A Base-Stabilized Terminal Borylene Complex of Osmium Derived from Reaction between a Dichloroboryl Complex and 8-Aminoquinoline[**]

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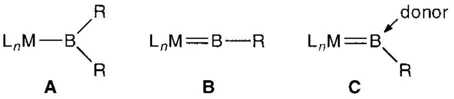
Two classes of terminal boron ligand have been structurally characterized, namely, boryl (**A**)[1] and borylene (**B**).[2] A theoretical analysis of the bonding characteristics of terminal borylene ligands shows that these ligands, which are isolobal with CO, have both good σ-donor and π-acceptor properties.[3] However, because of the high electrophilicity of the boron center, complexes of these ligands are likely to be stable only when sterically protecting and electron-releasing substituents are present on the boron atom, for example, $N(SiMe_3)_2$ or η^5-C_5Me_5 (Cp*).[2] Alternative strategies for stabilizing borylene complexes include placing the borylene ligand in a bridging situation between two metal centers,[4] utilizing very electron rich metal–ligand fragments, or coordination of a Lewis base to the boron atom, that is, formation of base-stabilized borylene complexes (**C**). Similar base-stabilized silylene complexes are a prominent feature of metal–silicon chemistry.[5]



Here we describe the synthesis of the dichloroboryl–osmium complex **1** as a precursor, which reacts with 8-aminoquinoline to provide **2a**, the first stable internally base-stabilized terminal borylene complex; the structure determination of the iodide derivative **2b**; and the further reaction of **2a** with ethanol to give the structurally characterized osmium-tethered ethoxyboryl complex **3**.

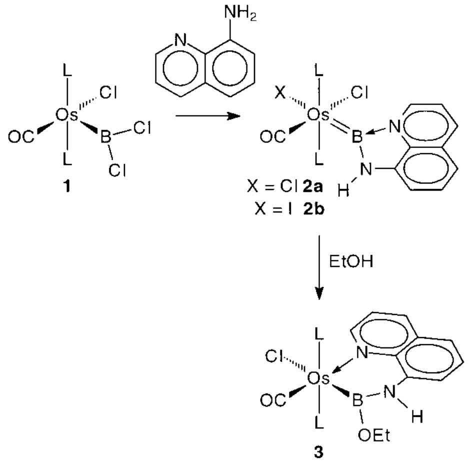
$[Os(BCl_2)Cl(CO)(PPh_3)_2]$ **1**

$[Os(=\overline{BNHC_9H_6N})Cl_2(CO)(PPh_3)_2]$ **2a**

$[Os(=\overline{BNHC_9H_6N})ClI(CO)(PPh_3)_2]$ **2b**

$[\overline{Os\{B(OEt)NHC_9H_6N}\}Cl(CO)(PPh_3)_2]$ **3**

Following the established route to five-coordinate boryl complexes of osmium(II),[6] treatment of $[Os(Ph)Cl(CO)(PPh_3)_2]$ with $HBCl_2 \cdot OEt_2$ produces bright yellow **1** (see the Experimental Section). The ^{11}B NMR spectrum for **1** exhibits a broad signal at $\delta = 52.5$. Complex **1** is a versatile synthon for many other boryl derivatives by virtue of the two good leaving groups on boron. For example, reaction with catechol ($catH_2$) gives $[Os(Bcat)Cl(CO)(PPh_3)_2]$, and treatment with ethanol gives $[Os\{B(OEt)_2\}Cl(CO)(PPh_3)_2]$.[1c] Reaction of **1** with 8-aminoquinoline gives the poorly soluble, red, base-stabilized borylene complex **2a** (Scheme 1). The more soluble, deep purple complex **2b**, in which the chloro ligand *trans* to boron is replaced with iodide, was formed by treatment of **2a** with tetrabutylammonium iodide. Both the ^1H and ^{13}C NMR spectra of **2b** (see the Experimental Section) are as expected for this formulation, but the signals for the borylene fragment and for the two triphenylphosphane ligands indicate the presence of two isomers. These isomers are interpreted as arising from two different orientations of the base-stabilized borylene ligand. The existence of these two isomers is also evident in the crystal structure, in which it is manifested as a disorder between the mutually *trans* Cl and CO ligands. The ^{11}B NMR spectrum of **2b** exhibits a broad signal at $\delta = 51.7$.



Scheme 1. Synthesis of base-stabilized borylene complexes and their reaction with ethanol. Complex **2b** is formed by treatment of **2a** with Bu_4NI. L = PPh_3.

The higher solubility of **2b** allowed crystals suitable for X-ray crystal structure determination to be obtained.[7] The molecular structure of **2b** is depicted in Figure 1. The overall geometry about osmium is approximately octahedral with mutually *trans* triphenylphosphane ligands and the iodo ligand *trans* to the borylene ligand. Hence, the chloro ligand *trans* to the borylene group was replaced by iodide ion, and this reflects a strong *trans* influence of the borylene ligand. The five-membered ring of the base-stabilized borylene ligand is almost coplanar with the equatorial ligand plane (angle between plane of borylene ligand and plane containing Os, Cl, I, CO is 8.3(2)°) and is sandwiched between two phenyl rings of the mutually *trans* triphenylphosphane ligands. The distances between the five-membered ring of the borylene ligand and the centroids of each of the two phenyl rings are only 3.271(3) and 3.192(5) Å. This arrangement suggests the existence of π–π stacking interactions between the three

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[**] This work was supported by the Marsden Fund administered by The Royal Society of New Zealand.

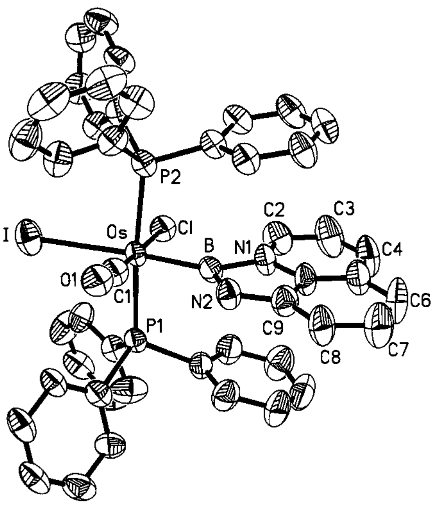
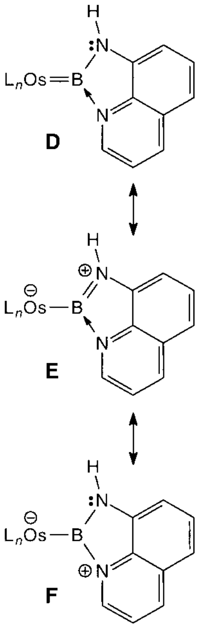


Figure 1. Molecular structure of **2b** (ORTEP) in the crystal (only one isomer shown). Selected bond lengths [Å] and angles [°]: Os-B 2.055(8), Os-C1 1.763(18), Os-I 2.8340(6), Os-Cl 2.476(7), Os-P1 2.3989(18), Os-P2 2.3833(18), B-N1 1.571(10), B-N2 1.440(10); C1-Os-B 84.3(6), C1-Os-I 85.8(5), C1-Os-Cl 179.0(5), I-Os-B 170.2(2), I-Os-Cl 93.62(12), P1-Os-P2 174.82(6), Cl-Os-B 96.2(3), Os-B-N1 131.6(5), Os-B-N2 129.1(5), B-N2-C9 113.6(6), B-N1-C10 109.8(6), N1-C10-C9 109.3(6), N2-C9-C10 108.0(6).

rings. The Os–B distance of 2.055(8) Å is the shortest of the range of Os–B distances we have observed in six-coordinate boryl complexes with either O or N substituents on boron. This distance is still longer than might be anticipated for a formal Os=B bond, but a pronounced shortening would not be expected for a base-stabilized borylene complex, since the valence-bond structures depicted in Scheme 2 (among others) must be considered. Base-stabilized silylene complexes also exhibit metal–silicon distances typical of single bonds rather than double bonds.[5] The two Os-B-N angles are approximately equal (ca. 130°), but the two B–N distances are markedly different (B–N2, 1.440(10), B–N1, 1.571(10) Å). The B–N2 distance is shorter than average and suggests a contribution from **E**. The B–N1 bond is also shorter than the average of all B–N(pyridine type) interactions reported in the CCSD. This is consistent with the presence of a particularly electrophilic boron center.



Scheme 2. Valence-bond structures for a base-stabilized osmium–borylene complex.

A theoretical study[3] on terminal borylene complexes drew attention to the expected electrophilicity of the boron atom in these complexes. Even the base-stabilized borylene complex **2a** displays this electrophilic character in undergoing a ready reaction with ethanol to form the ethoxy(amino)boryl complex **3**, experimental details of which will be published elsewhere. In this reaction the quinoline nitrogen atom shifts from boron to osmium to form an osmium-tethered boryl ligand (see Scheme 1). The structure of **3** is depicted in Figure 2. The Os–B distance of 2.072(3) Å is not significantly longer than the corresponding distance in **2b**. The B–O and B–N distances and Os-B-O and Os-B-N angles are all as expected. The Os–Cl distance of 2.6022(7) Å is the longest so far recorded.[8]

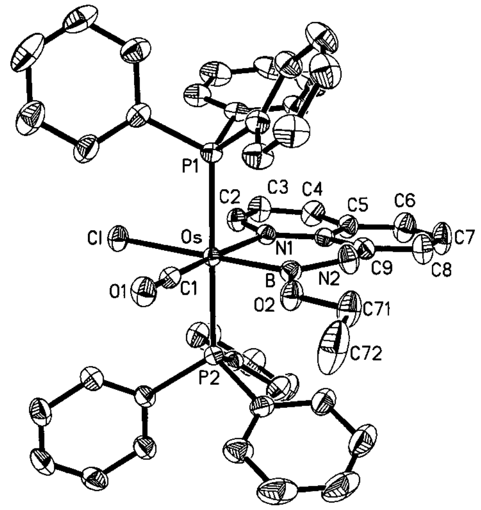


Figure 2. Molecular structure of **3** (ORTEP) in the crystal. Selected bond lengths [Å] and angles [°]: Os-B 2.072(3), Os-C1 1.843(3), Os-N1, 2.235(2), Os-Cl 2.6022(7), Os-P1 2.3799(7), Os-P2 2.3755(7), B-O2 1.401(4), B-N2 1.439(4); C1-Os-B 86.45(12), C1-Os-N1 174.50(10), C1-Os-Cl 93.19(8), N1-Os-B 88.05(10), N1-Os-Cl 92.31(6), P1-Os-P2 176.86(2), Cl-Os-B 179.31(8), B-N2-C9 132.2(2), Os-N1-C10 127.61(17), Os-B-O2 121.2(2), Os-B-N2 123.5(2).

The results reported here indicate that dichloroboryl ligands are potential precursors for numerous base-stabilized borylene ligands by reaction with potentially chelating hydroxyl and amino compounds.

Experimental Section

1: To a red suspension of $[Os(Ph)Cl(CO)(PPh_3)_2]$ (100 mg, 0.117 mmol) in benzene (15 mL) was added a solution of $HBCl_2 \cdot OEt_2$ in diethyl ether (0.15 mL, 1.0 M, 0.15 mmol). The mixture was then stirred at reflux temperature for 20 min. The resultant yellow solution was reduced to about 1 mL in vacuo, and hexane (20 mL) was added to precipitate a yellow solid, which was collected on a sintered glass crucible and washed with hexane. The product was purified by first placing it under vacuum for 30 min, then dissolving in benzene, filtering, reducing the solvent volume to about 1 mL and precipitation with hexane to give pure **1**. Yield 85 mg (85 %); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.36-7.46$ (m, 18 H, PPh_3), 7.55–7.60 (m, 12 H, PPh_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 128.37$ (t′,[9],$^{2,4}J$(C,P) = 11 Hz, *o*-PPh_3), 130.67 (s, *p*-PPh_3), 130.73 (t′, $^{1,3}J$(C,P) = 53 Hz, *ipso*-PPh_3), 134.46 (t′, $^{3,5}J$(C,P) = 11 Hz, *m*-PPh_3), 182.32 (t, ^2J(C,P) = 9 Hz, CO); ^{11}B NMR (128 MHz, C_6D_6, 25 °C, $BF_3 \cdot OEt_2$): $\delta = 52.5$; IR (Nujol): $\tilde{\nu}$ [cm^{-1}] = 1937vs (CO), 824s (B–Cl); elemental analysis calcd for $C_{37}H_{30}BCl_3OOsP_2$: C 51.68, H 3.52, Cl 12.37; found: C 51.87, H 3.79, Cl 12.34.

2a: A solution of **1** (85 mg, 0.0988 mmol) in benzene (10 mL) was added to 8-aminoquinoline (35 mg, 0.243 mmol) to produce a bright orange suspension, which was filtered through a sintered glass crucible. The orange solid was washed with EtOH, toluene, and hexane to give **2a** as a microcrystalline red solid. Yield 90 mg (87 %); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): major isomer: $\delta = 6.82$ (m, 1 H, $NC_9\mathit{H}_6NH$), 7.30 (m, 1 H, $NC_9\mathit{H}_6NH$), 7.49 (m, 1 H, $NC_9\mathit{H}_6NH$), 8.28 (s, 1 H, $NC_9H_6N\mathit{H}$), 8.40 (m, 1 H, $NC_9\mathit{H}_6NH$), 8.57 (m, 1 H, $NC_9\mathit{H}_6NH$); minor isomer: $\delta = 6.60$ (s, 1 H, $NC_9H_6N\mathit{H}$), 6.79 (m, 1 H, $NC_9\mathit{H}_6NH$), 7.46 (m, 1 H, $NC_9\mathit{H}_6NH$), 8.38 (m, 1 H, $NC_9\mathit{H}_6NH$), 10.31 (m, 1 H, $NC_9\mathit{H}_6NH$); overlapping signals of the two isomers: $\delta = 6.95-7.04$ (m, PPh_3), 7.15–7.28 (m, $NC_9\mathit{H}_6NH$), 7.82–7.90 (m, PPh_3); ^{13}C and ^{11}B NMR spectra were not obtained due to low solubility; IR (Nujol): $\tilde{\nu}$ [cm^{-1}] = 1902vs (CO); ^1H NMR shows 1.0 equiv of C_6H_6 present as solvent of crystallization; elemental analysis calcd for $C_{46}H_{37}BCl_2N_2OOsP_2 \cdot C_6H_6$: C 59.72, H 4.14, N 2.67; found: C 59.87, H 4.22, N 2.64.

2b: A solution of Bu_4NI (110 mg, 0.298 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of **2a** (90 mg, 0.093 mmol) in CH_2Cl_2 (15 mL), and the resultant mixture stirred for 40 min to give a dark red solution. Reduction of the solvent volume to about 1 mL in vacuo and addition of hexane gave an orange solid. The solid was collected on a sintered glass crucible and washed with EtOH, toluene, and hexane to give pure **2b** as a deep purple solid. Yield 93 mg (94%); ^1H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): major isomer: $\delta = 6.87$ (m, 1H, $NC_9\mathit{H}_6NH$), 7.52 (m, 1H, $NC_9\mathit{H}_6NH$), 8.25 (s, 1H, $NC_9H_6N\mathit{H}$), 8.40 (m, 1H, $NC_9\mathit{H}_6NH$), 8.46 (m, $NC_9\mathit{H}_6NH$), 8.65 (m, 1H, $NC_9\mathit{H}_6NH$); minor isomer: $\delta = 6.82$ (m, 1H, $NC_9\mathit{H}_6NH$), 7.23 (m, 1H, $NC_9\mathit{H}_6NH$), 7.49 (m, 1H, $NC_9\mathit{H}_6NH$), 8.27 (s, 1H, $NC_9H_6N\mathit{H}$), 8.57 (m, 1H, $NC_9\mathit{H}_6NH$), 10.11 (m, 1H, $NC_9\mathit{H}_6NH$); overlapping signals of both isomers: $\delta = 6.97-7.04$ (m, PPh_3), 7.29–7.35 (m, $NC_9\mathit{H}_6NH$), 7.75–7.87 (m, PPh_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): major isomer: $\delta = 127.48$ (t′,[9] $^{2,4}J(C,P) = 10$ Hz, *o*-PPh_3), 129.58 (s, *p*-PPh_3), 135.04 (t′, $^{3,5}J(C,P) = 10$ Hz, *m*-PPh_3); minor isomer: $\delta = 127.65$ (t′, $^{2,4}J(C,P) = 10$ Hz, *o*-PPh_3), 129.45 (s, *p*-PPh_3), 134.59 (t′, $^{3,5}J(C,P) = 10$ Hz, *m*-PPh_3); signals from other C atoms not observed due to low solubility; ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C, $BF_3 \cdot OEt_2$): $\delta = 51.7$; IR (Nujol): $\tilde{\nu}$ [cm^{-1}] = 1909m, 1892s, 1876s (CO); UV/Vis (CH_2Cl_2): $\lambda_{max} = 521.5$ nm; elemental analysis for $C_{46}H_{37}BClIN_2OOsP_2$: calcd: C 52.17, H 3.52, N 2.65; found: C 52.42, H 3.69, N 2.73.

Received: October 18, 1999 [Z14151]

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[7] Data for the X-ray structure analyses: **2b**: crystals from dichloromethane/benzene; $C_{46}H_{37}BClIN_2OOsP_2 \cdot 0.5\,C_6H_6$, $M_r = 1098.13$; crystal dimensions $0.28 \times 0.25 \times 0.08$ mm; monoclinic; space group $C2/c$; $a = 30.0757(4)$, $b = 20.6367(2)$, $c = 17.1417(2)$ Å, $\beta = 111.176(1)°$, $Z = 8$, $V = 9920.8(2)$ Å^3, $\rho_{calcd} = 1.470$ g cm^{-3}; $T = 203$ K; $2\theta_{max} = 55°$; of 30013 total reflections, 10794 were unique ($R_{int} = 0.0259$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 3.346$ mm^{-1}, $T_{min}/T_{max} = 0.454/0.775$). The structure was solved by Patterson methods and refined by full-matrix least-squares on F^2 on all data. The asymmetric unit cell contains one molecule of **2b**, in which the chloro and carbonyl ligands are disordered equally between the two sites, and half a molecule of benzene. $R_1 = 0.0518$ for the 8660 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.1712$ for all data. Goodness of fit on F^2 1.078. **3**: crystals from dichloromethane/toluene/*n*-hexane; $C_{48}H_{42}BClN_2O_2OsP_2 \cdot C_7H_8$, $M_r = 1069.37$; crystal dimensions $0.40 \times 0.28 \times 0.22$ mm; monoclinic; space group $P2_1/n$; $a = 16.6920(2)$, $b = 17.7366(1)$, $c = 17.6239(2)$ Å, $\beta = 106.510(1)°$, $Z = 4$, $V = 5002.65(9)$ Å^3, $\rho_{calcd} = 1.420$ g cm^{-3}; $T = 200$ K; $2\theta_{max} = 54°$; of 29951 total reflections, 10719 were unique ($R_{int} = 0.0220$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 2.708$ mm^{-1}, $T_{min}/T_{max} = 0.410/0.587$). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on F^2 on all data. The asymmetric unit cell contains one molecule of **3** and one molecule of toluene; $R_1 = 0.0247$ for the 9473 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.0630$ for all data. Goodness of fit on F^2 1.053. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-135052 (**2b**) and CCDC-135053 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

[8] Longest of the 629 determinations found in the CCSD.

[9] t′ denotes that the signal has apparent multiplicity; $^{n,m}J(C,P)$ is the sum of the two coupling constants $^{m}J(C,P)$ and $^{n}J(C,P)$, as explained in S. M. Maddock, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1996**, *15*, 1793–1803.

Orientation-Controlled Monolayer Assembly of Zeolite Crystals on Glass and Mica by Covalent Linkage of Surface-Bound Epoxide and Amine Groups**

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Efforts have been made during the last decade to develop zeolite thin films for separative, catalytic, and chemical sensor applications.[1–10] For practical purposes, they have usually been prepared on various substrates or supports since they are extremely fragile. The chemical methods to assemble zeolite thin films on substrates can generally be classified into two groups, namely, "direct growth"[1–5] and "postsynthetic crystal attachment".[6, 7] The former group usually involves in situ growth of the zeolite crystals or films on the substrates by immersing them into the synthesis gel.[1–4] For best results, the substrates are often chemically modified or pretreated with colloidal seed crystals. The unique pulsed laser ablation of preformed supported zeolites can also be classified into this group.[5] In the latter group, preformed zeolite crystals are chemically attached on substrates by ionic or covalent bonding by use of appropriate organic additives.[6, 7] For these

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[**] We thank the Ministry of Science and Technology, Korea, for financial support through the Creative Research Initiatives Program.