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An efficient synthesis of stable sulfur-containing phosphoranes derived from 2-mercapto-1-methylimidazole and 2-thiazoline-2-thiol

M. T. Maghsoodlou[a]; N. Hazeri[a]; S. M. H. Khorassani[a]; M. Nassiri[a]; G. Marandi[a]; G. Afshari[a]; U. Niroumand[a]
[a] Department of Chemistry, The University of Sistan and Balouchestan, Zahedan, Iran

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RESEARCH ARTICLE

An efficient synthesis of stable sulfur-containing phosphoranes derived from 2-mercapto-1-methylimidazole and 2-thiazoline-2-thiol

M. T. MAGHSOODLOU*, N. HAZERI, S. M. H. KHORASSANI, M. NASSIRI, G. MARANDI, G. AFSHARI and U. NIROUMAND

Department of Chemistry, The University of Sistan and Balouchestan, P. O. Box 98135-674, Zahedan, Iran

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Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong SH-acids, such as 2-mercapto-1-methylimidazole and 2-thiazoline-2-thiol. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords: Stable phosphorus ylide; Acetylenic esters; 2-Mercapto-1-methylimidazole and 2-Thiazoline-2-thiol; Triphenylphosphine; Geometrical isomers

1. Introduction

Phosphorus ylides are reactive systems which take part in many valuable reactions of organic synthesis [1–11]. These are most often prepared by treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the phosphine and an alkyl halide [1–5] and they are also obtained by Michael addition of phosphorus nucleophiles to activated olefins [1, 2]. Here, we describe an efficient synthetic route of the 2-mercapto-1-methylimidazole and also the 2-thiazoline-2-thiol-containing stable phosphorus ylides [12]. As has been noted earlier, the imidazole moiety and its derivatives are widely used in making medicines, and they also have biological activity [13]. Moreover, the thiazolines have antitumor properties [13].

With respect to the importance of the aforementioned purpose the present work was undertaken for the generation of stable sulfur-containing phosphoranes. In order to do this, the reaction of triphenylphosphine with dialkyl acetylenedicarboxylates (**1**) in the presence of

*Corresponding author. Tel: +98-541-2446565; Email: mt_maghsoodlou@yahoo.com

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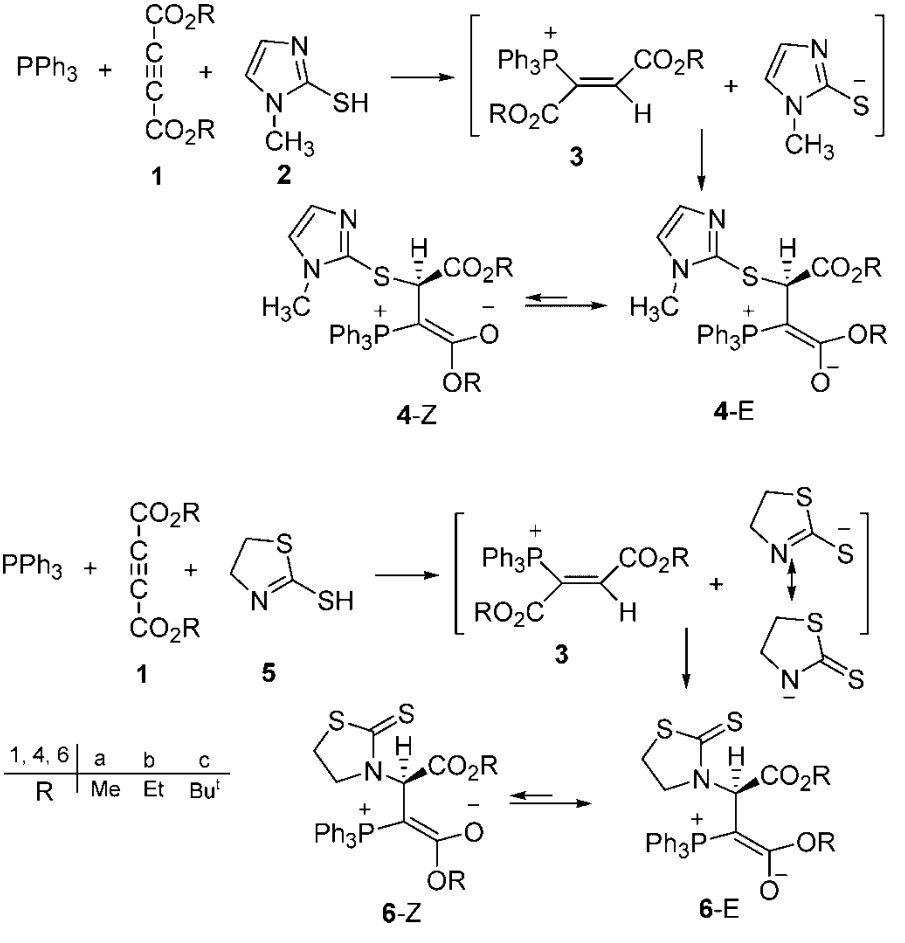
strong SH-acids (**2**) and (**5**) led to the vinyltriphenylphosphonium cation (**3**), which was subsequently followed by attack of the 2-mercapto-1-methylimidazole or 2-thiazoline-2-thiol anion to form the phosphoranes (**4**-*E*), (**4**-*Z*), (**6**-*E*), and (**6**-*Z*) in excellent yields (see scheme 1).



SCHEME 1

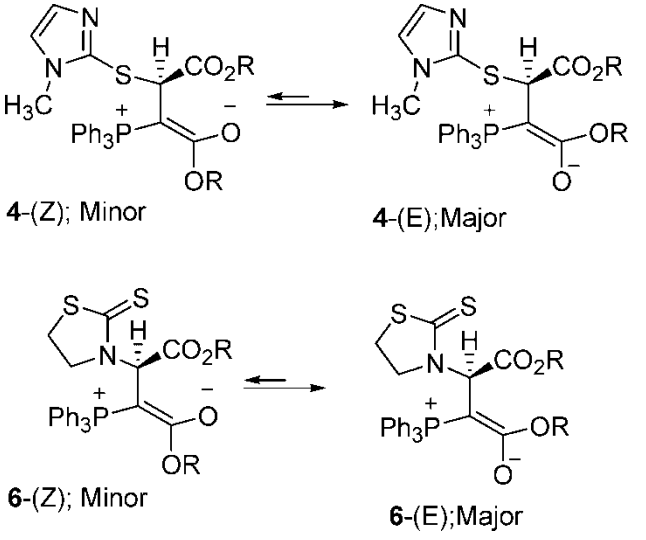
2. Results and discussion

The reactions of 2-mercapto-1-methylimidazole and 2-thiazoline-2-thiol with dialkyl acetylenedicarboxylates (**1**) in the presence of triphenylphosphine were carried out in ethyl acetate solvent at room temperature and were complete after approximately 8 hours.

The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphoranes (**4**) and (**6**). Any products other than (**4**) and (**6**) could not be detected by NMR spectroscopy. The ^{13}C NMR spectrum of compounds (**4a**) and (**6a**) exhibited a signal at δ (162.02) ppm and (195.25) ppm for the N-C-S and C=S units, respectively [14].

The structures of compounds (**4a–c**) and (**6a–c**) were deduced from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. Their mass spectra displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve loss of the side chains. The ^{1}H, ^{13}C, and ^{31}P NMR

spectra of ylides (**4a** and **b**) and (**6a** and **b**) are consistent with the presence of two isomers, but only one geometrical isomer was observed for the di-*tert*-butyl derivatives (**4c**) and (**6c**), presumably because of the bulky *tert*-butyl group. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and rotation around the partial double bond in (**4**-*E*), (**4**-*Z*), (**6**-*E*), and (**6**-*Z*) geometrical isomers is slow on the NMR timescale at ambient temperature (see scheme 2). ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds (**4a–c**) and (**6–c**) were described in the experimental section.



SCHEME 2

3. Experimental

Mps and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a Bruker DRX-500 Avance instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MH, respectively. Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine, dialkyl acetylenedicarboxylates (**1a–c**), 2-mercapto-1-methylimidazole (**2**), and 2-thiazoline-2-thiol (**5**) were purchased from Fluka (Buchs, Switzerland) and used without further purification.

3.1 *Preparation of dimethyl 2-(1-methylimidazole-2-sulfanyl)-3-(triphenylphosphanylidene) butanedioate* (**4a**)

General procedure. To a magnetically stirred solution of 2-mercapto-1-methylimidazole (0.11 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in 8 mL of ethyl acetate was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in 4 mL of ethyl acetate at −5 °C over 10 min. After approximately 8 hours of stirring at room temperature, the product was washed with cold diethyl ether (5 mL) and extracted as colorless crystals (0.50 g,

97%), mp 205–206 °C; IR (υ_{max}, cm^{-1}) 1740, 1620 (C=O); MS (*m/z*, %) 459 (M - CO_2Me, 15), 405 (M - heterocyclic, 50), 262 (PPh_3, 38), 183 (PPh2, 18), 108 (PPh, 25), 77 (Ph, 6).

Major isomer (*E*)-**4a** (65%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 3.12 (3H, s, NCH_3), 3.48 and 3.74 (6H, 2s, 2 OCH_3), 5.55 (1H, d, $^3J_{PH}$ 17.2 Hz, P-C-CH), 6.62 and 7.28 (2s, 2 H_{arom}, $C_3H_2N_2S$), 7.48–7.66 (15H, m, C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 34.62 (s, NCH_3), 43.35 (d, $^1J_{PC}$ 128.2 Hz, P=C), 49.21 and 52.62 (2s, 2 OCH_3), 60.40 (d, $^2J_{PC}$ 18.5 Hz, P-C-*CH*), 116.77 and 117.38 (2C, $C_3H_2N_2S$), 126.35 (d, $^1J_{PC}$ 92.2 Hz, C_{ipso}), 128.99 (d, $^3J_{PC}$ 11.8 Hz, C_{meta}), 132.25 (C_{para}), 133.61 (d, $^2J_{PC}$ 9.8 Hz, C_{ortho}), 162.03 (1C, $C_3H_2N_2S$, N-C-S), 170.35 (d, $^3J_{PC}$ 12.7 Hz, C=O), 171.56 (d, $^2J_{PC}$ 10.8 Hz, P-C=C). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 24.09 (Ph_3P^+-C).

Minor isomer (*Z*)-**4a** (35%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 3.13 (3H, s, NCH_3), 3.50 and 3.58 (6H, 2s, 2 OCH_3), 5.48 (1H, d, $^3J_{PH}$ 18.7 Hz, P-C-CH), 6.67 and 7.29 (2s, 2 H_{arom}, $C_3H_2N_2S$), 7.49–7.67 (15H, m, C_6H_5). ^{13}C NMR (125.8 Hz; $CDCl_3$) δ 34.60 (s, NCH_3), 43.33 (d, $^1J_{PC}$ 128.4 Hz, P=C), 50.22 and 52.50 (2s, 2 OCH_3), 60.23 (d, $^2J_{PC}$ 24.7 Hz, P-C-*CH*), 116.11 and 116.76 (2C, $C_3H_2N_2S$), 125.61 (d, $^1J_{PC}$ 93.1 Hz, C_{ipso}), 128.51 (d, $^3J_{PC}$ 12.2 Hz, C_{meta}), 132.23 (C_{para}), 133.60 (d, $^2J_{PC}$ 9.8 Hz, C_{ortho}), 162.43 (1C, $C_3H_2N_2S$, N-C-S), 170.34 (d, $^3J_{PC}$ 12.7 Hz, C=O), 171.23 (d, $^2J_{PC}$ 12.1 Hz, P-C=C). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 24.81 (Ph_3P^+-C).

3.2 *Preparation of diethyl 2-(1-methylimidazole-2-sulfanyl)-3-(triphenylphosphanylidene) butanedioate* (**4b**)

White powder (0.51 g, 94%), mp 109–111 °C; IR (υ_{max}, cm^{-1}) 1730, 1620 (C=O); MS (*m/z*, %) 433 (M-heterocyclic, 100), 284 (M-PPh_3, 8), 262 (PPh_3, 65), 211 (M-PPh_3-CO_2Et, 9), 182 (M-PPh_3-CO_2Et-Et, 45), 183 (PPh_2, 21), 108 (PPh, 79), 77 (Ph, 7).

Major isomer (*E*)-**4b** (72%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 0.47 and 1.31 (6H, 2t, $^3J_{HH}$ 7.0 Hz and 7.1 Hz, 2 O-C-CH_3), 3.51 (3H, s, NCH_3), 3.77 and 4.30 (4H, 2 m, 2 ABX_3 system, 2 O-CH_2-C), 5.54 (1H, d, $^3J_{PH}$ 17.5 Hz, P-C-CH), 6.62 and 7.36 (2s, 2 H_{arom}, $C_3H_2N_2S$), 7.50–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 14.02 and 14.90 (2s, 2 O-C-*CH*$_3$), 34.63 (s, NCH_3), 43.11 (d, $^1J_{PC}$ 127.0 Hz, P=C), 60.37 (d, $^2J_{PC}$ 17.9 Hz, P-C-*CH*), 61.32 and 61.37 (2C, 2 O*CH*$_2$$CH_3$), 116.63 and 117.59 (2C, $C_3H_2N_2S$), 126.54 (d, $^1J_{PC}$ 91.3 Hz, C_{ipso}), 128.51 (d, $^3J_{PC}$ 12.1 Hz, C_{meta}), 131.95 (d, $^4J_{PC}$ 2.6 Hz, C_{para}), 132.10 (d, $^2J_{PC}$ 9.8 Hz, C_{ortho}), 161.98 (1C, $C_3H_2N_2S$, N-C-S), 169.37 (d, $^3J_{PC}$ 13.0 Hz, C=O), 170.85 (d, $^2J_{PC}$ 13.4 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 23.03 (Ph_3P^+-C).

Minor isomer (*Z*)-**4b** (28%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 1.19 and 1.35 (6H, 2t, $^3J_{HH}$ 6.7 Hz and 6.9 Hz, 2 O*CH*$_2$*CH*$_3$), 3.53 (3H, s, NCH_3), 3.69 and 4.20 (4H, 2 m, 2 ABX_3 system, 2 O*CH*$_2$$CH_3$), 5.49 (1H, d, $^3J_{PH}$ 19.1 Hz, P-C-*CH*), 6.67 and 7.29 (2s, 2 H_{arom}, $C_3H_2N_2S$), 7.50–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 13.91 and 14.01 (2s, 2 O-C-*CH*$_3$), 34.33 (s, NCH_3), 43.13 (d, $^1J_{PC}$ 127.0 Hz, P=C), 60.35 (d, $^2J_{PC}$ 18.0 Hz, P-C-*CH*), 61.23 and 61.32 (2s, 2 OCH_2CH_3), 116.65 and 117.61 (2C, $C_3H_5N_2S$), 125.82 (d, $^1J_{PC}$ 90.2 Hz, C_{ipso}), 128.90 (d, $^3J_{PC}$ 12.2 Hz, C_{meta}), 131.97 (d, $^4J_{PC}$ 2.6 Hz, C_{para}), 132.12 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 163.26 (1C, $C_3H_2N_2S$, N-C-S), 169.70 (d, $^3J_{PC}$ 13.0 Hz, C=O), 170.83 (d, $^2J_{PC}$ 15.8 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 23.99 (Ph_3P^+-C).

3.3 *Preparation of di-tert-butyl 2-(1-methylimidazole-2-sulfanyl)-3-(triphenylphosphanylidene) butanedioate* (**4c**)

White powder (0.57 g, 97%), mp 162–164 °C; IR (υ_{max}, cm^{-1}) 1730, 1620, (C=O); MS (*m/z*, %) 488 (CO_2CMe_3, 22), 476 (M-heterocyclic, 30), 262 (PPh_3, 54), 183 (PPh_2, 30), 108 (PPh, 67).

Major rotamer (*E*)-**4c**: ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 0.97 and 1.54 (18H, 2s, 2 CMe_3), 3.47 (3H, s, N-CH_3), 5.33 (1H, d, $^{3}J_{PH}$ 17.7 Hz, P-C-CH), 6.61 (s, H_{arom}, $C_3H_2N_2S$), 7.47–7.68 (16H, m, 3 C_6H_5 and $C_3H_2N_2S$). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 28.24 and 28.30 (2s, 2 C*Me*$_3$), 34.81 (s, NCH_3), 42.42 (d, $^{1}J_{PC}$ 127.9 Hz, P=C), 61.01 (d, $^{2}J_{PC}$ 18.3 Hz, P-C-*CH*), 77.56 and 80.89 (2s, 2 O*C*Me$_3$), 116.50 and 116.73 (2C, $C_3H_2N_2S$), 127.06 (d, $^{1}J_{CP}$ 92.1 Hz, C_{ipso}), 128.76 (d, $^{3}J_{PC}$ 12.2 Hz, C_{meta}), 132.12 (C_{para}), 133.68 (d, $^{2}J_{PC}$ 9.7 Hz, C_{ortho}), 161.92 (1C, N-C-S, $C_3H_2N_2S$), 169.28 (d, $^{3}J_{PC}$ 12.5 Hz C=O), 169.33 (d, $^{2}J_{PC}$ 11.4 Hz P-C=*C*). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 23.59 (Ph_3P^+-C).

3.4 *Preparation of dimethyl 2-(2-mercapto-2-thiazolin-3-yl)-3-(triphenylphosphanylidene) butanedioate* (**6a**)

White powder (0.49 g, 95%), mp 154–156 °C; IR (υ_{rmax}, cm^{-1}) 1745, 1636 (C=O), 1431 (C=S); MS (*m*/*z*, %) 523 (M, 10), 464 (M - CO_2Me, 5), 405 (M - heterocyclic, 65), 262 (PPh_3, 100), 183 (PPh_2, 50), 118 (heterocyclic, 15), 108 (PPh, 41).

Major isomer (*E*)-**6a** (75%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 3.13 and 3.78 (6H, 2s, 2 OCH_3), 3.16 (2H, m, CH_2N), 4.40 (2H, m, CH_2S), 5.41 (1H, d, $^{3}J_{PH}$ 17.5 Hz, P–C–CH), 7.49–7.67 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 28.15 (s, C-C-N), 41.28 (d, $^{1}J_{PC}$ 126.34 Hz, P=C), 49.24 (s, C-C-S), 52.57 and 54.01 (2s, 2 OCH_3), 61.37 (d, $^{2}J_{PC}$ 17.9 Hz, P–C–*CH*), 126.33 (d, $^{1}J_{PC}$ 92.1 Hz, C_{ipso}), 129.13 (d, $^{3}J_{PC}$ 12.2 Hz, C_{meta}), 132.36 (C_{para}), 133.47 (d, $^{2}J_{PC}$ 9.6 Hz, C_{ortho}), 169.82 (d, $^{3}J_{PC}$ 13.0 Hz, C=O), 171.07 (d, $^{2}J_{PC}$ 12.3 Hz, P-C=*C*), 195.13 (s, C=S). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 24.48 (Ph_3P^+-C).

Minor isomer (*Z*)-**6a** (25%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 3.53 and 3.75 (6H, 2s, 2 OCH_3), 3.25 (2H, m, CH_2N), 4.56 (2H, m, CH_2S), 5.39 (1H, d, $^{3}J_{PH}$ 18.8 Hz, P–C–CH), 7.49–7.67 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 27.98 (s, C-C-N), 42.34 (d, $^{1}J_{PC}$ 139.4 Hz, P=C), 50.21 (s, C-C-S), 52.38 and 53.78 (2s, 2 OCH_3), 60.96 (d, $^{2}J_{PC}$ 17.5 Hz, P–C–*CH*), 125.67 (d, $^{1}J_{PC}$ 92.5 Hz, C_{ipso}), 129.13 (d, $^{3}J_{PC}$ 12.2 Hz, C_{meta}), 132.35 (C_{para}), 133.45 (d, $^{2}J_{PC}$ 9.9 Hz, C_{ortho}), 170.29 (d, $^{3}J_{PC}$ 17.9 Hz, C=O), 170.83 (d, $^{2}J_{PC}$ 13.5 Hz, P-C=C), 195.25 (s, C=S). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 25.24 (Ph_3P^+-C).

3.5 *Preparation of diethyl 2-(2-mercapto-2-thiazolin-3-yl)-3-(triphenylphosphanylidene) butanedioate* (**6b**)

White powder (0.51 g, 94%), mp 113–115 °C; IR (υ_{max}, cm^{-1}) 1745, 1634 (C=O), 1457 (C=S); MS (*m*/*z*, %) 551 (M, 3), 478 (M - CO_2Et, 5), 433 (M - heterocyclic, 10), 262 (PPh_3, 100), 183 (PPh_2, 43), 118 (heterocyclic, 10), 108 (PPh, 20).

Major isomer (*E*)-**6b** (70%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 0.46 and 1.31 (6H, 2t, $^{3}J_{HH}$ 7.1 Hz and 7.3 Hz, 2 O–C–CH_3), 3.17 (2H, m, CH_2N), 3.46–4.30 (4H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3), 4.44 (2H, m, CH_2S), 5.39 (1H, d, $^{3}J_{PH}$ 17.8 Hz, P–C–CH), 7.48–7.69 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 13.91 and 14.29 (2s, 2 O-C-*CH*$_3$), 28.17 (s, C-C-N), 41.04 (d, $^{1}J_{PC}$ 126.1 Hz, P=C), 54.10 (s, C-C-S), 57.92 and 61.16 (2s, 2 O-CH_2-C), 61.39 (d, $^{2}J_{PC}$ 18.1 Hz, P–C–*CH*), 126.52 (d, $^{1}J_{PC}$ 92.1 Hz, C_{ipso}), 129.04 (d, $^{3}J_{PC}$ 11.7 Hz, C_{meta}), 132.27 (C_{para}), 133.56 (d, $^{2}J_{PC}$ 11.4 Hz, C_{ortho}), 169.36 (d, $^{3}J_{PC}$ 13.1 Hz, C=O), 170.22 (d, $^{2}J_{PC}$ 12.3 Hz, P-C=C), 195.00 (s, C=S). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 24.48 (Ph_3P^+-C).

Minor isomer (*Z*)-**6b** (30%): ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 1.17 and 1.20 (6H, 2t, $^{3}J_{HH}$ 7.1 Hz and 7.4 Hz, 2 OCH_2CH_3), 3.27 (2H, m, CH_2N), 3.45–4.32 (4H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3), 4.60 (2H, m, CH_2S), 5.37 (1H, d, $^{3}J_{PH}$ 19.2 Hz, P–C–CH), 7.48–7.69 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 14.85 and 15.29 (2s, 2 O-C-*CH*$_3$), 27.78 (s, C-C-N), 42.22 (d, $^{1}J_{PC}$ 127.1 Hz, P=C), 53.93 (s, C-C-S), 58.51 (s, O*CH*$_2$CH$_3$), 60.84 (d, $^{2}J_{PC}$ 17.2 Hz, P–C–*CH*), 61.24 (s, O*CH*$_2$CH$_3$), 125.89 (d, $^{1}J_{PC}$ 92.3 Hz, C_{ipso}), 128.53 (d,

$^{3}J_{PC}$ 10.1 Hz, C_{meta}), 132.26 (C_{para}), 133.47 (d, $^{2}J_{PC}$ 10.6 Hz, C_{ortho}), 169.92 (d, $^{3}J_{PC}$ 12.0 Hz, C=O), 170.04 (d, $^{2}J_{PC}$ 12.2 Hz, P-C=C), 195.18 (s, C=S). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 25.42 (Ph_3P^+-C).

3.6 *Preparation of di-tert-butyl 2-(2-mercapto-2-thiazolin-3-yl)-3-(triphenylphosphanylidene) butanedioate* (**6c**)

White powder (0.58 g, 96%), mp 105–107 °C; IR (υ_{max}, cm^{-1}) 1739, 1641 (C=O), 1456 (C=S); MS (*m*/*z*, %) 607 (M, 5), 506 (M-CO_2t-Bu, 5), 262 (PPh_3, 100), 183 (PPh_2, 56), 118 (heterocyclic, 15), 108 (PPh, 30).

Major isomer (*E*)-**6c**: ^{1}H NMR (500.1 MHz; $CDCl_3$) δ 0.94 and 1.53 (18H, 2s, 2 CMe_3), 3.15 (2H, m, CH_2N), 4.04 (2H, m, CH_2S), 5.19 (1H, d, $^{3}J_{PH}$ 18.2 Hz, P-C-CH), 7.47–7.69 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 28.04 (s, C-C-N), 28.21 and 28.34 (2s, 2 C*Me*$_3$), 40.49 (d, $^{1}J_{PC}$ 126.7 Hz, P=C), 54.15 (s, C-C-S), 61.98 (d, $^{2}J_{PC}$ 17.2 Hz, P–C–CH), 77.67 and 81.05 (2s, 2 $OCMe_3$), 127.10 (d, $^{1}J_{PC}$ 91.9 Hz, C_{ipso}), 128.85 (d, $^{3}J_{PC}$ 12.3 Hz, C_{meta}), 132.11 (d, $^{4}J_{PC}$ 2.5 Hz, C_{para}), 133.60 (d, $^{2}J_{PC}$ 9.7 Hz, C_{ortho}), 168.76 (d, $^{3}J_{PC}$ 12.2 Hz, C=O), 168.74 (d, $^{2}J_{PC}$ 12.2 Hz, P-C=*C*), 194.47 (s, C=S). ^{31}P NMR (202.4 MHz; $CDCl_3$) δ 24.06 (Ph_3P^+-C).

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