Asymmetric Catalysis

Tandem 1,4-Addition/Enantioselective Protonation Catalyzed by Rhodium Complexes: Efficient Access to α-Amino Acids**

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The 1,4-addition of organometallic reagents (Michael-type additions) to electron-deficient alkenes catalyzed by transition metals has emerged as a powerful tool in organic synthesis for constructing carbon–carbon bonds.[1] Efficient asymmetric versions of this reaction have been developed in which a chiral ligand complexed to a transition metal allows efficient enantioselective introduction of a chiral center in the β position of the unsaturated substrate.[2] Useful examples

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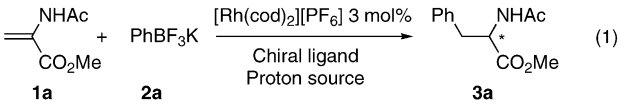
include the asymmetric 1,4-addition of organozinc reagents catalyzed by chiral copper complexes[2,3] and of organoboronic acids and derivatives catalyzed by chiral rhodium complexes.[4] Such carbometalation transformations generate a transient metal enolate, which can further react with electrophiles in a tandem process[5] or more commonly in a two-step process that requires the introduction of the electrophilic partner subsequent to generation of the enolate by carbometalation.[6] It is believed that in these processes the stereochemistry of the generated α center is generally governed by the stereochemistry of the β center. Examples are rare of catalytic asymmetric transformations where the stereochemical outcome is determined at the quenching step of the generated oxa-π-allylmetal intermediate, not at the insertion step of the organometallic reagent[5a,d] (Scheme 1).

Herein we show that conjugate addition of organometallic reagents to *N*-acylamidoacrylate mediated by a chiral rhodium catalyst together with in situ enantioselective protonation[7–10] using achiral phenol derivatives furnishes a variety of α-amino acid derivatives[11] with good to excellent efficiency. A similar approach, but based on radical chemistry, has recently been described by Sibi et al. for radical conjugate additions to α-aminoacrylates[12a] and α-methacrylate[12b] followed by hydrogen atom transfer.

We chose potassium trifluoro(organo)borates as organometallic partners for this tandem 1,4-addition/enantioselective protonation because of their high stability and ease of preparation and purification.[13] Moreover, such compounds have proven to be highly reactive in transition-metal-catalyzed reactions such as cross-coupling reactions[14] and asymmetric 1,4-additions.[15] In particular, we have shown that potassium trifluoro(organo)borates added efficiently to dehydroamino esters to afford racemic non-natural α-amino esters.[16]

We initially tested the feasibility of tandem 1,4-addition/enantioselective protonation by the addition of potassium trifluoro(phenyl)borate (**2a**) to methyl 2-acetylamidoacrylate (**1a**) in the presence of a catalytic amount of the cationic rhodium complex $[Rh(cod)_2][PF_6]$ (cod = cycloocta-1,5-diene) and a chiral ligand [Eq. (1)] using different protonating agents.

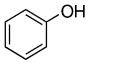
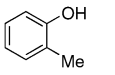
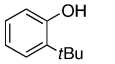
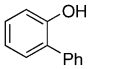
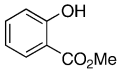
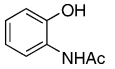
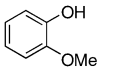
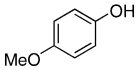
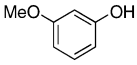


(1)

Disappointing results were obtained using water as the protonating agent of the in situ generated oxa-π-allylrhodium intermediate.[17] The *ee* values were usually below 28%, irrespective of the chiral ligand tested[18] (Table 1, entry 1). Moreover, results were not always reproducible with respect to the level of asymmetric induction obtained. From these results it appeared that water was not able to protonate one face of the rhodium enolate selectively when common chiral ligands were used.[8,9]

Thus, we investigated the use of more-hindered proton sources in this transformation. It appeared that carboxylic acids or sulfonic acids were not suitable and resulted in a blocking of the catalytic cycle,[19] with no Michael addition product observed (entries 2 and 3). However, quantitative conversions were achieved and more significant *ee* values were observed in the presence of phenol derivatives. For example, the α-amino ester **3a** was obtained in 81% yield and 18% *ee* using phenol and (S)-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl ((*S*)-binap) as the chiral ligand (entry 4). Encouraged by this result, a large variety of phenol derivatives were screened to improve the asymmetric induction achieved during the protonation step. It appeared that the *ee* values were highly dependent on the structure of the protonating phenol (Table 1).

Table 1: Effect of the proton source in the 1,4-addition/enantioselective protonation.[a]

Entry	Proton source	Conv. [%][b]	Yield [%][c]	*ee*[d] [%]
1	H_2O	100	quant.	0–28[18]
2	$(Ph)_2CHCO_2H$	0		
3	CSA[e]	0		
4		88	81	18
5		100	63	37
6		39	28	44
7		100	77	69
8		57	36	26
9		69	23	3
10		100	91	83
11		77	75	45
12		100	84	51

[a] Reactions conducted using 0.5 mmol of **1a** and 2 equiv of **2a** with 3 mol% of $[Rh(cod)_2][PF_6]$, and 3.3 mol% of (*S*)-binap in toluene at 110°C for 20 h. [b] Determined by GC analysis. [c] Yields of isolated products. [d] Determined by HPLC analysis using a Daicel Chiralcel OD-H chiral column. [e] Camphor sulfonic acid.

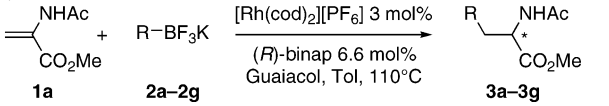
Higher *ee* values were generally achieved with *ortho*-substituted phenols.[20] Moreover, increasing steric hindrance in this position generally resulted in an increase in the *ee* value (entries 4–6). Even though we cannot rationalize the relation between the electronic nature of the *ortho* substituent and the level of asymmetric induction at present, it appeared that the highest *ee* values were generally obtained using moderately chelating substituents (compare entries 7 and 10 with 8 and 9). The reaction was not complete and the *ee* values were generally low when better complexing *ortho* substituents such as CO_2Me (entry 8) or NHAc (entry 9) were used. The highest *ee* values were achieved using inexpensive and nontoxic 2-methoxyphenol (guaiacol), which resulted in

the highly reproducibile formation of α-amino ester **3a** in 91% yield and 83% *ee* (entry 10). Once again the other isomers of methoxyphenol gave a lower level of asymmetric induction, even if they were efficient proton sources (entries 11 and 12).

Despite further optimizations by the screening of various chiral ligands and solvents, no improvements were observed for either the *ee* values or yields; the highest *ee* values were achieved using binap as the chiral ligand and toluene (or dioxane) as the solvent. However, a slight improvement in the *ee* values could be obtained by using two equivalents of chiral diphosphane to one equivalent of rhodium (89.5% *ee* compared to 83% *ee* with 1.1 equivalents of binap).

We tested the generality of the reaction under these optimized conditions ($[Rh(cod)_2][PF_6]$ and 2.2 equivalents of (*R*) or (*S*)-binap as the catalyst precursor in the presence of one equivalent of guaiacol) by treating substrate **1a** with various potassium trifluoro(organo)borates (Table 2).

Table 2: Tandem 1,4-addition/enantioselective protonation of RBF_3K to dehydroamino esters.[a]



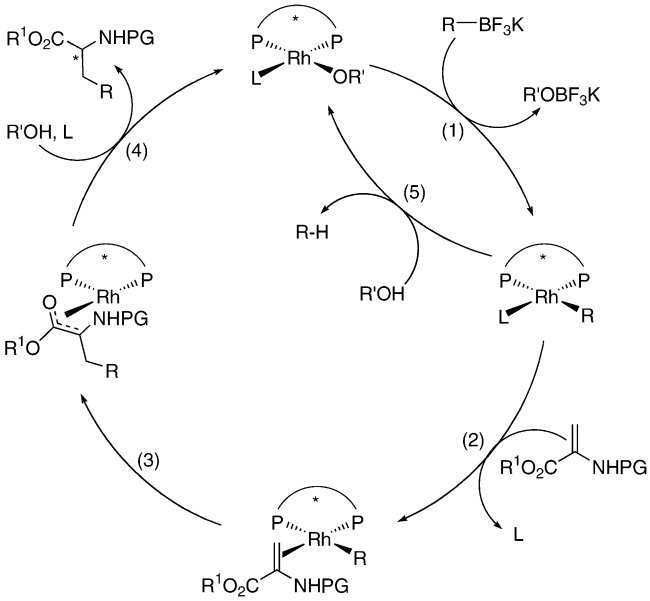
1a **2a–2g** **3a–3g**

Entry	RBF_3K	Product	Yield [%]	*ee*[b] [%]
1	**2a**	**3a**	89	89.5 (*S*)
2	**2b**	**3b**	89	89.5 (*S*)
3	**2c**	**3c**	88	86.5 (*S*)
4	**2d**	**3d**	82	83 (*S*)
5	**2e**	**3e**	75	81 (*S*)
6	**2f**	**3f**	68	81 (*S*)
7	**2g**	**3g**	96[c]	88 (*S*)

[a] Reactions conducted using 0.5 mmol of **1a**, 2 equiv of **2a**, 1 equiv of guaiacol, and 1 equiv of guaiacol with 3 mol% of $[Rh(cod)_2][PF_6]$ and 6.6 mol% of (*R*)-binap in toluene at 110°C for 20 h. [b] Determined by HPLC analysis using a Daicel Chiralcel OD-H column. The absolute configuration was determined by the sign of the optical rotation or HPLC retention time, and is given in parentheses. [c] Isolated as an inseparable mixture with 30% of the 3,4-isomer.

From these preliminary results it appeared that a great variety of aryl alanine derivatives are accessible using this tandem carbometalation/enantioselective protonation process[21] (Table 2). Enantioselectivity ranging from 81 to nearly 90% *ee* was generally achieved. Heterocyclic (entry 6) and functionalized (entry 5) derivatives are also accessible using this strategy; the latter can undergo further cross-coupling reactions to introduce higher diversity. It appeared that alkenyl-substituted alanine derivatives are produced efficiently with good *ee* values and yields from potassium alkenyltrifluoroborates (entry 7), although some isomerization of the double bond was observed, presumably through rhodium-catalyzed double-bound migration. This result represents an interesting feature of this carbometalation since these substrates are not easily accessible,[22] even from efficient asymmetric hydrogenation processes.[23] The absolute configuration of the carbometalation adducts were established by comparison of the sign of the optical rotation or chiral HPLC retention time with those of configurationally assigned compounds. From these results it appeared that products with an *S* configuration were obtained using (*R*)-binap, that is, protonation of the rhodium enolate intermediate takes place on the *Re* face of the amidoacrylate (Scheme 1).

Some general features concerning the mechanism of this transformation may be postulated on the basis of recent work carried out by Hayashi et al.[17] (Scheme 1). The initial step (step 1) should consist of the transmetalation of the organoboron reagent, but we have no evidence that potassium trifluoro(organo)borates directly transmetalate Rh^I species. Preferential coordination of one face of the amidoacrylate (eventually involving a second coordination of the NHAc group), followed by insertion of the R substituent then affords an oxa-π-allylrhodium intermediate (steps 2 and 3). In the last



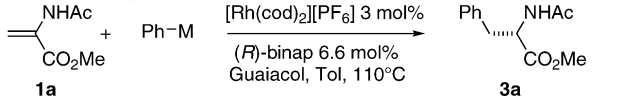
Scheme 1. Proposed reaction mechanism. PG = protecting group.

step (step 4), that is, protonation of the rhodium enolate, proton transfer can occur either by H-transfer from the rhodium center or by external protonation of the enolate, but it is quite evident that steric hindrance and/or coordination of the *ortho* substituent on the phenol plays a key role. Deuterium-labeling as well as computational studies are currently underway to get insights into this protonation step.

Overall, it is important to note that in all the reactions examined, the phenol derivatives not only allowed high *ee* values to be reached but that no reduction of the boron derivative was observed, which is very often a competitive process on protonation with water[4] (Scheme 1, path 5). Moreover, this phenol is easily and quantitatively recovered at the end of the reaction by simple acidification/extraction procedures.

The scope of the present tandem 1,4-additon/enantioselective protonation was further extended by studying the organometallic partner that could carbometalate dehydroamino ester **1a**. Indeed, we tested some other organometallic reagents, such as tin, silicon, and other boron derivatives, under the previously described conditions and using guaiacol as the proton source (Table 3). Of the organoboron compounds tested (entries 1–3) it appeared that only potassium trifluoro(organo)borates were able to transfer their organic moiety with high yields and *ee* values. The 1,4-addition was not efficient (42% yield) with phenylboronic acid **2b** because of competitive reduction (Scheme 1, path 5) and the *ee* value was surprisingly low. This lower asymmetric induction may be explained by the fact that boronic acids can act as competitive proton sources relative to guaiacol and are not able to induce enantiofacial discrimination (Scheme 1). On the other hand, pinacol ester derivative **2c** (entry 3) does not transmetalate rhodium under these conditions, and no 1,4-addition adduct was observed.

Table 3: Other organometallic reagents used in the tandem 1,4-addition/enantioselective protonation.[a]



1a **3a**

Entry	Ph-M	Yield [%]	*ee*[b] [%]
1	$PhBF_3K$ **2a**	89	89.5
2	$PhB(OH)_2$ **2b**	42	42
3	PhBpin[c] **2c**	0	
4	Ph_2SiCl_2 **2d**	0	
5	**2d**/NaF[d]	0	
6	$PhSnBu_3$ **2e**	52	88
7	$PhSnMe_3$ **2f**	89	71

[a] Reactions were conducted using 0.5 mmol of **1a** and 2 equiv of RM with 3 mol% of $[Rh(cod)_2][PF_6]$ and 6.6 mol% of (*R*)-binap in toluene at 110–115°C for 20 h. [b] Determined by HPLC analysis using a Daicel Chiralcel OD-H or OJ column. [c] Bpin: pinacolborane. [d] 1 equiv of NaF was used.

Organosilane **2d** did not react at all, even in the presence of fluoride ions[24] (entries 4 and 5), which are known to favor transmetalation of silicon derivatives to transition metals.[25] In contrast to organoboronic acid derivatives, organostannanes[26] also proved to be suitable in this reaction (entries 5 and 6) and provided α-amino acids in good yields and high enantioselectivities, which were comparable to potassium trifluoro(organo)borates.

We have shown that the concept of rhodium-catalyzed tandem carbometalation/enantioselective protonation is a highly efficient process for the introduction of an organic substituent in the β position of an electron-deficient alkene with concomitant control of the chirality of the α center. In this tandem process, the use of phenol derivatives, and particularly nontoxic and inexpensive guaiacol, as the proton source was crucial for achieving satisfactory levels of enantioselectivity and for the reproducibility of the reaction. This proton source may be easily recovered and completely suppresses the competitive reduction of the organometallic reagent that is usually observed in these rhodium-catalyzed reactions.[4] Application of dehydroamino esters in this reaction allowed access to diversely substituted α-amino esters in high yields and *ee* values (up to 90%) using binap as the chiral ligand.

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[18] Maximum *ee* values obtained with selected ligands: (*S*)-binap (16%), (*S*)-6,6′-dimethoxy-2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl (MeOBiphep, 28%), (*R*,*S*)-(−)-1-[2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (josiphos, 28%), (*S*)-6,6′-dimethoxy-2,2′-bis[di(4-dimethylaminophenyl)-phosphanyl)-1,1′-biphenyl ((*S*)-pDMA-MeObiphep, 11%), (*R*)-6,6′-dimethoxy-2,2′-bis[di(2-furyl)phosphanyl)-1,1′-biphenyl ((*R*)-2-furylMeObiphep, 18%), (*S*,*R*)-1-[2-(dicyclohexylphosphanyl)ferrocenyl]ethyldiphenylphosphane ((*S*,*R*)-Cy_2PFPPh_2, 10%), (*R*)-6,6′-dimethoxy-2,2′-bis[di(3,5-di-*tert*-butylphenyl)-phosphanyl)-1,1′-biphenyl ((*R*)-3,5-*t*BuMeOBiphep, 9%).

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[20] *Ortho*-substituted phenols that are capable of forming chelate complexes have been used successfully in the diastereoselective protonation of enolate intermediates: N. Krause, *Angew. Chem.* **1994**, *106*, 1845 – 1847; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1764 – 1765; review: N. Krause, S. Ebert, A. Haubrich, *Liebigs Ann.* **1997**, 2409 – 2418.

[21] Typical procedure: A septum-capped vial equipped with a magnetic stirring bar was charged with dehydroamino ester **1a** (0.5 mmol, 71.6 mg), potassium (4-bromophenyl)trifluoroborate **2e** (2 equiv, 1 mmol, 263 mg), $[Rh(cod)_2][PF_6]$ (3 mol%, 6.9 mg), and (*R*)-binap (6.6 mol%, 20.6 mg). The vial was closed and evacuated under vacuum and then placed in an argon atmosphere. Degassed toluene (2 mL) and distilled guaiacol (1 equiv, 0.5 mmol, 55 μL) were added and the mixture was stirred in a preheated oil bath at 110–115 °C for 20 h. After cooling the vessel to room temperature, the reaction mixture was purified by column chromatography (ethyl acetate/cyclohexane 3:2) on silica gel to afford **3e** as a white solid (113 mg, 75% yield). $[\alpha]_D^{25} = +79$ ($c = 1.03$, $CHCl_3$). HPLC (M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125 – 10138): Daicel Chiralcel OJ, hexane/propan-2-ol 90/10, 0.5 mL min^{-1}, 215 nm, $t_R = 25.3$ (*S*) and 29.2 min (*R*).

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