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Preparation and Ligand Properties of Thionylimino Derivatives of Arsenic(III). X-ray Crystal Structure of $Cr(CO)_5(Ph_2AsNSO)$

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The reactions of M^+NSO^- ($M^+ = K^+$ or $(Me_2N)_3S^+$) with Ph_2AsCl or $RAsCl_2$ in acetonitrile produce Ph_2AsNSO (**1**) or $RAs(NSO)_2$ (R = *t*-Bu (**2a**), Ph (**2b**)). Treatment of $Cr(CO)_5(THF)$ with **1** or **2** gives $Cr(CO)_5(Ph_2AsNSO)$ (**3**) or $Cr(CO)_5[RAs(NSO)_2]$ (R = *t*-Bu (**4a**), Ph (**4b**)), respectively. An X-ray structural determination of **3** shows that the ligand adopts a cis configuration and is bonded to chromium via the arsenic atom. Crystal data: monoclinic, space group $P2_1/c$, $a = 12.389(4)$ Å, $b = 10.293$ (3) Å, $c = 16.031$ (6) Å, $\beta = 104.50$ (1)°, $V = 1979.1$ Å^3, $Z = 4$. The structure was solved by Patterson techniques and refined by full-matrix least-squares techniques to give a final $R = 0.056$ and $R_w = 0.057$. The bond distances in the ligand are d(As–N) = 1.889 (6), d(N–S) = 1.496 (7), and d(S–O) = 1.457 (9) Å, and the bond angles at nitrogen and sulfur are 127.5 (4) and 120.2 (4)°, respectively. The reaction of **2b** with $Pt(C_2H_4)(PPh_3)_2$ results in As–N bond cleavage to give *cis*-$Pt(PPh_3)_2(NSO)_2$ in good yield. The thermolysis of **2b** produces the eight-membered ring $Ph_2As_2S_2N_4$. Complexes of the type *cis*-$Cr(CO)_4(R_2As_2S_2N_4)$ (R = *t*-Bu (**5a**), Ph (**5b**)) are obtained from the reaction of $R_2As_2S_2N_4$ and *cis*-$Cr(CO)_4(C_7H_8)$.

Introduction

Compounds of the type I or II (E = P or As) are likely to be versatile ligands in view of the variety of bonding modes to metal centers exhibited by the heterocumulenes RNSO.[1] Thionylimino

$$\underset{\text{I}}{R_2ENSO} \qquad \underset{\text{II}}{RE(NSO)_2}$$

derivatives[2] of trivalent group 15 elements are unknown as the free ligand,[3,4] although we recently reported the preparation[5a] and X-ray structural characterization[5b] of the first metal complex of I ($R_2E = Ph_2P$). Such complexes are obtained by the metathetical reactions of $(CO)_5M(R_2PCl)$ (M = Cr, Mo; R = Me, Ph) with KNSO in acetonitrile.[6] However, attempts to use this approach to prepare the free ligands I (E = P) have been unsuccessful[7] even when very bulky groups (e.g., R = *t*-Bu, 1,3,5-*t*-$Bu_3C_6H_2$) are attached to phosphorus.[8]

We describe here the preparation and spectroscopic characterization of the new ligands Ph_2AsNSO (**1**) and $RAs(NSO)_2$ (R = *t*-Bu (**2a**), Ph (**2b**)) and an investigation of their interaction with zerovalent chromium and platinum centers. The X-ray structure of $Cr(CO)_5(Ph_2AsNSO)$ has been determined, and the preparation of *cis*-$Cr(CO)_4(R_2As_2S_2N_4)$ (R = *t*-Bu, Ph) 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 literature methods: KNSO,[9] *t*-$BuAsCl_2$,[10] $PhAsCl_2$,[11] $Ph_2As_2S_2N_4$,[12] *t*-$Bu_2As_2S_2N_4$,[13] and $Pt(C_2H_4)(PPh_3)_2$.[14] Ph_2AsCl (Strem) and $Cr(CO)_6$ (Aldrich) were used as received and KO-*t*-Bu (Alfa) was sublimed before use. The preparation of $(TAS)^+NSO^-$ ($(TAS)^+ = (Me_2N)_3S^+$) was first reported by Mews et al.,[15] but details were not available until recently.[16] Consequently, we developed the procedure described below for the preparation of this salt.

Table I. Selected IR Data for Thionylimino and Sulfur Diimido Derivatives of Arsenic and Their Metal Carbonyl Complexes

	ν_{as},[a] cm^{-1}	ν_s,[a] cm^{-1}	ν(CO),[b] cm^{-1}
Ph_2AsNSO	1234	1084	
t-$BuAs(NSO)_2$	1246, 1232	1090	
$PhAs(NSO)_2$	1224, 1197	1079	
$Cr(CO)_5(Ph_2AsNSO)$	1234	1095	2071 (m), 1995 (w), 1956 (vs)
$Cr(CO)_5[t\text{-}BuAs(NSO)_2]$	1256, 1240	1102	2075 (m), 2003 (w), 1957 (vs)
$Cr(CO)_5[PhAs(NSO)_2]$	1238	1090	2095 (m), 2022 (w), 1948 (vs)
cis-$Cr(CO)_4$-$[t\text{-}Bu_2As_2S_2N_4]$	1159	1052	2021 (m), 1950 (m), 1926 (s), 1919 (s)
cis-$Cr(CO)_4$-$[Ph_2As_2S_2N_4]$	1134	1044	2025 (m), 1948 (m), 1920 (s), 1911 (s)
t-$Bu_2As_2S_2N_4$[c]	1219, 1202	1079, 1050	
$Ph_2As_2S_2N_4$[d]	1194, 1178	1078	

[a] Nujol mulls with the exception of Ph_2AsNSO and *t*-$BuAs(NSO)_2$, which were recorded as neat liquids. ν_{as} and ν_s refer to the asymmetric and symmetric stretching modes of NSO or NSN (see text for discussion of assignments). [b] In CCl_4 solution. [c] Data taken from ref 36. [d] This work.

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr windows), neat liquids, or CCl_4 solutions on a Nicolet DX-5 FTIR spectrophotometer. ^1H NMR spectra were recorded by use of a Hitachi Perkin-Elmer R-24B spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si in $CDCl_3$. ^{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. 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, The University of Calgary, and Guelph Chemical Laboratories, Ltd.

Preparation of $(TAS)^+NSO^-$. Me_3SiNSO (7.5 g, 55.4 mmol) was added dropwise over a period of 1 h to a solution of $(TAS)^+Me_3SiF_2^-$ (16.2 g, 58.6 mmol)[17] in THF (200 mL) at 23 °C. A yellow precipitate

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is formed immediately. The reaction mixture was stirred for a further 30 min. Filtration and washing with THF (2 × 50 mL) yielded $(TAS)^+NSO^-$ (11.2 g, 49.6 mmol) as a moisture-sensitive yellow solid. IR: ν_{as}(NSO) 1261 s, ν_s(NSO) 991 s, δ(NSO) 493 m cm^{-1}.

Preparation of Ph_2AsNSO (1). A solution of Ph_2AsCl (1.0 g, 3.8 mmol) in acetonitrile (5 mL) was added dropwise to a stirred suspension of KNSO (0.38 g, 3.8 mmol) in acetonitrile (10 mL) at −40 °C. The reaction mixture was allowed to reach 23 °C and stirred for an additional 2 h. Removal of the solvent under vacuum and extraction of the oily residue with pentane (20 mL), followed by removal of KCl by filtration, yielded a yellow oil. An analytically pure sample of Ph_2AsNSO (0.76 g, 2.6 mmol) was obtained by vacuum distillation; bp 115–118 °C (0.1 Torr). Anal. Calcd for $C_{12}H_{10}AsNOS$: C, 49.49; H, 3.47; N, 4.81. Found: C, 51.01; H, 3.80; N, 4.62. IR data are given in Table I.

Preparation of *t*-BuAs(NSO)$_2$ (2a). A solution of $(TAS)^+NSO^-$ (2.01 g, 8.9 mmol) in acetonitrile (5 mL) was added dropwise to a solution of *t*-BuAsCl$_2$ (0.89 g, 4.4 mmol) in acetonitrile (15 mL) at −40 °C. The reaction mixture was allowed to reach 23 °C and was stirred for 16 h. Removal of the solvent under vacuum and extraction with hexane (40 mL), followed by removal of $(TAS)^+Cl^-$ by filtration, yielded *t*-BuAs(NSO)$_2$ (0.87 g, 3.4 mmol) as a pale yellow liquid. An analytically pure sample was obtained by vacuum distillation; bp 42–43 °C (0.05 Torr). Anal. Calcd for $C_4H_9AsN_2O_2S_2$: C, 18.46; H, 3.49; N, 10.77. Found: C, 18.32; H, 3.70; N, 10.88.

Preparation of $PhAs(NSO)_2$ (2b). A similar procedure was used to prepare $PhAs(NSO)_2$ (0.75 g, 2.7 mmol) from $(TAS)^+NSO^-$ (1.65 g, 7.3 mmol) and $PhAsCl_2$ (0.82 g, 3.7 mmol). Compound **2b** was obtained as a pale yellow liquid, which can be crystallized from hexane as pale yellow crystals, mp 23 °C. Satisfactory analytical data could not be obtained for this extremely moisture-sensitive solid, but the thermolysis to give $Ph_2As_2S_2N_4$ is described below. IR data for **2a** and **2b** are given in Table I.

Thermal Decomposition of $PhAs(NSO)_2$. $PhAs(NSO)_2$ (1.74 g, 6.8 mmol) was heated at 100 °C (0.1 Torr) for 8 h. The resulting orange oil was recrystallized from CH_2Cl_2/hexane (1:1) to give orange crystals of $Ph_2As_2S_2N_4$ (0.71 g, 1.6 mmol). MS: *m/e* 424 (M^+). The IR spectrum was identical with that of a sample prepared from $PhAsCl_2$ and $Me_3SiNSNSiMe_3$.[12] Characteristic bands are given in Table I.

Reaction of $PhAs(NSO)_2$ with $Pt(C_2H_4)(PPh_3)_2$. A solution of $PhAs(NSO)_2$ (0.16 g, 0.62 mmol) in toluene (10 mL) was added dropwise to a solution of $Pt(C_2H_4)(PPh_3)_2$ (0.49 g, 0.66 mmol) in toluene (30 mL) at −17 °C. The reaction mixture was then stirred at 23 °C for 17 h. A yellow precipitate was isolated by filtration and identified as *cis*-Pt(PPh$_3$)$_2$(NSO)$_2$ (0.27 g, 0.32 mmol). Removal of solvent from the filtrate yielded a brown solid that was recrystallized from acetonitrile to give additional *cis*-Pt(PPh$_3$)$_2$(NSO)$_2$ (0.10 g, 0.12 mmol). Anal. Calcd for $C_{36}H_{30}N_2O_2P_2PtS_2\cdot0.5CH_3CN$: C, 51.17; H, 3.66; N, 4.03. Found: C, 50.85; H, 3.76; N, 4.01. ^{31}P NMR: δ +8.8, $^1J_{^{195}Pt-^{31}P}$ = 3191 Hz. IR (Nujol): 1243 vs, 1228 s, 1098 m, 1062 m, 753 w, 743 w, 734 w, 703 m, 692 s, 547 m, 527 s, 521 w, 513 w, 497 m cm^{-1}.

Preparation of $Cr(CO)_5(Ph_2AsNSO)$ (3). A solution of Ph_2AsNSO (0.69 g, 2.6 mmol) in THF (10 mL) was added dropwise to a solution of $Cr(CO)_5(THF)$ (2.6 mmol) in THF (40 mL) at 0 °C. The reaction mixture was allowed to reach 23 °C and was stirred for 16 h. Removal of the solvent in vacuo followed by recrystallization of the residue from hexanes (15 mL) yielded $Cr(CO)_5(Ph_2AsNSO)$ (0.82 g, 1.8 mmol) as yellow crystals. Anal. Calcd for $C_{17}H_{10}AsCrNO_6S$: C, 42.25; H, 2.09; N, 2.90. Found: C, 43.05; H, 2.07; N, 2.79. IR data are given in Table I.

Preparation of $Cr(CO)_5[RAs(NSO)_2]$ (R = Ph (4b), *t*-Bu (4a)). A solution of $PhAs(NSO)_2$ (0.22 g, 0.80 mmol) in THF (10 mL) was added dropwise to a solution of $Cr(CO)_5(THF)$ (0.80 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at 23 °C for 16 h. Removal of solvent under vacuum and extraction with hexanes (20 mL) yielded $Cr(CO)_5[PhAs(NSO)_2]$ (0.29 g, 0.61 mmol) as an orange oil.

A similar procedure was used to obtain $Cr(CO)_5$[*t*-BuAs(NSO)$_2$] (0.86 g, 1.9 mmol) as an orange oil from *t*-BuAs(NSO)$_2$ (0.60 g, 2.3 mmol) and $Cr(CO)_5(THF)$ (2.3 mmol). IR spectroscopic data for $Cr(CO)_5[RAs(NSO)_2]$ (R = *t*-Bu, Ph) are given in Table I.

Preparation of *cis*-Cr(CO)$_4$(Ph$_2$As$_2$S$_2$N$_4$) (5b). A solution of $Cr(CO)_4(C_7H_8)$ (0.06 g, 0.23 mmol) in toluene (10 mL) was added to a solution of $Ph_2As_2S_2N_4$ (0.10 g, 0.23 mmol) in toluene (20 mL). No reaction occurred at room temperature, so the yellow reaction mixture was heated at reflux for 5 h to give a brown solution. Removal of solvent gave a brown residue, which was redissolved in toluene (15 mL) and passed through a silica gel column (5 × 0.5 cm) to give a dark red solution. The volume of this solution was reduced to 1 mL, and then slow evaporation of the solvent in air gave dark red, diamond-shaped crystals of *cis*-Cr(CO)$_4$(Ph$_2$As$_2$S$_2$N$_4$) (0.08 g, 0.14 mmol). Anal. Calcd for $C_{16}H_{10}As_2CrN_4O_4S_2$: C, 32.65; H, 1.75; N, 9.52. Found: C, 32.25; H, 1.67; N, 9.30. MS(EI): *m/e* 588 (M^+). IR data are given in Table I.

Table II. Crystallographic Parameters

formula	$C_{17}H_{10}AsCrNO_6S$
fw	483.25
space group	$P2_1/c$
a, Å	12.389 (4)
b, Å	10.293 (3)
c, Å	16.031 (6)
β, deg	104.50 (1)
V, Å^3	1979.1
Z	4
D_{calcd}, gm/cm^3	1.622
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
temp, °C	23 (1)
scan range, deg	$1.5(0.74 + 0.34 \tan \theta)$
scan speed, deg min^{-1}	1–3
max θ, deg	25
octants collcd	$\pm h,+k,+l$
no. of unique reflcns collcd	3440
no. of reflcns obsd ($I > 3\sigma(I)$)	2178
μ(Mo Kα), cm^{-1}	21.5
abs cor: min; max	0.641; 1.491
no. of variables	245
no. of observns	2178
max Δ/σ	0.04
GOF	1.16
agreement factors[a]	
R	0.056
R_w	0.057

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

Preparation of *cis*-Cr(CO)$_4$(*t*-Bu$_2$As$_2$S$_2$N$_4$) (5a). A mixture of $Cr(CO)_4(C_7H_8)$ (0.250 g, 1.0 mmol) and *t*-Bu$_2$As$_2$S$_2$N$_4$ (0.384 g, 1.0 mmol) in toluene (75 mL) was heated at reflux for 5 h. The dark brown solution was filtered, and solvent was removed under vacuum to give purple needles of *cis*-Cr(CO)$_4$(*t*-Bu$_2$As$_2$S$_2$N$_4$) (0.48 g, 0.88 mmol). Anal. Calcd for $C_{12}H_{18}As_2CrN_4O_4S_2$: C, 26.28; H, 3.32; N, 10.22. Found: C, 25.93; H, 3.24; N, 9.93. IR data are given in Table I.

X-ray Analysis. The crystal data and experimental details are given in Table II. The crystal chosen for data collection was a pale orange block of approximate dimensions 0.5 × 0.5 × 0.6 mm. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry of 25 accurately centered reflections ($12 < \theta < 20°$). The choice of space group was uniquely determined by the systematic absences and confirmed by using the program TRACER.[18] Data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer using the ω–2θ scan technique. As a check on crystal and electronic stability three representative reflections were measured very 60 min. The intensities of these reflections remained constant within experimental error throughout data collection, so no decay correction was applied. The data were corrected for Lorentz and polarization effects[19] and an empirical absorption correction (program DIFABS[20]) was applied. Details concerning data collection and reduction can be found in ref 21.

The structure was solved by using the Patterson method, which revealed the position of the As atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculation in idealized positions with isotropic thermal parameters set to $1.1B_{iso}$ of the bonded atom. H parameters were not refined. Refinement was carried out by full-matrix least squares on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where the weight *w* is defined as $(\sigma^2(F) + 0.00002F^2)^{-1}$. Scattering factors were taken from Cromer and Waber[22] and ref 23 (H atoms), and anomalous

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Table III. Position Parameters ($\times 10^4$) and B_{eq} ($Å^2 \times 10$) for the Non-Hydrogen Atoms of $Cr(CO)_5(Ph_2AsNSO)$

atom	x	y	z	$B_{eq}{}^a$
As	2704.1 (6)	3482.6 (8)	4404.8 (4)	55.1 (4)
Cr	905.5 (9)	2766.0 (13)	3517.8 (7)	60.3 (7)
S	4175 (2)	3581 (3)	3146 (1)	87 (1)
N	3654 (4)	4234 (6)	3782 (3)	68 (3)
O(6)	3992 (5)	2201 (8)	2964 (4)	115 (5)
C(1)	260 (6)	4371 (9)	3717 (5)	64 (5)
O(1)	−152 (5)	5315 (6)	3837 (4)	84 (4)
C(2)	−454 (6)	2268 (8)	2819 (5)	70 (4)
O(2)	−1294 (4)	1947 (6)	2395 (4)	95 (4)
C(3)	500 (6)	2071 (8)	4478 (5)	61 (4)
O(3)	234 (5)	1642 (6)	5054 (4)	94 (4)
C(4)	1275 (7)	3458 (12)	2527 (5)	101 (6)
O(4)	1507 (6)	3831 (11)	1932 (4)	154 (6)
C(5)	1492 (7)	1122 (11)	3333 (5)	88 (6)
O(5)	1801 (5)	114 (8)	3221 (5)	123 (5)
C(11)	2704 (5)	4974 (8)	5130 (4)	52 (4)
C(12)	2484 (6)	6154 (11)	4749 (5)	68 (5)
C(13)	2425 (7)	7257 (9)	5234 (7)	78 (5)
C(14)	2579 (7)	7155 (11)	6101 (7)	82 (6)
C(15)	2780 (7)	5983 (13)	6487 (5)	81 (6)
C(16)	2866 (6)	4872 (8)	6005 (5)	66 (5)
C(21)	3737 (5)	2337 (9)	5157 (4)	56 (4)
C(22)	3422 (7)	1113 (10)	5330 (6)	71 (5)
C(23)	4167 (8)	306 (8)	5882 (5)	77 (5)
C(24)	5223 (7)	701 (10)	6237 (5)	74 (5)
C(25)	5533 (6)	1929 (11)	6080 (6)	83 (6)
C(26)	4795 (6)	2737 (9)	5541 (5)	78 (5)

[a] B_{eq} = one-third the trace of the B_{ij} matrix.

dispersion effects were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[24] An isotropic extinction parameter was refined to give a value of 3.1 (2) $\times 10^{-4}$. The model converged with final agreement factors of $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.056$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.057$. The highest peak in the final difference Fourier had a height of 2.0 (1) e/Å^3 and is associated with the As atom. The final atomic coordinates are given in Table III.

Results and Discussion

Synthesis of Ph_2AsNSO (1) and $RAs(NSO)_2$ (R = *t*-Bu (2a), Ph (2b)). In contrast to their phosphorus analogues, which have only been obtained in complexes with metals,[5] thionylimino derivatives of arsenic(III) are readily obtained in high yields by the metathetical reactions of Ph_2AsCl or $RAsCl_2$ (R = *t*-Bu, Ph) with salts of the NSO^- anion in acetonitrile. They are isolated as pale yellow, moisture-sensitive liquids (**1** and **2a**) or as a low melting solid (**2b**).

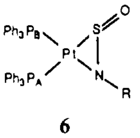
$$R_{3-n}AsCl_n + nM^+NSO^- \rightarrow R_{3-n}As(NSO)_n + nMCl \quad (1)$$

1, R = Ph, $n = 1$
2a, R = *t*-Bu, $n = 2$
2b, R = Ph, $n = 2$

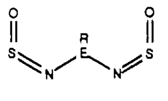
$$M^+ = (TAS)^+, K^+$$

Although Me_3SiNSO is a suitable reagent for the synthesis of $S(NSO)_2$ from SCl_2[25] and $Me_3SiNSNSiMe_3$ has been used for the preparation of $RAs(NSN)_2AsR$ (R = Me,[26] Ph,[12] mesityl[12]), we found that Me_3SiNSO is not sufficiently reactive for the synthesis of **1** or **2** from Ph_2AsCl or $RAsCl_2$ respectively. The use of $(TAS)^+NSO^-$ is preferable to KNSO for the preparation of (thionylimino)arsines in view of the solubility of the former salt in acetonitrile and the tendency for KNSO to promote the condensation reaction to give the corresponding sulfur diimides.[5b]

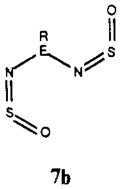
Spectroscopic Characterization of $R_{3-n}As(NSO)_n$. Compounds **1**, **2a**, and **2b** exhibit strong bands characteristic of the NSO group in their IR spectra (Table I). These bands are observed in the ranges 1200–1245 and 1080–1090 cm^{-1}, corresponding to ν_{as}(NSO) and ν_s(NSO), respectively. Previous IR studies of RNSO derivatives have shown that these two stretching modes are not strongly coupled.[27,28] There is disagreement, however, over the assignment of the individual bands to ν(NS) or ν(SO). For the series XNSO (X = F, Cl, Br, I) Eysel noted a more pronounced shift in the *lower* energy vibration and attributed this band to ν(NS).[27] This assignment has been adopted by other workers in their vibrational analysis of $S(NSO)_2$ (II (R E = S)),[29,30] an isoelectronic analogue of **2a** and **2b**. Close inspection of Eysel's numerical data,[27] however, reveals that there is not a clear-cut trend in the shifts of the ν_{as}(NSO) and ν_s(NSO) frequencies when X is changed. In contrast, Meij et al. attributed the *higher* energy vibration to ν(NS) on the basis of IR investigations of ^{15}N-labeled sulfinylanilines, ArNSO.[28] Support for this assignment comes from the observation that the lower energy vibration is shifted much less than the higher energy vibration of ArNSO upon side-on η^2-(N=S) coordination to Pt in **6** (R = Ar).[31] Thus the evidence from ^{15}N labeling and coordination complexes of ArNSO supports the assignment of the lower energy band to ν(SO) and the higher energy band to ν(NS), and it seems reasonable to adopt these assignments for **1**, **2a**, and **2b**.



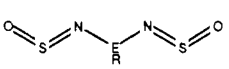
6



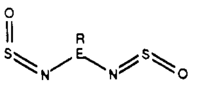
7a



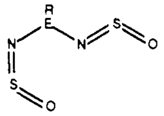
7b



7c



7d



7e

The stretching frequencies for **2a** and **2b** are shifted to higher frequencies by ca. 40–50 cm^{-1} compared to the corresponding bands for $S(NSO)_2$, which occur at 1185 and 1035 cm^{-1}.[29,30] Furthermore, two ν(NS) bands are observed for **2a** and **2b**. These observations merit some comment in the light of the known structure of $S(NSO)_2$. For a planar arrangement five isomers are feasible: cttc (**7a**), cctc (**7b**), tttt (**7c**), cttt (**7d**), and cctt (**7e**) (where c = cis and t = trans with reference to the geometry of substituents about the individual S–N and E–N bonds). In the solid state, structure **7a** is adopted for RE = S.[29,30] MNDO calculations indicate that the preference for this arrangement can be attributed to interactions between the negatively charged oxygen centers and the positively charged central sulfur atom.[32] Both a Coulombic attraction and an in-phase (weakly bonding) contribution in the HOMO are possible.[33] These calculations also revealed that structure **7b** is only ca 5 kJ mol^{-1} higher in energy than **7a** (RE = S). The observation of two ν(NS) bands for **2a** and **2b** suggests inequivalent NSO groups, i.e. a structure of lower symmetry than **7a** (C_{2v}). In addition, the shift to higher frequencies for vibrations involving the NSO groups when S is replaced by RAs indicates shorter and stronger S=N and S=O bonds in **2a** and **2b**, probably due to diminished interactions (or the absence of interactions) between the terminal oxygen atoms

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(33) The separation between a terminal oxygen and the central sulfur atom in $S(NSO)_2$ is 3.13 Å,[29,30] ca. 0.1 Å less than the sum of the van der Waals' radii.

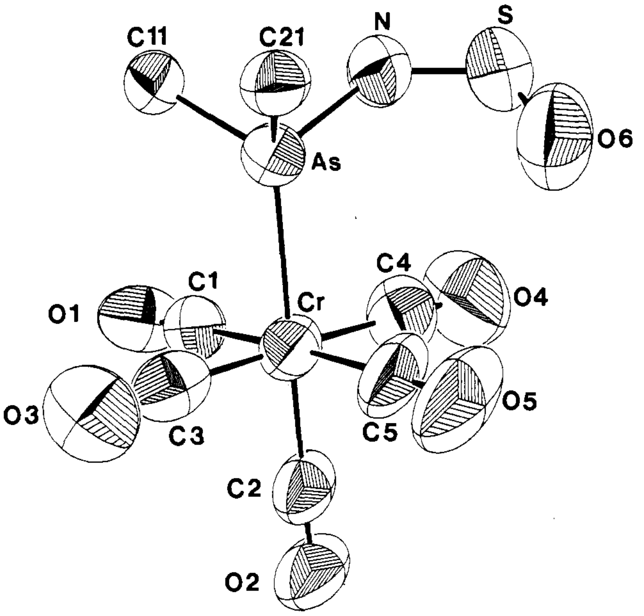

Figure 1. ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $Cr(CO)_5(Ph_2AsNSO)$ (**3**). Only the α-carbon atoms of phenyl groups are shown for clarity.

and arsenic.[34] Previous structural studies have revealed only cis isomers for RNSO derivatives.[5b,35] This fact together with the MNDO calculations for $S(NSO)_2$ and the IR data discussed above suggests that **7b** (or a nonplanar version) is the most likely arrangement for **2a** and **2b**. However, the X-ray structure determination is a challenging proposition for these low-melting, highly moisture-sensitive compounds. Consequently, we turned our attention to an investigation of the ligand behavior of **1**, **2a**, and **2b** in order to obtain crystalline derivatives that could be structurally characterized.

Preparation of $Cr(CO)_5(Ph_2AsNSO)$ (3) and $Cr(CO)_5[RAs(NSO)_2]$ (R = Ph (4a), *t*-Bu (4b)). The (thionylimino)arsines Ph_2AsNSO and $RAs(NSO)_2$ (R = Ph, *t*-Bu) react readily with $Cr(CO)_5(THF)$ to give complexes in which only the arsenic atom is coordinated to the metal and the NSO groups remain intact.

$$R_{3-n}As(NSO)_n + Cr(CO)_5(THF) \xrightarrow{THF} Cr(CO)_5[R_{3-n}As(NSO)_n] \quad (2)$$

3, R = Ph, n = 1
4a, R = *t*-Bu, n = 2
4b, R = Ph, n = 2

The characteristic infrared stretching vibrations of the NSO group in Ph_2AsNSO are not shifted substantially upon complexation (Table I), suggesting that the ligand is attached to chromium via the arsenic atom. This conclusion is confirmed by the X-ray structural determination of **3** described below.

The complexes **4a** and **4b** are extremely moisture-sensitive and satisfactory analytical data could not be obtained for these orange oils. Their infrared spectra show the typical pattern of a $Cr(CO)_5$ group in the 1900–2100-cm^{-1} region, and there is little change in the vibrational frequencies associated with the NSO groups of $RAs(NSO)_2$ upon complexation (Table I). Thus the spectroscopic evidence also suggests coordination to the metal via arsenic for these complexes.

Crystal and Molecular Structure of $Cr(CO)_5(Ph_2AsNSO)$ (3). The crystal structure of **3** 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. The structure of **3** is very similar to that of $Mo(CO)_5(Ph_2PNSO)$.[5b]

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $Cr(CO)_5(Ph_2AsNSO)$

Cr–As	2.438 (1)	S–O(6)	1.457 (9)
Cr–C(1)	1.896 (9)	C(1)–O(1)	1.14 (1)
Cr–C(2)	1.846 (7)	C(2)–O(2)	1.14 (1)
Cr–C(3)	1.877 (9)	C(3)–O(3)	1.14 (1)
Cr–C(4)	1.899 (10)	C(4)–O(4)	1.13 (1)
Cr–C(5)	1.894 (11)	C(5)–O(5)	1.14 (1)
As–N	1.889 (6)	As–C(11)	1.926 (8)
N–S	1.496 (7)	As–C(21)	1.926 (7)
As–Cr–C(1)	90.0 (2)	Cr–C(1)–O(1)	178.2 (7)
As–Cr–C(2)	178.0 (3)	Cr–C(2)–O(2)	179.1 (7)
As–Cr–C(3)	91.7 (2)	Cr–C(3)–O(3)	178.7 (6)
As–Cr–C(4)	89.9 (2)	Cr–C(4)–O(4)	177.7 (11)
As–Cr–C(5)	91.8 (2)	Cr–C(5)–O(5)	177.0 (8)
C(1)–Cr–C(2)	89.1 (3)	Cr–As–N	114.5 (2)
C(1)–Cr–C(3)	89.0 (4)	As–N–S	127.5 (4)
C(1)–Cr–C(4)	90.8 (4)	N–S–O(6)	120.2 (4)
C(1)–Cr–C(5)	177.3 (4)	Cr–As–C(11)	117.1 (2)
C(2)–Cr–C(3)	90.0 (3)	Cr–As–C(21)	123.2 (2)
C(2)–Cr–C(4)	88.3 (4)	N–As–C(11)	95.0 (3)
C(2)–Cr–C(5)	89.1 (4)	N–As–C(21)	100.2 (3)
C(3)–Cr–C(4)	178.4 (3)		
C(3)–Cr–C(5)	88.9 (4)		
C(4)–Cr–C(5)	91.2 (5)		

The geometry around the chromium atom is approximately octahedral. The AsNSO moiety is planar to within 0.01 Å and tilted at an angle of 32.0° with respect to the plane through the C(1)C(3)C(5)C(4)Cr unit, which is planar to within 0.01 Å. The Ph_2AsNSO ligand adopts a *cis* configuration with respect to the S–N bond. The value of the bond angle at the sulfur atom of 120.2 (4)° is somewhat larger and the bond angle of 127.5 (4)° at nitrogen is significantly smaller than the corresponding bond angles in $Mo(CO)_5(Ph_2PNSO)$ (118.6 (3) and 129.2 (4)°, respectively).[5b] Nevertheless the angle at nitrogen is still larger than that found for other RNSO compounds, e.g. 122.7 (2)° in $Ph_2CNSNSO$.[35] The S–O bond length of 1.457 (9) Å is typical, but the N–S bond length of 1.496 (7) Å is somewhat shorter than the corresponding value of ca. 1.53 Å found for other RNSO compounds.[35] The As–N bond length of 1.889 (6) Å is in the range 1.87–1.89 (1) Å found for $Ph_2AsNSNAsPh_2$[13] and $Ar_2As_2S_2N_4$ (Ar = Ph, mesityl),[12] and it has been shown that there is no significant change in the As–N bond lengths of $t\text{-}Bu_2As_2S_2N_4$ upon coordination to an $Os_3(CO)_{10}$ moiety.[36] The Cr–CO distance of 1.846 (7) Å found for the CO group trans to As is significantly shorter than the mean value of the other Cr–CO bond lengths [1.892 (10) Å], indicating that the Ph_2AsNSO ligand is a weaker π-acceptor than CO.

Reaction of $PhAs(NSO)_2$ with $Pt(C_2H_4)(PPh_3)_2$. Ligands of the type ArNSO adopt a side-on η^2-(N=S) coordination mode in Pt complexes of type **6**,[31] and the treatment of $S(NSO)_2$ with $Pt(C_2H_4)(PPh_3)_2$ promotes SO_2 elimination to give $PtS_2N_2(PPh_3)_2$.[37] We have investigated the reaction of **2b** with $Pt(C_2H_4)(PPh_3)_2$ in order to determine the initial site of interaction of zerovalent platinum with **2b** and any subsequent metal-promoted reactions of the coordinated ligand.

^{31}P NMR spectroscopy indicated that the initial product contains inequivalent Ph_3P groups. A characteristic AX pattern of 1:4:1 triplets, each split further into doublets, was observed with chemical shifts of +22.7 (P_A) and 10.7 (P_B), with coupling constants $^1J_{^{195}Pt-^{31}P} = 2152$ and $^2J_{^{31}P_A-^{31}P_B} = 23.0$ and $^1J_{^{195}Pt-^{31}P} = 3158$ and $^2J_{^{31}P_A-^{31}P_B} = 23.1$ Hz, respectively. This product probably involves side-on coordination to Pt via one of the N=S units as depicted in **6** [R = As(Ph)NSO],[38] but it is thermally unstable

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[34] The separation between the oxygen and arsenic atoms in $Cr(CO)_5(Ph_2AsNSO)$ is 3.39 Å; cf. 3.4 Å for the sum of the van der Waals' radii.

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[37] Chivers, T.; Edelmann, F.; Behrens, U.; Drews, R. *Inorg. Chim. Acta* **1986**, *116*, 145.

[38] This mode of bonding has been established by X-ray crystallography for **6** (R = Ar) in which the ^{31}P resonance with the largest $^1J_{^{195}Pt-^{31}P}$ value has been assigned to the PPh_3 group trans to N on the basis of ^{31}P NMR data for the 100% ^{15}N-enriched complexes.[31]

with respect to As–N bond cleavage to give *cis*-$Pt(PPh_3)_2(NSO)_2$, which was isolated in ca. 70% yield. The identity of the final product is based on elemental analyses, characteristic infrared frequencies at 1243 and 1228 (ν_{as} NSO) and 1098 and 1062 (ν_sNSO) cm^{-1}, the observation of a single 1:4:1 triplet in the $^{31}P\{^1H\}$ NMR spectrum at δ +8.8 with $^1J_{^{195}Pt-^{31}P}$ = 3191 Hz, and the isolation of an identical product from the reaction of $Pt(C_2H_4)(Ph_3P)_2$ with 2 mol of Me_3SiNSO.[39,40] The appearance of two IR bands for both ν_{as}(NSO) and ν_s(NSO) indicates inequivalent NSO groups in *cis*-$Pt(PPh_3)_2(NSO)_2$.[41]

Conversion of $R_{3-n}As(NSO)_n$ into $R_{3-n}As(NSN)_2AsR_{3-n}$ and Preparation of *cis*-$Cr(CO)_4(R_2As_2S_2N_4)$ (R = *t*-Bu (5a), (5b)). The treatment of metal complexes of I (E = P) with potassium *tert*-butoxide produces the corresponding sulfur diimides in high yields.[5b] By contrast, the reactions of **1**, **2a**, or **2b** with potassium *tert*-butoxide were accompanied by extensive cleavage of As–N bonds,[42] and only low yields of sulfur diimides could be obtained. The self-condensation reaction of (thionylimino)arsines can, however, be promoted by heating.

$$2PhAs(NSO)_2 \xrightarrow{100\ °C} Ph_2As_2S_2N_4 + SO_2 \qquad (3)$$

Attempts to convert **4a** or **4b** to complexes of $R_2As_2S_2N_4$ by thermolysis were unsuccessful, but such complexes were obtained by direct reaction of the ligands with labile metal carbonyl derivatives.[43]

$$\begin{aligned} Cr(CO)_4C_7H_8 + R_2As_2S_2N_4 \xrightarrow{-C_7H_8} {} & cis\text{-}Cr(CO)_4(R_2As_2S_2N_4) \\ & \mathbf{5a},\ R = t\text{-}Bu \\ & \mathbf{5b},\ R = Ph \end{aligned} \qquad (4)$$

Conclusion. A preliminary investigation of the coordination chemistry of the novel ligands Ph_2AsNSO and $RAs(NSO)_2$ (R = Ph, *t*-Bu) has revealed the expected pattern of coordination through arsenic with the 16-electron fragment $Cr(CO)_5$. Side-on N═S coordination followed by As—N bond cleavage occurs with the 14-electron fragment $(Ph_3P)_2Pt$. The latter tendency may prove to be a limiting factor in studies of complex formation by these new ligands.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant (T.C.) and an infrastructure grant for the X-ray structural service. A generous gift of $(Me_3N)_3S^+$-$Me_3SiF_2^-$ from Dr. F. Edelmann (Universität Göttingen) is gratefully acknowledged.

Registry No. **1**, 113585-02-7; **2a**, 113585-03-8; **2b**, 113585-04-9; **3**, 113585-05-0; **4a**, 113585-07-2; **4b**, 113585-06-1; **5a**, 113585-09-4; **5b**, 113585-08-3; TAS^+NSO^-, 111718-75-3; $(TAS)^+Me_3SiF_2^-$, 59218-87-0; Me_3SiNSO, 7522-26-1; Ph_2AsCl, 712-48-1; KNSO, 73400-02-9; *t*-$BuAsCl_2$, 4262-41-3; $PhAsCl_2$, 696-28-6; $Me_3SiNSNSiMe_3$, 18156-25-7; $Ph_2As_2S_2N_4$, 70369-32-3; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $Cr(CO)_5(THF)$, 15038-41-2; *cis*-$Pt(PPh_3)_2(NSO)_2$, 108450-77-7; $Cr(CO)_4(C_7H_8)$, 12146-36-0.

Supplementary Material Available: Tables SI–SIII, giving anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond lengths and bond angles for non-hydrogen atoms (3 pages); Table SIV, giving observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(40) Short, R.; Hursthouse, M. B.; Purcell, T. G.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1987**, 407. In contrast, the reaction of $(Ph_3P)_2Pt(C_2H_4)$ with $Hg(NSO)_2$ has been shown to give *trans*-$(Ph_3P)_2Pt(NSO)_2$ (40%): IR ν_{as}(NSO) 1218 s and ν_s(NSO) 1099 s cm^{-1}; NMR $\delta(^{31}P)$ +19.0 ($^1J_{^{195}Pt-^{31}P}$ = 2854 Hz). These authors also report that the reaction of *cis*-$PtCl_2(PPh_3)_2$ with $Hg(NSO)_2$ gives a product with $\delta(^{31}P)$ +8.1 and $^1J_{^{195}Pt-^{31}P}$ = 3257 Hz. This product was assumed to be *cis*-$Pt(PPh_3)_2(NSO)_2$, but it was not isolated.

(41) (a) Plenio, H.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1483. (b) Herberhold, M.; Neumann, F.; Süss-Fink, G.; Thewalt, U. *Inorg. Chem.* **1987**, *26*, 3612. These recent papers describe the synthesis and crystal structure of $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$, which adopts conformation **7a** with equivalent NSO groups: IR ν_{as}(NSO) 1235 and ν_s(NSO) 1075 cm^{-1}.

(42) Herberhold, M.; Ehrenreich, W.; Bühlmeyer, W.; Guldner, K. *Chem. Ber.* **1986**, *119*, 1424. Cleavage of As–N bonds is also observed in the reaction of *t*-$Bu_2AsNSNAs$-*t*-Bu_2 with KO-*t*-Bu to give *t*-$Bu_2AsNSN^-K^+$.

(43) Edelmann, F.; Spang, C.; Noltemeyer, M.; Sheldrick, G. M.; Keweloh, N.; Roesky, H. W. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1987**, *42B*, 1107. After the submission of this paper the preparation of **5b** and the X-ray structural characterization of the molybdenum analogue, *cis*-$Mo(CO)_4(Ph_2As_2S_2N_4)$, was reported.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Complexes of Technetium(III) with Sterically Hindered Arenethiolates and Their Interactions with Small π-Accepting Molecules

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A series of neutral Tc(III) compounds with sterically hindered arenethiolate ligands is reported. They contain a $Tc(SAr)_3$ core (SAr = 2,3,5,6-tetramethylbenzenethiolate (tmbt) or 2,4,6-triisopropylbenzenethiolate (tibt)) capped by two π-accepting ligands (MeCN, *i*-PrNC, py, or CO) to form a trigonal bipyramid and are air stable, diamagnetic, 14-electron compounds. Although the acetonitrile ligands in the parent compound $Tc(SAr)_3(MeCN)_2$ do not self-exchange with solvent MeCN-d_3, they are readily displaced by CO or *i*-PrNC to yield $Tc(SAr)_3(CO)_2$ or $Tc(SAr)_3(i\text{-}PrNC)_2$, respectively. One of the carbonyl ligands in $Tc(SAr)_3(CO)_2$ is labile, and this property has been exploited to prepare the monocarbonyl complexes $Tc(SAr)_3(CO)(MeCN)$ and $Tc(SAr)_3(CO)(py)$. Single-crystal X-ray structure determinations were carried out on $Tc(SC_{10}H_{13})_3(CH_3CN)_2$ (crystal data: monoclinic, a = 11.227 (1) Å, b = 15.784 (1) Å, c = 20.411 (1) Å, β = 105.36 (1)°, space group $P2_1/n$, Z = 4, final R = 0.066, R_w = 0.073), $Tc(SC_{10}H_{13})_3(CO)(CH_3CN)$ (monoclinic, a = 13.072 (2) Å, b = 15.153(2) Å, c = 17.149 (2) Å, β = 98.46 (1)°, space group $P2_1/n$, Z = 4, final R = 0.046, R_w = 0.059), and $Tc(SC_{10}H_{13})_3(CO)(C_5H_5N)$ (triclinic, a = 10.773 (1) Å, b = 18.018 (1) Å, c = 9.034 (1) Å, α = 93.67 (1)°, β = 96.05 (1)°, γ = 87.08 (1)°, space group $P\bar{1}$, Z = 2, final R = 0.044, R_w = 0.063). The coordination sphere is similar for all three structures, in which the sulfur atoms sit in the equatorial plane of a trigonal bipyramid and the π-accepting ligands occupy the axial positions. Two of the aryl rings are consistently on the same side of the plane defined by the sulfur atoms, while the other is on the opposite side. Spectroscopic data suggest that every compound in the series shares this conformation.

Due to its role in a number of enzymatic systems, the chemistry of transition-metal thiolate complexes has received much attention.[2] However, the analogous technetium chemistry remains essentially unexplored. The affinity of Tc(V) oxo complexes for