

Tridentate Amido Carbene Ligands in Early-Transition-Metal Coordination Chemistry

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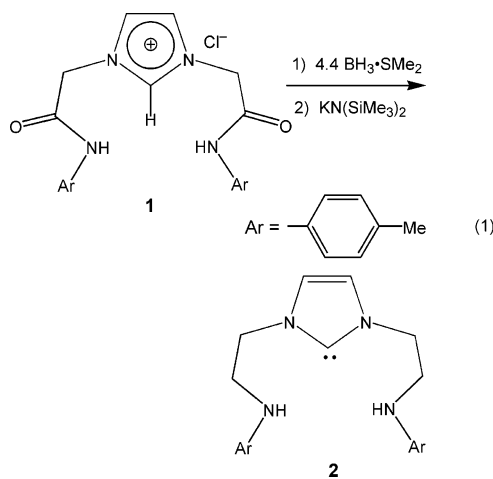
Summary: Coordination of the new tridentate N-heterocyclic carbene ligand precursor (*p*-Me-C₆H₄NHCH₂-CH₂)₂N₂C₃H₂ to Zr(IV) generates an [NCN] donor set where the N represents an amido unit and the C corresponds to the N-heterocyclic carbene. This ancillary ligand allows for the isolation and structural characterization of zirconium amido, chloro, and alkyl derivatives; the carbene donor is rendered stable to dissociation because of its central disposition between two anionic amido units.

Investigation into the use of N-heterocyclic carbene (NHC) ligands in modern coordination chemistry and homogeneous catalysis has become extremely popular, almost to the point of being de rigueur. In a remarkably short period of time, NHC donors have gone from academic curiosities to essential ancillary ligands throughout the periodic table.¹ The ubiquity of NHC's is due to their strong donor properties, which are enhanced by the diversity of N substituents and heterocyclic ring sizes that provide for some tunability of stereoelectronic effects.² Probably the aspect that has most propelled the use of NHC's to frenetic levels has been their ability to replace phosphine ligands to generate catalyst precursors more robust and versatile than their phosphine congeners.³

With respect to the use of NHC's with the early transition elements (groups 3–6) and the lanthanides, less is known about how susceptible these neutral donors are to dissociation.^{4a} For d⁰ systems such as Zr(IV), neutral ligands are prone to exchange typically via dissociation. In an effort to construct systems which would reduce the tendency for ligand dissociation, we have designed and synthesized a potentially tridentate carbene donor system that has the neutral NHC donor

flanked by two amido ligands. This is modeled after related diamidophosphine ligands that we have reported previously.⁵ Two recent publications have described a bidentate amidocarbene and a tridentate amidodicarbene.⁴ Samarium and yttrium complexes stabilized by a bidentate amidocarbene did show displacement of the carbene donor by Me₂NCH₂CH₂NMe₂ and Ph₃P=O.^{4a}

To construct an NHC with two pendant amine arms, the reduction of a bis(amide) imidazolium chloride was examined. The reaction of borane–dimethyl sulfide with an easily assembled amide precursor⁶ (**1**) gives the desired bis(amino)–imidazolium chloride in reasonable yield. Subsequent deprotonation by KN(SiMe₃)₂ selectively generates the expected free NHC **2** (eq 1). Both



¹H and ¹³C NMR spectra are consistent with a symmetrical molecule; diagnostic of the carbene moiety is the absence of the resonance attributed to the iminium proton (at C₂), an upfield shift in the heterocycle protons in the C_{4,5} positions, and a weak ¹³C resonance at 211.4 ppm for the carbene carbon.⁷

The incorporation of the [NCN] precursor **2** onto zirconium is easily achieved by either amine or alkyl elimination via protonolysis reactions. For example, aminolysis of Zr(NEt₂)₄ with **2** proceeds smoothly at room temperature to afford ^{tol}[NCN]Zr(NEt₂)₂ (**3**) (^{tol}[NCN] = (*p*-Me-C₆H₄NCH₂CH₂)₂N₂C₃H₂) in good

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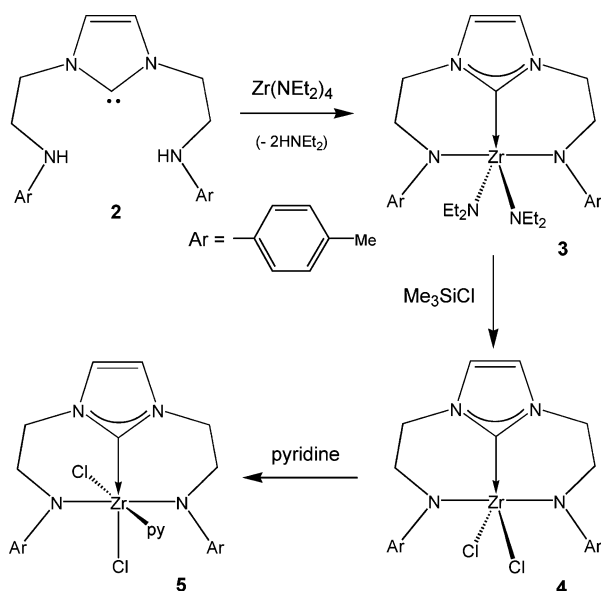
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yield. Complex **3** was characterized by ^1H and ^{13}C NMR



spectroscopy, which showed resonances attributable to equivalent NEt_2 moieties along with equivalent amido sidearms of the $^{\text{tol}}[\text{NCN}]$ unit; on the basis of these data a C_{2v} -symmetric geometry can be assigned to this five-coordinate complex. The ^{13}C NMR spectrum shows a resonance at 188.8 ppm due to the coordinated carbene carbon. Treatment of **3** with excess Me_3SiCl in toluene over 2 days gives the dichloride $^{\text{tol}}[\text{NCN}]\text{ZrCl}_2$ (**4**) in quantitative yield. The dichloride is extremely insoluble in common organic solvents, which may indicate a dimeric structure in the solid state;⁸ although no solution spectroscopic data could be obtained, the empirical formula of **4** was confirmed by mass spectrometry and elemental analysis. To solubilize this material, pyridine was added to a suspension of **4**, and this resulted in the benzene-soluble pyridine adduct $^{\text{tol}}[\text{NCN}]\text{ZrCl}_2(\text{py})$ (**5**), which allowed full characterization by spectroscopic and X-ray diffraction studies. The NMR data for **5** clearly show the presence of resonances for coordinated pyridine along with the $[\text{NCN}]$ resonances; the Zr–carbene carbon in **5** appears as a weak singlet at 187.9 ppm.

Crystals of **5** were grown from concentrated benzene solution and analyzed by single-crystal X-ray diffraction; the ORTEP diagram is shown in Figure 1. In the solid state, the zirconium center is coordinated by the tridentate $^{\text{tol}}[\text{NCN}]$ ligand in addition to pyridine. The two chlorides adopt a mutually cis disposition, with the $[\text{NCN}]$ ligand in a meridional orientation to generate a pseudo-octahedral arrangement around the central Zr atom. Both of the six-membered chelate rings of $[\text{NCN}]$ are nearly planar, with $\text{N}(2)\text{--C}(1)\text{--Zr}(1)\text{--N}(4)$ and $\text{N}(1)\text{--C}(1)\text{--Zr}(1)\text{--N}(3)$ torsion angles of -1.2 and -7.5° , respectively; however, each ring has the carbon α to the amido donor sitting above or below in the solid state. The $\text{Zr}(1)\text{--C}(1)$ bond length (2.391(5) Å) is significantly shorter than previously characterized lengths of Zr–

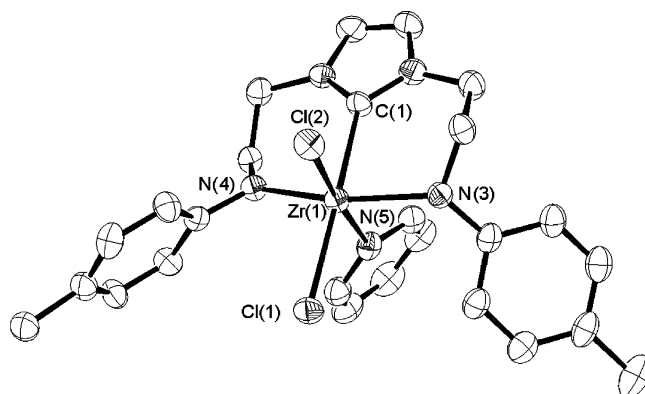
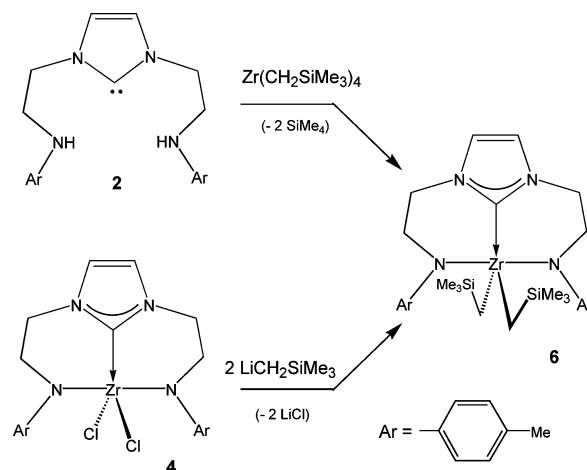


Figure 1. ORTEP view of $^{\text{tol}}[\text{NCN}]\text{ZrCl}_2(\text{py})$ (**5**), depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Zr}(1)\text{--C}(1) = 2.391(5)$, $\text{Zr}(1)\text{--N}(3) = 2.167(4)$, $\text{Zr}(1)\text{--N}(4) = 2.109(4)$, $\text{C}(1)\text{--Zr}(1)\text{--N}(5) = 84.02(18)$, $\text{N}(4)\text{--Zr}(1)\text{--Cl}(1) = 94.77(14)$, $\text{N}(4)\text{--Zr}(1)\text{--N}(3) = 155.27(16)$, $\text{N}(4)\text{--Zr}(1)\text{--Cl}(1) = 94.77(14)$, $\text{C}(1)\text{--Zr}(1)\text{--Cl}(1) = 170.38(14)$.

based NHC compounds (2.432(3)–2.456(3) Å),⁹ likely a result of the ligand architecture that pulls the carbene donor closer to the metal. The Zr–N amido bond lengths average to 2.138(4) Å and are comparable to those of other Zr–amide complexes.¹⁰ The Zr–Cl bond distances are not unusual. The Zr–N bond length of the pyridine donor is 2.398(5) Å and is normal.

The preparation of the bis(trimethylsilyl)methyl zirconium complex $^{\text{tol}}[\text{NCN}]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$ (**6**) was performed by both alkylation and protonolysis methods.



The reaction of $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$ with **2** led to the desired product **6** via SiMe_4 elimination. This complex could also be synthesized from the reaction of dichloride **4** and 2 equiv of $\text{LiCH}_2\text{SiMe}_3$; however, a better yield is obtained via the alkane elimination method at -30°C . Complex **6** was isolated as air- and moisture-sensitive pale yellow crystals. On exposure to light, solutions of **6** darkened to unidentified products within ~ 1 h. To our knowledge, **6** is the first reported zirconium dialkyl with an NHC-based ancillary ligand. The X-ray diffraction study

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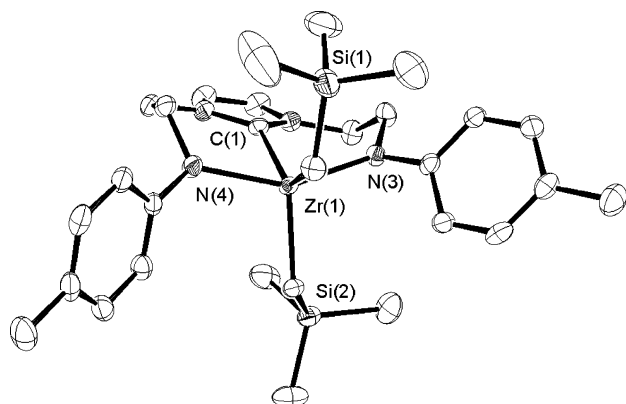


Figure 2. ORTEP view of $^{\text{tol}}[\text{NCN}]\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$ (**6**), depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Zr}(1)\text{--C}(1) = 2.415(3)$, $\text{Zr}(1)\text{--N}(3) = 2.173(2)$, $\text{Zr}(1)\text{--N}(4) = 2.135(2)$, $\text{Zr}(1)\text{--C}(23) = 2.238(3)$, $\text{Zr}(1)\text{--C}(24) = 2.254(3)$; $\text{N}(3)\text{--Zr}(1)\text{--C}(1) = 78.23(9)$, $\text{N}(4)\text{--Zr}(1)\text{--C}(1) = 76.27(9)$, $\text{C}(24)\text{--Zr}(1)\text{--C}(1) = 115.29(10)$, $\text{N}(4)\text{--Zr}(1)\text{--N}(3) = 148.73(9)$.

(Figure 2) of a single crystal of **6** revealed a distorted-trigonal-bipyramidal geometry around the zirconium metal center. The zirconium–carbene bond length ($\text{Zr}(1)\text{--C}(1)$) is 2.415(3) Å, which is slightly longer than that found in **5** but still shorter than the corresponding bond distances reported for NHC zirconium complexes of the type *trans*- ZrCl_4L_2 ($\text{L} = \text{NHC}$).⁹ The [NCN] ligand in **6** is more distorted from meridional than that found in **5**; the $\text{N}4\text{--Zr--N}3$ bond angle is only 148.73(9)° in **6**, considerably less than the analogous angle of 155.27(16)° found in **5**. The only organometallic group 4 complexes previously reported are the titanocene and zirconocene methyl cations $[\text{Cp}_2\text{MMe}(\text{IPr})]^+$ ($\text{M} = \text{Ti}, \text{Zr}$; $\text{IPr} = 1,3$ -diisopropylimidazol-2-ylidene), which contain a neutral monodentate NHC; only the titanocene complex was structurally characterized.¹¹

The aspect of carbene lability in $^{\text{tol}}[\text{NCN}]\text{ZrCl}_2(\text{py})$ (**5**) was addressed in two ways: in the first, the ^{13}C NMR spectrum of **5** in d_5 -pyridine, a strongly coordinating solvent, was measured and compared to that obtained in noncoordinating d_6 -benzene; in particular, the chemi-

cal shift of the N-heterocyclic carbene carbon resonance was monitored. In d_5 -pyridine this resonance was observed at 181.0 ppm, while in d_6 -benzene, it appeared at 187.9 ppm; the free carbene resonance observed for **2** is found at 211.4 ppm in d_6 -benzene. A second experiment involved the addition of 10 equiv of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ to a d_6 -benzene solution of **5**; in this case no change in the ^{13}C NMR resonance of the carbene carbon was observed. Both of these experiments are consistent with the carbene carbon atom of the NHC in the [NCN] ancillary ligand remaining bound to the Zr center, confirming that the flanking amido donors do anchor the NHC to the Zr(IV) center.

In conclusion, we have demonstrated the synthesis and coordination chemistry of a potentially dianionic, tridentate N-heterocyclic carbene system. By flanking the NHC with two amine pendant donor groups, which can be deprotonated to generate two anionic amido donors, the carbene donor has been forced to bind to Zr(IV) by virtue of its position in the chelate array. Procedures that involve protonolysis and alkylation are tolerated and have been used to synthesize both halide and alkyl zirconium compounds in good yields. The stability of the NHC donor to dissociation in this particular tridentate motif suggests that its influence on the chemistry of early metals will be measurable. Further research in this area will involve not only ancillary ligand modification but also the application of these and related complexes in homogeneous catalysis and dinitrogen activation.¹²

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Supporting Information Available: Text, tables, and figures giving complete experimental details and information on X-ray data collection and processing for **5** and **6** (PDF); X-ray data for **5** and **6** are also given as CIF files. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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