

In this paper, we prepared viologen-containing, bilayer-immobilized films by the polyion complex method<sup>3a</sup> and controlled the permeability across a film cast on a platinum minigrid sheet by electrochemical redox reactions. A schematic illustration of the apparatus is shown in Figure 1.

The bilayer-immobilized, polyion-complex film was prepared as follows, according to the Kunitake's method.<sup>3a</sup> Equivalent amounts of an aqueous dispersion of bilayer-forming  $2C_{16}$ -bpy<sup>2+</sup> $2ClO_4^-$  amphiphiles<sup>8</sup> and an aqueous of sodium poly(styrene sulfonate) PSS<sup>-</sup> (MW >  $2 \times 10^6$ ) were mixed. The precipitates, pale yellow powders (recovery: 90%), were dissolved in chloroform and cast on a Pt minigrid (100 mesh) supported on a polyethylene tube (see Figure 1). The polyion-complex film ( $2C_{16}$ -bpy<sup>2+</sup>-PSS<sup>-</sup> $ClO_4^-$ ) was transparent, water-insoluble, and estimated to be 100  $\mu$ m thick from SEM observations. X-ray diffraction analyses<sup>9</sup> showed that  $2C_{16}$ -bpy<sup>2+</sup> amphiphiles form extended lamellae parallel to the film plane in polyion complexes with PSS<sup>-</sup>, as well as other bilayer-immobilized films.<sup>3</sup> The  $2C_{16}$ -bpy<sup>2+</sup>-PSS<sup>-</sup> and the reduced  $2C_{16}$ -bpy<sup>•+</sup>-PSS<sup>-</sup> films showed phase transition temperatures ( $T_c$ ) at 24 and 38 °C from DSC measurements, respectively, as well as other bilayer films.<sup>3</sup>

Permeation of the freely water-soluble, nonionic fluorescent probe **1**<sup>10</sup> across the bilayer film cast on a Pt-grid was followed fluorometrically at 340 nm (excited at 280 nm) in 0.1 M NaClO<sub>4</sub> aqueous solution according to the apparatus of the thermostated quartz cell in Figure 1. Typical time courses of permeation of probe **1** under an intermittent potential applied to the electrode/film in a nitrogen atmosphere are shown in Figure 2. The bilayer film showed a relatively high resistance to the permeation of probe **1** [ $P = (2.28-2.63) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ], as well as other polymer membranes.<sup>1,4,6</sup>

A cyclic voltammetry study of viologen films cast on a Pt electrode in 0.1 M NaClO<sub>4</sub> aqueous solution showed two well-known peaks at -0.55 V vs. SCE in cathodic region ( $2C_{16}$ -bpy<sup>2+</sup>/ $2C_{16}$ -bpy<sup>•+</sup>) and at -0.35 V vs. SCE in anodic region ( $2C_{16}$ -bpy<sup>•+</sup>/ $2C_{16}$ -bpy<sup>2+</sup>). The peak currents were largely dependent on the fluidity of bilayer films: the reduction of  $2C_{16}$ -bpy<sup>2+</sup> to  $2C_{16}$ -bpy<sup>•+</sup> films occurred only in the fluid-liquid-crystalline state of  $2C_{16}$ -bpy<sup>2+</sup> bilayer films above the  $T_c = 24$  °C, but not in the solid state below the  $T_c$ .

Upon applying the potential of -0.50 V vs. SCE to the Pt grid/film, the film turned from pale yellow to violet within 30 s which shows the reduction of the dicationic  $2C_{16}$ -bpy<sup>2+</sup> to the radical cationic  $2C_{16}$ -bpy<sup>•+</sup> bilayers, and then the permeability was decreased by a factor of 3.3 ( $P = 7.72 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) at 30 °C. Upon switching off the Pt grid/film potential to 0 V even after a long duration (5-10 min) at 30 °C, the violet  $2C_{16}$ -bpy<sup>•+</sup> bilayers were oxidized again to the yellow  $2C_{16}$ -bpy<sup>2+</sup> bilayer film in 30 s and the permeability reverted to the original fast rate. These permeability changes due to the redox of  $2C_{16}$ -bpy<sup>2+</sup>/ $2C_{16}$ -bpy<sup>•+</sup> bilayer films on a Pt grid could be reproduced repeatedly in the range 25-35 °C. In contrast, the permeation of probe **1** was hardly affected by the -0.5-V potential on Pt grid/film at 40 °C in contrast to 25 °C, although the redox reaction of viologen films was confirmed to occur on Pt grid at 40 °C.

Redox-sensitive permeations at 30 °C but not at 40 °C of Figure 2 may be explained by the transition of the  $T_c$  between the oxidized  $2C_{16}$ -bpy<sup>2+</sup> bilayers (24 °C) and the reduced  $2C_{16}$ -bpy<sup>•+</sup> bilayers (38 °C). At a temperature of 30 °C, the oxidized  $2C_{16}$ -bpy<sup>2+</sup> bilayers are in the liquid crystalline state above  $T_c = 24$  °C and

probe **1** can permeate smoothly through the fluid and disordered bilayers, while the reduced  $2C_{16}$ -bpy<sup>•+</sup> bilayers are in the solid state below  $T_c = 38$  °C and have a high resistance to the permeation. In contrast, at 40 °C, both  $2C_{16}$ -bpy<sup>2+</sup> and  $2C_{16}$ -bpy<sup>•+</sup> bilayers are in the fluid state above their  $T_c$  values and showed a similar high permeability independent of their redox forms. Thus, the permeability changes may be attributed to the fluidity change of the bilayer film on a Pt grid because of the  $T_c$  transitions of bilayers by redox reactions. The change of membrane charges by redox reactions should be unimportant for the permeation of nonionic probes.

The permeability of chloride anions through polypyrrole films deposited on a Au grid has been reported to be changed by the positive charge formation on the film by electrochemical redox reactions.<sup>7</sup> This ion gate film of polypyrrole, however, showed slow responses, taking 15-30 min for the permeability change, and the poor reproducibility because of the morphological damages of the polymer film by redox reactions.<sup>7b</sup> In contrast, our viologen-containing bilayer films showed high fluid stability and the quick response for a permeability change, because the electrochemical redox reaction was converted to the fluidity change of bilayer films. A fluid, bilayer-immobilized film which is electrically switchable by redox reactions would provide a new idea for studying signal-receptive permeability-controllable membranes.

**Acknowledgment.** We thank Professor T. Kunitake for helpful comments on preparations of bilayer-immobilized films.

## Phosphine Oxides and LiAlH<sub>4</sub>-NaBH<sub>4</sub>-CeCl<sub>3</sub>: Synthesis and Reactions of Phosphine-Boranes

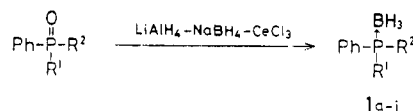
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Phosphine-boranes ( $R_3PBH_3$ ) have attracted little attention of chemists.<sup>1</sup> We wish to report a novel synthesis and some characteristic reactions of this class of compounds.

Our one-pot synthesis of phosphine-boranes from phosphine oxides employs a new reagent system, LiAlH<sub>4</sub>-NaBH<sub>4</sub>-CeCl<sub>3</sub>. Various phosphine oxides reacted smoothly with this reagent in THF at room temperature under N<sub>2</sub> to afford the corresponding phosphine-boranes (**1a-i**) in good yields (Table I).<sup>2</sup> It is note-



(1) Preparation and reaction of phosphine-boranes have only been described in a few scattered papers. (a) Frisch, M. A.; Heal, H. G.; Mackle, H.; Madden, I. O. *J. Chem. Soc.* **1965**, 899. (b) Nainan, K. C.; Ryschkewitsch, *Inorg. Chem.* **1969**, 8, 2671. (c) Mathur, M. A.; Myers, W. H.; Sisler, H. H.; Ryschkewitsch, G. E. *Inorg. Synth.* **1974**, 15, 128. (d) Schmidbaur, H.; Weiss, E.; Zimmer-Gasser, B. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 782. (e) Rosser, R.; Mills, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1041. (f) Kuznetsov, N. T. *Zh. Neorgan. Khim.* **1964**, 9, 1817.


(2) General procedure for the preparation of phosphine-boranes: Cerium chloride ( $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ) (3.3 g, 9 mmol) was quickly powdered in a mortar and was placed in a 50-mL two-necked flask. The flask was heated with stirring in vacuo to 140 °C during 1 h, maintained at this temperature for 2 h, and cooled to room temperature. Dry THF (20 mL) was then added with stirring under N<sub>2</sub>. After 0.5 h, NaBH<sub>4</sub> (0.34 g, 9 mmol) was added and stirring was continued for 1 h. The flask was immersed in an ice bath and phosphine oxide (3 mmol) was added, and finally LiAlH<sub>4</sub> (0.14 g, 3.6 mmol) was added by portions. The ice bath was removed and the mixture was stirred at room temperature for 2-15 h. The reaction mixture was diluted with benzene (ca. 15 mL) and poured slowly to ice-water containing 12 N HCl (4 mL). The mixture was filtered through Celite and the organic layer was separated. The aqueous layer was extracted twice with benzene. The combined extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The residue was subjected to chromatography on a short column of silica gel to give phosphine-borane. When the product was crystalline solid, it was recrystallized from hexane-benzene.

(8) The new compound  $2C_{16}$ -bpy<sup>2+</sup> was synthesized by monoquaternization of excess 4,4'-bipyridine with *N*-(2-bromoethyl)- $\alpha,\alpha$ -dihexadecylacetamide (mp 94-95 °C), followed by methylation with methyl bromide: mp 190 → 228 °C (liquid crystalline behavior),  $R_f$  0.4 ( $\text{CHCl}_3/\text{CH}_3\text{OH}/\text{CH}_3\text{COOH}/\text{H}_2\text{O} = 60:30:5:5$ ). The counteranions of  $2C_{16}$ -bpy<sup>2+</sup> were changed from  $2\text{Br}^-$  to  $2\text{ClO}_4^-$  in excess aqueous NaClO<sub>4</sub> before preparing polyion complexes.

(9) When the incident X-ray beam was parallel to the film plane which was held vertically, highly oriented diffractions with 3.8-nm spacings corresponding to the bilayer thickness were observed.

(10) Preparation and permeation of the fluorescent probe **1** across the capsule membrane are reported elsewhere: Okahata, Y.; Iizuka, N.; Nakamura, G.; Seki, T. *J. Chem. Soc., Perkin Trans. 2*, in press.

Table I. Phosphine-Boranes (1)<sup>a</sup>

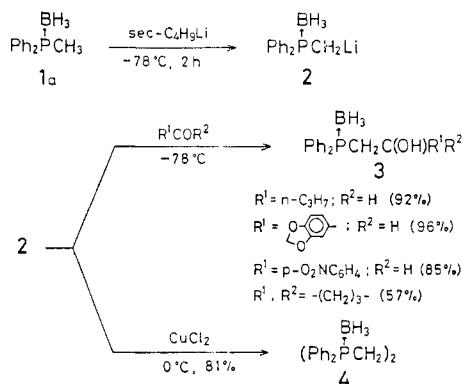
1	R <sup>1</sup>	R <sup>2</sup>	yield <sup>b,c</sup>	mp, °C
1a	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	96	50–51
1b	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	93	oil
1c	C <sub>6</sub> H <sub>5</sub>		89	34
1d	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CHOHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	72	oil
1e	<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	62	75–76
1f	1-C <sub>10</sub> H <sub>7</sub>	CH <sub>3</sub>	90	95–96
1g	C <sub>6</sub> H <sub>5</sub>	H	65	43–44
1h	1-C <sub>10</sub> H <sub>7</sub>	H	66	oil
1i	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	82	oil

<sup>a</sup>All reactions were carried out in THF at room temperature. See ref 2. <sup>b</sup>Isolated yield. <sup>c</sup>All products were fully characterized by IR and <sup>1</sup>H NMR spectroscopies and satisfactory elemental analyses were obtained.

worthy that this reaction did not proceed in the absence of cerium(III) chloride. Trivalent cerium<sup>3</sup> presumably plays dual roles in this reaction; it activates phosphine oxides by coordination so that the deoxygenation with LiAlH<sub>4</sub> proceeds readily<sup>4</sup> and it activates NaBH<sub>4</sub> to facilitate reaction with intermediates phosphines to form phosphine-boranes.<sup>5</sup>

This new method involves the following characteristic features: (1) Products are obtained directly from phosphine oxides with a simple procedure. (2) The reaction is quite general; not only tertiary but also secondary phosphine oxides are converted into phosphine-boranes. (3) Nontoxic and inexpensive cerium(III) chloride is used as the activating reagent.

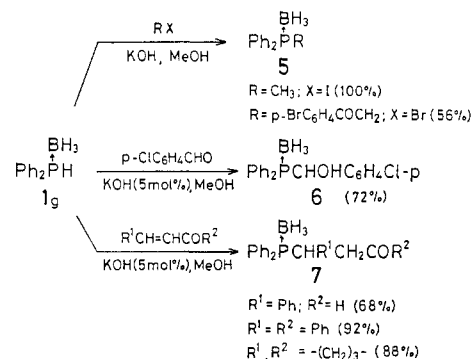
We have examined the reactivity of phosphine-boranes. The methyl group of **1a** was metalated with *sec*-butyllithium in THF at -78 °C.<sup>6</sup> The generated carbanion **2** reacted with carbonyl



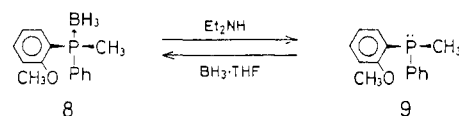
compounds to give the corresponding addition products **3** possessing borane moiety. The carbanion underwent copper(II)-promoted oxidative coupling<sup>7,8</sup> without impairment of the borane functionality to furnish **4**.

Compound **1g**, which has a P-H bond, also exhibited high reactivity. Thus, **1g** reacted rapidly at room temperature in the

presence of KOH with alkyl halides, aldehydes, and  $\alpha,\beta$ -unsaturated carbonyl compounds to yield various phosphine-borane derivatives (**5–7**).



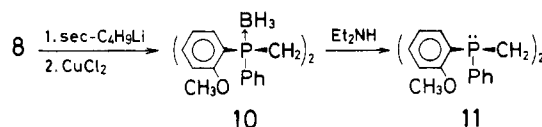
Another striking finding is that BH<sub>3</sub> group of phosphine-boranes was removed by the reaction with an amine such as diethylamine. This reaction has been proven to proceed in a stereospecific manner with retention of configuration. (*S*)-(*o*-Methoxyphenyl)methylphenylphosphine-boranes (**8**) (mp 66.5–67.5 °C, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +24.1° (*c* 1.5, MeOH) (89% ee)<sup>9</sup>), prepared by the stereospecific reaction of optically active phosphine **9**<sup>10</sup> with



BH<sub>3</sub>·THF at 25 °C for 2 h, was converted in essentially quantitative yield into **9** ([ $\alpha$ ]<sub>D</sub><sup>25</sup> -38.3° (*c* 1.7, MeOH) (89% ee))<sup>11</sup> on treatment with large excess of diethylamine at 50 °C for 8 h.

The reactions described above provide efficient syntheses of a variety of phosphine derivatives which are difficultly accessible by other previously existing methods. It is particularly worthy to mention that in these reaction sequences the BH<sub>3</sub> group acts both as an activating group and as a protecting group. That is, it activates the adjacent methyl group as well as the P-H bond to deprotonation with a strong base; at the same time it protects the labile phosphine group.

On the basis of these unique reactivities of phosphine-boranes, we have developed a new route to optically pure 1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine] (**11**), which



is an extremely useful ligand in catalytic asymmetric hydrogenation.<sup>8</sup> The *S* enantiomer **8** (89% ee) was converted via oxidative coupling to (*S,S*)-1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine-borane] (**10**) (mp 162.5–163.0 °C, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -70.2° (*c* 1.3, CHCl<sub>3</sub>)) in 65% yield.<sup>12</sup> This compound was then treated with diethylamine at 50 °C for 10 h to afford **11** (mp 102–103 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +87.0° (*c* 1.0, CHCl<sub>3</sub>))<sup>13</sup> in 84% yield. This method is favorably compared with the previous one<sup>8</sup> and is applicable to the synthesis of other analogous phosphine ligands.

(9) Enantiomeric excess of this compound was determined by high-performance liquid chromatography (HPLC) analysis with "CHIRALCEL OK" prepared by Daicel Chemical Industries, Ltd.

(10) This compound was synthesized by the reduction of (*S*)-(*o*-methoxyphenyl)methylphenylphosphine oxide ([ $\alpha$ ]<sub>D</sub><sup>25</sup> -24.2° (*c* 1.3, MeOH) (93% ee)) with HSiCl<sub>3</sub>-NEt<sub>3</sub> according to a literature procedure. Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *132*, 274. The stereospecific reduction of the phosphine oxide with LiAlH<sub>4</sub>-CeCl<sub>3</sub> was also attempted. However, the phosphine produced was predominantly racemized.

(11) The value of ee was estimated by measuring the optical rotation of the phosphine oxide ([ $\alpha$ ]<sub>D</sub><sup>25</sup> +23.2° (*c* 1.3, MeOH) (89% ee)) derived from this phosphine.

(12) The meso isomer was easily removed by preparative layer chromatography on silica gel.

(13) Reported values:<sup>8</sup> mp 102–104 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -85.0° (*c* 1.0, CHCl<sub>3</sub>).

(3) Utilization of cerium chloride in organic syntheses has been reported. (a) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454. (b) Luche, J.-L.; Gemal, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 5848. (c) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904. (d) Imamoto, T.; Sugiura, Y.; Takiyama, N. *Tetrahedron Lett.* **1984**, *25*, 4233.

(4) Phosphine oxides were rapidly deoxygenated by LiAlH<sub>4</sub>-CeCl<sub>3</sub> in THF at 20–40 °C to afford phosphines in excellent yields. This method is of greater advantage than the one using LiAlH<sub>4</sub> alone and is useful particularly for the reduction of sterically crowded phosphine oxides, although it is not stereospecific (see ref 10).

(5) In a separate experiment it was found that tertiary or secondary phosphines reacted smoothly with NaBH<sub>4</sub>-CeCl<sub>3</sub> to afford phosphine-boranes in essentially quantitative yields. In contrast, no traces of phosphine-boranes were produced in the absence of CeCl<sub>3</sub>.

(6) Schmidbaur et al. reported that diphosphanomethane-bis(boranes) could be metalated and C-alkylated. See ref 1d.

(7) Maryanoff, C. A.; Maryanoff, B. E.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 5839.

(8) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

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