

# Lithium Bis(2-phenylphosphidoethyl)phenylphosphine: A Reactive Phosphorus Intermediate

Lucas J. Mason, Alexander J. Moore, Amy Carr, and Monte L. Helm

Chemistry Department, Fort Lewis College, Durango, CO 81301

Received 12 May 2006; revised 9 August 2006

**ABSTRACT:** *Bis(2-phenylphosphinoethyl)phenylphosphine, PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>, reacts with lithium in tetrahydrofuran to give the corresponding lithium bis(2-diphenylphosphidoethyl)phenylphosphine, Li<sub>2</sub>[PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]. The lithium diphosphide is identified by NMR spectroscopy and further characterized through arylation with excess bromobenzene to reform the starting phosphine, PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>. Initial reactivity studies of the diphosphide, PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub><sup>-2</sup>, with some alkylhalides are also described. © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:675–678, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20351*

## INTRODUCTION

Organophosphides are of considerable importance in the synthesis of a variety of neutral mono- and bi-dentate phosphorus ligands. Issleib and coworkers performed many of the first studies of monophosphides, establishing the versatility of these compounds as a starting point for the synthesis of neutral-substituted monophosphines [1,2]. More recently, a number of studies

have been conducted on the synthesis and reactivity of diphosphides [3–6]. For example, Chou and coworkers used diphosphides of the type [–PhP(CH<sub>2</sub>)<sub>n</sub>PPh–], n = 2–6, to form a variety of neutral *P*-chiral bis(alkylphenylphosphino)alkanes [7]. Furthermore, Gallagher et al. have used similar diphosphides in the synthesis of diphosphorus heterocycles [5,8]. Much of the research into the formation and reaction chemistry of the diphosphides is driven by the potential for use as ligands for homogeneous catalysis.

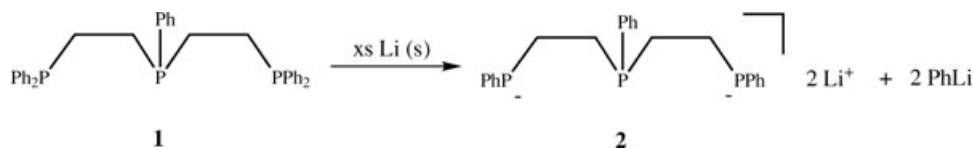
Tridentate phosphine ligands have recently been found to be useful as ligands in catalytic synthesis of organic compounds [9–12]. For example, the chiral ttp\* [(*S,S*)-PhP(CH<sub>2</sub>CHMeCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] can be used in metal complexes of rhodium and ruthenium for catalytic asymmetric hydrogenation of olefins [11]. In light of the growing interest in tridentate phosphine ligands, we set out to explore the formation and reaction chemistry of the phosphide compound derived from the tridentate phosphine ligand PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> (**1**). This report describes the synthesis and initial reactivity studies of the new lithium diphosphide Li<sub>2</sub>[PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (**2**).

## RESULTS AND DISCUSSION

Reaction of PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> (**1**) with lithium in tetrahydrofuran (THF) results in formation of a dark red solution of Li<sub>2</sub>[PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (**2**), as shown in Scheme 1. The reaction does not proceed to any measurable extent until it is initiated through ultrasonic radiation, a technique used in reactions

Correspondence to: Monte L. Helm; e-mail: helm.m@fortlewis.edu.

Contract grant sponsor: Fort Lewis College.  
Contract grant sponsor: Research Corporation.  
Contract grant number: DS0332.  
© 2007 Wiley Periodicals, Inc.



SCHEME 1

of diphosphine  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  with lithium to form the corresponding diphosphide [5,13]. Reaction times vary with concentration of the starting phosphine, (**1**), but generally ranged between 30 and 90 min at  $0^\circ\text{C}$ , resulting in near quantitative formation of **2** as analyzed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Increased temperature did not result in faster reaction times, but often lead to formation of phosphorus-containing decomposition products. The reaction solution that contains **2**, as well as 2 equivalents of  $\text{PhLi}$ , is extremely air sensitive and decomposes readily when exposed to oxygen or water. The solid  $\text{Li}_2[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$  salt is isolated from the reaction mixture through fractional crystallization with pentane.

The characterization of **2** is based on NMR spectral data and through reaction with bromobenzene to reform the starting triphosphine (**1**). Formation of **2** in the reaction mixture is clearly evident by the presence of characteristic sharp  $\text{AX}_2$   $^{31}\text{P}\{^1\text{H}\}$  NMR triplet ( $-23.3$  ppm) and doublet ( $-54.1$  ppm) resonances. The triplet and doublet chemical shifts of **2** are observed upfield from the starting material by 7.0 ppm and 42 ppm, respectively, and the  $^3J_{\text{PP}}$  coupling has increased from 28.2 Hz in **1** to 44.6 Hz in **2** (Fig. 1). The sixfold difference in the chemical shift of the doublet over the triplet indicates that formation of the anionic phosphorus atoms has occurred selectively at the terminal phosphorus positions. The observed differences in the  $^{31}\text{P}$  NMR spectrum between **1** and **2** are consistent with those previously reported for the two-phosphorus anionic system [4,5]. There was no indication of formation of the monoanionic species that would show a distinctive AMX splitting pattern, a result also consistent with the previously studied two-phosphorus systems [13]. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra show the expected peaks and chemical shifts consistent with formation of **2**, as well as confirm separation from other reaction products. Further characterization (MS, elemental analysis) was not accomplished because of the extremely air-sensitive nature of **2**.

Regeneration of the starting material (**1**) can be accomplished through addition of 4 equivalents of bromobenzene to the reaction mixture containing **2** (Scheme 2,  $\text{R} = \text{Ph}$ ). Since formation of **2** entails production of 2 equivalents of phenyl lithium

(Scheme 1), 4 equivalents of bromobenzene are required to neutralize this reactive byproduct. The presence of **1** after the reaction is complete is easily proven through observation of its known  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Further confirmation was accomplished through isolation of **1** from the reaction mixture by column chromatography followed by  $^1\text{H}$  NMR and melting point analysis, both of which match the previously reported data for this compound. Finally, solid **1** was isolated in 92% yield after this reaction sequence, indicating that although the  $\text{Li}_2[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$  salt was not isolated in high yield, it is formed in near quantitative yield in solution.

Initial reactivity studies of **2** with a series of alkyl halides resulted in formation of neutral tripodal phosphines (Scheme 2). Formation of the neutral phosphines are tentatively confirmed through  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In the cases where  $\text{R} \neq \text{Ph}$ , the neutral phosphines formed have *P*-chiral terminal phosphine atoms. As a result, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of these compounds show overlapping  $\text{AXX}'$  splitting patterns of the mixture of diastereomers, where the center "A" phosphorus resonance appears as a pseudotriplet. In all cases, however, formation of the neutral phosphines is indicated by the observed downfield chemical shift of the terminal phosphorus atoms observed upon alkylation of **2**. The  $^{31}\text{P}\{^1\text{H}\}$  chemical shifts of the neutral phosphines (reported as the center of the pseudotriplet and multiplet resonances) along with the coupling constant observed for the pseudotriplet are reported in Table 1. Attempts to purify or separate the mixture diastereomers for further characterization proved unsuccessful.

In summary, formation of the di-anionic  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2^{2-}$ , (**2**), is readily accomplished through reaction of  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ , (**1**), with lithium under ultrasonic radiation. Initial reactivity studies of the phosphide **2** indicate that it can be used as a reactive intermediate to form neutral tripodal phosphine ligands. Given the importance of multidentate phosphine ligands, the identification of this reactive phosphorus intermediate is an important advance for development of tridentate phosphine ligands for use in catalytic systems.

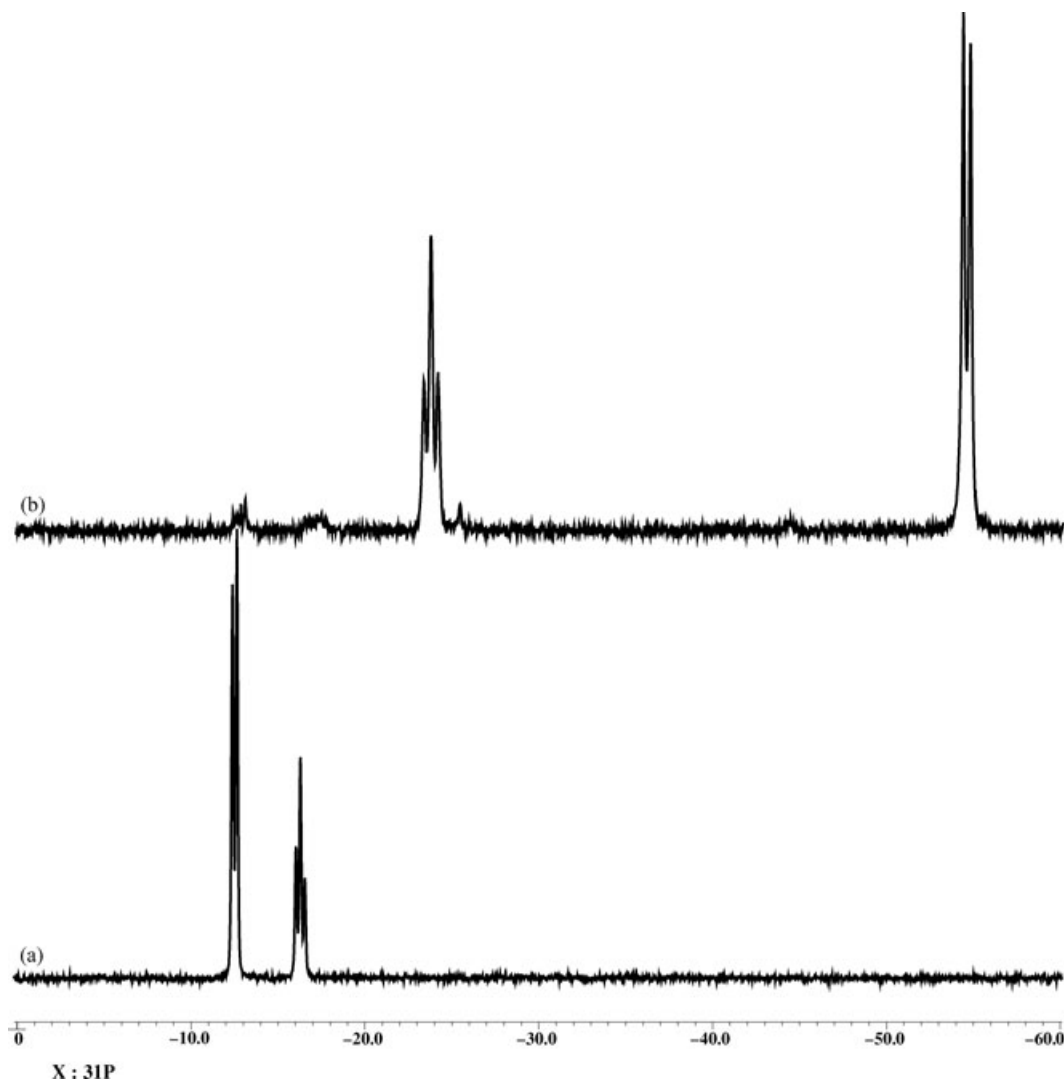
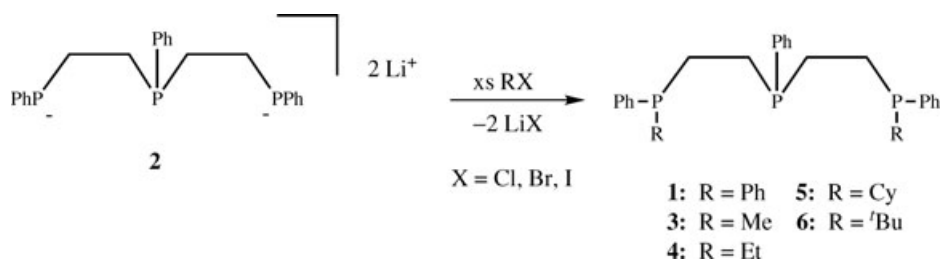


FIGURE 1  $^{31}\text{P}\{^1\text{H}\}$  NMR( $d_6$ -THF, 23°C) spectra of (a) **1** and (b) **2**.

### EXPERIMENTAL

Standard procedures for the manipulation of air-sensitive materials were employed. Unless otherwise stated, all manipulations were carried out at ambient temperature under an atmosphere of

dry nitrogen gas using an inert atmosphere glove box or standard Schlenk, syringe and high-vacuum line techniques. Solvents were dried, freshly distilled under nitrogen, and degassed prior to use. The  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  (**1**) was purchased from Aldrich and was used as received. The lithium was



SCHEME 2

TABLE 1  $^{31}\text{P}\{^1\text{H}\}$  NMR Chemical Shifts of Neutral *P*-Chiral Phosphines

Compound	Alkyl Halide Reacted with <b>2</b>	Chemical Shift Center <i>P</i> -Atom (ppm)	Chemical Shift Terminal <i>P</i> -Atoms (ppm)	$^3J_{\text{PP}}$ Coupling Constants (Hz)
<b>3</b>	MeI	-16.9	-31.7	23.5
<b>4</b>	EtI	-15.9 to -16.8	-15.9 to -16.8	-
<b>1</b>	PhBr	-16.3	-12.5	28.2
<b>5</b>	CyBr <sup>a</sup>	-15.7	+7.4	24.8
<b>6</b>	<sup>t</sup> BuCl	-16.2	+8.2	24.4

<sup>a</sup>Cy = cyclohexyl.

purchased from Aldrich, freshly cut and stored in an inert glove box under argon. All NMR spectra were recorded on a JEOL GSX-270 spectrometer ( $^1\text{H}$  270.166 MHz;  $^{13}\text{C}$  67.933 MHz;  $^{31}\text{P}$  109.365 MHz). The  $^{31}\text{P}$  chemical shifts downfield from 85%  $\text{H}_3\text{PO}_4$  (external) are reported as positive (+ $\delta$ ).

#### Lithium Bis(2-phenylphosphidoethyl)phenylphosphine (**2**)

To a solution of small Li pieces (0.050 g, 7.2 mmol) in THF (1 mL), bis[2-(diphenylphosphino)ethylphenylphosphine] (0.267 g, 0.50 mmol) dissolved in THF (1 mL) was added. The mixture was placed in an ultrasonicator at 0°C and was irradiated for 30 min, after which the dark red solution was separated from the remaining Li through cannula filtration. Approximately 15 mL of pentane was added, resulting in precipitation of an orange solid of pure **2** (0.600 g, 30% yield).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ ):  $\delta$  -23.3 (t, 1P, *PPh*,  $^3J_{\text{PP}} = 36.1$ ), -54.1 (d, 2P, -*PPh*);  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  7.48 (mult., 1H,  $\text{C}_6\text{H}_5$ ), 7.23 (mult., 4H,  $\text{C}_6\text{H}_5$ ), 6.88 (broad s, 4H,  $\text{C}_6\text{H}_5$ ), 6.62 (mult., 4H,  $\text{C}_6\text{H}_5$ ), 6.21 (mult. 2H,  $\text{C}_6\text{H}_5$ ), 2.03 (broad mult., 8H,  $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}$  (THF- $d_8$ ):  $\delta$  132.9, 132.6, 129.0, 128.5, 127.9, 127.0 (s/mult.,  $\text{C}_6\text{H}_5$ ), 29.2, 18.7 (mult.,  $\text{CH}_2$ ).

Reaction of the dark red solution from above (after separation from Li), which shows only the presence of **2** by  $^{31}\text{P}\{^1\text{H}\}$  NMR, is reacted with excess bromobenzene (0.385 mL, 3.68 mmol), followed by purification through a column of silica (230–400 mesh, 2.5 × 20 cm) resulted in isolation of pure starting material, bis[2-(diphenylphosphino)ethyl]phenylphosphine (0.241 g, 92% yield, analyzed by mp and  $^1\text{H}$  NMR).

#### Reactions of **2** with alkylhalides

The reaction of **2** with MeI is described here; reaction with other alkylhalides followed the same

general procedure. To a solution of **2** (1.2 mmol) in THF (10 mL), 4 equivalents of MeI (0.30 mL, 4.8 mmol) was added dropwise, upon which the dark red solution became clear. After removal of the solvents,  $\text{CH}_2\text{Cl}_2$  (5 mL) was added, and the mixture was purified through column chromatography (230–400 mesh, 2.5 × 20 cm) using  $\text{CH}_2\text{Cl}_2$  as the eluting solvent. Removal of the solvents resulted in an oil consisting mainly of bis[2-(methylphenylphosphino)ethyl]phenylphosphine.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -16.9 (pseudotriplet, 1P, *PPh*,  $^3J_{\text{PP}} = 23.5$ ), -31.7 (center of multiplet, 2P, *PPhMe*).

#### REFERENCES

- [1] Issleib, K.; Boettcher, W. *Synth React Inorg Met-Org Chem* 1976, 6, 179–190.
- [2] Issleib, K. *Z Chem* 1962, 2, 163–173.
- [3] Uhlig, F.; Hummeltenberg, R. *J Organomet Chem* 1993, 452, C9–C10.
- [4] Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F.; Moss, I. *Inorg Chim Acta* 1988, 141, 157–159.
- [5] Brooks, P.; Gallagher, M. J.; Sarroff, A. *Aust J Chem* 1987, 40, 1341–1351.
- [6] Chou, T.-s.; Tsao, C.-H.; Hung, S. C. *J Organomet Chem* 1986, 312, 53–58.
- [7] Chou, T.-s.; Tsao, C.-H.; Hung, S. C. *J Org Chem* 1985, 50, 4329–4332.
- [8] Brooks, P. J.; Gallagher, M. J.; Sarroff, A.; Bowyer, M. *Phosphorus, Sulfur, Silicon Relat Elem* 1989, 44, 235–247.
- [9] Hintermann, L.; Perseghini, M.; Barbaro, P.; Togni, A. *Eur J Inorg Chem* 2003, 601–609.
- [10] Barbaro, P.; Bianchini, C.; Giambastiani, G.; Togni, A. *Chem Commun (Cambridge, UK)* 2002, 2672–2673.
- [11] Lee, H. M.; Yang, C.; Jia, G. *J Organomet Chem* 2000, 601, 330–334.
- [12] Barbaro, P.; Togni, A. *Organometallics* 1995, 14, 3570–3573.
- [13] Brooks, P.; Craig, D. C.; Gallagher, M. J.; Rae, A. D.; Sarroff, A. *J Organomet Chem* 1987, 323, C1–C4.