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Preparation and Condensation Reactions of Metal Complexes of R_2PNSO (R = Me, Ph) with Potassium *tert*-Butoxide: X-ray Crystal Structure of $(CO)_5Mo(Ph_2PNSO)$

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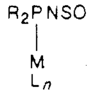
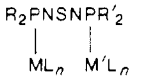
The reaction of KNSO with $(CO)_5M(R_2PCl)$ (M = Cr, Mo; R = Me, Ph) in acetonitrile yields complexes of the type $(CO)_5M(R_2PNSO)$ (**1a–d**). An X-ray crystal structure determination of $(CO)_5Mo(Ph_2PNSO)$ (**1d**) shows that the Ph_2PNSO ligand adopts a cis configuration and is coordinated to molybdenum via the phosphorus atom. Crystal data: monoclinic, space group $C2/c$, $a = 30.236$ (3) Å, $b = 11.034$ (1) Å, $c = 12.056$ (1) Å, $\beta = 96.762$ (4)°, $V = 3993.9$ (6) Å^3, $Z = 8$. The structure was solved by Patterson techniques and refined by full-matrix least squares to give a final $R = 0.038$ and $R_w = 0.030$. The bond distances are d(P–N) = 1.699 (5), d(S–N) = 1.501 (6), and d(S–O) = 1.481 (7) Å, and the bond angles at nitrogen and sulfur are 129.2 (4) and 118.6 (3)°, respectively. Complexes **1a–d** react with potassium *tert*-butoxide in a 2:1 molar ratio to give the homodinuclear complexes $(CO)_5M(R_2PNSNPR_2)M(CO)_5$ (**2a–d**) in good yields. Treatment of **1a–d** with potassium *tert*-butoxide in a 1:1 molar ratio produces adducts of the type $(CO)_5M(R_2PNS(O)OBu\text{-}t)^-K^+$ (**3a–d**). The reactions of these adducts with $(CO)_5M'(R_2PNSO)$ ($M \neq M'$) or $(CO)_5M(R'_2PNSO)$ ($R \neq R'$) produce symmetrical products in addition to heterodinuclear complexes of $R_2PNSNPR_2$ or homodinuclear complexes of the unsymmetrical ligand $R_2PNSNPR'_2$, respectively. The mechanism of these condensation reactions of **1a–d** in the presence of potassium *tert*-butoxide is discussed in terms of the product distribution as determined by ^{31}P NMR spectroscopy.

Introduction

Recently we reported the preparation of **1d**, the first metal complex of a ligand of the type R_2PNSO from the reaction of $(CO)_5Mo(Ph_2PCl)$ with KNSO in acetonitrile.[1] We also observed the formation of small amounts of **2d** in this reaction and speculated that it was formed from **1d** via a base-catalyzed reaction, since purified samples of **1d** did not produce **2d** in the absence of a base.[1]



$$\underset{\underset{L_n}{M}}{R_2PNSO}$$



$$R_2P(ML_n)NSNP(M'L_n)R'_2$$

1a, $ML_n = Cr(CO)_5$, R = Me
b, $ML_n = Cr(CO)_5$, R = Ph
c, $ML_n = Mo(CO)_5$, R = Me
d, $ML_n = Mo(CO)_5$, R = Ph

2a, $ML_n = M'L_n = Cr(CO)_5$, R = R′ = Me
b, $ML_n = M'L_n = Cr(CO)_5$, R = R′ = Ph
c, $ML_n = M'L_n = Mo(CO)_5$, R = R′ = Me
d, $ML_n = M'L_n = Mo(CO)_5$, R = R′ = Ph
e, ML_n $M'L_n = Cr(CO)_5$, R = Me, R′ = Ph
f, $ML_n = Cr(CO)_5$, $M'L_n = Mo(CO)_5$, R = R′ = Ph

We have now carried out a detailed investigation of the base-catalyzed condensation reaction and find that complexes of type **1a–d** react with potassium *tert*-butoxide to give high yields of homodinuclear complexes of $R_2PNSNPR_2$ (**2a–d**). Two other methods are available for the preparation of such complexes: (a) the metathetical reaction of $ML_n(R_2PCl)$ with K_2SN_2[1,2] and (b) direct reaction of $t\text{-}Bu_2PNSNPBu_2\text{-}t$ with metal carbonyl complexes containing easily displaceable ligands.[3] The latter method can only be used for R = Bu-*t*, since other ligands of the type $R_2PNSNPR_2$ (R = Et, Cy, Ph) are unstable.[4]

The reactions of organic thionylamines, RNSO,[5] with potassium *tert*-butoxide to give sulfur diimides[5] are known to proceed via the intermediate formation of adducts, $RNS(O)OBu\text{-}t^-K^+$.[6] By analogy, the corresponding reactions of metal complexes of R_2PNSO could provide a more versatile route to complexes of type 2. For example, the reaction of the potassium *tert*-butoxide adduct of **1a** with either **1b** or **1c** might provide a source of either homodinuclear complexes of *unsymmetrical* ligands $R_2PNSNPR'_2$, e.g. **2e**, or *heterodinuclear* complexes of $R_2PNSNPR_2$, e.g. **2f**. We describe here experiments designed to prepare these complexes. The mechanism of the base-catalyzed condensation reactions of 1 is discussed in the light of the observed product distributions as found by ^{31}P NMR spectroscopy. The X-ray structure of **1d** is also reported.

Experimental Section

Reagents and General Procedures. All experimental procedures were performed under an atmosphere of dry nitrogen or argon. Solvents were dried by heating under reflux with the appropriate drying agents and distilled before use. The following chemicals were prepared by the literature methods: K_2SN_2,[7] $(CO)_5Cr(Ph_2PCl)$,[8] $(CO)_5Cr(Me_2PCl)$,[9] $(CO)_5Mo(Me_2PCl)$.[10] For the successful preparation of KNSO from Me_3SiNSO and KOBu-*t*,[11] we found it necessary to sublime commercial KOBu-*t* (Alfa) before use and to carry out the reaction in THF at 50 °C. The preparation of $(CO)_5Mo(Ph_2PNSO)$ (**1d**),[1] $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ (**2d**),[1] and $(CO)_5CrP(Ph)_2NSN$-

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Table I. ^{31}P NMR and IR Data for 1a, 1b, 1c, 2a, and 2c

	$\delta(^{31}P)^a$	$\delta(P(CH_3)_2)^b$ ($^2J_{HP}$, Hz)	ν_{as},^{c} cm^{-1}	ν_s,^{c} cm^{-1}	$\nu(CO)$,^{d} cm^{-1}
1a	113.3	2.01 (d) (6.4)	1250	1108	2069 msh, 1988 w, 1952 s, 1946 s
1b	116.5		1232	1100, 1089	2069 msh, 1989 w, 1954 s, 1944 s
1c	86.4	1.99 (d) (6.4)	1247	1106	2077 msh, 1993 w, 1967 s, 1956 s
2a	106.0	1.90 (d) (6.6)	1180	1076	2063 msh, 1961 w, 1951 s, 1944 s
2c	80.2	1.90 (d) (5.2)	1194	1079	2073 msh, 1957 s, 1951 s

[a] In $CDCl_3$ at 20 °C; chemical shifts are in ppm relative to external 85% H_3PO_4 in D_2O. [b] In $CDCl_3$ at 20 °C; chemical shifts are in ppm relative to external Me_4Si in $CDCl_3$. [c] Nujol mulls. ν_{as} and ν_s refer to the asymmetric and symmetric stretching modes of NSN or NSO (see text for discussion of assignments). [d] In hexane.

$(Ph)_2PCr(CO)_5$ (**2b**)[2b] have been described previously.

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr windows) or hexane solutions on a Nicolet DX-5 FTIR spectrometer. ^{31}P NMR spectra were obtained on a Varian XL-200 spectrometer. Chemical shifts are reported in parts per million downfield from 85% H_3PO_4 in D_2O. ^1H NMR spectra were recorded by use of a Hitachi Perkin-Elmer R-24B spectrometer. Chemical shifts are reported in parts per million downfield from external Me_4Si in $CDCl_3$. 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 $(CO)_5Cr(Me_2PNSO)$ (1a). A solution of $(CO)_5Cr(Me_2PCl)$ (0.29 g, 1.01 mmol) in acetonitrile (5 mL) was added dropwise to a stirred suspension of KNSO (0.10 g, 0.99 mmol) in acetonitrile (10 mL) at -40 °C. The reaction mixture was allowed to warm to 23 °C, and then solvent was removed in vacuo to give a dark brown oil which was extracted with *n*-hexane (5 mL). The *n*-hexane solution was cooled to -20 °C to give dark orange crystals of **1a** (0.22 g, 0.70 mmol), which melted above ca. 15 °C. Anal. Calcd for $C_7H_6CrNO_6PS$: C, 26.67; H, 1.92; N, 4.45. Found: C, 26.58; H, 1.78; N, 4.16. Spectroscopic data are summarized in Table I.

Preparation of $(CO)_5Cr(Ph_2PNSO)$ (1b). Compound **1b** (0.34 g, 0.77 mmol) was obtained as dark orange crystals (mp 82–84 °C) from the reaction of $(CO)_5Cr(Ph_2PCl)$ (0.42 g, 1.02 mmol) and KNSO (0.10 g, 0.99 mmol) using the procedure described above for **1a**. Anal. Calcd for $C_{17}H_{10}CrNO_6PS$: C, 46.48; H, 2.30; N, 3.19. Found: C, 46.48; H, 2.40; N, 2.95. Spectroscopic data are summarized in Table I.

Preparation of $(CO)_5Mo(Me_2PNSO)$ (1c). Compound **1c** (0.29 g, 0.83 mmol) was obtained as a pale orange liquid from the reaction of $(CO)_5Mo(Me_2PCl)$ (0.36 g, 1.08 mmol) and KNSO (0.11 g, 1.08 mmol) using the procedure described above for **1a**. Anal. Calcd for $C_7H_6MoNO_6PS$: C, 23.41; H, 1.69; N, 3.90. Found: C, 23.63; H, 1.70; N, 3.75. Spectroscopic data are summarized in Table I.

Hydrolysis of $(CO)_5M(R_2PNSO)$ Complexes. $(CO)_5Mo(Ph_2PNSO)$ (**1d**) was prepared from $(CO)_5Mo(Ph_2PCl)$ (0.91 g, 2.0 mmol) and KNSO (0.22 g, 2.2 mmol) in acetonitrile (30 mL). Wet solvents were used in the workup procedure. Chromatography on a silica-60 column (20 × 2 cm) using a mixture of pentane/CH_2Cl_2 (4:1) as eluant yielded $(CO)_5Mo(Ph_2PNSNPPh_2)Mo(CO)_5$ (0.11 g, 0.12 mmol) and $(CO)_5Mo(Ph_2PNH_2)$ (0.72 g, 1.65 mmol) (IR, $\nu(NH)$ 3457, 3361 cm^{-1}; $\delta(^{31}P)$ 66.7). The hydrolysis product had the same IR spectrum and ^{31}P NMR chemical shift as an authentic sample of $(CO)_5Mo(Ph_2PNH_2)$ prepared from $(CO)_5Mo(Ph_2PCl)$ by the literature procedure.[12]

Similarly the hydrolysis of **1a**, **1b**, or **1c**, prepared in situ, gave, respectively, $(CO)_5Cr(Me_2PNH_2)$ ($\delta(^{31}P)$ 75.8 $\delta(CH_3)$ 1.64, $^2J_{CH_3-P}$ = 7.0 Hz), $(CO)_5Cr(Ph_2PNH_2)$ ($\delta(^{31}P)$ 87.0), or $(CO)_5Mo(Me_2PNH_2)$ ($\delta(^{31}P)$ 52.2, $\delta(CH_3)$ 1.62, $^2J_{CH_3-P}$ = 6.8 Hz (cf. lit.[12] $\delta(CH_3)$ 1.62, $^2J_{CH_3-P}$ = 6.4 Hz).

Preparation of $(CO)_5Cr(P(Me)_2NSN(Me)_2P)Cr(CO)_5$ (2a). A solution of $(CO)_5Cr(Me_2PCl)$ (0.29 g, 1.01 mmol) in acetonitrile (10 mL) was added dropwise to a stirred suspension of K_2SN_2 (0.07 g, 0.50 mmol) in acetonitrile (10 mL) at -40 °C. The reaction mixture was allowed to warm to 23 °C. After 16 h solvent was removed in vacuo and the brown oily residue was extracted with *n*-hexane (20 mL). The *n*-hexane solution was cooled to -20 °C to give red-brown crystals of **2a** (0.27 g, 0.48 mmol), mp 74–76 °C. Anal. Calcd for $C_{14}H_{12}Cr_2N_2O_{10}P_2S$: C, 29.69; H, 2.14; N, 4.95. Found: C, 29.29; H, 2.26; N, 4.52. Spectroscopic data are summarized in Table I.

Preparation of $(CO)_5Mo(P(Me)_2NSN(Me)_2P)Mo(CO)_5$ (2c). Pale orange crystals of **2c** (0.46 g, 0.70 mmol), mp 62–64 °C, were obtained from the reaction of $(CO)_5Mo(Me_2PCl)$ (0.64 g, 1.93 mmol) and K_2SN_2 (0.14 g, 1.01 mmol) using the procedure described above for **2c**. Anal. Calcd for $C_{14}H_{12}Mo_2N_2O_{10}P_2S$: C, 25.70; H, 1.85; N, 4.28. Found: C, 25.61; H, 1.95; N, 4.22. Spectroscopic data are summarized in Table I.

Preparation of 2a–d by the Reaction of 1a–d with Potassium *tert*-Butoxide. Compound **1a**, **1b**, **1c**, or **1d** reacts with potassium *tert*-butoxide in a 2:1 molar ratio in benzene or acetonitrile to give **2a**, **2b**, **2c**, or **2d**, respectively. A typical reaction procedure is described below.

A dark orange solution of **1b** (0.43 g, 0.98 mmol) in benzene (20 mL) was added dropwise to a stirred suspension of potassium *tert*-butoxide (0.05 g, 0.45 mmol) in benzene (10 mL) to give a pale yellow solution which becomes orange after the addition of ca. 50% of the solution of **1b**. Subsequently, this orange color intensified and the reaction mixture was heated at reflux for 1 h. Removal of solvent in vacuo gave a dark orange oil which was extracted with *n*-hexane (20 mL). The *n*-hexane solution yielded dark red crystals of **2b** (0.31 g, 0.38 mmol) identified by infrared and ^{31}P NMR spectra. In a similar manner dark orange crystals of **2d** (0.94 g, 1.01 mmol) were obtained by the reaction of **1d** (1.33 g, 2.75 mmol) with potassium *tert*-butoxide (0.16 g, 1.40 mmol) in acetonitrile (10 mL).

The preparation of **2a** and **2c** from **1a** and **1c**, respectively, were also carried out by using the procedure described above, and the products were identified by comparison of their infrared and ^{31}P NMR spectra with those of authentic samples.

Preparation of $(CO)_5Cr(Me_2PNS(O)OBu\text{-}t)^-K^+$ (3a). A solution of **1a** (0.63 g, 2.0 mmol) in benzene (5 mL) was added dropwise to a stirred suspension of potassium *tert*-butoxide (0.20 g, 1.8 mmol) in benzene (5 mL). A white precipitate of **3a** (0.59 g, 1.4 mmol) was obtained immediately. This adduct is insoluble in chloroform or acetonitrile and decomposes to the corresponding sulfur diimide in THF. Good analytical data could not be obtained due to the extreme moisture sensitivity of the solid. IR (Nujol): 1293 w, 1280 w, 1253 w, 1242 w, 1174 w, 1071 s, 1001 s, 933 m, 903 m, 863 s, 852 m, 832 m, 782 m, 759 s, 709 m, 690 s, 682 s, 666 s, 655 s, 478 m, 459 w, 441 w cm^{-1}.

Reaction of $(CO)_5Mo(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (3d) with $(CO)_5Cr(Ph_2PNSO)$ (1b). A solution of **1d** (0.20 g, 0.41 mmol) in acetonitrile (5 mL) was added dropwise to a stirred suspension of potassium *tert*-butoxide (0.05 g, 0.04 mmol) in acetonitrile (10 mL). To the resulting brown-yellow solution of **3d** was added dropwise a solution of **1b** (0.18 g, 0.41 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 16 h. The solvent was removed in vacuo, and extraction with *n*-hexane yielded a dark orange oil (0.28 g) identified as a mixture of **2b**, **2d**, and **2f** by ^{31}P NMR spectroscopy.

Reaction of $(CO)_5Cr(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (3b) with $(CO)_5Cr(Me_2PNSO)$ (1a). A solution of **1b** (0.44 g, 1.0 mmol) in benzene (5 mL) was added dropwise to a stirred suspension of potassium *tert*-butoxide (0.11 g, 1.0 mmol) in benzene (10 mL) until the first indication of a persistent orange color. At this point all potassium *tert*-butoxide had dissolved. To this solution of **3b** was added dropwise a solution of **1a** (0.31 g, 1.0 mmol) in benzene (10 mL). The reaction mixture was heated at reflux for 1 h. The solvent was removed in vacuo, and extraction with *n*-hexane yielded a dark orange oil (0.43 g) identified as a mixture

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Table II. Crystallographic Parameters

formula	$C_{17}H_{10}MoNO_6PS$
fw	483.25
space group	$C2/c$
a, Å	30.236 (3)
b, Å	11.034 (1)
c, Å	12.056 (1)
β, deg	96.762 (4)
V, Å^3	3993.9 (6)
Z	8
D_{calcd}, g cm^{-3}	1.607
$F(000)$	1920
radiatn, Å	$\lambda = 1.54056$ (Ni prefilter)
temp, °C	21
scan range, $\Delta\omega$, deg	$1.5\ (0.74 + 0.142 \tan \theta)$
scan speed, deg min^{-1}	0.5–3.3
max θ, deg	60
octants, collcd	$\pm h, -k, -l$
no. of unique reflctns	2966
no. of obsd reflctns ($>3\sigma$)	1850
cryst dimens, mm	0.2 × 0.26 × 0.30
μ (Mo Kα), cm^{-1}	75.99
min/max abs correctn	0.802, 1.357
weighting formula	$[\sigma^2(F) + 0.00003F^2]^{-1}$
no. of reflectns used in final cycle[a]	2464
no. of variables in final cycle	244
GOF	1.065
R, R_w[b]	0.038, 0.030
max shift/error in final cycle	0.006

[a] Including those for which $I > 3\sigma(I)$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|^2/\sum w|F_o|^2]^{1/2}$.

Table III. Positional Parameters (×10^4) and B_{eq} (×10) for the Non-Hydrogen Atoms of $(CO)_5Mo(PPh_2NSO)$

atom	x	y	z	B_{eq}[a]
Mo	4171.9 (1)	3642.2 (4)	1127.2 (4)	38.7 (2)
C(1)	4653 (2)	2388 (6)	1017 (6)	52 (4)
O(1)	4924 (1)	1685 (4)	915 (4)	76 (3)
C(2)	4632 (2)	4939 (6)	1126 (5)	43 (3)
O(2)	4893 (1)	5701 (4)	1149 (4)	58 (2)
C(3)	4043 (2)	3698 (7)	−567 (6)	57 (4)
O(3)	3950 (2)	3708 (5)	−1502 (4)	85 (3)
C(4)	3705 (2)	4951 (6)	1112 (5)	49 (4)
O(4)	3449 (1)	5726 (4)	1062 (4)	77 (3)
C(5)	4268 (2)	3588 (6)	2826 (5)	44 (3)
O(5)	4301 (1)	3591 (5)	3778 (3)	63 (2)
P	3632 (1)	1956 (2)	1195 (1)	47 (1)
N	3327 (2)	1652 (5)	−49 (4)	68 (3)
S	2991 (1)	2435 (3)	−731 (2)	102 (2)
O(6)	2867 (2)	3609 (6)	−259 (5)	118 (4)
C(11)	3213 (2)	1995 (6)	2169 (5)	49 (3)
C(12)	3122 (2)	3029 (6)	2716 (5)	54 (4)
C(13)	2797 (2)	3065 (6)	3437 (6)	65 (4)
C(14)	2553 (2)	2060 (8)	3579 (6)	74 (5)
C(15)	2645 (2)	1000 (7)	3081 (7)	78 (5)
C(16)	2972 (2)	952 (6)	2347 (6)	67 (4)
C(21)	3885 (2)	492 (6)	1477 (6)	58 (4)
C(22)	4130 (3)	298 (6)	2487 (7)	75 (5)
C(23)	4355 (3)	−753 (8)	2749 (8)	104 (7)
C(24)	4346 (5)	−1626 (10)	1980 (12)	132 (10)
C(25)	4106 (5)	−1495 (11)	957 (10)	144 (10)
C(26)	3869 (3)	−410 (8)	704 (7)	97 (6)

[a] $B_{eq} = {}^1/_3$ the trace of the $\mathbf{B}_{ij}$ matrix.

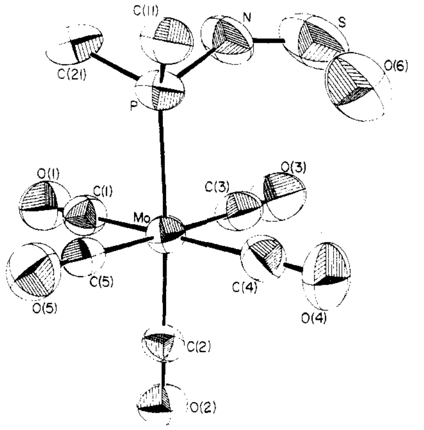

Figure 1. ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $(CO)_5Mo(Ph_2PNSO)$ (**1d**). Only the α-carbon atoms of phenyl groups are shown for clarity.

of **2a**, **2b**, and **2e** by ^{31}P NMR spectroscopy.

X-ray Analysis. The crystal data and experimental conditions are given in Table II. The crystal chosen for data collection was sealed in a capillary tube under nitrogen and held in place with a thin layer of grease. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections ($25 < \theta < 29.5°$). The space group was determined by the systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$), the centric distribution of E values (k curve),[13] and the successful solution of the structure. The data were collected on an Enraf-Nonius CAD4F automated diffractometer using the ω–2θ scan technique. The data were corrected for background, Lorentz, and polarization effects as well as a small degree of crystal decay (<3% drop in intensity of three standard reflections). The data were corrected for absorption by using an empirical method (DIFABS)[14] in order to account for the grease, a small amount of impurity on the surface of the crystal, and the capillary used. Details concerning data collection and reduction can be found in ref 15.

Atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann,[16] the H scattering factors were taken from ref 17, and real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[18] The structure was solved by Patterson techniques (location of the Mo atom) followed by a series of least-squares and difference Fourier syntheses. Refinement was carried out by full-matrix least-squares techniques based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$. H atoms were clearly observed on a difference Fourier map and included in the model in calculated positions with isotropic thermal parameters set to $1.1B_{equiv}$ of the bonded C atom, but not refined. The region about the phenyl ring connected through C(21) was examined for possible disorder, but a simple disorder model could not be found, suggesting a high degree of libration for these atoms. In the final cycles all non-hydrogen atoms were refined with anisotropic thermal parameters and an isotropic extinction coefficient was refined to a value of 3.9 (1.1) × 10^{-5}. The final atomic coordinates are given in Table III.

Results and Discussion

Synthesis of Transition-Metal Complexes of R_2PNSO (R = Me, Ph). The metathetical reaction of KNSO with chromium or molybdenum pentacarbonyl complexes of chlorodialkyl- or chlorodiphenylphosphines is a convenient route for the synthesis of the corresponding complexes of the novel R_2PNSO ligand, **1a**–**d**, in 70–75% yield.

$$(CO)_5M(R_2PCl) + KNSO \rightarrow (CO)_5M(R_2PNSO) + KCl$$

These complexes are obtained as orange solids (R = Ph) or liquids (R = Me). They can be handled in air in the solid state but undergo hydrolysis in solution to give $(CO)_5M(R_2PNH_2)$. These hydrolysis products can be

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Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $(CO)_5Mo(Ph_2PNSO)$

Bond Distances			
Mo-C(1)	2.024 (6)	S-O(6)	1.481 (7)
Mo-C(2)	1.996 (6)	C(1)-O(1)	1.144 (8)
Mo-C(3)	2.035 (7)	C(2)-O(2)	1.149 (7)
Mo-C(4)	2.017 (6)	C(3)-O(3)	1.129 (8)
Mo-C(5)	2.035 (6)	C(4)-O(4)	1.151 (8)
Mo-P	2.484 (2)	C(5)-O(5)	1.140 (7)
P-N	1.699 (5)	P-C(11)	1.827 (6)
N-S	1.501 (6)	P-C(21)	1.803 (7)
Bond Angles			
C(1)-Mo-C(2)	89.1 (2)	P-Mo-C(5)	87.8 (2)
C(1)-Mo-C(3)	90.6 (3)	Mo-C(1)-O(1)	177.5 (6)
C(1)-Mo-C(4)	175.1 (3)	Mo-C(2)-O(2)	178.2 (5)
C(1)-Mo-C(5)	91.6 (3)	Mo-C(3)-O(3)	176.6 (6)
C(2)-Mo-C(3)	91.7 (3)	Mo-C(4)-O(4)	176.6 (6)
C(2)-Mo-C(4)	88.5 (2)	Mo-C(5)-O(5)	176.4 (5)
C(2)-Mo-C(5)	90.3 (2)	Mo-P-N	114.2 (3)
C(3)-Mo-C(4)	85.3 (3)	Mo-P-C(11)	120.8 (2)
C(3)-Mo-C(5)	177.1 (2)	Mo-P-C(21)	114.2 (2)
C(4)-Mo-C(5)	92.7 (3)	N-P-C(11)	103.1 (3)
P-Mo-C(1)	88.3 (2)	N-P-C(21)	99.5 (3)
P-Mo-C(2)	176.7 (2)	C(11)-P-C(21)	102.2 (3)
P-Mo-C(3)	90.4 (2)	P-N-S	129.2 (4)
P-Mo-C(4)	94.3 (2)	N-S-O(6)	118.6 (3)

readily detected by their characteristic ^{31}P NMR chemical shifts.

$$(CO)_5M(R_2PNSO) + H_2O \rightarrow (CO)_5M(R_2PNH_2) + SO_2$$

When a small excess of KNSO was used in the synthesis of **1a–d**, small amounts of **2a–d** were also obtained. It seems likely that the formation of **2a–d** is a result of a base-catalyzed condensation reaction similar to that described below for the reactions of **1a–d** with potassium *tert*-butoxide. No other minor products were observed.

Crystal and Molecular Structure of $(CO)_5Mo(Ph_2PNSO)$ (1d). The crystal structure of **1d** consists of discrete molecular units with no unusual molecular contacts. Figure 1 shows an ORTEP drawing with the atomic numbering scheme for the molecule. Selected bond lengths and bond angles are given in Table IV. Complex **1d** has approximately octahedral geometry about the molybdenum atom. The PNSO moiety is planar to within 0.02 Å and is tilted at an angle of 30.9° with respect to the plane through C(1)C(3)C(4)C(5)Mo unit, which is planar to within 0.04 Å. The Ph_2PNSO ligand adopts a cis configuration with respect to the S–N bond. Previous structural studies have revealed only cis isomers for RNSO derivatives, e.g. R = H (microwave),[19] R = Me (electron diffraction),[20] R = Ar (IR and Raman spectra of ^{15}N-enriched compounds),[21] R = Ph_2CNS (X-ray),[22] and R = OSNS (X-ray).[23] The cis conformation is also retained in the S-bonded complex $(Ph_3P)_2Pt(ArNSO)$ (X-ray).[24]

The value of the bond angle at the sulfur atom of 118.6 (3)° is close to the values of 117–118° found in previous X-ray studies of RNSO compounds,[22,23] but the bond angle of 129.2 (4)° at nitrogen is larger than the corresponding values reported for $Ph_2CNSNSO$ (122.7 (2)°)[22] or $S(NSO)_2$ (mean value is ca. 124°).[23] The S–O bond length of 1.481 (7) Å is longer, and the S–N bond length of 1.501 (6) Å is shorter than the corresponding values for $Ph_2CNSNSO$ (1.453 (3) and 1.529 (2) Å)[22] or $S(NSO)_2$ (mean values of 1.455 and 1.535 Å).[23] The P–N bond length of 1.699 (5) Å is shorter than the value of 1.77 Å usually quoted for P–N single bonds.[25] This may indicate some $N(p_\pi)$–$P(d_\pi)$ contribution to this bond (cf. **2d**).[3] No unusual trends were observed in the structural parameters associated with the Mo–CO or Ph groups.

Table V. Variable-Temperature ^{31}P NMR Spectra of 2a–f[a]

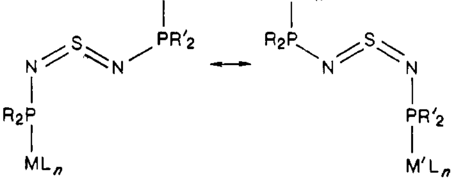
	$\delta(^{31}P)$	
	at 20 °C	at -90 °C
2a	109.4	111.1, 108.1
2b[b]	116.4	117.8, 114.2
2c	84.1	85.9, 83.1
2d[b]	93.7	96.0, 90.5
2e	115.9, 109.2	114.5, 109.5
2f	116.4, 93.9	117.4, 113.4, 95.5, 91.3

[a] In acetone-d_6. [b] Data taken from ref 2b.

Spectroscopic Data for 1a–d. as indicated in Table I, complexes of the ligands R_2PNSO (R = Me, Ph) show two characteristic bands in their infrared spectra at 1230–1250 cm^{-1} [ν_{as}(NSO)] and ca. 1100 cm^{-1} [ν_s(NSO)]. The latter is of lower intensity. Earlier studies of the vibrational spectra of NSO compounds[26] and more recent investigations of ^{15}N-labeled sulfinylanilines, ArNSO,[21] have shown that these two stretching modes are not strongly coupled and can thus be assigned as ν(NS) and ν(SO), respectively. The characteristic NSO deformation mode, which appears at 600–700 cm^{-1},[21,26] was obscured by other bands in this region in the infrared spectra of **1a–d**.

The ^{31}P NMR chemical shifts of **1a–d** are shifted 25–35 ppm upfield from the corresponding R_2PCl complexes and 5–7 ppm downfield from the corresponding $R_2PNSNPR_2$ complexes **2a–d**.[2b]

Fluxional Behavior of the Dinuclear Complexes 2a–f. An X-ray structural determination of **2d** has shown that the sulfur diimide ligand adopts a cis,trans conformation in the solid state.[1] Consistently, the ^{31}P NMR spectra of **2b** or **2d** in acetone-d_6 at -90 °C show two signals of equal intensity attributable to phosphorus atoms in cis and trans positions with respect to an S=N bond. At 25 °C, however, a sharp singlet is observed for both **2b** and **2d**. This dynamic behavior has been interpreted in terms of a rapid cis,trans → trans,cis interconversion.[1,2] The ^{31}P NMR spectra of the $Me_2PNSNPMe_2$ complexes **2a** and **2c** exhibit identical behavior (Table V), and it is reasonable to assume that a similar process is taking place for these complexes.



cis, trans trans, cis

By analogy, homodinuclear complexes of an unsymmetrical sulfur diimide ligand, e.g. **2e**, or heterodinuclear complexes of a symmetrical sulfur diimide ligand, e.g. **2f**, should both display four signals at low temperatures and two signals at room temperature. Thus, when M ≠ M′

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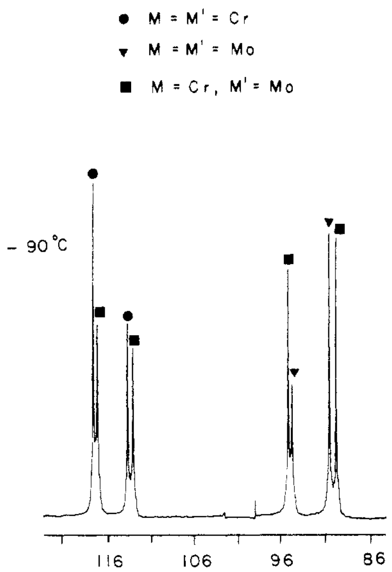

Figure 2. ^{31}P NMR spectrum at −90 °C in acetone-d_6 of the mixture of products $(CO)_5M(P(Ph)_2NSN(Ph)_2P)M'(CO)_5$ from the reaction of $(CO)_5Mo(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (**3d**) and $(CO)_5Cr(Ph_2PNSO)$ (**1b**). Chemical shifts are in ppm relative to external 85% H_3PO_4 in D_2O.

and R = R′ four signals are expected in the low-temperature-limiting ^{31}P NMR spectrum due to cis and trans phosphorus atoms attached to either M or M′. When the cis,trans and trans,cis isomers are interconverting rapidly, however, the different conformations of the phosphorus atoms would be averaged on the NMR time scale so that only two signals due to phosphorus atoms attached to different metals will be observed. A similar pattern of behavior is expected when M = M′ and R ≠ R′. Attempts to prepare **2e** and **2f** are described below.

Condensation Reactions of $ML_n(R_2PNSO)$. The formation of sulfur diimides via a condensation reaction involving thionylamines, usually in the presence of a catalyst such as $AlCl_3$, $SnCl_4$, pyridine, or alkoxides, is a well-documented reaction.[6,27-29] This transformation has been studied in detail for sulfinylanilines and potassium *tert*-butoxide, and the intermediate formation of an adduct has been established.[6]

$$2ArNSO + 2KOBu\text{-}t \rightarrow 2ArNS(O)OBu\text{-}t^-K^+ \xrightarrow{2ArNSO} 2ArNSNAr + K_2S_2O_6 + t\text{-}Bu_2O$$

The reaction of **1a**, **1b**, **1c**, or **1d** with potassium *tert*-butoxide in a 2:1 molar ratio, either in acetonitrile at 23 °C for 17 h or in benzene at reflux for 1 h, produced the corresponding sulfur diimide **2a**, **2b**, **2c**, or **2d**, respectively, in 70–75% yields. When a 1:1 molar ratio was employed for this reaction, however, the characteristic dark orange color of the R_2PNSO complexes disappeared immediately to give a pale yellow solution of the potassium *tert*-butoxide adducts. In one case, $(CO)_5Cr(Me_2PNS(O)OBu\text{-}t)^-K^+$ (**3a**), the adduct was obtained as a white precipitate from benzene solution, but the full characterization of this and other adducts has been hampered by their extreme sensitivity to moisture and rapid decomposition to the corresponding sulfur diimides in solution.

The attempted preparation of a heterodinuclear complex of $Ph_2PNSNPPh_2$ by the reaction of a solution of $(CO)_5Mo(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (**3d**) with **1b** in benzene at reflux produced the homodinuclear complexes **2b** and **2d** in addition to **2f** as indicated by ^{31}P NMR spectroscopy (Figure 2). The low-temperature-limiting spectrum showed two signals each for **2b** and **2d** that could be assigned on the basis of the known ^{31}P chemical shifts of these homodinuclear complexes.[2b] In addition, four signals attributable to the cis,trans and trans,cis isomers of **2f** were observed. When the temperature of a solution of this mixture was raised to +20 °C, only two signals were observed at 116.4 and 93.9 ppm. Since the ^{31}P chemical shifts of **2b** and **2d** in acetone-d_6 at +20 °C occur at 116.4 and 93.7 ppm, respectively,[2b] we interpret this to indicate that the two signals expected for **2f** under conditions of rapid interconversion (vide supra) are accidentally degenerate with those found for **2b** and **2d**. This interpretation seems reasonable as the two signals for **2f** represent phosphorus atoms attached to Cr and Mo, respectively, in averaged cis,trans environments. It was not possible to separate this mixture of products due to their similar solubilities.

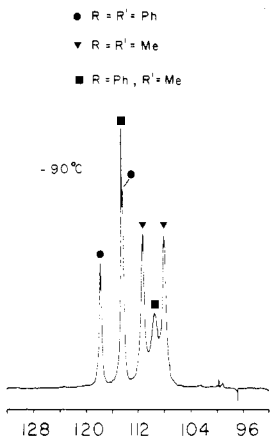

Figure 3. ^{31}P NMR spectrum at −90 °C in acetone-d_6 of the mixture of products $(CO)_5Cr(P(R)_2NSN(R')_2P)Cr(CO)_5$ from the reaction of $(CO)_5Cr(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (**3b**) and $(CO)_5Cr(Me_2PNSO)$ (**1a**). Chemical shifts are in parts per million relative to external 85% H_3PO_4 in D_2O.

$$\underset{\textbf{3d}}{(CO)_5Mo(Ph_2PNS(O)OBu\text{-}t)^-K^+} + \underset{\textbf{1b}}{(CO)_5Cr(Ph_2PNSO)} \rightarrow \underset{\textbf{2b,d,f}}{(CO)_5M(Ph_2PNSNPPh_2)M'(CO)_5}$$

M = M′ = Cr, **2b**; M = M′ = Mo, **2d**; M = Cr, M′ = Mo, **2f**

Similarly, the attempted preparation of a complex of the unsymmetrical ligand $Me_2PNSNPPh_2$ by treatment of $(CO)_5Cr(Ph_2PNS(O)OBu\text{-}t)^-K^+$ (**3b**) with 1 molar equiv of **1a** in boiling benzene produced complexes of symmetrical sulfur diimides **2a** and **2b** in addition to the desired product **2e**. In this case the low-temperature-limiting ^{31}P NMR spectrum of the mixture of products shows six rather than the expected eight signals (Figure 3). Two pairs of these signals are assigned to the homodinuclear complexes **2a** and **2b** on the basis of their known chemical shifts. The other two signals are attributed to the complex of an unsymmetrical sulfur diimide ligand, **2e**, *in one isomeric form*. Although it is not possible to make an unambiguous assignment of the two signals observed in the low-temperature ^{31}P NMR spectra of complexes of type **2**, we have shown that the upfield chemical shifts are most likely associated with the phosphorus atom in the cis conformation and the downfield shifts can be attributed to the trans phosphorus atom when M = M′.[2b] For **2e** shifts from 115.9 to 114.5 ppm for the Ph_2P group and from 109.2 to 109.5 ppm for the Me_2P group are observed upon lowering

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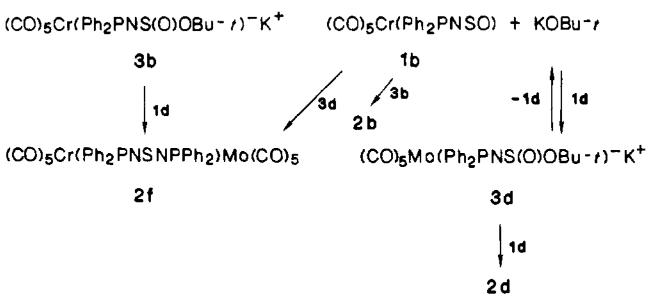
Scheme I



the temperature (Table V). This suggests that these two groups are in cis and trans conformations, respectively; i.e., only one isomeric form of **2e** exists at low temperature.

$$\underset{\mathbf{3b}}{(CO)_5Cr(Ph_2PNS(O)OBu\text{-}t)^-K^+} + \underset{\mathbf{1a}}{(CO)_5Cr(Me_2PNSO)} \rightarrow \underset{\mathbf{2a,b,e}}{(CO)_5Cr(R_2PNSNPR'_2)Cr(CO)_5}$$

$R = R' = Me$, **2a**; $R = R' = Ph$, **2b**; $R = Me$, $R' = Ph$, **2e**

In order to explain the formation of all three products in these reactions we propose that dissociation of the potassium *tert*-butoxide adduct occurs as indicated in Scheme I for the formation of **2b**, **2d**, and **2f**. In support of this suggestion we observed the formation of **2b** when **3b** is heated alone at reflux in benzene.

Finally, when a solution of **3b** in benzene was heated at reflux in the presence of **2a**, a small quantity of **2e** (2%) was formed in addition to **2b**. We conclude from this result that a second mechanism, i.e. the reaction of sulfur diimide complexes with the potassium *tert*-butoxide adducts, plays a minor role in the determination of the final products in the base-catalyzed condensation reactions of **1a–d**.

In summary, we have found that the reaction of $(CO)_5M(R_2PNSO)$ with potassium *tert*-butoxide is an excellent route to homodinuclear complexes of $R_2PNSNPR_2$. Although this synthetic approach can be extended to the formation of heterodinuclear complexes of this ligand or homodinuclear complexes of the unsymmetrical ligand $R_2PNSNPR'_2$, these products are formed together with symmetrical products. The separation of these mixtures is difficult due to the similar solubility properties of all three products.

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Registry No. **1a**, 108894-83-3; **1b**, 108894-84-4; **1c**, 108894-85-5; **1d**, 109007-84-3; **2a**, 108894-86-6; **2b**, 108894-87-7; **2c**, 108894-88-8; **2d**, 100815-29-0; **2e**, 108894-89-9; **2f**, 108894-90-2; **3a**, 108894-91-3; **3b**, 108894-92-4; **3d**, 108894-93-5; $(CO)_5Cr(Me_2PCl)$, 34629-15-7; $(CO)_5Cr(Ph_2PCl)$, 18461-36-4; $(CO)_5Mo(Me_2PCl)$, 34629-16-8; $(CO)_5Mo(Ph_2PCl)$, 23581-74-0; $(CO)_5Mo(Ph_2PNH_2)$, 38268-63-2; $(CO)_5Cr(Me_2PNH_2)$, 108894-94-6; $(CO)_5Cr(Ph_2PNH_2)$, 108894-95-7; $(CO)_5Mo(Me_2PNH_2)$, 38271-10-2; KNSO, 73400-02-9; K_2SN_2, 82495-69-0; KOBu-*t*, 865-47-4; Me_2PCl, 811-62-1; Ph_2PCl, 1079-66-9; Me_2PNSO, 108836-37-9; Ph_2PNSO, 108836-38-0; $Me_2PNHS(O)OBu$-*t*, 108836-39-1; $Ph_2PNHS(O)OBu$-*t*, 108836-40-4.

Supplementary Material Available: Listings of positional and thermal parameters and all bond distances and bond angles (3 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Small-Ring Cyclic Cumulenes: Synthesis and X-ray Crystal Structure of Bis(triphenylphosphine)chloro(η^2-1,2,3-cyclononatriene)rhodium

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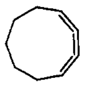
Reaction of the strained cumulene 1,2,3-cyclononatriene (**1**) with Wilkinson's catalyst (**2**; chlorotris(triphenylphosphine)rhodium) yields an air-stable crystalline complex (**6**). The complex shows a cumulenic infrared absorption at 1992 cm^{-1}. Complex **6** crystallizes in the orthorhombic space group *Pbca* (No. 61) with $a = 23.629$ (6) Å, $b = 23.912$ (30) Å, $c = 13.173$ (8) Å, and $Z = 8$. The X-ray crystal structure shows that the cumulene is complexed via the in-plane central double bond and is trans to the chlorine atom. C-7 of the cyclic cumulene shows two distinct locations in the crystal structure (50% probability each), which is best described in terms of a "flapping" disorder.

Introduction

We have recently reported the synthesis and characterization of 1,2,3-cyclononatriene (**1**), which may be the smallest isolable cyclic butatriene.[1,2] Molecular orbital calculations led to the prediction that the normally linear butatriene moiety should be bent ca. 15–19° in **1**, due to



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