2,4-*N*,*N'*-Bis(dialkylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes

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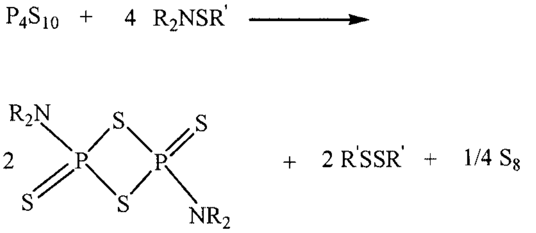
Keywords: Donor-acceptor systems / N-ligands / Fluorinated ligands / Sulfur / Phosphorus

Dialkylamide derivatives of the monometadithioxaphosphoric acid stabilised by pyridine as a donor, i.e. $[(C_5H_5N)PS_2NR_2]$, readily react with $AlCl_3$. The elimination of the donor and formation of the adduct $C_5H_5N{\cdot}AlCl_3$ liberates the unstable $\sigma^3\lambda^5$-phosphoranes (PS_2NR_2). The latter are stabilised by [2+2] "cycloaddition-dimerization" leading to the title compounds $[PS_2NR_2]_2$ in nearly quantitative yields. The synthesis and characterisation of two compounds possessing NR_2 substituents of very different basicities clearly demonstrate the generalisation of such a procedure as an easy way of accessing further derivatives in this class.

Introduction

Whereas studies of dithiadiphosphetane disulfides $(PS_2X)_2$ (X = alkyl, aryl, alkylthio, arylthio, and some "exotic substituents" such as ferrocenyl[1] or $[W(CO)_5]$[2]) have been well documented, with more than 20 published crystal structures[3], literature reports of the same class of substances with X = NR_2 remain rare, speculative or have been shown to be incorrect. During the reaction between P_4S_3 and $S[N(CH_3)_2]_2$, Fluck et al. observed the formation of the title compound $[PS_2NMe_2]_2$ (**1a**).[4] From numerous signals appearing in the ^{31}P NMR spectra of the reaction products, the authors assigned a singlet at $\delta = 23.9$ ppm to compound **1a**. The decrease of its intensity in the mixture was concomitant with the formation of crystals. The remaining components of the reaction mixture were not characterised. After successful completion of the process, the isolated crystals showed practically no solubility in common organic solvents. By means of mass spectrometric, IR and Raman data the composition of the crystals was postulated as a mixture of the dimer **1a** and the trimer $[PS_2NMe_2]_3$. An X-ray investigation of a crystal from the heterogeneous solid mixture revealed the structure of **1a**, the only known crystal structure, up to now, of a bis(dialkylamido)dithiadiphosphetane. By attempting to reproduce the synthesis of Fluck et al.[4], we succeeded in the preparation of **1a** with a yield of about 7%. The ^{31}P NMR spectra taken from the product mixture revealed the inaccessibility of this synthesis: the main peaks were unknown and did not correspond to **1a**. Furthermore we were unable to confirm the reported[4] insolubility of **1a** in common organic solvents. Thus, **1a** prepared in nearly quantitative yield by our method [see Equation (2)] allows at least the convenient measuring of ^{31}P NMR spectra in toluene.

In 1994 Nizamov et al.[5] reported the reaction between P_4S_{10} and R_2NSR' as a high yield synthesis for the title compounds **1a** or $[PS_2NEt_2]_2$ **1b**, respectively.



(1)

1a R = Me, R' = Et, *i*Pr
1b R = Et, R' = Et, *i*Pr, *i*Bu

The authors' interpretation of the data obtained from Equation (1) is, however, clearly incorrect. All of the ^{31}P NMR spectra taken from the reaction products showed no signals in the chemical shift region which is typical for compounds having a dithiadiphosphetane ring (δ = 20−26 ppm, see below), but signals at much lower field (between δ = 90 and 120 ppm). Because the elemental analysis[5] of the reaction products supports the presence of compounds with a composition equal to **1a** and **1b**, the reported $\delta(^{31}P)$ values of the NMR spectra could only be explained if the reaction products are isomers of **1** with a P_2N_2 four membered ring such as 1,3-dialkyl-2,4-bis(alkylthio)-2,4-dithioxo-1,3-diaza-2λ^5,4λ^5-diphosphetidines[6] and/or some cyclic oligomers, $[R_2NPS_2]_n$ (n = 3,4). However, the various signals listed in reference 5 which result from the main products of the reaction between P_4S_{10} and alkylsulfendialkylamides (R_2NSR'), show that Equation (1) clearly results in a mixture of undefined (not identified) products with no measurable formation of **1**. Altogether, the data from the

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literature reveal that at the present time, a suitable approach to the synthesis of **1** does not exist.

Results

During our investigations into the differences in the structures and reactivities of amides of the donor stabilised monometadithioxaphosphoric acid with various alkyl substituents, $(C_5H_5N)PS_2NR_2$ (**2**), we developed an easy synthesis for **1** by treating **2** with the Lewis acid $AlCl_3$.

R	**2** (^{31}P NMR Signal)
CH_3	**2a** (122.0 ppm)[7]
CH_2CH_3	**2b** (122.9 ppm)[8]
CH_2CF_3	**2c** (120.9 ppm)

$$\underset{\textbf{2a–c}}{2\,(C_5H_5N)PS_2NR_2} + 2AlCl_3 \longrightarrow 2\,C_5H_5N{\cdot}AlCl_3 + \underset{\textbf{1a–c}}{[PS_2NR_2]_2} \tag{2}$$

1 (^{31}P NMR Signal)
1a (23.9 ppm)[4]
1b (21.8 ppm)[8]
1c (25.7 ppm)

The starting compounds **2** can be obtained very pure and in high yields by treating the pyridine stabilized $\sigma^4\lambda^5$-dithiochlorophosphorane, Py→PS_2Cl, with the corresponding *sec*-amines.[9] The single-crystal X-ray diffraction investigations of **2b**[10] and **2c**[11] (Figure 1) show the distorted tetrahedral surroundings of the P atoms in both compounds. By comparing the two structures, one can recognize that the lengthening of the $P-N_{amide}$ bond in **2c**, caused as expected by the influence of the CF_3 groups, does not affect the $P-N_{donor}$ and P=S distances at all.

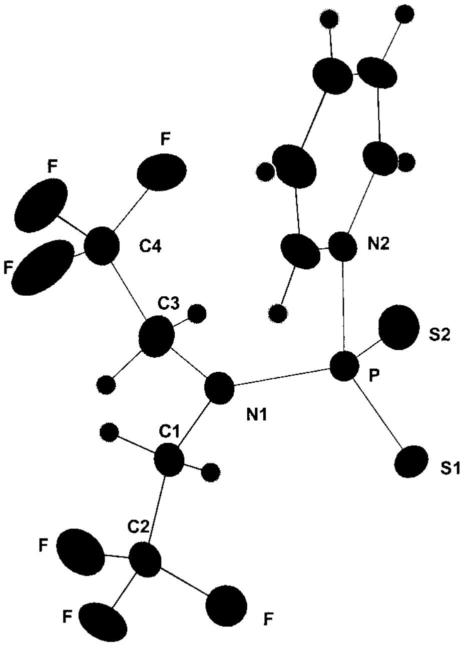

Figure 1. Structure of **2c** (DIAMOND[12], ellipsoids are shown at the 60% probability level) and selected bond lengths [pm] and angles (°) for **2c**/**2b**: P−S1 194.1(1)/194.9(2), P−S2 194.8(1)/195.2(1), P−N1 168.6(1)/164.0(1), P−N2 189.3(1)/189.8(2), N1−C1 146.2(2)/148.3(1), N1−C3 146.9(2)/148.0(1), C1−C2 151.6(2)/151.4(1), C3−C4 150.6(3)/152.2(1), S1−P−S2 122.81(3)/120.42(6), N1−P−N2 99.62(7)/101.82(5), N1−P−S1 111.65(5)/113.48(6), N1−P−S2 111.02(5)/112.58(8), N2−P−S1 103.14(5)/101.74(5), N2−P−S2 105.32(5)/103.65(5), C1−N1−C3 117.11(13)/115.56(7), C1−N1−P 121.84(11)/120.78(9), C3−N1−P 121.06(11)/123.60(4)

Our high temperature ^{31}P NMR investigations confirm the formation of small amounts of **1b** by heating **2b**, an observation already noted by Meisel and Donath.[8] This observation has been explained by the liberation of $\sigma^3\lambda^5$-PS_2NEt_2 intermediates from **2b** at high temperatures as reactive species which undergo [2+2] cycloaddition reactions. This hypothesis[8] has been strongly supported by our results which make it seem very plausible. The reaction of **2** with the strong Lewis acid $AlCl_3$ which forms the adduct Py → $AlCl_3$ with the donor base pyridine, results exclusively in the formation of **1**, Equation (2).[13]

The molecular structures of **1b**[14] (Figure 2) and **1c**[15] show a completely planar P_2S_2 four member ring in each case, with a *trans* arrangement of the exocyclic ligands. The P centres are in distorted tetrahedral environments. The tetrahedra are joined along a common edge (built by the endocyclic S atoms) to the dimeric molecules **1**. The significant difference in the bond lengths between the two endocyclic S atoms and phosphorus within the dithiadiphosphetane ring reveals the tendency for a monomer formation in **1b** and **1c** but, surprisingly, not in **1a**. In Table 1 some selected bond angles and distances are given.

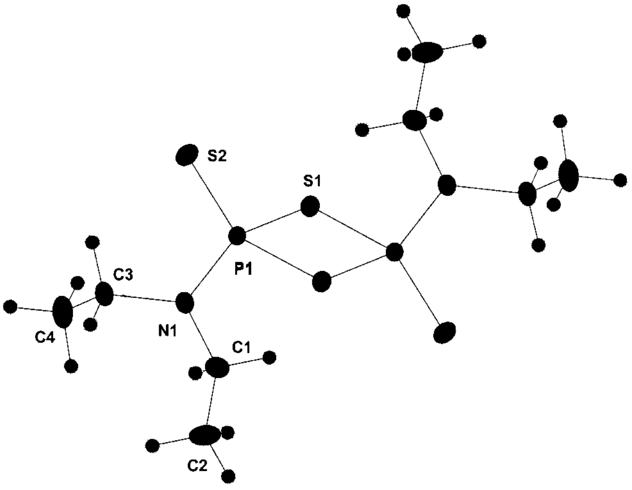

Figure 2. Structure of **1b** (DIAMOND,[12] ellipsoids are shown at the 60% probability level)

Table 1. Selected bond lengths [pm] and angles (°) (* atoms generated by symmetry)

	P1−S1	P1−S1*	P1−S2	P1−N1	N1−C1	N1−C3	C1−C2	C3−C4
1a[4]	212.2(1)	212.2(1)	192.6(1)	163.3(3)	145.0(5)	145.1(6)		
1b	210.9(1)	215.2(1)	193.8(1)	163.8(2)	149.1((3)	147.4(3)	152.0(3)	151.6((3)
1c	209.7(1)	213.8(1)	190.8(1)	167.7(1)	146.8(2)	146.0(2)	151.5(2)	150.6(2)
	P1−S1−P1*	S1−P1−S1*	S2−P1−S1*	S1−P1−N1	S2−P1−N1	P1−N1−C1	P1−N1−C3	C1−N1−C3
1a[4]	86.86(3)	93.14(3)	115.57(4)	107.83(9)	114.66(9)	120.5(2)	124.0(2)	115.5(3)
1b	87.75(6)	92.25(6)	114.80(7)	110.00(8)	115.00(8)	119.7(2)	121.8(2)	116.9(2)
1c	86.44(2)	93.56(2)	115.35(2)	107.77(5)	114.12(0)	119.5(1)	122.0(1)	117.0(1)

Equation (2) which we have dealt with in this work leads, in its first step and under mild conditions, to the formation of reactive $\sigma^3\lambda^5$ phosphoranes. The subsequent [2+2] cycloaddition reaction immediately forms the stable dimeric title compounds **1**. At present we are investigating the viability of the analogous reactions of Py→$POSNR_2$ and Py→PO_2NR_2 with $AlCl_3$. By successfully applying these reactions it may be possible to access the corresponding dimeric compounds with P_2O_2 or P_2OS four membered rings.

Experimental Section

General Remarks: All experiments were performed under purified dry argon in a glove box and/or on a glass high-vacuum line. Py→PS_2Cl was prepared according to the literature procedure from P_4S_{10}, pyridine and $PSCl_3$ [16]. Toluene was heated to reflux over Na and freshly distilled prior to use. The NMR spectra were recorded with a 400 MHz Bruker spectrometer at the appropriate ^{31}P, ^{1}H, ^{13}C and ^{19}F frequencies using H_3PO_4, TMS and F11 as external standards, respectively.

Single-crystals suitable for X-ray analyses were isolated and prepared in a cold stream of nitrogen. Data collection was carried out with an IPDS diffractometer (Stoe & Cie) at 180 K using graphite-monochromated Mo-K_α radiation (71.073 pm) and a cryostream cooler (Oxford Cryosystems). The data set was collected in the φ-oscillation scan mode. The structures were solved[17] and refined[18] with SHELX 97 (see refs.[10−15]). CCDC-232449 (for **1b**), -232450 (for **1c**), -232451 (for **2b**) and -232448 (for **2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of 1: Compound **2** (5 mmol) was partially dissolved in toluene (15 mL) in a 50-mL Schlenk tube. To this suspension was added an equivalent amount of $AlCl_3$ (668 mg) dissolved in toluene (15 mL) and the reaction mixture became a clear solution. Within 1−2 hours the reaction was complete and the adduct $C_5H_5N{\cdot}AlCl_3$ separated as an oil and/or solid participate. The clear toluene phase was separated, its volume reduced to about 1/3 by evaporation of the solvent and stored overnight at −20 °C for crystallisation. The resultant crystals were separated, washed with toluene and dried in vacuo.

1b: Yield 80.5%, $C_8H_{20}N_2P_2S_2$ (334.45): calcd. C 28.73, H 6.03, N 8.38, P 18.52, S 38.34; found C 27.87, H 6.43, N 8.13, P. 18.92, S 38.29. NMR spectroscopic data ([D_8]toluene): ^{31}P NMR: δ = 21.8 ppm. ^{1}H NMR: δ = 0.92 (t, $^{3}J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 3.42 (d/q, $^{3}J_{H,P}$ = 17.7, $^{3}J_{H,H}$ = 6.9 Hz, 4 H, CH_2) ppm. ^{13}C NMR: δ = 13.7 (s, CH_3), *δ* = 41.6 (s, CH_2) ppm.

1c: Yield 73.1%, $C_8H_8F_{12}N_2P_2S_4$ (550.33): calcd. N 5.09, P 11.26, S 22.3; found N 4.93, P 11.82, S 23.77. NMR spectroscopic data [D_8]toluene: ^{31}P NMR: δ = 25.7 ppm. ^{1}H NMR: δ = 3.93 (d/q, $^{3}J_{H,P}$ = 16.2, $^{3}J_{H,F}$ = 8.3 Hz, 4 H, CH_2) ppm. ^{13}C NMR: δ = 47.3 (q, $^{2}J_{C,F}$ = 33.5 Hz, CH_2), *δ* = 124.6 (q, $^{1}J_{C,F}$ = 282.1 Hz, CF_3) ppm. ^{19}F NMR: δ = −68.04 (t, $^{3}J_{F,H}$ = 8.3 Hz, CF_3) ppm.

Synthesis of 2: Py → PS_2Cl (10 mmol) was partially dissolved in toluene (25 mL) in a 75 mL Schlenk tube. To this suspension was added the corresponding *sec*-amine dissolved in toluene (10 mL). Two equivalents were used for **2b** and a single equivalent together with one equivalent of pyridine for **2c**. The reaction mixtures became clear solutions and after heating for 2 hours at 60 °C under an Argon atmosphere the reactions were complete. The precipitated amine hydrochlorides were filtered after cooling to room temperature and the clear filtrates stored overnight at −20 °C for crystallisation. The crystals were separated, washed with toluene and dried in vacuo.

2b: Yield 73.5%, $C_9H_{15}N_2PS_2$ (246.32): calcd. C 43.88, H 6.14, N 11.37, P 12.57, S 26.03; found C 43.20, H 6.14, N 10.93, P 12.85, S 26.07. NMR spectroscopic data (CD_3CN): ^{31}P NMR: δ = 123.3 ppm. ^{1}H NMR: δ = 0.95 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 3.50 (d/q, $^{3}J_{H,P}$ = 15.2, $^{3}J_{H,H}$ = 7.1 Hz, 4 H, CH_2), 7.81 (m, 2 H, β-CH), 8.25 (m, 1 H, γ-CH), 9.45 (m, 2 H, α-CH) ppm. ^{13}C NMR: δ = 14.2 (d, $^{3}J_{C,P}$ = 2.2 Hz, CH_3), 42.2 (d, $^{2}J_{C,P}$ = 3.6 Hz, CH_2), 126.9 (s, β-CH), 142.9(s, α-CH), 144.4 (s, γ-CH) ppm.

2c: Yield 69.1%, $C_9H_9F_6N_2PS_2$ (354.27): calcd. N 7.91, P 8.74, S 18.1; found N 7.51, P 9.26, S 18.46. NMR spectroscopic data (CD_3CN): ^{31}P NMR: δ = 120.9 ppm. ^{1}H NMR: δ = 4.47 (d/q, $^{3}J_{H,P}$ = 13.2, $^{3}J_{H,F}$ = 8.9 Hz, 4 H, CH_2), 7.9 (m, 2 H, β-CH), 8.4(m, 1 H, γ-CH), 8.7 (m, 2 H, α-CH) ppm. ^{13}C NMR: δ = 49.0 (q/d, $^{2}J_{C,F}$ = 32.7, $^{2}J_{C,P}$ = 5.0 Hz, CH_2), 125.8 (q/d, $^{1}J_{C,F}$ = 282, $^{3}J_{C,P}$ = 2.2 Hz, CF_3), 127.9 (s, β-CH), 143.1 (s, α-CH), 146.2 (s, γ-CH) ppm. ^{19}F-NMR: δ = −68.19 (t, $^{3}J_{F,H}$ = 8.9 Hz, CF_3) ppm.

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[10] Crystal data for **2b**: Pale yellow colour, crystal size $0.54 \times 0.42 \times 0.32$ mm, orthorhombic, space group *Pbca* (no. 61), a = 1729.6(12), b = 1735.8(23), c = 1665.5(15) pm, V = 5001(9) $\times 10^6$ pm^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.309 g·cm^{-3}, $F(000)$ = 2080, $\mu(\text{Mo-}K_\alpha)$ = 0.520 mm^{-1}; (h,k,l) = (± 17, 0 to +18, 0 to +12), θ = 2.06−21.77°, 4941 measured reflections (R_{int} = 0.0886), 272 parameters, $R1$ = 0.0693, 2214 reflections with $I > 2\sigma(I)$, $wR2$ = 0.1861 for 2625 unique reflections, ρ_{final}(max./min.) = 0.587/−1.065 $\times 10^{-6}$ e·pm^{-3}.

[11] Crystal data for **2c**: Colourless, crystal size $0.80 \times 0.72 \times 0.60$ mm, monoclinic, space group *P*21/*n* (No. 14), a = 1102.2(3), b = 1095.0(3), c = 1180.0(3) pm, β = 97.94(3)°, V = 1410.6(7) $\times 10^6$ pm^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.668 g·cm^{-3}, $F(000)$ = 712, $\mu(\text{Mo-}K_\alpha)$ = 0.548 mm^{-1}; (h,k,l) = (±13, ±13, ±14), θ = 2.63−25.75°, 9303 measured reflections (R_{int} = 0.0265), 217 parameters, $R1$ = 0.0295, 2428 reflections with $I > 2\sigma(I)$, $wR2$ = 0.0757 for 2655 unique reflections, ρ_{final}(max./min.) = 0.524/−0.385 $\times 10^{-6}$ e·pm^{-3}.

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[13] All compounds of reaction (2) were fully characterised by elemental analyses and single-crystal X-ray diffraction studies. The crystal structures of **2a** and $C_5H_5N{\cdot}AlCl_3$ will be published in a separate paper.

[14] Crystal data for **1b**: Colourless, crystal size $0.68 \times 0.60 \times 0.24$ mm, triclinic space group *P*-1 (no. 2), a = 658.0(2), b = 695.6(3), c = 891.9(5) pm, α = 86.17(6)°, β = 72.72(5)°, γ = 78.84(4)°, V = 382.4(3) $\times 10^6$ pm^3, Z = 1, $\rho_{\text{calcd.}}$ = 1.452 g·cm^{-3}, $F(000)$ = 176, $\mu(\text{Mo-}K_\alpha)$ = 0.808 mm^{-1}; (h,k,l) = (±7, ±8, ±10), θ = 3.47−25.25°, 3789 measured reflections (R_{int} = 0.0919), 114 parameters, $R1$ = 0.0285, 1207 reflections with $I > 2\sigma(I)$, $wR2$ = 0.0762 for 1255 unique reflections, ρ_{final}(max./min.) = 0.374/−0.341 $\times 10^{-6}$ e·pm^{-3}.

[15] Crystal data for **1c**: Colourless, crystal size $0.52 \times 0.40 \times 0.28$ mm, monoclinic space group P 21/*c* (no. 14), a = 1125.95(17), b = 580.54(5), c = 1432.6(2) pm, β = 99.572(17)°, V = 923.4(2) $\times 10^6$ pm^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.979 g·cm^{-3}, $F(000)$ = 544, $\mu(\text{Mo-}K_\alpha)$ = 0.802 mm^{-1}; (h,k,l) =(±13, ±6, ±17), θ = 2.88−25.23°, 5749 measured reflections (R_{int} = 0.0285), 143 parameter, $R1$ = 0.0227, 1526 reflections with $I > 2\sigma(I)$, $wR2$ = 0.0591 for 1645 unique reflections, ρ_{final}(max./min.) = 0.316/−0.270 $\times 10^{-6}$ e·pm^{-3}.

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Received April 29, 2004