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THE PREPARATION OF DIALKYLTHIOPHOSPHONATOAMINES. X-RAY STRUCTURES OF $(EtO)_2PSNHC_6H_4NO_2$ AND $[(EtO)_2PSNHC_6H_4NO_2]_2PdCl_2$

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Abstract—Reaction of RR′NH with $(EtO)_2P(S)Cl$ gave $(EtO)_2P(S)NRR'$ (R, R′ = Bu, Et, Me, H but not all combinations, R = H, R′ = p-$O_2NC_6H_4$- = the title compound). The crystal structures of the title compounds show that the aryl-N-P-S backbone is approximately co-planar both in the free compound and its palladium complex. In the palladium complex, the ligands are tilted with respect to the coordination plane. Copyright © 1996 Elsevier Science Ltd

Although the chemistry of dialkyldithiophosphates has been extensively investigated[1,2] there have been few reports on the dialkylthiophosphonatoamines. In these compounds both sulfur and nitrogen atoms have the potential to coordinate to metal centres. There is also the opportunity for coordination as both a neutral and as an anionic ligand, through abstraction of a hydrogen from the nitrogen atom. The few reported examples of complexes of aminothiophosphonates ($[(RO)_2PSNR']^-$) and phosphinites ($[R_2PSNR']^-$) are usually extremely air sensitive. There is one reported example of a thiophosphinatoamine coordinating to a metal as a neutral ligand.[3] Addition of Ph_2PSNH_2 to $Mn(CO)_5Br$ produced a monomeric product in which the neutral ligand was chelated to the metal centre.[4] Here, we report the preparation and characterisation of a range of thiophosphonatoamines together with the X-ray structures of $(EtO)_2P(S)NHC_6H_4NO_2$ and $[(EtO)_2P(S)NHC_6H_4NO_2]_2PdCl_2$.

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EXPERIMENTAL

Starting materials were commercial materials (Aldrich/BDH). CH_2Cl_2 was dried and distilled over CaH_2 under nitrogen. Hexane, $CDCl_3$ (98%), toluene and acetone were used as received. ^1H (89.6 MHz), ^{31}P-$\{^1H\}$, (109.4 and 202.5 MHz) were recorded ($CDCl_3$ solution) on Jeol FX90Q and Jeol JNM EX270 spectrometers. Infrared spectra were recorded as KBr discs on a Perkin Elmer 1720X FT spectrometer. Microanalyses were carried out by the Imperial College Microanalytical Service.

Thiophosphonatoamines

The N-substituted thiophosphonatoamines, $(EtO)_2PSNEt_2$, $(EtO)_2PSNH^nBu$, $(MeO)_2PSNEt_2$ and $(MeO)_2PSNH^nBu$ were prepared by the reaction of diethyl or dimethyl-chlorothiophosphate with diethylamine and ^{n}butylamine, based on a published procedure.[5]

In a typical reaction a solution of $(RO)_2PSCl$ in THF (50 mmol in 100 cm^3) was added slowly to a rapidly stirred solution of the relevant amine,

HNRR′, in THF (150 mmol in 200 cm^3). A water bath was used to keep the reaction flask at room temperature. Once all of the chlorophosphate had been added (1/2 h) stirring was continued at room temperature for 1 hr. The mixture was then heated to reflux for 2 h. After cooling the precipitated amine hydrochloride was filtered off and the solvent removed from the solution *in vacuo*. The resulting oil was purified by vacuum distillation.

$(EtO)_2PSNEt_2$ **1**: b.p. 100°C, 10 mm Hg. Yield 7.8 g, 69%. Found: C, 40.5; H, 7.9; N, 5. δ, M^+ 225; $C_8H_{20}NO_2PS$ requires: C, 42.6; H, 8.9; N, 6.2%; $M^+ = 225$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 74.5 ppm (s). ν_{max}/cm^{-1} 608 ν(PS), 718 ν(PN).

$(EtO)_2PSNH^nBu$ **2**: b.p. 120°C, 5 mm Hg. Yield 7.3 g, 65%. Found: C, 42.1; H, 8.3; N, 6.1; M^+ 225; $C_8H_{20}NO_2PS$ requires: C, 42.6; H, 8.9; N, 6.2%; $M^+ = 225$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 70.8 ppm (s). ν_{max}/cm^{-1} 646 ν(PS), 799 ν(PN).

$(MeO)_2PSNEt_2$ **3**: b.p. 88°C, 10 mm Hg. Yield 7.2 g, 73%. Found: C, 36.5; H, 7.5; N, 7.5; M^+ 197; $C_6H_{16}NO_2PS$ requires: C, 36.5; H 8.2; N, 7.1%; $M^+ = 197$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 78.7 ppm (s). ν_{max}/cm^{-1} 594 ν(PS), 724 ν(PN).

$(MeO)_2PSNH^nBu$ **4**: b.p. 117°C, 5 mm Hg. Yield 7.0 g, 71%. Found: C, 36.0; H, 7.9; N, 7.1; M^+ 197; $C_6H_{16}NO_2PS$ requires: C, 36.5; H, 8.2; N, 7.1%; $M^+ = 197$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 74.9 ppm (s). ν_{max}/cm^{-1} 638 ν(PS), 813 ν(PN).

$(EtO)_2PSNH_2$, $(MeO)_2PSNH_2$ and $(PhO)_2PSNH_2$ were prepared by the reaction of diethyl, dimethyl and diphenyl-chlorothiophosphate with ammonia. In a typical reaction ammonia was passed through a stirred solution of $(RO)_2PSCl$ in THF (50 mmol in 100 cm^3) for 1.5 h. After the first 0.5 h, the solution was warmed to reflux. Heating was continued for a further 1 h; after the NH_3 flow was stopped. After cooling the precipitated amine hydrochloride was filtered off and the solvent removed from the resulting solution *in vacuo*. The resulting oil was purified by vacuum distillation. In the case of $(PhO)_2PSNH_2$ the product was a solid and was recrystallised from CH_2Cl_2 and hexane.

$(EtO)_2PSNH_2$ **5**: b.p. 86°C, 0.5 mm Hg. Yield 6.4 g, 76%. Found: C, 28.5; H, 6.4; N, 8.5; M^+ 169; $C_4H_{12}NO_2PS$ requires: C, 28.4; H, 7.1; N, 8.3%; $M^+ = 169$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 72.5 ppm (s). ν_{max}/cm^{-1} 617 ν(PS), 778 ν(PN).

$(MeO)_2PSNH_2$ **6**: b.p. 102°C, 10 mm Hg. Yield 4.3 g, 61%. Found: C, 17.1; H, 5.0; N, 9.9; $C_2H_8NO_2PS$ requires: C, 17.0; H, 5.7; N, 9.9%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 76.5 ppm (s). ν_{max}/cm^{-1} 604 ν(PS), 785 ν(PN).

$(PhO)_2PSNH_2$ **7**: m.p. 107°C. Yield 12.47 g, 94%. Found: C, 54.5; H, 4.6; N, 4.9; M^+ 265; $C_{12}H_{12}NO_2PS$ requires: C, 54.3; H, 4.6; N, 5.3%; $M^+ = 265$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 62.8 ppm (s). ν_{max}/cm^{-1} 689, 631 ν(PS), 743 ν(PN).

O,O-Diethyl, N-paranitrophenylthiophosphonatoamine **8**

A solution of paranitroaniline (94 mmol, 13 g) and diethyl-chlorothiophosphate (27 mmol, 5 g) in THF (150 cm^3) was heated to reflux for a week. The solution was cooled and filtered and the solvent was removed *in vacuo* leaving a yellow oily solid. The crude product was heated *in vacuo* and then redissolved in the minimum CH_2Cl_2 and loaded onto a silica column. A large volume of pentane was passed through the column followed by CH_2Cl_2 to remove the product. The solvent was removed from the fraction leaving a yellow solid. Repeated recrystallisation from CH_2Cl_2 and petrol (60–80°) gave a crystalline sample of $(EtO)_2P(S)NHC_6H_4NO_2$. The product remained contaminated with traces of an unidentified orange solid.

$(EtO)_2P(S)NHC_6H_4NO_2$ **8**: Yield 2.8 g, 37%. Found: C, 47.6; H, 5.5; N, 11.8; M^+ 290; $C_{10}H_{15}N_2O_4PS$ requires: C, 41.4; H, 5.2; N, 9.6%; $M^+ = 290$. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 62.4 ppm (s). ν_{max}/cm^{-1} 673 (PS), 748 and 774 (PN).

Bis(O,O-diethyl, N-paranitrophenylthiophosphonatoamine) palladium dichloride

The thiophosphonatoamine **8** (43 mg), prepared as above, was added to a suspension of sodium tetrachloropalladate (20 mg) in acetone (5 cm^3) and the mixture was stirred for 24 h. The resulting deep red solution was filtered and the solvent was removed *in vacuo* leaving a mixture of orange and red solids. Recrystallisation from chloroform and petrol (60–80°) gave $[(EtO)_2P(S)NHC_6H_4NO_2]_2PdCl_2$ as red needles.

$[(EtO)_2P(S)NHC_6H_4NO_2]_2PdCl_2$ **9**: Yield 38 mg, 73%. Found: C, 31.2; H, 2.9; N, 7.2; $C_{20}H_{30}N_4O_8P_2S_2PdCl_2$ requires: C 31.7; H, 4.0; N, 7.4%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 55.9 ppm (s). ν_{max}/cm^{-1} 752 and 763 (PN).

Crystallography

8 $C_{10}H_{15}N_2O_4PS$, $M = 290.3$, triclinic, space group $P\bar{1}$, $a = 7.098(3)$, $b = 8.132(3)$, $c = 12.902(4)$ Å, $\alpha = 92.31(3)$, $\beta = 97.87(3)$, $\gamma = 111.34(3)°$, $U = 684$ Å^3, $Z = 2$, $D_c = 1.41$ g cm^{-3}, crystal dimensions $0.02 \times 0.14 \times 0.23$ mm, μ(Cu-K_α) = 3.31 mm^{-1}, $F(000) = 304$. Siemens P4/PC diffractometer, ω-scan method, graphite monochromated Cu-K_α radiation (2θ range 3.0–116°), 1802 independent reflections, 1352 observed ($|F_o| > 4.0\sigma|F_o|$), corrected for Lorentz and polar-

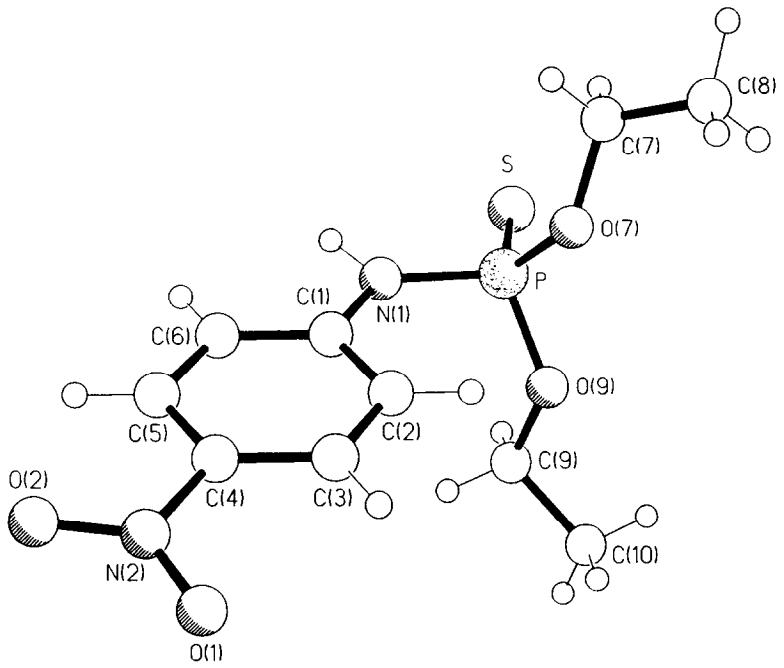

Fig. 1. Crystal structure of $(EtO)_2PSNHC_6H_4NO_2$ **8**.

isation factors, numerical (face indexed) absorption correction, maximum and minimum transmission factors 0.933 and 0.589, respectively. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. Hydrogen atoms were assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C/N)$ and allowed to ride on their parent carbon/nitrogen atoms. Refinement was by full matrix least squares, based on F, to $R = 0.045$ and $Rw = 0.047$ where $w^{-1} = \sigma^2(F) + 0.0005F^2$. The maximum and minimum residual electron densities in the final ΔF map were 0.19 and -0.22 e $Å^{-3}$ and the mean and maximum shifts/errors in the final refinement were 0.003 and 0.042, respectively.

9 $C_{20}H_{30}Cl_2N_4O_8P_2PdS_2$, $M = 757.8$, monoclinic, space group $P2_1/c$, $a = 12.260(4)$, $b = 9.216(4)$, $c = 14.574(5)$ Å, $\beta = 110.64(2)$, $U = 1541$ $Å^3$, $Z = 2$, $D_c = 1.63$ g cm^{-3}, crystal dimensions $0.20 \times 0.30 \times 0.33$ mm, μ(Mo-K_α) = 1.06 mm^{-1}, $F(000) = 768$. Siemens P4/PC diffractometer, ω-scan method, graphite monochromated Mo-K_α radiation (2θ range 4.0–50°), 2714 independent reflections ($R_{int} = 2.04\%$), 2184 observed ($|F_o| > 4.0\sigma\,|\,F_o$), corrected for Lorentz and polarisation factors, numerical (face indexed) absorption correction, maximum and minimum transmission factors 0.824 and 0.735, respectively. The structure was solved by direct methods and the non hydrogen atoms refined anisotropically. Hydrogen atoms were assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C/N)$ and allowed to ride on their parent carbon/nitrogen atoms. Refinement was by full matrix least squares to $R = 0.032$ and $Rw = 0.035$ where $w^{-1} = \sigma^2(F) + 0.0007F^2$. The maximum and minimum residual electron densities in the final ΔF map were 0.31 and -0.29 e $Å^{-3}$ and the mean and maximum shifts/errors in the final refinement were 0.000 and 0.001, respectively. Computations were carried out using SHELXTL PC[6].

RESULTS AND DISCUSSION

The reaction of either $(EtO)_2PSCl$ or $(MeO)_2PSCl$ with primary and secondary amines or with ammonia to give $(RO)_2P(S)NHR'$ is rapid and quantitative at room temperature. Attempts to slow it down by cooling generally resulted in lower yields and the formation of by-products. Most of the products formed were oils which could be conveniently purified by distillation. The products gave satisfactory microanalyses, mass spectra, NMR, and the expected IR spectra. The reaction of $(EtO)_2PSCl$ with *p*-nitroaniline was much slower than any of the other reactions and the product was a solid. O,O′-Diethyl,N-*p*-nitrophenyl thiophosphonatoamine is a bright orange solid but we were unable to free it of traces of another orange solid. Attempts to purify the compound by recrystallisation, column chromatography and gel permeation chromatography all failed to produce an analytically pure sample. However mass spectrometry and X-ray crystallography of some of the major compound formed confirmed that the synthesis has proceeded as anticipated (Fig. 1). The

bond lengths at phosphorus are normal with P=S and P—N being 1.911(2) and 1.654(3) Å respectively whilst the P—O distances are 1.557(4) and 1.564(3) Å. The distorted tetrahedral geometry at phosphorus has enlarged O—P—S angles [117.5(2), 118.3(1)°] and a contracted O—P—O angle of 95.8(2)° (Table 1). Overall, the molecule has approximate, non-crystallographic, C_s symmetry with the phosphorus and sulfur atoms lying only 0.2 and 0.4 Å out of the mean plane of the aryl ring. The geometry at N(1) is effectively trigonal though the C—N—P angle is somewhat enlarged at 129.7(3)°. Within the lattice the molecules are linked by weak N—H···O hydrogen bonds between N(1)H and one of the oxygen atoms of the nitro group to form loosely linked chains that extend along the crystallographic *b* direction [N···O 3.19, H···O 2.24 Å, N—H···O 165°]. Adjacent chains, which are of opposite polarity, are aligned parallel with partial overlap of their aryl rings [mean interplanar separation 3.50 Å and associated centroid···centroid distance 4.15 Å] consistent with weak π–π stacking interactions between the H-bonded chains.

Table 1. Selected bond lengths (Å) and angles (°) for $(EtO)_2PSNHC_6H_4NO_2$ **8**

S—P	1.911(2)	S—P—N(1)	110.3(1)
P—N(1)	1.654(3)	S—P—O(7)	118.3(1)
P—O(7)	1.557(4)	N(1)—P—O(7)	106.8(2)
P—O(9)	1.564(3)	S—P—O(9)	117.5(2)
N(1)—C(1)	1.399(5)	N(1)—P—O(9)	106.7(2)
O(7)—C(7)	1.388(7)	O(7)—P—O(9)	95.8(2)
O(9)—C(9)	1.439(7)	P—N(1)—C(1)	129.7(3)

Stirring $(EtO)_2P(S)NHC_6H_4NO_2$ with Na_2PdCl_4 in acetone produces a deep red solution which after concentration and recrystallisation of the product gives red crystals of the S-coordinated $[(EtO)_2P(S)NHC_6H_4NO_2]_2PdCl_2$ **9**. This result is a little surprising; with the electron withdrawing properties of the *p*-nitrophenyl group the hydrogen on the nitrogen might be expected to be fairly acidic. As anticipated, the IR spectrum of this complex closely resembles the IR spectrum of the uncoordinated ligand whilst the ^{31}P NMR spectrum of **9** is simply a singlet at 55.9 ppm, a change of only 6.5 ppm from the uncoordinated ligand.

The X-ray structure of **9** reveals (Fig. 2) a square planar arrangement about the palladium atom which is located on a crystallographic centre of symmetry. The chloro and S-coordinated ligands are thus *trans*. The individual ligands retain their approximate C_s symmetry upon coordination although they are more distorted than in **8**. Thus the phosphorus and sulfur atoms lie 0.54 and 0.49 Å respectively from the mean plane of the aryl ring. Furthermore, the nitrogen atom undergoes a slight pyramidalisation upon coordination of the ligand with the nitrogen atom lying 0.21 Å from the plane of its substituents. Interestingly, the planes of the

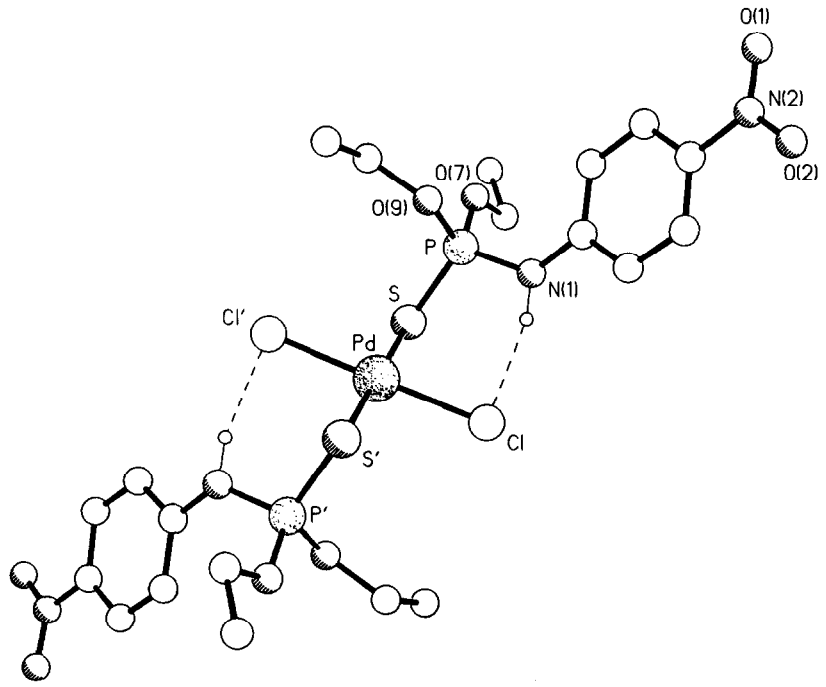

Fig. 2. Crystal structure of $[(EtO)_2PSNHC_6H_4NO_2]_2PdCl_2$ **9**.

aryl groups within the ligands are steeply inclined [by 71°] to the palladium coordination plane. The co-ordination of $(EtO)_2PSNHC_6H_4NO_2$ to palladium is accompanied by a lengthening of the P—S bond length [1.911(2) *cf* 1.972(2) Å] and a shortening of the P—N distance [1.625(3) *cf* 1.654(4) Å], compared to the uncoordinated ligand (Table 2). The S—P—N angle is unaffected, but there is a distinct increase in the O—P—O angle from 95.8(2)° to 102.6(1)° upon coordination whilst both S—P—O angles are decreased as the bonding arrangement around the phosphorus moves closer to a regular tetrahedron. There are strong intramolecular hydrogen bonds between the N—H protons and the chloro ligands [H···Cl 2.23, N···Cl 3.16 Å, N—H···Cl 166°]. Inspection of the packing of the molecules does not reveal any major interactions. The only motif is a parallel but offset head to tail stacking of the *para*-NO_2 groups with an interplanar separation of 3.47 Å and an associated ring-centroid to ring-centroid distance of 5.55 Å.

Table 2. Selected bond lengths (Å) and angles (°) for $[(EtO)_2PSNHC_6H_4NO_2]_2PdCl_2$ **9**

Pd—Cl	2.306(1)	Cl—Pd—S	92.2(1)
Pd—S	2.344(1)	Cl—Pd—S′	87.8(1)
S—P	1.972(2)	S—Pd—S′	180.0(1)
P—N(1)	1.625(3)	Pd—S—P	100.2(1)
P—O(7)	1.557(3)	S—P—N(1)	110.0(1)
P—O(9)	1.554(3)	S—P—O(7)	111.3(1)
N(1)—C(1)	1.412(6)	N(1)—P—O(7)	110.5(2)
O(7)—C(7)	1.464(7)	S—P—O(9)	116.8(1)
O(9)—C(9)	1.457(5)	N(1)—P—O(9)	105.4(2)
		O(7)—P—O(9)	102.6(1)
		P—N(1)—C(1)	127.5(2)

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