BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (2), 545—546 (1977)

Metal Phosphinylides and Phosphinothioylides. VII.[1] The Structure of $[Ph_2PX]M$ (X=O, S) in Solution and Their Disproportionation

Koshiro GODA, Hideyuki GOMI, Masaaki YOSHIFUJI, and Naoki INAMOTO
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received August 31, 1976)

Synopsis. The species $[Ph_2PO]M$ in THF were found to exist as Ph_2P–O–M by ^{31}P-NMR, and $[Ph_2PS]MgCl$ as Ph_2P–S–MgCl by Raman spectrum. The species $[Ph_2PS]M$ undergo easy disproportionation by heating.

The species $[Ph_2PX]M$ (X=O, S) have been prepared by the reaction of sodium or magnesium with diphenylphosphinic (**1a**)[2,3] or diphenylphosphinothioic chloride (**1b**)[3] (Method A) and by the reaction of butyllithium[3] or Grignard reagents[4] with diphenylphosphine oxide (**2a**) or sulfide (**2b**) (Method B).

$$\underset{\mathbf{1}}{Ph_2P(X)Cl} + M \longrightarrow \underset{\mathbf{3}}{[Ph_2PX]M} \qquad \text{(Method A)}$$

a, X=O; b, X=S

$$\underset{\mathbf{2}}{Ph_2P(X)H} + R'M \text{ (or M)} \longrightarrow \underset{\mathbf{3}}{[Ph_2PX]M} \qquad \text{(Method B)}$$

a, X=O; b, X=S

The following equilibrium is possible in a solution of **3**.

$$\underset{\mathbf{4}}{Ph_2P\text{–}X\text{–}M} \rightleftarrows \underset{\mathbf{4'}}{Ph_2P(X)M}$$

It was found from ^{31}P-NMR data that $[(EtO)_2PO]M$ exists as $(EtO)_2P$–O–M in solution.[5] The present paper describes the results of a reexamination of the reactions of **1** with metals by means of ^{31}P-NMR and the structure of **3** in solution.

The reactions by Methods A and B were carried out in tetrahydrofuran (THF) at room temperature under nitrogen. The ^{31}P-NMR data are given in Tables 1 and 2. The yields of **3** were nearly quantitative based on the ^{31}P-NMR spectra, except for the case of M=MgCl in Method A (Table 1). We see that reactions of **1**, especially **1b**, with metals are very complicated,

TABLE 1. ^{31}P-NMR DATA OF REACTION MIXTURE OF **1** WITH METAL (M) IN THF (METHOD A)

M	X=O δ_P (ppm)	X=O Assignment	X=S δ_P (ppm)	X=S Assignment	Yield (%)[a]
none	−42.8	**1a**	−79.8	**1b**	
Li	−93.8	$[Ph_2PO]$-Li	16.2	Ph_2PPPh_2	2
			−37.0	$Ph_2P(S)$-$P(S)Ph_2$	20
			−59.8	$Ph_2P(S)SLi$	46
Mg	−17.7	$[Ph_2PO]$-MgCl	15.9	Ph_2PPPh_2	4
			−37.9	$Ph_2P(S)$-$P(S)Ph_2$	23
			−59.0	$Ph_2P(S)$-SMgCl	46

a) Based on the peak areas in the ^{31}P-NMR spectra.

TABLE 2. ^{31}P-NMR DATA OF $[Ph_2PX]M$ IN THF (METHOD B)

RM or M	X=O δ_P (ppm)	X=O Assignment	X=S δ_P (ppm)	X=S Assignment
none	−22.9 (J=490 Hz)	**2a**	−20.8 (J=468 Hz)	**2b**
n-BuLi	−93.8	$[Ph_2PO]$-Li	−20.7	$[Ph_2PS]$-Li
n-BuMgCl	−90.0	$[Ph_2PO]$-MgCl	−14.3	$[Ph_2PS]$-MgCl
NaH			−22.3	$[Ph_2PS]$-Na
K			−25.0	$[Ph_2PS]$-K

indicating dimerization, desulfurization, and disproportionation of **3b**.[3] Thus, for the preparation of **3**, Method B is preferable to Method A.

The phosphorus atom in **3a** is trivalent (**4** type) in THF (Tables 1 and 2), except for the case of M=MgCl in Method A.[6] However, the structure of **3b** could not be determined, due to δ_P values being similar to those of **2b**. Thus, the Raman spectrum of $[Ph_2PS]MgCl$ prepared by Method B was compared with spectra of some model compounds (Table 3). From the results the structure was determined to be **4** type. In the case of M=Li and Na, no Raman spectra could be obtained because of the emission of fluorescence.

TABLE 3. RAMAN SPECTRA

Compound	$\nu_{P=S}$ (cm^{-1})	ν_{P-S} (cm^{-1})
$Ph_2P(S)H$ (THF)	650	—
$Ph_2P(S)OMe$ (THF)	638	—
$Ph_2P(S)SMe$ (THF)	658	537
$Ph_2P(O)SMe$ (THF)	—	568
Ph_2PSEt (neat)	—	515
$[Ph_2PS]MgCl$ (THF)	—	530

Easy disproportionation of **3b** was confirmed by the following experiments. Reaction of **1b** with lithium in THF at room temperature for 24 h afforded *S*-methyl diphenylphosphinodithioate (**5**) and methyldiphenylphosphine sulfide (**6**) in a ratio of 5:1 after treatment first with methyl iodide and then sulfur.

$$2[Ph_2PS]Li \longrightarrow \underset{\mathbf{5}}{Ph_2P(S)SLi} + Ph_2PLi$$

$$\downarrow MeI \qquad \downarrow MeI \qquad S_8 \downarrow MeI$$

$$\underset{\mathbf{6}}{2Ph_2P(S)Me} \qquad \underset{\mathbf{5}}{Ph_2P(S)SMe} \qquad \mathbf{6}$$

Refluxing of a mixture of **2b** and butyllithium in THF also gave **5** and **6** after a similar treatment (see Experi-

mental).

In this connection, a large contribution of metal diphenylphosphinodithioate is considered to take place in the reactions of $[Ph_2PS]M$ with THF.[7]

Experimental

^{31}P-NMR spectra were measured with a Hitachi R-20B-R-204 PB spectrometer using 85% phosphoric acid as an external standard. Raman spectra were taken with a JEOL-JSP-RS 4000 spectrometer.

Materials. Diphenylphosphinic (**1a**) and diphenylphosphinothioic chlorides (**1b**), diphenylphosphine oxide (**2a**) and sulfide (**2b**) were prepared by the methods described in a previous paper.[3] The following compounds were prepared by the reported methods: *O*-methyl diphenylphosphinothioate,[8] *S*-methyl diphenylphosphinodithioate,[9] and ethyl diphenylphosphinothioate.[10]

Preparation of S-Methyl Diphenylphosphinothioate. To a mixture of 13.4 g (57 mmol) of diphenylphosphinothioic acid and 2.5 g (63 mmol) of sodium hydroxide in 50 ml of THF was added 6 ml of methyl iodide, and the mixture was stirred for 3 h at room temperature. After washing with water and extraction with benzene, the extract was distilled *in vacuo*, bp 190 °C/0.2 Torr yield 13.0 g (92%). The distillate solidified on standing, mp 49.0—50.5 °C (from cyclohexane). IR (KBr): 1435, 1118 (P–Ph), 1202 (P=O), and 565 cm^{-1} (P–S); NMR (CCl_4): δ 2.10 (d, $J_{PSCH}=13$ Hz, 3H, SMe) and 7.2—8.0 (m, 10H, P–Ph); ^{31}P-NMR (THF): $\delta_P-38.6$ ppm.

Found: C, 62.91; H, 5.06; S, 13.05%. Calcd for $C_{13}H_{13}OPS$: C, 62.89; H, 5.28; S, 12.91%.

Disproportionation of $[Ph_2PS]Li$. A mixture of 1.405 g (6.4 mmol) of **2b**, 0.336 g (7.9 mmol) of lithium chloride, 12 mmol of butyllithium in hexane (8 ml), and 30 ml of THF was refluxed for 3 h and 1 ml of methyl iodide was added. The presence of methyldiphenylphosphine, **5**, and **6** was shown by means of gas chromatography (H 523 on Diasolid at 210 °C). Sulfur (0.38 g, 1.5 mmol) was added to the reaction mixture and the mixture was refluxed for several minutes. Only **5** and **6** were observed in the ratio 27: 73.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education. The authors thank Dr. Issei Harada and Mr. Shuji Imazeki for the measurement of Raman spectra.

References

1) For VI see: K. Goda and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **49**, 1175 (1976).
2) L. Horner and P. Beck, *Chem. Ber.*, **93**, 1371 (1960); L. Horner, P. Beck, and V. G. Toscano, *ibid.*, **94**, 1317, 1323 (1961).
3) T. Emoto, H. Gomi, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **47**, 2449 (1974); K. Goda, H. Gomi, M. Yoshifuji, and N. Inamoto, *ibid.*, **47**, 2453 (1974).
4) R. F. Cann, S. Warren, and M. R. Williams, *J. Chem. Soc, Perkin Trans. 1*, **1972**, 2377.
5) K. Moedritzer, *J. Inorg. Nucl. Chem.*, **22**, 19 (1961).
6) The structure is unknown but a possible one might be of the **4'** type such as $Ph_2P(O)$–MgCl and $[Ph_2P(O)]_2Mg$.
7) K. Goda, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 2484 (1975).
8) T. A. Mastryukova, T. A. Melent'eva, and M. I. Kobachnik, *Zh. Obshch. Khim.*, **35**, 1197 (1965); *Chem. Abstr.*, **63**, 11605 (1965).
9) W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).
10) A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **42**, 549 (1910).