

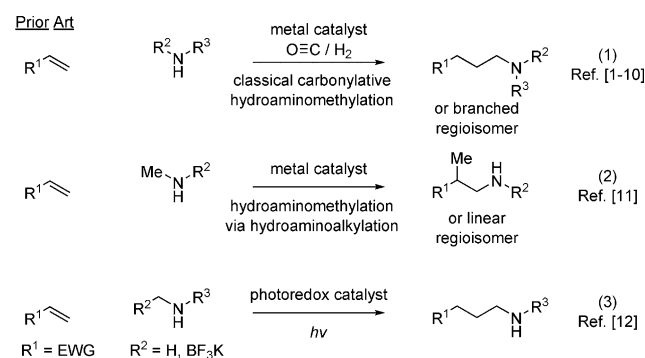


Hydroaminomethylation Beyond Carbonylation: Allene–Imine Reductive Coupling by Ruthenium-Catalyzed Transfer Hydrogenation**

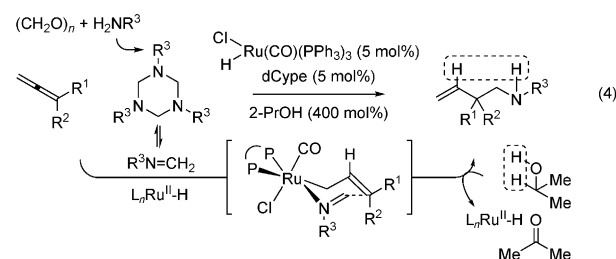
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Abstract: Ruthenium(II)-catalyzed hydrogen transfer from 2-propanol mediates reductive coupling of 1,1-disubstituted allenes with formaldimines with complete branch-regioselectivity, thus representing a new method for hydroaminomethylation beyond classical hydroformylation/reductive amination.

Hydroaminomethylation,^[1] the successive one-pot hydroformylation/reductive amination, is an important, atom-efficient method for amine synthesis [Scheme 1, Eq. (1)].



This Work: Hydroaminomethylation by transfer hydrogenation



Subsequent to Reppe's discovery of hydroaminomethylation at BASF in 1949,^[2] relatively few studies were disclosed.^[3] However, in the last 15 years, due in large part to the elegant

work of Eilbracht,^[4] hydroaminomethylation has been intensively investigated^[1] and utilized for the preparation of diverse pharmaceutical ingredients,^[5] including cinacalcet (Sensipar, Mimpara),^[5,6a] ibutilide (Corvert),^[5,6b] and fexofenadine (Allegra, Fexidine, Telfast, Fastofen, Tilfur, Vifas, Telfexo, Allerfexo).^[5,6c] Recent advances in hydroaminomethylation include the use of ammonia as a reactant,^[4c,7] regioselective reactions of terminal^[8a] and internal^[8b] alkenes through ligand control^[8] or the use of directing groups,^[9] the evolution from rhodium-based to ruthenium-based catalysts,^[10] and the emergence of noncarbonylative strategies, including hydroaminoalkylation^[11] [Scheme 1, Eq. (2)] and photoredox catalysis [Scheme 1, Eq. (3)].^[12] The vast majority of hydroaminomethylation protocols apply to α -olefins. To our knowledge, the hydroaminomethylation of other π -unsaturated reactants, such as dienes or allenes, is unknown.^[13] Herein we report a new strategy for hydroaminomethylation based on 2-propanol-mediated reductive coupling of 1,1-disubstituted allenes and formaldimines derived in situ from 1,3,5-tris(aryl)-hexahydro-1,3,5-triazines [Scheme 1, Eq. (4)]. These processes deliver branched products of hydroaminomethylation bearing all-carbon quaternary centers.^[13–20]

Initial experiments were inspired by our earlier studies on the ruthenium-catalyzed reductive coupling of formaldehyde with allenes,^[13,14] dienes,^[13,15] and alkynes.^[13,16] Using the allene **1a** and hexahydro-1,3,5-triazine **2a**, a crystalline solid prepared from paraformaldehyde and *p*-anisidine,^[21] a series of catalysts derived from the commercial ruthenium complex [HClRu(CO)(PPh₃)₃] were evaluated for their ability to induce reductive coupling by 2-propanol-mediated transfer hydrogenation (Table 1). In the absence of an exogenous ligand or upon use of tricyclohexylphosphine as a ligand, small quantities of the desired homoallylic neopentyl amine **3a** were formed as a single regioisomer. Chelating phosphine ligands were more effective at enforcing higher conversion. Eventually, it was found that upon use of dCype as a ligand, the desired homoallylic amine **3a** could be obtained in 83 % yield.

Under optimized reaction conditions using the ruthenium catalyst derived in situ from [HClRu(CO)(PPh₃)₃] and dCype, the scope of the allene partner was explored in reductive couplings to **2a** (Table 2). The 1,1-dialkylsubstituted allenes **1a–f** were each converted to the respective homoallylic neopentyl amines **3a–f** in good to excellent yields with complete regiocontrol. As illustrated in the formation of adducts **3c** and **3e**, this method allows the creation of congested all-carbon quaternary centers which are vicinal to tertiary stereocenters. The 1-methyl-1-aryl-disubstituted

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Table 1: Selected ligand-based optimization experiments in the reductive coupling of the allene **1a** with triazine **2a**.^[a]

Ligand	Yield [%] ^[a]
---	7
PCy ₃ (10 mol%)	8
dppf (5 mol%)	27
dippf (5 mol%)	26
dppm (5 mol%)	24
dCypm (5 mol%)	43
dppe (5 mol%)	51
dCype (5 mol%)	83

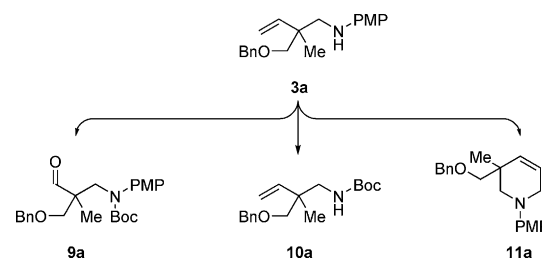
^[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. PMP = *para*-methoxyphenyl.
 dppf, R = Ph
 dippf, R = *i*Pr
 dCypm, n = 1, R = Ph
 dCypm, n = 1, R = *c*-Hex
 dppe, n = 2, R = Ph
 dCype, n = 2, R = *c*-Hex

Table 2: Ruthenium-catalyzed hydroaminomethylation of the allenes **1a–l** with the triazine **2a** to form homoallylic neopentyl amines **3a–l**.^[a]

1a , R ¹ = Me, R ² = CH ₂ OBn 1d , R ¹ = Me, R ² = CH ₂ OTBS 1g , R ¹ = Me, R ² = Ph 1j , R ¹ = Me, R ² = <i>p</i> -FC ₆ H ₄	1b , R ¹ = Et, R ² = CH ₂ OBn 1e , R ¹ = Me, R ² = <i>c</i> -Hex 1h , R ¹ = Me, R ² = <i>p</i> -MeOC ₆ H ₄ 1k , R ¹ = Me, R ² = <i>p</i> -CF ₃ C ₆ H ₄	1c , R ¹ = <i>i</i> Pr, R ² = CH ₂ OBn 1f , R ¹ = R ² = Me 1i , R ¹ = Me, R ² = benzodioxole 1l , R ¹ = Me, R ² = 3,5-Cl ₂ C ₆ H ₃
 3a , 83% yield	 3b , 85% yield	 3c , 50% yield
 3d , 77% yield	 3e , 74% yield ^[b]	 3f , 86% yield
 3g , 74% yield	 3h , 72% yield	 3i , 67% yield
 3j , 69% yield	 3k , 81% yield	 3l , 70% yield

^[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. ^[b] **1e** (400 mol%). TBS = *tert*-butyldimethylsilyl.

allenes **1g–l** react to form the corresponding neopentyl amines **3g–l**, which bear aryl-substituted all-carbon quaternary centers, in good yield as single regioisomers. Monosubstituted allenes did not engage in efficient coupling under these reaction conditions. To illustrate the utility of adducts **3a–l**, the homoallylic amine **3a** was selectively transformed to



Scheme 2. Selected elaborations of hydroaminomethylation product **3a** to form the compounds **9a**, **10a**, and **11a**. Yields are of material isolated by silica gel chromatography. For **9a**: 1) Boc₂O, Et₃N, DMAP, CH₂Cl₂, 25 °C, 47%. 2) O₃, CH₂Cl₂, −78 °C, 86%. For **10a**: 1) CAN, MeCN/H₂O (1:1), 25 °C, 79%. 2) Boc₂O, Et₃N, CH₂Cl₂, 25 °C, 92%. For **11a**: 1) BrCH₂CH=CH₂, K₂CO₃, DMF, 25 °C, 88%. 2) Grubbs-II, CH₂Cl₂, 25 °C, 90%. See the Supporting Information for further experimental details. Boc = *tert*-butoxycarbonyl, DMAP = 4-(*N,N*-dimethylamino)pyridine, DMF = *N,N*-dimethylformamide.

compounds **9a–11a**, which embody diverse functional group arrays (Scheme 2).

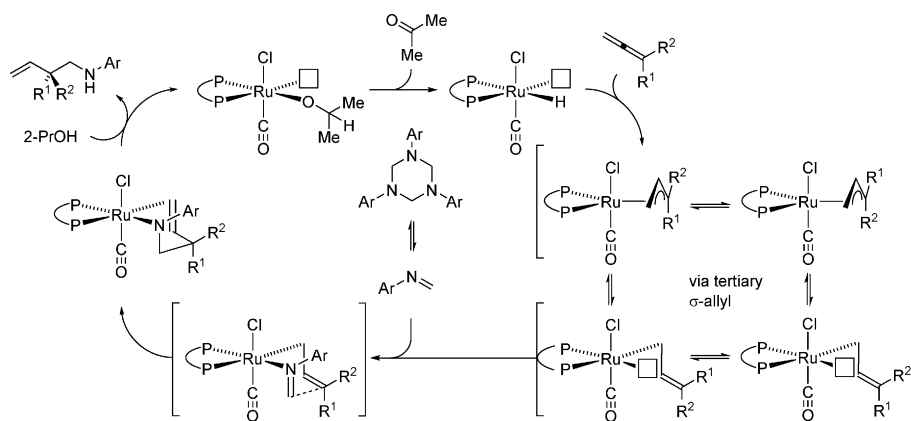
To further evaluate reaction scope, the *N*-substituted hexahydro-1,3,5-triazines, **2a–f** were exposed to **1a** under the standard conditions (Table 3). The reaction is most efficient

Table 3: Ruthenium-catalyzed hydroaminomethylation of **1a** with the triazines **2a–f** to form homoallylic neopentyl amines **3a–8a**.^[a]

Reaction scheme for Table 3: Allene 1a (200 mol%) reacts with triazine 2a-f (33.3 mol%, 100 mol% imine) in the presence of a Ru catalyst ($\text{Cl-Ru(CO)(PPh}_3)_3$, 5 mol%), dCype (5 mol%), 2-PrOH (400 mol%), PhMe (0.5 M), at 105 °C for 24 h to form product 3a-8a.		
2a , Ar = <i>p</i> -MeOC ₆ H ₄ 2d , Ar = Ph	2b , Ar = <i>p</i> -Me ₂ NC ₆ H ₄ 2e , Ar = <i>p</i> -FC ₆ H ₄	2c , Ar = <i>o</i> -MeOC ₆ H ₄ 2f , Ar = 5-(2-MeO-Pyr)
 3a , 83% yield	 4a , 82% yield	 5a , 53% yield
 6a , 61% yield	 7a , 70% yield	 8a , 62% yield

^[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details.

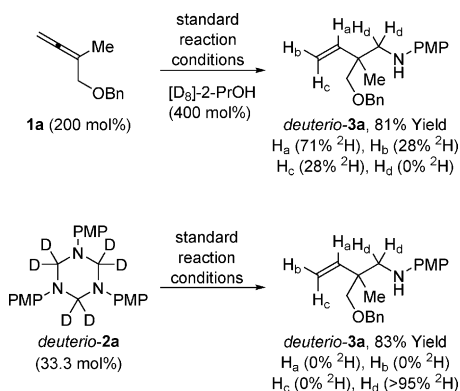
for electron-rich, *para*-substituted *N*-phenyl reactants, as illustrated in the formation of the adducts **3a** and **4a**. Nonetheless, *ortho*-anisidine substituted hexahydro-1,3,5-triazine **2c** delivers the adduct **5a** in moderate yield. Additionally, the parent *N*-phenyl triazine **2d** and *N-para*-fluorophenyl triazine **2e** provide the adducts **6a** and **7a**, respectively, in good yield. Finally, as demonstrated in the formation of the *N*-pyridyl-substituted adduct **8a**, heteroaromatic *N*-substituents are tolerated. Under these initially developed reaction conditions, *N*-alkyl, *N*-acyl, and *N*-sulfonyl triazines and alkyl-substituted *N*-PMP imines do not participate in catalytic C–C coupling.



Scheme 3. General catalytic mechanism for allene hydroaminomethylation by ruthenium-catalyzed C–C bond-forming transfer hydrogenation.

A general catalytic mechanism has been proposed (Scheme 3). The ruthenium hydride complex derived from $[\text{HClRu}(\text{CO})(\text{PPh}_3)_3]$ and dCype hydrometallates the allene to form a nucleophilic allylruthenium complex. The stoichiometric reaction of $[\text{HXRu}(\text{CO})(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}, \text{Br}$) with allenes (or dienes) to furnish π -allylruthenium complexes has been reported.^[22] Such π -allylruthenium species are highly fluxional in nature, thus undergoing rapid geometrical isomerization by way of the σ -bound haptomers.^[23] Coordination of the pentacoordinate σ -allylruthenium species to the formaldimine initiates addition through a closed transition structure to form the homoallylic ruthenium amide. Protolytic cleavage of the amidoruthenium intermediate by 2-propanol releases the product and provides the indicated ruthenium 2-propoxide, which upon β -hydride elimination forms acetone and regenerates the starting ruthenium hydride.

To gain further insight into the catalytic mechanism, deuterium-labelling studies were performed (Scheme 4). Reductive coupling of **1a** to **2a** using $[\text{D}_8]$ -2-propanol delivers *deuterio-3a*, which incorporates significant quantities of deuterium at the interior vinylic position (H_a) and, to a lesser extent, the terminal vinylic positions (H_b and H_c). This pattern of deuterium incorporation suggests allene hydrometallation is fast and reversible and occurs with incomplete regioselectivity. Incomplete deuterium incorporation at the interior vinylic position of *deuterio-3a* (71 % ^2H)



Scheme 4. Deuterium-labeling experiments.

likely stems from β -hydride elimination of the allylruthenium species to form dienes, which are detected in crude reaction mixtures and may account for the requirement of a superstoichiometric amount of allene. Adventitious water also may diminish the extent of deuterium incorporation.^[24] The coupling of **1a** to the deuterated triazine *deuterio-2a* delivers *deuterio-3a*, which completely retains deuterium adjacent to nitrogen (> 95 % ^2H), thus indicating that the C–N bond of the amine product is not subject to reversible dehydrogenation under these reaction conditions.

In summary, we report a new strategy for the hydroaminomethylation of π -unsaturated reactants beyond classical hydroformylation/reductive amination: the reductive coupling of allenes and *N*-aryl formaldimines by ruthenium-catalyzed transfer hydrogenation.^[25] These transformations exploit highly tractable saturated *s*-triazines, derived from paraformaldehyde and aryl amines as latent imines, and deliver adducts bearing all-carbon quaternary centers with complete control of regioselectivity. Related hydroaminomethylations of alkynes, 1,3-dienes, and 1,3-enynes are currently under exploration in our laboratory.

Keywords: allenes · green chemistry · ruthenium · synthetic methods · transfer hydrogenation

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