Boryl Complexes

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Boryl Anion Attacks Transition-Metal Chlorides To Form Boryl Complexes: Syntheses, Spectroscopic, and Structural Studies on Group 11 Borylmetal Complexes**

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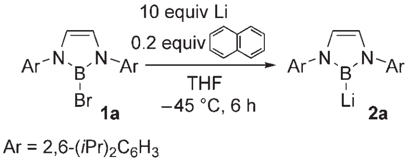
Transition-metal boryl complexes[1] have been proposed as intermediates in many catalytic transformations of boron-containing substrates.[2] Since some isolated boryl complexes show unique catalytic acitivity,[2,3] syntheses of boryl complexes would provide the possibility for new catalytic reactions. However, methods for the synthesis of boryl complexes are still limited. In fact, the following three types of reactions are the major methodologies to introduce a boryl ligand:[1] 1) salt elimination through the reaction of anionic metal carbonyl complexes with haloboranes;[4] 2) oxidative addition of a boron–heteroatom bond to low-valent transition metals;[5] and 3) σ-bond metathesis reactions between alkyl metal complexes and hydroboranes in the presence of light[6] or oxygen-substituted metal complexes and diborane.[7,8] Hence, generally obtainable boryl complexes should be classified into 1) multicarbonyl complexes, 2) metal complexes of which the precursors are active for oxidative addition, and 3) metal complexes that have appropriate alkylmetal or alkoxymetal precursors. Thus, a new and general methodology for the synthesis of boryl complexes would enable access to new types of boryl complexes. Recently, we reported the reduction of bromoborane **1a** to the corresponding boryllithium compound **2a** [Eq. (1)].[9] The nucleophilic character of **2a** prompted us to develop the introduction of boryl ligands via nucleophilic attack on transition-metal halides.[10]

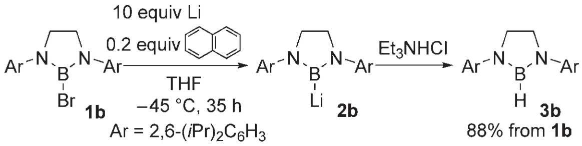


(1)

N-heterocyclic carbene (NHC) ligands, which are isoelectronic to boryllithium species **2a**, are among the strongest electron-donor ligands known.[11] Steric and electronic properties of NHCs can be easily tuned by modification of their substituents and skeleton.[12] For example, the saturation of the C–C backbone of an NHC was reported to lead to a more electron-rich metal center and to accelerate the Ru-catalyzed olefin metathesis reaction.[13] Therefore, we decided to synthesize the C–C-saturated boryllithium compound **2b** to compare its electronic properties with **2a**.

Herein, we report the synthesis of boryllithium species **2b** with a saturated C–C backbone and reactions of **2a** and **2b** with Group 11 metal chlorides to form the corresponding borylmetal complexes by nucleophilic borylation.[14] Spectroscopic and structural studies on the boryl complexes are also described.

The C–C-saturated boryllithium species **2b** was synthesized by a method similar to that reported for **2a** (Scheme 1).[9] Reduction of bromoborane precursor **1b** with an excess of lithium powder and a catalytic amount of naphthalene in THF caused the appearance of a broad singlet in the ^{11}B NMR spectrum at $\delta_B = 51.9$ ppm ($h_{1/2} = 773$ Hz) attributable to **2b**. The downfield shift of the ^{11}B signal of **2b** relative to that of **2a** ($\delta_B = 45.4$ ppm)[9] obeyed the trend observed for other diazaborolidine derivatives.[15] The THF solution of **2b** was quenched with Et$_3$NHCl to give the corresponding hydroborane **3b**, which could be characterized by X-ray crystallography (see the Supporting Information) in 88% yield of isolated product from **1b**. Compound **2b** was also characterized by ^{1}H and ^{13}C NMR spectroscopy of the reaction mixture in [D$_8$]THF.



Scheme 1. Generation of boryllithium compound **2b** with a saturated backbone.

IMes borylmetal complexes **4a**,**b**–**6a**,**b** (IMes = *N*,*N'*-bis(2,4,6-trimethylphenyl)-imidazole-2-ylidene; **a** denotes unsaturated backbone, **b** denotes saturated backbone) and PPh$_3$–borylgold(I) complexes **7a**,**b** were synthesized through addition of boryllithium compounds **2a**,**b** to equal amounts of IMes- or PPh$_3$-ligated Group 11 metal chlorides in THF

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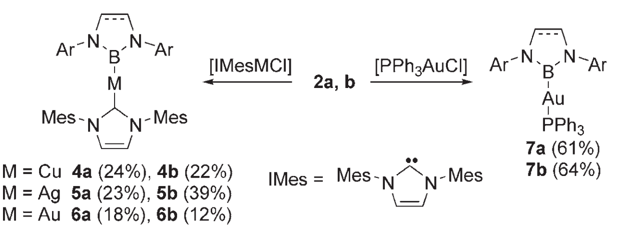
(Scheme 2). All complexes were characterized by spectroscopic, elemental, and X-ray analyses and were shown to have a linear, two-coordinate structure (see Figures 1 and 2 for structures of **5a** and **7a**; see Table 1 and the Supporting Information for structures of the other complexes).[16] Complexes **5a**,**b**–**7a**,**b** are the first examples of fully characterized borylsilver and borylgold complexes.



Scheme 2. Syntheses of Group 11 borylmetal complexes with boryllithium compounds **2a**,**b** (yields of isolated product).

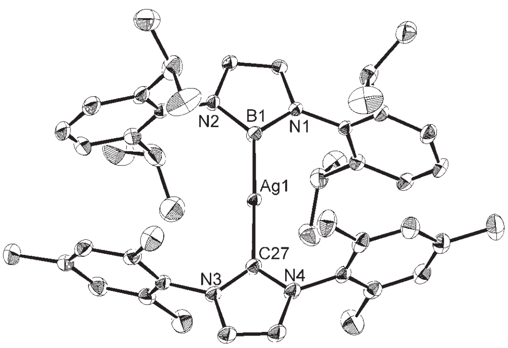


Figure 1. Crystal structure of **5a**. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity.

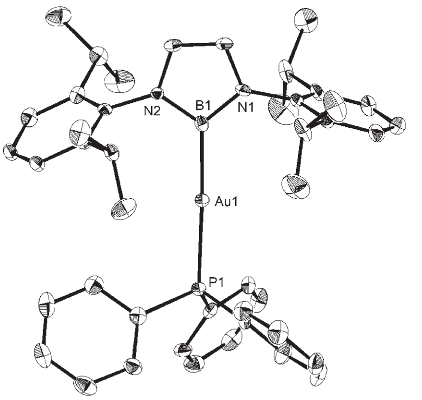


Figure 2. Crystal structure of **7a**. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 1: Observed chemical shifts (NMR spectroscopy) of the ^{11}B, ^{13}C(carbene carbon atom) and ^{31}P nuclei and selected bond lengths obtained from crystallographic data for **4a**,**b**–**7a**,**b** and reference compounds **8**–**14**.

Complex	δ_B	δ_C	δ_P	M–B [Å]	M–C/P [Å]
4a	38.9	185.3		1.980(2)	1.918(2)
4b	44.7	185.2		1.983(3)	1.915(3)
5a	40.7	194.6		2.118(2)	2.1207(18)
5b	46.5	194.8		2.122(4)	2.124(4)
6a	45.1	217.0		2.074(4)	2.078(4)
6b	49.9	216.3		2.069(3)	2.070(3)
7a	45.4		57.7	2.076(6)	2.3469(13)
7b	49.5		57.8	2.086(5)	2.3574(11)
free IMes (**8**)		219.7			
IMesCuCl (**9**)		178.7			
IMesAgCl (**10**)		184.0			2.056(7)
IMesAuCl (**11**)		173.4			1.998(5)
PPh$_3$AuCl (**12**)			33.5		2.235(3)
PPh$_3$AuPh (**13**)			44.0		2.296(2)
PPh$_3$AuMe (**14**)			47.7		2.279(8)

In the borylcopper complexes **4a**,**b**, the Cu–B and Cu–C bond lengths are shorter than those in the recently isolated borylcopper complex [IMesCuB(pinacolate)] (**15**; 2.002(3) and 1.937(2) Å).[8] The B-Cu-C angles in **4a**,**b** are almost linear (179.43(9) and 179.41(15)°), which satisfies the steric repulsion between the bulky diaminoboryl and diaminocarbene ligands. This structure is in contrast to that of **15**, which has a bent B-Cu-C angle (168.07(16)°)[8] that is probably due to packing forces. Borylsilver complexes **5a**,**b** possess two-center-two-electron (2c-2e) Ag–B bonds that are shorter than the silver–boron interactions (2.35–2.76 Å)[17] in the previously reported hydroborane silver complexes, which have 3c-2e bonds consisting of boron, hydrogen, and silver atoms. Similarly, borylgold complexes **6a**,**b**–**7a**,**b** also have 2c-2e Au–B bonds that are shorter than the gold–boron interactions (2.14–2.68 Å)[18] in cage compounds containing gold and boron atoms in which the boron atom forms one or more multicenter–multielectron bonds.

The stronger *trans* influence of a boryl ligand[19,20] than that of a chloride ligand is demonstrated by the smaller silver–carbon coupling constants $^{1}J_{\text{C-Ag}}$ in **5a** (81 and 88 Hz to ^{107}Ag and ^{109}Ag, respectively) and **5b** (83, 95 Hz) than those in [IMesAgCl] (**10**; 234, 270 Hz).[21] It is noteworthy that strong interaction between the central silver atom and boryl ligand causes the signal of the olefinic protons in the five-membered ring of **5a** to be a doublet, owing to coupling with silver ($^{4}J_{\text{Ag-H}} = 2$ Hz, couplings to ^{107}Ag and to ^{109}Ag not resolved).[22] From the chemical shifts, the following three features were found (Table 1): 1) all boryl complexes **4a**,**b**–**7a**,**b** showed characteristic downfield ^{11}B signals in the range of 38–50 ppm as observed for common dialkoxyboryl or diaminoboryl transition-metal complexes;[1] 2) in the ^{13}C NMR spectra of **4a**,**b**–**6a**,**b**, resonances for the carbene carbon atom were shifted downfield compared to those of reference compounds **9**–**11**.[21,23,24] Notably, ^{13}C chemical shifts of the carbene carbon atom in borylgold(I) carbene complexes **6a**,**b** were close to those of the free carbene IMes (**8**);[23] and 3) the differences in the ^{13}C or ^{31}P chemical shifts between unsaturated system **a** and saturated system **b** are generally small.

X-ray crystallographic analyses of **4a**,**b**–**7a**,**b** further support the large *trans* influence of boryl ligands (Table 1): 1) the M–C$_{\text{carbene}}$ bonds in **5a**,**b** and **6a**,**b** are longer than those of reference [IMesMCl] complexes **10** and **11** (M = Ag,[21] Au[24]); and 2) the Au–P bonds in **7a**,**b** are longer than those in a series of PPh$_3$–Au$^{\text{I}}$ complexes **12**–**14**[25] that have an additional anionic ligand (Cl$^-$, Ph$^-$, or Me$^-$). The difference in *trans* influence between unsaturated and saturated systems generally seems to be negligible, although the Au−P bond in **7b** is slightly longer than that in **7a**. The order of M−B and M−C bond lengths among **4a**,**b**–**6a**,**b** is Cu < Au < Ag, which reflects the ionic radii (Cu < Ag < Au) and the relativistic effect[26] that leads the gold atom to be smaller than silver atom. Borylgold complexes **6a**,**b** and **7a**,**b** showed no significant intermolecular aurophilic interaction,[27] which is probably due to the bulky boryl ligands.

In conclusion, we have demonstrated the nucleophilic substitution by boryllithium compounds **2a**,**b** on Group 11 metal chloride complexes to form boryl complexes **4a**,**b**–**7a**,**b**. Complexes **5a**,**b**–**7a**,**b** are the first examples of borylsilver and borylgold complexes that have 2c-2e M−B bonds. This methodology may be applicable to the synthesis of other boryl complexes. The NMR spectra and solid-state structures of the resulting boryl complexes revealed that the boryl ligand is one of the strongest known σ donors.[20] Saturation of the boryl ligand skeleton had little influence on its donor ability. The further reactivity of these boryl complexes is under investigation.

Experimental Section

2b: In a glovebox, **1b** (50 mg, 106 μmol) and naphthalene (2.7 mg, 21 μmol) were dissolved in [D$_8$]THF (1 mL). Lithium powder (7.4 mg, 1.07 mmol) was added to the solution at −45 °C, and the resulting suspension was stirred for 35 h at −45 °C to afford a dark red suspension. An aliquot of this suspension was transferred into a screw-capped NMR tube to record the NMR spectra. ^{1}H NMR ([D$_8$]THF, 500 MHz): $\delta = 1.21$ (d, $J = 7$ Hz, 12 H), 1.22 (d, $J = 7$ Hz, 12 H), 3.44 (s, 4 H), 3.84 (sep, $J = 7$ Hz, 4 H), 6.97 (dd, $J = 9$ Hz, 6 Hz, 2 H), 7.02 ppm (d, $J = 7$ Hz, 4 H); ^{13}C NMR ([D$_8$]THF, 125 MHz): $\delta =$ 25.46 (CH$_3$), 25.55 (CH$_3$), 28.9 (CH), 55.1 (CH$_2$), 123.5 (CH), 124.7 (CH), 149.3 (quaternary C), 149.7 ppm (quaternary C); ^{11}B NMR ([D$_8$]THF, 160 MHz): $\delta = 51.9$ ppm (br s).

4a,**b**–**7a**,**b**: In a glovebox, **1a** or **1b** (1 equiv) and naphthalene (0.40 equiv) were dissolved in THF (10 mL per mmol of **1**). Lithium powder (10 equiv) was added to the solution at −45 °C, and the resulting suspension was stirred for 20 h at −45 °C to afford a dark red suspension. The suspension was filtered through a celite pad to remove excess lithium and lithium naphthalenide. The filtrate was added at −45 °C to a THF solution (see the Supporting Information for each condition) of metal chloride complex (1.0 equiv), and the resulting suspension was stirred for 1 h at room temperature. After solvents were evaporated under reduced pressure, hexane was added to the residue. The resulting suspension was filtered through a celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate, and recrystallization from toluene gave colorless crystals of the desired product. An analytically pure sample was obtained by recrystallization from hexane or toluene. Details of spectroscopic and analytical data for each compound are described in the Supporting Information.

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[16] Details of the crystal data and a summary of the intensity data collection parameters for **3b** and **4a**,**b**–**7a**,**b** are listed in Table S1 (see the Supporting Information). ORTEP drawings of these complexes are illustrated in Figures S1–S9 in the Supporting Information. In each case, a suitable crystal was mounted with cooled mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71069$ Å) to $2\theta_{\max} = 55°$. The structures were solved by direct methods with SIR-97 (A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119) and refined by full-matrix least-squares techniques against F^2 SHELXL-97 (G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, **1997**) The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions. CCDC-648270 (**3b**), CCDC-648271 (**4a**), CCDC-648272 (**4b**), CCDC-648273 (**5a**), CCDC-648274 (**5b**), CCDC-648275 (**6a**), CCDC-648276 (**6b**), CCDC-648277 (**7a**), and CCDC-648278 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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