Tetrapodal Pentadentate Ligands with NS_4 and NP_4 Donor Sets: An Elusive Tetrathiol, and a Sterically Encumbered Tetraphosphane

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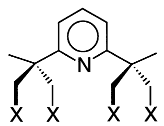
Tetrapodal Pentadentate Ligand, Polythiols, Polyphosphanes

With the intention of preparing tetrapodal pentadentate ligands having NS_4 or NP_4 donor sets, we investigated reactions of the previously reported tetratosylate 2,6-$C_5H_3N[CMe(CH_2OTs)_2]_2$ (**2**) with thiourea or diphenylphosphide, but found them not to proceed cleanly, and to give mixtures of products. A derivative of **2** better suited to nucleophilic substitution is the corresponding tetrabromide 2,6-$C_5H_3N[CMe(CH_2Br)_2]_2$(2,6-bis-(2-bromo-1-bromomethyl-1-methyl-ethyl)-pyridine, **3**), which is obtained in excellent yield from **2** by treatment with LiBr in dimethylsulfoxide. The reaction of **3** with 4 eq of thiourea in refluxing ethanol gives a single product. Substitution is not quantitative, however, and the product likely is a bis(thiouronium) bis(bromide) salt. Similarly, the reaction of **3** with 4 eq of potassium *O*-ethyl xanthogenate displaces only two out of the four bromo substituents under the chosen conditions; workup then leads to what is formulated as a bis(thietane) derivative formed by intramolecular cyclisation. By contrast, nucleophilic substitution with NaSEt in ethanol is quantitative, and the thioether 2,6-$C_5H_3N[CMe(CH_2SEt)_2]_2$(2,6-bis-(2-ethylsulfanyl-1-ethylsulfanylmethyl-1-methyl-ethyl)-pyridine, **4**) has been isolated in close to 60% yield. Likewise, and in spite of the considerable steric bulk amassed in the molecule, the reaction of **3** with an excess of $KPPh_2$ in THF proceeds smoothly (even at –50 °C), to give the tetraphosphane 2,6-$C_5H_3N[CMe(CH_2PPh_2)_2]_2$ (2,6-bis-{2-(diphenyl-phosphanyl)-1-[(diphenyl-phosphanyl)-methyl]-1-methyl-ethyl}-pyridine, **5**) in 65% yield. In order to assess possible pathways of oxidative degradation relevant to the coordination chemistry of this ligand, **5** was treated with NO in CH_2Cl_2 or ether at different temperatures. In two cases, reaction was observed to produce the oxide 2,6-$C_5H_3N[CMe(CH_2P(=O)Ph_2)_2]_2$ (**6**) as a colourless solid in near quantitative yield, with concomitant formation of N_2O. All compounds have been characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (as applicable); IR spectroscopic and elemental analysis data are reported, and the crystal structure of **6** has been determined.

Introduction

In octahedral complexes, tetrapodal pentadentate ligands help to create a single "labile" coordination site for reactivity studies of small monodentate ligands. We chose to investigate systems of high overall symmetry, and introduced the pentaamine **1** [1, 2]. Its NN_4 donor set, while having a geometry similar to that of a porphyrin with an additional axial base, is unique for its predominant σ donor character. We expect transition metal ions complexed by **1** to be electron-rich and at the same time stabilised with respect to complex fragments of the type $[M(NH_3)_5]^{n+}$, which contain only monodentate donors. Whereas complexes such as $[Fe^{II}(NH_3)_5)X]^+$ (X = halide) are unknown, chelated $[(\mathbf{1})Fe^{II}Br]^+$ is stable under ambient conditions and has been used to prepare a series of derivatives $[(\mathbf{1})Fe^{II}L]^{n+}$ (L = CO, NO, NO^+, NO_2^-) by ligand exchange. The reactivity of the nitro complex is unusual in that coordinated nitrite can be reduced to NO in the presence of protons and a suitable reducing agent (MeOH), a pattern reminiscent of the action of heme-dependent nitrite reductases [3].

The pentaamine **1** is obtained by a sequence of reactions that enables, in principle, the variation of



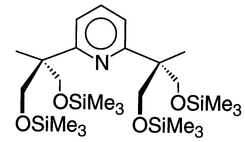
1: X = NH_2
2: X = OTs
3: X = Br
4: X = SEt
5: X = PPh_2
6: X = $P(O)Ph_2$

the basal donor set, which is introduced towards the end of the sequence by nucleophilic substitution. As the redox potential of a complex fragment is to a large part also a function of the nature of the donor atoms, we extended our study to include thiol and phosphane ligands, and aimed to derive NS_4 and NP_4 ligands from intermediates in the synthesis of **1**. We report here on attempts to obtain pure samples of the tetraalcohol 2,6-$C_5H_3N[CMe(CH_2OH)_2]_2$, on the reactivity of the tetratosylate 2,6-$C_5H_3N[CMe(CH_2OTs)_2]_2$ (**2**) and the tetrabromide 2,6-$C_5H_3N[CMe(CH_2Br)_2]_2$ (**3**) towards thiourea, potassium *O*-ethyl xanthogenate, sodium ethanethiolate and potassium diphenylphosphide, and on the complete oxidation of the tetraphosphane 2,6-$C_5H_3N[CMe(CH_2PPh_2)_2]_2$ (**5**) to give the oxide, 2,6-$C_5H_3N[CMe(CH_2P(=O)Ph_2)_2]_2$ (**6**). Complexation studies with **5** are in progress and will be reported elsewhere.

Results and Discussion

Attempted purification of the tetraalcohol 2,6-$C_5H_3N[CMe(CH_2OH)_2]_2$

Pure tetraalcohol had been obtained previously as the hemihydrate [4], but its water content proved a disadvantage in a number of subsequent reactions (see the attempted synthesis of a tetrachloride, below). Also, we sought a straightforward method for purifying tetraalcohol that had been obtained in an impure form. To this end, crude tetraalcohol was deprotonated with potassium hydride in hexane and treated with 4 eq of trimethylsilylchloride, to give a brown oil containing the tetrakis(trimethylsilyl)-ether (Formula **A**, 2,6-bis-[1-methyl-2-(trimethyl-silanyloxy)-1-(trimethyl-silanyloxymethyl)-ethyl]-pyridine) as the main product. The mass spectrum (FD) has the expected parent ion as the most intense peak at m/z = 543. In addition to signals due to impurities, the ^1H NMR spectrum shows signals for the pyridine, the diastereotopic methylene, the methyl and the trimethylsilyl protons having the expected patterns and correct intensities [5].

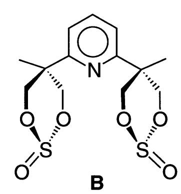


A

We expected the product to be sufficiently volatile to allow distillation, and decomposition with ammonium fluoride was envisaged to regenerate the tetraalcohol. Even kugelrohr distillation, however, failed to achieve appreciable purification, and this approach was abandoned.

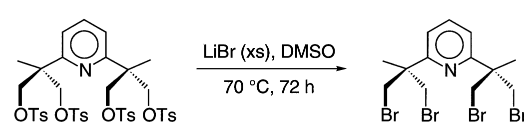
*2,6-$C_5H_3N[CMe(CH_2X)_2]_2$ (X = Cl; X = Br: **3**)*

We pursued the synthesis of tetrahalide analogues of the tetraalcohol in order to obtain useful starting materials for nucleophilic substitution reactions. Attempts to prepare a tetrachloride from the tetraalcohol by reaction with $SOCl_2$ in pyridine [6] were hampered by the presence of water and invariably gave mixtures of products. An intense signal in the mass spectrum (FD) at m/z = 351 (90 %) is assigned to the bis(ester) of sulfurous acid [7], 2,6-bis-(5-methyl-2-oxo-2λ^4-[1,3,2]dioxathian-5-yl)-pyridine, shown in Formula **B**, but a signal for the desired chloro derivative is not observed. We therefore focussed on the synthesis of a tetrabromide.



B

The reaction of pure tetratosylate **2** with an excess of LiBr in anhydrous DMSO at elevated temperature yields, after aqueous workup, a yellow-brown viscous oil, which is the virtually pure tetrabromide "pyBr_4", **3** (2,6-bis-(2-bromo-1-bromomethyl-1-methyl-ethyl)-pyridine). The isolated yield is close to 99% (eq. (1)). In the mass spectrum of **3** (FD), the parent ion signal clusters around m/z = 507 (= M[py(^{79}Br)$_4$] + 4) and shows the isotope pattern



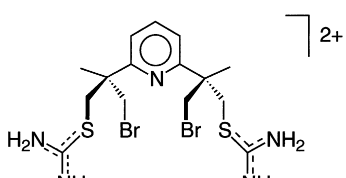
(1)

2 **3**

expected for a tetrabromo derivative. In the ^{1}H NMR spectrum, the protons on the pyridine ring give rise to a triplet (7.69 ppm) and doublet (7.23 ppm) with correct integrated intensities (1 : 2, AB_2 system), while the diastereotopic methylene protons show a characteristic set of two doublets (AB system) at *ca.* 3.9 ppm, and the six methyl protons give rise to a singlet at 1.61 ppm. The compound dissolves easily in ether, CH_2Cl_2, and THF. Its ready formation parallels the near quantitative reaction of the tetratosylate with sodium azide under similar conditions in the original synthesis of the pentaamine **1** [8].

Reaction of 2,6-$C_5H_3N[CMe(CH_2Br)_2]_2$ with thiourea

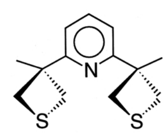
A general method for the preparation of alkylthiols starts from the corresponding alkyl halide, which is converted into an *S*-alkyl thiouronium salt by reaction with thiourea, and subsequently decomposed in alkaline solution [9 - 12]. The reaction of the tetrabromide **3** with a slight excess (4.4 eq) of thiourea in refluxing ethanol yields, after work-up, a yellow paste whose ^{1}H NMR spectrum indicates a mixture of products. After treatment of this mixture with aqueous NaOH, neutralisation with aqueous HCl, and extraction with diethyl ether, the obtained material shows no indication of the desired tetrathiol (^{1}H NMR, MS). However, crystallisation of the initially obtained mixture of products from aqueous picric acid provides a yellow microcristalline material. Its ^{1}H NMR spectrum has a broadened two-line feature at 9.03 ppm assigned to the diastereotopic NH_2 protons of a thiouronium salt and a singlet for the picrate protons at 8.58 ppm. From a comparison of integrals of these and the methylene group signals we conclude that the product is best formulated as a bis(thiouronium) salt, in which only two out of four bromo substituents have been replaced with a thioureido group (Formula **C** shows one of the three possible isomers, in which like substituents are diametrically opposite). The substitution reaction under the chosen conditions is thus incomplete, and it has not been pursued further.



C

Reaction of 2,6-$C_5H_3N[CMe(CH_2Br)_2]_2$ with potassium O-ethyl xanthogenate

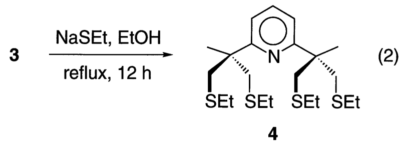
Instead of thiourea, potassium *O*-ethyl xanthogenate [13, 14] or potassium thioacetate [15, 16] have also been used as “masked” sulfhydryl group equivalents. The reaction of the tetrabromide **3** with an excess (6 eq) of potassium *O*-ethyl xanthogenate in DMSO at 70 °C for 72 h, followed by aqueous work-up, gives a yellow paste whose MS data suggest a derivative containing a maximum of three xanthogenate residues. Treatment of this paste with ethylenediamine at 40 °C, followed by hydrolysis as described in the literature [14], and final purification (*cf.* Experimental) give a yellowish powder whose MS and ^{1}H NMR data are compatible with the formulation of a bis(thietane) (2,6-bis-(3-methyl-thietan-3-yl)-pyridine, Formula **D**). The molecular mass of this material corresponds to the peak of highest intensity in the mass spectrum, and the ^{1}H NMR spectrum is conspicuous for the absence of SH signals, while showing all the other expected signals with correct integrated intensities. Thietane formation is known to be facile in 1,3-disubstituted trimethylene derivatives, in which an initially introduced thiolate function displaces, in a second step, a leaving group in the 3-position by nucleophilic substitution [17]. Therefore, the bis(thiouronium) salt shown in Formula **C** is expected also to give the bis(thietane) product when worked up with ethylenediamine [17].



D

*2,6-$C_5H_3N[CMe(CH_2SEt)_2]_2$ (**4**)*

In contrast to the other reactions described here which involve sulfur nucleophiles, the reaction of the tetrabromide **3** with sodium ethanethiolate (in refluxing ethanol) proceeds smoothly and with complete substitution (eq. (2)). Sodium bromide precipitates and may thus be conveniently removed. Evaporation of the solvent leaves **4** as a yellow oil (isolated yield: 58%), with ^{1}H and ^{13}C patterns char-



acteristic of a C_{2v}-symmetrical derivative (see Experimental). Future work will address the question whether the derivatisation is similarly straightforward with benzylthiolate, as benzyl thioethers may be cleaved selectively on the benzyl side to leave the corresponding thiol [18], so that this reaction may finally provide a viable route to the tetrathiol 2,6-$C_5H_3N[CMe(CH_2SH)_2]_2$.

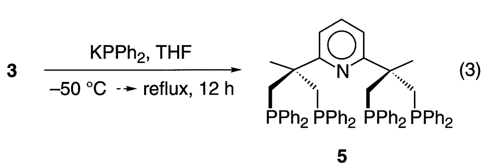
2,6-$C_5H_3N[CMe(CH_2PPh_2)_2]_2$ (**5**)

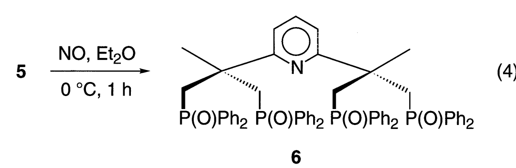
The reaction of polytosylates with alkali phosphides is an established method of preparation for polyphosphanes [19 - 21]. An initial series of experiments, however, employing the tetratosylate **2** and $LiPPh_2$ or $KPPh_2$, gave ill-defined brown mixtures of products, and neither NMR spectroscopy nor mass spectrometry indicated the formation of the target molecule. One of the underlying reasons may be the basicity of the phosphide anion, and its abstraction of tosylate methyl protons, instead of reacting by nucleophilic displacement of the leaving group [22, 23]. As an alternative starting material in the synthesis of polyphosphanes, polyhalides have been used to advantage, some of them having neopentyl-like residues as in our system [24 - 26]. This motivated our synthesis of the tetrabromide **3**, as described above. Treatment of a solution of **3** in THF at –50 °C with a slight excess (0.2 eq) of potassium diphenylphosphide [27], followed by raising the temperature slowly and refluxing for 12 h, gives a mixture from which, after aqueous workup, the tetraphosphane **5** may be isolated as a colourless foamy solid in up to 65% yield (eq. (3)). In the ^1H NMR spectrum, the diastereotopic methylene protons (AB system) give rise to two characteristic doublets of doublets between 2.5 and 2.8 ppm, due to geminal $^1H^1H$ and $^1H^{31}P$ coupling. Comparison of the $\{^1H\}\{^{31}P\}^{13}C$ and $\{^1H\}^{13}C$ NMR spectra has allowed the complete assignment of the carbon resonances (see Experimental). In the ^{31}P spectrum, a broad signal at –24.7 ppm is assigned to the phosphorus atoms of the diphenylphosphanyl groups. The chemical shifts of the methylene protons and carbon and phosphorus atoms in **3** are comparable to those determined for other poly(diphenylphosphanyl) compounds [25, 28]. The mass spectrum has a prominent signal (> 90% intensity) due to the molecular ion at *m/z* = 928, as expected. The tetraphosphane is readily soluble in CH_2Cl_2, THF, toluene, ether and refluxing ethanol, and sparingly soluble in hexane. It is insoluble in ethanol and methanol at room temperature. Oxidation of the solvent-free solid by aerobic oxygen is sluggish (if it occurs at all; no change in the ^{31}P spectrum is observed after several hours), and the compound may be stored indefinitely under dry dinitrogen at room temperature.

2,6-$C_5H_3N[CMe(CH_2P(=O)Ph_2)_2]_2$ (**6**)

With a view to the later synthesis of tetraphosphane complexes of the type $[(\mathbf{5})M(NO)]^{n+}$ (M = Ru, Fe), we studied conditions under which the ligand would be susceptible to oxidation by nitric oxide (nitrogen monoxide, NO). Since the reaction may be expected to produce the phosphane oxide, with concomitant formation of nitrous oxide (dinitrogen oxide, N_2O) [29, 30], we chose a 1 : 2 stoichiometry ($RPPh_2$:NO). Solutions of **5** in CH_2Cl_2 at –78 °C, 0 °C, and 25 °C, respectively, were each treated with 8 eq of NO gas, and their IR spectra recorded periodically. Whereas no reaction was observed at –78 °C and 0 °C, a ready reaction occurred at 25 °C to produce the oxide **6** (2,6-bis-[2-(diphenyl-phosphinoyl)-1-(diphenyl-phosphinoylmethyl)-1-methyl-ethyl]-pyridine; (eq. (4)). The formation of N_2O is conveniently followed by monitoring a growing band at 2222 cm^{-1}, which is due to the N=N stretching vibration.

For quantitative formation of the oxide, the tetraphosphane is best treated with an excess of NO in diethylether at room temperature (see Experimental) [29]. Compound **6** has been isolated





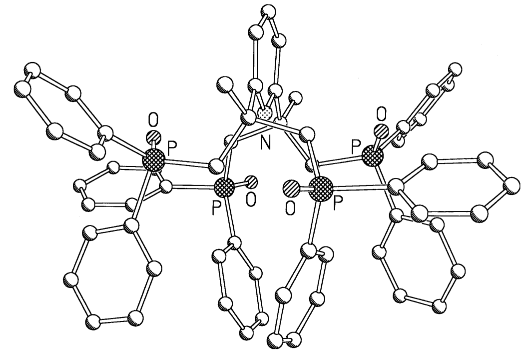


Fig. 1. Molecular structure of one of the two symmetry-independent molecules in **6** (for clarity, a ball-and-stick representation is shown, and hydrogen atoms have been omitted).

as a colourless powder in 94% yield. The product is characterised by a new strong absorption in the IR spectrum at 1183 cm^{-1}, which is assigned to the P=O stretching vibration. The ^1H, ^{13}C, and ^{31}P NMR data reflect the pairwise diastereotopicity of the phenyl rings but are otherwise in accord with values reported for other α,ω-bis(diphenyl-phosphinoyl) alkanes [31]. The only striking difference is in the ^1J(P-C) coupling constants involving the *ipso* carbon atoms. At *ca.* 190 Hz in the case of **6**, these coupling constants are almost three times as large as in the case of the diphosphane-derived oxides [31]. Compound **6** dissolves easily in CH_2Cl_2 but is virtually insoluble in diethyl ether.

The tetraphosphane oxide crystallises from methylene chloride as the hydrate with 0.5 equivalents of CH_2Cl_2 (**6** · H_2O · 0.5 CH_2Cl_2). Single crystals were of sufficient quality to allow determination of the solid-state structure (Fig. 1). The substituents on the phosphorus atoms adopt a distorted tetrahedral geometry. The P=O bond lengths involving P12, P13 and P15 are similar (average value: 147.5 pm), while the P=O bond at P14 is significantly shorter (140.0 pm). The average P-C bond length (P-C_{Aryl} and P-C_{Alkyl}) is 182.0 pm. These values, with the exception of the P=O bond length involving P14, are comparable to those found for 1,3-bis-(diphenyl-phosphinoyl)-propane: d(P-C_{Aryl}/C_{Alkyl}) = 179.9 pm, d(P=O) = 149.1 pm [31]. Likewise, the angles $\angle(OPC_{Aryl/Alkyl})$ and $\angle(C_{Aryl/Alkyl}PC_{Aryl/Alkyl})$ are in the ranges 110.8(4)° - 118.4(4)° and 100.5(4)° - 109.7(4)°, respectively, and thus of the same magnitude as in 1,3-bis-(diphenyl-phosphinoyl)-propane (111.1° - 114.1° and 106.7° - 109.8°, respectively) [31].

Concluding Remarks

The present work shows that ligands with square-pyramidally juxtaposed donor sets other than NN_4 are, in principle, accessible from intermediates of the synthesis of the pentaamine 2,6-$C_5H_3N[CMe(CH_2NH_2)_2]_2$. While the tetratosylate **2** is unsuitable for a direct tetraphosphane synthesis, it may be converted into the corresponding tetrabromide **3** in high yield, which then undergoes a clean reaction with $KPPh_2$ to yield the corresponding NP_4 ligand. The tetraphosphane **5** is the first polyphosphane of this topology. Preliminary experiments show that, inspite of its considerable steric bulk, **5** does indeed form mononuclear complexes (M = Ru, Co) in which the ligand acts as a square-pyramidal coordination cap. The preparation of a tetrathiol (NS_4) from the tetrabromide and thiourea was unsuccessful under the chosen conditions. However, NMR spectroscopic results indicate that substitution (albeit incomplete) does occur in ethanol. Current work addresses the question whether a more nucleophilic sulfhydryl equivalent (such as thioacetate) may effect complete substitution. Alternatively, since complete substitution has been achieved with ethanethiolate as the nucleophile, the analogous reaction with benzylthiolate and subsequent cleavage of the corresponding thioether may finally provide access to a tetrapodal polythiol having an NS_4 donor set.

Experimental Section

Materials and instrumentation: Manipulations were performed under an atmosphere of dried nitrogen, using standard Schlenk techniques. Reagents were AR grade or better and were purchased from Merck, Fluka, and Aldrich. The tetratosylate 2,6-$C_5H_3N[CMe(CH_2OTs)_2]_2$ and $KPPh_2$ · 2 THF were prepared as described previously [4, 27]. IR spectra (KBr discs or solutions in CaF_2 cuvettes) were recorded on a Perkin Elmer 16PC FT-IR instrument; solution spectra were compensated for solvent absorptions. NMR spectra were measured on JEOL JNM-EX 270, Lambda LA 400 and ALPHA 500 spectrometers, and mass spectra on a JEOL MSTATION 700 spectrometer. Only the absolute values of NMR coupling constants have been determined. Elemental analyses were performed using a Carlo Erba Elemental Analyser 1106.

2,6-$C_5H_3N[CMe(CH_2Br)_2]_2$ (**3**). To a warm solution (70 °C) of the tetratosylate **2** (26.02 g, 29.84 mmol) in DMSO (430 ml) was added dry LiBr (15.55 g, 179 mmol, 6 eq) in one portion, and the mixture stirred at 70 °C for 72 h. The added LiBr dissolved within 30 min, and towards the end of the reaction the solution had taken on a light brown colour. Workup was then carried out in air, with no precautions taken to exclude water from the solvents. After the solution had cooled to room temperature, water (690 ml) was added with stirring to give a white milky precipitate. Stirring was continued for 10 min, and the mixture then extracted with ether (5×200 ml). The combined ether phases were extracted once with water (70 ml), and dried over Na_2SO_4. Ether was distilled off on a rotary evaporator to leave the tetrabromide **3** as a yellow oil which was dried *in vacuo*. The material is virtually pure (^{1}H NMR) and was used in subsequent reactions without further purification. Yield: 14.9 g (99%). MS (FD$^+$, THF): m/z(%) = 507 [py(Br)$_4$]$^+$ (100). ^{1}H NMR (270 MHz, $CDCl_3$, R. T.): δ/ppm = 7.69 (AB_2, 3 lines, 1 H, py-H^4), 7.23 (AB_2, 2 lines, 2 H, py-H^{3,5}), 3.93 (d, ^2J(HH) = 9.9 Hz, 4 H, -C*H*H-Br), 3.84 (d, ^2J(HH) = 9.9 Hz, 4 H, -CH*H*-Br), 1.61 (s, 6 H, -C*H*$_3$). {^{1}H}^{13}C NMR (270 MHz, DMSO-d$_6$, R. T.): δ/ppm = 159.64 (py-C2/6), 137.31 (py-C4), 119.40 (py-C3/5), 45.60 (>C<), 42.14 (-*C*H$_2$-), 22.53 (-*C*H$_3$).

2,6-$C_5H_3N[CMe(CH_2SCH_2CH_3)_2]_2$ (**4**). To a solution of sodium metal (freshly cut under hexane, 1.27 g, 55.2 mmol) in ethanol (50 ml) was added ethanethiol (3.42 g, 4.1 ml, 55.0 mmol), and the mixture stirred at room temperature for 15 min. A solution of the tetrabromide **3** (5.58 g, 11.0 mmol) in ethanol (10 ml) was then added, and the mixture refluxed for 12 h. A crystalline precipitate (NaBr) began to appear after 1 h. The suspension was allowed to cool to room temperature, filtered, and the filtrate taken to dryness to leave **4** as a yellow oil. Yield: 2.74 g (58 %). ^{1}H NMR (270 MHz, $CDCl_3$, R. T.): δ/ppm = 7.56 (AB_2, 3 lines, 1 H, py-H^4), 7.14 (AB_2, 2 lines, 2 H, py-H^{3,5}), 3.13 (d, ^2J(HH) = 12.6 Hz, 4 H, -C*H*H-), 2.96 (d, ^2J(HH) = 12.5 Hz, 4 H, -CH*H*-), 2.31 (quart, ^3J(HH) = 7.4 Hz, 8 H, -C*H*$_2$-CH$_3$), 1.50 (s, 6 H, -C*H*$_3$), 1.11 (t, ^3J(HH) = 7.4 Hz, 12 H, -CH$_2$-C*H*$_3$). {^{1}H}^{13}C NMR (270 MHz, $CDCl_3$, R. T.): δ/ppm = 162.96 (py-C2/6), 136.15 (py-C4), 118.63 (py-C3/5), 46.34 (>C<), 43.36 (-*C*H$_2$-), 27.93 (-*C*H$_2$-CH$_3$), 23.12 (-*C*H$_3$), 14.96 (-CH$_2$-*C*H$_3$).

2,6-$C_5H_3N[CMe(CH_2PPh_2)_2]_2$ (**5**). A suspension of $KPPh_2 \cdot 2$ THF (25.4 g, 63.5 mmol) in THF (150 ml) was cooled to –50 °C in an acetone/dry ice bath. To this was added a solution of **3** (7.6 g, 15 mmol) in THF (50 ml) during 4 h, during which time the suspension changed colour from red to yellow-orange. The reaction mixture was allowed, together with the cold bath, to warm to room temperature, and subsequently heated to reflux for 12 h. Upon cooling to room temperature, the mixture was further cooled to 0 °C in an ice bath, and quenched with degassed water (120 ml). The organic phase was separated, and the aqueous phase extracted with absolute ether (5 × 100 ml). The combined organic phases were dried over Na_2SO_4, taken to dryness, and the remaining yellowish paste dried *in vacuo*. It was triturated with absolute ethanol (50 ml) with stirring at 50 °C for 2 h. Upon decantation of the yellowish liquid, the remaining colourless paste was triturated with *n*-hexane overnight. The hexane solution was then decanted, the sirupy paste dissolved in absolute CH_2Cl_2, the solution taken to dryness, and the residue dried *in vacuo* to yield the tetraphosphane as a colourless foamy solid. The hexane solution deposited further product upon cooling to –20 °C for 24 h. Yield: 9.04 g (65.0%). The elemental analysis is as yet unsatisfactory due to variable amounts of occluded solvent: $C_{61}H_{57}NP_4$ (928.03): calcd. C, 78.95; H, 6.19; N, 1.51; found C, 75.41; H, 5.81; N, 1.33 C. IR (KBr, cm^{-1}): 3048, 2959, 1583, 1573, 1479, 1455, 1432 (P-Ph), 738, 694, 508. MS (FD$^+$, CH_2Cl_2): m/z (%) = 928 [py(PPh$_2$)$_4$]$^+$ (90). ^{1}H NMR (400 MHz, CD_2Cl_2, R. T.): δ/ppm = 7.31 - 6.89 (m (br), 43 H, py-H^4, py-H^{3,5}, C$_{ortho}$-H, C$_{ortho}$'-H, C$_{meta}$-H, C$_{meta}$'-H, C$_{para}$-H, C$_{para}$'-H), 2.76 (dd (br), ^2J(HH) = 14.15 Hz, ^2J(HP) = 4.64 Hz, 4H, -C*H*H-), 2.52 (dd (br), ^2J(HH) = 14.13 Hz, ^2J(HP) = 1.46 Hz, 4 H, -CH*H*-), 1.24 (s (br), 6 H, -C*H*$_3$). ^{31}P NMR (400 MHz, CD_2Cl_2, R. T.): δ/ppm = –24.72 (s (br)). {^{1}H}{^{31}P}^{13}C NMR/{^{1}H}^{13}C NMR (500 MHz, CD_2Cl_2, R. T.): δ/ppm = 165.51 (t, ^3J(CP) = 3.1 Hz, 2 C, py-C2/6), 140.80 (d, ^1J(CP) = 12.93 Hz, 4 C, C$_{ipso}$/C$_{ipso}$'), 140.78 (d, ^1J(CP) = 14.48 Hz, 4 C, C$_{ipso}$/C$_{ipso}$'), 136.46 (s, 1 C, py-C4), 133.64 (d, ^2J(CP) = 20.69 Hz, 8 C, C$_{ortho}$/C$_{ortho}$'), 133.31 (d, ^2J(CP) = 20.18 Hz, 8 C, C$_{ortho}$/C$_{ortho}$'), 128.88 (d, ^3J(CP) = 7.76 Hz, 8 C, C$_{meta}$/C$_{meta}$'), 128.82 (s, 4C, C$_{para}$/C$_{para}$'), 128.75 (d, ^3J(CP) = 6.72 Hz, 8 C, C$_{meta}$/C$_{meta}$'), 128.59 (s, 4C, C$_{para}$/C$_{para}$'), 118.47 (s, 2 C, py-C3/5), 44.93 (t, ^2J(CP) = 15.26 Hz, 2 C, >C<), 43.37 (dd, ^1J(CP) = 16.29 Hz, ^3J(CP) = 9.57 Hz, 4 C, -*C*H$_2$-), 26.79 (t, ^3J(CP) = 10.6 Hz, 2 C, -*C*H$_3$).

2,6-$C_5H_3N[CMe(CH_2P(=O)Ph_2)_2]_2$ (**6**). *Reactivity studies with NO:* Three solutions of 100 mg aliquots of **5** (0.11 mmol) in CH_2Cl_2 (10 ml) were kept at –78 °C, 0 °C, and 25 °C, respectively, and to each was added NO (19.3 ml, 0.86 mmol). Solution IR spectra were recorded at hourly intervals. No reaction was observed in the first two cases after 4 h, and the mixtures were discarded. The mixture at room temperature showed a prominent band at 2222 cm^{-1} (N_2O, N=N str) already after 1 h. Reaction was allowed to proceed for 16 h, after which time the mixture was taken to dryness to leave **6** as a colourless powder whose spectroscopic data were identical to those of material obtained by the following procedure. *Preparative scale:* Into a clear, colourless solution of the tetraphosphane **5** (1.85 g, 2.0 mmol) in ether (40 ml), cooled to 0 °C, was passed a gentle stream of NO during 5 min. A fine, powdery solid began to appear after *ca.* 30 s. Stirring was continued for 30 min at 0 °C and for a further 30 min at room temperature. The solid was then filtered off, washed with ether (3 × 8 ml), and dried *in vacuo*. Yield: 1.93 g (94.0 %). **6** · 0.5 Et_2O, $C_{61}H_{57}NO_4P_4$ · 0.5 Et_2O (1029.09): calcd. C 73.53, H 6.07, N 1.36; found C 73.78, H 6.35, N 1.24. IR (KBr, cm^{-1}): 3053, 2964, 1576, 1482, 1457, 1436 (P-Ph), 1261, 1183 (P=O), 1116, 1100, 1067, 1026, 997, 804, 742, 714, 696, 593, 556, 508. MS (FD^+, CH_2Cl_2): *m/z* (%) = 992 $[py(P(O)Ph_2)_4]^+$ (100). ^1H NMR (270 MHz, CD_2Cl_2, R. T.) δ/ppm = 7.61 - 6.91 (m (br), 43 H, py-H^4, py-$H^{3,5}$, C_{ortho}-H, C_{ortho}'-H, C_{meta}-H, C_{meta}'-H, C_{para}-H, C_{para}'-H), 3.44 (dd, ^2J(HH) = 15.03 Hz, ^2J(HP) = 9.95 Hz, 4 H, -C*H*H-), 2.89 (ddd, ^2J(HH) = 14.37 Hz, ^2J(HP) = 12.02 Hz, ^4J(HP) = 1.17 Hz, 4 H, -CH*H*-), 1.49 (s, 6 H, -CH_3). ^{31}P NMR (400 MHz, CD_2Cl_2, R. T.): δ/ppm = 26.97 (s). $\{^1H\}^{13}C$ NMR (270 MHz, CD_2Cl_2, R. T.): δ/ppm = 163.01 (t, ^3J(CP) = 29.91 Hz, 2C, py-C2/6), 136.62 (s, 1 C, py-C4), 135.66 (d, ^1J(CP) = 193.87 Hz, 4 C, C_{ipso}/C_{ipso}'), 135.57 (d, ^1J(CP) = 192.86 Hz, 4 C, C_{ipso}/C_{ipso}'), 131.18 (s (br), 8 C, C_{para}/C_{para}'), 130.65 (d, ^2J(CP) = 22.69 Hz, 4 C, C_{ortho}/C_{ortho}'), 130.52 (d, ^2J(CP) = 23.72 Hz, 4 C, C_{ortho}/C_{ortho}'), 128.56 (d, ^3J(CP) = 22.68 Hz, 4 C, C_{meta}/C_{meta}'), 128.53 (d, ^3J(CP) = 22.68 Hz, 4 C, C_{meta}/C_{meta}'), 117.82 (s, 2 C, py-C3/5), 43.91 (t, ^2J(CP) = 15.47 Hz, 2 C, >C<), 40.11 (dd, ^1J(CP) = 139.23 Hz, ^3J(CP) = 25.77 Hz, 4 C, -CH_2-), 26.33 (t, ^3J(CP) = 19.59 Hz, 2 C, -CH_3).

Attempted derivatisations and purifications

2,6-$C_5H_3N[CMe(CH_2OSiMe_3)_2]_2$. Potassium hydride (0.45 g, 11.2 mmol) was suspended in hexane (10 ml), and the mixture cooled to 0 °C in an ice bath. After addition of a solution of crude tetraalcohol (0.71 g, ≤ 2.8 mmol) in THF (7 ml), stirring was continued for 15 min at 0 °C. The mixture was then allowed to warm to room temperature during 30 min, and gas evolution (H_2) was observed. The resulting yellow-brown suspension was cooled to –60 °C in a methanol / dry ice bath, and a solution of Me_3SiCl (1.42 ml, 11.2 mmol) in hexane (10 ml) added dropwise. After the addition, stirring was continued for 1 h at –60 °C and another 12 h at room temperature, during which time the colour of the suspension changed from brown to yellow. Precipitated KCl was removed by filtration / centrifugation, and the yellow filtrate taken to dryness in an oil pump vaccum, to leave a brown oil. Kugelrohr (bulb-to-bulb) distillation failed to achieve appreciable purification. MS (FD^+, CH_2Cl_2): *m/z* (%) = 543 $[py(OTMS)_4]^+$ (100). ^1H NMR (270 MHz, DMSO-d_6, R. T.): δ/ppm = 7.69 (AB_2, 3 lines, 1 H, py-H^4), 7.27 (AB_2, 2 lines, 2 H, py-$H^{3,5}$), 3.84 (d, ^2J(HH) = 10.8 Hz, 4 H, -C*H*H-OSiMe_3), 3.77 (d, ^2J(HH) = 10.8 Hz, 4 H, -CH*H*-OSiMe_3), 1.29 (s, 15 H, 6 H, -CH_3 [+ impurities]), 0.0 (s, 36 H, -Si$(CH_3)_3$).

Reaction of the tetrabromide **3** *with thiourea.* A solution of **3** (2.53 g, 5.0 mmol) in THF (10 ml) was added dropwise to a suspension of thiourea (1.37 g, 22.0 mmol, 4.4 eq) in ethanol (30 ml), and the mixture heated to reflux for 6 h. A clear solution resulted upon warming, whose colour gradually turned yellow. No precipitate formed upon cooling to room temperature at the end of the reaction, and the solution was taken to dryness to leave a yellow paste (*ca*. 2.3 g) which was dried *in vacuo*. Half of this was hydrolysed with base following the procedure of Harley-Mason *et al.* [9], but analysis of the product provided no indication for the formation of the target tetrathiol. The other half was dissolved in refluxing ethanol, and the hot solution added to a refluxing aqueous solution of picric acid (1% m/m). Upon cooling to room temperature, the solution deposited a yellow microcrystalline powder which was filtered off, washed with ethanol/ether (1:1), and dried in a stream of dry dinitrogen. ^1H NMR data suggest this material to be a bis(thiouronium) bis(picrate) derivative of the tetrabromide **3**: ^1H NMR (270 MHz, DMSO-d_6, R. T.): δ/ppm = 9.03 (d (br), ^2J(HH) = 9.4 Hz, 8 H, thiouronium-), 8.58 (s, 4 H, picrate), 7.90 ("t", 1H, py-H^4), 7.45 ("d", 2 H, py-$H^{3,5}$), 3.78 - 3.53 (m, 8 H, -CH_2-), 1.52 (s, 6 H, -CH_3).

Reaction of the tetrabromide **3** *with potassium O-ethyl xanthogenate*. A solution of **3** (5.07 g, 10.0 mmol) in DMSO (150 ml) under dry dinitrogen was warmed to 70 °C with stirring, solid potassium O-ethyl xanthogenate (9.62 g, 60.0 mmol) – which had previously been dried in an oil pump vacuum – added in one portion, and the mixture stirred at 70 °C for 72 h. The xanthogenate initially formed a yellow sludge, which dissolved within 2 h to give a clear solution, which gradually took on a yellowish colour. Workup was performed in air. After the solution had cooled to room temperature, water (240 ml) was added, the mixture stirred for 10 min, and then extracted with ether (5 × 100 ml). The combined ether phases were extracted with water (30 ml) and dried over Na_2SO_4. After removal of the solvent and drying *in vacuo*, the remaining yellow paste was treated with ethylenediamine (20 ml) at 40 °C for 12 h. After cooling to room temperature, the solution was added to a water / ice mixture (80 ml) to produce a milky precipitate. The pH was adjusted to 5 by addition of aqueous HCl, and the suspension extracted with ether (5 × 100 ml). The combined ether phases were dried over Na_2SO_4. Removal of the solvent and drying *in vacuo* gave a yellowish powder formulated as the bis(thietane) derivative: MS(FD^+,

Table 1. Crystallographic data for compound **6**.

Composition	$\mathbf{6} \cdot H_2O \cdot 0.5\ CH_2Cl_2$
Empirical formula	$C_{61.5}H_{60}ClNO_5P_4$
Formula weight	1052.43
Crystal system	orthorhombic
Space group (no.)	$Pca2_1$ (no. 29)
a [Å]	26.914(3)
b [Å]	14.090(1)
c [Å]	28.732(3)
Z	8
V [Å^3]	10896(2)
ρ_{calcd} [g cm^{-3}]	1.283
Diffractometer	Siemens P4
λ[a] [Å]	0.71073
Crystal size [mm^3]	$0.70 \times 0.62 \times 0.48$
T [°C]	200(2)
Absorption correction	psi scans
T_{min}/T_{max}	0.651/0.687
Scan	ω
2Θ Range	$4 \leq \Theta \leq 52$
Measured reflections	15976
Unique reflections	12041
Observed reflections[b]	6305
μ(Mo-K$_\alpha$) [mm^{-1}]	0.238
Refined parameters	1316
Data/parameter ratio	9.2
$wR2$ (all data)[c]	0.1934
$R1$ (obs. data)[d]	0.0747
ρ_{fin} (max/min) [e Å^{-3}]	0.608/–0.385
Weighting scheme[e]	$k = 0.0792$ / $l = 0.08784$
Abs. structure parameter	–0.01(12)

[a] Mo-K$_\alpha$, graphite monochromator; [b] with $F_o \geq 4\,\sigma(F)$; [c] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\} / \{\Sigma w(F_o^2)^2]\})^{0.5}$; [d] $R1 = \Sigma\,||F_o| - |F_c|| / \Sigma |F_o|$ for $F > 4\sigma(F)$; [e] $w = 1/[\sigma^2(F_o^2) + (k \cdot P)^2 + l \cdot P]$ and $P = (F_o^2 + 2 \cdot F_c^2)/3$.

CH_2Cl_2): *m/z* (%) = 251 [py(S)$_2$]$^+$ (100), 283 [py(S)(S$_2$)]$^+$ (10). ^{1}H NMR (270 MHz, DMSO-d$_6$, R. T): δ/ppm = 7.76 (AB$_2$, 3 lines, 1 H, py-H^4), 7.17 (AB$_2$, 2 lines, 2 H, py-H^{3,5}), 3.79 (d, ^2J(HH) = 4.5 Hz, 4 H, (-C*H*H)$_2$S), 3.01 (d, ^2J(HH) = 4.5 Hz, 4 H, (-CH*H*)$_2$S), 1.66 (s, 6 H, -C*H*$_3$) (no signals for -SH).

Crystallography

Selected distances and angles for compound **6** are discussed in the text; crystal data are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 5.10 (Bruker AXS, 1998). The unit cell contains two symmetry-independent molecules. One of the solvent water molecules is disordered, with alternative occupations of 76(2)% (O2) and 24(2)% (O4). The hydrogen atoms were calculated in geometrically optimised positions, and their isotropic displacement parameters tied to those of the adjacent carbon or oxygen atoms by a factor of 1.2 and 1.5, respectively. Positions for the hydrogen atoms of the water molecules were obtained from a difference Fourier synthesis and not refined. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 195312. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk]

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[1] S. Schmidt, F. W. Heinemann, A. Grohmann, Eur. J. Inorg. Chem. 1657 (2002).
[2] C. Zimmermann, F. W. Heinemann, A. Grohmann, Eur. J. Inorg. Chem. 547 (2001).
[3] J. Pitarch López, F. W. Heinemann, R. Prakash, B. A. Heß, O. Horner, J.-L. Oddou, J.-M. Latour, A. Grohmann, Chem. Eur. J., in press (2002).
[4] S. Schmidt, L. Omnès, F. W. Heinemann, J. Kuhnigk, C. Krüger, A. Grohmann, Z. Naturforsch. **53b**, 946 (1998).
[5] A. Grohmann, F. W. Heinemann, P. Kofod, Inorg. Chim. Acta 286, 98 (1999).
[6] J. P. Mason, D. J. Gasch, J. Am. Chem. Soc. **60**, 2816 (1938).
[7] S. Oae, Organic Chemistry of Sulfur, Plenum Press, New York (1977).
[8] A. Grohmann, F. Knoch, Inorg. Chem. **35**, 7932 (1996).
[9] J. Harley-Mason, J. Chem. Soc. 320 (1947).
[10] B. C. Cossar, J. O. Fournier, D. L. Fields, D. D. Reynolds, J. Org. Chem. **27**, 93 (1962).
[11] P. Barbaro, C. Bianchini, G. Scapacci, D. Masi, P. Zanello, Inorg. Chem. **33**, 3180 (1994).

[12] A. T. Yordanov, J. T. Mague, D. M. Roundhill, Inorg. Chem. **34**, 5084 (1995).
[13] K. Mori, Y. Nakamura, J. Org. Chem. **34**, 4170 (1996).
[14] H. Uneme, H. Mitsudera, T. Kamikado, Y. Kono, Y. Manabe, M. Numata, Biosci. Biotech. Biochem. **56**, 2023 (1994).
[15] H. Spies, M. Glaser, H.-J. Pietzsch, F. E. Hahn, O. Kintzel, T. Lügger, Angew. Chem. **106**, 1416 (1994).
[16] T.-C. Zheng, M. Burkart, D. E. Richardson, Tetrahedron Lett. **40**, 603 (1999).
[17] T. Eicher, S. Hauptmann, Chemie der Heterocyclen, Thieme, Stuttgart (1994).
[18] T. W. Greene, P. G. M. Wuts, Protective Groups in Organic Synthesis, 2nd ed., Wiley, New York (1991).
[19] H. Brunner, H.-J. Lautenschlager, Synthesis, 706 (1989).
[20] J. Holz, A. Börner, A. Kless, S. Borns, S. Trinkhaus, R. Selke, D. Heller, Tetrahedron: Asymmetry **6**, 1973 (1995).
[21] B. R. Cameron, F. C. J. M. van Veggel, D. N. Reinhoudt, J. Org. Chem. **60**, 2802 (1995).
[22] G. Reinhard, R. Soltek, G. Huttner, A. Barth, O. Walter, L. Zsolnai, Chem. Ber. **129**, 97 (1996).
[23] G. Huttner, personal communication.
[24] J. Ellermann, K. Dorn, Chem. Ber. **99**, 6537 (1966).
[25] H. Schmidbaur, A. Stützer, P. Bissinger, Z. Naturforsch. **47b**, 640 (1992).
[26] Normally, neopentyl systems react so slowly in nucleophilic substitutions that such reactions are considered synthetically useless: J. March, Advanced Organic Chemistry, 4^{th} ed., p. 339, Wiley, New York (1992). For an early example of findings to the contrary, see: R. Riemschneider, O. Göhring, P. Groß, A. Rook, K. Brendel, C. Faria, Monatsh. Chem. **96**, 147 (1965).
[27] K. Issleib, A. Tzschach, Chem. Ber. **92**, 1118 (1959).
[28] A. Muth, A. Asam, G. Huttner, A. Barth, L. Zsolnai, Chem. Ber. **127**, 305 (1994).
[29] R. Longhi, R. O. Ragsdale, R. S. Drago, Inorg. Chem. **1**, 768 (1962).
[30] M. D. Lim, I. M. Lorkovic, P. C. Ford, Inorg. Chem. **41**, 1026 (2002).
[31] P. Calcagno, B. M. Kariuki, S. J. Kitchin, J. M. A. Robinson, D. Philp, K. D. M. Harris, Chem. Eur. J. **6**, 2338 (2000).