



Communication

Rhodium catalyzed tandem Diels-Alder/hydrolysis reactions of 2-boron-substituted 1,3-dienes

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ABSTRACT

2-Boron substituted 1,3-dienes have been prepared and used in preliminary experiments to demonstrate that it is possible to effect rhodium catalyzed Diels-Alder/hydrolysis tandem reactions.

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1. Introduction

Our group [1] and the Tada group [2] independently reported the preparation and Diels-Alder reactions of pyridine cobaloxime dienyl complexes over 10 years ago. Since that time, we have reported a number of synthetic routes to these and other related types of cobalt dienyl complexes as well as their subsequent cycloaddition and demetallation chemistry [3–5], and other groups have now made use of the cycloadducts thus prepared [6] as well as the methodology [7]. We initially tried to develop a cobalt catalyzed Diels-Alder sequence rather than the stoichiometric cobalt chemistry we originally described. We proposed a sequence which relied on a cobalt hydride catalyst and hydrocobaltation of an enyne to generate a cobalt substituted diene but the last step of that proposed cycle proved problematic [3].

We have now subsequently reported the preparation of 2-BF₃ substituted 1,3-butadiene **1** and demonstrated that it can be used in sequential Diels-Alder/cross coupling reactions [8,9]. Given the Miyaura [10] and Hayashi [11] group's published results in rhodium catalyzed 1,4-additions of organoboron species, we wondered if boron substituted dienes could be used in a somewhat related rhodium catalyzed Diels-Alder/hydrolysis sequence (Scheme 1). With all of our experience in cobalt dienyl chemistry referenced above [3–5], we hoped that many of the reaction characteristics which we had discovered for cobalt dienyl chemistry (rapid Diels-Alder rates, *exo* selectivity, enantioselectivity with chiral metal dienes) would hold true if we could prepare related rho-

dium dienyl complexes **2**. Our preliminary results to test this hypothesis are outlined in this communication.

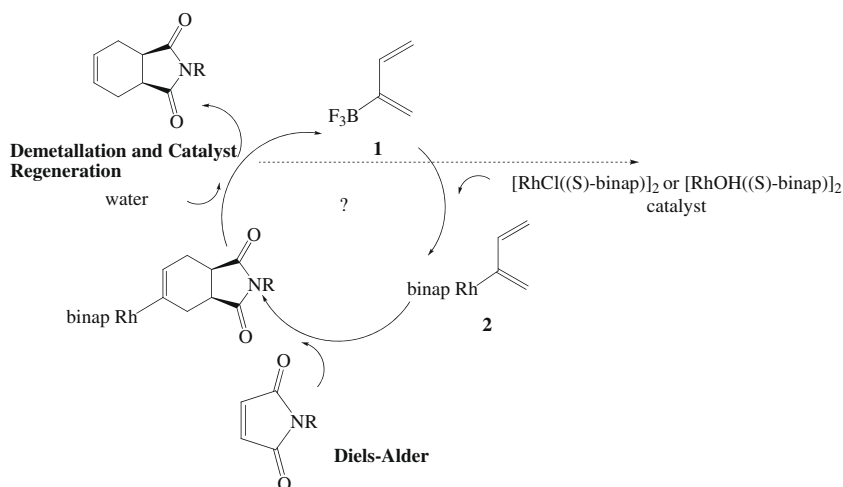
2. Results

As mentioned above, we had the dienyl trifluoroborate **1** in hand to test in this sequence but were somewhat worried about it as an initiator due to its low organic solvent solubility. All of our attempts to make the simple boronic acid substituted 2-(B(OH)₂)-1,3-butadiene have always proven unsuccessful, perhaps due to the acid sensitivity of that compound. We were however, able to prepare the trihydroxyboron substituted diene **4** on gram scale (Scheme 2). This compound was characterized by ¹H, ¹³C, and ¹¹B NMR and could also be used to test the sequence in Scheme 1. We had also prepared a tetrabutylammonium salt **5** from the potassium salt **1**.

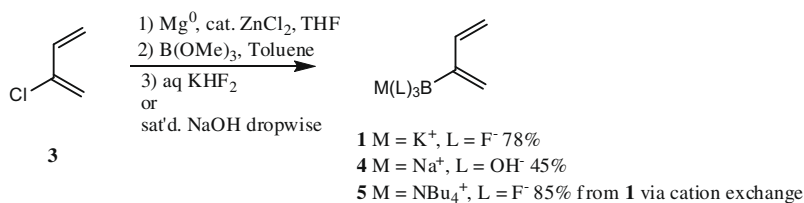
For the sequence outlined in Scheme 1 to be successful, a number of potential relative rate problems have to be overcome: (1) conditions have to be determined where background uncatalyzed Diels-Alder reactions of the boron dienes **1**, **4**, **5** have been suppressed. (2) Conditions have to be determined where hydrolysis of the boron diene or rhodium diene to produce butadiene have been suppressed. (3) Once condition 1 is satisfied, conditions where the rate of Diels-Alder reactions of rhodium dienes with α,β -unsaturated carbonyl compounds surpass the rate of 1,4 addition reactions with unsaturated carbonyl compounds have to be determined. (4) Once condition 2 is satisfied, the Rh–carbon bond in the Diels-Alder cycloadduct has to be more susceptible to hydrolysis than the Rh–carbon bond in the diene **2**. We were confident this last condition would be satisfied given our prior work on the

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Scheme 1. Rhodium catalyzed reactions of boron dienes.

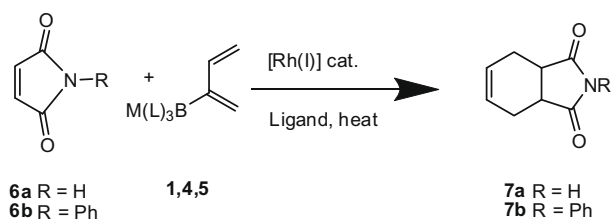


Scheme 2.

stability of related cobalt–carbon bonds in Diels–Alder cycloadducts compared to cobalt–carbon bonds in 2-cobalt-1,3-dienes [3] and Isono and Lautens recent report on hydrolysis of related Rh–alkene bonds [12].

First, the potassium salt of the BF_3 substituted diene **1** was used with either maleimide or N-phenyl maleimide **5a** or **5b** as a dienophile to determine the temperature limits for uncatalyzed and catalyzed Diels–Alder reactions (Scheme 3, Table 1). Two different Rh-catalysts in the presence of BINAP ligands were screened to check the feasibility of the protocol. All reactions were carried out in the presence of 5–10 mol% of a cationic rhodium source. Cationic rhodium was selected because of its role as an effective catalyst in the addition processes of potassium organotrifluoroborates in the Hayashi chemistry [13].

At 100 °C, diene **1** reacted completely with maleimide **6a** in 22 h using a toluene–water mixture or 2 h in wet acetone (entry 1). Under these conditions, both uncatalyzed Diels–Alder chemistry and C–B hydrolysis are both problems. At room temperature (entries 2–5) diene **1** was unreactive with dienophile **6a** or **6b** with or without the use of rhodium catalysis. In these cases diene **1** was recovered unreacted so C–B hydrolysis had been avoided. At intermediate temperatures (50–70 °C) diene **1** was unreactive without rhodium (entry 7) and gratifyingly we isolated cycloadduct **7b** in 62% yield when the RhOTf catalyst was used (entry 6).



Scheme 3.

We saw a higher yield of cycloadduct **7b** when we used the OTf salt (entry 6) as opposed to the BF_4 salt catalyst (entry 8). Switching from toluene–water to dioxane–water mixtures offered no advantage (entries 8 and 9). Use of diphenylphosphinoferrocene (dppf) instead of BINAP (entry 10) also offered no advantage. The recent report by Gilbertson and co-workers that catalytic silver salts enhanced rhodium catalyzed intramolecular [4 + 2 + 2] reactions caused us to also try silver as an additive (entry 11) but this also had little effect [14]. Treatment of the $\text{Rh}(\text{COD})$ catalyst system with an atmosphere of hydrogen for 30 min prior to ligand addition produced a slight improvement in yield (entry 12) whereas performing the reaction with no BINAP produced the highest yield (entry 13) consistent with Hayashi's recent report that rhodium diene catalysts are much more reactive than rhodium phosphine catalysts in the related 1, 4 addition chemistry [15]. Diene **5** was comparable to **1** under similar reaction conditions (entries 14 and 15) and since the preparation of **5** requires an extra synthetic step beyond the preparation of **1**, it was not pursued further. Lastly, we also tried the trihydroxyboron substituted diene **4** in the rhodium catalyst/BINAP protocol and it also provided product in reasonable isolated yield (entry 16) but the lower yield of the method used to prepare **4** originally also caused us not to pursue this diene further.

In conclusion, we have demonstrated that we can effect rhodium catalyzed Diels–Alder reactions of boron substituted dienes. We will report extensions of this chemistry into rhodium catalyzed Diels–Alder reactions of other main group element substituted dienes in due course.

3. Experimental

3.1. General procedures

The proton nuclear magnetic resonance (^1H NMR) spectra were obtained using a Bruker Avance 300 MHz spectrometer operating

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