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Unexpected Synthesis of New Phosphonium Salts from R_3PCS_2 and $[Cp_2ZrHCl]_n$

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Synthetic utility of the Schwartz reagent ($[Cp_2ZrHCl]_n$, **1**) in organic[1] or main group element[2] chemistry is well documented. Indeed, a number of applications of **1** have been described, such as regioselective cis-addition to alkenes or alkynes, reduction of aldehydes, ketones, nitriles, phosphaalkenes, and phosphaimines, ring opening of oxygen, nitrogen, or phosphorus heterocycles, etc.

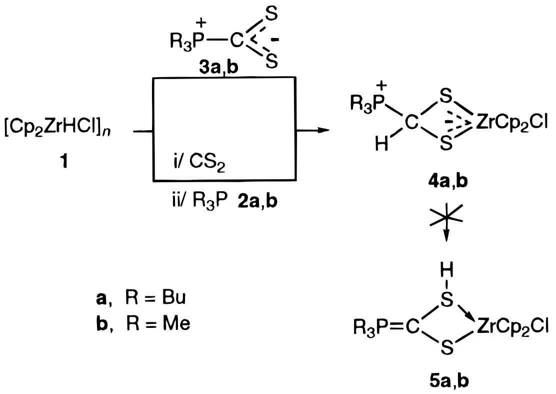
We report here new useful methodology for preparation of various new phosphonium salts involving the reaction of electrophiles with a zirconated phosphonio dithiolate complex (**4**) prepared from R_3PCS_2 and **1**.

The adduct R_3PCS_2[3] **3a** (R = Bu) or **3b** (R = Me) obtained from carbon disulfide and the corresponding phosphine R_3P **2** reacts readily with **1** in dichloromethane solution at −20 °C to give the 1:1 complex **4a** or **4b** (Scheme 1). Spectroscopic data (especially heteronuclear $^1H\{^{31}P\}-^{13}C\{^{31}P\}$ COSY experiments) are in agreement with the proposed structure arising from the direct hydrozirconation of the thiocarbonyl bond of **3a** or **3b** and subsequent stabilization of the $ZrCp_2Cl$ fragment with a sulfur−zirconium dative bond. Compound **4a** or **4b** can be alternatively prepared by first adding carbon disulfide to **1** and then treatment of the resulting complex with R_3P. **4a** is isolated in high yield as a yellowish crystalline product. The nature of substituents on phosphorus strongly affects the stability of these complexes: **4a** decomposes in solution over 1 day but is stable as a powder for several weeks at −25 °C, while **4b** has to be used as generated in situ. It should be noted that no 1,2-hydrogen shift which would have resulted in the formation of complexe **5a** or **5b** has been detected.

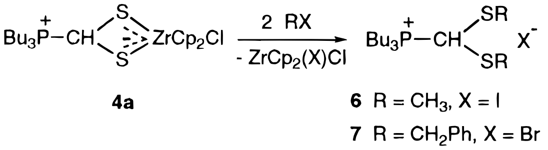
4a is unreactive toward secondary and tertiary alkyl halides but easily reacts with methyl iodide and benzyl bromide (2 equiv/1 equiv of **4a**) with formation in high yield of S,S′-dialkylated phosphonium salts **6** and **7** (Scheme 2). Similarly, addition of 2 equiv of acetyl chloride (CH_3COCl) to **4a** (1 equiv) affords the bis-thioacylated phosphonium salt **8** isolated as a colorless oil (Scheme 2). **8** displays characteristic signals in ^1H NMR [δ_{CH} 5.88 (d, $^2J_{HP}$ = 11.4 Hz)] and ^{13}C NMR [δ_{CH} 32.3 (d, $^1J_{CP}$ = 48.4 Hz)].

Surprisingly, treatment of **4a** (1 equiv) with CH_3COCl (1 equiv) affords the new methylenephosphonium salt **9** and the adduct **3a**; **9** is also formed when 1 equiv of **4a** is reacted with 0.5 equiv of CH_3COCl, but in this case one-half of the starting compound **4a** still remains in the reaction mixture (Scheme 3). The ionic nature of **9** is corroborated by anionic exchange reaction with $NaBPh_4$.

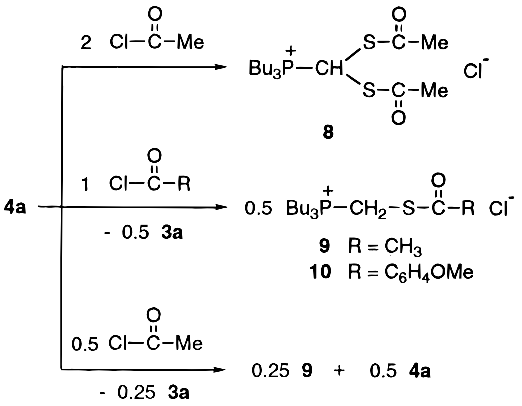
Scheme 1

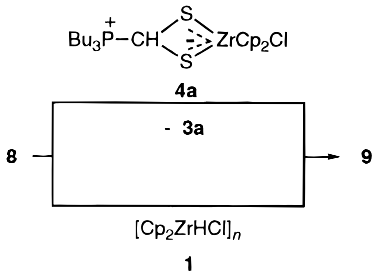


Scheme 2



Scheme 3





These results can be explained by considering that, whatever the ratio of the two starting reagents, the first step of the reaction is the bis-acylation of **4a** with formation of **8**; then derivative **8** may react further with **4a** which acts as a source of hydrogen to give **9** and **3**. Such an assumption is corroborated by several observations: (i) addition of **4a** to an *isolated* sample of **8** gives cleanly the methylenephosphonium salt **9** and **3a**, (ii) a similar hydride transfer is observed when **8** is treated with **1**—in this case **9** is formed as the sole phosphorus product of the reaction in quantitative yield, and (iii) deuterium experiment with $Bu_3PC(D)S_2ZrCp_2Cl$ (**4a**-d_1)[4] and $CH_3C(O)Cl$ gave $[Bu_3PCD_2SC(O)CH_3]^+$ Cl^- (**9**-d_2). Therefore hydrogen abstraction from solvent or a cyclo-

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[1] Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, pp 667−702.

[2] See, for example: Majoral, J.-P.; Zablocka, M.; Igau, A.; Cénac, N. *Chem. Ber.* **1996**, *129*, 879−886 and references cited therein.

[3] Issleib, K.; Brack, A. *Z. Anorg. Allg. Chem. B* **1954**, *277*, 271−274.

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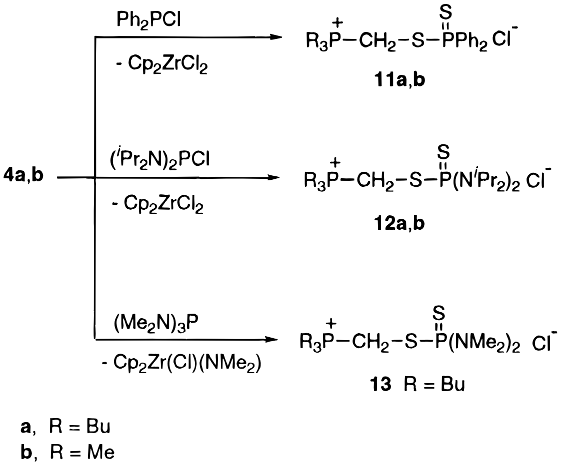
Scheme 4



pentadienyl group can be rejected. A similar reaction done with anisoyl chloride and **4a** gives **10** under the same experimental conditions.

Remarkably, the treatment of **4a** or **4b** with chlorophosphines (R_2PCl, R = Ph, N^iPr_2) in dichloromethane leads to other new methylene thiophosphorylated phosphonium salts **11a,b** or **12a,b** (Scheme 4). Similarly addition of tris(dimethylamino)phosphine to **4a** gives the salt **13**.[5] The structural assignment of derivatives **11**−**13** is based on ^{31}P, ^{1}H, and ^{13}C NMR data and mass spectrometry. ^{13}C NMR spectra exhibit a doublet at 20−26 ppm ($47 < {}^1J_{CP} < 55$ Hz) for the SCH_2P^+ group, and ^{1}H NMR spectra reveal characteristic peaks for the same group at 4.0−4.2 ppm. Furthermore the molecular structure of **11b** is confirmed by a single-crystal X-ray structure determination.[6]

The mechanism of this unusual reaction has not been unequivocally established but can be regarded as a three-step process, i.e., (1) nucleophilic substitution at sulfur in **4a** (or **4b**), (2) then sulfurization on the tricoordinated phosphorus atom, and (3) hydrogen transfer in order to form the PCH_2SR sequence.

In conclusion, in this preliminary report, we present a simple but efficient procedure of preparing a variety of unusual phosphonium salts via addition of electrophiles to new and useful reagents, the complexe **4a** or **4b**. Mechanistic studies and preparation and use of other phosphonium salts are currently in progress as well as investigations concerning the reactivity of various adducts of the type **4**.

Experimental Section

General. All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, ether), lithium aluminum hydride (pentane), P_2O_5 (CH_3CN), or CaH_2 (CH_2Cl_2). C_6D_6 and $CDCl_3$ were treated respectively with $LiAlH_4$ and CaH_2, distilled, and stored under argon. $[Cp_2ZrHCl]_n$ (Schwartz reagent) (**1**) was synthesized by the method of Buchwald.[7]

NMR chemical shifts are expressed in ppm upfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). The ^{13}C NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra.

Phosphonio *gem*-Dithiolate Complex 4a. A solution of tributylphosphine−carbon disulfide adduct **3a** (0.790 g, 2.84 mmol) in 4 mL of dichloromethane was added dropwise to a suspension of $[Cp_2ZrHCl]_n$ (0.730 g, 2.84 mmol) in 4 mL of CH_2Cl_2 at −20 °C. The resulting solution was stirred for 2 h until complete dissolution of the Schwartz reagent. Evaporation of the solvent gave an oily residue which was washed several times with 2 mL of toluene. Compound **4a** was obtained as a white powder in 68% yield (1.03 g).

4a: $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 32.4; ^{1}H NMR (CD_2Cl_2) δ 0.98 (t, $^3J_{HH}$ = 7.1 Hz, 9H), 1.50 (m, 6H), 1.56 (m, 6H), 2.17 (m, 6H), 4.78 (d, $^2J_{HP}$ = 5.5 Hz, 1H), 6.08 (s, 5H), 6.17 (s, 5H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 12.7, 16.0 (d, $^1J_{CP}$ = 49.9 Hz), 23.5 ($^3J_{CP}$ = 4.1 Hz), 23.8 (d, $^2J_{CP}$ = 14.3 Hz), 31.0 (d, $^1J_{CP}$ = 45.0 Hz), 112.5, 112.7; MS *m/z* 541 (M^+).

Phosphonio *gem*-Dithiolate Complex 4b. A solution of trimethylphosphine−carbon disulfide adduct **3b** (0.032 g, 0.21 mmol) in 0.8 mL of deuterated dichloromethane was added dropwise to $[Cp_2ZrHCl]_n$ (0.055 g, 0.21 mmol) at −20 °C. The resulting mixture was stirred for 2 h until complete dissolution of the Schwartz reagent occurred. The resulting orange solution was directly characterized by ^{31}P, ^{1}H, and ^{13}C NMR. Attempts to isolate **4b** led to decomposition.

4b: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 27.0; ^{1}H NMR (CD_2Cl_2) δ 1.78 (d, $^2J_{HP}$ = 13.0 Hz, 9H), 4.62 (d, $^2J_{HP}$ = 7.2 Hz, 1H), 6.17 (br s, 5H), 6.08 (br s, 5H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 5.3 (d, $^1J_{CP}$ = 58.8 Hz), 33.8 (d, $^1J_{CP}$ = 51.2 Hz), 113.3.

[Bis(*S*-methylthio)methyl]tributylphosphonium Iodide (6). Methyl iodide (1.14 g, 8.03 mmol) was added dropwise to a stirred solution of **4a** (0.77 g, 1.44 mmol) in 5 mL of dry dichloromethane at 20 °C. After stirring for 0.5 h the resulting yellow solution was evaporated, and 3 mL of toluene was added. The precipitate of zirconium dihalide was filtered off and the solvent removed. Repeated additions of toluene followed by filtrations allowed to totally remove zirconium dihalide. **6** was obtained in 73% yield as yellow crystals (0.46 g) after final purification performed by column chromatography (silica gel, eluent acetonitrile, R_f = 0.8).

6: $^{31}P\{^1H)$ NMR ($CDCl_3$) δ 42.1; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, $^3J_{HH}$ = 7.1 Hz, 9H), 1.48 (m, 6H), 1.61 (m, 6H), 2.45 (m, 6H), 2.51 (d, $^4J_{HP}$ = 1.0 Hz, 6H), 6.07 (d, $^2J_{HP}$ = 13.7 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.4, 16.6 (d, $^3J_{CP}$ = 3.8 Hz), 19.4 (d, $^1J_{CP}$ = 45.4 Hz), 24.1 (d, $^2J_{CP}$ = 23.7 Hz), 24.3 (d, $^3J_{CP}$ = 13.3 Hz), 42.5 (d, $^1J_{CP}$ = 47.5 Hz); MS *m/z* 436. Anal. Calcd for $C_{15}H_{34}IPS_2$: C, 41.28; H, 7.85; S, 14.69. Found: C, 41.85; H, 7.87; S, 14.36.

[Bis(*S*-benzylthio)methyl]tributylphosphonium Chloride (7). Benzyl bromide (47 mL, 0.40 mmol) was added to a stirred solution of **4a** in 1.5 mL of dry dichloromethane at 20 °C. The reaction mixture was stirred for 1 h, solvent was removed, 2 mL of toluene was added, and the zirconium dihalide was separated by filtration. Evaporation of the solvent gave an oily residue which was extracted with 35 mL of diethyl ether. Evaporation of diethyl ether gave **7** as a white oily powder (0.075 g, 70% yield).

7: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 41.5; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 9H), 1.44 (m, 12H), 2.40 (m, 6H), 4.10 (s, 4H), 6.14 (d, $^2J_{HP}$ = 14.8 Hz, 1H), 7.20−7.35 (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.2, 19.0 (d, $^1J_{CP}$ = 45.5 Hz), 23.9 (d, $^2J_{CP}$ = 20.4 Hz), 24.0, 37.9 (d, $^3J_{CP}$ = 3.0 Hz), 40.9 (d, $^1J_{CP}$ = 48.7 Hz), 127.7, 128.6, 129.2, 135.9; MS *m/z* 541.

[Bis(*S*-(methylcarbonyl)thio]methyl]tributylphosphonium Chloride (8). Acetyl chloride (0.110 g, 1.40 mmol) was added to a solution of **4a** (0.376 g, 0.70 mmol) in 5 mL of dichloromethane at −30 °C. The resulting solution was allowed to warm up to 20 °C; then the solvent was removed and 1 mL of THF added to allow slow crystallization of **8** at −25 °C as white crystals (0.173 g, 61% yield). When an excess of acetyl chloride is used, **8** was quantitatively formed.

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(4) $Bu_3PC(D)S_2ZrCp_2Cl$ is easily prepared from Bu_3PCS_2 and $[Cp_2Zr(D)Cl]_n$.

(5) In this preliminary work, resulting zirconated species were not systematically characterized.

(6) Atomic coordinates, bond lengths and angles, thermal parameters, and structure factors for compound **11b** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

(7) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

8: ^{31}P{^{1}H} NMR (CDCl$_3$) δ 46.1; ^{1}H NMR (CDCl$_3$) δ 0.72 (t, $^3J_{HH}$ = 6.8 Hz, 9H), 1.31 (m, 12H), 2.30 (s, 6H), 2.42 (m, 6H), 5.88 (d, $^2J_{HP}$ = 11.4 Hz, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 12.9, 18.9 (d, $^1J_{CP}$ = 45.1 Hz), 23.3 (d, $^3J_{CP}$ = 9.9 Hz), 23.4 (d, $^2J_{CP}$ = 11.6 Hz), 29.7, 32.3 (d, $^1J_{CP}$ = 48.4 Hz), 189.3; MS *m/z* 401. Anal. Calcd for $C_{17}H_{34}ClO_2PS_2$: C, 50.91; H, 8.54. Found: C, 50.41; H, 8.46.

Methylene Thioacetyl Phosphonium Salt 9. Acetyl chloride (0.070 g, 0.89 mmol) was added dropwise to a stirred solution of **4a** (0.476 g, 0.89 mmol) in 5 mL of CH_2Cl_2 at −40 °C. The solution was allowed to warm to 20 °C, and the solvent was then evaporated. The residue was washed with ether (5 × 10 mL) to give **9** as a colorless oil (0.14 g, 96% yield).

9: ^{31}P {^{1}H} NMR (CDCl$_3$) δ 36.7; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, $^3J_{HH}$ = 6.6 Hz, 9H), 1.32−1.72 (m, 12H), 2.34 (m, 6H), 2.39 (s, 3H), 4.23 (d, $^2J_{HP}$ = 9.0 Hz, 1H); ^{13}C {^{1}H} NMR (CDCl$_3$) δ 13.3, 17.8 (d, $^1J_{CP}$ = 49.3 Hz), 18.7 (d, $^1J_{CP}$ = 46.8 Hz), 23.5 (d, $^3J_{CP}$ = 4.8 Hz), 23.8 (d, $^2J_{CP}$ = 15.5 Hz), 30.1, 192.5. Anal. Calcd for $C_{15}H_{32}ClOPS$: C, 55.11; H, 9.87; S, 9.81. Found: C, 55.58; H, 9.86; S, 9.16.

Methylene Thioanisoyl Phosphonium Salt 10. A solution of anisoyl chloride (0.120 g, 0.69 mmol) in 1.5 mL of CH_2Cl_2 was added dropwise to a stirred solution of **4a** (0.370 g, 0.69 mmol) in 3 mL of CH_2Cl_2 at −78 °C. After the solution was warmed to room temperature, the solvent was evaporated and the residue washed with pentane (2 × 5 mL) and then with toluene (3 mL). Acetonitrile was added (3 mL); the solution was kept for several hours at −20 °C and then filtered. After solvent removal, **10** was obtained as an oil which slowly crystallized (0.120 g, 83% yield).

10: ^{31}P{^{1}H} NMR (CDCl$_3$) δ 36.6; ^{1}H NMR (CDCl$_3$) δ 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 9H), 1.53 (m, 12H), 2.49 (m, 6H), 3.87 (s, 3H), 4.48 (d, $^2J_{HP}$ = 8.8 Hz, 2H), 6.95 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.91 (d, $^3J_{HH}$ = 9.0 Hz, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 13.1, 17.2 (d, $^1J_{CP}$ = 47.9 Hz), 18.67 (d, $^1J_{CP}$ = 46.6 Hz), 23.4 (d, $^3J_{CP}$ = 4.1 Hz), 23.6 (d, $^2J_{CP}$ = 15.9 Hz), 55.5, 114.0, 127.2, 129.7, 164.6, 186.3. Anal. Calcd for $C_{21}H_{36}ClO_2PS$: C, 60.20; H, 8.66; S, 7.65. Found: C, 59.81; H, 8.39; S, 7.38.

Methylene Thiophosphorylated Phosphonium Salt 11a. A solution of chlorodiphenylphosphane (0.380 g, 1.72 mmol) in 3 mL of dichloromethane was added dropwise to a stirred solution of **3a** (0.920 g, 1.72 mmol) in 7 mL of dichloromethane at −78 °C. The reaction mixture was stirred until the temperature gradually rose to rt. The resulting yellow solution was evaporated and the oily residue washed with pentane (2 × 5 mL). Toluene (5 mL) was added, a precipitate was filtered off, and evaporation of the solvent left **11a** as a yellow oil (0.414 g, 96% yield).

11a: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 70.0 (d, $^3J_{PP}$ = 10.2 Hz), 36.7 (d, $^3J_{PP}$ = 10.2 Hz); ^{1}H NMR (CD$_2$Cl$_2$) δ 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 9H), 1.48 (m, 12H), 2.41 (m, 6H), 4.15 (dd, $^3J_{HP}$ = 9.2 Hz, $^2J_{HP}$ = 12.5 Hz, 2H), 7.15−7.95 (m, 10H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 13.3, 19.3 (d, $^1J_{CP}$ = 46.4 Hz), 20.5 (d, $^1J_{CP}$ = 47.1 Hz), 23.8 (d, $^3J_{CP}$ = 6.3 Hz), 23.9 (d, $^3J_{CP}$ = 27.2 Hz), 129.1 (d, $^2J_{CP}$ = 13.6 Hz), 131.5 (d, $^3J_{CP}$ = 11.5 Hz), 132.8 (d, $^1J_{CP}$ = 86.1 Hz), 132.9; MS *m/z* 468. Anal. Calcd for $C_{25}H_{39}ClP_2S_2$: C, 59.92; H, 7.84. Found: C, 60.39; H, 7.50.

Methylene Thiophosphorylated Phosphonium Salt 11b. A suspension of the phosphine−carbon disulfide adduct **3b** (0.120 g, 0.77 mmol) in 4 mL of CH_2Cl_2 was added to a stirred suspension of the Schwartz reagent (0.200 g, 0.77 mmol) in 1 mL of CH_2Cl_2 at −20 °C. The resulting mixture was stirred for 3 h and then cooled to −78 °C. Chlorodiphenylphosphine (0.170 g, 0.77 mmol) in CH_2Cl_2 (1.5 mL) solution was added; the reaction mixture was allowed to warm up to room temperature and then was stirred for 10 h. The solution was filtered and the solvent removed. Acetonitrile (3 mL) was added and the precipitate filtered again. The filtrate was evaporated and the residue washed with toluene (3 × 40 mL) to give **11b** as a brown powder (0.129 g, 90% yield). Recrystallization from acetonitrile gives crystals suitable for X-ray diffraction studies.

11b: ^{31}P{^{1}H} (CDCl$_3$) δ 69.1 (d, $^3J_{PP}$ = 7.5 Hz), 31.8 (d, $^3J_{PP}$ = 7.5 Hz); ^{1}H NMR (CDCl$_3$) δ 2.00 (d, $^2J_{HP}$ = 14.4 Hz, 9H), 4.01 (dd, $^3J_{HP}$ = 9.2 Hz, $^2J_{HP}$ = 14.2 Hz, 2H), 7.28−7.75 (m, 10H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 8.2 (d, $^1J_{CP}$ = 55.1 Hz), 23.3 (d, $^1J_{CP}$ = 53.0 Hz), 128.6 (d, $^2J_{CP}$ = 13.7 Hz), 131.0 (d, $^3J_{CP}$ = 11.4 Hz), 132.2 (d, $^1J_{CP}$ = 86.5 Hz), 132.4. Anal. Calcd for $C_{14}H_{21}ClP_2S_2$: C, 44.86; H, 5.65. Found: C, 45.21; H, 5.47.

Methylene Thiophosphorylated Phosphonium Salt 12a. A solution of bis(diisopropylamino)chlorophosphine (0.200 g, 0.76 mmol) in 2 mL of THF was added dropwise to a stirred solution of **3a** (0.410 g, 0.76 mmol) in 3 mL of THF at −40 °C. The solution was warmed up to room temperature and then stirred for 1 h. After evaporation of the solvent the brown oily residue was washed with pentane (5 mL) and then dried. Toluene (5 mL) was added, and the precipitate formed was separated by filtration. Removal of solvent gave **12a** as a brown oil (0.173 g, 83% yield).

12a: ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 83.1 (d, $^3J_{PP}$ = 25.7 Hz), 36.7 (d, $^3J_{PP}$ = 25.7 Hz); ^{1}H NMR (C$_6$D$_6$) δ 1.00 (t, $^3J_{HH}$ = 7.3 Hz, 9H), 1.29 (d, $^3J_{HH}$ = 6.7 Hz, 12H), 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 12H), 1.54 (pseudo sext, $^3J_{HH}$ = 7.2 Hz, 6H), 1.76 (m, 6H), 2.92 (m, 6H), 3.62 (sept, $^3J_{HH}$ = 6.7 Hz, 2H), 3.67 (sept, $^3J_{HH}$ = 6.7 Hz, 2H), 4.67 (dd, $^2J_{HP}$ = $^3J_{HP}$ = 11.1 Hz, 2H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 14.3, 20.4 (d, $^1J_{CP}$ = 46.9 Hz), 22.7, 22.8 (d, $^1J_{CP}$ = 47.2 Hz), 24.3, 24.8 (d, $^3J_{CP}$ = 4.4 Hz), 24.8 (d, $^2J_{CP}$ = 15.5 Hz), 46.9, 48.5 (d, $^2J_{CP}$ = 4.0 Hz). Anal. Calcd for $C_{25}H_{57}ClN_2P_2S_2$: C, 54.87; H, 10.50. Found: C, 54.27; H, 10.18.

Methylene Thiophosphorylated Phosphonium Salt 12b. A suspension of the phosphine−carbon disulfide adduct (Me_3PCS_2) (0.087 g, 0.55 mmol) in 5 mL of CH_2Cl_2 was added at −20 °C to a stirred suspension of the Schwartz reagent (0.138 g, 0.55 mmol) in 1 mL of dichloromethane. After being stirred for 2 h, the solution was cooled to −78 °C, and a solution of bis(diisopropylamino)chlorophosphine (0.148 g, 0.55 mmol) in 1 mL of CH_2Cl_2 was added via cannulae. After being warmed to rt and stirred for 10 h, the solution was filtered off and the solvent removed to give a brown residue which was washed with pentane (8 × 10 mL) and dried under vacuum. Acetonitrile was added, and the precipitate of Cp_2ZrCl_2 was filtered off. Removal of the solvent gave **12b** as a brown powder (0.050 g, 47% yield).

12b: ^{31}P{^{1}H} NMR (CDCl$_3$) δ 82.7 (d, $^3J_{PP}$ = 19.7 Hz), 31.6 (d, $^3J_{PP}$ = 19.7 Hz); ^{1}H NMR (CDCl$_3$) δ 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 12H), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 12H), 2.25 (d, $^2J_{HP}$ = 14.3 Hz, 9H), 3.71 (sept, $^3J_{HH}$ = 6.9 Hz, 2H), 3.75 (sept, $^3J_{HH}$ = 6.9 Hz, 2H), 3.93 (dd, $^2J_{HP}$ = 12.9 Hz, $^3J_{HP}$ = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 9.2 (d, $^1J_{CP}$ = 55.4 Hz), 22.4, 23.7, 26.3 (d, $^1J_{CP}$ = 53.3 Hz), 48.0, 48.1; MS *m/z* 385. Anal. Calcd for $C_{16}H_{39}ClN_2P_2S_2$: C, 45.64; H, 9.34. Found: C, 45.10; H, 9.09.

Methylene Thiophosphorylated Phosphonium Salt 13. Tris(dimethylamino)phosphine (0.018 g, 0.11 mmol) was added to a stirred solution of **3a** (0.052 g, 0.10 mmol) in 1 mL of CH_2Cl_2 at rt. The resulting solution was stirred for 2 h and then evaporated to give an oily residue which was washed with pentane (2 × 3 mL). **13** was extracted with toluene (2 mL) (0.018 g, 84% yield).

13: ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 99.7 (d, $^3J_{PP}$ = 20.1 Hz), 36.1 (d, $^3J_{PP}$ = 20.1 Hz); ^{1}H NMR (C$_6$D$_6$) δ 0.98 (t, $^3J_{HH}$ = 7.0 Hz, 9H), 1.47 (m, 6H), 1.66 (m, 6H), 2.51 (d, $^3J_{HP}$ = 13.8 Hz, 12H), 2.77 (m, 6H), 4.56 (dd, J_{HP} = 10.5, 10.7 Hz, 2H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 14.3, 20.3 (d, $^1J_{CP}$ = 46.8 Hz), 22.6 (d, $^1J_{CP}$ = 44.7 Hz), 24.8, 24.9 (d, $^2J_{CP}$ = 20.5 Hz), 37.8; MS *m/z* 398. Anal. Calcd for $C_{17}H_{41}ClN_2P_2S_2$: C, 46.93; H, 9.50. Found: C, 46.71; H, 9.32.

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Supporting Information Available: ORTEP drawing and details of the data acquisition for compound **11b** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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