Five-Coordinate Ruthenium(II) and Osmium(II) Boryl Complexes

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The five-coordinate ruthenium boryl complexes, $Ru(BR_2)Cl(CE)(PPh_3)_2$ (E = O, BR_2 = $BO_2C_6H_4$ (**1a**); E = O, BR_2 = $BO_2C_{10}H_6$ (**1b**); E = O, BR_2= $B(NH)_2C_6H_4$ (**1d**); E = O, BR_2 = $B(NH)SC_6H_4$ (**1e**); E = S, BR_2 = $BO_2C_6H_4$ (**2a**); E = S, BR_2 = $B(NH)SC_6H_4$ (**2e**); E = *N*-*p*-tolyl, BR_2 = $BO_2C_6H_4$ (**3a**)), result from the reactions of $RuHCl(CE)(PPh_3)_3$ with the appropriate borane. Related osmium compounds, $Os(BR_2)Cl(CE)(PPh_3)_2$ (E = O, BR_2 = $BO_2C_6H_4$ (**4a**); E = O, BR_2 = $BO_2C_6H_3CH_3$ (**4c**); E = O, BR_2 = $B(NH)_2C_6H_4$ (**4d**); E = O, BR_2 = $B(NH)SC_6H_4$ (**4e**); E = S, BR_2 = $BO_2C_6H_4$ (**5a**)), cannot be prepared from the hydrides but are formed from reactions between $Os(Ph)Cl(CE)(PPh_3)_2$ and the appropriate borane. A boryl complex of ruthenium of formula $Ru(BO_2C_6H_4)Cl(PPh_3)_2{\cdot}H_2O$ (6) results from reaction of $RuHCl(PPh_3)_3$ with $HBO_2C_6H_4$ (catecholborane). IR, ^1H NMR, and ^{13}C NMR data for the new boryl complexes are reported.

Introduction

Recent growth in the area of transition metal−boron chemistry has, in part, been driven by the increased interest associated with transition-metal-catalyzed hydroboration.[1] Catecholborane is known to hydroborate olefins, but the uncatalyzed reaction requires elevated temperatures. In contrast, the metal-mediated reactions proceed at ambient temperatures. Oxidative-addition reactions are thought to be of key importance in these reactions. Indeed, Männig and Nöth proposed a mechanism for olefin hydroboration catalyzed by $RhCl(PPh_3)_3$, which involved the oxidative addition of the B−H bond of catecholborane to the d^8 center as the first step in the catalytic cycle.[2]

Endeavors that are aimed at more clearly defining the role of the metal catalyst in these reactions are complemented by studies that focus on the full spectroscopic characterization and structural determination of metal boryl complexes. These compounds are usually derived from the stoichiometric oxidative-addition reactions of R_2BH, predominantly catecholborane, to d^8 metal centers.[3] Examples involving ruthenium or osmium are absent among the fully characterized transition metal boryl complexes reported to date, although boryl complexes of these metals are implied by the effectiveness of these metals in catalytic processes involving boranes.[3m,o,q] Furthermore, a large portion of the structurally characterized complexes involving M-B bonds, excluding the boraolefin complexes, are derived from the catecholboryl moiety. Consequently, little is known about the variations in metal−boron bond length or the reactivity of the metal−boron bond as boron substitution patterns vary among closely related complexes.[3l] Equally important are variations of the ancillary ligands on the metal. In order to gauge the effects of these ligands on the metal−boron bond, it would be valuable to have a series of complexes available that contain different π-acids, such as CO, CS, and CNR.

The work reported in this paper describes the first coordinatively unsaturated boryl complexes of ruthenium and osmium. These complexes were derived from the oxidative addition of boranes, R_2BH, to the appropriate metal complex starting materials. The development of a set of closely related complexes that differ only by systematic variation of the boryl ligand substituents is also described.

Results and Discussion

Ruthenium Boryl Carbonyl Complexes, $Ru(BR_2)Cl(CO)(PPh_3)_2$. Treatment of the ruthenium hydride $RuHCl(CO)(PPh_3)_3$ with the benzannelated heteroborolenes shown in Scheme 1 generates the corresponding yellow, coordinatively unsaturated boryl carbonyl complexes $Ru(BR_2)Cl(CO)(PPh_3)_2$. This method for the synthesis of ruthenium−heteroatom bonds is also effective for the production of transition metal silyl[4] and

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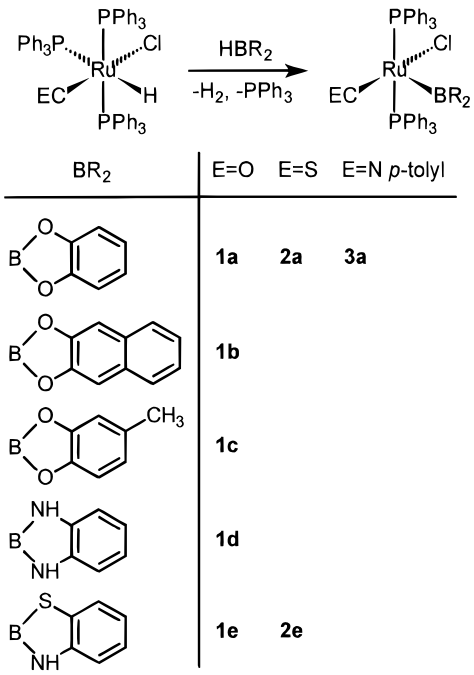
Scheme 1



stannyl[5] complexes. No evidence has been obtained regarding the mechanism of these M-B bond forming reactions. One possibility is that the reaction proceeds via dissociation of triphenylphosphine followed by oxidative addition of the B−H bond of the borane, leading to formation of an intermediate Ru(IV) species. Elimination of dihydrogen from this intermediate would result in the formation of the observed product. An alternative possibility could involve σ-bond metathesis, as discussed by Hartwig.[3o]

The boranes listed in Scheme 1 react with $RuHCl(CO)(PPh_3)_3$ at very different rates. Whereas most of the boranes had completely reacted after 30 min heating in benzene under reflux, the diazaborole, 2,3-dihydro-1*H*-1,3,2-benzodiazaborole, required reflux in toluene to achieve complete reaction.

As an alternative to using $RuHCl(CO)(PPh_3)_3$, the reaction between the boranes and the phenyl complex, $Ru(Ph)Cl(CO)(PPh_3)_2$, was found to be equally effective. If this reaction proceeds via a Ru(IV) intermediate, the eliminated molecule would be benzene rather than dihydrogen. This route offers no synthetic advantage. However, reaction with the styryl complex, $Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2$, and chatecholborane is much faster, being complete within 30 s at room temperature. Reactions with other organoruthenium complexes, $RuRX(CO)(PPh_3)_2$, were not examined. For most purposes, reactions between boranes and $RuHCl(CO)(PPh_3)_3$ offered a satisfactory synthesis in that yields were high and purity of products was good.

The generality of this route was examined by investigating other boranes. Attempted reactions between the boranes $HB(NMe)_2$, $HB(NMe)_2C_6H_4$, and $HB(NMe)_2C_2H_4$ and the ruthenium complexes $RuHCl(CO)(PPh_3)_3$, $Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2$, and $Ru(Ph)Cl(CO)(PPh_3)_2$ all failed to produce boryl complexes. Likewise, reactions with 1,3,2-dithiaborolane and 9-BBN (9-borabicyclo[3.3.1]nonane) were unsuccessful.

IR data for all new compounds are presented in Table 1. Each of the boryl ligands has distinctive bands which are useful for characterizing the products. The strong ν(CO) absorptions for these monocarbonyl complexes generally occur at higher values than those for the corresponding, five-coordinate ruthenium(II) aryl or silyl derivatives. An interesting comparison is between $Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ (ν(CO) = 1944/1935 (solid-state splitting) cm^{-1}) and $Ru(SiEt_3)Cl(CO)(PPh_3)_2$[6] ($\nu$(CO) = 1904 cm^{-1}). Change of substituents on the boryl ligand has a moderate effect on the ν(CO) position (see Table 1).

No structure determination has been carried out on these coordinatively unsaturated compounds. However, the structure of the related boryl complex $Os[B(OEt)_2]Cl(CO)(PPh_3)_2$, which was prepared by a different route, has been determined.[7] This supports the square pyramidal geometry that is depicted for the five coordinate boryl complexes in Schemes 1 and 2. Reactions in which a sixth ligand is introduced to produce octahedral derivatives, together with structure determinations of several of these saturated compounds will be described in a subsequent paper.

Ruthenium Boryl Thiocarbonyl Complexes, $Ru(BR_2)Cl(CS)(PPh_3)_2$, and Ruthenium Boryl Isocyanide Complexes, $Ru(BR_2)Cl(CN\text{-}p\text{-}tolyl)(PPh_3)_2$. By using as precursors either $RuHCl(CS)(PPh_3)_3$ or $RuHCl(CN\text{-}p\text{-}tolyl)(PPh_3)_3$, three more boryl complexes have been prepared (see Scheme 1). The yields are lower and oxygen sensitivity is greater, especially for the isocyanide complex, than for the corresponding carbonyl derivatives. IR, ^1H NMR, and ^{13}C NMR data are presented in Tables 1−3.

Synthesis of $Ru(BO_2C_6H_4)Cl(PPh_3)_2{\cdot}H_2O$. In an endeavor to prepare a coordinatively unsaturated boryl derivative with no accompanying π-acid ligand, the reaction between $RuHCl(PPh_3)_3$ and catecholborane was investigated. A pink product was obtained, which was very oxygen sensitive. The IR spectrum and elemental analysis were consistent with the formulation $Ru(BO_2C_6H_4)Cl(PPh_3)_2{\cdot}H_2O$. In the absence of a crystal structure determination, it is not possible to decide whether or not the water molecule is a ligand and, therefore, whether the compound is four- or five-coordinate. The solution instability of this compound prevented satisfactory NMR data from being obtained; however, further support for this formulation comes from the reaction with CO, which produced $Ru(BO_2C_6H_4)Cl(CO)_2(PPh_3)_2$, a compound identical to that produced by addition of CO to $Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$. The full characterization of the dicarbonyl compound will be described subsequently.[7]

Osmium Boryl Carbonyl Complexes, $Os(BR_2)Cl(CO)(PPh_3)_2$, and a Boryl Thiocarbonyl Complex, $Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$. In marked contrast to the facile synthesis of ruthenium boryl complexes from ruthenium hydride precursors, the osmium hydrides $OsHCl(CE)(PPh_3)_3$ (E = O, S) did not yield any osmium boryl complexes when treated with a variety of boranes.

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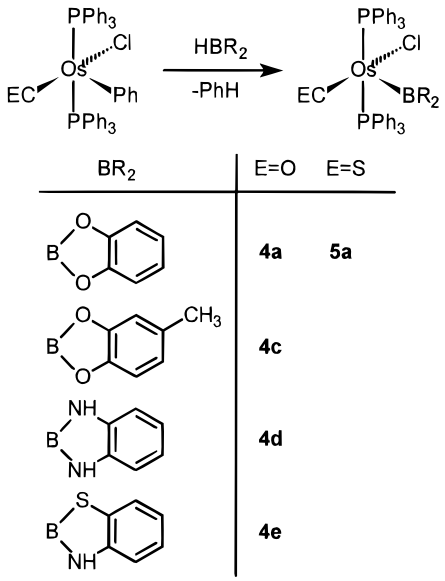
Table 1. Infrared Data (cm^{-1})[a] for Boryl Complexes

complex	ν(C≡E) (E = O, S, N-*p*-tolyl)	other bands[c]
$Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1a)**	1944 vs, 1935 vs[b]	1472, 1231, 1192 w, 1136 m, 1107 sh, 1094 vs, 1038 w, 808 m
$Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$ **(1b)**	1950 vs, 1933 vs[b]	1456, 1238, 1157 w, 1132 m, 1090 vs, 1038 m, 852 w
$Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1d)**	1923 vs	3466 m ν(NH), 1586 w, 1400 vs, 1339 w, 1307 vs, 1262, 1185 m, 1036 m, 834 m
$Ru(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(1e)**	1937 vs, 1921 vs, 1907 vs[b]	3408 m ν(NH), 1305 m, 1246 m, 1142 w, 1125 w, 874 w
$Ru(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(2a)**	1292 vs	1470, 1229, 1188 w, 1134 m, 1109 m sh, 1092 vs, 1040 m, 808 m
$Ru(B(NH)SC_6H_4)Cl(CS)(PPh_3)_2$ **(2e)**	1275 vs	3426 w br ν(NH), 1586 w, 1305 m, 1244 m, 1158 w, 871 m, 801 m
$Ru(BO_2C_6H_4)Cl(CN$-*p*-tolyl$)(PPh_3)_2$ **(3a)**	2070 sh, 2020 sh, 1989 brd, 1962 sh[b]	1506 m, 1474, 1231, 1190 w br, 1136 m, 1130 m, 1109 sh, 1092 vs, 1026 m, 822 m, 808 m
$Ru(BO_2C_6H_4)Cl(PPh_3)_2$ **(6)**		1232, 1202 w, 1146 w, 1123 sh, 1071 vs, 1028 w, 808 m
$Os(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4a)**	1923 vs	1234, 1142 m, 1109 m sh, 1096 vs, 807 m
$Os(BO_2C_6H_3CH_3)Cl(CO)(PPh_3)_2$ **(4c)**	1923 vs	1491 sh, 1248 m, 1211 m, 1166 w, 1148 m, 1130 m, 1105 vs, 1096 vs, 818 w sh, 804 m
$Os(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4d)**	1898 vs	3472 m ν(NH), 1404 vs, 1310, 1270 m, 1185 w, 1039 m, 838 w
$Os(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(4e)**	1924 sh, 1906 vs, 1894 vs[b]	3409 m ν(NH), 1304 m, 1245 m, 1142 w, 889 w, 875 w, 810 w
$Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(5a)**	1302 vs	1471, 1231, 1188 w, 1140 m, 1109 sh, 1097 vs, 1032 m, 807 m

[a] All intensities strong unless denoted otherwise. [b] Solid state splitting. [c] Bands associated with boryl ligand unless denoted otherwise.

Scheme 2



Fortunately, however, replacement of OsHCl(CE)-$(PPh_3)_3$ with Os(Ph)Cl(CE)$(PPh_3)_2$ leads to the new osmium boryl compounds described in Scheme 2. Yields were good, and the compounds displayed similar spectral properties to their ruthenium analogues (Tables 1−3). Again, not every reaction was successful and the following boranes $HB(NMe)_2C_6H_4$, $HB(NMe)_2C_2H_4$, $HB(NMe_2)_2$, $HBS_2C_2H_4$, and 9-BBN failed to react with Os-(Ph)Cl(CO)$(PPh_3)_2$.

Reactivity at Boron in These New Boryl Complexes. Chatecholborate esters normally react with acids to cleave the catecholate group from the boron. Furthermore, manganese boryl complexes undergo immediate cleavage of the Mn−B bond on treatment with acids or water, with the formation of a metal hydride.[3a] Remarkably, the compounds described here showed little reactivity toward acids and could be recovered unchanged after treatment with aqueous hydrochloric acid.

Summary. Preparative routes to ruthenium boryl and osmium boryl complexes, which possess a range of heterosubstituted benzannelated borole ligands, have been developed. These compounds display enhanced stability toward both oxygen and moisture compared with many of the other metal boryl complexes that have been reported. In no case was there any evidence for the introduction of more than one boryl ligand. The coordinative unsaturation of these new complexes allows for investigation of migratory insertions involving the boryl ligand, and these studies will be reported in subsequent publications. This unsaturation, together with the presence of a labile chloride ligand, also allows for further variation of the supporting ligands at the metal center.

Experimental Section

General Considerations. The general experimental and spectroscopic techniques employed in this work were the same as those described previously.[6] NMR spectra were recorded as $CDCl_3$ solutions at 298 K. ^1H NMR spectra were referenced to tetramethylsilane (0.00 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Ruthenium trichloride and osmium tetraoxide were obtained commercially from Johnson Mathey Chemicals Ltd. $RuHCl(CO)(PPh_3)_3$,[8] RuHCl(CS)-$(PPh_3)_3$,[9] Ru(Ph)Cl(CO)$(PPh_3)_2$,[10] Ru(*trans*-CH=CHPh)Cl(CO)-$(PPh_3)_2$,[11] $RuHCl(PPh_3)_3$,[12] $OsHCl(CO)(PPh_3)_3$,[13] Os(Ph)Cl(CO)-$(PPh_3)_2$,[10] Os(Ph)Cl(CS)$(PPh_3)_2$,[14] RuHCl(CN-*p*-tolyl)$(PPh_3)_3$,[15] catecholborane,[16] BH_3·THF,[17] and $HBCl_2$·OEt_2,[18] were prepared according to literature methods. The boranes 2,3-dihydro-1*H*-1,3,2-benzodiazaborole, 2,3-dihydro-1,3,2-benzothiazaborole, 1,3-dimethyl-2*H*-1,3,2-benzodiazaborole, and those derived from 4-methylcatechol and 2,3-dihydroxynaphthalene were prepared via a modification of Morales' method.[19]

$Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ (1a). $RuHCl(CO)(PPh_3)_3$ (0.250 g, 0.262 mmol) was partially dissolved in benzene (25

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Table 2. ^{1}H NMR Data (δ) for Boryl Complexes

complex	^{1}H, δ (ppm)[a]
$Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1a)**	6.86 (m, 2H, $O_2C_6H_4$), 7.02 (m, 2H, $O_2C_6H_4$), 7.29−7.60 (m, 30H, PPh_3)
$Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$ **(1b)**	6.90−8.95 (m, 36H, $O_2C_{10}H_6$, PPh_3)
$Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1d)**	5.93 (s, 2H, $(NH)_2C_6H_4$), 6.68 (m, 2H, $(NH)_2C_6H_4$), 6.73 (m, 2H), $(NH)_2C_6H_4$), 7.30−7.52 (m, 30H, PPh_3)
$Ru(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(1e)**	6.38 (s, 1H, $(NH)SC_6H_4$), 6.59 (dd, 1H, $(NH)SC_6H_4$, J_{HH} = 7.8, 0.9), 6.82 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.5, 0.9), 6.97 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.6, 1.1), 7.10−7.68 (m, 31H, PPh_3, $(NH)SC_6H_4$)
$Ru(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(2a)**	6.86 (m, 2H, $O_2C_6H_4$), 7.01 (m, 2H, $O_2C_6H_4$), 7.27−7.65 (m, 30H, PPh_3)
$Ru(B(NH)SC_6H_4)Cl(CS)(PPh_3)_2$ **(2e)**	6.53 (s, 1H, $(NH)SC_6H_4$), 6.70 (dd, 1H, $(NH)SC_6H_4$, J_{HH} = 7.8, 0.8), 6.83 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.5, 1.1), 7.00 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.6, 1.2), 7.25−7.63 (m, 31H, PPh_3, $(NH)SC_6H_4$)
$Ru(BO_2C_6H_4)Cl(CN\text{-}p\text{-tolyl})(PPh_3)_2$ **(3a)**	2.22 (s, 3H, $CNC_6H_4CH_3$), 6.02 (d, 2H, $CNC_6H_4CH_3$, J_{HH} = 8.3), 6.79 (d, 2H, $CNC_6H_4CH_3$, J_{HH} = 8.2), 6.83 (m, 2H, $O_2C_6H_4$), 7.00 (m, 2H, $O_2C_6H_4$), 7.20−7.67 (m, 30H, PPh_3)
$Os(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4a)**	6.81 (m, 2H, $O_2C_6H_4$), 6.97 (m, 2H, $O_2C_6H_4$), 7.30−7.60 (m, 30H, PPh_3)
$Os(BO_2C_6H_3CH_3)Cl(CO)(PPh_3)_2$ **(4c)**	2.29 (s, 3H, $O_2C_6H_3CH_3$), 6.61 (m, 1H, $O_2C_6H_3CH_3$), 6.82 (m, 2H, $O_2C_6H_3CH_3$), 7.23−7.59 (m, 30H, PPh_3)
$Os(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4d)**	5.59 (s, $(NH)_2C_6H_4$), 6.62 (m, 2H, $(NH)_2C_6H_4$), 6.68 (m, 2H, $(NH)_2C_6H_4$), 7.30−7.52 (m, 30H, PPh_3)
$Os(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(4e)**	5.86 (s, 1H, $(NH)SC_6H_4$), 6.52 (dd, 1H, $(NH)SC_6H_4$, J_{HH} = 7.8, 0.9), 6.77 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.5, 1.2), 6.92 (td, 1H, $(NH)SC_6H_4$, J_{HH} = 7.6, 1.3), 7.31−7.57 (m, 31H, PPh_3, $(NH)SC_6H_4$)
$Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(5a)**	6.81 (m, 2H, $O_2C_6H_4$), 6.97 (m, 2H, $O_2C_6H_4$), 7.27−7.64 (m, 30H, PPh_3)

[a] Coupling constants in hertz.

mL), and then catecholborane (0.084 mL, 0.787 mmol) was added. The mixture was then heated under reflux for 30 min, during which time all suspended material dissolved and a yellow solution resulted. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded $Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$. Recrystallization from benzene/*n*-hexane afforded pale lemon yellow microcrystals of pure **1a** (0.212 g, 100%). ^{1}H and ^{13}C NMR indicated $^1/_3$ equiv of benzene present as solvate. Anal. Calcd for $C_{43}H_{34}BClO_3P_2Ru\cdot{}^1/_3C_6H_6$: C, 64.80; H, 4.35; Cl, 4.25. Found: C, 64.71; H, 4.58; Cl, 4.57.

$Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$ (1b). $RuHCl(CO)(PPh_3)_3$ (0.750 g, 0.787 mmol) was partially dissolved in benzene (30 mL), and then 2,3-naphtho-2*H*-1,3,2-dioxaborole as a THF solution (1.230 mL, 1.6 M, 1.969 mmol) was added. The mixture was then heated under reflux for approximately 30 min. During the initial heating, all suspended material dissolved and the solution developed a yellow color. With further heating, the solution color slowly intensified, eventually giving rise to a brown solution for 30 min. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded $Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$. This product was then washed with a small portion of cold methanol. Recrystallization from benzene/*n*-hexane afforded light tan microcrystals of pure $Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$ (0.545 g, 81%). Anal. Calcd for $C_{47}H_{36}BClO_3P_2Ru$: C, 65.79; H, 4.23. Found: C, 65.52; H, 4.89.

$Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ (1d). $RuHCl(CO)(PPh_3)_3$ (0.300 g, 0.315 mmol) was partially dissolved in toluene (25 mL), and then 2,3-dihydro-1*H*-1,3,2-benzodiazaborole (0.372 g, 3.150 mmol) was added. The mixture was then heated under reflux for 20 min, during which time all suspended material dissolved and a bright yellow solution resulted. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded $Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$. Recrystallization from benzene/*n*-hexane afforded bright yellow microcrystals of pure $Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ (0.245 g, 96%). ^{1}H and ^{13}C NMR show $^1/_3$ equiv of benzene present as solvate. Anal. Calcd for $C_{43}H_{36}BClN_2OP_2Ru\cdot{}^1/_3C_6H_6$: C, 64.96; H, 4.60; N, 3.37. Found: C, 65.08; H, 4.83; N, 4.09.

$Ru(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ (1e). $RuHCl(CO)(PPh_3)_3$ (1.000 g, 1.050 mmol) was partially dissolved in benzene (40 mL), and then 2,3-dihydro-1,3,2-benzothiazaborole (0.567 g, 4.200 mmol) was added. The solution was then heated under reflux for 30 min, during which time all suspended material dissolved and a deep yellow solution resulted. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded **1e** as a pale yellow powder. Recrystallization from benzene/*n*-hexane gave light yellow microcrystals of pure $Ru(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ (0.860 g, 100%). Anal. Calcd for $C_{43}H_{35}BClNOP_2RuS$: C, 62.75; H, 4.29; N, 1.70. Found: C, 62.57; H, 4.40; N, 1.79.

$Ru(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ (2a). $RuHCl(CS)(PPh_3)_3$ (0.250 g, 0.258 mmol) was dissolved in benzene (15 mL), and then catecholborane (0.058 mL, 0.542 mmol) was added. The solution was then heated under reflux for 30 min, during which time an orange solution resulted. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded **2a** as a pale yellow powder. Recrystallization from benzene/*n*-hexane afforded pale yellow microcrystals of pure $Ru(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ (0.157 g, 74%). Anal. Calcd for $C_{43}H_{34}BClO_2P_2RuS$: C, 62.67; H, 4.16. Found: C, 62.77; H, 4.19.

$Ru(B(NH)SC_6H_4)Cl(CS)(PPh_3)_2$ (2e). $RuHCl(CS)(PPh_3)_3$ (0.250 g, 0.258 mmol) was dissolved in benzene (25 mL), and then 2,3-dihydro-1,3,2-benzothiazaborole (0.174 g, 1.291 mmol) was added. The solution was then heated under reflux for 30 min, during which time an intense red-orange solution resulted. Concentration of the solvent *in vacuo* followed by slow addition of *n*-hexane afforded $Ru(B(NH)SC_6H_4)Cl(CS)(PPh_3)_2$. Recrystallization from benzene/*n*-hexane gave light tan microcrystals of pure **2e** (0.170 g, 78%). Anal. Calcd for $C_{43}H_{35}BClNP_2RuS_2$: C, 61.55; H, 4.20; N, 1.67. Found: C, 61.70; H, 4.67; N, 2.37.

$Ru(BO_2C_6H_4)Cl(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (3a). $RuHCl(CN\text{-}p\text{-tolyl})(PPh_3)_3$ (0.300 g, 0.288 mmol) was partially dissolved in benzene (15 mL), and then catecholborane (0.092 mL, 0.864 mmol) was added. The mixture was heated under reflux for 15 min, during which time the suspended material dissolved and an intense yellow solution resulted. Reduction of the solvent volume *in vacuo* followed by slow addition of *n*-hexane yielded a bright yellow precipitate of **3a**. Recrystallization with benzene/*n*-hexane afforded vibrant yellow microcrystals of pure $Ru(BO_2C_6H_4)Cl(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (0.195 g, 75%). ^{1}H and ^{13}C NMR indicated $^1/_2$ equiv of benzene present as solvate. Anal. Calcd for $C_{50}H_{41}BClO_2NP_2Ru\cdot{}^1/_2C_6H_6$: C, 67.93; H, 4.43; N, 1.47. Found: C, 68.00; H, 4.73; N, 1.50.

$Ru(BO_2C_6H_4)Cl(PPh_3)_2$ (6). $RuHCl(PPh_3)_3$ (1.000 g, 1.082 mmol) was suspended in benzene (20 mL), and then catecholborane (0.461 mL, 4.327 mmol) was added. The solution was heated briefly under reflux for 10 min. During this time, all the suspended material dissolved, giving a yellow-brown solution. Concentration of the solvent *in vacuo* followed by

Table 3. ^{13}C NMR Data (δ) for Boryl Complexes

complex	^{13}C, δ (ppm)[a]
$Ru(BO_2C_6H_4)Cl(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ **(3a)**	21.1 (s, $CNC_6H_4CH_3$), 110.4 (s, $O_2C_6H_4$), 120.3 (s, $O_2C_6H_4$), 124.8 (s, $CNC_6H_4CH_3$), 128.1 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 128.3 (s, 4°, $CNC_6H_4CH_3$), 128.9 (s, $CNC_6H_4CH_3$), 129.5 (s, P*Ph*$_3$ *para*), 133.2 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 134.4 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.0$), 135.4 (s, 4°, $CNC_6H_4CH_3$), 150.2 (s, 4°, $O_2C_6H_4$), 173.0 (t, 4°, $CNC_6H_4CH_3$, $^{2}J_{CP} = 15.1$)
$Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1a)**	110.8 (s, $O_2C_6H_4$), 120.9 (s, $O_2C_6H_4$), 128.4 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 130.2 (s, P*Ph*$_3$ *para*), 131.9 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 134.3 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.0$), 149.8 (s, 4°, $O_2C_6H_4$), 199.3 (t, 4°, *C*O, $^{2}J_{CP} = 13.1$)
$Ru(BO_2C_{10}H_6)Cl(CO)(PPh_3)_2$ **(1b)**	106.2 (s, $O_2C_{10}H_6$), 124.0 (s, $O_2C_{10}H_6$), 127.4 (s, $O_2C_{10}H_6$), 128.4 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 129.8 (s, 4°, $O_2C_{10}H_6$), 130.2 (s, P*Ph*$_3$ *para*), 131.8 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 134.2 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.0$), 149.4 (s, 4°, $O_2C_{10}H_6$), 199.2 (t, 4°, *C*O, $^{2}J_{CP} = 12.8$)
$Ru(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(1d)**	108.7 (s, $(NH)_2C_6H_4$), 117.4 (s, $(NH)_2C_6H_4$), 128.3 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 103.1 (s, P*Ph*$_3$ *para*), 132.2 (t′, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 44.2$), 134.3 (t′, 4°, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 137.0 (s, 4°, $(NH)_2C_6H_4$), 200.1 (t, 4°, *C*O, $^{2}J_{CP} = 13.6$)
$Ru(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(1e)**	111.0 (s, $(NH)SC_6H_4$), 118.8 (s, $(NH)SC_6H_4$), 123.5 (s, $(NH)SC_6H_4$), 123.9 (s, $(NH)SC_6H_4$), 128.2 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 130.1 (s, P*Ph*$_3$ *para*), 131.2 (s, 4°, $(NH)SC_6H_4$), 131.6 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 134.3 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.0$), 145.5 (s, 4°, $(NH)SC_6H_4$), 199.8 (t, 4°, *C*O, $^{2}J_{CP} = 13.6$)
$Ru(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(2a)**[b]	110.9 (s, $O_2C_6H_4$), 120.9 (s, $O_2C_6H_4$), 128.2 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.0$), 130.2 (s, P*Ph*$_3$ *para*), 131.2 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 46.2$), 134.6 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 149.7 (s, 4°, $O_2C_6H_4$)
$Ru(B(NH)SC_6H_4)Cl(CS)(PPh_3)_2$ **(2e)**[b]	111.3 (s, $(NH)SC_6H_4$), 119.0 (s, $(NH)SC_6H_4$), 123.5 (s, $(NH)SC_6H_4$), 124.0 (s, $(NH)SC_6H_4$), 128.1 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.2 (s, P*Ph*$_3$ *para*), 131.1 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 131.3 (s, 4°, $(NH)SC_6H_4$), 134.7 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 145.7 (s, 4°, $(NH)SC_6H_4$)
$Os(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4a)**	110.6 (s, $O_2C_6H_4$), 120.5 (s, $O_2C_6H_4$), 128.3 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.2 (s, P*Ph*$_3$ *para*), 131.8 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 51.4$), 134.4 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 150.2 (s, 4°, $O_2C_6H_4$), 181.9 (t, 4°, *C*O, $^{2}J_{CP} = 8.4$)
$Os(BO_2C_6H_3CH_3)Cl(CO)(PPh_3)_2$ **(4c)**[c]	21.3 (s, $O_2C_6H_3CH_3$), 109.9 (s, $O_2C_6H_3CH_3$), 111.4 (s, $O_2C_6H_3CH_3$), 120.7 (s, $O_2C_6H_3CH_3$), 128.3 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.2 (s, P*Ph*$_3$ *para*), 131.8 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 51.4$), 134.4 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 148.1 (s, 4°, $O_2C_6H_3CH_3$), 150.2 (s, 4°, $O_2C_6H_3CH_3$), 181.9 (t, 4°, *C*O, $^{2}J_{CP} = 9.1$)
$Os(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ **(4d)**	108.5 (s, $(NH)_2C_6H_4$), 117.1 (s, $(NH)_2C_6H_4$), 128.2 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.2 (s, P*Ph*$_3$ *para*), 132.2 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 49.4$), 134.4 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 137.6 (s, 4°, $(NH)_2C_6H_4$), 183.1 (t, 4°, *C*O, $^{2}J_{CP} = 9.1$)
$Os(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ **(4e)**	110.9 (s, $(NH)SC_6H_4$), 118.6 (s, $(NH)SC_6H_4$), 123.3 (s, $(NH)SC_6H_4$), 123.9 (s, $(NH)SC_6H_4$), 128.3 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.3 (s, P*Ph*$_3$ *para*), 131.6 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 45.2$), 132.2 (s, 4°, $(NH)SC_6H_4$), 134.5 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.0$), 146.5 (s, 4°, $(NH)SC_6H_4$), 183.1 (t, *C*O, $^{2}J_{CP} = 8.6$)
$Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ **(5a)**[b]	110.7 (s, $O_2C_6H_4$), 120.6 (s, $O_2C_6H_4$), 128.2 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.0$), 130.3 (s, P*Ph*$_3$ *para*), 131.1 (t′, 4°, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 53.4$), 134.7 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.0$), 150.0 (s, 4°, $O_2C_6H_4$)

[a] Coupling constants in hertz t′ denotes signal has apparent triplet multiplicity, $^{m,n}J_{CP}$ is the sum of the two coupling constants $^{m}J_{CP}$ and $^{n}J_{CP}$ as explained in ref 6, 4° denotes a quaternary carbon (determiend by a DEPT 135 pulse sequence experiment). [b] *C*S not observed. [c] One quaternary $O_2C_6H_3CH_3$ not observed.

slow addition of *n*-hexane precipitated mustard-colored $Ru(BO_2C_6H_4)Cl(PPh_3)_2$. This was recrystallized in the following manner. The mustard-colored complex was dissolved in 1:1 benzene/*n*-hexane to give a deep red solution, which was then filtered. The solvent volume was reduced *in vacuo*, and then *n*-octane was slowly added to give salmon pink microcrystals of pure $Ru(BO_2C_6H_4)Cl(PPh_3)_2$ (0.518 g, 61%). ^{1}H NMR showed 1 equiv of water present as solvate. Anal. Calcd for $C_{42}H_{34}BClO_2P_2Ru\cdot H_2O$: C, 63.21; H, 4.55; Cl, 4.44. Found: C, 63.47; H, 4.76; Cl, 4.11.

$Os(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ (4a). $Os(Ph)Cl(CO)(PPh_3)_2$ (0.200 g, 0.234 mmol) was dissolved in benzene (15 mL), and then catecholborane (0.027 mL, 0.257 mmol) was added. The red solution was heated under reflux for 5 min, or until the red color discharged (approximately 20 min). During this time, the solution changed from red to a rich orange-yellow. The solvent was then concentrated *in vacuo*, and this often initiated crystallization. Crystallization was completed by the slow addition of *n*-hexane. The bright yellow crystals of analytically pure $Os(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ (0.192 g, 92%) were collected by filtration. Anal. Calcd for $C_{43}H_{34}BClO_3OsP_2$: C, 57.57; H, 3.82. Found: C, 57.88; H, 4.14.

$Os(BO_2C_6H_3CH_3)Cl(CO)(PPh_3)_2$ (4c). $Os(Ph)Cl(CO)(PPh_3)_2$ (0.500 g, 0.585 mmol) was dissolved in benzene (20 mL), and 4-methylcatecholborane as a THF solution (0.402 mL, 1.6 M, 0.643 mmol) was then added. The red solution was heated under reflux until the red color discharged (10−20 min). During this time, the solution changed from red to a rich orange-yellow. Isolation of the product proceeded, as for **4a** above, to afford analytically pure mustard yellow microcrystals of $Os(BO_2C_6H_3CH_3)Cl(CO)(PPh_3)_2$ (0.437 g, 82%). ^{1}H and ^{13}C NMR indicated $^1/_3$ equiv of benzene present as solvate. Anal. Calcd for $C_{44}H_{36}BClO_3OsP_2\cdot{}^1/_3C_6H_4$: C, 58.95; H, 4.09. Found: C, 58.94; H, 4.24.

$Os(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$ (4d). $Os(Ph)Cl(CO)(PPh_3)_2$ (0.200 g, 0.234 mmol) and 2,3-dihydro-1*H*-1,3,2-benzodiazaborole (0.061 g, 0.514 mmol) were dissolved in benzene (20 mL). The red solution was then heated under reflux for 10 min. During this time, the solution changed from red to a deep rich yellow. Concentration of the solvent *in vacuo* followed by the slow addition of *n*-hexane gave $Os(B(NH)_2C_6H_4)Cl(CO)(PPh_3)_2$. Recrystallization from benzene/*n*-hexane afforded yellow microcrystals of analytically pure $Os(B(NH)_2C_6H_4)Cl(PPh_3)_2$ (0.144 g, 69%). Anal. Calcd for $C_{43}H_{36}BClN_2OOsP_2$: C, 57.69; H, 4.05; N, 3.13. Found: C, 57.69; H, 3.91; N, 2.81.

$Os(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ (4e). $Os(Ph)Cl(CO)(PPh_3)_2$ (0.300 g, 0.351 mmol) was dissolved in benzene (20 mL), and 2,3-dihydro-1,3,2-benzothiazaborole (0.052 g, 0.386 mmol) added. The red solution was then heated under reflux for 20 min, over which time the red solution color changed to orange. Reduction of the solvent volume *in vacuo* followed by slow addition of *n*-hexane afforded a yellow precipitate of **4e**. Recrystallization from benzene/*n*-hexane afforded yellow mi-

crocrystals of analytically pure $Os(B(NH)SC_6H_4)Cl(CO)(PPh_3)_2$ (0.301 g, 94%). Anal. Calcd for $C_{43}H_{35}BClNOOsP_2S$: C, 56.62; H, 3.87; N, 1.54. Found: C, 56.29; H, 4.32; N, 1.67.

$Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ (5a). $Os(Ph)Cl(CS)(PPh_3)_2$ (0.200 g, 0.230 mmol) was dissolved in benzene (15 mL). To this solution, catecholborane (0.073 mL, 0.689 mmol) was added. The orange solution was then heated under reflux for 10 min, during which time the solution turned yellow. The solvent was then concentrated *in vacuo*, a process which often initiated crystallization. Precipitation of $Os(BO_2C_6H_4)Cl(CS)(PPh_3)_2$ was completed by the slow addition of *n*-hexane. This product was collected and then washed with a small portion of cold methanol followed by *n*-hexane to afford bright yellow crystals of analytically pure $Os(BO_2C_6H_4)Cl(CS)()PPh_3)_2$ (0.146 g, 70%). Anal. Calcd for $C_{43}H_{34}BClO_2OsP_2S$: C, 56.56; H, 3.75. Found: C, 56.41; H, 4.31.

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