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PAPER

Intermolecular hydroamination of oxygen-substituted allenes. New routes for the synthesis of *N*,*O*-chelated zirconium and titanium amido complexes†

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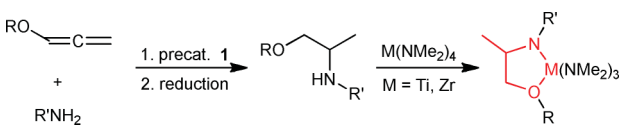
Intermolecular hydroamination of heteroatom-substituted allenes with a bulky arylamine was carried out using a bis(amidate) bis(amido) titanium(IV) complex (**1**) as a precatalyst. The reaction of 2,6-dimethylaniline with oxygen-substituted allene **2c** or **2d** in the presence of complex **1** gives the ketimine regioisomer as the exclusive product. Reduction of such ketimine products resulted in the formation of amino ethers that were further employed as proligands for the formation of *N*,*O*-chelating five-membered titana- and zirconacycles. Such sterically demanding *N*,*O*-chelating ligands result in the high-yielding preparation of mono-ligated products. Solid-state molecular structures of all the complexes revealed distorted trigonal bipyramidal geometry about the metal centers, with a dative bond between the metal and the oxygen donor atom. These new complexes obtained using hydroamination as the key-step in ligand preparation were also shown to be useful cyclohydroamination precatalysts in their own right.

Introduction

The transition metal-catalyzed addition of N–H to C–C multiple bonds such as alkynes, alkenes, and allenes is an important transformation in organic synthesis. This reaction termed hydroamination presents an atom economic way of synthesizing N-containing compounds, including amines, enamines, imines, and hydrazones, which are valuable substrates and intermediates in research and industrial processes.[1–7] A large number of metal-containing complexes including alkali and alkaline earth metals,[1,7–15] early transition metals,[1–4,16–25] late transition metals,[1,2,4,6,26–35] and lanthanides[1,4–6,36–39] have been described as competent catalysts for the hydroamination reaction. Despite these impressive reports, the use of alkenes as co-substrate with amines in the intermolecular variant still remains a significant challenge.[1,5,6,40] The difficulties encountered using alkenes can be mitigated by the selection of allenes as substrates because the C–C π-bond of an allene is about 10 kcal mol^{-1} less stable in comparison to that of a simple alkene.[41,42] However, the intermolecular hydroamination of allenes has received much less attention in comparison to alkynes and functional group tolerance in the allene substrate has not been extensively explored.

The bulk of reported allene hydroamination reactions are catalyzed by late transition metals,[29,41,43–61] notably gold[29,41,44,46–48,52–52,56–61] and palladium.[43,49–51] The use of lanthanide complexes as precatalysts for allene hydroamination has also been studied by Marks and co-workers.[62–66] A few examples of early transition metal-catalyzed intramolecular[67–70] and intermolecular[71–73] allene hydroamination have also been disclosed. All of the above reports involve alkyl- or aryl-substituted allenes, including our work disclosing a rare example of early transition metal-catalyzed intermolecular hydroamination of substituted allenes with less reactive alkylamine substrates.[74] However, to the best of our knowledge, the intermolecular hydroamination of oxygen-substituted allenes, in which the heteroatom is directly attached to the highly reactive allene moiety, has yet to be reported.[71] The product of such a reaction would provide facile access to a new class of monoanionic *N*,*O*-chelating ligand suitable for generating five-membered metallacycles (Scheme 1), rather than the four-membered metallacycles of complex **1** (Fig. 1) and other amidate and ureate complexes previously reported by our group[75–90] and others.[17,91–93]



Scheme 1 Hydroamination for a modular synthesis of *N*,*O*-chelating ligands suitable for the formation of five-membered metallacycles.

The development of four-membered *N*,*O*-chelating metallacycles of early-transition metals including amidates and ureates has received attention in recent years.[17,76,78,79,81,83–92] This is due in part to the facile protonolysis approach to synthesizing these complexes which allows access to well-defined monomeric species. These complexes have been successfully applied in catalytic synthesis of a variety of N-containing molecules.[17,74–77,79,80,82,83,85,86,89–92] Similarly,

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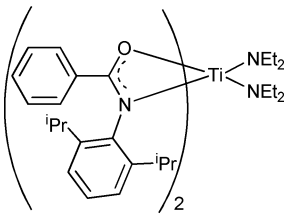


1

Fig. 1 Highly reactive and regioselective hydroamination precatalyst.

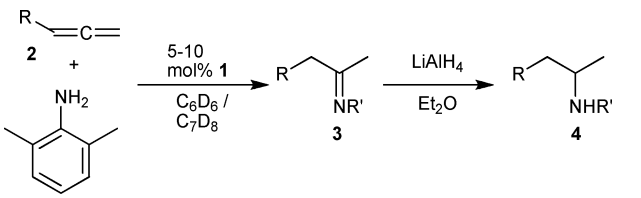
six-membered alkoxy-imine type, *N*,*O*-chelating complexes of early transition metals have been widely studied for a range of reactions with significant application in olefin polymerization.[94–97] In contrast, five-membered *N*,*O*-chelating complexes of early transition metals are much less investigated.[67,98–123] In principle, such five-membered *N*,*O*-chelating complexes should be easily accessible *via* protonolysis reactions with appropriate amino ether proligands (Scheme 1). Importantly, the development of a modular synthetic route to this class of proligands could serve to access a broad range of complexes suitable for investigation in catalytic applications. Here, we report the use of **1** (Fig. 1) for the hydroamination reaction of oxygen-substituted allenes with a bulky arylamine to give ketimines with excellent regioselectivity. Upon reduction, the amino ether proligands obtained can then be used to synthesize C_1-symmetric five-membered zirconium and titanium metallacyclic complexes with *N*,*O*-chelating ligands (Scheme 1). The synthetic details, characterization, and application of these new complexes in cyclohydroamination are described in this report.

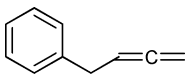
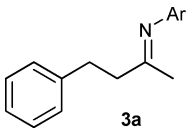
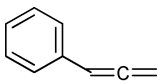
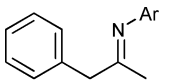
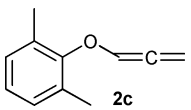
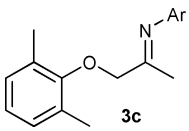
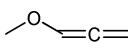
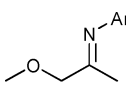
Results and discussion

Intermolecular hydroamination of heteroatom-substituted allenes

Complex **1** (Fig. 1) is an efficient precatalyst for the regioselective intermolecular hydroamination of aryl or alkyl substituted allenes with a bulky arylamine to exclusively afford the ketimine products (Table 1, entries 1 & 2).[74] These observations are consistent with previous reports of early transition metal-catalyzed intermolecular hydroamination of allenes with amines which also afford the ketimine products.[71–73] In an investigation of substrate scope we note that complex **1** is tolerant of oxygen-substituted allenes, thus, 1 equiv. of 2,6-dimethylphenoxyallene (**2c**) reacts fully with 1 equiv. of 2,6-dimethylaniline in the presence of 5 mol% of **1** within 2 h at 90 °C as observed by ^{1}H NMR spectroscopy (Table 1, entry 3). The success of this reaction is consistent with a high level of functional group tolerance of complex **1**. This is in contrast to Cp derived Ti precatalysts, which were reported to be unsuccessful for the hydroamination of heteroatom-substituted allenes.[71] Interestingly, even with late-transition metals where functional group tolerance is anticipated to be improved, we are unaware of any reported examples of the catalytic intermolecular hydroamination reaction of oxygen-substituted allenes in which the heteroatom is directly attached to the allene moiety. By choosing the bulky 2,6-dimethylaniline as the amine substrate we can access a preferred substituent ideal for incorporation into a ligand as it provides the requisite steric protection for electrophilic early transition metals such as Ti and Zr. The reaction of **2c** with 2,6-dimethylaniline proceeds efficiently at 90 °C (Table 1, entry 3) but can also be carried out at a lower temperature of 65 °C, although a longer time of 24 h is required. The disappearance of the allene signals between δ 5.20 and 6.90 and the appearance of new signals between δ 1.91 and 4.57 (singlets) in the ^{1}H NMR spectrum suggests the preferential formation of ketimine **3c**. The ketimine products **3** are then reduced to the corresponding secondary amines **4** for ease of isolation and characterization.

Table 1 Intermolecular hydroamination of substituted allenes with a bulky arylamine



Entry	Allene	Product	t^c/h	Yield^d (%)
1[a]	 **2a**	 **3a**	24	93
2[a]	 **2b**	 **3b**	7	76
3[a]	 **2c**	 **3c**	2	76
4[b]	 **2d**	 **3d**	24	68

[a] 5 mol% **1**; allene, 1.25 mmol; amine, 1.25 mmol, 90 °C. [b] 10 mol% **1**; allene, 1.50 mmol; amine, 1.25 mmol, 110 °C. [c] Time required to reach >96% conversion. [d] Isolated yield of the corresponding secondary amine following reduction with lithium aluminum hydride or sodium cyanoborohydride/zinc chloride.

Mechanistically, the hydroamination reaction using precatalyst **1** is postulated to proceed *via* a [2 + 2] cycloaddition mechanism, as has been previously proposed for alkyne hydroamination using this Ti catalyst system[90] and other group 4 complexes.[124] This mechanistic proposal is supported by unproductive attempts to mediate intermolecular hydroamination of allenes with morpholine, a known preferred secondary amine for intermolecular alkyne[77] and allene hydroamination.[29,44,55,56]

The alkoxy-substituted allene, methoxyallene (**2d**), also reacts with 2,6-dimethylaniline in the presence of 10 mol% of **1** to afford ketimine **3d**. Here, complete consumption of the amine is achieved within 24 h at 110 °C (Table 1, entry 4). The somewhat reduced yield of 68% is attributed to the fact that methoxyallene **2d** is volatile (b.p. 52 °C)[125] and at elevated reaction temperatures, an appreciable quantity is present in the gas phase. Most importantly, this result shows that steric protection of the oxygen substituent is

not required and that precatalyst **1** is compatible with the inclusion of sterically accessible neutral donor atoms.

It is well known that the isomerization of alkynes is one of the general methods of synthesizing allenes,[126] and indeed this methodology is utilized in the preparation of allenes **2c** and **2d**.[125,127] Thus, to exclude allene-alkyne isomerization and subsequent hydroamination catalysis during this reaction protocol, control experiments with the alkyne isomer of **2d**, methyl propargyl ether, have been performed. In this case 2,6-dimethylaniline does not react with methyl propargyl ether despite a catalyst loading of 10 mol%, and a reaction time of 24 h at 110 °C. The lack of reactivity with this alkyne eliminates the possibility of allene isomerization to the alkyne prior to undergoing hydroamination with the amine.

Thus by achieving the first examples of oxygen-substituted allene hydroamination with precatalyst **1** we have established a catalytic route for the preparation of a new family of monoanionic *N*,*O*-chelating ligands. This class of ligand provides access to five-membered metallacycles upon complexation of these proligands with variable steric and electronic properties.

Zirconium and titanium amido complexes

One of our main interests is the development of bidentate *N*,*O*-chelating ligands for early transition metal complexes.[75–81,83,85–90] Previous to this work, we have only investigated four-membered *N*,*O*-chelating ligands. Thus, by using the amino ethers **4c** and **4d** (Fig. 2), obtained from the reduction of ketimine products **3c** and **3d** respectively, we can obtain new monoanionic *N*,*O*-chelating ligands for group 4 metal complex formation. For ease of presentation and discussion these proligands will be referred to as **HL**^{1} (**4d**) and **HL**^{2} (**4c**) (Fig. 2).

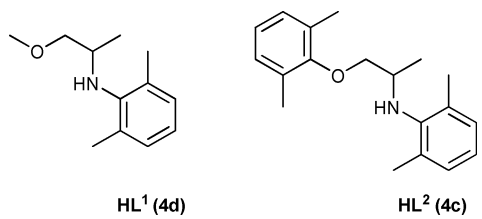
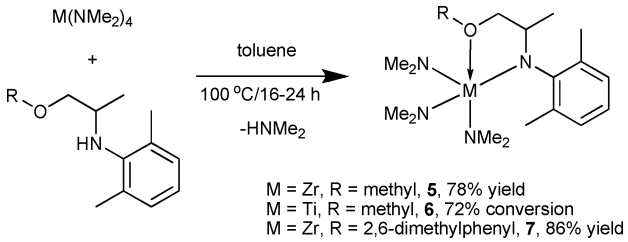


Fig. 2 Racemic proligands for preparing *N*,*O*-chelated group 4 complexes.

Initial synthetic efforts focused on the investigation of the least sterically demanding proligand. Thus, the protonolysis reaction using equimolar quantities of **HL**^{1} and Zr(NMe$_2$)$_4$ in toluene for 16 h at 100 °C gives complex **5** as a colourless solid in 78% isolated yield (Scheme 2). Notably, attempts to install two ligands using 2 equiv. of **HL**^{1} and 1 equiv. of Zr(NMe$_2$)$_4$ at 100 °C after 16 h still give only complex **5** with only one ancillary ligand. This is clearly observed by ^{1}H NMR spectroscopy of the reaction mixture, which displays the signals associated with Zr**L**^{1}(NMe$_2$)$_3$ (**5**), along with those of the free proligand in a 1 : 1 ratio.

The ^{1}H NMR spectrum of complex **5** reveals that the methyl protons adjacent to the stereogenic center in **L**^{1} resonate at a higher field (δ 0.56) relative to those of **HL**^{1} (δ 1.15), whereas the methyl protons of the *N*-aryl group in **L**^{1} are shifted downfield and are inequivalent as manifested by two distinct singlets at δ 2.34 and 2.45, each integrating to three protons. This inequivalence



Scheme 2 Synthesis of zirconium and titanium (amidoether)trisamido complexes.

suggests that there is hindered rotation about the N–C*aryl* bond in **L**^{1}. Recrystallization of complex **5** from hot hexanes produced crystals that are amenable to X-ray crystallographic studies.

The solid state molecular structure of **5** reveals geometry about zirconium that is distorted trigonal bipyramidal; with the oxygen of **L**^{1} and one of the dimethylamido nitrogens (N2) occupying the axial positions (Fig. 3). The crystallographic structure contains a mirror plane that passes through the aryl ring, N2, and between N3 and N3_8. In addition, atoms C1, C2, and O1 are disordered about the plane. This is clearly seen when the structure is viewed along the crystallographic *a*-axis. The torsion angle (43.2(5)°) of the five-membered chelate ring indicates significant deviation from planarity. The Zr1–N1 bond distance of 2.127(2) Å (Fig. 3) of the ligand **L**^{1} is shorter than Zr–N bond distances in *N*,*O*-chelating amidate complexes (2.183–2.470 Å) that have been extensively studied in our group.[87,128] The CH$_3$O–Zr distance (2.369(3) Å) is in the range of similar dative interactions in the literature;[109,119,129–132] and is also comparable to the values observed for five-membered Zr metallacycles featuring this interaction.[119,129] However, this Zr–O bond distance (2.369(3) Å) is significantly longer than the Zr–O bond distances in *N*,*O*-chelating amidate complexes (2.093–2.252 Å).[78,87,128] Table 2 features the experimental details of the X-ray diffraction studies.

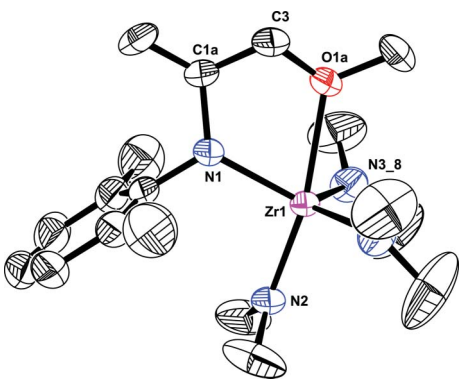


Fig. 3 ORTEP representation of the solid-state molecular structure of complex **5** plotted with 50% probability ellipsoids. Symmetry equivalent atoms are indicated with the "_8" character, and were generated with the symmetry operation (x, $-y$ + 1/2, z). Selected bond lengths (Å) and angles (°): Zr1–O1, 2.369(3); Zr1–N1, 2.127(2); Zr1–N2, 2.064(2); Zr1–N3, 2.068(2); N2–Zr1–N1, 100.22(9); N3–Zr1–N1, 119.45(6); N2–Zr1–O1, 167.65(9); N3–Zr1–O1, 94.30(10); O1a–C3–C1a–N1 (chelate ring dihedral angle), 43.2(5).

The reaction of equimolar quantities of **HL**^{1} and Ti(NMe$_2$)$_4$ is much slower and does not go to completion even with a prolonged reaction time. After 48 h at 100 °C, the conversion to

Table 2 Crystallographic parameters for $ZrL^1(NMe_2)_3$ (**5**), $TiL^1(NMe_2)_3$ (**6**), and $ZrL^2(NMe_2)_3$ (**7**)

	$ZrL^1(NMe_2)_3$ (**5**)	$TiL^1(NMe_2)_3$ (**6**)	$ZrL^2(NMe_2)_3$ (**7**)
Formula	$C_{18}H_{36}N_4OZr$	$C_{18}H_{36}N_4OTi$	$C_{25}H_{42}N_4OZr$
F_w	415.73	372.41	505.85
Crystal size/mm	$0.25 \times 0.2 \times 0.07$	$0.2 \times 0.2 \times 0.2$	$0.25 \times 0.1 \times 0.1$
Colour, habit	Colourless, prism	Red, prism	Colourless, prism
Space group	*Pnma*	*Pnma*	*Pbca*
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic
a/Å	17.2760(12)	17.289(2)	16.5820(15)
b/Å	13.5998(9)	13.0762(13)	17.7264(4)
c/Å	9.8227(5)	9.6677(8)	18.8172(15)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V/Å^3	2307.8(3)	2185.6(4)	5531.1(7)
Z	4	4	8
ρ_{calcd} (g cm^{-1})	1.196	1.132	1.215
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)	Mo-Kα ($\lambda = 0.71073$ Å)	Mo-Kα ($\lambda = 0.71073$ Å)
T/K	173	173	173
F(000)	880	808	2144
μ(Mo-Kα)/mm^{-1}	0.487	0.403	0.419
θ range (°)	2.36–27.74	2.36–25.23	2.00–27.73
$2\theta_{max}$ (°)	55.5	50.5	55.5
Total no. of reflns	46 460	17 022	154 892
No. of unique reflns $I = 2\sigma(I)$	2818	2046	6474
R (int)	0.0379	0.0585	0.0669
Structure soln	SIR92	SIR92	SIR92
No. of variables	139	136	291
Rfln/param ratio	20.27	15.04	22.25
R_1 (all data)	0.0421	0.0611	0.0579
wR_2 (all data)	0.0817	0.1144	0.0764
R_1 ($I > 2\sigma(I)$)	0.0290	0.0413	0.0303
wR_2 ($I > 2\sigma(I)$)	0.0744	0.1032	0.0681
Goodness of fit	1.069	1.046	1.013

$TiL^1(NMe_2)_3$ (**6**) is 72% as determined by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of this particular mixture shows two different doublets between δ 0 and 1.5, with the one at higher field (δ 0.55) being assigned to the protons of the methyl group adjacent to the stereocenter in L^1. This signal is diagnostic of the formation of metal complex **6** as it is shifted about 0.60 ppm upfield from the proligand doublet that corresponds to the protons of the same methyl group. Once again, the methyl protons on the aryl group in the complex are inequivalent and appear as singlets at δ 2.27 and 2.36. They are shifted downfield from the aryl-methyl protons of the proligand, which appear as a single signal at δ 2.20.

Crystals suitable for X-ray crystallographic studies were obtained from a hot benzene solution. The complex **6** is isomorphous to **5** (Fig. 4); a similar distorted trigonal bipyramidal coordination geometry can be seen about the metal center, with the oxygen atom datively bonded to the titanium center and the ligand L^1 forming a five-membered chelate. The crystallographic structure also contains a mirror plane similar to that described for complex **5**, with atoms C1 and O1 being disordered about the plane. Metrical parameters are all consistent with the smaller atomic radius of the titanium metal center.

Amido metal complex formation with HL^2 as a proligand and $Zr(NMe_2)_4$ has also been carried out. The presence of an aryl group as opposed to an alkyl group on the oxygen of HL^2 should result in the formation of complexes with different electronic properties upon metal complex formation. Proligand HL^2 reacts with $Zr(NMe_2)_4$ in a 1 : 1 molar ratio at 100 °C in toluene to afford $ZrL^2(NMe_2)_3$ (**7**) in 86% yield upon recrystallization from hot hexanes.

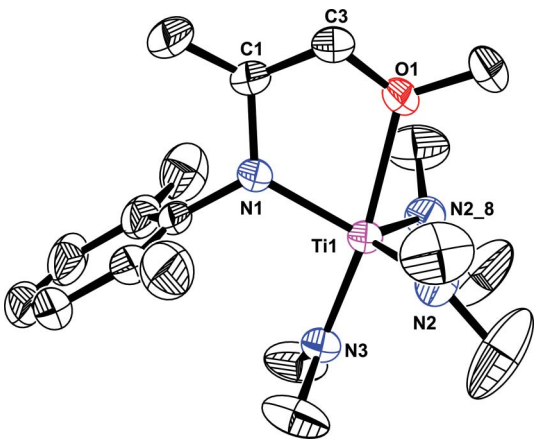


Fig. 4 ORTEP representation of the solid-state molecular structure of complex **6** plotted with 50% probability ellipsoids. Symmetry equivalent atoms are indicated with the "_8" character, and were generated with the symmetry operation (x, $-y + 1/2$, z). Selected bond lengths (Å) and angles (°): Ti1–O1, 2.255(3); Ti1–N1, 1.984(3); Ti1–N2, 1.925(2); Ti1–N3, 1.921(3); N3–Ti1–N1, 99.53(12); N2–Ti1–N1, 120.20(7); N3–Ti1–O1, 169.27(11); N2–Ti1–O1, 94.47(11); O1–C3–C1–N1 (chelate ring dihedral angle), 44.3(4).

The ^{1}H NMR spectrum of **7** indicates hindered rotation about the N–C*aryl* bond in L^2 as manifested by two singlets at δ 2.50 and 2.56 representing the protons of the methyl substituents on

the phenyl ring. In contrast, the methyl protons on the phenoxy ring appear as a singlet at δ 2.26. The methyl protons of the dimethylamido ligands are noted as a singlet at δ 2.81, a likely consequence of rapid exchange of pseudo axial and equatorial ligands on the NMR time scale.

X-ray crystallographic analysis shows that **7** is a C_1-symmetric complex with an *N*,*O*-chelating ligand in which the oxygen atom of the ligand interacts with the zirconium center in a dative fashion (Fig. 5). Once again, the geometry about zirconium is a distorted trigonal bipyramid with the oxygen of the ligand and one of the dimethylamido nitrogens (N2) in the axial positions. The five-membered chelate ring is significantly distorted from planarity as indicated by the torsion angle (46.40(19)°) between the atoms of the metallacycle. The bond distance of 2.4882(12) Å between the oxygen donor atom and the zirconium metal center in **7** is much longer than the value of 2.369(3) Å noted in complex **5** (Fig. 3). This suggests a much weaker interaction of the oxygen functionality with the metal center in complex **7** and is likely due to steric effects of the bulky aryl substituent as well as the reduced nucleophilicity of the lone pairs on oxygen due to the conjugated aryl ring. While this Zr–O bond distance is quite long, it should be noted that even longer Zr–O bond distances have been previously reported.[104,133]

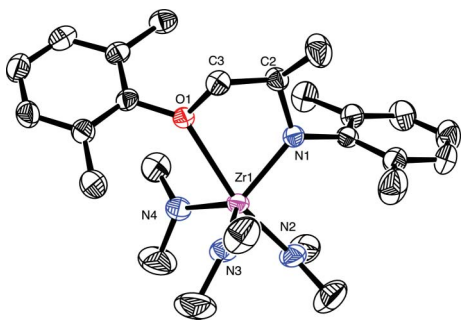
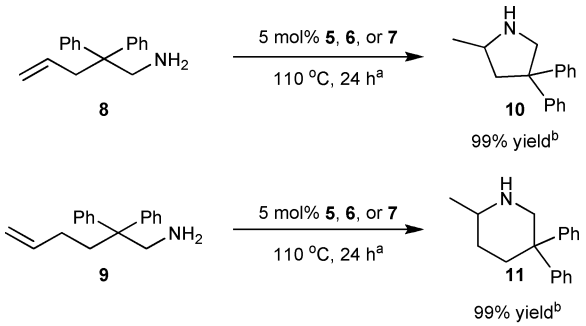


Fig. 5 ORTEP representation of the solid-state molecular structure of complex **7** plotted with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Zr1–O1, 2.4882(12); Zr1–N1, 2.1263(15); Zr1–N2, 2.0763(17); Zr1–N3, 2.0617(17); Zr1–N4, 2.0830(18); N3–Zr1–N2, 98.29(7); N3–Zr1–N4, 116.62(7); N2–Zr1–O1, 162.00(5); N3–Zr1–O1, 98.57(6); O1–C3–C2–N1 (chelate ring dihedral angle), 46.40(19).

Similar to the reaction with **HL¹**, attempts to prepare bis-ligated zirconium complex using **HL²** were unsuccessful as only one ligand could be installed. Furthermore, neither 1 nor 2 equiv. of **HL²** react with $Ti(NMe_2)_4$ using the established protonolysis methodology, even at a high temperature of 100 °C and reaction times of up to 24 h. Based upon the sluggish reactivity observed during the preparation of Ti complex **6** with **L¹**, the lack of reactivity of **HL²** observed here is attributed to steric factors.

Preliminary catalytic investigation

Preliminary catalytic studies with compounds **5–7** show that these complexes are effective precatalysts for the cyclohydroamination of aminoalkenes. Complete cyclization of aminoalkenes **8** and **9** into α-substituted pyrrolidine **10** and α-substituted piperidine **11** respectively, occurs with 5 mol% of either complex **5**, **6**, or **7** within 24 h at 110 °C (reaction time not optimized, Scheme 3). On-going investigations focus on comparing reactivity of complexes with



[a] Reaction time not optimized.
[b] Yield determined by ^{1}H NMR Spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Scheme 3 Intramolecular cyclohydroamination catalyzed by five-membered titana- and zirconacycles.

varying substituents and on synthesizing enantiopure versions of these proligands and complexes for subsequent use in enantioselective hydroamination reactions.

Summary and future directions

In summary, the intermolecular hydroamination of oxygen-substituted allenes with a bulky aniline using catalyst precursor **1** efficiently affords ketimine products. Thus, the hydroamination of oxygen-substituted allenes with 2,6-dimethylaniline provides an efficient and modular synthetic route toward amino ether proligands for the synthesis of *N*,*O*-chelated zirconium and titanium metal complexes. In the solid-state, these complexes adopt distorted trigonal bipyramidal geometry about the metal center and contain a five-membered metallacycle with dative bonding between the oxygen donor atom and the metal center. Interestingly, six-coordinate bis-ligated complexes could not be prepared by protonolysis, even with high reaction temperatures and long reaction times. Preliminary investigations revealed that these complexes are competent precatalysts for the cyclohydroamination of aminoalkenes. This family of proligands is particularly attractive, as enantioselective reduction protocols could be used, thereby granting access to new complexes that may be useful for asymmetric catalysis. Thus, the investigation of a variety of five-membered N,O-chelates including enantiopure variants is currently underway.

Experimental procedures

General methods

All moisture/air sensitive reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques or an MBraun Unilab glove box unless otherwise stated. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on 300 MHz or 400 MHz Bruker Avance spectrometers at ambient temperature; chemical shifts are reported in parts per million (ppm) relative to the signal for the residual proton in the solvent indicated. Thin layer chromatography was performed on silica gel (Macheney-Nagel Silica Gel 60) aluminum plates (layer 0.20 mm). Column chromatography was performed using SiliaFlash F60 silica gel 70–230 mesh. GC–MS spectra were obtained on an Agilent series 6890 gas chromatography system equipped with a 5973 mass

selective detector. Mass spectrometry and elemental analysis were performed at the Department of Chemistry, University of British Columbia. Single crystal X-ray diffraction measurements were performed on a Bruker X8 APEX diffractometer using a Mo-Kα radiation source ($\lambda = 0.71013$ Å) at 173 K.

Materials

THF, hexanes, and toluene were purified over columns of alumina. Amines were dried over CaH_2 and distilled under vacuum or nitrogen. $Ti(NEt_2)_4$, $Ti(NMe_2)_4$, and $Zr(NMe_2)_4$ were purchased from Strem and used as received. d_8-Toluene, and d_6-benzene, were degassed by freeze-pump-thaw process, and stored over 4 Å molecular sieves in the glove box. Bis(amidate) bis(amido) precatalyst **1** was prepared as described previously.[90] Phenylallene **2a**,[134] benzylallene **2b**,[135] 2,6-dimethylphenoxyallene **2c**,[127] methoxyallene **2d**,[125] 2,2-diphenyl-4-pentenylamine **8**,[136] and 2,2-diphenyl-5-hexenylamine **9**[136] were synthesized according to literature procedures. Hexanes solutions of proligands **HL²** and **HL¹** were dried over anhydrous magnesium sulphate for 2 h after which the solid was filtered off and the solvents removed prior to the proligands being used in metal complex formation. All other reagents were purchased from Aldrich, Acros, or Fisher Scientific and used without further purification. The spectral data for the following products are consistent with literature values: *N*-(4-phenylbutan-2-yl)-2,6-dimethylaniline **4a**,[74] *N*-(1-phenylpropan-2-yl)-2,6-dimethylaniline **4b**,[137] *N*-(1-methoxypropan-2-yl)-2,6-dimethylaniline **4d**,[138] 2-methyl-4,4-diphenylpyrrolidine **10**,[136] and 2-methyl-5,5-diphenylpiperidine **11**.[139]

Representative procedure for intermolecular hydroamination of allenes

All catalytic reactions were set up inside of the glove box and then transferred into a J. Young NMR tube equipped with a Teflon cap for further manipulation outside of the glove box. The NMR tubes were heated in an oil bath set at the temperature indicated in Table 1 for the specific substrates combination.

Example: synthesis of *N*-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,6-dimethylaniline (4c)

A mixture of 200 mg (1.25 mmol) of 2,6-dimethylphenoxyallene, 151 mg (1.25 mmol) of 2,6-dimethylaniline, 47 mg (5 mol%) of **1**, and 0.35 mL of d_8-toluene in a J. Young NMR tube equipped with a Teflon cap (total volume in NMR tube is 0.6 mL) was heated at 90 °C (in an oil bath) for 2 h. The reaction mixture was cooled to room temperature, and then added to a mixture of 157 mg (2.50 mmol) of sodium cyanoborohydride and 170 mg (1.25 mmol) of zinc chloride in 40 mL of THF or methanol, followed by stirring at room temperature for 16 h. The reaction was quenched by the addition of 20 mL of saturated aqueous sodium carbonate solution. The precipitated was filtered and washed with dichloromethane (25 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined extracts were dried over anhydrous magnesium sulphate, the solid was filtered off and the solvents removed by rotary evaporation. The crude product was purified by column chromatography using hexanes/ethyl acetate 40 : 1 to give the product in 76% yield (268 mg, 0.946 mmol).

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 1.36 (3H, d, J = 6.2 Hz, CHCH_3), 2.27 (6H, s, Ar–CH_3), 2.32 (6H, s, Ar–CH_3), 3.51 (1H, br s, Ar–NH), 3.69–3.78 (2H, m, CH_2CH), 3.86 (1H, m, CH_2CH), 6.82 (1H, m, Ar–H), 6.93 (1H, m, Ar–H), 7.01 (4H, m, Ar–H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, δ): 16.5, 18.8, 19.2, 52.6, 75.6, 121.6, 124.0, 129.1, 129.1, 129.3, 131.1, 144.6, 155.6; GC–MS (EI) m/z: 283 (M^+), 148 {M^+–[$CH_2O(CH_3)_2C_6H_3$]}; Anal. Calcd for $C_{19}H_{25}ON$: C, 80.52; H, 8.89; N, 4.94. Found: C, 80.33; H, 8.83; N, 5.20.

$ZrL^1(NMe_2)_3$ (5)

A solution of 300 mg (1.55 mmol) of **HL¹** in 10 mL of toluene was added to 0.415 g (1.55 mmol) of $Zr(NMe_2)_4$ in 20 mL of toluene at 0 °C *via* cannula transfer. The reaction was stirred at 100 °C overnight. All volatiles were removed *in vacuo* and the solid product formed was dissolved in hexanes and filtered through Celite in the glove box. The hexanes were removed *in vacuo* to give a colourless solid in 78% yield (503 mg, 1.21 mmol). Crystals were obtained by dissolving the solid in hot hexanes and slowly cooling to room temperature. ^{1}H NMR (C_6D_6, 400 MHz, δ): 0.56 (3H, d, J = 6.4 Hz, CHCH_3), 2.34 (3H, s, Ar–CH_3), 2.45 (3H, s, Ar–CH_3), 2.92 (18H, br s, N(CH_3)$_2$), 2.99 (3H, s, OCH_3), 3.19 (1H, m, CH_2CH), 3.26 (1H, dd, J = 7.6, 4.6 Hz, CH_2CH), 3.83 (1H, m, CH$_2$CH), 6.88 (1H, m, Ar–H), 7.10 (1H, d, J = 7.3 Hz, Ar–H), 7.19 (1H, d, J = 7.3 Hz, Ar–H); ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, δ): 17.3, 19.8, 21.4, 43.3, 56.4, 60.2, 82.8, 122.8, 128.6, 128.7, 134.2, 136.2, 151.1; MS(EI) m/z: 414 (M^+); Anal. Cacld for $C_{18}H_{36}N_4OZr$: C, 52.00; H, 8.73; N, 13.48. Found: C, 51.93; H, 8.69; N, 13.71.

$TiL^1(NMe_2)_3$ (6)

The synthesis procedure for complex **6** is analogous to that described above for complex **5**, with $Ti(NMe_2)_4$ being used instead of $Zr(NMe_2)_4$. Complex **6** was characterized in the presence of unreacted proligand. ^{1}H NMR (C_6D_6, 300 MHz, δ): 0.55 (3H, d, J = 6.5 Hz, CHCH_3), 2.27 (3H, s, Ar–CH_3), 2.36 (3H, s, Ar–CH_3), 3.03 (18H, br s, N(CH_3)$_2$), 3.06 (3H, s, OCH_3), 3.20–3.53 (2H, m, CH_2CH), 4.08 (1H, m, CH$_2$CH), 6.74–7.06 (3H, m, Ar–H); MS(EI) m/z: 372 (M^+), 328 (M^+–NMe_2).

$ZrL^2(NMe_2)_3$ (7)

This complex was synthesized from **HL²** (535 mg, 1.89 mmol) and $Zr(NMe_2)_4$ (505 mg, 1.89 mmol) as colourless solid in 86% yield (821 mg, 1.62 mmol) according to the procedure outlined above for complex **5**. ^{1}H NMR (C_6D_6, 300 MHz, δ): 0.63 (3H, d, J = 5.8 Hz, CHCH_3), 2.29 (6H, s, Ar–CH_3), 2.50 (3H, s, Ar–CH_3), 2.56 (3H, s, Ar–CH_3), 2.81 (18H, s, N(CH_3)$_2$), 3.47 (1H, m, CH_2CH), 4.16 (2H, m, CH_2CH, CH$_2$CH), 6.86 (3H, m, Ar–H), 6.94 (1H, m, Ar–H), 7.14 (1H, m, Ar–H), 7.24 (1H, m, Ar–H); ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, δ): 17.1, 17.2, 19.9, 21.6, 43.4, 57.6, 82.7, 123.2, 125.8, 128.9, 129.0, 130.0, 131.4, 134.2, 137.1, 151.4, 157.3; MS(EI) m/z: 504 (M^+); Anal. Cacld for $C_{25}H_{42}N_4OZr$: C, 59.36; H, 8.37; N, 11.08. Found: C, 58.96; H, 7.97; N, 10.74.

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References

1 T. E. Mueller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795.
2 R. Severin and S. Doye, *Chem. Soc. Rev.*, 2007, **36**, 1407.
3 A. L. Odom, *Dalton Trans.*, 2005, 225.
4 K. C. Hultzsch, *Adv. Synth. Catal.*, 2005, **347**, 367.
5 S. Hong and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673.
6 P. W. Roesky and T. E. Mueller, *Angew. Chem., Int. Ed.*, 2003, **42**, 2708.
7 J. Seayad, A. Tillack, C. G. Hartung and M. Beller, *Adv. Synth. Catal.*, 2002, **344**, 795.
8 A. G. M. Barrett, C. Brinkmann, M. R. Crimmin, M. S. Hill, P. Hunt and P. A. Procopiou, *J. Am. Chem. Soc.*, 2009, **131**, 12906.
9 M. Arrowsmith, M. S. Hill and G. Kociok-Kohn, *Organometallics*, 2009, **28**, 1730.
10 C. Quinet, L. Sampoux and I. E. Marko, *Eur. J. Org. Chem.*, 2009, 1806.
11 W. Zhang, J. B. Werness and W. Tang, *Org. Lett.*, 2008, **10**, 2023.
12 M. R. Crimmin, I. J. Casely and M. S. Hill, *J. Am. Chem. Soc.*, 2005, **127**, 2042.
13 P. Horrillo-Martinez and K. C. Hultzsch, *Tetrahedron Lett.*, 2009, **50**, 2054.
14 T. Ogata, A. Ujihara, S. Tsuchida, T. Shimizu, A. Kaneshige and K. Tomioka, *Tetrahedron Lett.*, 2007, **48**, 6648.
15 P. Horrillo-Martinez, C. Hultzsch Kai and F. Hampel, *Chem. Commun.*, 2006, 2221.
16 R. O. Ayinla, T. Gibson and L. L. Schafer, *J. Organomet. Chem.*, 2011, **696**, 50.
17 G. Zi, F. Zhang, L. Xiang, Y. Chen, W. Fang and H. Song, *Dalton Trans.*, 2010, **39**, 4048.
18 A. L. Reznichenko and K. C. Hultzsch, *Organometallics*, 2010, **29**, 24.
19 T. Janssen, R. Severin, M. Diekmann, M. Friedemann, D. Haase, W. Saak, S. Doye and R. Beckhaus, *Organometallics*, 2010, **29**, 1806.
20 K. Weitershaus, B. D. Ward, R. Kubiak, C. Mueller, H. Wadepohl, S. Doye and L. H. Gade, *Dalton Trans.*, 2009, 4586.
21 L. Ackermann, R. Sandmann and L. T. Kaspar, *Org. Lett.*, 2009, **11**, 2031.
22 C. Mueller, W. Saak and S. Doye, *Eur. J. Org. Chem.*, 2008, 2731.
23 S. Majumder and A. L. Odom, *Organometallics*, 2008, **27**, 1174.
24 H. Kim, T. Livinghouse and P. H. Lee, *Tetrahedron*, 2008, **64**, 2525.
25 J. Cho, T. K. Hollis, T. R. Helgert and E. J. Valente, *Chem. Commun.*, 2008, 5001.
26 K. D. Hesp, S. Tobisch and M. Stradiotto, *J. Am. Chem. Soc.*, 2010, **132**, 413.
27 X. Shen and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2010, **49**, 564.
28 Z. Zhang, S. D. Lee and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2009, **131**, 5372.
29 X. Zeng, M. Soleilhavoup and G. Bertrand, *Org. Lett.*, 2009, **11**, 3166.
30 X. Zeng, G. D. Frey, R. Kinjo, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2009, **131**, 8690.
31 J.-W. Pissarek, D. Schlesiger, P. W. Roesky and S. Blechert, *Adv. Synth. Catal.*, 2009, **351**, 2081.
32 H. M. Peng, J. Zhao and X. Li, *Adv. Synth. Catal.*, 2009, **351**, 1371.
33 N. T. Patil, R. D. Kavthe, V. S. Raut and V. V. N. Reddy, *J. Org. Chem.*, 2009, **74**, 6315.
34 A. Iglesias and K. Muniz, *Chem.–Eur. J.*, 2009, **15**, 10563.
35 R. L. Giles, J. D. Sullivan, A. M. Steiner and R. E. Looper, *Angew. Chem., Int. Ed.*, 2009, **48**, 3116.
36 P. Yin and T.-P. Loh, *Org. Lett.*, 2009, **11**, 3791.
37 A. V. Pawlikowski, A. Ellern and A. D. Sadow, *Inorg. Chem.*, 2009, **48**, 8020.
38 J. Hannedouche, I. Aillaud, J. Collin, E. Schulz and A. Trifonov, *Chem. Commun.*, 2008, 3552.
39 I. Aillaud, D. Lyubov, J. Collin, R. Guillot, J. Hannedouche, E. Schulz and A. Trifonov, *Organometallics*, 2008, **27**, 5929.
40 A. L. Reznichenko, H. N. Nguyen and C. Hultzsch Kai, *Angew. Chem., Int. Ed.*, 2010, **49**, 8984.
41 Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2006, **128**, 9066.
42 A. Padwa, M. A. Filipkowski, M. Meske, S. S. Murphree, S. H. Watterson and Z. Ni, *J. Org. Chem.*, 1994, **59**, 588.
43 S. Qiu, Y. Wei and G. Liu, *Chem.–Eur. J.*, 2009, **15**, 2751.
44 N. Nishina and Y. Yamamoto, *Tetrahedron*, 2009, **65**, 1799.
45 A. Tsuhako, D. Oikawa, K. Sakai and S. Okamoto, *Tetrahedron Lett.*, 2008, **49**, 6529.
46 V. Lavallo, G. D. Frey, B. Donnadieu, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2008, **47**, 5224.
47 Z. Zhang, C. F. Bender and R. A. Widenhoefer, *J. Am. Chem. Soc.*, 2007, **129**, 14148.
48 R. L. LaLonde, B. D. Sherry, E. J. Kang and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 2452.
49 M. Meguro and Y. Yamamoto, *Tetrahedron Lett.*, 1998, **39**, 5421.
50 M. Al-Masum, M. Meguro and Y. Yamamoto, *Tetrahedron Lett.*, 1997, **38**, 6071.
51 L. Besson, J. Gore and B. Cases, *Tetrahedron Lett.*, 1995, **36**, 3857.
52 A. N. Duncan and R. A. WidenHoefer, *Synlett*, 2010, 419.
53 R. L. LaLonde, Z. J. Wang, M. Mba, A. D. Lacker and F. D. Toste, *Angew. Chem., Int. Ed.*, 2010, **49**, 598.
54 K. Aikawa, M. Kojima and K. Mikami, *Angew. Chem., Int. Ed.*, 2009, **48**, 6073.
55 K. L. Toups and R. A. WidenHoefer, *Chem. Commun.*, 2010, **46**, 1712.
56 N. Nishina and Y. Yamamoto, *Synlett*, 2007, 1767.
57 Z. Zhang, C. F. Bender and R. A. Widenhoefer, *Org. Lett.*, 2007, **9**, 2887.
58 N. Morita and N. Krause, *Eur. J. Org. Chem.*, 2006, 4634.
59 N. T. Patil, L. M. Lutete, N. Nishina and Y. Yamamoto, *Tetrahedron Lett.*, 2006, **47**, 4749.
60 N. Nishina and Y. Yamamoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 3314.
61 A. M. Manzo, A. D. Perboni, G. Broggini and M. Rigamonti, *Tetrahedron Lett.*, 2009, **50**, 4696.
62 H. F. Yuen and T. J. Marks, *Organometallics*, 2009, **28**, 2423.
63 B. D. Stubbert and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 4253.
64 V. M. Arredondo, S. Tian, F. E. McDonald and T. J. Marks, *J. Am. Chem. Soc.*, 1999, **121**, 3633.
65 V. M. Arredondo, F. E. McDonald and T. J. Marks, *Organometallics*, 1999, **18**, 1949.
66 V. M. Arredondo, F. E. McDonald and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 4871.
67 J. R. Petersen, J. M. Hoover, W. S. Kassel, A. L. Rheingold and A. R. Johnson, *Inorg. Chim. Acta*, 2005, **358**, 687.
68 J. M. Hoover, J. R. Petersen, J. H. Pikul and A. R. Johnson, *Organometallics*, 2004, **23**, 4614.
69 L. Ackermann, R. G. Bergman and R. N. Loy, *J. Am. Chem. Soc.*, 2003, **125**, 11956.
70 L. Ackermann and R. G. Bergman, *Org. Lett.*, 2002, **4**, 1475.
71 J. S. Johnson and R. G. Bergman, *J. Am. Chem. Soc.*, 2001, **123**, 2923.
72 P. J. Walsh, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 1708.
73 L. L. Anderson, J. Arnold and R. G. Bergman, *Org. Lett.*, 2004, **6**, 2519.
74 R. O. Ayinla and L. L. Schafer, *Inorg. Chim. Acta*, 2006, **359**, 3097.
75 J. A. Bexrud and L. L. Schafer, *Dalton Trans.*, 2010, **39**, 361.
76 L. J. E. Stanlake and L. L. Schafer, *Organometallics*, 2009, **28**, 3990.
77 D. C. Leitch, P. R. Payne, C. R. Dunbar and L. L. Schafer, *J. Am. Chem. Soc.*, 2009, **131**, 18246.
78 D. C. Leitch, J. D. Beard, R. K. Thomson, V. A. Wright, B. O. Patrick and L. L. Schafer, *Eur. J. Inorg. Chem.*, 2009, 2691.
79 P. Eisenberger, R. O. Ayinla, J. M. P. Lauzon and L. L. Schafer, *Angew. Chem., Int. Ed.*, 2009, **48**, 8361.
80 J. A. Bexrud, P. Eisenberger, D. C. Leitch, P. R. Payne and L. L. Schafer, *J. Am. Chem. Soc.*, 2009, **131**, 2116.
81 L. J. E. Stanlake, J. D. Beard and L. L. Schafer, *Inorg. Chem.*, 2008, **47**, 8062.
82 Z. Zhang, D. C. Leitch, M. Lu, B. O. Patrick and L. L. Schafer, *Chem.–Eur. J.*, 2007, **13**, 2012.
83 M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak and L. L. Schafer, *Angew. Chem., Int. Ed.*, 2007, **46**, 354.
84 A. V. Lee and L. L. Schafer, *Eur. J. Inorg. Chem.*, 2007, 2243.
85 J. A. Bexrud, C. Li and L. L. Schafer, *Organometallics*, 2007, **26**, 6366.

86 R. K. Thomson, J. A. Bexrud and L. L. Schafer, *Organometallics*, 2006, **25**, 4069.
87 R. K. Thomson, F. E. Zahariev, Z. Zhang, B. O. Patrick, Y. A. Wang and L. L. Schafer, *Inorg. Chem.*, 2005, **44**, 8680.
88 R. K. Thomson, B. O. Patrick and L. L. Schafer, *Can. J. Chem.*, 2005, **83**, 1037.
89 C. Li, R. K. Thomson, B. Gillon, B. O. Patrick and L. L. Schafer, *Chem. Commun.*, 2003, 2462.
90 Z. Zhang and L. L. Schafer, *Org. Lett.*, 2003, **5**, 4733.
91 G. Zi, X. Liu, L. Xiang and H. Song, *Organometallics*, 2009, **28**, 1127.
92 A. L. Gott, A. J. Clarke, G. J. Clarkson and P. Scott, *Organometallics*, 2007, **26**, 1729.
93 G. R. Giesbrecht, A. Shafir and J. Arnold, *Inorg. Chem.*, 2001, **40**, 6069.
94 H. Makio, H. Terao, A. Iwashita and T. Fujita, *Chem. Rev.*, 2011, ASAP.
95 Y. Suzuki, H. Terao and T. Fujita, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1493.
96 H. Makio and T. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1532.
97 G. W. Coates, *J. Chem. Soc., Dalton Trans.*, 2002, 467.
98 D. Zaher, A. K. Tomov, V. C. Gibson and A. J. P. White, *J. Organomet. Chem.*, 2008, **693**, 3889.
99 K. V. Zaitsev, M. V. Bermeshev, S. S. Karlov, Y. F. Oprunenko, A. V. Churakov, J. A. K. Howard and G. S. Zaitseva, *Inorg. Chim. Acta*, 2007, **360**, 2507.
100 K. Vijayakrishna and G. Sundararajan, *Polymer*, 2006, **47**, 3363.
101 R. M. Porter, A. A. Danopoulos and G. Reid, *Inorg. Chem.*, 2006, **45**, 6516.
102 R. M. Porter and A. A. Danopoulos, *Polyhedron*, 2006, **25**, 859.
103 C. Wang, G. Erker, G. Kehr, K. Wedeking and R. Frohlich, *Organometallics*, 2005, **24**, 4760.
104 R. M. Porter, A. A. Danopoulos, G. Reid and L. R. Titcomb, *Dalton Trans.*, 2005, 427.
105 R. S. Ghadwal, R. C. Mehrotra and A. Singh, *J. Chem. Res.*, 2005, 352.
106 J. Chen, Z.-J. Zheng, L. Pan, D. Pan and Y.-S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1562.
107 S. A. Blum, V. A. Rivera, R. T. Ruck, F. E. Michael and R. G. Bergman, *Organometallics*, 2005, **24**, 1647.
108 S. A. Blum, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 2003, **125**, 14276.
109 P. N. O'Shaughnessy, K. M. Gillespie, C. Morton, I. Westmoreland and P. Scott, *Organometallics*, 2002, **21**, 4496.
110 P. E. O'Connor, D. J. Berg and T. Barclay, *Organometallics*, 2002, **21**, 3947.
111 B. Rhodes, J. C. W. Chien, J. S. Wood, A. Chandrasekaran and M. D. Rausch, *J. Organomet. Chem.*, 2001, **625**, 95.
112 P. E. O'Connor, D. J. Morrison, S. Steeves, K. Burrage and D. J. Berg, *Organometallics*, 2001, **20**, 1153.
113 L.-C. Liang, R. R. Schrock and W. M. Davis, *Organometallics*, 2000, **19**, 2526.
114 R. R. Schrock, R. Baumann, S. M. Reid, J. T. Goodman, R. Stumpt and W. M. Davis, *Organometallics*, 1999, **18**, 3649.
115 M. A. Flores, M. R. Manzoni, R. Baumann, W. M. Davis and R. R. Schrock, *Organometallics*, 1999, **18**, 3220.
116 R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang and R. R. Schrock, *J. Am. Chem. Soc.*, 1999, **121**, 7822.
117 R. R. Schrock, F. Schattenmann, M. Aizenberg and W. M. Davis, *Chem. Commun.*, 1998, 199.
118 R. Baumann and R. R. Schrock, *J. Organomet. Chem.*, 1998, **557**, 69.
119 F. Amor, A. Butt, K. E. du Plooy, T. P. Spaniol and J. Okuda, *Organometallics*, 1998, **17**, 5836.
120 M. Aizenberg, L. Turculet, W. M. Davis, F. Schattenmann and R. R. Schrock, *Organometallics*, 1998, **17**, 4795.
121 L. Lee, D. J. Berg and G. W. Bushnell, *Organometallics*, 1997, **16**, 2556.
122 R. Baumann, W. M. Davis and R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 3830.
123 A. G. Vaughan, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 7994.
124 F. Pohlki and S. Doye, *Chem. Soc. Rev.*, 2003, **32**, 104.
125 F. J. Weiberth and S. S. Hall, *J. Org. Chem.*, 1985, **50**, 5308.
126 H. H. A. M. Hassan, *Curr. Org. Synth.*, 2007, **4**, 413.
127 S. Borresen and J. K. Crandall, *J. Org. Chem.*, 1976, **41**, 678.
128 R. K. Thomson, Ph.D. Dissertation, University of British Columbia, 2008.
129 W. J. Evans, M. A. Ansari and J. W. Ziller, *Inorg. Chem.*, 1999, **38**, 1160.
130 A. A. H. Van der Zeijden and C. Mattheis, *Organometallics*, 1997, **16**, 2651.
131 A. Caselli, L. Giannini, E. Solari and C. Floriani, *Organometallics*, 1997, **16**, 5457.
132 A. A. H. van der Zeijden, C. Mattheis, R. Frohlich and F. Zippel, *Inorg. Chem.*, 1997, **36**, 4444.
133 B. D. Santarsiero and E. J. Moore, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 433.
134 L. Brandsma and A. D. Verkruijsse, *Synthesis of Acetylenes, Allenes and Cummulenes*, Elsevier, New York, 1981.
135 P. Crabbe, H. Fillion, D. Andre and J.-L. Luche, *J. Chem. Soc., Chem. Commun.*, 1979, 859.
136 S. Hong, S. Tian, M. V. Metz and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 14768.
137 A. Heutling, F. Pohlki and S. Doye, *Chem.–Eur. J.*, 2004, **10**, 3059.
138 R. Dorta, D. Broggini, R. Kissner and A. Togni, *Chem.–Eur. J.*, 2004, **10**, 4546.
139 C. Mueller, C. Loos, N. Schulenberg and S. Doye, *Eur. J. Org. Chem.*, 2006, 2499.

