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

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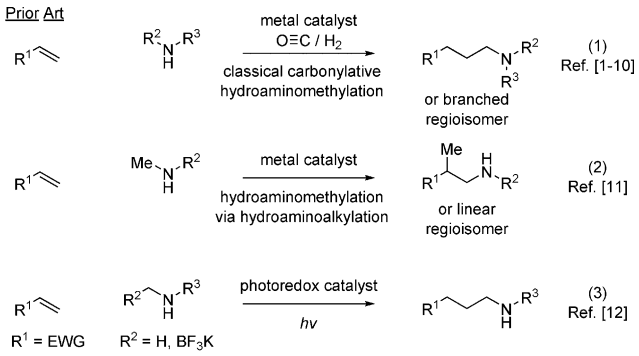
Abstract: *Ruthenium(II)-catalyzed hydrogen transfer from 2-propanol mediates reductive coupling of 1,1-disubstituted allenes with formaldimines with complete branch-regioselectivity, thus representing a new method for hydroaminomethylation beyond classical hydroformylation/reductive amination.*

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



Scheme 1. Classical and contemporary strategies for the hydroaminomethylation of π-unsaturated reactants.

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 $[HClRu(CO)(PPh_3)_3]$ 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 $[HClRu(CO)(PPh_3)_3]$ 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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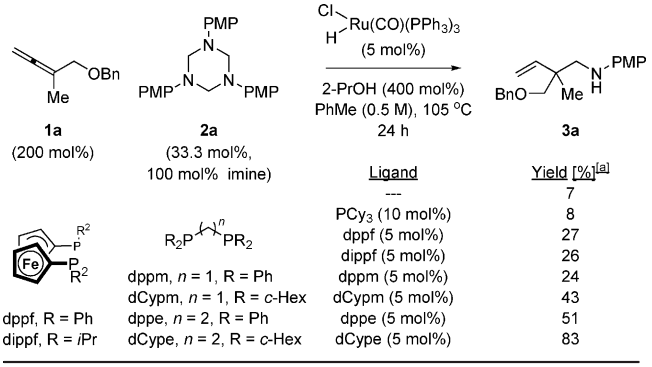
Table 1: Selected ligand-based optimization experiments in the reductive coupling of the allene **1a** with triazine **2a**.[a]



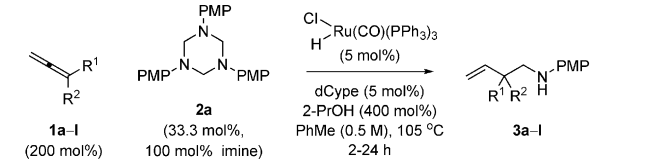
Ligand	Yield [%][a]
---	7
PCy_3 (10 mol%)	8
dppf (5 mol%)	27
dippf (5 mol%)	26
dppm (5 mol%)	24
dCypm (5 mol%)	43
dppe (5 mol%)	51
dCype (5 mol%)	83

dppf, R = Ph; dippf, R = *i*Pr

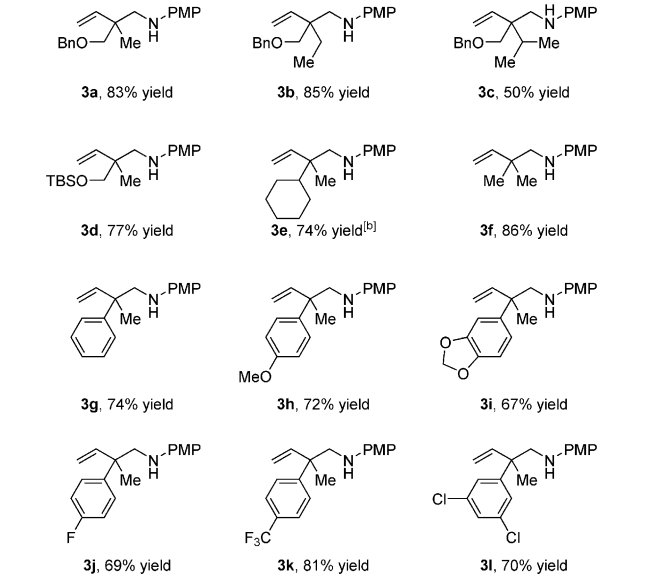
dppm, *n* = 1, R = Ph; dCypm, *n* = 1, R = *c*-Hex; dppe, *n* = 2, R = Ph; dCype, *n* = 2, R = *c*-Hex

[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. PMP = *para*-methoxyphenyl.

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

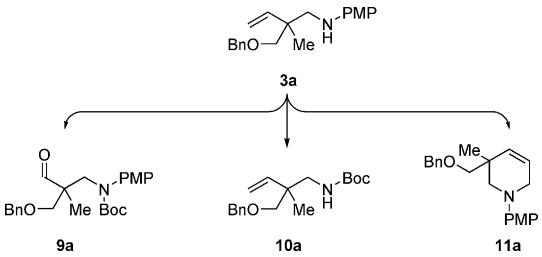


1a, R^1 = Me, R^2 = CH_2OBn; **1b**, R^1 = Et, R^2 = CH_2OBn; **1c**, R^1 = *i*Pr, R^2 = CH_2OBn
1d, R^1 = Me, R^2 = CH_2OTBS; **1e**, R^1 = Me, R^2 = *c*-Hex; **1f**, R^1 = R^2 = Me
1g, R^1 = Me, R^2 = Ph; **1h**, R^1 = Me, R^2 = *p*-$MeOC_6H_4$; **1i**, R^1 = Me, R^2 = benzodioxole
1j, R^1 = Me, R^2 = *p*-FC_6H_4; **1k**, R^1 = Me, R^2 = *p*-$CF_3C_6H_4$; **1l**, R^1 = Me, R^2 = 3,5-$Cl_2C_6H_3$



[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

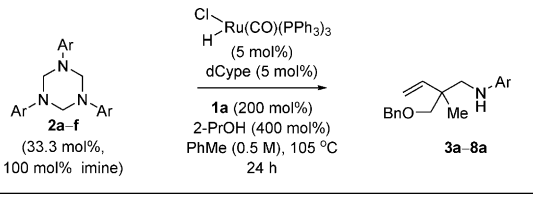


Scheme 2. Selected elaborations of hydroaminomethylation product **3a** to form the compounds **9a**, **10a**, and **11a**. Yields are of material isolated by silica gel chromatography. For **9a**: 1) Boc_2O, Et_3N, DMAP, CH_2Cl_2, 25 °C, 47%. 2) O_3, CH_2Cl_2, −78 °C, 86%. For **10a**: 1) CAN, $MeCN/H_2O$ (1:1), 25 °C, 79%. 2) Boc_2O, Et_3N, CH_2Cl_2, 25 °C, 92%. For **11a**: 1) $BrCH_2CH{=}CH_2$, K_2CO_3, DMF, 25 °C, 88%. 2) Grubbs-II, CH_2Cl_2, 25 °C, 90%. See the Supporting Information for further experimental details. Boc = *tert*-butoxycarbonyl, DMAP = 4-(*N*,*N*-dimethylamino)pyridine, DMF = *N*,*N*-dimethylformamide.

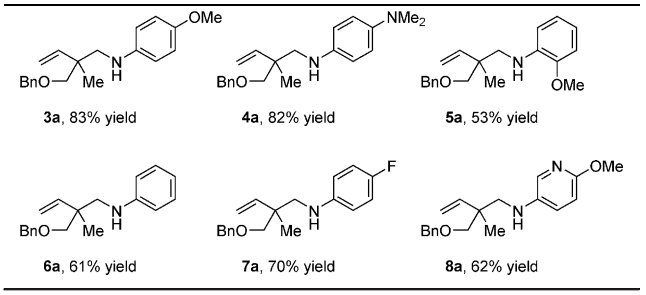
compounds **9a–11a**, which embody diverse functional group arrays (Scheme 2).

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]

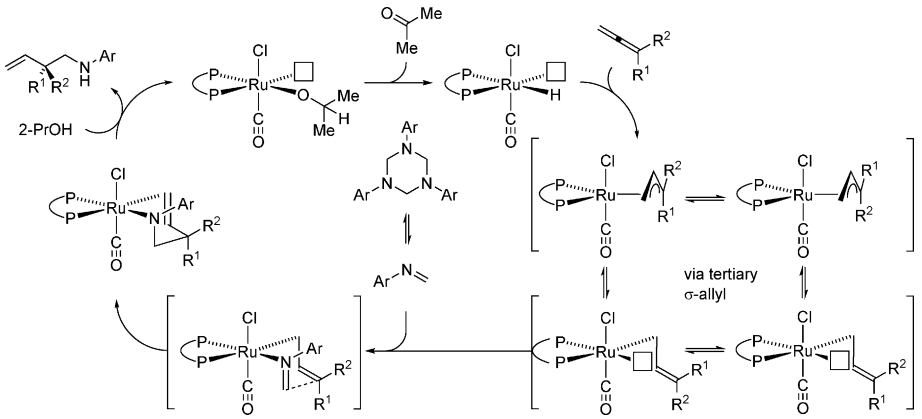


2a, Ar = *p*-$MeOC_6H_4$; **2b**, Ar = *p*-$Me_2NC_6H_4$; **2c**, Ar = *o*-$MeOC_6H_4$
2d, Ar = Ph; **2e**, Ar = *p*-FC_6H_4; **2f**, Ar = 5-(2-MeO-Pyr)



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

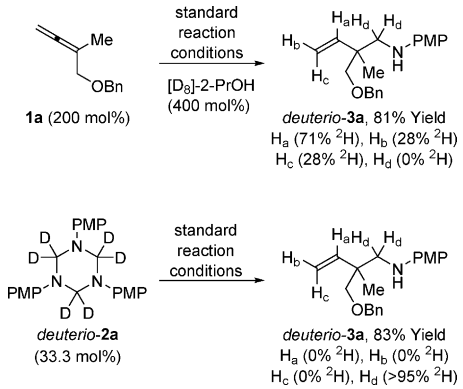
for electron-rich, *para*-substituted *N*-phenyl reactants, as illustrated in the formation of the adducts **3a** and **4a**. Nonetheless, *ortho*-anisidine substituted hexahydro-1,3,5-triazine **2c** delivers the adduct **5a** in moderate yield. Additionally, the parent *N*-phenyl triazine **2d** and *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 $[HClRu(CO)(PPh_3)_3]$ and dCype hydrometallates the allene to form a nucleophilic allylruthenium complex. The stoichiometric reaction of $[HXRu(CO)(PPh_3)_3]$ (X = Cl, 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. Protonolytic 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 $[D_8]$-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 % ^{2}H) 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 % ^{2}H), thus indicating that the C–N bond of the amine product is not subject to reversible dehydrogenation under these reaction conditions.



Scheme 4. Deuterium-labeling experiments.

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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