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Article

Zirconium Alkyl Complexes Supported by Ureate Ligands: Synthesis, Characterization, and Precursors to Metal−Element Multiple Bonds[†]

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A series of bis(ureate) zirconium complexes bearing reactive alkyl ligands have been prepared and fully characterized. A sterically demanding, nontethered ureate ligand was successfully employed in the synthesis of a dibenzyl complex; however synthesis can be complicated by suspected ligand disproportionation and redistribution. In contrast, tethered bis(ureate) ligands, including a chiral, C_2-symmetric ligand, are reliable supports for sterically accessible, mononuclear dibenzyl and bis(neopentyl) complexes. These coordinatively unsaturated species react with pyridine to form seven-coordinate adducts that exhibit remarkable thermal and photochemical stability. The reactive nature of the dibenzyl derivative can be exploited in the synthesis of imido complexes via protonolysis with 2,6-diisopropylaniline. A monometallic imido, supported by a sterically open ureate ligand, can be prepared in this manner with the use of excess pyridine; however, NMR spectroscopy indicates that this species undergoes dimerization in solution. When the reaction is performed in the absence of pyridine, only the dimeric complex is obtained.

Introduction

Transition metal alkyl complexes represent a broad and versatile class of organometallic compounds that are widely used throughout synthetic chemistry.[1] Group 4 alkyl derivatives in particular possess a rich chemistry, being extensively used as initiators in the production of polyolefins[2] and as reagents and/or catalysts for organic synthesis.[3] The range of known structures spans from simple, homoleptic tetra(alkyl) species[4] to group 4 alkyl fragments supported by a variety of ancillary ligand frameworks.[2,5] A plethora of research has been directed toward developing the latter category, with the goal of inducing new reactivity patterns through steric and electronic manipulation. Within this theme of exploring ligand-driven reactivity, our research group has developed a series of modular, mixed donor ligands for the generation of very electropositive early transition metal centers.[6] We have used one such ligand class, amidates, in the synthesis of group 3, 4, and 5 amido complexes, many of which exhibit remarkable reactivity in catalytic C−N, C−O, and C−C bond forming reactions.[7−9]

[†] Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth for his leadership and outstanding contributions to organometallic chemistry.

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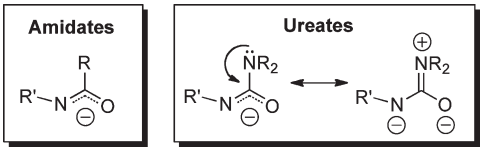

Figure 1. Electronic comparison of amidate and ureate ligands.

Notably, mixed amidate-amido complexes display significant multiple-bond character between the metal center and the amido ligands, thereby increasing the formal electron count at these electron-deficient metal centers. In contrast, there are relatively few reports of early transition metal amidate complexes with σ-bonding, two-electron donor ligands, such as halides or alkyls.[10] This has been attributed in part to the propensity of these species to form ill-defined bridging aggregates in an effort to increase electron donation to the metal center. Recently, we have described a synthetic protocol to reliably access a small group of amidate-supported dichlorides; however, the success of this methodology is highly ligand dependent.[10a] In addition, the resulting complexes are susceptible to fluxional behavior and geometric isomerization in solution. The few reported examples of amidate-supported alkyls have exhibited similar tendencies.[10b,c] The first example of an amidate-supported Hf−dibenzyl complex was reported in 2005 and was isolated as the THF adduct.[10c] More recently, Scott and co-workers utilized several biaryl-tethered amidate ligands in the preparation of Ti− and Zr−dibenzyl compounds for hydroamination catalysis.[10b] These complexes display various amidate coordination modes, solution-phase isomerization, and formation of dinuclear species through bridging interactions. In addition, several synthetic attempts were reported as unsuccessful, leading to unidentifiable product mixtures. These difficulties highlight the importance and challenge of *N,O* ligand design in the pursuit of discrete, well-behaved complexes.

In order to examine the electronic effects exerted by tight bite-angle *N,O* chelates, our group has recently explored the use of electron-rich ureate ligands in the synthesis of group 4 complexes.[10a,11] Sterically analogous to amidates, ureates possess an electron-donating amino group attached to the central carbon atom (Figure 1). It has been envisaged that the use of this electron-rich ligand would stabilize highly electropositive metal complexes, facilitating their isolation and characterization, while promoting the same unique reactivity exhibited by amidate derivatives. Indeed, the use of this alternate ligand set allows for facile preparation of group 4 dichloride complexes[10a] and has resulted in the identification of a highly active hydroamination catalyst.[11]

Herein, we report the preparation and characterization of the first examples of ureate-supported zirconium dibenzyl and bis(neopentyl) compounds. While use of a nontethered ureate ligand gives limited success in the formation of dialkyls, tethered bis(ureate) ligands are reliable supports for sterically accessible, coordinatively unsaturated dialkyl derivatives. In contrast to the aforementioned amidates reported by Scott,[10b] these ureate complexes do not undergo isomerization or dimerization. Furthermore, we have examined the reactivity of these

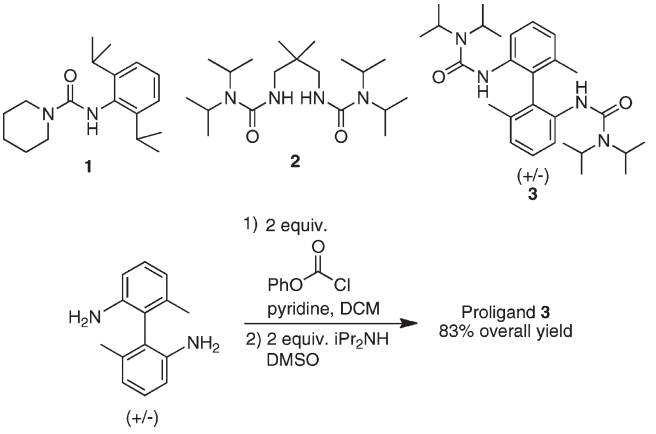

Figure 2. Proligands employed in this study; synthesis of **3**.

compounds with neutral donors, resulting in the formation of pyridine adducts that are thermally and photochemically stable for months under inert atmosphere. Finally, we demonstrate the potential of this class of compounds as organometallic precursors for the synthesis of other ureate-supported metal complexes, namely, the first ureate-supported zirconium imido complexes.

Results and Discussion

Synthesis of Dialkyl Complexes. Through the work of several research groups, including our own, several reliable synthetic protocols have been developed for the installation of amidate and ureate ligands.[6−12] Foremost among these routes is a direct reaction between an organic amide or urea proligand and a metal complex containing ligands that are susceptible to cleavage by protonation. These protonolysis reactions generally lead to products that are easily isolated and purified due to the absence of salt-containing byproducts. All previously reported examples of amidate-supported dibenzyl complexes were prepared in this fashion using $M(CH_2Ph)_4$ (M = Ti, Zr, Hf);[10b,c] we therefore have chosen a similar protocol for the synthesis of analogous bis(ureate) complexes. The urea proligands included in this investigation are shown in Figure 2. Syntheses of compounds **1** and **2** have been previously established,[10a,11] while the preparation of **3** is disclosed here. These frameworks have been chosen to vary the steric properties of the ureate ligands and to compare with known amidate compounds possessing comparable substitution patterns. Specifically, proligands **1** and **3** are structurally similar to amides used previously to prepare highly active catalysts for the hydroamination of alkynes and alkenes.[8a−g,i]

Treatment of $Zr(CH_2Ph)_4$ with two equivalents of **1** at −78 °C in THF results in the formation of dibenzyl complex **4** in moderate recrystallized yield (Scheme 1, top pathway). ^{1}H NMR spectroscopy of the purified compound confirms the formulation as L_2ZrBn_2: relative integration of the isopropyl methine multiplet and the benzyl methylene singlet gives a 1:1 ratio. The NMR spectra also give an indication of the

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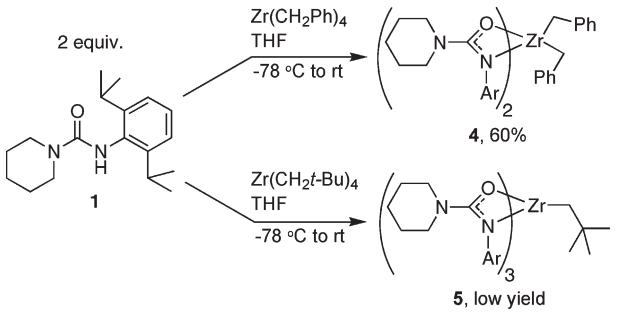
Scheme 1. Synthesis of Dibenzyl Complex 4 and Unexpected Formation of Tris(Ureate) 5



solution-phase coordination geometry. There are two inequivalent signals for the isopropyl methyl groups, resonating as doublets at δ 1.11 and 1.38, while there is a single multiplet for the methine protons at δ 3.16. In addition, one singlet at δ 2.39 is observed for the methylene protons of the benzyl ligands. The ^{13}C NMR spectrum contains signals for seven aliphatic carbons, including one at δ 75.4 for the carbons attached to zirconium, and a diagnostic signal at δ 166.8 for the central carbon of a κ^2-chelating ureate. No evidence of THF coordination is observed by NMR spectroscopy, in contrast to the aforementioned bis(amidate) hafnium dibenzyl complex.[10c] These spectral features are indicative of a C_2-symmetric coordination geometry, with two equivalent κ^2-(*N,O*) ureate ligands and two equivalent benzyl groups. The inequivalence of the isopropyl methyl groups is due to hindered rotation about the *i*Pr−Ar bond, as hindered rotation about N−Ar or inequivalent ligand environments would similarly split the methine protons into two groups. All of this is consistent with **4** as a six-coordinate, distorted octahedral complex. The likely coordination mode has the benzyl ligands in a *cis*-disposition and the ureate nitrogens oriented *trans*, proposed by analogy to amidate complexes with a sterically similar ligand.[13] Unfortunately, attempts to grow single crystals of **4** for definitive assignment by X-ray crystallography have thus far been unsuccessful.

Performing an analogous reaction with $Zr(CH_2tBu)_4$ and **1** leads to a mixture of products, from which was isolated an unexpected, tris(ureate) neopentyl complex (**5**) in low yield (Scheme 1, bottom pathway). Careful control of reaction stoichiometry and use of alternate solvents (toluene, hexanes) does not improve the reaction outcome. Furthermore, increasing the proligand-to-zirconium ratio to 3:1 also leads to a mixture of products and a similar low yield of **5**. ^{1}H NMR spectroscopy and mass spectrometry of the reaction mixture are not consistent with the intended bis(ureate) complex and instead indicate its composition as $L_3Zr(CH_2tBu)$ (**5**). Fortunately, cooling a pentane solution of the crude product mixture to −35 °C led to the deposition of single crystals; the solid-state molecular structure as determined by X-ray diffraction is shown in Figure 3.

The complex is seven-coordinate, with three κ^2-ureate ligands; however, the ligand arrangement about zirconium does not conform to the typical pentagonal-bipyramidal or monocapped octahedral geometries. If the ureate ligands are instead viewed as occupying only *one* coordination site, the geometry can be assigned as distorted tetrahedral: the average angle between any two carbons, either as the central atom in the ureate chelate or as the neopentyl methylene, through zirconium is 109.20(9)° (average deviation: 10.49°). Each of the three ureate ligands adopts a nonsymmetric binding mode, where the Zr−O lengths (2.134(1)−2.199(1) Å) are markedly

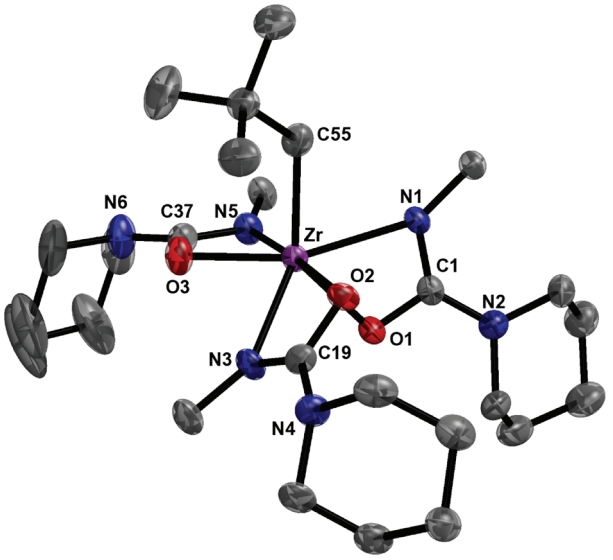
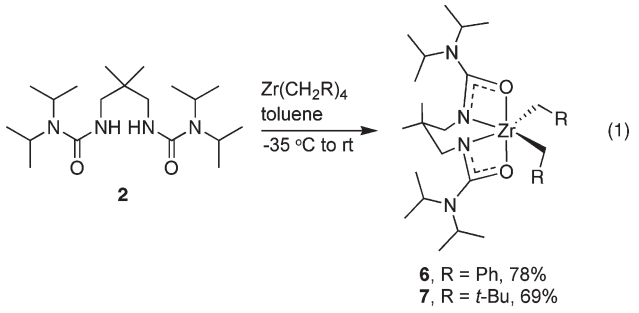


Figure 3. ORTEP representation of the molecular structure of **5** (ellipsoids plotted at 50% probability, hydrogens and all but *ipso*-carbons of aromatic groups removed for clarity, disordered pentane solvent removed with SQUEEZE routine) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 2.401(2); Zr−N3, 2.276(3); Zr−N5, 2.359(2); Zr−O1, 2.134(1); Zr−O2, 2.199(2); Zr−O3, 2.136(2); Zr−C55, 2.279(3); C1−N1, 1.325(3); C1−O1, 1.309(3); C1−N2, 1.354(2); average ureate bite angle, 58.13(8); average angle between C−Zr−C′, 109.2(9); sum of angles about N2, N4, N6: 359.9(6), 354.4(6), 355.6(9); N1−C1−N2−C14: 19.7(4).

shorter than the Zr−N lengths (2.276(3)−2.401(2) Å). This is likely due to steric crowding between the three bulky 2,6-diisopropylphenyl groups attached to the nitrogen atoms. As in previously characterized ureate complexes, the disubstituted amino group attached to the chelate shows evidence of electron donation.[10a] The sum of the angles about nitrogen atoms N2, N4, and N6 is approximately 360°, indicating sp^2-hybridization. In addition, the C−N bond lengths in the $[N_2CO]$ core are all between 1.320(3) and 1.361(4) Å, consistent with electron delocalization and multiple-bond character. Finally, the torsion angles between the plane about the distal nitrogen and that of the NCO-chelate range from 0° to 30°, with an average of 15.8(4)°, indicating a largely coplanar arrangement. All of these metrical data are indicative of π-electron donation by the NR_2 group, resulting in an electron-rich chelating ureate.

In order to rationalize the undesired formation of complex **5**, we postulated that disproportionation reactions through ligand redistribution are responsible. This would explain the inability to reliably isolate **5** even with proper stoichiometry. Previously, we have employed tethered ureate ligands to minimize ligand fluxionality in zirconium dichloride complexes;[10a] a similar strategy was examined in this case, with the use of tethered urea proligands **2** and **3**. Equation 1 outlines the preparation of ureate-supported benzyl (**6**) and neopentyl (**7**) derivatives from proligand **2** and $Zr(CH_2R)_4$, in 78% and 69% yield, respectively, as analytically pure solids. Unlike the situation outlined above with proligand **1**, the formation of bis(neopentyl) complex **7** is accomplished with minimal contamination by side products. A ^{1}H NMR spectrum of the crude product mixture in the synthesis of **7** does indicate the presence of a by-product, which we have tentatively assigned as the homoleptic tetrakis(ureate) complex; however, this impurity is insoluble in

pentane and therefore easily removed by filtration. Lowering the reaction temperature (−78 °C) further reduces the amount of this byproduct, but does not prevent its formation.



(1)

The NMR spectral characteristics of compounds **6** and **7** are very similar, differing only in the signals associated with the alkyl ligands and minor chemical shift changes for the ureate signals. The ^{1}H NMR spectra contain single resonances for each type of proton, including those of the isopropyl groups attached to the distal ureate nitrogen; ^{13}C NMR spectroscopy reveals a similar high degree of magnetic equivalence. This indicates not only high molecular symmetry but also fast rotation about the iPr$_2$N−C bond, suggesting reduced π-donation by the distal nitrogen atoms. In order to compare this solution-phase behavior with solid-state structural parameters, we sought to apply X-ray crystallographic characterization. Repeated attempts to grow single crystals of compound **6** resulted in microcrystalline material that gave weak diffraction patterns; however, single crystals of compound **7** were obtained from a cold pentane solution. The solid-state molecular structure of **7** is shown in Figure 4, confirming the ligand arrangement about zirconium. The complex is six-coordinate, with the four donor atoms of the bis(ureate) ligand in a planar arrangement. As for **5**, there is no immediately obvious six-coordinate geometry to which this complex conforms; it is therefore best described as distorted tetrahedral (average C−Zr−C′ angle: 109.33(6)°, average deviation: 9.71°). An examination of the metrical parameters of complex **7** once again reveals evidence of π-electron donation by the distal nitrogens (sp^2-hybridized nitrogens, electron delocalization, coplanar arrangement), in contrast to the solution-phase behavior noted above. These conflicting facts suggest that while electron donation by the distal nitrogen atoms may occur, it is not strong enough to prevent rotation about the iPr$_2$N−C bond in solution. It should be noted that analogous tethered bis(amidate) dibenzyl complexes of zirconium and hafnium are only isolable as the THF adducts.[13]

Given the challenges encountered previously in the preparation of tethered bis(amidate) zirconium benzyl complexes,[10b,13] the isolation of base-free, monometallic, nonfluxional complexes **6** and **7** points to a significant difference between the stabilization afforded by amidates and ureates. In order to further compare these ligand sets, biaryl-tethered proligand **3**, analogous to the proligands used by Scott and co-workers,[10b] was used to prepare zirconium dialkyl compounds **8** and **9** in 75% and 54% recrystallized yield (eq 2). ^{1}H NMR spectroscopy indicates that the ligand binds in a C_2-symmetric fashion, as the methyl groups attached to the biaryl tether are equivalent. The methylene protons of the Zr−CH_2R group resonate as an AB quartet in both cases, due to the axial chirality of the ureate ligand. ^{13}C NMR spectra of **8** and **9** contain a single resonance for the ureate carbon at ∼168 ppm, diagnostic of a κ^2-chelating binding mode. All of these spectral features are in striking contrast to those observed previously for biaryl-tethered bis(amidate) benzyl compounds.

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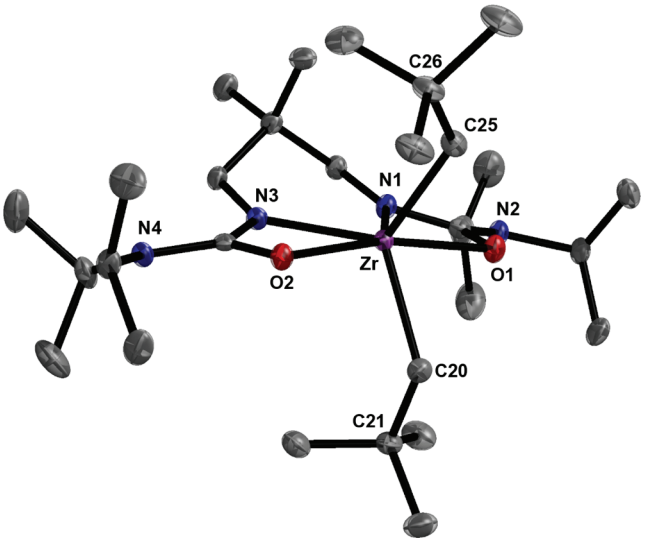
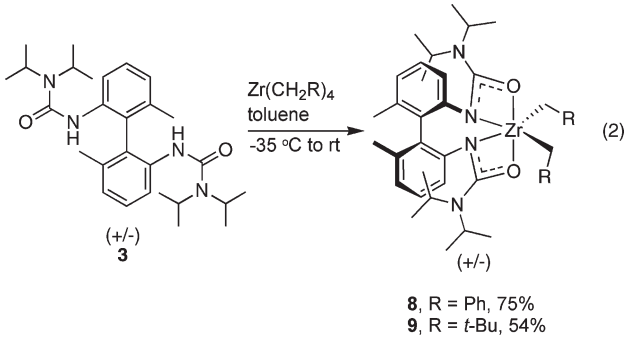


Figure 4. ORTEP representation of the molecular structure of **7** (ellipsoids plotted at 50% probability, hydrogens removed for clarity) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 2.193(2); Zr−N3, 2.183(1); Zr−O1, 2.208(1); Zr−O2, 2.240(1); Zr−C20, 2.266(2); Zr−C25, 2.259(2); C1−N1, 1.331(2); C1−O1, 1.295(2); C1−N2, 1.351(2); N1−Zr−O1, 59.32(4); N1−Zr−N3, 76.33(5); average angle between C−Zr−C′, 109.3(6); Zr−C20−C21, 123.8(1); Zr−C25−C26, 130.7(1); sum of angles about N2, N4: 359.5(3), 359.2(3); N1−C1−N2−C5: 14.7(3).



(2)

A major difference in the solution-phase behavior between the alkyl-tethered complexes (**6**, **7**) and the biaryl-tethered complexes (**8**, **9**) is in the disposition of NMR signals corresponding to the diisopropylamino substituents on the ureate chelate. As noted above, fast rotation about the iPr$_2$N−C bond on the NMR time scale is observed for **6** and **7**, resulting in equivalent methyl and methine protons. The ^{1}H NMR signals for isopropyl groups in **8** and **9**, however, are inequivalent and broad. The two sets of methine resonances are separated by ∼1 ppm. The methyl signals are similarly separated, with the upfield resonance (centered around δ 0.75) further split into two broad, overlapping signals. This splitting of the upfield isopropyl methyl resonance is presumably due to the chiral environment about the metal center, rendering these methyl groups diastereotopic. The isopropyl carbons appear as very broad resonances in the ^{13}C NMR spectra, preventing a reliable chemical shift assignment in the case of **8**. These observations are indicative of

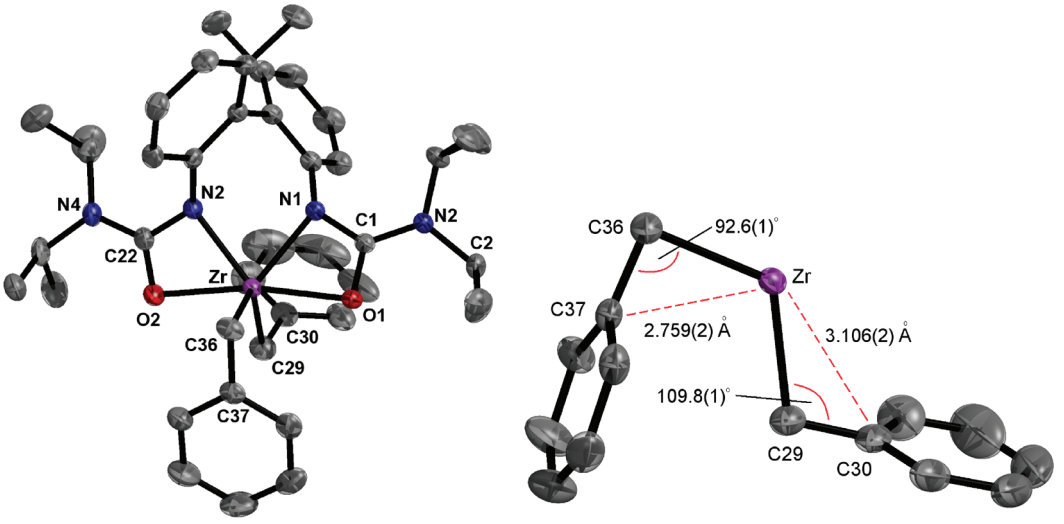


Figure 5. ORTEP representation of the molecular structure of **8** (left) and abbreviated structure showing η^2-benzyl interaction (right) (ellipsoids plotted at 50% probability, hydrogens removed for clarity) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 2.195(1); Zr−N3, 2.183(1); Zr−O1, 2.221(1); Zr−O2, 2.257(1); Zr−C25, 2.265(2); Zr−C29, 2.282(2); C1−N1, 1.334(2); C1−O1, 1.294(2); C1−N2, 1.346(2); N1−Zr−O1, 59.31(5); N1−Zr−N3, 75.34(5); average angle between C−Zr−C′, 109.8(6); Zr−C29−C30, 109.8(1); Zr−C36−C37, 92.6(1); sum of angles about N2, N4: 359.6(3), 359.2(3); N1−C1−N2−C5: 14.3(3).

slow rotation about the iPr$_2$N−C bond, in stark contrast to the situation for **6** and **7**. There are two possible explanations for this difference: first, greater steric compression by the biaryl tether relative to the alkyl tether hinders rotation about this bond; and second, the electron-withdrawing aromatic substituents on the ureate nitrogen induce a greater degree of π-donation by the diisopropylamino lone pair.

Single crystals of **8** were deposited from a cold pentane solution; the solid-state molecular structure is shown in Figure 5 (left). The complex adopts a coordination geometry analogous to that of the alkyl-tethered complex **7** described above. Metrical evidence for π-donation from the iPr$_2$N group is also apparent. This further supports the electron-donation hypothesis for the hindered rotation about the iPr$_2$N−C bond observed in solution. One other noteworthy aspect of the structure of **8** is that one of the benzyl ligands adopts a formal η^2-bonding mode (Figure 5, right). The Zr−C−C angle (92.6(1)°) and Zr−C$_{ipso}$ distance (2.759(2) Å) are in the range of other reported η^2-interactions;[14] however, the second benzyl ligand is clearly η^1-bound. Due to the lack of solution-phase NMR spectroscopic evidence for η^2-benzyl ligands, we propose that this interaction is not maintained in solution and that both benzyls be considered as time-averaged η^1-ligands. Single crystals of complex **9** were also obtained, although the crystal morphology (leaf) led to a weak diffraction pattern. However, based on the similar solution-phase spectroscopic features, we propose that **9** is structurally analogous to **8**.

Formation of Pyridine Adducts. The isolation of tethered bis(ureate) zirconium complexes **6**−**9** as stable, monometallic, donor-free dialkyls is remarkable given the difficulties associated with related tethered bis(amidate) complexes.[10b,13] Other titanium and zirconium complexes supported by the alkyl-tethered bis(ureate) derived from proligand **2** have been isolated as base-stabilized, seven-coordinate species, even when electron-rich amido ligands are present.[10a,11] We have therefore tested whether the dialkyls described above constitute coordinatively saturated species or if the presence of a neutral donor would readily generate seven-coordinate complexes. Addition of excess pyridine (>2 equiv) to C_6D_6 solutions of compounds **6**−**9** results in an immediate color change from colorless to bright orange. In each case, the ^{1}H NMR spectra contain broad signals for the *ortho*-protons of the pyridine centered at δ 8.65, which is close to that of free pyridine (δ 8.53). On the basis of this relatively unperturbed chemical shift and the absence of clear signals that would correspond to a coordinated pyridine molecule, we propose that fast neutral ligand exchange occurs on the NMR time scale. For biaryl-tethered ureate complexes **8** and **9**, the resonances corresponding to the isopropyl protons become sharp and well resolved after pyridine addition, in contrast to the signals observed for the parent complexes. In particular, the broad signals for the isopropyl methyl groups resolve into two sets of nearly overlapping doublets, which integrate for 12 protons each. This further splitting occurs due to the chiral environment about zirconium, as proposed above for complexes **8** and **9**. The pyridine adducts formed in this manner are surprisingly thermally robust: heating a solution of **9** in the presence of five equivalents of pyridine to 110 °C for several hours results in no detectable decomposition.

While the above spectroscopic experiments strongly suggest the formation of seven-coordinate, pyridine-stabilized complexes, they do not give an indication of the exact nature of these species. Therefore, complexes **6-py** and **8-py** were prepared on a larger scale by the reaction of **2** or **3** with Zr(CH$_2$Ph)$_4$ in the presence of a slight excess of pyridine; the compounds were recrystallized in 70% and 49% yield. These pyridine-stabilized alkyls are stable to ambient heat and light under an inert atmosphere for months. The NMR spectra of **6-py** and **8-py** contain similar features to those observed in the aforementioned small-scale reactions; however, the pyridine *ortho*-proton signals are shifted downfield to δ 9.38 for **6-py** and δ 8.85 for **8-py**. Signals for free pyridine are not observed, suggesting that in the absence of excess pyridine, ligand exchange and/or loss does not occur or that the equilibrium heavily favors the seven-coordinate species. Furthermore, subjecting solid **6-py** and **8-py** to high vacuum for 24 hours at room temperature does not remove the pyridine donor.

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Table 1. Crystallographic Parameters

	5	7	8	6-py	8-py	10	11
formula	$C_{59}H_{92}N_6O_3Zr$	$C_{29}H_{60}N_4O_2Zr$	$C_{42}H_{54}N_4O_2Zr$	$C_{43}H_{69}N_5O_2Zr$	$C_{47}H_{59}N_5O_2Zr$	$C_{41}H_{65}N_7O_2Zr$	$C_{62}H_{110}N_{10}O_4Zr_2$
fw	1024.61	588.03	738.11	779.25	817.21	779.22	1242.04
cryst size (mm)	1.00 × 0.80 × 0.50	0.50 × 0.50 × 0.30	0.80 × 0.50 × 0.40	0.25 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.40 × 0.40 × 0.20	1.00 × 0.70 × 0.20
color, habit	colorless, prism	colorless, prism	yellow, prism	orange, irregular	orange, block	orange, prism	yellow, oval
cell setting	trigonal	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P63$	$P21/c$	$P21/c$	$P\bar{1}$	$C2221$	$P21/n$	$P21/n$
a (Å)	24.5106(9)	13.7893(4)	11.7720(8)	12.697(1)	15.151(2)	13.7003(5)	12.8587(8)
b (Å)	24.5106(9)	15.7596(4)	15.169(1)	13.748(1)	18.936(3)	20.8396(7)	29.109(2)
c (Å)	18.9897(7)	15.9037(4)	22.643(2)	14.213(1)	15.576(3)	15.3980(5)	18.121(1)
α (deg)	90	90	90	69.300(4)	90	90	90
β (deg)	90	107.1760(10)	101.173(3)	69.631(4)	90	94.5140(10)	91.361(3)
γ (deg)	120	90	90	78.194(4)	90	90	90
V(Å^3)	9879.7(2)	3301.96(15)	3966.7(5)	2166.4(3)	4468.8(12)	4382.6(4)	6780.8(8)
Z	6	4	4	2	4	4	4
ρ_{calcd} (g cm^{-1})	1.033	1.173	1.236	1.195	1.215	1.181	1.217
radiation	Mo Kα (λ = 0.71073 Å)						
F(000)	3312	1252	1560	836	1728	1664	2656
μ (Mo Kα) (cm^{-1})	2.08	3.61	3.16	2.93	2.87	2.91	3.57
$2\theta_{max}$ (deg)	50.04	55.00	60.22	55.82	70.72	49.98	54.98
total no. of reflns	99 073	24 563	45 994	31 903	16 782	24 316	59 909
no. of unique reflns	11 533 (R_{int} = 0.0566)	7524 (R_{int} = 0.0315)	11 674 (R_{int} = 0.0343)	9956 (R_{int} = 0.0242)	7914 (R_{int} = 0.0144)	7144 (R_{int} = 0.1084)	15 448 (R_{int} = 0.0273)
no. of reflns with $I = 2\sigma(I)$	9273	6040	8888	8848	7172	4741	12 859
no. of variables	638	357	452	462	255	474	731
R_1 (F^2, all data)	0.0424	0.0423	0.0556	0.0426	0.0321	0.1395	0.0433
wR_2 (F^2, all data)	0.0792	0.0666	0.0890	0.0989	0.0697	0.1319	0.0768
R_1 (F, $I = 2\sigma(I)$)	0.0310	0.0278	0.0340	0.0354	0.0257	0.0364	0.0306
wR_2 (F, $I = 2\sigma(I)$)	0.0764	0.0619	0.0773	0.0933	0.0645	0.0919	0.0699
goodness of fit	0.973	1.021	1.031	1.065	1.091	1.064	1.049

The molecular structures of both **6-py** and **8-py** as determined by X-ray crystallography are shown in Figures 6 and 7, respectively. In each case, the complex is seven-coordinate, C_2-symmetric, distorted pentagonal bipyramidal, with the benzyl ligands in a *trans*-disposition about the metal center; the equatorial plane is comprised of the ureate ligand and the pyridine donor. The ureate has undergone little structural reorganization from the six-coordinate complexes characterized above, with Zr−N and Zr−O bond distances that are basically unchanged. The zirconium−pyridine distances are quite short (2.378(1) and 2.397(2) Å), approaching the zirconium−benzyl lengths (2.350(1)−2.373(2) Å). Comparing the Zr−C distances between **8** and **8-py** reveals a significant lengthening (0.068−0.085 Å), due to the increased electron count of the pyridine adduct. Neither **6-py** nor **8-py** shows any evidence of η^2-benzyl interactions.

Use of Organometallic Precursors in the Synthesis of Imido Complexes. Group 4 imidos are an important class of compounds that exhibit remarkable stoichiometric reactivity, including [2+2] cycloadditions with a variety of unsaturated organic substrates,[15] and hydrocarbon C−H activation.[16] Furthermore, they have been implicated as key catalytic intermediates in a variety of group 4 catalyzed organic transformations, including imine metathesis,[17] carboamination,[18] hydroamination,[8b,d,e,i,15,19] and hydroaminoalkylation.[20] Several synthetic routes have been applied to the synthesis of these

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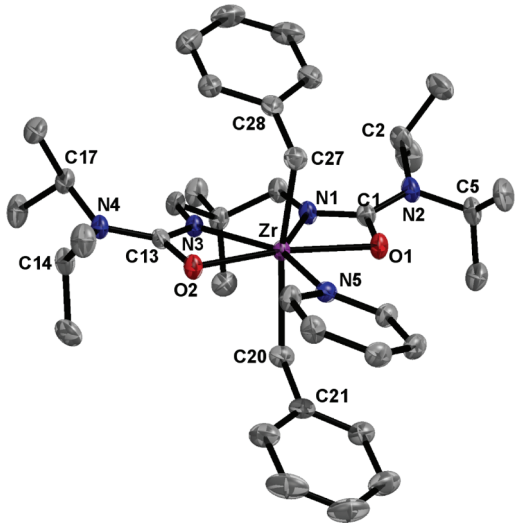

Figure 6. ORTEP representation of the molecular structure of **6-py** (ellipsoids plotted at 50% probability, hydrogens and pentane solvent removed for clarity) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 2.177(2); Zr−N3, 2.186(1); Zr−N5, 2.397(2); Zr−O1, 2.216(1); Zr−O2, 2.197(2); Zr−C20, 2.365(2); Zr−C27, 2.373(2); C1−N1, 1.326(2); C1−O1, 1.300(2); C1−N2, 1.360(3); N1−Zr−O1, 59.49(6); N1−Zr−N3, 77.56(6); C20−Zr−C27, 156.54(8); C20−Zr−N5, 80.02(7); C27−Zr−N5, 76.59(7); Zr−C20−C21, 126.7(2); Zr−C27−C28, 108.2(1); sum of angles about N2, N4: 359.8(6), 360.0(6); N1−C1−N2−C2: 22.9(3).

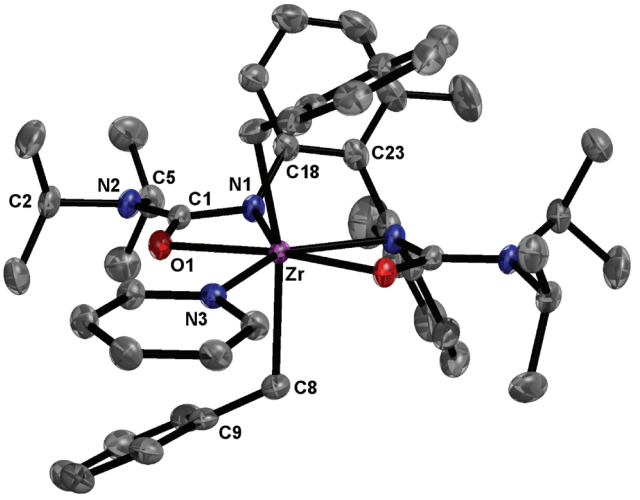

Figure 7. ORTEP representation of the molecular structure of **8-py** (ellipsoids plotted at 50% probability, hydrogens removed for clarity) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 2.200(1); Zr−N3, 2.378(1); Zr−O1, 2.1965(9); Zr−C8, 2.350(1); C1−N1, 1.356(2); C1−O1, 1.283(2); C1−N2, 1.337(2); N1−Zr−O1, 60.06(4); N1−Zr−N1*, 79.13(4); C8−Zr−C8*, 154.83(5); C8−Zr−N3, 77.42(5); Zr−C8−C9, 117.3(1); sum of angles about N2: 359.4(3); N1−C1−N2−C5: 20.4(2); C18−C23−C23*−C18*: 68.5(2).

species,[21−25] most involving salt metathesis reactions.[21−23] Mountford and co-workers have developed titanium and zirconium starting materials of the form $M(NR)Cl_2py_2$, which provide a convenient source of the metal−imido fragment.[21] Through treatment of these starting materials with alkali-metal salts of a variety of ancillary ligands, many group 4 imido complexes have been successfully prepared.[22] Another common route involves a two-step process, in which an amido species of the form $L_nM(NHR)(R')$ is generated by salt metathesis, followed by thermally induced α-proton abstraction to give $L_nM(NR)$ and R′H.[16,23]

An alternate method to synthesize group 4 imido complexes is through direct aminolysis between bis(amido) or dialkyl compounds and one equivalent of a primary amine.[25] Previously, we have used this route to prepare several amidate-supported titanium and zirconium imides from $L_2M(NMe_2)_2$ precursors.[6,8d,8e] These imido complexes have been examined as models for catalytic hydroamination intermediates and are themselves effective precatalysts for the hydroamination of both alkynes and alkenes. Recently, we established that the tethered bis(ureate) complex $LZr(NMe_2)_2 \cdot HNMe_2$ (where L is the ureate ligand derived from proligand **2**) exhibits unique catalytic reactivity for a group 4 system with respect to hydroamination.[11] As part of our mechanistic investigations on this catalyst system, we sought to synthesize and characterize zirconium imido complexes supported by the same tethered bis(ureate) ligand and to investigate their reactivity patterns.

In contrast to the aforementioned synthesis of amidate-supported imides, attempts to prepare imido species from $LZr(NMe_2)_2 \cdot HNMe_2$ led to incomplete protonolysis even at elevated temperatures. In order to overcome this problem, dialkyl compound **6** was used as an alternate starting material. In protonolysis reactions, dialkyl compounds are superior to bis(amido)s due to the higher basicity of the alkyl ligands and the generation of inert hydrocarbon byproducts. Accordingly, treatment of **6** with one equivalent of 2,6-diisopropylaniline in the presence or absence of pyridine leads to the formation of monometallic (**10**) or dimeric (**11**) imido complexes (Scheme 2).

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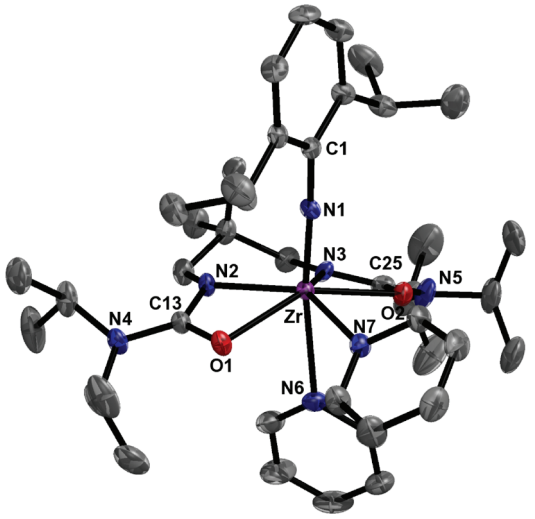
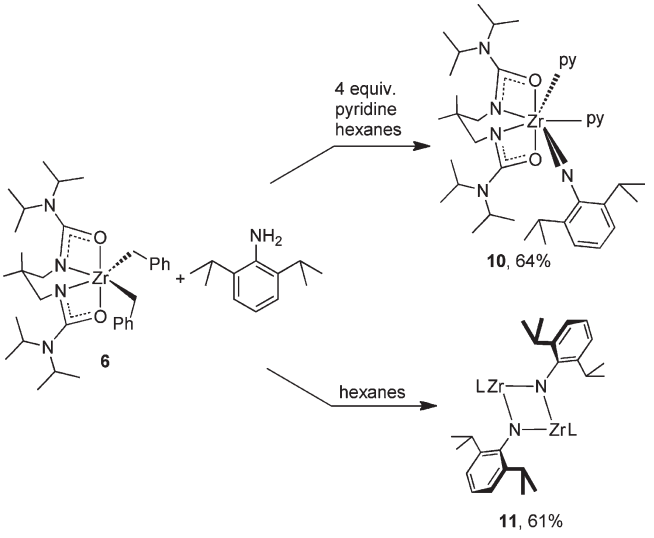


Figure 8. ORTEP representation of the molecular structure of **10** (ellipsoids plotted at 50% probability, hydrogens removed for clarity) with selected bond lengths (Å) and bond and torsion angles (deg): Zr−N1, 1.891(3); Zr−N2, 2.245(3), Zr−O1, 2.244(2); Zr−N6, 2.579(3); Zr−N7, 2.375(3); C13−N2, 1.322(4); C13−O1, 1.290(4); C13−N4, 1.369(4); N2−Zr−O1, 58.44(9); Zr−N1−C1, 177.6(3); O1−C13−N4−C14, 20.2(5).

Scheme 2. Synthesis of Monometallic and Dimeric Imido Complexes 10 and 11 through Aminolysis of Dibenzyl Compound 6



Each of the previously mentioned amidate-supported imido complexes have been stabilized by the presence of a neutral donor, either pyridine or triphenylphosphine oxide, facilitating their isolation and characterization. A similar strategy has therefore been employed in the preparation of complex **10**. Treatment of **6** with 2,6-diisopropylaniline and four equivalents of pyridine results in a red suspension that can be clarified by gentle heating. On standing overnight at room temperature, this solution yields an orange crystalline product (**10**, 64% yield). The solid-state molecular structure is shown in Figure 8, confirming the identity of **10** as a seven-coordinate, distorted pentagonal bipyramidal, monometallic imido complex. As for complex **7**, the ureate ligand adopts a planar arrangement. The two pyridine donors are *cis*-disposed, one in an equatorial position and the other axial. The imido ligand is axial, *trans* to the axial pyridine donor. The Zr−N1 distance of 1.891(3) Å and Zr−N1−C1 angle of 177.6(3)° are consistent with a zirconium−nitrogen triple bond, characteristic of an imido linkage. The pyridine that is *trans* to the imido is weakly bound (Zr−N6, 2.579(3) Å) due to the strong *trans*-influence of the −NAr ligand. A previously reported six-coordinate amidate-supported zirconium imido complex adopts a related pentagonal-pyramidal coordination geometry, with the imido group also in the axial position.[8e] In that case, the steric properties of the amidate ligands enable the isolation of a six-coordinate species.

Combustion analysis of the crystalline material confirms the empirical formula and purity of compound **10**; however, solution-phase NMR spectroscopy reveals a more complicated situation. The ^{1}H NMR spectrum of a solution of crystalline **10** indicates the presence of two compounds in a 1:1 ratio; in addition, two broad *ortho*-Py−H signals were observed, assigned to exchanging bound and free pyridine. The addition of excess pyridine (10 equivalents) to this solution increased the ratio of components to 2:1. After heating to 65 °C for one hour followed by cooling to room temperature, only one compound was observed, assigned as the monometallic imido **10**. The ^{1}H NMR spectral features of this compound after the above treatment are sharp and well resolved. The methyl groups on the alkyl tether are inequivalent, and the methylene protons diastereotopic, indicating different magnetic environments above and below the plane of the ligand. Relative ^{1}H NMR signal integrations confirm a 1:1 ratio between the ureate ligand and the imido fragment.

The solution-phase behavior of compound **10** allows us to consider that, while stable in the solid state, **10** is in equilibrium with a base-free, dimeric imido species (**11**) while in solution, even in the presence of a neutral donor. This tendency to dimerize may come as a result of the weak bond between the zirconium center and the pyridine *trans* to the imido and the sterically accessible nature of the bis(ureate) ligand. Considering the size of the substituent on the imido nitrogen, favorable dimer formation is remarkable; only three examples of dimeric group 4 imidos with this bulky aryl group have been reported.[21a,26] In order to confirm this dimerization hypothesis, **11** was independently synthesized by treating compound **6** with 2,6-diisopropylaniline in the absence of a neutral donor. Analytically pure crystals of **11** were isolated from the reaction mixture in 61% yield. On the basis of electron-impact mass spectrometry and X-ray crystallography (Figure 9), we have established that **11** is indeed a dimeric, base-free imido complex. Thus, ^{1}H NMR spectroscopy of **11** confirms its identity as the second component present in solution with the untreated compound **10**. Consistent with the anticipated reactivity of complex **11**, the treatment of this compound with an excess of pyridine and heat forms complex **10** in solution phase.

The molecular structure of **11** reveals that each zirconium center is six-coordinate, with distorted tetrahedral-type geometry as described above for **7** and **8**. One striking structural feature is unique to this complex: the bis(ureate) ligand distorts itself to accommodate the bulky aryl group on the imido nitrogens. Rather than adopting a planar conformation, as observed for every titanium or zirconium complex supported by this same ligand,[10a,11] the two ureate chelates bend upward, away from the 2,6-diisopropylphenyl group, while maintaining a tetradentate binding mode. Notably, treatment of either **10** or **11** with a variety of alkynes results in no reaction, in contrast with many other group 4 imido complexes that undergo [2+2]

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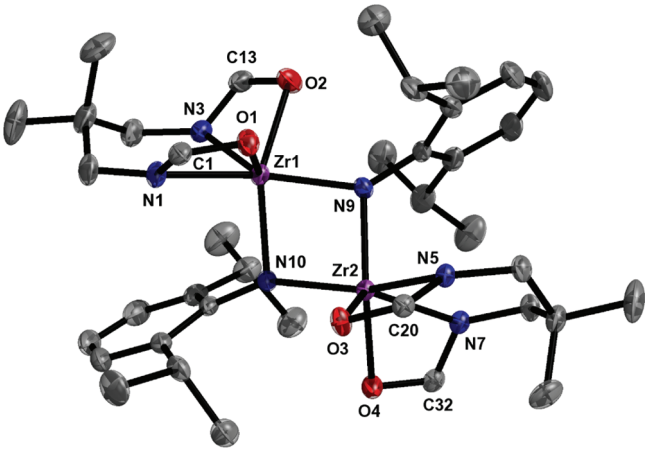

Figure 9. ORTEP representation of the molecular structure of **11** (ellipsoids plotted at 50% probability, hydrogens and N(*i*Pr)$_2$ groups removed for clarity) with selected bond lengths (Å) and angles (deg): Zr1−N1, 2.279(1); Zr1−N3, 2.243(1), Zr1−O1, 2.147(1); Zr1−O2, 2.192(1); Zr1−N9, 2.073(1); Zr2−N9, 2.125(1); Zr1−N10, 2.080(1); Zr2−N10, 2.089(1); C1−N1, 1.312(2); C1−O1, 1.314(2); C1−N2, 1.360(2); N1−Zr1−O1, 59.25(5); N1−Zr1−N3, 78.46(5); C1−Zr1−C13, 105.31(5); C1−Zr1−N9, 122.89(5); C1−Zr1−N10, 107.50(5); N9−Zr1−N10, 80.36(5); Zr1−N9−Zr2, 97.97(6).

cycloadditions with C−C unsaturations.[15] This lack of reactivity has implications for the mechanistic pathway of catalytic hydroamination using tethered ureate-supported complexes; these investigations are currently ongoing.

Summary and Outlook

The successful use of electron-rich ureates as supporting ligands for zirconium dialkyl fragments has been outlined here for a range of compounds. While the use of nontethered ureates has led to limited success in the isolation of discrete dialkyl species, tethered bis(ureate) ligands are effective supports for several derivatives. Despite the sterically accessible zirconium center in many of these complexes, fluxional behavior, ligand redistribution, and bridging interactions are not observed. The coordinatively unsaturated nature of dialkyl complexes with tethered bis(ureate) ancillary ligands has been established through their reaction with pyridine, resulting in adducts that exhibit stability relative to thermal and photochemical degradation. Finally, the utility of these compounds as starting materials for further organometallic synthesis has been demonstrated in the preparation of the first ureate-supported imido complexes. Interestingly, the resultant imido complexes are not viable for stoichiometric [2+2] cycloadditions with alkynes, despite the high catalytic activity for hydroamination exhibited by related bis(amido) complexes. Given the unique reactivity exhibited by many related group 4 amidate and ureate complexes, we are currently exploring the use of this family of compounds as catalysts for carbon−element bond forming reactions. Particularly relevant in this regard are complexes derived from chiral proligand **3**, which could be applied to enantioselective catalysis. The results of these and related studies will be reported in due course.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry, oxygen-free dinitrogen using a glovebox or standard Schlenk techniques unless otherwise noted. Dichloromethane was distilled from calcium hydride. Tetrahydrofuran, toluene, hexanes, and pentane were purified and dried by passage through a column of activated alumina and sparged with dinitrogen. d_6-Benzene and d_8-toluene were degassed by several freeze−pump−thaw cycles and dried over activated 4 Å molecular sieves for at least 24 hours before use in NMR experiments. All common organic reagents were purchased from Aldrich and either used as received (for proligand synthesis) or distilled from calcium hydride and stored under an inert atmosphere (for reaction with Zr complexes). $ZrCl_4$ was purchased from Strem and used as received. Proligands **1** and **2** were synthesized as previously reported.[10a] The zirconium starting materials $Zr(CH_2Ph)_4$[4d] and $Zr(CH_2CMe_3)_4$[4b] were prepared as described in the literature. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker 300 or 400 MHz Avance spectrometer; chemical shifts are given relative to residual protio solvent at 298 K unless otherwise noted. All ^{13}C NMR spectra were obtained as proton-decoupled. Mass spectra were recorded on 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 on 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 and Mr. Neal Yonson.

Synthesis of Proligand 3. 2,2′-Diamino-6,6′-dimethylbiphenyl (4.20 g, 19.8 mmol) was dissolved in dichloromethane (40 mL). The solution was cooled to 0 °C prior to the addition of pyridine (3.91 g, 4.17 mL, 49.5 mmol), followed by the addition of phenyl chloroformate (6.52 g, 5.24 mL, 41.6 mmol). The solution was left to warm to room temperature with stirring overnight. The reaction was quenched by the addition of 1 M HCl (50 mL). The organic layer was separated and washed with a further portion of 1 M HCl (50 mL) and brine (50 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave the bis(phenylcarbamate) as an off-white solid (8.55 g, 4.78 mmol, 96% yield), which was used in the next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.01 (6H, s, 2 × −C*H*$_3$), 6.48 (2H, s, 2 × −N*H*−), 7.09 (4H, d, J = 7.8 Hz, 4 × Ph−*H*), 7.15−7.41 (10H, m, 6 × Ph−*H* and 4 × Ar−*H*), 8.14 (2H, d, J = 8.17 Hz, 2 × Ar−*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.8, 118.8, 122.7, 126.8, 127.3, 130.4, 130.7, 136.7, 138.6, 151.5, 152.8. MS(ESI): m/z 475 (M^+ + Na). The second step was performed without rigorous exclusion of air or moisture. The bis(phenylcarbamate) (8.55 g, 18.9 mmol) was dissolved in dimethylsulfoxide (50 mL). Diisopropylamine (4.02 g, 5.58 mL, 39.7 mmol) was added via syringe. The solution was stirred overnight at room temperature, during which time a solid product precipitated. Dichloromethane (75 mL) was added to clarify the suspension. The organic phase was washed successively with water (2 × 75 mL), 1 M HCl (75 mL), water (75 mL), 1 M NaOH (75 mL), and brine (75 mL). The organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified by recrystallization from a hexanes/ethyl acetate mixture to yield **3** as off-white crystals (7.58 g, 16.3 mmol, 86% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.92 (12H, d, J = 6.9 Hz, 2 × −CH(C*H*$_3$)$_2$), 0.94 (12H, d, J = 6.9 Hz, 2 × −CH(C*H*$_3$)$_2$), 1.93 (6H, s, 2 × −C*H*$_3$), 3.75 (4H, m, J = 6.9 Hz, 4 × −C*H*(CH$_3$)$_2$), 6.01 (2H, s, −N*H*−), 6.95 (2H, d, J = 7.5 Hz, 2 × Ar−*H*), 7.24 (2H, t, J = 7.9 Hz, 2 × Ar−H_{meta}), 8.21 (2H, d, J = 8.3 Hz, 2 × Ar−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.9, 20.9, 21.0, 44.9, 117.8, 124.0, 129.3, 137.3, 138.4, 154.3 (one quaternary carbon not observed). MS(ESI): m/z 467 (M^+ + H). Anal. Calcd for $C_{28}H_{42}N_4O_2$: C, 72.07; H, 9.07; N, 12.01. Found: C, 72.18; H, 9.00; N, 11.86.

Synthesis of 4. This reaction was performed with exclusion of ambient light. Proligand **1** (0.300 g, 1.042 mmol) and $Zr(CH_2Ph)_4$ (0.237 g, 0.521 mmol) were dissolved in THF (10 mL) at −78 °C in a foil-wrapped Schlenk tube. 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 0.265 g (60% yield) of **4** as colorless microcrystals. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.05−1.25 (12H, m, 2 × (−CH_2−)$_3$), 1.21 (12H, d, J = 7.2 Hz, 2 × CH(CH_3)$_2$), 1.45 (12H, d, J = 7.2 Hz, 2 × −CH(CH_3)$_2$), 2.46 (4H, s, Zr(CH_2-Ph)$_2$), 3.02 (8H, br m, 2 × (−CH_2−)$_2$N), 3.24 (4H, m, J = 6.8 Hz, 4 × CH(CH$_3$)$_2$), 6.96 (2H, m, Ar−H), 7.18 (6H, m, Ar−H), 7.25 (8H, m, Ar−H). ^{13}C NMR (C_6D_6, 100 MHz): δ 24.7, 25.3, 25.8, 26.6, 28.4, 45.9, 75.4, 121.5, 124.6, 126.0, 128.7, 141.5, 143.9, 147.2, 166.8. MS(EI): m/z 755 (M^+ − CH_2Ph); Anal. Calcd for $C_{50}H_{68}N_4O_2Zr$: C, 70.79; H, 8.08; N, 6.60. Found: C, 70.42; H, 8.12; N, 6.42.

Synthesis of 5. This reaction was performed with exclusion of ambient light. Proligand **1** (0.288 g, 1.00 mmol) and Zr(CH$_2$-CMe$_3$)$_4$ (0.188 g, 0.500 mmol) were dissolved in THF (10 mL) at −78 °C in a foil-wrapped Schlenk tube. 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 a few colorless crystals of **5** (yield not determined). ^{1}H NMR (C_6D_6, 400 MHz, 338 K): δ 1.30 (18H, br m, 3(−CH_2−)$_3$), 1.39 (27H, m, 3 × −CH(CH_3)$_2$) + C(CH_3)$_3$), 1.50 (18H, d, J = 9.3 Hz, 3 × −CH(CH_3)$_2$), 3.12 (12H, br m, 3(−CH_2−)$_2$N), 3.82 (6H, br m, 6 × CH(CH$_3$)$_2$), 7.22−7.30 (9H, m, Ar−H), neopentyl methylene protons obscured. ^{13}C NMR (C_6D_6, 100 MHz, CH$_2$ and C determined from DEPT): δ 24.9 (CH$_2$), 25.6, 26.7 (CH$_2$), 28.4, 35.0, 36.2 (C), 46.2 (CH$_2$), 82.2 (CH$_2$), 124.4, 125.1, 143.3 (C), 144.1 (C), 166.4 (C). MS(EI): m/z 951 (M^+ − CH$_2t$Bu). Satisfactory elemental analysis could not be obtained due to difficulty obtaining pure material in sufficient quantity.

Synthesis of 6. This reaction was performed with exclusion of ambient light. A foil-wrapped 20 mL scintillation vial was charged with Zr(CH$_2$Ph)$_4$ (0.228 g, 0.500 mmol) and a Teflon-coated stir bar. A separate vial was charged with **2** (0.178 g, 0.500 mmol). Toluene was added to both vials (5 mL each), and both solutions were cooled to −35 °C. The proligand solution was added dropwise to the stirring solution of Zr(CH$_2$Ph)$_4$. The resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo* and the crude solid redissolved in hexanes. The hexanes solution was filtered through Celite, concentrated, and cooled to −35 °C to give colorless microcrystals of **6** (0.245 g, 78% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.85 (6H, 2 × CH_3), 1.27 (24H, d, J = 6.7 Hz, 4 × CH(CH_3)$_2$), 2.47 (4H, s, Zr(CH_2Ph)$_2$), 2.94 (4H, s, 2 × CH_2), 3.49 (4H, sept, J = 6.7 Hz, 4 × CH(CH$_3$)$_2$), 7.05 (2H, t, J = 7.2 Hz, 2 × Ph−H_{para}), 7.39 (4H, t, J = 8.0 Hz, 4 × Ph−H_{meta}), 7.47 (4H, d, J = 7.2 Hz, 4 × Ph−H_{ortho}). ^{13}C NMR (C_6D_6, 100 MHz, CH$_2$ and C determined from DEPT): δ 21.9, 24.7, 35.8 (C), 46.8, 57.1 (CH$_2$), 62.0 (CH$_2$), 121.0, 128.3, 129.0, 144.6 (C), 170.0 (C); MS(EI) m/z 535 (M^+ − CH$_2$Ph). Anal. Calcd for $C_{33}H_{52}N_4O_2Zr$: C, 63.11; H, 8.35; N, 8.92. Found: C, 62.80; H, 8.43; N, 9.00.

Synthesis of 6-py. This reaction was performed with exclusion of ambient light. A foil-wrapped Schlenk tube was charged with Zr(CH$_2$Ph)$_4$ (0.639 g, 1.40 mmol) and a Teflon-coated stir bar. A separate tube was charged with **2** (0.500 g, 1.40 mmol) and pyridine (0.111 g, 118.3 μL, 1.40 mmol). Toluene was added to both flasks (10 mL each), and the Zr(CH$_2$Ph)$_4$ solution was cooled to −78 °C. The proligand solution was cannula transferred to the stirring solution of Zr(CH$_2$Ph)$_4$. The resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo* and the crude solid redissolved in hexanes. The hexanes solution was filtered through Celite, concentrated, and cooled to −35 °C to give orange crystals of **6-py** (0.687 g, 70% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.08 (6H, s, C(CH_3)$_2$), 1.37 (24H, d, J = 6.8 Hz, 4 × CH(CH_3)$_2$), 2.14 (4H, s, 2 × −CH_2Ph), 3.02 (4H, s, 2 × CH_2), 3.73 (4H, br m, 4 × CH(CH$_3$)$_2$), 6.81 (2H, t, J = 7.2 Hz, 2 × Ph−H_{para}), 6.89 (2H, t, J = 6.4 Hz, 2 × Py−H_{meta}), 6.94 (4H, d, J = 7.6 Hz, 4 × Ph−H_{ortho}), 7.04 (1H, t, J = 7.6 Hz, Py−H_{para}), 7.18 (4H, t, J = 7.6 Hz, 4 × Ph−H_{meta}), 9.38 (2H, br m, 2 × Py-H_{ortho}). ^{13}C NMR (C_6D_6, 100 MHz, CH$_2$ and C determined from DEPT): δ 22.1, 25.7, 36.1 (C), 46.7, 56.4 (CH$_2$), 58.3 (CH$_2$), 117.4, 123.7, 124.8, 127.4, 135.9, 147.9, 154.7 (C), 168.8 (C). MS-(EI): m/z 535 (M^+ − py, CH$_2$Ph). Anal. Calcd for $C_{38}H_{57}N_5O_2Zr$: C, 64.54; H, 8.12; N, 9.90. Found: C, 64.25; H, 8.28; N, 9.82.

Synthesis of 7. This reaction was performed with exclusion of ambient light. A foil-wrapped 20 mL vial was charged with Zr(CH$_2$CMe$_3$)$_4$ (0.211 g, 0.562 mmol) and a Teflon-coated stir bar. A separate vial was charged with **2** (0.200 g, 0.562 mmol). Toluene was added to both vials (5 mL each), and both solutions were cooled to −35 °C. The proligand solution was added dropwise to the stirring solution of Zr(CH$_2$CMe$_3$)$_4$. The resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo* and the crude solid redissolved in pentane. The pentane solution was filtered through Celite, concentrated, and cooled to −35 °C to give colorless crystals of **7** (0.225 g, 69% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.88 (6H, 2 × CH_3), 1.23 (4H, s, Zr(CH_2CMe$_3$)$_2$), 1.36 (24H, d, J = 6.7 Hz, 4 × CH(CH_3)$_2$), 1.53 (18H, s, Zr(CH$_2$-C(CH_3)$_3$), 3.12 (4H, s, 2 × CH_2N), 3.61 (4H, sept, J = 6.7 Hz, 4 × CH(CH$_3$)$_2$). ^{13}C NMR (C_6D_6, 100 MHz, CH$_2$ and C determined from DEPT): δ 22.1, 25.0, 34.9, 35.0 (C), 36.2 (C), 46.9, 57.5 (CH$_2$), 81.8 (CH$_2$), 170.4. MS(EI) gave no molecular ion or diagnostic fragments due to suspected instability to the ionization conditions. Anal. Calcd for $C_{29}H_{60}N_4O_2Zr$: C, 59.23; H, 10.28; N, 9.53. Found: C, 59.61; H, 10.45; N, 9.52.

Synthesis of 8. This reaction was performed with exclusion of ambient light. A foil-wrapped 20 mL scintillation vial was charged with Zr(CH$_2$Ph)$_4$ (0.195 g, 0.429 mmol) and a Teflon-coated stir bar. A separate vial was charged with **3** (0.200 g, 0.429 mmol). Toluene was added to both vials (5 mL each), and both solutions were cooled to −35 °C. The proligand solution was added dropwise to the stirring solution of Zr(CH$_2$Ph)$_4$. The resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo*, and the crude solid was redissolved in hexanes. The hexanes solution was filtered through Celite, concentrated, and cooled to −35 °C to give pale yellow crystals of **8** (0.237 g, 75% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.67−0.85 (12H, br m, 2 × −CH(CH_3)$_2$), 1.30−1.52 (12H, br m, 2 × −CH(CH_3)$_2$), 2.13 (6H, s, 2 × Ar−CH_3), 2.41 (4H, AB q, J = 9.9 Hz, Zr(CH_2Ph)$_2$), 2.99 (2H, br m, 2 × CH(CH$_3$)$_2$), 3.97 (2H, br m, 2 × −CH(CH$_3$)$_2$), 6.65 (2H, d, J = 7.7 Hz, 2 × Ar−H), 7.00 (2H, d, J = 7.4 Hz, 2 × Ar−H), 7.06 (4H, d, J = 7.5 Hz, 4 × Ph−H_{ortho}), 7.21−7.34 (8H, m, 2 × Ar−H + 4 × Ph−H_{meta} + 2 × Ph−H_{para}). ^{13}C NMR (C_6D_6, 100 MHz, CH$_2$ and C determined from DEPT): δ 19.7, 65.3 (CH$_2$), 119.9, 121.8, 124.6, 127.2, 128.7, 128.8, 132.1 (C), 137.0 (C), 143.9 (C), 145.3 (C), 168.3 (C), broad resonances (δ 15−50) for the isopropyl carbons are not assigned. MS(EI) gave no molecular ion or diagnostic fragments due to suspected instability to the ionization conditions. Anal. Calcd for $C_{42}H_{54}N_4O_2Zr$: C, 68.34; H, 7.37; N, 7.59. Found: C, 68.56; H, 7.77; N, 7.36.

Synthesis of 8-py. This reaction was performed with exclusion of ambient light. A foil-wrapped Schlenk tube was charged with Zr(CH$_2$Ph)$_4$ (0.195 g, 0.429 mmol) and a Teflon-coated stir bar. A separate tube was charged with **3** (0.200 g, 0.429 mmol) and pyridine (0.039 g, 36.1 μL, 0.43 mmol). Toluene was added to both flasks (10 mL each), and the Zr(CH$_2$Ph)$_4$ solution was cooled to −78 °C. The diurea solution was cannula transferred to the stirring solution of Zr(CH$_2$Ph)$_4$. This resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo* and the crude solid redissolved in hexanes. The hexanes solution was filtered through Celite, concentrated, and cooled to −35 °C to give orange crystals of **8-py** (0.171 g, 49% yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.75−0.82 (12H, br m, 2 × CH(CH_3)$_2$), 1.37−1.45 (12H, br m, 2 × CH(CH_3)$_2$), 1.85 (2H, d, J = 8.6 Hz, Zr−CH_2Ph), 1.96 (2H, d, J = 8.6 Hz, Zr−CH_2Ph), 2.17 (6H, s, 2 × Ar−CH_3), 3.00 (2H, br m, 2 × CH(CH$_3$)$_2$), 4.13 (2H, br m,

2 × C*H*(CH_3)$_2$), 6.39 (4H, m, 4 × Ar−*H*), 6.67 (4H, m, 4 × Ar−*H*), 6.90 (7H, m, 7 × Ar−*H*), 6.97 (2H, d, J = 7.3 Hz, 2 × Ar−*H*), 7.06 (2H, t, J = 7.6 Hz, 2 × Ar−*H*), 8.85 (2H, br m, 2 × Py−H_{ortho}). ^{13}C NMR (C_6D_6, 100 MHz, CH_2 and *C* determined from DEPT): δ 19.0, 20.9, 22.0, 22.5, 24.0, 46.4, 49.2, 62.9 (*C*H_2), 119.1, 120.0, 124.7, 125.4, 125.6, 128.1, 128.2, 133.0 (*C*), 136.4, 137.9 (*C*), 147.2 (*C*), 169.7 (*C*), one pyridine carbon not observed. MS(EI): m/z 645 (M^+ − py, CH_2Ph). Anal. Calcd for $C_{47}H_{59}N_5O_2Zr$: C, 69.08; H, 7.28; N, 8.57. Found: C, 69.32; H, 7.31; N, 8.58.

Synthesis of 9. This reaction was performed with exclusion of ambient light. A foil-wrapped 20 mL scintillation vial was charged with $Zr(CH_2CMe_3)_4$ (0.161 g, 0.429 mmol) and a Teflon-coated stir bar. A separate vial was charged with **3** (0.200 g, 0.429 mmol). Toluene was added to both vials (5 mL each), and both solutions were cooled to −35 °C. The proligand solution was added dropwise to the stirring solution of Zr-(CH_2CMe_3)$_4$. The resulting mixture was allowed to warm to room temperature with stirring overnight. The solvent was removed *in vacuo* and the crude solid redissolved in pentane. The pentane solution was filtered through Celite, concentrated, and cooled to −35 °C to give colorless leaf crystals of **9** (0.161 g, 54% yield); the crystal morphology was not conducive to X-ray diffraction analysis. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.70−0.88 (12H, br m, 2 × CH(C*H*$_3$)$_2$), 1.42 (18H, s, Zr(CH_2C(C*H*$_3$)$_3$)$_2$), 1.45 (4H, AB q, J = 12.2 Hz, Zr(C*H*$_2$CMe$_3$)$_2$), 1.57−1.68 (12H, br m, 2 × −CH(C*H*$_3$)$_2$), 2.11 (6H, s, 2 × Ar−C*H*$_3$), 3.12 (2H, br m, 2 × C*H*(CH_3)$_2$), 4.06 (2H, br m, 2 × −C*H*(CH_3)$_2$), 6.96 (4H, m, 4 × Ar−*H*), 7.09 (2H, t, J = 7.7 Hz, 2 × Ar−*H*). ^{13}C NMR (C_6D_6, 100 MHz): δ 18.3 (br), 19.7, 20.9 (br), 21.8 (br), 22.9 (br), 34.7, 35.1, 45.8 (br), 47.9 (br), 85.5, 119.8, 124.5, 126.9, 132.1, 137.0, 145.1, 168.0. MS(EI): m/z 625 (M^+ − CH_2CMe_3). Anal. Calcd for $C_{38}H_{62}N_4O_2Zr$: C, 65.37; H, 8.95; N, 8.03. Found: C, 65.31; H, 9.19; N, 7.99.

Synthesis of 10. Complex **6** (0.100 g, 0.159 mmol), 2,6-diisopropylaniline (0.0282 g, 30.1 μL, 0.159 mmol), and pyridine (0.0497 g, 53.0 μL, 0.637 mmol) were dissolved in hexanes with gentle heating. The solution was left to stand at room temperature overnight, during which time orange crystals of **10** formed. Yield: 0.079 g (64%). ^{1}H NMR (C_6D_6, 400 MHz, excess pyridine added): δ 0.93 (3 H, s, C*H*$_3$), 1.21 (12 H, d, J = 6.6 Hz, 2 × CH(C*H*$_3$)$_2$), 1.51 (12 H, d, J = 6.5 Hz, 2 × CH(C*H*$_3$)$_2$), 1.57 (15 H, d and obscured s, J = 6.9 Hz, 2 × CH(C*H*$_3$)$_2$ and C*H*$_3$), 3.43 (2 H, d, J = 11.6 Hz, C*H*$_2$), 3.65 (2 H, d, J = 11.6 Hz, C*H*$_2$), 3.82 (4 H, sept, J = 6.7 Hz, 4 × C*H*(CH_3)$_2$), 4.74 (2 H, sept, J = 6.9 Hz, 2 × C*H*(CH_3)$_2$), 6.79 (4 H, m, 4 × Py−*H*), 6.83 (1 H, t, J = 7.4 Hz, Ar−H_{para}), 7.11 (4 H, br m, 4 × Py−*H*), 7.26 (2 H, d, J = 7.6 Hz, 2 × Ar−H_{meta}), 8.60 (4 H, br m, 4 × Py−H_{ortho}). ^{13}C NMR (C_6D_6, 100 MHz, CH_2 and *C* assigned from DEPT, excess pyridine added): δ 22.4, 22.7, 25.7, 27.1, 27.4, 37.2 (*C*), 46.2, 57.7 (*C*H_2), 113.7, 121.4, 123.5, 135.5, 142.1 (*C*), 150.1, 154.7 (*C*), 164.2 (*C*). MS(EI): m/z 620 (M^+ − 2 py). Anal. Calcd for $C_{41}H_{65}N_7O_2Zr$: C, 63.20; H, 8.41; N, 12.58. Found: C, 62.97; H, 8.23; N, 12.65.

Synthesis of 11. Complex **6** (0.100 g, 0.159 mmol) and 2,6-diisopropylaniline (0.0282 g, 30.1 μL, 0.159 mmol) were dissolved in hexanes with gentle heating. The solution was left to stand at room temperature overnight, during which time colorless crystals of **11** formed. Yield: 0.060 g (61%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 0.67 (3H, s, C*H*$_3$), 0.78 (3H, s, C*H*$_3$), 1.05−1.45 (24H, br m, 4 × CH(C*H*$_3$)$_2$), 1.67 (12H, br m, 2 × CH(C*H*$_3$)$_2$), 2.80 (2H, br m, C*H*$_2$), 3.00 (2H, br d, J = 12 Hz, C*H*$_2$), 3.42 (4H, br m, 4 × C*H*(CH_3)$_2$), 4.38 (2H, br m, 2 × C*H*(CH_3)$_2$), 7.13 (1H, t, J = 7.6 Hz, Ar−H_{para}), 7.44 (2H, d, J = 7.6 Hz, 2 × Ar−H_{meta}). ^{1}H NMR (C_6D_6, 400 MHz, 343 K): δ 0.72 (6H, br s, 2 × C*H*$_3$), 1.24 (24H, br m, 4 × CH(C*H*$_3$)$_2$), 1.61 (12H, d, J = 6.8 Hz, 2 × CH(C*H*$_3$)$_2$), 2.90 (4H, br m, 2 × C*H*$_2$), 3.49 (4H, sept, J = 6.8 Hz, 4 × C*H*(CH_3)$_2$), 4.34 (2H, sept, J = 6.8 Hz, 2 × C*H*(CH_3)$_2$), 7.04 (1H, t, J = 7.6 Hz, Ar−H_{para}), 7.37 (2H, d, J = 7.6 Hz, 2 × Ar−H_{meta}). ^{13}C NMR (C_6D_6, 100 MHz, 298 K, CH_2 and *C* assigned from DEPT): δ 20.8 (br), 22.6 (br), 23.7 (br), 24.0, 26.0, 27.4 (br), 38.4 (*C*), 47.2 (br), 57.0 (br, *C*H_2), 118.4, 121.9, 153.1 (*C*), two quaternary carbons not observed. ^{13}C NMR (C_6D_6, 100 MHz, 343 K): δ 21.0−22.8 (br), 24.1, 28.5 (br), 38.3, 47.2, 57.1, 118.4, 121.9, 138.1, 153.2, 170.0. MS(EI): m/z 1240 (M^+), 620 (LZrNAr$^+$). Anal. Calcd for $C_{62}H_{110}N_{10}O_4Zr_2$: C, 59.95; H, 8.93; N, 11.28. Found: C, 60.08; H, 8.85; N, 11.22.

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Supporting Information Available: Representative NMR spectra for new compounds and CIF for solid-state molecular structures. This material is available free of charge via the Internet at http://pubs.acs.org.