

dithiols.³ The very large shift in the case of the gold complex, as compared to the complexes of divalent metals, is explained by the higher positive charge of the central atom, which will cause an increased drift of electrons towards the selenium atoms.

The position of the $=CSe_2$ stretching band of the ligand, near 850 cm^{-1} , appears to be almost unchanged in the spectra of the complexes. A ligand infrared band, at 467 cm^{-1} , is shifted towards lower frequencies in the spectra of the complexes, and is assigned to a deformation mode of the $=CSe_2$ group. The ligand further exhibits infrared bands near 1200 cm^{-1} and 600 cm^{-1} . These bands, which are only weak in the spectra of the complexes, will be discussed elsewhere in another connection.⁴

Electronic spectra. The ligand (as the potassium or tetraphenylphosphonium salt) has an absorption maximum at 370 nm and the same maximum is found, with only small variations, in the spectra of the metal complexes. Whilst the zinc and cadmium complexes exhibit only this band, most of the transition metal complexes exhibit an additional band (Table 1) which, like the corresponding band of the 1,1-dithiolate complexes,⁵ is assigned to an $M \rightarrow L^*$ intramolecular charge transfer. Finally, the lowest bands of the Ni(II), Pt(II), Cu(II), Co(III) complexes are assigned to spin-allowed $d-d$ transitions.

Experimental. The infrared spectra (KBr discs) were recorded on a Perkin-Elmer model 337 grating spectrophotometer and the electronic spectra (acetone solutions) on a Perkin-Elmer model 137 ultraviolet-visible spectrophotometer.

1. Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **24** (1970) 1088.
2. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* **22** (1968) 1107.
3. Fackler, J. P. and Coucouvanis, D. *J. Am. Chem. Soc.* **88** (1966) 3913.

4. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand. In press.*
5. Werden, B., Billig, E. and Gray, H. B. *Inorg. Chem.* **5** (1966) 78.

Received March 6, 1970.

Phosphinodithioformates

III. *P,P*-Disubstituted Thiophosphinoylthioformamides

OTTO DAHL and OLE LARSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

During an investigation of some derivatives of phosphinodithioformic acid, R_2PCSSH , the aminolysis of esters of thiophosphinoylthioformic acid, $R^1P(S)CSSR^2$ (I), to give thiophosphinoylthioformamides, $R^1P(S)CSNR^2R^4$ (II), has been studied. Previously, such amides have been prepared from secondary phosphine sulfides and thiocyanic acid or isothiocyanates,¹ and by the reaction of secondary phosphines with isothiocyanates, followed by treatment with sulfur.² Both methods are limited to the preparation of unsubstituted or *N*-monosubstituted amides, in contrast to the method described here.

Esters of the type (I), $R^1 =$ ethyl or phenyl, $R^2 =$ methyl, ethyl or benzyl,³ reacted readily with ammonia and moderately sterically hindered primary aliphatic amines; for example, isopropylamine reacted readily in ether solution, whereas *tert*-butylamine reacted very slowly. No amides could be obtained from (I) and aromatic amines. In the case of secondary

Table 1. Yields, melting points and analyses for *P,P*-disubstituted thiophosphinoylthioformamides.

No.	Compound	Yield, %	M.p., °C	Formula	Analyses (C, H, N, S)
IIa	(C ₂ H ₅) ₂ P(S)CSNH ₂	40 ^a	114–116	C ₈ H ₁₂ NPS ₂	Found: 33.25 6.67 7.74 35.59 Calc.: 33.13 6.67 7.73 35.38
IIb	(C ₂ H ₅) ₂ P(S)CSNHCH ₃	85 ^b	67–68.5	C ₉ H ₁₄ NPS ₂	Found: 36.61 7.16 7.02 32.87 Calc.: 36.90 7.23 7.17 32.84
IIc	(C ₂ H ₅) ₂ P(S)CSN(CH ₃) ₂	60 ^b	32–32.5	C ₇ H ₁₆ NPS ₂	Found: 40.00 7.76 6.52 30.82 Calc.: 40.16 7.71 6.69 30.64
IId	(C ₂ H ₅) ₂ P(S)CSNHC ₂ H ₅	30 ^b	24–24.5	•	Found: 39.92 7.62 6.84 30.85
IIe	(C ₂ H ₅) ₂ P(S)CSNHCH(CH ₃) ₂	45 ^c	22.5–23.5	C ₉ H ₁₈ NPS ₂	Found: 43.25 7.95 6.32 29.00 Calc.: 43.02 8.12 6.27 28.72
IIf	(C ₂ H ₅) ₂ P(S)CSN(CH ₃) ₄	75 ^d	78–79	C ₉ H ₁₈ NPS ₂	Found: 46.05 7.76 5.96 27.35 Calc.: 45.93 7.71 5.95 27.25
IIg	(C ₂ H ₅) ₂ P(S)CSNH ₂	40 ^a	129–130.5 ^f	C ₁₂ H ₁₈ NPS ₂	Found: 55.68 4.41 4.99 23.08 Calc.: 56.30 4.36 5.05 23.13
IIh	(C ₂ H ₅) ₂ P(S)CSNHCH ₃	50 ^d	93.5–95.5 ^g	C ₁₄ H ₁₄ NPS ₂	Found: 57.68 4.94 4.72 22.10 Calc.: 57.70 4.84 4.81 22.01
IIi	(C ₂ H ₅) ₂ P(S)CSN(CH ₃) ₂	40 ^e	191–193	C ₁₃ H ₁₆ NPS ₂	Found: 59.02 5.35 4.45 20.93 Calc.: 58.99 5.28 4.59 21.00
IIj	(C ₂ H ₅) ₂ P(S)CSNHC ₂ H ₅	35 ^d	87–89	•	Found: 58.90 5.33 4.53 21.30
IIk	(C ₂ H ₅) ₂ P(S)CSN(CH ₃) ₃	35 ^d	185–187	C ₁₃ H ₂₀ NPS ₂	Found: 62.85 6.00 4.09 18.53 Calc.: 62.58 5.84 4.05 18.56

Solvents used for recrystallization: ^aMethylene chloride-pentane, ^b80 % methanol, ^cpentane,

^dethanol, ^e2-propanol. ^fLit.¹ 132–135°C. ^gLit.¹ 98–100°C, ^h103°C.

amines, dimethylamine, pyrrolidine, and piperidine furnished the corresponding amides readily, whereas no amides could be isolated from the red-brown oils obtained from reacting (I) with diethylamine or higher homologues. Probably, the aminolyses have to be fast in order to compete with a base-induced decomposition of (I). The physical properties of the amides prepared are listed in Table 1.

The proton magnetic resonance (¹H-NMR) spectra of compounds containing the P(O)C(O)N grouping have been studied by Siddall III *et al.*^{4,5} who observed long-range coupling from phosphorus to the protons in the *N*-substi-

tuents, and doubling of the signals from the *N*-substituents due to slow rotation about the carbonyl-nitrogen bond. The same phenomena were observed in the ¹H-NMR spectra of the thioamides II (Table 2). In these compounds the long-range coupling from phosphorus to the α -hydrogens of the *N*-alkyl groups (J_{PCNCH}) is of approximately the same magnitude as both that found for the oxygen analogues⁴ and that of the corresponding coupling (J_{PCSCH}), found for the dithioesters (I).⁵ However, the coupling to the β -hydrogens (J_{PCNCH}) is smaller than that to the α -hydrogens, in contrast to the results obtained for most of the

Table 2. ¹H-NMR chemical shifts ^{a,b} (τ) and coupling constants (*J*, Hz) of *P,P*-disubstituted thiophosphinoylthioformamides (ca. 5 % solutions in CDCl₃).

No.	N-C-H (α)	N-C-C-H (β)	N-H ^e	<i>J</i> _{PCNCH}	<i>J</i> _{PCNCCH}	<i>J</i> _{HNCH} ^g	<i>J</i> _{HCCH(N)}
IIb	6.70 (2 × 2 ^c)		ca. 0.2	1.7		5.2	
IIc	6.53 (2 × 1) 6.02 (2 × 1)			1.6 1.0			
IId	6.24 (m ^d)	8.67 (3 × 1)	ca. 0.4	1.7		5.7	7.4
IIe	5.35(m)	8.68 (2 × 2)	ca. 0.5	1.8	ca. 0.3	ca. 4.8	6.4
IIh	6.72 (2 × 2)		ca. -0.3	1.9		5.3	
IIi	6.48 (2 × 1)			ca. 1.1			
III ^h	7.12 (2 × 1) 6.93 (2 × 1)			1.5 1.0			
IIj	6.25 (m)	8.65 (3 × 2)	ca. 0.0	1.8	ca. 0.5	5.6	7.5

^aThe signals from the *P*-ethyl and *P*-phenyl groups have been omitted as the chemical shifts and coupling constants are close to those found for the corresponding esters.^b The values given in the table represent the centres of the multiplets. ^cMultiplicity of signal. ^dMultiplet. ^eVery broad. ^fNot resolved. ^gThe splitting assigned to this coupling disappeared upon shaking with acidified D₂O. ^hIn C₆D₆.

compounds studied by Siddall III,⁴ and also in contrast to the results for the dithioesters (I).³ Obviously, no simple relations exist between the magnitude of these long-range couplings and the number of bonds which separate hydrogen and phosphorus. Apart from the narrow spacing due to coupling with phosphorus, a further doubling of signals from the *N*-alkyl groups of IIc was observed in CDCl₃ solution, whereas no such doubling was found for III in CDCl₃. However, III in C₆D₆ showed a similar doubling. Apparently, the signals from the methyl groups in III are accidentally coincident in CDCl₃. This doubling is most probably due to slow rotation about the thiocarbonyl-nitrogen bond. Thus, the two pairs of signals exhibited by IIc moved towards each other with increasing temperature and coalesced at 107 ± 5°C (in (CD₃)₂SO). Moreover, the coupling constants *J*_{PCNCH} are different for the two signals, corresponding to *N*-methyl groups *cis* or *trans* to phosphorus.

Experimental. The yellow thioamides (IIa-k) were obtained by the following general procedure: The methyl ester (I) (10⁻³ mol) was dissolved in ether (10 ml) and excess amine was added at room temperature. In most cases the reaction was completed within a minute and was accompanied by evolution of methanethiol and a change of colour from red to yellow. The solution was evaporated to dryness and the product was purified by re-crystallization. The physical data are given in Table 1.

1. Ojima, I., Akiba, K. and Inamoto, N. *Bull. Chem. Soc. Japan* **42** (1969) 2975.
2. Issleib, K. and Harzfeld, G. *Z. anorg. allgem. Chem.* **351** (1967) 18.
3. Dahl, O. and Larsen, O. *Acta Chem. Scand.* **23** (1969) 3613.
4. Siddall III, T. H. and Prohaska, C. A. *Applied Spectroscopy* **21** (1967) 9.
5. Siddall III, T. H. and Stewart, W. E. *Spectrochim. Acta A* **24** (1968) 81.

Received March 12, 1970.