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Full Paper

CCC-NHC Pincer Zr Diamido Complexes: Synthesis, Characterisation, and Catalytic Activity in Hydroamination/Cyclisation of Unactivated Amino-Alkenes, -Alkynes, and Allenes*

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2-(1,3-Bis-3′-butylimidazol-1′-yl-2′-ylidene)phenylene)bis(dimethylamido) iodo zirconium(IV) (**3**) and 2-(1,3-bis-3′-butylimidazol-1′-yl-2′-ylidene)phenylene)bis (dimethylamido) bromo zirconium(IV) (**4**), have been prepared via a modification of the solvent and stoichiometry from the previously reported methodology. The reactivity of **3** and **4** in hydroamination/cyclisation is reported. Both diamido complexes have been found to improve catalytic activity as compared with the previously reported mono-amido analogues. Complexes **3** and **4** were observed to be selective for primary amines over secondary amines in hydroamination/cyclisation. The lack of reactivity with secondary amines is consistent with a mechanism involving requisite formation of a Zr-imido intermediate.

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Introduction

Hydroamination/cyclisation of unactivated amino-alkenes is an active area of research that is of interest to both the organic and organometallic chemist.[1] The products of these reactions are nitrogen-containing building blocks that are found in natural products, biologically active molecules, and pharmaceuticals.[2] These desirable moieties have prompted the development of efficient methods for the formation of C–N bonds, which typically involve the use of transition-metal catalysts.[2d–f,3] Methods for the synthesis of nitrogen-containing heterocycles by transition-metal catalysed intramolecular amine additions into unactivated amino-alkenes have recently been developed and have expanded the range of tools available to the synthetic chemist.[4] Hydroamination of alkenes is attractive as an atom-economic transformation,[1b,5] however the electrostatic repulsion between the nitrogen lone pair and electron rich π-system of the olefin results in a high activation energy,[6] thus requiring the use of a catalyst to allow the reaction to occur. Amidates, diphosphonic amides, biaryl diamines, ureates, and pyridylamido complexes were reported in the catalytic hydroamination/cyclisation of unactivated aminoalkenes, and the asymmetric synthesis of pyrrolidines and piperidines.[3a,7] The use of organolathanides in hydroaminations/cyclisation has also been reported.[4c,8] Metal-based catalysts have been employed extensively in the hydroamination/cyclisation of alkynes and allenes,[9] and the reactions with unactivated amino-alkenes has been especially popular in recent years.[10] Several groups worldwide have developed chiral Zr moieties that can enantioselectively catalyse the formation of five-, six-, and seven-membered N-heterocycles (NHCs) (Chart 1).[2a,11] A review of earth-abundant metals in hydroamination has been recently reported.[12]

Pincer ligands are a large and important class of organometallic compounds.[13] Examples of early transition metal complexes with rigid tridentate pincer ligands incorporating one or more NHCs are sparse.[13] These complexes have proven to be useful catalytic reagents in various types of reactions. This activity is due to their strong sigma donor ability and greater stability compared with their phosphine counterparts.[14] These properties have led to many applications in catalysis, solar cells, and biomedical fields.[15] Since the pyridylene moiety coordinates readily, many CNC-NHC pincer complexes have been reported.[3b,15c,16] However, fewer examples of CCC-NHC pincer complexes have been reported.

The synthesis, characterisation, and catalytic hydroamination activity of CCC-NHC pincer Zr mono-amido complexes have recently been reported.[11c,17] In that work it was found that the mono-amido complexes (Scheme 1, **5**, **6**) required a

*Dedicated to the memory of Professor B. Bosnich and the clarity of thought he brought to the most significant problems.

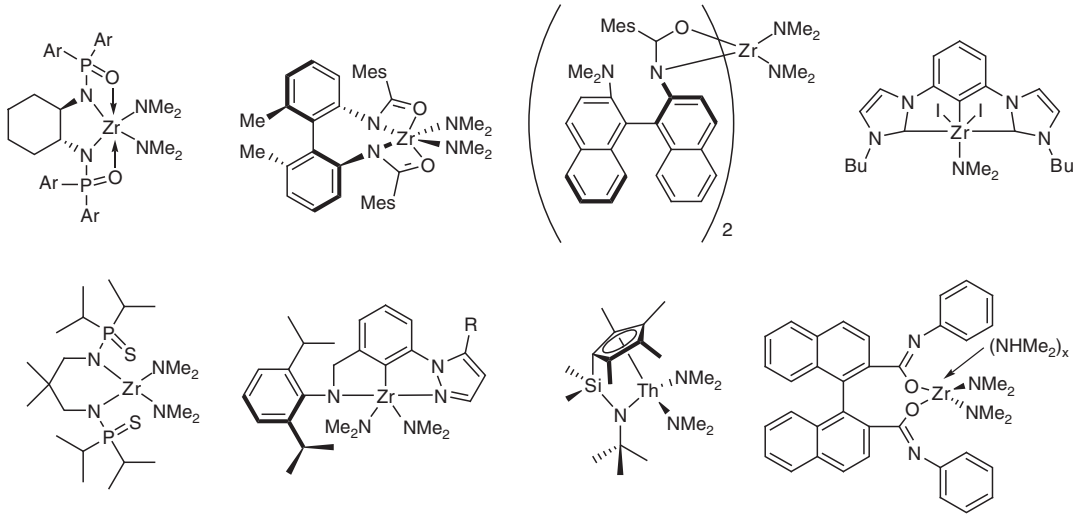
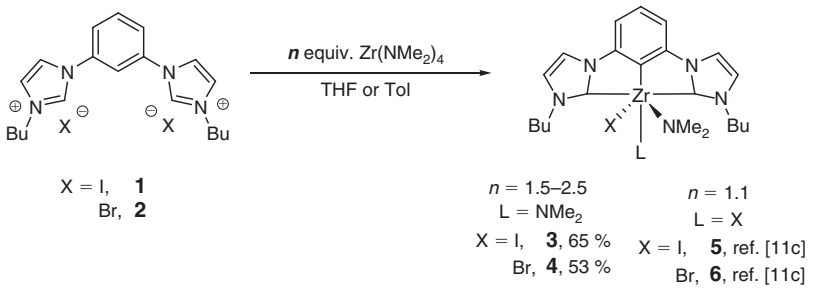


Chart 1. Recently reported catalysts for hydroamination/cyclisation. See text for literature references.



Scheme 1. Synthesis of CCC-NHC pincer Zr complexes.

minimum concentration for catalytic activity and only became active above 80°C. Such a requirement was consistent with an amido exchange at metal centres to generate the requisite Zr-imido complex for cyclisation. Therefore it was hypothesised that a diamido complex would provide a more efficient catalyst and allow a reduction in reaction temperature. Furthermore, in evaluating metals it was found that for the CCC-NHC complexes that Zr gave the fastest pre-catalysts. Herein, we report an expansion of the previous methodology to form 2-(1,3-bis-3′-butylimidazol-1′-yl-2′-ylidene)phenylene)bis(dimethylamido) iodo zirconium(IV) (**3**), and 2-(1,3-bis-3′-butylimidazol-1′-yl-2′-ylidene)phenylene)bis(dimethylamido)bromo zirconium(IV) (**4**), and their activity in the hydroamination/cyclisation of unactivated amino-alkenes, -alkynes, and allenes.

Results and Discussion

Synthesis and Characterisation

The diamido complexes **3** or **4** were readily obtained in pure form by using excess of the [$Zr(NMe_2)_4$] reagent with the appropriate salt, **1** or **2**, and replacing the previously reported solvent, DCM, with THF or toluene (Scheme 1).[18] This method provides the diamido complexes through the use of excess $Zr(NMe_2)_4$, whereas use of 1.1 equiv. provided the monoamido complexes **5** and **6**. Due to improved solubility in THF shorter reaction times and less solvent could be employed during the synthesis, but both methods were efficient. In some instances THF remained in the crystalline lattice (see below), so if a coordinating solvent might interfere with subsequent catalytic reactions, toluene may be the preferred synthetic solvent. Typical changes in the NMR spectra of the metalation were observed, and X-ray quality crystals (see below) were readily obtained from the reaction mixtures. Each was isolated by decanting the mother liquor from the crystals that were formed upon cooling, washing with hexanes, and drying. Upon isolation of the crystalline material the ^{1}H NMR spectra indicated the loss of the imidazolium proton signal around 11.4–11.6 ppm and the loss of the proton signal at 8.5 ppm in the aromatic region, which was consistent with the formation of the CCC-NHC pincer Zr complexes.

X-Ray Crystallography

The previously reported literature[18a] describes the synthesis and characterisation of the CCC-NHC pincer $ZrI(NMe_2)_2$ complex **3**. In this previous report, analysis of the crystal data showed that 9 % of the crystals were the mono-amido structure and 91 % were the di-amido structure. The crystallographic data below show 100 % diamido structure and no presence of the mono-amido. During the synthesis of complex **3** or **4**, the reaction mixtures yielded both cubic and needle crystals appropriate for single crystal X-ray diffraction. *ORTEP* illustrations of the molecular structure of complex **3** are shown in Fig. 1 and that of **4** are shown in Fig. 2. The coordination sphere around the metal centre is the typical distorted octahedron. The Zr–$C_{carbene}$ bonds (C10, C7) in complex **3** are 2.402(3)Å and 2.429(3)Å, and the Zr–$C_{carbene}$ bonds (C10, C7) in complex **4** are 2.407(4)Å and 2.384(4)Å. The Zr–I bond distance in complex **3** was 3.0864(3)Å, in comparison to the previously reported diamido structure of 3.07615(18)Å.[18a]

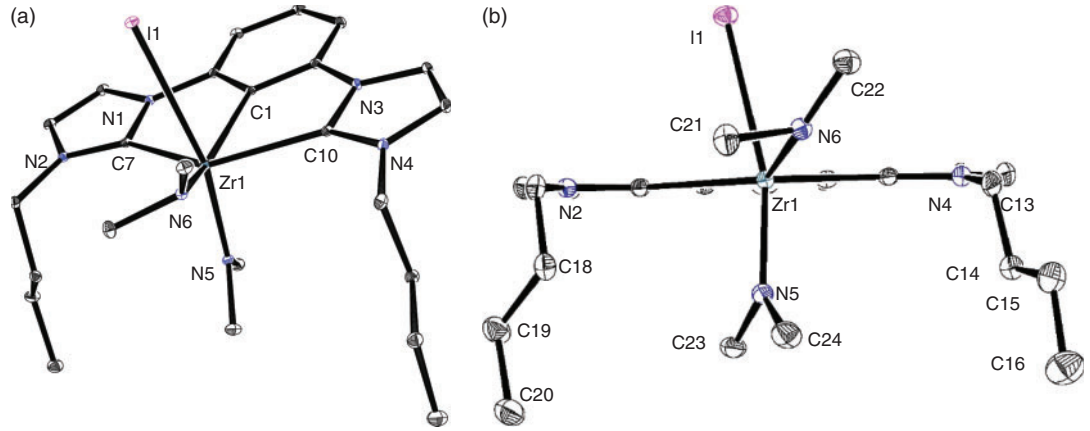


Fig. 1. An *ORTEP* molecular drawing of iodo complex **3** (a) illustrating the meridional tridentate binding and (b) illustrating the meso(cis) conformation of the butyl groups. Thermal ellipsoids are shown at 50 % probability and hydrogens were omitted for clarity. Selected bond angles (°), selected bond lengths (Å): C(10)–Zr(1)–C(7), 136; N(5)–Zr(1)–I(1), 165; N(6)–Zr(1)–C(1), 150; N(5)–Zr(1)–N(6), 102; Zr(1)–I(1), 3.0864(3); Zr(1)–C(7), 2.429(3); Zr(1)–C(10), 2.402(3); Zr(1)–C(1), 2.325(3); Zr(1)–N(5), 2.053(3); Zr(1)–N(6), 2.068(2).

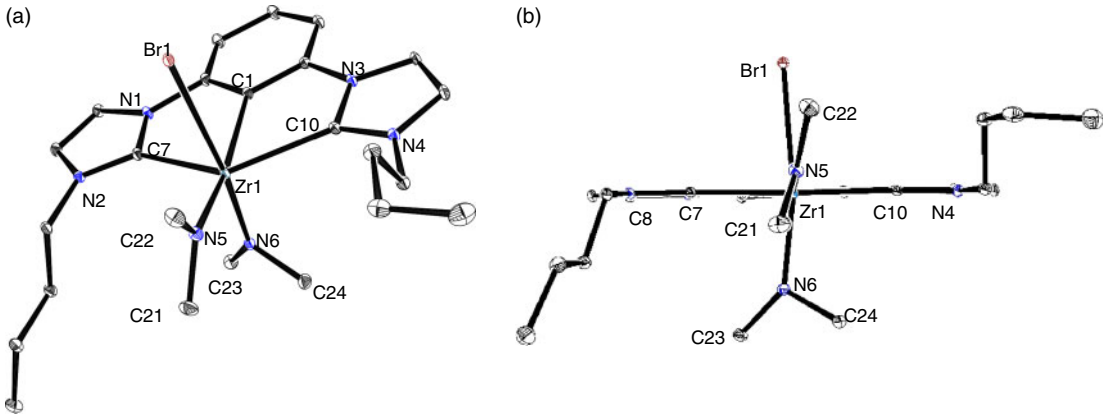
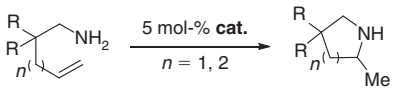


Fig. 2. An *ORTEP* molecular drawing of bromo complex **4** (a) illustrating the meridional tridentate binding and (b) illustrating the racemic (trans) conformation of the butyl groups. Thermal ellipsoids are shown at 50 % probability, and hydrogens and the THF are omitted for clarity. Selected bond angles (°), selected bond lengths (Å): C(10)–Zr(1)–C(7), 136; N(5)–Zr(1)–Br(1), 87; N(6)–Zr(1)–C(1), 93; N(5)–Zr(1)–N(6), 100; Zr(1)–Br(1), 2.8087(5); Zr(1)–C(7), 2.384(4); Zr(1)–C(10), 2.407(4); Zr(1)–C(1), 2.339(4); Zr(1)–N(5), 2.116(3); Zr(1)–N(6), 2.047(3).

Significant differences between the ligand conformations were noted between the iodo and bromo complexes (Figs 1b and 2b). The butyl groups are in a 'meso' conformation for iodo complex **3** (Fig. 1b), but are in a 'racemic' conformation for bromo complex **4** (Fig. 2b). It may be noted that the iodide is also bent from the standard octahedral angle, (C(7)–Zr(1)–I(1); 76.7°. In addition, there are distortions of the angles around nitrogen (N6) of the amido group for the iodo complex **3**, which are C(10)–Zr(1)–N(6); 92.613° and Zr(1)–N(6)–C(22); 143.865°. The bromo complex, **4**, has angles of C(10)–Zr(1)–N(5); 132.784 and Zr(1)–N(5)–C(22); 110.363, much closer to the normal 120° of a trigonal planar geometry. This distortion appears to be due to steric interactions between the large iodo ligand, the methyls of the amido ligand, and the methylene of the butyl chain. It may be rationalised based on two reinforcing factors. First the methylene carbon (C13) of the butyl chain and the methyl carbon (C22) of the amido group are 3.547Å apart, indicating that they are significantly closer than the Van der Waals minimum energy distance of 4.0 Å for Me–Me interactions.[19] Also, the C^{Me}–I distances are very short at 3.752 Å to C(22) and 3.884 Å to C(21). Second, the angles around N(6) are 109.7°, 97.9°, and 143.9°, which sums to 351.5°. Based on the sum alone it seems close to the 360° value for a planar structure. If the individual angles are examined the large distortions of 143.9° and 97.9° account for the total appearing to be near planarity. The distortions, therefore, may be entirely explained on the basis of a steric interaction with the larger iodo ligand (compare to the Br structure) and not an electronic repulsive interaction.

Catalyst Optimisation and Amino-Alkene Substrate Scope

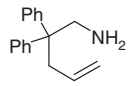
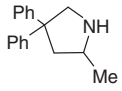
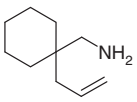
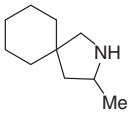
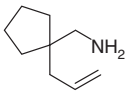
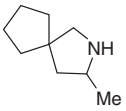
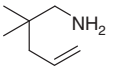
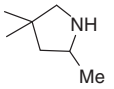
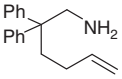
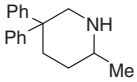
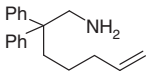
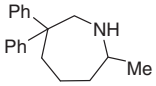
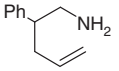
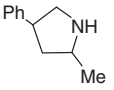
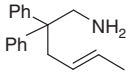
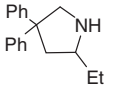
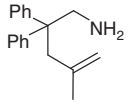
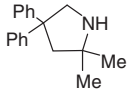
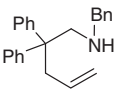
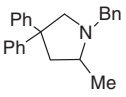
The previously employed 5 mol-% loading of pre-catalyst was selected for evaluation of the diamido complexes **3** or **4** for the hydroamination of alkenes as illustrated in Scheme 2. Initial evaluation was made for the formation of pyrrolidines (Table 1, entry 1) and piperidines (Table 1, entry 5) at different temperatures. Generally, the diamido complexes were found to have much faster reaction rates than the previously reported analogous mono amido complexes.[17] Reaction rates providing synthetically useful yields were observed at 160 and 40°C, and in some cases with a slow reaction being observed even at room temperature. Since room temperature reaction rates were slow, it was decided to evaluate both 40 and 160°C to provide guidance for future studies. It was determined that by using 5 mol-% Zr-I



Scheme 2. Hydroamination/cyclisation of unactivated amino-alkenes.

pre-catalyst **3**, quantitative conversions were obtain after 40–50 min of heating (Table 1, entry 1 and entry 5 at 160°C). Since the halogen present in the pre-catalyst had previously been demonstrated to have a large impact on the reaction rates,

Table 1. Catalyst and substrate scope for intramolecular hydroaminations

Entry[A]	Amine	Heterocycle	T[B] [°C]	Time [h], Conversion [%]	
				3 (ZrI)	**4** (ZrBr)
1			RT 40 160[D]	72, 11 96, 65 50 min, 100	72, 9 186, 37 1.5, 100
2			40 160	96, 21 3, 100	240, 8 10, >98
3			40 160	96, 3 29, 83	240, 4 25, 45
4			40 160	96, 2 64, 68	72, 0 24, 15
5			RT 40 160	72, 43 72, 85 40 min, 86	95, 44 38, 84 3, 92
6			40 160	24, 0[C] 24, 0[C]	24, 0[C] 24, 0[C]
7			40 160	48, 0[C] 24, 19	48, 0[C] 24, 6
8			40 160	24, 0[C] 24, 0[C]	24, 0[C] 24, 0[C]
9			40 160	24, 0[C] 24, 0[C]	24, 0[C] 24, 0[C]
10			40 160	96, 18 7, 98	48, 0 5, >98
11			40 160	24, 0[C] 24, 0[C]	24, 0[C] 24, 0[C]

[A]All reactions were performed in toluene-d_8 with the NMR tube immersed in a 160 or 40°C heating bath using 5 mol-% precatalyst (**3** or **4**). All conversions were determined by NMR spectroscopy.
[B]RT = room temperature, ~21°C.
[C]No reaction.
[D]~6 % oxidative amination product observed.

Zr-Br complex **4** was also evaluated. Generally, the bromide-containing complex **4** was found to have a slower rate than the iodide-containing complex **3** (Table 1). Formation of five-membered rings was efficient as long as the substrate contained substituents that facilitated ring closure due to the gem-dialkyl effect (Table 1, entries 1–4 versus 7 and 8). Having only a mono-substituted substrate (entry 7) or no substituent (entry 8) produced low conversion to no reaction. While five- and six-membered rings were formed efficiently, seven-membered ring precursors (entry 6) did not undergo reaction. A substituent on the terminus of the alkene (entry 9) also shut down reactivity. Internal substitution of the alkene (entry 10) resulted in a slower reaction, but good conversions were obtained at extended reaction times yielding a tetra-substituted carbon atom (entry 10). Attempted cyclisation of a secondary amine (entry 11) gave no reaction. Good activity was also noted for 2.5 and 1 mol-% catalyst loading at the same concentration of Zr pre-catalyst. It should be noted that for Table 1, entry 1 we were able to identify a side product at 80°C or higher that is the oxidative amination product that is otherwise obtained in Table 2, entry 1 (see Supplementary Material). This pyrroline product was present in approximately the same amount as that of the catalyst present, and, therefore, its production is consistent with a catalyst decomposition pathway. The diamido complexes **3** and **4** were found to be much more efficient catalysts than their mono-amido counterparts with reactivity observable at or near room temperature.

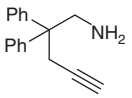
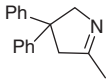
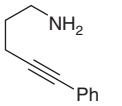
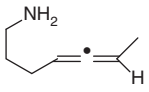
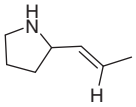
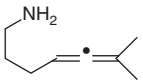
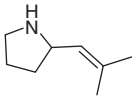
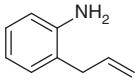
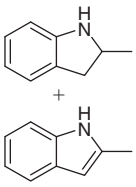
Other Hydroamination Substrates

Further evaluation of the substrate scope using complex **3** or **4** was made using 5 mol-% catalyst loading at room temperature or 160°C (Table 2) for hydroamination/cyclisation of alkyne and allene substrates. Intramolecular reactivity with alkyne substrates (entries 1 and 2) was found to be efficient and rapid even at room temperature for both **3** and **4** producing quantitative yields in minutes. In contrast, allene substrates gave no reaction even after extended periods at 160°C (entries 3 and 4). An aniline substrate (entry 5) was evaluated for the preparation of dihydroindoles. This substrate reacted slowly with the concomitant formation of the indole in an ~3.4 : 1 ratio, which was the first observation of an oxidative amination process for these Zr catalysts. Due to the aromatic nature of indole, the oxidation of indolene was not surprising. The fate of the hydrogen was not determined for these reactions. Finally, the intermolecular hydroamination of unactivated alkenes, alkynes, and allenes is also a highly desired process, but is difficult to obtain.[20] Intramolecular hydroaminations of alkenes, alkynes, and allenes have been widely reported by several groups, but intermolecular reactions are typically slow and require much longer reaction times. Attempted intermolecular hydroaminations using **3** or **4** produced no reaction.

Comparison of Hydroamination/Cyclisation Rates

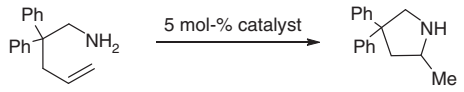
Recalling that the Zr monoamido diiodo complex **5** was the fastest of our previously reported complexes, data for comparison

Table 2. Substrate scope for hydroamination

Entry[A]	Amine	Product	T^B [°C]	Time [h], Conversion [%]	
				3 (ZrI)	**4** (ZrBr)
1			RT 160	2, 100 30 min, 100	1.5, 100 30 min, 100
2			RT	1, 99	30 min, 99
3			RT	24, 0[C]	24, 0[C]
4			RT 160	24, 0[C] 41, 0	24, 0[C] 68, 0
5			160	192, 71 192, 21	

[A]All reactions were performed in toluene-d_8 with the NMR tube immersed in a 160°C heating bath using 5 mol-% precatalyst (**3** or **4**). All conversions were determined by NMR spectroscopy.
[B]RT = room temperature.
[C]No reaction.

Table 3. Comparison of CCC-NHC Zr complex rates



Entry	Catalyst	Time [h]	*T* [°C]	Yield [%]
1	**3**, ZrI	96	40	65
2	**4**, ZrBr	93	40	23
3	**5**, ZrI_2	18	80	0[A]

[A]Ref. [11c].

of the diamido versus monoamido relative rates were collected in Table 3 for the conversion of the diphenyl substrate. Both diamido complexes **3** and **4** were observed to have significant rates of catalysis at 40°C with an observed yield of 65 % at 96 h for **3** (entry 1) versus 23 % at 93 h for **4** (entry 2). In contrast, no reaction was observed when the catalysis with monoamido diiodo complex **5** was conducted at 80°C (entry 3). Furthermore, as noted in Table 1, entry 1 both diamido complexes were found to have slow conversion at room temperature. This dramatic difference in the temperature required for initiation of the reaction is the biggest advantage of the diamido complexes, which has significant implications for stereoselective applications. While the diamido complexes are a significant improvement for the CCC-NHC type catalysts, their rates of reaction are still significantly less than the best catalysts as depicted in Chart 1.

Conclusions

The synthesis, characterisation, and the X-ray molecular structures of CCC-NHC pincer Zr diamido complexes **3** and **4** have been reported. These complexes were found to have improved reaction rates for hydroamination in comparison to the previously reported monoamido complexes. In addition, reactivity was reported for alkyne hydroamination and the formation of indole and dihydroindole. The hypothesis that having two amido ligands would lead to a faster catalyst has been borne out by the results obtained to date. Furthermore, the lack of reactivity of secondary amines is consistent with the formation of a Zr-imido in the catalytic cycle. Work continues to develop improved reaction rates for hydroamination catalysts based on the CCC-NHC ligand architecture.

Experimental

General Procedures

All reactions were done under an inert atmosphere using standard Schlenk techniques or a glove box unless noted otherwise. Al_2O_3 (basic, 50–200 μm) was stored in an oven at 130°C before use. Amine substrates were made by previously reported literature procedures and distilled before use.[17] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on 300 or 600 MHz Bruker instruments. Chemical shifts (δ) were expressed in ppm downfield to TMS at δ 0 and referenced to the residual solvent peak.[21] CD_2Cl_2, THF, toluene, toluene-d_8, and amine substrates were dried by passing through activated alumina.[22] 1,3-Bis(imidazol-1′-yl)benzene, 1,3-bis(3′-butylimidazol-1′-yl) benzene diiodide, and 1,3-bis(3′-butylimidazol-1′-yl)benzene dibromide were obtained via previously reported procedures.[17,18,23] $Zr(NMe_2)_4$ was freshly sublimed before use. All catalytic reactions were performed in a screw-cap NMR tube with toluene-d_8, and immersed in an oil bath at the temperature indicated in Tables 1 and 2. Products were readily identified based on their ^1H NMR signature.

Synthesis and Characterisation of CCC-NHC Zr Complexes

Method A – THF

*Preparation of 2-(1,3-Bis(*N*-butyl-imidazol-2ylidene)phenylene)bis(dimethylamido)(iodo) zirconium(IV) (**3**).* Solid 1,3-bis (1′-butylimidazol-3′-yl) benzene diiodide (0.273 g, 0.472 mmol) was added to a solution of $Zr(NMe_2)_4$ (0.314 g, 1.17 mmol) in THF (3 mL) and stirred for 10 min followed by heating in a 120°C oil bath for 10 min. The clear, bright yellow solution was allowed to cool slowly, and crystals formed. The supernatant was decanted. The product was washed with hexanes (2 × 2 mL) and dried under vacuum (0.191 g, 65 %). A crystal suitable for single crystal X-ray diffraction was selected from this sample. δ_H (CD_2Cl_2, 600 MHz) 7.66 (d, *J* 1.7, 2H), 7.42 (t, *J* 7.8, 1H), 7.27 (d, *J* 1.7, 2H), 7.26 (d, *J* 7.8, 2H), 4.01 (t, *J* 7.4, 4H), 3.01 (s, 12H), 1.78 (quint, *J* 7.5, 4H), 1.39 (sext, *J* 7.5, 4H), 0.99 (t, *J* 7.4, 6H). δ_C (150 MHz, CD_2Cl_2) 189.3, 158.4, 148.8, 132.1, 123.2, 116.7, 111.6, 52.1, 38.5, 34.1, 20.4, 14.1. Anal. Calc. for $C_{24}H_{37}IN_6Zr$: C 45.92, H 5.94, N 13.39. Found: C 45.93, H 5.97, N 13.17 %.

*Preparation of 2-(1,3-Bis(*N*-butyl-imidazol-2-ylidene)-phenylene)bis(dimethylamido)(bromo) zirconium(IV) (**4**).* Solid 1,3-bis(1′-butylimidazol-3′-yl)benzene dibromide (0.229 g, 0.472 mmol) was added to a solution of $Zr(NMe_2)_4$ (0.314 g, 1.17 mmol) and THF (3 mL). The mixture was sonicated for 10 min, and heated at 120°C for 10 min. The clear, bright yellow solution was allowed to cool slowly, and crystals formed. The supernatant was decanted. The product was washed with hexanes (2 × 2 mL) and dried under vacuum (0.103 g, 38 %). A crystal suitable for single crystal X-ray diffraction was selected from this sample, which contained THF in the crystalline lattice. After further drying under high vacuum at 70°C, an NMR sample was taken, which did not contain THF. δ_H (toluene-d_8, 300 MHz) ~7.06 (t, 1H, overlaps toluene), 6.84 (d, *J* 1.4, 2H), 6.76 (d, *J* 7.7, 2H), 6.26 (d, *J* 1.3, 2H), 4.01 (t, *J* 7.7, 4H), 3.56 (m, 4H, THF), 3.15 (s, 12H), 1.67 (quint, *J* 8.9, 4H), 1.45 (m, 4H, THF), 1.28 (sext, *J* 8.7, 4H), 0.90 (t, *J* 7.3, 6H).

Method B – Toluene

*Preparation of 2-(1,3-Bis(3′-butyl-imidazol-2′-ylidene)phenylene)bis(dimethylamido)(iodo) zirconium(IV) (**3**).* 1,3-Bis (imidazol-1′-yl)benzene diiodide (924 mg, 1.59 mmol), $Zr(NMe_2)_4$ (1.06 g, 3.99 mmol), and toluene (200 mL) were combined in a storage flask. The resulting mixture was stirred for 3 h in a 160°C oil bath. After cooling to room temperature, 70 % of the volatiles were removed under reduced pressure yielding a yellow solid. The precipitate was collected by vacuum filtration. After drying under reduced pressure, a light yellow solid was obtained (650 mg, 62 %). δ_H (CD_2Cl_2, 300 MHz) 7.68 (d, *J* 1.5, 2H), 7.42 (t, *J* 7.5, 1H), 7.29 (d, *J* 1.5, 2H), 7.12 (d, *J* 7.8, 2H), 4.01 (t, *J* 7.5, 4H), 3.01 (s, 12H), 4.46 (s, 4H), 1.78 (quint, *J* 7.5 4H), 1.38 (sextet, *J* 7.5, 4H), 0.98 (t, *J* 7.2, 6H). δ_C (75.5 MHz, CD_2Cl_2) 189.2, 158.3, 148.8, 132.1, 123.2, 116.7, 111.6, 52.0, 38.5, 34.0, 20.4, 14.1.

*Preparation of 2-(1,3-Bis(3′-butyl-imidazol-2′-ylidene)-phenylene)bis(dimethylamido)(bromo) zirconium(IV) (**4**).* 1,3-Bis(imidazol-1′-yl)benzene dibromo (990 mg, 2.04 mmol), $Zr(NMe_2)_4$ (1.36 g, 5.12 mmol), and toluene (200 mL) were combined in a storage flask. The resulting mixture was stirred

for 16 h in a 160°C oil bath. After cooling to room temperature, 70 % of the volatiles were removed under reduced pressure yielding a yellow solid. The precipitate was collected by vacuum filtration. After drying under reduced pressure, a light yellow solid was obtained (368 mg, 62 %). δ_H (500 MHz, CD_2Cl_2) 7.56 (s, 2H), 7.42 (t, *J* 7.5, 1H), 7.13 (s, 2H), 7.12 (s, 2H), 4.18 (t, *J* 7.5, 4H), 2.94 (s, 12H), 1.84 (quint, *J* 7.5, 4H), 1.43 (sextet, *J* 7.5, 4H), 0.99 (t, *J* 7.5, 6H). δ_C (125 MHz, CD_2Cl_2) 193.0, 165.4, 148.0, 129.0, 121.4, 115.97, 110.4, 51.6, 42.1, 34.0, 20.5, 14.1.

Typical Catalysis Procedure

In a screw cap NMR tube unactivated amino alkene (~25 mg, 1 equiv.), 2-(1,3-bis(*N*-butyl-imidazol-2-ylidene) phenylene)bis(dimethylamido)(iodo) zirconium(IV) (**3**, 3.9 mg, 0.05 equiv., 5 mol-%) and 0.5 mL of d_8-toluene were combined in a glove box followed by heating in a 160°C oil bath. The reaction progress was monitored by ^{1}H NMR spectroscopy.

*5-Methyl-3,3-diphenyl-3,4-dihydro-2*H*-pyrrole* (Table 3, entry 1). In a screw cap NMR tube 2,2-diphenyl-4-pentyn-1-amine (0.025 g, 0.106 mmol), 2-(1,3-bis(*N*-butyl-imidazol-2-ylidene) phenylene)bis(dimethylamido)(iodo) zirconium (IV) (0.004 g, 0.0054 mmol), and 0.4 mL of toluene-d_8 was combined in a glove box, which was immersed in a 160°C oil bath. The progress of the reaction was monitored by using ^{1}H NMR spectroscopy. δ_H (C_6D_6, 300 MHz) 7.08–6.95 (m, 10H), 4.38–4.36 (br sextet, *J* 1.5, 2H), 2.68 (br s, 2H), 1.75–1.74 (br t, *J* 1.6, 3H).

Crystallographic Data

The X-ray crystal structure data have been deposited with Cambridge Crystallographic Data Centre (**3**: CCDC# 982132, and **4**: CCDC# 982133).

Supplementary Material

^{1}H and ^{13}C NMR data for complexes **3** and **4**, along with details of the X-ray data collection and table of metric data are available on the Journal's website.

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