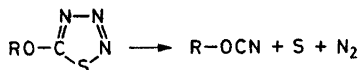


Formation of Triphenylphosphine Sulfide, Triphenylarsine Sulfide, Triphenylstibine Sulfide, and Attempts to Obtain Nitrogen Complexes from 5-Alkoxy-1,2,3,4-thiatriazoles

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During investigations of the mechanism of the transformation of 5-alkoxy-1,2,3,4-thiatriazoles into alkyl cyanates,<sup>1</sup> which takes place according to the stoichiometric equation:



some attempts were made to "trap" the nitrogen and sulfur formed in this reaction. Sulfur must primarily be eliminated as sulfur atoms, which would be expected to react as "active sulfur". This was borne out by addition of triphenylphosphine, triphenylarsine, or triphenylstibine to a solution of 5-ethoxy-1,2,3,4-thiatriazole in ether. Whereas this solution on standing at room temperature normally becomes turbid because of the formation of sulfur (S<sub>8</sub>), it remained clear when the above-mentioned compounds had been added; the corresponding sulfides could be isolated in almost quantitative yields from the solution. The phosphine sulfide and arsine sulfide were obtained directly in an analytically pure state (C, H, and S analyses) whereas the stibine sulfide contained some free sulfur. Melting points and infrared spectra<sup>2</sup> agreed with those reported in the literature. It is remarkable that triphenylarsine sulfide (m.p. 164–165°C, cf. Ref. 2) is formed so easily in this way, since it could not be prepared from triphenylarsine and sulfur.<sup>2</sup>

On the other hand, triphenylamine and triphenylbismuth, added to the decomposing thiatriazole, were recovered unchanged, with sulfur separating from the solution.

Since it would be very interesting to isolate an amine *N*-sulfide, which represents a hitherto unknown class of compound, several analogous experiments were carried out in which other tertiary amines (trimethylamine, pyridine, quinoline) were added to the thiatriazole; these gave negative results, however.

When 5-ethoxy-1,2,3,4-thiatriazole was added to a chloroform solution of the iridium or rhodium complexes, [Ir(Ph<sub>3</sub>P)<sub>2</sub>(CO)Cl] and [Rh(Ph<sub>3</sub>P)<sub>2</sub>(CO)Cl], gas was evolved immediately and the solution became turbid (in the case of the rhodium complex the colour of the solution changed from light yellow to reddish-brown). After 10 min at 40°C the solution was clarified by centrifugation. On addition of pentane a golden-yellow (Ir compound) or yellow-brown (Rh compound) solid precipitated. The infrared spectra of these products showed that, in both cases, the original CO band at *ca.* 1970 cm<sup>-1</sup> had almost disappeared while new intense bands at 2240 cm<sup>-1</sup> and 2050 cm<sup>-1</sup> (Ir compound) and 2115 cm<sup>-1</sup> (Rh compound) had appeared. The 2050 cm<sup>-1</sup> and the 2115 cm<sup>-1</sup> absorptions are quite close to those reported for the N<sub>2</sub> absorption frequency (2095 and 2152 cm<sup>-1</sup>, respectively) in iridium<sup>3</sup> and rhodium<sup>4</sup> complexes which are known to contain coordinated molecular nitrogen. However, a mass spectrometric investigation revealed that no nitrogen was given off from these products on thermal decomposition. Also the intensities of these bands are not diminished by heating the products for several hours at 65°C. It must then be concluded that the bands at 2050 cm<sup>-1</sup> and 2115 cm<sup>-1</sup> are due to CO. Other examples are known<sup>5</sup> where the CO frequency is near 2100 cm<sup>-1</sup>.

The band at 2240 cm<sup>-1</sup> is assigned to an NCO group vibration. The formation of cyanato (or isocyanato) complexes from alkyl cyanates and metal halides has been found to be a general reaction.<sup>6</sup> The alkyl cyanates do not become bound as such but react with halide ions to form alkyl halides and cyanate ions, which then replace the halogenide ions in the complex. Thus the above-mentioned iridium and rhodium complexes reacted with ethyl cyanate to form complexes with the compositions [Ir(Ph<sub>3</sub>P)<sub>2</sub>(CO)(NCO)] and [Rh(Ph<sub>3</sub>P)<sub>2</sub>(CO)(NCO)]. These were chlorine-free and exhibited the CO band at 1970 cm<sup>-1</sup> with an intensity comparable to that of the parent compounds. In addition they exhibited the cyanate band at 2240

$\text{cm}^{-1}$ . Alkyl cyanates<sup>7</sup> and cyanic acid have a strong absorption band near  $2250\text{ cm}^{-1}$  and a coordinated isocyanate ion has been reported<sup>8</sup> to absorb at  $2180\text{--}2200\text{ cm}^{-1}$ .

It is remarkable that no nitrogen complex is formed from 5-ethoxy-1,2,3,4-thiatriazole and the iridium complex  $[\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$  since this is known to form a nitrogen complex when it reacts with organic azides.<sup>3</sup> The reaction with 5-ethoxy-1,2,3,4-thiatriazole was carried out at both a lower temperature ( $0^\circ\text{C}$ ) and in other solvents, but in no case could the nitrogen complex be isolated. The reason for this is possibly that the ligand triphenylphosphine is converted to triphenylphosphine sulfide during the reaction with the thiatriazole, and this may also be the cause of the shift of the CO frequency which is not observed when the complexes react with ethyl cyanate. It proved impossible to purify these products by recrystallization and analyses were variable and did not correspond to any simple formula. They indicate, however, that chlorine has been exchanged by cyanate. The infrared spectra exhibit all bands of triphenylphosphine and triphenylphosphine sulfide.

Several other phosphine complexes, phosphine-carbonyl complexes, carbonyl-olefin complexes, and carbonyl complexes of vanadium, chromium, manganese, iron, molybdenum, rhenium, platinum, and tungsten were treated with 5-ethoxy-1,2,3,4-thiatriazole, but in no case did the infrared spectra of the reaction products indicate the formation of nitrogen complexes.

*Experimental. Triphenylphosphine sulfide.* A solution of 2.62 g of triphenylphosphine in 5 ml of diethyl ether was added to a solution of 1.31 g of 5-ethoxy-1,2,3,4-thiatriazole<sup>9</sup> in 5 ml of ether, and the mixture was kept for 12 h at room temperature. Triphenylphosphine sulfide separated as a colourless crystalline solid, which was filtered off and washed with ether. Yield 2.4 g (82%) with m.p.  $161\text{--}162^\circ\text{C}$  (lit.<sup>10</sup> 161). (Found: C 73.21; H 5.20; S 10.90. Calc.: C 73.40; H 5.12; S 10.90). Triphenylarsine sulfide and triphenylstibine sulfide were obtained similarly.

*Formation of cyanate (or isocyanate) complexes.* One ml of a 0.28 M solution of ethyl cyanate<sup>11</sup> in ether was added to a solution of 50 mg of the complex  $[\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$  or  $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$  in 5 ml of chloroform. After 12 h a precipitate had formed. The iridium compound was yellow, the rhodium compound yellow-brown (the solution in this case became red-brown a few minutes after the addition of the cyanate). The precipitates were collected and washed with ether and dried in vacuum. The compounds (according to their infrared spectra) contain both OCN and CO, but no chlorine. Iridium compound: Found: C 57.4; H 3.76. Calc. for  $[\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})(\text{NCO})]$  or  $\text{C}_{36}\text{H}_{30}\text{IrNO}_2\text{P}_2$ : C 56.5; H 4.12. Rhodium compound: Found: C 65.3; H 4.41. Calc. for  $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})(\text{NCO})]$  or  $\text{C}_{36}\text{H}_{30}\text{NO}_2\text{RhP}_2$ : C 63.1; H 4.60. Infrared spectra (KBr): 1960 vs, 2250 vs (Ir compound), 1980 vs, 2240 vs (Rh compound).

1. Jensen, K. A., Burmester, S. and Bak, T. A. *Acta Chem. Scand.* **21** (1967) 2792.
2. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 1875.
3. Collman, J. P. and Kang, J. W. *J. Am. Chem. Soc.* **88** (1966) 3459; Collman, J. P., Kubota, M., Sun, J.-Y. and Vastine, F. *J. Am. Chem. Soc.* **89** (1967) 169.
4. Ukhin, L. Yu., Shvetsov, Yu. A. and Khidekel, M. L. *Izv. Akad. Nauk. SSSR Ser. Khim.* **6** (1967) 957.
5. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1963, pp. 176–182.
6. Jensen, K. A., Holm, A. and Huges-Jensen, E. *Acta Chem. Scand.* To be published.
7. Groving, N. and Holm, A. *Acta Chem. Scand.* **19** (1965) 443.
8. Forster, D. and Goodgame, D. M. L. *J. Chem. Soc.* **1965** 1286.
9. Jensen, K. A., Holm, A. and Thorkilsen, B. *Acta Chem. Scand.* **18** (1964) 825.
10. Strecker, W. and Grossmann, C. *Ber.* **49** (1916) 63, p. 74.
11. Jensen, K. A. and Holm, A. *Acta Chem. Scand.* **18** (1964) 826.

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