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COMMUNICATION

Structure–activity relationships in group 3 metal catalysts for asymmetric intramolecular alkene hydroamination. An investigation of ligands based on the axially chiral 1,1′-binaphthyl-2,2′-diamine motif†

Helena M. Lovick, Duk K. An and Thomas S. Livinghouse*

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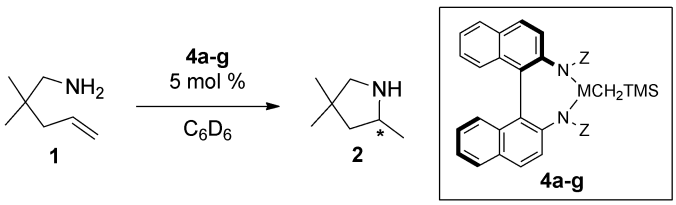
From a series of *N*,*N*′-disubstituted-1,1′-binaphthyl-2,2′-diamines, several group 3 metal complexes were synthesized *via* an *in situ* procedure. These chiral complexes were subsequently applied to catalysis of intramolecular alkene hydroamination. Significant structure–activity relationships were observed, most notably a reversal of stereoselectivity for cyclopentyl *versus* diphenylmethyl substituents.

The intramolecular hydroamination of alkenes constitutes a powerful and atom-economical method for the synthesis of nitrogen-containing heterocycles. Although main-group metal complexes have been used as catalysts for alkene hydroamination,[1a] the most general cases for the synthesis of amines and their derivatives involve transition metal catalysis using complexes of rhodium,[1b–d] ruthenium,[1e–f] nickel,[1g–i] palladium,[1j–p] and gold[1q–s] as well as the group 3[2a–g] and group 4[2h–o] metals. The seminal group 3 metallocenes developed by Marks and coworkers[2] for hydroamination/cyclization have subsequently been joined by a variety of nonmetallocene complexes of the group 3 metals as catalysts for this important reaction.[3,4]

We have previously disclosed that chelating bis(thiophosphinic amidate)s and chelating diamido complexes of the group 3 metals are potent catalysts for intramolecular alkene hydroamination.[5a,b] Asymmetric variations of this important reaction have been reported in which the most frequently encountered sources of asymmetry have derived from the axially chiral 1,1′-binaphthyl-2,2′-diamine[3a–f] and 6,6′-dimethyl-1,1′biphenyl-2.2′-diamine[3g–i] platforms. Alternatively, sterically congested 1,1′-binaphthyl-2,2′-diol,[3j] *trans*-1,2-cyclohexane- and related diamine derivatives[3k] have found utility as chirality sources. In this communication we present a study of the enantioselectivities and rates associated with the cyclization of 1-amino-2,2-dimethyl-4-pentene (**1**) to the optically enriched pyrrolidine **2** catalyzed by Y, Sm, and Lu complexes **4**, based on the 1,1′-binaphthyl-2,2′-diamine motif (Scheme 1).



Scheme 1 Intramolecular hydroamination catalyzed by complexes **4a–g**.

Synthesis of proligands

Proligands **3a** and **3b** were synthesized by the sequential dilithiation of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine or (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine (*n*-BuLi) followed by phosphinylation with chlorodiisopropyl phosphine (2.2 equiv.) and final treatment with elemental sulfur or selenium respectively.[4d] Proligands **3c** and **3d** were prepared by the exhaustive reductive amination ($NaBH_4$, H_2SO_4, MeOH) of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with cyclopentanone[3b] or 2-indanone respectively. Proligand **3e** was obtained by dialkylation of the aforementioned diamine with chlorodiphenylmethane. Proligands **3f** and **3g** were synthesized by the Pd(0)-catalyzed cross-coupling of this precursor with 2-bromo-1-isopropylbenzene or 1-bromonaphthalene respectively (Scheme 2).[5]

Generation of group 3 precatalysts

We have previously shown that Group 3 precatalysts can be accessed by the treatment of the appropriate proligand with homoleptic amides of the type $M[N(TMS)_2]_3$.[4a–f] Unfortunately this process, although successful for some of the proligands reported here, (*e.g.*, 1 h at 60 °C for **3a** or **3b**) was extremely lethargic for others (requiring 2 weeks at 120 °C for **3c**). We therefore applied a procedure first advanced by Anwander[6] for the *in situ* generation of the desired complexes. Optimally, reaction of the appropriate MCl_3-tetrahydrofuranate [$YCl_3(THF)_{3.5}$, $SmCl_3(THF)_{3.5}$, or $LuCl_3(THF)_3$] suspended in THF with Me_3SiCH_2Li (3.4 equiv., 1 M in *p*-xylene) immediately generated homoleptic group 3 alkyls of the type **5**. Subsequent addition of the proligand of interest resulted in elimination of Me_4Si with concomitant formation of the precatalysts **4** (Scheme 3). The direct use of preformed THF solutions of **4** for asymmetric hydroamination/cyclization

Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA. E-mail: livinghouse@chemistry.montana.edu

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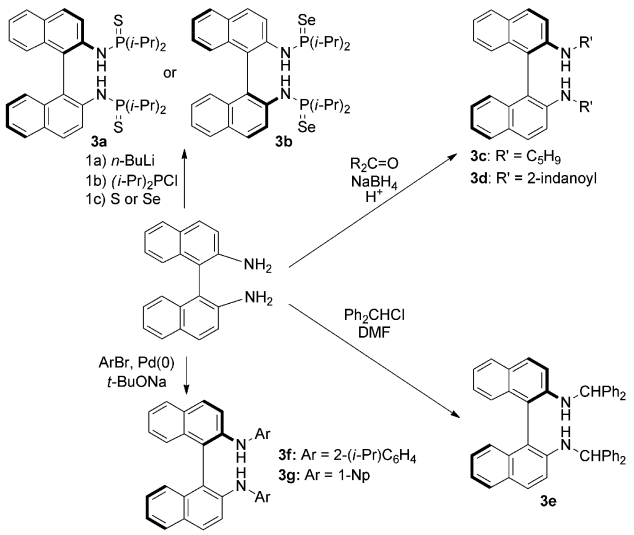
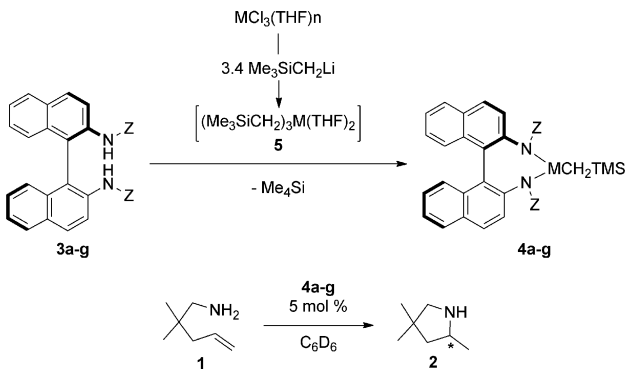


Scheme 2 Preparation of proligands.



Scheme 3 *In situ* generation of group 3 metal catalysts.

proved undesirable due to extended reaction times and diminished enantioselectivities. This was conveniently circumvented by simply evaporating the majority of the THF *in vacuo* followed by the addition of C_6D_6 and subsequent introduction of 1-amino-2,2-dimethyl-4-pentene (**1**). It is none the less significant that precatalysts generated from either the direct "amine elimination" approach (involving $M[N(TMS)_2]_3$) or the preformed homoleptic alkyls $M(CH_2TMS)_3\cdot(THF)_2$ (**5**) proceeded to give pyrrolidine **2** with virtually identical ee's within experimental error (*i.e.*, for $\mathbf{4a}_Y$, 61 and 56% ee respectively).

Results and discussion

The internal hydroamination of 2,2-dimethylpent-4-ene-1-amine (**1**) was selected for examination since cyclization of this substrate would be facilitated by the Thorpe–Ingold effect.[4e] We have previously demonstrated that chelating bis(thiophosphinic amidate)s are versatile supporting ligands for the metals of group 3 and 4.[4d,e] We initiated this investigation by evaluating the NPS and NPSe proligands **3a** and **3b** as chirality sources in asymmetric internal alkene hydroamination. As had been hoped, precatalyst $\mathbf{4a}_Y$, generated from **3a** and $\mathbf{5}_Y$ readily catalyzed the conversion of **1** to the corresponding pyrrolidine **2** with good (56%) enantioselectivity.[7] As might be expected, the corresponding

Table 1 NPS and NPSe ligand assays

Entry	Proligand	Metal	t^a	ee^b (config)^c
1	**3a**	Y	36 h	56% (*S*)
2	**3a**	Sm	36 h	38% (*S*)
3	**3a**	Lu	18 h	64% (*S*)
4	**3b**	Y	36 h	−56% (*R*)
5	**3b**	Sm	48 h	−42% (*R*)
6	**3b**	Lu	24 h	−58% (*R*)

[a] >95% conversion as determined by ^{1}H NMR Spectroscopy. [b] Enantiomeric excess; based on integration of ^{1}H NMR spectrum using (*R*)-(−)-*O*-acetylmandelic acid.[2j] [c] Assigned based on NMR spectroscopy of the (*S*)-(+)-α-trifluoromethylphenylacetyl chloride derivative.[3i]

samarium complex $\mathbf{4a}_{Sm}$, that possesses a metal center larger than yttrium, exhibited reduced selectivity, providing **2** with an ee of 38%. Similarly, $\mathbf{4a}_{Lu}$, with a smaller metal center than yttrium, proved slightly more selective, furnishing **2** in 64% ee. The latter results are consistent with the early findings of Marks and Gagné, who observed that catalytic turn-over frequencies for internal hydroamination decrease in direct relation to decreasing atomic radius of the metal center within group 3 metallocenes.[8] A closely related set of enantioselectivities were obtained for group 3 complexes derived from the NPSe proligand **4b**, with the expected reversal of antipodal selectivity (Table 1).

The comparatively simple proligand *N*,*N*′-dicyclopentyl-1,1′-binaphthyl-2,2′-diamine (**3c**) has been shown to be one of the most effective proligands leading to chelating diamide complexes that possess respectable enantioselectivity in internal alkene hydroamination.[3a–d] In light of this, we initiated a study to elucidate factors that might influence structure–activity relationships in connection with variation of *N*-alkyl substitution. Subjection of the known proligand **3c** to the standard metallation protocol using $\mathbf{5}_Y$ cleanly generated $\mathbf{4c}_Y$, that, when used for the enantiocontrolled cyclization of **1** (2 d, 23 °C) afforded **2** in 72% ee, in agreement with literature results.[3a,c] As would be expected, the corresponding samarium precatalyst $\mathbf{4c}_{Sm}$ provided **2** more rapidly (1.5 d, 23 °C) but with slightly suppressed ee (66%). The lutetium analog $\mathbf{4c}_{Lu}$ proved less active, requiring fully 30 d at 23 °C (or 1.5 d at 60 °C) providing **2** with 70% (or 66%) ee respectively.

We subsequently explored minor and major perturbations on the *N* and *N*′- substituents of 1,1′-binaphthyl-2,2′-diamine. Accordingly, the utilization of the *N*,*N*′-2-indanoyl proligand **4d** gave rise to the facile generation of the precatalysts $\mathbf{4d}_Y$, $\mathbf{4d}_{Sm}$, and $\mathbf{4d}_{Lu}$. These, in turn, catalyzed the conversion of **1** to scalemic **2** in 70, 48, and 70% ee at 23 °C in 4.5, 9, and 24 d respectively. In sharp contrast to these results, the sterically encumbered precatalysts $\mathbf{4e}_Y$ and $\mathbf{4e}_{Sm}$ that possessed *N*,*N*′-2-(diphenylmethyl) substituents catalyzed the conversion of **1** to scalemic **2** in 75 and 72% ee at 23 °C in 7 d and 5 h respectively, but with a surprising and unexpected *inversion* of enantioselectivity. The less reactive complex, $\mathbf{4e}_{Lu}$, required 1.5 d at 60 °C for >95% conversion and gave **2** in 33% ee, also with inverted enantioselectivity (Table 2).

In 2003, Reetz and coworkers reported an efficient method for the synthesis of sterically hindered *N*,*N*′-diaryl-1,1′-binaphthyl-2,2′-diamines using a modification of the Buchwald *N*-arylation procedure.[5] Given the opportunity provided by this precedent, proligands **3f** and **3g** were assembled and subsequently evaluated as chirality sources for the enantioselective conversion of **1** to **2**.

Table 2 Alkyl substituted proligand assays

Entry	Proligand	Metal	t^a	ee^b (config)
1	**3c**	Y	2 d	72% (*S*)
2	**3c**	Sm	1.5 d	66% (*S*)
3	**3c**	Lu	30 d	70% (*S*)
4	**3c**	Lu	1.5 d^c	66%^{c}(*S*)
5	**3d**	Y	4.5 d	70% (*S*)
6	**3d**	Sm	9 d	48% (*S*)
7	**3d**	Lu	24 d	70% (*S*)
8	**3e**	Y	7 d	−75% (*R*)
9	**3e**	Sm	5 d	−72% (*R*)
10	**3e**	Lu	1.5 d^c	−33%^{c}(*R*)

^{a} >95% conversion as determined by ^{1}H NMR spectroscopy. ^{b} Enantiomeric excess. ^{c} Reaction was performed at 60 °C.

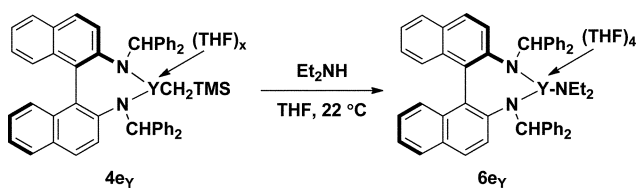
Table 3 Aryl substituted proligand assays

Entry	Proligand	Metal	t^a	ee^b (config)
1	**3f**	Y	12 h	28% (*S*)
2	**3f**	Sm	3 h	38% (*S*)
3	**3f**	Lu	16 h	32% (*S*)
4	**3g**	Y	27 h	12% (*S*)
5	**3g**	Sm	4 h	16% (*S*)
6	**3g**	Lu	24 h	12% (*S*)

^{a} Reactions were performed at 60 °C; >95% conversion as determined by ^{1}H NMR spectroscopy. ^{b} Enantiomeric excess.

The preliminary results obtained with Y, Sm, and Lu precatalysts derived from **3f** and **3g** were disappointing as prolonged reaction times were necessary to achieve >95% conversion and the observed enantiomeric excesses were uniformly low (Table 3). It should be emphasized that we have not yet isolated rigorously pure complexes of the type $\mathbf{4f}_M$ and $\mathbf{4g}_M$. Should these entities possess low catalytic activity, as a consequence of an unfavorable steric and/or electronic environment at the metal center, the observed decrease in enantioselectivity would be consistent with a competing reaction pathway involving a more reactive *achiral* catalyst derived from the homoleptic metallating agents **5**.

In order to determine the nature of metal species formed *via* the *in situ* methodology, we attempted the isolation of monoalkyl complex $\mathbf{4e}_Y$. Unfortunately, in coordinating (THF) and noncoordinating (C_6D_6) solvents, the decomposition of complex $\mathbf{4e}_Y$ occurs (<2 d at 22 °C). This observation is consistent with the reported instability of other alkyl group 3 metal amide complexes.[6] To circumvent this difficulty, we prepared the more robust triamide complex $\mathbf{6e}_Y$ *via* aminolysis of the yttrium-alkyl bond of $\mathbf{4e}_Y$ with diethylamine (Scheme 4).[6] Addition of diethylamine to a solution of $\mathbf{4e}_Y$ in THF at ambient temperature provided rapid access to $\mathbf{6e}_Y$ (less than five minutes for complete ligand exchange).



4e$_Y$ 6e$_Y$

Scheme 4 Synthesis of an enantiopure yttrium triamide complex.

Unlike its precursor, $\mathbf{4e}_Y$, triamide $\mathbf{6e}_Y$ was stable for several days in THF. After filtration, the volatiles were removed to provide $\mathbf{6e}_Y$. Within the ^{1}H NMR spectrum of $\mathbf{6e}_Y$ (in C_6D_6) the resonances for the *N*-methylene group of the diethylamido ligand and the *N*-methine resonances of the 1,1′-binaphthyl-2,2′-diamine were shifted downfield in comparison to their unligated counterparts. Furthermore, the ^{1}H NMR spectrum of $\mathbf{6e}_Y$ is consistent with four molecules of THF per 1,1′-binaphthyl-2,2′-diamine unit. Interestingly, there are two distinct *O*-methylene resonances for the coordinated THF molecules shifted upfield from free THF. Additionally, the C_2 symmetry of $\mathbf{6e}_Y$ is evidenced by the sharp singlet for the methine resonance (5.922 ppm in THF).

Conclusions

In summary, we have optimized an experimentally facile method for the *in situ* generation of chiral non-metallocene complexes of the group 3 metals based on ligand exchange using preformed homoleptic alkyls $M(CH_2TMS)_3\cdot(THF)_2$ (**5**). Little difference was observed in the catalytic activity/selectivity profiles for the NPS and NPSe complexes $\mathbf{4a}_M$ and $\mathbf{4b}_M$. *N*-Alkyl substituted complexes $\mathbf{4c}_M$–$\mathbf{4e}_M$ provided the highest enantioselectivities in this study, with a remarkable reversal of enantioselection observed for $\mathbf{4e}_M$, consistent with a significant steric perturbation at the catalytic site. Although the attempted isolation of $\mathbf{4e}_Y$ failed due to its intrinsic instability, the isolation of the corresponding triamide derivative $\mathbf{6e}_Y$ was achieved. The synthesis and evaluation of additional chelating diamine and related proligands as well as the activity/selectivity signatures of their *isolated* complexes will be the topics of a future report from this laboratory.

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