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Asymmetric Catalysis

Highly Diastereo- and Enantioselective Palladium-Catalyzed [3+2] Cycloaddition of Vinyl Aziridines and α,β-Unsaturated Ketones**

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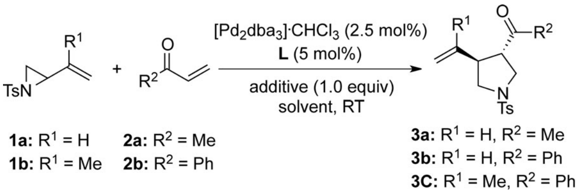
Abstract: *A palladium-catalyzed asymmetric [3+2] cycloaddition reaction of vinylaziridines with α,β-unsaturated ketones, wherein the alkenes have a single activator, is realized in high diastereo- and enantioselectivity, thus affording 3,4-disubstituted pyrrolidines in high yields with excellent ee values. The introduction of a methyl group at C1 of the vinyl group the vinylaziridines greatly improves the stereochemistry of the reaction. A plausible transition state is proposed.*

Transition-metal-catalyzed tandem Michael addition/intramolecular cyclization (intermolecular [3+2] cycloaddition) of vinylaziridines with electron-deficient alkenes provides a general, efficient, and powerful approach for constructing pyrrolidines,[1] an important subunit in natural products and biologically active molecules as well as the building blocks in organic synthesis.[2] Since the pioneering work of Yamamoto on the [3+2] cycloaddition reaction of the electron-deficient alkenes with *N*-tosylvinylaziridines in 2002,[3a] many protocols have been developed.[3–5] Knight et al. disclosed the synthesis of substituted pyrrolidines through a palladium-catalyzed decarboxylative cyclization strategy[3b,c] by using an *N*-sulfonyl-5-vinyloxazolidin-2-one as a vinylaziridine equivalent.[3e] However, the big limitation is that two electron-withdrawing groups are needed for to activate the alkene as a Michael addition acceptor. Moreover, despite generating products with multiple chiral centers, no catalytic asymmetric version of the reaction has been reported for a long time. The breakthrough appeared when Ooi and co-workers reported the first catalytic asymmetric [3+2] cycloaddition reaction of 5-vinyloxazolidinones and electron-deficient alkenes under palladium catalysis,[4] however, alkenes with two activators were still needed. Very recently, Aggarwal and co-workers realized the palladium-catalyzed [3+2] cycloaddition reaction in high diastereoselectivity by using optically active vinyl aziridines with methyl vinyl ketone or ethyl thiolacrylate.[5a] He also successfully applied his methodology to the formal synthesis of (−)-α-kainic acid.[5] Though the highest yield was only 66%, it is the only example of the [3+2] cycloaddition reaction of vinyl aziridines with monoactivated alkenes to date. Unfortunately the enantioselective version of the reaction was not reported. Thus, it is a challenge to realize catalytic asymmetric reaction of vinyl aziridines with alkenes using a single activator. We have been involved with a program of intermolecular cycloaddition of aziridines and oxiranes with unsaturated compounds,[6] and have realized the palladium-catalyzed enantioselective tandem Michael addition/intramolecular cyclization of vinyl epoxides with nitroalkenes.[6b] Further studies revealed that the alkenes with only one activator could be used as a starting material in the palladium-catalyzed enantioselective tandem Michael addition/intramolecular cyclization of vinyl aziridines, thus affording desired products in high yields with high *ee* values. Herein we disclose our preliminary results on this reaction.

Initially, the reaction of vinyl the aziridine **1a** with methyl vinyl ketone (**2a**) in THF in the presence of $[Pd_2dba_3]\cdot CHCl_3/PPh_3$ as the catalyst was studied, but no desired product was afforded (entry 1, Table 1). However, 65% yield of **3a** was obtained when 100 mol% of Bu_4NCl was

Table 1: Investigations on the reaction conditions for palladium-catalyzed [3+2] cycloaddition of the vinylaziridines **1** and vinyl ketones **2**.[a]



(1)

1a: R^1 = H
1b: R^1 = Me
2a: R^2 = Me
2b: R^2 = Ph
3a: R^1 = H, R^2 = Me
3b: R^1 = H, R^2 = Ph
3C: R^1 = Me, R^2 = Ph

Entry	**1**	**2**	**L**	Additive	Yield [%][b]	*trans/cis*[c]	*ee* [%][d]	
							trans	*cis*
1	**1a**	**2a**	PPh_3	–	n.r.	–	–	–
2	**1a**	**2a**	PPh_3	$n Bu_4NCl$	65	1:2	–	–
3	**1a**	**2a**	PPh_3	$n Bu_4NBr$	82	1:1	–	–
4	**1a**	**2a**	**L1**	$n Bu_4NBr$	93	1:2	−14	−13
5	**1a**	**2a**	**L2**	$n Bu_4NBr$	71	3:1	23	−5
6	**1a**	**2b**	PPh_3	$n Bu_4NBr$	44	5:1	–	–
7	**1a**	**2b**	PPh_3	KBr	98	1.5:1	–	–
8	**1a**	**2b**	**L3**	KBr	94	2:1	94	90
9	**1b**	**2b**	**L3**	KBr	78	13:1	92	90

[a] Molar ratio of $[Pd_2dba_3]\cdot CHCl_3$/**L**/**1**/**2**/additive = 2.5:5:100:200:100. Solvent: THF. [b] Yield of isolated product. [c] Determined by H^1 NMR spectroscopy. [d] Determined by HPLC analysis using a chiral stationary phase. A minus sign means that the product has the opposite configuration. dba = dibenzylidene acetone, THF = tetrahydrofuran, Ts = 4-toluenesulfonyl.

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used as an additive (entry 2), according to the Aggarwal protocol.[5a] The yield increased to 82 % when Bu_4NBr was used (entry 3). In both cases, the d.r. of the product was about 1:1, which was not significantly improved when the chiral ligands **L1** and **L2** (Figure 1) were used. With **L1** and **L2** the d.r. value were 1:1 and 3:1, respectively, while the *ee* values were 5 and 23 %, respectively (entries 4 and 5). The d.r. value increased to 5:1 but the yield decreased to 44 % when phenyl vinyl ketone (**2b**), instead of **2a**, was the Michael acceptor under the $[Pd_2dba_3]\cdot CHCl_3/PPh_3/Bu_4NBr$/THF conditions (entry 6). However, the product **3b** was obtained in 98 % yield with 1.5:1 d.r. if KBr was used as the additive (entry 7). From the reaction mechanism,[3] the stereochemistry should be established in the second step and the intramolecular cyclization can be seen as an intramolecular allylic alkylation reaction. Thus, the SIOCPhox ligand developed in our group, with which high diastereo- and enantioselectivities were obtained in the palladium-catalyzed asymmetric allylic alkylation of different nucleophiles, was tested.[7] Indeed, excellent enantioselectivity was afforded, with *ee* values of 90 and 94 % for the *cis* and *trans* diastereomers by using (R_{phos},R_a)-SIOCPhox (**L3**) as the ligand (entry 8). However, the d.r. value was still 2:1 and the yield was 94 %. In the allylic alkylation reaction, the introduction of a substituent at the C2-position of the allyl subunit should increase the steric interactions between the allyl electrophile and nucleophile so as to influence the stereochemical outcome of the reaction. Keeping this in mind, the vinyl aziridine **1b**, with a methyl substituent at C1 of the vinyl group, was used in the reaction. Pleasingly, the reaction of **1b** with **2b** proceeded well to afford the product **3c** in 78 % yield with a 13:1 d.r. and the *ee* value of the major diastereomer being 92 % (entry 9).

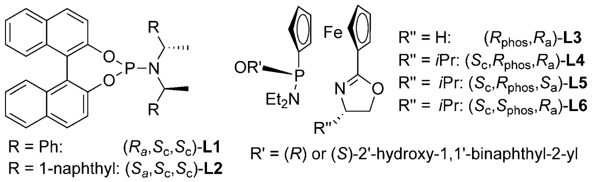


Figure 1. Feringa's ligands and ferrocene-based ligands SIOCPhox.

Encouraged by these results, the impact of the reaction parameters on the reaction shown in Table 1 was investigated further. The results are compiled in Table 2. It can be seen that the reaction with Feringa's ligand ,(R_a,S,S)-**L1**, gave a good yield but almost no diastereoselectivity and very low enantioselectivity (entry 1). Further screening of the ferrocene-based SIOCPhox ligands uncovered that a cycloadduct with a high *ee* value but lower d.r. value was generated when (S_c,R_{phos},R_a)-**L4** was used (entry 3). In contrast, no desired product was obtained by using (S_c,R_{phos},S_a)-**L5** as the ligand and only a low yield of **3c** was afforded when (S_c,S_{phos},S_a)-**L6** was used (entries 4 and 5). These results indicate that both substituents on the oxazoline ring and the combination of chiral elements within the ligands play an important role in the reaction. Several commercially available chiral ligands, including (*S*)-*t*BuPHOX, (S,S_p)-*t*BuFcPHOX, and (*R*,*R*)-DACH-phenyl Trost's ligand, were also examined, however, reaction did not occurred (not shown in table). The screening of the additives indicated that both the potassium cation and bromide anion were vital for the reaction.[8] The absence of KBr led to a sharp decrease of diastereoselectivity and a little reduction of enantioselectivity while the yield was still high (entry 6 versus entry 2). The use of other additives containing either a potassium cation or bromide anion gave inferior results compared with that using KBr (entries 7–11 versus entry 2). Examination of solvent effects revealed that the reaction in THF provided better diastereoselectivity and higher enantioselectivity than those in toluene, CH_2Cl_2, and *N*,*N*-dimethylformamide (DMF; entries 12–14). Lowering the reaction temperature did not improve the stereoselectivity of the reaction significantly (entry 15).

Table 2: Impact of reaction parameters for palladium-catalyzed asymmetric [3+2] cycloaddition of vinylaziridine (**1b**) and phenyl vinyl ketone (**2b**).[a]

Entry	Ligand	Solvent	Additive	Yield [%][b]	*trans*/*cis*[c]	*ee* [%][d]
1	(R_c,S_{phos},S_a)-**L1**	THF	KBr	78	1:1	–
2	(R_{phos},R_a)-**L3**	THF	KBr	78	13:1	92
3	(S_c,R_{phos},R_a)-**L4**	THF	KBr	96	3.5:1	82
4	(S_c,R_{phos},S_a)-**L5**	THF	KBr	n.r.	–	–
5	(S_c,S_{phos},R_a)-**L6**	THF	KBr	20	1.7:1	–
6	(R_{phos},R_a)-**L3**	THF	–	86	7:1	86
7	(R_{phos},R_a)-**L3**	THF	Bu_4NBr	77	17:1	52
8	(R_{phos},R_a)-**L3**	THF	NaBr	73	14:1	86
9	(R_{phos},R_a)-**L3**	THF	CsBr	92	9:1	90
10	(R_{phos},R_a)-**L3**	THF	KI	70	22:1	24
11	(R_{phos},R_a)-**L3**	THF	KCl	83	8:1	88
12	(R_{phos},R_a)-**L3**	toluene	KBr	98	4.6:1	72
13	(R_{phos},R_a)-**L3**	CH_2Cl_2	KBr	95	5:1	70
14	(R_{phos},R_a)-**L3**	DMF	KBr	68	8:1	40
15[e]	(R_{phos},R_a)-**L3**	THF	KBr	65	13:1	94

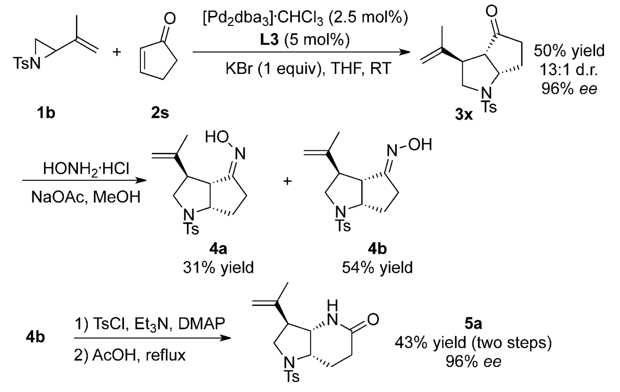
[a] Molar ratio of $[Pd_2dba_3]\cdot CHCl_3$/**L**/**1b**/**2b**/add. = 2.5:5:100:200:100. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] Determined for the *trans* isomer by HPLC using a chiral stationary phase. [e] Reaction run at 0 °C.

The substrate scope of the reaction was examined under the optimized reaction conditions and the results are shown in Table 3. A wide range of vinyl ketones (**2**), not only aromatic and heteroaromatic, but also aliphatic ketones are suitable Michael acceptors and provide the corresponding pyrrolidines **3** in high yields with high d.r. and *ee* values. When the R group of the vinyl ketones **2** is an electron-rich aromatic ring, the reaction proceeded smoothly to afford the corresponding pyrrolidines (**3b**–**h**) in high yields with high diastereo- and enantioselectivities (entries 2–6), and when the R group is an electron-deficient aromatic ring, the corresponding adducts (**3i**–**n**) were obtained in good yield with 75–88 % *ee* and 5.6:1–20:1 d.r. (entries 7–12). The reaction of **2n**, having a bulkier naphthyl group, also proceeded efficiently to afford the product **3o** in 90 % yield with 25:1 d.r. and 89 % *ee* (entry 13). The heteroaromatic ketone **2r** was a suitable substrate (entry 18). Noticeably, the reaction of the alkyl vinyl ketones **2** also provided the products **3p**–**s** in 72–85 % yield along with greater than 95 % *ee* and 19:1–30:1 d.r. (entries 14–17).The substituent R^1

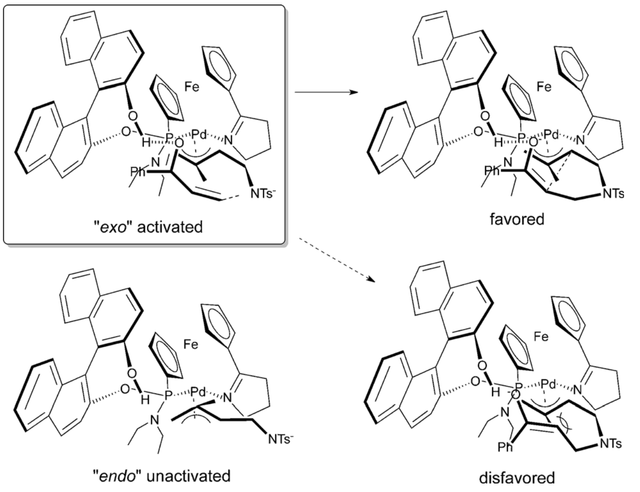
Table 3: Substrate scope for the palladium-catalyzed asymmetric [3+2] cycloaddition of the vinylaziridines **1** and vinyl ketones **2**.[a]

Entry	R^1 (**1**)	R^2 (**2**)	Yield [%][b]	*trans*/*cis*[c]	*ee* [%][d]
1	Me (**1b**)	Ph (**2b**)	78 (**3c**)	13:1	92
2	Me (**1b**)	*p*-MeC_6H_4 (**2c**)	86 (**3d**)	11:1	95
3	Me (**1b**)	*o*-MeC_6H_4 (**2d**)	89 (**3e**)	21:1	94
4	Me (**1b**)	*p*-$MeOC_6H_4$ (**2e**)	88 (**3f**)	14:1	96
5	Me (**1b**)	*o*-$MeOC_6H_4$ (**2f**)	84 (**3g**)	12:1	97
6	Me (**1b**)	*m*-$MeOC_6H_4$ (**2g**)	85 (**3h**)	7.5:1	92
7[e]	Me (**1b**)	*p*-FC_6H_4 (**2h**)	75 (**3i**)	6.3:1	82
8[e]	Me (**1b**)	*p*-ClC_6H_4 (**2i**)	88 (**3j**)	5.6:1	79
9	Me (**1b**)	*p*-BrC_6H_4 (**2j**)	90 (**3k**)	8:1	75
10	Me (**1b**)	*m*-BrC_6H_4 (**2k**)	90 (**3l**)	7.7:1	85
11	Me (**1b**)	*o*-BrC_6H_4 (**2l**)	85 (**3m**)	20:1	85
12	Me (**1b**)	*p*-$CF_3C_6H_4$ (**2m**)	87 (**3n**)	9:1	77
13	Me (**1b**)	2-naphthyl (**2n**)	90 (**3o**)	25:1	89
14[f]	Me (**1b**)	Me (**2a**)	85 (**3p**)	23:1	95
15	Me (**1b**)	Et (**2o**)	78 (**3q**)	19:1	97
16	Me (**1b**)	*n*-pentyl (**2p**)	72 (**3r**)	30:1	99
17	Me (**1b**)	cyclohexyl (**2q**)	75 (**3s**)	20:1	98
18	Me (**1b**)	2-furanyl (**2r**)	72 (**3t**)	14:1	63
19	Et (**1c**)	Ph (**2b**)	98 (**3u**)	7:1	91
20	H (**1a**)	Ph (**2b**)	94 (**3b**)	2:1	94 (90)[g]
21	*i*Pr (**1d**)	Ph (**2b**)	99 (**3v**)	2.1:1	82 (91)[g]
22	Ph (**1e**)	Ph (**2b**)	83 (**3w**)	2.5:1	82

[a] Molar ratio of $[Pd_2dba_3]\cdot CHCl_3$/**L3**/**1**/**2**/KBr = 2.5:5:100:200:100, solvent: THF, reaction time: 12 h. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy. [d] Determined for the *trans* isomer by HPLC using a chiral stationary phase. [e] Run at 0 °C. [f] KBr was not added. [g] The *ee* value for the *cis* isomer.



Scheme 1. Palladium-catalyzed asymmetric [3+2] cycloaddition of the vinylaziridine **1b** and 2-cyclopentenone (**2s**). Transformations of the product **3x**. DMAP = 4-(*N*,*N*-dimethylamino)pyridine.



Scheme 2. Proposed working model for the enantioselection.

of the vinyl aziridines **1** greatly affects the diastereoselectivity (entries 19–22). The reaction afforded the product **3u** in high yield with high d.r. and *ee* values when R^1 was Et (entry 19), and the pyrrolidines **3b**, **3v**, and **3w** were obtained in high yields with high *ee* values but lower d.r. values when R^1 was H, Ph, and isopropyl, respectively (entries 21–23).

Additionally, 2-cyclopentenone (**2s**) was also a suitable substrate for this asymmetric [3+2] cycloaddition, thus giving the adduct **3x** in 50% yield with 13:1 d.r. and 96% *ee* (Scheme 1). The compound **3x** reacted with hydroxylamine to afford the *Z*-oxime **4a** and *E*-oxime **4b** in 31 and 54% yield, respectively. Protection of the **4b** with a tosyl group and subsequent Beckmann rearrangement in the presence of acetic acid afforded the bicyclic compound **5a** with 96% *ee* and in 43% yield over two steps. 2-Cyclohexenone and 2-cycloheptenone were also tested under the same reaction conditions, however, no reaction occurred. Probably the ring tension of the five-membered ring **2s** favors the reaction.

The absolute configuration of the product **3k** was determined to be 3*S*,4*R* by the X-ray diffraction analysis of its single crystal.[9] On the basis of the absolute configuration of **3k**, together with the palladium-catalyzed allylic tandem reaction, a working model was tentatively proposed to explain the diastereo- and enantioselectivities of the reaction (Scheme 2). The tosyl-protected nitrogen anion attacks the vinyl ketone to form an enolate intermediate, which then attacks the π-allyl palladium complex. According to the X-ray diffraction analysis of (π-phenylallyl)Pd complexed with **L3**,[10] the *exo* transition state should be favored, while the *endo* transition state is disfavored. Perhaps the presence of the hydroxy group of the ligand favors the formation of the *exo* intermediate while KBr plays the role in promoting the conversion of **1** into the intermediate.[8b,c] In contrast, we suppose that the methyl group at C2 of the allyl subunit plays a significant role in promoting the diastereoselectivity. To avoid the steric congestion with methyl group, the enolate approaches the π-allyl palladium from the other side. However, replacing the methyl with ethyl, isopropyl, or hydrogen, will lead to a sharp decrease in diastereoselection. Maybe it is due to the rotation of these groups reducing the difference of two sides. Further investigations are needed to improve our understanding of the transition state as well as the reaction mechanism.

In conclusion, we have successfully developed a palladium-catalyzed asymmetric [3+2] cycloaddition reaction of vinylaziridines with alkenes, having a single activator, in high diastereo- and enantioselectivity. The significant influence of substituents on the vinyl group of the aziridines was explored. This information should be useful for similar reactions of vinyl oxiranes and vinyl cyclopropanes with activated alkenes. Additional studies on the reactions of three-membered rings,

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with appended vinyl groups, and activated alkenes, as well as their applications in organic synthesis are underway.

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[9] The deposition number of compound **3k**: CCDC 1032989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For its structural detail, see the Supporting Information.

[10] CCDC 1033402 (complex (π-phenylallyl)Pd(R_{phos},R_{a})-**L3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For its structural details, see the Supporting Information.

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