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Thermochemistry and Molecular Structure of a Remarkable Agostic Interaction in a Heterobifunctional Ruthenium−Boron Complex

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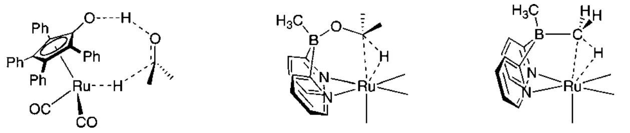
Hydrocarbon functionalization is an important reaction class in organic synthesis and has a central role in applications ranging from utilization of hydrocarbon feedstocks to fine-chemical synthesis.[1] In this area, our group is developing ligand−metal bifunctional catalysts that manipulate hydrides. Our general approach to C−H functionalization involves cooperative effects between a transition metal and a ligand-centered coordination-directing element. This is analogous to hydrogen-bond-directed oxidation catalysts such as Noyori's (Ts-DPEN)(cym)RuCl systems[2] and the cyclopentadienone-ligated systems from Shvo[3] and Casey[4] (Figure 1A), except that a Lewis acid directing group such as boron (Figure 1B) does not require a protic functionality in the substrate. In this communication, we report the synthesis, X-ray structure, and unique thermochemistry of an unusually strong C−H agostic methyl bridge between boron and ruthenium (Figure 1C). This agostic complex has structural homology to a potential transition state for boron-directed C−H cleavage (Figure 1B).



A: H$^+$-directed C-H cleavage **B**: B-directed C-H cleavage **C**: B-CH$_3$ Agostic C-H

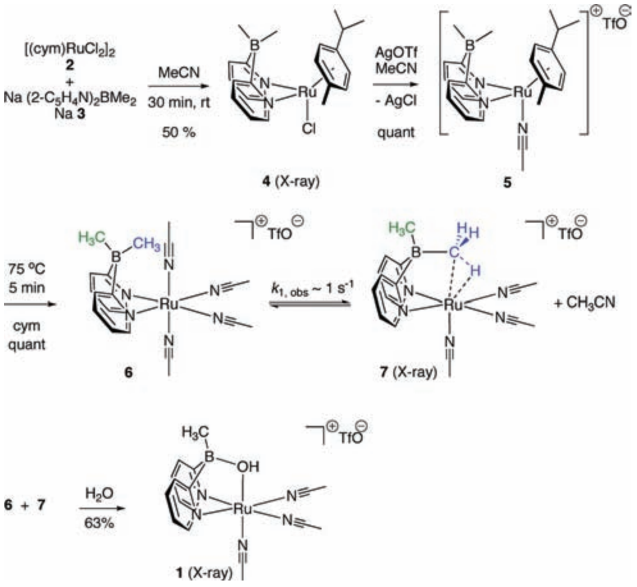
Figure 1. An agostic boron methyl has structural homology to transition states for coordination-directed C−H activation reactions.

Our design of a boron-pendant ruthenium-based oxidation catalyst requires a ligand that is robust under mild conditions. Along these lines, we became interested in the dimethylbis(2-pyridyl)borate ligand (**3**) as a platform from which a heterobimetallic boron−transition metal hydride abstraction system could be constructed.[5] Pt(II) and Pt(IV) complexes of this ligand are known and are stable toward dioxygen at elevated temperatures.[6] A Pt(II) complex of **3** shows no reactivity between the borate and the metal, but the Pt(IV) congener participates in slow methyl transfer from boron to platinum with the intermediacy of an agostic bridge.

Analogous to the Pt(IV) complex, we observe that a boron methyl on **3** forms an agostic interaction to ruthenium when ligated to Ru(II). This occurs with expulsion of an acetonitrile ligand from the metal (Scheme 1). Unlike the analogous platinum system, the equilibrium between **6** and **7** is very rapid. To our knowledge, this is the first characterization of an alkyl group bridging boron and ruthenium in this way. Moreover, formation of the agostic bond occurs in the presence of acetonitrile, thus defining a very rare example of ligand displacement from a coordinatively saturated metal by a C−H bond.[7] In fact, hydrolysis of this bridging methyl affords a *μ*-OH complex that has reactivity analogous to that of the Shvo catalyst.[8]

The syntheses of agostic complex **7** and precatalyst **1** are outlined in Scheme 1. The route is initiated with the formation of chlororuthenium adduct **4** from **3**[5] and **2**. Treatment of **4** with AgOTf in acetonitrile-d_3 in a J. Young NMR tube affects rapid formation of **5** [^{1}H δ(B−Me) = +0.09, +0.04 ppm]; solvent then displaces cymene in minutes at elevated temperature to give an equilibrating mixture of **6** and **7** (1:1 at 90 °C), which can be hydrolyzed to give **1** [^{1}H δ(B−Me) = +0.29 ppm].

Scheme 1. Synthesis of Bis(2-pyridyl)borate-Ligated Ruthenium Complexes



The spectral data for **7** feature ^{1}H resonances at +0.18 and −5.13 ppm ($\Delta\delta$ = 5.3 ppm). While the downfield shift is consistent with bonding only at boron, the peak at −5.13 ppm is more consistent with an agostic interaction. In an attempt to arrest the agostic interaction, solutions of **6** + **7** were cooled to −40 °C in acetonitrile-d_3 and −95 °C in dichloromethane-d_2. The upfield signal remained a singlet in each case, indicating rapid interconversion among the three hydrogens of the bridging methyl at these temperatures. A 25 °C HMBC spectrum of the equilibrating mixture elucidated the carbon chemical shifts of the boron-bound carbon atoms and illustrated that the upfield methyl group in **7** was bound both to boron (correlation to the other BMe ^{13}C: 8 ppm) and ruthenium (correlation to acetonitrile ligands ^{13}C: 125 ppm). The low $^1J_{C-H}$ values provide further evidence for an agostic interaction.[9] Although $^1J_{C-H}$ values for the boron methyls of **6** and **7** could not be observed directly (see the Supporting Information), each was measured in a ^{13}C-coupled HSQC experiment: $^1J_{C-H}$(agostic) = 100 Hz; $^1J_{C-H}$(free) = 107 Hz in **7**. For comparison, **6** has $^1J_{C-H}$ (free) = 109 Hz. Further comparison of the spectral details for **6** and **7** is presented in the Supporting Information. The nearest examples of

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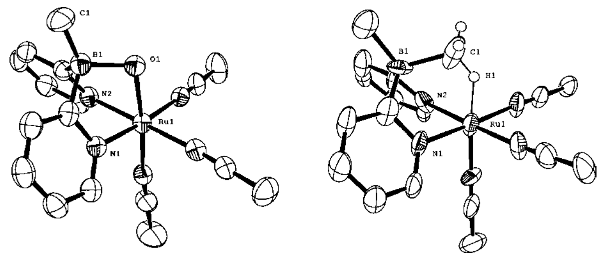


Figure 2. ORTEP diagrams of **1** (left) and **7** (right). Selected hydrogens and the counterions have been omitted for clarity. Ellipsoids are drawn at the 50% level.[11] For comparison sake, the bond lengths (Å) for the agostic BMe−M interactions in **7** and [(**3**)$Pt^{IV}Me_3$] are Ru1−H1, 1.72; B1−C1, 1.66; Ru1−C1, 2.53; Ru1−B1, 2.89, and Pt1−H1, 2.02; B1−C1, 1.68; Pt1−C1, 2.76; Pt1−B1, 3.08, respectively.

a metal-bound alkyl borate in the literature include a Pt(IV) case[6] and a bis(pyrazolyl)diethylborate-ligated Mo(II) complex.[10]

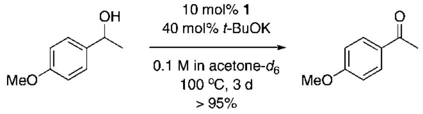
Importantly, the NMR data for **7** show that the lifetimes of **6** and **7** are on the order of 1 s in solution, and [**7**]/[**6**] decreases at lower temperature. Nonetheless, low-temperature vapor diffusion enabled crystallization of **7** in dichloromethane at low acetonitrile concentration. Remarkably, these crystals enabled collection of an X-ray structure that clearly defines the atomic connectivity in **7** (Figure 2). A direct comparison of the X-ray structures of **1** and **7** illustrates the positions of the dipyridylborate ligand with an oxygen or agostic bridge (Figure 2). The agostic C−H in **7** was positioned using the electron difference map. The Ru1−C1 bond distance of 2.53 Å in **7** is in contrast to the bond distance of 2.10 Å for Ru1−O1 in **1**.

The thermochemistry for the equilibration of **6** and **7** was measured by NMR spectroscopy. This equilibrium has a linear van't Hoff plot from 20 to 80 °C with $\Delta H = 5.5(2)$ kcal/mol and $\Delta S = 20.1(5)$ eu. The conversion of **7** to **6** was conveniently studied by NMR magnetization transfer: at 85 °C, bridge cleavage has $k_{-1,\mathrm{obs}} \approx 1\ \mathrm{s}^{-1}$. The mechanism for conversion of **7** to **6** has kinetic order with respect to [MeCN], which is consistent with a rapid pre-equilibrium followed by rate-determining acetonitrile association or concerted displacement of the agostic bond from **7**. The microscopic reverse of this reaction involves the very rare[7b] situation that an agostic bond displaces a ligand from an 18-electron metal center. Determination of second-order rate constants k_{-1} by inversion−recovery enabled the determination of the activation parameters for cleavage of the agostic interaction, which were found to be $\Delta H^{\ddagger} = 13.3(6)$ kcal/mol and $\Delta S^{\ddagger} = -27.5(43)$ eu using Eyring analysis over a range of 41 °C.

Complex **1** shows catalytic reactivity in the oxidation of *p*-methoxyphenethylalcohol (Scheme 2). Heating 10 mol % **1** with alcohol and 40 mol % *t*-BuOK in acetone resulted in >95% yield of the corresponding ketone. The mechanism of this reaction is unknown.

In summary, we have reported here the first example of an agostic bridge between boron and ruthenium atoms. The structure of this agostic bridge was established by a combination of NMR and X-ray diffraction methods. Cleavage of the bridge has kinetic order with respect to [acetonitrile], indicating that bridge dissociation is either a rapid pre-equilibrium or concerted displacement. Thus, this is a very rare situation in which an agostic interaction is in equilibrium with a tightly binding ligand. A hydrolyzed form of this ligand−metal bifunctional complex is a catalyst for transfer dehydrogenation of alcohols, although the mechanism of this reaction has not been established. We are currently investigating the mechanism of this oxidation and optimizing the heterobifunctional motif for general hydride manipulation reactions.

Scheme 2. Catalytic Reactivity of **1**



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Supporting Information Available: Experimental procedures, kinetics data, graphical spectra, and crystallographic data (CIF) for compounds **1**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) CCDC 738031, 738030, and 755444 contain supplementary crystallographic data for compounds **1**, **4**, and **7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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