4862 *Organometallics* **2002,** *21,* 4862−4872

Tethered Boryl and Base-Stabilized Borylene Osmium Complexes from the Reaction of $Os(BCl_2)Cl(CO)(PPh_3)_2$ with 2-Aminopyridine

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Received April 29, 2002

Reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-aminopyridine in the presence of ethanol leads to a mixture of two products. In the first, replacement of one chloride on the dichloroboryl ligand through condensation with the amino function and coordination of the pyridine nitrogen atom to osmium leads to the tethered, six-coordinate boryl complex $\overline{\mathrm{Os[BCl(NHC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**1**). In the second, the direction of addition of the aminopyridine is reversed, leading to the tethered, pyridine-stabilized borylene complex $\overline{\mathrm{Os[B(OEt)(NC_5H_4N}}\mathrm{H)]Cl(CO)(PPh_3)_2}$ (**2**). The five-membered chelate ring formed in **1** is stable and persists through reactions involving replacement of chloride both at osmium and at boron. When **1** is treated with NaBr or with $NaBH_4$, replacement of chloride at osmium occurs exclusively, leaving the B−Cl bond intact and giving $\overline{\mathrm{Os[BCl(NHC_5H_4N}}\mathrm{)]Br(CO)(PPh_3)_2}$ (**3**) or $\overline{\mathrm{Os[BCl(NHC_5H_4N}}\mathrm{)]H(CO)(PPh_3)_2}$ (**4**), respectively. Replacement of chloride at boron requires the assistance of $AgSbF_6$, and the following derivatives of **1** have been characterized: $\overline{\mathrm{Os[B(OH)(NHC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**5**) (with 1 equiv of $AgSbF_6$), $[\overline{\mathrm{Os\{B(OH)(NHC_5H_4N}}\mathrm{)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**6**) (with 2 equiv of $AgSbF_6$ in MeCN), and $[\overline{\mathrm{Os\{B(OEt)(NHC_5H_4N}}\mathrm{)\}(CO)_2(PPh_3)_2]SbF_6}$ (**7**) (with 2 equiv of $AgSbF_6$ and CO in the presence of EtOH). Reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-(methylamino)pyridine leads to only one product, the tethered, pyridine-stabilized borylene complex $\overline{\mathrm{Os[BCl(NC_5H_4N}}\mathrm{Me)]Cl(CO)(PPh_3)_2}$ (**8**). Four further pyridine-stabilized borylene complexes have been derived from **8**. Reaction of **8** with $NaBH_4$ gives $\overline{\mathrm{Os[BCl(NC_5H_4N}}\mathrm{Me)]H(CO)(PPh_3)_2}$ (**9**), and **9** is hydrolyzed by water to $\overline{\mathrm{Os[B(OH)(NC_5H_4N}}\mathrm{Me)]Cl(CO)(PPh_3)_2}$ (**10**). Ethanol converts **8** to $\overline{\mathrm{Os[B(OEt)(NC_5H_4N}}\mathrm{Me)]Cl(CO)(PPh_3)_2}$ (**11**), and 2 equiv of $AgSbF_6$ in acetonitrile converts **8** to $[\overline{\mathrm{Os\{B(OEt)(NC_5H_4N}}\mathrm{Me)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**12**). Crystal structures of complexes **2**−**6** and **9** are reported.

Introduction

Compounds with transition-metal−boron two-center−two-electron (2c−2e) bonds (L_nM-BR_2) have been widely studied in the past decade, primarily because of the recognition that these compounds are key intermediates in the metal-catalyzed syntheses of boron-functionalized organics. Several reviews have covered developments in this area.[1] We have recently reported that treatment of the coordinatively unsaturated dichloroboryl complex $Os(BCl_2)Cl(CO)(PPh_3)_2$ with 2-hydroxypyridine produces the tethered boryl complex $\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$, in which one B−Cl bond has condensed with the hydroxy function and the pyridine nitrogen coordinates to osmium.[2] In this paper we examine the reaction between the same dichloroboryl complex and 2-aminopyridine. Three possible ways in which 2-aminopyridine might interact with the dichloroboryl complex are depicted in Chart 1. In structure **I** both nitrogen atoms of the 2-aminopyridine interact with the boron center, displacing one of the chlorides to osmium and so producing a base-stabilized borylene complex. This sort of behavior has been observed for reaction with 8-aminoquinoline.[3] However, while the reaction with 8-ami-

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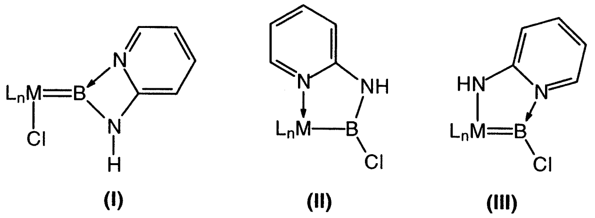
(1) (a) Wadepohl, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2441. (b) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (c) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. (d) Marder, T. B.; Norman, N. C. In *Topics in Catalysis;* Leitner, W., Blackmond, D. G., Eds.; Baltzer Science: Amsterdam, 1998; Vol. 5, p 63. (e) Smith, M. R., III. *Prog. Inorg. Chem.* **1999**, *48*, 505. (f) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.

(2) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 1714.

(3) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 948.

10.1021/om0203431 CCC: \$22.00

Chart 1. Possible Modes of Interaction of 2-Aminopyridine with a Coordinatively Unsaturated Dichloroboryl Metal Complex



noquinoline gives a favorable five-membered chelate ring, the corresponding reaction with 2-aminopyridine would give a much less favorable four-membered chelate ring, and therefore formation of product **I** seems unlikely. A second possibility, **II** in Chart 1, is analogous to the simple condensation product observed for reaction with 2-hydroxypyridine:[2] viz., a complex with a tethered, amino-substituted boryl ligand still bearing one chloride substituent. A third possibility, **III** in Chart 1, has the direction of addition of the 2-aminopyridine reversed such that an osmium−amido linkage is formed and the pyridine nitrogen coordinates to boron, producing a tethered, base-stabilized borylene complex. Surprisingly, a mixture of products exhibiting both structural types **II** and **III** is observed in the reaction with 2-aminopyridine. With 2-(methylamino)pyridine the product formed is of structural type **III** exclusively. Further reactions of these novel complexes are described, along with six crystal structure determinations; the latter provide both structural confirmation and data for examining trends in bond distances and angles for the bonds attached to boron.

Results and Discussion

Reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-Aminopyridine. Reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-aminopyridine gives two products which are easily separated, because one is insoluble in ethanol and the other both dissolves in and reacts with ethanol (see Scheme 1). The ethanol-insoluble compound, which is colorless, forms in approximately 40% yield and has been identified as $Os[BCl(NHC_5H_4N)]Cl(CO)(PPh_3)_2$ (**1**). This is the nitrogen analogue of the tethered boryl complex derived from reaction with 2-hydroxypyridine and described previously.[2] The second product (postulated as **A** in Scheme 1) dissolves in and reacts with ethanol to give a yellow solid isolated in approximately 25% yield. This has been identified as the tethered, pyridine-stabilized borylene complex $Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2$ (**2**). The full characterization of **2**, including a crystal structure determination (see Figure 1), is discussed below.

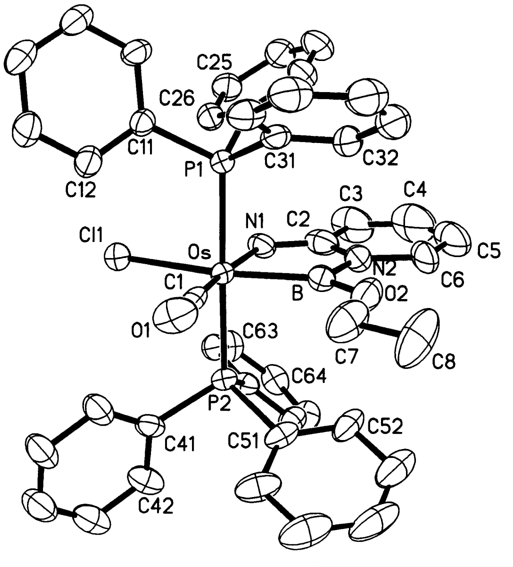
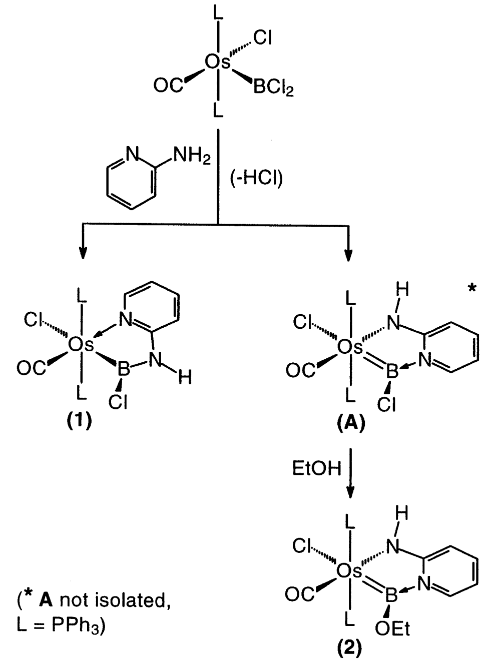


Figure 1. Molecular structure of $Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2$ (**2**) with thermal ellipsoids at the 50% probability level.

Scheme 1



(* **A** not isolated, L = PPh$_3$)

Characterization and Further Reactions of $Os[BCl(NHC_5H_4N)]Cl(CO)(PPh_3)_2$ (1). The spectroscopic data for **1**, and for all other new compounds reported in this paper, are presented in Table 1 (IR), Table 2 (^1H NMR), Table 3 (^{13}C NMR), and Table 4 (^{11}B NMR). On the basis of these spectroscopic data for **1**, an unambiguous assignment to one of the three structures shown in Chart 1 was not possible. Fortunately, crystal structures were obtained for two derivatives of **1**, where the boron ligand remains unchanged and an Os−Cl bond is replaced either by bromide to give $Os[BCl(NHC_5H_4N)]Br(CO)(PPh_3)_2$ (**3**) or by hydride to give $Os[BCl(NHC_5H_4N)]H(CO)(PPh_3)_2$ (**4**) (see Scheme 2). The remarkable lack of reactivity of the B−Cl bond indicated in these transformations is further reinforced by the observation that **1** can be recovered unchanged after prolonged periods of heating in the presence of ethanol. This extraordinary inertness must be attributed in part to the presence of two effective π-donor substituents (NH and Os) on boron.

Compound **3** has spectroscopic data closely similar to **1**, and the molecular structure of **3** is shown in Figure

Table 1. Infrared Data (cm^{-1})[a] for Tethered Osmium Boryl and Borylene Complexes

complex	ν(C=O)	other bands
$\mathrm{\overline{Os[BCl(NHC_5H_4N})]Cl(CO)(PPh_3)_2}$ (**1**)	1906 vs	3260 m, 1616 m, 1276 m, 1159 m, 1125 m, 1112 m, 1017 w, 918 w, 902 s, 836 m
$\mathrm{\overline{Os[B(OEt)(NC_5H_4NH})]Cl(CO)(PPh_3)_2}$ (**2**)	1895 vs	3363 w, 1645 s, 1555 s, 1308 w, 1292 s, 1261 m, 1033 m, 865 m, 820 w
$\mathrm{\overline{Os[BCl(NHC_5H_4N})]Br(CO)(PPh_3)_2}$ (**3**)	1908 vs	3266 m, 1616 m, 1274 w, 1160 w, 1127 m, 1112 m, 1073 m, 1017 w, 918 w, 900 s, 837 m
$\mathrm{\overline{Os[BCl(NHC_5H_4N})]H(CO)(PPh_3)_2}$ (**4**)	1877 vs	3405 w, 1243 w, 1166 w, 1158 m, 1101 m, 1073 m, 891 w, br, 812 m
$\mathrm{\overline{Os[B(OH)(NHC_5H_4N})]Cl(CO)(PPh_3)_2}$ (**5**)	1876 vs	3322 w, 1614 m, 1281 w, 1260 w, 1168 m, 961 m
$\mathrm{[\overline{Os\{B(OH)(NHC_5H_4N})\}(CO)(MeCN)(PPh_3)_2]\ SbF_6}$ (**6**)	1919 vs	3305 m, 1623 m, 1297 w, 1285 w, 1268 w, 1171 m, 964 w
$\mathrm{[\overline{Os\{B(OEt)(NHC_5H_4N})\}(CO)_2(PPh_3)_2]SbF_6}$ (**7**)	1948 s, 2022 s	3369 m, 1623 m, 1306 m, 1267 m, 1220 m, 1202 w, 1160 m, 1127 w
$\mathrm{\overline{Os[BCl(NC_5H_4NMe})]Cl(CO)(PPh_3)_2}$ (**8**)	1907 vs	1643 m, 1555 s, 1535 m, 1273 m, 1171 w, 1155 w, 939 w, 903 m, 846 m
$\mathrm{\overline{Os[BCl(NC_5H_4NMe})]H(CO)(PPh_3)_2}$ (**9**)	1885 vs	1867 m (Os−H), 1641 m, 1558 m, 1535 w, 1313 w, 1271 m, 1165 m, 862 m, 830 w
$\mathrm{\overline{Os[B(OH)(NC_5H_4NMe})]Cl(CO)(PPh_3)_2}$ (**10**)	1879 vs	1638 s, 1551 s, 1537 w, 1331 w, 1284 m, 1252 m, 1017 m, 835 w, 801 m, 790 m
$\mathrm{\overline{Os[B(OEt)(NC_5H_4NMe})]Cl(CO)(PPh_3)_2}$ (**11**)	1892 vs	1637 s, 1551 s, 1411 m, 1331 w, 1295 m, 1261 m, 1034 m, 909 w, 845 m
$\mathrm{[\overline{Os\{B(OEt)(NC_5H_4NMe})\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**12**)	1929 vs	1638 s, 1549 s, 1334 w, 1315 w, 1296 s, 1261 s, 1164 m, 1156 m, 1142 m, 1034 m, 904 w, 853 m

[a] Spectra recorded as Nujol mulls between KBr plates. [b] Solid-state splitting.

2 with bond distances and bond angles presented in Table 7. The complex is pseudooctahedral with mutually trans triphenylphosphine ligands. The tethered boryl ligand is of structural type **II** in Chart 1: i.e., the same structure as that found for the previously reported compound $\mathrm{\overline{Os[BCl(OC_5H_4N})]I(CO)(PPh_3)_2}$, obtained from reaction with 2-hydroxypyridine but with the O atom replaced by NH. The overall structures are closely related, as a detailed structural comparison makes clear. The Os−B distances in **3** (2.047(7) and 2.053(8) Å) are just slightly longer than in the O analogue (2.039(4) Å), but the B−Cl distances are significantly longer in **3** (1.811(7) and 1.812(9) Å) than in the O analogue (1.773(4) Å). The B−N distances in **3** (1.437(8) and 1.417(11) Å) are close to the mean of reported B−N distances.[4] It is interesting to note that although the B−Cl bond in **3** is longer than in the O analogue, the B−Cl bond in **3** (and in the closely related **1**) is much less reactive. This reduced reactivity must have kinetic origins and be associated with the better π-donor properties of the NH group to boron relative to the O atom, thus reducing the electrophilicity of the boron atom in **1** and **3**.

The reaction of **1** with $NaBH_4$ produces **4**, and the osmium-bound hydride ligand is observed in the ^1H NMR as a triplet signal at −4.22 ppm ($J_{HP} = 24.2$ Hz), consistent with coupling to two mutually trans triphenylphosphine ligands. The crystal structure confirms this, and the molecular structure of **4** is shown in Figure 3, with bond distances and bond angles presented in Table 8. The structure reveals that the hydride ligand has been introduced to the osmium (hydride located, Os−H, 1.62(3) Å), through replacement of chloride and the B−Cl bond remains. The structure of the tethered boryl ligand is closely similar to that found in **3**, but the Os−B distance is lengthened to 2.104(3) Å through the trans influence of the hydride ligand.

Replacement of chloride on boron in **1** is achieved through treatment with either 1 or 2 equiv of $AgSbF_6$. With 1 equiv of $AgSbF_6$ in undried THF the product isolated is the tethered hydroxyboryl complex $\mathrm{\overline{Os[B(OH)(NHC_5H_4N})]Cl(CO)(PPh_3)_2}$ (**5**) (see Scheme 2). With 2 equiv of $AgSbF_6$ in undried THF containing MeCN, the product is the cationic analogue of **5**, where chloride on osmium has been replaced by MeCN, giving $\mathrm{[\overline{Os\{B(OH)(NHC_5H_4N})\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**6**). An unambiguous assignment for the B−OH proton in the ^1H NMR spectrum was made only in compound **5**, where this signal is observed as a singlet at 4.12 ppm. Crystal structures for **5** and **6** confirm the presence of the tethered hydroxyboryl ligands in both of these complexes, and molecular structures are depicted in Figures 4 and 5, respectively, with bond distances and angles in Tables 9 and 10, respectively. The overall geometries of the tethered boryl ligands (excluding the Os−B distances) in **5** and **6** do not differ significantly from those observed in **3** and **4**. However, the Os−B distance in the neutral complex **5** is slightly shorter (2.085(3) Å)

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(4) Cambridge Crystallographic Data Base.

Table 2. ^{1}H NMR Data[a] for Tethered Osmium Boryl and Borylene Complexes

complex	^{1}H, δ (ppm)
$\mathrm{Os[BCl(NHC_5H_4N)]Cl(CO)(PPh_3)_2}$ (**1**)	5.69 (apparent dt, J = 6.6 Hz, J = 1.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.40 (apparent d, J = 8 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.68 (s, 1H, $\mathrm{NC_5H_4N\mathit{H}}$), 7.11 (app dt, J = 7.5 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.16−7.24 (m, 19H, $\mathrm{PPh_3}$ and $\mathrm{NC_5\mathit{H_4}NH}$), 7.52−7.60 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2}$ (**2**)	0.55 (t, J = 7.0 Hz, 3H, $\mathrm{OCH_2\mathit{Me}}$), 2.58 (q, J = 7.0 Hz, 2H, $\mathrm{OC\mathit{H_2}Me}$), 5.30 (s, 1H, $\mathrm{NC_5H_4N\mathit{H}}$), 5.59 (apparent d, J = 9.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 5.80 (apparent t, J = 6.6 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.56 (apparent t, J = 7.5 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.29 (m, 18H, $\mathrm{PPh_3}$), 7.38 (d, J = 6.6 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.54−7.58 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{Os[BCl(NHC_5H_4N)]Br(CO)(PPh_3)_2}$ (**3**)	5.64 (apparent dt, J = 6.5 Hz, J = 1.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.40 (apparent d, J = 8.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.70 (s, 1H, $\mathrm{NC_5H_4N\mathit{H}}$), 7.11 (apparent dt, J = 7.8 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.15−7.23 (m, 18H, $\mathrm{PPh_3}$), 7.54−7.60 (m, 12H, $\mathrm{PPh_3}$), 7.70 (d, J = 6.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$)
$\mathrm{Os[BCl(NHC_5H_4N)]H(CO)(PPh_3)_2}$ (**4**)	−4.22 (t, $^2J_{\mathrm{HP}}$ = 24.2 Hz, 1H, $\mathrm{Os\mathit{H}}$), 5.22 (apparent dt, J = 6.6 Hz, J = 1.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.25 (apparent d, J = 8.5 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.92 (m, 3H, $\mathrm{NC_5\mathit{H_4}N\mathit{H}}$), 7.16−7.24 (m, 18H, $\mathrm{PPh_3}$), 7.56−7.62 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{Os[B(OH)(NHC_5H_4N)]Cl(CO)(PPh_3)_2}$ (**5**)	4.12 (s, 1H, $\mathrm{BO\mathit{H}}$), 5.69 (apparent dt, J = 6.5 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 5.87 (s, 1H, $\mathrm{NC_5H_4N\mathit{H}}$), 6.30 (apparent d, J = 8.2 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.03 (apparent dt, J = 7.7 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.18−7.24 (m, 18H, $\mathrm{PPh_3}$), 7.51−7.56 (m, 12H, $\mathrm{PPh_3}$), 7.77 (apparent d, J = 6.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$)
$\mathrm{[Os\{B(OH)(NHC_5H_4N)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**6**)[b]	2.10 (s, 3H, $\mathrm{\mathit{Me}CN}$), 6.13 (apparent t, br, J = 6.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.21 (apparent d, J = 8.4 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.90 (s, 1H, $\mathrm{BO\mathit{H}}$ or $\mathrm{NC_5H_4N\mathit{H}}$), 7.14 (apparent t, J = 7.7 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.24 (s, 1H, $\mathrm{BO\mathit{H}}$ or $\mathrm{NC_5H_4N\mathit{H}}$), 7.31−7.35 (m, 12H, $\mathrm{PPh_3}$), 7.38−7.42 (m, 6H, $\mathrm{PPh_3}$), 7.52−7.57 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{[Os\{B(OEt)(NHC_5H_4N)\}(CO)_2(PPh_3)_2]SbF_6}$ (**7**)	1.16 (t, J = 7.0 Hz, 3H, $\mathrm{OCH_2\mathit{Me}}$), 3.53 (q, J = 7.0 Hz, 2H, $\mathrm{OC\mathit{H_2}Me}$), 5.97 (apparent dt, J = 6.6 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.48 (apparent d, J = 8.3 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NH}$), 6.89 (s, 1H, $\mathrm{NC_5H_4N\mathit{H}}$), 7.14−7.19 (m, 2H, $\mathrm{NC_5\mathit{H_4}NH}$), 7.29−7.43 (m, 30H, $\mathrm{PPh_3}$)
$\mathrm{Os[BCl(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**8**)	1.42 (s, 3H, $\mathrm{NC_5H_4N\mathit{Me}}$), 5.89 (apparent dt, J = 6.6 Hz, J = 1.1 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.04 (apparent d, J = 9.5 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.94 (m, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.23−7.28 (m, 18H, $\mathrm{PPh_3}$), 7.40 (apparent d, J = 6.7 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.59−7.64 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{Os[BCl(NC_5H_4NMe)]H(CO)(PPh_3)_2}$ (**9**)	−4.59 (t, $^2J_{\mathrm{HP}}$ = 24.6 Hz, 1H, $\mathrm{Os\mathit{H}}$), 1.49 (s, 3H, $\mathrm{NC_5H_4N\mathit{Me}}$), 5.64 (apparent d, J = 9.4 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 5.77 (apparent t, J = 6.7 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.76 (m, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.23−7.26 (m, 18H, $\mathrm{PPh_3}$), 7.58−7.64 (m, 12H, $\mathrm{PPh_3}$), 7.72 (apparent d, J = 6.9 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$)
$\mathrm{Os[B(OH)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**10**)	1.28 (s, 3H, $\mathrm{NC_5H_4N\mathit{Me}}$), 4.59 (s, 1H, $\mathrm{BO\mathit{H}}$), 5.83 (apparent dt, J = 7.0 Hz, J = 1.0 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 5.97 (apparent d, J = 9.5 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.95 (m, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.0 (apparent d, J = 6.7 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.24−7.28 (m, 18H, $\mathrm{PPh_3}$), 7.59−7.65 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{Os[B(OEt)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**11**)	0.52 (t, J = 7.0 Hz, 3H, $\mathrm{OCH_2\mathit{Me}}$), 1.83 (s, 3H, $\mathrm{NC_5H_4N\mathit{Me}}$), 2.95 (q, J = 6.9 Hz, 2H, $\mathrm{OC\mathit{H_2}Me}$), 5.90 (apparent d, J = 9.6 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 5.92 (apparent t, J = 6.2 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.91 (m, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.22−7.29 (m, 18H, $\mathrm{PPh_3}$), 7.38 (apparent d, J = 6.6 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.56−7.61 (m, 12H, $\mathrm{PPh_3}$)
$\mathrm{[Os\{B(OEt)(NC_5H_4NMe)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**12**)	0.79 (t, J = 7.0 Hz, 3H, $\mathrm{OCH_2\mathit{Me}}$) 1.94 (s, 3H, $\mathrm{NC\mathit{Me}}$ or $\mathrm{NC_5H_4N\mathit{Me}}$), 2.20 (s, 3H, $\mathrm{NC\mathit{Me}}$ or $\mathrm{NC_5H_4N\mathit{Me}}$), 3.33 (q, J = 7.1 Hz, 2H, $\mathrm{OC\mathit{H_2}Me}$), 5.63 (apparent d, J = 9.4 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 5.93 (apparent t, J = 6.3 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 6.73 (m, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$), 7.31−7.39 (m, 30H, $\mathrm{PPh_3}$), 7.52 (apparent d, J = 6.4 Hz, 1H, $\mathrm{NC_5\mathit{H_4}NMe}$)

[a] Spectra recorded in $\mathrm{CDCl_3}$ at 25 °C. Chemical shifts are referenced to $\mathrm{Me_4Si}$ (δ 0.00). Splitting patterns and line shapes are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. [b] Spectra recorded in $\mathrm{(CD_3)_2CO}$ at 25 °C.

than the corresponding distance in the cationic complex **6** (2.105(4) Å). This is perhaps surprising in view of the greater importance of σ-bonding rather than of π-bonding for the M−B bond, as revealed by calculations.[5] The expectation would be, therefore, that these predominantly σ-bonding ligands would bind more strongly to a cationic metal center than to a neutral center. The result here suggests that the π-component to the Os−B bond should not be ignored. For compound **5** the B−OH distance is 1.383(4) Å and the B−N distance is 1.465(4) Å. The corresponding distances for **6** are 1.374(5) and 1.464(5) Å, respectively. These values are close to the means of all previously recorded B−O distances (1.371, SD 0.035 Å) and B−N distances (1.424, SD 0.043 Å).[4] The Os−Cl bond distance in **5** (2.5606(7) Å) is comparable to the Os−Cl bond distance in the related compound $\mathrm{Os[B(NH\mathit{n}\text{-}Bu)(OC_5H_4N)]Cl(CO)(PPh_3)_2}$ (2.5653(6) Å),[2] and both are at the long end limits of the observed range for Os−Cl (mean 2.389, SD 0.067 Å).[4] The observed chemical lability of this chloride is therefore not surprising. In fact, the reaction of **1** with 1 equiv of $\mathrm{AgSbF_6}$ probably proceeds by initial chloride removal from osmium, creating a cationic complex in which hydrolysis of the chloroboryl ligand is facilitated. The chloride released in this process then returns to osmium, giving the observed product **5**. Compounds **5** and **6** can be interconverted, as shown in Scheme 2.

Treatment of **1** with 2 equiv of $\mathrm{AgSbF_6}$ in ethanol and in the presence of CO produces a cationic dicarbonyl complex containing the tethered ethoxyboryl ligand $\mathrm{[Os\{B(OEt)(NHC_5H_4N)\}(CO)_2(PPh_3)_2]SbF_6}$ (**7**) (see Scheme 2). Ethanol must compete successfully with adventitious water in this case for the boron center, since neither **5**

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(5) (a) Giju, K. T.; Bickelhaupt, F. M.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 4776. (b) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.

Table 3. ^{13}C NMR Data[a] for Tethered Osmium Boryl and Borylene Complexes

complex	^{13}C, δ (ppm)
$\mathrm{Os[BCl(NHC_5H_4N)]\text{-}Cl(CO)(PPh_3)_2}$ (**1**)	108.40 (NC_5H_4NH), 115.07 (NC_5H_4NH), 127.60 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.33 (*p*-PPh$_3$), 132.92 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.16 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 136.92 (NC_5H_4NH), 149.12 (NC_5H_4NH), 161.65 (NC_5H_4NH), 189.76 (t, $^2J_{CP}$ = 11 Hz, CO)
$\mathrm{Os[B(OEt)(NC_5H_4NH)]\text{-}Cl(CO)(PPh_3)_2}$ (**2**)	16.33 (OCH$_2$*Me*), 62.39 (O*C*H$_2$Me), 104.46 (NC_5H_4NH), 115.27 (NC_5H_4NH), 127.58 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.32 (*p*-PPh$_3$), 131.48 (NC_5H_4NH), 133.71 (t′, $^{1,3}J_{CP}$ = 48 Hz, *i*-PPh$_3$), 134.16 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 136.59 (NC_5H_4NH), 164.52 (NC_5H_4NH), 190.47 (t, $^2J_{CP}$ = 10 Hz, CO)
$\mathrm{Os[BCl(NHC_5H_4N)]\text{-}Br(CO)(PPh_3)_2}$ (**3**)	108.47 (NC_5H_4NH), 115.50 (NC_5H_4NH), 127.54 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.30 (*p*-PPh$_3$), 133.25 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.20 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 137.15 (NC_5H_4NH), 150.95 (NC_5H_4NH), 161.62 (NC_5H_4NH), 189.86 (t, $^2J_{CP}$ = 11 Hz, CO)
$\mathrm{Os[BCl(NHC_5H_4N)]\text{-}H(CO)(PPh_3)_2}$ (**4**)	108.55 (NC_5H_4NH), 115.70 (NC_5H_4NH), 127.41 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.03 (*p*-PPh$_3$), 134.02 (t′, $^{3,5}J_{CP}$ = 12 Hz, *m*-PPh$_3$), 135.99 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 136.08 (NC_5H_4NH), 157.83 (NC_5H_4NH), 162.86 (NC_5H_4NH), 192.58 (t, $^2J_{CP}$ = 11 Hz, CO)
$\mathrm{Os[B(OH)(NHC_5H_4N)]\text{-}Cl(CO)(PPh_3)_2}$ (**5**)	107.97 (NC_5H_4NH), 113.57 (NC_5H_4NH), 127.65 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.29 (*p*-PPh$_3$), 133.40 (t′, $^{1,3}J_{CP}$ = 49 Hz, *i*-PPh$_3$), 134.02 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 136.79 (NC_5H_4NH), 149.25 (NC_5H_4NH), 163.02 (NC_5H_4NH), 191.31 (t, $^2J_{CP}$ = 11.5 Hz, CO)
$\mathrm{[Os\{B(OH)(NHC_5H_4N)\}(CO)\text{-}(MeCN)(PPh_3)_2]SbF_6}$ (**6**)[b]	111.79 (NC_5H_4NH), 115.49 (NC_5H_4NH), 129.08 (t′, $^{2,4}J_{CP}$ = 9 Hz, *o*-PPh$_3$), 131.03 (*p*-PPh$_3$), 132.51 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.51 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 139.00 (NC_5H_4NH), 147.85 (NC_5H_4NH), 164.19 (NC_5H_4NH), resonances due to MeCN and CO not obsd
$\mathrm{[Os\{B(OEt)(NHC_5H_4N)\}\text{-}(CO)_2(PPh_3)_2]SbF_6}$ (**7**)	16.74 (OCH$_2$*Me*), 60.91 (O*C*H$_2$Me), 113.73 (NC_5H_4NH), 116.80 (NC_5H_4NH), 128.59 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 130.94 (*p*-PPh$_3$), 131.02 (t′, $^{1,3}J_{CP}$ = 55 Hz, *i*-PPh$_3$), 133.12 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 139.59 (NC_5H_4NH), 150.89 (NC_5H_4NH), 164.18 (NC_5H_4NH), 183.77 (t, $^{2,2}J_{CP}$ = 9.5 Hz, CO), 184.89 (t, $^2J_{CP}$ = 7.5 Hz, CO)
$\mathrm{Os[BCl(NC_5H_4NMe)]\text{-}Cl(CO)(PPh_3)_2}$ (**8**)	32.36 (NC_5H_4N*Me*), 104.58 (NC_5H_4NMe), 113.33 (NC_5H_4NMe), 127.67 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.44 (*p*-PPh$_3$), 132.67 (NC_5H_4NMe), 133.75 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.20 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 136.36 (NC_5H_4NMe), other resonances not obsd due to low solubility
$\mathrm{Os[BCl(NC_5H_4NMe)]\text{-}H(CO)(PPh_3)_2}$ (**9**)	46.42 (NC_5H_4N*Me*), 103.44 (NC_5H_4NMe), 111.90 (NC_5H_4NMe), 127.43 (t′, $^{2,4}J_{CP}$ = 9 Hz, *o*-PPh$_3$), 129.20 (*p*-PPh$_3$), 132.18 (NC_5H_4NMe), 134.24 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 135.20 (NC_5H_4NMe), 136.23 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 164.53 (NC_5H_4NMe), 192.09 (t, $^2J_{CP}$ = 12 Hz, CO)
$\mathrm{Os[B(OH)(NC_5H_4NMe)]\text{-}Cl(CO)(PPh_3)_2}$ (**10**)	spectrum not obtained due to low solubility
$\mathrm{Os[B(OEt)(NC_5H_4NMe)]\text{-}Cl(CO)(PPh_3)_2}$ (**11**)	16.36 (OCH$_2$*Me*), 33.06 (NC_5H_4N*Me*), 62.53 (O*C*H$_2$Me), 103.92 (NC_5H_4NMe), 112.21 (NC_5H_4NMe), 127.50 (t′, $^{2,4}J_{CP}$ = 9 Hz, *o*-PPh$_3$), 129.22 (*p*-PPh$_3$), 132.56 (NC_5H_4NMe), 134.28 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 135.04 (t′, $^{1,3}J_{CP}$ = 48 Hz, *i*-PPh$_3$), 137.14 (NC_5H_4NMe), 163.83 (NC_5H_4NMe), 189.46 (t, $^2J_{CP}$ = 10.5 Hz, CO)
$\mathrm{[Os\{B(OEt)(NC_5H_4NMe)\}(CO)\text{-}(MeCN)(PPh_3)_2]SbF_6}$ (**12**)	2.90 (NC*Me*), 16.59 (OCH$_2$*Me*), 37.12 (NC_5H_4N*Me*), 63.67 (O*C*H$_2$Me), 105.36 (NC_5H_4NMe), 111.73 (NC_5H_4NMe), 128.31 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 130.56 (*p*-PPh$_3$), 131.23 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 131.99 (NC_5H_4NMe), 133.34 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 137.81 (NC_5H_4NMe), 164.12 (NC_5H_4NMe), 187.15 (t, $^2J_{CP}$ = 9.5 Hz, CO), resonance due to Me*C*N not obsd

[a] Spectra recorded in CDCl$_3$ at 25 °C. Chemical shifts are referenced to CDCl$_3$ (δ 77.00). t′ denotes that the signal has apparent triplet multiplicity. $^{m,n}J_{CP}$ is the sum of the two coupling constants $^mJ_{CP}$ and $^nJ_{CP}$, as explained in ref 6. [b] Spectra recorded in (CD$_3$)$_2$CO at 25 °C.

nor **6** shows any evidence of undergoing an exchange reaction when in the presence of ethanol.

Characterization of $\mathbf{Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2}$ (2). The remarkable second product from reaction between $\mathrm{Os(BCl_2)Cl(CO)(PPh_3)_2}$ and 2-aminopyridine, followed by treatment with ethanol (see Scheme 1), is the tethered, pyridine-stabilized borylene complex $\mathrm{Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2}$ (**2**). A reasonable precursor for **2** is the chloro−borylene analogue of **2**, which is labeled **A** in Scheme 1. In the coordinatively unsaturated complex $\mathrm{Os(BCl_2)Cl(CO)(PPh_3)_2}$ there are two potential acceptor sites, one at osmium and the other at boron. Equally, for 2-aminopyridine there are two donor sites, one localized at the pyridine nitrogen and the other at the amino nitrogen. The formation of the two products depicted in Scheme 1, **1** and **A**, could be rationalized as following from initial coordination of pyridine to osmium (and NH$_2$ to boron) or of pyridine to boron (and NH$_2$ to osmium), respectively. The B−Cl bond in **A** must be more reactive than the B−Cl bond in **1**, as replacement of chloride by ethoxide to give **2** occurs readily. This might be expected for a "borylene" formulation where the boron center will be very electrophilic. Indeed, the *N*-methyl-substituted analogue of **A**, compound **8**, which is described below, does undergo ethanolysis of the B−Cl bond. The definitive characterization of **2** depended upon a crystal structure determination. The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are given in Table 6.

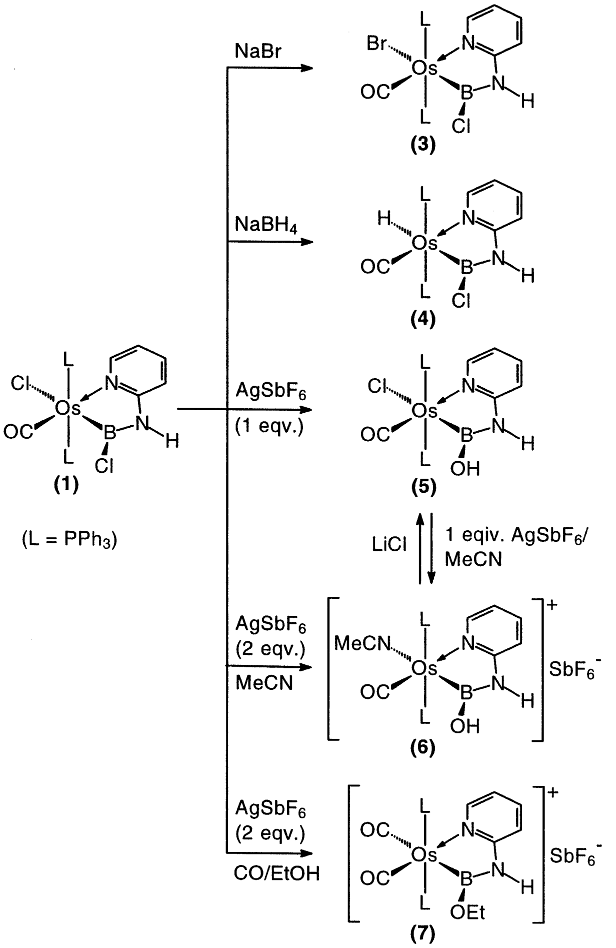
We choose to compare the structure of **2** with that of complex **5** because both complexes have the same set of donor atoms around both osmium and boron. Complex **5** has a pyridine N bound to osmium and an NH group bound to boron and is therefore considered as a regular boryl complex. Complex **2** has the reverse arrangement of the two N donors, i.e., pyridine N bound to boron and

Table 4. ^{11}B NMR Data[a] for Tethered Osmium Boryl and Borylene Complexes

complex	^{11}B, δ (ppm)
$\mathrm{Os[BCl(NHC_5H_4N)]Cl(CO)(PPh_3)_2}$ (**1**)	60.9
$\mathrm{Os[B(OEt)(NC_5H_4NH)]Cl(CO)(PPh_3)_2}$ (**2**)	52.1
$\mathrm{Os[BCl(NHC_5H_4N)]Br(CO)(PPh_3)_2}$ (**3**)	60.2
$\mathrm{Os[BCl(NHC_5H_4N)]H(CO)(PPh_3)_2}$ (**4**)	73.1
$\mathrm{Os[B(OH)(NHC_5H_4N)]Cl(CO)(PPh_3)_2}$ (**5**)[b]	
$\mathrm{[Os\{B(OH)(NHC_5H_4N)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**6**)[c]	48.7
$\mathrm{[Os\{B(OEt)(NHC_5H_4N)\}(CO)_2(PPh_3)_2]SbF_6}$ (**7**)	54.6
$\mathrm{Os[BCl(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**8**)[b]	
$\mathrm{Os[BCl(NC_5H_4NMe)]H(CO)(PPh_3)_2}$ (**9**)[d]	84.6
$\mathrm{Os[B(OH)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**10**)[b]	
$\mathrm{Os[B(OEt)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**11**)	53.2
$\mathrm{[Os\{B(OEt)(NC_5H_4NMe)\}(CO)(MeCN)(PPh_3)_2]SbF_6}$ (**12**)	54.6

[a] Spectra recorded in $\mathrm{CDCl_3}$ at 25 °C. Chemical shifts are referenced to $\mathrm{BF_3{\cdot}OEt_2}$ (δ 0.00). [b] Spectrum not obtained due to low solubility. [c] Recorded in $\mathrm{CDCl_3}$/acetone. [d] Recorded in $\mathrm{CDCl_3/CH_2Cl_2}$.

Scheme 2



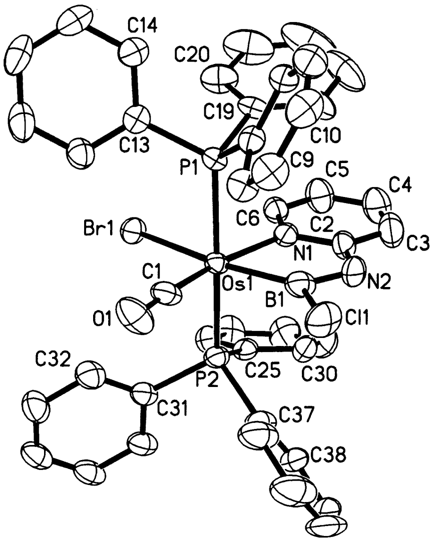


Figure 2. Molecular structure of $\mathrm{Os[BCl(NHC_5H_4N)]Br(CO)(PPh_3)_2}$ (**3**) with thermal ellipsoids at the 50% probability level.

an amido NH bound to osmium, and can therefore be formally considered as a pyridine-stabilized borylene complex, as drawn in Scheme 1. Despite these differences in formal representation there are remarkably small differences in most bond distances and angles, suggesting that the formal distinction is somewhat artificial. The Os−B distance in **2** is 2.066(5) Å, whereas the corresponding distance in **5** is 2.085(3) Å. Similarly, the angle Os−B−O is 140.2(4)° in **2** and 136.5(2)° in **5**. In each molecule the B−O distance (1.361(6) Å in **2** and 1.383(4) Å in **5**) is much shorter than the B−N distance (1.516(7) Å in **2** and 1.465(4) Å in **5**).

Reaction between $\mathrm{Os(BCl_2)Cl(CO)(PPh_3)_2}$ and 2-(Methylamino)pyridine. Unlike the reaction between $\mathrm{Os(BCl_2)Cl(CO)(PPh_3)_2}$ and 2-aminopyridine, the reaction with 2-(methylamino)pyridine gives only one product, the tethered, base-stabilized borylene complex $\mathrm{Os[BCl(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (**8**) (see Scheme 3). The structure of this compound and all of its derivatives (see Scheme 4) is based upon the crystal structure of compound **9**, the derivative in which the Os−Cl bond in **8** is replaced with an Os−H bond (see below). A satisfactory explanation for the exclusive formation of the "borylene" isomer from 2-(methylamino)pyridine must await further results.

Further Reactions of $\mathrm{Os[BCl(NC_5H_4NMe)]Cl(CO)(PPh_3)_2}$ (8). Treatment of **8** with $\mathrm{NaBH_4}$ results in replacement of the Os−Cl bond only, the B−Cl bond remaining unchanged and the product being complex, $\mathrm{Os[BCl(NC_5H_4NMe)]H(CO)(PPh_3)_2}$ (**9**) (see Scheme 4). The osmium-bound hydride ligand in **9** is observed in the ^{1}H NMR as a triplet signal at δ −4.59 (J_{HP} = 24.6 Hz), consistent with coupling to two mutually trans triphenylphosphine ligands. The chemical shift and coupling constant are very close to the values found for **4**. The mode of attachment of the (methylamino)pyridine fragment was determined by X-ray crystallography. The molecular structure of **9** is shown in Figure 6, and selected bond lengths and angles are given in Table 11. The molecular structure of **9** can be usefully compared with the structure of **4**, since the only differences between these two compounds are the orientation of the 2-aminopyridine fragment and the presence of a methyl group on nitrogen in **9**. Once again the structural parameters are strikingly similar. The Os−B (2.078(4) Å) and B−Cl (1.803(4) Å) distances found in **9** are

Table 5. Crystal and Refinement Data for 2−6 and 9

	2·CH_2Cl_2	**3**·1.5CH_2Cl_2	**4**	**5**	**6**·2Me_2CO	**9**
formula	$C_{45}H_{42}BCl_3N_2O_2OsP_2$	$C_{43.5}H_{37}BBrCl_4N_2OOsP_2$	$C_{42}H_{36}BClN_2OOsP_2$	$C_{42}H_{36}BClN_2O_2OsP_2$	$C_{50}H_{51}BF_6N_3O_4OsP_2Sb$	$C_{43}H_{38}BClN_2OOsP_2$
mol wt	1012.11	1088.41	883.13	899.13	1256.64	897.15
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	10.4645(1)	26.0038(3)	12.6570(2)	10.3340(1)	12.6292(1)	9.3471(5)
b, Å	12.0732(1)	19.2065(3)	13.7582(1)	27.6187(3)	13.7740(1)	12.4256(6)
c, Å	17.3518(2)	17.2856(2)	22.0517(1)	12.9728(2)	15.4020(1)	16.8918(8)
α, deg	97.124(1)	90.0	90.0	90.0	80.715(1)	83.745(1)
β, deg	93.237(1)	100.016(1)	105.297(1)	96.900(1)	77.679(1)	85.689(1)
γ, deg	98.381(1)	90.0	90.0	90.0	80.490(1)	75.116(1)
V, Å^3	2145.86(4)	8501.58(19)	3703.98(7)	3675.76(8)	2559.44(3)	1882.48(16)
Z	2	8	4	4	2	2
d(calcd), g cm^{-3}	1.566	1.701	1.584	1.625	1.631	1.583
F(000)	1008	4272	1752	1784	1240	892
μ, mm^{-1}	3.27	4.30	3.64	3.67	3.14	3.58
cryst size, mm	0.35 × 0.22 × 0.03	0.44 × 0.30 × 0.12	0.32 × 0.31 × 0.11	0.22 × 0.20 × 0.12	0.44 × 0.26 × 0.20	0.35 × 0.09 × 0.07
2*θ* (min−max), deg	1.2−27.5	1.3−27.5	1.7−27.5	1.5−27.5	1.4−27.4	1.2−27.5
no. of rflns collected	20 337	52 045	22 320	22 669	24 966	18 785
no. of indep rflns (R_{int})	9271 (0.0374)	18 726 (0.0324)	8152 (0.0194)	8144 (0.0204)	10 944 (0.0300)	8194 (0.0269)
A (min, max)	0.394, 0.908	0.253, 0.626	0.389, 0.690	0.499, 0.667	0.339, 0.573	0.367, 0.788
goodness of fit on F^2	1.052	1.048	1.069	1.171	1.044	1.047
R (obsd data)[a]						
R1	0.0325	0.0474	0.0213	0.0250	0.0315	0.0270
wR2	0.0722	0.01129	0.0496	0.0508	0.0812	0.0567
R (all data)						
R1	0.0426	0.0609	0.0255	0.0299	0.0362	0.0340
wR2	0.0824	0.1223	0.0517	0.0523	0.0850	0.0598

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Interatomic Distances			
Os−B	2.066(5)	Os−P(2)	2.3870(10)
Os−C(1)	1.870(5)	C(1)−O(1)	1.135(5)
Os−N(1)	2.104(3)	B−N(2)	1.516(7)
Os−Cl	2.5578(10)	B−O(2)	1.361(6)
Os−P(1)	2.3798(10)		
Interatomic Angles			
C(1)−Os−B	95.5(2)	P(1)−Os−B	89.41(13)
C(1)−Os−N(1)	173.39(16)	P(2)−Os−Cl	89.69(3)
C(1)−Os−Cl	101.92(13)	P(2)−Os−B	90.00(13)
C(1)−Os−P(1)	90.63(13)	Cl−Os−B	162.55(15)
C(1)−Os−P(2)	91.50(13)	O(1)−C(1)−Os	178.2(4)
N(1)−Os−B	77.90(18)	B−N(2)−C(2)	116.3(4)
N(1)−Os−Cl	84.65(10)	N(2)−C(2)−N(1)	115.3(4)
N(1)−Os−P(1)	88.55(10)	Os−N(1)−C(2)	119.1(3)
N(1)−Os−P(2)	89.30(10)	Os−B−N(2)	111.4(3)
P(1)−Os−P(2)	177.84(4)	Os−B−O(2)	140.2(4)
P(1)−Os−Cl	90.26(3)		

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex 3

molecule 1		molecule 2	
Interatomic Distances			
Os(1)−B(1)	2.047(7)	Os(2)−B(2)	2.053(8)
Os(1)−C(1)	1.832(6)	Os(2)−C(51)	1.823(8)
Os(1)−N(1)	2.195(5)	Os(2)−N(3)	2.191(6)
Os(1)−Br(1)	2.6933(6)	Os(2)−Br(2)	2.6740(7)
Os(1)−P(1)	2.3773(15)	Os(2)−P(3)	2.3835(16)
Os(1)−P(2)	2.3798(15)	Os(2)−P(4)	2.3865(17)
B(1)−N(2)	1.437(8)	B(2)−N(4)	1.417(11)
B(1)−Cl(1)	1.811(7)	B(2)−Cl(2)	1.812(9)
Interatomic Angles			
C(1)−Os(1)−B(1)	93.1(3)	C(51)−Os(2)−B(2)	94.0(3)
C(1)−Os(1)−N(1)	169.7(2)	C(51)−Os(2)−N(3)	170.3(3)
C(1)−Os(1)−Br(1)	101.87(18)	C(51)−Os(2)−Br(2)	100.2(2)
C(1)−Os(1)−P(1)	92.31(19)	C(51)−Os(2)−P(3)	91.9(2)
C(1)−Os(1)−P(2)	89.87(19)	C(51)−Os(2)−P(4)	92.5(2)
N(1)−Os(1)−B(1)	76.7(2)	N(3)−Os(2)−B(2)	76.4(3)
N(1)−Os(1)−Br(1)	88.37(12)	N(3)−Os(2)−Br(2)	89.41(14)
N(1)−Os(1)−P(1)	89.43(13)	N(3)−Os(2)−P(3)	89.15(14)
N(1)−Os(1)−P(2)	89.11(13)	N(3)−Os(2)−P(4)	87.25(14)
P(1)−Os(1)−P(2)	175.54(5)	P(3)−Os(2)−P(4)	173.90(6)
P(1)−Os(1)−B(1)	91.0(2)	P(3)−Os(2)−B(2)	92.2(2)
P(1)−Os(1)−Br(1)	84.81(4)	P(3)−Os(2)−Br(2)	89.08(4)
P(2)−Os(1)−Br(1)	90.94(4)	P(4)−Os(2)−Br(2)	85.96(4)
P(2)−Os(1)−B(1)	92.8(2)	P(4)−Os(2)−B(2)	91.7(2)
Br(1)−Os(1)−B(1)	164.56(19)	Br(2)−Os(2)−B(2)	165.7(3)
N(2)−B(1)−Cl(1)	111.5(4)	N(4)−B(2)−Cl(2)	111.3(6)
Os(1)−B(1)−N(2)	114.5(4)	Os(2)−B(2)−N(4)	114.9(5)
Os(1)−B(1)−Cl(1)	133.9(4)	Os(2)−B(2)−Cl(2)	133.8(5)

shorter than the corresponding distances in **4** (2.104(3) and 1.819(3) Å, respectively), although the differences are barely significant.

Although the conversion of **8** to **9** involves a solvent mixture containing ethanol, no reaction of the B−Cl bond was observed during the 15 min time of the reaction. However, when a benzene solution of **8** was heated under reflux, in the presence of ethanol, for 90 min, complete ethanolysis of the B−Cl bond occurs to form $Os[B(OEt)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2$ (**11**) (see Scheme 4). Likewise, prolonged treatment of a benzene solution of **9** with water converts **9** to $Os[B(OH)(NC_5H_4NMe)]Cl(CO)(PPh_3)_2$ (**10**). Presumably the HCl formed during hydrolysis of the B−Cl bond returns to cleave the Os−H bond. More rapid ethanolysis of the B−Cl bond in **8** occurs when **8** is treated with 2 equiv of $AgSbF_6$ in acetonitrile to give $[Os\{B(OEt)(NC_5H_4NMe)\}(CO)(MeCN)(PPh_3)_2]SbF_6$ (**12**). This cationic complex reacts with LiCl to give **11**.

Conclusions

The reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-hydroxypyridine, which we have reported previously,[2]

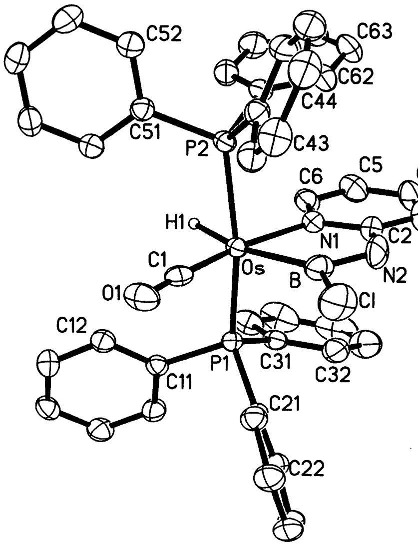


Figure 3. Molecular structure of Os[BCl(NHC$_5$H$_4$N)]H(CO)(PPh$_3$)$_2$ (**4**) with thermal ellipsoids at the 50% probability level.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Interatomic Distances			
Os−B	2.104(3)	Os−P(2)	2.3498(6)
Os−C(1)	1.835(3)	C(1)−O(1)	1.170(3)
Os−N(1)	2.175(2)	B−N(2)	1.438(4)
Os−H	1.62(3)	B−Cl	1.819(3)
Os−P(1)	2.3466(6)		
Interatomic Angles			
C(1)−Os−B	94.45(12)	P(1)−Os−B	97.19(9)
C(1)−Os−N(1)	170.28(10)	P(2)−Os−H	81.8(10)
C(1)−Os−H	104.3(10)	P(2)−Os−B	95.96(9)
C(1)−Os−P(1)	90.57(8)	H−Os−B	161.1(10)
C(1)−Os−P(2)	91.78(8)	O(1)−C(1)−Os	176.8(2)
N(1)−Os−B	76.7(2)	B−N(2)−C(2)	119.1(2)
N(1)−Os−H	85.4(10)	N(2)−C(2)−N(1)	114.5(2)
N(1)−Os−P(1)	89.76(6)	Os−N(1)−C(2)	116.86(18)
N(1)−Os−P(2)	90.23(6)	Os−B−N(2)	113.6(2)
P(1)−Os−P(2)	166.43(2)	Os−B−Cl	135.54(18)
P(1)−Os−H	84.7(10)		

gave a single product, the tethered boryl complex Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$. In contrast, the reaction between Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ and 2-aminopyridine reported here unexpectedly gives two products, depending upon the direction of addition of the two nitrogen donor atoms to the osmium and boron centers. One is Os[BCl(NHC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$, the NH analogue of Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$, and the other (after reaction with EtOH) is the novel, tethered, base-stabilized borylene complex Os[B(OEt)(NC$_5$H$_4$NH)]Cl(CO)(PPh$_3$)$_2$. With 2-(methylamino)pyridine the tethered base-stabilized borylene complex Os[BCl(NC$_5$H$_4$NMe)]Cl(CO)(PPh$_3$)$_2$ is formed exclusively. These compounds have been derivatized through reactions at either the osmium center or the boron center. Reactions at the boron center for the boryl complexes are very slow and only proceed effectively upon treatment with Ag$^+$. Reactions at the boron center for the "borylene" complexes occur more readily. Crystal structure determinations of six of these complexes substantiate the structure assignments and reveal little difference between the key structural parameters of the boryl and base-stabilized borylene formulations. The implication is that from a structural point of view the nature of the M−B bond in these base-stabilized borylene complexes is not greatly different from the nature of the M−B bond in regular boryl complexes.

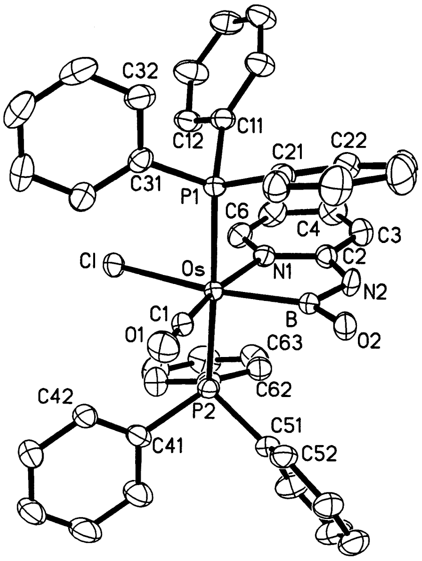


Figure 4. Molecular structure of Os[B(OH)(NHC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**5**) with thermal ellipsoids at the 50% probability level.

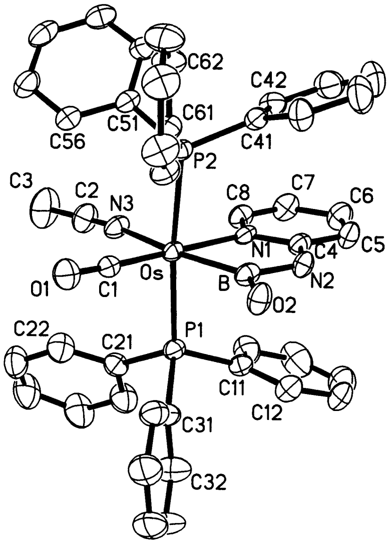


Figure 5. Molecular structure of [Os{B(OH)(NHC$_5$H$_4$N)}(CO)(MeCN)(PPh$_3$)$_2$]SbF$_6$ (**6**) with thermal ellipsoids at the 50% probability level.

Experimental Section

General Considerations. The general experimental and spectroscopic techniques employed in this work were the same as those described previously.[6] Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ was prepared as reported previously.[3]

Infrared spectra (4000−400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin-Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX

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[6] Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793.

Table 9. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Interatomic Distances			
Os−B	2.085(3)	Os−P(2)	2.3775(7)
Os−C(1)	1.835(3)	C(1)−O(1)	1.175(4)
Os−N(1)	2.197(2)	B−N(2)	1.465(4)
Os−Cl	2.5606(7)	B−O(2)	1.383(4)
Os−P(1)	2.3733(7)		

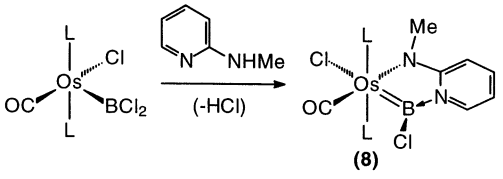
Interatomic Angles			
C(1)−Os−B	92.32(13)	P(1)−Os−B	89.23(9)
C(1)−Os−N(1)	169.65(11)	P(2)−Os−Cl	86.99(2)
C(1)−Os−Cl	101.72(9)	P(2)−Os−B	92.99(9)
C(1)−Os−P(1)	88.28(9)	Cl−Os−B	165.96(9)
C(1)−Os−P(2)	91.46(9)	O(1)−C(1)−Os	177.7(3)
N(1)−Os−B	77.35(11)	B−N(2)−C(2)	119.9(2)
N(1)−Os−Cl	88.61(6)	N(2)−C(2)−N(1)	115.4(2)
N(1)−Os−P(1)	90.87(6)	Os−N(1)−C(2)	114.76(19)
N(1)−Os−P(2)	89.79(6)	Os−B−N(2)	112.4(2)
P(1)−Os−P(2)	177.78(2)	Os−B−O(2)	136.5(2)
P(1)−Os−Cl	90.90(2)		

Table 10. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Interatomic Distances			
Os−B	2.105(4)	Os−P(2)	2.3913(9)
Os−C(1)	1.880(4)	C(1)−O(1)	1.149(5)
Os−N(1)	2.165(3)	B−N(2)	1.464(5)
Os−N(3)	1.179(3)	B−O(2)	1.374(5)
Os−P(1)	2.3956(9)		

Interatomic Angles			
C(1)−Os−B	98.57(16)	P(1)−Os−B	87.54(11)
C(1)−Os−N(1)	176.78(13)	P(2)−Os−N(3)	92.20(8)
C(1)−Os−N(3)	94.93(14)	P(2)−Os−B	88.71(11)
C(1)−Os−P(1)	93.31(11)	N(3)−Os−B	166.45(15)
C(1)−Os−P(2)	90.96(11)	O(1)−C(1)−Os	177.0(3)
N(1)−Os−B	78.37(14)	B−N(2)−C(4)	121.0(3)
N(1)−Os−N(3)	88.15(12)	N(2)−C(4)−N(1)	115.3(3)
N(1)−Os−P(1)	87.58(7)	Os−N(1)−C(4)	115.2(2)
N(1)−Os−P(2)	87.98(7)	Os−B−N(2)	110.2(2)
P(1)−Os−P(2)	174.69(3)	Os−B−O(2)	138.1(3)
P(1)−Os−N(3)	90.58(8)		

Scheme 3



400 at 25 °C. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were obtained by operating at 400.1 (^{1}H), 100.6 (^{13}C), 128.0 (^{11}B), and 162.0 MHz (^{31}P), respectively. Resonances are quoted in ppm and ^{1}H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the protio impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm), ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard, and ^{11}B NMR spectra to $BF_3{\cdot}OEt_2$ as an external standard. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

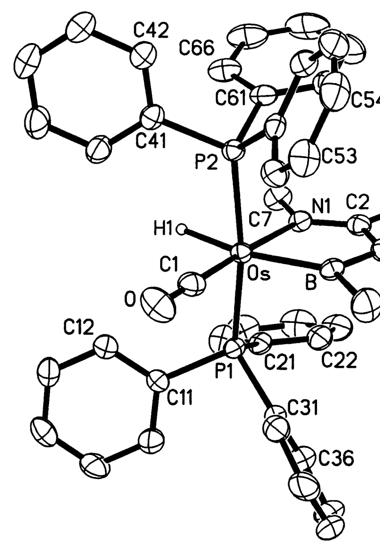
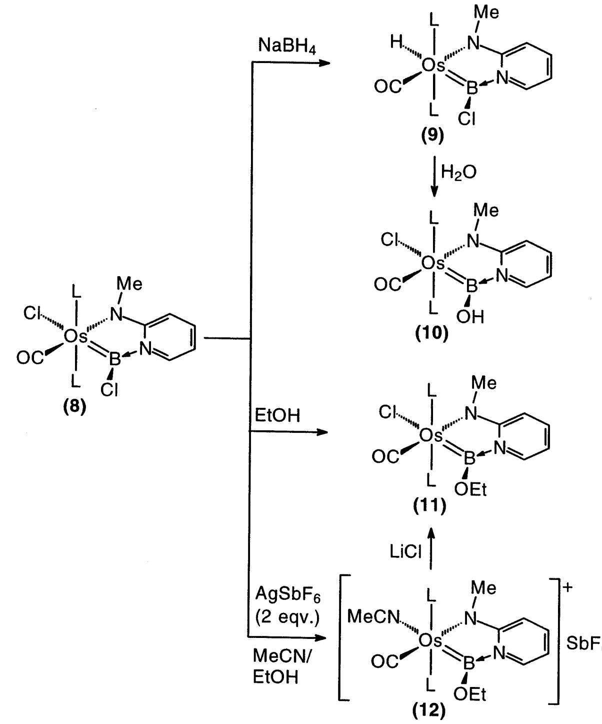


Figure 6. Molecular structure of Os[BCl(NC$_5$H$_4$NMe)]H(CO)(PPh$_3$)$_2$ (**9**) with thermal ellipsoids at the 50% probability level.

Scheme 4



Os[BCl(NHC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (1) and Os[B(OEt)(NC$_5$H$_4$NH)]Cl(CO)(PPh$_3$)$_2$ (2). A benzene solution of Os(BCl_2)Cl(CO)(PPh_3)$_2$ (0.366 g, 0.426 mmol) was added to 2-aminopyridine (50 mg, 0.53 mmol) to give a bright yellow solution with a pale precipitate. The reaction mixture was stirred for 20 min and concentrated in vacuo to ca. 1 mL. Addition of hexane gave a yellow precipitate, which was collected by filtration. The yellow solid was washed several times with EtOH, and the combined yellow washings were retained for isolation of **2** (see below). The remaining white solid was recrystallized from CH_2Cl_2/EtOH to give pure **1** (yield 158 mg, 40%). Anal. Calcd for $C_{42}H_{35}BCl_2N_2OOsP_2$: C, 54.98; H, 3.84; N, 3.05. Found: C, 55.26; H, 3.96; N, 2.92.

The yellow ethanol washings (see above) were allowed to stand for 20 min and then concentrated in vacuo to ca. 5 mL, to give a yellow precipitate, which was collected by filtration and washed with EtOH and hexane. The product was recrystallized from CH_2Cl_2/EtOH to give pure **2** (yield 100 mg, 25%). ^{1}H NMR spectroscopy showed 0.5 equiv of CH_2Cl_2 present as solvate. Anal. Calcd for $C_{44}H_{40}BClN_2O_2OsP_2{\cdot}0.5CH_2Cl_2$: C, 55.12; H, 4.26; N, 2.89. Found: C, 54.92; H, 4.25; N, 2.93.

Os[BCl(NHC$_5$H$_4$N)]Br(CO)(PPh$_3$)$_2$ (3). A solution of NaBr (100 mg) in H_2O/EtOH (1:7, 2 mL) was added to a solution of **1** (50 mg, 0.055 mmol) in THF, and the mixture was stirred for 1 h. Concentration of the solution to ca. 1 mL in vacuo formed a white precipitate. EtOH was added to complete precipitation of pure **3**, which was collected by filtration and

Table 11. Selected Bond Distances (Å) and Angles (deg) for Complex 9

Interatomic Distances			
Os−B	2.078(4)	Os−P(2)	2.3450(9)
Os−C(1)	1.843(4)	C(1)−O(1)	1.163(4)
Os−N(1)	2.136(3)	B−N(2)	1.502(4)
Os−H	1.78(3)	B−Cl	1.803(4)
Os−P(1)	2.3452(9)		
Interatomic Angles			
C(1)−Os−B	100.11(15)	P(1)−Os−B	94.42(11)
C(1)−Os−N(1)	176.27(13)	P(2)−Os−H	83.9(11)
C(1)−Os−H	98.5(11)	P(2)−Os−B	95.04(11)
C(1)−Os−P(1)	89.45(11)	H−Os−B	161.4(11)
C(1)−Os−P(2)	90.99(11)	O(1)−C(1)−Os	179.6(3)
N(1)−Os−B	76.17(12)	B−N(2)−C(2)	113.8(3)
N(1)−Os−H	85.3(11)	N(2)−C(2)−N(1)	116.6(3)
N(1)−Os−P(1)	90.59(8)	Os−N(1)−C(2)	118.8(2)
N(1)−Os−P(2)	89.59(8)	Os−B−N(2)	114.6(2)
P(1)−Os−P(2)	170.30(3)	Os−B−Cl	134.0(2)
P(1)−Os−H	86.4(11)		

washed with EtOH and hexane (yield 47 mg, 90%). Anal. Calcd for $C_{42}H_{35}BBrClN_2OOsP_2$: C, 52.44; H, 3.67; N, 2.91. Found: C, 52.11; H, 3.66; N, 2.97.

Os[BCl(NHC$_5$H$_4$N)]H(CO)(PPh$_3$)$_2$ (4). A solution of NaBH$_4$ (50 mg) in EtOH (3 mL) was added to a suspension of **1** (49 mg, 0.053 mmol) in CH_2Cl_2 (10 mL), and the resultant mixture was stirred for 15 min. The solvent was removed in vacuo, benzene was added to the solid residue, and the mixture was filtered to give a pale yellow solution. Concentration of the solution to ca. 1 mL in vacuo and addition of hexane gave pure **4** as a cream-colored precipitate which was collected by filtration and washed with EtOH and hexane (yield 42 mg, 89%). ^{31}P NMR ($CDCl_3$): δ 24.13 (s). Anal. Calcd for $C_{42}H_{36}BClN_2OOsP_2$: C, 57.12; H, 4.11; N, 3.17. Found: C, 57.17; H, 4.44; N, 3.05.

Os[B(OH)(NHC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (5). To a solution of [Os{B(OH)(NHC$_5$H$_4$N)}(CO)(MeCN)(PPh$_3$)$_2$]SbF$_6$ (**6**; 46 mg, 0.041 mmol) in THF (10 mL) was added LiCl (100 mg, 2.36 mmol) in 95% EtOH (2 mL), and the resultant colorless solution was stirred for 1 h. Concentration of the solution to ca. 1 mL in vacuo and addition of EtOH gave pure **5** as a white precipitate, which was collected by filtration and washed with EtOH and hexane (yield 30 mg, 81%). Anal. Calcd for $C_{42}H_{36}BClN_2O_2OsP_2 \cdot 0.25CH_2Cl_2$: C, 55.13; H, 3.99; N, 3.04. Found: C, 55.14; H, 4.07; N, 3.04. (This compound can also be produced by addition of 1 equiv of AgSbF$_6$ to **1** in THF. A solution of AgSbF$_6$ (25 mg, 0.073 mmol) in THF (5 mL) was added to a solution of **1** (60 mg, 0.065 mmol) in THF (10 mL), forming a precipitate of AgCl in a yellow solution. The AgCl was removed by filtration, and on concentration of the filtrate to ca. 1 mL in vacuo and addition of ethanol pure **5** was precipitated.)

[Os{B(OH)(NHC$_5$H$_4$N)}(CO)(MeCN)(PPh$_3$)$_2$]SbF$_6$ (6). A solution of AgSbF$_6$ (50 mg, 0.15 mmol) in THF (5 mL) was added to a solution of **1** (60 mg, 0.065 mmol) in THF (10 mL), forming a pale precipitate of AgCl in a yellow solution. The mixture was stirred for 10 min, and then MeCN (0.1 mL) was added, turning the solution colorless. The solvent was removed in vacuo, CH_2Cl_2 was added to the solid residue, and the resultant suspension was filtered through Celite. Addition of EtOH to the filtrate followed by removal of the CH_2Cl_2 in vacuo gave a white precipitate of pure **6**, which was collected by filtration and washed with EtOH and hexane (yield 50 mg, 67%). ^{31}P NMR ($CDCl_3$/acetone): δ 12.0 (s, br). Anal. Calcd for $C_{44}H_{39}BF_6N_3O_2OsP_2Sb$: C, 46.34; H, 3.45; N, 3.68. Found: C, 46.62; H, 3.54; N, 3.64.

[Os{B(OEt)(NHC$_5$H$_4$N)}(CO)$_2$(PPh$_3$)$_2$]SbF$_6$ (7). A solution of AgSbF$_6$ (40 mg, 0.12 mmol) in THF (5 mL) was added to a solution of **1** (51 mg, 0.065 mmol) in THF (10 mL) and EtOH (3 mL), forming a pale precipitate of AgCl in a yellow solution. The mixture was stirred for 10 min, and then a stream of CO gas was passed through it until the solution turned colorless. The solvent was removed in vacuo, CH_2Cl_2 was added, and the resultant suspension was filtered through Celite. Addition of hexane and removal of CH_2Cl_2 in vacuo gave a white precipitate of pure **7**, which was collected by filtration and washed with EtOH and hexane (yield 58 mg, 90%). Anal. Calcd for $C_{45}H_{40}BF_6N_2O_3OsP_2Sb$: C, 46.77; H, 3.49; N, 2.42. Found: C, 46.77; H, 3.47; N, 2.23.

Os[BCl(NC$_5$H$_4$NMe)]Cl(CO)(PPh$_3$)$_2$ (8). A solution of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ (170 mg, 0.198 mmol) in benzene (12 mL) was added to 2-(methylamino)pyridine (200 mg, 185 mmol) to produce a bright yellow precipitate. After it was stirred for 15 min, the mixture was concentrated in vacuo to ca. 3 mL and EtOH was added. Pure **8** was collected by filtration as a yellow solid and washed with EtOH and hexane (yield 172 mg, 94%). Anal. Calcd for $C_{43}H_{37}BCl_2N_2OOsP_2 \cdot C_6H_6$: C, 58.28; H, 4.29; N, 2.77. Found: C, 58.30; H, 4.27; N, 2.89.

Os[BCl(NC$_5$H$_4$NMe)]H(CO)(PPh$_3$)$_2$ (9). A solution of NaBH$_4$ (50 mg) in EtOH (3 mL) was added to a suspension of **8** (73 mg, 0.078 mmol) in CH_2Cl_2 (12 mL) and the resultant mixture stirred for 15 min. The solvent was removed in vacuo, benzene was added to the solid residue, and the mixture was filtered to give a yellow solution. Reduction of the solvent volume to ca. 1 mL in vacuo and addition of hexane gave pure **9** as a yellow precipitate, which was collected by filtration and washed with EtOH and hexane (yield 60 mg, 85%). ^{31}P NMR ($CDCl_3$/CH_2Cl_2): δ 21.36 (s). Anal. Calcd for $C_{43}H_{38}BClN_2OOsP_2$: C, 57.56; H, 4.27; N, 3.12. Found: C, 57.82; H, 4.60; N, 3.17.

Os[B(OH)(NC$_5$H$_4$NMe)]Cl(CO)(PPh$_3$)$_2$ (10). To a solution of **9** (81 mg, 0.090 mmol) in benzene (10 mL) was added H_2O (28 mg, 1.6 mmol), and the resultant mixture was stirred at room temperature for 16 h to give a yellow suspension. The solvent volume was reduced in vacuo to ca. 2 mL, and EtOH was added. Pure **10** was collected as a yellow solid by fitration and washed with EtOH and hexane (yield 46 mg, 56%). Anal. Calcd for $C_{43}H_{38}BClN_2O_2OsP_2$: C, 56.56; H, 4.19; N, 3.07. Found: C, 56.53; H, 4.50; N, 2.77.

Os[B(OEt)(NC$_5$H$_4$NMe)]Cl(CO)(PPh$_3$)$_2$ (11). Method 1. A suspension of **8** (100 mg, 0.107 mmol) in benzene (20 mL) and EtOH (5 mL) was heated under reflux for 90 min to give a bright yellow solution. Reduction of the solvent volume to ca. 1 mL in vacuo and addition of EtOH gave a yellow precipitate, which was collected by filtration and washed with EtOH and hexane. The product was recrystallized from CH_2Cl_2/EtOH to give pure **11** (yield 50 mg, 49%). ^{31}P NMR ($CDCl_3$): δ 3.99 (s). Anal. Calcd for $C_{45}H_{42}BClN_2O_2OsP_2$: C, 57.42; H, 4.50; N, 2.98. Found: C, 57.36; H, 4.45; N, 2.99.

Method 2. To a solution of **12** (60 mg, 0.051 mmol) in CH_2Cl_2 (10 mL) was added a solution of LiCl (0.15 g, 3.5 mmol) in EtOH (5 mL). The mixture was stirred for 10 min, and then the CH_2Cl_2 was removed in vacuo to give a yellow precipitate, which was collected by filtration and washed with EtOH and light petroleum (yield 42 mg, 88%).

[Os{B(OEt)(NC$_5$H$_4$NMe)}(CO)(MeCN)(PPh$_3$)$_2$]SbF$_6$ (12). Addition of a solution of AgSbF$_6$ (125 mg, 0.364 mmol) in THF (5 mL) to a suspension of **8** (154 mg, 0.165 mmol) in THF (10 mL) and EtOH (3 mL) afforded a bright yellow solution and a precipitate of AgCl. The mixture was stirred for 10 min, and then MeCN (0.5 mL) was added and the solution turned pale yellow. After it was stirred for 5 min, the solvent was removed in vacuo and CH_2Cl_2 was added to the solid residue. The resultant suspension was then filtered through Celite to give a yellow filtrate, which was concentrated in vacuo to ca. 1 mL. Addition of a mixture of light petroleum (20 mL) and EtOH (2 mL) gave pure **12** as a yellow precipitate, which was collected by filtration and washed with EtOH (2 × 2 mL portions) and then light petroleum (yield 126 mg, 64%). ^{31}P NMR (CDCl$_3$): δ 8.95 (s, br). Anal. Calcd for $C_{47}H_{45}BF_6N_3O_2OsP_2Sb$: C, 47.74; H, 3.84; N, 3.55. Found: C, 47.76; H, 3.94; N, 3.56.

X-ray Diffraction Studies of 2−6 and 9. Data were collected on a Siemens SMART CCD diffractometer at 203 K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using ω scans. The data were corrected for Lorentz and polarization effects and empirical absorption corrections applied using symmetry equivalents.[7] The structures were solved using SHELXS[8] and refined by full-matrix least squares of F^2 using SHELXL[9] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms, other than those bonded to osmium, were placed geometrically and allowed to ride on the carrier atom with 20% higher thermal parameters. The hydrogen atoms bound to osmium were located from electron density maps and their coordinates refined with thermal parameters tied to that of the osmium atom. For **3**, the asymmetric unit contains two independent molecules together with three molecules of dichloromethane. Data collection and refinement parameters are summarized in Table 5.

Acknowledgment. We thank the Marsden Fund, administered by the Royal Society of New Zealand, for supporting this work and for granting a Postdoctoral Fellowship award to A.W.

Supporting Information Available: Tables of crystal data, collection and refinement parameters, positional and anisotropic displacement parameters, and bond distances and angles for **2**−**6** and **9**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0203431

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