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Review

Enantioselective Heck reactions using chiral P,N-ligands☆

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Abstract

Palladium complexes with chiral phosphinooxazoline ligands are efficient catalysts for enantioselective Heck reactions with aryl or alkenyl triflates and cyclic olefins. In the arylation and alkenylation of 1,2-dihydrofuran, cyclopentene, 2,3-dihydro-4*H*-pyran, 4,7-dihydro-1,3-dioxepin, and *N*-methoxycarbonyl-2,3-dihydropyrrole high yields and good to excellent enantioselectivities have been obtained. In contrast to palladium-BINAP catalysts, the catalysts derived from phosphinooxazolines show a very low tendency to promote isomerization of the product by C–C double bond migration.

Keywords: Asymmetric catalysis; Oxazolines; Palladium; P,N-ligands

1. Introduction

The first examples of what today is called the Heck reaction were reported more than 25 years ago [1]. The pioneering work by Heck and his group [2] clearly demonstrated the potential of this new catalytic method and paved the way for further developments. Thanks to the efforts of numerous academic and industrial research groups, the Heck reaction has become one of the most versatile catalytic methods for C–C bond formation [3]. Its use as a key step in complex organic syntheses as well as the development of enantioselective versions are exciting results of recent research.

The generally accepted mechanism of the Heck reaction is shown in Scheme 1 [3,4]. In the overall process an aryl or alkenyl halide or triflate is coupled with an olefinic substrate and as a result a new C–C bond is formed by replacing an olefinic hydrogen atom with a carbon substituent. The catalytic cycle starts with the oxidative addition of the organic halide or triflate to a Pd(0) complex (step 1), followed by insertion of the olefin into the Pd–C bond of the intermediate σ-aryl or σ-alkenyl-palladium(II) complex (step 2). The resulting alkyl palladium(II) complex undergoes β-hydride elimination leading to a hydrido-palladium olefin complex (step 3). Dissociation of this π-complex leads to the product and a hydrido-palladium species (step 4). Finally, the catalytically active Pd(0) complex is regenerated by reductive elimination of HX (step 5). Depending on the structure of the substrate, several isomeric products can be formed in step 3. If the C–C double bond is restored in the original position (path a), no additional stereogenic center is created in the overall process. However, if β-hydride elimination takes a different direction (path b), the stereogenic C atom introduced in the insertion step is retained. In this case, the use of chiral palladium complexes makes it possible to carry out such reactions in an enantioselective manner.

The reaction sequence leading from the σ-alkyl-palladium intermediate to the final product is often complicated by *E*/*Z*-isomerization through reversible β-hydride elimination and re-insertion reactions and by migration of the C=C bond along the carbon skeleton of the product.

☆ Dedicated to Professors Richard F. Heck and Jiro Tsuji in recognition of their fundamental contribution to organopalladium chemistry and synthetic methodology.

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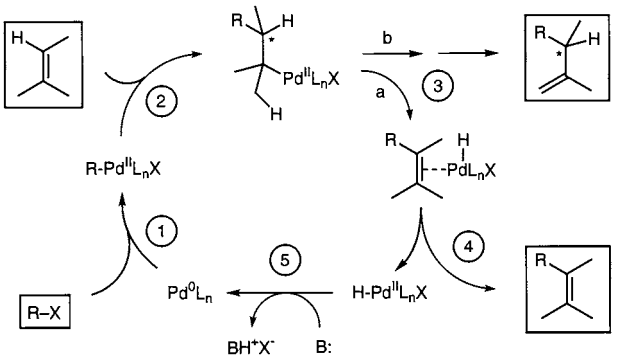


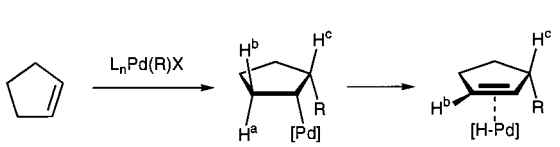
Scheme 1.

A plausible mechanism for this double bond migration involves re-insertion of the olefin into the Pd–H bond of the intermediate hydrido-palladium olefin complex with inverse regioselectivity followed by β-hydride elimination in the opposite direction.

The addition of the aryl- or alkenyl-palladium intermediate to the olefin (step 2) and the subsequent β-hydride elimination (step 3) both occur in a *syn* fashion. Thus, after the oxidative addition, the intermediate has to change its conformation in order to bring the Pd and the β-H atom in the required *syn* arrangement. In intermolecular Heck reactions with acyclic olefins several isomers may be formed because rotation around the C–C bonds adjacent to the Pd atom can generate several conformations with the prerequisite *syn* geometry for β-hydride elimination. Therefore, such reactions are often difficult to control and can lead to complex mixtures unless one specific pathway is favored by steric or electronic factors.

The situation is simpler if cyclic olefins are used as substrates (Scheme 2). In this case, oxidative addition leads to a geometrically defined σ-alkyl-palladium complex. Only one of the β-H atoms (H^a) is in the *syn* position required for β-hydride elimination. Therefore, the double bond is formed exclusively in the direction away from the R substituent and, consequently, the stereogenic center introduced in the previous step is retained. Thus, cyclic substrates are attractive candidates for the development of enantioselective variants of the Heck reaction. This has been recognized by Hayashi and coworkers who were the first to report enantioselective reactions of this type and in some cases obtained remarkably high ee's [5].

One of the reactions studied by Hayashi et al. [5], the coupling of phenyl triflate with 2,3-dihydrofuran, is shown in Scheme 3. Starting from a Pd(BINAP) catalyst, the intermediate phenyl-palladium complex adds regio- and enantioselectively to the C=C bond. For geometric reasons, the subsequent β-hydride elimination takes place exclusively at C(4) leaving the stereogenic center at C(2) intact. Under the reaction conditions, the C=C bond migrates by re-insertion into the Pd–H bond with reversed regioselectivity followed by β-hydride elimination to give the thermodynamically more stable 2,3-dihydrofuran derivative **2**. This double bond migration was found to involve kinetic resolution and, therefore, 2-phenyl-2,3-dihydrofuran (*R*)-**2**, which was the main product in this case, was obtained with high ee, even though the initial insertion of dihydrofuran into the palladium-phenyl bond proceeded only with moderate enantioselectivity. The extent of double bond migration, and consequently the product ratio **1**/**2** and the ee's depend on the reaction conditions, particularly on the nature of the base. Interestingly, in the analogous reaction with alkenyl triflates (cf. Scheme 4) [5b] the enantioface selection in the addition of the alkenyl-palladium intermediate to dihydrofuran is much higher and the corresponding 2-alkenyl-2,3-dihydrofuran derivatives can be obtained in high enantiomeric purity, even though no kinetic resolution process is observed in this case. Under the conditions shown in Scheme 4, the reaction leads exclusively to the more stable 2,3-dihydro derivative **3** whereas the 2,5-dihydro isomer is not observed.

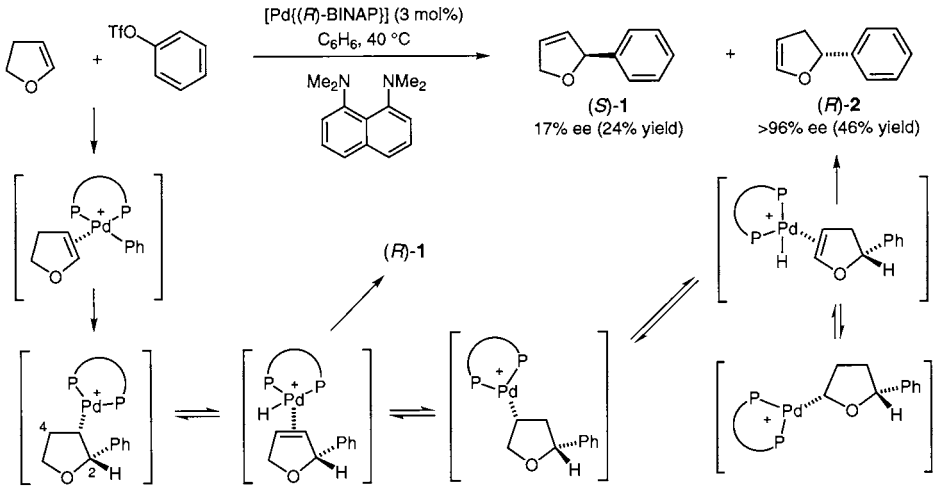


Scheme 2.

Scheme 3 illustrates that the reaction course can be quite complex involving several consecutive insertion and β-hydride elimination steps (see also [4]). Depending on the substrate structure, many different pathways leading to different isomers are possible. Therefore, it is not surprising that the enantioselectivity, the number of products and ratios of isomers can strongly depend on the nature of the base, the solvent, and other reaction parameters. Thus, the development of new enantioselective Heck reactions often requires extensive screening and optimization of many different variables.

Intramolecular Heck reactions also offer attractive possibilities for enantioselective transformations. In contrast to intermolecular reactions, the formation of quaternary asymmetric carbon atoms is possible in this case. In addition, the defined geometry of cyclic intermediates often controls the regioselectivity of both the oxidative addition and the subsequent β-hydride elimination. Shibasaki and Overman, the pioneers and leaders in this field, have reported remarkable examples of highly enantioselective intramolecular Heck reactions and have convincingly demonstrated the value of such transformations in the synthesis of complex natural products [3h,i,6].

When we started our work in this field, the only effective chiral ligand, that had been used for enantioselective inter- and intramolecular Heck reactions, was BINAP [7]. Although this versatile diphosphine ligand often allows very effective enantiocontrol, there are many cases where Pd–BINAP catalysts do not provide satisfactory results. In order to enhance the scope of

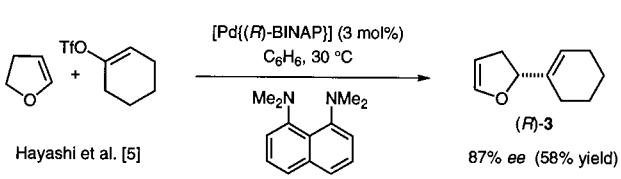


Scheme 3.

enantioselective Heck reactions, a search for other chiral ligands and catalysts is necessary. In the course of our work on phosphinooxazolines **4** [8], which have proven to be effective ligands for enantioselective palladium-catalyzed allylic alkylations [9–11], we decided to test if these ligands could be used for enantiocontrol in Heck reactions [12].

2. Phosphinooxazolines as chiral ligands in Heck reactions

The first experiments were quite encouraging. In the reaction of 2,3-dihydrofuran with 1-cyclohexenyl triflate we obtained up to 95% ee and good yields of the product (*R*)-**5**, using 3 mol% of catalyst prepared from $[Pd_2(dba)_3{\cdot}CHCl_3]$ (dba = dibenzylidene-acetone) and ligand **4c** (cf. Table 1). However, we had difficulties reproducing the ee values and yields which fluctuated from experiment to experiment. Eventually, we found chloroform, which was present as a crystal solvent in the commercially available Pd–dba complex used as catalyst precursor, to be the cause of this problem. With the analogous chloroform-free complex $[Pd_2(dba)_3{\cdot}(dba)]$ [13], high ee's of 98% and almost quantitative yields were obtained with very good reproducibility. Possibly, the chloroform undergoes oxidative addition under the reaction conditions affecting the performance of the catalyst [14]. In general, the catalyst



Scheme 4.

was found to be highly sensitive to halide ions. No reaction was observed in the presence of Et_4NCl or with a catalyst generated from [(**4c**)$PdCl_2$] and BuLi. For the same reason, aryl or alkenyl halides could not be used as substrates even in the presence of silver salts. In some reactions, $Pd(OAc)_2$ was used as a catalyst precursor and essentially the same enantioselectivities and yields were obtained as with $[Pd_2(dba)_3{\cdot}(dba)]$.

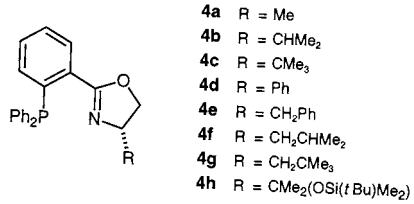
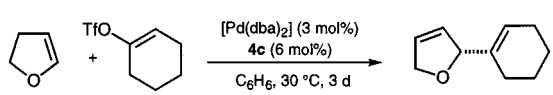


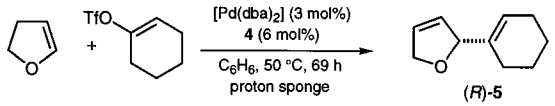
Table 1
Influence of the base



Base	Enantioselectivity (% ee)	Yield (%)[a]
1,8-Bis(dimethylamino) naphthalene	98	95
2,2,6,6-Tetramethylpiperidine	99	95
Triethylamine	>99	78
N,*N*-Diisopropylamine	>99	92
N,*N*-Diisopropylethylamine	99	98[b]
Sodium carbonate	98	34
Sodium acetate	98	50

[a] Determined by GC with *n*-tridecane as standard.
[b] Yield of purified product: 92%.

Table 2
Ligand screening



Ligand	R	Enantioselectivity (% ee)	Conversion (%)[a]
4e	CH_2Ph	90	24
4f	CH_2CHMe_2	95	18
4g	CH_2CMe_3	98	25
4c	CMe_3	98	95

[a] Determined by GC with n-tridecane as internal standard.

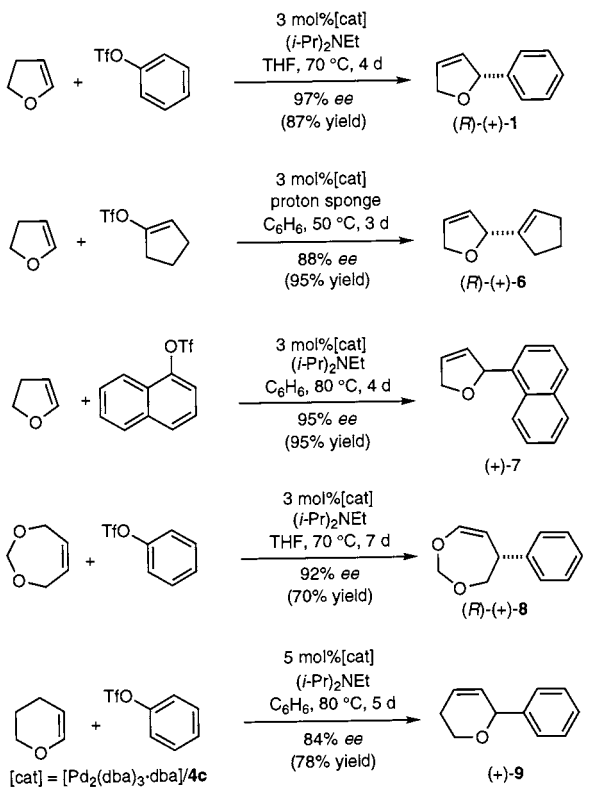
The reaction between 2,3-dihydrofuran and 1-cyclohexenyl triflate was chosen to screen different bases and ligands and to optimize the reaction conditions [12]. The influence of the base is shown in Table 1. While in the reactions with Pd(BINAP) catalysts, 1,8-bis-(dimethylamino)naphthalene (proton sponge) was the preferred base for optimum results [5b], in our case simpler bases such as triethylamine or *N*,*N*-diisopropylethylamine proved to be equally or even slightly more effective. Usually, one-and-a-half to two equivalents of ligand **4c** were used. With just one equivalent (3 mol% **4c**, 3 mol% [$Pd_2(dba)_3$·dba]) the ee's and yields were slightly lower (98 versus 99% ee, and 85 versus 95% yield).

The substituent at the stereogenic center of the oxazoline ligand has a distinct influence on the reactivity of the catalyst. The catalyst derived from the *tert*-butyloxazoline ligand **4c** gives $>90\%$ conversion after 2–3 days at 30–50°C or 1 day at 80°C. At 80°C the ee is slightly lower than at 50°C (96 versus 98% ee). Interestingly, with phosphinooxazolines containing less bulky groups at the stereogenic center, the reaction is much slower as reflected by the low conversion (Table 2). With ligand **4h**, containing a larger substituent, the reaction rate was twice as fast as with the *tert*-butyl derivative **4c** while the ee was almost the same [15]. The same trend was also observed with other substrates. These findings were unexpected because steric hindrance near the metal center often slows down a metal-catalyzed process and no obvious explanation can be offered at this stage.

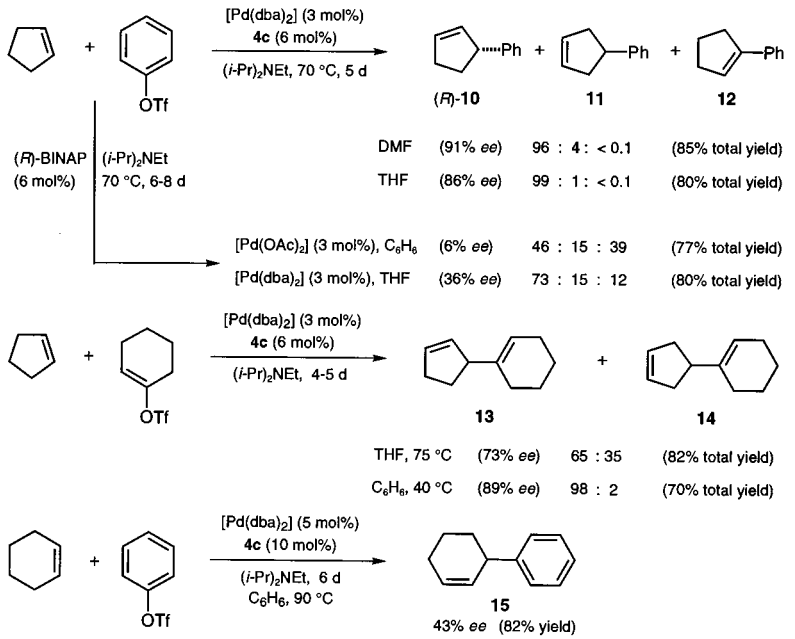
Reactions on a preparative scale confirmed the results of the screening experiments. Using 3 mol% of catalyst, prepared in situ from [$Pd_2(dba)_3$·dba] and 5–6 mol% of ligand **4c**, the 2,5-dihydrofuran derivative (*R*)-**5** was isolated in $>90\%$ yield and with excellent enantioselectivity. The corresponding 2,3-dihydrofuran derivative **3**, which is formed as the sole product in the Pd(BINAP)-catalyzed reaction (Scheme 4) [5b], was not detected. The reason for this striking difference between the BINAP- and the phosphinooxazoline-derived catalysts is not clear. Possibly, the π-complex between the phosphinooxazoline-palladium hydride and the olefin, which is formed after the first β-hydride elimination, is less stable than the corresponding BINAP-derived complex. Therefore, dissociation of the π-complex to the product **5** is faster than insertion of the olefin into the Pd–H bond (cf. Scheme 3).

Similar results were obtained with phenyl, 1-naphthyl and 1-cyclopentenyl triflate (Scheme 5). Arylation of 4,7-dihydro-1,3-dioxepin, which leads to a masked hydroxy-aldehyde, also proceeds with good enantioselectivity and satisfactory yield. The corresponding Pd(BINAP)-catalyzed process [16] was reported to give 72% ee and 84% yield in this reaction. Dihydropyran proved to be less reactive than dihydrofuran but at somewhat higher temperature also gave the desired product in good yield with 84% ee. With BINAP, a 3:2 mixture of 5,6- and 3,6-dihydro-2-phenyl-2*H*-pyran was formed with low enantioselectivity ($<20\%$ ee for both isomers).

The low tendency of Pd(phosphinooxazoline) catalysts to promote C–C double bond migration makes it possible to use substrates such as cyclopentene which are converted to mixtures of isomers with Pd(BINAP) catalysts (Scheme 6). The observed product distribution is dependent on the solvent and the base. The best ee's and highest conversions and yields were obtained in polar solvents such as DMF, DMF:H_2O (9:1),



Scheme 5.



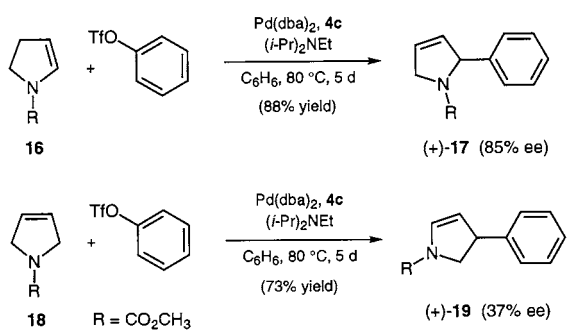
Scheme 6.

methanol, THF or 1,4-dioxane. THF and dioxane gave somewhat lower ee's (84–86% ee) but less C=C bond migration (**10**:**11** 99:1) than DMF or methanol. In benzene, both the enantioselectivity (82% ee) and conversion were lower than in the other solvents. Under optimized conditions, the desired chiral 3-substituted cyclopentene derivatives **10** and **13** were obtained in good yield and with high preference over the corresponding achiral isomers **11** and **14**. Other isomers such as **12** are formed only in trace amounts under these conditions, in contrast to the corresponding Pd(BINAP)-catalyzed reactions which lead to complex mixtures of isomers and low ee's due to extensive double bond migration. Ligands **4a**, **4b** and **4d**–**g** all gave low conversion and lower ee's (60–70%) than the standard ligand **4c**. Cyclohexene is less reactive and has to be heated to 90°C for 6 days to achieve full conversion. Under these conditions the desired product **15** is formed in good yield but with low ee.

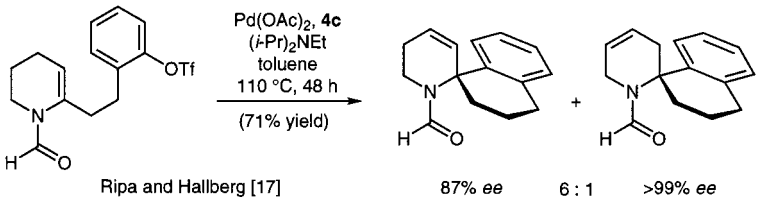
The reaction of the 2,3-dihydropyrrole derivative **16** with phenyl triflate also requires prolonged heating at relatively high temperature (Scheme 7). However, in this case the arylation product **17** can be obtained with an ee of 85% in good yield. The corresponding 2,3-dihydro isomer is not detected, whereas under similar conditions with a catalyst prepared from $Pd(OAc)_2$ and BINAP, the 2,3-dihydro isomer is formed as the main product in 68% yield with 74% ee while the minor isomer **17** is isolated in 27% yield with 27% ee. The analogous reaction of the 2,5-dihydropyrrole derivative **18** gives much lower enantioselectivity.

We have not studied any intramolecular Heck reactions. However, Ripa and Hallberg [17] have recently reported a palladium-catalyzed cyclization leading to a spiro ring system with high enantioselectivity in good yield, using the phosphinooxazoline **1c** as chiral ligand (Scheme 8). BINAP proved to be ineffective in this case.

A mechanistic rationalization of the observed selectivities seems premature because experimental data on the structure, relative stability, and reactivity of the intermediates in the catalytic cycle are still lacking. At present, we do not know if the enantioselectivity-determining step, the insertion of the olefin into the Pd–C bond, involves *cis* or *trans* coordination of the C=C bond relative to the P atom.



Scheme 7.



Scheme 8.

3. Other P,N-ligands

The effectiveness of phosphinooxazoline ligands in the reactions discussed above suggested that further investigation of related P,N-ligands could be profitable. Therefore, we tested the pyridine- and quinoline-derived ligands **20** and **21** [18] which we had synthesized in connection with another project. The design of these ligands was based on a study by Moberg et al. [19] who found a remarkably strong conformational preference of 2-(halomethyl)- and 2-(oxymethyl)pyridines for an *anti* arrangement of the N–C(2) and the C–X bond with a N–C–C–X dihedral angle of 180°. Assuming such a conformational preference for the phosphinoethyl-pyridine and -quinoline derivatives **20** and **21**, force field calculations suggest that the coordination geometry and the conformation of the diphenylphosphino group in metal complexes of these ligands and the phosphinooxazolines **4** are very similar. The steric and electronic properties of the pyridine or quinoline ring, on the other hand, differ strongly from those of the oxazoline ring. Therefore, we thought that pyridine- and quinoline ligands of this type could be a useful addition to the oxazoline-derived P,N-ligands.

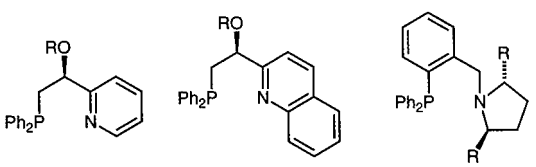


Table 3 shows some representative results obtained with ligands **20** and **21** [18]. With both the quinoline and the pyridine derivatives, high enantioselectivities could be achieved. Interestingly, the structure of the remote silyl group has a small but significant influence on the enantioselectivity. The reaction rates are similar to those observed with phosphinooxazoline-palladium complexes. Although the 2,5-dihydrofuran derivative **1** is still the main product, double bond migration does occur to some extent. The ratio between products **1** and **2** depends on the base and the reaction temperature.

A different class of P,N-ligands, the C_2-symmetric pyrrolidine derivatives **22** with a coordinating sp^3 N-atom, has been tested by Guiry et al. [20]. In the Heck reaction of 2,3-dihydrofuran with phenyl triflate, palladium catalysts prepared from these ligands proved to be considerably less reactive than analogous phosphinooxazoline complexes. At ambient temperature the 2,5-dihydro-isomer (*R*)-1 (cf. Table 3) was formed exclusively and with high enantioselectivity (>90% ee) using ligand **22b**. However, the reaction was very slow and even after several days conversion was low. At higher temperatures mixtures of the 2,5- and 2,3-dihydro-isomers (*R*)-1 and (*R*)-2 were formed in low enantiomeric purity.

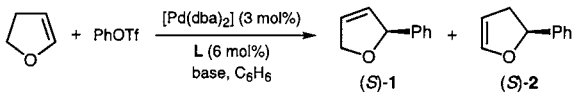
4. Conclusions

The high enantioselectivities obtained with phosphinooxazolines indicate a considerable scope for P,N-ligands in enantioselective Heck reactions. Because of the low extent of C–C double bond migration observed with these ligands, the product distribution can differ substantially from analogous Pd(BINAP)-catalyzed reactions. Thus, with certain substrates like 2,3-dihydrofuran, different isomers can be prepared selectively with high ee using either BINAP or phosphinooxazolines as ligands. In cases, where double bond migration leads to undesired mixtures of isomers or racemization, phosphinooxazolines are clearly superior to diphosphine ligands. Although at present, other P,N-ligands cannot compete with the phosphinooxazolines or BINAP, the encouraging results obtained with phosphinopyridines and -quinolines **20** and **21** suggest that the development and screening of new P,N-ligands might be profitable.

Phosphinooxazolines as well as other P,N-ligands like **20** or **21** are attractive catalyst components because they are readily synthesized from simple precursors [21] and because their modular structure allows the preparation of quite diverse libraries of ligands. By variation of the nitrogen-containing heterocycle, the phosphine group, and the back-bone, the ligand structure can be systematically optimized for a particular application.

Although impressive enantioselectivities have been achieved in various Heck reactions with BINAP and phosphinooxazolines as ligands, the reactivity of the catalysts developed so far is less satisfactory. Often, very long reaction times and relatively large amounts of catalyst are necessary for full conversion. Therefore, the

Table 3
Heck reaction using ligands **20** and **21**



Ligand	Base	Temperature (°C)	Time (days)	ee (**1**) (%)	**1**:**2**	Conversion (%)[a]
20a	Proton sponge	60	3	87	97:3	97
20b	*i*-PrNEt$_2$	60	3	92	98:2	83
21a	*i*-PrNEt$_2$	50	2	97	83:17	100
21b	Proton sponge	50	2	99	95:5	48

[a] Conversion determined by GC with *n*-tridecane as internal standard.

search for more reactive enantioselective catalysts remains a challenge for future research.

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