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ASYMMETRIC LEWIS ACID CATALYSIS OF ALUMINUM(SALALEN) COMPLEXES: FRIEDEL-CRAFTS REACTION OF INDOLE

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‡ Dedication to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

Abstract – We examined the Lewis acid catalysis of chiral Al(salalen)X complexes and found that complex **1b** (X = Br) serves as an efficient catalyst for the Friedel-Crafts reaction of indole with *N*-[(*E*)-alkenoyl]oxazolidin-2-ones. High enantioselectivity (up to 98% ee) was obtained under the optimized conditions.

INTRODUCTION

Recently, optically active metal(salalen) complexes (salalen = salen/salan hybrid)[1] have received increasing attention and the unique asymmetric catalysis has been demonstrated by us and other groups.[2-9] The catalytic performance of octahedral metal(salalen) complexes is mainly due to the following properties: i) they tend to adopt a *cis*-β structure, and the metal center is chiral, ii) an amine nitrogen donor atom of the ligand is chiral, and iii) two ancillary ligands that are *cis* to each other are sterically and electronically non-equivalent. As expected from these properties, metal(salalen) complexes can efficiently activate bidentate electrophiles or accelerate bimolecular reactions between precoordinating substrate and reagent. Indeed, asymmetric epoxidation using hydrogen peroxide, which is a kind of divalent ligand, and hydrophosphonylation between aldehyde and phosphite, which can precoordinate with metal ion, are catalyzed by metal(salalen) complexes in a highly enantioselective manner.[3,4] Moreover, vanadium- and chromium(salalen) complexes were recently found to serve as Lewis acid catalysts for asymmetric transcyanation and hetero Diels-Alder reactions, respectively.[5,6] On the other hand, electrophiles bearing two oxygen donor atoms such as *N*-(alkenoyl)oxazolidin-2-one have been

widely used as a Michael accepter. Considering the high oxophilicity of the aluminum ion and the above structural features, aluminum(salalen) complexes are expected to efficiently activate such bidentate electrophiles in a highly asymmetric atmosphere. Thus, we examined Friedel-Crafts reaction of indole with *N*-[(*E*)-alkenoyl]oxazolidin-2-ones as the electrophile in the presence of Al(salalen) complexes **1**.[10-12]

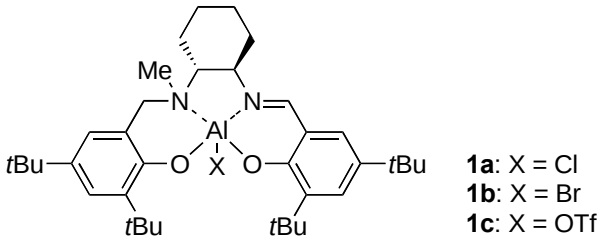
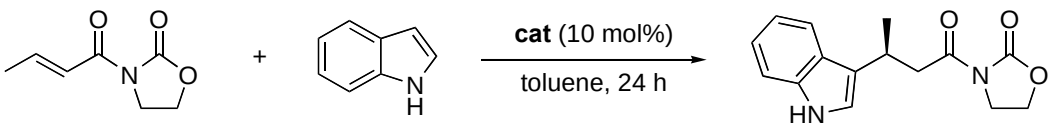


Figure 1 Al(salalen) complexes **1**.

RESULTS AND DISCUSSION

We first examined the reaction with *N*-[(*E*)-crotonoyl]oxazolidin-2-one in the presence of complex **1a** (X = Cl), which has been demonstrated to be an efficient catalyst for asymmetric hydrophosphonylation,[4] but no reaction occurred (Table 1, entry 1). In order to enhance the Lewis acidity, we prepared complex **1b** (X = Br)[13] and complex **1c** (X = OTf).[14] Complex **1b** slowly catalyzed the reaction at room temperature with moderate enantioselectivity (entry 2). Although the enantioselectivity was significantly improved as the reaction temperature was reduced, the yield was maximum at -15 °C and grossly diminished at lower temperatures (entries 3-5).[15,16] Complex **1c** also promoted the reaction but was less efficient in both enantioselectivity and yield compared to complex **1b** (entry 6). The reaction with **1c** at -30 °C was sluggish and the substrate was recovered intact.

Table 1. Asymmetric Friedel-Crafts reaction of indole using complex **1** as the catalyst.[a]



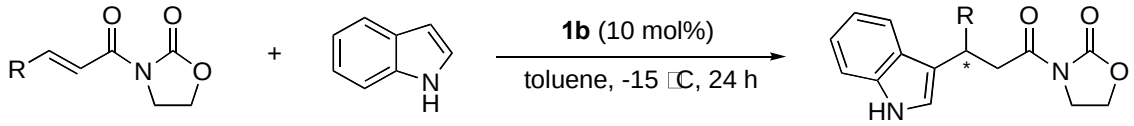
Entry	Catalyst	Temp./°C	Yield/%[b]	Ee/%[c]	Config.[d]
1	**1a**	RT[e]	NR[f]	-	-
2	**1b**	RT[e]	36	57	*S*
3	**1b**	0	62	78	*S*

4	**1b**	-15	65 (60)[g]	87	*S*
5	**1b**	-30	25	89	*S*
6	**1c**	-15	28	78	*S*

[a] Reactions were carried out with 0.10 mmol of *N*-[(*E*)-crotonoyl]oxazolidin-2-one, 0.15 mmol of indole, and 10 mol% of catalyst in toluene (1.0 ml) for 24 h. [b] Determined by ^{1}H NMR analysis (400MHz), based on the amount of the electrophile. [c] Determined by chiral HPLC analysis with CHIRALPAK AD-H column. [d] Determined by comparison of optical rotation after converting to the corresponding methyl ester (Ref. 12). [e] Room temperature. [f] No reaction. [g] Isolated yield.

Under the optimized conditions, we investigated the reactions with several *N*-[(*E*)-alkenoyl]oxazolidin-2-ones in the presence of complex **1b** (Table 2).[17-20] When the β-substituent was a primary alkyl group, the enantioselectivity was comparable to that obtained with *N*-[(*E*)-crotonoyl]-oxazolidin-2-one (entries 1 and 2). While the electrophiles with a secondary group at the position produced low yield with higher enantioselectivity, substitution with the more bulky *tert*-butyl group led to complete lack of reactivity (entries 3 and 4). The cinnamoyl derivative was also a reluctant substrate (entry 5). However, the reaction with an electron-withdrawing ester group proceeded smoothly in high yield with an excellent enantioselectivity of 98% ee (entry 6).

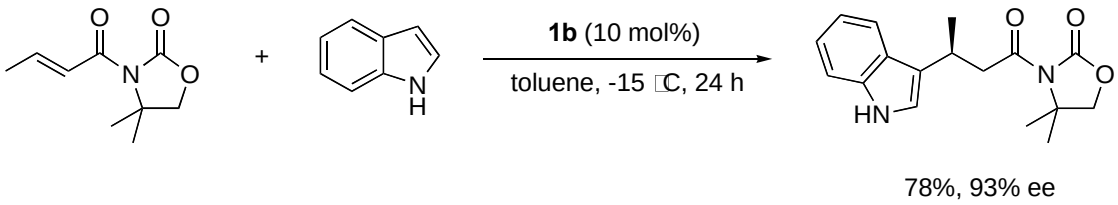
Table 2. Reactions between of *N*-[(*E*)-alkenoyl]oxazolidin-2-one and indole using complex **1b** as the catalyst.[a]



Entry	R	Yield/%[b]	Ee/%[c]
1	Et	60	88
2	nC$_7$H$_{15}$	46	87
3	iPr	28	92
4	tBu	NR[d]	-
5	Ph	NR[d]	-
6	CO_2Et	>99	98

[a] Reactions were carried out with 0.20 mmol of electrophiles, 0.30 mmol of indole, and 10 mol% of complex **1b** in toluene (2.0 mL). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] No reaction.

N-[(*E*)-Alkenoyl]oxazolidin-2-ones can exist in s-*cis* and s-*trans* conformers and the reactions of the two conformers may show opposite stereoselection to each other. Thus, we examined the reaction of *N*-[(*E*)-crotonoyl]-4,4-dimethyloxazolidin-2-one, in which the equilibration between the conformers should shift to the s-*trans* side due to steric effects (Scheme 1).[21] As we expected, the reaction proceeded with better enantioselectivity.[22]



Scheme 1.

In conclusion, we were able to demonstrate that aluminum(salalen)Br complex **1b** is an efficient catalyst for the asymmetric Friedel-Crafts reaction of indole with *N*-[(*E*)-alkenoyl]oxazolidin-2-ones as the electrophile. It was also found that the conformation of the *N*-alkenyl moiety and the electronic nature of the β-substituents significantly affect the yield and the enantioselectivity of the reaction.

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13. Complex **1b** was prepared as follows, according to the procedure for the synthesis of Al(salen)Br complex: A. Mitra, L. J. DePue, S. Parkin, and D. A. Atwood, *J. Am. Chem. Soc.*, 2006, **128**, 1147. To a rapidly stirred solution of diethylaluminum bromide in toluene, prepared in situ by the redistribution of triethylaluminum (0.94 M solution in toluene, 0.85 mL, 0.80 mmol) and aluminum bromide (1.0 M solution in dibromomethane, 0.40 mL, 0.40 mmol), was added salalen ligand (0.68 g, 1.2 mmol). The reaction mixture was refluxed for 8h. The volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2/heptane. Yellow crystal; 38%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92-1.02 (m, 1H), 1.11-1.30 (m, 21H), 1.39 (s, 9H), 1.52 (s, 9H), 1.74-1.87 (m, 3H), 2.27-2.36 (m, 1H), 2.47 (s, 3H), 2.54-2.61 (m, 1H), 3.33-3.36 (d, J = 13.2 Hz, 1H), 3.38-3.45

(m, 1H), 4.63-4.66 (d, J = 13.2 Hz, 1H), 6.81-6.82 (d, J = 2.4 Hz, 1H), 7.01-7.01 (d, J = 2.4 Hz, 1H), 7.23-7.24 (d, J = 2.4 Hz, 1H), 7.59-7.59 (d, J = 2.4 Hz, 1H), 8.45 ppm (s, 1H); HRMS (ESI): calcd for $C_{37}H_{56}AlN_2O_2$ $[M\text{-}Br]^+$: 587.4152; found: 587.4159.

14. Complex **1c** was prepared as follows. Salalen ligand (0.56 g, 1.0 mmol) was dissolved in CH_2Cl_2 at rt and a solution of trimethylaluminum in toluene (0.60 mL, 2.0 $molL^{-1}$) was added. After stirred for 1.5 h at rt, trifluoromethansulfonic acid (0.11 mL, 1.2 mmol) was added and the resultant mixture was stirred over night. The volatiles were removed under reduced pressure and the residue was crystallized from CH_2Cl_2/heptane. Yellow crystal; 26 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00-1.30 (m, 22H), 1.35 (s, 9H), 1.50 (s, 9H), 1.83-2.00 (m, 3H), 2.35-2.58 (m, 5H), 3.48-3.56 (d, J = 13.2 Hz, 1H), 3.60-3.69 (m, 2H), 4.17-4.24 (m, 1H), 6.81-6.82 (d, J = 2.0 Hz, 1H), 7.02-7.03 (m, 1H), 7.23-7.28 (m, 1H), 7.62-7.63 (d, J = 2.4 Hz, 1H), 8.45 ppm (m, 1H); HRMS (ESI): calcd for $C_{37}H_{56}AlN_2O_2$ $[M\text{-}OTf]^+$: 587.4152 found: 587.4150.
15. General procedure for Friedel-Crafts reaction of indole using Al(salalen) complex **1b** as the catalyst: Complex **1b** (13.4 mg, 10 mol%) was dissolved in toluene (1.6 mL) at −15 °C. A solution of *N*-(alkenoyl)oxazolidin-2-one in toluene (0.20 mL, 1.0 $molL^{-1}$) and a solution of indole in toluene (0.20 mL, 1.5 $molL^{-1}$) were added, and the resultant mixture was stirred for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture was extracted with EtOAc. The organic phase was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel to give a Friedel-Crafts adduct. Enantiomeric excess was determined by chiral HPLC analysis.
16. (*S*)-*N*-[3-(3'-Indolyl)butanoyl]oxazolidin-2-one: Colorless solid; 65%, 87% ee (CHIRALPAK AD-H, hexane/*i*PrOH 80:20); $[\alpha]_D^{24}$ −9.8 (*c* 0.58, $CHCl_3$); IR (KBr): 3400 (N-H), 1774 (C=O), 1695 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44-1.45 (d, J = 7.1 Hz, 3H), 3.18-3.24 (dd, J = 7.6, 15.9 Hz, 1H), 3.45-3.51 (dd, J = 6.8, 15.9 Hz, 1H), 3.69-3.78 (m, 1H), 3.85-3.97 (m, 2H), 4.18-4.25 (ddd, J = 7.1, 9.0, 9.0 Hz, 1H), 4.29-4.35 (ddd, J = 7.1, 8.9, 8.9 Hz, 1H), 7.06-7.06 (d, J = 2.4 Hz, 1H), 7.09-7.13 (ddd, J = 1.0, 7.1, 7.8 Hz, 1H), 7.16-7.20 (ddd, J = 1.2, 7.1, 8.1 Hz, 1H), 7.34-7.36 (m, 1H), 7.68-7.70 (d, J = 8.1 Hz, 1H), 7.99 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 27.5, 42.6, 42.6, 61.9, 111.0, 119.0, 119.1, 120.4, 120.4, 121.8, 126.3, 136.1, 153.3, 172.2 ppm; HRMS (ESI): calcd for $C_{15}H_{16}N_2O_3Na$ $[M+Na]^+$: 259.1053; found: 295.1048. The absolute configuration was determined by comparison of optical rotation after converting to the corresponding methyl ester (87% ee). $[\alpha]_D^{24}$ +2.9 (*c* 0.27, CH_2Cl_2) [lit.,[12] $[\alpha]_D^{25}$ +2.7 (c 1.10, CH_2Cl_2), 83% ee, (*S*)-isomer].
17. *N*-[3-(3'-Indolyl)pentanoyl]oxazolidin-2-one: Colorless solid; 60%, 88% ee (CHIRALCEL OD-H, hexane/*i*PrOH 80:20); $[\alpha]_D^{24}$ −13.1 (*c* 1.58, $CHCl_3$); IR (KBr): 3404 (N-H), 1774 (C=O), 1695 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85-0.88 (dd, J = 7.3, 7.3 Hz, 3H), 1.77-1.90 (m, 2H),

3.22-3.32 (m, 1H), 3.43-3.53 (m, 2H), 3.70-3.84 (m, 2H), 4.04-4.11 (m, 1H), 4.19-4.25 (ddd, *J* = 6.8, 8.0, 8.0 Hz, 1H), 7.00-7.00 (d, *J* = 2.2 Hz, 1H), 7.06-7.10 (m, 1H), 7.13-7.17 (m, 1H), 7.29-7.31 (d, *J* = 8.1 Hz, 1H), 7.65-7.67 (d, *J* = 7.8 Hz, 1H), 8.09 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2, 28.8, 34.6, 41.0, 42.6, 61.9, 111.0, 118.1, 118.9, 119.1, 121.4, 121.6, 126.7, 136.0, 153.3, 172.4 ppm; HRMS (ESI): calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$: 309.1210; found: 309.1215.

18. *N*-[3-(3'-Indolyl)decanoyl]oxazolidin-2-one: Colorless solid; 46%, 87% ee (CHIRALCEL OD-H, hexane/*i*PrOH 80:20); $[\alpha]_D^{24}$ –7.2 (*c* 1.90, $CHCl_3$); IR (KBr): 3398 (N-H), 1774 (C=O), 1686 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82-0.85 (t, *J* = 6.8 Hz, 3H), 1.20-1.26 (m, 10H), 1.71-1.87 (m, 2H), 3.22-3.27 (dd, *J* = 5.9, 15.6, 1H), 3.43-3.49 (dd, *J* = 8.5, 15.6 Hz, 1H), 3.53-3.60 (m, 1H), 3.72-3.85 (m, 2H), 4.06-4.12 (m, 1H), 4.21-4.27 (ddd, *J* = 6.8, 8.8, 8.8 Hz, 1H), 7.02-7.03 (d, *J* = 2.4 Hz, 1H), 7.07-7.10 (m, 1H), 7.14-7.17 (m, 1H), 7.31-7.33 (d, *J* = 8.1 Hz, 1H), 7.65-7.67 (d, *J* = 8.1 Hz, 1H), 8.03 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 27.7, 29.3, 29.7, 31.9, 33.0, 36.1, 41.4, 42.6, 61.9, 111.0, 118.7, 119.0, 119.1, 121.3, 121.7, 126.7, 136.1, 153.3, 172.4 ppm; HRMS (ESI): calcd for $C_{21}H_{28}N_2O_3Na$ $[M+Na]^+$: 379.1992; found: 379.1996.

19. *N*-[3-(3'-Indolyl)-4-methylpentanoyl]oxazolidin-2-one: Colorless solid; 28%, 92% ee (CHIRALPAK AD-H, hexane/*i*PrOH 80:20); $[\alpha]_D^{23}$ –24.0 (*c* 0.69, $CHCl_3$); IR (KBr): 3408 (N-H), 1774 (C=O), 1697 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.90 (d, *J* = 6.6 Hz, 3H), 0.97-0.98 (d, *J* = 6.6 Hz, 3H), 2.03-2.15 (dqq, *J* = 6.6, 6.6, 6.6 Hz, 1H), 3.24-3.29 (dd, *J* = 4.2, 15.1 Hz, 1H), 3.43-3.48 (ddd, *J* = 4.2, 6.6, 10.3 Hz, 1H), 3.51-3.58 (dd, *J* = 10.3, 15.1 Hz, 1H), 3.67-3.78 (m, 2H), 4.08-4.14 (ddd, *J* = 7.1, 9.0, 9.0 Hz, 1H), 4.19-4.25 (ddd, *J* = 6.8, 9.0, 9.0 Hz, 1H), 7.03-7.04 (d, *J* = 2.4 Hz, 1H), 7.07-7.11 (m, 1H), 7.13-7.18 (m, 1H), 7.31-7.33 (d, *J* = 8.1 Hz, 1H), 7.64-7.66 (d, *J* = 7.8 Hz, 1H), 8.03 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 20.8, 33.0, 38.4, 39.3, 42.7, 61.9, 110.9, 117.4, 119.1, 119.3, 121.6, 121.7, 127.4, 135.9, 153.3, 172.7 ppm; HRMS (ESI): calcd for $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$: 323.1366; found: 323.1374.

20. *N*-[3-Ethoxycarbonyl-3-(3'-indolyl)butanoyl]oxazolidin-2-one: Colorless solid; >99%, 98% ee (CHIRALPAK AD-H, hexane/*i*PrOH 80:20); $[\alpha]_D^{21}$ +124.3 (*c* 1.78, $CHCl_3$); IR (KBr): 3398 (N-H), 1778 (C=O), 1701 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19-1.22 (dd, *J* = 7.1, 7.1 Hz, 3H), 3.31-3.37 (dd, *J* = 3.9, 18.3 Hz, 1H), 3.94-4.13 (m, 4H), 4.15-4.23 (dq, *J* = 7.1, 10.7 Hz, 1H), 4.37-4.42 (m, 2H), 4.45-4.48 (dd, *J* = 3.9, 11.0 Hz, 1H), 7.12-7.16 (m, 2H), 7.18-7.22 (m, 1H), 7.35-7.37 (d, *J* = 8.1 Hz, 1H), 7.74-7.76 (d, *J* = 7.8 Hz, 1H), 8.19 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 38.0, 38.4, 42.4, 61.1, 62.2, 111.2, 112.2, 119.1, 119.6, 122.1, 122.2, 126.1, 135.9, 153.3, 171.5, 173.4 ppm; HRMS (ESI): calcd for $C_{17}H_{18}N_2O_5Na$ $[M+Na]^+$: 353.1108; found: 353.1113.

21. C. Chapuis and J. Jurczak, *Helv. Chim. Acta,* 1987, **70**, 436.

22. (*S*)-*N*-[3-(3'-Indolyl)butanoyl]-4,4-dimethyloxazolidin-2-one: Colorless needle; mp 136.4-136.8 °C; 78%, 93% ee (CHIRALPAK IA, hexane/*i*PrOH 90:10); $[\alpha]_D^{24}$ –5.8 (*c* 1.61, $CHCl_3$); IR (KBr): 3423 (N-H), 1774 (C=O), 1701 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.41-1.42 (d, *J* = 6.8 Hz, 3H), 1.42 (s, 3H), 1.44 (s, 3H), 3.17-3.23 (dd, *J* = 8.3, 15.9 Hz, 1H), 3.37-3.43 (dd, *J* = 6.6, 15.9 Hz, 1H), 3.66-3.75 (m, 1H), 3.86-3.92 (d, *J* = 8.3 Hz, 1H), 3.86-3.92 (d, *J* = 8.3 Hz, 1H), 7.01-7.01 (d, *J* = 2.4 Hz, 1H), 7.08-7.12 (m, 1H), 7.15-7.19 (m, 1H), 7.32-7.34 (d, *J* = 8.1 Hz, 1H), 7.69-7.71 (d, *J* = 7.8 Hz, 1H), 8.01 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 24.7, 24.8, 27.6, 44.5, 60.5, 75.1, 111.0, 119.1, 119.2, 120.2, 120.8, 121.8, 126.4, 136.1, 153.9, 173.1 ppm; HRMS (ESI): calcd for $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$: 323.1366; found: 323.1370. The absolute configuration was determined by comparison of optical rotation after converting to the corresponding methyl ester (92% ee). $[\alpha]_D^{25}$ +3.5 (*c* 0.18, CH_2Cl_2) [lit.,[12] $[\alpha]_D^{25}$ +2.7 (c 1.10, CH_2Cl_2), 83% ee, (*S*)-isomer].