adopts a cis,trans conformation in this complex.

FLUXIONAL BEHAVIOUR OF HOMODINUCLEAR COMPLEXES

The $^{31}P\{^1H\}$ NMR spectra of 4a-c in acetone-d_6 at -90°C show two equally intense singlets. These signals broaden and collapse to a single sharp peak when the temperature of the solution is slowly raised to +20°C consistent with a rapid cis,trans to trans,cis interconversion (Figure 3).[2]

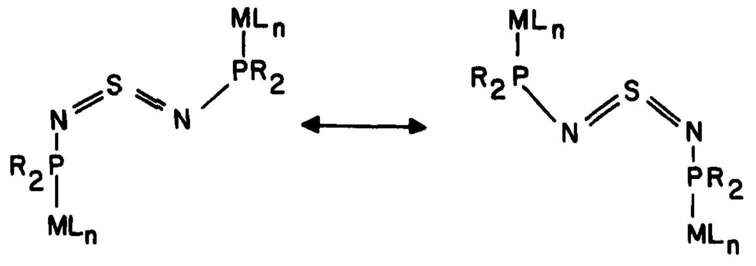


FIGURE 3. Cis,trans ↔ trans,cis interconversion for 4a-c

The ^{31}P NMR chemical shifts, coalescence temperatures and activation energies, E_a, for the cis,trans → trans,cis interconversion of 4a-c are given in Table I.

TABLE I Variable temperature ^{31}P NMR data for 4a-c

	$\delta(^{31}P_{cis})^a$	$\delta(^{31}P_{trans})^a$	$\delta(^{31}P)^b$	Coalescence temp.(°C)	E_a (kcal mol^{-1})
4a	114.2	117.8	116.4	-64	10.1
4b	90.5	96.0	93.7	-60	9.8
4c	143.1	149.1	147.2	-59	13.4

a. Chemical shifts for the non-equivalent P atoms at -90°C.
b. Chemical shifts at 20°C.

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