# Metal Phosphinylides and Phosphinothioylides. I. Formation of Metal Diphenylphosphinylides and Diphenylphosphinothioylides and the Reactions with Some Organic Halides and Aldehydes

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Lithium diphenylphosphinylide or diphenylphosphinothioylide ([$Ph_2PX$]Li; X=O, S), prepared from diphenylphosphine oxide or sulfide and *n*-butyllithium, reacted with methyl iodide, acetaldehyde and benzaldehyde to give the corresponding phosphine oxides or sulfides in good yields, indicating the formation of C–P bond. Formation of [$Ph_2PS$]MgCl from diphenylphosphinothioyl chloride (**1**) and magnesium was confirmed by the similar reactions. When **1** was allowed to react with magnesium or sodium for a long time, diphenylphosphides ([$Ph_2P$]-M) were produced by desulfurization, together with [$Ph_2PS$]M (M=MgCl, Na). Reaction of **1** with [$Ph_2PS$]M gave tetraphenyldiphosphine disulfide through formation of P-P bond, while diphenylphosphinyl chloride and [$Ph_2PO$]M reacted through formation of P–O bond. The difference has been explained by soft-hard-acid-base concept.

Tetraphenyldiphosphine disulfide is prepared by the reaction of diphenylphosphinothioyl chloride (**1**) with an alkyl Grignard reagent. The reaction mechanism has been considered as follows.[1)]

$$\underset{\mathbf{1}}{Ph_2P(S)Cl} + RMgBr \longrightarrow \underset{\mathbf{2'}}{Ph_2P(S)MgBr} + RCl$$

$$\mathbf{2'} + \mathbf{1} \longrightarrow Ph_2P(S)\text{-}P(S)Ph_2 + MgClBr \qquad (1)$$

Phosphinothioylmagnesium bromide (**2'**) has been assumed as the intermediate,[1)] but there is no report on the direct formation of phosphinothioylmagnesium chloride (**2**) from **1** and magnesium. There are several reports[2,3)] on formation of metal diphenylphosphinylides by reaction of dialkyl phosphite with excess amounts of phenylmagnesium bromide[2)] and by reaction of diphenylphosphinyl chloride with sodium or magnesium.[3)]

Metal diphenylphosphinylides and diphenylphosphinothioylides have two reaction centers, that is, the phosphorus and the oxygen or sulfur atoms.

$$Ph_2P(X)\text{-}M \rightleftharpoons Ph_2P\text{-}X\text{-}M \qquad [X=O, S]$$

In this paper, such compounds are represented as [$Ph_2PX$]M. It has been reported that metal derivatives (M=Li, Na, K, MgCl) of dialkyl phosphites exist as $(RO)_2P$–O–M from the $^{31}$P-NMR data.[4)] $^{31}$P-NMR measurements of [$Ph_2PX$]M are under investigation and will be reported in the near future.

This paper describes formation of **2** and other metal diphenylphosphinothioylides by metallation of diphenylphosphine sulfide (**3b**) and by reaction of some metals with **1**, and comparison of their reactions with those of metal diphenylphosphinylides prepared by similar methods.

First, lithium derivatives (**4**) were prepared from diphenylphosphine oxide (**3a**) or sulfide (**3b**) and *n*-butyllithium in tetrahydrofuran (THF) at 0 °C.

$$\underset{\mathbf{3}}{Ph_2P(X)H} + n\text{-}Bu\text{-}Li \longrightarrow \underset{\mathbf{4}}{[Ph_2PX]Li}$$

a, X=O; b, X=S

Reactions of **4a** with methyl iodide, acetaldehyde and benzaldehyde gave methyldiphenylphosphine oxide (**5a**) (93%), α-hydroxyethyldiphenylphosphine oxide (**6a**) (95%), and α-hydroxybenzyldiphenylphosphine oxide (**7a**) (63%), respectively. Similar reactions of **4b** gave the corresponding sulfides (**5b**, **6b** and **7b**) in 66, 81 and 63% yields, respectively.

In the case of reaction of **4b** with methyl iodide, methyl diphenylphosphinothionite could not be detected in the crude reaction mixture by means of NMR.

$$\underset{\mathbf{4}}{[Ph_2PX]Li} \xrightarrow{MeI} \underset{\mathbf{5}}{Ph_2P(X)Me}$$

$$\xrightarrow{RCHO} Ph_2P(X)CHOH\text{-}R$$

a, X=O; b, X=S

**6**, R=Me; **7**, R=Ph

In all cases, the reaction center seems to be the phosphorus atom.

Reactions of **1** with magnesium was carried out to prepare **2**. An equimolar mixture of **1** and magnesium was refluxed for 1 hr in THF. Treatment of the reaction mixture with water gave **3b** in 37% yield, indicating the formation of **2**.

Grignard-type reagent (**2**), prepared under the same condition, reacted with benzyl chloride, benzaldehyde and **1** to give benzyldiphenylphosphine sulfide (**8**), **7b** and tetraphenyldiphosphine disulfide (**9**) in 44, 31 and 36% yields, respectively. Formation of **9** from **1** and **2** supported the reaction (1).

$$\underset{\mathbf{1}}{Ph_2P(S)Cl} + Mg \xrightarrow[\text{refl. THF}]{1\text{ hr}} \underset{\mathbf{2}}{[Ph_2PS]MgCl}$$

$$\underset{\mathbf{3b}}{Ph_2P(S)H} \xleftarrow{H_2O} [Ph_2PS]MgCl \xrightarrow{PhCHO} Ph_2P(S)CHPh\text{-}OH \quad (\mathbf{7b})$$

$$\underset{\mathbf{8}}{Ph_2P(S)CH_2Ph} \xleftarrow{PhCH_2Cl} [Ph_2PS]MgCl \qquad \underset{\mathbf{1}}{Ph_2P(S)\text{-}P(S)Ph_2} \quad (\mathbf{9})$$

(**2**)

From the above results, it is expected that yields of **2** were below 50% under the above condition. Then, two equivalents of magnesium were used and the mixture was refluxed for 8—10 hr. Hydrolysis of the reaction mixture gave **3b** in only 0.6% yield, and produced **3a** and diphenylphosphinic acid in 77 and 14% yields, respectively, indicating the formation of $[Ph_2P]MgCl$ by desulfurization.

$$Ph_2P(S)Cl\ (\mathbf{1}) + 2\,Mg \xrightarrow[\text{refl. THF}]{\text{8—10 hr}} [Ph_2PS]MgCl + [Ph_2P]MgCl$$

$$[Ph_2PS]MgCl \xrightarrow{H_2O} Ph_2P(S)H\ (\mathbf{3b})$$

$$[Ph_2P]MgCl \xrightarrow{H_2O} Ph_2PH \xrightarrow{O_2} Ph_2P(O)H\ (\mathbf{3a}) \xrightarrow{O_2} Ph_2P(O)OH$$

The formation of **3a** and diphenylphosphinic acid is attributed to successive oxidation of diphenylphosphine initially formed during treatment.

The desulfurization was also indicated by formation of **7a** (7.5%) and **7b** (18%) in reaction with benzaldehyde.

Reaction of **1** with excess amounts of sodium in toluene for 115 hr at room temperature gave **9** (3.8%) and diphenylphosphinic acid (30%) after hydrolysis. The formation of the latter also indicates occurrence of desulfurization.

$$Ph_2P(S)Cl\ (\mathbf{1}) + Na \xrightarrow[\text{in PhMe}]{\text{115 hr, r. t.}} [Ph_2PS]Na + [Ph_2P]Na$$

$$[Ph_2PS]Na \xrightarrow{\mathbf{1}} Ph_2P(S)\text{-}P(S)Ph_2\ (\mathbf{9})$$

$$[Ph_2P]Na \xrightarrow{H_2O} Ph_2PH \xrightarrow{O_2} Ph_2P(O)OH$$

From the above results, it is suggested that reaction of **1** with the corresponding metal derivative ($[Ph_2PS]$-M) gives diphosphine disulfide, indicating the formation of P(S)–P(S) bond.

Reaction of diphenylphosphinyl chloride (**10**) with twice molar amounts of sodium was carried out in refluxed toluene for 5 hr. The resulting precipitates contained sodium diphenylphosphinylide (**11**) from result of hydrolysis, and reacted with **10** to give diphenylphosphinic acid in 55% yield.

$$Ph_2P(O)Cl\ (\mathbf{10}) + 2\,Na \rightarrow [Ph_2PO]Na\ (\mathbf{11}) \xrightarrow{\mathbf{10}} (Ph_2P(O)\text{-}OPPh_2)\ (\mathbf{12})$$

$$(\mathbf{12}) \xrightarrow{O_2} (Ph_2P(O)\text{-}O\text{-}P(O)Ph_2)\ (\mathbf{13}) \xrightarrow{H_2O} 2\,Ph_2P(O)OH$$

In this case, the crude product was found to contain diphenylphosphinic diphenylphosphonous anhydride (**12**) by IR and mass spectra. Therefore, the formation of diphenylphosphinic acid is attributed to oxidation[5] and hydrolysis of **12** during isolation and purification, because diphenylphosphinic anhydride (**13**) undergoes hydrolysis easily.[6]

Thus reaction of **10** with the corresponding metal derivative ($[Ph_2PO]M$) was found to afford the product through the formation of P–O–P(O) bond.

The difference in the reactions of $[Ph_2PX]M$ with $Ph_2P(X)Cl$ may be explicable in terms of soft-hard-acid-base.[7] The phosphorus and oxygen atoms of $[Ph_2PO]M$ are soft and hard, respectively, and the phosphorus atom of **10** is hard.[8] Thus, in the reaction of **11** with **10**, P–O–P(O) bond is formed. The phosphorus and sulfur atoms of $[Ph_2PS]M$ and also the phosphorus atom of **1** are all soft,[8] and moreover, tervalent phosphorus atom is more nucleophilic than sulfide anion.[9] Therefore, in the reaction of **2** with **1**, P(S)–P(S) bond is formed.

The following reactions support this consideration.[5,10]

$$Ph_2P(O)H \xrightarrow[Et_3N]{Ph_2PCl} Ph_2P(O)\text{-}PPh_2\ ^{10)}$$

$$Ph_2P(O)H \xrightarrow[\mathbf{10},\ Et_3N]{} Ph_2P\text{-}OP(O)Ph_2\ ^{5)}$$

One possible mechanism of desulfurization in preparation of $[Ph_2PS]M$ may be disproportionation as follows, because the reaction of **1** with magnesium in THF at 150 °C gave a small amount of diphenylphosphinodithioic acid.[11]

$$2[Ph_2PS]^- \longrightarrow Ph_2P^- + Ph_2P(S)S^-$$

In the preparation of $[Ph_2PS]M$ from **1** and metal, desulfurization took place by using excess amounts of metal or by heating for a long time. Therefore, the best method to prepare $[Ph_2PS]M$ is that from **3b** through hydrogen-metal exchange reaction, because of homogeneous and rapid reaction.

## Experimental

All melting and boiling points are uncorrected. The IR spectra were recorded on Hitachi EPI-G2 spectrophotometer, NMR spectra were measured with Hitachi R-24 and R-20B spectrometers using TMS as an internal standard, and $^{31}P$-NMR spectra were measured with a Hitachi R-20B spectrometer equipped with a phosphorus measurement unit R-204-PB (24.3 Hz) using 85% phosphoric acid as an external standard. Mass spectra were determined with Hitachi RMU-6L mass spectrometer. All reactions were carried out under nitrogen.

*Materials.* The following materials were prepared by the methods reported in the literature: diphenylphosphinothioyl chloride,[12] bp 155—157 °C/0.3 mmHg; diphenylphosphinyl chloride,[13] bp 155 °C/0.1 mmHg; diphenylphosphine sulfide,[14] mp 93—94 °C; diphenylphosphine oxide,[15] mp 45—48 °C. *n*-Butyllithium was used as 15% *n*-hexane solution.

*Reactions of Lithium Diphenylphosphinylide (**4a**).* *a) With Methyl Iodide*: A solution of **4a** prepared from diphenylphosphine oxide (**3a**) (2.66 g, 13.2 mmol) and *n*-butyllithium (13.2 mmol) in THF (50 ml) was stirred with methyl iodide (2.00 g, 14.0 mmol) in THF (10 ml) for 2.5 hr. After removal of THF, the residue was treated with water, and extracted with ether. After removal of ether from the dried extract, crude methyldiphenylphosphine oxide (**5a**) was recrystallized from *n*-hexane-benzene, mp 113.5—115 °C (lit,[16] 113—114 °C), yield 2.66 g (93%). NMR ($CDCl_3$): $\delta$ 2.02 (d, $J_{PCH}$ 13.6 Hz, 3H, Me) and 7.3—8.0 (m, 10H, 2Ph); $\delta_P$ ($CHCl_3$): −29.7 ppm.

*b) With Acetaldehyde*: A solution of **4a** prepared from **3a** (2.11 g, 10.4 mmol) and *n*-butyllithium (11 mmol) in THF (60 ml) was stirred with acetaldehyde (0.66 g, 14.9 mmol) for 2 hr. Similar work-up gave α-hydroxyethyldiphenylphosphine oxide (**6a**) (2.54 g, 95%), mp 131—132 °C (from benzene). IR (KBr): 3150 (OH) and 1170 $cm^{-1}$ (P=O); NMR ($CDCl_3$): $\delta$ 1.38 (d d, $J_{PCCH}$ 15.4, $J_{HH}$ 7.2 Hz, 3H, Me), 4.57 (q, $J_{PCH}$ *ca.* 0 Hz, 1H, CH), 5.02 (s, 1H, OH), and 7.3—8.1 (m, 10H, 2Ph); $\delta_p$ ($CHCl_3$): −32.9 ppm.

Found: C, 68.31; H, 6.00%. Calcd for $C_{14}C_{15}O_2P$: C, 68.29; H, 6.14%.

*c) With Benzaldehyde*: A solution of **4a** prepared from **3a** (1.98 g, 9.4 mmol) and *n*-butyllithium (10.4 mmol) in THF (40 ml) was refluxed with benzaldehyde (1.7 g, 16 mmol) in THF (15 ml) for 1.5 hr. The reaction mixture was poured into a mixture of ice and hydrochloric acid, and ether was added. Evaporation of the ethereal layer gave α-hydroxybenzyldiphenylphosphine oxide (**7a**) (1.9 g, 63%), mp 172—174 °C (from ethanol) (lit,[3a] 176 °C). $\delta_p$ (DMF): −26.9 ppm.

*Reactions of Lithium Diphenylphosphinothioylide (**4b**).* *a) With Methyl Iodide*: To a solution of diphenylphosphine sulfide (**3b**) (5.01 g, 23 mmol) in THF (50 ml) was added dropwise *n*-butyllithium (24 mmol) in hexane under ice-cooling with stirring over 30 min. The mixture was stirred at room temperature for 30 min. To the solution was added dropwise 3.47 g (24.4 mmol) of methyl iodide in 10 ml of THF with stirring under ice-cooling, and the mixture was stirred for 2 hr at room temperature. After removal of THF, the residue was treated with water, and extracted with ether. Removal of the ether from the dried extract gave oily material. The NMR spectrum was quite the same with that of the distillate (**5b**), bp 170—171 °C/1 mmHg (lit,[17] 181 °C/1.5 mmHg), yield 3.52 g (66%). NMR ($CCl_4$): $\delta$ 2.07 (d, $J_{PCH}$ 13.6 Hz, 3H, Me) and 7.2—8.0 (m, 10H, 2Ph); $\delta_p$ ($CHCl_3$): −35.9 ppm.

*b) With Acetaldehyde*: To a solution of **4b** prepared from **3b** (4.01 g, 18.4 mmol) in THF (50 ml) and *n*-butyllithium (19 mmol), acetaldehyde (0.83 g, 19 mmol) was added dropwise at room temperature and the mixture was stirred for 2 hr. Similar work-up gave oily materials, which solidified on standing to give **6b**, mp 84—86 °C (from *n*-hexane-ether), yield 3.91 g (81%). IR (KBr): 3300 (OH) and 590 $cm^{-1}$ (P=S); NMR ($CDCl_3$): $\delta$ 1.30 (d d, $J_{PCCH}$ 17, $J_{HH}$ 7.2 Hz, 3H, Me), 2.87 (s, 1H, OH), 4.72 (d q, $J_{PCH}$ 2.6, $J_{HH}$ 7.2 Hz, 1H, CH), and 7.3—8.2 (m, 10H, 2Ph); $\delta_p$ ($CHCl_3$): −49.0 ppm.

Found: C, 64.16; H, 5.57%. Calcd for $C_{14}H_{15}OPS$: 64.10; H, 5.77%.

*c) With Benzaldehyde*: A solution of **4b** prepared from **3b** (2.14 g, 9.8 mmol) and *n*-butyllithium (10 mmol) in THF (50 ml) was stirred with benzaldehyde (1.78 g, 16.8 mmol) for 20 hr. Similar work-up gave colorless crystals, which were recrystallized from carbon tetrachloride to give **7b**, mp 121—122.5 °C, yield 1.99 g (63%). IR (KBr): 3250 (OH) and 610 $cm^{-1}$ (P=S); NMR ($CDCl_3$); $\delta$ 3.92 (s, 1H, OH), 5.54 (d, $J_{PCH}$ 1.8 Hz, 1H, CH), and 6.8—8.15 (m, 15H, 3Ph); $\delta_p$ ($CHCl_3$): −52.3 ppm.

Found: C, 70.39; H, 5.30; S, 9.95%. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.29; S, 9.88%.

*Preparation of Diphenylphosphinothioylmagnesium Chloride (**2**) and the Hydrolysis.* *a) Shorter Reaction Time*: A mixture of diphenylphosphinothioyl chloride (**1**) (5.1 g, 20 mmol) and magnesium turnings (0.73 g, 30 mg atom) in THF (100 ml) was heated under reflux for 1 hr. The reaction mixture was decanted and the solution was evaporated *in vacuo*. After addition of ether to the residue, 10% aqueous ammonium chloride was poured into the ether solution, and the ether was removed from the dried ethereal layer. The residual oily material was crystallized with acetonitrile to give **3b** (1.6 g, 37%), mp 93—94 °C (lit,[14] 95—97 °C).

*b) Longer Reaction Time*: A mixture of **1** (4.5 g, 18 mmol) and magnesium turnings (875 mg, 36 mg atom) in THF (50 ml) was heated under reflux with vigorous stirring for 10 hr. Remaining magnesium (0.14 g, 6 mg atom) was removed by decantation and the solution was evaporated. The residue was dissolved in 50 ml of benzene and a small amount of water was added. The benzene layer was dried and removal of the benzene gave oily material, which was crystallized with ether to give diphenylphosphinic acid (0.56 g, 14%), mp 190—191 °C (lit,[18] 194 °C). After evaporation of the filtrate the residue was chromatographed on silica gel with dichloromethane to afford 2.8 g (77%) of **3a**, mp 46—48 °C (lit,[15] 51—54 °C), and 22 mg (0.6%) of **3b**, mp 92—93 °C.

*Reactions of **2**.* *a) With Benzyl Chloride*: A solution of **2** was prepared from **1** (5.1 g, 20 mmol), magnesium (0.5 g, 20 mg atom) and THF (60 ml) under a condition of shorter reaction time described above. To the solution was added benzyl chloride (2.6 g, 21 mmol) in THF (10 ml) at room temperature. After stirring for 20 min, the mixture was heated under reflux for 2 hr. After removal of THF, the residual oil dissolved in dichloromethane was dried with anhydrous sodium sulfate. After removal of the dichloromethane, the residual oil was mixed with a small amount of ethanol to precipitate benzyldiphenylphosphine sulfide (**8**) (2.7 g, 44%), mp 160—161 °C (from ethanol) (lit,[19] 162—163 °C).

*b) With Benzaldehyde*: 1) To a solution of **2** prepared by the same method described in a), was added dropwise benzaldehyde (2.12 g, 20 mmol) in THF (15 ml) at room temperature. After stirring for 1 hr, the mixture was heated gradually and then refluxed for 10 min. THF was removed, the residue was treated with 10% aqueous ammonium chloride, and extracted with dichloromethane. After evaporation of the dried extract, the residue was recrystallized from 2-propanol to give **7b** (2.0 g, 31%), mp 113—114 °C, which was identified by the IR spectrum.

2) A mixture of **1** (5.1 g, 20 mmol), magnesium (0.97 g, 40 mg atom) in 100 ml of THF was refluxed for 8 hr. After decantation, to the solution was added dropwise 2.1 g (20 mmol) of benzaldehyde in 10 ml of THF at room temperature, and the mixture was refluxed for 2 hr. The residue, which was obtained by a similar treatment to that described in 1), gave colorless crystals by addition of ether. The crystals were recrystallized from ethanol to give pure **7a** (0.49 g, 7.5%), mp 173—175 °C (lit,[3a] 176 °C). Standing of the ethereal filtrate gave 1.1 g (18%) of **7b**.

*c) With Diphenylphosphinothioyl Chloride (**1**)*: A mixture of **1** (7.9 g, 31 mmol), magnesium (0.82 g, 34 mg atom) and THF (60 ml) was refluxed for 1 hr. To the solution was added dropwise **1** (7.7 g, 30 mmol) in THF (40 ml) at room temperature. The mixture was refluxed for 6 hr. After filtration of magnesium chloride and removal of THF from the filtrate, the residual semi-solid was washed twice with water and extracted with dichloromethane. Removal of dichloromethane from the extract gave oily material, which crystallized by addition of a small amount of ethanol. The crystals were recrystallized from acetone-ethanol (9 : 1) to give **9** (4.7 g, 36%), mp 165—167 °C (lit,[20] 168.5 °C).

*Reaction of **1** with Sodium.* A solution of **1** (1.7 g, 6.8 mmol) in toluene (10 ml) was added dropwise to sodium (1.2 g, 52 mg atom) in toluene (10 ml) at room temperature, the mixture was stirred for 115 hr and poured into water,

The organic layer was evaporated after drying. Extraction with a small amount of acetonitrile gave diphenylphosphinic acid (4.4 g, 30%), mp 188—190 °C, as insoluble material. The acetonitrile solution gave a solid after evaporation. Recrystallization from ether gave **9** (56 mg, 3.8%), mp 167—168.5 °C.

*Reaction of Sodium Diphenylphosphinylide with Diphenylphosphinyl Chloride. (**10**).* To a suspension of sodium (0.97 g, 42 mg atom) in toluene (50 ml) was added dropwise **10** (4.9 g, 21 mmol) in toluene (50 ml), and the mixture was refluxed for 5 hr. Precipitates thus obtained were filtered off under nitrogen. Hydrolysis of a small amount of the precipitates gave **3a**. To a suspension of the dry precipitates (1.2 g), which contain an equimolar amount of sodium chloride, in xylene (25 ml) was added dropwise **10** (1.0 g, 4.2 mmol) in xylene (25 ml) at room temperature, and the mixture was refluxed for 12 hr. Treatment of the reaction mixture with water gave insoluble solid, which was identified as diphenylphosphinic acid (1.0 g, 55%) by IR. Evaporation of the organic layer gave white solid, which was found to be diphenylphosphinic acid mainly by IR. The IR spectrum showed a band at 960 $cm^{-1}$ (P–O–P). The mass spectrum also showed the absence of tetraphenyldiphosphine dioxide ($M^+$, *m/e* 402) and the presence of diphenylphosphinic anhydride ($M^+$, *m/e* 418).

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