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COMMUNICATION

C–N Bond formation *via* ligand-induced nucleophilicity at a coordinated triamidoamine ligand†

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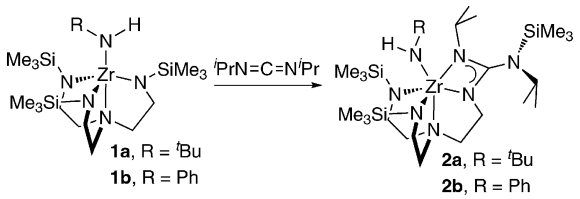
Reaction of $(N_3N)ZrX$ complexes (X = amido, Cl^-, CH_3^-) with carbodiimide substrates results in insertion into an Zr–N bond of the triamidoamine ligand rather than the Zr–X bond as has been observed for related $(N_3N)ZrX$ complexes (X = PR_2^-, AsR_2^-).

Efficient reactions that form new N–C bonds are attractive chemical transformations. In recent years, there has been a heightened interest in catalytic hydroamination reactions that produce substituted guanidine molecules, the value of which stem from the utility of these molecules, RN=(CNR′R′′)NHR, as chemical synthons, the core structure of some bioactive molecules, and organocatalysts.[1] Additionally, guanidinate anions are effective transition-metal and lanthanide ligands.[2]

At the forefront of catalytic preparation of guanidine molecules has been group 1–3 metal and lanthanide catalysts, though some others have been reported.[3] The dearth of group 4 metal catalysts other than Ti[3o–q] and the prior observation that triamidoamine-supported zirconium complexes are catalysts for hydroarsination and hydrophosphination reactions, including those with carbodiimide substrates,[4] suggested that the $(N_3N)Zr$ fragment (N_3N = $N(CH_2CH_2NSiMe_3)^{3-}$) may be viable for the catalytic hydroamination of carbodiimides. In the course of exploring such reactivity, an unusual but efficient activation of the coordinated triamidoamine ligand has been uncovered.

Treatment of zirconium-amido and -anilido complexes $(N_3N)ZrNHR$ (R = ^{t}Bu, **1a**; Ph, **1b**) with one equiv. of *N*,*N*′-diisopropylcarbodiimide at ambient temperature afforded the guanidinate-functionalized zirconium products [*N*,*N*,*N*,*N*,*N*,*N*-$N(CH_2CH_2NSiMe_3)_2\{CH_2CH_2NC(N^iPr)(N^iPrSiMe_3)\}$]$ZrNHR$ (R = ^{t}Bu, **2a**; R = Ph, **2b**) as analytically pure, colorless powders in 65 and 97% yield, respectively [eqn (1)]. Reactions with excess quantities of carbodiimide failed to give clean products.



(1)

Complexes **2a** and **2b** display apparent C_1 symmetry by ^{1}H and ^{13}C NMR spectroscopy with three inequivalent trimethylsilyl substituents. Some indicative spectral features of these compounds include four inequivalent methyl resonances of the isopropyl substituents as well as NH resonances at δ = 4.15 and 6.35 in the ^{1}H NMR spectra and imine carbon resonances at δ = 170.8 and 171.7 in the ^{13}C NMR spectra for complexes **2a** and **2b**, respectively. Assignments of chemical shifts for inequivalent methylene and methyl moieties in the ^{1}H and ^{13}C NMR spectra were accomplished with ^{1}H–^{13}C HMQC experiments.

The spectroscopically assigned molecular structure of complex **2a** was confirmed by X-ray crystallography. Single crystals were obtained by cooling a concentrated ether solution of the complex to −30 °C for extended periods, and the molecular structure of **2a** is shown in Fig. 1. This six-coordinate complex deviates significantly from an idealized octahedron at zirconium, and the angles are more acute than those of a bicapped tetrahedron.[5] Thus, the zirconium center of **2a** appears to be in a distorted skew-trapezoidal bipyramidal geometry. This geometry was originally described for bis(bidentate)dialkyltin complexes, but by using the *tert*-butyl amido, N(5), and amine, N(4), nitrogen atoms as unique positions and defining bidentate chelates as the N(2)/N(1) and N(3)/N(6) pairs, the $\phi_E \sim 76.5°$ and $\phi_B \sim 134.5°$ parameters of **2a** compare favorably to tin complexes with this geometry.[6] The nitrogen atom bond subject to insertion, N(3), now has Zr–N(3) = 2.198(1) Å, which is elongated over typical $Zr–N_{amido}$ bonds in $(N_3N)Zr$ complexes,[4,7] implying there is some delocalization of the lone pair to C(17). Furthermore, the sum of angles at C(17) = 360.0 (2)° and the C–N bond lengths of N(3)–C(17) = 1.335(2) Å and N(6)–C(17) = 1.326(2) Å are consistent with delocalization between N(3)–C(17)–N(6) and a CN_3, guanidinate-like unit. The C(18)–N(7)–Si(3) plane is approximately perpendicular to the plane N(3)–C(17)–N(6) suggesting there is no π-delocalization between C(17) and

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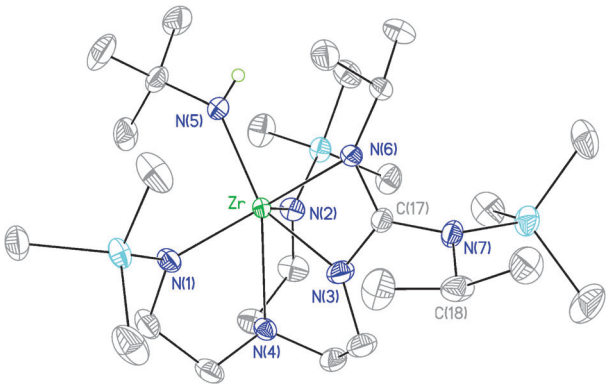
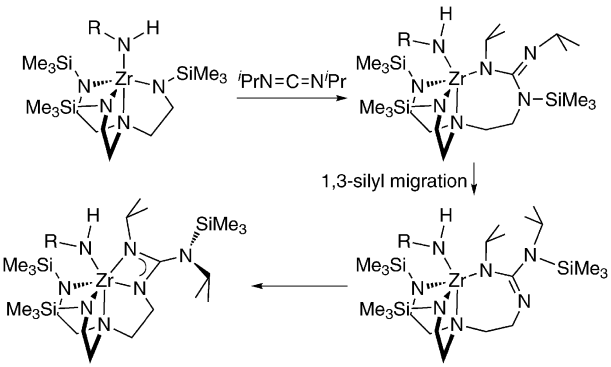
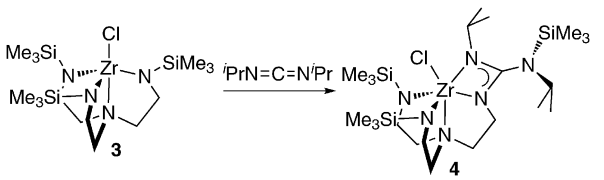


Fig. 1 Perspective view of **2a** with ellipsoids drawn at 50% probability level. Hydrogen atoms except H(5), which was located from the electron difference map, are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(1) = 2.138(1), Zr–N(2) = 2.135(1), Zr–N(3) = 2.198(1), Zr–N(4) = 2.511(1), Zr–N(5) = 2.090(1), Zr–N(6) = 2.405(1), N(3)–C(17)–N(6) = 111.3(1), N(3)–C(17)–N(7) = 123.3(1), N(6)–C(17)–N(7) = 125.4(1), C(13)–N(5)–H(5) = 107.4(1), C(13)–N(5)–Zr = 134.0(1).



Scheme 1 Proposed mechanism for the formation of **2**.



(2)

N(7). The *tert*-butyl amido ligand of **2a** appears to be engaged in ligand-to-metal π-donation based on the sum of angles at N(5) = 360.0(2)° and Zr–N(5) = 2.090(1) Å, which is comparable to that of complex **1** where Zr–N(5) = 2.071(3) Å.[7c]

The reactivity of (N_3N)Zr-amido complexes toward carbodiimide substrates differs substantially from what has previously been observed for the related pnictogen derivatives. For the terminal phosphide complexes $(N_3N)ZrPRR'$ (R = aryl or alkyl; R′ = R or H), reaction with carbodiimides results in 1,2-insertion into the Zr–P bond followed by η^3-coordination of the resultant phosphaguanidinate ligand, and arsenido derivatives display similar reactivity with heterocumulenes.[4] However, Cole and Junk have observed a similar reaction between symmetric alkyl carbodiimides and a 2-aminopyridine ligand on group 1 metals.[8] Based on prior observation of insertion chemistry at the Zr–X bond of $(N_3N)ZrX$ species and the report by Cole, a tentative mechanism for this transformation consisting of 1,2-insertion into the M–N bond of the triamidoamine ligand followed by 1,3-silyl migration to allow κ^5 coordination is proposed (Scheme 1). Presumably coordination of both isopropyl-substituted nitrogen atoms would be sterically unfavorable, which promotes the 1,3-silyl migration.

Despite these reactions not affording the intended guanidinate products, functionalization of tris(2-aminoethyl)amine ligands support the range of chemistry, particularly bioinorganic chemistry, in which these ligands participate.[9] Interestingly, reactivity that results in functionalization of this type of tren-type tetradentate N4 donor while coordinated remain limited.[10] More commonly, reported reactions decompose the triamidoamine ligand.[11]

Reaction of $(N_3N)ZrCl$ (**3**) with one equiv. of *N*,*N*′-diisopropylcarbodiimide at ambient temperature in benzene solution gave the related product as an analytically pure, colorless powder in 98% yield [eqn (2)].

Complex **4** displayed highly similar ^1H and ^{13}C NMR spectroscopic features as compared to complexes **2a** and **2b**. In particular, the imine carbon resonance at δ = 171.7 in the ^{13}C NMR spectrum was highly indicative. A single crystal X-ray diffraction study provided absolute confirmation of the structure and is shown in Fig. 2.

Single crystals of **4** were obtained by cooling a concentrated pentane solution of **4** to −30 °C for 12 h. Like **2a**, the geometry around Zr is best described as skew-trapezoidal bipyramid. The guanidinate unit is planar at C(16) (sum of angles ~360°), and the N–C bond lengths, N(3)–C(16) = 1.340(2) Å and N(5)–C(16) = 1.326(2) Å compare favorably with **2a**. These data are consistent with delocalization. Interestingly, the Zr–N(4) bond of **4** is shorter than that for other $(N_3N)Zr$ complexes, which is presumably due to the electron withdrawing character of the chloride ligand.[4,7]

The difference in the insertion reactivity between $(N_3N)ZrX$ derivatives is suggested by the nature of Zr–X bonding, where

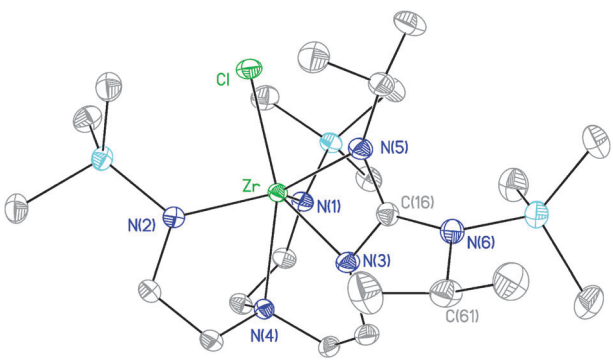
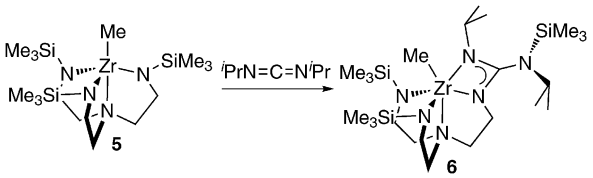


Fig. 2 Perspective view of **4** with ellipsoids drawn at 50% probability level. Hydrogen atoms except H(5) are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(1) = 2.109(2), Zr–N(2) = 2.110(2), Zr–N(3) = 2.163(2), Zr–N(4) = 2.389(1), Zr–N(5) = 2.336(2), Zr–Cl = 2.5014(8), N(3)–C(16)–N(5) = 109.9(1), N(3)–C(16)–N(6) = 124.4(1), N(5)–C(16)–N(6) = 125.7(1).

the amido and anilido derivates show evidence for ligand-to-metal π-donation from nitrogen to zirconium, but P and As congeners do not.[4,7] Amido derivatives also exhibit stronger Zr–X bonds according to computations.[7c] Thus, it was unclear with these substrates whether π-donation, which is likely present in both Zr–Cl and Zr–N bonds, or bond strength is the cause for this reactivity.

To test the whether π-bonding may or may not be causal for this unusual reactivity, another $(N_3N)ZrX$ (**5**) complex with a σ-only donor was explored. Treatment of $(N_3N)ZrMe$[12] with one equiv. of *N*,*N*′-diisopropylcarbodiimide in benzene solution exclusively reacted at the Zr–N bond to afford [*N*,*N*,*N*,*N*,*N*-$N(CH_2CH_2NSiMe_3)_2\{CH_2CH_2NC(N^iPr)(N^iPrSiMe_3)\}$]ZrMe (**6**) in 63% yield [eqn (3)]. The same C_1 symmetry and as well as similar ^1H and ^{13}C NMR spectroscopic features allow for the ready identification of **6** in comparison to complexes **2** and **4**.



(3)

The solid state structure of **5** is that of the expected σ-donor methyl ligand,[13] and according to computational studies, complex **5** has a stronger Z–X bond than related Zr-phosphide complexes.[7c] A similar trend was noted for the amido complexes relative to the phosphide complexes.

These observations lead to the conclusion that while there is a driving force for insertion into M–X bonds for these triamidoamine-supported zirconium complexes, other factors can thwart the expected Zr–X insertion and activate $M–N_{amido}$ bonds of the triamidoamine ligand. Current evidence supports the notion that the relative Zr–X bond strength allows for this previously unseen reactivity at the $M–N_{amido}$ bonds of the triamidoamine ligand. This somewhat unusual transformation with carbodiimides represents a mild and facile route to guanidinate-substituted triamidoamine ligands.

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