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N,O-Chelates of Group 4 Metals: Contrasting the Use of Amidates and Ureates in the Synthesis of Metal Dichlorides

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A series of dichloride complexes of titanium and zirconium with amidate and ureate ancillary ligands have been prepared. Three examples of bis(amidate)dichlorotitanium and zirconium complexes were effectively synthesized through salt metathesis with metal tetrachloride as starting materials. Optimum results were achieved using sodium amidate salts formed from sodium bis(trimethylsilyl)amide and neutral amide proligands, while other methods were ineffective. Use of electron-donating ureate ligands in lieu of amidates enables preparation through alternate routes. Protonolysis of $Ti(NMe_2)_2Cl_2$ and $Zr(NMe_2)_2Cl_2(dme)$ with urea proligands leads to dichlorobis(ureate) complexes in good yield. Using a tethered bis(ureate) ligand eliminates the fluxional behaviour and coordination isomerism observed for both bis(amidate) and bis(ureate) zirconium complexes.

Introduction

The use of easily prepared classes of organic compounds as ancillary ligands is a key facet of organometallic and coordination chemistry. Since the 1950s, cyclopentadienyl (Cp) ligands and related derivatives have dominated the field, with countless examples of complexes reported from across the periodic table.[1,2] Such Cp-based ligands are, however, not easily modified. This limitation has led to the use of new ligand sets, which are based on alternative donor motifs, in the past few decades.[3–5] One strategy is to adopt a modular approach to ligand design, combining ease of synthesis with a readily modified ligand architecture. Such steric and electronic tuning of the environment surrounding the metal centre can enable variable reactivity.[3]

Two particular sets of non-Cp-based ligands that have received wide attention are amidinates[4] and guanidinates.[5] These ligand sets are used extensively to form group 4 complexes, some of which exhibit remarkable reactivity.[6–13] In many cases, group 4 chloride complexes with amidinate or guanidinate ancillary ligands are used as precatalysts, particularly for olefin polymerization,[8c,8e,9,14b] and starting materials to access a wide range of compounds, including alkyl,[7b,7c,7e,8d,8e,8h,8j,10b,11a,11b,12a] imido,[12c–12e] low valent,[7b] and dinitrogen complexes.[7b,7d,8i]

Related amidate ligands have recently been exploited in constructing group 3 and 4 based metal complexes and catalytic systems.[14–16] Given the ease and efficiency with which amide proligands can be prepared, this class of ligands is an attractive motif for investigation. Over the past five years, our group has shown that titanium and zirconium bis(amidate) bis(amido) complexes are efficient catalysts for the hydroamination of alkynes,[16a,16b,16g,16k,16m] allenes[16e] and alkenes,[16f,16i,16j] and the α-alkylation of amines (hydroaminoalkylation).[16n] We have also shown that amidates are an effective support for group 4 imido[16f,16k] alkyl,[16d] and metallaaziridine[16n] complexes. However, fully characterized bis(amidate) dichlorides have remained elusive, with only one partially characterized example reported.[15] Such compounds are potentially versatile starting materials for the synthesis of a wide variety of amidate-supported complexes. During the course of our investigations on amidate ligands, we have discovered that such bis(amidate) dichlorides are difficult to access, prone to fluxional behaviour in solution, and challenging to characterize. These observations may rationalize the marked paucity of such compounds in organometallic literature.

Bis(amidate) dichloride complexes are anticipated to be very electron-deficient. In an effort to explore electronic effects upon complex stability, we also chose to investigate ureate ligands in the synthesis of group 4 dichloride complexes. Ureates, which are readily accessed through the use of urea proligands, contain an electron-donating amino group on the chelate backbone (Figure 1), analogous to that of guanidinates. There are sparse examples of group 4 ureate complexes prepared by isocyanate insertion into

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metal amide bonds.[17] Here, we install ureates as easily modifiable ancillary ligands using simple protonolysis reactions.

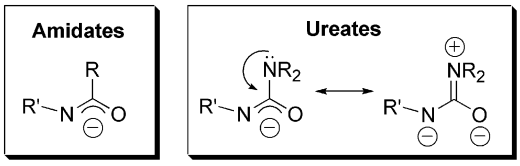


Figure 1. Comparison of electron-donating properties of amidate and ureate ligands.

This report describes the preparation of amidate and ureate dichloride complexes by several routes, including salt metathesis, reaction of $L_2M(NMe_2)_2$ complexes with chlorotrimethylsilane, and protonolysis of $M(NMe_2)_2Cl_2$ precursors. Importantly, the use of a tethered bis(ureate) ligand system, which eliminates solution-phase geometric isomerization, results in well-defined dichloride complexes of both titanium and zirconium which can be prepared reliably and in high yield.

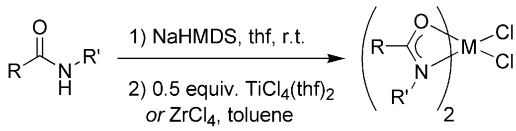
Results and Discussion

Synthesis of Amidate-Supported Dichloride Complexes

The only literature example to date of a group 4 bis(amidate) dichloride complex, reported by Arnold and coworkers in 2001, was prepared through several routes, one of which was the reaction of the dilithium salt of a bridged diamide with $TiCl_4(thf)_2$.[15] ^1H NMR spectroscopy revealed the formation of the dichloride complex; however, satisfactory elemental analysis could not be obtained. Following this result, preliminary work in our research group on traditional salt metathesis preparations of group 4 amidate complexes employed *n*-butyllithium as a base to form lithium amidates in situ, which were subsequently reacted with metal tetrachloride as the starting materials. These reactions invariably led to product mixtures which resisted attempts at purification and identification. Our hypothesis is that the lithium chloride produced in these reactions remains coordinated, resulting in ill-defined "ate" complexes.

A screen of a variety of strong bases was undertaken to identify a general route to amidate salts that exhibited the desired reactivity. These experiments revealed that sodium amidates, generated by the reaction of amides with sodium bis(trimethylsilyl)amide (NaHMDS), react with titanium and zirconium tetrachlorides to give bis(amidate) dichloride complexes in good yield without incorporation of sodium chloride [Equation (1)]. The use of a bulky base in this reaction appears to be important, as NaH was ineffective in these reactions.

The sodium amidate salts were generated by reacting the amide proligand with NaHMDS in thf at room temperature. After removal of the volatiles in vacuo, the crude amidate salts were used directly without further purification. The subsequent salt metathesis reactions were performed by adding half an equivalent of $TiCl_4(thf)_2$ or $ZrCl_4$ to the



(1)

reaction vessel containing the crude amidate salt, followed by the addition of toluene. After stirring overnight, the solutions were filtered and concentrated slowly under vacuum at 70 °C. Subsequent cooling to room temperature resulted in crystallization over the course of several days (yield: 68–76%). Three examples of group 4 bis(amidate) dichloride complexes have been prepared using this protocol (Figure 2).

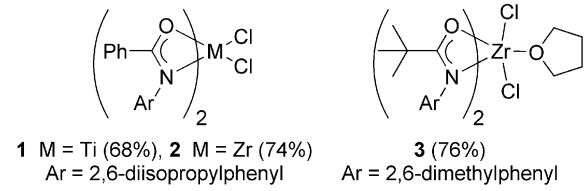


Figure 2. Amidate-supported group 4 dichlorides prepared by salt metathesis.

Titanium complex **1** was prepared in 68% yield as deep red rectangular crystals using *N*-(2′,6′-diisopropylphenyl)-benzamide as a proligand. The ^1H NMR spectrum of **1** reveals two distinct resonances for the methyl protons of the isopropyl groups on the *N*-aryl ring of the ligand (doublets at δ = 1.02 and 1.12 ppm); moreover, the methine protons of the isopropyl groups produce a broad resonance. In contrast, the aromatic protons on the phenyl group at-

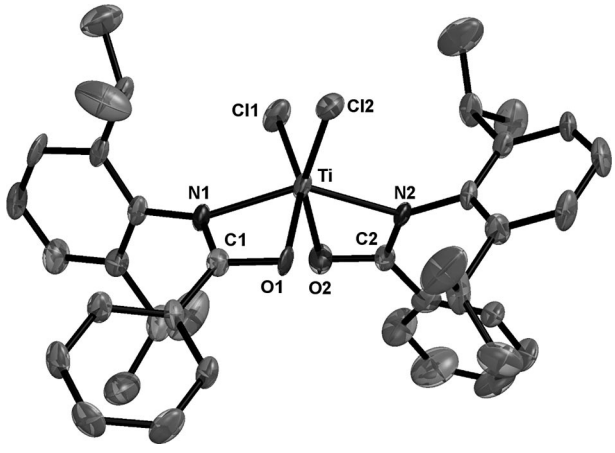


Figure 3. ORTEP representation of one of the independent molecules of **1** (ellipsoids plotted at 50% probability, toluene molecule and hydrogen atoms omitted for clarity) with selected bond lengths [Å] and angles [°] averaged between the two molecules: Ti–N1, 2.074(5); Ti–O1, 2.038(4); Ti–N2, 2.062(4); Ti–O2, 2.036(5); Ti–Cl1, 2.246(2); Ti–Cl2, 2.235(2); C1–N1, 1.315(8); C1–O1, 1.306(7); C2–N2, 1.314(8); C2–O2, 1.308(7); N1–Ti–O1, 63.9(2); N2–Ti–O2, 63.9(2); Cl1–Ti–Cl2, 98.81(8); N1–C1–O1, 112.4(6); N2–C2–O2, 111.4(5).

tached to the carbonyl give well resolved signals. These observations suggest that the two ligands are equivalent, with hindered rotation around the N–C_{aryl} bond responsible for the two isopropyl signals. This is consistent with the solution phase behaviour of the corresponding bis(amidate) bis(amido) complex reported previously.[16b]

A single crystal of **1** was subjected to X-ray crystallographic analysis. The asymmetric unit consists of two independent molecules of **1**, as well as one molecule of toluene from the recrystallization solvent. One of these molecules is depicted in Figure 3. Crystallographic data for all X-ray structure determinations is summarized in Table 1.

Table 1. Crystallographic data for **1**, **3**·[DMP(NH,O)*t*Bu], **7**, **8**·thf, **10**, and **11**.

	1	**3**·[DMP(NH,O)*t*Bu]	**7**
Formula	$C_{83}H_{96}Cl_4N_4O_4Ti_2$	$C_{39}H_{55}Cl_2N_3O_3Zr$	$C_{30}H_{42}Cl_2N_4O_2Ti$
F_w	1451.24	775.98	609.48
Crystal size [mm]	0.20 × 0.20 × 0.15	0.15 × 0.10 × 0.05	0.25 × 0.15 × 0.10
Colour, habit	red, block	colourless, prism	yellow, plate
Cell setting	orthorhombic	triclinic	monoclinic
Space group	*Pbn*21	$P\bar{1}$	*C*2/*c*
a [Å]	10.3501(7)	13.230(1)	24.072(6)
b [Å]	24.9023(20)	13.620(1)	12.611(3)
c [Å]	31.0070(26)	14.080(1)	17.219(4)
α [°]	90	108.574(3)	90
β [°]	90	94.061(2)	130.581(8)
γ [°]	90	118.708(2)	90
V [Å^3]	7991.8(3)	2031.5(3)	3970.0(16)
Z	4	2	4
$\rho_{calcd.}$ [g cm^{-1}]	1.206	1.269	1.020
Radiation		Mo-K_α (λ = 0.71073 Å)	
F(000)	3064	816	1288
μ (Mo-K_α) [cm^{-1}]	3.83	4.40	3.76
$2\theta_{max}$ [°]	50.10	45.2	45.08
Total number of reflections	97762	24588	4849
Number of unique reflections	14115 (R_{int} = 0.0535)	5203 (R_{int} = 0.046)	2583 (R_{int} = 0.1305)
Number of reflections with $I = 2\sigma(I)$	12224	4092	1466
Number of variables	874	468	183
R_1 (F^2, all data)	0.080	0.075	0.1608
wR_2 (F^2, all data)	0.199	0.137	0.2496
R_1 [F, $I = 2\sigma(I)$]	0.069	0.054	0.0969
Goodness of fit	1.127	1.04	1.052
	8·thf	**10**	**11**
Formula	$C_{42.5}H_{67}Cl_2N_4O_3Zr$	$C_{27}H_{51}N_5O_2Ti$	$C_{21}H_{45}N_5O_2Zr$
F_w	844.12	596.53	561.74
Crystal size [mm]	0.25 × 0.10 × 0.10	0.80 × 0.50 × 0.20	0.35 × 0.15 × 0.10
Colour, habit	colourless, chip	yellow, prism	colourless, prism
Cell setting	triclinic	triclinic	orthorhombic
Space group	*P* –1	$P\bar{1}$	*C* m c 21
a [Å]	10.532(2)	10.7519(6)	15.9460(8)
b [Å]	12.162(3)	12.4824(7)	12.4515(6)
c [Å]	17.907(4)	12.6443(7)	13.9449(6)
α [°]	81.666(10)	89.296(2)	90
β [°]	76.329(10)	79.739(2)	90
γ [°]	82.263(10)	73.967(2)	90
V [Å^3]	2193.3(9)	1603.67(15)	2768.8(2)
Z	2	2	4
$\rho_{calcd.}$ [g cm^{-1}]	1.278	1.235	1.348
Radiation		Mo-K_α (λ = 0.71073 Å)	
F(000)	896	640	1184
μ (Mo-K_α) [cm^{-1}]	4.13	4.64	6.15
$2\theta_{max}$ [°]	56.04	66.50	65.54
Total no. of reflections	30543	36303	8184
Number of unique reflections	10267 (R_{int} = 0.0339)	9995 (R_{int} = 0.0255)	3987 (R_{int} = 0.0157)
Number of reflections with $I = 2\sigma(I)$	7861	8592	3904
Number of variables	528	350	161
R_1 (F^2, all data)	0.0634	0.0396	0.0196
wR_2 (F^2, all data)	0.1025	0.0858	0.0485
R_1 [F, $I = 2\sigma(I)$]	0.0389	0.0396	0.0189
Goodness of fit	1.053	1.034	1.095

The two amidate ligands are arranged in a *cis* fashion in a distorted octahedral geometry, giving the complex pseudo-C_2 symmetry. The minor differences in the bond lengths and angles between the two ligands, and the two molecules, are likely due to crystal packing. The Ti–O1 bond [2.038(4) Å] is only slightly shorter than the Ti–N1 bond [2.074(5) Å]; in addition, the C1–O1 [1.306(7) Å] and C1–N1 [1.315(8) Å] bonds of the amidate backbone are similar, suggestive of significant electron delocalization. The Ti–Cl bond lengths (2.246(2) Å and 2.235(2)) are typical for related amidinate complexes.[12a]

Comparison of these metrical parameters with the corresponding titanium bis(amidate) bis(amido) complex[16b] reveals a tighter complexation in the case of the dichloride. While the C–N and C–O bond lengths are similar in both complexes, the dichloride has shorter Ti–O [2.038(4) Å vs. 2.146(1) Å], and Ti–N [2.074(5) Å vs. 2.156(1) Å] bonds. These shorter bonds can be attributed to the more electropositive titanium center of **1** (formal electron count: 12 e^-), due to poorer electron-donation by the chloro ligands relative to that of amidos. Sterics may also play a role in this disparity, as the smaller chloro ligands may enable a tighter complexation of the amidates than the dimethylamido moieties.

Salt metathesis using sodium amidate salts is also effective in the synthesis of zirconium dichloride complexes. Zirconium complex **2**, possessing the same ancillary ligand as **1**, was prepared as above in 74% yield. NMR spectra of this complex are markedly different than for **1**. The ^{1}H NMR spectrum contains four sharp doublets corresponding to the methyl protons of the isopropyl groups at δ = 0.89, 1.02, 1.36, and 1.56 ppm, and two sharp septets corresponding to the methine protons at δ = 4.05 and 4.27 ppm. Furthermore, broad signals at δ = 1.26 and 4.43 ppm are indicative of one equivalent of bound thf. This spectroscopic evidence suggests a C_1 coordination geometry in which the two amidate ligands bind with the nitrogen of one amidate *cis* to the oxygen of the other. With one thf ligand also bound, a seven-coordinate species would result (**2**·thf). The ^{13}C NMR spectrum is also consistent with this assignment, as it indicates two inequivalent ligand environments. X-ray diffraction was not performed on this compound; however, based on solid-state molecular structures of complexes **3**·[DMP(NH,O)*t*Bu] (Figure 6) (DMP = 2,6-dimethylphenyl) and **8**·thf (Figure 8, vide infra), the proposed structure of **2**·thf is shown in Figure 4.

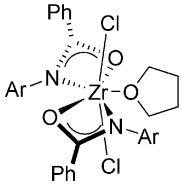


Figure 4. Proposed structure of **2**·thf (Ar = 2,6-diisopropylphenyl).

Zirconium dichloride complex **3**, prepared from *N*-(2,6-dimethylphenyl)pivalamide as a proligand, was synthesized in 76% yield using the same protocol as for **1** and **2**. This compound exists as two distinct isomers in solution, denoted **3a** and **3b**, as evidenced by ^{1}H NMR spectroscopy. Integration of diagnostic signals gives a ratio of **3a** to **3b** of 3:1. Three singlets are observed between δ = 0.86 and 1.13 ppm corresponding to the methyl protons of the *tert*-butyl groups: two resonances, at δ = 0.86 and 1.13 ppm, belonging to **3a** and one at δ = 1.02 to **3b**. The same pattern is observed for the methyl groups from the 2,6-dimethylphenyl substituent: signals at δ = 2.53 and 2.75 ppm corresponding to **3a** and one at δ = 2.40 to **3b**. Broad resonances at δ = 1.06, 1.35, 4.43 and 4.64 are indicative of bound thf on both **3a** and **3b**. Based on this spectroscopic evidence, **3a** likely corresponds to a C_1-symmetric coordination isomer, as proposed for **2**. Isomer **3b**, on the other hand, has the ligands as equivalent, with either an *N-trans* and/or an *O-trans* configuration (Figure 5).

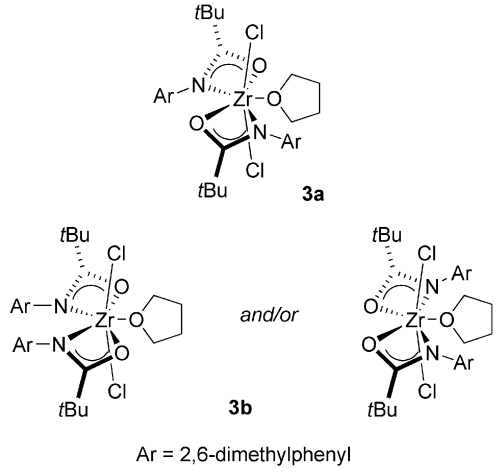


Figure 5. Proposed structures of **3a** and **3b** based on ^{1}H NMR spectroscopy.

Heating the sample causes the spectrum to simplify, and increases the ratio of **3a** to **3b** considerably; at 378 K, only **3a** is observed. In addition, the independent signals for the aryl methyl groups of **3a** coalesce into one broad signal at this temperature. Cooling the sample to room temperature following heating returns the spectrum to its original form. These results suggest a rapid dynamic equilibrium between **3a** and **3b**, which shifts in favor of **3a** at higher temperature. However, a van't Hoff plot generated from the K_{eq} values determined for this process between 318 K and 358 K is non-linear over this temperature range (see Supporting Information). This suggests that this is not a simple equilibrium; there may be more species involved than **3a** and **3b** which cannot be observed by ^{1}H NMR spectroscopy.

Attempts to remove the thf ligand from **3** under vacuum to give an anticipated six-coordinate complex were unsuccessful. An NMR-scale experiment did reveal that the thf can be replaced by triphenylphosphane oxide; however, there still appeared to be two isomers in solution. X-ray diffraction on a crystal grown from a hexanes solution of **3** did not yield the expected structure. Instead, the structure corresponded to a byproduct, **3**·[DMP(NH,O)*t*Bu], con-

taining a neutral amide as a donor in place of the thf. This neutral amide likely results from the presence of adventitious water. The complex is pentagonal bipyramidal, with the chloride ligands occupying the apical positions while the donor atoms of the two monoanionic amidate ligands, oriented in the same fashion as that proposed for **3a**, and one neutral amide occupy the equatorial plane. The molecule is disordered between two different orientations, one of which is shown in Figure 6. The overall coordination geometry is analogous to that proposed for the structures of **2**·thf and **3a**.

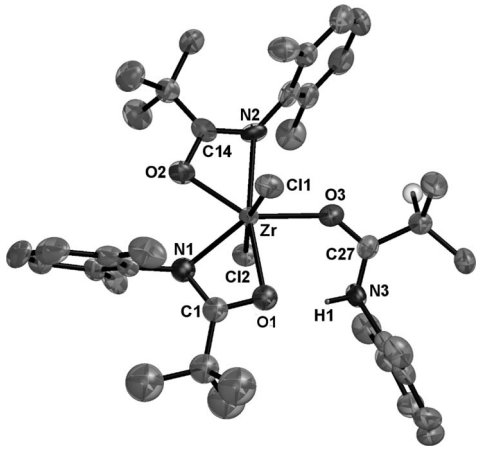


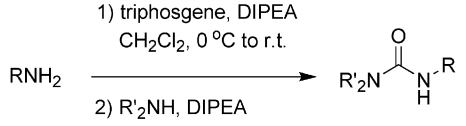
Figure 6. ORTEP representation of the primary orientation of **3**·[DMP(NH,O)*t*Bu] (ellipsoids plotted at 50% probability, hydrogen atoms except H1 omitted for clarity, H1 refined from unassigned electron density, see Supporting Information for second orientation) with selected bond lengths [Å] and angles [°] for pictured orientation: Zr–N1, 2.272(4); Zr–O1, 2.202(4); Zr–N2, 2.319(4); Zr–O2, 2.093(4); Zr–O3, 2.168(4); Zr–Cl1, 2.436(2); Zr–Cl2, 2.470(2); C1–N1, 1.302(8); C1–O1, 1.307(6); C14–N2, 1.298(7); C14–O2, 1.324(6); C27–N3, 1.294(7); C27–O3, 1.290(6); N1–Zr–O1, 58.35(17); N2–Zr–O2, 58.8(2); Cl1–Zr–O3, 87.7(1); Cl1–Ti–Cl2, 168.23(6); N1–C1–O1, 113.5(5); N2–C14–O2, 112.2(5); N3–C27–O3, 117.3(5).

These results show that salt metathesis using sodium amidates can be used to synthesize bis(amidate) dichlorides of group 4 metals; however, the success of this method has been observed to be ligand dependant. In some other cases, sodium amidates gave uncharacterizable mixtures of products. Notably, the incorporation of sterically bulky substituents is a prerequisite for discrete complex formation and characterization. Other common routes, including reaction of bis(amidate) bis(amido) compounds with excess chlorotrimethylsilane and protonolysis reactions using $M(NR_2)_2Cl_2$ starting materials do not yield the desired compounds, commonly giving mixed chloro/amido species. If the difficulties encountered in these preparations are due to the electron-deficient nature of the resulting bis(amidate) dichlorides, moving to a more electron-rich version of the amidate ligand should alleviate this problem. In order to test this hypothesis, we have used ureates as alternate ancillary ligands for group 4 metals.

Urea Proligand Design and Synthesis

In keeping with our previous work on group 4 amidates,[16] we sought to apply the same modular approach to the preparation of ureate complexes. Previous syntheses of group 4 ureates have involved the insertion of an isocyanate into a metal–amido bond.[17a] Lappert and co-workers were the first to prepare bis(amido) bis(ureate) complexes of the group 4 metals by this route using phenylisocyanate in 1970; however, no molecular structures or reactivity were reported.[17b] Recently, Xie and co-workers[17c] and Huang and co-workers[17d] have synthesized zirconium and hafnium ureates as insertion products using indenyl-carboranyl and substituted pyrrolyl-supporting ligands, respectively.

Using these methods to synthesize a wide variety of group 4 ureate complexes has significant limitations. Due to the fact that the final ligand structure is dependant on the identity of the amido ligand that undergoes insertion, preparation of functionally varied ligands would require the synthesis of exotic metal-amido precursors. Moreover, many organic isocyanates can be difficult to work with. Organic ureas, on the other hand, are efficiently prepared via a one-pot procedure[18] and can act as proligands for the synthesis of ureate complexes. Reaction of a primary amine with triphosgene in the presence of a sterically demanding tertiary amine base generates an intermediate isocyanate in situ. This isocyanate is then reacted directly with the secondary amine which will become the backbone substituent to give an *N*,*N*′,*N*′-trisubstituted urea in excellent yield (Scheme 1). The products are crystalline and are easily handled. Purification can be achieved by flash chromatography, recrystallization, or vacuum sublimation as required. Proligands **4** and **5** were chosen to mimic the steric bulk of the amidate ligands used in this investigation.



4: R = 2,6-dimethylphenyl, R' = *i*Pr 90%
5: R = 2,6-diisopropylphenyl, $R'_2 = -(CH_2)_5-$ 99%

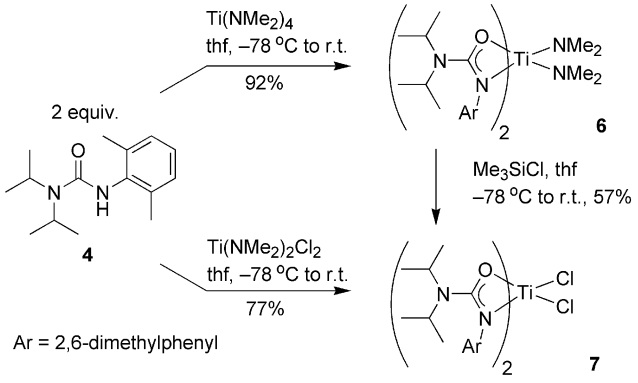
Scheme 1. Synthesis of urea proligands **4**,**5**.

Synthesis of Bis(ureate) Supported Dichloride Complexes

With a more electron-rich analogue of the amide proligand in hand, various synthetic routes to metal dichlorides were investigated. Because salt metathesis reactions form salt byproducts which can be laborious to remove, we sought a synthetic protocol which gives easily removed byproducts. In particular, aforementioned protonolysis routes using precursors of the type $M(NR_2)_2Cl_2$ seemed attractive. While $Ti(NMe_2)_2Cl_2$ was prepared according to a published procedure,[20] $Zr(NMe_2)_2Cl_2(dme)$ was synthesized through a conproportionation reaction between $Zr(NMe_2)_4$ and

$ZrCl_4(thf)_2$ in the presence of an excess of 1,2-dimethoxyethane in toluene, giving the product in 86% yield.

The synthesis of L_2TiCl_2 complex **7** using urea proligand **4** was accomplished in two ways: directly, involving protonolysis of **4** using $Ti(NMe_2)_2Cl_2$ in thf, and through the reaction of intermediate bis(amido) complex **6** and excess chlorotrimethylsilane (Scheme 2). Both routes are feasible, with the direct protonolysis method giving a higher overall yield (77% vs. 52%). ^{1}H NMR spectroscopy of the resulting dichloride complex **7** indicates that the two isopropyl groups on the backbone nitrogen are inequivalent, as two distinct resonances for the methyl protons are observed at δ = 0.54 and 1.38 ppm. This is in contrast to the corresponding signals for the bis(dimethylamido) complex **6**, which appear as a very broad peak between δ = 0.6 and 1.7. In addition, the methine protons of the isopropyl groups in **6** are broadened almost into the baseline between approximately δ = 3.5 and 3.7 ppm, while two distinct signals at δ = 2.90 and 3.59 ppm are observed in the case of dichloride **7**. These observations are consistent with a more restricted C–N bond rotation in **7**. This is likely due to a greater degree of electron donation from the backbone nitrogen in the dichloride complex **7** relative to the bis(amido) **6**, resulting in appreciable double bond character. This hindered rotation must be an electronic effect, since the isopropyl groups in both **6** and **7** are distal to the metal center. Furthermore, **7** is less sterically crowded overall than **6**.



Scheme 2. Synthesis of **7**.

Compound **7** was recrystallized from a hot toluene solution to give crystals for X-ray crystallography. The solid-state molecular structure is shown in Figure 7. Complex **7** exhibits distorted octahedral geometry and is rigorously C_2-symmetric, with the two chloride ligands oriented *cis* to one another. Evidence of electron donation from the backbone nitrogen is apparent, consistent with aforementioned spectroscopic evidence. The sum of the bond angles about N2 is 360(2)°, the C1–N1 and C1–N2 bond lengths are similar [1.35(1) Å vs. 1.37(2) Å], and there is a high degree of coplanarity between the chelate ring and the trigonal plane about N2 [torsion angle 7(1)°]. Guanidinate ligands exhibit similar behaviour when bound to electropositive early transition metals.[5,7e]

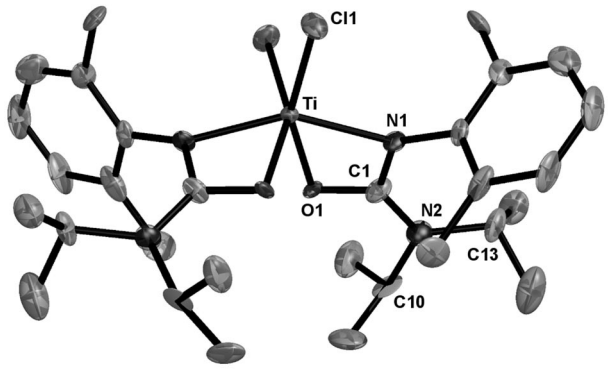
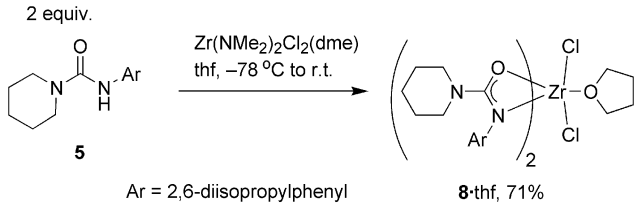


Figure 7. ORTEP representation of the molecular structure of **7** (ellipsoids plotted at 50% probability, disordered toluene molecule removed with SQUEEZE,[23] hydrogen atoms omitted for clarity) with selected bond lengths [Å], bond and torsion angles [°]: Ti–N1, 2.044(9); Ti–O1, 2.006(7); Ti–Cl1, 2.271(3); C1–N1, 1.35(1); C1–O1, 1.30(1); C1–N2, 1.37(2); N1–Ti–O1, 64.8(3); N1–Ti–N1*, 151.4(4); sum of angles about N2, 360(2); N1–C1–N2–C13, 7(1).

Formation of a dichlorobis(ureate)zirconium complex using proligand **5** and $Zr(NMe_2)_2Cl_2(dme)$ in thf gave adduct **8**·thf [Equation (2)]. The ^{1}H NMR spectrum of **8**·thf reveals a high degree of fluxional behaviour in solution, likely due to exchange of the labile thf ligand and conversion between geometric isomers. At higher temperature (345 K), the spectrum simplifies considerably and is consistent with a C_2-symmetric isomer.



(2)

Crystals for X-ray diffraction were obtained from pentane solutions of **8**·thf at –35 °C; the solid state molecular structure is shown in Figure 8. The geometry is distorted pentagonal bipyramidal, with the ureate ligands and the thf molecule in the equatorial positions. The chloride ligands occupy the apical sites and are slightly canted toward the thf ligand, with a Cl1–Zr–Cl2 angle of 165.24(2)°. The ureate ligands are arranged to give a molecule with C_1 symmetry, analogous to the geometry of **3**·[DMP(NH,O)*t*Bu]. As in complex **7**, there is evidence of electron delocalization between the tertiary amino substituent and the chelate ring [C1–N1 1.316(3) Å vs. C1–N2 1.337(3) Å, sum of angles about N2 is 357.6(6)°, torsion angle between O1–C1–N2–C2 is 8.8(3)°].

Subjecting **8**·thf to high vacuum for 48 h resulted in removal of the thf ligand to give **8**. The ^{1}H NMR spectrum of this compound is consistent with C_1 symmetry. Unfortunately, **8** is a poorly soluble microcrystalline solid; attempts to obtain single crystals of this compound for X-ray diffraction have failed.

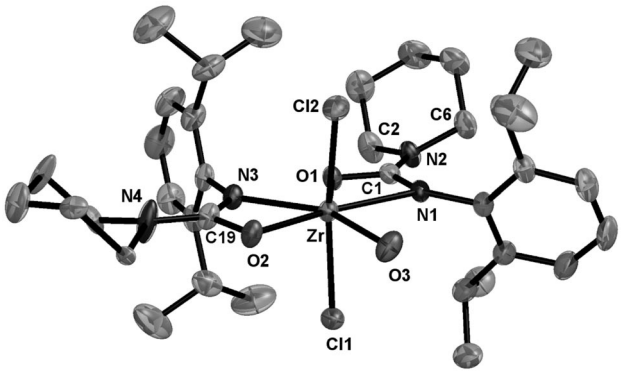
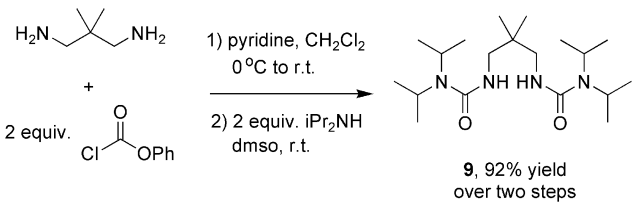


Figure 8. ORTEP representation of the molecular structure of **8**·thf (ellipsoids plotted at 50% probability, carbons of the thf ring, disordered pentane, and hydrogen atoms omitted for clarity, one conformation of the N4 piperidine ring shown) with selected bond lengths [Å], bond and torsion angles [°]: Zr–N1, 2.285(2); Zr–O1, 2.092(2); Zr–Cl1, 2.437(1); Zr–O3, 2.297(2); C1–N1, 1.316(3); C1–O1, 1.300(3); C1–N2, 1.337(3); N1–Zr–O1, 59.63(6); Cl1–Zr–Cl2, 165.24(2); sum of angles about N2, 357.6(6); O1–C1–N2–C2, 8.8(3).

A Tethered Bis(Ureate) Ligand for Dichloride Complexes

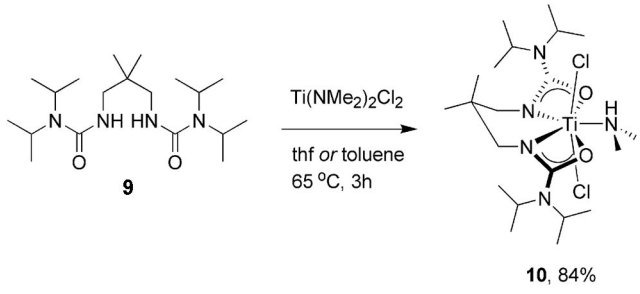
The bis(amidate) and bis(ureate) zirconium complexes discussed thus far both exhibit fluxional behaviour and/or geometric isomerism. To alleviate these problems, a tethered urea was envisioned as a proligand to form discrete, well-defined dichloride complexes. An analogous tethered bis(amidate) ligand has been used to synthesize seven-coordinate, pentagonal bipyramidal zirconium and hafnium dibenzyl complexes.[16d] This ligand coordinates the metal center in the equatorial plane, akin to the geometry observed for zirconium complexes **3**·[DMP(NH,O)*t*Bu] and **8**·thf.

The aforementioned urea synthesis cannot be applied to the preparation of tethered bis(urea) proligands. Reaction of a diamine with triphosgene would presumably lead to the formation of the cyclic urea as a major byproduct. In order to circumvent this, a strategy involving activated carbamate intermediates was employed.[19] Addition of two equivalents of phenyl chloroformate to 2,2-dimethyl-1,3-diaminopropane in the presence of pyridine leads to the quantitative formation of the bis(phenylcarbamate). This compound reacts with two equivalents of diisopropylamine in DMSO at room temperature to give the urea **9** in 92% overall yield [Equation (3)].



(3)

Preparation of a tethered bis(ureate)titanium dichloride was accomplished by the reaction of one equivalent of **9** with $Ti(NMe_2)_2Cl_2$ in thf or toluene. This reaction led to the exclusive formation of **10** [Equation (4)], with no observation of side-products or bridging oligomers.



(4)

The ^{1}H NMR spectrum of **10** contains one set of resonances for the ligand protons. In addition, this compound contains one equivalent of dimethylamine as a neutral donor, even when synthesized using thf as a solvent. A doublet at δ = 2.91 ppm and a broadened multiplet at δ = 3.64 ppm correspond to the methyl groups and the N*H* proton, respectively. Unlike titanium bis(ureate) **7**, there is only one signal corresponding to the methyl protons of the isopropyl groups, a doublet at δ = 1.17 ppm, indicative of a lower barrier to rotation about the C–N bond. Determination of the $\Delta G^{\ddagger}$ of rotation by variable temperature NMR spectroscopy gives a value of 9.0 ± 0.5 kcal mol^{-1} for **10** at the coalescence temperature, while for **7** the value is 16.1 ± 0.5 kcal mol^{-1} (see Supporting Information). The presence of a neutral donor likely results in a more electron-rich titanium center, lowering the amount of electron-density donated by the backbone diisopropylamino substituents. Subjecting **10** to high vacuum at 65 °C does not remove the dimethylamine.

The solid-state molecular structure of **10** is shown in Figure 9. The titanium center has distorted pentagonal-bipyramidal geometry, with the chloride ligands in the apical positions and the ligand donor atoms in the equatorial plane, including a neutral dimethylamine ligand. This geometry is entirely analogous to the zirconium complexes previously discussed; this is the first example of a seven-coordinate titanium complex with amidate or ureate ligands we have observed. The Ti–N5 length is much longer than the Ti–N1 length [2.2889(9) Å vs. 2.0345(9) Å], and N5 is pyramidalized, characteristic of a neutral amine donor rather than an anionic amido ligand. The Ti–Cl bond lengths in **10** are also considerably longer than those of either bis(amidate) **1** or bis(ureate) **7** [2.246(2) Å for **1**, 2.271(3) Å for **7**, 2.3751(3) Å for **10**]. In the solid state, there is evidence of electron donation from the diisopropylamino substituents: C1–N1 1.334(1) Å vs. C1–N2 1.343(1) Å, the sum of angles about N2 is 359.8(3)°, and the torsion angle between O1–C1–N2–C5 is 13.82°. This contrasts with the aforementioned spectroscopic data, which suggests a lesser degree of electron donation from the amino groups at room temperature in solution.

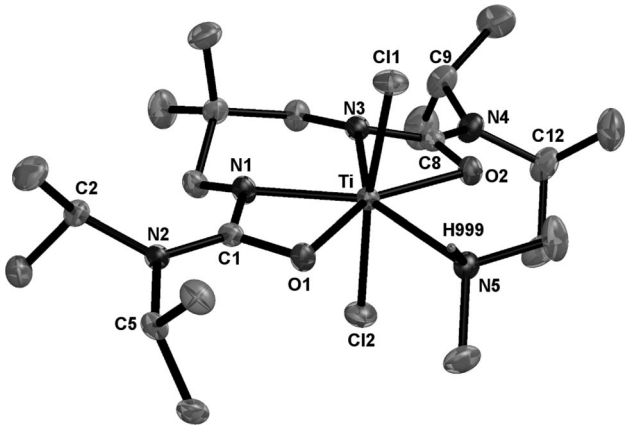


Figure 9. ORTEP representation of the molecular structure of **10** (ellipsoids plotted at 50% probability, benzene molecule and hydrogen atoms except H999 not shown, H999 refined from unassigned electron density) with selected bond lengths [Å], bond and torsion angles [°]: Ti–N1, 2.0345(9); Ti–O1, 2.0583(8); Ti–N3, 2.0709(9); Ti–O2, 2.0190(7); Ti–N5, 2.2889(9); Ti–Cl1: 2.3751(3); C1–N1, 1.334(1); C1–O1, 1.297(1); C1–N2, 1.343(1); N1–Ti–O1, 63.63(3); Cl1–Ti–Cl2, 172.46(1); sum of angles about N2, 359.8(3); O1–C1–N2–C5, 13.82.

Synthesis of the corresponding zirconium complex **11** was accomplished in the same manner as above. Performing the reaction in thf led to a mixture of two products in a 1:1 ratio as seen by ^{1}H NMR spectroscopy. One product is the dimethylamine adduct, as for titanium compound **10**, while the other is the thf adduct. Performing the reaction in toluene leads to the exclusive formation of the dimethylamine adduct in 89% yield. The spectroscopic data are completely analogous to the titanium congener, with the only major difference being an upfield shift for the N*H* proton to δ = 2.97 ppm. The solid state molecular structure of **11** is shown in Figure 10, and is analogous to that of **10**. There is a mirror plane which bisects the molecule, rendering both halves of the ligand equivalent. The Zr–Cl bond lengths are slightly longer than zirconium complexes **3**·[DMP(NH,O)-*t*Bu] and **8**·thf, possibly due to tighter complexation by the tethered ligand: the Zr–N_{ureate} bond length is considerably shorter in **11** [2.170(1) Å] than **3**·[DMP(NH,O)*t*Bu] [average Zr–$N_{amidate}$: 2.296(4) Å] or **8**·thf [average Zr–N_{ureate}: 2.231(1) Å].

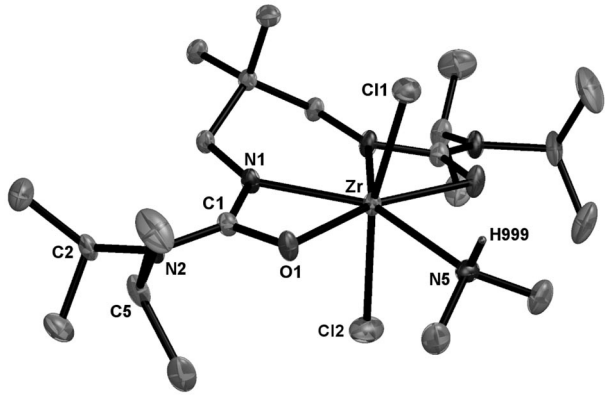


Figure 10. ORTEP representation of the molecular structure of **11** (ellipsoids plotted at 50% probability, hydrogen atoms except H999 not shown, H999 refined from unassigned electron density) with selected bond lengths [Å], bond and torsion angles [°]: Zr–N1, 2.170(1); Zr–O1, 2.176(1); Zr–N5, 2.445(2); Zr–Cl1: 2.4846(5); C1–N1, 1.332(2); C1–O1, 1.310(2); C1–N2, 1.345(2); N1–Zr–O1, 60.19(3); Cl1–Zr–Cl2, 162.98(2); sum of angles about N2, 359.9(3); O1–C1–N2–C5, 12.02.

Conclusions

Group 4 dichloride complexes are classic and versatile starting materials for organometallic chemistry. While the preparation of these types of complexes is typically straightforward, no general synthesis of bis(amidate) or bis(ureate) dichlorides has existed until now. This fact is somewhat surprising, given the multitude of closely related amidinate- and guanidinate-supported dichlorides reported to date. A minor adjustment to traditional salt metathesis chemistry has yielded a feasible synthetic route to amidate dichlorides. Protonolysis of bis(amido)dichlorotitanium and zirconium precursors is effective when employing a more electron-rich urea proligand, which simplifies purification. In addition, modifying the ligand to include a tether to prevent solution-phase isomerization equilibria gives easily characterized titanium and zirconium bis(ureate) dichlorides reliably and in high yield. The development of these new protocols has been a critical challenge in realizing the full potential of this new class of complexes, and hopefully will allow access to the same manner of rich chemistry displayed by analogous amidinate and guanidinate dichlorides.

Experimental Section

General: All reactions were performed under dry, oxygen-free nitrogen using a glove box or standard Schlenk techniques unless otherwise noted. Dichloromethane was distilled from calcium hydride. Thf, benzene, toluene, hexanes and pentane were purified and dried by passage through a column of activated alumina and sparged with nitrogen. [D_6]Benzene and [D_8]toluene were degassed by several freeze-pump-thaw cycles and dried with activated 4-Å molecular sieves for at least 24 h before use in NMR experiments. All common reagents, including $Ti(NMe_2)_4$, and amines used for proligand synthesis were purchased from Aldrich and used as received. $Zr(NMe_2)_4$ and $ZrCl_4$ were purchased from Strem and used as received. $TiCl_4(thf)_2$,[20] $ZrCl_4(thf)_2$,[20] $Ti(NMe_2)_2Cl_2$,[21] *N*-(2′,6′-diisopropylphenyl)benzamide,[16b] and *N*-(2′,6′-dimethylphenyl)-pivalamide[16l] were prepared according to literature protocols. ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker 300 MHz or 400 MHz Avance spectrometer; chemical shifts are given relative to residual *protio* solvent at 298 K unless otherwise noted. Mass spectra were recorded with either a Kratos MS-50 spectrometer using an electron-impact (70 eV) source or a Bruker Esquire~LC using an electrospray ionization source. Elemental analyses were recorded with a Carlo Erba Elemental Analyzer EA 1108. Single crystal X-ray structure determinations were performed at the Department of Chemistry, University of British Columbia by Dr. Brian O. Patrick, Mr. Robert K. Thomson, or Mr. Neal Yonson.

Synthesis of 1: *N*-(2,6-Diisopropylphenyl)benzamide (2.042 g, 7.262 mmol) and sodium bis(trimethylsilyl)amide (1.330 g, 7.262 mmol) were dissolved in thf (100 mL) at room temperature. The solution was stirred for 3 h prior to the removal of the solvent in vacuo. $TiCl_4(thf)_2$ (1.212 g, 3.631 mmol) and toluene (100 mL) were added, and the resulting slurry stirred overnight. The red solution was then filtered through Celite to remove sodium chloride. The solvent was slowly removed under reduced pressure at 70 °C without stirring until crystals began to form along the side of the flask. The flask was then closed to vacuum, cooled to room temperature, and left standing overnight. The resulting deep red crystalline product was collected on filter paper and dried (1.670 g, 68% yield). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.02 [d, J = 4.6 Hz, 12 H, 2 -CH(CH_3)$_2$], 1.12 [d, J = 5.1 Hz, 12 H, 2 -CH(CH_3)$_2$], 3.91 [m, 4 H, 4 -CH(CH$_3$)$_2$], 6.74 (t, J = 8.0 Hz, 4 H, 4 Ph-H_{meta}), 6.88 (t, J = 6.4 Hz, 2 H, 2 Ph-H_{para}), 7.18 (m, 6 H, 6 Ar-H), 7.66 (d, J = 8.6 Hz, 4 H, 4 Ph-H_{ortho}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 23.0 24.2, 24.7, 25.9, 28.1, 29.8, 123.6 (two signals), 125.7, 129.1, 129.6, 131.3, 133.1, 135.3, 142.3, 142.6, 182.5 ppm. MS (EI): m/z = 678 (M^+). $C_{41.5}H_{52}Cl_2N_2O_2Ti$ (**1** + 1/2 C_7H_8, 729.67): calcd. C 68.69, H 6.53, N 4.12; found C 68.60, H 6.94, N 4.25.

Synthesis of 2: Prepared analogous to **1** above using *N*-(2,6-diisopropylphenyl)benzamide (2.018 g, 7.178 mmol), sodium bis(trimethylsilyl)amide (1.314 g, 7.178 mmol), and $ZrCl_4$ (0.836 g, 3.59 mmol). Colorless crystals (1.922 g, 74% yield). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.89 [d, J = 6.8 Hz, 6 H, -CH(CH_3)$_2$], 1.02 [d, J = 6.8 Hz, 6 H, -CH(CH_3)$_2$], 1.27 (m, 4 H, thf:-CH_2CH_2CH_2CH$_2$-), 1.36 [d, J = 6.7 Hz, 6 H, -CH(CH_3)$_2$], 1.56 [d, J = 6.6 Hz, 6 H, -CH(CH_3)$_2$], 4.05 [m, 2 H, 2 -CH(CH$_3$)$_2$], 4.27 [m, 2 H, 2 -CH(CH$_3$)$_2$], 4.43 (m, 4 H, thf -CH_2OCH_2-), 6.64 (t, J = 7.8 Hz, 2 H, 2 Ph-H_{meta}), 6.77 (t, J = 7.6 Hz, 1 H, Ph-H_{para}), 6.83 (t, J = 7.3 Hz, 1 H, Ph-H_{para}), 6.85 (t, J = 7.8 Hz, 2 H, 2 Ph-H_{meta}), 7.12 (m, 3 H, 3 Ar-H), 7.27 (m, 3 H, 3 Ar-H), 7.49 (d, J = 7.8 Hz, 2 H, 2 Ph-H_{ortho}), 7.76 (d, J = 7.7 Hz, 2 H, 2 Ph-H_{ortho}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 23.7, 24.1, 24.2, 24.3, 24.7, 24.8, 25.2, 25.4, 25.8, 26.1, 26.5, 27.5, 27.9, 28.3, 28.7, 28.9, 75.0, 120.0, 125.2, 126.6, 127.3, 127.9, 128.1, 129.5, 129.6, 129.9, 130.2, 130.5, 131.0, 131.1, 131.7, 132.5, 139.3, 141.1, 143.1, 144.0, 179.8, 181.1 ppm. MS (EI): m/z = 722 [M^+]. $C_{38}H_{44}Cl_2N_2O_2Zr$ (no thf, 722.91): calcd. C 63.14, H 6.13, N 3.88; found C 62.86, H 6.53, N 4.28.

Synthesis 3: Prepared analogous to **1** above using *N*-(2,6-dimethylphenyl)pivalamide (8.00 g, 38.97 mmol), sodium bis(trimethylsilyl)amide (7.15 g, 38.97 mmol), and $ZrCl_4$ (4.54 g, 19.48 mmol). Colorless crystals (8.45 g, 76% yield). Spectroscopic evidence indicates two geometric isomers in solution, labeled **3a** and **3b**, in a ratio of 3:1. Proton integrations cited are for each individual compound, and not indicative of the ratio of **3a**:**3b**. A single crystal of a byproduct, **3**·[DMP(NH,O)*t*Bu], was analyzed by X-ray diffraction (vide supra). This compound was not characterized further. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.86 [s, 9 H, -C(CH_3)$_3$, **3a**], 1.02 [s, 18 H, 2 -C(CH_3)$_3$, **3b**], 1.06 (br. m, 4 H, thf:-CH_2CH_2CH_2CH$_2$-, **3a**), 1.13 [s, 9 H, -C(CH_3)$_3$, **3a**], 1.35 (br. m, 4 H, thf -CH_2CH_2CH_2CH$_2$-, **3b**), 2.40 (s, 6 H, 2 Ar-CH_3, **3b**), 2.53 (s, 3 H, Ar-CH_3, **3a**), 2.75 (s, 3 H, Ar-CH_3, **3a**), 4.43 (m, 4 H, thf -CH_2OCH_2-, **3a**), 4.64 (m, 4 H, thf -CH_2OCH_2-, **3b**), 6.52 (d, J = 7.23 Hz, 2 H, 2 Ar-H, **3b**), 6.64 (br. t, 1 H, Ar-H, **3b**), 6.83 (br. m, 2 H, 2 Ar-H, **3a**), 7.02 (br. m, 2 H, Ar-H, **3a**) ppm. MS (EI): m/z = 640 [M^+], 568 [M^+ – thf]. $C_{30}H_{44}Cl_2N_2O_3Zr$ (642.82): calcd. C 56.05, H 6.90, N 4.36; found C 56.88, H 6.98, N 4.46 (analysis was complicated by the presence of the byproduct **3**·[DMP(NH,O)-*t*Bu]).

Synthesis of 4: 2,6-Dimethylaniline (0.489 g, 0.500 mL, 4.03 mmol) was dissolved in dichloromethane (10 mL). The solution was cooled to 0 °C. Solid triphosgene (0.419 g, 1.41 mmol) was added in one portion and the solution stirred for 5 min. *N*,*N*-Diisopropylethylamine (1.04 g, 1.40 mL, 8.06 mmol) was added and the cold bath removed. The reaction was stirred for 45 min. Diisopropylamine (0.407 g, 0.570 mL, 4.03 mmol) was slowly added, followed by another equivalent of *N*,*N*-diisopropylethylamine (0.520 g, 0.700 mL, 4.03 mmol). The reaction was stirred for an additional 30 min at room temperature. The solution was diluted with 1 M HCl (50 mL) and dichloromethane (30 mL). The organic phase was washed with 1 M HCl (3 × 50 mL) and dried with $MgSO_4$. Removal of the solvent gave the crude urea, which was purified by flash chromatography (hexanes/ethyl acetate, 1:1) to give **4** as a white solid (0.90 g, 90% yield). This compound was dried in vacuo for 18 h prior to use in protonolysis reactions. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.32 [d, J = 6.88 Hz, 12 H, -CH(CH_3)$_2$], 2.23 (s, 3 H, -CH_3), 4.02 [m, J = 6.89 Hz, 2 H, -CH(CH$_3$)$_2$], 5.57 (br. s, 1 H, -NH-), 7.03 (m, 3 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.91, 22.81, 46.74, 127.20, 129.24, 136.95, 137.64, 156.29 ppm. MS (ESI): m/z = 249 [M^+ + H], 271 [M^+ + Na]. HRMS: m/z calcd for $C_{15}H_{25}N_2O$ [M^+ + H]: 249.1967; found 249.1971. $C_{15}H_{24}N_2O$ (248.37): calcd. C 72.54, H 9.74, N 11.28; found C 72.69, H 9.77, N 11.47.

Synthesis of 5: Prepared analogous to **4** using 2,6-diisopropylaniline (1.95 g, 2.08 mL, 11.0 mmol), triphosgene (1.309 g, 3.500 mmol), *N*,*N*-diisopropylethylamine (3.88 g, 5.25 mL, 30.0 mmol) and piperidine (0.851 g, 0.99 mL, 10.0 mmol). White solid (2.85 g, 99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 [d, J = 6.85 Hz, 12 H, 2 -CH(CH_3)$_2$], 1.54–1.65 [m, 6 H, (-CH_2-)$_3$], 3.11 [m, J = 6.88 Hz, 2 H, 2 -CH(CH$_3$)$_2$], 3.454 [m, 4 H, (-CH_2-)$_2$N-], 5.70 (br. s, 1 H, -NH-), 7.10–7.23 (m, 3 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.81, 24.77, 26.09, 28.79, 45.87, 123.42, 127.64, 132.97, 146.62, 156.71 ppm. MS (ESI): m/z = 289 [M^+ + H], 311 [M^+ + Na]. HRMS: m/z calcd. for $C_{18}H_{29}N_2O$ [M^+ + H]: 289.2280; found 289.2278. $C_{18}H_{28}N_2O$ (288.43): calcd. C 74.96, H 9.78, N 9.71; found C 75.01, H 9.49, N 10.00.

Synthesis of $Zr(NMe_2)_2Cl_2$(dme): This compound was prepared using a different route to that previously published.[22] $Zr(NMe_2)_4$ (1.00 g, 3.745 mmol) and $ZrCl_4(thf)_2$ (1.41 g, 3.745 mmol) were dissolved in toluene (10 mL each) in separate flasks. The slurry of $ZrCl_4(thf)_2$ was cooled to –78 °C prior to the addition of $Zr(NMe_2)_4$ via cannula. 1,2-Dimethoxyethane (1.00 mL) was subsequently added via syringe. The solution was warmed to room temperature and then heated to 60 °C for four hours. The solvent was removed in vacuo. The crude solid was suspended in pentane and filtered. The collected solid was washed with several portions of pentane and subsequently dried in vacuo to give a pale yellow powder (2.19 g, 86% yield) which was used without further purification. ^{1}H NMR (300 MHz, C_6D_6): δ = 3.14 (br. m, 10 H, CH_3OCH_2CH_2OCH_3), 3.26 [s, 12 H, -N(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 44.8, 62.4, 72.0 ppm.

Synthesis of 6: Urea **4** (0.400 g, 1.61 mmol) was dissolved in thf (15 mL). The resulting slurry was cooled to –78 °C. $Ti(NMe_2)_4$ (0.181 g, 0.806 mmol) in thf (5 mL) was added via cannula. The solution was warmed to room temperature with stirring over a period of three hours. The solvent was removed in vacuo and the crude solid redissolved in hexanes. This solution was filtered through a bed of Celite and the solvent was removed. Recrystallization from pentane at –35 °C afforded **6** as yellow-orange crystals (0.467 g, 92% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ = 0.62–1.67 [br. m, 24 H, 4 -CH(CH_3)$_2$], 2.52 (s, 12 H, 4 Ar-CH_3), 3.10 [s, 12 H, 2 -N(CH_3)$_2$], 3.46–3.74 [br. m, 4 H, 4 -CH(CH$_3$)$_2$], 6.92 (t, J = 7.31 Hz, 2 H, 2 Ar-H), 7.09 (d, J = 7.44 Hz, 4 H, 4 Ar-H) ppm.

^{13}C NMR (C_6D_6, 100 MHz): δ = 19.62, 20.9–23.9 (br), 46.1–47.1 (br), 47.89, 123.83, 133.57, 146.63, 166.05 (one aromatic carbon not observed) ppm. MS (EI): *m*/*z* = 630 [M^+], 586 [$M^+ - NMe_2$]. $C_{34}H_{58}N_6O_2Ti$ (630.75): calcd. C 64.74, H 9.27, N 13.32; found C 64.14, H 9.50, N 13.01.

Synthesis of 7. Route A: Urea **4** (0.500 g, 2.02 mmol) and $Ti(NMe_2)_2Cl_2$ were dissolved in thf (20 mL) at –78 °C. The solution was warmed to room temperature with stirring overnight. The solvent was removed in vacuo and the crude solid triturated with pentane. This slurry was filtered and the yellow solid collected. No further purification was required, giving **7** (0.471 g, 77% yield). Recrystallization from toluene afforded yellow crystals used for X-ray diffraction. **Route B:** Titanium complex **6** (0.200 g, 0.317 mmol) was dissolved in thf (10 mL). The solution was cooled to –78 °C. Chlorotrimethylsilane (0.345 g, 0.400 mL, 3.17 mmol) was added via syringe. The cold bath was removed and the solution stirred overnight at room temperature. The compound was isolated as described above (0.110 g, 57% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ = 0.54 [d, *J* = 6.60 Hz, 12 H, 2 -CH(C*H*$_3$)$_2$], 1.38 [d, *J* = 6.74 Hz, 12 H, 2 -CH(C*H*$_3$)$_2$], 2.67 (s, 12 H, 4 Ar-C*H*$_3$), 2.90 [m, *J* = 6.46 Hz, 2 H, 2 -C*H*(CH$_3$)$_2$], 3.59 [m, *J* = 6.39 Hz, 2 H, 2 -C*H*(CH$_3$)$_2$], 6.92 (m, 2 H, Ar-*H*), 7.02 (m, 4 H, Ar-*H*) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 18.48, 19.36, 19.79, 21.11, 21.51, 46.60, 47.17, 125.69, 128.09, 132.72, 145.90, 166.08 ppm. MS (EI): *m*/*z* = 612 [M^+], 577 [M^+ – Cl]. HRMS: *m*/*z* calcd. for $C_{30}H_{46}N_4O_2{}^{35}Cl_2{}^{48}Ti$ (M^+): 612.24773; found 612.24742. $C_{30}H_{46}Cl_2N_4O_2Ti$ (613.51): calcd. C 58.73, H 7.56, N 9.13; found C 59.22, H 7.68, N 9.53.

Synthesis of 8: As above from route A using urea **5** (0.500 g, 1.74 mmol) and $Zr(NMe_2)_2Cl_2$(dme) (0.295 g, 0.868 mmol). The resulting product was **8**·thf as colourless crystals (0.499 g, 71% yield). These crystals were subject to high vacuum for 48 h to remove the thf ligand, giving **8** quantitatively. **8**·thf: ^{1}H NMR (C_6D_6, 400 MHz, 345 K): δ = 1.20 (m, 12 H), 1.21 (m, 4 H, H_{thf}), 1.36 [d, *J* = 6.80 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.57 [d, *J* = 6.40 Hz, 12 H, CH(C*H*$_3$)$_2$], 2.55 (m, 8 H), 2.90 [m, 8 H, C*H*(CH$_3$)$_2$ and H_{thf}], 3.59 [m, *J* = 6.39 Hz, 2 H, C*H*(CH$_3$)$_2$], 6.92 (m, 2 H, Ar-*H*), 7.02 (m, 4 H, Ar-*H*) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 345 K): δ = 24.68, 24.80, 25.85, 26.06, 26.55, 28.55, 41.45, 46.08, 124.49, 126.40, 141.78, 166.03 ppm. **8**: ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.00–1.40 [m, 12 H, 2 (-C*H*$_2$-)$_3$], 1.18 [m, 12 H, 2 CH(C*H*$_3$)$_2$], 1.31 [d, *J* = 6.80 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.37 [d, *J* = 7.20 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.51 [d, *J* = 6.40 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.67 [d, *J* = 6.40 Hz, 3 H, CH(C*H*$_3$)$_2$], 2.85 [br. m, 2 H, (-C*H*$_2$-)$_2$N-], 2.93 [br. m, 2 H, (-C*H*$_2$-)$_2$N-], 3.08 [br. m, 4 H, (-C*H*$_2$-)$_2$N-], 3.43 [m, *J* = 6.40 Hz, 2 H, 2 -C*H*(CH$_3$)$_2$], 4.24 [m, *J* = 6.80 Hz, 1 H, -C*H*(CH$_3$)$_2$], 4.34 [m, *J* = 6.80 Hz, 1 H, -C*H*(CH$_3$)$_2$], 6.94–7.13 (m, 4 H, Ar-*H*), 7.20–7.36 (m, 2 H, Ar-*H*) ppm. MS (EI): *m*/*z* = 736 [M^+]. $C_{36}H_{54}Cl_2N_4O_2Zr$ (736.98): calcd. C 58.67, H 7.36, N 7.60; found C 58.68, H 7.76, N 7.37.

Synthesis of Diphenyl (2,2-Dimethyl-1,3-propanediyl)bis(carbamate): 1,3-Diamino-2,2-dimethylpropane (5.00 g, 5.85 mL, 49.0 mmol) was dissolved in dichloromethane (150 mL). The solution was cooled to 0 °C prior to the addition of pyridine (9.70 g, 9.90 mL, 122.5 mmol), followed by the addition of phenyl chloroformate (16.1 g, 12.95 mL, 103.0 mmol). The solution was left to warm up to room temperature with stirring overnight. The reaction was quenched by the addition of 1 M HCl (100 mL). The organic layer was separated and washed with a further portion of 1 M HCl (100 mL), brine (100 mL), and dried with $MgSO_4$. Removal of the solvent in vacuo gave a thick yellow oil, which solidified upon standing, in quanitative yield. The crude product was used in further steps without purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.97 (s, 6 H, 2 -C*H*$_3$), 3.11 (d, *J* = 6.85 Hz, 4 H, 2 -CH$_2$-), 5.95 (br. t, 2 H, 2 -N*H*), 7.15 (d, *J* = 7.59 Hz, 4 H, 4 Ar-H_{ortho}), 7.23 (t, *J* = 7.34 Hz, 2 H, 2 Ar-H_{para}) 7.39 (m, 4 H, 4 Ar-H_{meta}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.36, 36.76, 47.80, 121.69, 125.44, 129.43, 151.20, 155.97 ppm. MS (ESI): *m*/*z* = 365 [M^+ + Na].

Synthesis of 9: This reaction was performed without the exclusion of water or air. Diphenyl (2,2-Dimethyl-1,3-propanediyl)bis(carbamate) (1.11 g, 3.25 mmol) was dissolved in dimethyl sulfoxide (10 mL). Diisopropylamine (0.657 g, 0.91 mL, 6.50 mmol) was added via syringe. The solution was stirred overnight at room temperature, during which time a solid product precipitated. Dichloromethane (30 mL) was added to clarify the suspension. The organic phase was washed successively with water (2 × 50 mL), 1 M HCl (50 mL), water (50 mL), 1 M NaOH (50 mL), and brine (50 mL). The organic phase was dried with $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by recrystallization from ethyl acetate to give **9** as white crystals (1.06 g, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.83 [s, 6 H, -C(C*H*$_3$)$_2$], 1.23 [d, *J* = 6.80 Hz, 24 H, 4 -CH(C*H*$_3$)$_2$], 2.99 (d, *J* = 6.40 Hz, 4 H, 2 -C*H*$_2$-), 3.84 [m, *J* = 6.80 Hz, 4 H, 4 -C*H*(CH$_3$)$_2$], 5.31 (br. t, 2 H, 2 -N*H*) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.36, 24.63, 37.61, 46.21, 47.57, 158.69 ppm. MS (ESI): *m*/*z* = 379 [M^+ + Na]. $C_{19}H_{40}N_4O_2$ (356.55): calcd. C 64.00, H 11.31, N 15.71; found C 64.15, H 11.29, N 15.72.

Synthesis of 10: Urea **9** (0.7530 g, 2.115 mmol), and $Ti(NMe_2)_2Cl_2$ (0.4374 g, 2.115 mmol) were dissolved in toluene (10 mL). The solution was heated to 65 °C with stirring for three hours. The solvent was removed and the crude solid subject to high vacuum at 65 °C overnight. The residue was recrystallized from benzene with heating to give **10** as yellow crystals (0.923 g, 84% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.17 [d, 24 H, *J* = 6.80 Hz, 4 -CH(C*H*$_3$)$_2$], 1.28 [s, 6 H, -C(C*H*$_3$)$_2$], 2.91 [d, 6 H, *J* = 6.40 Hz, HN(C*H*$_3$)$_2$], 3.53 [m, 4 H, *J* = 6.80 Hz, 4 -C*H*(CH$_3$)$_2$], 3.54 (s, 4 H, 2 -C*H*$_2$-), 3.63 [br. m, 1 H, *H*N(CH$_3$)$_2$]. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.44, 26.85, 36.19, 42.68, 47.86, 59.28, 171.80 ppm. MS (EI): *m*/*z* = 472 [M^+ – $HNMe_2$]. $C_{21}H_{45}Cl_2N_5O_2Ti$ (518.41): calcd. C 48.66, H 8.75, N 13.51; found C 48.47, H 8.63, N 13.80.

Synthesis of 11: As above from **9** (1.00 g, 2.81 mmol), and $Zr(NMe_2)_2Cl_2$(dme) (0.955 g, 2.81 mmol). Colourless crystals (1.40 g, 89% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.18 [d, *J* = 6.80 Hz, 24 H, 4 -CH(C*H*$_3$)$_2$], 1.18 [s, 6 H, overlapping with previous, -C(C*H*$_3$)$_2$], 2.66 [d, *J* = 6.40 Hz, 6 H, HN(C*H*$_3$)$_2$], 2.97 [br. m, 1 H, *H*N(CH$_3$)$_2$], 3.35 (s, 4 H, 2 -C*H*$_2$-), 3.57 [m, *J* = 6.80 Hz, 4 H, 4 -C*H*(CH$_3$)$_2$] ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 22.42, 26.63, 37.01, 40.17, 47.53, 57.34, 170.13 ppm. MS (EI): *m*/*z* = 516 [M^+ – $HNMe_2$]. $C_{21}H_{45}Cl_2N_5O_2Zr$ (561.75): calcd. C 44.90, H 8.07, N 12.47; found C 45.14, H 7.96, N 12.49.

CCDC-269304 (for **1**), -722755 (for **7**), 722756 (for **3**·[DMP(NH,O)*t*Bu]), 722757 (for **8**·thf), 722758 (for **10**), 722759 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Further crystallographic details for complexes **1** and **3**·[DMP(NH,O)*t*Bu], van't Hoff plot for the equilibrium between **3a** and **3b**, and $\Delta G^{\ddagger}$ determination by variable temperature NMR for the C–N*i*Pr$_2$ bond rotation of **7** and **10**.

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