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Organometallic Complexes of Bulky, Optically Active, C_3-Symmetric Tris(4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl)phenylborate (To^{P}*)

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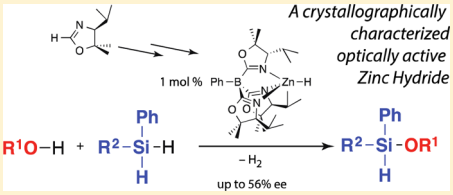
Supporting Information

ABSTRACT: A bulky, optically active monoanionic scorpionate ligand, tris(4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl)phenylborate (To^{P}*), is synthesized from the naturally occurring amino acid L-valine as its lithium salt, Li[To^{P}*] (**1**). That compound is readily converted to the thallium complex Tl[To^{P}*] (**2**) and to the acid derivative H[To^{P}*] (**3**). Group 7 tricarbonyl complexes To^{P}*M(CO)$_3$ (M = Mn (**4**), Re (**5**)) are synthesized by the reaction of MBr(CO)$_5$ and Li[To^{P}*] and are crystallographically characterized. The ν_{CO} bands in their infrared spectra indicate that π back-donation in the rhenium compounds is greater with To^{P}* than with non-methylated tris(4*S*-isopropyl-2-oxazolinyl)phenylborate (To^{P}). The reaction of H[To^{P}*] and $ZnEt_2$ gives To^{P}*ZnEt (**6**), while To^{P}*ZnCl (**7**) is synthesized from Li[To^{P}*] and $ZnCl_2$. The reaction of To^{P}*ZnCl and KO*t*Bu followed by addition of $PhSiH_3$ provides the zinc hydride complex To^{P}*ZnH (**8**). Compound **8** is the first example of a crystallographically characterized optically active zinc hydride. We tested its catalytic reactivity in the cross-dehydrocoupling of silanes and alcohols, which provided Si-chiral silanes with moderate enantioselectivity.

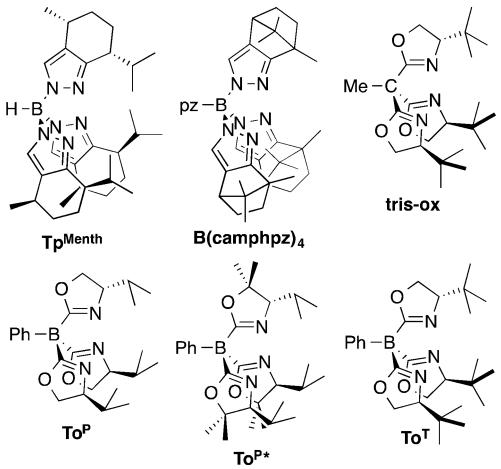


INTRODUCTION

Bulky scorpionate ligands, such as tris(3-mesitylpyrazolyl)-borate (Tp^{Ms}), tris(3,5-dimethylpyrazolyl)borate (Tp*), and tris(3-*tert*-butyl-5-methylpyrazolyl)borate ($Tp^{tBu,Me}$),[1] stabilize reactive groups across the periodic table in complexes of transition metals,[2] lanthanides,[3] and main-group metals.[4] Optically active tris(pyrazolyl)borate ligands also offer the opportunity to explore C_3 symmetry in stereoselective reactions and in catalysis (see Tp^{menth} or B(camphpz)$_4$ in Chart 1).[5] However, unsymmetrically substituted pyrazoles may form either B–N1 or B–N2 linkages, and combinations of these linkages give diastereomeric mixtures rather than stereochemically pure compounds. In addition, the B–N bond in pyrazolylborate ligands is susceptible to isomerization or cleavage.[5b,6] This process can be mediated by metal ions,[7] and it may limit the application of optically active tris(pyrazolyl)borates in enantioselective catalysis. Oxazolinylborate-based ligands with B–C2 linkages circumvent these isomerization issues, and a series of oxazolinylborate-based scorpionate ligands have previously been reported, including achiral tris(4,4-dimethyl-2-oxazolinyl)phenylborate (To^{M})[8] and optically active tris(4*S*-isopropyl-2-oxazolinyl)phenylborate (To^{P})[9] and tris(4*S*-*tert*-butyl-2-oxazolinyl)phenylborate (To^{T}).[10] Alternatively, neutral C_3-symmetric tris-ox ligands RC(Ox^{R})$_3$ also circumvent the isomerization issues associated with optically active pyrazolylborates.[11] The anionic nature of tris(2-oxazolinyl)borates, however, also impacts the electronic properties and reactivity of the resulting complexes.

The 4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl group (Ox^{iPr,Me_2}) has been widely used in a variety of chiral ligands for catalytic reactions such as cyclopropanation,[12] allylic oxidation,[13] α-tosyloxylation,[14] and the Henry reaction (nitro-aldol reaction)[15] and in other enantioselective syntheses.[16] In addition, the mixed cyclopentadienylbis(oxazolinyl)borate ligand containing Ox^{iPr,Me_2} is highly effective in enantioselective hydroamination/cyclization of aminoalkenes[17] and more active than the analogue derived from 4*S*-*tert*-butyl-2-oxazoline. This Ox^{iPr,Me_2} group also has a potential advantage over the alternative bulky 4-*tert*-butyl-2-oxazoline-based ligands in that

Chart 1. C_3-Symmetric Pyrazolyl and Oxazoline-Based Scorpionate Ligands



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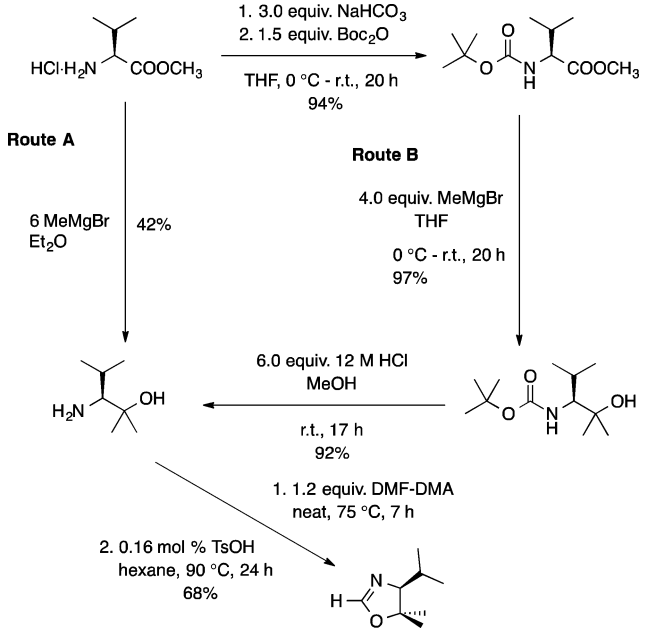
it is synthesized from naturally occurring L-valine. We were therefore motivated to synthesize the C_3-symmetric tridentate ligand tris(4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl)phenylborate (To^P*) and compare its coordination compounds and reactivity to those of previously synthesized achiral and chiral tris(oxazolinyl)borate ligands.

Here we describe the preparation of To^P*, its salts for transmetalation reactions, and a few of its organometallic compounds. Group 7 carbonyl complexes allow an evaluation of the electronic and steric properties of the To^P* ligand through single-crystal X-ray diffraction and infrared spectroscopic studies. In addition, we have investigated the capability of To^P* to support monomeric zinc compounds, including an optically active zinc hydride complex. We present the application of the latter compound in catalytic cross-dehydrocoupling of silanes and alcohols.

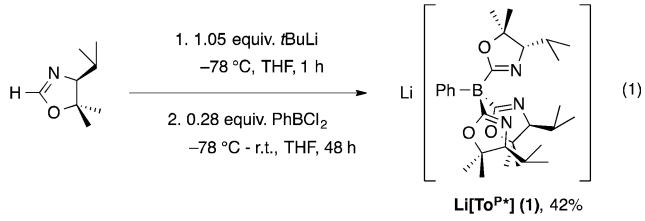
RESULTS AND DISCUSSION

Synthesis of 4*S*-Isopropyl-5,5-dimethyl-2-oxazoline (2H-Ox^{iPr,Me_2}). The synthesis of 4*S*-isopropyl-5,5-dimethyl-2-oxazoline (2H-Ox^{iPr,Me_2}) was previously communicated as part of the preparation of $H[PhB(Ox^{iPr_2,Me_2})_2C_5H_5]$.[17b] However, the previous synthesis involves the direct methylation of L-valine methyl ester, which gives the intermediate 2*S*-amino-1,1,3-trimethylbutanol in low yield and requires a large excess of MeMgBr, limiting the overall yield of 2H-Ox^{iPr,Me_2} (Scheme 1, route A). An alternative route (route B) begins with the reported preparation of L-valine methyl ester hydrochloride.[18] Instead of its direct methylation with MeMgBr, L-valine methyl ester hydrochloride is neutralized and protected using di-*tert*-butyl dicarbonate (Boc_2O).[19] The protected ester is then converted to the alcohol using MeMgBr, purified through column chromatography, and deprotected.[19] Although the second preparation involves more steps than the first, the overall yield is higher than that obtained from direct methylation. Cyclization of the amino alcohol to give 2H-Ox^{iPr,Me_2} follows the classical synthesis.[20]

Scheme 1. Routes to 2H-Ox^{iPr,Me_2}



Synthesis and Characterization of Tris(4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl)phenylborate (To^P*) Transfer Agents. The preparation of Li[To^P*] (**1**) is based on the general route for the syntheses of tris(oxazolinyl)borate ligands and involves deprotonation of 2H-Ox^{iPr,Me_2} followed by reaction with 0.3 equiv of $PhBCl_2$ (eq 1). However, the substituents of



(1)

Li[To^P*] (**1**), 42%

the 2-oxazoline affect the optimal base, reaction concentration, and reaction time needed to prepare the tris(2-oxazolinyl)borate. In our experience, bulkier substituents require more aggressive bases to quantitatively deprotonate the 2-oxazoline at C2 to give the 2-lithio-2-oxazolide. For this reason, the preparation of bulky To^P* employs *t*BuLi to generate 2-lithio-4*S*-isopropyl-5,5-dimethyl-2-oxazolide (2Li-Ox^{iPr,Me_2}). A second key to a good yield is a concentrated reaction mixture ([2H-Ox^{iPr,Me_2}] ~ 0.5 M) because the deprotonation reaction appears to be slow and dilute conditions give impure products. Quantitative deprotonation of the oxazoline is critical because mixtures of the 2-oxazoline, 2-lithio-2-oxazolide, and dichlorophenylborane produce unidentified and inseparable side products.[8] Moreover, 2Li-Ox^{iPr,Me_2} is employed in a slight excess (0.28 equiv of $PhBCl_2$) because the separation of bis(oxazolinyl)phenylborane and **1** is difficult. The yellow crude Li[To^P*] can be purified to give a white solid after pentane washes. The To^P* ligand is the permethylated derivative of tris(4*S*-isopropyl-2-oxazolinyl)phenylborate (To^P) and is named in analogy to isoelectronic pentamethylcyclopentadiene (Cp*) and tris(3,5-dimethylpyrazolyl)hydridoborate (Tp*).

The ^{1}H NMR spectrum of a benzene-d_6 solution of Li[To^P*] contained broad alkyl and aryl resonances, as is typically observed in the lithium tris(oxazolinyl)borate salts, presumably as a result of aggregation and exchange of coordinated and noncoordinated oxazoline groups. In contrast, a sharp and well-defined ^{1}H NMR spectrum was obtained for Li[To^P*] dissolved in acetonitrile-d_3. The presence of one set of 4*S*-isopropyl-5,5-dimethyl-2-oxazolinyl ^{1}H NMR resonances suggests a C_3-symmetric structure in which the stereochemical integrity of the 4*S*-isopropyl moiety is maintained (i.e., *S*,*S*,*S*-To^P* is obtained from 2H-$Ox^{4S\text{-}iPr,Me_2}$). The ratio of the integrations for the alkyl and phenyl groups indicates that three oxazolines and one phenyl group are bonded to boron. This conclusion is also supported by the ^{11}B chemical shift of −17.8 ppm, which is in the region typical of four-coordinate anionic borates.[21] Similar ^{11}B NMR chemical shifts were observed for Li[To^M] (−16.9 ppm),[8] Li[To^P] (−16.8 ppm),[9] and Li[To^T] (−17.0 ppm).[10] A broad peak in the $^{13}C\{^1H\}$ NMR spectrum at 185 ppm is assigned to the oxazoline C2 that is bonded to boron. The IR spectrum (KBr) contained only one strong, broad peak in the ν_{CN} region at 1583 cm^{-1}. Although the carbon elemental analysis was consistently lower than expected, this material was sufficiently pure to use for the synthetic applications described in this paper.

Li[To^P*] may be used directly for some preparations, but a few other reagents were synthesized to facilitate coordination of To^P* to reactive metal centers. The thallium reagent, Tl[To^P*]

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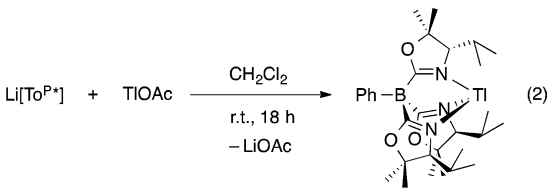
Organometallics 2015, 34, 3508−3519

(**2**), is synthesized by the reaction of Li[To^{P}*] and thallium(I) acetate in methylene chloride at room temperature (eq 2). The



Tl[To^{P}*] (2), 43%

initially yellow suspension becomes milky gray over 30 min as a result of the formation of the insoluble lithium acetate. Crude Tl[To^{P}*] is obtained as a brown solid after workup, and it is further purified by pentane washes to give an off-white solid. Compound **2** is partially soluble in benzene-d_6 and acetonitrile-d_3, and like Li[To^{P}*], it gives broad ^{1}H NMR signals in benzene-d_6 and sharp resonances of a C_3-symmetric species in acetonitrile-d_3. The oxazoline resonances of **2** were shifted slightly with respect to those of Li[To^{P}*], but overall the NMR and IR spectra of the two compounds were very similar.

The identity of **2** and the tridentate interaction of To^{P}* and Tl are supported by a single-crystal X-ray diffraction study (Figure 1). In the crystallographically determined solid-state

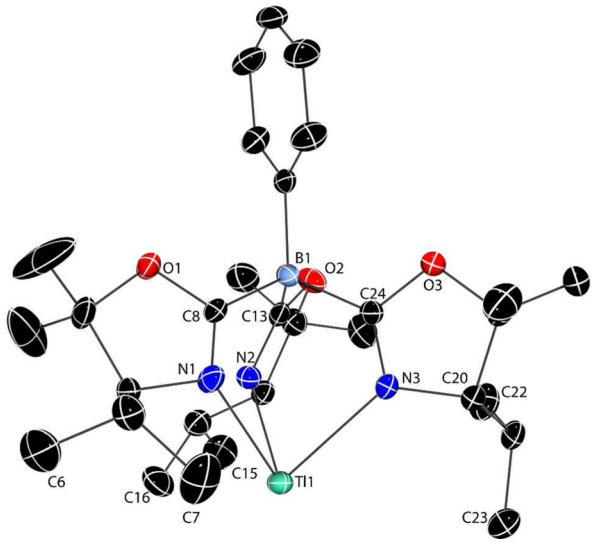
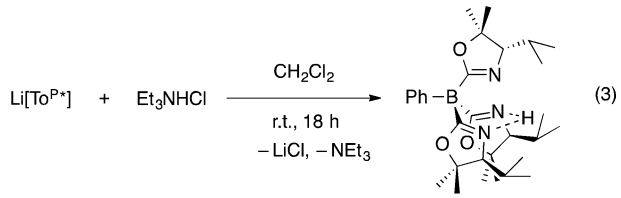


Figure 1. Rendered thermal ellipsoid plot of Tl[To^{P}*] (**2**) with ellipsoids at 35% probability. H atoms have been omitted for clarity. Selected interatomic distances (Å): Tl1–N1, 2.493(2); Tl1–N2, 2.647(2); Tl1–N3, 2.493(2). Selected interatomic angles (deg): N1–Tl1–N2, 78.09(6); N2–Tl1–N3, 81.37(7); N3–Tl1–N1, 75.27(7).

structure, the nitrogen atoms of the three oxazolines are coordinated to the Tl center in a tridentate bonding motif. In each oxazoline, one methyl in each isopropyl group points toward the thallium atom. The geometry is not pseudo-C_3-symmetric because the Tl1–N2 distance (2.647(2) Å) is significantly longer than the Tl1–N1 and Tl1–N3 distances (2.493(2) Å). In addition, one of the oxazolines coordinates through N3 such that the three N-bonded atoms (Tl1, C24, and C20) and the boron center are essentially planar (e.g., the Tl1–N3–C24–B1 torsion angle is 4.6(4)°), whereas the other two oxazolines coordinate to the thallium center in a canted fashion. This twist is characterized by large Tl1–N1–C8–B1 and Tl1–N2–C13–B1 torsion angles of −35.3(4) and −37.3(4)°, respectively. Finally, the conformations of the isopropyl groups are inequivalent in the three oxazolines. The isopropyl group on the N3 ring is oriented with one methyl group (C23) pointing in front of the ligand, whereas the isopropyl substituents on the N1 and N2 rings have both methyl groups (C6, C7, C15, C16) pointing forward.

The steric properties of To^{P}* are assessed in terms of the solid angle, which describes the surface area resulting from the projection of the ligand in question onto a sphere surrounding the complex.[22] The solid angle of To^{P}*, determined from the X-ray crystallographic coordinates of **2** analyzed by Solid-G,[23] is 6.67 steradians, which corresponds to 53.1% of a sphere's surface area. For comparison, the solid angle of To^{M}, also bonded to Tl, is 6.09 steradians (48.5%). Thus, a greater percentage of the area around Tl is occupied by To^{P}* than by To^{M}.

The protonated ligand H[To^{P}*] (**3**) is formed after Li[To^{P}*] is subjected to flash column chromatography in air or upon exposure of Li[To^{P}*] to air or bench-grade solvents. H[To^{P}*] is most quickly and conveniently prepared by the reaction of Li[To^{P}*] and triethylammonium chloride (eq 3).



H[To^{P}*] (3), 45%

H[To^{P}*] is isolated in moderate yield as a slightly sticky white solid, and it is readily soluble in benzene-d_6. In contrast to the characteristic two doublets and two singlets for the methyl groups in the ^{1}H NMR spectra of 2H-Ox^{iPr,Me_2}, Li[To^{P}*], and Tl[To^{P}*], three broad resonances at 0.75 (9H), 1.1 (18H), and 1.2 ppm (9H) were observed for H[To^{P}*]. An ^{1}H–^{13}C HMQC experiment indicated that the broad singlet at 1.1 ppm results from the overlap of one of the isopropyl methyl groups and one 5-methyl group. A signal in the ^{11}B NMR spectrum at −17.8 ppm indicated that the four B–C bonds were unaffected by the acidic treatment. In addition, two intense IR absorption bands at 1601 and 1583 cm^{-1} indicate that two types of oxazoline rings are present in the molecule. These bands are assigned to nonprotonated and N-protonated oxazoline groups, respectively. The depiction of **3** with the proton bonded to two oxazolines is based on analogy to H[To^{M}], which crystallizes with two oxazolines pointing the same direction.[8]

Synthesis and Characterization of To^{P}*M(CO)$_3$ (M = Mn (4), Re (5)). Monovalent group 7 carbonyl compounds provide a metric for comparing the electron-donating abilities of *fac*-coordinating tridentate ligands through the IR frequencies of the carbonyl stretching modes. The complexes To^{P}*Mn(CO)$_3$ (**4**) and To^{P}*Re(CO)$_3$ (**5**) are synthesized by the reaction of Li[To^{P}*] with manganese and rhenium pentacarbonyl bromide, respectively (eq 4).

The NMR spectra of **4** and **5** in benzene-d_6 confirmed their anticipated pseudo-C_3 symmetry. The ^{1}H NMR spectrum of the manganese compound **4** was well-resolved. In the ^{1}H NMR spectrum of **5**, a large virtual doublet at 1.06 ppm integrating to 27H resulted from overlapping singlet and doublet signals assigned to methyls of the 5,5-dimethyl and 4-isopropyl groups. An ^{1}H–^{13}C HMQC experiment supported this assignment.

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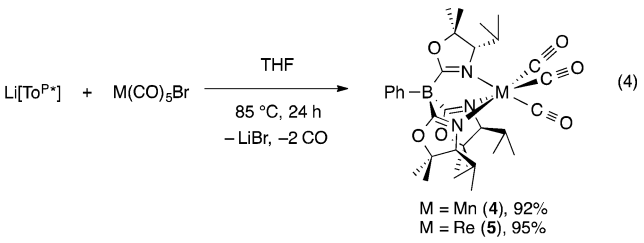

The $^{13}C\{^1H\}$ NMR spectra of **4** and **5** contained broad downfield signals for the carbonyl carbons at 223 and 199 ppm, respectively, in addition to To^P* resonances. The ^{15}N NMR chemical shifts of **5**, obtained from $^1H-^{15}N$ HMBC experiments, were upfield of those of To^{M}Re(CO)$_3$ but similar to those of To^{P}Re(CO)$_3$. The IR spectra (KBr) contained the expected symmetric and asymmetric carbonyl (2000−1800 cm^{-1}) and oxazoline ν_{CN} (~1600 cm^{-1}) bands. The spectral data, as well as data for previously reported isoelectronic To^M, To^P, Tp, and Tp* compounds, are summarized in Table 1.[24]

The symmetric CO stretching modes of complexes **4** and **5**, measured both in the solid state and in CH_2Cl_2 solution, are slightly lower in energy than those of the corresponding group 7 compounds of To^M and To^P. The asymmetric stretches of **5** in CH_2Cl_2 are also slightly lower in energy than those of To^{M}Re(CO)$_3$ and To^{P}Re(CO)$_3$. The ν_{CO} data from the symmetric and asymmetric modes suggest that π back-donation from manganese or rhenium to the carbonyl ligands is affected by 5,5-dimethylation of the oxazoline. The averages of the symmetric and asymmetric stretching frequencies for the ligands across the series of rhenium compounds are lower for the tris(oxazolinyl)borate complexes than for their Tp and Tp* analogues. By this measure of electron donation, the tris(oxazolinyl)borate ligands are more electron-donating than Tp and Tp* and To^P* is the most electron-donating among the five borate ligands, which follow the trend To^P* > To^P > To^M > Tp* > Tp.

To^P*Re(CO)$_3$ may be reversibly oxidized by one electron, as demonstrated by a cyclic voltammetry (CV) experiment (Figure 2). The $E_{1/2}$ value for To^P*Re(CO)$_3$ is identical to that for To^{P}Re(CO)$_3$, and the additional methyl groups in To^P* do not affect the redox potential of the rhenium center.

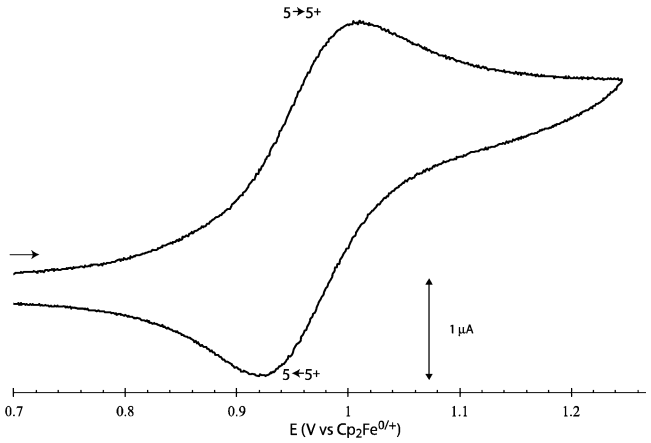

Figure 2. Cyclic voltammogram of 1.0 mM **5** in CH_2Cl_2/0.10 M $[NBu_4][BF_4]$. Conditions: 298 K, 2 mm Pt electrode, 10 mV/s.

X-ray quality crystals of **4** and **5** are obtained from concentrated solutions containing a mixture of toluene and pentane cooled at −30 °C (see Figure 3 for a thermal ellipsoid plot of To^P*Re(CO)$_3$ and the Supporting Information for a thermal ellipsoid plot of To^P*Mn(CO)$_3$). The manganese and rhenium compounds are isostructural and crystallize in the same orthorhombic space group ($P2_12_12_1$). The primary differences between **4** and **5** are related to the M−L distances and unit cell sizes. The *a* and *c* dimensions of To^P*Re(CO)$_3$ are 0.05 and 0.25 Å longer, respectively, than those of the manganese complex. The Re−C and Re−N interatomic distances are ca. 0.1 Å longer than the distances associated

Table 1. Summary of the Characteristic Data for Manganese and Rhenium Tricarbonyl Complexes Bearing To^P*, with Related Data for To^M, To^P, Tp, and Tp* Complexes Given for Comparison

compound	ν_{CO} (cm^{-1})	$(\nu_{sym} + 2\nu_{asym})/3$ (cm^{-1})	ν_{CN} (cm^{-1})[a]	$E_{1/2}$[b]	^{15}N NMR (ppm)
To^P*Mn(CO)$_3$ (**4**)[c]	2013, 1903 (KBr)	1946	1592	–	not detected
	2016, 1911 (CH_2Cl_2)				
To^P*Re(CO)$_3$ (**5**)[c]	2008, 1886 (KBr)	1933	1584	0.97	−197
	2012, 1894 (CH_2Cl_2)				
To^{M}Mn(CO)$_3$[d]	2018, 1899 (KBr)	1948	1592	–	−172
	2020, 1912 (CH_2Cl_2)				
To^{M}Re(CO)$_3$[d]	2012, 1892 (KBr)	1938	1582	1.00	−177
	2019, 1898 (CH_2Cl_2)				
To^{P}Mn(CO)$_3$[d]	2016, 1961 (KBr)	1944	1601	–	not detected
	2017, 1908 (THF)				
To^{P}Re(CO)$_3$[d]	2010, 1892 (KBr)	1936	1589	0.97	−196
	2014, 1897 (CH_2Cl_2)				
TpMn(CO)$_3$[e]	2026, 1932, 1915 (KBr)	1966	n.a.	–	n.a.
	2035, 1932 (CH_2Cl_2)[d]				
TpRe(CO)$_3$[e]	2020, 1896 (KBr)	1950	n.a.	0.98	n.a.
	2026, 1912 (CH_2Cl_2)[d]				
Tp*Mn(CO)$_3$[e]	2023, 1912 (KBr)	1957	n.a.	–	n.a.
	2027, 1922 (CH_2Cl_2)[d]				
Tp*Re(CO)$_3$[e]	2017, 1893 (KBr)	1941	n.a.	0.82	n.a.
	2018, 1903 (CH_2Cl_2)[d]				

[a]KBr. [b]In V vs $Cp_2Fe^{0/+}$; the redox potential for To^P*Mn(CO)$_3$ was not determined. [c]This work. [d]See ref 24a. [e]See ref 24b.

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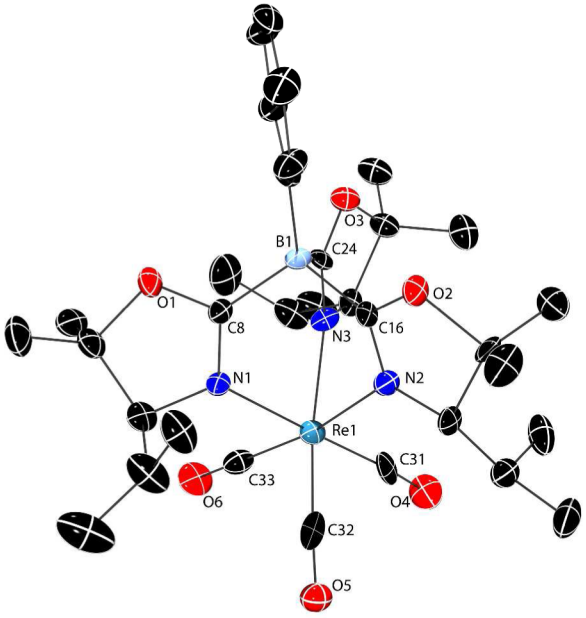
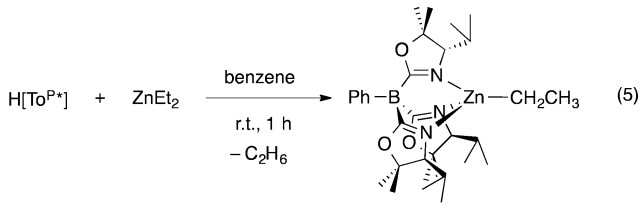


Figure 3. Rendered thermal ellipsoid plot of To^{P}*Re(CO)$_3$ (**5**) with ellipsoids shown at 35% probability. H atoms have been omitted for clarity. Selected interatomic distances (Å): Re1−N1, 2.186(8); Re1−N2, 2.203(7); Re1−N3, 2.189(7); Re1−C31, 1.93(1); Re1−C32, 1.87(1); Re1−C33, 1.94(1). Selected interatomic angles (deg): N1−Re1−N2, 83.6(3); N2−Re1−N3, 80.1(3); N3−Re1−N1, 84.8(3); C31−Re1−C32, 86.1(4); C32−Re1−C33, 90.1(4); C33−Re1−C31, 89.4(4); Re1−N1−C8−B1, −15(2); Re1−N2−C16−B1, −10(2); Re1−N3−C24−B1, −6(2).

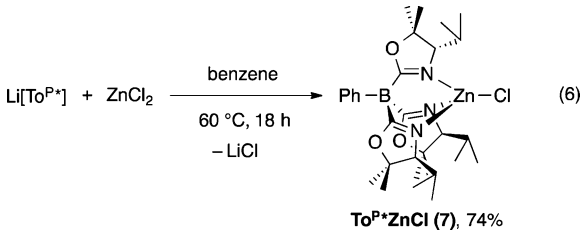
with the manganese center. Apart from these minor differences, the two compounds adopt similar molecular structures. The metal centers are coordinated in a distorted octahedral environment, and the carbonyl groups are positioned between the oxazoline rings. However, the carbonyls are not equally situated between the oxazoline nitrogen, as determined by the interligand distances between atoms in the metal's first coordination sphere. In **5**, for example, one of the carbonyl carbons, C33, is 2.85 Å from N1 and 3.08 Å from N3. These distances may be readily rationalized by the observation that the isopropyl group on the N3 oxazoline ring is pointing at the carbonyl ligand containing C33. This distortion is repeated for N2−C31−N3, but the carbon of the carbonyl between N1 and N2 (C32, trans to N3) is nearly equidistant from the two oxazoline nitrogens (difference of 0.08 Å).

Synthesis and Characterization of To^{P}*ZnX (X = Et (6), Cl (7), H (8)). The reaction of diethylzinc and H[To^{P}*] affords To^{P}*ZnEt (**6**) (eq 5). Ethane is formed within 5 min in a



micromolar-scale reaction monitored by ^{1}H NMR spectroscopy. The product forms in essentially quantitative yield and is easily isolated as an analytically pure white solid after evaporation of volatile materials. The ^{1}H NMR spectrum contained the expected ratio of the integrations of the ethyl and pseudo-C_3-symmetric To^{P}* signals, supporting the assigned ligand ratio. As in the group 7 compounds, an ^{1}H−^{15}N HMBC experiment revealed one nitrogen signal at −177 ppm that was correlated to the oxazoline and isopropyl methine ^{1}H NMR resonances. The IR spectrum (KBr) contained one strong CN stretching band at 1585 cm^{-1}. These data indicate that the three oxazoline rings are equivalent and coordinated to zinc.

To^{P}*ZnEt is converted to To^{P}*ZnCl (**7**) by reaction with triethylammonium chloride. A more direct synthetic route to To^{P}*ZnCl involves the reaction of Li[To^{P}*] and zinc chloride in benzene at elevated temperature (eq 6). The well-resolved



features of the ^{1}H NMR spectrum of To^{P}*ZnCl were readily distinguished from the broad signals of the Li[To^{P}*] starting material. Two sharp doublets at 0.94 and 1.22 ppm ($^3J_{HH}$ = 6.6 Hz, 9H each) and two singlets observed at 0.98 and 1.03 ppm (9H each), assigned to the CH*Me*$_2$ and 5,5-dimethyl groups, respectively, were distinct from the broad signals obtained in the ^{1}H NMR spectrum of Li[To^{P}*]. The IR spectrum (KBr) showed one strong band at 1579 cm^{-1} assigned to a CN stretch, supporting the structural assignment.[25] This assignment was confirmed by a single-crystal X-ray diffraction study (Figure 4). In the solid-state structure, the isopropyl groups on the oxazoline are oriented to place one methyl group in each oxazoline (C3, C11, and C17) in front of the metal center. The conformation of the ligand, particularly the orientation of the

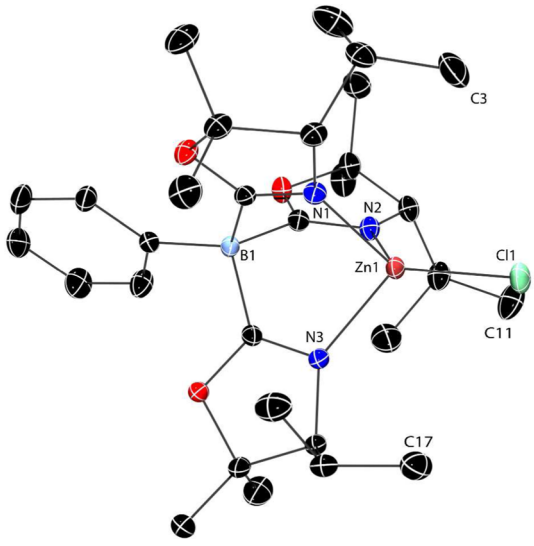


Figure 4. Rendered thermal ellipsoid plot of To^{P}*ZnCl (**7**) with ellipsoids at 35% probability. H atoms have been omitted for clarity. Selected interatomic distances (Å): Zn1−N1, 2.047(1); Zn1−N2, 2.0249(9); Zn1−N3, 2.023(1); Zn1−Cl1, 2.1831(4). Selected interatomic angles (deg): N1−Zn1−N2, 93.70(4); N2−Zn1−N3, 93.81(4); N3−Zn1−N1, 94.21(4); N1−Zn1−Cl1, 121.15(3); N2−Zn1−Cl1, 121.63(3); N3−Zn1−Cl1, 124.53(3).

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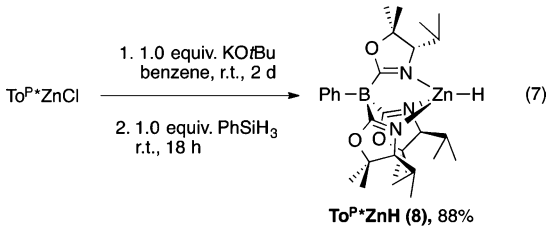
Organometallics 2015, 34, 3508−3519

isopropyl groups in Tl[To^{P}*], To^{P}*ZnCl, and To^{P}*M(CO)$_3$, changes with the changing coordination number of the metal center. The conformation in this complex is similar to that observed in the X-ray crystal structure of To^{P}*ZnH and will be discussed in the structure of that compound (below).

Compound **7** reacts with potassium *tert*-butoxide at room temperature to give To^{P}*ZnO*t*Bu. ^{1}H NMR spectra of To^{P}*ZnO*t*Bu dissolved in benzene-d_6 or methylene chloride-d_2, however, contained broad peaks in the alkyl region, and the species did not provide a characteristic set of signals. It is likely that the O*t*Bu ligand competes as a donor with the oxazolines, giving oligomeric Zn−O−Zn structures that exchange on the NMR time scale and give broad resonances. Instead, To^{P}*ZnO*t*Bu is assigned on the basis of its reactivity toward $PhSiH_3$ to form To^{P}*ZnH (**8**) and PhH_2SiO*t*Bu (eq 7).



(7)

The ^{1}H NMR spectrum of **8**, acquired in benzene-d_6, contained a singlet at 4.61 ppm characteristic of a zinc hydride resonance.[26] The C_3-symmetric molecule provided a spectrum that contained one set of oxazoline resonances. An ^{1}H−^{15}N HMBC experiment correlated the oxazoline nitrogen signal at −179 ppm (referenced to the nitromethane scale) to the zinc hydride resonance, the oxazoline C4−*H* resonance, and the isopropyl methine resonance at 1.63 ppm. The IR spectrum (KBr) revealed one strong band at 1587 cm^{-1} assigned to the oxazoline C═N stretching mode and a medium intensity peak at 1766 cm^{-1} assigned to ν_{ZnH}. The related compounds To^{M}ZnH (1745 cm^{-1}) and Tp^{tBu}ZnH (1770 cm^{-1}) have ν_{ZnH} bands in a similar range.

X-ray-quality crystals of To^{P}*ZnH are grown from a concentrated pentane solution at −30 °C (Figure 5). To the best of our knowledge, To^{P}*ZnH is the first example of a crystallographically characterized optically active mononuclear zinc hydride. The Zn−H interatomic distance (1.44(3) Å) is the shortest among crystallographically characterized terminal zinc hydride compounds reported in the Cambridge Structural Database. For comparison, the Zn−H distance in TptmZnH (Tptm = tris(2-pyridylthio)methyl) is 1.51(3) Å,[26e] and the C-metalated dimeric compound $[\{\mu\text{-}\kappa^3\text{-HC(NHC)}_2\}\text{ZnH}]_2$ (NHC = methylidyne-3,3′-bis(*N*-*tert*-butylimidazol-2-ylidene)) has a Zn−H distance of 1.61(3) Å,[27] while the distance in aminophenolate-supported LZnH (L = 2,4-di-*tert*-butyl-6-{[(2′-dimethylaminoethyl)methylamino]methyl}phenolate) is 1.75(3) Å.[28] Like To^{P}*ZnCl, the zinc atom in To^{P}*ZnH is coordinated in a distorted tetrahedral geometry in which the N−Zn−H angles (average 125 ± 1°; see Figure 5 for individual values and crystallographic estimated standard deviations) are much larger than the N−Zn−N angles (average 91 ± 1°). These angles show an increased distortion from To^{P}*ZnCl, which has smaller N−Zn−Cl angles (average 122 ± 1°) and larger N−Zn−N angles (average 93.9 ± 0.2). This distortion is also manifested in the B−Zn distance, which is longer in To^{P}*ZnH than in To^{P}*ZnCl by ca. 0.1 Å. The three isopropyl groups inherit the same conformation as in **7**, in which only one methyl from each isopropyl group is placed in front of the metal and the other methyl of the isopropyl group points at the next oxazoline donor. Overall, the conformation of the isopropyl groups conforms to the C_3 symmetry associated with this ligand in the solid-state structure.

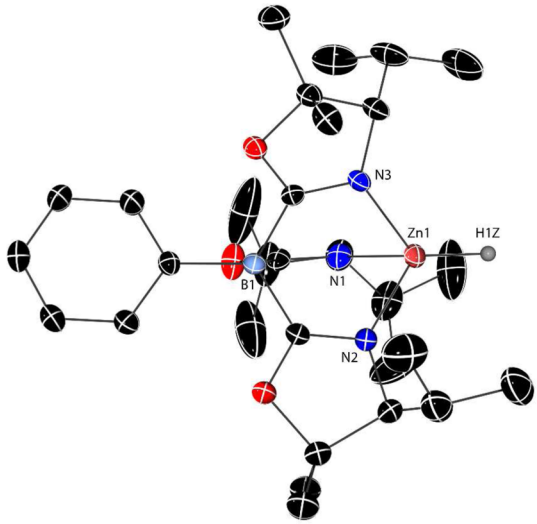


Figure 5. Rendered thermal ellipsoid plot of To^{P}*ZnH (**8**) with ellipsoids at 35% probability. H atoms have been omitted for clarity, except for the hydride. Selected interatomic distances (Å): Zn1−N1, 2.071(2); Zn1−N2, 2.062(2); Zn1−N3, 2.060(2); Zn1−H1Z, 1.44(3). Selected interatomic angles (deg): N1−Zn1−N2, 90.53(9); N2−Zn1−N3, 91.95(9); N3−Zn1−N1, 90.85(8); N1−Zn1−H1Z, 126(1); N2−Zn1−H1Z, 123(1); N3−Zn1−H1Z, 124(1).

Enantioselective Dehydrogenative Silylation of Alcohols. The achiral tris(oxazolinyl)boratozinc hydride complex To^{M}ZnH is a catalyst for the dehydrogenative silylation of alcohols with silanes.[29] Complex **8** was tested as catalyst for the dehydrogenative coupling of alcohols with the prochiral silanes phenylmethylsilane and 1-naphthylphenylsilane as a catalytic route to enantioenriched Si-chiral silanes (Table 2). This transformation might provide an alternative approach to such silicon-centered optically active molecules to complement kinetic resolutions of racemic chiral tertiary silanes via dehydrocoupling[30] and other synthetic routes to compounds containing stereogenic silicon centers.[31] A previous example of asymmetric dehydrocoupling employed a chiral rhodium complex as the catalyst.[32] To^{P}*ZnCl was also a catalyst with *t*BuOK (i.e., as To^{P}*ZnO*t*Bu) but was inactive without the activator. To^{P}*ZnMe is only slowly activated for dehydrocoupling.

Low enantioselectivity was observed for the combination of methanol and phenylmethylsilane (Table 2, entry 1). However, an encouraging increase in enantioselectivity was obtained from ethanol and $PhMeSiH_2$ (entry 2). An excess amount of silane was used in these two experiments, as well as some of the following trials, in order to suppress the formation of dialkoxysiloxanes through another dehydrogenative silylation of the desired products. The dehydrogenative coupling of 3,5-dimethylphenol and phenylmethylsilane gives lower enantiomeric excess (entry 3). In addition, the reactions of 1-naphthylphenylsilane and methanol, ethanol, isopropanol, and 3,5-dimethylphenol give low % ee. In the end, To^{P}*ZnH is most effective for the specific combination of EtOH and $PhMeSiH_2$, and trends for extending and enhancing this activity are not currently obvious with this ligand−metal combination.

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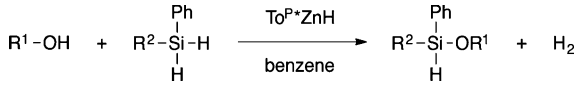
Organometallics 2015, 34, 3508−3519

Table 2. Enantioselective Dehydrogenative Silylation of Alcohols with Prochiral Silanes Catalyzed by 8



entry	R^1	R^2	cat. loading (mol %)	temp. (°C)	time	conv. (%)	yield (%)[a]	ee (%)[b]
1[c]	Me	Me	1.0	25	4 h	100	79	6
2[d]	Et	Me	1.0	25	8 h	100	75	56
3[e]	3,5-$Me_2C_6H_3$	Me	2.0	25	4 days	100	81	24
4[c]	Me	1-Np	1.0	25	6 h	100	90	16
5[d]	Et	1-Np	1.0	25	10 h	100	91	22
6[f]	*i*Pr	1-Np	1.0	25	14 days	91	67	4
7[e]	3,5-$Me_2C_6H_3$	1-Np	2.0	25	14 days	100	80	7
8[e]	3,5-$Me_2C_6H_3$	1-Np	2.0	35	26 h	100	80	8
9[e]	3,5-$Me_2C_6H_3$	1-Np	2.0	60	12 h	100	80	11

[a]Isolated yields. [b]Determined by HPLC (Chiracel-ODH) with hexane as the eluent. [c]10 mL of benzene, 2.61 mM **8**, 524 mM silane, 259 mM alcohol. [d]10 mL of benzene, 1.74 mM **8**, 350 mM silane, 172 mM alcohol. [e]2 mL of benzene, 8.70 mM **8**, 437 mM silane, 434 mM 3,5-$Me_2C_6H_3OH$. [f]2 mL of benzene, 8.70 mM **8**, 865 mM silane, 850 mM *i*PrOH.

Attempts to increase the % ee by lowering the temperature also slowed the reaction too much. However, a number of first-row metal compounds catalyze the dehydrocoupling of silanes and protic reagents, and we are currently investigating To^{P}*M-complexes in this capacity.

CONCLUSION

To^{P}* is a new C_3-symmetric tridentate monoanionic ligand that forms coordination compounds related to those formed by reported tris(oxazolinyl)borate ligands, namely, the achiral ligand To^{M} and the chiral ligands To^{P} and To^{T}. In particular, octahedral group 7 tricarbonyl compounds and tetrahedral zinc To^{P}*-supported compounds may be readily prepared, as well as lithiated, thalliated, and protonated ligands for transmetalation. The 5,5-dimethyl substitution affects the steric profile of the tris(oxazolinyl)borate ligand, as described by the larger solid angle of To^{P}* than of To^{P}. The 5,5-dimethylation in To^{P}* also affects the ν_{CO} in group 7 tricarbonyls, although the redox potentials are similar for To^{M}, To^{P}, and To^{P}*. To^{P}*ZnH also provides some stereoselectivity in the cross-coupling of alcohols and silanes to give Si-chiral siloxanes, with the caveat that the results were highly substrate-dependent.

EXPERIMENTAL SECTION

General Procedures. All of the reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, pentane, tetrahydrofuran, and methylene chloride were dried and deoxygenated using an IT PureSolv system. Benzene-d_6 was heated to reflux over Na/K alloy and vacuum-transferred. Acetonitrile-d_3 and chloroform-*d* were heated to reflux over CaH_2 and vacuum-transferred. Thionyl chloride, *N*,*N*-dimethylformamide dimethyl acetal (DMF-DMA), and dichlorophenylborane were purchased from Sigma-Aldrich and were distilled and then stored in separate storage flasks equipped with resealable Teflon valves under an inert atmosphere before use. Methylmagnesium bromide solution (3.0 M in diethyl ether), *tert*-butyllithium solution (1.7 M in pentane), and dimethylzinc solution (2.0 M in toluene) were purchased from Sigma-Aldrich and were transferred and then stored in separate storage flasks equipped with resealable Teflon valves under an inert atmosphere before use. L-Valine was purchased from Acros Organics. Di-*tert*-butyl dicarbonate (Boc_2O) was purchased from TCI America. *p*-Toluenesulfonic acid monohydrate was purchased from Fisher Scientific. Thallium(I) acetate and 1-naphthylphenylsilane were purchased from Sigma-Aldrich and stored in a glovebox in their original bottles. Diethylzinc was purchased from Strem Chemicals and stored inside a glovebox in its original Swagelok cylinder. Zinc chloride was purchased from Fluka Analytical and stored in a glovebox. Potassium *tert*-butoxide and 3,5-dimethylphenol were purchased from Sigma-Aldrich and were sublimed and then stored in a glovebox. Manganese and rhenium pentacarbonyl bromide were synthesized according to the literature procedures[33] starting from manganese(0) carbonyl and dirhenium decacarbonyl, respectively. Manganese pentacarbonyl bromide was used without further sublimation, while rhenium pentacarbonyl bromide was further purified by sublimation. Triethylammonium chloride was synthesized from triethylamine and hydrochloric acid. Phenylsilane and phenylmethylsilane were synthesized by reduction of trichlorophenylsilane and dichloro(methyl)phenylsilane with $LiAlH_4$, respectively. Methanol, ethanol, and isopropanol for the catalysis were heated to reflux with activated magnesium metal and then distilled and stored over 4 Å molecular sieves in a glovebox.

^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectra were collected on Varian VRX 300 MHz, Varian MR 400 MHz, and Bruker Avance II 600 MHz NMR spectrometers. ^{15}N NMR chemical shifts were determined by $^{1}H-^{15}N$ HMBC experiments on a Bruker Avance II 600 MHz NMR spectrometer. ^{15}N chemical shifts were originally referenced to an external liquid NH_3 standard and recalculated to the CH_3NO_2 chemical shift scale by adding −381.9 ppm. ^{29}Si chemical shifts were determined by $^{1}H-^{29}Si$ HMBC experiments collected on a Bruker Avance II 600 MHz spectrometer. Infrared spectra were recorded on a Bruker Vertex spectrometer. Elemental analyses were performed using a PerkinElmer 2400 Series II CHN/S analyzer at the Iowa State Chemical Instrumentation Facility. $[\alpha]_D$ values were measured on an ATAGO AP-300 polarimeter with a wavelength of 589 nm in a 50 mm observation tube at 20 °C. HPLC analyses were carried out on a Waters Alliance HPLC system with an e2695 separation module and a 2489 dual-wavelength detector. The electrochemistry was performed in a glovebox under a nitrogen atmosphere using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat interfaced to a personal computer. Voltammetry scans were recorded using a platinum disk with a diameter of 2 mm (PAR) as the working electrode. The disk was polished with 0.05 μm micropolish alumina suspension (Buehler), washed with distilled water and acetone, and finally sonicated for 5 min before use. A Ag/AgCl pseudoreference electrode was employed, and the system was calibrated against the $Cp_2Fe^{0/+}$ redox couple. Mass spectrometry data for the isolated Si-chiral silanes were acquired using an Agilent Technologies 7890A GC system (HP-5 ms column) coupled with a 5975C inert MSD with a Triple-Axis detector.

L-Valine Methyl Ester Hydrochloride. Following the literature procedure,[18] methanol (300 mL) was added to a three-neck round-bottom flask connected to an oil bubbler, and the flask was cooled in an ice−salt bath. Under nitrogen purge, thionyl chloride (47.6 mL, 0.653 mol) was added dropwise over 2 h. L-Valine (70.0 g, 0.598 mol) was then added to the solution in one portion, and the mixture was heated to 60 °C to dissolve all of the solids. The solution was then

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Organometallics 2015, 34, 3508−3519

heated for another hour. The solvent and excess reagents were removed by distillation. The resulting white solid was dried in vacuo for several hours and then dissolved in a minimal amount of methanol (90 mL). Diethyl ether (900 mL) was then poured into the methanol solution, and the mixture was cooled to −30 °C overnight, during which the product crystallized as white crystals. The solid was collected, washed with cold diethyl ether, and dried in vacuo to give L-valine methyl ester hydrochloride as a white solid (90.7 g, 0.541 mol, 90.4%). ^{1}H NMR (chloroform-*d*, 300 MHz): δ 8.9 (br, 3H, *H*Cl·H_2NCH(CHMe$_2$)COOCH$_3$), 3.93 (d, $^3J_{HH}$ = 4.5 Hz, 1H, HCl·H_2NC*H*(CHMe$_2$)COOCH$_3$), 3.84 (s, 3H, HCl·H_2NCH(CHMe$_2$)-COOC*H*$_3$), 2.47 (m, 1H, HCl·H_2NCH(C*H*Me$_2$)COOCH$_3$), 1.16 (vt, 6H, HCl·H_2NCH(CH*Me*$_2$)COOCH$_3$).

Boc-L-valine Methyl Ester. Following the literature procedure,[19] L-valine methyl ester hydrochloride (70.0 g, 0.418 mol) was dissolved in tetrahydrofuran/methanol (4:1, 750 mL), and the solution was cooled to 0 °C. Solid NaHCO$_3$ (105.4 g, 1.255 mol) was added to the solution in one portion, immediately followed by the addition of solid Boc$_2$O (137 g, 0.628 mol). The mixture was then warmed to room temperature, stirred for 20 h, and quenched with water (500 mL). The organic layer was extracted with diethyl ether (3 × 300 mL). The ether extracts were combined, washed with saturated aqueous NaHCO$_3$ solution (3 × 100 mL) and then brine (3 × 100 mL), dried over MgSO$_4$ for several hours, filtered, and then concentrated under reduced pressure to give the crude product as an oil. Purification of the crude product with flash column chromatography (silica gel; hexane/ethyl acetate = 9:1 → 6:1) gave the pure product as a clear colorless oil (90.7 g, 0.392 mol, 93.8%). R_f = 0.4 (silica gel; hexane/ethyl acetate = 9:1). ^{1}H NMR (chloroform-*d*, 300 MHz): δ 5.03 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Me$_3$COC(O)N*H*CH(CHMe$_2$)COOCH$_3$), 4.20 (dd, $^3J_{HH}$ = 4.8, 9.0 Hz, 1H, Me$_3$COC(O)NHC*H*(CHMe$_2$)COOCH$_3$), 3.71 (s, 3H, Me$_3$COC(O)NHCH(CHMe$_2$)COOC*H*$_3$), 2.09 (m, 1H, Me$_3$COC-(O)NHCH(C*H*Me$_2$)COOCH$_3$), 1.42 (s, 9H, *Me*$_3$COC(O)NHCH-(CHMe$_2$)COOCH$_3$), 0.93 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me$_3$COC(O)-NHCH(CH*Me*$_2$)COOCH$_3$), 0.87 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me$_3$COC-(O)NHCH(CH*Me*$_2$)COOCH$_3$).

3*S*-(Boc-amino)-2,4-dimethyl-2-pentanol. Following the literature procedure,[34] Boc-L-valine methyl ester (70.0 g, 0.303 mol) was degassed through three freeze−pump−thaw cycles and dissolved in tetrahydrofuran (1.5 L). The solution was cooled to 0 °C, and methylmagnesium bromide solution (400.0 mL, 3.0 M in diethyl ether, 1.2 mol) was added dropwise over 3 h. The resulting brown solution with some white precipitate was warmed to room temperature and stirred for 20 h, during which the precipitate dissolved. The solution was cooled to 0 °C again and carefully quenched with a saturated aqueous solution of NH$_4$Cl (800 mL). The aqueous layer was extracted with diethyl ether (2 × 250 mL), and the ether extracts were combined with the organic layer and washed with brine (2 × 600 mL), dried over Na$_2$SO$_4$ for several hours, filtered, and concentrated under reduced pressure to give the crude product as a slightly yellow oil. The crude product was then purified with flash column chromatography (silica gel; hexane/ethyl acetate = 9:1 → 4:1) to give the pure product as a white solid (67.7 g, 0.293 mol, 96.7%). R_f = 0.4 (silica gel; hexane/ethyl acetate = 4:1). ^{1}H NMR (chloroform-*d*, 400 MHz): δ 4.87 (d, $^3J_{HH}$ = 10.0 Hz, 1H, Me$_3$COC(O)N*H*CH(CHMe$_2$)CMe$_2$OH), 3.37 (dd, $^3J_{HH}$ = 2.4, 10.4 Hz, 1H, Me$_3$COC(O)NHC*H*(CHMe$_2$)-CMe$_2$OH), 2.08 (m, 1H, Me$_3$COC(O)NHCH(C*H*Me$_2$)CMe$_2$OH), 1.43 (s, 9H, *Me*$_3$COC(O)NHCH(CHMe$_2$)CMe$_2$OH), 1.24 (s, 3H, Me$_3$COC(O)NHCH(CHMe$_2$)C*Me*$_2$OH), 1.21 (s, 3H, Me$_3$COC(O)-NHCH(CHMe$_2$)C*Me*$_2$OH), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Me$_3$COC-(O)NHCH(CH*Me*$_2$)CMe$_2$OH), 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Me$_3$COC(O)NHCH(CH*Me*$_2$)CMe$_2$OH).

2*S*-Amino-1,1,3-trimethylbutanol. Following a modified literature procedure,[18] 3*S*-(Boc-amino)-2,4-dimethyl-2-pentanol (50.0 g, 0.216 mol) was dissolved in methanol (1 L), and the solution was cooled to 0 °C. Hydrochloric acid (108.0 mL, 12.1 M, 1.307 mol) was diluted with methanol (500 mL) and added dropwise to the solution over 30 min. The resulting solution was warmed to room temperature and stirred for 17 h. The volatiles were then removed under reduced pressure, and the residue was diluted with diethyl ether (500 mL). The mixture was cooled to 0 °C, and NaOH powder (80 g, 2.0 mol) was added in portions. The resulting yellow solution with a white precipitate was stirred at room temperature for another hour after it cooled. The mixture was filtered and then concentrated under reduced pressure to give the crude product as a red oil, which was purified by distillation at 97 °C and 30 mmHg to give a clear, colorless oil (26.0 g, 0.198 mol, 91.7%). ^{1}H NMR (chloroform-*d*, 400 MHz): δ 2.41 (d, $^3J_{HH}$ = 2.8 Hz, 1H, H_2NC*H*(CHMe$_2$)CMe$_2$OH), 1.92 (m, 1H, H_2NCH(C*H*Me$_2$)CMe$_2$OH), 1.19 (s, 3H, H_2NCH(CHMe$_2$)-C*Me*$_2$OH), 1.11 (s, 3H, H_2NCH(CHMe$_2$)C*Me*$_2$OH), 0.97 (d, $^3J_{HH}$ = 7.2 Hz, 3H, H_2NCH(CH*Me*$_2$)CMe$_2$OH), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3H, H_2NCH(CH*Me*$_2$)CMe$_2$OH).

4*S*-Isopropyl-5,5-dimethyl-2-oxazoline. A modification of Meyers' procedure for the synthesis of 2-oxazoline using 2*S*-amino-1,1,3-trimethylbutanol was implemented.[20] DMF-DMA (13.7 mL, 103 mmol) was added to degassed 2*S*-amino-1,1,3-trimethylbutanol (11.1 g, 84.6 mmol). This mixture was allowed to reflux at 75 °C for 7 h. The volatiles were removed under reduced pressure, and the mixture was triturated with hexane (4 × 30 mL). Then *p*-toluenesulfonic acid monohydrate (26.5 mg, 0.139 mmol) and hexane (40 mL) were added. An addition funnel containing approximately 40 mL of activated 4 Å molecular sieves was placed on top of the flask, and a condenser was placed on top of the addition funnel. The solution was heated at 90 °C for 24 h, and the condensed liquid was washed over the sieves as the reaction proceeded. The reaction mixture was washed with saturated aqueous NaHCO$_3$ solution (30 mL) and then with brine (50 mL). The aqueous layers were combined and back-extracted with diethyl ether (6 × 25 mL), and then the organic extracts were combined with the organic layer, dried over Na$_2$SO$_4$ overnight, and filtered. Concentration of the filtrate gave a dark-red oil that was distilled at 85 °C and 18 mmHg to provide 4*S*-isopropyl-5,5-dimethyl-2-oxazoline as a clear colorless oil (8.11 g, 57.4 mmol, 67.8%). ^{1}H NMR (chloroform-*d*, 600 MHz): δ 6.74 (s, 1H, C*H*NCH(CHMe$_2$)-CMe$_2$O), 3.23 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CHNC*H*(CHMe$_2$)CMe$_2$O), 1.80 (m, 1H, CHNCH(C*H*Me$_2$)CMe$_2$O), 1.45 (s, 3H, CHNCH-(CHMe$_2$)C*Me*$_2$O), 1.29 (s, 3H, CHNCH(CHMe$_2$)C*Me*$_2$O), 1.08 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CHNCH(CH*Me*$_2$)CMe$_2$O), 0.98 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CHNCH(CH*Me*$_2$)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 152.74 (CHNCH(CHMe$_2$)CMe$_2$O), 85.17 (CHNCH-(CHMe$_2$)CMe$_2$O), 80.07 (CHNCH(CHMe$_2$)CMe$_2$O), 29.56 (CHNCH(CHMe$_2$)CMe$_2$O), 29.48 (CHNCH(CHMe$_2$)C*Me*$_2$O), 21.53 (CHNCH(CH*Me*$_2$)CMe$_2$O), 21.48 (CHNCH(CHMe$_2$)-C*Me*$_2$O), 21.20 (CHNCH(CH*Me*$_2$)CMe$_2$O). ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ −143. IR (KBr, cm^{-1}): 3069 w, 2973 s, 2874 m, 1686 w, 1632 s (CN), 1471 m, 1462 m, 1386 m, 1372 m, 1336 w, 1304 w, 1272 w, 1243 w, 1202 w, 1172 m, 1134 m, 1114 m, 1082 s, 1015 m, 934 m, 894 m, 856 w, 813 w, 769 w. $[\alpha]_D^{20}$ = −35.2 (C$_6$H$_6$).

Li[To^P*] (1). 4*S*-Isopropyl-5,5-dimethyl-2-oxazoline (0.966 g, 6.84 mmol) was degassed through three freeze−pump−thaw cycles and dissolved in tetrahydrofuran (15 mL). The solution was cooled to −78 °C, and *t*BuLi solution (4.40 mL, 1.7 M in pentane, 7.48 mmol) was added dropwise. The resulting bright-yellow solution was stirred at −78 °C for another hour. PhBCl$_2$ (0.250 mL, 1.93 mmol) was then added dropwise, and the solution was stirred at −78 °C for another hour and gradually warmed to room temperature and stirred for 48 h. The solvent was then removed in vacuo, and the resulting yellow solid was extracted with benzene (2 × 15 mL). The benzene extracts were combined and evaporated in vacuo, and the crude product was then washed with pentane (2 × 5 mL) and dried in vacuo to give the product as a white solid (0.417 g, 0.809 mmol, 41.9%). ^{1}H NMR (acetonitrile-d_3, 600 MHz): δ 7.5 (br, 2H, *o*-C$_6$H$_5$), 7.04 (t, $^3J_{HH}$ = 6.6 Hz, 2H, *m*-C$_6$H$_5$), 6.96 (t, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-C$_6$H$_5$), 3.2 (br, 3H, CNC*H*(CHMe$_2$)CMe$_2$O), 1.76 (m, 3H, CNCH(C*H*Me$_2$)CMe$_2$O), 1.21 (s, 9H, CNCH(CHMe$_2$)C*Me*$_2$O), 1.16 (s, 9H, CNCH(CHMe$_2$)-C*Me*$_2$O), 0.99 (d, $^3J_{HH}$ = 6.6 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O), 0.95 (d, $^3J_{HH}$ = 6.6 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O). ^{13}C{^{1}H} NMR (acetonitrile-d_3, 150 MHz): δ 185 (br, *C*NCH(CHMe$_2$)CMe$_2$O), 150 (br, *ipso*-C$_6$H$_5$), 135.33 (*o*-C$_6$H$_5$), 126.88 (*m*-C$_6$H$_5$), 125.02 (*p*-C$_6$H$_5$), 83.48 (CNCH(CHMe$_2$)CMe$_2$O), 79.81 (CNCH(CHMe$_2$)CMe$_2$O), 30.05 (CNCH(CHMe$_2$)CMe$_2$O and CNCH(CHMe$_2$)C*Me*$_2$O), 22.13

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Organometallics 2015, 34, 3508−3519

(CNCH(CHMe_2)CMe_2O), 21.78 (CNCH(CHMe_2)CMe_2O), 20.48 (CNCH(CHMe_2)CMe_2O). ^{11}B NMR (acetonitrile-d_3, 128 MHz): δ −17.8. ^{15}N{^{1}H} NMR (acetonitrile-d_3, 71 MHz): δ −163. IR (KBr, cm^{-1}): 3068 w, 3044 w, 2970 s, 2932 m, 2875 m, 1653 w, 1635 w, 1583 s (CN), 1560 w, 1471 m, 1432 w, 1386 m, 1369 m, 1247 w, 1213 m, 1194 m, 1173 m, 1138 m, 1096 w, 1019 m, 948 m, 895 w, 742 w, 709 w. Anal. Calcd for $C_{30}H_{47}BLiN_3O_3$: C, 69.90; H, 9.19; N, 8.15. Found: C, 65.02; H, 8.79; N, 7.51. Mp: 238−241 °C.

Tl[To^P*] (2). Thallium(I) acetate (0.182 g, 0.691 mmol) was added to a solution of Li[To^P*] (**1**) (0.293 g, 0.568 mmol) in methylene chloride (15 mL). The resulting yellow suspension with a white precipitate was stirred at room temperature for 18 h, during which it turned to a gray suspension. The suspension was then filtered, and the filtrate was evaporated in vacuo to give the crude product as a brown solid, which was then washed with pentane (3 × 10 mL) to give the product as an off-white solid (0.174 g, 0.244 mmol, 43.0%). ^{1}H NMR (acetonitrile-d_3, 600 MHz): δ 7.6 (br, 2H, o-C$_6$H$_5$), 7.02 (t, $^3J_{HH}$ = 6.6 Hz, 2H, m-C$_6$H$_5$), 6.94 (t, $^3J_{HH}$ = 6.6 Hz, 1H, p-C$_6$H$_5$), 3.2 (br, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.71 (m, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.20 (s, 9H, CNCH(CHMe$_2$)CMe_2O), 1.15 (s, 9H, CNCH(CHMe$_2$)-CMe_2O), 0.98 (d, $^3J_{HH}$ = 5.4 Hz, 9H, CNCH(CHMe_2)CMe$_2$O), 0.92 (d, $^3J_{HH}$ = 5.4 Hz, 9H, CNCH(CHMe_2)CMe$_2$O). ^{13}C{^{1}H} NMR (acetonitrile-d_3, 150 MHz): δ 185 (br, CNCH(CHMe$_2$)CMe$_2$O), 151 (br, $ipso$-C$_6$H$_5$), 135.70 (o-C$_6$H$_5$), 126.60 (m-C$_6$H$_5$), 124.65 (p-C$_6$H$_5$), 82.80 (CNCH(CHMe$_2$)CMe$_2$O), 80.13 (CNCH(CHMe$_2$)CMe$_2$O), 30.21 (CNCH(CHMe$_2$)CMe_2O), 30.12 (CNCH(CHMe$_2$)CMe$_2$O), 22.09 (CNCH(CHMe_2)CMe$_2$O), 21.88 (CNCH(CHMe$_2$)CMe_2O), 20.43 (CNCH(CHMe_2)CMe$_2$O). ^{11}B NMR (acetonitrile-d_3, 128 MHz): δ −18.0. ^{15}N{^{1}H} NMR (acetonitrile-d_3, 71 MHz): δ −160. IR (KBr, cm^{-1}): 3068 w, 3044 w, 2971 s, 2932 m, 2875 m, 1653 w, 1584 s (CN), 1458 m, 1436 m, 1386 m, 1368 m, 1274 w, 1247 w, 1215 m, 1173 w, 1141 m, 1096 w, 1019 w, 989 w, 964 w, 948 m, 895 w, 809 w, 742 w, 709 m. Anal. Calcd for $C_{30}H_{47}BN_3O_3Tl$: C, 50.54; H, 6.65; N, 5.89. Found: C, 53.76; H, 7.05; N, 6.15. Mp: 249−251 °C.

H[To^P*] (3). Triethylammonium chloride (0.174 g, 1.26 mmol) was added to a solution of Li[To^P*] (**1**) (0.539 g, 1.05 mmol) in methylene chloride (15 mL). The resulting yellow suspension with a white precipitate was stirred at room temperature for 18 h, during which it turned to a white suspension. The suspension was then filtered, and the filtrate was evaporated in vacuo to give the crude product, which was extracted with pentane (2 × 10 mL). The pentane extracts were combined and cooled to −30 °C, and the white precipitate was isolated and dried in vacuo to give the product as a sticky slightly yellow solid (0.242 g, 0.475 mmol, 45.2%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.06 (d, $^3J_{HH}$ = 6.6 Hz, 2H, o-C$_6$H$_5$), 7.44 (t, $^3J_{HH}$ = 6.6 Hz, 2H, m-C$_6$H$_5$), 7.24 (t, $^3J_{HH}$ = 6.6 Hz, 1H, p-C$_6$H$_5$), 3.07 (d, $^3J_{HH}$ = 8.4 Hz, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.63 (m, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.24 (s, 9H, CNCH(CHMe$_2$)CMe_2O), 1.1 (br, 18H, CNCH(CHMe_2)CMe$_2$O (9H) and CNCH(CHMe$_2$)-CMe_2O (9H)), 0.75 (d, $^3J_{HH}$ = 5.4 Hz, 9H, CNCH(CHMe_2)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 187 (br, CNCH(CHMe$_2$)-CMe$_2$O), 147 (br, $ispo$-C$_6$H$_5$), 134.96 (o-C$_6$H$_5$), 127.72 (m-C$_6$H$_5$), 126.04 (p-C$_6$H$_5$), 86.18 (CNCH(CHMe$_2$)CMe$_2$O), 77.77 (CNCH-(CHMe$_2$)CMe$_2$O), 29.59 (CNCH(CHMe$_2$)CMe_2O), 29.28 (CNCH-(CHMe$_2$)CMe$_2$O), 21.57 (CNCH(CHMe$_2$)CMe_2O), 21.42 (CNCH-(CHMe_2)CMe$_2$O), 21.25 (CNCH(CHMe_2)CMe$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ −17.8. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): −173. IR (KBr, cm^{-1}): 3074 w, 3047 w, 2971 s, 2932 m, 2871 m, 2836 w, 1653 w, 1624 m, 1601 s (CN), 1583 m (CN), 1559 w, 1489 m, 1471 m, 1409 m, 1380 m, 1368 m, 1334 m, 1277 w, 1200 w, 1141 m, 1117 w, 1096 w, 1024 m, 970 m, 930 w, 888 w, 852 w, 792 w, 756 m. Anal. Calcd for $C_{30}H_{48}BN_3O_3$: C, 70.72; H, 9.50; N, 8.25. Found: C, 71.03; H, 9.91; N, 8.29. Mp: 126−128 °C.

To^P*Mn(CO)$_3$ (4). Manganese pentacarbonyl bromide (0.0567 g, 0.206 mmol) was added to a solution of Li[To^P*] (**1**) (0.106 g, 0.206 mol) in tetrahydrofuran (15 mL). The solution was heated to 85 °C for 24 h. The solvent was then removed under reduced pressure, and the resulting solid was extracted with benzene (2 × 15 mL). The benzene extracts were combined and filtered through a short plug of grade III neutral alumina (1.5 mL). The filtrate was evaporated in vacuo to give the product as a yellow solid (0.123 g, 0.190 mol, 92.2%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.23 (d, $^3J_{HH}$ = 7.2 Hz, 2H, o-C$_6$H$_5$), 7.48 (t, $^3J_{HH}$ = 7.2 Hz, 2H, m-C$_6$H$_5$), 7.25 (t, $^3J_{HH}$ = 7.2 Hz, 1H, p-C$_6$H$_5$), 3.6 (br, 3H, CNCH(CHMe$_2$)CMe$_2$O), 2.67 (m, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.12 (s, 9H, CNCH(CHMe$_2$)CMe_2O), 1.11 (s, 9H, CNCH(CHMe$_2$)CMe_2O), 1.05 (d, $^3J_{HH}$ = 7.2 Hz, 9H, CNCH(CHMe_2)CMe$_2$O), 0.90 (d, $^3J_{HH}$ = 7.2 Hz, 9H, CNCH-(CHMe_2)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 223.2 (CO), 189 (br, CNCH(CHMe$_2$)CMe$_2$O), 143 (br, $ipso$-C$_6$H$_5$), 136.20 (o-C$_6$H$_5$), 127.30 (m-C$_6$H$_5$), 126.11 (p-C$_6$H$_5$), 88.38 (CNCH-(CHMe$_2$)CMe$_2$O), 80.09 (CNCH(CHMe$_2$)CMe$_2$O), 31.69 (CNCH-(CHMe$_2$)CMe_2O), 30.23 (CNCH(CHMe$_2$)CMe$_2$O), 23.11 (CNCH-(CHMe$_2$)CMe_2O), 18.85 (CNCH(CHMe_2)CMe$_2$O), 17.35 (CNCH-(CHMe_2)CMe$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ −18.7. IR (KBr, cm^{-1}): 3074 w, 3046 w, 3019 w, 2975 m, 2935 m, 2878 m, 2013 s (CO), 1903 s (CO), 1592 m (CN), 1470 w, 1391 w, 1371 w, 1258 m, 1147 w, 1127 w, 1024 m. Anal. Calcd for $C_{33}H_{47}BMnN_3O_6$: C, 61.21; H, 7.32; N, 6.49. Found: C, 61.40; H, 7.41; N, 6.38. Mp: 164−167 °C.

To^P*Re(CO)$_3$ (5). Rhenium pentacarbonyl bromide (0.0800 g, 0.197 mmol) was added to a solution of Li[To^P*] (**1**) (0.102 g, 0.198 mmol) in tetrahydrofuran (15 mL). The solution was heated to 85 °C for 24 h. The solvent was then removed under reduced pressure, and the resulting solid was extracted with benzene (2 × 15 mL). The benzene extracts were combined and filtered through a short plug of grade III neutral alumina (1.5 mL). The filtrate was evaporated in vacuo to give the product as a yellow solid (0.146 g, 0.187 mmol, 94.9%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.19 (d, $^3J_{HH}$ = 7.2 Hz, 2H, o-C$_6$H$_5$), 7.48 (t, $^3J_{HH}$ = 7.2 Hz, m-C$_6$H$_5$), 7.26 (t, $^3J_{HH}$ = 7.2 Hz, 1H, p-C$_6$H$_5$), 3.6 (br, 3H, CNCH(CHMe$_2$)CMe$_2$O), 2.63 (m, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.07−1.05 (m, 27H, CNCH(CHMe_2)-CMe$_2$O (9H) and CNCH(CHMe$_2$)CMe_2O (18H)), 0.86 (d, $^3J_{HH}$ = 7.2 Hz, 9H, CNCH(CHCMe_2)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 199 (br, CO), 189 (br, CNCH(CHMe$_2$)CMe$_2$O), 136.15 (o-C$_6$H$_5$), 127.36 (m-C$_6$H$_5$), 126.35 (p-C$_6$H$_5$), 89.04 (CNCH-(CHMe$_2$)CMe$_2$O), 80.53 (CNCH(CHMe$_2$)CMe$_2$O), 31.43 (CNCH-(CHMe$_2$)CMe_2O), 30.19 (CNCH(CHMe$_2$)CMe$_2$O), 22.84 (CNCH-(CHMe$_2$)CMe_2O), 18.49 (CNCH(CHMe_2)CMe$_2$O), 17.60 (CNCH-(CHMe_2)CMe$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ −18.2. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ −197. IR (KBr, cm^{-1}): 3074 w, 3047 w, 3003 w, 2974 m, 2934 m, 2877 m, 2008 s (CO), 1886 s (CO), 1584 m (CN), 1553 w, 1463 w, 1391 m, 1372 m, 1296 m, 1261 m, 1201 m, 1154 m, 1125 m. Anal. Calcd for $C_{33}H_{47}BN_3O_6Re$: C, 50.90; H, 6.08; N, 5.40. Found: C, 50.97; H, 6.47; N, 5.36. Mp: 189−191 °C.

To^P*ZnEt (6). Diethylzinc (22.0 μL, 0.215 mmol) was added to a solution of H[To^P*] (**3**) (0.109 g, 0.214 mmol) in benzene (10 mL). The resulting solution was stirred at room temperature for 1 h. The solvent was then removed in vacuo to give the product as a white solid (0.122 g, 0.202 mmol, 94.4%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.27 (d, $^3J_{HH}$ = 6.6 Hz, 2H, o-C$_6$H$_5$), 7.50 (t, $^3J_{HH}$ = 6.6 Hz, 2H, m-C$_6$H$_5$), 7.26 (t, $^3J_{HH}$ = 6.6 Hz, 1H, p-C$_6$H$_5$), 3.3 (br, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.83 (t, $^3J_{HH}$ = 6.6 Hz, 3H, ZnCH$_2$CH_3), 1.65 (m, 3H, CNCH(CHMe$_2$)CMe$_2$O), 1.08 (s, 9H, CNCH-(CHMe$_2$)CMe_2O), 1.0 (br, 18H, CNCH(CHMe_2)CMe$_2$O (9H) and CNCH(CHMe$_2$)CMe_2O (9H)), 0.92 (d, $^3J_{HH}$ = 6.0 Hz, 9H, CNCH(CHMe_2)CMe$_2$O), 0.8 (br, 2H, ZnCH_2CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 191 (br, CNCH(CHMe$_2$)CMe$_2$O), 144 (br, $ipso$-C$_6$H$_5$), 136.45 (o-C$_6$H$_5$), 127.15 (m-C$_6$H$_5$), 125.86 (p-C$_6$H$_5$), 87.61 (CNCH(CHMe$_2$)CMe$_2$O), 77.40 (CNCH(CHMe$_2$)CMe$_2$O), 30.09 (CNCH(CHMe$_2$)CMe_2O), 29.89 (CNCH(CHMe$_2$)CMe$_2$O), 21.96 (CNCH(CHMe_2)CMe$_2$O), 21.62 (CNCH(CHMe$_2$)CMe_2O), 18.99 (CNCH(CHMe_2)CMe$_2$O), 14.26 (ZnCH$_2$CH$_3$), 0.51 (ZnCH_2CH$_3$). ^{11}B NMR (benzene-d_6, 128 MHz): −18.0. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ −177. IR (KBr, cm^{-1}): 3080 w, 3047 m, 2970 s, 2932 s, 2851 m, 1585 s (CN), 1558 w, 1495 w, 1466 m, 1386 m, 1371 m, 1336 w, 1254 s, 1231 s, 1202 m, 1191 m, 1139 s, 1109 w, 1019 m, 993 m, 947 m, 888 w, 839 w, 816 m, 747 m, 703 m. Anal. Calcd for $C_{32}H_{52}BN_3O_3Zn$: C, 63.74; H, 8.69; N, 6.97. Found: C, 63.30; H, 8.65; N, 6.96. Mp: 130−132 °C.

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To^{P}*ZnCl (7). Zinc chloride (0.108 g, 0.792 mmol) was added to a solution of Li[To^{P}*] (**1**) (0.406 g, 0.788 mmol) in benzene (20 mL). The solution was then heated at 60 °C for 18 h. The resulting yellow solution with a white precipitate was filtered, and the filtrate was evaporated in vacuo to give a yellow solid, which was triturated with pentane and dried in vacuo to give the product as a yellow solid (0.355 g, 0.583 mmol, 74.0%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.22 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, *o*-C_6H_5), 7.49 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, *m*-C_6H_5), 7.26 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 3.42 (d, $^{3}J_{HH}$ = 3.0 Hz, 3H, CNC*H*(CHMe$_2$)CMe$_2$O), 1.65 (m, 3H, CNCH(C*H*Me$_2$)CMe$_2$O), 1.22 (d, $^{3}J_{HH}$ = 6.6 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O), 1.04 (s, 9H, CNCH(CHMe$_2$)C*Me*$_2$O), 0.98 (s, 9H, CNCH(CHMe$_2$)C*Me*$_2$O), 0.94 (d, $^{3}J_{HH}$ = 6.6 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 191 (br, *C*NCH(CHMe$_2$)CMe$_2$O), 136.30 (*o*-C_6H_5), 127.30 (*m*-C_6H_5), 126.26 (*p*-C_6H_5), 88.91 (CNCH-(CHMe$_2$)CMe$_2$O), 76.86 (CNCH(CHMe$_2$)CMe$_2$O), 29.99 (CNCH-(CHMe$_2$)C*Me*$_2$O), 29.66 (CNCH(CHMe$_2$)CMe$_2$O), 22.51 (CNCH-(CH*Me*$_2$)CMe$_2$O), 21.47 (CNCH(CHMe$_2$)C*Me*$_2$O), 18.94 (CNCH-(CH*Me*$_2$)CMe$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ −17.9. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ −184. IR (KBr, cm^{-1}): 3079 w, 3046 w, 2969 s, 2932 m, 2875 m, 1579 s (CN), 1466 m, 1390 m, 1372 m, 1339 w, 1290 m, 1257 s, 1192 w, 1141 s, 1110 w, 1023 m, 951 m, 885 m. Anal. Calcd for $C_{30}H_{47}BClN_3O_3Zn$: C, 59.13; H, 7.77; N, 6.90. Found: C, 58.78; H, 8.05; N, 6.80. Mp: 249−251 °C.

To^{P}*ZnH (8). Potassium *tert*-butoxide (0.0393 g, 0.350 mmol) was added to a solution of To^{P}*ZnCl (**7**) (0.213 g, 0.350 mmol) in benzene (15 mL). The solution was then stirred at room temperature for 2 days. Phenylsilane (43.5 μL, 0.353 mmol) was then added, and the resulting solution was stirred at room temperature for another 18 h. The solution was then filtered, and the filtrate was evaporated in vacuo. The residue was washed with pentane (2 × 5 mL) and dried in vacuo to give the product as a white solid (0.177 g, 0.308 mmol, 88.0%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.29 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, *o*-C_6H_5), 7.52 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, *m*-C_6H_5), 7.27 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 4.61 (s, 1H, ZnH), 3.4 (br, 3H, CNC*H*(CHMe$_2$)-CMe$_2$O), 1.63 (m, 3H, CNCH(C*H*Me$_2$)CMe$_2$O), 1.19 (d, $^{3}J_{HH}$ = 7.2 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O), 1.07 (s, 9H, CNCH(CHMe$_2$)-C*Me*$_2$O), 1.02 (s, 9H, CNCH(CHMe$_2$)C*Me*$_2$O), 0.98 (d, $^{3}J_{HH}$ = 6.6 Hz, 9H, CNCH(CH*Me*$_2$)CMe$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 191 (br, *C*NCH(CHMe$_2$)CMe$_2$O), 144 (br, *ipso*-C_6H_5), 136.47 (*o*-C_6H_5), 127.18 (*m*-C_6H_5), 125.96 (*p*-C_6H_5), 87.84 (CNCH-(CHMe$_2$)CMe$_2$O), 77.62 (CNCH(CHMe$_2$)CMe$_2$O), 30.15 (CNCH-(CHMe$_2$)C*Me*$_2$O), 29.78 (CNCH(CHMe$_2$)CMe$_2$O), 22.81 (CNCH-(CH*Me*$_2$)CMe$_2$O), 21.46 (CNCH(CHMe$_2$)C*Me*$_2$O), 19.16 (CNCH-(CH*Me*$_2$)CMe$_2$O). ^{11}B NMR (benzene-d_6, 128 MHz): δ −18.0. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ −179. IR (KBr, cm^{-1}): 3082 w, 3045 w, 2964 m, 2931 m, 2873 m, 1766 m (ZnH), 1587 s (CN), 1464 m, 1389 w, 1371 m, 1286 w, 1254 m, 1234 m, 1202 w, 1194 w, 1140 m, 1112 w, 1022 m, 1001 w, 950 m, 885 w. Anal. Calcd for $C_{30}H_{48}BN_3O_3Zn$: C, 62.67; H, 8.42; N, 7.31. Found: C, 62.53; H, 8.30; N, 7.10. Mp: 186−189 °C.

PhMeHSiOMe. Phenylmethylsilane (0.720 mL, 5.24 mmol) and To^{P}*ZnH (0.0150 g, 0.0261 mmol) were dissolved in benzene (10 mL), and methanol (0.105 mL, 2.59 mmol) was added to the solution. Bubbles formed immediately, and the resulting clear and colorless solution was stirred at room temperature for 4 h before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 53 °C and 15 mmHg to give the product as a clear and colorless liquid (0.312 g, 2.05 mmol, 79.2%). The spectral data for PhMeHSiOMe matched the literature values.[29] ^{1}H NMR (benzene-d_6, 600 MHz): δ 7.56 (m, 2H, *o*-C_6H_5), 7.20 (m, 3H, *p*- and *m*-C_6H_5), 5.17 (q, $^{3}J_{HH}$ = 3.0 Hz, $^{1}J_{SiH}$ = 207 Hz, 1H, SiH), 3.30 (s, 3H, OMe), 0.33 (d, $^{3}J_{HH}$ = 2.4 Hz, 3H, SiMe). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 136.38 (*ipso*-C_6H_5), 134.55 (*o*-C_6H_5), 130.71 (*p*-C_6H_5), 128.65 (*m*-C_6H_5), 52.04 (OMe), −2.59 (SiMe). ^{29}Si{^{1}H} NMR (benzene-d_6, 119 MHz): δ −0.61. GC−MS: $C_8H_{12}OSi$ *m*/*z* 152 (M$^+$). $[\alpha]_D^{20}$ = −212.42 (C_6H_6).

PhMeHSiOEt. Phenylmethylsilane (0.480 mL, 3.49 mmol) and To^{P}*ZnH (0.0100 g, 0.0174 mmol) were dissolved in benzene (10 mL), and ethanol (0.100 mL, 1.71 mmol) was added to the solution. Bubbles formed immediately, and the resulting clear and colorless solution was stirred at room temperature for 8 h before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 61 °C (10 mmHg) to give the product as a clear and colorless liquid (0.213 g, 1.28 mmol, 74.9%). The spectral data for PhMeHSiOEt matched the literature values.[29] ^{1}H NMR (benzene-d_6, 600 MHz): δ 7.60 (m, 2H, *o*-C_6H_5), 7.20 (m, 3H, *p*- and *m*-C_6H_5), 5.25 (q, $^{3}J_{HH}$ = 3.0 Hz, $^{1}J_{SiH}$ = 206 Hz, 1H, SiH), 3.60 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 1.08 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 0.36 (d, $^{3}J_{HH}$ = 2.4 Hz, 3H, SiMe). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 136.87 (*ipso*-C_6H_5), 134.56 (*o*-C_6H_5), 130.64 (*p*-C_6H_5), 128.63 (*m*-C_6H_5), 60.47 (OCH$_2$CH$_3$), 18.72 (OCH$_2$CH$_3$), −2.12 (SiMe). ^{29}Si{^{1}H} NMR (benzene-d_6, 119 MHz): δ −3.45. GC−MS: $C_9H_{14}OSi$ *m*/*z* 166 (M$^+$). $[\alpha]_D^{20}$ = +22.01 (C_6H_6).

PhMeHSi(O-3,5-C$_6$H$_3$Me$_2$). Phenylmethylsilane (0.120 mL, 0.874 mmol) and To^{P}*ZnH (0.0100 g, 0.0174 mmol) were dissolved in benzene (2 mL), and 3,5-dimethylphenol (0.106 g, 0.868 mmol) was added to the solution. The resulting clear and colorless solution was stirred at room temperature for 4 days before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 101 °C (0.1 mmHg) to give the product as a clear and colorless oil (0.170 g, 0.701 mmol, 80.8%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 7.63 (m, 2H, *o*-C_6H_5), 7.16 (m, *p*- and *m*-C_6H_5, overlapped with benzene-d_6), 6.73 (s, 2H, *o*-$C_6H_3Me_2$), 6.50 (s, 1H, *p*-$C_6H_3Me_2$), 5.55 (q, $^{3}J_{HH}$ = 3.0 Hz, $^{1}J_{SiH}$ = 213 Hz, 1H, SiH), 2.06 (s, 6H, $C_6H_3Me_2$), 0.44 (d, $^{3}J_{HH}$ = 3.0 Hz, 3H, SiMe). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 156.32 (*ipso*-$C_6H_3Me_2$), 139.79 (*m*-$C_6H_3Me_2$), 135.72 (*ipso*-C_6H_5), 134.56 (*o*-C_6H_5), 130.95 (*p*-C_6H_5), 128.73 (*m*-C_6H_5), 124.39 (*p*-$C_6H_3Me_2$), 117.90 (*o*-$C_6H_3Me_2$), 21.62 ($C_6H_3Me_2$), −2.01 (SiMe). ^{29}Si{^{1}H} NMR (benzene-d_6, 119 MHz): δ −5.23. GC−MS: $C_{15}H_{18}OSi$ *m*/*z* 242 (M$^+$). $[\alpha]_D^{20}$ = −198.31 (C_6H_6).

1-NpPhHSiOMe. 1-Naphthylphenylsilane (1.150 mL, 5.25 mmol) and To^{P}*ZnH (0.0150 g, 0.0261 mmol) were dissolved in benzene (10 mL), and methanol (0.105 mL, 2.59 mmol) was added to the solution. Bubbles formed immediately, and the resulting clear and colorless solution was stirred at room temperature for 6 h before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 120 °C (0.1 mmHg) to give the product as a clear and colorless oil (0.617 g, 2.33 mmol, 90.0%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.38 (m, 1H, $C_{10}H_7$), 7.93 (d, $^{3}J_{HH}$ = 6.6. Hz, 1H, $C_{10}H_7$), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *o*-C_6H_5), 7.67 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, $C_{10}H_7$), 7.61 (m, 1H, $C_{10}H_7$), 7.27 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C_6H_5), 7.20 (m, 2H, $C_{10}H_7$), 7.11 (m, 3H, *m*-C_6H_5 (2H) and $C_{10}H_7$ (1H)), 5.94 (s, $^{1}J_{SiH}$ = 212 Hz, 1H, SiH), 3.44 (s, 3H, OMe). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 138.05 ($C_{10}H_7$), 137.61 ($C_{10}H_7$), 136.34 (*ipso*-C_6H_5), 135.29 (*o*-C_6H_5), 134.20 ($C_{10}H_7$), 134.09 ($C_{10}H_7$), 131.91 ($C_{10}H_7$), 131.69 ($C_{10}H_7$), 130.90 ($C_{10}H_7$), 130.45 ($C_{10}H_7$), 128.85 (*m*-C_6H_5), 127.11 ($C_{10}H_7$), 126.49 ($C_{10}H_7$), 125.96 (*p*-C_6H_5), 52.68 (OMe). ^{29}Si{^{1}H} NMR (benzene-d_6, 119 MHz): δ −7.86. GC−MS: $C_{17}H_{16}OSi$ *m*/*z* 264 (M$^+$). $[\alpha]_D^{20}$ = +9.20 (C_6H_6).

1-NpPhHSiOEt. 1-Naphthylphenylsilane (0.770 mL, 3.51 mmol) and To^{P}*ZnH (0.0100 g, 0.0174 mmol) were dissolved in benzene (10 mL), and ethanol (0.100 mL, 1.71 mmol) was added to the solution. Bubbles formed immediately, and the resulting clear and colorless solution was stirred at room temperature for 10 h before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 140 °C (0.1 mmHg) to give

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the product as a clear and colorless oil (0.435 g, 1.56 mmol, 91.2%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.42 (m, 1H, $C_{10}H_7$), 7.97 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $C_{10}H_7$), 7.73 (d, $^3J_{HH}$ = 7.2 Hz, 2H, *o*-C_6H_5), 7.67 (d, $^3J_{HH}$ = 7.8 Hz, 1H, $C_{10}H_7$), 7.61 (m, 1H, $C_{10}H_7$), 7.29 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 7.20 (m, 2H, $C_{10}H_7$), 7.13 (m, 3H, *m*-C_6H_5 (2H) and $C_{10}H_7$ (1H)), 5.99 (s, $^1J_{SiH}$ = 211 Hz, 1H, SiH), 3.74 (m, 2H, OCH_2CH_3), 1.12 (t, $^3J_{HH}$ = 6.6 Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 150 MHz): δ 138.05 ($C_{10}H_7$), 137.61 ($C_{10}H_7$), 136.34 (*ipso*-C_6H_5), 135.31 (*o*-C_6H_5), 134.22 ($C_{10}H_7$), 134.10 ($C_{10}H_7$), 131.86 ($C_{10}H_7$), 131.69 ($C_{10}H_7$), 130.82 ($C_{10}H_7$), 130.45 ($C_{10}H_7$), 128.85 (*m*-C_6H_5), 127.01 ($C_{10}H_7$), 126.47 ($C_{10}H_7$), 125.97 (*p*-C_6H_5), 61.22 (OCH_2CH_3), 18.66 (OCH_2CH_3). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 119 MHz): δ −10.96. GC−MS: $C_{18}H_{18}OSi$ *m*/*z* 278 (M^+). $[\alpha]_D^{20}$ = +3.66 (C_6H_6).

1-NpPhHSiO*i*Pr. 1-Naphthylphenylsilane (0.380 mL, 1.73 mmol) and To^P*ZnH (0.0100 g, 0.0174 mmol) were dissolved in benzene (2 mL), and isopropanol (0.130 mL, 1.70 mmol) was added to the solution. The resulting clear and colorless solution was stirred at room temperature for 14 days before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 146 °C (0.1 mmHg) to give the product as a clear and colorless oil (0.333 g, 1.14 mmol, 67.1%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.43 (m, 1H, $C_{10}H_7$), 8.01 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $C_{10}H_7$), 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-C_6H_5), 7.70 (d, $^3J_{HH}$ = 8.4 Hz, 1H, $C_{10}H_7$), 7.62 (m, 1H, $C_{10}H_7$), 7.30 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 7.20 (m, 2H, $C_{10}H_7$), 7.13 (m, 3H, *m*-C_6H_5 (2H) and $C_{10}H_7$ (1H)), 6.02 (s, $^1J_{SiH}$ = 211 Hz, 1H, SiH), 4.11 (m, 1H, $OCHMe_2$), 1.19 (d, $^3J_{HH}$ = 6.0 Hz, 3H, $OCHMe_2$), 1.13 (d, $^3J_{HH}$ = 6.0 Hz, 3H, $OCHMe_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 150 MHz): δ 138.01 ($C_{10}H_7$), 136.32 ($C_{10}H_7$), 135.75 (*ipso*-C_6H_5), 135.29 (*o*-C_6H_5), 134.24 ($C_{10}H_7$), 133.73 ($C_{10}H_7$), 131.81 ($C_{10}H_7$), 130.74 ($C_{10}H_7$), 129.48 ($C_{10}H_7$), 129.07 ($C_{10}H_7$), 128.69 (*m*-C_6H_5), 126.90 ($C_{10}H_7$), 126.44 ($C_{10}H_7$), 125.81 (*p*-C_6H_5), 68.18 ($OCHMe_2$), 25.76 ($OCHMe_2$), 25.70 ($OCHMe_2$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 119 MHz): δ −13.70. GC−MS: $C_{19}H_{20}OSi$ *m*/*z* 292 (M^+). $[\alpha]_D^{20}$ = +17.18 (C_6H_6).

1-NpPhHSi(O-3,5-$C_6H_3Me_2$). 1-Naphthylphenylsilane (0.190 mL, 0.867 mmol) and To^P*ZnH (0.0100 g, 0.0174 mmol) were dissolved in benzene (2 mL), and 3,5-dimethylphenol (0.106 g, 0.868 mmol) was added to the solution. The resulting clear and colorless solution was stirred at room temperature for 14 days before it was filtered through a short plug of Celite (5 mL). The Celite plug was further washed with benzene (3 mL × 2). The clear and colorless filtrates were combined with the wash, and the mixture was purified by distillation. The product was distilled at 250 °C (0.1 mmHg) to give the product as a clear and colorless oil (0.246 g, 0.694 mmol, 80.0%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.44 (m, 1H, $C_{10}H_7$), 8.01 (d, $^3J_{HH}$ = 6.6 Hz, 1H, $C_{10}H_7$), 7.76 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-C_6H_5), 7.67 (d, $^3J_{HH}$ = 7.8 Hz, 1H, $C_{10}H_7$), 7.59 (m, 1H, $C_{10}H_7$), 7.23 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 7.18 (m, 2H, $C_{10}H_7$), 7.11 (m, 3H, *m*-C_6H_5 (2H) and $C_{10}H_7$ (1H)), 6.83 (s, 2H, *o*-$C_6H_3Me_2$), 6.47 (s, 1H, *p*-$C_6H_3Me_2$), 6.34 (s, $^1J_{SiH}$ = 218 Hz, 1H, SiH), 1.99 (s, 6H, $C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 150 MHz): δ 156.48 (*ipso*-$C_6H_3Me_2$), 139.87 (*m*-$C_6H_3Me_2$), 139.69 ($C_{10}H_7$), 137.86 ($C_{10}H_7$), 136.47 (*ipso*-C_6H_5), 135.42 (*o*-C_6H_5), 134.31 ($C_{10}H_7$), 134.23 ($C_{10}H_7$), 132.21 ($C_{10}H_7$), 132.13 ($C_{10}H_7$), 131.16 (*p*-C_6H_5), 129.57 (*m*-C_6H_5), 127.24 ($C_{10}H_7$), 126.57 ($C_{10}H_7$), 125.86 (*p*-$C_6H_3Me_2$), 124.62 ($C_{10}H_7$), 118.48 ($C_{10}H_7$), 117.82 (*o*-$C_6H_3Me_2$), 21.56 ($C_6H_3Me_2$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 119 MHz): δ −13.32. GC−MS: $C_{24}H_{22}OSi$ *m*/*z* 354 (M^+). $[\alpha]_D^{20}$ = +11.96 (C_6H_6).

■ ASSOCIATED CONTENT

Supporting Information

Rendered thermal ellipsoid plot of To^P*Mn(CO)$_3$ (**4**), spectra of To^P* compounds, characterization of catalytic products, and crystallographic information files (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00225.

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Notes

The authors declare no competing financial interest.

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