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A Cationic Palladium(II) Complex-Catalyzed Diels-Alder Reaction

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Abstract: A cationic palladium(II) complex, $[PdL_2(RCN)_2](BF_4)_2$, has been found to catalyze the Diels-Alder reaction of α, β-unsaturated carbonyl compounds with dienes, affording the corresponding cycloadducts in good yields. Excellent enantioselectivity can be achieved in the reaction of *N*-acryloyloxazolidinone and cyclopentadiene by use of a chiral ligand, BINAP. © 1998 Elsevier Science Ltd. All rights reserved.

The Diels-Alder reaction is usually catalyzed by a variety of Lewis acids, such as halides of trivalent boron or aluminum and tetravalent titanium or tin. These typical Lewis acids, however, present some problems in that they are very sensitive to moisture, moreover the turnover number is low in many cases. Recently, it has been recognized that certain transition metal complexes display considerable Lewis acidic character and can be used as catalysts instead of the typical Lewis acids. These complexes have a number of merits, e.g., stability to air and moisture, high turnover number, and a well-defined structure. For example, copper complexes with chiral N-N and N-P ligands were reported to catalyze the asymmetric Diels-Alder reaction[1] and hetero Diels-Alder reaction[2] with good enantioselectivity. η^5-Cyclopentadienyl and salen ruthenium complexes were utilized for the hetero Diels-Alder reaction[3] and Diels-Alder reaction,[4] respectively. Recently, chiral η^6-arene ruthenium complexes[5] and chiral η^5-pentamethylcyclopentadienyl rhodium complexes[6] have been reported to catalyze the asymmetric Diels-Alder reaction between cyclopentadiene and methacrolein. We previously reported that the hetero Diels-Alder reaction of nonactivated simple dienes with aldehydes is catalyzed by cationic palladium(II) complexes, $[PdL_2(RCN)_2](BF_4)_2$, affording the corresponding 5,6-dihydro-2*H*-pyrans.[7] During the course of our studies on catalytic activities of the palladium(II) cationic complexes, we found for the first time that the cationic palladium(II) complexes act as good catalysts for the Diels-Alder reaction of α, β-unsaturated carbonyl compounds with dienes (Scheme 1) and that the cationic palladium complex with a chiral ligand, BINAP, achieves excellent enantioselectivity for the reaction of *N*-acryloyloxazolidinone (**1d**) with cyclopentadiene (**2b**) and cyclohexadiene (**2c**).

Typically, 5 mmol of α, β-unsaturated carbonyl compounds and 5.5 mmol of dienes were stirred in 5 ml of CH_2Cl_2 in the presence of 1 mol% of cationic palladium complex $[Pd(PPh_3)_2(CH_3CN)_2](BF_4)_2$ (**I**)[8] at ambient temperature for 20 h. The resulting cyclic compounds were purified by distillation or column chromatography.

The results are summarized in Table 1. The reaction of acrolein (**1a**) with isoprene (**2a**) proceeded smoothly at low catalyst loading of 1 mol% affording the cyclization product in 72 % yield. The reaction of methyl vinyl ketone (**1b**) with **2a** gave the product in 55 % yield. Methyl acrylate (**1c**) did not react with **2a**.

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Scheme 1

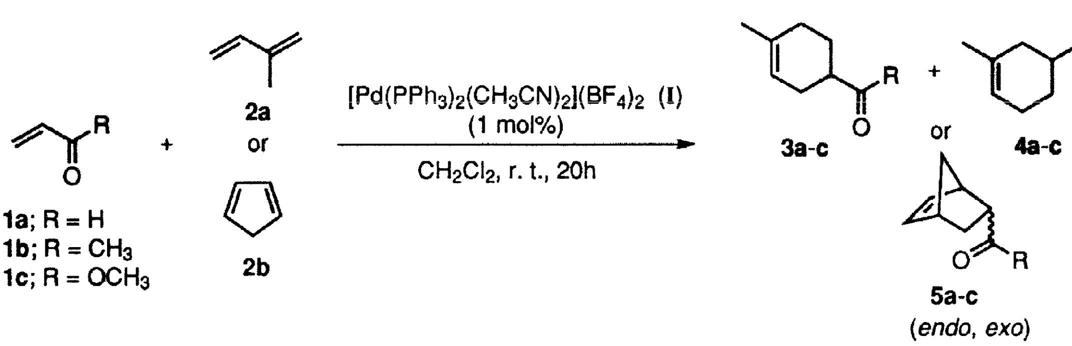

Table 1. Diels-Alder reaction of **1** with **2**.

Entry	Dienophile **1**	Diene **2**	Yield(%)[a]	Isomer ratio[a]
1	**1a**	**2a**	72 (**3a** + **4a**)	n. d.
2	**1b**	**2a**	55 (**3b** + **4b**)	98 (**3b**) / 2 (**4b**)
3	**1c**	**2a**	0 (**3c** + **4c**)	-
4	**1a**	**2b**	88 (**5a**)	84 (*endo*) / 16 (*exo*)
5	**1b**	**2b**	94 (**5b**)	94 (*endo*) /6 (*exo*)
6	**1c**	**2b**	17 (**5c**)	89 (*endo*) /11 (*exo*)

a) Determined by GLC.

The reactions of cyclopentadiene (**2b**) with **1a**, **1b**, and **1c** gave the products **5a-c** in higher yields of 88 %, 94 %, and 17 %, respectively, than the reactions with **2a**. Neutral palladium complexes such as $Pd(PPh_3)_2Cl_2$ or $Pd(CH_3CN)_2Cl_2$ did not show any catalytic activity at all. Polar coordinative solvents such as acetonitrile or THF inhibited the reaction to give no cyclization products. The higher reactivity of cationic palladium complexes where weakly coordinating anions or solvent ligands are involved is responsible in part for the easier access of substrate molecules to the coordination sites around the metal center. Another factor may be the increased electrophilicity of the palladium center.

Then, we prepared the chiral cationic complexes, $[Pd(S\text{-BINAP})(PhCN)_2]X_2$ (**IIa**: X = BF_4, **IIb**: X = PF_6) by treatment of $Pd(S\text{-BINAP})Cl_2$[9] with AgX in the presence of benzonitrile,[7] to carry out the asymmetric Diels-Alder reaction. These complexes are stable and can be handled in the air. Enantiomer excess was determined by HPLC using a chiral column.[10] Since only modest enantioselectivities were observed with **1a** or **1b**, *N*-acryloyloxazolidinone (**1d**) was employed as the dienophile (Scheme 2). The reactions were carried out using 1.0 mmol of **1d** and 5.0 equiv of **2** in the presence of 10 mol% of **II** in CH_2Cl_2 (1 ml) at -50 or 0 °C. The results are summarized in Table 2. Although the reaction of **1d** with **2b** catalyzed by **IIa** at 0 °C gave the product **5d** with low enantioselectivity (49 %ee, entry 1), the reaction at -50 °C gave (2*R*)-**5d** in 99 %ee and 95 % yield (entry 2) showing the complete enantioselectivity. Lower enantioselection (77 %ee) was obtained by changing the counterion in the catalyst from BF_4 (**IIa**) to PF_6 (**IIb**, entry 3). The reaction of **1d** with 1,3-cyclohexadiene (**2c**) was slower than that of **1d** with **2b** and required longer reaction time (72 h) and higher reaction temperature (0 °C), yielding the cycloadduct **5e** in 43 % yield with good enantiomeric excess (92 %ee). Unfortunately, the reaction of β-substituted

Scheme 2

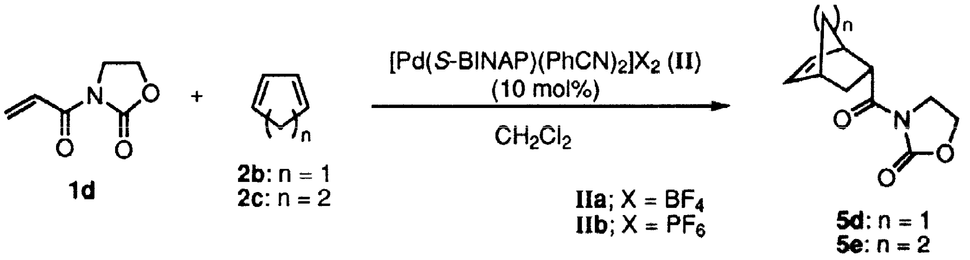

Table 2. Diels-Alder reaction of **1d** with **2**.

Entry	Diene 2	X in II	Temp.(°C)	Time(h)	Yield(%)[a]	*endo*/*exo*[b]	Ee(%)[c]
1	**2b**	BF_4	0	24	96 (**5d**)	92/2	49 (*R*)
2	**2b**	BF_4	-50	24	95 (**5d**)	95/5	99 (*R*)
3	**2b**	PF_6	-50	24	98 (**5d**)	96/4	77 (*R*)
4	**2c**	BF_4	0	72	43 (**5e**)	98/2	92

a) Isolated yield. b) Determined by GLC. c) Ee of *endo* isomers. See note 10.

dienophile such as *N*-crotonoyloxazolidinone or *N*-cinnamoyloxazolidinone with **2b** was very sluggish affording the product in poor yield.

A proposed chiral induction model is illustrated by the acryloyl substrate **1d** in Fig. 1. It is thought that **1d** is L_2-coordinated to the palladium-*S*-BINAP complex via the two carbonyl oxygen atoms affording the square-planar complex in the intermediate. The attack of **2b** at the *endo*-*Si*-face of the acryloyl group of **1d** is favored to afford the observed (2*R*)-cycloadducts, while the attack at the *Re*-face may be obstructed by the equatorial phenyl group of *S*-BINAP.

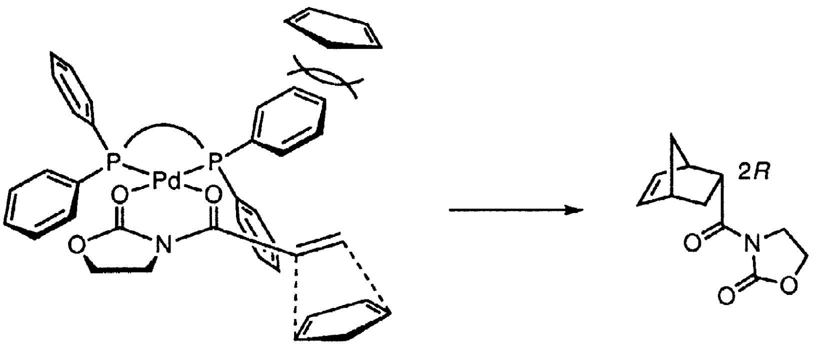

Fig. 1. A proposed chiral induction model for the reaction of **1d** with **2b**.

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10. Enantiomer excess of **5d** and **5e** was determined by Daicel Chiralcel OD column (10% 2-PrOH in hexane), and Daicel Chiralpak AD column (10% 2-PrOH in hexane), respectively. Absolute configuration was determined by measurement of optical rotation.