ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 10022–10024

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COMMUNICATION

Enantioselective hydrovinylation *via* asymmetric counteranion-directed ruthenium catalysis†

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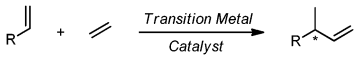
Received 28th April 2011, Accepted 22nd July 2011
DOI: 10.1039/c1cc12499d

The first Ru-catalyzed enantioselective hydrovinylation has been realized by using an asymmetric counteranion-directed catalysis strategy. Styrene derivatives react with ethylene in excellent yields and promising enantioselectivity using this approach.

The hydrovinylation of olefins with ethylene is a highly attractive and perfectly atom economic carbon–carbon-bond forming reaction based on feedstock chemicals (eq (1))[1].



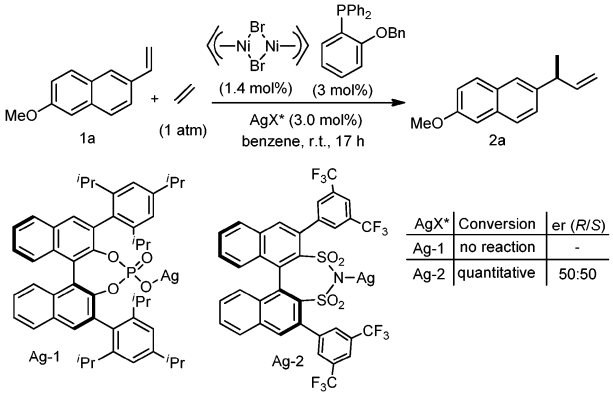
(1)

Typical catalysts are based on nickel[2–5] but cobalt,[6] palladium,[7] and ruthenium complexes[8,9] have also been described. Asymmetric hydrovinylation catalysis goes back to pioneering studies by Wilke *et al.*, who in 1972 used $[(allyl)NiCl]_2$/(−)-dimenthylmethylphosphane/$Et_3Al_2Cl_3$ to catalyze the reaction of 1,3-cyclooctadien with ethylene to 3-vinylcyclooctene in up to 85 : 15 er.[2] The reaction has been significantly advanced in more recent years by studies of Rajanbabu *et al.*,[3] Leitner *et al.*,[4] and Zhou *et al.*,[5] who have provided state of the art enantioselective Ni-catalysts. Herein, we report the first asymmetric hydrovinylation, which is catalyzed by a ruthenium complex. Our approach capitalizes from an asymmetric counteranion directed catalysis strategy and gives promising enantioselectivies in the hydrovinylation of styrene derivatives.

The generally accepted mechanism of the Ni-catalyzed hydronvinylation of styrene suggests involvement of a cationic nickel hydride with a weakly coordinating anion.[3] Insertion of styrene into the Ni–H-bond following coordination of ethylene, its insertion into the Ni–C-bond, and β-hydride elimination, then leads to the product. All steps in this mechanism, including the stereo-determining one, formally involve cationic intermediates, which to us implies the opportunity for the utilization of enantiopure counteranions in an asymmetric counteranion-directed catalysis (ACDC) approach.[10,11]

In our initial studies we have therefore prepared dozens of different Ni-complexes with chiral counteranions. However, quite to our disappointment, these species proved to be either unreactive or did not furnish enantioselectivity in any of the hydrovinylations we have investigated. Two examples shall illustrate this (Scheme 1): subjecting olefin **1a** under an atmosphere of ethylene to a catalyst system comprised of dimeric allyl nickel bromide, (2-(benzyloxy)phenyl)diphenyl-phosphine, and silver phosphate **Ag-1**, did not lead to the formation of even traces of the expected hydrovinylation product. In contrast, when we utilized chiral disulfonimide **Ag-2**, which we have recently introduced in the context of Lewis acid organocatalysis,[12] product **2a** was formed in quantitative yield but with no enantioselectivity. Similar results were obtained with many different Ni-salt/chiral anion/achiral phosphine-combinations.[13]

We next switched our attention to Ru-catalysts. Despite the discovery of ruthenium salt catalysis of hydrovinylation reactions already in 1965,[8] there has not been a single example of an asymmetric variant.[9] Our interest in Ru-based catalysts was spurred by the previous observation of strong counteranion effects in the hydrovinylation, suggesting the possibility of an asymmetric version by incorporating a chiral non-racemic counteranion.[9] In 2001, Yi and co-workers reported a pentavalent ruthenium hydride complex, $RuHCl(CO)(PCy_3)_2$ (**Ru-1**), that promotes the hydrovinylation of olefins with ethylene.[9a] In subsequent years, first Rajanbabu and co-workers and later Connell and co-workers developed cationic variants by combining **Ru-1** with silver salts (Scheme 2).[3f,9e] Inspired by these observations and as a part of our continuing interest in



Scheme 1 Attempts towards an enantioselective hydrovinylation *via* asymmetric counteranion-directed Ni-catalysis.

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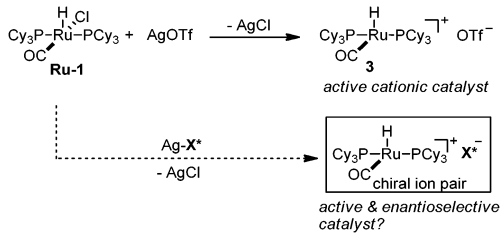
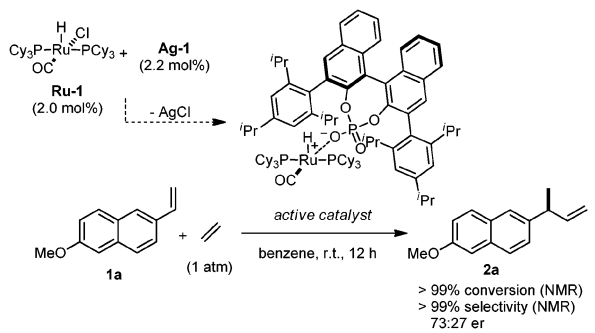
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1cc12499d



Scheme 2 An ACDC strategy for the design of an asymmetric Ru-catalyzed hydrovinylation reaction.

asymmetric-counteranion-directed-transition-metal catalysis,[11] we hypothesized that replacing the chloride anion at the Ru-complex with an enantiopure counteranion to furnish a chiral catalyst might allow for the development of enantioselective Ru-hydrovinylation catalysis. The synthesis of such a chiral Ru-complex was anticipated to be achievable by treating **Ru-1** with a silver salt that bears a chiral counteranion.

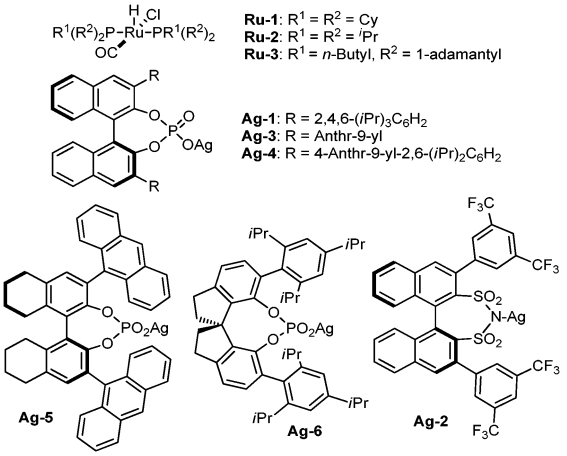
Indeed, initial feasibility studies provided encouragement for our reaction design. Activating complex **Ru-1** (2.0 mol%) with silver phosphate **Ag-1** (2.2 mol%) gave a catalyst for the hydrovinylation of **1a** at room temperature that smoothly yielded the desired product **2a** in excellent yield and with an er of 73 : 27 (eq (2)). The formation of the isomerized product was not observed.



(2)

We next investigated the effect of different phosphine ligands on our Ru-catalyst. During the extensive screening of a variety of phosphine ligands to prepare analogs of **Ru-1**, we found that most of the frequently used phosphine ligands, with the notable exception of triisopropylphosphine and di-(1-adamantyl)-*n*-butylphosphine, are either not suitable for the preparation or the corresponding ruthenium complexes or their complexes are unreactive (for details, see Electronic Supplementary Information (ESI)†). Analogs **Ru-2**[14a] and **Ru-3** can be easily obtained by the treatment of $RuCl_3 \cdot nH_2O$ or $[RuCl_2(COD)]_2$ with triisopropylphosphine and di-(1-adamantyl)-*n*-butylphosphine under the reported conditions, respectively.[14] In the meantime, different chiral phosphates as silver salts, bearing substituents at different positions of the 3,3′-aryl groups, including our recently developed spirocyclic phosphate **Ag-6**,[15] were investigated for the asymmetric hydrovinylation of **1a** with ethylene to **2a** at room temperature in benzene for 12 h. Table 1 shows the details of the screening results. Remarkably, the disulfonimide anion introduced by **Ag-2** fails entirely to produce catalytically active ruthenium complexes, a stark difference to the corresponding

Table 1 Enantioselectivity for the asymmetric hydrovinylation of **1a** with ethylene to **2a** catalyzed by diverse Ru/chiral Ag salts



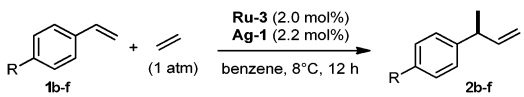
Entry[a]	Ru-cat.	Ag salt	Conv. (%)[b]	Selectivity(%)[b]	er[c]
1	**Ru-1**	**Ag-1**	> 99	> 99	73 : 27
2		**Ag-2**	n.r.	—	—
3		**Ag-3**	> 99	> 99	75 : 25
4		**Ag-4**	97	98	74 : 26
5		**Ag-5**	95	96	74 : 26
6		**Ag-6**	97	97	74 : 26
7	**Ru-2**	**Ag-1**	> 99	> 99	70 : 30
8	**Ru-3**	**Ag-1**	> 99	> 99	77 : 23

[a] Reaction conditions: **1a** (0.2 mmol), ethylene (1 atm), [**Ru**] (2.0 mol%), [**Ag**] (2.2 mol%), benzene (1 mL), 22 °C, 12 h. [b] Determined by ^{1}H-NMR analysis of the crude reaction mixture. [c] Determined by HPLC.

Ni-catalysis (Scheme 1). The best result was obtained with ion-pair catalyst based on **Ru-3** and **Ag-1**, which gave an er of 77 : 23 and > 99% NMR yield (entry 8). Further optimization, which included lowering the temperature, the examination of other solvents, and the study of isocyanide and *N*-heterocyclic carbenes to replace the CO or phosphine-ligand did not lead to further improvements of the enantioselectivity.

Finally, we conducted a small exploration of the substrate scope of our asymmetric hydrovinylation using the best catalyst system (**Ru-3**/**Ag-1**). As illustrated in Table 2, the asymmetric hydrovinylation of styrene derivatives **1b–f** gave

Table 2 Symmetric hydrovinylation of styrene derivatives[a]



Entry	Product (R=)	Conv. (%)[c]	Selectivity (%)[c]	er[d]
1	**2b** (H)	> 99	> 99	68 : 32
2	**2c** (Me)	> 99	> 99	67 : 33
3	**2d** (OMe)	> 99	> 99	67 : 33
4	**2e** (Br)	> 99	> 99	72 : 28
5[b]	**2f** (CO_2Me)	96	96	68 : 32

[a] Reaction conditions: **1** (0.2 mmol), ethylene (1 atm), **Ru-3** (2.0 mol%), **Ag-1** (2.2 mol%), benzene (1 mL), 8 °C, 12 h. [b] At r.t. [c] Determined by ^{1}H-NMR analysis of the crude reaction mixture. [d] Determined by chiral GC or HPLC.

generally quantitative conversion to the desired products **2b–f** in high selectivity but moderate enantioselectivity.

In summary, the first ruthenium-catalyzed asymmetric hydrovinylation has been discovered.[16] The reaction is based on the utilization of our ACDC-strategy. It is interesting to speculate on the role of the anion and the nature and stereochemistry (chiral at Ru) of our actual catalyst complex. Future structural and mechanistic studies are expected to shed light on this fascinating aspect of our reaction. Furthermore, improvements of our catalyst system and additional applications of chiral anions in Ru-catalysis are anticipated.

We thank S. Müller, H. v. Thienen, and S. Liao for providing chiral acids. This work was supported by the Max-Planck-Society.

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