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Cationic Ruthenium Complexes with an Arylspiroborate Counterion Derived from 3,5-Di-*tert*-butylcatechol

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Abstract: We have prepared ruthenium complexes containing the $Bbutcat_2^-$ anion (butcat = 3,5-di-*tert*-butylcatecholato) and the first single crystal X-ray diffraction study of a ruthenium arylspiroborate complex is presented. These new ruthenium complexes have been examined for their ability to catalyse the addition of diorganyloxyboranes to vinylarenes, and results suggest that these compounds generate the corresponding alkenylboronate esters via a competing dehydrogenative borylation pathway.

Keywords: Arylspiroborate, Boron, Catalysis, Hydroboration, Ruthenium.

Introduction

Arylspiroborates are a remarkable family of compounds containing two catecholato groups bound to a central boron atom that are usually nontoxic, inexpensive and thermally, chemically and electrochemically stable. To date, these compounds have found only limited use in chemistry and industry. For instance, lithium salts of arylspiroborates are being considered for their potential as lithium batteries[1]. Although these compounds have low toxicity to mammals, including humans, they display considerable biological properties[2]. More specifically, arylspiroborates have shown considerable antifungal and termiticidal activities, and are thus being considered as potential candidates as leach resistant boron-based wood preservatives. These compounds have also been used as catalysts, or co-catalysts, for the Diels-Alder reaction[3a], methoxycarbonylation reactions[3b], and in amide and ester condensation reactions[3c].

Of particular interest to us is the ability of these species to bind to transition metals using different coordination sites. For instance, a nickel complex containing the parent $[Bcat_2]^-$ (cat = 1,2-$O_2C_6H_4$) anion is believed to coordinate to the metal using the Lewis basic oxygen atoms (Figure 1a)[4]. A similar bonding motif has been reported for a titanium compound (Figure 1b), isolated as a deactivated form of a titanium catalyst used in the hydroboration of alkenes[5]. Interestingly, rhodium complexes containing these ligands can have the metal fragment bound to the six-membered ring of one of the catecholato groups (Figure 1c)[6]. These rhodium complexes are active and selective catalysts for the hydroboration of a wide range of alkenes[6a]. Slippage of the rhodium fragment from an η^6 to η^4 to η^2 to an uncoordinated bonding mode will generate the necessary coordination sites required for

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catalysis. Upon completion of catalysis the ligand can once again resume a stable η^6 coordination, leaving the metal complex in a relatively stable resting state. A similar bonding motif has been observed in the only ruthenium complex reported to date containing an arylspiroborate ligand, (η^6-catBcat)Ru(H)(PCy_3)$_2$ (Figure 1d) (Cy = cyclohexyl). This ruthenium complex is generated in minor amounts, along with the σ-borane complex $RuH_2(\eta^2\text{-}HBcat)(\eta^2\text{-}H_2)(PCy_3)_2$, from the addition of HBcat to the bis(dihydrogen) complex $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ [7] and has only been characterized spectroscopically.

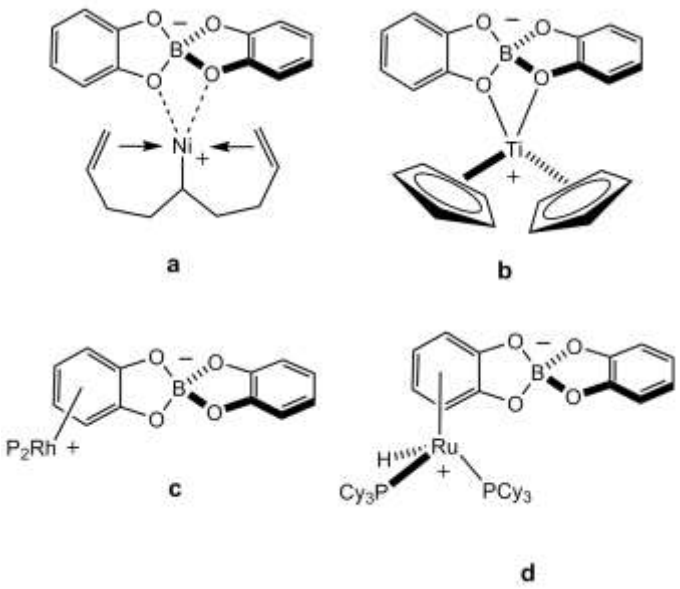


Figure 1. Metal complexes containing arylspiroborates.

Our interest in designing new catalyst precursors for borylation reactions, naturally led us to investigate new arylspiroborate ligands. We have recently prepared the unique thallium salt **1**, Tl[Bbutcat$_2$] (where butcat = 3,5-di-*tert*-butylcatecholato), and begun to examine its reactivity with metal chlorides[8]. In this study we report our findings from the addition of **1** to $RuCl_2(PPh_3)_3$ in an effort to expand the scope of these interesting ligands in organometallic chemistry and in catalysis.

Results and Discussion

Addition of one equivalent of thallium salt **1** to a solution of $RuCl_2(PPh_3)_3$ in acetonitrile gave a number of ruthenium phosphine complexes, as evidenced by several peaks in the ^{31}P NMR spectrum, along with the formation of thallium chloride (characterized by decomposition point). A peak at δ -5.3 ppm in the ^{31}P NMR spectrum also shows that at least some of the phosphine is dissociating in solution while the peak at δ 13.3 ppm in the ^{11}B NMR spectrum confirms that the arylspiroborate remains intact. The ^{1}H and ^{13}C NMR data suggest that the arylspiroborate does not coordinate to the metal centre as no significant change for any of these resonances is observed[9]. Although attempts to isolate the resulting ruthenium complexes proved unsuccessful, we were able to get a few single crystals of one isomer and have carried out an X-ray diffraction study on compound **2**, the molecular structure of which is shown in figure 2 and crystallographic data presented in table 1. Complex **2**, *cis,mer*-[RuCl(NCCH$_3$)$_3$(PPh_3)$_2$][Bbutcat$_2$], was crystallized from a solution of acetonitrile at -5 ^{o}C and confirms that the arylspiroborate does not coordinate to the metal

center in the solid state. The ruthenium atom is arranged in a roughly octahedral environment with a meridional arrangement of coordinating acetonitrile ligands. Two phosphine ligands remain attached to the metal center in a *cis* geometry, with one phosphine ligand trans to the chloride atom. All bond lengths and angles are similar to those reported for related species[10]. This isomer does not appear to be present in any significant amount in solution as a compound containing two magnetically inequivalent phosphines is not observed in the ^{31}P NMR spectra.

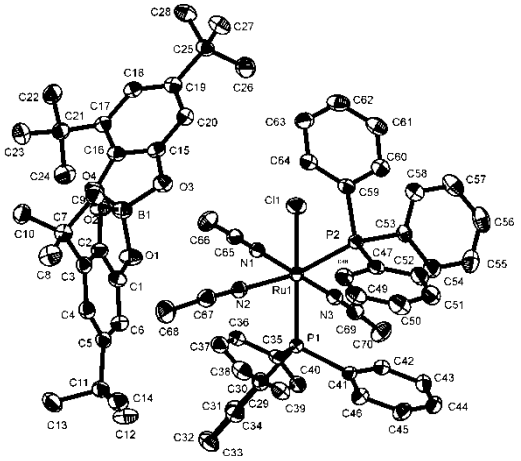
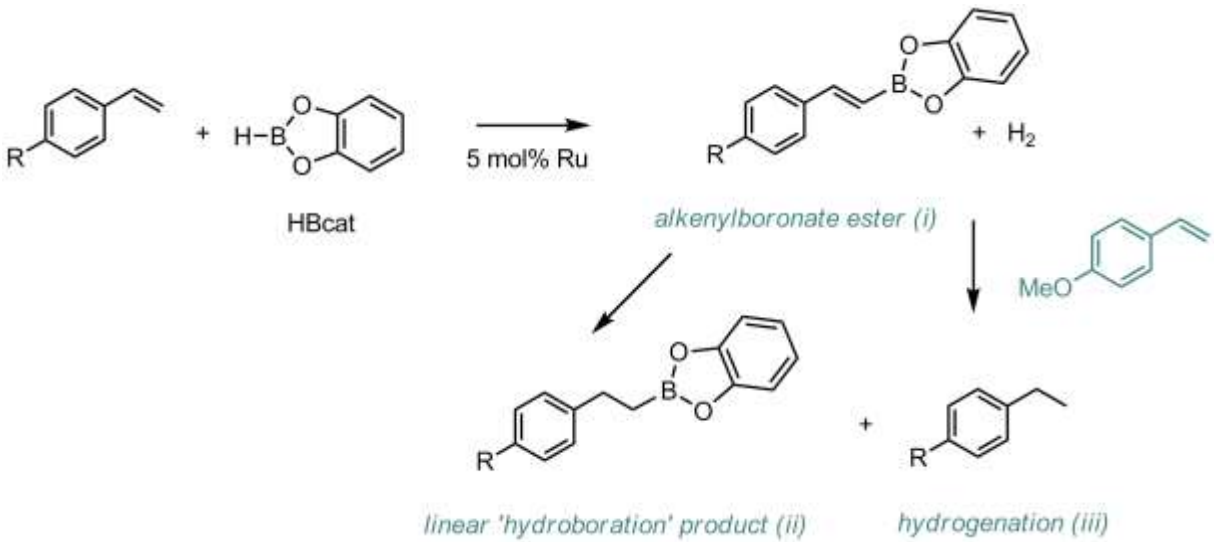


Figure 2. The molecular structure of **2** with atom labelling scheme.

Thermal ellipsoids are drawn at the 50 % probability level with hydrogen atoms and one molecule of solvent acetonitrile omitted for clarity. Selected bond distances (Å): Ru(1)-N(1) 2.0223(18), Ru(1)-N(3) 2.0249(18), Ru(1)-N(2) 2.0810(17), Ru(1)-P(2) 2.3349(7), Ru(1)-P(1) 2.3515(7), Ru(1)-Cl(1) 2.4491(7), B(1)-O(4) 1.479(3), B(1)-O(1) 1.482(3), B(1)-O(3) 1.486(3), B(1)-O(2) 1.492(3); Selected bond angles (°): N(1)-Ru(1)-N(3) 177.85(7), N(1)-Ru(1)-N(2) 85.53(7), N(3)-Ru(1)-N(2) 92.72(7), N(1)-Ru(1)-P(2) 88.57(5), N(3)-Ru(1)-P(2) 92.94(5), N(2)-Ru(1)-P(2) 168.53(5), N(1)-Ru(1)-P(1) 94.89(5), N(3)-Ru(1)-P(1) 86.25(5), N(2)-Ru(1)-P(1) 87.06(5), P(2)-Ru(1)-P(1) 103.260(19), O(4)-B(1)-O(1) 112.68(19), O(4)-B(1)-O(3) 104.75(17), O(1)-B(1)-O(3) 112.0(2), O(4)-B(1)-O(2) 112.3(2), O(1)-B(1)-O(2) 104.60(17), O(3)-B(1)-O(2) 110.66(19).

Interestingly, addition of two equivalents of thallium salt **1** to a solution of $RuCl_2(PPh_3)_3$ in acetonitrile gave the expected thallium chloride along with the formation of only one new phosphinoruthenium species, tentatively assigned as $[Ru(NCCH_3)_4(PPh_3)_2][Bbutcat_2]_2$ **3**. Once again, free triphenylphosphine is observed at δ -5.3 ppm in the ^{31}P NMR spectrum along with a peak at δ 39.7 ppm for **3**. The ^{1}H, ^{13}C and ^{11}B NMR data all suggest the bulky arylspiroborate is not coordinated directly to the metal center. Unfortunately, all attempts at generating a single crystal of **3** for an X-ray diffraction studied proved unsuccessful and we were not able to determine the geometry of the two phosphine ligands. Nevertheless, we then examined the *in situ* addition of one and two equivalents of the thallium salt **1** to $RuCl_2(PPh_3)_3$ for the corresponding ruthenium complexes to potentially act as catalysts in the hydroboration of vinylarenes[11]. Reactions were carried out using 4-vinylanisole as the substrate of choice, as the methoxy group provides a useful diagnostic in the ^{1}H NMR spectra and the arene peaks are well-defined doublets.

We have found that addition of catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) did not give the expected 'hydroboration' products, but did generate compounds arising from a competing 'dehydrogenative borylation' pathway. This reaction is generally believed to result from an initial oxidative addition of the borane to the metal center to give a hydrido boryl (BR_2) metal intermediate, followed by coordination of the alkene and subsequent insertion into the M-B bond. The next step in this process is a selective β-hydride elimination to give the *trans*-alkenylboronate ester along with formation of one equivalent of dihydrogen (Scheme 1)[12]. The liberated dihydrogen can either add catalytically to the aforementioned *trans*-alkenylboronate ester to give a linear 'hydroboration' product, or to unreacted vinylarene to generate the corresponding 'hydrogenation' product. In this study we have found that the alkenylboronate ester is formed in 15 %, the linear product in 61 % and the hydrogenation product in 24 % (Table 2). The ability to generate alkenylboronate esters has recently received much attention owing to the use of these valuable precursors in Suzuki-Miyaura cross-coupling reactions[13]. This result is in contrast to a previous report using the neutral ruthenium species $RuCl(PPh_3)_4$, which found that the alcohol derived from the linear hydroboration product, upon oxidative work-up, was the major species (77 %)[14]. Reactions with pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) did not improve selectivities and similar product distributions were achieved using this borane. Altering the electronic nature of the vinylarene by using 4-fluorostyrene also did not improve product selectivities. Attempts to catalyze these reactions using **2** or **3** and bulkier diorganyloxyboranes proved unsuccessful[15]. Similar selectivities were achieved in reactions using the *in situ* addition of $AgBF_4$ to $RuCl_2(PPh_3)_3$, illustrating that the arylspiroborate had little effect on the course of the reaction.



Scheme 1. Ruthenium catalyzed addition of catecholborane (HBcat) to vinylarene derivatives.

Table 1. Crystallographic data collection parameters for *cis-*,*mer* $[RuCl(NCCH_3)_3(PPh_3)_2][Bbutcat_2]\cdot CH_3CN$.

CCDC deposit no.	824993
Formula	$C_{72}H_{82}BClN_4O_4P_2Ru$
fw	1276.69
Crystal system	triclinic
Space group	P-1
a, Å	15.018(3)
b, Å	16.348(3)
c, Å	16.603(3)
α, deg	97.266(3)
β, deg	114.604(2)
γ, deg	110.359(3)
V, Å^3	3294.10(11)
Z	2
ρ_{calcd}, mg m^{-3}	1.287
Crystal size, mm^3	0.60 x 0.40 x 0.12
Temperature, K	173(1)
Radiation	MoKα (λ = 0.71073)
μ, mm^{-1}	0.378
Total reflections	22992
Total unique reflections	14288
No. of variables	782
R_{int}	0.0200
Theta range, deg	1.57 to 27.50
Largest difference peak/hole, e Å^{-3}	1.053/-0.676
S (GoF) on F^2	1.056
R1[a] (I>2σ(I))	0.0346
wR2[b] (all data)	0.0937

[a] $R1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0412 * P)^2 + (2.2046 * P)]$ where $P = (\max(F_o^2, 0) + 2 * F_c^2)/3$.

Table 2. The catalyzed addition of HBcat and HBpin to vinylarenes using either **2** or **3**.

Entry[a]	Reagent	Catalyst System	Borane	i	ii	iii
1	R = OMe	1 eq **1**/ $RuCl_2(PPh_3)_3$	HBcat	15	61	24
2	R = OMe	2 eq **1**/ $RuCl_2(PPh_3)_3$	HBcat	17	66	17
3	R = F	1 eq **1**/ $RuCl_2(PPh_3)_3$	HBcat	18	62	20
4	R = F	2 eq **1**/ $RuCl_2(PPh_3)_3$	HBcat	24	62	14
5	R = OMe	1 eq **1**/ $RuCl_2(PPh_3)_3$	HBpin	20	65	15
6	R = OMe	2 eq **1**/ $RuCl_2(PPh_3)_3$	HBpin	22	68	10
7	R = F	1 eq **1**/ $RuCl_2(PPh_3)_3$	HBpin	20	66	14
8	R = F	2 eq **1**/ $RuCl_2(PPh_3)_3$	HBpin	20	68	12

[a] All reactions were carried out in C_6D_6 at rt and product ratios (%) were determined by ^{1}H NMR spectroscopy using 5 mol% of ruthenium.

Conclusion

We have prepared ruthenium complexes containing the $Bbutcat_2^-$ anion (butcat = 3,5-di-*tert*-butylcatecholato) and the first single crystal X-ray diffraction study of a ruthenium arylspiroboronate ester complex is presented. The borate ligand does not coordinate to the metal center directly, presumably due to steric congestion caused by the bulky *tert*-butyl groups. These new ruthenium complexes have been examined for their ability to catalyse the addition of diorganyloxyboranes to vinylarenes, and results suggest that these compounds are effective in generating the corresponding alkenylboronate esters via a competing dehydrogenative borylation pathway. Further studies with related ruthenium systems are currently underway and results of which will be presented in due course.

Acknowledgements

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Experimental Section

Reagents and CD_3CN were purchased from Aldrich Chemicals and used as received. $RuCl_2(PPh_3)_3$[16] and $Tl(Bbutcat_2)$[8] were synthesized as previously reported. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^1H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz; ^{31}P 109 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B), and H_3PO_4 (^{31}P)] and coupling constants (*J*) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m), broad (br), and overlapping (ov). Reactions were performed under an atmosphere of dinitrogen.

General Experimental

To a stirred yellow CD_3CN (0.75 mL) solution of $RuCl_2(PPh_3)_3$ (125 mg, 0.13 mmol) was added a colourless CD_3CN (0.75 mL) solution of the appropriate amount of $Tl(Bbutcat_2)$. The reactions were allowed to proceed for 18 hours at room temperature at which point the mixtures were filtered to remove TlCl which had precipitated as a white solid. The clear yellow solutions were examined by multinuclear NMR spectroscopy. Crystals of **2** suitable for an X-ray crystallographic study formed upon storing the solution at rt for 3 days.

$RuCl_2(PPh_3)_3$ + $Tl(Bbutcat_2)$

Selected spectroscopic NMR data: ^1H NMR δ (ppm): 7.51-7.12 (ov m, Ar), 6.57 (d, J = 2.0 Hz, Ar), 6.56 (d, J = 2.0 Hz, Ar), 1.34 (s, *t*-butyl), 1.27 (s, *t*-butyl); ^{11}B NMR δ 13.3 (sharp); ^{13}C NMR{^1H} δ 151.8, 147.3, 139.4, 138.0, 137.4 (d, J_{CP} = 10.9 Hz), 134.9 (t, J_{CP} = 4.7 Hz), 133.8, 133.6 (d, J_{CP} = 19.7 Hz), 131.9, 131.8, 130.1, 129.0, 128.8 (d, J_{CP} = 6.8 Hz), 128.4, 128.1 (br), 127.6, 126.3, 125.4, 117.4, 110.7, 104.1, 34.2, 33.8, 31.5, 29.1, 0.5 (app sept, J = 20.8 Hz); ^{31}P NMR{^1H} δ 44.7 (br), 41.4 (br), 39.0, 29.3, 28.2, 26.6, -5.3.

$RuCl_2(PPh_3)_3$ + 2 Tl($Bbutcat_2$)

Selected spectroscopic NMR data: NMR δ (ppm): 7.48 (m, Ar), 7.39-7.12 (ov m, Ar), 6.59 (d, *J* = 2.0 Hz, Ar), 6.57 (d, *J* = 2.0 Hz, Ar), 1.35 (s, *t*-butyl), 1.28 (s, *t*-butyl); ^{11}B NMR δ 13.3 (sharp); ^{13}C NMR{^{1}H} δ 151.8, 147.3, 139.4, 138.0, 137.4 (d, J_{CP} = 11.4 Hz), 134.9 (t, J_{CP} = 4.7 Hz), 133.8, 133.7, 133.6 (d, J_{CP} = 19.7 Hz), 131.2, 131.1, 130.9, 130.5, 130.3, 129.0, 128.9, 128.8 (d, J_{CP} = 6.2 Hz), 128.3, 125.4, 117.4, 110.7, 104.0, 34.2, 33.8, 31.5, 29.1, 0.4 (app sept, *J* = 20.8 Hz); ^{31}P NMR{^{1}H} δ 39.7, -5.3.

General procedure for the hydroboration of vinylarenes: To a stirred C_6D_6 (0.5 mL) solution of alkene and the desired ruthenium catalyst (5 mol %) was added the appropriate borane (2 molar equiv.) in C_6D_6 (0.5 mL). The reaction was allowed to proceed at room temperature for 18 h at which point the reaction was analyzed by multinuclear NMR spectroscopy and compared to known compounds[6].

X-ray Crystallography

Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)[17] and corrected for absorption (SADABS)[18]. The structure was solved by direct methods and refined by full-matrix least squares on F^2(SHELXTL)[19]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

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