Published in final edited form as:

Angew Chem Int Ed Engl. 2017 November 13; 56(46): 14667–14671. doi:10.1002/anie.201708189.

Diols as Dienophiles: Bridged Carbocycles *via* Ruthenium(0) Catalyzed Transfer Hydrogenative Cycloadditions of Cyclohexadiene or Norbornadiene**

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The Influence of Alcohols

Highly *exo*-selective ruthenium(0) catalyzed transfer hydrogenative cycloadditions of 1,2-diols with cyclohexadiene or norbornadiene are described. Novel bridged bicyclic ring systems are accessible from the diol, α -ketol or 1,2-dione oxidation levels with complete control of diastereoselectivity.

Keywords

Cycloaddition; Diol; C-C Bond Formation; Ruthenium; Hydrogen Transfer; Homogenous Catalysis

Bridged carbocycles are ubiquitous structural motifs in naturally occurring or unnatural bioactive compounds.^[1] Transition metal catalyzed cycloadditions^[2] are among the most powerful methods for the construction of complex ring systems, however, despite longstanding effort, nearly all reported processes exploit π -unsaturated reactants and are conducted in a redox-neutral mode.^[3–5] Recently, in connection with the development of catalytic hydrogen transfer reactions that convert lower alcohols to higher alcohols,^[6,7] we discovered a ruthenium catalyzed [4+2] cycloaddition of acyclic dienes that is *redox independent* - vicinal diols, ketols or diones may serve as dienophiles.^[8,9] These unusual cycloadditions, which deliver substituted cyclohexene diols, occur through a catalytic mechanism involving diol dehydrogenation to form a vicinal dicarbonyl species, which upon oxidative coupling delivers a ruthenacyclic intermediate.^[10] Subsequent intramolecular

**The Welch Foundation (F-0038) and the NIH (RO1-GM069445) are acknowledged for partial support of this research. The Japan Student Services Organization (JASSO) and the Japan Society for the Promotion of Science (JSPS) are acknowledged for graduate fellowship (HS) and research fellowship (KF) fellowship support, respectively. We thank Mr. Justin Jurczyk for the preparation of some diols used in this study.

carbonyl allylruthenation followed by transfer hydrogenolysis delivers the cycloadduct and returns ruthenium to its zero-valent form. Application of this reactivity pattern to *cyclic* dienes, such as cyclohexadiene (CHD), and related compounds, such as norbornadiene (NBD), would significantly broaden access to bridged carbocycles. However, competing aromatization (CHD to benzene) and catalyst deactivation (Ru-NBD complexes) rendered the feasibility of such processes uncertain. Here, we report that cyclohexadiene and norbornadiene are efficient partners for diol-mediated cycloaddition, delivering bridged carbocycles with complete levels of *exo*-selectivity (Figure 1). We also demonstrate the redox-independent nature of these processes, which may be conducted from the diol, ketol or dione oxidation levels.

In an initial set of experiments, cyclohexadiene **1a** (500 mol%) and cyclopentane diol **2a** (100 mol%) were exposed to the ruthenium catalyst prepared *in situ* from Ru₃(CO)₁₂ (2 mol %) and various phosphine ligands (12 mol% for monodentate ligands; 6 mol% for chelating ligands) in toluene solvent (2.0 M) at 140 °C. From this initial ligand screen, it was found that the ruthenium(0) catalyst modified by bis(diphenylphosphino)ethane (dppe) delivered the hydroxy substituted bridged bicycle **3a** in 77% yield with complete levels of *exo*-selectivity. As depicted above (Figure 1), our collective studies on the ruthenium(0) catalyzed C-C coupling of alcohols^[6c] are consistent with catalytic mechanisms involving diene-dione oxidative coupling to form oxaruthenacycles. In certain cases, such oxaruthenacycles are isolable,^[10] suggesting they likely represent resting states in the catalytic cycle and potentially contribute to diminished catalytic efficiency. Carboxylic acid additives are known to co-catalyze the hydrogenolysis^[11] and transfer hydrogenolysis^[12] of oxa- and azametallacycles. Hence, a series of carboxylic acid additives were evaluated in the ruthenium(0) catalyzed coupling of cyclohexadiene **1a** and cyclopentane diol **2a**. To our delight, upon application of the aforesaid conditions in the presence of 3,5-dimethylbenzoic acid (10 mol%), the bicyclic product of [4+2] cycloaddition **3a** was obtained in 95% yield after isolation by silica gel chromatography. These conditions enabled conversion of both cyclic diols **2a–2e** to the corresponding products of [4+2] cycloaddition **3a–3e** in good yield with complete *exo*-selectivity (Table 1). Acyclic diol **2f** also participated in cycloaddition to form adduct **3f** as a single diastereomer, along with a small quantity of the ketol *dehydro-3f*. The cycloaddition was insensitive to diol stereochemistry. The dihydride complex H₂Ru(CO)(PPh₃)₃ (6 mol%) catalyzed the cycloaddition of cyclohexadiene **1a** with cyclopentane diol **2a** to form **3a** in 93% yield under otherwise standard conditions.

The documented ability of Ru₃(CO)₁₂ to catalyze olefin isomerization^[13] suggested the feasibility of engaging non-conjugated dienes in [4+2] cycloaddition. In the event, exposure of 1,4-cyclohexadiene *iso-1a* and cyclopentane diol **2a** to standard reaction conditions led to the formation of the bridged bicycle **3a** in 95% yield after isolation by silica gel chromatography (eq. 1). An even more powerful application of tandem olefin isomerization-cycloaddition is found in the reaction of 1,5,9-cyclododecatriene **1b** with diol **2d** to form cycloadduct **3d'** (eq. 2). Here, olefin isomerization results in the generation of a conjugated triene *iso-1b*, which exists in equilibrium with the corresponding [6.4.0] bicycle *iso-1b'* through electrocycloization.^[14] Ruthenium(0) catalyzed cycloaddition onto the [6.4.0] bicycle provides cycloadduct **3d'** as a single diastereomer.

(eq. 1)

(eq. 2)

The use of norbornadiene **1c** in thermal *homo*-Diels-Alder reactions is longstanding,^[15] as are metal catalyzed variants.^[16] Motivated by this precedent and the utility of *homo*-Diels-Alder cycloadducts with respect to the synthesis of diquinanes,^[17] the ruthenium(0) catalyzed cycloaddition of norbornadiene **1c** with cyclopentane diol **2a** was explored. To our delight, after only a minor adjustment to reaction temperature, the product of cycloaddition **4a** was formed in 80% yield with complete *exo*-diastereoselectivity. These conditions were applicable to cyclic diols **2a–2e** and **2g** (Table 2). Unlike cyclohexadiene **1a**, norbornadiene **1c** did not engage in efficient coupling with acyclic diols. The dihydride complex $\text{H}_2\text{Ru}(\text{CO})(\text{PPh}_3)_3$ (6 mol%) catalyzed the cycloaddition of norbornadiene **1c** with cyclopentane diol **2a** to form **4a** in 67% yield under otherwise standard conditions.

The present diol-mediated cycloadditions are oxidative processes in which one equivalent of diene **1a–1c** serves as a sacrificial hydrogen acceptor. However, as illustrated by the reactions of dienes **1a** and **1c** with ketol *dehydro-2d* (Scheme 1, eq. 4 and 7) or dione *didehydro-2d* (Scheme 1, eq. 5 and 8), redox-neutral and reductive cycloaddition also is possible. Redox-neutral cycloadditions do not require a sacrificial oxidant or reductant and, hence, preclude generation of stoichiometric byproducts. Reductive cycloadditions mediated by formic acid (200 mol%) generate carbon dioxide as the sole stoichiometric byproduct.

A general catalytic mechanism and stereochemical model accounting for *exo*-selectivity have been proposed, as illustrated in couplings of cyclohexadiene **1a** and norbornadiene **1c** with diol **2a** (Scheme 2). The cycloaddition is initiated *via* dehydrogenation of diol **2a** to the dione *didehydro-2a*.^[18–20] Reversible^[10] ruthenium(0)-mediated oxidative coupling of dione *didehydro-2a* to cyclohexadiene **1a** and norbornadiene **1c** delivers oxa-ruthenacycles **IA** and **IC**, respectively.^[21,22] Formation of the second C-C bond occurs in a diastereoselective fashion by way of transition structures **IIA** and **IIC**. Transfer hydrogenolytic cleavage of the resulting metallacycles **IIIA** and **IIIC** mediated by diol **2a** or ketol *dehydro-2a* releases the cycloadducts **3a** and **4a**. The carboxylic acid cocatalyst is

postulated to accelerate transfer hydrogenolysis of the sterically congested metalacycle **IIIa** *via* protonolytic cleavage of a ruthenium-oxygen bond to form a more accessible and substitutionally labile ruthenium carboxylate (not shown).^[12b] It should be noted that although ethylene and α -olefins engage in diol-mediated C-C coupling under the conditions of ruthenium(0)^[12a] or osmium(0)^[12c,d] catalysis, the more highly substituted *mono*-olefins cyclohexene and norbornene do not engage in C-C coupling in the presence or absence of a carboxylic acid cocatalyst, likely due to unfavorable equilibria associated with the reversible nature of the oxidative coupling event.^[10] Indeed, we have shown that such unfavorable equilibria can be overcome upon use of enol carboxylates as coupling partners, which deliver transient β -acyloxy-oxametallacycles that are “captured” through the elimination of carboxylate.^[12c] Reactions conducted under an atmosphere of carbon monoxide do not result in lactone formation or other products of carbonylation. Finally, whereas the carbonyl complex $\text{H}_2\text{Ru}(\text{CO})(\text{PPh}_3)_3$ is capable of catalyzing the present diol-mediated cycloadditions of cyclohexadiene **1a** and norbornadiene **1c**, the related complex lacking a carbonyl ligand, $\text{H}_2\text{Ru}(\text{PPh}_3)_4$, is inactive. A carbonyl ligand may be required to facilitate alkoxide exchange at ruthenium by way of an acylruthenium intermediate.^[23]

In summary, we report highly *exo*-selective ruthenium(0) catalyzed transfer hydrogenative cycloadditions of cyclohexadiene **1a** or norbornadiene **1c** with 1,2-diols **2a–2g** to form bridged carbocycles. A remarkable feature of these transformations relates to their redox-independent nature, which allows cycloaddition to be conducted from the diol, ketol or dione oxidation levels, and the ability to engage either conjugated- or non-conjugated dienes. These processes contribute to growing class of transfer hydrogenative cycloadditions^[8,9] that provide entry to structural space beyond that accessible through classical cycloaddition methodology. Future studies will focus on the development of related transfer hydrogenative cycloadditions and their application to target-oriented synthesis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Bridged Carbocycles via Classical Diels-Alder and Homo-Diels-Alder Reactions

This Work: Bridged Carbocycles using Diols as Dienophiles via Ru Catalysis

Figure 1. Classical Diels-Alder and *homo*-Diels-Alder cycloadditions to form bridged carbocycles and related transfer hydrogenative variants.

Scheme 1.

Redox level independent cycloaddition of cyclohexadiene **1a** and norbornadiene **1c** with diol **2d**, ketol *dehydro-2d* and dione *didehydro-2d*.^a

^aYields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

Cycloadditions of Cyclohexadiene 1a

Cycloadditions of Norbornadiene 1c

Scheme 2.

General mechanism and stereochemical model accounting for *exo*-selectivity.

Table 1

Ruthenium catalyzed cycloaddition of cyclohexadiene **1a** with diols **2a–2f** to form bridged bicycles **3a–3f**.^a

1a (500 mol%)	2a-2f (100 mol%)		
2a , 1,2-cyclopentane diol	2b , 3,4-tetrahydrofuran diol	2c , 1,2-dihydroindene diol	
2d , acenaphthylene diol	2e , H ₆ -5,6-phthalimide diol	2f , 1,2-propane diol

3a , 95% Yield >20:1 dr		3b , 99% Yield >20:1 dr (X-Ray)

		3c , 81% Yield ^b >20:1 dr

3d , 85% Yield >20:1 dr		3e , 91% Yield ^c >20:1 dr (X-Ray)

		3f , 58% Yield ^d >20:1 dr	

^aYields are of material isolated by silica gel chromatography. PMP = *p*-methoxyphenyl.^b*rac*-BINAP (6 mol%)^cWithout 3,5-Me₂BzOH, 150 °C.^ddCype (6 mol%). The ketol *dehydro-3f* was formed in 13% yield. See Supporting Information for further experimental details.

Table 2

Ruthenium catalyzed cycloaddition of norbornadiene **1c** with diols **2a–2e**, **2g** to form bridged bicycles **4a–4e**, **4g**.^a

1c (500 mol%)	2a–2e, 2g (100 mol%)	4a–4e, 4g
2a , 1,2-cyclopentane diol 2d , acenaphthylene diol	2b , 3,4-tetrahydrofuran diol 2e , H ₆ -5,6-phthalimide diol	2c , 1,2-dihydroindene diol 2g , 1,2-cyclohexane diol
 4a , 80% Yield >20:1 dr	 4b , 63% Yield ^b >20:1 dr	 4c , 82% Yield >20:1 dr (X-Ray)
 4d , 91% Yield >20:1 dr (X-Ray)	 4e , 85% Yield >20:1 dr (X-Ray)	 4g 54% Yield (from diol 2g) 62% Yield (from ketol <i>dehydro-2g</i>) >20:1 dr

^aYields are of material isolated by silica gel chromatography. PMP = *p*-methoxyphenyl.

^bdppb (6 mol%), 150 °C, dioxane (2.0 M). See Supporting Information for further experimental details.