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Ruthenium-Catalyzed C–C Coupling of Amino Alcohols with Dienes via Transfer Hydrogenation: Redox-Triggered Imine Addition and Related Hydroaminoalkylations

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Supporting Information

ABSTRACT: Ruthenium-catalyzed hydrogen transfer from 4-aminobutanol to butadiene results in the pairwise generation of 3,4-dihydro-2*H*-pyrrole and an allylruthenium complex, which combine to form products of imine *anti*-crotylation. In couplings of 1-substituted-1,3-dienes, novel C2 regioselectivity is observed. As corroborated by deuterium labeling studies, kinetically preferred hydrometalation of the terminal olefin of the 1-substituted-1,3-diene delivers a 1,1-disubstituted π-allylruthenium complex that isomerizes to a thermodynamically more stable monosubstituted π-allylruthenium complex, which undergoes imine addition with allylic inversion through a closed transition structure. Direct ruthenium-catalyzed diene hydroaminoalkylations with pyrrolidine also are described.

Although several early transition metal-based catalysts for hydroaminoalkylation have been described,[1] the development of related late transition metal-catalyzed amine C–H functionalizations has proven challenging.[1−3] Indeed, with the exception of the ruthenium(0)-catalyzed C–C coupling of hydantoins with dienes,[3] all other late-transition-metal catalysts for hydroaminoalkylation require pyridyl directing groups in combination with mono-olefin reactants.[2] Our laboratory has developed a suite of redox-triggered carbonyl additions wherein hydrogen transfer from alcohols to π-unsaturated reactants delivers transient carbonyl–organometal pairs that combine to furnish products of formal alcohol C–H functionalization or "hydrohydroxyalkylation".[4] Accordingly, we envisioned a protocol for formal late transition metal-catalyzed hydroaminoalkylation wherein dehydrogenation of 4-aminobutanol at oxygen would initiate intramolecular Schiff base formation[5] and hydrometalation of exogenous diene. The resulting imine–allylruthenium pair would then combine to form products of formal hydroaminoalkylation (Figure 1, bottom). Here, we report that the ruthenium catalyst generated from HClRu(CO)-$(PPh_3)_3$ and 1,3-bis(dicyclohexylphosphino)propane (dCypp) promotes the formal hydroaminoalkylation of 4-aminobutanol with butadiene and higher conjugated dienes to form 2-substituted pyrrolidines with complete levels of branched regioselectivity and good to excellent levels of *anti*-diastereoselectivity.[6,7] Further, we report preliminary studies on direct ruthenium-catalyzed hydroaminoalkylation, as exemplified by the coupling of pyrrolidine with butadiene and isoprene.

To probe the feasibility of redox-triggered imine addition, butadiene (**1a**) was exposed to 4-aminobutanol (**2a**) under

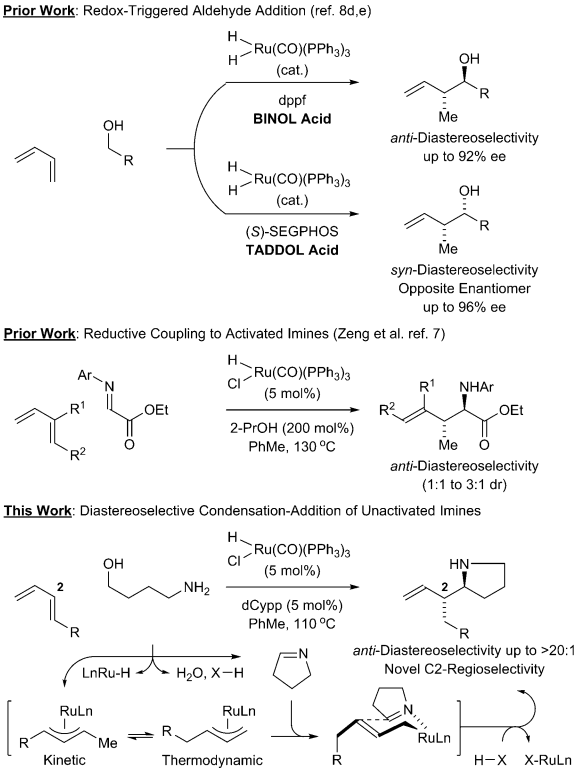

Figure 1. Redox-triggered carbonyl and imine addition catalyzed by ruthenium involving diene pronucleophiles.

conditions similar to those employed in related C–C couplings of primary alcohols with dienes (Figure 1, top).[8] In initial experiments, catalysts generated *in situ* from HClRu(CO)-$(PPh_3)_3$ (5 mol %) and various phosphine ligands were evaluated (Table 1). To facilitate isolation of the reaction products, the crude reaction mixtures were subjected directly to *N*-tosylation conditions. Among chelating phosphine ligands, 1,3-bis(diphenylphosphino)propane (dppp) was quite effective, providing the desired imine addition product **4a** in 80% yield but with modest levels of *anti*-diastereoselectivity (Table 1, entry 7). This result led us to evaluate the catalyst modified by dCypp (Table 1, entry 9), which provided adduct **4a** in 54% yield with complete levels of *anti*-diastereoselectivity, as determined by ^{1}H NMR analysis of the crude reaction mixture. Through further

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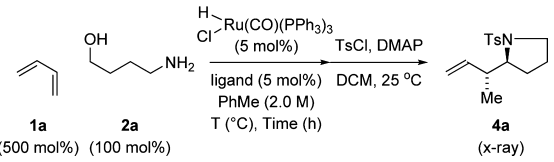
Table 1. Selected Optimization Experiments in the Ruthenium-Catalyzed Coupling of Butadiene (1a) with 4-Aminobutanol (2a)[a]



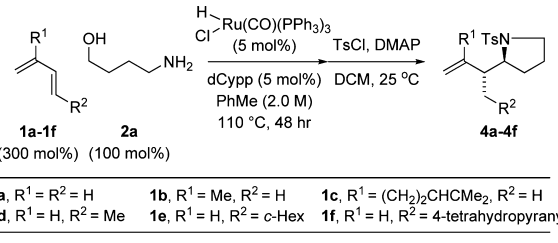
Entry	Ligand	T (°C)	Time (hr)	Yield **4a**	dr (*anti:syn*)
1	---	130	24	trace	---
2[b]	PCy_3	130	24	trace	---
3	*rac*-BINAP	130	24	11%	2:1
4	BIPHEP	130	24	23%	4:1
5	dppf	130	24	15%	3:1
6	dppe	130	24	20%	4:1
7	dppp	130	24	80%	3:1
8	dCype	130	24	52%	7:1
9	dCypp	130	24	54%	>20:1
10	dCypp	130	48	35%	>20:1
11	dCypp	150	24	27%	>20:1
12	dCypp	110	24	42%	>20:1
⇨13[c]	**dCypp**	**110**	**48**	**75%**	**>20:1**

[a]Yields are of material isolated by silica gel chromatography. [b]PCy_3 (10 mol%). [c]Average isolated yield from four experiments. See the Supporting Information for further details.

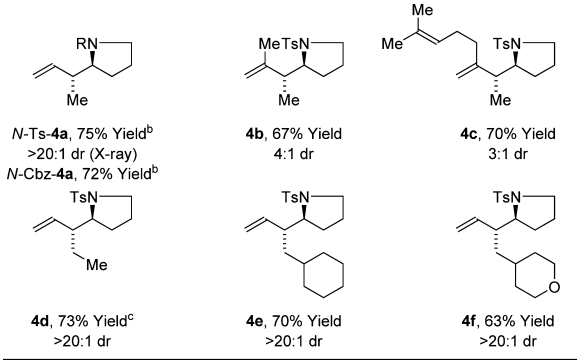
variation of temperature and reaction time, optimal conditions for the highly diastereoselective (>20:1 dr) coupling of **1a** with **2a** to form **4a** in 75% yield were identified (Table 1, entry 13).

With these conditions in hand, the coupling of **2a** with various conjugated dienes **1a**−**1f** was explored (Table 2). As illustrated in the couplings of **1a**, isoprene (**1b**), and myrcene (**1c**), a gradual decline in *anti*-diastereoselectivity with increasing size of the diene 2-substituent due to allylic 1,2-strain is observed.[8c] In

Table 2. Regio- and Diastereoselective Ruthenium-Catalyzed C−C Coupling of Conjugated Dienes 1a−1f with 2a[a]

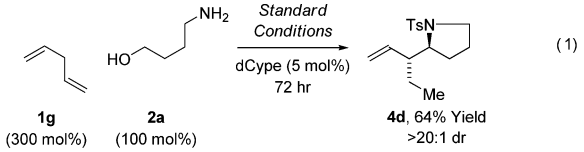


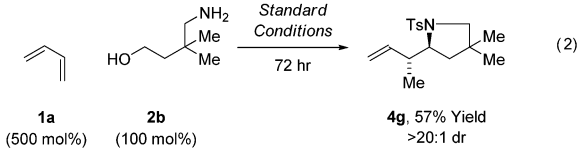
1a, $R^1 = R^2 = H$ **1b**, R^1 = Me, $R^2 = H$ **1c**, $R^1 = (CH_2)_2CHCMe_2$, $R^2 = H$
1d, $R^1 = H$, R^2 = Me **1e**, $R^1 = H$, R^2 = *c*-Hex **1f**, $R^1 = H$, R^2 = 4-tetrahydropyranyl

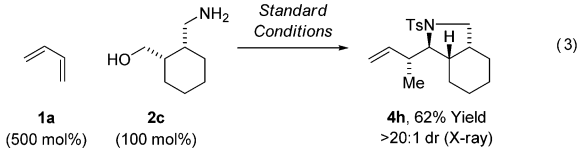


[a]Yields are of material isolated by silica gel chromatography. [b]**1a** (500 mol%). [c]dCype was used as the ligand. Diastereoselectivities were determined by ^{1}H NMR analysis of crude reaction mixtures. See the Supporting Information for further details.

the coupling of 1,3-pentadiene (**1d**), C−C coupling occurs at the diene 2-position to furnish the adduct **4d** with complete levels of *anti*-diastereoselectivity. Similarly, the 1-cyclohexyl-substituted diene **1e** and 1-(4-tetrahydropyranyl)-substituted diene **1f** engage in C−C coupling at the diene 2-position to furnish adducts **4e** and **4f**, respectively, with complete levels of *anti*-diastereoselectivity. As will be discussed (*vide infra*), coupling to the diene 2-position, exemplified by the formation of **4d**−**4f**, suggests reversible diene hydrometalation in advance of imine addition. Reversible hydrometalation enables nonconjugated dienes, such as 1,4-pentadiene (**1g**), to serve as conjugated diene equivalents, as shown in the formation of **4d** (eq 1). Whereas







attempted reactions of **1a** with 5-aminopentanol failed to provide the corresponding 2-substituted piperidine, it was found that the more highly substituted 4-aminobutanols **2b** and **2c** participate in redox-triggered imine addition to form adducts **4g** (eq 2) and **4h** (eq 3), respectively, with complete levels of *anti*-diastereoselectivity, as determined by ^{1}H NMR spectroscopy. Functionalized dienes, such as chloroprene or alkoxy-substituted dienes, do not participate in C−C coupling under these conditions.

In the couplings of **2a** with conjugated dienes **1a**−**1f**, alcohol dehydrogenation triggers pairwise generation of an imine electrophile, 3,4-dihydro-2*H*-pyrrole, and a ruthenium hydride that hydrometalates the diene to form a nucleophilic allylruthenium complex. It was reasoned that such nucleophile−electrophile pairs could be generated through the redox-triggered coupling of dienes with pyrrolidine itself, constituting a rare example of late transition metal-catalyzed hydroaminoalkylation in the absence of a directing group.[2,3] However, as observed empirically in the present couplings of **2a**, alcohol dehydrogenation occurs in preference to amine dehydrogenation, suggesting that such processes would pose significant challenges, which proved to be the case. Nevertheless, after screening of various ruthenium complexes, it was found that the catalyst generated *in situ* through the acid−base reaction of $H_2Ru(CO)(PPh_3)(dppp)$ and ferrocene carboxylic acid or $C_7F_{15}CO_2H$ promotes the hydroaminoalkylation of conjugated dienes **1a** and **1b** with pyrrolidine (**3a**) to form adducts **4a** and **4b**, respectively, in good yields with good levels of *anti*-diastereoselectivity (Scheme 1, eq 4). Finally, with the trimeric imine derived from pyrrolidine, *dehydro*-**3a**, 2-propanol-mediated reductive coupling to form *N*-Cbz-**4a** could be achieved,

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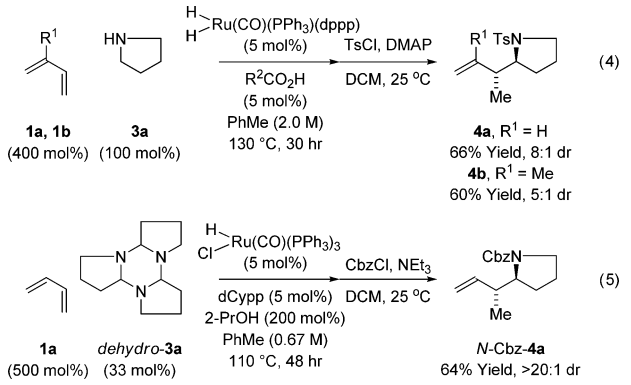
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

Scheme 1. Ruthenium-Catalyzed Hydroaminoalkylation of Conjugated Dienes 1a and 1b with Pyrrolidine and the Related 2-Propanol-Mediated Reductive Coupling of *dehydro*-3a[a]



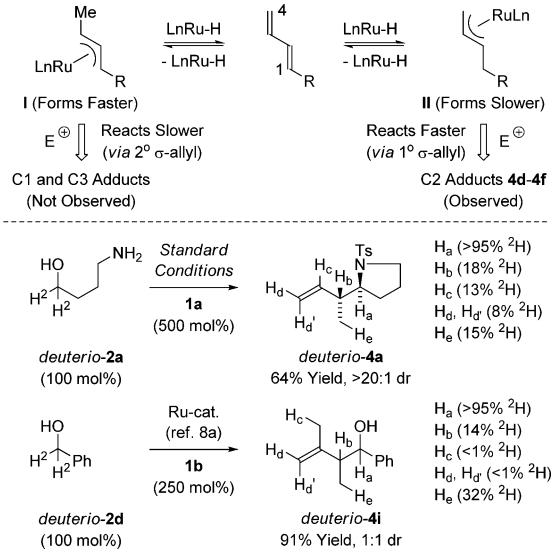
[a]Yields are of material isolated by silica gel chromatography. For the reaction of **1a**, R^2CO_2H = ferrocene carboxylic acid. For the reaction of **1b**, $R^2CO_2H = C_7F_{15}CO_2H$.

corroborating intervention of the imine in catalytic couplings of **2a** or **3a** (Scheme 1, eq 5).

Coupling at the diene 2-position, as illustrated by the formation of adducts **4d**–**4f**, represents a regioselectivity that has not been reported in intermolecular metal-catalyzed carbonyl or imine reductive coupling.[6−13] Olefin coordination is a prelude to hydrometalation, and the stability of late-transition-metal–olefin π-complexes decreases with increasing degree of olefin substitution.[14] As observed in the stoichiometric reaction of $HClRu(CO)(PPh_3)_3$ with 1,3-pentadiene to provide the 1,3-dimethyl-substituted π-allylruthenium isomer,[15] hydrometalation of 1-substituted-1,3-dienes at the less substituted olefin to form the π-allylruthenium complex **I** is kinetically preferred.[14] However, the resulting terminally disubstituted π-allyl **I** is less stable than the isomeric monosubstituted π-allylruthenium complex **II**.[16] Thus, if hydrometalation is reversible, the initially formed disubstituted π-allyl **I** may isomerize[8b,17] to form the π-allylruthenium complex **II**, which can engage in imine addition by way of the (*E*)-σ-allylruthenium haptomer to deliver the observed reaction products **4d**–**4f** (Scheme 2).

To determine whether diene hydrometalation is reversible, *deuterio*-**2a** was subjected to the standard conditions for ruthenium-catalyzed C–C coupling with **1a** (Scheme 2). Significant levels of deuterium incorporation were observed at all of the vinylic positions (H_c, H_d, and $H_{d'}$), the allylic position (H_b), and the methyl group (H_e), corroborating reversible diene hydrometalation. Notably, deuterium was completely retained at the methine adjacent to nitrogen (H_a), suggesting that alcohol dehydrogenation is not reversible because of rapid capture of the resulting aldehyde via imine formation. Retention of deuterium at H_a also suggests that the transient imine is not subject to hydrogenation–dehydrogenation and that the amine product derived upon C–C coupling is kinetically inert with respect to dehydrogenation–hydrogenation, likely as a result of coordination of the homoallylic olefin to ruthenium, which blocks an otherwise vacant coordination site required for β-hydride elimination. The incorporation of deuterium across all of the diene-derived carbon atoms of *deuterio*-**4a** differs dramatically from the pattern of deuterium incorporation observed in the previously reported reaction of *deuterio*-**2d** with **1b**, which was conducted under similar conditions.[8a] These data further

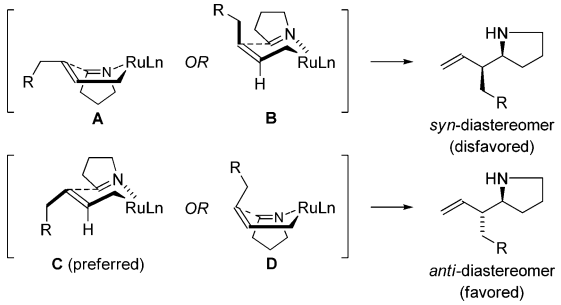
Scheme 2. Rationale for the C2 Regioselectivity Observed in the Formation of Adducts 4d–4f and Deuterium Labeling Studies Corroborating Reversible Diene Hydrometalation



emphasize the highly reversible nature of diene hydrometalation events under the present conditions for the reaction of 1-substituted dienes with **2a** (Scheme 2).

The regioselectivity and *anti*-diastereoselectivity observed in the formation of adducts **4a**–**4h** can be understood on the basis of stereochemical models **A**–**D** (Scheme 3). Imine addition is

Scheme 3. Stereochemical Models A–D for Imine Addition



postulated to occur by way of the primary σ-allylruthenium haptomer with allylic inversion through a closed transition structure. As stereochemical models **A** and **B** would generate *syn*-diastereomers, these pathways are excluded. The stereochemical model **D** requires intervention of the (*Z*)-σ-allylruthenium isomer, which is unlikely as the deuterium labeling studies corroborated thermodynamic control in the formation of the allylruthenium intermediate. Thus, stereochemical model **C**, wherein imine addition occurs through a chairlike transition structure by way of the (*E*)-σ-allylruthenium isomer, is preferred.

With regard to scope, attempts were made to develop an enantioselective variant of the present diene–amino alcohol C–C couplings. Numerous chiral ligands were evaluated, but high levels of enantiomeric enrichment could be achieved only in the formation of the minor diastereomeric reaction products. Attempts also were made to utilize α-olefins and styrenes as coupling partners, but these reactions failed entirely.

In summary, we have reported the first redox-triggered additions of dienes to unactivated imines, as illustrated in the

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formal hydroaminoalkylation of conjugated dienes **1a**−**1f** using amino alcohols **2a**−**2c** to deliver adducts **4a**−**4h**. The present protocol for redox-triggered imine addition bypasses the stoichiometric use of premetalated carbanions and hence, the generation of stoichiometric metallic byproducts, as required in conventional methods for imine addition. In the present transformations, water is the sole stoichiometric byproduct. Furthermore, as illustrated in the reaction of dienes **1a** and **1b** with **3a**, preliminary studies of direct amine C−H functionalization have been described, constituting a rare example of late transition metal-catalyzed hydroaminoalkylation in the absence of directing groups.[2,3] Future studies will focus on the development of improved second-generation catalysts for amine C−H functionalization via redox-triggered imine addition.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for new compounds, including scanned images of ^{1}H and ^{13}C NMR spectra, and single-crystal X-ray diffraction data for **4a** and **4h** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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