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Chiral Octahedral Complexes of Co^{III} As a Family of Asymmetric Catalysts Operating under Phase Transfer Conditions

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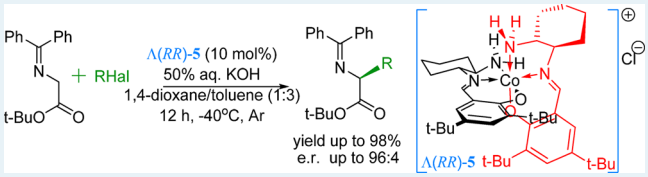
Supporting Information

ABSTRACT: Stereochemically inert and positively charged chiral complexes of Co^{III} prepared from Schiff bases derived from chiral diamines and salicylaldehydes were shown to be efficient catalysts of the asymmetric phase transfer benchmark reaction of alkylation of O'Donnell's substrate with alkyl halides. The enantiomeric purities of the reaction products were up to 92%.



KEYWORDS: *cobalt Schiff base, phase transfer asymmetric catalysis*

INTRODUCTION

The field of asymmetric phase transfer (APT) catalytic enolate alkylation,[1−7] as a part of a larger field of ion-pairing catalysis,[8−10] has been intensively studied in recent years. The reasons for this are that this type of catalysis is intrinsically "green," inexpensive, and versatile. APT catalysis is already being applied to industrial production.[11,12] Denmark et al. recently summarized the existing mechanistic understandings and catalyst types present in APT catalyzed enolate alkylation.[13,14] The area is still dominated by positively charged, chiral, quaternary ammonium salts derived from cinchona alkaloids.[1−7] In recent years, purely synthetic chiral ammonium catalysts were also developed by Maruoka, Lygo, Denmark, and other groups.[13−18] Unfortunately, the cinchona skeleton is difficult to modify, and the preparation of purely synthetic Maruoka type catalysts is synthetically challenging. Additionally, the catalysts themselves are expensive. Thus, there is a need to develop novel, simple, inexpensive, and versatile APT catalysts, capable of easy modification to fine-tune them to particular reactions. In addition, it would be highly desirable to introduce to the catalysts some features not present in the classic ammonium type agents. An emerging class of novel bifunctional chiral quaternary ammonium salt catalysts with additional hydroxyl groups as hydrogen bond donors is an example of recent modifications introduced to the family of the catalysts.[19]

In previous work, we successfully elaborated chiral negatively charged stereochemically inert complexes of Co^{III} as ACDC type[9] catalysts for asymmetric synthesis.[20−22] Recently, positively charged Co^{III} complexes were developed by some of us as catalysts for the cyanosilylation of aldehydes with high catalytic efficiency, but low enantioselectivity.[23] In this manuscript, we report the use of novel chiral positively charged complexes of Co^{III} as catalysts of asymmetric enolate alkylation under PT conditions.

RESULTS AND DISCUSSION

Complexes **1**−**4** were prepared from Schiff bases derived from chiral diamines and salicylaldehydes by reaction with the corresponding Co^{III} salts, as illustrated in Scheme 1 for a cyclohexenediamine example. Complex **5**, analogous to **1d** but with a Cr^{III} central metal ion instead of Co^{III}, was prepared from the same Schiff base, starting with $CrCl_3$ as described in the Experimental Section, Supporting Information.

The structures of all the positively charged complexes (**1**−**5**) prepared in this study are depicted in Figure 1. The structure of anionic complex Co^{III}, **6**, is also presented in Figure 1. Compounds **1d** and **3** were analyzed by X-ray crystallography. Their X-ray structures are presented in Figure 2 and indicate Λ(*R*,*R*)-**1d** and Δ(*S*,*S*)-**3** configurations with Λ or Δ configurations attributed according to left or right helical mutual orientations of their tridentate ligands relative to the C_2 symmetry axis.[2] The absolute configurations of **1a**,**b**,**c**,**e**, **2**, **4**, and **5** were assigned by the comparison of their CD spectra with those of Λ(*R*,*R*)-**1d** and Λ(*S*,*S*)-**3** (see the Supporting Information). The formation of all the positively charged complexes is highly enantioselective, with complexes of only the Λ configuration obtained from Schiff bases of (*R*)-cyclohexenediamine and complexes of Δ configuration obtained from (*S*)-cyclohexenediamine. The Schiff bases derived from (*S*)-aminomethylpyrrolidine were obtained exclusively with the Λ configuration.

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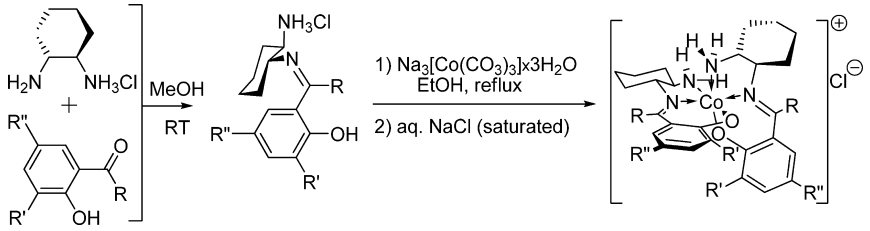
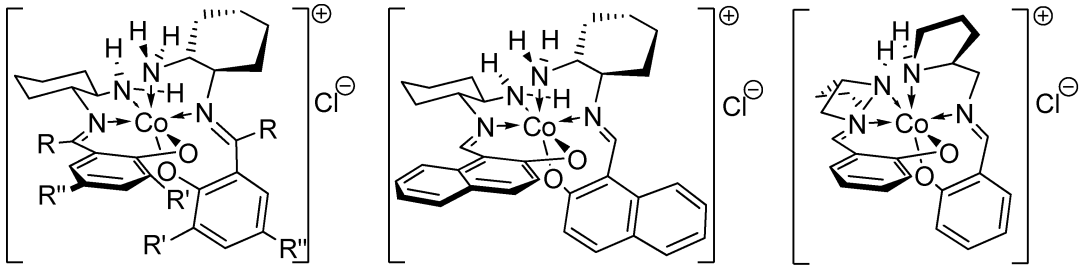
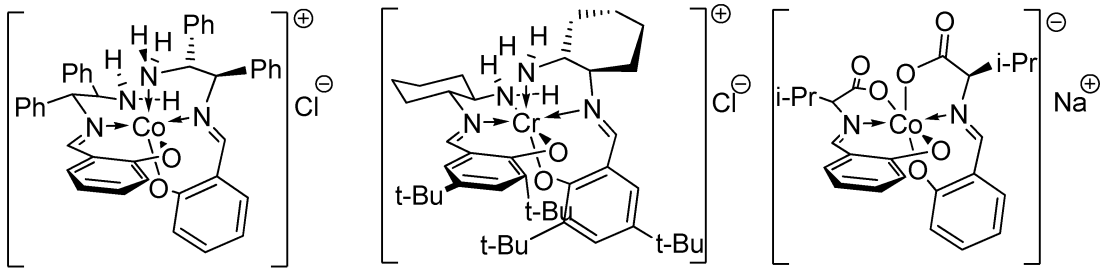
Scheme 1. The Synthetic Protocol Used for Catalyst Preparation





Λ(*R*,*R*)-**1a-f** Λ(*R*,*R*)-**2** Λ(*S*,*S*)-**3**



Λ(*R*,*R*)-**4** Λ(*R*,*R*)-**5** Λ(*R*,*R*)-**6**

Figure 1. Structures of catalysts **1**–**6**. (**a**) R = R′ = R″ = H. (**b**) R = R″ = H, R′ = allyl. (**c**) R = R″ = H, R′ = *t*-Bu. (**d**) R = H, R′ = R″ = ^{t}Bu. (**e**) R = R′ = H, R″ = Ph. (**f**) R = Ph, R′ = R″ = H.

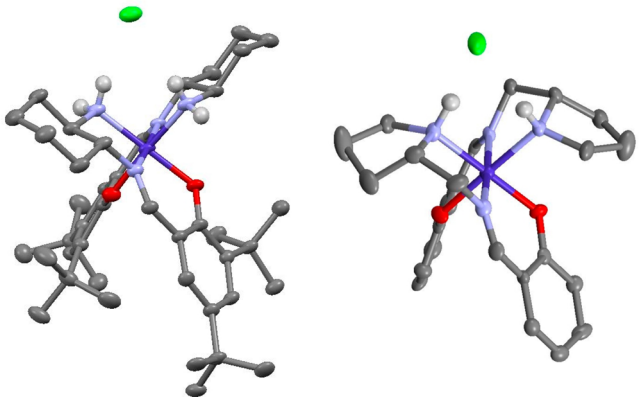


Figure 2. X-ray structures of Λ(*R*,*R*)-**1d** and Δ(*S*,*S*)-**3** with chlorine counteranions.

A salient feature of the stereochemically inert complexes is a set of hydrogen bonds connecting the complex cation with the halide counteranion. Only two NH bonds were engaged in this interaction in the case of **1d**. The other two NH bonds remained unattached and oriented toward π planes of the aromatic moieties of the second tridentate ligand. In the case of **3**, both present NH groups were engaged in the hydrogen bonds with the chlorine anion as indicated by the distances of NH···Cl^{-} equal to 2.448 Å in the case of **1d** and 3.168 Å in the case of **3**.

Complex **1a** was tested in its capacity to exchange chloride anions with aqueous solutions of KF, KBr, and KI (see Scheme 2). As can be seen from Table 1, all the anions are easily

Scheme 2. Ion Exchange of Chlorine Counteranions of 1a with Those of Potassium Salts in a System Water/CH_2Cl_2

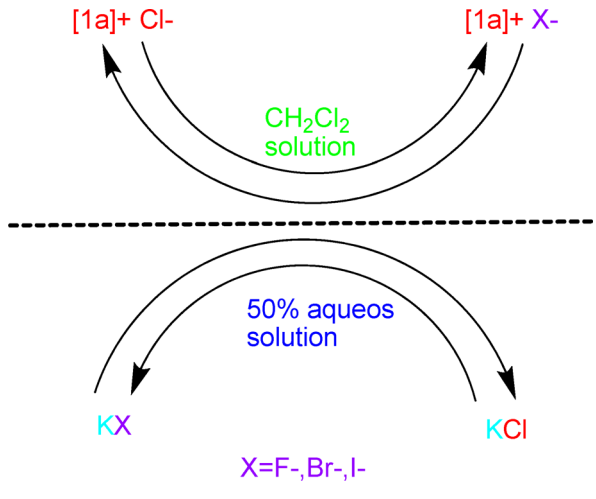


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Table 1. Ion Exchange of [1a]Cl with KX in Water/CH_2Cl_2 Mixture[a]

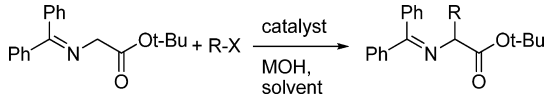
run	KX	$[\mathbf{1a}]^+Cl^-$, %[b]	$[\mathbf{1a}]^+X^-$, %[b]
1	KF	45	55
2	KBr	13	87
3	KI	10	90

[a]Reaction conditions: 10 mg of $[\mathbf{1a}]^+Cl^-$ (0,0189 mmol), 2 mL of CH_2Cl_2, 10 equiv of 50% aq. KX (0.189 mmol) was stirred at ambient temperature for 2 h. [b]The ratio of $[\mathbf{1a}]^+Cl^-$ and $[\mathbf{1a}]^+X^-$ in CH_2Cl_2 was assessed by employing X-ray fluoresence analysis determining the ratio of Co/Cl in the organic layer and additionally with ^{19}F NMR in the case of $X = F^-$.

transferred by the positively charged complex in CH_2Cl_2 solution. Notably, this also included the fluorine ion. The structure of **1a** was not changed, as shown by ^1H NMR and CD spectra of the series of $[\mathbf{1a}]^+X^-$. Most likely, it was the set of the hydrogen bonds provided by **1a** (Figure 2) that stabilized the anions in CH_2Cl_2. The phenomena of anion coordination by multiple hydrogen bonds of synthetic receptors is well-known and reviewed.[24,25] It underlies the leveling effect of the complex on the equilibrium of Scheme 2 making the extraction coefficient of Br and I very similar and fluorine anion exchange with Cl anion and extraction possible.

The asymmetric phase transfer alkylation of the O'Donnell substrate by alkyl halides was chosen as a model reaction to test the catalytic activity of complexes **1**–**6** (Scheme 3). The

Scheme 3. Alkylation of O'Donnell's Substrate Catalyzed by Co^{III} Complexes 1–6



positively charged complex was expected to form an ion pair with the carbanion to be transferred into the organic phase where the chiral ion pair would undergo the alkylation reaction. An NH–O hydrogen bond and electrostatic plus lipophilic interactions could lead to the prevalence of one enantiogenic form of the enolate in the ion pair.

The catalytic activities of the complexes were initially investigated using benzyl bromide as the alkylating agent. First, different bases were tested in the reaction promoted by complex **1a** (Table 2, runs 1–6). The best base was found to be either solid or aqueous potassium hydroxide (runs 1–3). Sodium hydroxide was much less efficient, and lithium hydroxide gave no product (runs 5, 6). Another good base was $CsOH \times H_2O$ (run 4). Under the reaction conditions, the enantiomeric purity of the resulting phenylalanine was 53–61% with $\Delta(S,S)$-**1a** furnishing (*R*)-amino acid (runs 1, 2, 4) and $\Lambda(R,R)$-**1a** giving the (*S*)-enantiomer (run 3). There was no influence of the nature of the base cation on the enantiomeric purity of the product. Different solvents were also tested, and the best enantioselectivity was obtained using 1,4-dioxane (run 8, compare with runs 2, 3, 7, 9, 10).

A control experiment proved that a significant loss of product occurred during chromatographic separation of the product on silica. An NMR experiment of the reaction mixture with a standard added proved that the real yield of the alkylation product was in the range of 80–90% (Table 2, run 8, figures in brackets).

Table 2. Alkylation of O'Donnell's Substrate by Benzyl Bromide at Ambient Temperature, Promoted by $\Delta(S,S)$-1a[a]

run	base (MOH)	solvent	time (h)	yield (%)[b]	e.r.[c]
1	50% aq KOH	CH_2Cl_2	1.5	67	76.5(*R*):23.5(*S*)
2	KOH	CH_2Cl_2	1.5	69	79.5(*R*):20.5(*S*)
3[d]	KOH	CH_2Cl_2	1.5	66	80.5(*S*):19.5(*R*)
4	$CsOH.H_2O$	CH_2Cl_2	1.5	73	80(*R*):20(*S*)
5	NaOH	CH_2Cl_2	22	32	72.5(*R*):27.5(*S*)
6	LiOH	CH_2Cl_2	4	n.d.	n.d.
7	KOH	toluene	1	75	69(*R*):31(*S*)
8[e]	KOH	1,4-dioxane	1	62 (80–90)	84.5(*R*):15.5(*S*)
9	KOH	THF	1.5	60	82.5(*R*):17.5(*S*)
10	KOH	Et_2O	1.5	54	65.5(*R*):34.5(*S*)

[a]Reaction conditions: 0.101 mmol (30 mg) O'Donnell's substrate, 10 mol % catalyst, 1 mL of solvent, 3 equiv solid metal hydroxide, and 1.25 equiv BnBr unless indicated otherwise. [b]Yield of pure alkylated Schiff base after purification by silica gel chromatography. [c]Enantiomeric purity was established by chiral HPLC analysis. [d]Promoted by $\Lambda(R,R)$-**1a**. [e]The figures in brackets are the chemical yields assessed by NMR, using an internal standard.

Other catalysts **1**–**6** were tested in the reaction under the conditions of Table 2, run 8, and the data are summarized in Table 3. Evidently, the introduction of large alkyl groups in

Table 3. Alkylation of O'Donnell's Substrate by Benzyl Bromide at Ambient Temperature, Promoted by Catalysts 1–6[a]

run	catalyst	yield (%)[b]	e.r.[c]
1	$\Lambda(R,R)$-**1b**	54	83(*S*):17(*R*)
2	$\Lambda(R,R)$-**1c**	55	86(*S*):14(*R*)
3	$\Lambda(R,R)$-**1d**	65 (80–90)	88.5(*S*):11.5(*R*)
4[d]	$\Lambda(R,R)$-**1d**	80	85(*S*):15(*R*)
5	$\Lambda(R,R)$-**1e**	65	89(*S*):11(*R*)
6	$\Lambda(R,R)$-**1f**	57	racemate
7	$\Lambda(R,R)$-**2**	64	86.5(*S*):13.5(*R*)
8	$\Lambda(S,S)$-**3**	34	53.5(*S*):46.5(*R*)
9	$\Lambda(R,R)$-**4**	55	57(*S*):43(*R*)
10[d,e]	$\Lambda(R,R)$-**1d**	79	83(*S*):17(*R*)
11	$\Lambda(R,R)$-**5**	65	85(*S*):15(*R*)
12	$\Lambda(R,R)$-**6**	20	racemate

[a]Reaction conditions: 0.101 mmol (30 mg) O'Donnell's substrate, 10 mol % catalyst, 1 mL 1,4-dioxane, 3 equiv 50% aq. KOH and 1.25 equiv BnBr for 1 h at ambient temperature unless indicated otherwise; see footnotes to Table 1. No dependence of the enantioselectivity on the reaction volume was observed. [b]Yield of pure alkylated Schiff base after purification by silica gel chromatography. [c]Enantiomeric purity was established by chiral HPLC analysis. [d]Solid KOH was used. [e]The catalyst was recovered from the previous experiment and reused.

positions 3 and 5 of the salicylaldehyde moiety increased the enantioselectivity of the alkylation (compare Table 2, run 8 and Table 3, runs 1–5). In the case of complex **1d**, the asymmetric induction reached 78%. Almost the same effect was brought about by the enlargement of the aromatic Schiff base to a naphthol derivative **2** (Table 3, run 7). The introduction of a phenyl group at the imine carbon atom (**1f**) resulted in a complete loss of any stereoselectivity during the catalysis (Table 3, run 6). The aminomethylpyrrolidine derived complex $\Delta(S,S)$-**3** was a sluggish catalyst, and there was almost no asymmetric induction in the reaction (Table 3, run 8).

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Surprisingly, diphenylethylenediamine derivative **4**, although catalytically active, furnished almost no asymmetric induction in the reaction (Table 3, run 9). Thus, complex **1d** was the most active APT catalyst under the experimental conditions. Remarkably, aqueous KOH was a superior base to the solid version (Table 2, run 3 and 4). The complexes could be recovered from the reaction mixture and reused without a significant loss of catalytic activity or enantioselectivity (Table 3, run 10). The Cr^{III} derived catalyst was almost as active as analogous **1d**, furnishing the same chemical yield of the product and enentioselectivity (Table 3, run 11). Under the same conditions, catalyst **6** was sluggish, and the product was racemic (Table 3, runs 12). The conversion is most likely a result of a blank reaction, which was shown to take place under the experimental conditions with the same rate.

Figure 3 illustrates the dependence of the enantioselectivity and the chemical yield of the alkylation catalyzed by Δ(*S*,*S*)-**1d**

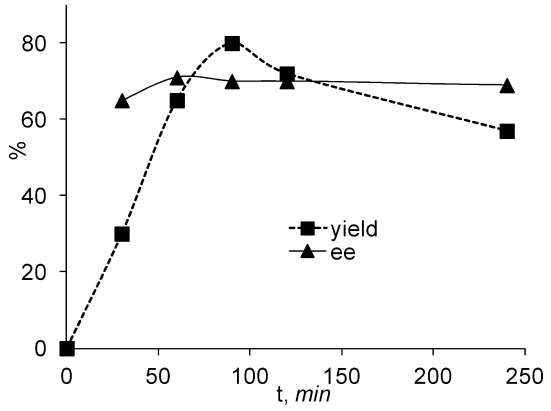

Figure 3. Variation of the enantiomeric purity and the chemical yield of the alkylation product with reaction time carried out using a solid KOH/dioxane system promoted by complex **1d**.

on the reaction time. Evidently, there was no racemization of the product during the alkylation, but a sizable decrease in the chemical yield of the reaction was observed at longer reaction times.

There was no dependence of the enantiomeric excess of the product on the **1d** catalyst loading in the range of 3−10 mol % in dioxane. However, when using just 1 mol % of the catalyst, the enantiomeric excess of the product dropped to just 34%. The competitive uncatalyzed alkylation reaction was shown to be responsible for the adverse effect of low catalyst loading on the enantioselectivity. A further increase of the catalyst loading to 15 mol % led to a decrease in the enantioselectivity, probably due to catalyst self-association, as was observed earlier in the case of anionic Co^{III} complexes.[20]

Further improvement in the enantioselectivity of the reaction came from varying the temperature of the experiments, as summarized in Table 4.

The experiments at low temperatures were conducted in a 3:1 mixture of toluene and dioxane to avoid solvent crystallization. There was a clear tendency for the enantioselectivity of the alkylation to increase as the reaction temperature was reduced (Table 4, runs 1−6). Although the maximum enantioselectivity was observed at −78 °C (Table 4, run 6), the reaction was too slow at this temperature, and −40 °C was chosen as the optimal temperature to conduct further alkylations with other alkyl halides. Notably, the enantioselectivity of the alkylation was almost independent of the alkyl halide structure and gave amino acid derivatives with 85−94% enantiomeric excess (Table 4, runs 5, 7−11). As expected, aliphatic alkyl iodides were slow to react compared to activated halides but still gave reasonable chemical yields (Table 4, runs 8,9).

Table 4. Alkylation of O'Donnell's Substrate with Different Alkyl Halides at Varying Temperatures Promoted by Λ(*R*,*R*)-1d in 3:1 Toluene/Dioxane in the Presence of aq. KOH[a]

run	alkyl halide	*T* (°C)	*T* (h)	yield (%)[b]	e.r.[c]
1[d]	BnBr	65	1.5	65	81(*S*):19(*R*)
2[d]	BnBr	25	1.5	65	89(*S*):11(*R*)
3[e]	BnBr	25	7	66	89(*S*):11(*R*)
4	BnBr	−15	3	61	92.5(*S*):7.5(*R*)
5	BnBr	−40	12	62 (88[f])	95(*S*):5(*R*)
6	BnBr	−78	6	10	97(*S*):3(*R*)
7	4-$FC_6H_4CH_2Br$	−40	12	61	96(*S*):4(*R*)
8	MeI	−40	12	30	93.5(*S*):6.5(*R*)
9	EtI	−40	12	21	96(*S*):4(*R*)
10	Allyl Br	−40	12	58	93.5(*S*):6.5(*R*)
11	Propargyl Br	−40	12	41	93(*S*):7(*R*)

[a]Reaction conditions, see footnote to Table 3. [b]Yield of pure alkylated Schiff base after purification by silica gel chromatography. [c]Enantiomeric purity was established by chiral HPLC analysis. [d]Conducted in pure dioxane. [e]Conducted in a 1:1 mixture of dioxane and toluene. [f]Determined by NMR analysis of the reaction mixture before chromatography.

Another closely related PT reaction catalyzed by the novel catalyst family was Michael addition of methyl acrylate to O'Donnel's substrate (Scheme 4). The condensation was catalyzed by Λ(*R*,*R*)-**1d** in CH_2Cl_2 at ambient temperature to give (*S*)-glutamic acid with e.r. 87.5(*S*):12.5(*R*) in a chemical yield of 89%.

The mechanism of the catalytic activity of the positively charged complexes is, at present, a subject of debate. Although the direct participation of the central metal ion in the catalytic stage of the C−C bond forming reactions could not be entirely excluded at this experimental stage, it looked more likely that the mechanism of the reaction was that of a regular phase transfer conversion. The following arguments support this notion: The complexes are capable of promoting ion exchange similarly to traditional ammonium salts and other anion receptors (see Table 1).

The complexes of Co^{III} (d^6) are stereochemically inert and coordinatively saturated. Any direct involvement of the metal ion in the transition state of the alkylation would demand a significant energy expenditure of preliminary ligand dissociation and structure reorganization.[26] Still, the complex catalyst can be easily recovered from the reaction mixture without any loss of its catalytic activity (Table 3, run 10) and with unchanged chemical structure and configuration.

Complexes of Co and Cr, **1d** and **5**, have almost the same catalytic activity and asymmetric inducing ability (Table 3, runs 3 and 11). Had the central metal ion directly participated in the transition state of the reaction, such dependence would have been highly unusual. On the other hand, if the coordinated ligand had the main role to play in the phase transfer, it would be a highly expected event.

Negatively charged Co complex **6** was a very poor catalyst of the alkylation reactions (Table 3, runs 12). Evidently, had the

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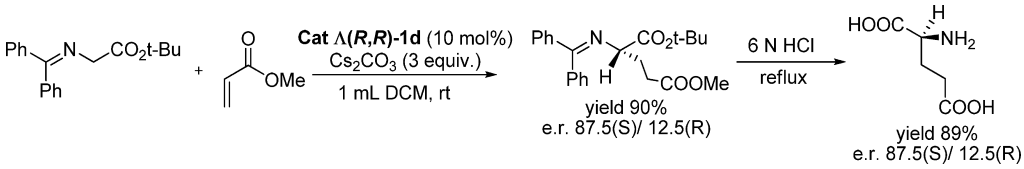
Scheme 4. Michael Addition of O'Donnell Substrate to Methyl Acrylate, Catalyzed by Λ(*R*,*R*)-1d



central metal ion a decisive influence on the catalytic activity, the catalyst would be expected to have much higher activity.

Michael addition was also catalyzed by **1d** with the same sense of chirality of the final product as in the case of alkyl halide alkylation. Such behavior is expected for classical APTC reactions.

CONCLUSIONS

The experiments demonstrated that the strategy of using chiral, stereochemically inert, positively charged complexes of Co^{III} as a catalyst system in the benchmark reaction of O'Donnell substrate alkylation under APTC conditions was successful. The complexes are easy to prepare and modify. Another feature of the catalysts not present in chiral ammonium cations was their hydrogen bond donating properties and potential redox properties. Work is ongoing to further modify the complexes and explore their applications in other areas of organic catalysis and anion coordination applications.

ASSOCIATED CONTENT

Supporting Information

All procedures for the preparation of novel complexes **1**−**5** and their characterization; general procedures alkylation and Michael addition of glycine *tert*-butyl ester benzophenone Schiff base; proton and carbon NMR as well as IR and CD spectra of novel reported compounds **1**−**5**; X-ray diffraction data for complexes **1d** and **3**; and CIF files of single crystals **1d** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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