Synthesis and NHC Lability of d^0 Lithium, Yttrium, Titanium, and Zirconium Amido Bis(N-heterocyclic carbene) Complexes

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The synthesis of lithium(I) complexes of the neutral and anionic salts of a tridentate aminobis(N-heterocyclic carbene) ligand, L, are reported (L = $N\{CH_2CH_2(1\text{-}C[NCHCHNMes])\}_2$), along with the X-ray diffraction determined molecular structure of the imidazolium proligand $[H_2N\{CH_2CH_2(1\text{-}HC\text{-}[NCHCHNMes])\}_2][Br]_3$ (H_4LBr_3). The transamination reaction between the lithium chloride adduct of HL and $Y[N\{SiMe_3\}_2]_3$ affords yttrium amidocarbene complexes, while the transamination reaction between the imidazolium proligand and $Ti(NMe_2)_4$ or $Zr(NMe_2)_4$ affords a titanium or zirconium amidocarbene complex, respectively. The molecular structure of one of the yttrium products, $Y(L)(N\{SiMe_3\}_2)Cl$, is reported. The reactivity of a selection of the complexes with phosphine oxides is compared.

1. Introduction

N-heterocyclic carbenes (NHCs) have been widely used as replacements for phosphines as supporting σ-bases in homogeneous late-metal catalyst systems and as rate-accelerating additives in organic reactions catalyzed by Lewis acidic metal cations.[1] There are few examples of functionalized NHC complexes of early-transition-metal complexes.[2−5]

We have been studying the chemistry of NHC ligands with an incorporated anionic functional group, to allow us to isolate discrete carbene complexes of Lewis acidic transition-metal cations and lanthanides. We have found that the group 1 salts of alkoxide, amide, and amino-functionalized NHC ligands can be readily synthesized to form kinetically inert complexes.[6−10] We have also demonstrated that these tethered NHCs can readily be bound to d^0 early transition metals such as yttrium and titanium and also to lanthanides and actinides.[2,11−13]

We have previously described a simple, one-pot route to the proligand of the tridentate aminocarbene ligand HL (L = $N\{CH_2CH_2(1\text{-}C[NCHCHNMes])\}_2$) and its ability to form linear 1D chains with silver halides, $[Ag(HL)X]_2$ (**A**; X = Cl, Br) (Chart 1).[14] One other potentially tridentate aminodicarbene ligand has also been reported by Douthwaite et al.,[15] an *N-tert*-butyl-functionalized analogue prepared via a multistep synthesis. The amido complex was prepared by NH deprotonation subsequent to palladium(II) coordination, affording $[(N\{CH_2CH_2(C[NCHCHNBu^t])\}_2)PdCl]$ (**B**). For the study of group 4 metals, Fryzuk has also recently reported diamidocarbene ligands, which, tethered to the metal by two amido groups, form more rigid tridentate ligands in which the metal−NHC binding is enforced by the chelate, **C**.[16,17] Bis(phenolate) ligands with a central donor carbene group have also been reported, and the alkene polymerization reactivity of the titanium and zirconium complexes has been described.[18,19] No group 3 or f-block chemistry of ligands containing tridentate NHC-containing ligands has yet been reported.

Here, we describe the use of lithium bases to prepare lithium chloride adducts of HL and L^-. We also report the generation of yttrium(III), titanium(IV), and zirconium(IV) L adducts formed through transamination chemistry. The molecular structures of one of the yttrium amidodicarbene complexes and of the proligand are also reported.

2. Results and Discussion

2.1. Lithium Adducts of L. Treatment of a colorless suspension of H_4LCl_3 (**1**) in THF with 3 molar equiv of a lithium *n*-butyl solution in hexanes at −30 °C affords a pale, cloudy, straw-colored slurry which slowly dissolves as the reaction mixture is stirred at this temperature. After 4 h, the reaction mixture is now a straw-colored solution, from which the lithium aminodicarbene chloride complex $(LiCl)_3{\cdot}NH\{CH_2CH_2\text{-}$

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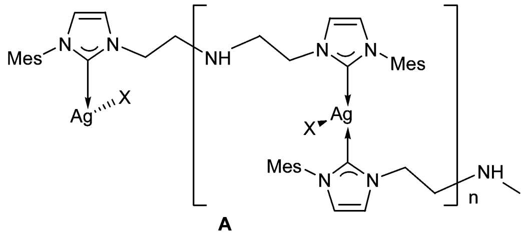
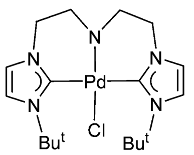
Chart 1



A



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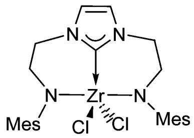
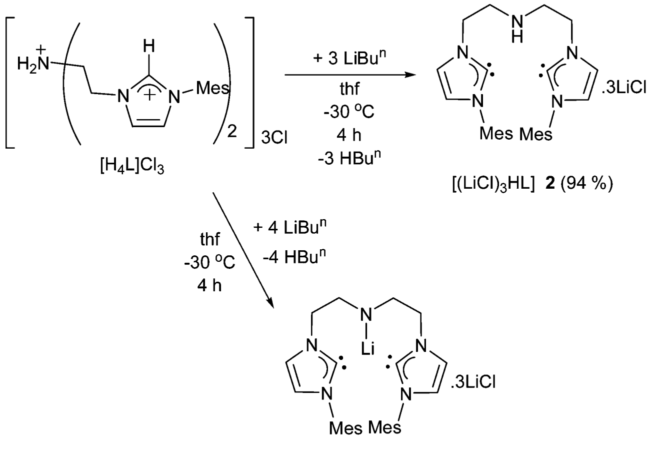


C

Scheme 1



$[H_4L]Cl_3$

$[(LiCl)_3HL]$ **2** (94 %)

$[(LiCl)_3LiL]$ **3** (88 %)

(C[NCHCHNMes])}$_2$ (**2**; [(LiCl)$_3$HL]) may be isolated after removal of volatiles under reduced pressure and washing of the cream-colored powder with diethyl ether (Scheme 1).

Complex **2** has been characterized by multinuclear NMR spectroscopy and elemental analysis. Although we have been unable to grow single crystals suitable for an X-ray diffraction experiment to date, comparison of the physical properties of **2** with those of previous lithium halide NHC adducts synthesized within the group would suggest formation of a cluster of lithium chloride ions with Li−carbene bonds and NH−chloride hydrogen-bonding interactions at the surface of the cluster. Deprotonation of **1** with 4 equiv of lithium *n*-butyl affords cream-colored **3**, the lithium amide salt, as a powdery solid, which also retains the LiCl but is soluble in THF. Attempts to remove the lithium chloride by solvent extraction (diethyl ether and toluene) are successful in removing the salt but so far always result in ligand decomposition.

2.2. X-ray Crystal Structure of the Proligand Salt 1a. We have been able to determine the structure of the bromide analogue of **1**, [H$_4$L]Br$_3$ (**1a**) (Figure 1), from a single-crystal X-ray diffraction study. The bromide **1a** was made from a reaction to form **1** from the bis(bromoethyl)amine instead of the chloride.

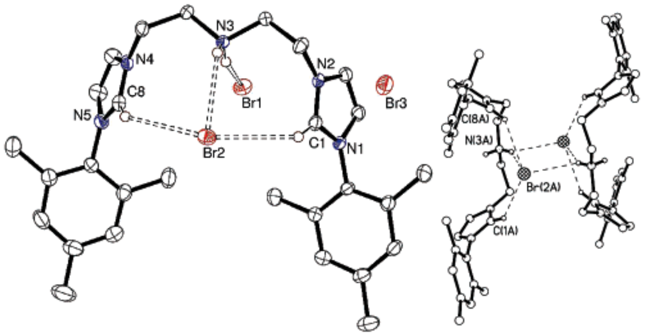
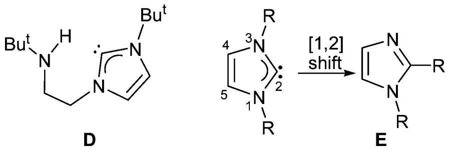


Figure 1. Views of [H$_4$L]Br$_3$ (**1a**): (left) displacement ellipsoid drawing of the molecular structure, showing intramolecular H-bonding interactions with the bromide counterions; (right) part of the dimeric structure formed by hydrogen-bonding interactions with Br2. Lattice solvent and non-NH or imidazolium CH hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): C(1)−N(1) = 1.332(3), C(1)−N(2) = 1.333(3); N(1)−C(1)−N(2) = 108.7(2).

Chart 2



D **E**

The solid-state structure of **1a** is C-shaped; the backbone diethylamine group curves to generate an approximately C_{2v}-symmetric ligand in which the two imidazolium groups point toward the same bromide ion, Br2, with hydrogen-bonding interactions suggested by the calculated distances H1−Br2 = 3.599 Å, and H8−Br2 = 2.899 Å. The central ammonium group also forms a hydrogen bond to this bromide (H2n−Br2 = 2.725 Å) and to another bromide (H1n−Br1 2.351 Å), which forms an additional hydrogen bond with a lattice chloroform CH (H30−Br1 = 2.490 Å). The remaining bromide, Br3, shows several close contacts with aliphatic ligand CH groups and, notably, a contact with one carbene carbon, C8, at a normal angle to the ring plane, in line with the π-system, at a distance of 3.365 Å.

The thermal instability of the free base HL and the lithium salt LiL surprised us, since we can distill the aminomonocarbene ligand *t*-BuNHCH$_2$CH$_2${C(NCHCHN-*t*-Bu)} (**D**; Chart 2) at 100 °C, with analytical purity, in good yield. Reactions at room temperature and higher to deprotonate H$_4$LCl$_3$ using the same lithium bases have so far yielded only intractable materials, which we characterize as products of unselective ligand deprotonations. The most facile, and thus anticipated, decomposition route for these carbene ligands is via a [1,2]-migration of the N-hydrocarbyl group, to form products of type **E** (Chart 2), but we see no evidence of rearranged carbenes in the NMR spectra.[20−22] We also note that ligands with relatively acidic C−H groups in the position α to the ring are often decomposed by only mildly basic reagents.[23]

Despite the fragility of the free base HL, we have been able to explore chemistry to make both group 3 and group 4 adducts of monoanionic L from the lithium chloride adducts of HL and LiL.

2.3. Yttrium Adducts of L. Treatment of the aminodicarbene [(LiCl)$_3$HL] with stoichiometric YN″$_3$ (N″ = N(SiMe$_3$)$_2$) in tetrahydrofuran affords a cream-colored solution from which YLClN″ (**4**) can be isolated as colorless needles by extraction with and then recrystallization from diethyl ether, in 49% yield. NMR spectroscopy and elemental analysis confirm the retention

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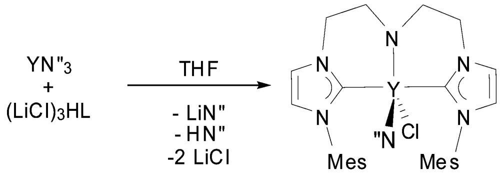
of only one silylamido N'' anion in the product **3** and the elimination of Li'' as well as HN'' as byproducts, observed by ^1H NMR spectroscopy (eq 1).



4 (49 %) **(1)**

The ^1H NMR spectrum of **4** in d_6-benzene shows four distinct CH_2 resonances arising from distinct environments of the two ligand ethylene groups, at 3.07, 3.47, 4.20, and 4.37 ppm. In contrast, the ^1H NMR spectrum of square-planar **B** showed no observable resonances for backbone hydrogen atoms, due to a rapid interconversion of the two C_2-symmetric isomers on the NMR time scale. This rapid atropisomerism is also observed in many pyridyl-bridged tridentate NHC complexes.[24-27] The ^{13}C NMR spectrum of **4** shows a NHC carbene resonance at 194.3 ppm that is an yttrium-coupled doublet: $^1J_{CY} = 48.0$ Hz. This coupling is comparable to that in previous yttrium NHC complexes[28] but lower than in the bidentate amidocarbene adducts reported by us.[2] The coupling constant is also comparable to those found for C_{ipso} resonances in yttrium aryl compounds.[29]

The molecular structure of **4** has also been determined by an X-ray diffraction study of a suitable crystal grown from a diethyl ether/hexanes solution (Figure 2).

The yttrium–NHC bond lengths in **4** are within reported literature values, although they are longer than in previous yttrium–NHC complexes synthesized within the group[8] and significantly longer than normal two-electron yttrium alkyl bond lengths. The geometry at the yttrium atom is distorted trigonal bipyramidal with the tricoordinate L *meridionally* configured. The NHC ligands occupy the axial positions with a C–Y–C angle of 157.28°. The Y1–N1 distance of 2.184(2) Å is short for Y amides.[30-32]

The reaction to afford **4** has been carried out multiple times, in either THF or toluene solvent, at temperatures of either −40 or 20 °C: in each case, only the yttrium monochloride complex **4** is formed. However, in one instance, a reaction between YN''_3 and an impure batch of **2** [$(LiCl)_3HL$] in THF at room temperature afforded a different, colorless yttrium complex, which precipitated out of the THF reaction mixture due to a significantly lower solubility in THF and which was characterized as $YLCl_2$ (**5**) (eq 2). Treatment of $YCl_3(THF)_3$ with 1 equiv of the lithium salt $LiL\cdot 3LiCl$ was anticipated to afford a straightforward route to **5**, but in our hands, no tractable product could be isolated from this reaction.

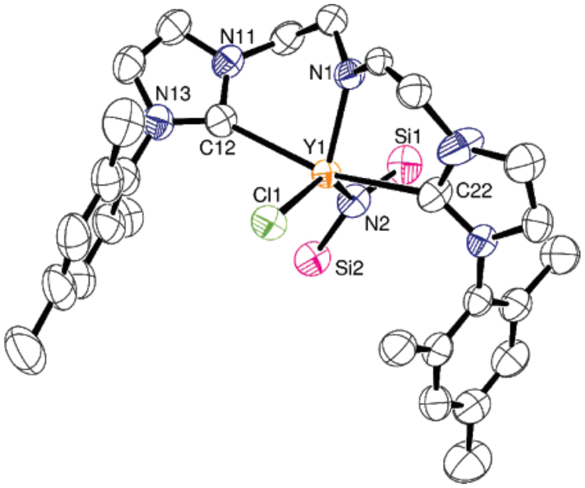
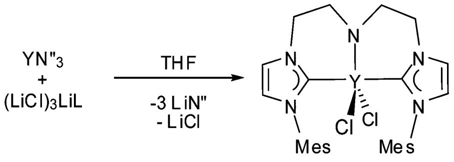


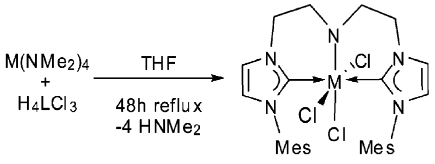
Figure 2. Displacement ellipsoid drawing of the molecular structure of **4**. Lattice solvent, silyl methyls, and hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Y(1)–C(12) = 2.574(3), Y(1)–C(22) = 2.565(3), Y(1)–N(1) = 2.184(2), Y(1)–N(2) = 2.273(2), Y(1)–Cl(1) = 2.6186(8); C(22)–Y(1)–C(12) = 157.28(10), N(1)–Y(1)–C(12) = 79.06(9), N(1)–Y(1)–C(22) = 82.58(10).



5 (46 %) **(2)**

The ^1H NMR spectrum of **5** in d_5-pyridine shows fewer resonances than that of **4**, due to the symmetrical nature of **5**. The two ligand ethylene groups are equivalent on the NMR time scale, observed at 3.60 and 4.66 ppm, in contrast to the four resonances observed in the ^1H NMR spectrum of **4**. The ^{13}C NMR spectrum of **5** contains a resonance at 192.8 ppm that is an yttrium-coupled doublet: $^1J_{CY} = 47$ Hz. The size of this coupling constant in almost identical with that for **4**.

2.4. Titanium and Zirconium Adducts of L. A mixture of the proligand H_4LCl_3 and a stoichiometric amount of $M(NEt_2)_4$ (M = Ti, Zr) was heated in THF for 48 h. During this time a green precipitate formed in the titanium amide containing reaction vessel, while a yellow precipitate formed in the zirconium amide containing reaction vessel. In each case, the powder was isolated by filtration and washed with THF to afford bright green powdery $TiLCl_3$ (**6**) and dark yellow powdery $ZrLCl_3$ (**7**) (eq 3). Comparison of the physical characteristics of both products with those of the other L adducts leads us to assume a *mer* coordination of the ligand about the zirconium cation.



M = Ti **6** (16 %)
M = Zr **7** (62 %) **(3)**

Both complexes, like **5** above, are poorly soluble in all common aprotic solvents, except pyridine. The ^1H NMR

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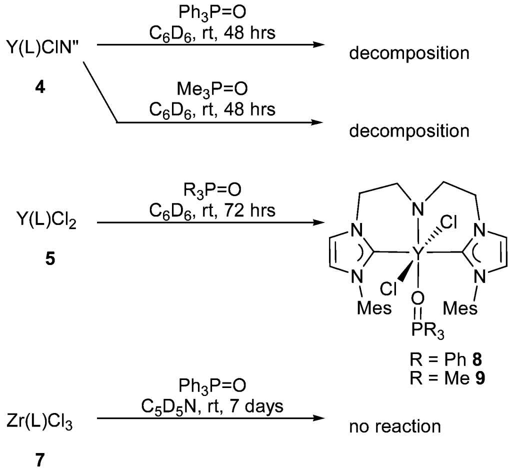
Scheme 2



spectrum of a d_5-pyridine solution of either contains two resonances characteristic of the CH_2 backbone protons. Only the zirconium complex had sufficient solubility for the carbene carbon resonance to be observed in the ^{13}C NMR spectrum; a single resonance at 186.2 ppm is measured for **7**, associated with a C_2- or C_{2v}-symmetric structure. This compares with the reported carbene resonance for **C** of 192.3 ppm.[33]

The five-coordinate zirconium complex **C** was also reported to be very insoluble but formed an octahedral pyridine adduct in solution with a ^{13}C NMR carbene resonance at 181.0 ppm.[16] No pyridine adduct could be formed from six-coordinate **7**.

2.5. Competition Reactions with Phosphine Oxides. Triphenylphosphine oxide is recognized as a good, solvating, two-electron donor for electropositive metal complexes. Trimethylphosphine oxide is used in this capacity less frequently. Solutions of the yttrium(III) and zirconium(IV) carbene complexes **4**, **5**, and **7** were each treated with 1.1 equiv of $O{=}PPh_3$, and **4** and **5** were treated also with $O{=}PMe_3$ (Scheme 2). The mixtures were monitored by multinuclear NMR spectroscopy to identify if one or both NHC groups could be displaced by the phosphine oxide.

Over storage at room temperature for 48 h, a benzene solution of **4** and $O{=}PPh_3$ turns brown, and a brown precipitate forms. NMR spectroscopic analysis suggests that one NHC is displaced with resonances for one coordinated and one uncoordinated NHC observed initially, but the resulting complex is not stable and precipitates out of solution. The precipitate formed is pyridine-soluble but is not a tractable product. The ^{31}P NMR of the reaction solution has one resonance at 25.9 ppm for $Ph_3P{=}O$.

Over storage at room temperature for 48 h, a benzene solution of **4** and $O{=}PMe_3$ also turns brown, and a brown precipitate forms. NMR spectroscopic analysis shows complete conversion of **4** into a new, highly symmetrical species after 10 min, possibly a phosphine oxide solvated adduct, but again the decomposition of this species is apparent over 48 h in solution. The precipitate formed is pyridine-soluble but is not a tractable product.

Over storage at room temperature for 72 h, a benzene solution of **5** and $O{=}PPh_3$ also turns brown, and a brown precipitate forms. Other than a small quantity of unreacted $O{=}PPh_3$, nothing remains in solution. The precipitate formed is pyridine-soluble; the ^{31}P NMR spectrum contains a single resonance assigned as a coordinated molecule of $Ph_3P{=}O$, while the ^1H NMR spectrum suggests the formation of a C_2- or C_{2v}-symmetrical product which contains one yttrium-coordinated $O{=}PPh_3$ and two yttrium-coordinated carbenes, implying that the simple, six-coordinate adduct **8** in Scheme 2 has been formed. A single carbene resonance (^{13}C NMR spectrum) at 193.1 ppm is an yttrium-coupled doublet ($^1J_{YC} = 38$ Hz), very similar in shift and coupling constant to those of **5**, supporting this assignment.

Over storage at room temperature for 72 h, a benzene solution of **5** and $O{=}PMe_3$ also turns brown, and a brown precipitate forms. The ^1H NMR spectrum of the benzene soluble material suggests that the solution contains only a small amount of decomposition products, and a new, poorly soluble compound with a resonance at 52.7 ppm in the ^{31}P NMR spectrum due to yttrium-bound $Me_3P{=}O$. The precipitate is the same material, and is pyridine-soluble; the ^1H NMR spectrum of the again supports the formation of a symmetrical product with one yttrium-bound $Me_3P{=}O$, and both carbenes coordinated, **9** in Scheme 2. The ^{13}C NMR spectrum of **9** again contains one resonance attributed to the carbenes at 193.0 ppm, which is an yttrium coupled doublet, $^1J_{YC} = 38$ Hz.

Due to the poor solubility of the zirconium complex **7** in benzene and THF, a d_5-pyridine solution of **7** and $O{=}PPh_3$ was stored at room temperature for 7 days. At the end of this time, a small quantity of yellow **7** had precipitated out of the solution, while NMR analysis of the remaining solution showed that no reaction had taken place.

The formation of **8** and **9** as six-coordinate yttrium adducts is presumably possible in the latter two cases, as the chloride ligands are not too bulky, but if there is insufficient space for both donors (oxide and carbene), then the phosphine oxide competes effectively, displacing the carbene, forming complexes in these cases which cannot be isolated.

3. Conclusions

To conclude, we have described two different synthetic routes to early-transition-metal complexes of a monoanionic bis(carbene) amido ligand. The thermal sensitivity of the carbene ligand HL in the absence of stabilizing metal halide precludes the isolation of the free ligand and constrains the synthesis of HL and LiL to low-temperature deprotonation routes. However, both transamination and salt elimination based synthetic routes using these lithium chloride adducts of L allow access to the first examples of group 3 and group 4 complexes of a monoanionic bis(carbene) ligand. Treatment of some of the complexes with phosphine oxide competitors confirms that the yttrium−carbene bonds are significantly more labile than the zirconium−carbene bonds, but the complexes in these systems that contain labilized carbenes decompose before we are able to isolate them.

4. Experimental Section

4.1. General Details. All manipulations of air-sensitive materials were carried out under a dry, oxygen-free argon or dinitrogen atmosphere, using standard Schlenk techniques (rotary pump for vacuum 10^{-4} mbar), or in a glovebox (Mbraun Unilab or Saffron) under dry dinitrogen. All NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating frequency 300 MHz (^1H), 75 MHz (^{13}C), or 116 MHz (^7Li), with the variable-temperature unit set to 300 K unless otherwise stated. Chemical shifts are reported in parts per million and are referenced to residual solvent proton resonances calibrated against external TMS. Mass spectra (EI) were run by Mr. A. Hollingworth on a VG Autospec instrument. Elemental analyses were determined by Dr. S. Boyer at London Metropolitan

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University. All solvents used (diethyl ether, tetrahydrofuran, hexane, toluene, dichloromethane, 1,2-dichloromethane, acetonitrile, and pyridine) either were degassed and purified by passage through activated alumina towers prior to use or were freshly distilled from the appropriate drying reagent under dinitrogen and thoroughly degassed prior to use (pyridine from CaH_2). NMR spectroscopic grade d_6-benzene and d_5-pyridine were dried over potassium metal, thoroughly degassed by the freeze−thaw method, and transferred under reduced pressure before use. The syntheses of $[H_4L]Cl_3$ and $[H_4L]Br_3$ have been previously described.[14]

4.2. Preparations. Preparation of [(LiCl)$_3$HL] (2). To a stirred slurry of H_4LCl_3 (4.00 g, 7.26 mmol) in THF (20 cm^3) was added n-butyllithium (2.5 M solution in hexanes, 8.71 cm^3, 21.78 mmol) dropwise at −30 °C over 10 min. This mixture was stirred at −30 °C for 4 h, and then volatiles were removed at reduced pressure to yield a pale brown solid. The solid was washed with hexane (20 cm^3) and then diethyl ether (20 cm^3). This yielded **2** as an off-white solid. Yield: 3.91 g, 94.2%. Anal. Found (calcd) for $C_{28}H_{35}N_5Li_3Cl_3$: C, 59.04 (59.13); H, 6.24 (6.20); N, 12.50 (12.31). ^{1}H NMR (C_5D_5N): 7.43 (s, 2H, C*H*), 6.88 (s, 2H, C*H*), 6.70 (s, 4H, Ar), 4.65 (m, 4H, C*H*$_2$), 3.26 (m, 4H, C*H*$_2$), 2.19 (s, 6H, *p*-C*H*$_3$) and 1.95 (s, 12H, *o*-C*H*$_3$); NH not seen. ^{13}C{^{1}H} NMR (C_5D_5N): 203.9 (N*C*N), 138.5 (Ar), 137.5 (Ar), 129.0 (Ar), 121.2 (*C*H), 120.8 (*C*H), 51.6 (*C*H$_2$), 51.0 (*C*H$_2$), 20.9 (*p*-*C*H$_3$), 17.9 (*o*-*C*H$_3$). ^{7}Li NMR (C_5D_5N): 4.09 (br).

Solvent Extraction Reactions with 2. To a solid of **2** (1.00 g, 1.76 mmol) was added toluene (10 cm^3) at room temperature, and the resultant suspension was stirred at room temperature for 48 h. This yielded a orange solution and white solid; the solution was filtered and the solid washed with toluene (10 cm^3) and added to the orange reaction solution. Volatiles were removed from this solution at reduced pressure to afford a brown solid. ^{1}H NMR spectral analysis of the brown solid showed no resonances for **2** or resonances that could be assigned to the LiCl free ligand.

The analogous reaction was carried out in diethyl ether and gave the same result.

Preparation of [(LiCl)$_3$LiL] (3). To a stirred slurry of H_4LCl_3 (5.07 g, 9.15 mmol) in THF (15 mL) was added n-butyllithium (2.5 M solution in hexanes, 14.84 cm^3, 36.85 mmol) dropwise at −30 °C. The cream-colored suspension was stirred at −30 °C for 4 h, and then the volatiles were removed under reduced pressure to yield a pale brown solid. The solid was washed with hexane (20 cm^3) and then diethyl ether (20 cm^3). This yielded **3** as an off-white solid. Yield: 88.3%. Anal. Found (calcd) for $C_{32}H_{42}N_5OLi_4Cl_3$ (**3**·THF): C, 59.95 (59.42); H, 6.63 (6.54); N, 10.73 (10.83). ^{1}H NMR (C_5D_5N, 300 MHz): 7.14 (2H, d, C*H*), 6.80 (2H, d, C*H*), 6.66 (4H, s, Ar), 4.42 (4H, m, C*H*$_2$), 3.80 (4H, m, C*H*$_2$), 3.62 (4H, t, THF), 2.16 (6H, s, *p*-C*H*$_3$), 2.00 (12H, s, *o*-C*H*$_3$), 1.58 (4H, q, THF). ^{13}C{^{1}H} NMR (C_5D_5N, 75.5 MHz): 203.4 (N*C*N), 138.7 (Ar), 137.1 (Ar), 128.9 (Ar), 121.6 (*C*H), 119.2 (*C*H), 67.9 (THF), 62.5 (*C*H$_2$), 54.6 (*C*H$_2$), 25.9 (THF), 20.9 (*p*-*C*H$_3$), 18.2 (*o*-*C*H$_3$). ^{7}Li NMR (C_5D_5N, 116.6 MHz): 2.91 (br), −2.35 (s).

Preparation of [YLCl(N{SiMe$_3$}$_2$)] (4). A mixture of **2** (1.50 g, 2.64 mmol) and $Y(N(SiMe_3)_2)_3$ (1.27 g, 2.64 mmol) in THF (10 cm^3) was stirred at room temperature for 8 h. Volatiles were then removed at reduced pressure to yield a brown solid, which was washed with hexane (2 × 10 cm^3). The product was recrystallized from diethyl ether at 0 °C to give **4** as white needles. Yield: 0.94 g, 49.1%. Anal. Found (calcd) for $C_{34}H_{52}N_6ClSi_2Y$: C, 56.17 (56.30); H, 7.37 (7.23); N, 11.54 (11.59). ^{1}H NMR (C_6D_6): 6.78 (s, 4H, Ar), 6.18 (d, 2H, ^3J = 1.5 Hz, C*H*), 5.99 (d, 2H, ^3J = 1.5 Hz, C*H*), 4.37 (m, 2H, C*H*$_2$), 4.20 (m, 2H, C*H*$_2$), 3.47 (m, 2H, C*H*$_2$), 3.07 (m, 2H, C*H*$_2$), 2.33 (s, 6H, C*H*$_3$), 2.08 (s, 6H, C*H*$_3$), 2.01 (s, 6H, C*H*$_3$), 0.15 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 194.3 (N*C*N, d, $^1J_{CY}$ = 48 Hz), 138.4 (Ar), 137.0 (Ar), 136.9 (Ar), 134.4 (Ar), 129.8 (Ar), 128.9 (Ar), 121.0 (*C*H), 120.2 (*C*H), 57.7 (*C*H$_2$), 50.9 (*C*H$_2$), 21.0 (*C*H$_3$), 19.3 (*C*H$_3$), 18.5 (*C*H$_3$), 5.5 (N(Si(*C*H$_3$)$_3$)$_2$). MS(EI): *m*/*z* 452 (10%), 306 (28%), 187 ([MesIm + H]$^+$, 10%), 161 (36%), 146 ([PhIm + 2H]$^+$, 100%), 135 ([MesNH$_2$]$^+$, 37%), 130 (42%), 120 ([Mes]$^+$, 22%).

Preparation of [YLCl$_2$] (5). A mixture of $(LiCl)_3HL$ (5.00 g, 8.79 mmol) and $Y(N(SiMe_3)_2)_3$ (4.22 g, 8.79 mmol) in THF (50 mL) was stirred at room temperature for 16 h. During this time a colorless precipitate formed in the brown solution. The reaction mixture was filtered to isolate a colorless solid, which was washed with THF (2 × 25 cm^3) and dried under reduced pressure to yield pure **5**. Yield: 2.40 g, 45.5%. Anal. Found (calcd) for $C_{28}H_{34}Cl_2N_5Y$: C, 55.89 (56.01); H, 5.80 (5.71); N, 11.52 (11.66). ^{1}H NMR (C_5D_5N, 300 MHz): 7.29 (2H, d, C*H*), 6.88 (2H, d, C*H*), 6.40 (4H, s, Ar), 4.66 (4H, br, C*H*$_2$), 3.60 (4H, br, C*H*$_2$), 2.33 (6H, s, C*H*$_3$), 2.06 (12H, s, *o*-C*H*$_3$), 2.04 (6H, s, *p*-C*H*$_3$). ^{13}C{^{1}H} NMR (C_5D_5N, 75.5 MHz): 192.9 (N*C*N, d, $^1J_{CY}$ = 48 Hz), 137.9 (Ar), 136.7 (Ar), 128.8 (Ar), 122.3 (*C*H), 119.8 (*C*H), 56.8 (*C*H$_2$), 53.5 (*C*H$_2$), 20.9 (*p*-*C*H$_3$), 18.2 (*o*-*C*H$_3$). MS (EI): *m*/*z* 561 (10%), 442 ([HL]$^+$, 38%), 426 ([HL − CH$_4$]$^+$, 43%), 399 (45%), 360 (70%), 306 (95%), 279 (73%), 201 (65%), 187 ([Mes − Im]$^+$, 65%), 135 (100%).

Reaction of [(LiCl)$_3$LiL] (3) with YCl$_3$(THF)$_3$. A Schlenk tube was charged with **3** (270 mg, 0.47 mmol), $YCl_3(THF)_3$ (200 mg, 0.49 mmol), and THF (5 cm3). The resultant solution was stirred at room temperature for 12 h, yielding a brown solution. Removal of volatiles from the brown solution under reduced pressure afforded a brown solid. The ^{1}H NMR spectrum of the brown solid in d_5-pyridine contained no resonances for $Y(L)Cl_2$.

Preparation of [TiLCl$_3$] (6). An ampule was charged with **1** (1.00 g, 1.81 mmol) and $Ti(NEt)_4$ (0.61 g, 1.81 mmol). To this was added THF (10 cm^3), and the resulting mixture was heated at 80 °C for 48 h. During this time, a brown solution and green solid formed. The solution was filtered and the solid washed with THF (2 × 5 cm^3) and dried under reduced pressure to afford **6** as a green powder. Yield: 16%, 167 mg. ^{1}H NMR (C_5D_5N): 7.37 (br, 2Hs, C*H*), 6.90 (br, 2Hs, C*H*), 6.44 (br, 4Hs, Ar), 4.47 (br, 8Hs, C*H*$_2$), 2.20 (br, 12Hs, *o*-C*H*$_3$), 2.00 (br, 6Hs, *p*-C*H*$_3$). ^{13}C{^{1}H} NMR (C_5D_5N): 137.4, 134.6, 129.8, 129.0 (all Ar), 121.7 (*C*H), 120.8 (*C*H), 59.4 (*C*H$_2$), 50.9 (*C*H$_2$), 20.9 (*p*-*C*H$_3$), 18.8 (*o*-*C*H$_3$). The carbene resonance was not observed, probably due to the poor solubility of the complex. MS (EI): *m*/*z* 592 ([M − 2H]$^+$, 5%), 558 ([M − Cl − H]$^+$, 100%), 540 (15%), 461 ([TiL − 2CH$_3$ + H]$^+$, 22%), 446 ([TiL − 3CH$_3$]$^+$, 37%), 398 ([L − 3CH$_3$]$^+$, 36%), 371 (66%). Anal. Found (calcd) for $C_{28}H_{34}Cl_3N_5Ti$: C, 56.35 (56.54); H, 5.81 (5.76); N, 11.85 (11.77).

A Schlenk tube was charged with **2** (200 mg, 0.31 mmol), $TiCl_3(NMe_2)$ (62 mg, 0.31 mmol), and THF (5 cm^3) and the resulting mixture stirred at room temperature for 24 h, yielding a brown solution. Removal of volatiles from the solution under reduced pressure afforded a brown solid that could not be identified by NMR spectroscopy.

Preparation of [ZrLCl$_3$] (7). To a slurry of H_4LCl_3 (1.00 g, 1.81 mmol) in THF (10 cm^3) was added a solution of $Zr(NEt_2)_4$ (0.69 g, 1.81 mmol) in THF (10 cm^3) at room temperature. The mixture was heated at 70 °C for 2 days to give a yellow solid in a brown solution. The yellow solid was collected by filtration and washed with THF (2 × 10 cm^3) to yield pure **7**. Yield: 0.78 g, 62.3%. Anal. Found (calcd) for $C_{28}H_{34}N_5Cl_3Zr$: C, 52.58 (52.70); H, 5.44 (5.37); N, 10.90 (10.97). ^{1}H NMR (C_5D_5N, 300 MHz): 1.99 (6H, s, *p*-C*H*$_3$), 2.21 (12H, s, *o*-C*H*$_3$), 3.85 (4H, m, C*H*$_2$), 4.46 (4H, m, C*H*$_2$), 6.69 (4H, s, Ar), 7.04 (2H, d, C*H*), 7.40 (2H, d, C*H*). ^{13}C{^{1}H} NMR (C_5D_5N, 75.5 MHz): 18.6 (*o*-*C*H$_3$), 21.0 (*p*-*C*H$_3$), 51.8 (*C*H$_2$), 56.0 (*C*H$_2$), 121.4 (*C*H), 122.2 (*C*H), 129.1 (Ar), 136.5 (Ar), 138.3 (Ar), 186.2 ($C_{carbene}$). MS (EI): *m*/*z* 637 ([M]$^+$, 100%), 600 ([M − Cl]$^+$, 45%).

4.3. Displacement Reactions. Reaction of Y(L)ClN″ with Ph$_3$P═O. A mixture of **4** (22 mg, 0.03 mmol) and triphenylphosphine oxide (9 mg, 0.03 mmol) in C_6D_6 (0.5 cm^3) at room temperature yielded a brown solution and brown solid after 2 days. Benzene-soluble material: ^{31}P{^{1}H} NMR spectroscopy (C_6D_6) shows trace unreacted O═PPh$_3$. Benzene-insoluble material: ^{31}P{^{1}H} NMR (C_5D_5N) 26.7 (Ph$_3$*P*═O); ^{1}H NMR (C_5D_5N) 7.75−7.65 (m, 5H, Ar), 7.32−7.58 (m, 10H, Ar).

Reaction of Y(L)ClN″ with Me$_3$P═O. A mixture of **4** (45 mg, 0.06 mmol) and triphenylphosphine oxide (6 mg, 0.06 mmol) was stored in C_6D_6 (0.5 cm^3) at room temperature for 48 h, after which time a brown solid had formed in a brown solution. Benzene-soluble material after 10 min: ^{1}H NMR (C_6D_6) 6.76 (s, 4H, Ar), 6.65 (s, 2H, C*H*), 6.37 (s, 2H, C*H*), 3.99 (m, 4H, C*H*$_2$), 2.90 (m, 4H, C*H*$_2$), 2.12 (s, 6H, *p*-C*H*$_3$), 2.07 (s, 12H, *o*-C*H*$_3$); no signal measurable in ^{31}P NMR spectrum. Benzene-insoluble material: ^{31}P{^{1}H} NMR (C_5D_5N) 41.1; ^{1}H NMR shows no resonances that could be attributed to a complex or ligand.

Reaction of Y(L)Cl$_2$ with Ph$_3$P═O To Give 8. A mixture of **5** (38 mg, 0.06 mmol) and triphenylphosphine oxide (18 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was reacted at room temperature for 5 days, yielding a brown solution and the brown solid **8**. The solution was decanted away from **8**. ^{1}H NMR (C_5D_5N): 7.93−7.87 (m, 5H, OPPh$_3$), 7.45−7.42 (m, 10H, OPPh$_3$), 6.84 (br, 4H, Ar), 6.78 (s, 2H, C*H*), 6.63 (s, 2H, C*H*), 4.33 (m, 2H, C*H*$_2$), 3.57 (m, 2H, C*H*$_2$), 3.06 (m, 2H, C*H*$_2$), 2.91 (m, 2H, C*H*$_2$), 2.24 (s, 6H, C*H*$_3$), 2.07 (s, 6H, C*H*$_3$), 1.89 (s, 6H, C*H*$_3$). ^{31}P{^{1}H} NMR (C_5D_5N): 37.5. ^{13}C{^{1}H} NMR (C_5D_5N): 193.1 (N*C*N, d, $^{1}J_{CY}$ = 38 Hz), 137.8, 136.8, 135.8, 132.8, 129.0, 128.8 (all Ar), 122.2 (*C*H), 119.7 (*C*H), 56.9 (*C*H$_2$), 53.6 (*C*H$_2$), 20.9 (*p*-*C*H$_3$), 18.3 (*o*-*C*H$_3$).

Reaction of Y(L)Cl$_2$ with Me$_3$P═O To Give 9. A mixture of **5** (45 mg, 0.07 mmol) and O═PMe$_3$ (7 mg, 0.08 mmol) in C_6D_6 (0.5 cm^3) was reacted at room temperature for 5 days, yielding a brown solution and the brown solid **9**. The solution was decanted away from **9**. ^{1}H NMR (C_5D_5N): 7.16 (s, 2H, C*H*), 6.79 (s, 2H, C*H*), 6.43 (s, 4H, Ar), 4.65 (br, 4H, C*H*$_2$), 3.68 (br, 4H, C*H*$_2$), 2.09 (s, 12H, *o*-C*H*$_3$), 2.06 (s, 6H, *p*-C*H*$_3$), 1.65 (br, 9H, (C*H*$_3$)$_3$P═O). ^{31}P{^{1}H} NMR (C_5D_5N): 56.7. ^{13}C{^{1}H} NMR (C_5D_5N): 193.0 (N*C*N, d, $^{1}J_{CY}$ = 38 Hz), 137.8 (Ar), 136.8 (Ar), 128.8 (Ar), 122.2 (*C*H), 119.7 (*C*H), 56.9 (*C*H$_2$), 53.5 (*C*H$_2$), 20.9 (*p*-*C*H$_3$), 18.3 (*o*-*C*H$_3$), 16.9 and 15.9 (P*C*H$_3$).

Reaction of Zr(L)Cl$_3$ and Ph$_3$P═O. A yellow mixture of Zr(L)Cl$_3$ (42 mg, 0.07 mmol) and triphenylphosphine oxide (20 mg, 0.07 mmol) in C_5D_5N (0.5 cm^3) was heated to 90 °C, affording a brown solution and yellow solid after 10 days. NMR spectroscopy of the mixture showed only starting materials.

4.4. X-ray Crystallography. Crystals of **1a** were examined on a Bruker AXS SMART 1000 area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystals of **4** were examined on a SMART 1k CCD area detector diffractometer at DL9.8 (λ = 0.6928 Å) at Daresbury. The structures was solved by direct methods and refined by least-squares methods on F^2 values, with anisotropic displacement parameters for non-H atoms and with constrained riding hydrogen geometries (except ammonium hydrogens, which were freely refined); U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom.

Crystal data for **1a**: colorless block, 0.55 × 0.35 × 0.32 mm, $C_{28}H_{38}N_5Br_3 \cdot CHCl_3$, M_r 803.73, triclinic, $P\bar{1}$, 150 (2) K, a = 10.596(2) Å, b = 11.496(2) Å, c = 14.619(3) Å, α = 95.065(3)°, β = 92.839(3)°, γ = 100.834(3)°, V 1738.2(9) Å^3, Z = 2, D_{exptl} = 1.536 Mg m^{-3}, μ = 3.74 mm^{-1}. T_{min} = 0.561, T_{max} = 1.000, 15 654, 7803, and 6780 measured, independent, and observed reflections, R_{int} = 0.015, θ_{max} = 27.6°, $R[F^2 > 2\sigma(F^2)]$ = 0.032, $R_w(F^2)$ = 0.087, S = 1.05, 7797 reflections, 375 parameters, $\Delta\rho_{max}$ = 1.06 e Å^{-3}, $\Delta\rho_{min}$ = −0.70 e Å^{-3}.

Crystal data for **4**: pale red plate, 0.15 × 0.12 × 0.02 mm, $C_{34.25}H_{52.58}ClN_6Si_2Y$, monoclinic, $P2_1/n$, 120(2) K, a = 15.9217(6) Å, b = 31.6519(12) Å, c = 18.4820(7) Å, α = 90.00°, β = 104.618(2)°, γ = 90.00°, V = 9012.5(6) Å^3, Z = 8, D_{exptl} = 1.074 Mg m^{-3}, μ = 1.43 mm^{-1}. T_{min} = 0.827, T_{max} = 1.000, 75 591, 18 301, and 14 001 measured, independent, and observed reflections, R_{int} = 0.0449, θ_{max} = 27.6°, $R\,[F^2 > 2\sigma(F^2)]$ = 0.059, $R_w(F^2)$ = 0.2023, S = 1.09, 18 301 reflections, 817 parameters.

Computer programs: Bruker SMART, version 5.625 (Bruker, 1998); Bruker SAINT, version 6.36a (Bruker, 2000); Bruker SHELXTL (Bruker, 2001); SIR92 (Altomare et al., 1994); enCIFer (Allen et al., 2004); PLATON (Spek, 2003). CCDC xxx and xxx contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: CIF files giving crystallographic data for compounds **1a** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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