



**HAL**  
open science

## Synthesis of S-Alkyl Phosphinocarbothioates with Switch between P(III) and P(V) Derivatives

Andrii Karpus, Jean-Claude Daran, Rinaldo Poli, Stéphane Mazières, Mathias Destarac, Eric Manoury

► **To cite this version:**

Andrii Karpus, Jean-Claude Daran, Rinaldo Poli, Stéphane Mazières, Mathias Destarac, et al.. Synthesis of S-Alkyl Phosphinocarbothioates with Switch between P(III) and P(V) Derivatives. *Journal of Organic Chemistry*, 2019, 84 (15), pp.9446-9453. 10.1021/acs.joc.9b00590 . hal-02273507

**HAL Id: hal-02273507**

**<https://hal.science/hal-02273507v1>**

Submitted on 17 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Synthesis of S-alkyl phosphinocarbodithioates with switch between P(III) and P(V) derivatives

Andrii Karpus,<sup>[a,b]</sup> Jean-Claude Daran,<sup>[a]</sup> Rinaldo Poli,<sup>[a]</sup> Stéphane Mazières,<sup>\*[b]</sup> Mathias A. Destarac,<sup>[b]</sup> and Eric Manoury <sup>\*[a]</sup>

[a] Dr. A. Karpus, Dr. J.-C. Daran, Prof. R. Poli, Dr. E. Manoury  
CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT,  
205 Route de Narbonne, BP 44099, 31077 Toulouse, France. E-mail: [eric.manoury@lcc-toulouse.fr](mailto:eric.manoury@lcc-toulouse.fr)

[b] Dr. A. Karpus, Dr. S. Mazières, Prof. M. Destarac  
Laboratoire des IMRCP, Université Paul Sabatier, CNRS UMR 5623  
118 route de Narbonne 31062 Toulouse, France. E-mail: [mazieres@chimie.ups-tlse.fr](mailto:mazieres@chimie.ups-tlse.fr)

**Abstract:** Simple and effective synthetic pathways are described to prepare compounds  $R_2P(X)C(S)SCH(Me)Ph$  with the P atom either in the oxidation state V [ $R/X = t\text{-Bu/O}$  (**6**),  $Ph/S$ , (**7**),  $t\text{-Bu/S}$  (**8**),  $t\text{-Bu/Se}$  (**9**)] or III [ $R/X = Ph/BH_3$  (**4**),  $t\text{-Bu/BH}_3$  (**5**),  $t\text{-Bu/lone pair}$  (**10**)]. Compound **9** is the first example of carbodithioate ester with a  $P=Se$  group and for the first time a phosphinocarbodithioate with a free phosphine function (compound **10**) is described. Stabilization of the latter crucially depends on the steric protection by the  $t\text{-Bu}$  groups, since an analogous derivative with  $R = Ph$  is observable but too unstable for isolation. Compound **10** can be reversibly protonated to yield the  $[t\text{-Bu}_2PHC(S)SCH(Me)Ph]^+$  cation (**10-H<sup>+</sup>**), which was isolated as a  $BF_4^-$  salt. A few interconversion processes resulting in the facile addition/removal or exchange of the X group in this family of compounds are also described.

The phosphorus atom oxidation state and the nature of electron-withdrawing group have a significant impact on the spectral properties.

## Introduction

Phosphinocarbodithioates

(Figure 1a) have been widely used as ambidentate ligands in coordination chemistry to bind lead(IV),<sup>1,2</sup> mercury(II),<sup>2</sup> tin(IV),<sup>3</sup> and iron(II)<sup>4</sup> via the S atom, or niobium(II)<sup>5</sup> and tungsten(II)<sup>6</sup> via the P atom. The phosphacarbodithioate structural motif often acts as bidentate ligand in complexes with ruthenium<sup>7</sup> and iron<sup>8</sup> that mimic certain biological systems.

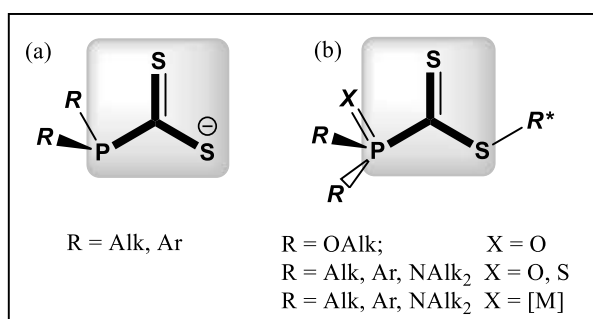


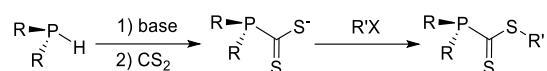
Figure 1. Phosphinocarbodithioate structural motifs.

Many phosphinocarbodithioate ester derivatives have been synthesized by alkylation of the corresponding carbodithioate anions in which the phosphino group, with various substituents like alkoxy, aryl or dialkyl amino is protected (Figure 1b) by covalent bonding ( $X = \text{O, S, BH}_3$ )<sup>8,9,10</sup> or by metal coordination ( $X = [\text{M}], \text{M} = \text{W, Ru, Fe, Cr, Mo, Mn}$ )<sup>6-8,11,12,13,14,15</sup> but, to the best of our knowledge, no carbodithioate ester with an unprotected phosphino group has so far been described. The present contribution addresses the convenient preparation of the first example of a stable compound of general formula  $t\text{-Bu}_2\text{PC}(\text{S})\text{SR}$  which involves a phosphorus atom with a free lone pair, as well as several  $t\text{-Bu}_2\text{P}(\text{X})\text{C}(\text{S})\text{SR}$  derivatives ( $X = \text{BH}_3, \text{O, S, Se}$ ) and describes simple protocols for the addition/removal/exchange of the X group.

## Results and Discussion

### Synthesis

Our synthetic exploration started with the ubiquitous diphenylphosphino group by direct alkylation of the phosphinocarbodithioate salts (Scheme 1). The reaction of secondary phosphines ( $R_2PH$ ) in a mixture of carbon disulfide and a weak base such as triethylamine or potassium phenolate at ambient temperature results in the formation of the corresponding triethylammonium or potassium phosphinodithioformates in high yields.<sup>16</sup>

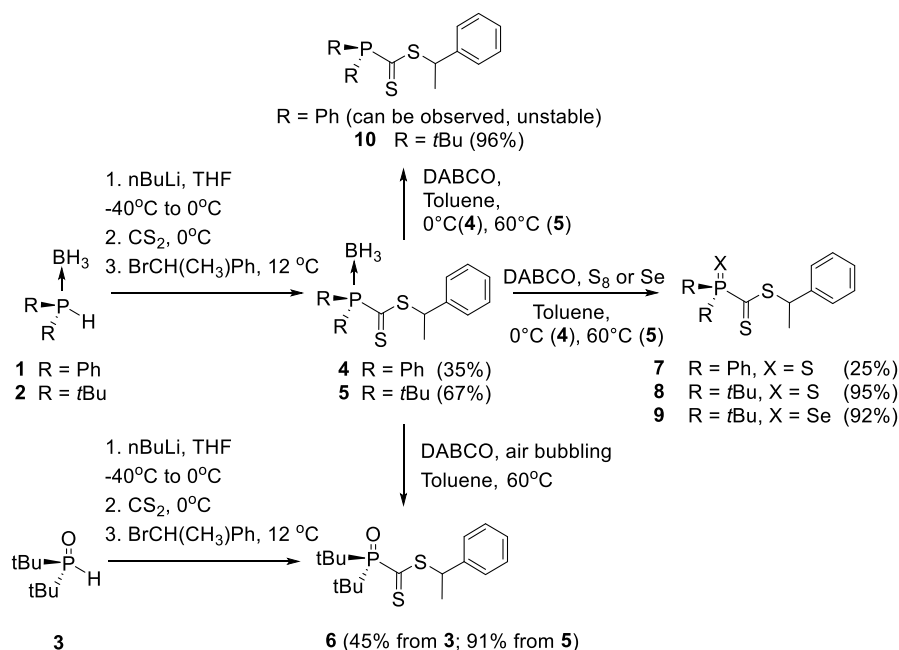


Scheme 1. Direct alkylation of phosphinocarbodithioate salts.

A deep red solution of lithium diphenylphosphinodithioformate was generated by reaction of diphenylphosphine with *n*-BuLi in THF followed by the addition of CS<sub>2</sub>. The subsequent addition of 1-bromo-1-phenylethane led to an immediate color change to orange and to the precipitation of a brownish solid. The analysis of the reaction mixture revealed a mixture of unidentified species and the absence of the desired alkylation product. Other attempts to obtain the target product by reducing the P=O or P=S functions from previously described Ph<sub>2</sub>P(X)C(S)SCH(Me)Ph (X = O, S)<sup>10</sup> using known protocols<sup>17,18</sup> were equally ineffective. The use of stronger reducing agents (LiAlH<sub>4</sub>, P(NMe<sub>2</sub>)<sub>3</sub>, etc.) led to disappearance of the initial deep violet color, which is typical of the conjugated –C(S)SR function, immediately after the reducing agent addition (even at -20°C) without a significant shift of the <sup>31</sup>P{<sup>1</sup>H} NMR resonance from the starting compound value. In case of the less active NaBH<sub>4</sub>, no reaction was observed.

We then considered the deprotection of a phosphine-borane derivative. An ester of formula Ph<sub>2</sub>P(BH<sub>3</sub>)C(S)SMe has already been described. It was synthesized by methylation of the carbodithioate salt Ph<sub>2</sub>PC(S)S<sup>-</sup>K<sup>+</sup> by MeI in CS<sub>2</sub> followed by addition of a borane THF solution but no yields were given.<sup>8</sup> Due to the relative acidity of secondary phosphine-borane adducts, compound **4** could be prepared according to a slightly modified literature method.<sup>10</sup> The diphenylphosphine-borane adduct was first deprotonated by *n*-BuLi. Subsequent treatment of

the obtained anion with an excess of carbon disulfide led to the formation of the corresponding salt  $\text{Ph}_2(\text{BH}_3)\text{CS}_2\text{Li}^+$ , which could be detected immediately after addition of the first  $\text{CS}_2$  drops by the appearance of a characteristic deep red color. Nevertheless, the generated solution was treated directly with 1-bromo-1-phenylethane to yield the target compound **4**. Protection of the reaction mixture from light at this stage improved the yield (35% versus 18% in case of light exposure). Compound **4** is not air-sensitive in the solid state or in solution, but slowly decomposes at room temperature. However, it can be stored at 4°C for weeks without noticeable change. In order to remove the  $\text{BH}_3$  group from the phosphorus atom a set of experiments was performed using morpholine,  $\text{Et}_3\text{N}$  and DABCO. In all reactions,  $^{31}\text{P}$  NMR monitoring indicated full consumption of **4** (broad doublet at  $\delta = 45.0$  ppm) after 0.5 h at room temperature (or 0°C in the case of DABCO), while a narrow singlet at  $\delta = 37.1$  ppm appeared as the major new resonance (see supplemental Figure S1). We assigned this resonance to the desired free phosphine derivative,  $\text{Ph}_2\text{PC}(\text{S})\text{SCH}(\text{Me})\text{Ph}$ . However, the product decomposed in solution after 1h at ambient temperature, or during the purification step (Figure S2), as indicated by a color change from dark-violet to bright orange. When the deboration of compound **4** was performed in the presence of  $\text{S}_8$  (see Scheme 2), the previously described  $\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}(\text{Me})\text{Ph}$ , **7**,<sup>10</sup> was isolated in appreciable yields (25%). A control experiment showed no reaction between compound **4** and  $\text{S}_8$  in the absence of DABCO in the 0°C – 25°C temperature range, whereas a mixture of decomposition products with only traces of **7** was obtained at higher temperatures, as indicated by  $^{31}\text{P}$  NMR.



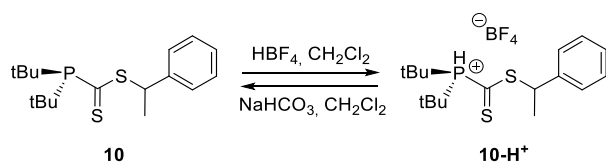
Scheme 2. Synthesis of phosphinocarbodithioates **4-10**. The numbers in brackets display isolated yield of compounds

Since  $\text{Ph}_2\text{PC}(\text{S})\text{SCH}(\text{Me})\text{Ph}$  proved to be unstable, subsequent efforts were redirected to an analogous system with two bulky alkyl groups. The direct transformation of di-*tert*-butylphosphine by the usual reaction sequence (treatment of its lithium salt with an excess of carbon disulfide and further alkylation) was unsuccessful, just as the same procedure described above for the diphenylphosphine reagent. The use of the di-*tert*-butylphosphine-borane complex **2** under the same reaction conditions gave the corresponding (*S*-methylbenzyl (di-*tert*-butylphosphino)carbodithioate)trihydroboron **5** in 67% yield (Scheme 2). The product is air stable at room temperature and does not thermally degrade in solution up to  $100^\circ\text{C}$  under argon. Treatment of compound **5** with DABCO in toluene at  $60^\circ\text{C}$  led nearly quantitatively to compound **10** (Scheme 2), which is air sensitive but can be purified and handled under an argon atmosphere. In the solid state, it slowly converts to corresponding oxide **6** upon exposure to air (12% of oxide after 24 h at ambient temperature).

The deboration of **5** could also be accomplished at ambient temperature by stirring with excess  $\text{Et}_3\text{N}$  in THF or in dioxane overnight. Subsequent removal of all volatile components in high

vacuum led to the quantitative recovery of compound **10**, thus avoiding the tedious column flash-chromatographic separation at the product purification stage. The phosphinoyl compound **6** can be prepared either by deboration of **5** in air or by direct synthesis from the readily available di-*tert*-butylphosphine oxide **3**, applying the usual reaction sequence: (i) deprotonation with *n*-BuLi, (ii) treatment with an excess of CS<sub>2</sub> and (iii) alkylation of the generated carbodithioate salt with 1-bromo-1-phenylethane (Scheme 2). The sulfur (**8**) and selenium (**9**) derivatives can be obtained selectively and nearly quantitatively by treatment of **5** with DABCO in the presence of S<sub>8</sub> and Se powder, respectively. Compound **9** is, to the best of our knowledge, the first example of carbodithioate ester with a P=Se group directly connected. It is worth pointing out that compound **8** has also been obtained from **10** by treatment with S<sub>8</sub> at 60°C in toluene solution without significant decrease of the final product yield, relative to the one-pot deboration-sulfuration of **5**. A control experiment showed no reaction between **5** and S<sub>8</sub> in the absence of DABCO in the 25°C – 60°C temperature range; only the <sup>31</sup>P NMR resonance of **5** at δ = 67.9 ppm was observed after 24 h.

Treatment of **10** with an excess amount of the strong acid HBF<sub>4</sub> led to the protonated product **10-H<sup>+</sup>** (Scheme 3). The protonation is reversible; treatment of **10-H<sup>+</sup>** with an aqueous sodium bicarbonate solution led to the quantitative recovery of **10**. The [**10-H**][BF<sub>4</sub>] salt could be obtained nearly quantitatively from **10** and the equimolar amount of acid in CH<sub>2</sub>Cl<sub>2</sub> at 0°C. It is an air-stable, hygroscopic, pink waxy solid, insoluble in Et<sub>2</sub>O and alkanes, which can be used as a convenient precursor of **10**.



Scheme 3. Reversible protonation of compound **10** in CH<sub>2</sub>Cl<sub>2</sub>.

### Spectroscopic properties

$^{31}\text{P}\{^1\text{H}\}$  NMR is a useful tool for following the chemical changes around the phosphorus atom (see Table 1).

Table 1. Selected NMR data for compounds  $t\text{-Bu}_2\text{P}(\text{X})\text{C}(\text{S})\text{SCH}(\text{CH}_3)\text{Ph}$

Compound	$^{31}\text{P}$ NMR ( $\delta/\text{ppm}$ )	$^{13}\text{C}$ {H} NMR ( $\underline{\text{C}}\text{S}_2$ , $\delta/\text{ppm}$ )
<b>5</b> (X = BH <sub>3</sub> )	67.9 ( $^1J_{\text{BP}} = 70.7$ Hz)	231.1 ( $J_{\text{CP}} = 11.8$ Hz)
<b>6</b> (X = O)	56.4	239.0 ( $J_{\text{CP}} = 45.2$ Hz)
<b>8</b> (X = S)	84.9	234.9 ( $J_{\text{CP}} = 30.3$ Hz)
<b>9</b> (X = Se)	86.6 ( $^1J_{\text{PSe}} = 710.4$ Hz)	231.6 ( $J_{\text{CP}} = 22.9$ Hz)
<b>10</b> (X = nothing)	67.4	247.5 ( $J_{\text{CP}} = 60.1$ Hz)
<b>10-H<sup>+</sup></b> (X = H <sup>+</sup> )	38.5 ( $J_{\text{PH}}^1 = 479.6$ Hz)	210.5 ( $J_{\text{CP}} = 49.1$ Hz)

The resonance of compound **10**, at 67.4 ppm, is unusually downfield shifted, at essentially the same position as that of its borane precursor **5** (67.9 ppm). Such a strong downfield  $^{31}\text{P}$  NMR chemical shift for a free phosphine has already been reported for sterically hindered di- and tri- $t\text{-Bu}$  phosphine derivatives.<sup>19</sup> The resonance of **10** is downfield shifted from that of **6** (56.4 ppm), but upfield from those of **8** (84.9 ppm) and **9** (86.6 ppm). The latter exhibits the expected satellites because of coupling to the  $^{77}\text{Se}$  isotope (7.6% abundance). Correspondingly, a doublet is observed in the  $^{77}\text{Se}$  NMR spectrum at -384.4 ppm ( $^1J_{\text{SeP}} = 710.8$  Hz). The  $^1J_{\text{PSe}}$  value is known to respond to the phosphorus atom hybridization, increasing as the  $s$  character of the phosphorus orbital used in P-Se bonding increases.<sup>20</sup> The value measured for **10** is intermediate between those of triaryl and trialkyl phosphine derivatives and quite close to that of compound  $\text{PhMe}_2\text{P}=\text{Se}$ , indicating that the C(S)SR group has intermediate electron-donating effect



between those of an aryl and an alkyl group. As such, **10** is expected to react as a ligand and as a base, in agreement with the reversible protonation leading to the stable phosphonium derivative **10-H<sup>+</sup>** (*vide supra*). The latter exhibits the expected resonance in the <sup>31</sup>P NMR spectrum as a broad doublet (Figure S3), collapsing to a singlet in the decoupled <sup>31</sup>P{<sup>1</sup>H} spectrum (Figure S4) and a corresponding doublet (<sup>1</sup>J<sub>HP</sub> = 471.1 Hz) in the <sup>1</sup>H NMR spectrum at δ = 7.01 ppm (Figure S5).

The <sup>13</sup>C NMR spectra also give interesting information, particularly in terms of the C(S)S- group resonance (Table 1). Replacing Ph with *t*-Bu groups on the phosphorus atom from **4** to **5** shows that the carbon chemical shift of the C(S)S- group remains essentially unchanged (from 230.6 for **4** to 231.1 ppm for **5**), while <sup>1</sup>J<sub>CP</sub> decreases dramatically from 25.9 to 11.8 Hz. For the **5-9** series of derivatives, the C(S)S- resonance remains within a narrow chemical shift range (231.1 - 238.9 ppm), whereas it is significantly more downfield shifted for **10** (247.5 ppm) and upfield shifted for **10-H<sup>+</sup>** (210.5 ppm). This resonance also shows a much greater <sup>1</sup>J<sub>CP</sub> value for **10** (60.1 Hz) than for all other derivatives (in the 11.8 – 47.8 Hz range).

The IR spectra exhibit characteristic stretching bands for the thiocarbonyl moiety (C=S) with a frequency that is modulated by the P=X substituent: 1045 cm<sup>-1</sup> (**4**), 1073 cm<sup>-1</sup> (**5**), 1079 cm<sup>-1</sup> (**6**), 1069 cm<sup>-1</sup> (**8**), 1066 cm<sup>-1</sup> (**9**), 1066 cm<sup>-1</sup> (**10**) and 1051 cm<sup>-1</sup> (**10-H<sup>+</sup>**). The corresponding frequencies for the stretching bands of the (C=S) moieties for the known diphenyl-substituted analogues, Ph<sub>2</sub>P(X)C(S)SCH(Me)Ph, are much higher (1097 cm<sup>-1</sup> and 1190 cm<sup>-1</sup> for X = O and S, respectively).<sup>21</sup> The B-H bonds in compounds **4** and **5** also provided strong absorption bands, as expected (2370 cm<sup>-1</sup> for **4** and 2393 cm<sup>-1</sup> for **5**). The P=O bond stretching vibration in compound **6** was found at a lower wavenumber than in the diphenyl analogue (1157 cm<sup>-1</sup> vs. 1190 cm<sup>-1</sup>)<sup>10</sup> and the same trend was also shown by the P=S vibration (651 cm<sup>-1</sup> for **8** vs. 722 cm<sup>-1</sup> in the diphenyl analog<sup>10</sup>). The P=Se stretching vibration in compound **9** was found at a

much lower wavenumber, 548 cm<sup>-1</sup>, in the expected range for P=Se stretching vibrations (440-600 cm<sup>-1</sup>)<sup>21</sup> close to the value measured for Ph<sub>2</sub>P(Se)NSiMe<sub>3</sub> (567 cm<sup>-1</sup>).<sup>22</sup>

### X-ray structural analyses

The molecular structures of **6**, **8** and **9** are quite similar (Figure 2, Table S1), based on a phosphorus atom linked to two *tert*-butyl groups, a carbodithioate substituent and O, S or Se atoms for **6**, **8** and **9** respectively. The full geometric parameters of their crystal structures are listed in Table S1, while selected bond lengths (Å) and angles (°) are collected in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for all structures

	<b>6</b>	<b>8</b>	<b>9</b>
P – C(S2)	1.8498(14)	1.859(4) / 1.863(4)	1.857(3)
P – C(C3)	1.8532(15)	1.885(4) / 1.867(5)	1.888(3)
P – C(C3)	1.8578(15)	1.877(4) / 1.868(5)	1.882(3)
P – X	1.4862(10)	1.9616(15) / 1.9579(16)	2.1172(8)
C = S	1.6391(14)	1.635(5) / 1.638(5)	1.638(3)
C – S	1.7150(14)	1.728(4) / 1.712(4)	1.718(3)
S – C	1.8328(14)	1.838(4) / 1.837(5)	1.834(3)
C(S2) – P – X	109.31(6)	109.31(6)	109.88(10)
C(C3) – P – X	109.68(7)	110.22(15) / 110.28(17)	110.24(10)
C(C3) – P – X	109.87(6)	111.43(17) / 110.8(2)	111.08(13)
C(S2) – P – C(C3)	104.82(6)	103.13(18) / 105.0(2)	103.67(16)
C(S2) – P – C(C3)	107.44(7)	107.6(2) / 105.9(2)	107.26(14)
C(C3) – P – C(C3)	115.47(7)	114.4(2) / 114.0(3)	114.39(15)

In compound **8** there are two roughly identical molecules within the asymmetric unit as shown in the molecular overlay of Figure S6. The weighted r.m.s. fit is 0.226 Å for 9 heavy atoms (S21, S22, S23, P2, C21, C24 C241, C244 and C247), with a maximum deviation of 0.579 Å for the S23 atom. These two independent molecules are connected through C-H $\cdot\cdot\cdot$  $\pi$  interactions (Table S2). In all compounds there are C-H $\cdot\cdot\cdot$ X (O, S, Se) intermolecular interactions that stabilize the packing.

In all compounds the non-substituted S atom of the carbodithioate group is located *anti* to the X (O, S, Se) atom with respect to the P1-C1 bond. The X-P1-C1-S2 torsion angles are 172.00(8) $^\circ$  for **6**, 169.9(2) $^\circ$ [178.2(2) $^\circ$ ] for **8** and 170.4(2) $^\circ$  for **9**. Similar conformations have also been observed in related compounds such as Ph<sub>2</sub>P(O)C(S)SCH(Me)Ph with a torsion angle of 175.1 $^\circ$ ,<sup>10</sup> (c-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>P(S)C(S)SMe (180 $^\circ$ )<sup>23</sup> and Ph<sub>2</sub>P(S)C(S)SCH(Me)Ph (153 $^\circ$ ).<sup>10</sup> Most bond lengths and angles are similar; the nature of the P-bonded X group has no significant effect on the P-C(S) and C=S bond lengths. The P-C(S) bonds in the *t*-Bu<sub>2</sub>P(X)- derivatives are shorter than in the previously described Ph<sub>2</sub>P(O)- and (N*i*Pr<sub>2</sub>)<sub>2</sub>P(O)- derivatives (1.848 and 1.868 Å, respectively).<sup>10</sup> As expected, the P=X bond length increases with an increase of the X atom size: 1.4862(10) Å for P=O (**6**), 1.9616(15)[1.9579(16)] Å for P=S (**8**) and 2.1172(8) Å for P=Se (**9**). A search in the Cambridge Structural Database using the C<sub>2</sub>P(=X)(CS<sub>2</sub>) fragment reveals only 19 hits, with only 3 referring to carbodithioate derivatives,<sup>10,23</sup> the remaining corresponding to di- or trithiate rings. However, a comparison of the P=X distances for the whole reference set shows that the P=O distance in compound **6** (1.486(1) Å) falls within the previously observed range (1.481 to 1.492 Å),<sup>1,10,24,25,26,27,28</sup> whereas the P=S distances in two independent molecules of compound **8** (1.962(2) and 1.958(2)) are slightly longer than the previously observed ones (1.946 to 1.952 Å)<sup>10,23</sup> and the P=Se distance in compound **9** (2.1172(8) Å) is also slightly longer than the previously observed ones (2.098 and 2.103 Å).<sup>10,23,27,28,29,30</sup>

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1889097- 1889099. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

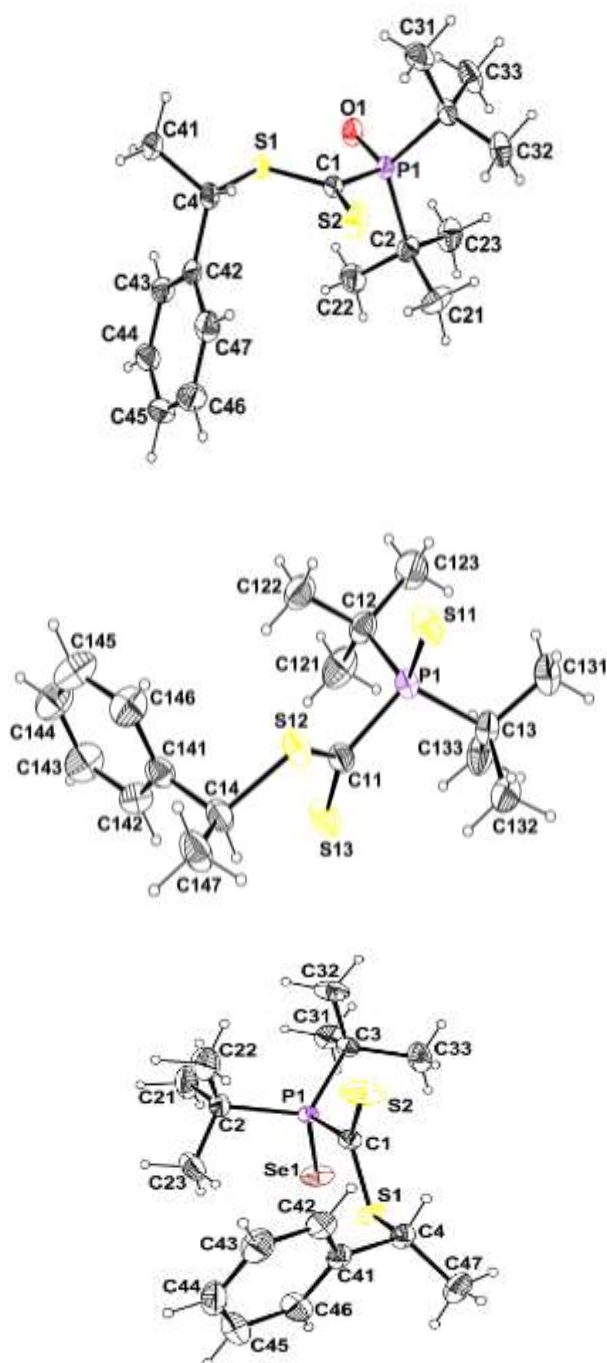


Figure 2. Molecular views of compound **6** (above) **8** (center) and **9** (below) with the atom labelling scheme. Only one of the two independent molecules in the asymmetric unit is drawn for compound **8**. The ellipsoids are drawn at the 50% probability level. The H atoms are represented as small circle of arbitrary radii.

## Conclusions

A simple gram-scale synthetic pathway was used to obtain efficiently six new *S*-(1-phenylethyl) phosphinocarbothioates, five of which bear the same di-*tert*-butylphosphino fragment. Various interconversions of these compounds have been accomplished under mild conditions in nearly quantitative yields. All the new compounds of the study have an appropriate structure to operate as a chain transfer agent in the RAFT (reversible addition-fragmentation chain transfer) process.<sup>31,32,33</sup> Indeed, various *S*-alkyl phosphinocarbothioates have been efficiently applied as chain transfer agents showing excellent results for a wide variety of activated monomers such as styrene, acrylates and acrylamides. The modularity and the interconversions of the new compounds described in this report may be of interest in RAFT polymerization. This study is ongoing and will be reported in due course.

## Experimental Section

### General experimental

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Melting points were determined on a Boetius apparatus and were uncorrected. Solvents were carefully dried by conventional methods and distilled under argon before use. Column chromatography was performed on Carlo Erba silica gel 60A, 70 - 200  $\mu\text{m}$  size. Di-*tert*-butylphosphine borane,<sup>34</sup> diphenylphosphine borane<sup>35</sup> and di-*tert*-butylphosphine oxide<sup>36</sup> were

prepared according to literature procedures. Chlorodiphenylphosphane (97%, TCI), di-*tert*-butylchlorophosphane (96%, Alfa Aesar) di-*tert*-butylphosphine (98%, Sigma Aldrich), 1,4-diazabicyclo[2.2.2]octane (97%, TCI), *n*-butyllithium (1.6 M solution in hexanes, Sigma Aldrich), (1-bromoethyl)benzene (97%, Sigma Aldrich), and tetrafluoroboric acid (diethyl ether complex, Sigma Aldrich) were used as received. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded with a Bruker Avance 400 FT-NMR spectrometer. The resonances were calibrated relative to the residual solvent resonances and are reported with positive values downfield from TMS. For all characterized compounds, the peak assignments in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were based on COSY, HSQC and HMBC 2D experiments. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray or chemical ionization method.

**General synthetic procedure for 4–6:** The phosphine borane or phosphine oxide (6.24 mmol) solution in THF (100 mL) was treated with a slight excess of *n*-butyllithium (4.1 mL, 1.6 M in hexane, 1.05 eq.) at  $-40^\circ\text{C}$ . The resulting bright yellow mixture was allowed to warm up to  $0^\circ\text{C}$  and further stirred for 1h. A large excess of  $\text{CS}_2$  (2.2 mL, 33.6 mmol) was then added dropwise at  $0^\circ\text{C}$  to yield a dark red solution. The mixture was covered with aluminum foil, and was allowed to warm up to  $12^\circ\text{C}$  and stirred for 15 min. (1-Bromoethyl)benzene (1.10 mL, 9.87 mmol) was then added, and the dark red solution was stirred for additional 4 h at  $12\text{--}15^\circ\text{C}$ . After solvent removal under reduced pressure, the residual product was eluted through a silica gel chromatographic column using hexane/toluene (1:1 v/v) as mobile phase, followed by evaporation of the product-containing fractions. All compounds were obtained as oily materials. Recrystallization from a dichloromethane/pentane mixture (1:10) led to the solid compounds. The spectral data for compounds 4–6 are shown in the Supporting Information (Figures S7 to S20).

Compound **4**: (S-(1-phenylethyl) (diphenylphosphino)carbodithioate)trihydroboron. Pink amorphous solid. Yield 0.831 g, 35%. mp = 52-54°C (bleaching). **<sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)** δ: 7.80-7.68 (4H, m, Ph), 7.60- 7.43 (8H, m, Ph), 7.37-7.30 (3H, m, Ph), 5.25 (1H, qd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HP</sub> = 2.0 Hz, CHCH<sub>3</sub>), 1.73 (3H, dd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>5</sup>J<sub>HP</sub> = 1.0 Hz, CHCH<sub>3</sub>), 1.60-0.78 (3H, m, BH<sub>3</sub>). **<sup>11</sup>B{<sup>1</sup>H} (128 MHz, CDCl<sub>3</sub>)** δ: -36.8 (br s). **<sup>13</sup>C{<sup>1</sup>H} (125 MHz, CDCl<sub>3</sub>)** δ: 230.6 (d, <sup>1</sup>J<sub>CP</sub> = 25.9 Hz, C(S)S), 140.0 (<sup>Ph</sup>C-CHCH<sub>3</sub>), 133.7 (d, J<sub>CP</sub> = 9.4 Hz, <sup>Ph</sup>CH), 133.6 (d, J<sub>CP</sub> = 9.3 Hz, <sup>Ph</sup>CH), 132.0 (d, J<sub>CP</sub> = 2 Hz, 2C <sup>Ph</sup>CH para), 128.75 (J<sub>CP</sub> = 10.4 Hz, <sup>Ph</sup>CH), 128.71 (<sup>Ph</sup>CH), 128.71 (J<sub>CP</sub> = 10.5 Hz, <sup>Ph</sup>CH), 127.4 (d, <sup>1</sup>J<sub>CP</sub> = 3.7 Hz, <sup>Ph</sup>C-P), 127.3 (d, <sup>1</sup>J<sub>CP</sub> = 3.7 Hz, <sup>Ph</sup>C-P), 50.5 (CHCH<sub>3</sub>), 20.3 (CHCH<sub>3</sub>). **<sup>31</sup>P{<sup>1</sup>H} (162 MHz, CDCl<sub>3</sub>)** δ: 45.0 (br m). **HRMS (ESI):** m/z: [M+H]<sup>+</sup> Calcd for for C<sub>21</sub>H<sub>23</sub>BPS<sub>2</sub> 381.1066 Found 381.1105.

Compound **5**: (S-(1-phenylethyl) (di-*tert*-butylphosphino)carbodithioate)trihydroboron. Pink amorphous solid. Yield 1.406 g, 67%. MP = 59-61°C. **<sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)** δ: 7.38-7.25 (5H, m, Ph), 5.18 (1H, qd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>4</sup>J<sub>HP</sub> = 1.9 Hz, CHCH<sub>3</sub>), 1.70 (3H, d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHCH<sub>3</sub>), 1.43 (9H, d, <sup>3</sup>J<sub>HP</sub> = 13.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, d, <sup>3</sup>J<sub>HP</sub> = 13.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.59-0.58 (3H, m, BH<sub>3</sub>). **<sup>11</sup>B{<sup>1</sup>H} (128 MHz, CDCl<sub>3</sub>)** δ: -41.0 (br d, <sup>1</sup>J<sub>BP</sub> = 51.4 Hz). **<sup>13</sup>C{<sup>1</sup>H} (125 MHz, CDCl<sub>3</sub>)** δ: 231.11 (d, <sup>1</sup>J<sub>CP</sub> = 11.8 Hz, C(S)S), 140.37 (<sup>Ph</sup>C-CHCH<sub>3</sub>), 128.55 (<sup>Ph</sup>CH), 127.97 (<sup>Ph</sup>CH), 127.73 (<sup>Ph</sup>CH), 49.41 (CHCH<sub>3</sub>), 35.73 (d, <sup>1</sup>J<sub>CP</sub> = 20.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 35.69 (d, <sup>1</sup>J<sub>CP</sub> = 20.7 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.57 (C(CH<sub>3</sub>)<sub>3</sub>), 28.46 (C(CH<sub>3</sub>)<sub>3</sub>), 19.94 (CHCH<sub>3</sub>). **<sup>31</sup>P{<sup>1</sup>H} (162 MHz, CDCl<sub>3</sub>)** δ: 67.9 (br d, <sup>1</sup>J<sub>BP</sub> = 70.7 Hz). **HRMS (ESI):** m/z: [M-H]<sup>+</sup> Calcd for for C<sub>17</sub>H<sub>29</sub>BPS<sub>2</sub> 339.1541 Found 339.1548.

Compound **6**: S-(1-phenylethyl) di-*tert*-butylphosphinoylcarbodithioate. Pink solid. Yield 0.950 g, 45%. MP = 96-98°C. **<sup>1</sup>H (400 MHz, CDCl<sub>3</sub>)** δ: 7.36-7.18 (5H, m, Ph), 5.17 (1H, qd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HP</sub> = 1.8 Hz, CHCH<sub>3</sub>), 1.65 (3H, dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>5</sup>J<sub>HP</sub> = 0.6 Hz, CHCH<sub>3</sub>), 1.35 (9H, d, <sup>3</sup>J<sub>HP</sub> = 14.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (9H, d, <sup>3</sup>J<sub>HP</sub> = 14.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>). **<sup>13</sup>C{<sup>1</sup>H} (125 MHz,**

**CDCl<sub>3</sub>**  $\delta$ : 239.0 (d,  $^1J_{CP}$  = 45.2 Hz, C(S)S), 140.6 ( $^{Ph}C-CHCH_3$ ), 128.5 ( $^{Ph}CH$ ), 127.8 ( $^{Ph}CH$ ), 127.7 ( $^{Ph}CH$ ), 47.3 (d,  $^3J_{CP}$  = 1.6 Hz, CHCH<sub>3</sub>), 37.17 (d,  $^1J_{CP}$  = 55.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 37.15 (d,  $^1J_{CP}$  = 55.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 27.17 (C(CH<sub>3</sub>)<sub>3</sub>), 27.09 (C(CH<sub>3</sub>)<sub>3</sub>), 20.2 (CHCH<sub>3</sub>).  **$^{31}P\{^1H\}$  (162 MHz, CDCl<sub>3</sub>)  $\delta$ : 56.4. HRMS (DCI, CH<sub>4</sub>): m/z: [M+H]<sup>+</sup> Calcd for for C<sub>17</sub>H<sub>28</sub>OPS<sub>2</sub> 343.1319 Found 343.1319.**

**Alternative synthetic procedure for 6:** A solution of compound **5** (1.27 mmol) in toluene (30 mL) in a Schlenk tube covered with aluminum foil was treated with DABCO (0.357 g, 3.16 mmol). Air was bubbled through the solution during heating at 60° with stirring for 6 h. After removal of the solvent under reduced pressure, the residual product was eluted through a silica gel chromatographic column using hexane/toluene (1:1 v/v), followed by evaporation of the product-containing fractions to yield the product in an oily form. Recrystallization from a dichloromethane/pentane mixture (1:10) led to 0.276 g (91%) of the product as a crystalline solid.

**General synthetic procedure for 7–9:** A solution of **4** or **5** (1.27 mmol) in toluene (30 mL) under Ar atmosphere in a Schlenk tube covered with aluminum foil was treated with either sulfur (0.203 g, 6.32 mmol) or selenium (0.503 g, 6.32 mmol) powder, and with DABCO (0.357 g, 3.16 mmol). The reaction mixture was stirred for 6 h at 0°C (**4**) or 60°C (**5**). After solvent removal under reduced pressure, the residual product was eluted through a silica gel chromatographic column using hexane/toluene (1:1 v/v), followed by evaporation of the product-containing fractions. All compounds were obtained as oily materials. Recrystallization from a dichloromethane/pentane mixture (1:10) led to the crystalline compounds. The spectral data for compounds **8–9** are shown in the Supporting Information (Figures S21 to S30).

**Compound 7:** S-(1-phenylethyl) diphenylthiophosphinoylcarbodithioate. Pink amorphous solid. Yield 0.126 g, 25%. All characterization data match with the previously reported ones.<sup>10</sup>



Compound **8**: S-(1-phenylethyl) di-*tert*-butylthiophosphinoylcarbodithioate. Red-pink solid. Yield 0.432 g, 95%. MP = 78-79°C.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40-7.22 (5H, m, Ph), 4.97 (1H, qd,  $^3J_{\text{HH}} = 7.1$  Hz,  $^4J_{\text{HP}} = 2.3$  Hz,  $\text{CHCH}_3$ ), 1.69 (3H, dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^5J_{\text{HP}} = 0.9$  Hz,  $\text{CHCH}_3$ ), 1.48 (9H, d,  $^3J_{\text{HP}} = 16.0$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 1.38 (9H, d,  $^3J_{\text{HP}} = 16.0$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 234.9 (d,  $^1J_{\text{CP}} = 30.3$  Hz,  $\text{C}(\text{S})\text{S}$ ), 140.6 ( $^{\text{Ph}}\text{C}-\text{CHCH}_3$ ), 128.5 ( $^{\text{Ph}}\text{CH}$ ), 128.0 ( $^{\text{Ph}}\text{CH}$ ), 127.7 ( $^{\text{Ph}}\text{CH}$ ), 50.1 ( $\text{CHCH}_3$ ), 40.72 (d,  $^1J_{\text{CP}} = 36.2$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 40.69 (d,  $^1J_{\text{CP}} = 36.0$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 28.2 ( $\text{C}(\text{CH}_3)_3$ ), 28.0 ( $\text{C}(\text{CH}_3)_3$ ), 19.9 ( $\text{CHCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$ : 84.9. HRMS (DCI,  $\text{CH}_4$ ): m/z:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{28}\text{PS}_3$  359.1091 Found 359.1093.

Compound **9**: S-(1-phenylethyl) di-*tert*-butylselenophosphinoylcarbodithioate. Red-green solid. Yield 0.474 g, 92%. MP = 85-87°C.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40-7.15 (5H, m, Ph), 4.93 (1H, qd,  $J = 7.2$  Hz,  $J_{\text{HP}} = 2.4$  Hz,  $\text{CHCH}_3$ ), 1.70 (3H, dd,  $J = 7.2$  Hz,  $J_{\text{HP}} = 1.1$  Hz,  $\text{CHCH}_3$ ), 1.52 (1H, d,  $J_{\text{HP}} = 16.4$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 1.41 (1H, d,  $J_{\text{HP}} = 16.4$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 231.6 (d,  $J_{\text{CP}} = 22.9$  Hz,  $\text{C}(\text{S})\text{S}$ ), 140.5 ( $^{\text{Ph}}\text{C}-\text{CHCH}_3$ ), 128.5 ( $^{\text{Ph}}\text{CH}$ ), 128.0 ( $^{\text{Ph}}\text{CH}$ ), 127.7 ( $^{\text{Ph}}\text{CH}$ ), 51.4 ( $\text{CHCH}_3$ ), 40.86 (d,  $^1J_{\text{CP}} = 28.1$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 40.74 (d,  $^1J_{\text{CP}} = 27.2$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 28.6 ( $\text{C}(\text{CH}_3)_3$ ), 28.4 ( $\text{C}(\text{CH}_3)_3$ ), 19.8 ( $\text{CHCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$ : 86.6 ppm (s + satellite d ( $J_{\text{PSe}} = 710.4$  Hz)).  $^{77}\text{Se}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : -384.4 ppm (d,  $^1J_{\text{PSe}} = 710.8$  Hz). HRMS (DCI,  $\text{CH}_4$ ): m/z:  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{26}\text{PS}_2\text{Se}$  405.0379 Found 405.0451.

**General synthetic procedure for 10**: A solution of compound **5** (1.47 mmol) in toluene (30 mL) in a Schlenk tube covered with aluminum foil was treated with DABCO (0.357 g, 2.92 mmol). The reaction mixture was stirred for 6h at 60°C. After removal of the solvent under reduced pressure, the residual product was eluted through a silica gel chromatographic column using hexane/toluene (1:1 v/v), followed by evaporation of the product-containing fractions.

The spectral data for compound **10** are shown in the Supporting Information (Figures S31 to S34).

Compound **10**: S-(1-phenylethyl) di-*tert*-butylphosphinocarbodithioate. Red-pink waxy solid. Yield 0.459 g, 96%.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40-7.20 (5H, m, Ph), 7.02 (1H, d,  $^3J_{\text{HH}} = 7.1$  Hz,  $\text{CHCH}_3$ ), 5.27 (1H, q of d,  $^3J_{\text{HH}} = 7.1$  Hz,  $^4J_{\text{HP}} = 3.5$  Hz,  $\text{CHCH}_3$ ), 1.69 (3H, d,  $^3J_{\text{HH}} = 7.1$  Hz,  $\text{CHCH}_3$ ), 1.31 (9H, d,  $^3J_{\text{HP}} = 12.3$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 1.25 (9H, d,  $^3J_{\text{HP}} = 12.3$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 247.5 (d,  $^1J_{\text{CP}} = 60.1$  Hz,  $\text{C}(\text{S})\text{S}$ ), 141.1 ( $^{\text{Ph}}\text{C}-\text{CHCH}_3$ ), 128.5 ( $^{\text{Ph}}\text{CH}$ ), 127.8 ( $^{\text{Ph}}\text{CH}$ ), 127.4 ( $^{\text{Ph}}\text{CH}$ ), 49.1 (d,  $^3J_{\text{CP}} = 17.4$  Hz,  $\text{CHCH}_3$ ), 35.0 (d,  $^1J_{\text{CP}} = 27.6$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 34.9 (d,  $^1J_{\text{CP}} = 27.4$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 29.9 (d,  $^2J_{\text{CP}} = 13.9$  Hz,  $2\text{C}(\text{CH}_3)_3$ ), 19.4 ( $\text{CHCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$ : 67.4. **HRMS (DCI,  $\text{CH}_4$ )**:  $m/z$ :  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{26}\text{PS}_2$  325.1214 Found 325.1214.

**General synthetic procedure for 10-H+**: A solution of compound **10** (0.253 g, 0.775 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL) in a Schlenk tube covered with aluminum foil was treated with  $\text{HBF}_4\text{-Et}_2\text{O}$  (130  $\mu\text{L}$ , 0.930 mmol) at  $0^\circ\text{C}$ . The reaction mixture was stirred for 10 min at  $0^\circ\text{C}$ . After removal of the solvent under reduced pressure, the residual product was washed with  $\text{Et}_2\text{O}$  (3x10 mL) and pentane (2x10 mL) and finally dried under vacuum. The spectral data are shown in the Supporting Information (Figures S35 to S39).

Compound [**10-H**] $[\text{BF}_4]$ : di-*tert*-butyl-(((1-phenylethyl)thio)carbonothioyl)phosphonium tetrafluoroborate. Red-pink waxy solid. Yield 0.306 g, 95%.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40-7.28 (5H, m, Ph), 7.01 (1H, d,  $^1J_{\text{HP}} = 471.1$  Hz,  $\text{PH}$ ), 5.21 (1H, qd,  $^3J_{\text{HH}} = 7.3$  Hz,  $^4J_{\text{HP}} = 2.0$  Hz,  $\text{CHCH}_3$ ), 1.82 (3H, dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^5J_{\text{HP}} = 1.2$  Hz,  $\text{CHCH}_3$ ), 1.61 (9H, d,  $^3J_{\text{HP}} = 18.1$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 1.48 (9H, d,  $^3J_{\text{HP}} = 18.0$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 210.5 (d,  $^1J_{\text{CP}} = 49.1$  Hz,  $\text{C}(\text{S})\text{S}$ ), 138.3 ( $^{\text{Ph}}\text{C}-\text{CHCH}_3$ ), 128.9 ( $^{\text{Ph}}\text{CH}$ ), 128.7 ( $^{\text{Ph}}\text{CH}$ ), 127.9 ( $^{\text{Ph}}\text{CH}$ ), 52.1 ( $\text{CHCH}_3$ ), 37.3 (d,  $^1J_{\text{CP}} = 26.7$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 37.0 (d,  $^1J_{\text{CP}} = 27.2$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 27.2 ( $\text{C}(\text{CH}_3)_3$ ), 27.1 ( $\text{C}(\text{CH}_3)_3$ ), 19.8 ( $\text{CHCH}_3$ ).  $^{31}\text{P}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$ : 38.5 (d,  $^1J_{\text{HP}} = 479.6$  Hz).

**HRMS (DCI,  $\text{CH}_4$ )**:  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{17}\text{H}_{28}\text{PS}_2$  327.1365 Found 327.1368.

**X-ray structural analyses.** Suitable crystals for the X-ray structural analyses were obtained for compounds **6**, **8** and **9** by slow evaporation of the solvent from saturated acetonitrile solutions. The single crystals were mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of either an Agilent Technologies GEMINI EOS diffractometer for **6** and **8** or a Bruker Nonius APEXII for **9**. The structures were solved by using the integrate space-group and crystal structure determination SHELXT<sup>37</sup> software and refined by least-squares procedures on  $F^2$  using SHELXL-2014.<sup>38</sup> All H atoms attached to C atoms were introduced in calculation in idealised positions and treated as riding models. The Flack's parameters<sup>39</sup> for the structures of **8**, 0.44(3), and **9**, 0.504(8), indicate the occurrence of a twin by inversion. In compound **8**, there are two roughly identical molecules within the asymmetric unit. **Figure S6** shows a molecular overlay of the two molecules. One of them presents a disorder on two *t*Bu C atoms. The disordered models were treated using the tools (PART, SADI, EADP) available in SHELXL. The drawing of the molecules was realised with the help of ORTEP32.<sup>40,41</sup> Crystal data and refinement parameters are shown in Table S1.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS publication website at DOI:

Copies of <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR, IR and UV-visible spectroscopies, crystallographic data.

### Acknowledgements

We thank the Agence Nationale de la Recherche for support of this work through grant ANR-16-CE29-0014-RAFTSWITCH. Additional support from the CNRS (Centre National de la Recherche Scientifique) is also gratefully acknowledged.

## ORCID

Andrii Karpus [0000-0002-5760-3086](https://orcid.org/0000-0002-5760-3086)

[Jean-Claude Daran](https://orcid.org/0000-0003-4833-7895) 0000-0003-4833-7895

Rinaldo Poli: 0000-0002-5220-2515

Stephane Mazières: 0000-0003-1266-4659

Mathias Destarac: 0000-0002-9718-2239

Eric Manoury: 0000-0001-7991-8890

**Keywords:** S-alkyl phosphinocarbodithioates • free phosphine • phosphine-borane •  
phosponium • selenium •

## References

---

(1) Ólafsson, S. N.; Flensburg, C.; Andersen, P. Lead(IV) complexes with phosphinoyldithioformates,  $R_2P(O)CS_2^-$  ( $R = Ph$  or  $PhCH_2$ ). Syntheses and characterization. Crystal structures of  $PPh_4S_2CP(O)Ph^{2-} \cdot 0.5H_2O$ ,  $PbPh_2[S_2CP(O)Ph^{2-}]_2$  and  $PbPh_2Cl[S_2CP(O)Ph^{2-}]$ . *J. Chem. Soc., Dalton Trans.* **2000**, 4360-4368.

(2) Ólafsson, S. N.; Kvaran, A.; Jonsdottir, S.; Suman, S. G. Non-rigid coordination behavior of the ambidentate phosphinoyldithioformate ligands,  $S_2CP(O)R^{2-}$  ( $-$ ), ( $R = Ph, CH_2Ph$ ) in organometallic Lead(IV) and Mercury(II) compounds. *J. Organomet. Chem.* **2018**, 854, 38-48.

(3) Ólafsson, S. N.; Bjornsson, R.; Helgason, O.; Jonsdottir, S.; Suman, S. G. Coordination geometry determination of stannane compounds with phosphinoyldithioformate ligands using multinuclear NMR, Sn Mossbauer and DFT methods. *J. Organomet. Chem.* **2016**, 825, 125-138

(4) Shi, Y.-C.; Cheng, H.-R.; Tan, H. Syntheses of novel Fe/S clusters via reactions of  $Fe_3(CO)_{12}$  and  $Et_4N Ph_2PCS_2$  with electrophiles. *J. Organomet. Chem.* **2012**, 716, 39-48.

(5) Antinolo, A.; Evrard, D.; Garcia-Yuste, S.; Otero, A.; Perez-Flores, J. C.; Reguillo-Carmona, R.; Rodriguez, A. M.; Villasenor, E. Synthesis, characterization, and reactivity of isocyanidophosphidoniobocene derivatives: X-ray diffraction structures of new isocyanideniobocene complexes,  $Nb(\eta^5-C_5H_4SiMe_3)_2(CNR)(PMePh_2)$  I,  $R = Xylyl, Cy$ . *Organometallics* **2006**, 25, 3670-3677.

(6) Yih, K.-H.; Lee, G.-H.; Wang, Y. Syntheses and Crystal Structures of Tungsten Complexes with Various Ligands Containing (1,3-Dithioliumyl)diphenylphosphine. *Organometallics* **2001**, 20, 2604-2610.

(7) Gutierrez-Alonso, A.; Ballester-Reventos, L.; Perez-Garcia, V.; Ruiz-Valero, C. Cyclopentadienylruthenium complexes with sulfur donor ligands. 3. Coordinative ability of P,S-donor ligands - X-ray structure of  $Ru(\eta^5-CH_3C_5H_4)(Ph_2PCSNPh)(PPh_3)$ . *Polyhedron* **1990**, 9, 2163-2169

(8) Yen, T.-H.; He, Z.-C.; Lee, G.-H.; Tseng, M.-C.; Shen, Y.-H.; Tseng, T.-W.; Liaw, W.-F.; Chiang, M.-H. Reduced thione ligation is preferred over neutral phosphine ligation in diiron biomimics regarding electronic functionality: a spectroscopic and computational investigation. *Chem. Commun.* **2017**, 53, 332-335.

- 
- (9) Dahl, O.; Larsen, O. Phosphinodithioformates. II. *S*-Alkyl *P,P*-Disubstituted Thiophosphinoyldithioformates *Acta Chem. Scand.* **1969**, *23*, 3613-3615.
- (10) Mazières, S.; Kulai, I.; Geagea, R.; Ladeira, S.; Destarac, M. Phosphinoyl and Thiophosphinoylcarbodithioates: Synthesis, Molecular Structure, and Application as New Efficient Mediators for RAFT Polymerization. *Chem. Eur. J.* **2015**, *21*, 1726-1734.
- (11) Yih, K. H.; Lin, Y. C.; Cheng, M. C.; Wang, Y. Novel pathway for the intermolecular cyclization of the((propargylthio)thiocarbonyl)diphenylphosphine ligand in tungsten complexes. *Organometallics* **1994**, *13*, 1561-1563.
- (12) Yih, K. H.; Lin, Y. C.; Cheng, M. C.; Wang, Y. Syntheses, reactivities and molecular structures of tungsten complexes containing the diphenylphosphinodithioformate ligand. *J. Chem. Soc., Dalton Trans.* **1995**, 1305-1313.
- (13) Chen, C. L.; Lo, Y. H.; Lee, C. Y.; Fong, Y. H.; Shih, K. C.; Huang, C. C. Novel W(II) complexes for reversible addition-fragmentation chain transfer (RAFT) polymerizations. *Inorg. Chem. Commun.* **2010**, *13*, 603-605
- (14) Geagea, R.; Ladeira, S.; Mazières, S.; Destarac, M. Chromium and Molybdenum Pentacarbonyl Complexes of Phosphinocarbodithioates: Synthesis, Molecular Structure and Behaviour in RAFT Polymerisation. *Chem. Eur. J.* **2011**, *17*, 3718-3725.
- (15) Kulai, I.; Karpus, A.; Soroka, L.; Valyaev, D. A.; Bourdon, V.; Manoury, E.; Poli, R.; Destarac, M.; Mazières, S. Manganese Phosphinocarbodithioate for RAFT Polymerization with Sunlight-Induced Chain End Post-Treatment. *Polym. Chem.* **2019**, *10*, 266-277.
- (16) Dahl, O.; Gelting, N. C.; Larsen, O. Phosphinodithioformates. I. Reactions of secondary phosphines with carbon disulfide in the presence of bases. *Acta Chem. Scand.* **1969**, *23*, 3369-3375.
- (17) Rajendran, K. V.; Gilheany, D. G. Simple unprecedented conversion of phosphine oxides and sulfides to phosphine boranes using sodium borohydride. *Chem. Commun.* **2012**, *48*, 817-819.
- (18) Omelanczuk, J.; Mikolajczyk, M. A general synthesis of optically active phosphines, phosphinites and thiophosphinites from alkylthio(alkylseleno)phosphonium salts and tris(dimethylamino)phosphine as a thiophilic agent. *Tetrahedron* **1984**, *25*, 2493-2496.
- (19) Kühn, O., *Phosphorus-31 NMR Spectroscopy: A Concise Introduction for the Synthetic Organic and Organometallic Chemist*. Springer-Verlag: Berlin Heidelberg, 2009; p 1-132.
- (20) Beckmann, U.; Süslüyan, D.; Kunz, P. C. Is the  $^1J_{\text{PSe}}$  coupling constant a reliable probe for the basicity of phosphines? A  $^{31}\text{P}$  NMR study. *Phosphorus Sulfur and Silicon and the Related Elements* **2011**, *186*, 2061-2070.
- (21) Vereshchagina, Y.A., Klimovitskii, A. E., Ishmaeva, E. A., Alimova, A. Z., Malysheva, S. F. Polarity and Vibrational Spectra of Bis(2-phenylethyl)- and Bis(2-phenylpropyl)phosphine Selenides. *Russ. J. Org. Chem.* **2012**, *48*, 1003-1004
- (22) Chivers, T., Parvez, M., Seay, M. A. An Acyclic Nitrogen-Phosphorus-Selenium Anion: Preparation, Structure, and reactions of  $(\text{K}[\text{Ph}_2\text{P}(\text{Se})\text{NSiMe}_3]\cdot\text{THF})_2$  with Iodine and Chlorodiphenylphosphine Sulfide. *Inorg. Chem.* **1994**, *33*, 2147-2150.
- (23) Hoskins, B. F.; Tiekink, E. R. T. The crystal structure of *S*-methyl 1-dicyclohexyl(thiophosphoryl) dithioformate -  $(\text{-C}_6\text{H}_{11})_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe}$ . *Austr. J. Chem.* **1988**, *41*, 405-408
- (24) Kulpe, S.; Seidel, I. Alpha-substituted phosphoryl compounds. (III) - The crystal and molecular structure of diphenyl 1,3-benzodithiolyl-(2)-phosphinoyl,  $\text{C}_{19}\text{H}_{15}\text{OPS}_2$ . *Kristall Und Technik-Crystal Research and Technology* **1980**, *15*, 3-10.
- (25) Juaristi, E.; Valle, L.; Morauzeta, C.; Valenzuela, B. A.; Josephnathan, P. Axial preference of 2- 1,3 dithianyldiphenylphosphine oxide - A strong S-C-P anomeric interaction. *J. Org. Chem.* **1982**, *47*, 5038-503.

- 
- (26) Juaristi, E.; Valenzuela, B. A.; Valle, L. Conformational analysis of S-C-P anomeric interactions. 2. X-ray crystallographic evidence against the importance of NS- sigma-star C-P conjugation in axial 2-1,3 dithianyldiphenylphosphine oxide. *J. Org. Chem.* **1984**, 49, 3026-3027.
- (27) Mikolajczyk, M.; Balczewski, P.; Wieczorek, M. W.; Bujacz, G.; Antipin, M. Y.; Struchkov, Y. I. organosulfur compounds. 45. Crystal and molecular structure of 2-diphenylthiophosphinoyl-1,3,5-trithiane. *Phosphorus Sulfur and Silicon and the Related Elements* **1988**, 37, 183-188.
- (28) Wieczorek, M. W.; Bujacz, G. D.; Majzner, W. R.; Graczyk, P. P.; Mikolajczyk, M. Crystal and molecular structure of diastereomeric 2-phosphoryl-substituted, 2-thiophosphoryl-substituted, and 2-selenophosphoryl-substituted 1,3-dithianes. *Heteroatom Chemistry* **1995**, 6, 377-386.
- (29) Mikolajczyk, M.; Luczak, T.; Graczyk, P. P.; Wieczorek, M. W.; Blaszczyk, J.; Bujacz, G. D.; Majzner, W. R. Solid state conformation of the anomeric effect in 2-phosphoryl-, 2-thiophosphoryl- and 2-selenophosphoryl-substituted 1,3-dithiolanes. *J. Organomet. Chem.* **1997**, 536, 355-360.
- (30) Wieczorek, M. W.; Bujacz, G. D.; Majzner, W. R.; Graczyk, P. P.; Mikolajczyk, M. Crystal and molecular structure of diastereomeric 2-diphenylthiophosphinoyl-cis(4,6-dimethyl)-1,3-dithianes. *Heteroatom Chemistry* **1998**, 9, 537-541.
- (31) Barner-Kowollik, C., *Handbook of RAFT Polymerization*. Wiley-VCH: Weinheim, 2008
- (32) Moad, G.; Rizzardo, E.; Thang, S. H. Living Radical Polymerization by the RAFT Process - A Third Update. *Austr. J. Chem.* **2012**, 65, 985-1076.
- (33) Destarac, M. On the Critical Role of RAFT Agent Design in Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization. *Polym. Rev.* **2011**, 51, 163-187.
- (34) Frew, J. J. R.; Damian, K.; Van Rensburg, H.; Slawin, A. M. Z.; Tooze, R. P.; Clarke, M. L. Palladium(II) Complexes of New Bulky Bidentate Phosphanes: Active and Highly Regioselective Catalysts for the Hydroxycarbonylation of Styrene. *Chem. Eur. J.* **2009**, 15, 10504-10513.
- (35) He, Y.; Hinklin, R. J.; Chang, J. Y.; Kiessling, L. L. Stereoselective N-glycosylation by Staudinger ligation. *Org. Lett.* **2004**, 6, 4479-4482.
- (36) Smoll, K. A.; Kaminsky, W.; Goldberg, K. I. Photolysis of Pincer-Ligated Pd-II-Me Complexes in the Presence of Molecular Oxygen. *Organometallics* **2017**, 36, 1213-1216.
- (37) Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, 71, 3-8.
- (38) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, 71, 3-8.
- (39) Flack, H. D.; Bernardinelli, G. The use of X-ray crystallography to determine absolute configuration. *Chirality* **2008**, 20, 681-690.
- (40) Burnett, M. N.; Johnson, C. K., *ORTEP-III, Report ORNL-6895*. . Oak Ridge National Laboratory: Oak Ridge, Tennessee, U.S. , 1996.
- (41) Farrugia, L. J. ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Cryst.* **1997**, 30, 565.

---

**(Graphical Abstract for Table of Content)**

