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Borane complex of amino-functionalized phosphine

Abstract: Phosphine compounds [2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**1**) and [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**2**) containing Y,C,Y-chelating ligands were treated with BH$_3$·SMe$_2$. Coordination of BH$_3$·SMe$_2$ by **2** produced complex {[2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Ph$_2$P}·(BH$_3$)$_3$ (**3**). Compound **3** was characterized by means of elemental analyses, ^{1}H, ^{11}B, ^{13}C, ^{31}P NMR spectroscopy, and by single crystal X-ray diffraction analysis.

Keywords: borane; NMR; phosphine; X-ray diffraction; YCY-chelating ligands.

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Introduction

Ether-functionalized phosphines such as tris(2,6-dimethoxyphenyl)phosphine (TDMPP), tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), and their related phosphines combine characteristics of high basicity and steric bulkiness (Horner and Hoffmann, 1956; Horner et al., 1968; Knowles et al., 1972, 1975; Knowles, 1983; Haefner et al.,1991; Baker et al., 1992, 1993; Haefner and Dunbar, 1992; Dunbar et al., 1994). Transition metal complexes with ether-functionalized phosphine ligands have been found to exhibit enhanced reactivity due to the presence of weak *P,O*-chelation producing metal-ether interactions that are often labile both in the solid state and in solution (Yamamoto et al., 1995, 1996; Han and Yamamoto, 1998). In was also demonstrated that elimination of alkyl groups is possible in these transition metal complexes of O,P,O-ligands to produce new covalent transition metal-oxygen bonds (Empsall et al., 1974, 1975, 1976; Jones et al., 1974; Miller and Shaw, 1974; Lindner and Bader, 1991; Lindner et al., 1993, 1994; Weissman et al., 2004). By contrast, corresponding amino-functionalized N,P,N-chelating ligands, widely used in the chemistry of transition metals, form six- and five-membered rings as the result of *P,N*-chelation to transition metal center (del Campo et al., 1999; Mirkin, 1999; Braunstein and Naud, 2001; Uchiike et al., 2008; Canovese et al., 2009; Maggini, 2009). As a result of this behavior, ether- and amino-functionalized phosphines are referred to as 'hemi-labile' ligands (Espinet and Soulantica, 1999; Slone et al., 1999; Gianneschi et al., 2005; Angell et al., 2006; Moxham et al., 2006; Weng et al., 2007). Previously, we have shown different coordination ability of ether- and amino-functionalized phosphines [2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**1**) and [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**2**) towards MCl$_2$ (M is Pd, Pt) (Chart 1) (Řezníček et al., 2011, 2012).

In addition, ether- or amino-functionalized phosphines are also able to form stable phosphine borane complexes (Brunel et al., 1998; Carboni and Monnier, 1999). The phosphine borane complexes can be used in catalyst or are active in an activation of small molecule (Imamoto et al., 1998; Welch et al., 2006; Welch and Stephan 2007; Chase and Stephan, 2008). In the course of our systematic studies on the chemistry of **1** and **2**, here we report their different reactivity towards BH$_3$·SMe$_2$.

Results and discussion

Treatment of [2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**1**) with BH$_3$·SMe$_2$ did not provide any isolable product. By contrast, the same reaction of [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**2**) with 3 eq. of BH$_3$·SMe$_2$ yielded complex {[2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Ph$_2$P}·(BH$_3$)$_3$ (**3**), in quantitative yield (Scheme 1).

Complex **3** was characterized with the help of ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectroscopy. The ^{31}P[^{1}H] NMR spectrum showed a resonance at δ +16.6 ppm that is shifted downfield compared with the starting **2** (δ -17.2 ppm) (Carré et al., 1997). The ^{1}H NMR spectrum of **3** showed singlet of methylene C*H*$_2$N groups at δ 3.59 ppm and a broad resonance at δ 1.58 ppm for B*H*$_3$ moiety. The ^{11}B NMR spectrum revealed,

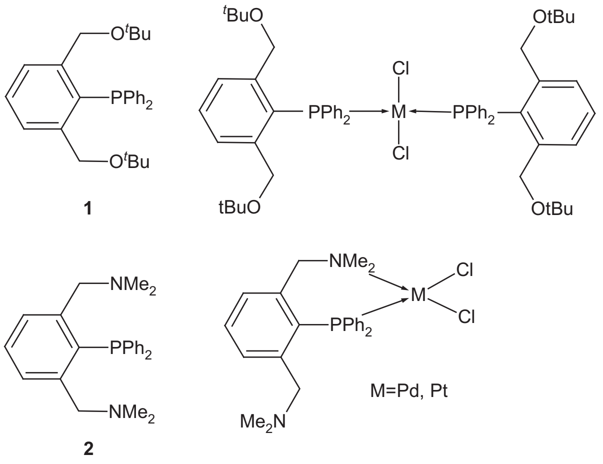


Chart 1 Compounds **1** and **2** and their Pd and Pt complexes.

however, two resonances at δ -8.7 ppm and δ -35.9 ppm as emerging a presence of non-equivalent BH_3 groups.

Single crystals of **3** suitable for X-ray diffraction analysis were obtained by crystallization from toluene solution at +4°C. The molecular structure of **3**, selected bond lengths, and angles are shown in Figure 1; the crystallographic data are given in Table 1.

Thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1-B1 1.881(4), N1-B2 1.621(3), N1a-B2a 1.621(3), C1-P1-B1 117.49(18), C1-P1-C13a 87.23(10), C1-P1-C8 105.47(10).

The molecular structure proved the presence of two non-equivalent BH_3 groups. Whereas one boron atom B1 coordinates the central phosphorus atom P1, the remaining two BH_3 groups coordinate CH_2NMe_2 moieties of ligand L^2. The central phosphorus atom P1 is four coordinate with deformed tetrahedral arrangement with bonding angles C1-P1-B1 (117.49(18)°), C1-P1-C13a (87.23(10)°), and C1-P1-C8 (105.47(10)°). The P1-B1 bond length (1.881(4) Å) is close to the sum of covalent radii of both atoms (Σ_{cov}(B,P)=1.96 Å) (Pyykkö et al., 2005; Pyykkö and Atsumi, 2009a) and indicates the presence of strong P→B intramolecular interaction in **3**. Similarly the N1-B1 and N1a-B1a bond lengths (1.621(3) and 1.621(3) Å) are somewhat longer than the sum of covalent radii of both atoms (Σ_{cov}(B,N)=1.56 Å) (Pyykkö et al., 2005; Pyykkö and Atsumi, 2009b) and suggest the presence of strong N→B coordination in **3**.

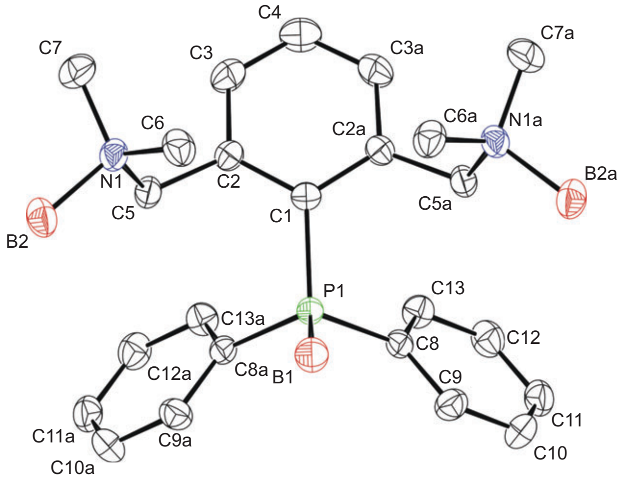
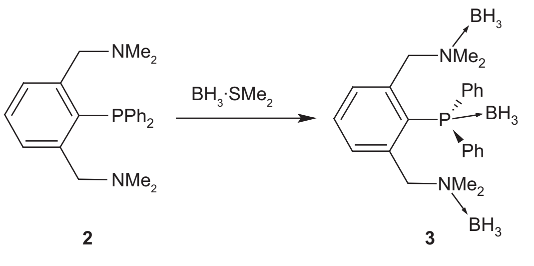


Figure 1 ORTEP view of compound **3**.



Scheme 1 Synthesis of phosphine borane complex (L^{2}PPh$_2$)·(BH_3)$_3$ (**3**).

	3
Empirical formula	$C_{24}H_{38}B_3N_2P$
Color	Colorless
Crystal system	Orthorhombic
Space group	*P n m a*
a, Å	15.0600(6)
b, Å	20.1280(11)
c, Å	8.4051(13)
α, °	90
β, °	90
γ, °	90
Z	4
mm^{-1}	0.121
D_x, Mg m^{-3}	1.090
Crystal size, mm	0.30×0.26×0.19
Crystal shape	Block
Range, deg	1–27.5
ρ max/min, e/Å^3	0.542/-0.351
Number of reflections measured	14 120
Number of unique reflections, R_{int}^{a}	29780.0737
Number of observed refs.	2086
Number of parameters	142
S^b, all data	1.125
Final R^c, I>2σ(I)	0.0590
$wR2^c$, all data	0.1373

Table 1 Crystal data and structure refinement for compound **3**.

[a] $R_{int}=\Sigma|F_o^2-F_{o,mean}^2|/\Sigma F_o^2$.

[b] $GOF=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{diffrs}-N_{params})]^{1/2}$ for all data.

[c] $R(F)=\Sigma\,||F_o|-|F_c||/\Sigma|F_o|$for observed data, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

In conclusion, we have demonstrated different reactivity of ether- and amino-functionalized phosphines $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]PPh_2$ (**1**) and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PPh_2$ (**2**) towards $BH_3{\cdot}SMe_2$. Compound **2** easily coordinates three molecules of BH_3 to provide complex $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ph_2P\}{\cdot}(BH_3)_3$ (**3**).

Experimental section

General methods

The starting compounds $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]PPh_2$ and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PPh_2$ were prepared according to the literature (Carré et al., 1997; Řezníček et al., 2011, 2012). $BH_3{\cdot}Me_2S$ complex was purchased by Sigma Aldrich (Sokolovská, Praha, Czech Republic). All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried by standard methods, distilled prior to use. ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer at 300 K in $CDCl_3$. ^1H, ^{13}C, ^{11}B, and ^{31}P NMR chemical shifts δ are given in ppm and referenced to internal Me_4Si (^1H and ^{13}C), H_3PO_4 (^{31}P), and external $BF_3{\cdot}Et_2O$ (^{11}B). Elemental analyses were performed on an LECO-CHNS-932 analyzer.

Synthesis of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ph_2P{\cdot}(BH_3)_3$ (3)

Solution (2.0 M) of $BH_3{\cdot}Me_2S$ (2.78 ml, 5.56 mmol) was added dropwise to toluene solution (15 ml) of **2** (0.59 g, 1.59 mmol). The formation of white suspension occurred within 1 h and the reaction mixture was stirred for an additional 19 h. Suspension was concentrated to 5 ml and filtrated off. The solid was separated and dried under reduced pressure to give **3** (yield 0.61 g, 92%). For **3**: mp 169–171°C; Anal. Calcd. for $C_{24}H_{38}B_3N_2P$ (417.97 g/mol): C, 68.44; H, 9.80. Found: C, 68.47; H, 9.82. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.58 (bs, 9H, B*H*); 2.37 (s, 12H, NCH_3); 3.59 (s, 4H, CH_2N); 7.40–7.97 (m, 13H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.0 (NCH_3); 67.9 (CH_2N, $^3J(^{13}C, ^{31}P)=6$ Hz); 129.5 (C(3',5'); $^3J(^{13}C, ^{31}P)=10$ Hz); 131.8 (C(2',6'), $^2J(^{13}C, ^{31}P)=7$ Hz); 131.8 (C(3,5), $^3J(^{13}C, ^{31}P)=7$ Hz); 132.1 C(4'); 132.7 C(4); 135.0 (C(2,6), $^2J(^{13}C, ^{31}P)=7$ Hz); 135.0 (C(1), $^1J(^{13}C, ^{31}P)=46$ Hz); 138.5 (C(1'), $^1J(^{13}C, ^{31}P)=16$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.6; ^{11}B NMR ($CDCl_3$, 128 MHz): δ -8.7 and -35.9.

Crystallography

Compound **3** was dissolved in toluene and allowed to crystallize at 4°C. Obtained material was suitable for X-ray analysis. X-Ray data (Table 1) for colorless crystals of **3** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with MoK_α radiation (λ=0.71073 A), a graphite monochromator, and ϕ and χ scan mode. Data reductions were performed with DENZO-SMN (Otwinowski and Minor, 1997). Absorption was corrected by integration methods (Coppens, 1970). Structures were solved by direct methods (Sir92) (Altomare et al., 1993) and refined by full matrix least-square based on F^2 (SHELXL97) (Sheldrick, 1997). Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)=1.2\ U_{eq.}$ (pivot atom) or of $1.5\ U_{eq.}$ for the methyl moiety with C—H=0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic rings, respectively. H atoms of the BH_3 groups were placed into idealized positions with B—H bond lengths of 0.96 Å. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC no. 882969 for **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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