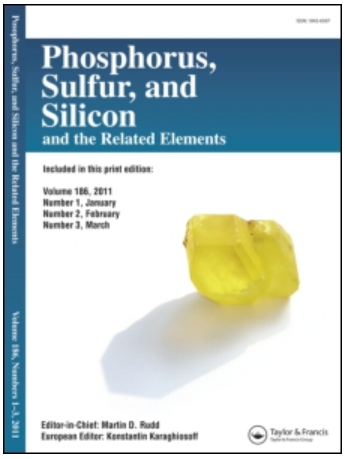

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Synthesis and Characterization of Diaminodithio- and Aminotrithiophosphoric Acid Esters

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Synthesis and Characterization of Diaminodithio- and Aminotrithiophosphoric Acid Esters

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The synthesis and characterization of a series of five new diaminodithiophosphoric acid esters $(R^1R^2N)_2P(S)SR$ *and five new aminotrithiophosphoric acid esters* $(R^1R^2N)P(S)(SR)_2$ *are described. The structure of two of these compounds, the diaminodithio derivative* $(iPr_2N)_2P(S)SCH_2Ph$ *and the aminotrithio derivative* $(iPr_2N)P(S)(SCH_2Ph)_2$*, has been determined by single crystal X-ray diffraction. These series of compounds are potentially usable as agents for reversible addition-fragmentation chain transfer polymerization.*

Keywords Aminotrithiophosphoric acid esters; amines; diaminodithiophosphoric acid esters; reversible addition-fragmentation chain transfer (RAFT) agents; thiols

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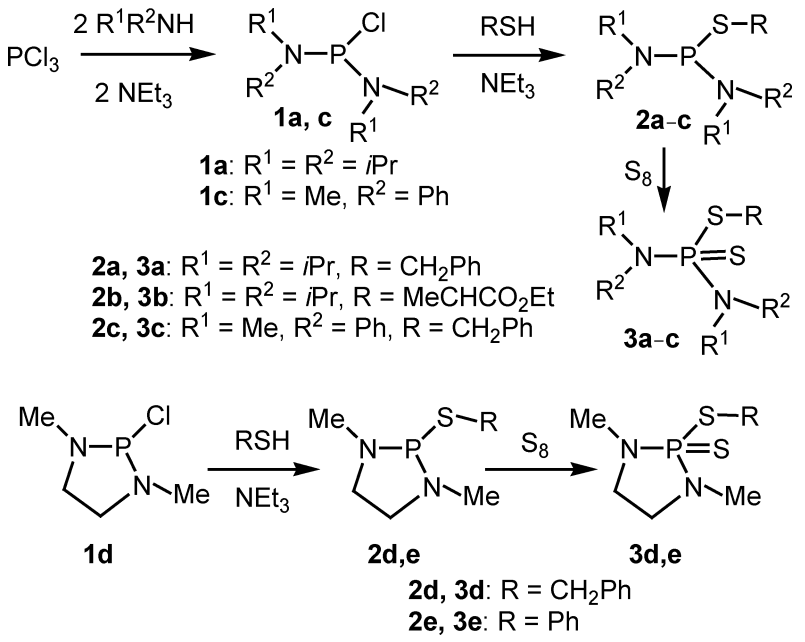
I. INTRODUCTION

Thiocarbonyl thio compounds S=C(Z)SR are the most effective agents for the Reversible Addition-Fragmentation Chain Transfer (RAFT) process, which is used to produce narrow polydispersity polymers.[1] RAFT polymerizations are applicable to a wide variety of monomers and reaction conditions, and afford the possibility to finally control the molecular weight and macromolecular architectures (block copolymers, star polymers from dendrimers,[2] etc.). Both Z and R substituents of the thiocarbonyl thio compounds have been shown to have a tremendous importance on the efficiency of the RAFT process.[3]

Recently, it has been demonstrated by some of us that dithioesters can be directly generated using tetrathiophosphates;[4] whether these thiophosphates themselves can be considered as RAFT agents or not remained unclear. However, taking into account the analogy often demonstrated between phosphorus and carbon,[5] we decided to synthesize a series of phosphorus analogs of thiocarbonyl thio compounds, i.e., $S{=}P(Z^1)(Z^2)SR$, in which the Z^1, Z^2, and R substituents can be varied. Obviously, phosphorus derivatives possess one substituent more than carbon analogs, offering a larger palette of modifications, which should enable a subtle balance between the effects of Z^1, Z^2, and R substituents. We decided to synthesize a large series of compounds in which none, one, or two of the Z substituents are also SR groups. A brief survey of the literature concerning these types of compounds shows that cases $Z^1 = Z^2 = OR$, SR, or CR_3 are well known; an example of the last two cases was already reported to be able to control radical polymerizations.[6] On the other hand, examples of such compounds in which $Z^1 = NR^1R^2$ and $Z^2 = SR$ or $Z^1 = Z^2 = NR^1R^2$ are less known. Here we report the synthesis of all the previously unknown types of compounds, which we have prepared in view of the search for new RAFT agents; all of them are amino derivatives.

II. RESULTS AND DISCUSSION

Many dithio or trithio derivatives of phosphorus are synthesized starting from P_4S_3, P_4S_{10}, Davy's or Lawesson's reagent, or $S{=}PX_3$, i.e., from reagents possessing already PS linkages. In first attempts, we tried to use such reagents for obtaining $S{=}P(NR^1R^2)_2SR$ and $S{=}P(NR^1R^2)(SR)_2$ derivatives, but in our hands, they did not provide the desired compounds with a sufficiently good yield and purity. On the other hand, PCl_3 appears as a more powerful and versatile reagent, particularly when bulky or poorly reactive substituents are to be used. The first family of



SCHEME 1

compounds we synthesized using a one-pot process starting from PCl_3 belongs to the diaminodithiophosphoric acid ester series (Scheme 1).

The first substitution reaction might be carried out to introduce either one SR or two NR^1R^2 substituents. The second possibility appears as the most suitable, because it leads to relatively stable diaminochlorophosphines of type **1**. The substituents on nitrogen were chosen in order to have a maximal diversity with a small number of compounds. An alkyl (**1a**),[7] an aryl (**1c**),[8] and a cyclic (**1d**)[9] derivative were obtained using known procedures. These compounds can be either isolated or used directly in a one-pot process.

The second substitution reaction was carried out at low temperature with three different thiols: a "linear" alkylthiol, leading to **2a**, **2c**, and **2d**; a functionalized branched alkythiol leading to **2b**; and an arylthiol leading to **2e**. It is important to use a strictly stoichiometric amount of the thiol (or even a slight deficiency) to avoid the replacement of one amino group by the highly nucleophilic thiol. This problem was not observed in cases **d** and **e**, where the cyclic substituent precluded the breaking of the P—N bonds. The reaction was only monitored by ^{31}P NMR, and no attempt was made to isolate these new tricoordinated phosphorus compounds. Finally, S_8 was added to all the

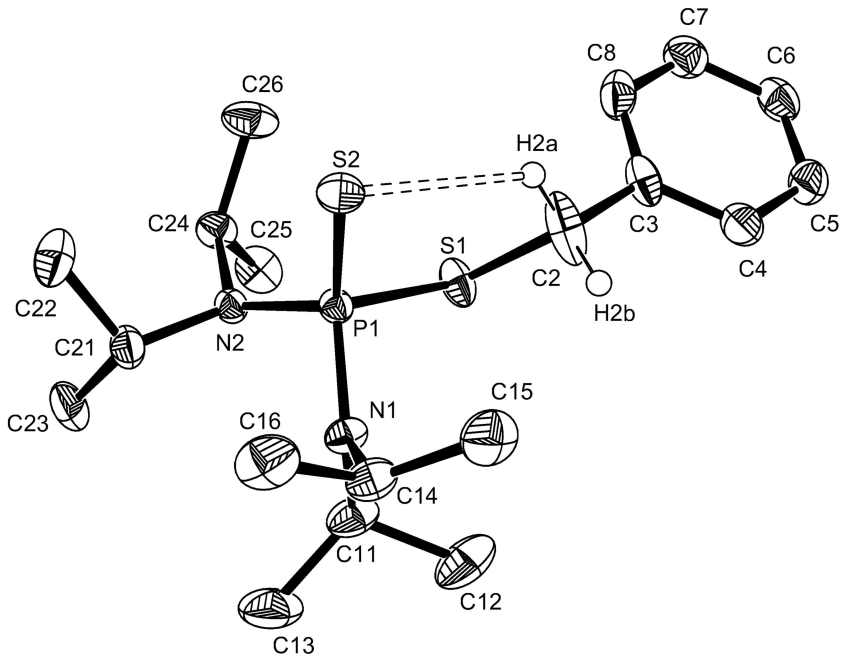


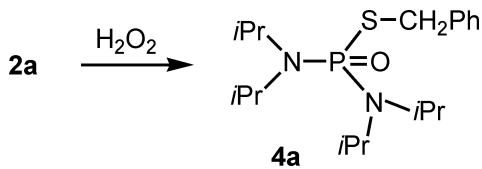
FIGURE 1 ORTEP drawing of compound **3a**. Selected bond lengths (Å) and angles (deg.): S(2)-P(1) 1.948(1); S(1)-P(1) 2.123(1); P(1)-N(1) 1.655(1); P(1)-N(2) 1.667(1); N(1)-P(1)-N(2) 104.6(1); S(2)-P(1)-S(1) 111.6(1); N(1)-P(1)-S(1) 106.8(1); N(1)-P(1)-S(2) 113.9(1); N(2)-P(1)-S(1) 101.1(1); N(2)-P(1)-S(2) 117.6(1).

samples, either at r.t. or at −20°C. The completion of the reactions is shown again by ^{31}P NMR. The R^1, R^2, and R substituents had only a weak influence on δ^{31}P (84–92 ppm); even the chemical shift of the cyclic derivatives was in the same range. Besides ^{31}P NMR, these compounds were also characterized by ^{1}H and ^{13}C NMR, as well as elemental analyses. Furthermore, single crystals suitable for X-ray diffraction studies were obtained for compound **3a** from ethanol at −30°C. The ORTEP drawing is shown in Figure 1, the crystallographic data are summarized in Table I. All bond lengths were in the expected range. However, a slight interaction was detected between the sulphur of the thiophosphoryl group and a proton of the benzylic group. The distance S2···H2a = 2.63(26) Å was smaller than the sum of van der Waals radii (2.8 Å). Furthermore, the X-ray structure showed that the accessibility to S2 was relatively hindered by the bulky diisopropylamino substituents.

TABLE I Crystal Data and Structure Refinement for 3a and 7f

	3a	**7f**
Formula	$C_{19}H_{35}N_2PS_2$	$C_{20}H_{28}NPS_3$
M. W.	386.58	409.58
Temperature (K)	160(2)	180(2)
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/a	P 2_1/c
a/Å	a = 15.4247(12)	a = 8.754(2)
b/Å	b = 9.1409(7)	b = 14.366(2)
c/Å	c = 16.4146(13)	c = 17.670(6)
β/°	106.382(9)	91.61(4)
V/Å^3	2220.4(3)	2221.4(10)
Z	4	4
Density (calculated)	1.156	1.225
Absorption Coeff./mm^{-1}	0.316	0.409
F(000)	840	872
Crystal size/mm^3	0.32 × 0.13 × 0.09	0.24 × 0.12 × 0.08
θ range for data collect./°	2.58 to 26.02	2.31 to 24.40
Index ranges	$-18 \le h \le 18$ $-11 \le k \le 11$ $-20 \le l \le 20$	$-10 \le h \le 10$ $-16 \le k \le 16$ $-20 \le l \le 20$
Reflections collected	16357	14438
Independent reflections	4211 [R(int) = 0.0309]	3612 [R(int) = 0.1485]
Max./min. transmission	0.9721/09057	0.9680/0.9082
Data/restraints/parameters	4211/0/232	3612/0/230
Goodness-of-fit on F^2	1.028	0.925
Final $R_{indices}$ [I > 2sigma(I)]	R1 = 0.0304, wR2 = 0.0743	R1 = 0.0585, wR2 = 0.1441
$R_{indices}$ (all data)	R1 = 0.0387, wR2 = 0.0779	R1 = 0.1106 wR2 = 0.1766
Largest diff. peak and hole	0.306 and −0.282 e. Å^{-3}	0.332 and −0.491 e. Å^{-3}

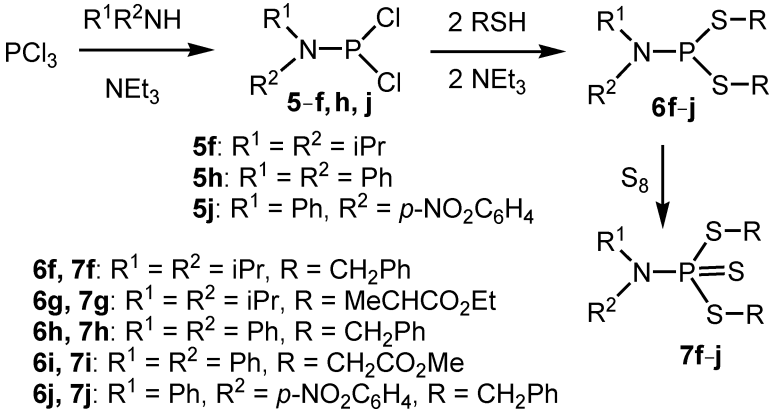
Obviously, the oxides corresponding to compounds **3** could be obtained by using an oxidant such as H_2O_2 in the last step instead of S_8. We have carried out the experiment with **2a**, to finally isolate oxide **4a** (Scheme 2). This compound might serve as a negative probe



SCHEME 2

for the control of RAFT polymerizations, since carbonylthio derivatives (O=C(Z)SR) have no activity in the RAFT process.

A second series of experiments analogous to those shown in Scheme 1 was then carried out using only one equivalent of amine (instead of two equivalents). In this case, alkyl (**5f**) and phenyl (**5h**, **5j**) substituents were used. These compounds are characterized only by ^{31}P NMR of the crude product and were directly used in a one-pot process, reacting with two equivalents of linear or branched thiols at low temperature. A strictly stoichiometric amount of thiols were needed to minimize the substitution of the amino groups by thiol. Compounds **6f**–**6j** were not isolated but were reacted directly with S_8 at r.t. to afford compounds **7f**–**7j** (Scheme 3).



SCHEME 3

Compounds **7f**–**7j** were first characterized by ^{31}P NMR; here again, all the chemical shifts were in the same range (88–100 ppm). Two signals in a 1/1 ratio were observed for **7g** (and also for **6g**), corresponding to two diastereomers due to the presence of two asymmetric carbon atoms. ^{1}H NMR spectra of all compounds **7**, except **7g**, indicated, the presence of diastereotopy for both protons of the CH_2 group of the R substituents. Single crystals suitable for X-ray diffraction studies were obtained for compound **7f** from ethanol at –30°C. The ORTEP drawing is shown in Figure 2. All bond lengths were in the expected range and correlated well with those found for **3a**. No interaction was detected between S3 and the benzyl group in the structure of **7f**, and access to S3 appeared easier than for **3a**.

This series of 10 new monoaminotrithio and diaminodithio derivatives of phosphorus pertains to a larger series of thiophosphorus derivatives that have been tested as agents for RAFT polymerizations.[10]

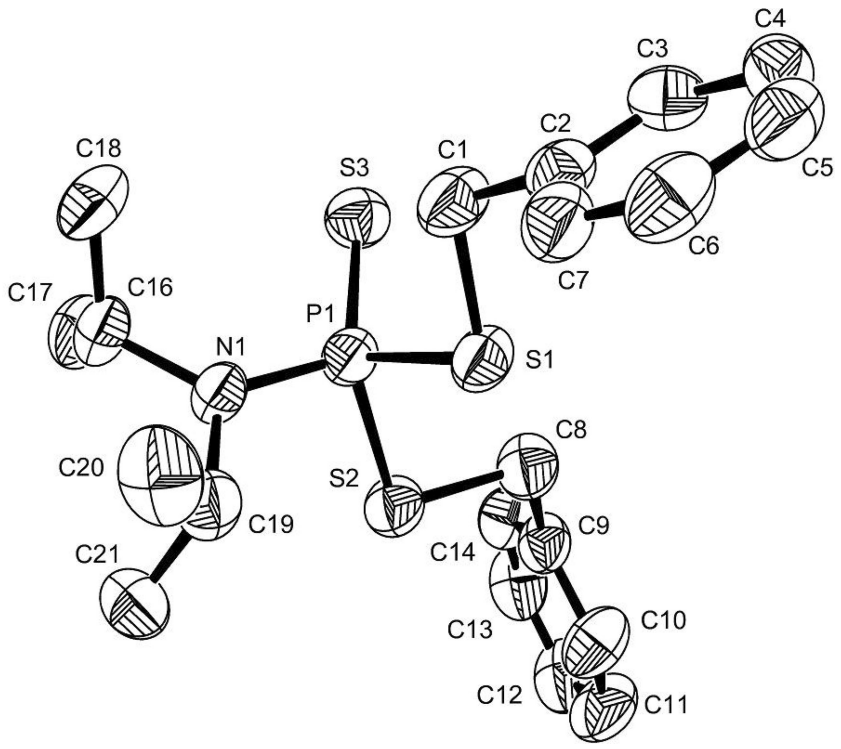


FIGURE 2 ORTEP drawing of compound **7f**. Selected bond lengths (Å) and angles (deg.): P(1)-S(3) 1.940(2); P(1)-S(1) 2.103(2); P(1)-S(2) 2.105(2); P(1)-N(1) 1.643(4); S(3)-P(1)-S(1) 112.2(1); S(3)-P(1)-S(2) 114.5(1); S(2)-P(1)-S(1) 100.6(1); N(1)-P(1)-S(3) 118.2(1); N(1)–P(1)-S(2) 102.4(2); N(1)-P(1)-S(1) 107.1(2).

III. EXPERIMENTAL

All manipulations were carried out using standard high vacuum and dry-argon techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or DPX 300 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P and $SiMe_4$ for ^{1}H and ^{13}C. The assignment of the ^{13}C NMR signals has been done using J_{mod} experiments. Solvents were dried and distilled prior to use (THF over sodium/benzophenone, CH_2Cl_2 over phosphorus pentoxide) and degassed when phosphines were used.

a. Procedure for Preparation of Compounds 3

The diaminochlorophosphines **1a**,**c**,**d** were prepared from PCl_3 and the corresponding amine; they were either isolated or used crudely. A slight

deficiency of thiol (0.95 equiv.) was added dropwise to a solution of **1a**,**c**,**d** (1 equiv.) and NEt_3 (0.95 equiv.) either in THF at −78°C or in CH_2Cl_2 (30 mL per g of **1a**,**c**,**d** in both cases) at −50°C. The resulting mixture was allowed to reach r.t. overnight; then it was cooled again at −20°C, and a slight excess of S_8 (1.1 equiv.) was added. The reaction needed 2 to 72 h to go to completion. After filtration, the solution was poured into the same volume of aqueous HCl (10%) and then extracted with diethylether (five times the amount of water). The organic phases were recovered and washed with a saturated solution of K_2CO_3 or Na_2CO_3 (same amount of water as previously), dried over $MgSO_4$, filtered, and evaporated to dryness. Compounds **3a**, **3d**, and **3e** were obtained as crystalline white powders; compounds **3b** and **3c** were obtained as thick pale yellow oils. The yields that follow are the overall yields from PCl_3.

3a: (50% yield) $^{31}P\{^1H\}$ NMR ($CDCl_3$): 84.5; ^1H NMR ($CDCl_3$): 1.33 (d, $^3J_{HH} = 6.9$ Hz, 12H, CH_3), 1.42 (d, $^3J_{HH} = 6.9$ Hz, 12H, CH_3), 3.84 (sept of d, $^3J_{HH} = {}^3J_{PH} = 6.9$ Hz, 4H, CH), 4.17 (d, $^3J_{PH} = 9.5$ Hz, 2H, CH_2), 7.34 (m, 5H, C_6H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.4 (s, CH_3), 23.5 (s, CH_3), 38.5 (s, CH_2), 47.2 (d, $^2J_{PC} = 4.7$ Hz, CH), 127.0 (s, C_{Ar}), 128.3 (s, C_{Ar}), 129.2 (s, C_{Ar}), 137.2 (d,$^3J_{PC} = 9.8$ Hz, C^i_{Ar}); anal. calcd. for $C_{19}H_{35}N_2PS_2$ (386.6): C, 59.03; H, 9.13; N, 7.25; found: C, 59.12; H, 9.17; N, 7.14.

3b: (48% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 84.6; ^1H NMR ($CDCl_3$): 1.26 (m, 27H, CH_3), 1.55 (d, $^3J_{HH} = 7.2$ Hz, 3H, C<u>H</u>$_3$CHS), 3.77 (sept of d, $^3J_{HH} = {}^3J_{PH} = 6.7$ Hz, 4H, CHN), 4.16 (m, 3H, CH_2O, CHS); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 14.1 (s, <u>C</u>H_3CH_2O), 20.2 (d, $^3J_{PC} = 3.8$ Hz, <u>C</u>H_3CHS), 22.4 (d, $^3J_{PC} = 4.3$ Hz, <u>C</u>H_3CHN), 23.6 (d,$^3J_{PC} = 3.3$ Hz, <u>C</u>H_3CHN), 45.7 (s, CHS), 47.4 (d, $^2J_{PC} = 3.8$ Hz, CHN), 47.5 (d, $^2J_{PC} = 3.9$ Hz, CHN), 61.1 (s, CH_2O), 173.1 (s, CO_2Et).

3c: (55% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 91.1; ^1H NMR ($CDCl_3$): 3.12 (d, $^3J_{PH} = 11.9$ Hz, 6H, CH_3N), 3.97 (d, $^3J_{PH} = 13.2$ Hz, 2H, CH_2S), 7.32 (m, 15H, H_{Ar}); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 38.6 (s, CH_2S), 39.6 (d, $^2J_{PC} = 4.7$ Hz, CH_3N), 126.3 (s, C^p_{ArN}), 127.3 (s, C^p_{ArC}), 127.7 (d, $^3J_{PC} = 4.0$ Hz, C^o_{ArN}), 128.5 (s, C^o_{ArC}), 128.8 (s, C^m_{ArN}), 129.2 (s, C^m_{ArC}), 137.5 (d, $^3J_{PC} = 2.0$ Hz, C^i_{ArC}), 145.1 (d, $^2J_{PC} = 2.8$ Hz, C^i_{ArN}); anal. calcd for $C_{21}H_{23}N_2PS_2$ (398.5): C, 63.29; H, 5.82; N, 7.03; found: C, 63.43; H, 5.94; N, 6.91.

3d: (48% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 91.8; ^1H NMR ($CDCl_3$): 2.56 (d, $^3J_{PH} = 13.5$ Hz, 6H, CH_3N), 3.1 (m, 4H, CH_2N), 3.9 (d, $^3J_{PH} = 15.1$ Hz, 2H, CH_2S), 7.3 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 31.4 (d, $^2J_{PC} = 7.1$ Hz, CH_3), 38.9 (s, CH_2S), 48.3 (d, $^2J_{PC} = 7.0$ Hz, CH_2N), 127.4 (s, C_{Ar}), 128.5 (s, C_{Ar}), 128.8 (s, C_{Ar}), 138.2 (s, C^i_{Ar}); anal. calcd for $C_{11}H_{17}N_2PS_2$ (272.4): C, 48.51; H, 6.29; N, 10.29; found: C, 48.59; H, 6.35; N, 10.22.

3e: (50% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 85.0; ^1H NMR ($CDCl_3$): 2.42 (m, 2H, CH_2), 2.78 (d, $^3J_{PH} = 12.7$ Hz, 6H, CH_3N), 2.98 (m, 2H, CH_2), 7.4 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 31.2 (d, $^2J_{PC} = 7.9$ Hz, CH_3), 47.8 (d, $^2J_{PC} = 7.0$ Hz, CH_2N), 128.8 (s, C_{Ar}), 128.9 (s, C_{Ar}), 129.1 (s, C_{Ar}), 135.2 (s, C^i_{Ar}); anal. calcd for $C_{10}H_{15}N_2PS_2$ (258.3): C, 46.49; H, 5.85; N, 10.84. found; C, 46.55; H, 5.89; N, 10.78.

b. Synthesis of Compound 4a

To a crude solution of **2a** (0.50 g) in THF (10 mL) cooled at −20°C was added an excess of H_2O_2 (30% in water) instead of S_8. Compound **4a** was isolated as colorless oil in 72% yield after a work-up analogous to that used for compounds **3**.

4a: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.7; ^1H NMR ($CDCl_3$): 1.27 (d, $^3J_{HH} = 7.1$ Hz, 12H, CH_3), 1.31 (d, $^3J_{HH} = 7.1$ Hz, 12H, CH_3), 3.59 (sept of d, $^3J_{HH} = {}^3J_{PH} = 7.1$ Hz, 4H, CH), 4.02 (d, $^3J_{PH} = 8.8$ Hz, 2H, CH_2), 7.34 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.9 (s, CH_3), 23.8 (s, CH_3), 30.6 (s, CH_2), 46.7 (d, $^2J_{PC} = 4.6$ Hz, CH), 126.9 (s, C_{Ar}), 128.4 (s, C_{Ar}), 129.2 (s, C_{Ar}), 137.5 (d,$^3J_{PC} = 9.7$ Hz, C^i_{Ar}).

c. Procedure for Preparation of Compounds 7

Compounds **7** were synthesized by the same method as compounds **3**, but two equivalents of thiol were used instead of one. Compounds **7f** and **7h** were obtained as crystalline white powders; **7g**, **7i**, and **7j** were obtained as thick pale yellow oils. The yields that follow are the overall yields from PCl_3.

7f: (62% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 89.9; ^1H NMR ($CDCl_3$): 1.29 (d, $^3J_{HH} = 6.9$ Hz, 12H, CH_3), 3.94 (sept. of d, $^3J_{HH} = {}^3J_{PH} = 6.9$ Hz, 2H, $CH_3C\underline{H}$), 4.20 (dd, $^2J_{HH} = {}^3J_{PH} = 12.0$ Hz, 2H, CH_2), 4.26 (dd, $^2J_{HH} = {}^3J_{PH} = 12.0$ Hz, 2H, CH_2), 7.32 (m, 10H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.9 (d, $^3J_{PC} = 9.0$ Hz, CH_3), 39.2 (d, $^2J_{PC} = 3.1$ Hz, CH_2), 49.3 (d, $^2J_{PC} = 3.1$ Hz, CH), 127.5 (s, C_{Ar}), 128.7 (s, C_{Ar}), 129.4 (s, C_{Ar}), 137.0 (d, $^3J_{PC} = 4.5$ Hz, C^i_{Ar}); anal. calcd for $C_{20}H_{28}NPS_3$ (409.6): C, 58.64; H, 6.89; N, 3.42; found: C, 58.67; H, 6.90; N, 3.40.

7g: Two diastereomers in a 1:1 ratio (45% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 88.2 (s), 88.6 (s); ^1H NMR ($CDCl_3$): 1.25 (m, 6H, $C\underline{H}_3CH_2O$), 1.32 (m, 12H, $C\underline{H}_3CHN$), 1.57 (dd, $^3J_{HH} = 7.3$ Hz, $^4J_{PH} = 0.7$ Hz, 3H, $C\underline{H}_3CHS$), 1.58 (d, $^3J_{HH} = 7.2$ Hz, 3H, $C\underline{H}_3CHS$), 3.89 (m, 4H, CHN, CHS), 4.18 (m, 4H, CH_2O).

7h: (52% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 92.8; ^1H NMR ($CDCl_3$): 4.09 (dd, $^2J_{HH} = {}^3J_{PH} = 13.0$ Hz, 2H, CH_2), 4.19 (dd, $^2J_{HH} = {}^3J_{PH} = 13.0$ Hz,

2H, CH_2), 7.37 (m, 20H, Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 39.8 (d, $^2J_{PC} = 3.7$ Hz, SCH_2), 127.0 (s, C_{Ar}), 127.6 (s, C_{Ar}), 128.7 (s, C_{Ar}), 129.1 (s, C_{Ar}), 129.2 (s, C_{Ar}), 129.4 (s, C_{Ar}), 136.3 (d, $^3J_{PC} = 7.3$ Hz, C^i_{ArCH2}), 143.5 (bs, C^i_{ArN}); Anal. Calcd for $C_{26}H_{24}NPS_3$ (477.76): C, 65.38; H, 5.06; N, 2.93. found; C, 65.46; H, 5.11; N, 2.88.

7i: (51% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 93.8; ^1H NMR ($CDCl_3$): 3.71 (s, 6H, CH_3O), 3.76 (m, 4H, SCH_2), 7.28 (m, 6H, Ar), 7.53 (m, 4H, Ar).

7j: (25% yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 100.4; ^1H NMR ($CDCl_3$): 4.07 (dd, $^2J_{HH}$=$^3J_{PH} = 11.0$ Hz, 2H, C<u>H</u>$_2$Ph), 4.13 (dd, $^2J_{HH} = {}^3J_{PH} = 11.0$ Hz, 2H, C<u>H</u>$_2$Ph), 6.96 (d, $^3J_{HH} = 7.8$ Hz, 2H, Ar), 7.30 (m, 15H, Ar), 8.1 (d, $^3J_{HH} = 7.8$ Hz, 2H, Ar).

d. X-Ray Structure Determination for Compounds 3a and 7f

Measurements were carried out on a one-circle IPDS STOE x-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å, 50 KV/30 mA power). The data were collected at low temperature at T = 160(2) K and 180(2) K for **3a** and **7f**, respectively. Frames were integrated with the aid of STOE, X-RED, Data Reduction for STADI4 and IPDS, Revision 1.08, STOE software.[11]

For **3a** a total of 100 frames were collected for a hemisphere of reflections. Based on a monoclinic crystal system, the integrated frames yielded a total of 16,357 reflections at a maximum 2θ angle of 52.04° of which 4211 were independent reflections ($R_{int} = 0.0309$, $R_{sig} = 0.0224$, completeness = 96.3%) and 3,559 (84.5%) reflections were greater than $2\sigma(I)$. Absorption corrections were applied (absorption coefficient $\mu = 0.316$ mm^{-1}; max/min transmission 0.9721 and 0.9057) using the DIFABS program.[12]

For **7f** a total of 150 frames were collected for a hemisphere of reflections. Based on a monoclinic crystal system, the integrated frames yielded a total of 14,438 reflections collected at a maximum 2θ angle of 48.80^o (3612 independent reflections, $R_{int} = 0.1485$, $R_{sig} = 0.1101$, completeness = 98.6 %) and 2025 (56.06) reflections were found greater than $2\sigma(I)$. Absorption corrections were applied (absorption coefficient $\mu = 0.409$ mm^{-1}; max/min transmission = 0.9680 and 0.9082) using the DIFABS program.[12]

Structures were solved by using direct methods, with the aid of SIR92[13] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 included in the WinGX programs version 1.64 04.[14] For all compounds, direct methods of phase determination followed by subsequent Fourier cycles of refinement led to an electron density map, from which most of the non-hydrogen atoms were identified. With

subsequent isotropic refinement, all of the non-hydrogen atoms were identified. Atomic coordinates, isotropic, and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The hydrogen atoms were included in the refinement in calculated positions, riding on the carbon atoms to which they were attached, except concerning compound **3a**, for which the two hydrogen atoms labelled H2a and H2b connected to the C(2) atom were isotropically refined. Drawings of molecules were realized with the aid of ORTEP32.[15] Atomic scattering factors were taken from international tables for x-ray crystallography.[16]

For **3a** the refinement converged at R1 = 0.0304 and wR2 = 0.0743, with intensity $I > 2\sigma(I)$. The largest peak/hole in the final difference map was 0.306 and -0.282 e.Å^{-3}. For **7f** the final values were R1 = 0.0585 and wR2 = 0.1441, with intensity $I > \sigma(I)$. The largest peak/hole in the final difference map was 0.332 and -0.491e.Å^{-3}.

d.1. Supplementary Data

Crystallographic data for both structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 295416 (**3a**) and 295417 (**7f**). Copies of the data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif.

REFERENCES

[1] (a) J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, et al., *Macromolecules*, **31,** 5559 (1998); (b) J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, et al., *Macromolecules*, **36,** 2273 (2003).

[2] V. Darcos, D. Taton, Y. Gnanou, P. Marchand, A. M. Caminade, J. P. Majoral, et al., *Chem. Commun.*, 2110 (2004).

[3] (a) M. Adamy, A. M. van Herk, M. Destarac, and M. J. Monteiro, *Macromolecules*, **36**, 2293 (2003); (b) M. Benaglia, E. Rizzardo, A. Alberti, and M. Guerra, *Macromolecules*, **38,** 3129 (2005).

[4] (a) A. Dureault, Y. Gnanou, D. Taton, M. Destarac, and F. Leising, *Angew. Chem. Int. Ed.*, **42,** 2869 (2003); (b) A. Dureault, D. Taton, M. Destarac, F. Leising, and Y. Gnanou, *Macromolecules*, **37,** 5513 (2004).

[5] K. B. Dillon, F. Mathey, and J. F. Nixon, *Phosphorus: the Carbon Copy* (Wiley, Chichester, 1998).

[6] D. Gigmes, D. Bertin, S. Marque, O. Guerret, and P. Tordo, *Tetrahedron Lett.*, **44,** 1227 (2003).

[7] R. B. King and P. M. Sundaram, *J. Org. Chem.*, **49,** 1784 (1984).

[8] F. L. Bowden, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. Perkin Trans. 1*, 516 (1973).

[9] F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Am. Chem. Soc.*, **89,** 6276 (1967).

[10] M. Destarac, F. Leising, D. Taton, A. Dureault, Y. Gnanou, J. P. Majoral, et al., World Patent WO 2003104288.
[11] STOE, X-RED, Data Reduction for STADI4 and IPDS, Revision 1.08, CAN 140:28164, AN 2003:971591.
[12] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, et al., *J. Appl. Cryst.*, **27,** 435 (1994).
[13] SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB]—Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, (1998).
[14] L. J. Farrugia, *J. Appl. Cryst.*, **32,** 837 (1999).
[15] L. J. Farrugia, *J. Appl. Cryst.*, **30,** 565 (1997).
[16] *International Tables for X-Ray Crystallography*, Vol. IV (Kynoch Press, Birmingham, England, 1974).