1714 *Organometallics* **2002,** *21,* 1714−1718

Tethered Osmium Boryl Complexes from the Reaction of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ with 2-Hydroxypyridine

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Received December 4, 2001

Reaction between Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ and 2-hydroxypyridine leads to the replacement of one chloride on the dichloroboryl ligand and coordination of the pyridine nitrogen atom to osmium, leading to the six-coordinate complex Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**1**). The five-membered chelate ring so formed is stable and persists through reactions involving replacement of chloride both at osmium and at boron. When **1** is treated with anhydrous HI, replacement of chloride at osmium occurs exclusively, leaving the B−Cl bond intact and giving Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (**2**). However, the following nucleophilic substitution reactions at boron occur readily in **1**: EtOH gives Os[B(OEt)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**3**), *n*-BuNH$_2$ gives Os[B(NH*n*-Bu)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**4**), and Et$_3$N·3HF gives Os[BF(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**5**). Crystal structures of complexes **2** and **4** are reported.

Introduction

Compounds with transition metal−boron, 2c-2e bonds (L$_n$M-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] In this paper we examine the reaction between the coordinatively unsaturated dichloroboryl complex Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ and 2-hydroxypyridine in the expectation that condensation between a B−Cl bond and the hydroxy function of the 2-hydroxypyridine will introduce a substituent to the boryl ligand with the capability of coordinating back to the osmium through the pyridine nitrogen atom. A favorable five-membered chelate ring would be formed in this process. In principle both B−Cl bonds could react but in the event condensation occurs only once, leaving a stable complex with a tethered boryl ligand still bearing one chloride substituent. This complex provides the opportunity of examining the reactivity of this remaining B−Cl bond through studying reactions with an alcohol, an amine, and fluoride ion. Crystal structure determinations confirm the presence of the chelate ring and allow an interesting comparison of structural changes consequent upon changing one of the substituents on the boryl ligand from chloride to an amino group.

Results and Discussion

Reaction between Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ and 2-Hydroxypyridine. We have previously reported that reaction between Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ and 8-aminoquinoline leads to a base-stabilized borylene complex.[2] In this case both nitrogen atoms of the 8-aminoquinoline bind to the boron atom with the formation of a five-membered ring. For 2-hydroxypyridine, similar behavior would lead to a less favorable four-membered ring at boron, whereas the alternative possibility of coordination of the pyridine nitrogen back to osmium forms a favorable five-membered ring. This second possibility is the observed result with the formation of Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**1**) (see Scheme 1). The spectroscopic data for **1**, and for all other new compounds reported in this paper, are presented in Table 1 (IR), Table 2 (^{1}H NMR), Table 3 (^{13}C NMR), and Table 4 (^{11}B NMR) and a discussion of these data is given below.

Treatment of **1** with anhydrous HI produces Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (**2**), in which iodide replaces chloride on osmium but the B−Cl bond is left unchanged. However, as shown in Scheme 2, the B−Cl bond in **1** does undergo reaction with ethanol, *n*-butylamine, or fluoride ion (as Et$_3$N·3HF) to give Os[B(OEt)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**3**), Os[B(NH*n*-Bu)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**4**), or Os[BF(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**5**), respectively. ν(CO) values in Table 1 fall into two groups. The higher values (ν(CO), 1911

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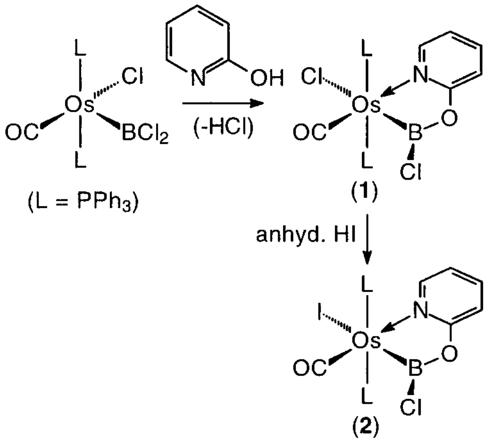
10.1021/om011029u CCC: $22.00

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

complex	ν(C=O)	other bands
$\overline{\text{Os[BCl(OC}_5\text{H}_4\text{N)]}}\text{Cl(CO)(PPh}_3)_2$ (**1**)	1911vs	1615m, 1302m, 1115m, 1073m, 1058s, 1037m, 1024m, 901s
$\overline{\text{Os[BCl(OC}_5\text{H}_4\text{N)]}}\text{I(CO)(PPh}_3)_2$ (**2**)	1919vs	1615w, 1302w, 1289w, 1113w, 1067m, 1054m, 1034m, 1023m, 915m
$\overline{\text{Os[B(OEt)(OC}_5\text{H}_4\text{N)]}}\text{Cl(CO)(PPh}_3)_2$ (**3**)	1895vs	1297m, 1279m, 1245w, 1150w, 1046w, 965m
$\overline{\text{Os[B(NH}n\text{-Bu)(OC}_5\text{H}_4\text{N)]}}\text{Cl(CO)(PPh}_3)_2$ (**4**)	1887vs	3449w, 1612m, 1331m, 1295m, 1267m, 1245m, 1151m, 1048w, 1020w, 945m, 873w
$\overline{\text{Os[BF(OC}_5\text{H}_4\text{N)]}}\text{Cl(CO)(PPh}_3)_2$ (**5**)	1921m, 1904vs[b]	1223m, 1062m, 1051m, 1030m, 1023m

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

Scheme 1



cm^{-1}, **1**; ν(CO), 1919 cm^{-1}, **2**) are associated with the two compounds bearing chloride on the boron atom. Lower values are observed for the compounds **3**−**5**, which bear oxygen, nitrogen, or fluorine on the boron atom. A possible explanation for this is that chloride is the least effective π-donor toward boron of this set of donor atoms, and therefore the corresponding increase in the Os−B π-interaction[3] results in higher values for ν(CO). The structural data to be discussed below are also compatible with this “competitive π-bonding model”, which has been used successfully to explain heteroatom substituent effects in metal carbene complexes.[4]

The ^{1}H NMR data in Table 2 are useful for characterization purposes but require no special comment. In the ^{13}C NMR data in Table 3 all five pyridine ring carbons are observed for each of the compounds **1**−**5**. Of special note is that the quaternary carbon of the pyridine ring in $\overline{\text{Os[BF(OC}_5\text{H}_4\text{N)]}}\text{Cl(CO)(PPh}_3)_2$ shows long-range coupling to fluorine, $^3J_{CF} = 12$ Hz. Another feature of the ^{13}C NMR data is that in all compounds the carbonyl carbon resonances appear as triplets through coupling to two equivalent phosphorus atoms, thus fixing the geometries of the complexes as depicted in the schemes and confirmed by the X-ray crystal structure determinations to be discussed below. It can be seen in the ^{11}B NMR data tabulated in Table 4 that the compounds bearing chloride on the boron (**1** and **2**) have chemical shift values of ca. 63 ppm. In contrast, the compounds in which chloride has been replaced by oxygen, nitrogen, or fluorine donor atoms (**3**−**5**) have chemical shift values of ca. 47 ppm. No other significant trends are apparent.

Crystal Structure Determinations. In this paper we report crystal structure determinations for complexes **2** and **4**. The crystal and refinement data are presented in Table 5, and selected bond distances and angles for these complexes are presented in Tables 6 and 7. The molecular structures of **2** and **4** are shown in Figures 1 and 2, respectively.

The structures reveal an octahedral arrangement of ligands about osmium for both complexes with the two triphenylphosphine ligands located mutually trans and the boryl and carbonyl ligands adjacent to one another. The Os−I bond in **2** (2.8674(3) Å) and the Os−Cl bond in **4** (2.5653(6) Å) are both at the long end limits of the corresponding ranges of previously observed values (Os−I, mean = 2.705 Å, standard deviation = 0.061; Os−Cl, mean = 2.389 Å, standard deviation = 0.067).[5] Clearly, in both cases the boryl ligand is exerting a pronounced trans-influence. The geometry of the chelate rings in both complexes is planar with the Os−N(pyridine) distances being 2.178(3) Å in **2** and 2.185(2) Å in **4**. The coordination about boron is planar, with the largest angle being Os−B−Cl for **2** (132.7(3)°) and Os−B−N for **4** (132.8(2)°). A particularly interesting comparison between the two structures centers on the marked differences in the bond distances about each boron atom. The shorter Os−B distance is found in **2** (2.039(4) Å) and the longer in **4** (2.075(3) Å). Correspondingly, the B−O distance in **2** (1.417(5) Å) is shorter than that in **4** (1.445(4) Å), and both are longer than the mean of all B−O distances reported for three-coordinate boron (mean, 1.371; SD, 0.035 Å).[5] The B−N distance in **4** is 1.398(4) Å, which is shorter than the mean of reported values (1.424; SD, 0.043 Å).[5] The B−Cl distance in **2** is 1.773(4) Å, which is also shorter than the mean of reported values (1.787; SD, 0.036 Å).[5] These trends in bond distances can be explained using the same “competitive π-bonding model” so successfully used by Schubert to rationalize the observed bond distances to carbon in transition metal heteroatom-substituted carbene complexes.[4] Hence, replacement of chloride on boron in **2**, with the more strongly π-donating NHn-Bu group in **4** has the effect of lessening the π-donation required of the O and Os substituents at boron, and this in turn results in a lengthening of both the B−O and Os−B bonds, as observed. Furthermore, the presence of the poorly π-donating Cl group in **2** contributes to the Os−B distance (2.039(4) Å) being the shortest Os−B distance we have observed in 26 crystal structure determinations of related octahedral osmium boryl

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(5) Cambridge Crystallographic Data Base.

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

complex	^{1}H, δ (ppm)
$\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**1**)	5.92 (apparent td, $J = 6.7$ Hz, $J = 1.2$ Hz, 1H, NC_5H_4O), 6.76 (apparent d, $J = 8.2$ Hz, 1H, NC_5H_4O), 7.16−7.24 (m, 19H, PPh_3 and NC_5H_4O), 7.47 (apparent d, $J = 5.5$ Hz, 1H, NC_5H_4O), 7.52−7.58 (m, 12H, PPh_3)
$\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]I(CO)(PPh_3)_2}$ (**2**)	5.81 (apparent td, $J = 6.7$ Hz, $J = 1.2$ Hz, 1H, NC_5H_4O), 6.76 (apparent d, $J = 8.2$ Hz, 1H, NC_5H_4O), 7.15−7.23 (m, 18H, PPh_3), 7.31 (apparent td, $J = 7.6$ Hz, $J = 1.8$ Hz, 1H, NC_5H_4O), 7.57−7.62 (m, 12H, PPh_3), 7.80 (apparent d, $J = 6.1$ Hz, 1H, NC_5H_4O)
$\overline{\mathrm{Os[B(OEt)(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**3**)	0.89 (t, $J = 7.2$ Hz, 3H, OCH_2Me), 3.40 (q, $J = 7.2$ Hz, 2H, OCH_2Me), 5.87 (apparent td, $J = 7.1$ Hz, $J = 1.2$ Hz, 1H, NC_5H_4O), 6.50 (apparent d, $J = 8.1$ Hz, 1H, NC_5H_4O), 7.16−7.24 (m, 19H, PPh_3 and NC_5H_4O), 7.54−7.60 (m, 12H, PPh_3), 7.62 (apparent d, $J = 5.5$ Hz, 1H, NC_5H_4O)
$\overline{\mathrm{Os[B(NH}n\mathrm{\text{-}Bu)(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**4**)	0.76 (t, $J = 7.2$ Hz, 3H, $NH(CH_2)_3Me$), 0.86 (m, 2H, $NH(CH_2)_2CH_2Me$), 0.96 (m, 2H, $NHCH_2CH_2CH_2Me$), 2.57 (m, 2H, $NHCH_2(CH_2)_2Me$), 5.80 (apparent td, $J = 6.6$ Hz, $J = 1.2$ Hz, 1H, NC_5H_4O), 6.55 (apparent dd, $J = 8.2$ Hz, $J = 0.6$ Hz, 1H, NC_5H_4O), 7.14−7.22 (m, 20H, PPh_3, NC_5H_4O and $NH(CH_2)_3Me$), 7.49−7.58 (m, 13H, PPh_3 and NC_5H_4O)
$\overline{\mathrm{Os[BF(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**5**)	5.91 (apparent td, $J = 6.7$ Hz, $J = 1.2$ Hz, 1H, NC_5H_4O), 6.57 (apparent d, $J = 8.2$ Hz, 1H, NC_5H_4O), 7.19−7.27 (m, 19H, PPh_3 and NC_5H_4O), 7.51 (apparent d, $J = 5.8$ Hz, 1H, NC_5H_4O), 7.54−7.59 (m, 12H, PPh_3)

[a] Spectra recorded in $CDCl_3$ at 25 °C. Chemical shifts are referenced to Me_4Si ($\delta = 0.00$). Splitting patterns and line shapes are indicated thus: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.

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

complex	^{13}C, δ (ppm)
$\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**1**)	110.06 (NC_5H_4O), 118.13 (NC_5H_4O), 127.78 (t′, $^{2,4}J_{CP} = 10$ Hz, *o*-PPh_3), 129.57 (*p*-PPh_3), 132.42 (t′, $^{1,3}J_{CP} = 52$ Hz, *i*-PPh_3), 134.09 (t′, $^{3,5}J_{CP} = 10$ Hz, *m*-PPh_3), 138.80 (NC_5H_4O), 147.88 (NC_5H_4O), 165.64 (NC_5H_4O), 189.13 (t, $^2J_{CP} = 11$ Hz, *C*O)
$\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]I(CO)(PPh_3)_2}$ (**2**)	110.26 (NC_5H_4O), 119.06 (NC_5H_4O), 127.64 (t′, $^{2,4}J_{CP} = 10$ Hz, *o*-PPh_3), 129.47 (*p*-PPh_3), 133.34 (t′, $^{1,3}J_{CP} = 52$ Hz, *i*-PPh_3), 134.10 (t′, $^{3,5}J_{CP} = 10$ Hz, *m*-PPh_3), 139.53 (NC_5H_4O), 152.71 (NC_5H_4O), 165.42 (NC_5H_4O), 189.70 (t, $^2J_{CP} = 11$ Hz, *C*O)
$\overline{\mathrm{Os[B(OEt)(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**3**)	17.00 (OCH_2Me), 58.86 (OCH_2Me), 109.35 (NC_5H_4O), 116.76 (NC_5H_4O), 127.57 (t′, $^{2,4}J_{CP} = 10$ Hz, *o*-PPh_3), 129.20 (*p*-PPh_3), 133.20 (t′, $^{1,3}J_{CP} = 49$ Hz, *i*-PPh_3), 134.21 (t′, $^{3,5}J_{CP} = 11$ Hz, *m*-PPh_3), 138.32 (NC_5H_4O), 148.04 (NC_5H_4O), 165.59 (NC_5H_4O), 189.49 (t, $^2J_{CP} = 11$ Hz, *C*O)
$\overline{\mathrm{Os[B(NH}n\mathrm{\text{-}Bu)(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**4**)	13.98 ($NH(CH_2)_3Me$), 19.93 ($NH(CH_2)_2CH_2Me$), 34.93 ($NHCH_2CH_2CH_2Me$), 40.61 ($NHCH_2(CH_2)_2Me$), 109.40 (NC_5H_4O), 116.06 (NC_5H_4O), 127.51 (t′, $^{2,4}J_{CP} = 10$ Hz, *o*-PPh_3), 129.02 (*p*-PPh_3), 133.23 (t′, $^{1,3}J_{CP} = 50$ Hz, *i*-PPh_3), 134.11 (t′, $^{3,5}J_{CP} = 11$ Hz, *m*-PPh_3), 138.15 (NC_5H_4O), 148.04 (NC_5H_4O), 166.90 (NC_5H_4O), 191.52 (t, $^2J_{CP} = 11.5$ Hz, *C*O)
$\overline{\mathrm{Os[BF(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ (**5**)	109.77 (NC_5H_4O), 117.64 (NC_5H_4O), 127.84 (t′, $^{2,4}J_{CP} = 10$ Hz, *o*-PPh_3), 129.60 (*p*-PPh_3), 132.85 (t′, $^{1,3}J_{CP} = 51$ Hz, *i*-PPh_3), 134.02 (t′, $^{3,5}J_{CP} = 10$ Hz, *m*-PPh_3), 138.68 (NC_5H_4O), 147.91 (NC_5H_4O), 164.63 (d, $^3J_{CF} = 12$ Hz, NC_5H_4O), 188.72 (t, $^2J_{CP} = 11.5$ Hz, *C*O)

[a] Spectra recorded in $CDCl_3$ at 25 °C. Chemical shifts are referenced to $CDCl_3$ ($\delta = 77.00$). t′ denotes 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.

complexes. Details of these other structures, all of which support this bonding model, will be discussed in subsequent papers.

Conclusions

A tethered boryl complex of osmium(II), bearing a reactive chloride substituent on boron, is accessible from reaction between $Os(BCl_2)Cl(CO)(PPh_3)_2$ and 2-hydroxypyridine. Related complexes are produced from facile nucleophilic substitution reactions occurring at the B−Cl bond of this tethered complex. Structure determination of $\overline{\mathrm{Os[BCl(OC_5H_4N}}\mathrm{)]I(CO)(PPh_3)_2}$ reveals a very short Os−B bond distance of 2.039(4) Å, whereas replacement of chloride at boron by NH*n*-Bu in $\overline{\mathrm{Os[B(NH}n\mathrm{\text{-}Bu)(OC_5H_4N}}\mathrm{)]Cl(CO)(PPh_3)_2}$ results in a longer Os−B bond distance of 2.075(3) Å. The observed trends in the bond distances about boron, Os−B, B−O, B−N, and B−Cl, can be understood in terms of a bonding model in which all the substituents at boron are involved in competitive π-donation to boron.

Experimental Section

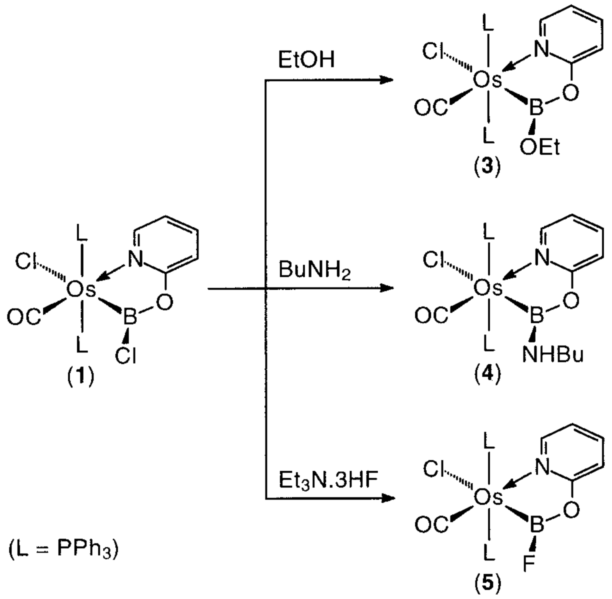
General Considerations. The general experimental and spectroscopic techniques employed in this work were the same as those described previously.[6] $Os(BCl_2)Cl(CO)(PPh_3)_2$ was prepared as reported previously.[2]

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

complex	^{11}B, δ (ppm)
Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**1**)	63.0
Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (**2**)	62.3
Os[B(OEt)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**3**)	47.5
Os[B(NH*n*-Bu)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**4**)	46.0
Os[BF(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**5**)	48.8

[a] Spectra recorded in CDCl$_3$ at 25 °C. Chemical shifts are referenced to BF$_3$·OEt$_2$ (δ = 0.00).

Scheme 2



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 400 at 25 °C. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were obtained operating at 400.1 (^{1}H), 100.6 (^{13}C), 128.0 (^{11}B), and 162.0 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^{1}H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-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$_3$·OEt$_2$ as an external standard. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (1). A solution of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ (255 mg, 0.297 mmol) in toluene (12 mL) was added to 2-hydroxypyridine (73 mg, 0.772 mmol) and the mixture stirred for 20 min. The resultant murky yellow solution was filtered and the filtrate concentrated to ca. 4 mL in vacuo. Standing at −20 °C for 3 days afforded colorless crystals of pure **1**, which were collected on a glass frit and washed with hexanes (yield 249 mg, 83%). ^{1}H NMR spectroscopy showed the presence of 1.0 equiv of toluene as solvate. Anal. Calcd for C$_{42}$H$_{34}$BCl$_2$NO$_2$OsP$_2$·C$_7$H$_8$: C, 58.23; H, 4.19; N, 1.39. Found: C, 58.03; H, 4.09; N, 1.47.

Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (2). A tetrahydrofuran solution of BH$_3$·THF (1.00 M, 0.10 mL, 0.10 mmol) was added to a solution of Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (50 mg, 0.054 mmol) in THF (10 mL). To produce anhydrous HI (through reaction between BH$_3$ and I$_2$), a solution of I$_2$ (25 mg, 0.10 mmol) in THF (5 mL) was then added dropwise to the above mixture and the resultant orange solution stirred for 10 min. Concentration of the solution in vacuo followed by addition of light petroleum gave pure **2** as a pale yellow precipitate, which was collected on a glass frit and washed with light petroleum (yield 51 mg, 93%). ^{31}P NMR (CDCl$_3$): δ 2.18 (s). Anal. Calcd for C$_{42}$H$_{34}$BClINO$_2$OsP$_2$: C, 49.94; H, 3.39; N, 1.39. Found: C, 49.81; H, 3.13; N, 1.42.

Table 5. Crystal and Refinement Data for 2 and 4

	2	**4**·0.5EtOH
formula	C$_{42}$H$_{34}$BClINO$_2$OsP$_2$	C$_{47}$H$_{44}$BClN$_2$O$_{2.5}$OsP$_2$
molecular wt	1010.00	975.25
cryst syst	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
a, Å	10.0292(2)	9.4822(1)
b, Å	16.2023(2)	11.5729(1)
c, Å	11.6971(2)	21.3401(1)
α, deg	90.0	82.024(1)
β, deg	94.761(1)	81.023(1)
γ, deg	90.0	67.463(1)
V, Å^3	1894.18(5)	2128.44(3)
Z	2	2
d(calc), g cm^{-3}	1.771	1.531
F(000)	980	976
μ, mm^{-1}	4.37	3.17
cryst size, mm	0.36 × 0.28 × 0.09	0.42 × 0.24 × 0.11
2θ (min−max), deg	1.7−27.1	1.9−27.1
no. of reflns collected	11 582	20 264
no. of ind reflns	7367, R_{int} 0.0212	9090, R_{int} 0.0212
A (min, max)	0.302, 0.694	0.349, 0.721
goodness of fit on F^2	0.790	1.087
R, wR2 (obsd data)[a]	0.0193 0.0513	0.0216 0.0508
R, wR2 (all data)	0.0201, 0.0528	0.0249, 0.0524

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

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

Interatomic Distances			
Os−B	2.039(4)	Os−P(2)	2.3894(10)
Os−C(1)	1.838(4)	C(1)−O(1)	1.162(5)
Os−N	2.178(3)	C(2)−O(2)	1.347(5)
Os−I	2.8674(3)	B−O(2)	1.417(5)
Os−P(1)	2.3912(10)	B−Cl	1.773(4)
Interatomic Angles			
C(1)−Os−B	91.7(2)	P(1)−Os−B	92.71(13)
C(1)−Os−N	166.58(16)	P(2)−Os−I	86.81(2)
C(1)−Os−I	99.92(15)	P(2)−Os−B	90.38(13)
C(1)−Os−P(1)	90.76(12)	I−Os−B	168.08(13)
C(1)−Os−P(2)	91.35(12)	O(1)−C(1)−Os	177.1(5)
N−Os−B	75.09(16)	B−O(2)−C(2)	115.8(3)
N−Os−I	93.38(9)	O(2)−C(2)−N	116.9(4)
N−Os−P(1)	87.47(9)	Os−N−C(2)	114.8(3)
N−Os−P(2)	91.21(9)	Os−B−O(2)	117.2(3)
P(1)−Os−P(2)	176.21(3)	Os−B−Cl	132.7(3)
P(1)−Os−I	89.72(2)	O(2)−B−Cl	110.0(3)

Os[B(OEt)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (3). A solution of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ (187 mg, 0.217 mmol) in benzene (15 mL) was added to 2-hydroxypyridine (50 mg, 0.53 mmol) to give a bright yellow solution together with a pale precipitate, which was stirred for 20 min. Addition of EtOH (3 mL) dissolved the precipitate, and the resultant solution was stirred for 20 min. Concentration of the solution in vacuo to ca. 1 mL followed by addition of EtOH gave pure **3** as a white precipitate, which was collected on a glass frit and washed with EtOH and hexanes (yield 139 mg, 69%). ^{1}H NMR spectroscopy showed 1 equiv of CH$_2$Cl$_2$ present as solvate. Anal. Calcd for

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

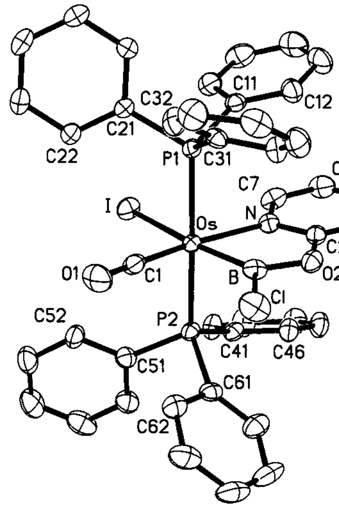

Figure 1. Molecular structure of Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (**2**) with thermal ellipsoids at the 50% probability level.

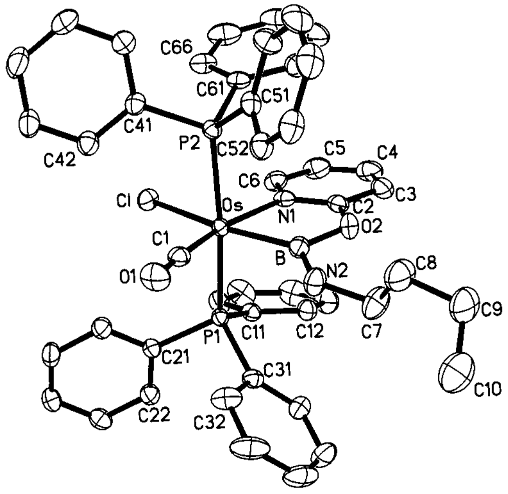

Figure 2. Molecular structure of Os[B(NH*n*-Bu)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (**4**) with thermal ellipsoids at the 50% probability level.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Interatomic Distances			
Os−B	2.075(3)	Os−P(2)	2.3741(6)
Os−C(1)	1.833(3)	C(1)−O(1)	1.175(3)
Os−N(1)	2.185(2)	C(2)−O(2)	1.341(3)
Os−Cl	2.5653(6)	B−O(2)	1.445(4)
Os−P(1)	2.3646(6)	B−N(2)	1.398(4)
Interatomic Angles			
C(1)−Os−B	89.39(12)	P(1)−Os−B	90.30(8)
C(1)−Os−N(1)	165.42(10)	P(2)−Os−Cl	86.50(2)
C(1)−Os−Cl	106.59(8)	P(2)−Os−B	96.28(8)
C(1)−Os−P(1)	91.21(8)	Cl−Os−B	163.79(9)
C(1)−Os−P(2)	90.56(8)	O(1)−C(1)−Os	174.7(2)
N(1)−Os−B	76.13(11)	B−O(2)−C(2)	116.7(2)
N(1)−Os−Cl	87.96(6)	O(2)−C(2)−N(1)	118.2(2)
N(1)−Os−P(1)	90.52(6)	Os−N(1)−C(2)	114.10(17)
N(1)−Os−P(2)	89.40(6)	Os−B−O(2)	114.54(19)
P(1)−Os−P(2)	173.21(2)	Os−B−N(2)	132.8(2)
P(1)−Os−Cl	86.71(2)		

C$_{44}$H$_{39}$BClNO$_3$OsP$_2$·CH$_2$Cl$_2$: C, 53.35; H, 4.08; N, 1.38. Found: C, 53.73; H, 4.15; N, 1.46.

Os[B(NH*n*-Bu)(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (4). A solution of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ (85 mg, 0.099 mmol) in benzene (10 mL) was added to 2-hydroxypyridine (23 mg, 0.242 mmol) to give a bright yellow solution together with a pale precipitate, which was stirred for 20 min. Addition of *n*-BuNH$_2$ (3 mL) gave a pale yellow solution, which was stirred for 40 min. Concentration of the mixture in vacuo to ca. 1 mL and addition of hexanes afforded colorless crystals, which were collected on a glass frit and washed with EtOH and hexanes to give pure **4** (yield 70 mg, 74%). ^{31}P NMR (CDCl$_3$): δ 11.90 (s). Anal. Calcd for C$_{46}$H$_{44}$BClN$_2$O$_2$OsP$_2$: C, 57.84; H, 4.64; N, 2.93. Found: C, 57.85; H, 4.47; N, 2.90.

Os[BF(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (5). A solution of Et$_3$N·3HF (0.10 mL, 0.61 mmol) in THF (10 mL) was added to Os[BCl(OC$_5$H$_4$N)]Cl(CO)(PPh$_3$)$_2$ (50 mg, 0.054 mmol) to give a pale yellow solution together with a pale precipitate. After stirring for 1 h, addition of EtOH (5 mL) and removal of the THF in vacuo afforded a white precipitate, which was collected on a glass frit and washed with EtOH and hexanes to give pure **5** (yield 40 mg, 81%). ^{19}F NMR (CDCl$_3$/CFCl$_3$): δ −45.2. ^{31}P NMR (CDCl$_3$): δ 11.56 (s). Anal. Calcd for C$_{42}$H$_{34}$BClFNO$_2$OsP$_2$: C, 55.92; H, 3.80; N, 1.55. Found: C, 55.71; H, 3.63; N, 1.52.

X-ray Diffraction Studies of 2 and 4. Data were collected on a Siemens SMART CCD difractometer at 200 K with graphite-monochromated Mo Kα radiation (λ 0.71073 Å) using ω scans. The data were corrected for Lorentz and polarization effects and absorption corrections applied using symmetry-related measurements.[7] The structures were solved using SHELXS[8] and refined by full matrix least squares using SHELXL[9] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and allowed to ride on the carrier atom. For **2** the absolute structure parameter[10] is 0.009(3). There is a molecule of ethanol disordered across a center of symmetry in **2**. The disorder is such that the hydroxyl oxygen of one disordered molecule is coincident with the methylene carbon of the second molecule.

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** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM011029U

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