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THE SYNTHESIS OF PHOSPHINO-, ARSINO- AND STIBINO-SUBSTITUTED SULFUR DIIMIDE HETEROCYCLES IN TRANSITION METAL COMPLEXES

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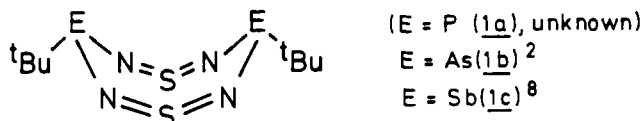
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Abstract The reaction of pentacarbonylchromium complexes $\text{Cr}(\text{CO})_5[\text{tBuECl}_2]$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$) with the salt K_2SN_2 (1:1) leads to the formation of either six- or eight-membered sulfur diimide heterocycles. Coordination compounds such as $\text{Cr}(\text{CO})_5[\text{tBuE}(\text{NSN})\text{SNH}]$ ($\text{E} = \text{P}, \text{As}$) and $\text{Cr}(\text{CO})_5[\text{tBuE}(\text{NSN})_2\text{E}^t\text{Bu}]$ ($\text{E} = \text{As}, \text{Sb}$) have been obtained, and the X-ray crystallographic structure of $(\text{CO})_5\text{Cr}[\text{tBuP}(\text{NSN})\text{SNH}]$ has been determined. A comparative structural study of transition metal complexes containing the boat-shaped eight-membered ring $\text{tBuAs}(\text{NSN})_2\text{As}^t\text{Bu}$ as a ligand (L) reveals high flexibility of the ring system. Non-bonding transannular $\text{As} \cdots \text{As}$ distances between 313 and 396 pm have been observed.

INTRODUCTION

In addition to bis(trimethylsilyl) sulfur diimide, $\text{S}(\text{N-SiMe}_3)_2$, the salt K_2SN_2 ¹ is a valuable starting material for the synthesis of sulfur diimide heterocycles. Thus, several arsenic(III)-containing rings ^{2,3} and cages ^{3,4} have been synthesized via the reactions of K_2SN_2 with arsenic(III) chlorides such as tBuAsCl_2 ², $\text{MeCH}(\text{As}^t\text{BuCl})_2$ ³, $\text{RCH}(\text{AsCl}_2)_2$ ($\text{R} = \text{H}, \text{Me}$) ³, $[\text{tBuNAsCl}]_2$ and AsCl_3 ⁴. The eight-membered ring $\text{tBuAs}(\text{NSN})_2\text{As}^t\text{Bu}$ (**1b**) - which is analogous to the known compounds $\text{RAs}(\text{NSN})_2\text{AsR}$ ($\text{R} = \text{methyl}$ ⁵, phenyl ⁶, mesityl ⁶) - can be prepared from tBuAsCl_2 and either

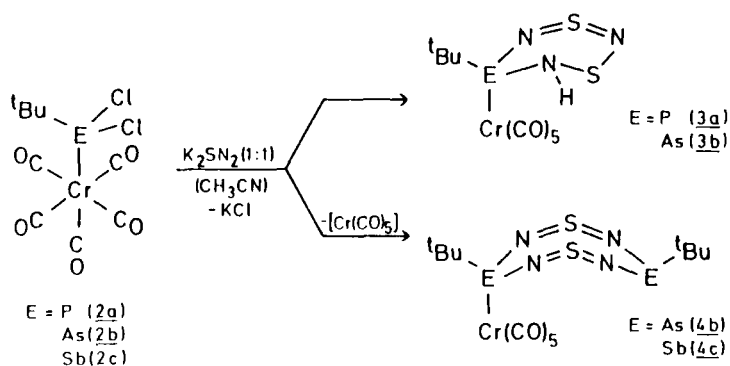
$S(N-SiMe_3)_2$ or K_2SN_2 , and the less stable antimony analogue 1c is similarly accessible from $tBuSbCl_2$. However, the corresponding phosphorus compound (1a) could not be obtained from $tBuPCl_2$ (cf. ⁷).



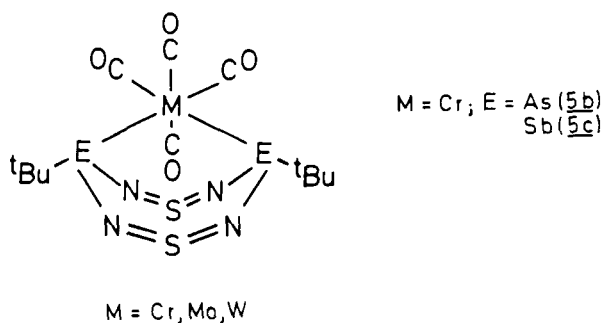
PREPARATION OF THE COMPLEXES

In an attempt to synthesize the missing boat-shaped ring system 1a in the protecting coordination sphere of a transition metal complex, the pentacarbonylchromium compound $Cr(CO)_5[tBuPCl_2]$ (2a) was treated with K_2SN_2 (1:1) in acetonitrile suspension. However, a PS_2N_2 six-membered ring system was formed. In addition to $Cr(CO)_5[\overline{tBuP(NSN)SNH}]$ (3a)⁹ (yield 20%), two aminophosphane complexes $Cr(CO)_5[P(tBu)(NH_2)_2]$ and $(CO)_5Cr[(tBu)(NH_2)P(NSN)P(tBu)(NH_2)]Cr(CO)_5$ (pair of enantiomers, ratio 5.5 : 1) were isolated in yields of 5 and 10%, respectively. The corresponding reactions of $Cr(CO)_5[PhPCl_2]$ and $Cr(CO)_5[PCl_3]$ with K_2SN_2 (1:1) led also to the formation of six-membered heterocycles, i.e. $Cr(CO)_5[\overline{RP(NSN)SNH}]$ ($R = Ph$ and NH_2 , respectively).

No products containing eight-membered phosphorus-nitrogen-sulfur rings were isolated, although Chivers et al. ⁷ have recently described the binuclear complex trans-(CO)₅Cr[(ⁱPr₂N)P(NSN)₂P(ⁿPr₂)]Cr(CO)₅, which contains an almost planar P₂N₄S₂ ring.



From the reaction of $Cr(CO)_5[{}^tBuAsCl_2]$ (2b) with K_2SN_2 , products with either six- or eight-membered rings (3b and 4b) were obtained. It was not possible to attach a second complex fragment ($[Cr(CO)_5]$ or $[CpMn(CO)_2]$ ($Cp = \eta^5$ -cyclopentadienyl)) to the free arsenic atom of $Cr(CO)_5[{}^tBuAs(NSN)_2As{}^tBu]$ (4b). However, both thermolysis and photolysis in solution convert 4b into the known chelate complex $Cr(CO)_4[{}^tBuAs(NSN)_2As{}^tBu]$ (5b) which can be directly synthesized ^{10,11} from 1b and the precursor of tetracarbonylchromium fragments, $Cr(CO)_4(nor-C_7H_8)$ ($nor-C_7H_8 =$ norbornadiene).



The reaction of $Cr(CO)_5[{}^tBuSbCl_2]$ (2c) with K_2SN_2 gave only the product containing the eight-membered ring, 4c. Attempted decarbonylation of 4c led to decomposition of the ring ligand 1c. However, chelate complexes $M(CO)_4[{}^tBuSb(NSN)_2Sb{}^tBu]$ ($M = Cr$ (5c), Mo , W) are directly accessible ⁶ from 1c and $Cr(CO)_4(nor-C_7H_8)$.

STRUCTURAL STUDIES

The molecular structure of $\text{Cr}(\text{CO})_5[\text{}^t\text{BuP}(\overline{\text{NSN}})\text{SNH}]$ (**3a**) is presented in Figure 1. The six-membered ring possesses a half-boat conformation with the hydrogen-bearing nitrogen atom protruding by 71 pm from the plane of the almost planar $\text{P}(\text{NSN})\text{S}$ unit.

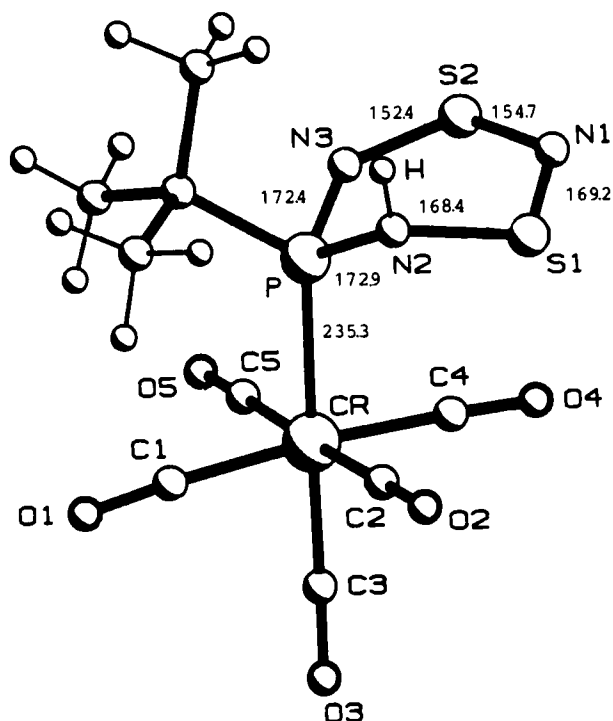


FIGURE 1 Molecular Structure of $\text{Cr}(\text{CO})_5[\text{}^t\text{BuP}(\overline{\text{NSN}})\text{SNH}]$ (**3a**)

The ring in **3a** contains both a sulfur diimide and a diamino sulfane sub-structure with angles of $103.7(3)^\circ$ at P, $108.2(4)^\circ$ at S1 and $120.1(4)^\circ$ at S2. The P-N distances correspond to single bonds. The sulfur diimide unit in **3a** is apparently less involved

in the π -electron system of the ring than in phosphorus(V) derivatives such as $\text{Ph}_2\overline{\text{PNSNSN}}$ ¹² $(\text{Me}_3\text{SiNH})_2\overline{\text{PNSNSN}}$ ¹³ and $[\text{Ph}_2\overline{\text{PNSNSNMe}}]^+$ ¹⁴.

A series of carbonylmetal complexes is now known which contain the eight-membered ring $\text{tBuAs(NSN)}_2\text{As}^{\text{tBu}}$ (**1b**) as a ligand (L).¹² As expected, the geometry of the hammock-like molecule **1b** - as indicated by the (nonbonding) transannular $\text{As}\cdots\text{As}$ distance and the As-N-S angle - depends on the coordination mode. The flexibility of the ring ligand **1b** (L) is illustrated in Figure 2 which shows an almost linear correlation between these two parameters.

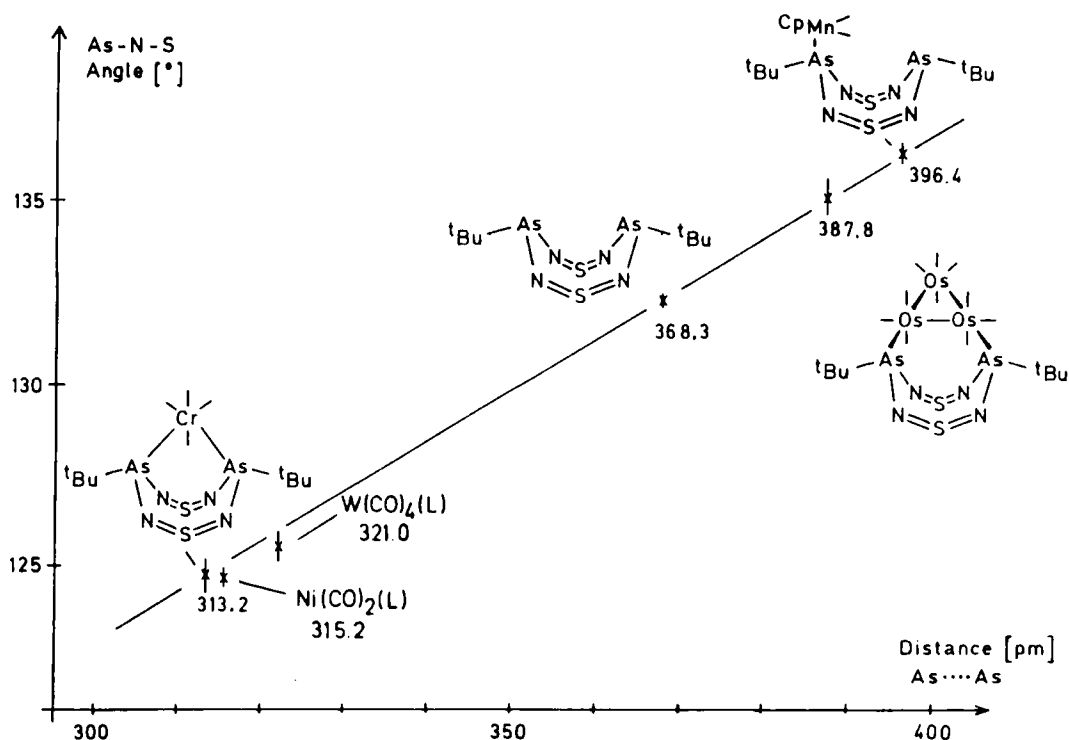


FIGURE 2 Carbonylmetal complexes containing $\text{tBuAs(NSN)}_2\text{As}^{\text{tBu}}$ (**1b**)

Compared with the free molecule ($L = 1b$) the ring ligand L is considerably compressed in chelate complexes such as $M(CO)_4(L)$ ($M = Cr, W$) and $Ni(CO)_2(L)$. On the other hand, the ring is opened when acting as a monodentate ligand in $CpMn(CO)_2(L)$, or as a bidentate ligand to two metal atoms in $Os_2(CO)_{10}(L)$.¹⁵

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