

New organophosphorus–sulfur heterocycles

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The synthesis of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfides from P_4S_{10} and the appropriate naphthalene compound has been accomplished. The reactions of naphthalene-1,8-diyl-1,3,2,4-dithiadiphosphetane 2,4-disulfide with methanol and 3,5-di-*tert*-butylcatechol have been performed. The crystal structure of a naphthalene relative of Lawesson's reagent has been determined.

Lawesson's reagent 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **1** is widely used for the thionation of organic molecules^{1,2} and as a starting material in the synthesis of phosphorus-containing rings.³ 2,4(Naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **2** which contains a *cis* dithiadiphosphetane ring with a naphthalene-1,8-diyl backbone has been briefly reported⁴ and has been used as a starting material for the synthesis of some phosphorus heterocyclic compounds.^{5–7} Since the preparation of **2** can be problematical we report here a full synthesis of it together with the synthesis of 2,4-(4-methoxynaphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **3**. Furthermore, the reactions of **2** with methanol and 3,5-di-*tert*-butylcatechol have been studied and the crystal structure of **3** determined and compared with some related systems.

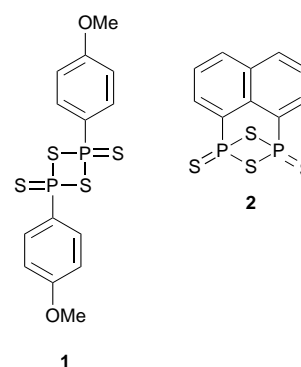
Experimental

All reactions were carried out under nitrogen gas. Toluene was distilled from sodium before use, diethyl ether from sodium–benzophenone. ALR Methanol was from Fisons and was used as received. The compounds P_4S_{10} , 1-bromonaphthalene, 1-methoxynaphthalene and 3,5-di-*tert*-butylcatechol were obtained from Aldrich and used as received. Proton (including double-irradiation experiments) and ^{31}P - $\{^1H\}$ NMR spectra were recorded ($CDCl_3$ unless otherwise stated) using a Bruker 250 MHz machine, ^{13}C - $\{^1H\}$ spectra and correlations with either a Bruker 250 or 400 MHz spectrometer, IR spectra on a Perkin-Elmer system 2000 and mass spectra using a Kratos MS80 spectrometer. Microanalyses were carried out by the Loughborough Chemistry Departmental service.

CAUTION: at the temperatures used the silicone oil-bath may start to smoke; these fumes and the hydrogen sulfide, sulfur compounds, halogens and phosphorus compounds should not be inhaled so these preparations should be carried out within an effective fume cupboard. The gases formed by the reaction mixtures can be mixed with nitrogen before being treated with sodium hypochlorite solution before release into the fume cupboard.

Preparations

2,4-(Naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide 2. 1-Bromonaphthalene (35 cm³, 52 g, 250 mmol) was stirred with P_4S_{10} (10.8 g, 24 mmol) in a round-bottomed flask (250 cm³) fitted with a thermometer and a reflux condenser; the flask was lowered into a preheated oil-bath (270 °C) after the temperature of the flask had reached 245 °C it was left in the bath for 4 min before it was removed. The flask was allowed to cool to room temperature with magnetic stirring before the



addition of diethyl ether or toluene (40 cm³). The solid was collected by filtration using a glass sinter. After washing with solvent the solid product was dried *in vacuo* to give a cream-yellow solid (1.76 g, 5.57 mmol, 11%) [Found (Calc.): C, 37.8 (38.0); H, 1.8 (1.9)%]. NMR: ^{31}P - $\{^1H\}$, δ 15.5; 1H , δ 8.9 (complex m, 2 H), 8.6 (complex m, 2 H) and 8.2 (complex m, 2 H). IR (cm⁻¹): 1597w, 1582w, 1555m, 1483m, 1436m, 1210w, 1159m, 1145w, 1071w, 992m, 901s, 826s, 759s, 741s, 670vs [$\nu(P=S)$], 573s, 535s, 506s, 432s, 386m, 327m and 289m. Mass spectra: electron impact (EI), m/z 316 (M^+), 252, 221, 186, 155, 124, 113, 95, 63, 47 and 31; positive-ion EI, m/z 316 (M^+), 284, 252, 223 and 189; expected isotropic distribution for the molecular ion.

The mother-liquor from the synthesis was examined by ^{31}P - $\{^1H\}$ NMR spectroscopy and found to be a complex mixture. Distillation of the mother-liquor from two preparations gave a mixture of bromonaphthalene and naphthalene (56 g), and an evil-smelling involatile residue.

2,4-(4-Methoxynaphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide 3. 1-Methoxynaphthalene (10 cm³, 10.9 g, 69 mmol) was stirred with P_4S_{10} (2.92 g, 6.6 mmol) in a round-bottomed flask (100 cm³) fitted with a thermometer and a reflux condenser; the flask was lowered into a preheated oil-bath (290 °C) after the temperature in the flask had reached 245 °C it was left in the bath for 4 min before it was removed. The flask was allowed to cool to room temperature with magnetic stirring before the addition of toluene (10 cm³). The mixture was stirred for several hours before the product was filtered off, washed with dry toluene (10 cm³) and then twice with diethyl ether (10 and then 15 cm³) before being dried *in vacuo*, to give a cream solid (1.21 g, 3.5 mmol, 26%). This product can be recrystallized from toluene. This reaction has been scaled up (to 11 g P_4S_{10}) successfully using a 250 cm³ flask. Single crystals suitable for X-ray studies were obtained from toluene [Found (Calc.): C, 37.6 (38.1); H, 2.0 (2.3)%]. NMR: ^{31}P - $\{^1H\}$, 17.5 (d), 16.9 (d) [$^2J(^{31}P-^{31}P) = 7.4$]; 1H , δ 8.8 (m, 1 H), 8.6 [ddd, $^4J(^1H-^1H) = 1.3$, $^3J(^1H-^1H) = 7.3$, $^3J(^{31}P-^1H) = 21$], 8.5 [dd, $^3J(^1H-^1H) = 8.3$,

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$^3J(^{31}\text{P}-^1\text{H}) = 21$ Hz] (combined integration for this peak and that at 8.6, 2 H), 7.8 (m, 1 H), 7.1 [dd, 1 H, $^4J(^{31}\text{P}-^1\text{H}) = 3.3$, $^3J(^1\text{H}-^1\text{H}) = 8.3$ Hz] and 4.2 (s, 3 H). IR (cm^{-1}): 3073w, 3004m, 2969m, 2926m, 2853w, 1601w, 1575m, 1561s, 1495m, 1456w, 1446m, 1407m, 1364w, 1350m, 1319w, 1263s, 1208m, 1186w, 1152m, 1104s, 1073w, 1014m, 946s, 885w, 827m, 801s, 759s, 741s, 698vs [$\nu(\text{P}=\text{S})$], 658vs [$\nu(\text{P}=\text{S})$], 597m, 547s, 513s, 483s and 430s. EI mass spectrum: m/z 346 (M^+), 314, 251, 219, 204, 189, 176, 158, 143, 115 and 63.

Reactions of compound 2

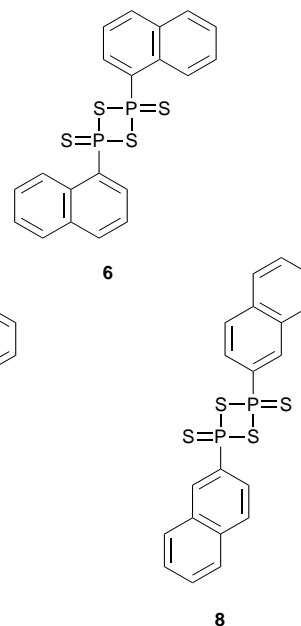
With 3,5-di-*tert*-butylcatechol. Compound **2** (0.5 g, 1.6 mmol) and 3,5-di-*tert*-butylcatechol (0.705 g, 3.2 mmol) were heated in toluene (20 cm^3) at reflux for 5 d. After cooling the mixture was stirred to cause the precipitation of a white solid which was filtered off, washed with hexane (10 cm^3) and dried to give **10** (0.25 g, 31%). NMR: ^{31}P - $\{^1\text{H}\}$, δ 74.4 (d), 71.2 (d) [$^2J(^{31}\text{P}-^{31}\text{P}) = 3.2$]; ^1H , δ 9.1 [ddd, $^4J(^1\text{H}-^1\text{H}) = 1$, $^3J(^1\text{H}-^1\text{H}) = 7$, $^3J(^1\text{H}-^{31}\text{P}) = 22$], 8.8 [ddd, 1 H, $^4J(^1\text{H}-^1\text{H}) = 2$, $^3J(^1\text{H}-^1\text{H}) = 7$, $^3J(^1\text{H}-^{31}\text{P}) = 24$], 8.2 (m, 2 H), 7.7 (m, 2 H), 7.3 (m) and 7.1 (m) (integration together gave 2 H), 1.5 (s, 9 H) and 1.2 (s, 9 H); ^{13}C - $\{^1\text{H}\}$, δ 149.1 (poorly resolved), 142.7 (dd, 5.3 and 2.5), 141.2 (dd, 18.3 and 4.8), 139.4 (dd, 12.5 and 3.8), 136.3, 136.2 (d, 10.6), 136.0 (d, 8.4), 135.4 (complex m), 133.7 (t, 12.3), 132.8 (d, 3.6), 129.6 (t, 8.8), 127.4 (dd, 11.4 and 2.7), 126.3 (d, 18.1), 125.4 (d, 19.0 Hz), 123.5 (poorly resolved m), 118.6 (poorly resolved m), 35.8, 35.2, 31.7 and 31.4; $^{31}\text{C}-^1\text{H}$ correlations and ^1H decoupling experiments were in accord with the formulation. IR (cm^{-1}): 3005w, 2960s, 2906m, 2868m, 1606w, 1581m, 1557w, 1495m, 1478m, 1460 (sh), 1445m, 1410s, 1395 (sh), 1365m, 1345w, 1326w, 1302s, 1261w, 1224s, 1213 (sh), 1201 (sh), 1160m, 1101m, 1027w, 1003w, 981s, 920s, 903s, 884s, 873 (sh), 837m, 825m, 795m, 775w, 769w, 759s, 748s, 704w, 678s, 663s, 652s, 636m, 616w, 596s, 571w, 554w, 537w, 518w, 507m, 490m, 474m, 455w, 423m, 390w, 371w, 322w and 303w. EI mass spectrum: m/z 504 (M^+), 489, 440, 251, 221, 189, 157, 119, 91, 57, 41 and 29; molecular ion 504.0577 ($^{12}\text{C}_{24}^{1}\text{H}_{26}^{16}\text{O}_2^{31}\text{P}_2^{32}\text{S}_3$ requires 504.0570, error 1.4 ppm).

With methanol. Compound **2** (0.77 g, 2.4 mmol) was placed in methanol (44 cm^3) and heated under reflux (6 h) before being allowed to cool. The solid was filtered off and recrystallized from ethyl acetate to give a white solid **11** (0.76 g, 85%) [Found (Calc.): C, 39.8 (39.75); H, 3.2 (3.35)%]. EI mass spectrum: m/z 362 (M^+), 330, 299, 283, 267 and 220. NMR: ^{31}P - $\{^1\text{H}\}$, δ 79.8 [d, $^2J(^{31}\text{P}-^{31}\text{P}) = 15.0$] and 66.4 [d, $^2J(^{31}\text{P}-^{31}\text{P}) = 15.0$]; ^1H , 8.8 (complex m, 2 H), 8.2 (m, 2 H), 7.7 (m, 2 H), 3.83 [d, 3 H, $^2J(^{31}\text{P}-^1\text{H}) = 16.3$] and 2.61 [d, 3 H, $^2J(^{31}\text{P}-^1\text{H}) = 17.9$ Hz]. IR (cm^{-1}): 2979m, 2933s, 2911s, 2829s, 1588w, 1554w, 1496m, 1447w, 1431w, 1324w, 1210w, 1173w, 1156m, 1023s, 897m, 828w, 798s, 760s, 667m, 649s, 621m, 598m, 567w, 526m, 511s and 485m.

Crystallography

Crystal data. $\text{C}_{11}\text{H}_8\text{OP}_2\text{S}_4$ **3**, $M = 346.4$, orthorhombic, space group $Pnma$, $a = 10.629(2)$, $b = 6.936(3)$, $c = 18.397(2)$ Å, $U = 1356$ Å 3 , $Z = 4$, $D_c = 1.70$ g cm^{-3} , crystal dimensions $0.20 \times 0.12 \times 0.20$ mm, $\mu(\text{Cu-K}\alpha) = 8.51$ mm^{-1} , $F(000) = 704$. Rigaku AFC7S diffractometer, ω -scan method, graphite-monochromated Cu-K α radiation (λ 1.54178 Å; 2θ range 3.0–120°); 1217 independent reflections ($R_{\text{int}} = 0.017$), 958 observed [$I > 3.0\sigma(I)$], corrected for Lorentz-polarization and absorption scans, maximum and minimum transmission factors 1.00 and 0.80.

The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. Hydrogen atoms were refined in idealized positions. Refinement on F to $R = 0.029$ and $R' = 0.031$. Weighting scheme employed: $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [S^2(C + R^2B) + (\rho F_o^2)^2]/Lp^2$



and $S =$ scan rate, $C =$ total integrated peak count, $R =$ ratio of scan time to background counting time, $B =$ total background count, $Lp =$ Lorentz-polarization factor and $p = p$ -factor. The maximum and minimum residual electron densities in the final ΔF map were 0.36 and -0.22 e Å $^{-3}$ and the maximum shift/error in the final refinement was 0.49. Computations were carried out using TEXSAN.⁸

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/431.

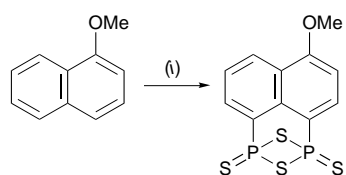
Results and Discussion

Reaction of 1-bromonaphthalene with P_4S_{10} at 240 °C leads to compound **2** in moderate yield. The synthesis is very sensitive to slight changes in the conditions used, so close attention to detail is needed; longer reaction times or lower temperatures lead to mixtures. On occasion we have obtained much higher yields (over 50%) than those reported here but 10–20% is most typical. Compound **2** was characterized spectroscopically and gave satisfactory NMR and IR data [δ_p 15.5, $\nu(\text{P}=\text{S})$ 670 cm^{-1}]; it is a reasonably air-stable solid with a mild odour. The mechanism of formation of **2** is unclear, but we believe a free-radical mechanism is likely. When 1-chloronaphthalene **4a** was substituted for the 1-bromonaphthalene **4** in the synthesis, almost no **2** was formed suggesting that cleavage of the carbon-halogen bond is a key step in the formation of **2**. By distillation of the mother-liquor from the synthesis of **2** we found that in addition to **4** some naphthalene **5** was present. This may have been formed from naphthyl radicals as a side product.

The reaction of naphthalene with P_4S_{10} has been reported to give **2**, 2,4-bis(1-naphthyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **6**, 2-(1-naphthyl)-4-(2-naphthyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **7** and 2,4-bis(2-naphthyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **8**.⁹ We postulated that by activating the 1 position of a naphthalene by means of an electron-donating group that the formation of a naphthalene-1,8-diyl dithiadiphosphetane system could be favoured. It was found that the reaction of 1-methoxynaphthalene **9** with P_4S_{10} gave **3** in reasonable yield (Scheme 1). The formation of **3** presumably proceeds *via* electrophilic aromatic substitution occurring first at the site *para* to the methoxy group. The resulting intermediate then cyclizes by means of another electrophilic aromatic

Table 1 Selected comparative bond lengths (Å) and angles (°) for compounds **2**,⁴ **3** and **11**⁵

	2	3	11
P(1)–S(1)	1.913(2)	1.907(2)	1.923(1)
P(9)–S(9)	1.912(2)	1.910(2)	1.936(1)
P(1)–S(19)	2.126(2)	2.123(1)	2.084(1)
P(9)–S(19)	2.122(1)	2.114(1)	2.079(1)
P(1)–C(1)	1.805(6)	1.784(4)	1.808(3)
P(9)–C(9)	1.809(6)	1.799(4)	1.807(3)
S(1)–P(1)–S(19)	118.2(1)	117.8(1)	105.6(1)
S(9)–P(9)–S(19)	118.6(1)	118.6(1)	111.5(1)
S(1)–P(1)–C(1)	117.5(2)	119.4(2)	117.7(1)
S(9)–P(9)–C(9)	116.9(2)	117.6(2)	117.4(1)
S(19)–P(1)–C(1)	103.7(1)	102.6(1)	108.2(1)
S(19)–P(9)–C(9)	103.6(1)	102.6(1)	108.2(1)
S(19)–P(1)–S(19*)	91.6(1)	92.1(1)	–
S(19)–P(9)–S(19*)	91.8(1)	92.6(1)	–
P(1)–S(19)–P(9)	80.0(1)	80.2(1)	103.0(1)
S(19)⋯S(19*)	3.05	3.06	–
π – π interplanar separation	3.56	3.51	3.34



Scheme 1 (i) P_4S_{10} , heat

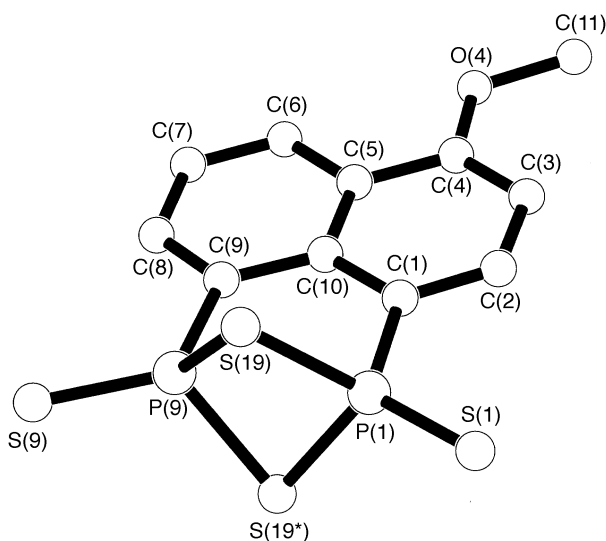


Fig. 1 Crystal structure of compound **3**

substitution reaction to give **3**. The ^{31}P NMR spectrum of **3** is an AX system with $^2J(^{31}P-^{31}P) = 7.4$ Hz which is similar to that (7 Hz) found for 2-(1,1'-dimethylferrocen-3-yl)-4-(*p*-methoxyphenyl)-1,3-dithiadiphosphetane disulfide¹⁰ and is approximately twice that of **10** (see below). The $\nu(P=S)$ at 670 cm^{-1} for **2** is split into two bands at 658 and 698 cm^{-1} for **3** as a consequence of the electronic effect of the methoxy group on the dithiadiphosphetane ring system. This group does not exert any steric effect on the phosphorus–sulfur ring system but does have an electronic effect through the aromatic naphthalene system.

In the crystal structure of compound **3** (Fig. 1, Table 1) all of the atoms except for S(19) [and hence S(19*)] lie in a crystallographic mirror plane and therefore are necessarily coplanar. The atom S(19) lies 1.53 Å above the naphthalene plane with an S(19)⋯S(19*) distance of 3.06 Å . The P=S bond lengths in **3**

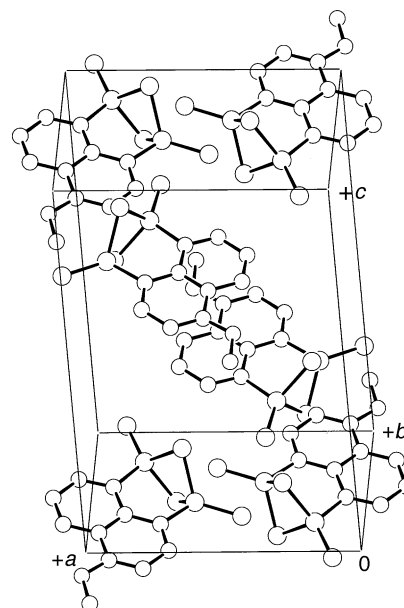
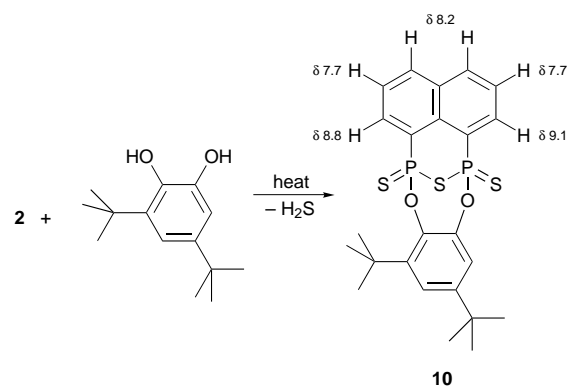


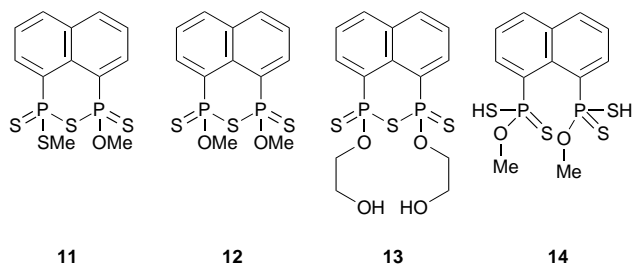
Fig. 2 Packing diagram of compound **3** illustrating the face-face π – π overlap



Scheme 2

are indistinguishable from those in **2** but significantly shorter than the equivalent bond lengths in **10**. Concomitant with this effect is a slight lengthening of the P(1)–S(19) and P(9)–S(19) in **2** and **3** relative to **10**. This effect is presumably a consequence of the difference in the electron-withdrawing effects of a bridging sulfur atom (in **2** or **3**) compared to alkoxy groups in **10**. Further support for this observation is the fact that the observation of similar trends in the P–S bond lengths of **10**⁷ and $RP(S)_2P(S)R$ ($R = \text{ferrocenyl}$).¹⁰ In **2** and **3** the internal ring angles differ markedly from $RP(S)_2P(S)R$ systems since in the latter the P_2S_2 rings are always planar. Thus when $R = \text{ferrocenyl}$ the internal P–S–P and S–P–S angles are $86.9(1)$ and $93.1(1)^\circ$ respectively compared to $80.2(1)$ and $92.6(1)/92.1(1)$ in **3**. The transannular S⋯S distance may 'fix' the ring angles since it seems insensitive to the R groups or ring folding at 3.05 , 3.06 and 3.08 Å in **2**, **3** and the ferrocenyl compound¹⁰ respectively. The P–S–P angles in **11** and **13** are $103.0(1)$ and $101.8(1)$ respectively reflecting the ability of the system to 'open up' with the loss of one ring atom. In **3** the molecules pack (Fig. 2) with the naphthalene rings face to face in a typical π – π overlap with an interplanar separation of 3.51 Å . There are long-range S(1)⋯S(19) interactions (3.49 Å) between adjacent molecules.

The reaction of compound **2** with 3,5-di-*tert*-butylcatechol has been mentioned in a preliminary communication;⁷ here the experimental details are given for the reaction (Scheme 2) forming **10** the seven-membered heterocyclic product. The reaction is most likely to involve attack of the hydroxyl oxygen atoms as nucleophiles on the electrophilic phosphorus atoms, followed



by elimination of hydrogen sulfide to give the product. The presence of the Bu^t groups may favour the formation of **10** at the expense of a polymer. When diferrocenyldithiadiphosphetane disulfide was treated with catechol we found¹⁰ that a mixture of at least three different compounds was obtained. Owing to the complex nature of the ¹³C NMR spectrum of **10** even at 100.6 MHz a ¹³C-¹H correlation was carried out in order to assist with the assignment of the carbon spectrum. The ¹H NMR spectrum was assigned with the aid of a double-irradiation experiment (see Scheme 2).

Refluxing compound **2** in methanol gives **11** in good yield. The formation of a more symmetric compound (**12**) with a pair of *P*-methoxy groups would be expected on the grounds of the oxophilic nature of phosphorus; such a product could form by the reaction of two molecules of methanol with **2** followed by elimination of a molecule of hydrogen sulfide, as is thought to be the case in the reaction of ethylene glycol and **2** to give **13**. We speculate that the first stage of the reaction of methanol with **2** is the formation of an intermediate **12** which is then

converted into **11**. Alternatively, intermediate **14** could reorganize then eliminate H₂O to give **11**. To date all attempts to trap **12** have been unsuccessful. Interestingly, we have not been able to extend the reaction to other alcohols.

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