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Optically active, bulky tris(oxazolinyl)borato magnesium and calcium compounds for asymmetric hydroamination/cyclization

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ABSTRACT

The synthesis of the new chiral, pseudo C_3-symmetric, monoanionic ligand tris(*4S-tert*-butyl-2-oxazolinyl)phenylborate $[To^T]^-$ is reported. The steric bulk, tridentate coordination, and anionic charge of $[To^T]^-$ are suitable for formation of complexes of the type To^TMX, where one valence is available for reactivity. With this point in mind, we prepared magnesium and calcium To^T complexes that resist redistribution to $(To^T)_2M$ compounds. Both To^TMgMe and $To^TCaC(SiHMe_2)_3$ contain tridentate To^T-coordination to the metal center, as shown by NMR spectroscopy, infrared spectroscopy, and X-ray crystallography. These compounds are active catalysts for the cyclization of three aminoalkenes to pyrrolidines, and provide non-racemic mixtures of pyrrolidines in enantiomeric excesses up to 36%.

1. Introduction

Group 2 organometallic compounds have potential advantages in homogeneous catalysis, as organomagnesium and organocalcium compounds are inexpensive, their starting materials are readily available, both metals are physiologically benign, and techniques for their manipulation are typically similar to those developed for Grignard reagents. However, their ionic bonding, facile configurational and structural exchange reactions, and thermodynamic stability of oxide and halide salts due to high lattice energies are particular challenges that inhibit the application of Group 2 metal compounds in catalysis. In this regard, the discovery by Parkin and coworkers that tris(pyrazolyl)boratomagnesium(II) compounds are resistant toward disproportionation reactions and provide compounds with well-defined coordination constitutions and geometries offers opportunities for organomagnesium compounds in catalysis [1]. Later, Chisholm reported achiral C_{3v} and chiral C_3-symmetric tris(pyrazolyl)boratomagnesium catalysts for lactide ring-opening polymerization [2]. More recently, magnesium and calcium diketiminate compounds (e.g. {nacnac}MR) have been shown to be highly active in hydroamination/cyclization of aminoalkenes [3,4] where sterically demanding substituents on the diketiminate hinder the formation of bis(diketiminate)magnesium and calcium complexes [5]. Additionally, interesting zwitterionic bis(carbene)- and tris(carbene)borato alkaline earth metal compounds have been reported and applied in hydroamination/cyclization [6]. A few reports of stereoselective hydroamination with calcium and magnesium-based catalysts have provided % ee's up to 6% and 14%, respectively [7].

We previously reported the synthesis of the achiral monoanionic tris(4,4-dimethyl-2-oxazolinyl)phenylborate $[\mathbf{To^M}]^-$ and its chemistry in zirconium, [8] iridium, aluminum, and yttrium complexes, [9] where the latter yttrium species are catalysts for the cyclization/hydroamination of aminoalkenes to pyrrolidines [10].

These tridentate monoanionic ligands are electronically similar to the well-known tris(pyrazolyl)borate ligands [11,12]. The tridentate monoanionic oxazolinylborate ligands also may be compared to Gade's neutral tridentate tris(oxazolinyl)ethane ligands (trisox) [13] whereas the anionic borate center in the tris(oxazolinyl)borates provides an additional electrostatic component to their interaction with metal centers. Compounds with the formula $[\{trisox\}LnR]^{2+}$ (Ln = Sc, Y, Lu, Tm, Er, Ho, Dy), generated in situ from $\{trisox\}LnR_3$ and $[Ph_3C][B(C_6F_5)_4]$, are catalysts for stereospecific polymerization of α-olefins [14]. Neutral tris(oxazolinyl)borate compounds of divalent metal centers, such as magnesium, calcium, and zinc, are isoelectronic with the putative dicationic trisox rare earth alkyls and might provide reactive complexes. In this context, we recently described a series of achiral tris(oxazolinyl)borato zinc compounds containing chloride, hydride, alkoxide, and disilazide ligands [15]. We were curious if tris(oxazolinyl)borato magnesium and calcium compounds might behave similarly, providing robust compounds

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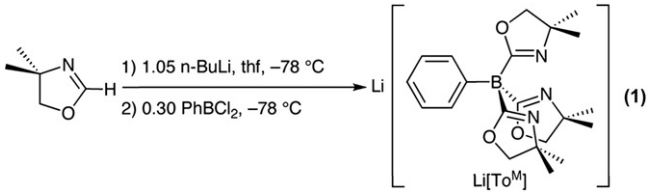
that could still access open coordination sites for chemical reactivity. Here we report the synthesis of tris(*4S-tert*-butyl-2-oxazolinyl)phenylborate $[To^T]^-$, its complexes with magnesium(II) and calcium(II), and their reactivity as catalysts for the hydroamination/cyclization of aminoalkenes.

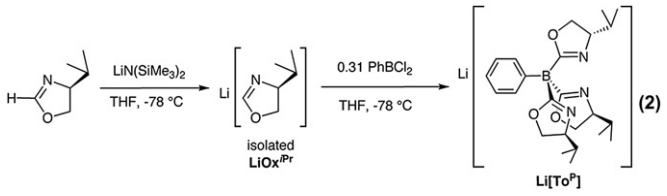
2. Results and discussion

2.1. Ligand synthesis

The preparation of Li[To^M] involves in situ deprotonation of 2H-4,4-dimethyl-2-oxazoline with *n*BuLi followed by reaction with 0.30 equivalents of $PhBCl_2$ (Eq. (1)) [8].

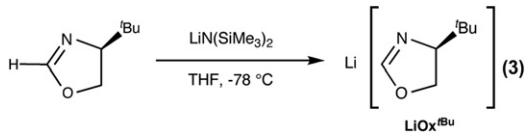


We also prepared a chiral analog from the readily-available, L-valine-derived *4S*-isopropyl-2-oxazoline to provide tris(*4S*-isopropyl-2-oxazolinyl)phenylborate [**To^P**]$^-$ [16]. In contrast to the synthesis of $[To^M]^-$, deprotonation of 2H-*4S*-isopropyl-2-oxazoline with *n*BuLi proceeds in lower yield (ca. 70%) [17] and treatment of the in situ prepared 2Li-*4S*-isopropyl-oxazolide with 0.31 equivalents of $PhBCl_2$ affords Li[To^P] only irreproducibly. Instead, preparation of Li[To^P] requires deprotonation of 2H-*4S*-isopropyl-2-oxazoline with the bulky disilazide base $LiN(SiMe_3)_2$, isolation of the 2Li-*4S*-isopropyl-oxazolide, and reaction of the isolated material with 0.31 equivalents. of $PhBCl_2$ (Eq. (2)). Thus, the seemingly straightforward synthesis of tris(oxazolinyl)borates as proligands for organometallic compounds has required optimization for each ligand, unlike the corresponding bis(oxazolinyl)borates described by Pfaltz that are prepared by in situ reaction of 2H-oxazolines, *t*BuLi, and Ph_2BCl [18].



Because development of new stereoselective catalytic reactions often requires several structurally and electronically similar ligands with a range of steric properties, we set out to prepare a tris(oxazolinyl)borate derived from L-*tert*-leucine, as the *tert*-butyl group will provide an increased steric demand. The tridentate, monoanionic nature of these tris(oxazolinyl)borate ligands appears well suited to Group 2 chemistry because the ligand–metal interaction is supported by sterics and electrostatics, as well as coordination bonding.

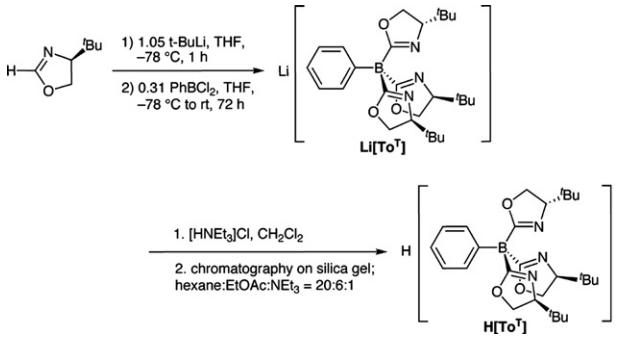
Reaction of 2H-*4S-tert*-butyl-2-oxazoline and $LiN(SiMe_3)_2$ provides 2Li-*4S-tert*-butyl-2-oxazolide (**LiOx^{tBu}**) (Eq. (3)). Although formation of $LiOx^{tBu}$ is quantitative in micromolar scale reactions, its isolation from the $HN(SiMe_3)_2$ byproduct proved difficult due to the high solubility of the oxazolide anion in pentane and diethyl ether. No evidence could be obtained for THF coordination to $LiOx^{tBu}$ that might be responsible for the enhanced solubility of the *tert*-butyl-oxazolide versus the 4*S*-isopropyl- or 4,4-dimethyl-oxazolides. Reaction of $LiOx^{tBu}$ with methanol-d_4 as solvent forms 2D-Ox^{tBu}, and the ^{1}H NMR spectrum of this mixture does not contain resonances from diethyl ether or THF that might rationalize the high solubility of $LiOx^{tBu}$ in hydrocarbon solvents. A ^{1}H NMR spectrum of isolated $LiOx^{tBu}$ in benzene-d_6 does not exhibit resonances due to residual THF, and addition of THF-d_8 to this benzene solution does not change the chemical shifts of the oxazolide in the ^{1}H NMR spectrum. Furthermore, the ^{7}Li NMR spectrum of $LiOx^{tBu}$ (1.22 ppm) in benzene-d_6 does not shift upon addition of THF. The IR spectrum of $LiOx^{tBu}$ (KBr) contained ν_{CN} bands due to both isocyanide (2000 cm^{-1}) and oxazolide (1635 cm^{-1}), and this is consistent with previous observations with 4,4-dimethyl-2-lithio-oxazolide and 4*S*-isopropyl-2-lithio-oxazolide [16,19].



This high solubility contrasts 2Li-4,4-dimethyl-oxazolide (**LiOx^{Me2}**) and 2Li-*4S*-isopropyl-oxazolide (**LiOx^{iPr}**) that are insoluble in hydrocarbons, diethyl ether, and THF once isolated, though the latter species dissolves in THF upon addition of $PhBCl_2$. The isolated anion $LiOx^{Me2}$ is insoluble in THF after isolation and was not useful for synthesis of Li[To^M], although it may be used in situ in THF. Thus, the procedure used for isolation of $LiOx^{iPr}$, which involves washing with diethyl ether to remove the $HN(SiMe_3)_2$, is not possible with $LiOx^{tBu}$. Neither repeated crystallization nor exposure to high vacuum (10^{-5} mTorr) for extended times (2 days) improved the purity of $LiOx^{tBu}$.

Fortunately, a one-pot procedure, in which 2H-*4S-tert*-butyl-2-oxazoline and *tert*-butyllithium are allowed to react in THF at −78 °C followed by treatment with 0.31 equivalents of $PhBCl_2$ at −78 °C affords the desired lithium tris(*4S-tert*-butyl-2-oxazolinyl)phenylborate (**Li[To^T]**, Eq. (4)) as indicated by a single resonance at δ −17.0 in the ^{11}B NMR spectrum in methanol-d_4. The ^{1}H NMR spectrum of crude Li[To^T] is consistent with formation of a C_3-symmetric product as evident by one set of oxazoline resonances at δ 0.86 (^{t}Bu), 3.75 (CH), and 3.89 (CH_2). Clearly, the yield of $LiOx^{tBu}$ obtained from an in situ 2H-*4S-tert*-butyl-2-oxazoline deprotonation with *tert*-butyllithium is much improved in comparison to $LiOx^{iPr}$. Apparently, the formation of a quaternary borate with three boron-oxazoline bonds requires pure oxazolide anion and cannot tolerate the lower yield of $LiOx^{iPr}$ or small amounts of $HN(SiMe_3)_2$.

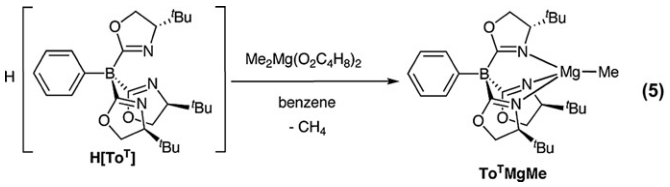
A crude sample of Li[To^T] (contaminated with LiCl) is converted to the protonated hydrogen tris(*4S-tert*-butyl-2-oxazolinyl)phenylborate **H[To^T]** (Eq. (4)) by treatment with triethylammonium chloride in methylene chloride, followed by filtration through alumina. Pure H[To^T] is isolated after silica gel column chromatography with the solvent mixture hexane:ethyl acetate:triethyl amine = 20:6:1. Only three oxazoline resonances δ 0.80 (^{t}Bu), 3.44



(CH), 3.78 (CH_2) are observed in the ^{1}H NMR spectrum of H[To^T] (benzene-d_6), providing support for an optically pure, C_3-symmetric species. As in [To^P]$^-$ chemistry, the oxazoline groups in *S,S,S*-H[To^T] are optically pure because small amounts of *4R-tert*-butyl-oxazoline would give diastereomers (e.g. *S,S,R*) that would have a ^{1}H NMR spectrum that is distinct from the *S,S,S*-H[To^T] diastereomer.

2.2. Synthesis and characterization of To^{T}MgMe and To^{T}CaC(SiHMe$_2$)$_3$

H[To^T] and $MgMe_2\cdot(O_2C_4H_8)_2$ react in benzene to afford To^{T}MgMe (Eq. (5)). The oxazolines in To^{T}MgMe are equivalent in the ^{1}H NMR spectrum, indicating that the magnesium compound's structure in solution is pseudo C_3-symmetric.



(5)

Thus, one resonance, observed at 0.72 ppm, was assigned to the *tert*-butyl moiety, and three resonances due to the oxazoline methine and methylene were detected at 3.45, 3.59 and 3.72 ppm. Additionally, the resonance due to the MgMe appeared at −0.65 ppm; the integrated ratio of this resonance versus the ^{t}Bu resonance was the expected 3 H:27 H. The ^{15}N{^{1}H} NMR chemical shift of −178.2 ppm was obtained from a ^{1}H−^{15}N HMBC experiment, which contained a crosspeak between the oxazoline nitrogen and oxazoline methine and methylene resonances. Unfortunately, through-bond coupling (3 bonds) between the coordinated oxazoline nitrogen and magnesium methyl was not detected. The ^{15}N{^{1}H} NMR chemical shift is only slightly different than the value of −174.5 ppm observed for H[To^T], but it is significantly upfield from that of 2H-*4S-tert*-butyl-2-oxazoline (−148.0 ppm). Evidence for a three-point interaction between [To^T]$^-$ and magnesium (versus rapid exchange of oxazoline in a bidentate ground state) is provided by the infrared spectrum that contains only one ν_{CN} at 1585 cm^{-1}. In contrast, the ν_{CN} of 2H-*4S-tert*-butyl-2-oxazoline and H[To^T] are 1635 and 1601 cm^{-1}, respectively [19] The steric impact of coordination of the large [To^T] ligand to the small magnesium(II) center is sufficient to inhibit coordination of THF and dioxane.

X-ray quality crystals of To^{T}MgMe were obtained from a concentrated toluene solution cooled to −78 °C. A single crystal diffraction study revealed that the tris(oxazolinyl)borate is coordinated to the magnesium center in a tridentate fashion in the solid state (Fig. 1). Pseudo-C_3 symmetry is evident, where the C_3 axis coincides with the B−Mg vector with the simplifying assumption that the B−C_{phenyl} is freely rotating in solution. Thus, the [To^T]$^-$ ligand forms a propeller-type shape around the magnesium center. The chiral $P2_12_12_1$ space group is consistent with the presence of only one enantiomer of To^{T}MgMe in the solid state.

The Mg1−C26 bond length is 2.102(1) Å; the Mg1−N1 and Mg1−N3 bond lengths are equivalent (2.108(1) and 2.109(1) Å), whereas the Mg1−N2 bond is slightly longer (2.118(1) Å). The steric bulk and chelating [To^T] ligand distort the bond angles of the Mg center from tetrahedral, as expected for a highly ionic compound. For example, the values for the ∠N−Mg−N angles are close to 90° (89.74(4)−91.56(4)°) whereas the ∠N−Mg−C angles are more open, ranging from 121.13(6) to 127.84(6)°. For comparison, the Mg−C bond distance in the related tris(pyrazolyl)borate compound Tp^{tBu}MgMe (Tp^{tBu} = tris(3-*tert*-butyl-pyrazolyl)borate) of 2.12(1) Å is the same within 3σ error, and the Mg−N bond distances 2.13(1), 2.137(7), and 2.137(7) Å are also essentially identical with those in To^{T}MgMe.[1] The N−Mg−N and N−Mg−C bond angles are similar (90.6(4)−91.3(3)°) and (122.7(4)−125.4(2)°) respectively. The similarity of Mg−N bond lengths in To^{T}MgMe and Tp^{tBu}MgMe, where *4S-tert*-butyl-oxazolinyl and 3-*tert*-butyl-pyrazolyl are expected to have distinct electronic properties, further emphasizes the substantial ionic character of these four-coordinate magnesium compounds.

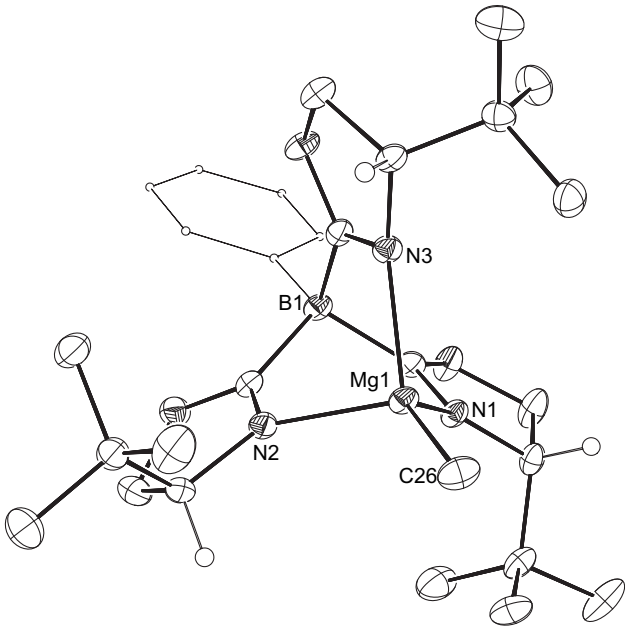
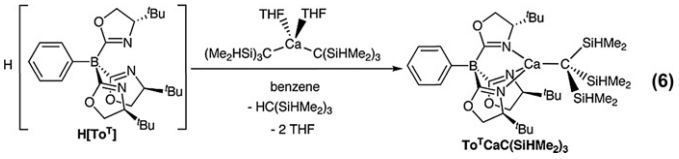


Fig. 1. An ORTEP diagram of To^{T}MgMe, drawn at 50% probability. Hydrogen atoms on the stereogenic centers are shown to highlight the configuration, and the C_6H_5 group is represented by a ball and stick structure (without the hydrogens) for clarity.

A better comparison between To^{T}MgMe and Tp^{tBu}MgMe involves their relative steric properties. The cone angle of Tp^{tBu} was previously estimated as 244°, [1] whereas the crystallographic coordinates of To^T from To^{T}MgMe provide an estimation of its cone angle as 233°. The cone angle measures the extent to which substituents on the pyrazole or oxazoline rings (i.e., *tert*-butyl) extend past the magnesium center. A second approach for assessing the steric properties of a ligand is provided by its solid angle, in which the metal center is treated as a point source of light and the complex is encompassed in an imaginary sphere [20]. The solid angle is the surface area of a shadow cast by a ligand on the inside of the sphere, providing an estimate of the overall steric impact of a ligand. We have calculated the solid angles for To^T and Tp^{tBu} from X-ray coordinates as 7.8 steradians (the percentage of the surface area of the surrounding sphere 'shaded' is 62%) and 8.9 steradians (71%), respectively, using the program Solid-G [21]. Taken together, the cone angles and solid angles show that the effective size of the To^T ligand is smaller than that of Tp^{tBu}. This steric difference is related to the hybridization of the carbons on the heterocyclic rings, such that planar, sp^2-hybridized C3 in the pyrazole directs the *tert*-butyl group past the magnesium center whereas sp^3 hybridization in the oxazoline ring points the *tert*-butyl group toward the backside of one of the adjacent oxazolines rather than in front of the metal center. For example, the closest hydrogen on one *tert*-butyl group is 2.5 Å from the nearest hydrogen on the back-side of an adjacent oxazoline ring in the (static) conformation observed in the solid state structure. Still, for a stereoselective reaction (such as an insertion) in which a substrate must penetrate the space between two oxazoline rings, the steric properties of To^T are expected to make a significant steric distinction between prochiral faces.

Furthermore, the solid angles of both To^T and Tp^{tBu} indicate that $(To^T)_2Mg$ and $(Tp^{tBu})_2Mg$ are not sterically reasonable complexes (at least when both ligands are bonded in a tridentate fashion). Thus, the moniker 'tetrahedral enforcer', often applied to Tp^{tBu}, [1] is also an appropriate descriptor of the steric properties of To^T. Consistently, To^TMgMe is thermally robust in solution, and no change in the ^1H NMR spectra were observed after heating in toluene-d_8 at 120 °C for five days. Additionally, To^TMgMe can be stored as a solid at room temperature in the absence of air and moisture for extended times without observable decomposition.

A related calcium complex is accessible by reaction of $H[To^T]$ and $Ca(C(SiHMe_2)_3)_2(THF)_2$ [22] in benzene, which yields $To^TCaC(SiHMe_2)_3$ and $HC(SiHMe_2)_3$ as a non-coordinating byproduct that can be removed under vacuum (Eq. (6)). On micromolar scale in benzene-d_6, the reaction is complete after 5 min, but to insure complete conversion in larger scale preparations, the reaction was allowed to stir for 1 h before workup.



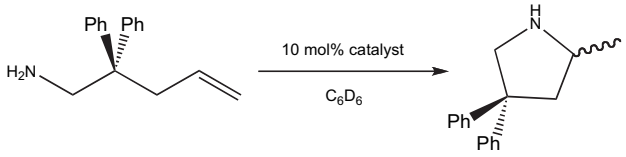
(6)

The compound $To^TCaC(SiHMe_2)_3$ is THF-free, and an intriguing aspect of the $-C(SiHMe_2)_3$ alkyl group is that it stabilizes the formally four-coordinate calcium center through additional β-agostic SiH interactions. Thus, the δ_{SiH} and $^1J_{SiH}$ of values 4.89 ppm and 153 Hz from the ^1H NMR spectrum and the ν_{SiH} values of 2106 and 1877 cm^{-1} in the infrared spectrum indicate the presence of β-agostic SiH groups, as are observed in the starting material $Ca(C(SiHMe_2)_3)_2(THF)_2$ [22] These data are consistent with a structure of $To^TCaC(SiHMe_2)_3$ containing one or two β-agostic SiH interactions that are fluxional on the ^1H NMR timescale but exchange slower than the IR timescale. The three oxazoline groups are equivalent on the ^1H NMR timescale. Additionally, no ν_{CN} bands from 1630 to 1615 cm^{-1} were detected that would correspond to non-coordinated oxazoline. Only a single ν_{CN} band at 1569 cm^{-1} was detected that was assigned as the symmetric normal stretching mode. These data indicate that all three oxazolines are coordinated to calcium and remain coordinated, at least for timeframes longer than the IR timescale.

2.3. Hydroamination/cyclization of aminoalkenes

We investigated our new optically active complexes To^TMgMe and $To^TCaC(SiHMe_2)_3$ as catalysts for the hydroamination/cyclization of the aminopentenes 2,2-diphenyl-1-amino-pent-4-ene, 2,2-dimethyl-1-amino-pent-4-ene, and C-(1-allyl-cyclohexyl)-methylamine as test substrates. The results are summarized in Tables 1–3. In general, the calcium compound $To^TCaC(SiHMe_2)_3$ catalyzes the cyclization of all three substrates at a significantly greater rate than hydroaminations catalyzed by To^TMgMe. While we expected that the presumed catalyst intermediate $To^TMNHCH_2CR_2CH_2CH{=}CH_2$ (R_2 = Ph_2, $-(CH_2)_5-$, Me_2) would be more reactive for M = Ca than M = Mg based on size and related rates of hydroamination/cyclizations catalyzed by diketiminate calcium and magnesium complexes, [3] initiation of $To^TCaC(SiHMe_2)_3$ is surprisingly fast given the unusual properties of the -C$(SiHMe_2)_3$ group [22]. This alkyl ligand is both sterically encumbered and relatively non-basic at the central carbon, and as a result Lewis acids such as $B(C_6F_5)_3$ react with a peripheral SiH rather than abstract the alkyl group in the typical fashion [23].

Table 1
Enantioselective hydroamination/cyclization of 2,2-diphenyl-4-penten-1-amine catalyzed by To^TMgMe and $To^TCaC(SiHMe_2)_3$.

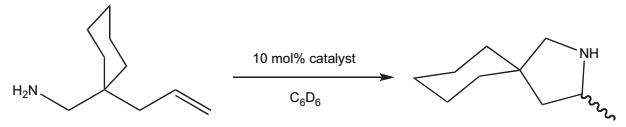


Entry	Catalyst	R	Time	Temperature	Conversion	% ee
1	To^TMgMe	Ph	24 h	RT	89%	0%
2	To^TMgMe	Ph	12 h	60 °C	≥99%	0%
3	$To^TCaC(SiHMe_2)_3$	Ph	5 min	RT	≥99%	0%

Although To^TMgMe and $To^TCaC(SiHMe_2)_3$ are efficient catalysts for the cyclization of 2,2-diphenyl-1-amino-pent-4-ene, the corresponding pyrrolidine product is obtained as a racemic mixture (Table 1). More promising results are obtained with C-(1-allyl-cyclohexyl)-methylamine, which is cyclized by To^TMgMe at 60 °C and by $To^TCaC(SiHMe_2)_3$ at room temperature to give the spiropyrrolidine product in 36% and 18% ee, respectively (Table 2). Additionally, the substrate 2,2-dimethyl-1-amino-pent-4-ene is cyclized by To^TMgMe with 27% ee and by $To^TCaC(SiHMe_2)_3$ with 18% ee. Interestingly, hydroamination/cyclization of 2,2-dimethyl-1-amino-pent-4-ene and C-(1-allyl-cyclohexyl)-methylamine with To^TMgMe gives rise to the *R* pyrrolidines whereas $To^TCaC(SiHMe_2)_3$ gives rise to the *S* pyrrolidines. We are currently working to elucidate the mechanism behind the stereo-defining step of To^TMgMe- and $To^TCaC(SiHMe_2)_3$-catalyzed hydroamination/cyclization given this interesting observation. However such differences in absolute configuration have also been reported in rare earth metal complex-catalyzed hydroaminations with scandium providing a different absolute configuration than larger metal centers [24]. Thus, the substituents on the alkyl chain appear to be the most important component of the aminoalkene for stereoselectivity in these cyclizations.

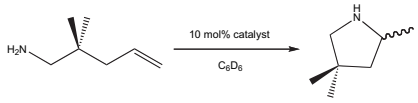
While the enantioselectivity of To^TMgMe and $To^TCaC(SiHMe_2)_3$ are relatively low in comparison to the highly selective catalysts of Hultzsch (Sc and Lu) [25] and Schafer (Zr) [26] these chiral oxazolinylborato magnesium and calcium catalysts provide the highest reported % ee's for Group 2-catalyzed hydroamination/cyclization. We are aware of only two reports of enantioselective hydroamination/cyclization with Group 2-based catalysts. Previously, Hultzsch and co-workers described chiral binaphthyl-derived tetraamine dimagnesium complexes that cyclize 2,2-diphenyl-1-amino-pent-4-ene with 14% ee, though 2,2-dimethyl-1-amino-pent-4-ene (4% ee) and C-(1-allyl-cyclohexyl)-methylamine (6% ee) were less successful [7b]. Additionally, Harder and co-workers

Table 2
Enantioselective hydroamination/cyclization of C-(1-allyl-cyclohexyl)-methylamine catalyzed by To^TMgMe and $To^TCaC(SiHMe_2)_3$.



Entry	Catalyst	Tim	Temperature	Conversion	% ee
1	To^TMgMe	24 h	RT	no conversion	n.a.
2	To^TMgMe	26 h	60 °C	93%	36% (*R*)
3	$To^TCaC(SiHMe_2)_3$	5 min	RT	≥99%	18% (*S*)
4	$To^TCaC(SiHMe_2)_3$ (1% cat)	7 d	80 °C	≤10%	n.d.

Table 3
Enantioselective hydroamination/cyclization of 2,2-dimethyl-4-penten-1-amine catalyzed by To^TMgMe and $To^TCaC(SiHMe_2)_3$.



	Catalyst	Time	Temperature	Conversion	% ee
1	To^TMgMe	7 d	RT	none	n.a.
2	To^TMgMe	5 d	80 °C	80%	27% (*R*)
3	$To^TCaC(SiHMe_2)_3$	5 min	RT	100%	18% (*S*)

reported that bis(oxazoline) disilazidocalcium catalyzes the cyclization of 2,2-diphenyl-1-amino-pent-4-ene in up to 10% ee [7a].

3. Conclusion

The contrasting stereoselectivity between the neutral Group 2 tris (oxazolinyl)borate catalyzed hydroamination/cyclization described here and the dicationic trisox scandium alkyls that polymerize α-olefins with high stereoregularity is striking. Both reactions are presumed to involve insertion of an olefin into an M–E bond, albeit Mg/Ca–N versus Sc–C bonds and intramolecular cyclization versus a chain and/or ligand mediated intramolecular process. Clearly, the factors that control stereoselective insertion in olefin polymerization are significantly different than the factors that influence cyclization of aminoalkenes in hydroamination reactions. A related comparison was considered by Marks and co-workers, who investigated C_1-symmetric and chiral *ansa*-lanthanoidocene complexes $Me_2Si(C_5Me_4)(C_5H_3R^*)LnR$ as catalysts for enantioselective hydrogenation and hydroamination/cyclization [27]. In those cases, good enantioselectivities were obtained for both reactions (up to 74% for hydroamination and up to 96% for hydrogenation), and olefin insertion was proposed as the stereochemistry defining step for both catalytic transformations.

4. Experimental

4.1. General procedures

All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N_2. Benzene-d_6, toluene-d_8 and tetrahydrofuran-d_8 were vacuum transferred from Na/K alloy and stored under N_2 in the glovebox. $Ca(C(SiHMe_2)_3)_2(THF)_2$ [22] $Me_2Mg\cdot(O_2C_4H_8)_2$ [28] 2,2-diphenyl-4-penten-1-amine [29] 2,2-dimethyl-4-penten-1-amine [30] and C-(1-allyl-cyclohexyl)-methylamine [31] were prepared by published procedures. All the aminoalkenes were degassed and stored with 4 Å molecular sieves in a glovebox prior to use. All other chemicals used here are commercially available. ^1H, ^{11}B, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were collected on a Bruker DRX-400 spectrometer or a Bruker Avance II 700 spectrometer with a Bruker Z-gradient inverse TXI $^1H/^{13}C/^{15}N$ 5 mm cryoprobe. $^{13}C\{^1H\}$ NMR chemical shifts of boron-bonded carbons were not observed in several cases due to the quadrupolar ^{11}B nucleus. ^{15}N chemical shifts were also determined on the Bruker Avance II 700 spectrometer by $^1H–^{15}N$ HMBC experiments; ^{15}N chemical shifts were originally referenced to liquid NH_3 and recalculated to the CH_3NO_2 chemical shift scale by adding −381.9 ppm ^{11}B NMR spectra were referenced to an external sample of $BF_3\cdot Et_2O$ and ^{29}Si NMR spectra were referenced to an external sample of tetramethylsilane. Accurate mass ESI mass spectrometry was performed using the Agilent QTOF 6530 equipped with the Jet Stream ESI source. An Agilent ESI test mix was used for tuning and calibration. Accurate mass data was obtained in the positive ion mode using a reference standard with ions at 121.05087 and 922.00979. The mass resolution (FWHM) was maintained at 18,000.

4.1.1. 2Li-4-tert-butyl-2-oxazoline [$LiOx^{tBu}$]

Hexamethyldisilazane (1.0 mL, 4.80 mmol) was added to a Schlenk flask followed by 15 mL of THF. The solution was cooled to −78 °C then *n*-butyllithium (1.92 mL, 4.80 mmol) was slowly added. The solution was allowed to stir for 45 min, and then a THF (5 mL) solution of degassed 4*S*-*tert*-butyl-2-oxazoline was added slowly via cannula. The solution immediately turned bright yellow. The yellow solution was stirred at −78 °C for 1 h then warmed to room temperature and allowed to stir for 2 h. All volatiles were removed *in vacuo*. The resulting yellow solid was dissolved in warm hexane and cooled to −30 °C. The resulting off-white solid was isolated by filtration at −30 °C and dried under vacuum to yield 0.461 g (3.46 mmol, 76%) of crude $LiOx^{tBu}$ that is contaminated with small amounts of $HN(SiMe_3)_2$. ^1H NMR (400 MHz, tetrahydrofuran-d_8): δ 4.02 (br d, $^2J_{HH}$ = 8.4 Hz, 1 H, $LiCNCHCMe_3CH_2O$), 3.74 (t, $^3J_{HH}$ = 9.6 Hz, 1 H, $LiCNCHCMe_3CH_2O$), 3.23 (br d, $^2J_{HH}$ = 7.2 Hz, 1 H, $LiCNCHCMe_3CH_2O$), 0.95 (s, 9 H, $LiCNCHCMe_3CH_2O$). $^{13}C\{^1H\}$ NMR (100 MHz, tetrahydrofuran-d_8): δ 156.98 ($LiCNCHCMe_3CH_2O$), 73.54 ($LiCNCHCMe_3CH_2O$), 65.64 ($LiCNCHCMe_3CH_2O$), 33.48 ($LiCNCHCMe_3CH_2O$), 27.27 ($LiCNCHCMe_3CH_2O$). ^7Li NMR (156 MHz, benzene-d_6): δ 1.22. IR (KBr, cm^{-1}): 2970 s, 2908 m, 2873 m, 2833 m, 2718 w, 2000 w (ν_{CN}; ring-opened isocyanide), 1635 w (ν_{CN}; oxazolide), 1479 m, 1465 m, 1400 w, 1367 m, 1336 w, 1243 w, 1222 w, 1190 w, 1020 w, 942 w, 922 w, 820 w, 779 w.

4.1.2. Li[To^T]

A solution of 4*S*-*tert*-butyl-2-oxazoline (2.77 g, 21.8 mmol) in THF (100 mL) was cooled to −78 °C in a dry ice/acetone bath. *tert*-Butyllithium (13.6 mL, 23.1 mmol, 1.7 M) was added in a dropwise fashion, and the solution turned from colorless to bright yellow. The reaction mixture was stirred for 30 min at −78 °C, and then $PhBCl_2$ (0.88 mL, 6.78 mmol) was slowly added. The yellow solution was allowed to slowly warm to room temperature and was then stirred for 72 h. The volatiles were evaporated, and the resulting yellow solid was extracted with diethyl ether to yield crude Li[To^T] (2.23 g, 4.71 mmol, 65%). The most efficient way to obtain pure $[To^T]^-$ is to transform Li[To^T] into H[To^T], but ^1H NMR and ^{11}B NMR spectroscopy are useful for verifying complete conversion to Li[To^T]. ^1H NMR (methanol-d_4): δ 7.42 (d, $^3J_{HH}$ = 5.6 Hz, 2 H, *ortho*-C_6H_5), 7.02 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *meta*-C_6H_5), 6.94 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, *para*-C_6H_5), 3.89 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, OCH_2), 3.75 (t, $^3J_{HH}$ = 8.4 Hz, 3 H, $NCHCMe_3$), 0.86 (s, 27 H, $NCHCMe_3$). ^7Li NMR (156 MHz, acetonitrile-d_3): δ 0.11. ^{11}B NMR (128 MHz, methanol-d_4): δ −17.0.

4.1.3. H[To^T]

Crude Li[To^T] (1.316 g, 2.78 mmol) was dissolved in methylene chloride (50 mL). $[HNEt_3]Cl$ (0.455 g, 3.31 mmol) was added, and the resulting yellow suspension was stirred overnight at room temperature. All volatile materials were evaporated under reduced pressure. The resulting pale yellow solid was redissolved in a minimal amount of methylene chloride and passed through a plug of grade III neutral alumina (16 mm × 76 mm) using methylene chloride (100 mL) as the eluent. The solvent was removed under vacuum to yield a pale yellow solid. The solid H[To^T]

was extracted with benzene (3 × 15 mL) to remove residual [$HNEt_3$]Cl. The filtrate was collected, and the solvent was removed under vacuum to yield a pale yellow solid. This crude product was purified by silica gel chromatography (16 mm × 140 mm, hexane: EtOAc:NEt_3 = 20:6:1, R_f = 0.27) to afford 0.714 g (1.53 mmol, 55%) of hydrogen tris(*4S-tert*-butyl-2-oxazolinyl)phenylborate (**H[To^T]**). H[To^T] was further dried over P_2O_5 in benzene without loss of yield. ^{1}H NMR (400 MHz, benzene-d_6): δ 8.12 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, *ortho*-C_6H_5), 7.46 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, *meta*-C_6H_5), 7.25 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *para*-C_6H_5), 3.78 (m, 6 H, OC*H*$_2$), 3.44 (dd, J_{HH} = 10.2 Hz, 7.6 Hz, 3 H, NC*H*CMe$_3$), 0.80 (s, 27 H, C*Me*$_3$). ^{13}C{^{1}H} NMR (175 MHz, benzene-d_6): δ 134.99 (*ortho*-C_6H_5), 127.88 (*meta*-C_6H_5), 126.36 (*para*-C_6H_5), 73.18 (N*C*HCMe$_3$), 39.16 (O*C*H$_2$), 33.86 (*C*Me$_3$), 26.14 (C*Me*$_3$). ^{11}B NMR (128 MHz, benzene-d_6): δ −16.5. ^{15}N NMR (70.9 MHz, benzene-d_6): δ −174.5. IR (KBr, cm^{-1}): 3069 w, 3045 w, 2955 s, 2901 m, 2869 m, 1601 s (C═N), 1478 m, 1423 m, 1392 w, 1362 w, 1208 w, 1176 w, 969 m. MS (ESI) exact mass Calculated for $C_{27}H_{42}BN_3O_3$: m/e 468.3392 ([M$^+$]), Found: 468.3398 (Δ −1.29 ppm). Mp 98–102 °C.

4.1.4. To^{T}MgMe

A yellow benzene solution of H[To^T] (0.441 g, 0.943 mmol) was slowly added to a rapidly stirring suspension of $Me_2Mg\cdot(O_2C_4H_8)_2$ (0.241 g, 1.04 mmol) in benzene at room temperature. Vigorous bubbling was observed upon addition. After addition was complete, the suspension was stirred for 2 h; excess $Me_2Mg\cdot(O_2C_4H_8)_2$, which is insoluble under reaction conditions, was removed by filtration. The filtrate was evaporated under reduced pressure, and the resulting solid was washed with pentane to yield To^{T}MgMe (0.384 g, 0.759 mmol, 80.5%). X-ray quality crystals are obtained by cooling a concentrated toluene solution of To^{T}MgMe to −78 °C. ^{1}H NMR (700 MHz, benzene-d_6): δ 8.22 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, *ortho*-C_6H_5), 7.52 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, *meta*-C_6H_5), 7.33 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, *para*-C_6H_5), 3.72 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 5.6 Hz, 3 H, OC*H*$_2$), 3.59 (v t, J_{HH} = 9.8 Hz, 3 H, OC*H*$_2$), 3.45 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 5.6 Hz, 3 H, NC*H*CMe$_3$), 0.72 (s, 27 H, C*Me*$_3$), −0.65 (s, 3 H, MgMe). ^{13}C{^{1}H} NMR (175 MHz, benzene-d_6): δ 193.76 (br, B-*C*NCHCMe$_3$CH$_2$O), 136.44 (*ortho*-C_6H_5), 127.23 (*meta*-C_6H_5), 126.16 (*para*-C_6H_5), 73.59 (N*C*HCMe$_3$), 70.28 (OCH$_2$), 34.11 (*C*Me$_3$), 26.28 (C*Me*$_3$), −13.69 (MgMe). ^{11}B NMR (128 MHz, benzene-d_6): δ −17.1. ^{15}N NMR (70.9 MHz, benzene-d_6): δ −178.2. IR (KBr, cm^{-1}): 3045 w, 2958 m, 2869 m, 1585 s (C═N), 1478 m, 1396 w, 1365 m, 1196 s, 966 m. Anal. Calcd for $C_{28}H_{44}BMgN_3O_3(C_4H_8O_2)$: C, 64.72; H, 8.83; N, 7.08. Found: C, 64.44; H, 8.87; N, 7.52. Mp 238–239 °C (dec).

4.1.5. To^{T}CaC(SiHMe$_2$)$_3$

Ca(C(SiHMe$_2$)$_3$)$_2$(THF)$_2$ (0.086 g, 0.153 mmol) was dissolved in benzene (5 mL). In a separate vial, H[To^T] (0.054 g, 0.116 mmol) was dissolved in benzene (5 mL) and was added to the Ca(C(SiHMe$_2$)$_3$)$_2$(THF)$_2$ solution along with an additional 5 mL of benzene. The reaction mixture was stirred for 1 h, and then all the volatiles were removed *in vacuo* to yield an orange solid. To^{T}CaC(SiHMe$_2$)$_3$ was extracted with pentane; the yellow pentane solution was placed under vacuum overnight to remove the HC(SiHMe$_2$)$_3$ byproduct to yield a pale yellow solid (49.2 mg, 0.071 mmol, 61%). ^{1}H NMR (400 MHz, benzene-d_6): δ 8.11 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *ortho*-C_6H_5), 7.49 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *meta*-C_6H_5), 7.30 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, *para*-C_6H_5), 4.89 (d, sept, $^1J_{SiH}$ = 153 Hz, $^3J_{HH}$ = 3.2 Hz, 3 H, SiH), 3.72 (dd, $^2J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 4 Hz, 3 H, OC*H*$_2$), 3.67 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 4 Hz, 3 H, NC*H*CMe$_3$), 3.48 (v t, J_{HH} = 9.2 Hz, 3 H, OC*H*$_2$), 0.73 (s, 27 H, NCHC*Me*$_3$), 0.52 (d, $^3J_{HH}$ = 3.2 Hz, 9 H, SiHC*H*$_3$), 0.50 (d, $^3J_{HH}$ = 3.2 Hz, 9 H, SiHC*H*$_3$). ^{13}C{^{1}H} (100 MHz, benzene-d_6): δ 135.97 (*ortho*-C_6H_5), 126.83 (*meta*-C_6H_5), 125.59 (*para*-C_6H_5), 74.15 (N*C*HCMe$_3$), 68.91 (O*C*H$_2$), 34.02 (NCH*C*Me$_3$), 25.84 (NCHC*Me*$_3$), 4.18 (*C*(SiHMe$_2$)$_3$), 3.73 (C(SiH*Me*$_2$)$_3$). ^{11}B NMR (128 MHz, benzene-d_6): δ −16.7. ^{15}N NMR (70.9 MHz, benzene-d_6): δ −163.7. ^{29}Si{^{1}H} NMR (79.5 MHz, benzene-d_6): δ −20.4. IR (KBr, cm^{-1}): 3044 w, 3074 w, 2958 m, 2903 m, 2870 w, 2106 m (SiH), 1877 w (SiH), 1569 m (C═N), 1478 w, 1254 w. Anal. Calcd for $C_{34}H_{62}BCaN_3O_3Si_3$(HC(SiHMe$_2$)$_3$): C, 55.55; H, 9.55; N, 4.74. Found: C, 55.67; H, 9.44; N, 4.61. Mp 226–227 °C (dec).

4.1.6. General conditions for hydroamination/cyclization

In a glovebox, To^{T}MgMe or To^{T}CaC(SiHMe$_2$)$_3$ catalyst (1 equivalent) and aminoalkene (10 equivalents) were massed in separate test tubes. The catalyst was dissolved in benzene-d_6 and transferred to a test tube containing the aminoalkene. This solution was either added to a dry NMR tube and capped with a septa for room temperature reactions or added to a dry NMR tube fitted with a J-Young valve for reactions at elevated temperatures. ^{1}H NMR spectra were taken at regular intervals.

4.1.7. Determination of % ee for cyclohexyl- and dimethyl-pyrrolidine

The NMR sample was transferred to a flask and all volatiles were vacuum transferred under reduced pressure. The solution is then transferred to an NMR tube. The amount of pyrrolidine is calculated from the ^{1}H NMR spectrum using tetrakis(trimethylsilyl)silane as an internal standard. Hünig's base (2 equivalents) and (*S*)-(+)-Mosher's chloride (1.2 equivalents) were added to the NMR tube. After 20 min, the NMR sample was added to a vial and all volatiles were removed *in vacuo*. The pyrrolidine-Mosher amide was extracted with pentane (3 × 2 mL) and the volatiles were removed. The % ee was then determined by integration of the ^{19}F NMR spectrum at 60 °C in chloroform-*d*.

4.1.8. Determination of % ee for diphenyl-pyrrolidine

The NMR sample was transferred to a small flask and the 4,4-diphenyl-2-methylpyrrolidine product was vacuum distilled using a Kugelrohr (~120 °C, 10^{-6} torr). The distillate was then transferred to an NMR tube with chloroform-*d*. The amount of pyrrolidine product was calculated from the ^{1}H NMR spectrum using tetrakis(trimethylsilyl)silane as an internal standard. Hünig's base (2 equivalents) and (*S*)-(+)-Mosher's chloride (1.2 equivalents) were added to the NMR tube. After 20 min, all volatiles were removed *in vacuo*. The amide product was extracted with pentane (3 × 2 mL) and the volatiles were removed. The % ee was then determined by integration of the ^{1}H NMR spectrum at ambient temperature in chloroform-*d*.

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Appendix A. Supplementary material

CCDC 787151 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.08.057.

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