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CCC–N-heterocyclic carbene pincer complexes: Synthesis, characterization and hydroamination activity of a hafnium complex

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ABSTRACT

Our methodology for the stoichiometric preparation of CCC–NHC pincer complexes of Zr has been extended to Hf. The CCC^{Bu}–NHC pincer Hf complex has been characterized by X-ray crystal structure analysis. Catalytic activity in the intramolecular hydroamination/cyclization of unactivated alkenes is reported and compared to the recently reported Zr analog. An improved, scaled-up CuO-catalyzed aryl amination of 1,3-dibromobenzene and an improved salt formation methodology for preparation of bis (butyl-imidazolium)benzene are reported also.

1. Introduction

The catalytic synthesis of C–N bonds is a long standing challenge in synthetic chemistry. The addition of N–H bonds to unactivated alkenes is an atom-economical approach to this challenge. The original contribution of Marks and Gagne with lanthanides sparked much exploration in this area [1]. Metals ranging from Pt, Pd, Rh, Ir, Au, Zr, and Ti have been reported to catalyze this addition reaction [2], and many groups have made recent contributions [3]. In addition, several asymmetric variants of this reaction have been reported [4].

Following the first reports of stable carbenes, push–pull carbenes by Bertrand et al. and N-heterocyclic carbenes (NHCs) by Arduengo et al. [5], various metal complexes incorporating NHC ligands have been successfully synthesized and applied in disparate scientific arenas [6,7]. The stronger σ donating ability with almost no π-backbonding has led to NHCs place as *phosphine complements* [7], and as a result, they are now common ligands in a variety of transition metal catalyzed reactions [8] such as hydrogenation [9], carbon–carbon bond formation [10], carbon–nitrogen bond formation [11] and olefin metathesis [12].

Pincer ligand metal complexes have been extensively studied and applied in catalytic reactions because they possess a unique coordination environment [13]. Several groups have reported NHC pincer complexes containing an aromatic ring as a central donor group as illustrated in Fig. 1. Due to the ease of coordination of the nitrogen in the pyridine moiety, many pyridinylene [14] and 2,6-lutidinyl [15] bridged CNC–NHC pincer complexes (**A**) have been reported for a wide range of transition metals. Fewer examples have been reported for xylene-bridged CCC–NHC pincer complexes **B**, $n = 1$ [16]. We have recently reported several syntheses of early and late transition metal complexes [17–19] of the phenylene-bridged architectures (**B**, $n = 0$). Others have also begun reporting examples based on this ligand architecture [20]. We recently reported a highly efficient stoichiometric synthesis of the (CCC^{Bu}–NHC)$ZrI_2(NMe_2)$ complex and its effectiveness as a catalyst for hydroamination/cyclization of unactivated alkenes [17].

There are several examples of Hf NHC complexes, and a few have been crystallographically characterized [21]. Fryzuk reported the crystallographic characterization of an Hf(diamido-NHC) pincer complex, [22] and Cavell reported a unique C-atom bridged carbene Hf pincer complex [23]. We report herein the successful extension of our Zr methodology to the preparation of an Hf analog and compare its reactivity to the Zr complex. Additionally, improved synthetic methods for the preparation of the ligand precursors are described.

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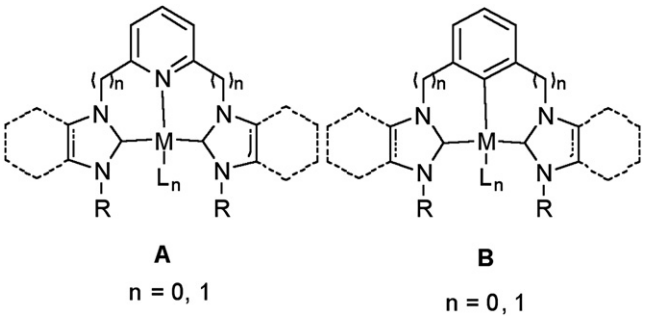


Fig. 1. Schematic of aryl-bridged CCC–NHC pincer complexes.

2. Results and discussion

2.1. Improved ligand precursor synthesis

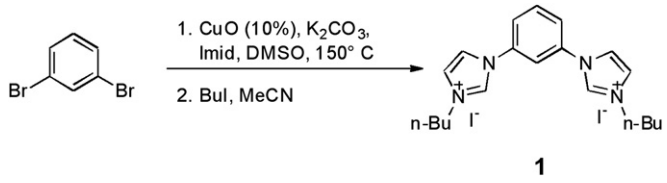
We report here a 10-fold scale-up of the synthesis of di(imidazolyl)benzene (Scheme 1, step 1). Filtration and concentration of the crude reaction mixture led to crystallization of the product in some cases. Pure material was routinely obtained on a 35 g scale. Use of MeCN as solvent for the bis(alkylation) procedure (Scheme 1, step 2) lead to faster reaction times and more efficient isolation procedures. Bis(imidazolium) salt **1** was routinely isolated in >90% yield by simple concentration and filtration.

2.2. Synthesis and characterization of CCC^{Bu}–NHC Hf pincer complex **3**

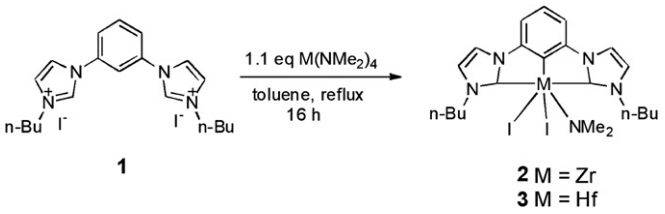
We recently reported that use of sublimed $Zr(NMe_2)_4$ allowed the efficient isolation of analytically pure CCC^{Bu}–NHC Zr complex **2** [17]. With appropriate technical preparations the use of a stoichiometric amount of $Hf(NMe_2)_4$ was employed to selectively and efficiently metallate ligand precursor **1** yielding the CCC^{Bu}–NHC Hf complex **3** (Scheme 2). Upon cooling the reaction a crystalline precipitate formed. This material proved to be analytically pure and was sufficient for single crystal X-ray diffraction analysis.

2.3. X-ray diffraction analysis of the molecular structure of CCC^{Bu}–NHC Hf complex **3**

An ORTEP® plot of the molecular structure of Hf complex **3** is presented in Fig. 2 along with selected metric data [24]. The coordination sphere was a distorted octahedron. The values of the bond distance and angles were within normal ranges and were typical of those previously reported for this class of molecules [22]. All of the average Hf–C distances were shorter than for the Zr complex. The bond distances for Hf–I and Hf–N5 did not differ significantly from the Zr complex. The C12–Hf–N5 angle was 99° compared to 107° in the Zr analog. The angle of the carbenes around the metal center (C3–Hf–C4) would be expected to be 180° in an idealized octahedron compared to the observed value of 138°, which is due to the constraints of the pincer structure. The trans I–Hf–N angle of 175° was near ideal. The Hf–I distance trans to the amido ligand was significantly longer than that trans to the aryl ligand (2.993(2) Å vs. 2.861(2) Å). Full metric data was included in the electronic supporting information. Additional data regarding data collection are included in Table 1.



Scheme 1. Improved ligand precursor syntheses.



Scheme 2. Metal complex synthesis.

2.4. Hydroamination/cyclization catalysis

Initial studies for hydroamination/cyclization were conducted with the unactivated primary alkenyl amine, 2,2-diphenyl-4-pentenamine, depicted in Table 2. At 5 mol% catalyst loading the production of the pyrrolidine product was clean and efficient. Therefore, the catalyst loading was decreased by a factor of ~2 in two additional experiments. Each time, complex **3** was found to be active and efficient yet required an increased reaction time to achieve the same level of conversion. The time required for conversion increased by a factor of ~2 with each reduction of catalyst loading by an equivalent factor. Such an anecdotal observation is consistent with a reaction that is first order. Significantly, pincer complex **3** was active even at 1 mol% catalyst loading.

Based on the data in Table 2, 5 mol% catalyst loading (entry 1) was chosen as optimal for evaluation of a series of substrates.

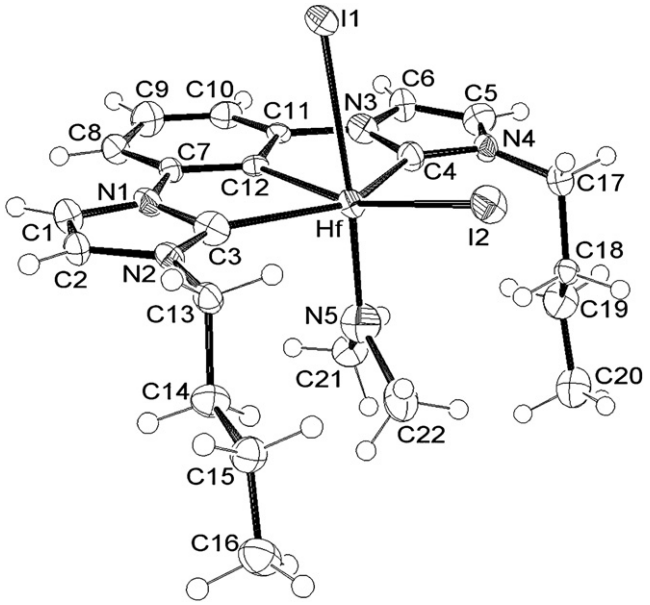


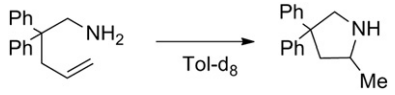
Fig. 2. ORTEP® plot at 50% thermal ellipsoids of CCC^{Bu}–NHC Hf pincer complex **3**. Selected structural bond distances (Å) and angles (deg): Hf–C12, 2.25(3) Å; Hf–C3, 2.34(3) Å, Hf–C4, 2.35(3) Å; Hf–I1, 2.993(2) Å; Hf–I2, 2.861(2) Å; Hf–N5, 1.98(3) Å C12–Hf–C3, 68.2(10)°; C12–Hf–C4, 69.4(10)°; C12–Hf–I1, 80.1(6)°; C12–Hf–I2, 164.1 (6)°; C12–Hf–N5, 98.6(11)°; C3–Hf–C4, 137.6(11)°; I1–Hf–I2, 84.58(6)°; N5–Hf–I1, 175.1(9)°.

Table 1
Crystal data and structure refinement for CCC^{Bu}–NHC Hf pincer complex, **3**.

Empirical formula	$C_{22}H_{31}HfI_2N_5$
Formula weight	797.81
Temperature (K)	101(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	
a (Å)	12.8134(8)
b (Å)	13.4801(6)
c (Å)	15.4005(10)
α (°)	90
β (°)	95.054(5)
γ (°)	90
Volume (Å^3)	2649.7(3)
Z	4
Density (calculated, Mg/m^3)	2.000
Absorption coefficient (mm^{-1})	6.284
F(000)	1504
Crystal size (mm)	0.20 × 0.20 × 0.20
θ range for data collection (°)	3.02 to 30.34
Index ranges	$-18 \le h \le 13$, $-18 \le k \le 18$, $-21 \le l \le 20$
Reflections collected	14894
Independent reflections	7163 [R(int) = 0.0552]
Completeness to $\theta = 30.34°$	89.9%
Absorption correction	Semi-empirical from equivalent
Max. and min. transmission	1 and 0.34895
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7163/168/271
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1466$, $wR_2 = 0.3374$
R indices (all data)	$R_1 = 0.1830$, $wR_2 = 0.3539$
Largest diff. peak and hole (e Å^{-3})	7.154 and −0.3146

Table 3 depicts these results and includes the data for Zr analog **2** for comparison [18]. The general reactivity patterns found with Zr complex **2** were also observed for Hf analog **3**. Pyrrolidines (entries 1–4) and piperidines (entry 5) were prepared in high yields, whereas the 7-membered heterocycle did not form (entry 6). A significant "*gem*-dialkyl" effect was observed when the rate of mono-substituted substrate was compared with the di-substituted substrates (entry 7 vs. entry 1) [25]. The extra substituent dramatically enhanced the rate of cyclization. Terminal substitution of the alkene prevented reaction completely (entry 8). Internal substitution of the alkene slowed but did not stop the reaction (entry 9), which is promising for asymmetric applications. Only primary amines underwent cyclization, since the dialkene (entry 10) underwent monocyclization only. The Hf catalyst was consistently slightly slower than the Zr catalyst in all examples evaluated. Both catalysts produced product at synthetically useful rates.

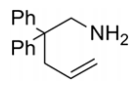
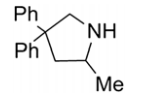
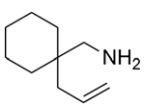
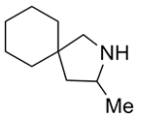
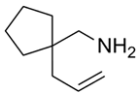
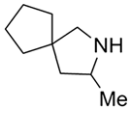
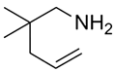
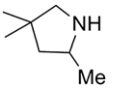
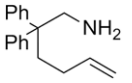
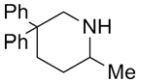
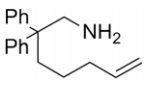
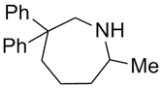
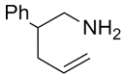
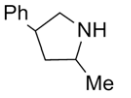
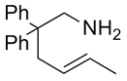
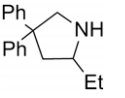
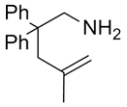
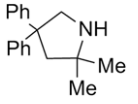
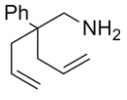
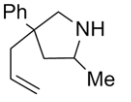
Table 2
Evaluation of catalyst loading for CCC^{Bu}–NHC Hf complex **3**.



Entry	Catalyst loading (mol%)	Temp (°C)	Time (h)	Conv (%)[a]
1	5	160	4.5	>98
2	2.5	160	7	>98
3	1	160	12	>98

[a] All conversions determined by ^{1}H NMR.

Table 3
Substrate survey of hydroamination catalytic activity at 5 mol% **3** in tol–d_8 at 160 °C.

Entry	Amine	Heterocycle	Hf[a]		Zr[b]	
			Time	conv (%)	Time	Conv (%)
1			4.5 h	>98%	50 min	>98%
2			14 h	>98%	3 h	>98%
3			28 h	83%	18 h	92%
4			48 h	81%	38 h	88%
5			12 h	93%	2 h	90%
6			48 h	–[c]	49 h	–[c]
7			30 h	19%	11 h	18%
8			48 h	–[c]	39 h	–[c]
9			35 h	>98%	8 h	>98%
10			5 h	>98%	1 h	>98%

[a] All conversions determined by ^{1}H NMR.
[b] All Zr data are from Ref. [17].
[c] No reaction.

3. Conclusions

The highly efficient stoichiometric synthesis of early transition metal CCC–NHC pincer complexes has been extended to an Hf analog, which was structurally similar to the Zr complex. The Hf

complex was found to be catalytically active for hydroamination/cyclization of unactivated alkenylamines, but it was slower than the Zr analog. Large scale synthesis of the CCC^{Bu}–NHC ligand precursor was accomplished.

4. Experimental section

4.1. General considerations

All experiments were performed with Schlenk techniques under an atmosphere of Ar or in an Ar filled glovebox except as noted. Hf$(NMe_2)_4$ was sublimed prior to use. Toluene, DMSO and CH_2Cl_2 were dried by passing through activated alumina [26]. MeOH and MeCN were used as received. The NMR spectra were recorded on Bruker 300 and 500 MHz instruments.

4.2. Preparation of bis(imidazolium) precursors

4.2.1. 1,3-Di-(imidazolyl)benzene

1,3-Dibromobenzene (25 mL, 207 mmol), imidazole (35g, 514 mmol), K_2CO_3 (72g, 520 mmol), CuO (2g, 25 mmol), and DMSO (200 mL) were combined in a 1 L round bottom flask. No precautions for excluding air were used. The solution was heated at 150 °C for 48 h. The reaction was cooled, checked by TLC, and filtered through Florosil® with MeOH. The resulting solution was concentrated, and crystallization yielded dark-yellow crystals. The crystals were washed with cold CH_2Cl_2 and dried yielding 17g of pale yellow crystals. A second batch of crystals was isolated similarly from the mother liquor, and it was purified by silica gel chromatography (10:1) eluting with CH_2Cl_2/MeOH (10:1) providing off-white crystals (19.4g) for a combined yield of 36.4 g, 83%. Alternatively, after concentration the crude product was purified by silica gel chromatography yielding 35.4g, 81% in a separate experiment. Spectroscopic data was identical to previously published data [27].

4.2.2. 1,3-Bis (1-butyl-imidazolium-3-yl) benzene iodide **1**

1,3-Bis-(imidazolyl) benzene (1.04 g, 4.95 mmol), butyl iodide (11.30 mL, 99.00 mmol) and MeCN (50 mL) were combined. The resulting mixture was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure to give a yellow solid (2.68 g, 94%). Spectroscopic data was identical to previously published data [27].

4.3. Preparation of CCC–NHC Hf complex

4.3.1. 2-(1,3-Bis(N-butyl-imidazol-2-ylidene)phenylene)bis (dimethylamido)(iodo)Hafnium (IV), **3**

1,3-Bis(1-butyl-imidazol-3-yl) benzene diiodide **1** (0.70 g, 1.22 mmol), Hf$(NMe_2)_4$ (0.48 g, 1.34 mmol) and toluene (40 mL) were combined and heated for 16 h in a 160 °C oil bath. The reaction was cooled to room temperature. During this period a solid precipitated. The precipitate was collected and dried under reduced pressure yielding a light yellow solid (0.67 g, 69%): ^{1}H NMR (CD_2Cl_2) δ 7.52 (s, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.10 (s, 2H), 4.4–4.6 (br m, 2H), 4.3–4.4 (br m, 2H), 3.07 (s, 6H), 1.94 (m, 4H), 1.47 (sex, J = 7.2 Hz, 4H), 1.00 (t, J = 7.2 Hz, 6H)); ^{13}C{^{1}H} (75.5 MHz, CD_2Cl_2): δ 201.0, 168.9, 146.8, 129.2, 122.0, 116.0, 110.8, 52.3, 43.1, 34.1, 20.3, 14.2. Anal. Calcd For $C_{22}H_{31}I_2N_5Hf$: C, 33.12; H, 3.92; N, 8.78. Found: C, 33.43; H, 3.90; N, 8.81.

4.4. X-ray structure determination for compound $C_{22}H_{31}HfI_2N_5$, **3**

4.4.1. Data collection

A thin, almost colorless crystal of dimensions approximately 0.20 × 0.20 × 0.20 mm, was retrieved from fluorocarbon oil, and placed in a 0.2–0.3 mm nylon loop. It extinguished fairly well under crossed polarizers. The loop was glued to a stout glass fiber, and mounted on a pin placed in a goniometer head. The crystal was flash frozen in the cold stream of the Oxford Cryostream to 101K. The crystallographic properties and data were collected using Mo Kα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 101(2) K [28]. A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. This crystal was the third specimen examined, and each was fairly mosaic (above 1.3°), and reflections were significantly broadened, but intensity did extend to below 1.0 Å. Data collection was carried out using Mo Kα radiation (graphite monochromator) with 8 runs consisting of 350 frames with a frame time of 50.0 s and a crystal-to-CCD distance of 50.000 mm. The runs were collected by omega scans of 1.0° width, and at detector positions of 28.781 and −30.499° in 2θ. The intensity data were corrected for absorption with an empirical correction [29]. Final cell constants were calculated from 4975 stronger reflections from the actual data collection after integration. See Table 1 for crystal and refinement information.

The structure was solved using direct methods in SHELXS-97, and refined using SHELXL-97 [30]. The space group P2(1)/n was determined based on the cell, intensity statistics, systematic absences, and successful solution structure and refinement. Non-H atoms from a single molecule were located in the initial E-map. They were refined at first with isotropic vibrational factors, then with anisotropic vibrational factors. H-atoms were then observable in difference electron density maps. Hydrogen atoms were placed in ideal positions; all were refined as riding atoms with relative isotropic displacement parameters. Soft restraints were used to keep some light atoms positive definite. The final full-matrix least-squares refinement converged to $R_1 = 0.1466$ (5038 reflections, F^2, $I > 2\sigma(I)$), and $wR_2 = 0.3539$ for all 7163 data, 271 parameters, 168 restraints (to keep light non-H atoms positive definite), goodness-of-fit (S) 1.026.

The cell was of the same general type and space group as the comparable Zr/I structure [18]. The structure is of the hafnium carbene complex with a non-chiral carbene ligand, two iodides (one axial and one equatorial), and an axial dimethylamido group. The butyl side chains are ordered. There are no close contacts that meet the definition of hydrogen-bonds, and most other contacts are of the H…H type.

All calculations were performed using Pentium computers using the current SHELX suite of programs.

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Appendix A. Supplementary data

CCDC 791008 (compound **3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplemental data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2010.10.004.

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