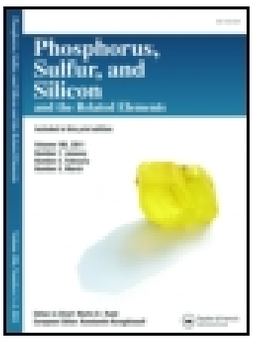


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

Selective P-C bond cleavage of tertiary phosphine boranes by sodium

Jian-Qiu Zhang, Jing-Jing Ye & Li-Biao Han

To cite this article: Jian-Qiu Zhang, Jing-Jing Ye & Li-Biao Han (2021): Selective P-C bond cleavage of tertiary phosphine boranes by sodium, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2021.1948851

To link to this article: https://doi.org/10.1080/10426507.2021.1948851

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2021.1948851

Taylor & Francis
Taylor & Francis Group

SHORT COMMUNICATION

Selective P-C bond cleavage of tertiary phosphine boranes by sodium

Jian-Qiu Zhang[a,b], Jing-Jing Ye[a,b], and Li-Biao Han[a,b]

[a]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [b]Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan

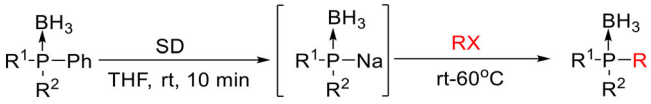
ABSTRACT

Herein reported is the facial modification of tertiary phosphine boranes R_3PBH_3 by selective cleaving the P-Ph bond by sodium in which the phosphide borohydride $R_2PNa(BH_3)$ is quantitatively generated and could be easily quenched by electrophiles to furnish a series of new phosphine boranes in high yields.

ARTICLE HISTORY
Received 8 March 2021
Accepted 23 June 2021

KEYWORDS
Phosphine borane; C-P bond cleavage; sodium

GRAPHICAL ABSTRACT



Introduction

Tertiary phosphines are extensively applied as ligands in transition metal-catalyzed reactions,[1] as organocatalysts in synthetic chemistry[2] and as reducing reagents in Staudinger,[3] Mitsunobu,[4] Wittig reaction,[5] etc. However, phosphines R_3P inherently bearing a lone pair of electrons at the phosphorus atom, in particular alkyl functionalized phosphines, are air-sensitive and easily oxidized to the corresponding phosphine oxides, leading to great difficulties in handling and purification of these compounds.[6] Conversion of the phosphines to the corresponding air-stable phosphine boranes ($R_3P{\cdot}BH_3$) upon treatment with a borane reagent ($BH_3{\cdot}THF$ or $BH_3{\cdot}SMe_2$) is a general and efficient strategy to slow down their oxidation, since the borane group is also easily removed by a base.[7–9] Based on our previously established works on the P-Ph bond cleavage of triphenylphosphine oxide $Ph_3P(O)$ and triphenylphosphine Ph_3P by sodium dispersion (sodium finely dispersed in paraffin oil with μm-scale sizes, hereafter abbreviated as SD), the corresponding reactive intermediate $Ph_2P(ONa)$ and Ph_2PNa was generated, respectively. And finally a range of new phosphine oxides $Ph_2P(O)R$ and phosphines Ph_2PR were easily obtained after quenching by electrophiles RX (Scheme 1A).[10–12] Thus, we wondered if this strategy would be also applied to triphenylphosphine borane $Ph_3P{\cdot}BH_3$ to react with sodium to generate the corresponding intermediate sodium phosphide boranes $Ph_2PNa(BH_3)$ *via* selective P-Ph bond cleavage (Scheme 1B). Since $Ph_3P{\cdot}BH_3$ is a common and inexpensive phosphine borane, if the above reaction proceeds readily, the other functionalized phosphine boranes that are difficult to prepared by the traditional methods[13] will be easily and directly obtained from $Ph_3P{\cdot}BH_3$. Although the metallation of phenylphosphine boranes $R_2PhP(BH_3)$ with lithium and potassium generating phosphide boranes $R_2P^-(BH_3)M^+$ (M = Li, K) has been reported,[13–15] employing the much cheaper and readily available sodium is a better choice. Thus, in this protocol, we report a direct modification of $R_2PhP(BH_3)$ with sodium, followed by the addition of alkyl halides, enabling access to a series of new phosphine boranes in good to excellent yields.

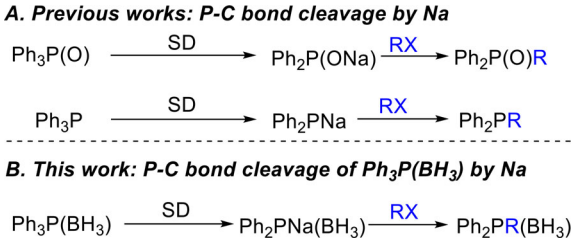
Results and Discussion

The study began by treating 0.2 mmol of triphenylphosphine borane ($Ph_3P{\cdot}BH_3$) **1a** with 0.42 mmol of SD at room temperature, the solution immediately changed to brown. After stirring the mixture for 2 h, as monitored by ^{31}P NMR spectra (Scheme 2), the original signal at δ 21.6 ($J_{B\text{-}P}$ = 53.5 Hz) of $Ph_3P{\cdot}BH_3$ totally disappeared and a new signal at δ − 31.1 ($J_{B\text{-}P}$ = 35.6 Hz) emerged, indicating that $Ph_2PNa(BH_3)$ **2a** was generated almost quantitatively. Furthermore, the final product diphenyl(*n*-octyl)phosphine borane **3a** ($Ph_2Pn\text{-}Oct(BH_3)$) with a signal at δ 16.5 ($J_{B\text{-}P}$ = 50.2 Hz) was obtained in quantitative yield by simple quenching with one equivalent of *n*-octyl bromide (*n*-OctBr) at room temperature. It was interesting that no byproduct via P-B bond cleavage was detected. And ^1H NMR spectra verified the formation of **3a** (Scheme 2B).

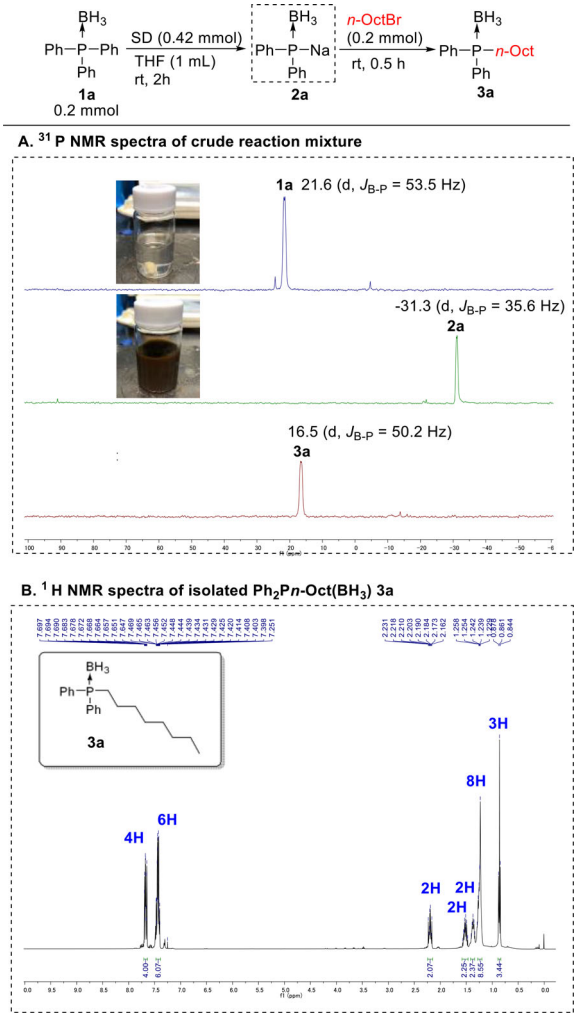
This interesting result led us to explore the reactivity of triphenylphosphine sulfide ($Ph_3P(S)$) upon treatment with SD. Thus, similarly, to a solution of 0.2 mmol of $Ph_3P(S)$ in

CONTACT Li-Biao Han libiao-han@aist.go.jp National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan
Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan.

Supplemental data for this article can be accessed online at https://doi.org/10.1080/10426507.2021.1948851.

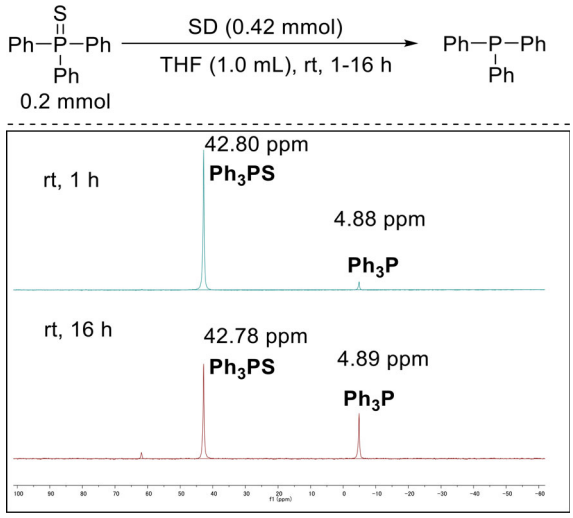


Scheme 1. Selective P-C bond cleavage by SD.



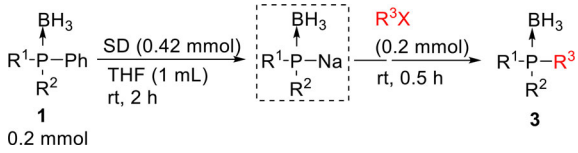
Scheme 2. Reaction of $Ph_3P{\cdot}BH_3$ **1a** with SD monitored by ^{31}P NMR and the ^{1}H NMR spectra of **3a.**

1.0 mL of THF was added dropwise SD at room temperature, and the reaction was monitored by ^{31}P NMR spectroscopy. As we can see from Scheme 3, after 1 hour of reaction time, the P-Ph bond of $Ph_3P(S)$ ($\delta = 42.8$ ppm) did not react with sodium at all and the P = S double bond was broken by SD, giving rise to the desulfurization product Ph_3P ($\delta = -4.9$ ppm) in 4% ^{31}P NMR yield. The yield of Ph_3P increased up to 31% after 16 hours (Scheme 3). Worth noticing is that almost no product stemming from P-Ph bond cleavage could be detected during the whole process. In contrast to the reactions of phosphine borane, these results disclosed an interesting fact that the P = S bond is more easily to be broken by SD than the P-Ph bond in both $Ph_3P(S)$



Scheme 3. Reaction of $Ph_3P(S)$ with SD.

Table 1. P-C bond cleavage of phosphine boranes[a].



Entry	R^1	R^2	R^3X	Yield/**3**	^{31}P NMR, δ/ppm
1	Ph	Ph	*n*-BuBr	**3b**, 92%	17.23/16.95
2[b]	Ph	Ph	*n*-BuCl	**3b**, 86%	17.22/16.92
3	Ph	Ph	*n*-BuI	**3b**, 86%	17.27/16.93
4	Ph	Ph	*n*-OctBr	**3a**, 92%	17.16/17.01
5	Ph	Ph	$PhCH_2Br$	**3c**, 94%	19.16/18.79
6[c]	Ph	Ph	$Br(CH_2)_4Br$	**3d**, 95%	16.5
7	Ph	Ph	*i*-PrCl	**3e**, n.r.	–
8	Ph	Ph	*i*-PrI	**3e**, 87%	25.86/25.49
9	Ph	Ph	*t*-BuBr	**3f**, n.d.	–
10[d]	Ph	*n*-Bu	*n*-BuBr	**3g**, 69%	16.67/16.30
11[d]	Et	Et	*n*-BuBr	**3h**, 72%	20.43/20.07

[a]Reaction conditions: Phosphine borane **1** (0.2 mmol), THF (1.0 mL), SD (0.42 mmol), rt, 2 h. Then R^3X (0.2 mmol), rt, 0.5 h, the yield was estimated by ^{31}P NMR based on **1** used.
[b]12 h at the 1st step.
[c]R^3X (0.1 mmol).
[d]30 h at the 1st step.

and Ph_3P, because no signal of Ph_2PSNa and Ph_2PNa appeared.

Because SD failed to cleave P-Ph bond of $Ph_3P(S)$, further emphasis was only placed on investigating the reactions of phosphine boranes with SD. As depicted in Table 1, the intermediate sodium phosphide borohydride $Ph_2PNa(BH_3)$ *in situ* generated from the reaction of $Ph_3P(BH_3)$ with SD was capable of reacting with a series of aliphatic halides to deliver new phosphine boranes with good efficiency. For example, all kinds of primary alkyl halides (chloride, bromide, iodide) could readily trap $Ph_2PNa(BH_3)$ to give the new phosphine boranes **3** in high yields (Table 1). Especially the less reactive *n*-butyl chloride, which did not react with Ph_2PONa at room temperature,[11] now could react with $Ph_2PNa(BH_3)$ efficiently, demonstrating that the reactivity of $Ph_2PNa(BH_3)$ is higher than that of Ph_2PONa. The quenching reaction proceeds smoothly with benzyl bromide and

1,4-dibromobutane, affording the corresponding phosphine borane **3c** and **3d** in 94% and 95% yield, respectively (entries 5 and 6). However, except for isopropyl iodide (entry 8), the reactions with isopropyl chloride (entry 7) and *tert*-butyl bromide (entry 9) did not take place, perhaps due to inert C-Cl bond of *i*-PrCl and large steric hindrance of *t*-BuBr. In addition, by prolonging the reaction time, treatment of diarylphosphine borane Ph_2Pn-Bu(BH_3) and dialkyl(aryl)phosphine borane $PhPEt_2(BH_3)$ with SD could also lead to the corresponding $R_2PNa(BH_3)$ intermediate. Finally, the new generated phosphine boranes were produced in moderated yields (Table 1, entries 10 and 11). Unfortunately, the coupling reactions of $Ph_2PNa(BH_3)$ with aromatic chloride such as *p*-chlorotoluene gave complicated results and no expected product could be detected even in the presence of a palladium catalyst.[11]

Conclusions

In conclusion, we have developed an efficient transformation of arylphosphine boranes *via* the selective P-Ph bond cleavage by using SD, which not only completes our previously established systematical studies on the P-C bond cleavage by sodium, but also provides a new approach to alkylated phosphine boranes.

Experimental

Materials

The solvent THF and reagents alkyl halides were purchased and used without further purification. Triphenylphosphine borane **1a** and SD (~10 mol/L) was provided by Tokyo Chemical Industry Co., Ltd. Ph_2n-BuP(BH_3) and $Et_2PhP(BH_3)$ was prepared from Ph_2n-BuP and Et_2PhP by treating with BH_3·THF solution, respectively. The Supplemental Materials contains sample ^1H, ^{13}C and ^{31}P NMR spectra for the product, 3 (multiple runs, Figures S1–S18).

Instrumentation

^1H, ^{31}P and ^{13}C NMR spectra were recorded with a JEOL JNM-ECS400 instrument operating at 400 MHz (^1H), 100 MHz (^{13}C), and 162 MHz (^{31}P). Chemical shifts for ^1H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Chemical shifts for ^{31}P NMR are given relative to H_3PO_4 (85% solution in D_2O, 0 ppm).

Synthesis

Experimental procedure for the preparation of Ph_2Pn-Oct(BH_3) 3a

A Schlenk tube was charged with triphenylphosphine borane $Ph_3P{\cdot}BH_3$ (0.2 mmol, 55.2 mg) and 1.0 mL of THF; then under stirring, SD (0.42 mmol, 42 µL) was added to the solution, and stirring of the mixture was continued at room temperature for 2 h. After removing the excess of sodium by a syringe filter the reaction mixture was quenched with *n*-OctBr (0.2 mmol, 35 µL) and stirred at room temperature for 0.5 h. The final mixture was added to 2.0 mL EtOAc and washed with H_2O (3 × 1 mL). Then the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by GPC to afford **3a** (56.2 mg, colorless oil, 0.18 mmol, 90% yield); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.70–7.65$ (m, 4H), 7.47–7.40 (m, 6H), 2.23–2.16 (m, 2H), 1.57–1.47 (m, 2H), 1.41–1.33 (m, 2H), 1.29–1.23 (m, 8H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 132.2$ (d, J_{PC} = 9.1 Hz), 131.2 (d, J_{PC} = 1.8 Hz), 129.8 (d, J_{PC} = 54.4 Hz), 128.9 (d, J_{PC} = 9.6 Hz), 31.9, 31.2 (d, J_{PC} = 13.7 Hz), 29.1 (d, J_{PC} = 7.6 Hz), 25.9, 25.6, 23.1, 22.7, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 16.5$ (J_{BP} = 57.2 Hz).

General experimental procedures for the reaction of phosphine boranes with sodium

A Schlenk tube was charged with phosphine borane $R_3P{\cdot}BH_3$ **1** (0.2 mmol) and 1.0 mL of THF; then under stirring SD (0.42 mmol, 42 µL) was added to the solution and stirring of the mixture was continued at room temperature for the indicated time (2 h, 12 h, 16 h, 30 h). Then the excess of sodium was removed by a syringe filter followed by quenching of the reaction mixture with RX (0.2 mmol) and stirring at room temperature for 0.5 h. The crude mixture was analyzed by ^{31}P NMR and the estimated yield of **3** was calculated by integration based on the phosphine borane **1** used.

Acknowledgements

This work was primarily supported by joint research between AIST and Maruzen Petrochemical Co., Ltd.

ORCID

Jian-Qiu Zhang http://orcid.org/0000-0002-5220-3200
Li-Biao Han http://orcid.org/0000-0001-5566-9017

References

[1] Adrio, L. A.; Hii, K. K. Application of Phosphine Ligands in Organic Synthesis. *Organomet. Chem.* **2009**, *35*, 62–92. DOI: 10.1039/b801380m.
[2] Guo, H.; Fan, Y. C.; Sun, Z.; Wu, Y.; Kwon, O. Phosphine Organocatalysis. *Chem. Rev.* **2018**, *118*, 10049–10293. DOI: 10.1021/acs.chemrev.8b00081.
[3] Bednarek, C.; Wehl, I.; Jung, N.; Schepers, U.; Bräse, S. The Staudinger Ligation. *Chem. Rev.* **2020**, *120*, 4301–4354. DOI: 10.1021/acs.chemrev.9b00665.
[4] Fletcher, S. The Mitsunobu reaction in the 21st century. *Org. Chem. Front.* **2015**, *2*, 739–752. DOI: 10.1039/C5QO00016E.
[5] Byrne, P. A.; Gilheany, D. G. The Modern Interpretation of the Wittig Reaction Mechanism. *Chem. Soc. Rev.* **2013**, *42*, 6670−−6696. DOI: 10.1039/C3CS60105F.
[6] Stewart, B.; Harriman, A.; Higham, L. J. Predicting the Air Stability of Phosphines. *Organometallics* **2011**, *30*, 5338–5343. DOI: 10.1021/om200070a.
[7] Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. Synthesis and Reactions of Phosphine-Boranes. Synthesis of

New Bidentate Ligands with Homochiral Phosphine Centers via Optically Pure Phosphine-Boranes. *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252. DOI: 10.1021/ja00169a036.

[8] Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. Borane Complexes of Trivalent Organophosphorus Compounds. Versatile Precursors for the Synthesis of Chiral Phosphine Ligands for Asymmetric Catalysis. *Synthesis* **1998**, *1998*, 1391–1415. DOI: 10.1055/s-1998-2166.

[9] Demchuk, O. M.; Jasinski, R.; Strzelecka, D.; Dziuba, K.; Kula, K.; Chrzanowski, J.; Krasowska, D. A Clean and Simple Method for Deprotection of Phosphines from Borane Complexes. *Pure Appl. Chem.* **2018**, *90*, 49–62. DOI: 10.1515/pac-2017-0313.

[10] Zhang, J.-Q.; Ye, J.; Huang, T.; Shinohara, H.; Fujino, H.; Han, L.-B. Conversion of Triphenylphosphine Oxide to Organophosphorus via Selective Cleavage of C-P, O-P, and C-H Bonds with Sodium. *Commun. Chem.* **2020**, *3*, 1–9. DOI: 10.1038/s42004-019-0249-6.

[11] Zhang, J.-Q.; Ikawa, E.; Fujino, H.; Naganawa, Y.; Nakajima, Y.; Han, L.-B. Selective C-P(O) Bond Cleavage of Organophosphine Oxides by Sodium. *J. Org. Chem*. **2020**, *85*, 14166–14173. DOI: 10.1021/acs.joc.0c01642.

[12] Ye, J.; Zhang, J.-Q.; Saga, Y.; Onozawa, S. Y.; Kobayashi, S.; Sato, K.; Fukaya, N.; Han, L.-B. Ready Approach to Organophosphines from ArCl via Selective Cleavage of C–P Bonds by Sodium. *Organometallics* **2020**, *39*, 2682–2694. DOI: 10.1021/acs.organomet.0c00295.

[13] Pellon, P. Phosphine-Boranes in Synthesis. Borane as an Efficient Protecting Group in the Preparation of Functionalized Phosphines. *Tetrahedron Lett.* **1992**, *33*, 4451–4452. DOI: 10.1016/S0040-4039(00)60107-7.

[14] Gourdel, Y.; Ghanimi, A.; Pellon, P.; Le Corre, M. Activation of Phosphines with Borane. *Tetrahedron Lett.* **1993**, *34*, 1011–1012. DOI: 10.1016/S0040-4039(00)77478-8.

[15] Stankevič, M.; Wójcik, K.; Jaklińska, M.; Pietrusiewicz, K. M. *Eur. J. Org. Chem.* In Situ Dearomatisation/Alkylation of Arylphosphane Derivatives. **2012**, *2012*, 2521–2534. DOI: 10.1002/ejoc.201200096.