Tetrapodal Pentadentate Ligands with NS₄ and NP₄ Donor Sets: An Elusive Tetrathiol, and a Sterically Encumbered Tetraphosphane

Christopher Zimmermann, Walter Bauer, Frank W. Heinemann, and Andreas Grohmann

a Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany
b Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestraße 42, D-91054 Erlangen, Germany

Reprint requests to Priv.-Doz. Dr. A. Grohmann. Fax: 09131-852 7367; E-mail: grohmann@anorganik.chemie.uni-erlangen.de
Z. Naturforsch. 57 b, 1256–1264 (2002); received August 5, 2002

Tetrapodal Pentadentate Ligand, Polythiols, Polyphosphanes

With the intention of preparing tetrapodal pentadentate ligands having NS₄ or NP₄ donor sets, we investigated reactions of the previously reported tetratosylate 2,6-C₅H₃N[CMe(CH₂OTs)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-C₅H₃N[CMe(CH₂Br)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(thiouanium) 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-C₅H₃N[CMe(CH₂SEt)₂]₂(2,6-bis-(2-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 KPHP₂ in THF proceeds smoothly (even at −50 °C), to give the tetraphosphane 2,6-C₅H₃N[CMe(CH₂PPh₂)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 CH₂Cl₂ or ether at different temperatures. In two cases, reaction was observed to produce the oxide 2,6-C₅H₃N[CMe(CH₂P(=O)Ph₂)₂]₂ (6) as a colourless solid in near quantitative yield, with concomitant formation of N₂O. All compounds have been characterised by ¹H, ¹³C and ³¹P 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 pentamine 1 [1, 2]. Its NN₄ 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(NH₃)₅]⁺⁺, which contain only monodentate donors. Whereas complexes such as [Fe⁺⁺(NH₃)₅]⁺⁺ (X = halide) are unknown, chelated [(I)Fe⁺⁺Br]⁺ is stable under ambient conditions and has been used to prepare a series of derivatives [(I)Fe⁺⁺L]⁺⁺ (L = CO, NO, NO⁺, NO₂⁻) 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 pentamine 1 is obtained by a sequence of reactions that enables, in principle, the variation of
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 phosphine ligands, and aimed to derive NS₄ and NP₄ ligands from intermediates in the synthesis of 1. We report here on attempts to obtain pure samples of the tetraalcohol 2,6-C₅H₅N[CMet(CH₂OH)₂]₂, on the reactivity of the tetrasalts 2,6-C₅H₅N[CMet(CH₂OTs)₂]₂ (2) and the tetrabromide 2,6-C₅H₅N[CMet(CH₂Br)₂]₂ (3) towards thiourea, potassium O-ethyl xanthogenate, sodium ethanethiolate and potassium diphenylphosphinodithiolate, and on the complete oxidation of the tetraphosphate 2,6-C₅H₅N[CMet(CH₂PPh₂)₂]₂ (5) to give the oxide, 2,6-C₅H₅N[CMet(CH₂P(O)Ph₂)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-C₅H₅N[CMet(CH₂OH)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-(trimethylsilylamoxy)-1-(trimethyl-silylaxoxymethyl)-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].

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-C₅H₅N[CMet(CH₂X)₂]₂ (X = Cl; X = Br: 3)

We pursued the synthesis of tetrachloride 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 SOCl₂ 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 sulfuric acid [7], 2,6-bis-(5-methyl-2-oxo-2λ⁴-[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.

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 "pyBr₄", 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(⁷⁹Br)₄] + 4) and shows the isotope pattern

![Reaction Scheme](image-url)
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 methyl 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$_2$Cl$_2$, 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$_5$H$_3$N[CMe(CH$_2$Br)$_2$]$_2$ with thiourea**

A general method for the preparation of alkylthiols starts from the corresponding alkyl halide, which is converted into an S-alkyl thiouonium 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 triathiol ($^1$H NMR, MS). However, crystallisation of the initially obtained mixture of products from aqueous picric acid provides a yellow microcrystalline 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 thiouonium salt and a singlet for the picro 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(thiouonium) 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.

**Reaction of 2,6-C$_5$H$_3$N[CMe(CH$_2$Br)$_2$]$_2$ 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(thiouuronium) salt shown in Formula C is expected also to give the bis(thietane) product when worked up with ethylenediamine [17].

![Reaction structure](image)

**2,6-C$_5$H$_3$N[CMe(CH$_2$Et)$_2$]$_2$ (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 tetraethyl $2,6$-$C_5$H$_3$N[CMe(CH$_2$SH)$_2$]$_2$. 

$2,6$-$C_5$H$_3$N[CMe(CH$_2$PPh$_2$)$_2$]$_2$ (5)

The reaction of polysulphides with alkali phosphides is an established method of preparation for polyphosphines [19 - 21]. An initial series of experiments, however, employing the tetrasulphide 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 polyphosphines, 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 tetraphosphate 5 may be isolated as a colourless foamy solid in up to 65% yield (eq. (3)). In the $^1$H 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 $^1$H$^1$H and $^1$H$^3$P coupling. Comparison of the $^1$H$^3$P$^{13}$C and $^1$H$^{13}$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 diphenylphosphinyl groups. The chemical shifts of the methylene protons and carbon and phosphorus atoms in 3 are comparable to those determined for other poly(diphenylphosphinyl) compounds [25, 28]. The mass spectrum has a prominent signal (> 90% intensity) due to the molecular ion at $m/z = 928$, as expected. The tetraphosphate is readily soluble in CH$_2$Cl$_2$, 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.

$2,6$-$C_5$H$_3$N[CMe(CH$_2$P=O)Ph$_2$]$_2$ (6)

With a view to the later synthesis of tetraphosphate complexes of the type [(5)M(NO)]$^{1+}$ (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 phosphoxide oxide, with concomitant formation of nitrous oxide (dinitrogen oxide, N$_2$O) [29, 30], we chose a 1 : 2 stoichiometry (RPPh$_2$:NO). Solutions of 5 in CH$_2$Cl$_2$ 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-(diphenylphosphinoyl)-1-(diphenylphosphinomethyl)-1-methyl-ethyl]-pyridine; (eq. (4))]. The formation of N$_2$O 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 tetraphosphate is best treated with an excess of NO in diethylether at room temperature (see Experimental) [29]. Compound 6 has been isolated
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 $\text{P=O}$ stretching vibration. The $^1\text{H}$, $^{13}\text{C}$, and $^{31}\text{P}$ NMR data reflect the pairwise diastereotopicity of the phenyl rings but are otherwise in accord with values reported for other $\alpha\,\omega$-bis(diphenyl-phosphinoyl) alkanes [31]. The only striking difference is in the $^1\text{J}(\text{P-C})$ 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 diphenosphate-derived oxides [31]. Compound 6 dissolves easily in CH$_2$Cl$_2$ but is virtually insoluble in diethyl ether.

The tetraphosphane oxide crystallises from methylene chloride as the hydrate with 0.5 equivalents of CH$_2$Cl$_2$ (6 · H$_2$O · 0.5 CH$_2$Cl$_2$). 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 ($\text{P-C}_{\text{Ar}}$ and $\text{P-C}_{\text{Alkyl}}$) 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: $d(\text{P-C}_{\text{Ar}}/\text{C}_{\text{Alkyl}}) = 179.9$ pm, $d(\text{P=O}) = 149.1$ pm [31]. Likewise, the angles $\angle(\text{OPC}_{\text{Ar}}/\text{Alkyl})$ and $\angle(\text{C}_{\text{Ar}}/\text{AlkylP-C}_{\text{Ar}}/\text{Alkyl})$ are in the ranges 110.8(4)$^\circ$ - 118.4(4)$^\circ$ and 100.5(4)$^\circ$ - 109.7(4)$^\circ$, respectively, and thus of the same magnitude as in 1,3-bis-(diphenyl-phosphinoyl)-propane (111.1$^\circ$ - 114.1$^\circ$ and 106.7$^\circ$ - 109.8$^\circ$, 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$_5$H$_3$N[CMe(CH$_2$NH$_2$)$_2$]$_2$. 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 KPP$_2$ 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 tetraethiol (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 sulfhydril 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 polythioly 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$_5$H$_3$N[CMe(CH$_2$OT)$_2$]$_2$ and KPP$_2$ · 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-Cl₂H₃N[CMet(CH₂Br)₂]₂ (3). To a warm solution (70 °C) of the tetratosylyte 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 Na₂SO₄. 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 (¹H 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). ¹H NMR (270 MHz, CDCl₃, R. T.): δ/ppm = 7.69 (AB₂, 3 lines, 1 H, py-H⁺), 7.23 (AB₂, 2 lines, 2 H, py-H⁺), 3.93 (d, J(HH) = 9.9 Hz, 4 H, -CH₂H-Br), 3.84 (d, J(HH) = 9.9 Hz, 4 H, -CH₂H-Br), 1.61 (s, 6 H, -CH₃). ¹³C NMR (270 MHz, DMSO-d₆, R. T.): δ/ppm = 159.64 (py-C(2)/6), 137.31 (py-C(4)), 119.40 (py-C(3)/5), 45.60 (>C<), 42.14 (-CH₂-), 22.53 (-CH₃).

2,6-C₃H₅N[CMet(CH₂SCH₂CH₃)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 %). ¹H NMR (270 MHz, CDCl₃, R. T.): δ/ppm = 7.56 (AB₂, 3 lines, 1 H, py-H⁺), 7.14 (AB₂, 2 lines, 2 H, py-H⁺), 3.13 (d, J(HH) = 12.6 Hz, 4 H, -CH₂H⁺), 2.96 (d, J(HH) = 12.8 Hz, 4 H, -CH₂H⁺), 2.31 (quart, J(HH) = 7.4 Hz, 8 H, -CH₂CH₃), 1.50 (s, 6 H, -CH₃), 1.11 (t, J(HH) = 7.4 Hz, 12 H, -CH₂CH₃). ¹³C NMR (270 MHz, CDCl₃, R. T.): δ/ppm = 162.96 (py-C(2)/6), 136.15 (py-C(4)), 118.63 (py-C(3)/5), 46.34 (>C<), 43.36 (-CH₂-), 27.93 (-CH₂CH₃), 23.12 (-CH₃). 14.96 (-CH₂CH₃).

2,6-C₅H₃N[CMet(CH₂P(=O)Ph₂)₂]₂ (5). A suspension of KPb₂ · 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 Na₂SO₄, 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 CH₂Cl₂, 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: C₆₃H₇₂N₃P₄ (928.03): calcd. C, 78.95; H, 6.19; N, 1.51; found C, 75.41; H, 5.81; N, 1.33. IR (KBr, cm⁻¹): 3048, 2959, 1583, 1573, 1479, 1455, 1432 (P-Ph), 738, 694, 508. MS (FD⁺, CH₂Cl₂): m/z (%) = 928 [py[PP₃]₂]⁺ (90). ¹H NMR (400 MHz, CDCl₃, R. T.): δ/ppm = 7.31 - 6.89 (m br), 43 H, py-H⁺, py-H⁺, 5.04, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H, Cortho-H. 1.76 (dd br), 2.62 (dd br), 2.56 (dd br), 2.46 (dd br), 2.30 (dd br), 1.45 (dd br), 1.74 (dd br). ¹³C NMR (400 MHz, CDCl₃, R. T.): δ/ppm = -24.72 (s br), 1.74 (₃₁P) ¹⁵C NMR/¹³C NMR (500 MHz, CDCl₃, R. T.): δ/ppm = 165.51 (t, 3.1 J(CP) = 3.1 Hz, 2 C, py-C(2)/6), 140.80 (d, 3.1 J(CP) = 12.95 Hz, 4 C, Cipso/Cipso'), 140.78 (d, 3.1 J(CP) = 14.8 Hz, 4 C, Cipso/Cipso'), 136.46 (s, 1 C, py-C(4)), 133.64 (d, 3.1 J(CP) = 20.69 Hz, 8 C, Cortho/Cortho'), 133.31 (d, 3.1 J(CP) = 20.18 Hz, 8 C, Cortho/Cortho'), 128.88 (d, 3.1 J(CP) = 7.76 Hz, 8 C, Cmeta/Cmeta), 128.82 (s, 4 C, Cpara/Cpara), 128.75 (s, 3 J(CP) = 6.72 Hz, 8 C, Cmeta/Cmeta), 128.59 (s, 4 C, Cpara/Cpara), 118.47 (s, 2 C, py-C(3)/5), 44.93 (t, 3.1 J(CP) = 15.26 Hz, 2 C, >C<), 43.37 (dd, 3.1 J(CP) = 16.29 Hz, 3 J(CP) = 9.57 Hz, 4 C, -CH₂-), 26.79 (t, 3 J(CP) = 10.6 Hz, 2 C, -CH₃).

2,6-C₅H₃N[CMet(CH₂P(=O)Ph₂)₂]₂ (6). Reactivity studies with NO: Three solutions of 100 mg aliquots of 5 (0.11 mmol) in CH₂Cl₂ (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 (N₂O, 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 ma-
tial 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 Et2O, C6H5H7N06P2. 0.5 Et2O (1029.09): calcld. 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⁺, CH3Cl2): m/z (%) = 992 [py(P(O)Pb)2]⁺ (100). 3H NMR (270 MHz, CD2Cl2, R. T.) δ/ppm = 7.61 - 6.91 (m, br), 43 H, py-H⁺, py-H3, Cortho-H, Cortho-H, Cmeta-H, Cmeta-H, Cpara-H, Cpara-H): 3.44 (dd, J(HH) = 15.03 Hz, J(HH) = 9.95 Hz, 4 H, -CH2-), 2.89 (ddd, J(HH) = 14.37 Hz, J(HH) = 12.02 Hz, 4 H, -CH2-H), 1.49 (s, 6 H, -CH3). 3P NMR (400 MHz, CD2Cl2, R. T.): δ/ppm = 26.97 (s). 1H NMR (270 MHz, CD2Cl2, R. T.): δ/ppm = 163.01 (s), J(JP) = 29.91 Hz, C2/C2), 136.62 (s, 1, Cpy-C4), 135.66 (d, J(JP) = 193.87 Hz, 4 C, Cpy/Cpy), 135.57 (d, J(JP) = 192.86 Hz, 4 C, Cpy/Cpy), 131.18 (s, 8 br, 8 C, Cpara-Cpara), 130.65 (d, J(JP) = 22.69 Hz, 4 C, Cortho/Cortho), 130.52 (d, J(JP) = 23.72 Hz, 4 C, Cortho/Cortho), 128.56 (d, J(JP) = 22.68 Hz, 4 C, Cmeta/Cmeta), 128.53 (d, J(JP) = 22.68 Hz, 4 C, Cmeta/Cmeta), 117.82 (s, 2 C, py-C3/5), 43.91 (t, J(JP) = 15.47 Hz, 2 C, py-C3/5), 40.11 (dd, J(JP) = 139.23 Hz, 3J(JP) = 25.77 Hz, 4 C, -CH2-), 26.33 (t, J(JP) = 19.59 Hz, 2 C, -CH3).

**Attempted derivatisations and purifications**

2.6-C5H5N[CMet(CH2OSiMe3)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 tetralcohol (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 (H2) was observed. The resulting yellow-brown suspension was cooled to –60 °C in a methanol / dry ice bath, and a solution of Me3SiCl (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 vacuum, to leave a brown oil. Kugelrohr (bulb-to-bulb) distillation failed to achieve appreciable purification. MS (FD⁺, CH2Cl2): m/z (%) = 543 [py(OTMS)3]⁺ (100). 1H NMR (270 MHz, DMSO-d6, R. T.): δ/ppm = 7.69 (ABz, 3 lines, 1 H, py-H⁺), 7.27 (ABz, 2 lines, 2 H, py-H3), 3.84 (d, J(JH) = 10.8 Hz, 4 H, -CH2OSiMe3), 3.77 (d, J(JH) = 10.8 Hz, 4 H, -CH2OSiMe3), 1.29 (s, 15 H, 6 H, -CH3 [+ impurities]), 0.0 (s, 36 H, -Si(CH3)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 tetrathioc. 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(thiourom) bis(picrate) derivative of the tetrabromide 3: 1H NMR (270 MHz, DMSO-d6, R. T.): δ/ppm = 9.03 (d, br, J(JH) = 9.4 Hz, 8 H, thiourom-), 8.58 (s, 4 H, picrate), 7.90 (t, J(JH) = 7.45 (d, 1H, picrate), 7.45 (d, 2 H, py-H3), 3.78 - 3.53 (m, 8 H, -CH2-), 1.52 (s, 6 H, -CH3).

**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 Na2SO4. 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 Na2SO4. Removal of the solvent and drying in vacuo gave a yellowish powder formulated as the bis(thiophene) derivative: MS(FD⁺).
Table 1. Crystalllographic data for compound 6.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>6 · H₂O · 0.5 CH₃Cl₂</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₆₁,H₉₀ClNO₅P₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1052.43</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group (no.)</td>
<td>Pca2₁ (no. 29)</td>
</tr>
<tr>
<td>a [Å]</td>
<td>26.914(3)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>14.090(1)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>28.732(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>10896(2)</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Siemens P4</td>
</tr>
<tr>
<td>λ [Å]</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal size [mm³]</td>
<td>0.70 × 0.62 × 0.48</td>
</tr>
<tr>
<td>T [°C]</td>
<td>200(2)</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>psi scans</td>
</tr>
<tr>
<td>T_min/T_max</td>
<td>0.651/0.687</td>
</tr>
<tr>
<td>Scan</td>
<td>ω</td>
</tr>
<tr>
<td>2θ Range</td>
<td>4 ≤ θ ≤ 52</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>15976</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>12041</td>
</tr>
<tr>
<td>Observed reflections[b]</td>
<td>6305</td>
</tr>
<tr>
<td>μ (Mo-Kα) [mm⁻¹]</td>
<td>0.238</td>
</tr>
<tr>
<td>Refined parameters</td>
<td>1316</td>
</tr>
<tr>
<td>Data/parameter ratio</td>
<td>9.2</td>
</tr>
<tr>
<td>wR2 (all data)[c]</td>
<td>0.1934</td>
</tr>
<tr>
<td>R1 (obs. data)[c]</td>
<td>0.0747</td>
</tr>
<tr>
<td>ρmax (max/min) [e Å⁻³]</td>
<td>0.608/−0.385</td>
</tr>
<tr>
<td>Weighting scheme[e]</td>
<td>k = 0.0792 / l = 0.08784</td>
</tr>
<tr>
<td>Abs. structure parameter</td>
<td>−0.01(12)</td>
</tr>
</tbody>
</table>

[a] Mo-Kα, graphite monochromator; [b] with F_o ≥ 4σ(F); [c] wR2 = (Σ[w(F_o² - F_c²)]²) / [Σ w(F_c²)]⁻¹; [d] R1 = Σ |F_o| - |F_c| / Σ |F_o| for F > 4σ(F); [e] w = 1/σ²(F_c) + (k · P)² + l · P and P = (F_o² + 2 · F_c²)/3.

CH₂Cl₂): n/cm² = 251 [py(S₂)₂]+ (100), 283 [py(S)₂]+ (10). H NMR (270 MHz, DMSO-d₆, R. T.): δ/ppm = 7.76 (AB₂, 3 lines, 1 H, py-H¹), 7.17 (AB₂, 2 lines, 2 H, py-H³,⁵), 3.79 (d, J(CH) = 4.5 Hz, 4 H, (-CH₂)₂S), 3.01 (d, J(CH) = 4.5 Hz, 4 H, (-CH₂)₂S), 1.66 (s, 6 H, -CH₃) (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 F² 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]

Acknowledgements

We thank Professor H. H. Karsch (Technische Universität München) and Professor D. Uguen (ECPM, Strasbourg) for valuable discussions, and we are grateful to Professor D. Sellmann for support of this work. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.