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Catalytic Enantioselective Addition of Cyclic β-Keto Esters with Activated Olefins and N-Boc Imines Using Chiral C_2-Symmetric Cationic Pd^{2+} N-Heterocyclic Carbene (NHC) Diaqua Complexes

Zhen Liu and Min Shi*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

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Summary: The asymmetric addition of cyclic β-keto esters to activated olefins and N-Boc imines was realized by using chiral cationic C_2-symmetric N-heterocyclic carbene (NHC) Pd^{2+} diaqua complexes ***1a,b*** *as the catalysts, producing the corresponding adducts in moderate to high yields (up to 95%) and with good to high enantioselectivities (up to 96% ee). Nevertheless, the most significant observation is that when the (R)-NHC Pd^{2+} diaqua complex was used in these reactions, different absolute configurations were observed in comparison to those obtained with catalysts obtained from (R)-phosphane ligands.*

Recently, N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and catalysis.[1] On the basis of recent achievements in this field, N-heterocyclic carbenes (NHCs) clearly are not just "phosphane mimics", as they are sometimes called in the literature, since NHCs as ligands or catalysts showed several advantages over their phosphine counterparts. The NHCs have the general advantage of being better σ donors and weaker π acceptors than phosphine ligands, and these ligands are also air and moisture stable. These advantages have attracted several research groups to search for new catalytic systems using NHCs as ancillary ligands for many catalytic reactions.[2] Recently, NHC−Pd complexes have significantly emerged as effective catalysts for a variety of coupling reactions.[3] However, to the best of our knowledge, the promise of a highly active and enantioselective NHC−Pd catalyst has not been fulfilled, even though many palladium-mediated transformations have opened up the possibility of the development of enantioselective catalysis.[4−6]

Michael- or Mannich-type addition reactions of acidic carbon nucleophiles to a variety of activated olefins or imines are some of the most important and practically useful carbon−carbon bond-forming reactions in organic synthesis.[7] In these reactions, the use of readily enolizable compounds such as β-keto esters as nucleophiles for the construction of chiral tertiary carbon centers have especially attracted much attention.[8] Thus far, a number of Pd enolates of ketones have been successfully applied to the above reactions, affording the corresponding adducts in high yields and good enantiomeric excesses under mild conditions.[9] For example, Sodeoka and co-workers originally reported that Pd (*R*)-phosphane ligand diaqua complexes reacted with 1,3-dicarbonyl compounds, such as β-keto esters, to give chiral Pd enolates. Using this novel Pd enolate chemistry, efficient catalytic enantioselective addition reactions with various electrophiles have been achieved.[10] On the other hand, we previously reported the synthesis of a series of the chiral cationic Pd^{2+} NHC diaqua complexes and their application in the catalytic enantioselective arylation of *N*-tosylarylimines with arylboronic acids.[11b]

*Fax: 86-21-64166128. Mshi@mail.sioc.ac.cn.

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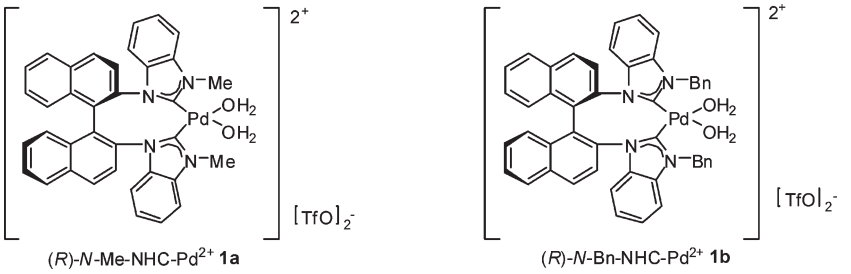
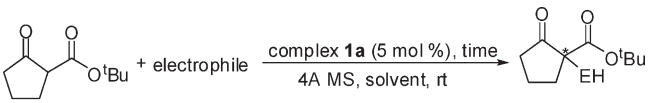


Figure 1. Chiral cationic Pd^{2+} NHC diaqua complexes **1a**,**b**.

Table 1. Catalytic Enantioselective Michael Addition of Cyclic *β*-Keto Ester 2a



2a **3**

entry	solvent	electrophile	time (h)	yield (%)[a]	ee (%)[b]
1	CH_2Cl_2	MVK	24	98 (**3a**)	71 (*S*)[c]
2[d]	CH_2Cl_2	MVK	24	86 (**3a**)	38 (*S*)
3[e]	CH_2Cl_2	MVK	24	96 (**3a**)	40 (*S*)
4	THF	MVK	24	80 (**3a**)	53 (*S*)
5	toluene	MVK	24	90 (**3a**)	39 (*S*)
6	DCE	MVK	24	89 (**3a**)	63 (*S*)
7	dioxane	MVK	24	76 (**3a**)	38 (*S*)
8[f]	CH_2Cl_2	MVK	24	69 (**3a**)	70 (*S*)
9[g]	CH_2Cl_2	MVK	24	98 (**3a**)	63 (*S*)
10	CH_2Cl_2	EVK	72	91 (**3b**)	19(-)
11	CH_2Cl_2	PVK	48	93 (**3c**)	0
12	CH_2Cl_2	nitroethene	48	90 (**3d**)	38(-)

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Determined by comparison of the sign of optical rotation with the literature value.[10g] [d] Complex **1b** was used. [e] 5 mol % of 4-$NO_2C_6H_4CO_2H$ was added. [f] The reaction was carried out at −10 °C. [g] The reaction was carried out at 35 °C.

Herein, we have turned our attention to the investigation of the catalytic activity of these chiral cationic Pd^{2+} NHC diaqua complexes in enantioselective addition reactions of cyclic *β*-keto esters with several electrophiles such as activated olefins and N-Boc imines. It was found that the corresponding adducts could be obtained in moderate to high yields (up to 95%) and with good to high enantioselectivities (up to 97% ee) under mild conditions. In this paper, we wish to report the details of these findings.

Results and Discussion

Synthesis of Chiral Cationic C_2-Symmetric Pd^{2+} N-Heterocyclic Carbene (NHC) Diaqua Complexes 1a,b. The chiral cationic Pd^{2+} NHC diaqua complexes **1a**,**b**, shown in Figure 1, were designed and synthesized in a six-step pathway starting from optically active binaphthyl-2,2′-diamine (BINAM) according to our previously reported procedure.[11]

Catalytic Enantioselective Michael Addition of Cyclic *β*-Keto Ester 2a. An initial experiment was carried out by reacting cyclic *β*-keto ester **2a** with methyl vinyl ketone (MVK) in the presence of the Pd^{2+} (*R*)-NHC diaqua catalyst **1a** (5 mol %) together with 4 Å molecular sieves at room temperature (20 °C). The reaction was conducted in CH_2Cl_2 at room temperature to afford **3a** in 98% yield and 71% ee with *S* configuration for the major enantiomer (Table 1, entry 1). It should also be noted that the Pd^{2+} (*R*)-Tol-BINAP diaqua catalyst produces product **3a** with an *R* configuration as the predominant species.[10g] In contrast to the Pd^{2+} (*R*)-NHC diaqua catalyst **1a**, catalyst **1b** was found to be less reactive in this reaction, giving **3a** in 86% yield and 38% ee under the standard conditions, presumably due to the fact that the sterically hindered *N*-benzyl group did not favor this reaction (Table 1, entry 2). Adding 5 mol % of 4-$NO_2C_6H_4CO_2H$ as the additive in the combination with catalyst **1a** produced **3a** in 96% yield and 40% ee (Table 1, entry 3). The examination of the solvent effects revealed that CH_2Cl_2 is the best choice if **1a** is used as the catalyst. Other solvents such as tetrahydrofuran (THF), toluene, 1,2-dichloroethane (DCE), and dioxane generally gave poor results in this reaction (Table 1, entries 4−7). Unfortunately, lowering or elevating the temperature resulted in poorer results (Table 1, entries 8 and 9). Therefore, the best reaction conditions involve carrying out the reaction in CH_2Cl_2 at room temperature (20 °C) using the Pd^{2+} (*R*)-NHC diaqua catalyst **1a** in the presence of molecular sieves 4 Å. Other Michael acceptors have also been tested under the optimized reaction conditions using catalyst **1a**. In addition to methyl vinyl ketone (MVK), ethyl vinyl ketone (EVK) and phenyl vinyl ketone (PVK) were also examined and we found that increasing the steric bulkiness resulted in a decrease in the enantioselectivity (entries 10 and 11). The asymmetric addition of cyclic *β*-keto ester **2a** to nitroethene also proceeded smoothly to give the corresponding adduct **3d** in 90% yield and 38% ee (entry 12).

Catalytic Diastereo- and Enantioselective Addition of *β*-Keto Esters to N-Boc Imines. The above success led us to investigate the diastereoselective addition of *β*-keto esters to N-Boc imines using Pd^{2+} (*R*)-NHC diaqua catalyst **1a**. Initially, we also examined the solvent and temperature effects in this reaction using phenyl-substituted N-Boc imine as the substrate and the results of these experiments are summarized in Table 2. It was found that the corresponding product **4a** was obtained in 91% yield along with 80% ee (anti:syn, dr = 3.5:1) when the reaction was carried out in CH_2Cl_2 at room temperature (20 °C) using catalyst **1a** (Table 2, entry 1). Interestingly, when the Pd^{2+} (*R*)-NHC diaqua complex was used for this asymmetric addition reaction, a different major diastereomer and absolute configuration were also observed in comparison to the product obtained with Pd^{2+} (*R*)-BINAP diaqua catalyst.[10h] Other solvents such as tetrahydrofuran (THF), toluene, and 1,2-dichloroethane (DCE) generally gave lower dr or ee values in this reaction (Table 2, entries 2−4). Furthermore, it was found that lowering the temperature could reduce the dr value of the product, leaving the ee value unchanged (Table 2, entry 5). Thus, we established the optimized reaction

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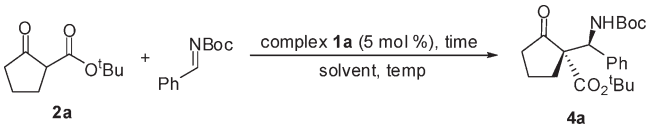
Table 2. Optimization of the Reaction Conditions for Catalytic Enantioselective Addition of β-Keto Ester 2a to N-Boc Imines



2a 4a

entry	solvent	temp	time (h)	yield (%)[a]	dr[b]	ee (%)[c]
1	CH_2Cl_2	room temp	72	91	3.5:1	80 (*S,S*)
2	THF	room temp	48	87	1.5:1	71 (*S,S*)
3	toluene	room temp	48	86	3:1	69 (*S,S*)
4	DCE	room temp	48	90	2:1	76 (*S,S*)
5	CH_2Cl_2	−10 °C	96	85	2:1	80 (*S,S*)

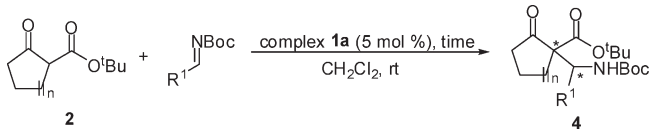
[a] Isolated yields. [b] dr (anti:syn); determined by ^{1}H NMR spectroscopic analysis of the crude products. [c] ee (anti); determined by chiral HPLC.

conditions for this reaction: using 5 mol % complex **1a** as the catalyst and CH_2Cl_2 as the solvent to perform the reaction at room temperature.

Next, the asymmetric additions of cyclic β-keto esters **2a**,**b** with a variety of N-Boc imines were evaluated under the optimal conditions. The results are summarized in Table 3. The corresponding adducts **4b**−**i** were generated in high yields (up to 95%) and good to excellent enantiomeric excesses (up to 95% ee) regardless of whether they have electron-donating or electron-withdrawing substituents on their benzene rings (Table 3, entries 1−8). Furthermore, the position of these substituents on the benzene rings is not restrictive for obtaining high enantioselectivities (Table 3, entries 1−5). To our delight, by using teh cationic Pd^{2+} diaquo complex **1a** as the catalyst, the N-Boc aliphatic imine substrate also efficiently gave the corresponding product **4j** in 92% yield and 96% ee as a single diastereomer (Table 3, entry 9). Moreover, this system was also applicable to the six-membered cyclic β-keto ester **2b**, affording the corresponding Mannich adducts **4k**,**l** in good yields along with high enantioselectivities (Table 3, entries 10 and 11). Interestingly, we found that, as for those N-Boc imines having an electron-withdrawing substituent on the ortho or meta position of their benzene rings, the diastereoselectivities of the products were different from those having substituents on the para position of their benzene rings under identical conditions on the basis of NMR spectroscopic data (Table 3, entries 1−3 and 10 vs entries 4 and 6−8). In these cases, the syn products were obtained as the major diastereomers, presumably due to steric effects and the electronic properties of the substrates. As for the *p*-CF_3-substituted imine, the syn product was formed as the major species, suggesting strong electronic effects on the diastereoselectivity in this asymmetric addition reaction (Table 3, entries 5 and 11). The corresponding adducts **4** were obtained with medium diastereoselectivity when they have para substituents on the benzene rings (Table 3, entries 4, and 6−8, except for the strongly electron withdrawing *p*-CF_3-substituted imine). Moreover, it was found that adducts **4** were produced in good to excellent diastereoselectivity when they have ortho or meta substituents on their benzene rings (Table 3, entries 1−3 and 10), presumably due to the fact that the sterically more bulky and strongly electron withdrawing substituents favor high diastereoselectivities in this asymmetric catalytic process.

To determine the absolute configuration of **4**, the structure of the major asymmetric addition product of 1-[(4-bromophenyl)-*tert*-butoxycarbonylaminomethyl]-2-oxocyclopentanecarboxylic

Table 3. Catalytic Diastereo- and Enantioselective Addition of β-Keto Esters 2 with N-Boc Imines



2 4

entry	*n*	R^1	time (h)	yield (%)[a]	dr[b]	ee (%)[c]
1	1 (**2a**)	2-ClC_6H_4	48	80 (**4b**)	1:5	73
2	1 (**2a**)	3-ClC_6H_4	48	95 (**4c**)	1:20	91
3	1 (**2a**)	3-$CF_3C_6H_4$	24	90 (**4d**)	1:20	94
4	1 (**2a**)	4-ClC_6H_4	48	91 (**4e**)	2:1	90 (*S,S*)
5	1 (**2a**)	4-$CF_3C_6H_4$	24	90 (**4f**)	1:10	95
6	1 (**2a**)	4-FC_6H_4	36	92 (**4g**)	2:1	83 (*S,S*)
7	1 (**2a**)	4-BrC_6H_4	48	89 (**4h**)	2:1	70 (*S,S*)
8	1 (**2a**)	4-$CH_3C_6H_4$	36	91 (**4i**)	2:1	80 (*S,S*)
9	1 (**2a**)	cyclohexyl	24	92 (**4j**)	*d*	96
10	2 (**2b**)	3-CF_3C6H_4	48	85 (**4k**)	1:10	88
11	2 (**2b**)	4-$CF_3C_6H_4$	48	79 (**4l**)	1:5	80

[a] Isolated yields. [b] dr (anti:syn); determined by ^{1}H NMR spectroscopic analysis of the crude products. [c] ee (major); determined by chiral HPLC. [d] Only one diastereoisomer was isolated.

acid *tert*-butyl ester (**4h**) was unequivocally determined by a single-crystal X-ray structural analysis. Its ORTEP drawing and its CIF data are presented in the Supporting Information.[12] The stereochemistry of the major product of **4h** was deduced as the *S,S* configuration at both the quaternary carbon and tertiary carbon centers.

A plausible catalytic cycle is outlined in Scheme SI-1 in the Supporting Information on the basis of Sodeoka's suggestion.[10g,h] First, the chiral bis(NHC)$_2$PdOH species **A** is generated from the palladium diaqua complex during the reaction along with the generation of a Brønsted acid (TfOH) and water. The chiral palladium species **A** reacts with the β-keto ester to give the chiral palladium enolate **B**, which undergoes the addition reaction with the electrophiles (E, activated olefins or N-Boc imines) to give intermediate **D** via intermediate **C**. Finally, tautomerization followed by ligand exchange with water gives the addition product and regenerates palladium species **A** (see the Supporting Information).

The generally accepted stable palladium enolate might be used to explain the observed absolute configuration of the products (Figure 2).[10g,h] Since the bis(NHC) ligand is less sterically hindered in comparison with the Pd^{2+} (*R*)-phosphane ligand diaqua catalyst, in which each phosphorus atom has two phenyl groups, the bulky ester (^{t}Bu) can locate at the same side of the NHC ligand in the enolate face. Thus, the *Re* face of the palladium enolate is blocked preferentially, and the incoming electrophiles would react with palladium enolate at the *Si* face in a highly enantioselective manner. On the other hand, the relative stereochemistry is derived from the face selection of the imines to the palladium enolate. The imines might react with the Pd enolate from the *Si* face with the aryl groups directed to the more advantageous space in the chiral environment according to their different steric bulks and the electronic properties through an open transition-state

(12) The crystal data of **4h** have been deposited with the CCDC with file number 741415. Crystal data: empirical formula $C_{22}H_{30}BrNO_5$, formula weight 468.38, crystal size 0.279 × 0.256 × 0.245 mm^3, colorless, prismatic habit, crystal system monoclinic, lattice type primitive, lattice parameters a = 9.9053(17) Å, b = 11.2911(18) Å, c = 11.0981(19) Å, α = 90°, β = 109.586(3)°, γ = 90°, and V = 1169.4(3) Å^3, space group $P2_1$, Z = 2, D_{calcd} = 1.330 g/cm^3, F_{000} = 488, R1 = 0.0671, wR2 = 0.1623, diffractometer Rigaku AFC7R.

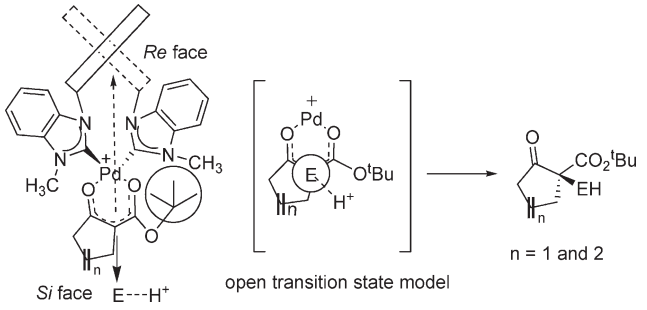


Figure 2. Proposed transition-state model.

model as suggested by Sodeoka.[10g,h,13] Thus, it seems to us that our enantioselective addition reaction occurs with the proposed geometry as depicted in Figure 2 in accord with the observed absolute and relative stereochemistry.

In conclusion, we have successfully established a series of new, efficient, chiral C_2-symmetric cationic Pd^{2+} NHC diaqua complex catalyzed systems for the asymmetric addition of cyclic β-keto esters to activated olefins and N-Boc imines. This system provides easy access to the corresponding adducts in moderate to high yields (up to 95%) and with good to high enantioselectivities (up to 96% ee). Interestingly, the most significant observation is that when the Pd^{2+} (*R*)-NHC diaqua complex was used for these reactions different absolute configurations were observed compared to those obtained with Pd^{2+} (*R*)-phosphane ligand diaqua catalysts.

Experimental Section

General Procedure for the Catalytic Enantioselective Addition of β-Keto Ester 2a to Activated Olefins Using C_2-Symmetric Cationic Pd^{2+} N-Heterocyclic Carbene (NHC) Diaqua Complexes. In a dried Schlenk tube, catalyst (0.01 mmol; **1a**, 9.6 mg; **1b**, 11 mg), activated olefins (0.4 mmol, 28−53 mg), β-keto ester **2a** (0.2 mmol, 37 mg), and 4A molecular sieves (50 mg) were dissolved in the solvent (0.5 mL) under an argon atmosphere. The solution was stirred at the appointed temperature. After the reaction was complete (monitored by TLC), the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1:20, v/v) as eluent to afford the products.

General Procedure for the Catalytic Enantioselective Addition of β-Keto Esters to N-Boc Imines Using C_2-Symmetric Cationic Pd^{2+} N-Heterocyclic Carbene (NHC) Diaqua Complexes. In a dried Schlenk tube, catalyst (0.01 mmol; **1a**, 9.6 mg; **1b**, 11 mg), N-Boc imines (0.4 mmol, 82−109 mg), and β-keto esters (0.2 mmol; **2a**, 37 mg; **2b**, 40 mg) were dissolved in CH_2Cl_2 (1.0 mL) under an argon atmosphere. The solution was stirred at room temperature. After the reaction was complete (monitored by TLC), the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1:20, v/v) as eluent to afford the products.

(*S*)-2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylic Acid *tert*-Butyl Ester (3a). This is a known compound.[10g] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.44 (9H, s), 1.81−2.07 (5H, m), 2.14 (3H, s), 2.22−2.30 (1H, m), 2.35−2.50 (3H, m), 2.69−2.77 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.5, 26.9, 27.8, 29.8, 34.5, 37.9, 38.8, 59.4, 81.9, 170.6, 208.0, 215.2. HPLC (Daicel AS column, 95:5 hexanes/^{i}PrOH, 0.7 mL/min, λ 230 nm, t_{major} = 17.0 min, t_{minor} = 15.1 min): 71% ee. $[\alpha]^{20}_D$ = −5.2° (*c* 0.92, $CHCl_3$). Yield: 98%.

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Supporting Information Available: Text, figures, tables, and a CIF file giving procedures for the synthesis of catalysts, experimental details and characterization data, a plausible reaction mechanism, chiral HPLC traces, and X-ray crystallographic data for **4h**. This material is available free of charge via the Internet at http://pubs.acs.org.

(13) An open transition state was proposed as an important candidate. See: Enders, D.; Ward, D.; Adam, J.; Raabe, G. *Angew. Chem., Int. Ed.* **1996**, *35*, 981.