

Molybdenum complexes bearing a diaminosubstituted-phosphiteboranyl ligand: Syntheses, structures, and reactivity involving the Mo–B, B–P, and B–H activation

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Received 24 March 2006; received in revised form 21 April 2006; accepted 24 April 2006

Available online 1 September 2006

Abstract

Photoreaction of diaminosubstituted-phosphiteborane, $\text{BH}_3\text{P}(\text{NMeCH}_2)_2(\text{OMe})$ with a methyl molybdenum complex, $(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R}_5 = \text{Me}_5, \text{Me}_4\text{H}, \text{H}_5$) yielded a phosphiteboranyl molybdenum complex, $(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{BH}_2\{\text{P}(\text{NMeCH}_2)_2(\text{OMe})\}$ ($\text{R}_5 = \text{Me}_5$: **2**, Me_4H : **3**, H_5 : **4**). In the reaction of **2** with MeI , the Mo–B bond was activated to give $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{Me}$, in the reaction with PMe_3 , the B–P bond was activated to give $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3(\text{BH}_2\text{PMe}_3)$. Complex **2** in solution was gradually converted into $(\eta^5\text{-C}_5\text{Me}_5)\text{MoH}(\text{CO})_2\{\text{P}(\text{NMeCH}_2)_2(\text{OMe})\}$ (**8**) via the B–H bond activation of **2**. Structures of **2**, **3**, and **8** were determined by single crystal X-ray diffraction studies.

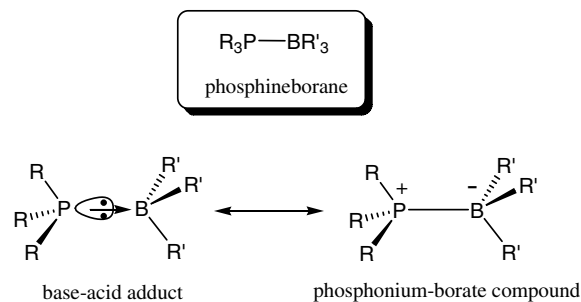
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Keywords: Phosphiteborane; Phosphiteboranyl complex; Bond activation; Photoreaction; Molybdenum; X-ray structure

1. Introduction

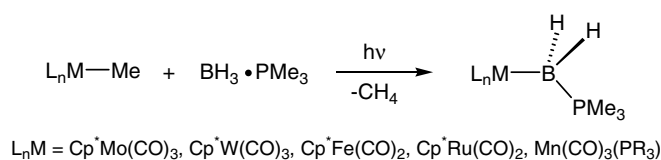
Phosphineborane ($\text{R}_3\text{PBR}'_3$) is generally considered to be a Lewis base–acid adduct, that is, the P–B bond consists of donation of lone-pair electrons on the phosphorus to the empty p orbital of the boron. On the other hand, phosphineborane also can be seen as a phosphonium-borate compound with a P–B covalent bond, if positive and negative charge is located on the P and the B, respectively. In the latter description, phosphineborane is isoelectronic to alkane. Phosphineborane may be described as a resonance hybrid somewhere between these two extremes. Phosphineborane complexes ($\text{L}_n\text{M-PR}_2\text{BR}'_3$) and phosphiteboranyl complexes ($\text{L}_n\text{M-BR}'_2\text{PR}_3$) attracted considerable attention. Since phosphineborane complexes are formally produced by the displacement of one substituent on the P of

phosphineborane by a transition fragment and phosphineboranyl complexes are formally produced by the displacement of one substituent on the B by a transition metal fragment, these complexes are isoelectronic to organo-transition-metal complexes.



B–H bond activation of BH_3PR_3 with a transition metal complex is a subject of growing interest, because this reaction can be considered as a model reaction of alkane C–H activation [1]. Many examples of B–H bond activation by

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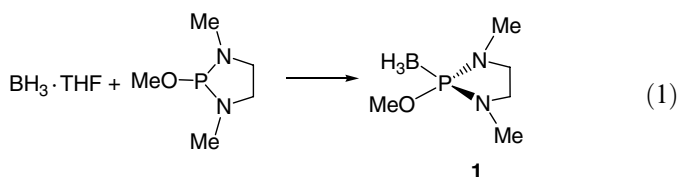
Scheme 1.

transition metal complexes have been reported for tri-coordinate boranes [2,3]. In contrast, little is known of B–H bond activation of tetra-coordinate (sp^3 -type) boranes such as $BH_3 \cdot PR_3$ [4,5]. Shimoi et al. reported elegant examples of B–H bond activation of tetra-coordinate borane (Scheme 1). The photolysis of $Cp^*M(CO)_3Me$ ($Cp^* = \eta^5-C_5Me_5$, $M = Mo, W$) in the presence of $BH_3 \cdot PMe_3$ produced $Cp^*M(CO)_3BH_2(PMe_3)$ [6]. They also synthesized $Cp^*M(CO)_2BH_2(PMe_3)$ ($M = Fe, Ru$) [7] and $Mn(CO)_3(PR_3)BH_2(PMe_3)$ ($PR_3 = PEt_3, PMe_2Ph$) [8]. Shimoi's method, that is, photoreaction of a methyl complex of transition metal with phosphineborane to produce phosphineboranyl complex seems to be useful. But examples shown to date are limited only for trimethylphosphineborane. Herein we demonstrate that photoreaction of $Cp^*Mo(CO)_3Me$ and its derivatives in the presence of several phosphorus compounds, such as diaminosubstituted-phosphiteborane, $BH_3P(NMeCH_2)_2(OMe)$ (**1**), produced phosphiteboranyl Mo complexes, such as $Cp^*Mo(CO)_3BH_2\{P(NMeCH_2)_2(OMe)\}$ (**2**). We also present the unprecedented reactivity of **2** involving Mo–B bond activation by MeI, B–P bond activation by PMe_3 , and B–H bond activation. A part of this work was reported preliminarily [9].

2. Results and discussion

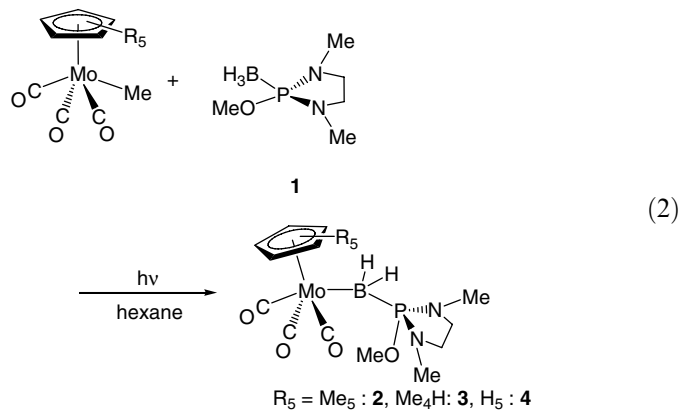
2.1. Synthesis and characterization of phosphiteboranyl molybdenum complexes

Treatment of $P(NMeCH_2)_2(OMe)$ [10] with $BH_3 \cdot THF$ yields a diaminosubstituted-phosphiteborane, $BH_3 \cdot P(NMeCH_2)_2(OMe)$ (**1**) in the analogous method [11], as a white solid in 98% yield, as shown in Eq. (1).



Photoreaction of **1** with some methyl molybdenum complexes ($\eta^5-C_5R_5$) $Mo(CO)_3Me$ ($R_5 = Me_5, Me_4H, H_5$) [12–14] at 0 °C in 1:1 molar ratio afforded corresponding phosphiteboranyl complexes ($\eta^5-C_5R_5$) $Mo(CO)_3BH_2\{P(NMeCH_2)_2(OMe)\}$ ($R_5 = Me_5$: **2**, Me_4H : **3**, H_5 : **4**) (Eq. (2)). The isolation yields were 43% for **2**

and 13% for **3**. Complex **4** could not be isolated due to its thermal instability. We sought optimized reaction conditions to get a better isolation yield, and found that the reaction of **1** with a slightly excess amount (1.36 times molar ratio) of $Cp^*Mo(CO)_3Me$ produces **2** in a 70% yield based on the Mo complex and in a 95% yield based on **1**. An analogous methyl complex of another transition metal, $Cp^*W(CO)_3Me$ and $Cp^*M(CO)_2Me$ ($M = Fe, Ru$), did not react with **1** under the same reaction conditions. This is in contrast to the results of the reaction with $BH_3 \cdot PMe_3$ (see Scheme 1).



The X-ray structures of **2** and **3** were determined by X-ray crystallography. The molecular structures of **2** and **3** are shown in Fig. 1(a) and (b), respectively, and selected bond distances and angles are summarized in Table 1. Both complexes have a phosphiteboranyl ligand, a C_5R_5 ligand with η^5 -fashion ($R_5 = Me_5$: **2**, Me_4H : **3**), and three carbonyl ligands around the Mo forming a four-legged piano-stool structure. The Mo–B bond distance is 2.472(4) Å in **2** and 2.487(3) Å in **3**, and slightly shorter than that of the previously reported phosphineboranyl complex, $Cp^*Mo(CO)_3\{BH_2(PMe_3)\}$ (2.497(5) Å) [6]. The B–P bond distance (1.903(4) Å: **2**, 1.908(3) Å: **3**) is obviously shorter than that of the corresponding phosphineboranyl complexes, $Cp^*M(CO)_3\{BH_2(PMe_3)\}$ ($M = Mo$: 1.949(5) Å, W : 1.952(7) Å) [6]. The bond distances of Mo–C(carbonyl) are almost the same for **2**, **3**, and $Cp^*Mo(CO)_3\{BH_2(PMe_3)\}$, irrespective of the geometrical position of CO (cis or trans to the boranyl ligand). The bond angles of Mo–B–P (123.4(2)° for **2**, 121.2(1)° for **3**) are similar to that of the phosphineboranyl complex (121.4(2)°) [6], showing that these borons have typical tetrahedral geometries.

The $^{31}P\{^1H\}$ NMR signals in **1–3** show broad quartet at δ 113.3 (q, $J_{BP} = 102.1$ Hz) for **1**, 103.6 (q, $J_{BP} = 127.6$ Hz) for **2**, and 103.9 (q, $J_{BP} = 127.2$ Hz) for **3**. In the ^{11}B NMR, the chemical shifts for **2** (δ –29.6, $J_{PB} = 130.0$ Hz, $J_{HB} = 120.4$ Hz) and **3** (δ –30.0, $J_{PB} = 130.0$ Hz, $J_{HB} = 110.7$ Hz) are at lower field than that for **1** (δ –42.2, dq, $J_{PB} = 102.1$ Hz, $J_{HB} = 96.3$ Hz). The similar tendency has been observed for $Cp^*Mo(CO)_3\{BH_2(PMe_3)\}$ [6].

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