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An efficient asymmetric hydrophosphonylation of unsaturated amides catalyzed by rare-earth metal amides [(Me₃Si)₂N]₃RE(μ-Cl)Li(THF)₃ with phenoxy-functionalized chiral prolinols†

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An asymmetric hydrophosphonylation reaction of diethyl phosphite with α,β-unsaturated amides catalyzed by [(Me₃Si)₂N]₃RE(μ-Cl)Li(THF)₃ (RE = Sc (**1**), Y (**2**), La (**3**), Yb (**4**) and Lu (**5**)) with H_2L^n ((*S*)-2,4-R_2-6-[[2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]methyl]phenol) (R = ${}^tBu$ (H_2L^1); R = 1-cumyl (H_2L^2) and R = 1-adm (H_2L^3)) was disclosed. The effects of different central metals and proligands on the addition reaction were tested and it was found that the combination of Sc complex **1** and ligand H_2L^2 gave the best results. An excellent chemical yield (up to 99%) and good to high enantioselectivities (varied from 73 to 89%) were achieved with a relatively broad scope of the unsaturated amides. The active species in the current system was also discussed.

Introduction

In recent years, the catalytic asymmetric synthesis of optically active phosphonates has attracted increasing attention due to their important applications in biology and medical science.[1] The asymmetric conjugate addition reactions of phosphite to α,β-unsaturated carbonyl compounds, including aldehydes,[2] ketones,[3] amides[4] and esters,[3i,4g,5] promoted by metal-based catalysts are regarded as simple and efficient methods for C–P bond formation. Among the investigations, the phospha-Michael reaction of α,β-unsaturated amides is quite limited, with only a few reports focused on the subject. As early as 2001, Quirion realized the synthesis of amidophosphonates, which was the first case of a phospha-Michael reaction of an α,β-unsaturated amide.[4a] Thirteen years later, Leung disclosed the first asymmetric phospha-Michael addition of diarylphosphines to *N*-enoyl phthalimides catalyzed by a chiral palladacycle catalyst.[4b] Soon after, they achieved the first catalytic asymmetric phospha-Michael addition of Ph₂PH to 4-oxo-enamides.[6] Almost at the same period, Wang successfully employed a dinuclear zinc catalyst to catalyze the

conjugate addition reactions of phosphite to α,β-unsaturated *N*-acylpyrroles.[4c–e,7] Subsequently, his group continued to develop the phospha-Michael reaction of dialkyl phosphine oxide with various α,β-unsaturated substrates, such as *N*-acylpyrroles, *N*-acylated oxazolidinones and β,β-disubstituted α,β-unsaturated carbonyl compounds. Most of them gave good yields and high enantioselectivities. In 2011, a palladium-catalyzed asymmetric addition of diarylphosphines to α,β-unsaturated *N*-acylpyrroles was explored by Duan and his results were as good as those previously reported.[4f] Ishihara conducted a 1,4-addition reaction to an α,β-unsaturated amide with chiral magnesium(II)binaphtholates in 2013, which gave an 80% yield and 94% enantioselectivity.[4g] However, the diversity of metal-based catalysts used in the phospha-Michael reaction of α,β-unsaturated amide still needs to be developed.

Our group has been devoted to studying lanthanide chemistry for several years.[8] Recently, we turned to investigate the enantioselective synthesis of some valuable target molecules using rare-earth metal catalysts. Fortunately, a series of rare-earth metal complexes together with phenoxy-functionalized chiral prolinols were proven to be highly efficient catalysts in the epoxidation of α,β-unsaturated ketones[9] and also effective in the Michael addition of malonates to unsaturated ketones.[10] All these wonderful results encouraged us to seek for new applications of the current catalytic system. Since the asymmetric phospha-Michael reaction of α,β-unsaturated amide is still challenging, herein, we report this novel transformation catalyzed using rare-earth amides [(Me₃Si)₂N]₃RE(μ-Cl)Li(THF)₃ with phenoxy-functionalized chiral prolinols.

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Results and discussion

First, to test the reactivity and selectivity of our catalytic systems, we prepared five rare-earth metal amides $[(Me_3Si)_2$-$N]_3RE(\mu$-Cl)Li(THF)$_3$ (RE = Sc (**1**), Y (**2**), La (**3**), Yb (**4**) and Lu (**5**)) according to the previous study.[11] Then, three phenoxy-functionalized chiral prolinols with bulky groups ((S)-2,4-di-R^2-6-[[2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]methyl]phenol) (R = ^{t}Bu (H_2L^1); R = cumyl (H_2L^2) and R = 1-adm (H_2L^3)) were synthesized as previously reported.[9] With the ytterbium amide **4** in hand, the model reaction of N-benzyl unsaturated amide **6** with HPO(OEt)$_2$ was carried out in the presence of the proligand H_2L^1. To our delight, the yields of the corresponding 1,4-adducts were satisfying and the enantiomeric excess was moderate, from 47% to 59% (Table 1, entries 1–3). The steric effect of the different proligands was investigated and the bulky cumyl groups in proligand H_2L^2 revealed a slight ascendant in controlling the enantioselectivity (Table 1, entries 2, and 4–5). A relatively low temperature is usually helpful to improve the enantioselectivity of the asymmetric reaction. Attempts to lower the reaction temperature in our case have a positive effect on the enantioselectivity. Although the yields dramatically dropped from 99% to 72% when the temperature was decreased, it was
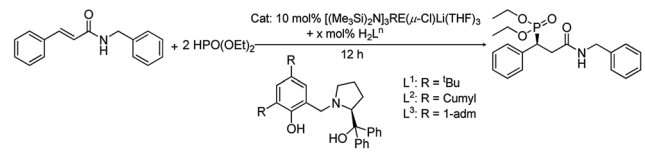
an acceptable yield, considering the good enantiomeric excess achieved (Table 1, entries 4, and 6–7).

The effects of the center rare-earth metals of the amides were next to be explored. As expected, the radius of the center metals significantly influenced both the yield and enantioselectivity, that is, the outcome of the transformation improved when the radius of center metals decreased. When scandium amide **1** was employed as the catalyst in the model reaction, the ee value reached 83%, while the yield was maintained at 80% (Table 1, entries 7–11). As we know, solvent often plays an important role in homogenous reactions, and some commonly used solvents were screened subsequently. Fortunately, the reaction gave an excellent yield and high enantioselectivity in 1,4-dioxane at 20 °C (Table 1, entries 11–16). Finally, the ratio of scandium amide $[(Me_3Si)_2N]_3Sc(\mu$-Cl)Li(THF)$_3$ to the proligand was tested again in 1,4-dioxane and the results showed that the model reaction proceeded better with a 1 : 2 molar ratio of the Sc complex to the proligand H_2L^2 at 20 °C (Table 1, entries 16–18). The effect of the ester moiety in different phosphites was then studied since it may have had an influence on the level of the asymmetric induction.[12] Dimethyl phosphite gave the target product in 69% yield and 75% ee, while diisopropyl phosphite gave a 21% yield and 81% ee. As to diphenyl phosphite, only a trace amount of the corresponding adduct was observed. As a result, the aliphatic ester moiety matched better in the enantioselective transformation in the present case, particularly diethyl phosphite (Table 1, entries 18–21).

Thus, various substrates were investigated using 10 mol% of Sc catalyst **1** in 1,4-dioxane at 20 °C in the presence of 20 mol% of proligand H_2L^2, and the results are summarized in Scheme 1. As we can see, almost all of the substrates participated in the reaction and gave excellent yields and good to high enantioselectivities under the optimal conditions. Whatever the substrate was, α,β-unsaturated secondary amides (**7a–7p**) or tertiary amides (**7q–7t**) bearing either aliphatic or aromatic N-substituents, the yields were excellent, from 90% to 99%, except in two cases (**7b** and **7c**). Perhaps the flexible n-butyl and i-propyl groups attached to the nitrogen atom in the molecule are relatively crowded and blocked the interaction between the catalyst and the substrate, which also affected the enantioselectivity (only 74% ee for **7b** and 64% ee for **7c**). In addition, there was no evidence that the electronic effect of the groups on the phenyl rings had an significant influence on the results. Moreover, we successfully realized the asymmetric hydrophosphonylation of unsaturated amide with an aliphatic acyl group in our system (**7l**).

To further investigate the possible active species in the current catalytic system based on the optimal molar ratio of the Sc amide **1** to proligand H_2L^2, crystals of **8** were obtained from the reaction of the Sc-based precatalyst **1** with 2 equiv. of proligand H_2L^2 in THF. The NMR spectra and elemental analysis results of crystal **8** were informative. One peak at 8.86 was assigned to the hydrogen of the hydroxyl group and was observed in the proton NMR spectrum; the chemical shifts at 1.64 and 1.36 were ascribed to the hydrogens in the $C(CH_3)_2$ group the peaks at 3.88 and 3.73 were ascribed to hydrogens of the methine in group NCH$_2$Ar. These observations prove the

**Table 1** Optimization of the reaction conditions[a]

Entry	Cat.	x	Ligand	T (°C)	Solvent	Yield[b] (%)	ee[c] (%)
1	Yb	10	H_2L^1	25	THF	99	47
2	Yb	15	H_2L^1	25	THF	96	59
3	Yb	20	H_2L^1	25	THF	99	58
4	Yb	15	H_2L^2	25	THF	99	59
5	Yb	15	H_2L^3	25	THF	99	58
6	Yb	15	H_2L^2	0	THF	99	61
7	Yb	15	H_2L^2	−20	THF	72	64
8	La	15	H_2L^2	−20	THF	10	70
9	Y	15	H_2L^2	−20	THF	69	64
10	Lu	15	H_2L^2	−20	THF	65	63
11	Sc	15	H_2L^2	−20	THF	80	83
12	Sc	15	H_2L^2	−20	Tol	22	80
13	Sc	15	H_2L^2	−20	DME	9	82
14	Sc	15	H_2L^2	−20	Et$_2$O	10	80
15	Sc	15	H_2L^2	−20	CH$_3$CN	99	57
16	Sc	15	H_2L^2	20	1,4-Dioxane	99	81
17	Sc	10	H_2L^2	20	1,4-Dioxane	92	78
18	Sc	20	H_2L^2	20	1,4-Dioxane	99	85
19[d]	Sc	20	H_2L^2	20	1,4-Dioxane	69	75
20[e]	Sc	20	H_2L^2	20	1,4-Dioxane	21	81
21[f]	Sc	20	H_2L^2	20	1,4-Dioxane	Trace	—

[a] Reactions were performed with unsaturated amide (0.5 mmol), HPO(OEt)$_2$ (1.0 mmol) in 2 mL solvent. [b] HPLC yield. [c] Determined by chiral HPLC analysis. [d] The reaction was conducted with dimethyl phosphite. [e] The reaction was conducted with diisopropyl phosphite. [f] The reaction was conducted with diphenyl phosphite.
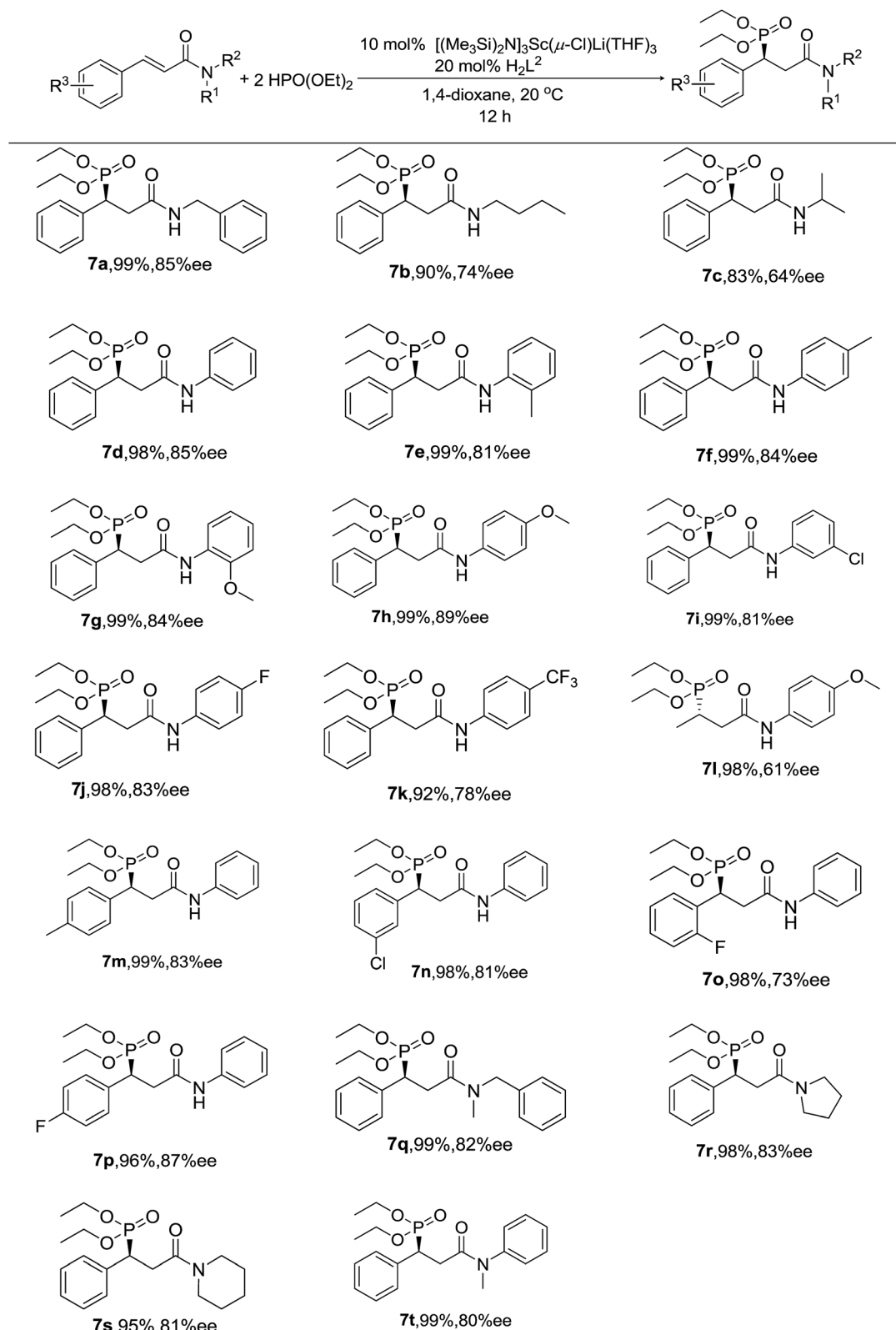
Scheme 1 The asymmetric hydrophosphonylation of unsaturated amides. Reactions were performed with the substrate (0.5 mmol), HPO(OEt)$_2$ (1.0 mmol) in 2 mL of 1,4-dioxane at 20 °C. The ee values were determined by chiral HPLC. The isolated yields are shown.

existence of the ligand in the crystal. Furthermore, the elemental analysis shows that the ratio of Sc : L^2 was 1 : 2, and the LiCl component was not observed. However, the crystals of **8**

obtained in the abovementioned reaction were not good enough for the X-ray diffraction analysis and only the skeleton of the molecular structure could be presumed. Fortunately,
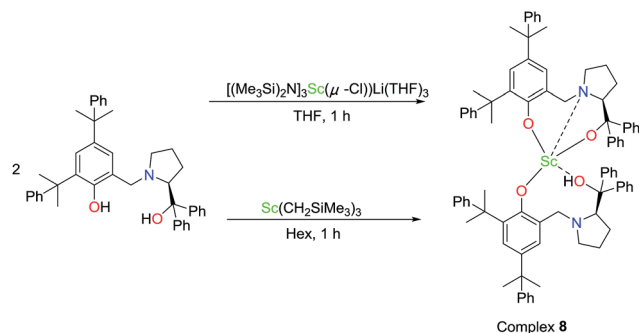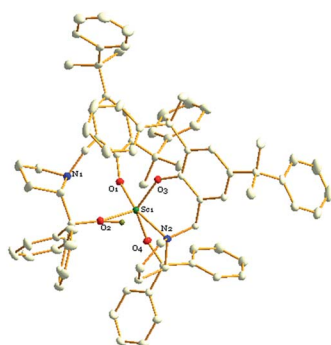
Scheme 2 Synthesis of complex **8**.

Fig. 1 The molecular structure of **8** showing 20% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sc(1)−O(1) 2.0350(16), Sc(1)−O(2) 1.9518(17), Sc(1)−O(3) 2.0141(16), Sc(1)−O(4) 1.9833(16), Sc(1)−N(2) 2.3539(19), O(2)−Sc(1)−O(4) 108.05(7), O(2)−Sc(1)−O(3) 115.27(7), O(4)−Sc(1)−O(3) 132.87(7), O(2)−Sc(1)−O(1) 97.92(7), O(4)−Sc(1)−O(1) 99.48(7), O(2)−Sc(1)−O(1) 92.29(6), O(2)−Sc(1)−N(2) 99.29(7), O(4)−Sc(1)−N(2) 74.83(7), O(3)−Sc(1)−N(2) 80.64(7), O(1)−Sc(1)−N(2) 162.78(7).

a colourless crystal of **8** suitable for the X-ray diffraction analysis could also be obtained by treating tris((trimethylsilyl)methyl) scandium with 2 equiv. of proligand H_2L^2 in hexane (Scheme 2). Finally, the definite solid structure of **8** [$L^2Sc(L^2H)$] was determined as expected and is depicted in Fig. 1. The scandium complex has a mononuclear structure with two chiral ligands in the unit cell. One hydrogen atom of the hydroxyl group in one of the chiral prolinolates remains to meet the requirement of the trivalence of the central metal.

Subsequently, complex **8** was added to the model reaction of the asymmetric hydrophosphonylation of N-benzyl unsaturated amide and the target molecule was obtained in 74% yield and 79% ee (Table 2, entry 1). Taking into consideration the difference between the catalyst system generated *in situ* and the abovementioned structure of complex **8**, 10 mol% of lithium chloride and 20 mol% of HNSiMe₃ were deliberately added to the reaction. The outcome was satisfactory with a 98% yield and 85% ee, almost the same as the *in situ* catalyst system (Table 2, entry 2). The following test without the addition of lithium chloride indicates that lithium chloride was essential. Numerous additives such as DBU, Et₃N, TMEDA, Cy₂NMe, and DABCO were added to make clear whether the aminosilane HNSiMe₃ was essential in the reaction. The results revealed that

Table 2 The effect of additives on the asymmetric hydrophosphonylation of unsaturated amides[a]

| Entry	Additive	Yield[b] (%)	ee[c] (%)
1[d]	—	74	79
2	HNSiMe₃	98	85
3[e]	HNSiMe₃	98	78
4	DBU	98	79
5	Et₃N	96	77
6	TMEDA	81	76
7	Cy₂NMe	73	77
8	DABCO	98	75

[a] Reactions were performed with unsaturated amide (0.5 mmol), HPO(OEt)₂ (1.0 mmol), complex **8** (10 mol%), LiCl (10 mol%), additive (20 mol%) in 2 mL of 1,4-dioxane at 20 °C. [b] HPLC yield. [c] Determined by chiral HPLC analysis. [d] Reaction was performed without LiCl and HNSiMe₃. [e] Reaction was performed without LiCl.

the base is helpful to the transformation; however, all the results are not as good as those achieved using aminosilane (Table 2, entries 4–8). Therefore, we came to the conclusion that the bases are beneficial for the asymmetric hydrophosphonylation of unsaturated amides and aminosilane is optimal. Because complex **8** was recrystallized in a mixed solvent of toluene and hexane, the lithium chloride molecule was removed after work up due to its poor solubility in toluene; it was almost impossible for us to gain the expected crystals bearing LiCl in the crystal cell with the current situation. A detailed study of the mechanism is underway in our laboratory.

Furthermore, the outcome of the model reaction on a gram scale was satisfactory with an appropriate prolonging of the reaction time (Scheme 3). The absolute configuration of the
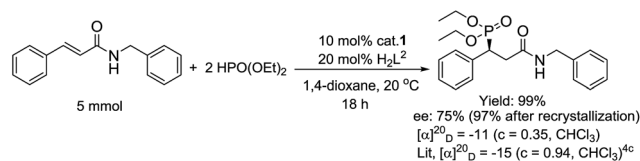
Scheme 3 The amplification reaction of the preparation of compound **7a** and its optical rotation analysis.
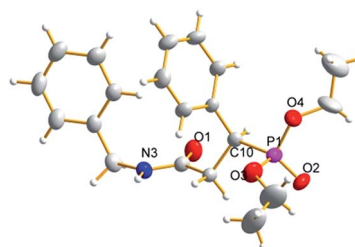
Scheme 4 The molecular structure of compound **7a**.

target phosphonate **7a** was determined by a combination of single crystal diffraction, chiral HPLC and optical rotation analysis (Schemes 3 and 4).

Conclusion

In summary, the asymmetric hydrophosphonylation of α,β-unsaturated amides was successfully catalyzed by rare-earth metal amides with phenoxy-functionalized chiral prolinols. After careful screening, 10 mol% of the Sc complex [(Me₃Si)₂-N]₃Sc(μ-Cl)Li(THF)₃ together with the proligand H₂L² ((S)-2,4-dicumyl-6-[[2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]methyl] phenol) in a 1 : 2 molar ratio were found to be the optimal catalytic conditions in 1,4-dioxane at 20 °C. Substrates bearing various groups were examined in this catalytic system, including secondary amides and tertiary amides, which gave excellent yields (up to 99%) and good to high enantioselectivities (73–89%). The absolute configuration of the target phosphonate was determined. During the exploration of the definite structure of the actual catalyst, complex **8** was obtained. It was proven to be an efficient catalyst in the presence of 1 equiv. LiCl and 2 equiv. base in the hydrophosphonylation reaction. We are still on the way to deduce the clear catalytic cycle occurring in the reaction.

Acknowledgements

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