Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 5788–5803
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and reactivity of zirconium and hafnium complexes incorporating chelating diamido-N-heterocyclic-carbene ligands

Liam P. Spencer, Michael D. Fryzuk *

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

Received 3 June 2005; received in revised form 14 July 2005; accepted 15 July 2005
Available online 9 November 2005

Abstract

Early transition metal complexes employing a diamido N-heterocyclic carbene (NHC) ligand set (denoted [NCN]) render the centrally disposed NHC moiety stable to dissociation. Aminolysis reactions with the mesityl-substituted ligand precursor (^{Mes}[NCN]H$_2$) and M(NMe$_2$)$_4$ (M = Zr, Hf) provide bis(amido)-NHC-metal complexes that can be further converted to chloro and alkyl derivatives. Activation of ^{Mes}[NCN]M(CH$_3$)$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] yields {^{Mes}[NCN]MCH$_3$}{B(C$_6$F$_5$)$_4$}, which is surprisingly inactive for the polymerization of 1-hexene. The zirconium cation did, however, show moderate ability to catalytically polymerize ethylene. The hafnium dialkyls are thermally stable with the exception of the diethyl complex, ^{Mes}[NCN]Hf(CH$_2$CH$_3$)$_2$, which undergoes β-hydrogen transfer and subsequent C–H bond activation with an *ortho*-methyl substituent on the mesityl group. The hafnium dialkyl complexes also insert carbon monoxide and substituted isocyanides to yield η^2-acyls and η^2-iminoacyls, respectively. In some circumstances, further C–C bond coupling occurs to yield enediolates and eneamidolate metallocycles. The molecular structures of ^{Mes}[NCN]Hf(CH$_2$CHMe$_2$)$_2$, ^{Mes}[NCN]Hf(η^2-(2,6-Me$_2$C$_6$H$_3$NCCH$_3$)(CH$_3$), ^{Mes}[NCN]Hf(η^2-(2,6-Me$_2$C$_6$H$_3$NCCH$_3$)$_2$, ^{Mes}[NCN]Hf(OC(CH$_3$)=C(CH$_3$)NXy), and [^{Mes}[NCN]Hf(OC(^{t}Bu)=C(^{t}Bu)O)]$_2$ are included.

Keywords: Hafnium; Zirconium; Tridentate ligand; N-heterocyclic carbene; Amido donors; Migratory insertion; Polymerization

1. Introduction

N-Heterocyclic carbenes (NHCs) have found widespread use as essential ancillary ligands throughout most of the periodic table. Initially regarded as academic curiosities, the re-emergence of NHCs has been driven in part by their ability to replace phosphine ligands in homogeneous catalysis and small molecule activation [1]. In particular, late transition metal complexes employing this ligand set show strong metal carbene bonds and slow dissociation rates [2], properties that furnish robust and versatile catalysts. Indeed, in many cases, late transition metal NHC complexes have shown enhanced catalytic performance as compared to their phosphine predecessors. However, with certain late transition metal complexes, NHCs have also been observed to undergo non-innocent migratory insertion chemistry with metal alkyls and hydrides, which results in the deleterious modification of the NHC unit [3].

With respect to the early transition metals, N-heterocyclic-carbenes are known to be susceptible to dissociation. For example, samarium and yttrium complexes stabilized by a bidentate amidocarbene ancillary ligand show this tendency in the presence of Me$_2$NCH$_2$CH$_2$NMe$_2$ and Ph$_3$P=O [4]. In an effort to prevent dissociation and further develop early transition metal NHC chemistry, we have designed and synthesized an [NCN] ligand set with an NHC flanked by two amido units. We recently communicated the isolation and structural characterization of several zirconium amido, chloro, and alkyl derivatives and found the carbene donor was rendered stable to dissociation due to its central disposition between the two anionic amido units [5]. In the present work, we have extended our studies to

* Corresponding author.
E-mail address: fryzuk@chem.ubc.ca (M.D. Fryzuk).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.07.121

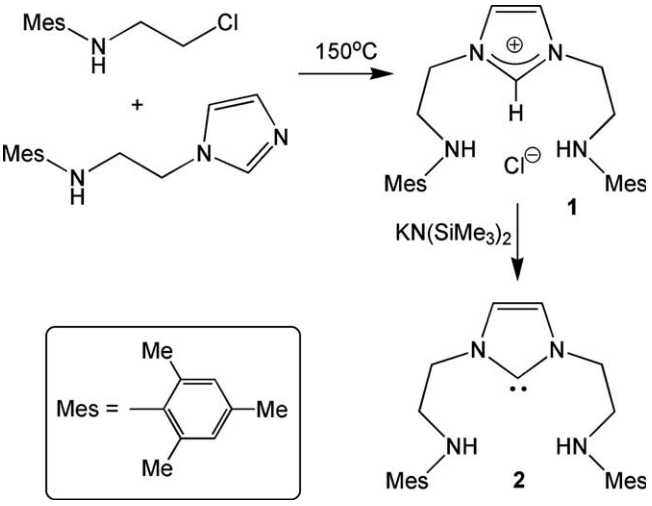
include the synthesis of hafnium-amido, -halide, and -alkyl compounds and, for the alkyl derivatives report their potential to polymerize ethylene and 1-hexene. We have also investigated the migratory insertion reactivity of the dialkyl derivatives with carbon monoxide and substituted isocyanides, and show that the NHC donor remains innocent during the insertion process.

2. Results and discussion

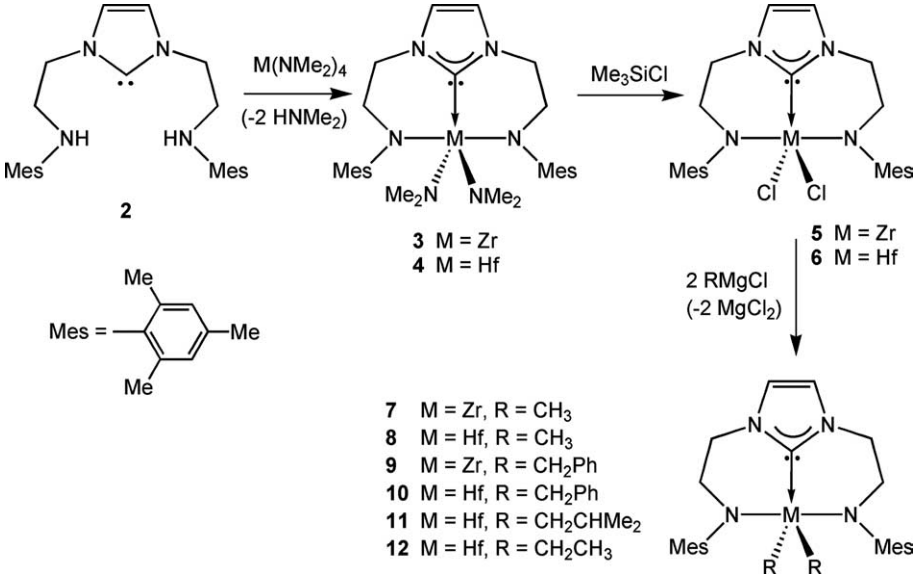
2.1. Synthesis of the dialkyl group 4 [NCN] complexes

We have recently reported the synthesis of an [NCN] ligand set and several group 4 zirconium complexes, including the first crystallographically characterized zirconium dialkyl containing an NHC donor [5]. The synthesis of the ligand was accomplished by reducing the carbonyl of a substituted bis(arylamide)imidazolium chloride precursor with BH_3. However, attempts to incorporate increased steric bulk on the aryl groups (i.e., 2,4,6-$Me_3C_6H_2$ or 2,6-$^{i}PrC_6H_3$) in a similar manner were unsuccessful; in these cases, BH_3 reduction under a variety of conditions only led to decomposition of the starting materials. Introduction of mesityl (2,4,6-$Me_3C_6H_2$) groups was accomplished by simply melting the appropriately substituted imidazole and β-chloroethylarylamine providing the imidazolium chloride, (^{Mes}[NCHN]H_2)$^{+}Cl^{-}$ (**1**), in near quantitative yield. Compound **1** can be selectively deprotonated with $KN(SiMe_3)_2$ to give the diamino-carbene (**2**) (Scheme 1). Synthesis of **2** was confirmed by the disappearance of the diagnostic iminium resonance of **1** at δ 9.35, along with an upfield shift in the imidazole ring proton resonances in the ^{1}H NMR spectrum, and a weak ^{13}C resonance at δ 215 attributable to the carbene carbon of **2**.

Protonolysis reactions involving **2** and $M(NMe_2)_4$ (M = Zr, Hf) provide for a convenient entry to ^{Mes}[NCN] group 4 complexes (Scheme 2). The ^{1}H NMR spectra of the bis(dimethylamido) complexes, **3** and **4** (Zr and Hf, respectively), suggest a C_{2v} symmetric species in solution with two multiplets for the equivalent ethylene spacers and singlets for the remaining proton environments. Both compounds also exhibit weak downfield ^{13}C resonances around δ 190, due to the M–$C_{carbene}$ carbon. The dimethylamido groups can be quantitatively removed to generate the corresponding dichlorides, **5** and **6**, with excess Me_3SiCl. The ^{1}H and ^{13}C NMR spectra of both **5** and **6** confirm the loss of dimethylamido groups, and weak ^{13}C M–$C_{carbene}$ resonances at δ 192.3 ppm and 198.2, for **5** and **6**, respectively, are observed. Interestingly, there is no change in the chemical shift of these latter resonances in any of the zirconium or hafnium compounds even in strongly coordinating pyridine over a period of several months, which confirms that there is no dissociation of the carbene carbon when flanked by two amido donors.



Scheme 1.



Scheme 2.

Alkylation of the dichlorides **5** and **6** by Grignard reagents proceeds smoothly to give the dialkyl products **7**–**12** exclusively. The zirconium dialkyl derivatives are more thermally sensitive in solution as compared to the hafnium analogues, decomposing to unidentifiable products over the period of one day; for this reason, zirconium complexes that have ethyl or isobutyl groups could not be isolated. With one exception, the hafnium dialkyls possess excellent thermal stability; no apparent decomposition was noted with the hafnium diisobutyl derivative **11** at 60 °C. In solution, the dialkyl products possess C_{2v} symmetry with diagnostic ^{13}C and ^{1}H resonances in the NMR spectra; for example, in **7**, both zirconium-methyl groups are equivalent and appear as a singlet at δ 0.33, and also equivalent are the four *ortho*-methyls on both mesityl substituents on the amido nitrogens. The solid-state molecular structure of **11** is shown in Fig. 1; crystallographic data are given in Table 1. The ligand assumes a puckered orientation with respect to a distorted trigonal bipyramidal metal centre. The mesitylamido donors are pseudo-*trans* oriented with N(4)–Hf(1)–N(3) being 151.49(8)°. The hafnium–carbene bond length (2.387(3) Å) is similar to the previously reported zirconium [NCN] complexes as are Hf–N amido (av. 1.361(3) Å) and Hf–C 2.250(3) Å) alkyl bond lengths [5,6].

In contrast to the thermal stability of the diisobutyl derivative **11**, the diethyl complex ^{Mes}[NCN]Hf(CH_2CH_3)$_2$ (**12**) decomposes at room temperature to give the metallated species **13** and ethane (δ 0.8) (Scheme 3). ^{1}H NMR studies of **13** reveal a C_1 symmetric species in solution with five inequivalent aryl-methyl resonances. There are two doublets at δ 1.00 and 2.51 indicative of two diastereotopic protons on the metallated –CH_2 resonance, consistent with a previously described metallated mesityl group [7].

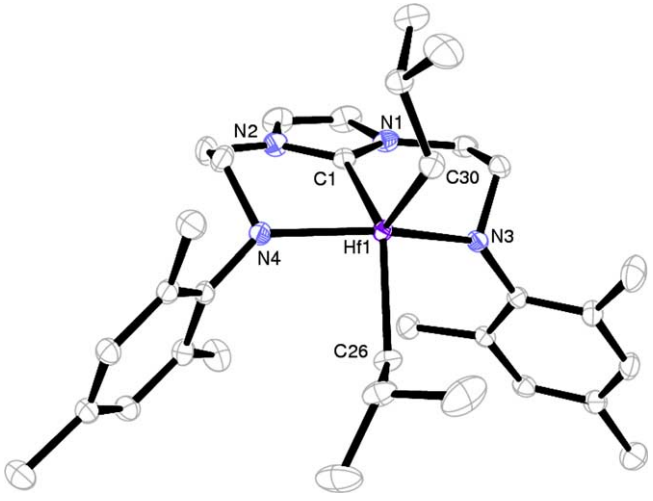


Fig. 1. ORTEP view of ^{Mes}[NCN]Hf(^{i}Bu)$_2$ (**11**) (1/2Et$_2$O omitted), depicted with 30% ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)–C(1) 2.385(3), Hf(1)–N(3) 2.101(2), Hf(1)–N(4) 2.126(2); N(3)–Hf(1)–N(4) 151.49(8), N(3)–Hf(1)–C(1) 80.33(9), N(4)–Hf(1)–C(1) 80.30(9), C(30)–Hf(1)–C(1) 118.02(9), C(26)–Hf(1)–C(1) 134.32(9).

Furthermore, two multiplets at δ −0.10 and 0.10 can be assigned to the diastereotopic protons of the remaining –HfCH_2 group, an observation previously made with a similarly metallated –HfCH_2CH_3 system [8]. Further proof of *ortho*-methyl bond activation was observed with a downfield shifted Hf–C ^{13}C resonance at δ 72.9, a chemical shift similar to that found for the benzylic carbons of the hafnium dibenzyl derivative **10**. Synthesis of the deuterated diethyl complex ^{Mes}[NCN]Hf(CD_2CD_3)$_2$ (d_{10}-**12**) provided information on the mechanism of this metallation. Decomposition of d_{10}-**12** results in the liberation of d_6-ethane (CD_3CD_3: identified by GC–MS), which suggests that β-hydrogen transfer [8] has occurred to give a reactive η^2-ethylene intermediate. This intermediate was not observed in solution but readily undergoes C–H bond activation with a neighbouring mesityl-methyl group to give the mono-protonated product, d_4-**13**; a broad singlet at 1.5 ppm integrating to one proton was found. Attempts to trap the η^2-ethylene intermediate with PMe_3 or pyridine have been unsuccessful.

2.2. Migratory insertion of isocyanides and carbon monoxide

2.2.1. Reactivity with aryl and alkyl isocyanides

The hafnium dimethyl derivative **8** reacts immediately in solution with one equivalent of xylyl isocyanide (XyNC) to give the mono-insertion product **14** (Scheme 4). The ^{1}H NMR spectrum is consistent with a C_s symmetric structure (equivalent N-mesityl groups and back bone linkers); the iminoacyl methyl resonance is found at 0.17 ppm. The η^2 coordination mode of the iminoacyl group was confirmed by ^{13}C NMR (N=*C*, δ 259) and IR (ν(C=N) 1575 cm^{-1}) spectroscopy and is a typical outcome for this kind of reaction [9]. In solution, only one of the two possible orientations of the η^2-iminoacyl unit is apparent. NOE measurements show a through space enhancement of the *ortho*-methyls of the N-xylyl group upon irradiation of the remaining Hf–Me resonance, which supports the isomer having the N-xylyl group pointing towards the Hf–Me. The solid-state molecular structure of **14** (Fig. 2) also verifies the η^2-iminoacyl coordination mode; crystallographic data are given in Table 1. The imino carbon atom is directly bound to hafnium centre with the Hf(1)–C(36) bond length at 2.251(2) Å, which is similar to related iminoacyl-zirconium complexes (2.23–2.25 Å). The bond angles of the triangle defined by Hf–C(28)–N(5) are typical of other structurally characterized group 4 η^2-iminoacyl complexes as is the imino C(28)–N(5) bond length [9]. The ancillary [NCN] ligand is distorted towards facial coordination with the N(4)–Hf(1)–N(3) angle being 133.65(7)°.

Addition of a second equivalent of xylyl isocyanide to **14** results in the exclusive formation of the bis(η^2-iminoacyl) product **15** (Scheme 4). The product contains a ν(C=N) band at 1568 cm^{-1}. The room temperature ^{1}H NMR spectrum of **15** in CD_2Cl_2 is consistent with a C_s symmetric species; however, cooling the solution to −40 °C was

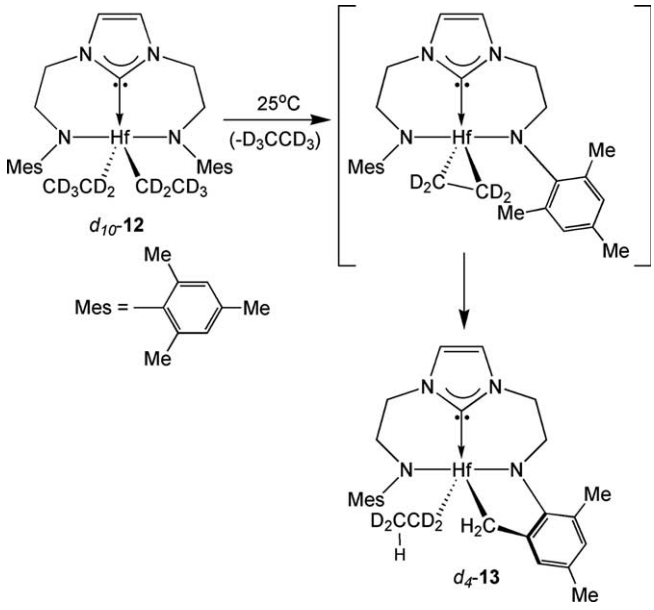
Table 1
General crystallographic data[a]

Compound	**11**	**14**	**15**	**18**	**23**
CCDC registry	271123	271124	271125	271126	271127
Formula	$C_{33}H_{50}HfN_4 \cdot C_2H_5O$	$C_{36}H_{47}Hf\ N_5 \cdot C_4H_8O$	$C_{90}H_{112}Hf_2N_{12} \cdot CH_2Cl_2$	$C_{37}H_{47}Hf\ N_5O \cdot C_2H_5O$	$C_{70}H_{100}Hf_2N_8O_4 \cdot 4C_6H_6$
Molecular weight	726.33	800.39	1803.82	801.35	1786.99
Colour, habit	Colourless, prism	Colourless, plate	Colourless, irregular	Yellow, irregular	Colourless, tablet
Crystal size (mm)	$0.15 \times 0.15 \times 0.15$	$0.40 \times 0.30 \times 0.10$	$0.20 \times 0.07 \times 0.04$	$0.10 \times 0.05 \times 0.03$	$0.15 \times 0.07 \times 0.04$
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	19.9312(3)	32.883(5)	15.6616(8)	10.9435(6)	12.377(5)
b (Å)	13.7149(3)	11.614(5)	16.3972(7)	20.0210(11)	18.530(5)
c (Å)	28.0013(6)	23.793(5)	21.5514(10)	17.3179(8)	21.408(5)
α (°)	90	90	70.757(2)	90	107.656(5)
β (°)	113.0590(10)	112.217(5)	73.887(2)	92.451(2)	103.930(5)
γ (°)	90	90	68.167(2)	90	100.104(5)
V (Å^3)	7042.7(2)	8412(4)	4774.1(4)	3790.9(3)	4374(2)
Z	4	4	2	4	2
D_{calc} (g cm^{-3})	1.355	1.378	1.255	1.404	1.357
$F(000)$	2952	3600	1844	1636	1840
μ(Mo Kα) (mm^{-1})	2.991	2.521	2.275	2.790	2.425
Transmission factors	0.8448–1.0000	0.7118–1.0000	0.8093–1.0000	0.7300–1.0000	0.6694–1.0000
$2\theta_{max}$ (°)	51.40	55.24	48.10	41.20	46.92
Index ranges (h, k, l)	−25, 26; −18, 18; −37, 37	−43, 43; −15, 15; −31, 30	−19, 19; −20, 18; −26, 25	−12, 13; −23, 23; −15, 20	−13, 13; −19, 19; −23, 22
Total number of reflections	97131	115842	108780	25826	44117
Number of unique reflections	8473	9958	19273	6703	11428
R_{merge}	0.0396	0.0388	0.0649	0.1030	0.1051
Number of reflections with $I \geqslant 2\sigma(I)$	6802	8511	13353	4186	7049
Number of variables	377	479	988	420	993
R (F^2, all data)	0.0337	0.0285	0.0963	0.1058	0.1106
R_w (F^2, all data)	0.0576	0.0478	0.2299	0.0834	0.1137
R (F, $I > 2\sigma(I)$)	0.0217	0.0203	0.0656	0.0479	0.0473
R_w (F, $I > 2\sigma(I)$)	0.0508	0.0454	0.2136	0.0713	0.0944
Goodness-of-fit	1.066	1.021	1.281	0.999	0.982
Largest difference in peak/hole (e Å^{-3})	1.241/−0.590	0.669/−0.672	6.701/−1.140	1.033/−1.275	1.340/−1.319

[a] Data common to all structures: Diffractometer, Bruker X8 APEX CCD; temperature (K), 173(2); wavelength (Å), 0.71073.

necessary to fully resolve all resonances. At this lower temperature, two unique environments were observed for each η^2-iminoacyl group consistent with the solid-state molecular structure of **15** (Fig. 3); crystallographic data are given in Table 1. Attempts to observe the characteristic iminoacyl ^{13}C resonance in solution were not possible likely due to fast exchange under the normal acquisition conditions. In the solid state, there are two independent molecules in the asymmetric unit cell with subtle variations in the η^2-iminoacyl bond lengths (only one of the molecules is used for structural analysis described below). Although formally seven-coordinate, **15** is best described as distorted trigonal bipyramidal about hafnium, with each of the η^2-iminoacyl groups occupying a single coordination site, one axial and one equatorial. The ^{Mes}[NCN] ligand is puckered towards a facial orientation with N(4)–Hf(1)–N(3) being 122.6(3)°, presumably to accommodate the additional steric constraints of two xylyl units. The two iminoacyl groups are oriented perpendicular to each other, which is further evidence of the considerable steric interactions in the solid state.

In general, thermolysis of groups 4 and 5 bis(η^2-iminoacyl) complexes results in the formation of enediamido metallacycles [10,11]. However, heating **15** in refluxing toluene resulted in no reaction, only recovery of starting materials (110 °C for >8 h). This was somewhat surprising as this transformation is reported to be facilitated by lowering the $\pi^*_{C=N}$ orbital via the presence of electron-withdrawing substituents or by having a relatively electron-rich metal centre [9]. Because NHCs are considered strongly σ-donating [1], this should have facilitated this transformation. To probe the effects of sterics on this process, isopropylisocyanide (^{i}PrNC) was added to **14** to generate the mixed bis(iminoacyl) species **17** (Scheme 4). Thermolysis of this material also resulted in no reaction even after extended reaction times at 110 °C. Finally, the bis(isopropyl)



Scheme 3.

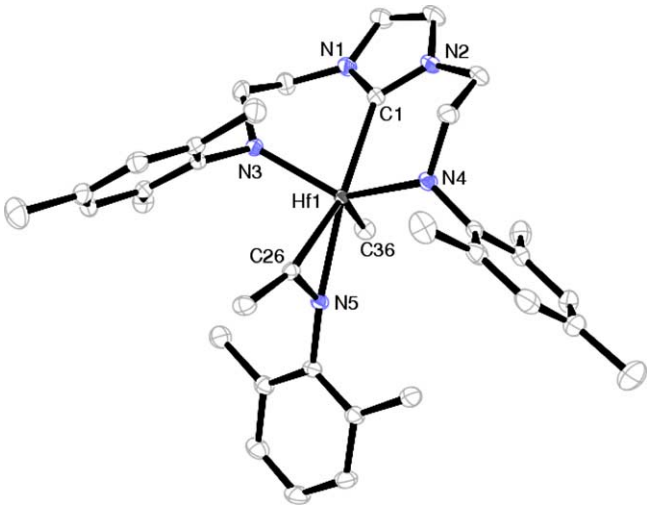
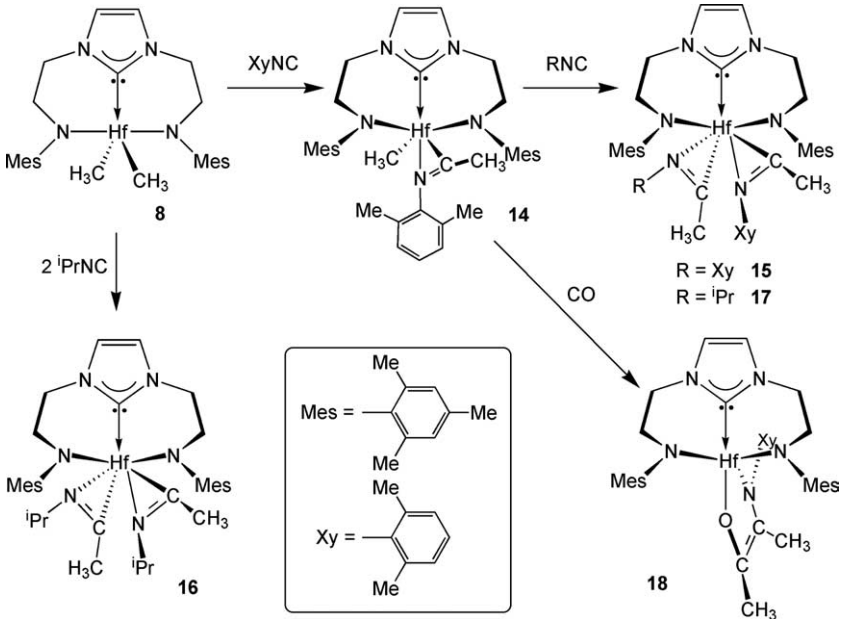


Fig. 2. ORTEP view of ^{Mes}[NCN]Hf(η^2-XyNCCH$_3$)(CH$_3$) (THF omitted) (**14**), depicted with 30% ellipsoids; all hydrogen atoms and mesityl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)–C(1) 2.387(2), Hf(1)–C(26) 2.251(2), Hf(1)–N(3) 2.1352(18), Hf(1)–N(4) 2.1117(18), Hf(1)–N(5) 2.2461(16); N(5)–C(26)–Hf(1) 73.05(11), N(4)–Hf(1)–N(3) 133.65(7), N(4)–Hf(1)–C(1) 77.25(7), N(3)–Hf(1)–C(1) 77.72(7).

iminoacyl was prepared by addition of two equiv of isopropyl isocyanide to the dimethyl complex **8** to generate **16** in excellent yields. This also turned out to be indefinitely stable to thermolysis as evidenced by no change in the ^{1}H NMR spectrum over a period of hours at 110 °C. Formation of an enediamido metallacycle is known to be affected by the steric bulk located on the nitrogen atom [12,13]. Moreover, for enediamide formation to occur, both η^2-iminoacyls must rotate into the preferred coplanar configuration, which would appear to be difficult in complexes **15**–**17** due to increased steric bulk around the metal centre [10,11,14–16].

2.2.2. Formation of an eneamidolate metallacycle

The hafnium methyl-iminoacyl complex **14** readily reacts with CO (1 atm) to generate the eneamidolate complex **18** (Scheme 4). The likely first step is insertion of CO into the remaining Hf–CH$_3$ bond; however, monitoring of this process by NMR spectroscopy did not provide any evidence for the presence of a mixed acyl-iminoacyl compound implying that the C=C bond formation process is quite facile. To our knowledge, only one other example of eneamidolate synthesis has been reported, but that



Scheme 4.

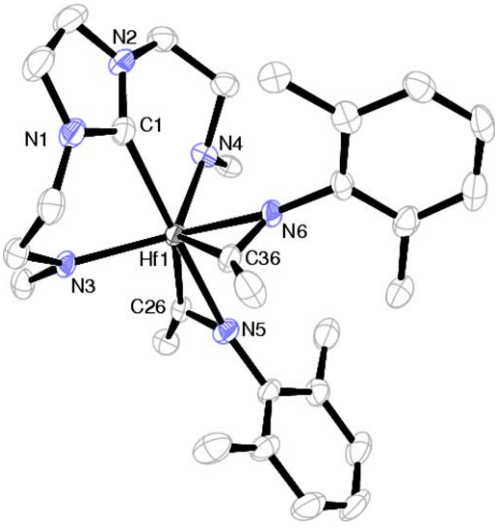


Fig. 3. ORTEP view of ^{Mes}[NCN]Hf(η^2-XyNCCH$_3$)$_2$ (CH_2Cl_2 omitted) (**15**), depicted with 30% ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf(1)–N(4) 2.146(8), Hf(1)–N(3) 2.154(7), Hf(1)–C(26) 2.249(9), Hf(1)–N(5) 2.250(8), Hf(1)–N(6) 2.305(7), Hf(1)–C(36) 2.306(10), Hf(1)–C(1) 2.377(10); N(4)–Hf(1)–N(3) 122.6(3), C(26)–Hf(1)–N(5) 34.0(3), N(4)–Hf(1)–C(1) 78.2(3), N(3)–Hf(1)–C(1) 76.2(3), N(6)–Hf(1)–C(36) 32.3(3).

example required forcing conditions (200–1000 psi of CO) [10]. The solid-state molecular structure of **18** is shown in Fig. 4, and confirms the presence of an eneamidolate ring; crystallographic data are given in Table 1. The C=C bond length (1.340(9) Å) compares well with previously described metallocyclopentene metallocycles [10,17]. The eneamidolate ring is distorted from a planar coordination, an observation prominent in most enediolate, eneamidolate and enediamides systems. This bending has been attributed

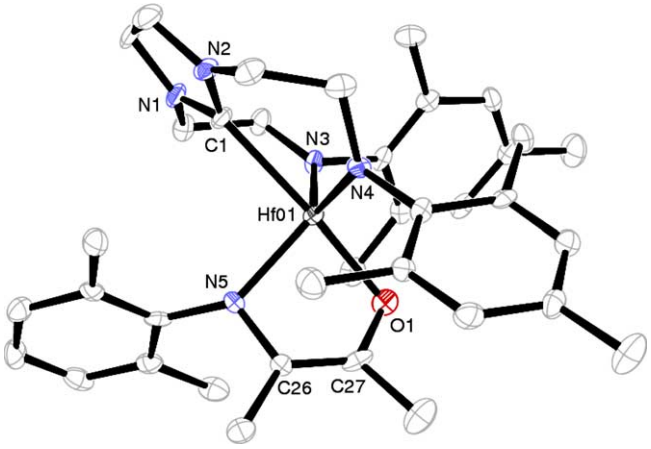
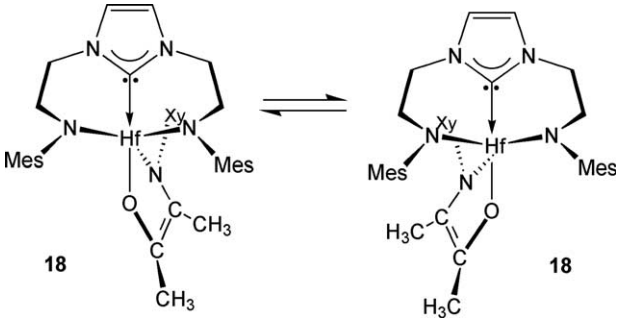


Fig. 4. ORTEP view of ^{Mes}[NCN]Hf(OC(CH$_3$)=C(CH$_3$)NXy) (1/2Et$_2$O omitted) (**18**), depicted with 30% ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf(01)–O(1) 2.032(4), Hf(01)–N(5) 2.061(5), Hf(01)–N(3) 2.077(5), Hf(01)–N(4) 2.082(5), Hf(01)–C(1) 2.348(6), Hf(01)–C(27) 2.660(6), Hf(01)–C(26) 2.728(7), C(26)–C(27) 1.340(9); O(1)–Hf(01)–N(5) 83.14(19), N(3)–Hf(01)–N(4) 124.5(2), N(3)–Hf(01)–C(1) 78.1(2), N(4)–Hf(01)–C(1) 81.2(2).

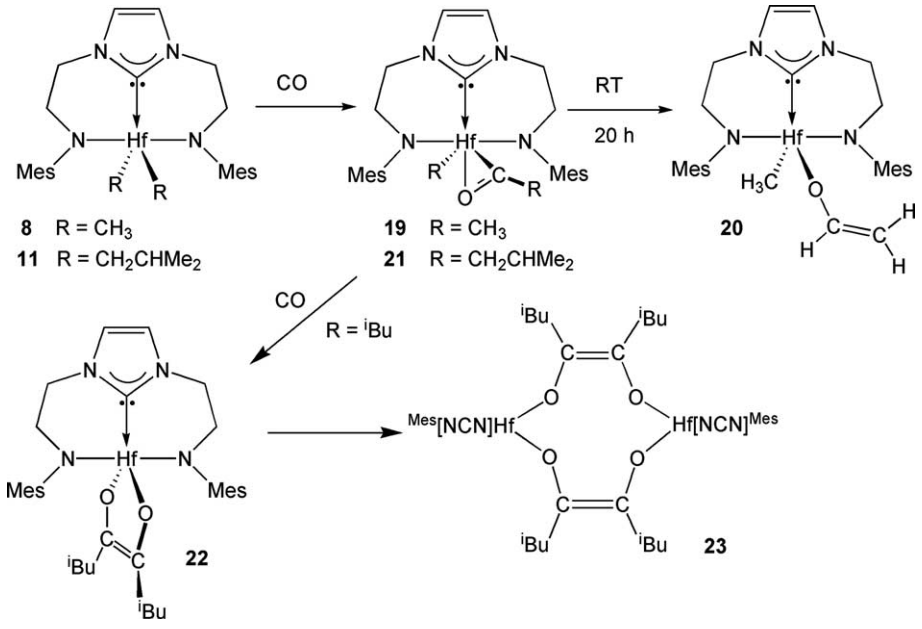
to a σ^2,π bonding interaction between the electron deficient metal centre and the olefinic portion of the metallocyclic backbone, a phenomenon observed in a similar Zr–butadiene system [17]. A fold angle of 24.0° was found for **18**, significantly less than previously reported compounds (~50°) [10,18], which may be reflective of the decreased Lewis acidity of the metal centre and/or the different kind of heterometallocycle. As a result, the Hf(1)···C(26) and Hf(1)···C(27) distances (2.728(7) and 2.660(6) Å, respectively) are significantly longer than the previously reported eneamidolate complex (2.549(8) and 2.581(8) Å) [10]. Once again, the ^{Mes}[NCN] ancillary ligand is distorted towards facial coordination as evidenced by the N(4)–Hf(1)–N(3) bond angle of 124.5(2)°. The molecule possesses C_1 symmetry in the solid state as a result of the σ^2,π interaction; however, C_s symmetry was observed in solution at room temperature due to ring flipping of this eneamidolate ring on the NMR time scale. The $\Delta G^{\ddagger}$ of 54.1 kJ mol^{-1} for the ring-flipping process (Eq. (1)) was estimated from the coalescence temperature (268 K), and is very similar to the value estimated for a Hf–enediamide complex (59.4 kJ mol^{-1}) [10]. Broad resonances for the O–*C*(CH$_3$)= and O–C(*C*H$_3$)= carbon nuclei were observed by ^{13}C NMR at δ 137.0 and 19.4, respectively.



(1)

2.2.3. Formation of a hafnium vinyl-enolate and enediolate metallacycle

Due to its ease of preparation and its enhanced thermal stability relative to zirconium dialkyl complexes, the hafnium dimethyl derivative **8** was chosen for reactivity studies with CO. Exposure of **8** to 1 atm of carbon monoxide for one day results in the formation of ^{Mes}[NCN]Hf(CH$_3$)-(O–CH=CH$_2$) (**20**), a hafnium vinyl-enolate (Scheme 5). Diagnostic resonances appear in the ^{1}H NMR spectrum at δ 3.47, 3.54, and 5.75, with appropriate geminal and vicinal coupling constants. The downfield resonance at δ 5.75, assigned to the α-O–C*H*= proton, splits further when ^{13}CO is substituted, giving typical $^1J_{^{13}C-^1H}$ coupling of 145 Hz [19]. The ^{Mes}[NCN] ligand resonances are diagnostic of a C_s symmetric compound and also apparent is the Hf–CH$_3$ resonance located at δ 0.37. The ^{13}C NMR reveals a Hf–NHC carbene signal at δ 196.2, as well as vinyl ^{13}C resonances at δ 120.2 and 139.0. From the solution NMR data, we are unable to provide information on the *mer* versus *fac* orientation of the [NCN] donors, and for



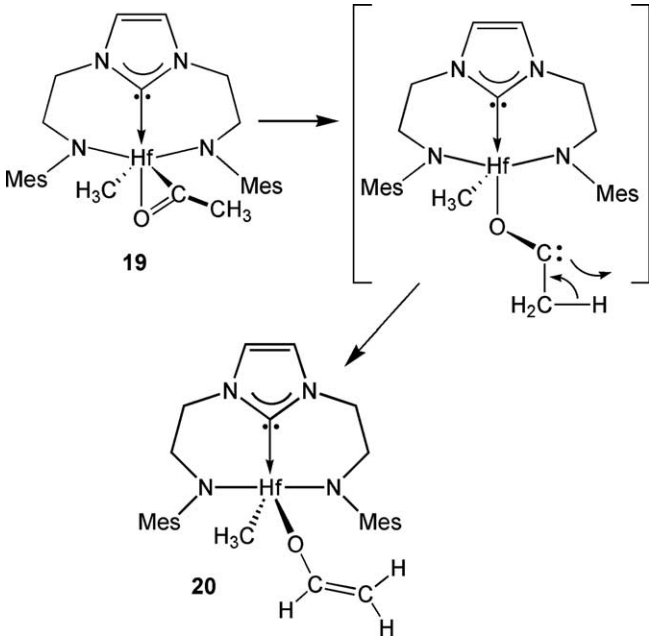
Scheme 5.

this reason, a *mer* geometry is shown, despite the fact that the mono insertion adduct of XyNC (cf., **14**) has a facial coordination of the ancillary ligand.

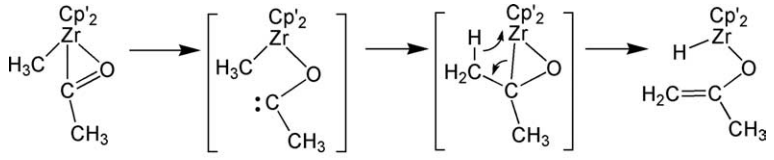
Monitoring the reaction of CO with the dimethyl complex shows the formation of the expected η^2-acyl intermediate ^{Mes}[NCN]Hf(η^2-COCH$_3$)(CH$_3$) (**19**), as evidenced by a singlet at δ 1.62 for the acetyl methyl protons; this resonance splits into a doublet with the use of ^{13}CO ($^1J_{^{13}C-^1H} = 7$ Hz), confirming that simple insertion has occurred. The ^{13}C NMR spectrum shows a resonance at δ 339.6, and is typical for the acyl carbonyl carbon of reported Hf(η^2-acyl) complexes [9]. IR spectroscopy was also useful in the determination of the Hf(η^2-acyl) with a ν(C=O) stretch observed at 1540 cm^{-1}, characteristic of similar compounds.

The rearrangement of the hafnium methyl–acetyl complex **19** to the methyl–vinyl enolate derivative **20** was unexpected. The reactivity of group 4 methyl–acetyl complexes has been ascribed to the oxy-carbene resonance form of the η^2-acyl moiety [19,20], which normally undergoes intramolecular coupling with the adjacent methyl group [21], followed by hydrogen abstraction by the metal to generate a metal hydrido-methylvinyl-enolate (Scheme 6).

In the case of the hafnium methyl–acetyl complex **19**, the formation of the vinyl enolate suggests that the oxy-carbene resonance form preferentially undergoes a hydrogen-atom shift from the methyl substituent of the carbene carbon to generate the observed vinyl enolate (Scheme 7). Presumably, the η^2-acetyl unit of **19** is oriented in such a



Scheme 7.



Scheme 6.

way as to disfavour C–C coupling with the Hf–CH_3 unit, and instead, hydrogen transfer from the methyl occurs. Whether or not this is a result of a geometric constraint caused by the different ancillary ligands or an electronic effect is unknown. Similar hydrogen and silyl group migrations have been reported for Cp_3ThR and $Cp^*_2ThR(Cl)$ derivatives upon reaction with CO [22]. Continued exposure of **20** towards CO results in the formation of an insoluble, white powder. ES-MS shows a molecular ion peak at 652 *m*/*z* indicative of a second CO insertion; however, the insolubility of the product has hampered further characterization efforts.

It has been shown that the nature of carbonylation products is dependent on substituents on the metal [23]. With this in mind, the carbonylation of the hafnium diisobutyl complex, **11**, was investigated. Exposure of **11** to 1 atm of CO for an extended period (3–4 days) results in the precipitation of colourless crystals in reasonable yield. Analysis by solid-sate X-ray diffraction indicated that this material is the dihafnium bis(enediolate) complex, (^{Mes}[NCN]Hf)$_2$(μ-OC(^{i}Bu)=C(Bu^i)O)$_2$ (**23**) (see Scheme 5). The ORTEP diagram is shown in Fig. 5; crystallographic data are given in Table 1. Examination of the C–C bond length clearly shows double bond character (av. 1.342(15) Å) and along with Hf–O bond lengths (av. 1.928(6) Å) are similar to other early transition metal enediolate complexes [24]. The [NCN] ligand distorts to a facial geometry having an N(4)–Hf(01)–N(3) bond angle of 124.4(3)° Hf–C alkyl and Hf–N amido bond lengths are similar to previously discussed complexes. In solution, the ^{1}H NMR resonance spectrum was consistent a C_s symmetric species in solution with two distinct *iso*-butyl resonances, consistent with the solid-state structure. In addition, **23** exhibits a weak ^{13}C resonance at 140.0 ppm indicative of an olefinic C=C bond ($^1J^{13}C$-$^{13}C = 20$ Hz with ^{13}CO).

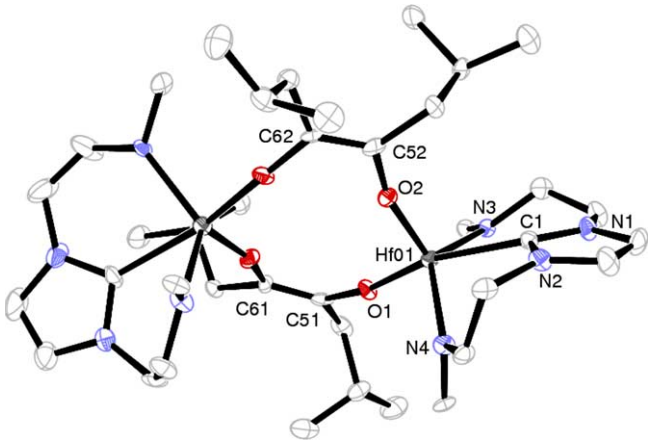


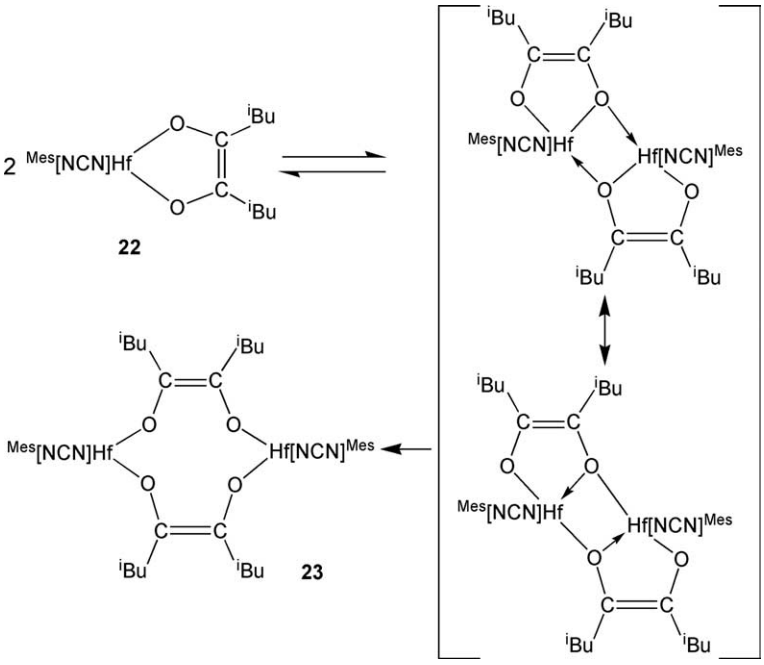
Fig. 5. ORTEP view of ^{Mes}[NCN]Hf(OC(^{i}Bu)=C(^{i}Bu)O)]$_2$(4C_6H_6 omitted) (**23**), depicted with 30% ellipsoids. For clarity, only the *ipso*-carbons of the mesityl groups have been included and all hydrogen atoms have been removed. Selected bond distances (Å) and angles (°): Hf(01)–O(2) 1.912(6), Hf(01)–O(1) 1.937(5), Hf(01)–N(4) 2.097(7), Hf(01)–N(3) 2.109(7), Hf(01)–C(1) 2.387(9), C(52)–C(62) 1.342(12), C(51)–C(61) 1.341(12); O(2)–Hf(01)–O(1) 105.4(2), N(4)–Hf(01)–N(3) 124.4(3), N(4)–Hf(01)–C(1) 77.1(3), N(3)–Hf(01)–C(1) 77.8(3), C(51)–O(1)–Hf(01) 169.4(6), C(52)–O(2)–Hf(01) 163.1(6).

The mechanism of the formation of the dinuclear bis(enediolate) was examined by monitoring the reaction of **11** with CO as a function of time using NMR spectroscopy. The first intermediate formed is the hafnium isobutyl–acyl species, **21**, clearly distinguished by a ^{13}C NMR resonance at 338.4 ppm, attributed to an Hf(O=C^iBu) resonance, analogous to other early transition metal η^2-acyl complexes [9]. The ^{1}H NMR spectrum reveals a C_s symmetric species in solution with two distinct *iso*-butyl resonances. The methylene protons α to the acyl carbonyl of one *iso*-butyl unit are observed as a doublet at 1.68 ppm, which splits further into a doublet of doublets when ^{13}CO was used ($^2J^{13}C$–H = 4.7 Hz). Again, the coordination mode of the ^{Mes}[NCN] ligand in **21**, *mer* versus *fac*, is not assignable with the NMR data available.

Continued exposure of **21** to CO results in the formation of a new product having C_{2v} symmetry in solution and distinct from the final dihafnium macrocycle **23**. Only one *iso*-butyl resonance is present in the ^{1}H NMR spectrum at room temperature, suggestive of a second CO molecule insertion into the remaining Hf–C bond. The ^{13}C NMR spectrum of this species displays a weak resonance at δ 140.6 indicative of a new C=C bond. This spectroscopic evidence is consistent with the formation of the mononuclear hafnium–enediolate, **22** (Scheme 5). The synthesis of this enediolate likely proceeds through a bis(η^2-acyl) species, the presence of which was not observed by ^{1}H NMR studies. In solution, the nuclearity of the enediolate **22** is assumed to be mononuclear; however, there are early transition metal enediolates reported in both monomeric and dimeric forms (Scheme 8), depending on the steric bulk of the alkyl group [23]. For example, when the alkyl group is bulky (R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$) monomeric species have been observed, and with smaller groups (R = H, CH_3, CH_2Ph), higher nuclearity species have been reported. Indeed, there are several reports of monomeric enediolates dimerizing to form dinuclear complexes [25,26]. In one example, such complexes show dynamic behaviour interconverting oxygen atoms through a low activation-energy process by a ten-membered metallacycle intermediate, similar in structure to the final product **23** [26].

A reasonable proposal for the formation of **23** is shown in Scheme 8, and involves dimerization of **22** via dative oxygen–hafnium interactions that are converted to covalent bonds, followed by ring-opening to generate the 10-membered dihafnium macrocycle. The driving force for the formation of the dinuclear complex **23** may be provided by better oxygen-to-hafnium π donation, an overlap that is more difficult in the mononuclear complex **22** with the five-membered enediolate ring [27]. Examination of the solid-state structure of **23** reveals a average Hf–O–C bond angle of 163.5(3)° and reflects such a π donation.

The reason for the differences in reactivity between alkyl substituents may be attributed to competitive dimerization



Scheme 8.

and insertion pathways. Such considerations have been attributed to the nucleophilic character of the alkoxy-carbene moiety and have been well documented in actinide and tantalum metallocene systems [22,28].

2.2.4. Hf and Zr cation formation and polymerization studies

Group 4 transition metal complexes with aryl-substituted amide ligands have been extensively examined as olefin polymerization catalysts [29]. In some circumstances, 1-hexene can be polymerized in a living fashion by bis(amide) substituted zirconium and hafnium complexes [30]. With these results in mind, the polymerization ability of zirconium and hafnium dimethyl complexes was examined.

The methyl cations, $[^{Mes}[NCN]M(CH_3)][B(C_6F_5)_4]$ (M = Zr, **24**; M = Hf, **25**), were generated in situ from dimethyl precursors **7** and **8** at −10 °C with $[Ph_3C][B(C_6F_5)_4]$. Due to the thermal sensitivity of the species generated, the products were identified by ^{1}H NMR spectroscopy in solution and not isolated. ^{1}H NMR spectra showed C_s symmetric products in solution with M–CH_3 resonances at δ 0.50 for **24** and δ 0.26 for **25**.

Treatment of **8** with triflic acid generates the hafnium methyl-triflate complex, ^{Mes}[NCN]Hf(OTf)(CH_3) (**26**), which is stable at room temperature. The ^{1}H NMR spectrum of **26** shows a C_s symmetric species in solution with a Hf–CH_3 resonance at δ 0.19, which is similar to previously described complexes [31].

Cationic **24** and **25** were evaluated as 1-hexene polymerization catalysts (see Section 4 for protocol). Upon work-up, a minor amount of a viscous substance was recovered that was identified as atactic poly-1-hexene in 4% yield [32]. These results were quite surprising in light of the many active amido-based non-metallocene group 4 catalysts [29]. It was recently found that 1-hexene polymerization with group 4 metal bearing diamido ^{Mes}[N(NMe)N] ancillary ligands underwent *ortho*-methyl C–H bond activation during polymerization [7]. Investigation of the decomposition products revealed an *ortho*-methyl C–H bond activated compound similar to **13**, in addition to other unidentifiable materials.

Generation of **24** in chlorobenzene in the presence of ethylene showed moderate catalytic ability to produce polyethylene (125 g mmol^{-1} h^{-1} atm^{-1}). It is important to note that immediately after exposure to ethylene, a noticeable exotherm was observed. Halting the polymerization experiment at increasingly longer times resulted in a decreased activity. This suggests that the active species, albeit catalytically active, was short-lived in solution decomposing to the previously described inactive complex.

3. Conclusion

In this work, a new tridentate diamido-N-heterocyclic carbene ligand precursor has been synthesized via a modification of an earlier procedure; this new method tolerates bulky aryl donors attached to the amine arms flanking the NHC. Incorporation of ^{Mes}[NCN] onto zirconium(IV) and hafnium(IV) complexes was accomplished by protonolysis of M(NMe_2)$_4$ to generate the bis(dimethyl)amido derivatives, which in turn could be converted to dichloro and dialkyl complexes by straightforward procedures.

We have already shown that dissociation of the carbene moiety from an electro-positive, early transition metal can be prevented by having the NHC positioned between two

amido donors. What was not known was how stable early transition metal NHC interactions would be to migratory insertion. We have investigated a variety of such fundamental processes and have found that the NHC moiety remains coordinated to the metal and does not participate in any way that disrupts or changes the NHC donor. For example, isocyanide insertions in hafnium–sp^3-carbon bonds all occur at the alkyls and result in iminoacyl derivatives. Tandem insertions involving isocyanides and carbon monoxide also take place just at the sp^3-metal carbon bond and leave the NHC unscathed. In addition, multiple insertions of CO result in the formation of enediolate species, presumably via the intermediacy of oxycarbene resonance forms, with no involvement of the NHC unit. Such outcomes will be important in future designs of ancillary ligands that incorporate NHC type donors.

Activation of the zirconium- and hafnium-dimethyl derivatives with $[Ph_3C][B(C_6F_5)_4]$ in the presence of 1-hexene yields marginal polymer formation. The cationic zirconium species does possesses moderate catalytic ability for ethylene polymerization. Hafnium alkyl complexes containing β-hydrogen atoms display different reactivity depending on the substitution. Diisobutyl substituted complexes show no decomposition, even at elevated temperatures; however, ethyl substituted complexes undergo facile β-hydrogen transfer at room temperature, presumably through a reactive hafnium η^2-ethylene intermediate, to yield a metallated hafnium species.

We are currently exploring the potential for the [NCN] ligand architecture to stabilize other early and late transition metal centres, with goals that involve small molecule activation and new catalytic processes.

4. Experimental

4.1. General considerations

Unless otherwise stated, all manipulations were performed under 1 atm of dry oxygen-free argon or nitrogen by means of standard Schlenk or glovebox techniques. $Zr(NEt_2)_4$ and $Hf(NEt_2)_4$ were purchased from Strem Chemicals and used as received. All other chemicals were purchased from Aldrich and used as received. 2,4,6-$Me_3C_6H_2NHC(O)CH_2Cl$, 2,4,6-$Me_3C_6H_2NHCH_2CH_2Cl$, and $(CD_3CD_2)MgBr$ were synthesized by the literature methods [33–35]. Hexanes, toluene, and tetrahydrofuran were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and Ridox catalyst. Deuterated solvents were dried according to the literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE 400 instrument operating at 400.0 MHz for ^1H. Elemental analyses, IR spectroscopy, and mass spectrometry (EI/MS) were performed at the Department of Chemistry at the University of British Columbia.

4.2. 2,4,6-$Me_3C_6H_2NHC(O)CH_2$(imidazole)

NaH (3.8 g, 158.3 mmol) and imidazole (9.73 g, 142.9 mmol) were combined in DMF (75 mL) and stirred for 30 min at 50 °C to give a clear brown solution. 2,4,6-$Me_3C_6H_2NHC(O)CH_2Cl$ (28.2 g, 142.9 mmol) was added portionwise over a period of 30 min to give an opaque solution. After stirring for 12 h, water (20 mL) was added and all solvents were removed under reduced pressure. The resulting brown residue was acidified with 2 M HCl (250 mL) and washed with Et_2O (3 × 150 mL). The aqueous solution was made basic with excess NaOH and extracted with CH_2Cl_2 (3 × 250 mL). The $CH_2Cl_2$was removed to give a white crystalline material, which was washed with hexanes (28.0 g, 86%). ^1H NMR ($CDCl_3$): δ 2.12 (s, 6H, –*o*-ArC*H*$_3$), 2.25 (s, 3H, –*p*-ArC*H*$_3$), 4.75 (s, 2H, –N$_{imid}$C*H*$_2$), 6.80 (s, 2H, –Ar*H*), 7.05 (s, 1H, –imid*H*), 7.10 (s, 1H, –imid*H*), 7.60 (s, 1H, –NC*H*N). ^{13}C NMR ($CDCl_3$): δ 18.2 (–*o*-*C*H$_3$), 20.5 (–*p*-*C*H$_3$), 57.0 (–N$_{imid}$*C*H$_2$), 123.0 (–imid*C*), 123.2 (–imid*C*), 128.5 (–Ar*C*), 130.5 (–Ar*C*), 130.7 (–Ar*C*), 135.1 (–N*C*N), 140.1 (–Ar*C*), 178.1 (–*C*(O)). Anal. Calc. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.00; H, 7.01; N, 17.10%.

4.3. 2,4,6-$Me_3C_6H_2NHCH_2CH_2$(imidazole)

2,4,6-$Me_3C_6H_2NHCOCH_2$(imidazole) (13.0 g, 56.8 mmol) and BH_3–SMe_2 (25.0 mL,125.0 mmol, 5.0 M in Et_2O) were combined in THF (500 mL) and refluxed overnight. The THF was removed under reduced pressure and 2 M HCl (63 mL, 2.2 equivalents) was added to the white residue. The solution was made basic with excess NaOH (8 equivalents) and extracted with CH_2Cl_2 (3 × 250 mL). The $CH_2Cl_2$was removed, and the clear oil recrystallized with boiling hexanes (9.8 g, 80%). ^1H NMR (d_6-DMSO): δ 2.03 (s, 6H, –*o*-ArC*H*$_3$), 2.15 (s, 3H, –*p*-ArC*H*$_3$), 3.19 (t, $J = 8$ Hz, –N$_{Ar}$C*H*$_2$), 3.68 (t, $J = 8$ Hz, 1H, –N*H*), 4.13 (t, $J = 8$ Hz, –N$_{imid}$C*H*$_2$), 6.80 (s, 2H, –Ar*H*), 6.85 (s, 1H, –imid*H*), 7.20 (s, 1H, –imid*H*), 7.64 (s, 1H, –NC*H*N). ^{13}C NMR (d_6-DMSO): δ 18.9 (–*o*-*C*H$_3$), 22.1 (–*p*-*C*H$_3$), 48.4 (–N$_{Ar}$*C*H$_2$), 48.9 (–N$_{imid}$*C*H$_2$), 121.0 (–imid*C*), 121.6 (–imid*C*), 126.4 (–Ar*C*), 128.8 (–Ar*C*), 129.0 (–Ar*C*), 134.2 (–N*C*N), 142.1 (–Ar*C*). Anal. Calc. for $C_{14}H_{19}N_3$: C, 73.33; H, 8.35; N, 18.32. Found: C, 73.05; H, 8.09; N, 18.15%.

4.4. (^{Mes}[NCHN]H$_2$)$^+$Cl$^-$ (**1**)

2,4,6-$Me_3C_6H_2NHCH_2CH_2Cl$ (6.0 g, 30.4 mmol) and 2,4,6-$Me_3C_6H_2NHCH_2CH_2$(imidazole) (6.5 g, 30.4 mmol) were combined and stirred at 150 °C for 2 h. After cooling, the resulting white solid was washed with THF (50 mL) and filtered to give a white crystalline powder (11.3 g, 87%). Recrystallization with boiling acetonitrile gave long colourless crystals. ^1H NMR (d_6-DMSO): δ 2.01 (s, 12H, –*o*-ArC*H*$_3$), 2.12 (s, 6H, –*p*-ArC*H*$_3$), 3.15 (q, $J = 8$ Hz,

4H, $-N_{Ar}CH_2$), 3.92 (t, $J = 8$ Hz, 1H, –N*H*), 4.40 (t, $J = 8$ Hz, 4H, $-N_{imid}CH_2$), 6.81 (s, 4H, –Ar*H*), 7.88 (s, 2H, –imid*H*), 9.35 (s, 1H, –NC*H*N). ^{13}C NMR (d_6-DMSO): δ 17.8 (–*o*-*C*H$_3$), 20.2 (–*p*-*C*H$_3$), 47.2 ($-N_{Ar}CH_2$), 49.2 ($-N_{imid}CH_2$), 122.6 (–imid*C*), 129.0 (–Ar*C*), 130.2 (–Ar*C*), 130.7 (–Ar*C*), 137.2 (–N*C*HN), 142.4 (–Ar*C*). Anal. Calc. for $C_{25}H_{35}ClN_4$: C, 70.32; H, 8.26; N, 13.12. Found: C, 70.15; H, 8.13; N, 13.02%.

4.5. $^{Mes}[NCN]H_2$ (2)

A THF solution of $KN(SiMe_3)_2$ (690 mg, 3.5 mmol) was slowly added dropwise to **1** (1.47 g, 3.5 mmol) suspended in THF (20 mL). The resulting pale yellow solution was stirred for 30 min and the volatiles were removed. The oily white solid was extracted with toluene (3×30 mL) and the solvent removed to give a white powder (1.4 g, 100%). The powder could be further purified by recrystallization with toluene at −30 °C to give long colourless needles. ^{1}H NMR (C_6D_6): δ 2.35 (s, 6H, –*p*-ArC*H*$_3$), 2.40 (s, 12H, –*o*-ArC*H*$_3$), 3.22 (q, $J = 8$ Hz, 4H, $-N_{Ar}CH_2$), 3.76 (t, $J = 8$ Hz, 4H, $-N_{imid}CH_2$), 4.15 (t, $J = 8$ Hz, 1H, –N*H*), 6.30 (s, 2H, –imid*H*), 6.82 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 20.0 (–*o*-*C*H$_3$), 24.5 (–*p*-*C*H$_3$), 48.5 ($-N_{Ar}CH_2$), 49.1 ($-N_{imid}CH_2$), 121.7 (–imid*C*), 126.9 (–Ar*C*), 127.5 (–Ar*C*), 130.1 (–Ar*C*), 145.0 (–Ar*C*), 215.0 (–N*C*N). Anal. Calc. for $C_{25}H_{34}N_4$: C, 76.88; H, 8.77; N, 14.35. Found: C, 76.54; H, 8.41; N, 14.28%.

4.6. $^{Mes}[NCN]M(NMe_2)_2$ (M = Zr (3), Hf (4))

The following procedure is representative of the synthesis of **3** and **4**. A cooled (−30 °C) THF (10 mL) solution of $Hf(NMe_2)_4$ (415 mg, 1.17 mmol) was slowly added dropwise to **2** dissolved in THF (20 mL). The mixture was warmed to room temperature gradually and stirred overnight. After the solvent was removed in vacuo and toluene (15 mL) added, the solution was filtered and the solvent removed to give a pale orange solid, which was recrystallized with Et_2O/hexanes at −30 °C to give a white powder (662 mg, 85%). **3**: ^{1}H NMR (C_6D_6): δ 2.21 (s, 6H, –*p*-ArC*H*$_3$), 2.40 (s, 12H, –*o*-ArC*H*$_3$), 2.67 (s, 12H, –N*Me*$_2$), 3.34 (m, 4H, $-N_{Ar}CH_2$), 3.61 (m, 4H, $-N_{imid}CH_2$), 6.02 (s, 2H, –imid*H*), 6.96 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 19.6 (–*o*-*C*H$_3$), 23.4 (–*p*-*C*H$_3$), 45.6 (–N*C*H$_3$), 48.8 ($-N_{Ar}CH_2$), 49.2 ($-N_{imid}CH_2$), 122.4 (–imid*C*), 130.5 (–Ar*C*), 132.3 (–Ar*C*), 132.9 (–Ar*C*), 140.2 (–Ar*C*), 190.9 (–Zr$C_{carbene}$). Anal. Calc. for $C_{29}H_{44}N_6Zr$: C, 61.33; H, 7.81; N, 14.80. Found: C, 61.20; H, 7.58; N, 14.45%.

4: ^{1}H NMR (C_6D_6): δ 2.19 (s, 6H, –*p*-ArC*H*$_3$), 2.39 (s, 12H, –*o*-ArC*H*$_3$), 2.70 (s, 12H, –N*Me*$_2$), 3.36 (m, 4H, $-N_{Ar}CH_2$), 3.55 (m, 4H, $-N_{imid}CH_2$), 5.95 (s, 2H, –imid*H*), 6.91 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 19.7 (–*o*-*C*H$_3$), 24.3 (–*p*-*C*H$_3$), 44.5 (–N*C*H$_3$), 49.0 ($-N_{Ar}CH_2$), 50.1 ($-N_{imid}CH_2$), 122.0 (–imid*C*), 129.8 (–Ar*C*), 132.8 (–Ar*C*), 133.3 (–Ar*C*), 142.3 (–Ar*C*), 195.7 (–Hf$C_{carbene}$). Anal. Calc. for $C_{29}H_{44}HfN_6$: C, 53.16; H, 6.77; N, 12.83. Found: C, 52.89; H, 6.44; N, 12.68%.

4.7. $^{Mes}[NCN]MCl_2$ (M = Zr (5), Hf (6))

The following procedure is representative of the synthesis of **5** and **6**. Chlorotrimethylsilane (1.03 mL, 8.14 mmol) was added dropwise to a toluene (20 mL) solution of **4** (533 mg, 0.81 mmol) with vigorous stirring. The white suspension was stirred overnight and collected by filtration to give a white powder, (495 mg, 95%). **5**: ^{1}H NMR (C_6D_5N): δ 2.24 (s, 6H, –*p*-ArC*H*$_3$), 2.28 (s, 12H, –*o*-ArC*H*$_3$), 3.79 (m, 2H, $-N_{Ar}CH_2$), 4.59 (m, 4H, $-N_{imid}CH_2$), 6.86 (s, 4H, –Ar*H*), 7.26 (s, 2H, –imid*H*). ^{13}C NMR (C_6D_5N): δ 19.9 (–*o*-*C*H$_3$), 24.7 (–*p*-*C*H$_3$), 52.3 ($-N_{Ar}CH_2$), 54.9 ($-N_{imid}CH_2$), 127.4 (–imid*C*), 130.9 (–Ar*C*), 133.6 (–Ar*C*), 134.1 (–Ar*C*), 144.8 (–Ar*C*), 192.3 (–Zr$C_{carbene}$). Anal. Calc. for $C_{25}H_{32}Cl_2N_4Zr$: C, 54.53; H, 5.86; N, 10.17. Found: C, 54.36; H, 5.44; N, 10.01%.

6: ^{1}H NMR (C_6D_5N): δ 2.26 (s, 6H, –*p*-ArC*H*$_3$), 2.31 (s, 12H, –*o*-ArC*H*$_3$), 4.09 (m, 2H, $-N_{Ar}CH_2$), 4.40 (m, 4H, $-N_{imid}CH_2$), 6.91 (s, 4H, –Ar*H*), 7.28 (s, 2H, –imid*H*). ^{13}C NMR (C_6D_5N): δ 20.1 (–*o*-*C*H$_3$), 25.7 (–*p*-*C*H$_3$), 54.2 ($-N_{Ar}CH_2$), 56.0 ($-N_{imid}CH_2$), 127.5 (–imid*C*), 131.2 (–Ar*C*), 134.3 (–Ar*C*), 134.8 (–Ar*C*), 145.3 (–Ar*C*), 198.2 (–Hf$C_{carbene}$). Anal. Calc. for $C_{25}H_{32}Cl_2HfN_4$: C, 47.07; H, 5.06; N, 8.78. Found: C, 46.85; H, 4.86; N, 8.53%.

4.8. $^{Mes}[NCN]M(CH_3)_2$ (M = Zr (7), Hf (8))

The following procedure is representative of the synthesis of **7** and **8**. The hafnium dichloride **6** (200 mg, 0.31 mmol) was dissolved in 5 mL THF and cooled to −30 °C, and CH_3MgCl (0.62 mmol, 3.0 M in THF) was added dropwise; the slightly yellow solution was stirred in the dark for 30 min. The THF was removed under reduced pressure and to the resulting residue was added a few drops 1,4-dioxane and toluene (5 mL). The resulting suspension was filtered through Celite and volatiles were removed to give a white solid which was recrystallized in toluene; yield (167 mg, 90%). **7**: ^{1}H NMR (C_6D_6): δ 0.33 (s, 6H, –ArC*H*$_3$), 2.20 (s, 6H, –*p*-ArC*H*$_3$), 2.43 (s, 12H, –*o*-ArC*H*$_3$), 3.37 (m, 4H, $-N_{Ar}CH_2$), 3.45 (m, 4H, $-N_{imid}CH_2$), 5.88 (s, 2H, –imid*H*), 6.98 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 18.6 (–*o*-*C*H$_3$), 20.0 (–*p*-*C*H$_3$), 48.4 (–Zr*C*H$_3$), 51.7 ($-N_{Ar}CH_2$), 52.3 ($-N_{imid}CH_2$), 118.5 (–imid*C*), 129.9 (–Ar*C*), 133.3 (–Ar*C*), 135.0 (–Ar*C*), 148.9 (–Ar*C*), 189.8 (–Zr$C_{carbene}$). Anal. Calc. for $C_{27}H_{38}N_4Zr$: C, 63.61; H, 7.51; N, 10.99. Found: C, 63.33; H, 7.32; N, 10.75%.

8: ^{1}H NMR (C_6D_6): δ 0.12 (s, 6H, –HfC*H*$_3$), 2.17 (s, 6H, –*p*-ArC*H*$_3$), 2.49 (s, 12H, –*o*-ArC*H*$_3$), 3.40 (m, 4H, $-N_{Ar}CH_2$), 3.49 (m, 4H, $-N_{imid}CH_2$), 5.90 (s, 2H, –imid*H*), 6.99 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 19.6 (–*o*-*C*H$_3$), 20.7 (–*p*-*C*H$_3$), 52.2 ($-N_{Ar}CH_2$), 54.1 (–Hf*C*H$_3$), 54.2 ($-N_{imid}CH_2$), 119.5 (–imid*C*), 129.6 (–Ar*C*), 132.3 (–Ar*C*), 135.3 (–Ar*C*), 152.1 (–Ar*C*), 196.1 (–Hf$C_{Carbene}$). Anal.

Calc. for $C_{27}H_{38}HfN_4$: C, 54.31; H, 6.41; N, 9.38. Found: C, 54.22; H, 6.26; N, 9.16%.

4.9. ^{Mes}[NCN]M(CH_2Ph)$_2$ (M = Zr (**9**), Hf (**10**))

The following procedure is representative of the synthesis of **9** and **10**. The hafnium dichloride **6** (200 mg, 0.31 mmol) was dissolved in 5 mL THF and cooled to −30 °C. $PhCH_2MgCl$ (0.62 mmol, 1.0 M in Et_2O) was added dropwise and the slightly yellow solution was stirred in the dark for 30 min. The THF was removed under reduced pressure and to the resulting residue was added a few drops 1,4-dioxane and Et_2O (5 mL). The resulting suspension was filtered through Celite and volatiles were removed to give a white solid which was recrystallized in Et_2O; yield (210 mg, 89%). **9**: ^{1}H NMR (C_6D_6): δ 1.92 (s, 4H, –ZrCH_2), 2.24 (s, 6H, –*p*-ArCH_3), 2.31 (s, 12H, –*o*-ArCH_3), 3.03 (m, 4H, –N_{Ar}CH_2), 3.56 (m, 4H, –N_{imid}CH_2), 5.77 (s, 2H, –imid*H*), 6.84 (d, $J = 8$ Hz, 4H, –*o*-CH_2Ph), 6.92 (t, $J = 8$ Hz, 2H, –*p*-CH_2Ph), 6.98 (s, 4H, –Ar*H*), 7.17 (t, $J = 8$ Hz, 4H, –*m*-CH_2Ph). ^{13}C NMR (C_6D_6): δ 20.2 (–*o*-*C*H_3), 24.3 (–*p*-*C*H_3), 49.3 (–N_{Ar}*C*H_2), 52.7 (–N_{imid}*C*H_2), 65.6 (–Zr*C*H_2), 121.6 (–imid*C*), 122.4 (–Ar *C*), 130.3 (–Ar*C*), 131.5 (–Ar*C*), 136.6 (–Ar*C*), 148.4 (–Ar*C*), 156.3 (–Ar*C*), 190.1 (–Zr$C_{Carbene}$). Some aromatic resonances obscured by C_6D_6 solvent. Anal. Calc. for $C_{39}H_{46}N_4Zr$: C, 70.75; H, 7.00; N, 8.46. Found: C, 70.43; H, 6.92; N, 8.35%.

10: ^{1}H NMR (C_6D_6): δ 1.85 (s, 4H, –HfCH_2), 2.26 (s, 6H, –*p*-ArCH_3), 2.36 (s, 12H, –*o*-ArCH_3), 3.04 (m, 4H, –N_{Ar}CH_2), 3.46 (m, 4H, –N_{imid}CH_2), 5.73 (s, 2H, –imid*H*), 6.82 (d, $J = 8$ Hz, 4H, –*o*-CH_2Ph), 6.90 (t, $J = 8$ Hz, 2H, –*p*-CH_2Ph), 7.02 (s, 4H, –Ar*H*), 7.18 (t, $J = 8$ Hz, 4H, –*m*-CH_2Ph). ^{13}C NMR (C_6D_6): δ 21.2 (–*o*-*C*H_3), 22.1 (–*p*-*C*H_3), 50.0 (–N_{Ar}*C*H_2), 51.4 (–N_{imid}*C*H_2), 73.5 (–Hf*C*H_2), 121.3 (–Ar*C*), 122.9 (–imid*C*), 129.6 (–Ar*C*), 130.9 (–Ar*C*), 135.5 (–Ar*C*), 147.9 (–Ar*C*), 155.6 (–Ar*C*), 196.5 (–Hf$C_{Carbene}$). Some aromatic resonances obscured by C_6D_6 resonances. Anal. Calc. for $C_{39}H_{46}HfN_4$: C, 62.51; H, 6.19; N, 7.48. Found: C, 62.42; H, 6.14; N, 7.42%.

4.10. ^{Mes}[NCN]Hf(R)$_2$ (R = CH_2CHMe_2 (**11**); R = CH_2CH_3 (**12**); R = CD_2CD_3 d_{10}-**12**)

The following procedure is representative of the synthesis of **11** and **12**. The hafnium dichloride **6** was dissolved in 5 mL THF and cooled to −30 °C. The Grignard reagent (2 equivalents) was added dropwise and the slightly yellow solution was stirred in the dark for 30 min. The THF was removed under reduced pressure and to the resulting residue was added a few drops 1,4-dioxane and Et_2O (5 mL). The resulting suspension was filtered through Celite and volatiles were removed to give a white solid, which was recrystallized with Et_2O. **11**: ^{1}H NMR (C_6D_6): δ 0.68 (d, $J = 8$ Hz, 4H, –HfCH_2), 1.02 (d, $J = 8$ Hz, 12H, –CH(CH_3)$_2$), 2.24 (s, 6H, –*p*-ArCH_3), 2.35 (n, $J = 8$ Hz, 2H, –CH_2C*H*(CH_3)$_2$), 2.46 (s, 12H, –*o*-ArCH_3), 3.23 (m, 2H, –N_{Ar}CH_2), 3.67 (m, 4H, –N_{imid}CH_2), 5.86 (s, 2H, –imid*H*), 7.00 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 13.7 (–CH_2CH(*C*H_3)$_2$), 19.4 (–*o*-*C*H_3), 20.5 (–*p*−*C*H_3), 32.3 (–CH_2*C*H(CH_3)$_2$), 50.5 (–N_{Ar}*C*H_2), 52.1 (–N_{imid}*C*H_2), 68.4 (–Hf*C*H_2), 118.4 (–imid*C*), 128.4 (–Ar*C*), 132.1 (–Ar *C*), 133.9 (–Ar*C*), 148.4 (–Ar*C*), 194.9 (–Hf$C_{Carbene}$). Anal. Calc. for $C_{33}H_{50}HfN_4$: C, 58.18; H, 7.40; N, 8.22. Found: C, 57.91; H, 7.05; N, 8.01%.

12: ^{1}H NMR (C_6D_6) δ 0.62 (q, $J = 8$ Hz, 4H, –HfCH_2), 1.49 (t, $J = 8$ Hz, 6H, –CH_2CH_3), 2.24 (s, 6H, –*p*-ArCH_3), 2.46 (s, 12H, –*o*-ArCH_3), 3.32 (m, 2H, –N_{Ar}CH_2), 3.55 (m, 4H, –N_{imid}CH_2), 5.90 (s, 2H, –imid*H*), 6.70 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 12.8 (–HfCH$_2$*C*H$_3$), 19.7 (–*o*-*C*H_3), 20.9 (–*p*-*C*H_3), 51.4 (–N_{Ar}*C*H_2), 52.5 (–N_{imid}*C*H_2), 66.1 (–Hf*C*H$_2$CH$_3$), 119.9 (–imid*C*), 129.6 (–Ar*C*), 131.8 (–Ar*C*), 134.9 (–Ar*C*), 152.9 (–Ar*C*), 196.4 (–Hf$C_{Carbene}$). Anal. Calc. for $C_{29}H_{42}HfN_4$: C, 55.72; H, 6.77; N, 8.96. Found: C, 55.24; H, 6.59; N, 8.87%.

d_{10}-**12**: ^{1}H and ^{13}C NMR spectra identical to **12** with the absence of –HfCH$_2$CH$_3$ resonances.

4.11. Decomposition of ^{Mes}[NCN]Hf(CH_2CH_3)$_2$ to form **13** and d_4-**13**

d_{10}-**12** (110 mg, 0.18 mmol) was dissolved in Et_2O and the pale yellow solution was stirred for 5 days. The Et_2O was removed under reduced pressure and hexanes added to precipitate a dark orange powder (99 mg, 95%). ^{1}H NMR (C_6D_6): δ −0.10 (dq, $J = 5.3$, 8 Hz, 1H, –HfCH_2CH$_3$), 0.010 (dq, $J = 5.3$, 8 Hz, 1H, –HfCH_2CH$_3$), 1.00 (d, $J = 12$Hz, 1H, –HfCH_2Ar), 1.01 (t, $J = 8$ Hz, 3H, –HfCH$_2$CH_3), 2.23 (s, 3H, –CH_3), 2.25 (s, 3H, –CH_3), 2.37 (s, 3H, –CH_3), 2.47 (s, 3H, –CH_3), 2.51 (d, $J = 12$Hz, 1H, –HfCH_2Ar), 2.58 (s, 3H, –CH_3), 3.19 (m, 3H, –NCH_2), 3.22 (m, 3H, –NCH_2), 3.27–3.31 (m, 3H, –NCH_2), 3.47 (m, 3H, –NCH_2), 3.62 (m, 3H, –NCH_2), 3.93 (m, 3H, –NCH_2), 4.16 (m, 3H, –NCH_2), 5.89 (d, J=2Hz, 1H, –imid*H*), 5.92 (d, $J = 2$Hz, 1H, –imid*H*), 6.77 (s, 1H, –Ar*H*), 6.97 (s, 1H, –Ar*H*), 7.04 (s, 2H, –Ar *H*). ^{13}C NMR (C_6D_6): δ 9.7 (–HfCH$_2$*C*H$_3$), 19.1 (–Ar*C*H$_3$), 19.3 (–Ar*C*H$_3$), 21.1 (–Ar*C*H$_3$), 21.3 (–Ar*C*H$_3$), 52.1 (–N *C*H$_2$), 53.8 (–N*C*H$_2$), 55.2 (–N*C*H$_2$), 55.3 (–N*C*H$_2$), 58.2 (–Hf*C*H$_2$CH$_3$), 72.9 (–Hf*C*H$_2$Ar), 119.5 (–imid*C*), 129.3 (–Ar*C*), 129.9 (–Ar*C*), 135.0 (–Ar*C*), 138.5 (–Ar*C*), 138.6 (–Ar*C*), 142.9 (–Ar*C*), 145.6 (–Ar*C*), 197.3 (–Hf$C_{Carbene}$). Some aromatic resonances obscured by C_6D_6 solvent. Anal. Calc. for $C_{27}H_{36}HfN_4$: C, 54.49; H, 6.10; N, 9.41. Found: C, 54.13; H, 5.86; N, 9.12%.

d_4-**13**: ^{1}H and ^{13}C NMR spectra identical to **13** with the absence of –HfCH$_2$CH$_3$ resonances, except for a broadened singlet at δ 0.9 in the ^{1}H NMR spectrum for $HfCD_2CD_2H$.

4.12. ^{Mes}[NCN]Hf(η^2-XyNCCH$_3$)(CH$_3$) (**14**)

To a cooled toluene (5 mL) solution of **8** (200 mg, 0.33 mmol) was added a cooled toluene (2 mL) solution

of xylyl isocyanide (44 mg, 0.33 mmol). The pale yellow solution was allowed to gradually warm to room temperature and stirred overnight. The solvent was removed and suspended in cold (−30 °C) hexanes. The solid was filtered and washed with cold hexanes to give a white powder. The solid was further recrystallized with Et_2O at −30 °C (183 mg, 74%). **14**: ^{1}H NMR (C_6D_6): δ 0.17 (s, 3H, –HfCH_3), 1.61 (s, 6H, –xylylCH_3), 1.63 (s, 3H, –CCH_3), 2.21 (s, 6H, –*p*-Ar_{Mes}–CH_3), 2.39 (s, 6H, –*o*-Ar_{Mes}–CH_3), 2.48 (s, 6H, –*o*-Ar_{Mes} CH_3), 3.08 (m, 2H, –N_{Ar}CH_2), 3.18 (m, 2H, –N_{Ar}CH_2), 3.81 (m, 2H, –N_{imid}CH_2), 4.07 (m, 2H, –N_{imid}CH_2), 6.06 (s, 2H, –imid*H*), 6.82–6.92 (m, 7H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 18.2 (–Ar*C*H_3), 19.7 (–Ar *C*H_3), 19.8 (–Ar*C*H_3), 20.5 (–Ar*C*H_3), 22.4 (–Ar*C*H_3), 34.2 (–Hf*C*H_3), 52.2 (–N_{Ar}*C*H_2), 56.9 (–N_{imid}*C*H_2), 118.7 (–imid*C*), 124.3 (–Ar*C*), 128.8 (–Ar*C*), 129.2 (–Ar*C*), 129.6 (–Ar*C*), 131.1 (–Ar*C*), 134.4 (–Ar*C*), 134.6 (–Ar*C*), 147.2 (–Ar*C*), 154.8 (–Ar*C*), 197.5 (–Hf*C*$_{carbene}$), 259.0 (–Hf*C*$_{iminoacyl}$). IR(nujol): ν(C=N) 1575 cm^{-1}. Anal. Calc. for $C_{36}H_{47}N_5Hf$: C, 59.37; H, 6.50; N, 9.62. Found: C, 59.23; H, 6.33; N, 9.46%.

NOESY NMR data (C_6D_6): δ (1H, 1H) the Hf–CH_3 resonance at δ 0.17 correlated with the xylyl-CH_3 at δ 1.61.

4.13. ^{Mes}[NCN]Hf(η^2-RNCCH$_3$)$_2$ (R = Xy (**15**); R = ^{i}Pr (**16**))

The following procedure is representative of the synthesis of **15** and **16**. To a toluene (2 mL) solution of **8** (200 mg, 0.33 mmol) was added a toluene (2 mL) solution of xylyl isocyanide (92 mg, 0.70 mmol). The pale yellow solution gradually turned dark purple (or orange in the case of **17**) and was stirred overnight, whereupon the solvent was removed quickly and Et_2O (2 mL) added to precipitate a white solid. Cooling of the solution, followed by filtration yielded colourless microcrystals (260 mg, 92%). **16**: ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.45 (br s, 18H, –CCH_3 and –$Ar_{XyC\ H3}$), 1.85 (br s, 12H, –*o*-Ar_{Mes}CH_3), 2.14 (br s, 6H, –*p*-Ar_{Mes}CH_3), 4.2 (br s, 8H, –NCH_2), 6.60 (br s, 4H, –Ar_{Mes}*H*), 6.80–6.85 (br s, 6H, –Ar_{Xy}*H*), 6.90 (s, 2H, –imid*H*). ^{1}H NMR (CD_2Cl_2, 233 K): δ 1.21 (s, 3H, –CCH_3), 1.27 (s, 6H, —Ar_{Xy}CH_3), 1.57 (s, 6H, —Ar_{Xy}CH_3), 1.78 (s, 6H, –*o*-Ar_{Mes}CH_3), 1.85 (s, 6H, –*o*-Ar_{Mes}CH_3), 2.10 (s, 6H, –*p*-Ar_{Mes}CH_3), 2.24 (s, 3H, –CCH_3), 2.80 (m, 2H, –NCH_2), 3.98 (m, 4H, –NCH_2), 4.27 (m, 1H, –NCH_2), 6.56 (s, 2H, –Ar_{Mes}*H*), 6.64 (s, 2H, –Ar_{Mes}*H*), 6.81 (m, 1H, –Ar_{Xy}*H*), 6.85 (m, 2H, –Ar_{Xy}*H*), 6.90 (s, 2H, –imid*H*). ^{13}C NMR (C_6D_6, 298 K): δ 18.5 (–Ar*C*H_3), 20.4 (–Ar*C*H_3), 20.8 (–Ar*C*H_3), 23.6 (–Ar*C*H_3), 52.7 (–N_{Ar}*C*H_2), 57.9 (–N_{imid}*C*H_2), 118.5 (–imid*C*), 124.7 (–Ar*C*), 125.6 (–Ar*C*), 129.1 (–Ar*C*), 129.9 (–Ar*C*), 130.3 (–Ar*C*), 135.1 (–Ar*C*), 156.5 (–Ar*C*), 196.5 (–Hf*C*$_{carbene}$). IR(nujol): ν(C=N) 1568 cm^{-1}. Anal. Calc. for $C_{45}H_{56}HfN_6$: C, 62.89; H, 6.57; N, 9.78. Found: C, 62.54; H, 6.19; N, 9.62%.

17: ^{1}H NMR (C_6D_6): δ 0.88 (d, $J = 7$ Hz, 12H, –CH(CH_3)$_2$), 1.32 (s, 6H, η^2-^{i}PrNCCH_3), 2.25 (s, 12H, –*o*-Ar_{Mes}–CH_3), 2.31 (s, 6H, –*p*-Ar_{Mes}–CH_3), 3.28 (m, 2H, –N_{Ar}CH_2), 3.47 (sept, $J = 7$ Hz, 2H, –C*H*(CH_3)$_2$), 3.55 (m, 2H, –N_{Ar}CH_2), 3.67 (m, 2H, –N_{imid}CH_2), 4.01 (m, 2H, –N_{imid}CH_2), 6.07 (s, 2H, –imid*H*), 6.93–7.07 (m, 13H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 20.4 (–Ar*C*H_3), 20.9 (–Ar*C*H_3), 21.1 (–C*C*H_3) 23.2, 48.8 (–N*C*H), 53.3 (–N_{Ar}*C*H_2), 56.4 (–N_{imid}*C*H_2), 119.4 (–imid*C*), 128.7 (–Ar*C*), 129.8 (–Ar*C*), 135.3 (–Ar*C*), 157.6 (–Ar*C*), 194.5 (–Hf*C*$_{carbene}$) 266.2 (–Hf*C*$_{imnoacyl}$). IR(nujol): ν(C=N) 1562 cm^{-1}. Anal. Calc. for $C_{35}H_{52}HfN_6$: C, 57.17; H, 7.13; N, 11.43. Found: C, 56.89; H, 7.00; N, 11.26%.

4.14. ^{Mes}[NCN]Hf(η^2-XyNCCH$_3$)(η^2-^{i}PrNCCH$_3$) (**17**)

To a toluene (2 mL) solution of **14** (100 mg, 0.14 mmol) was added a toluene (2 mL) solution of ^{i}PrNC (10 mg, mmol). No observable colour change was noted. The solution was stirred for 1 h, whereupon the solvent was removed quickly and Et_2O (2 mL) added to precipitate a white solid, which was washed with hexanes and dried in vacuo (96 mg, 86%). ^{1}H NMR (C_6D_6): δ 0.97 (d, $J = 7$ Hz, 6H, –CH(CH_3)$_2$), 1.23 (s, 3H, η^2-^{i}PrNCCH_3), 1.91 (s, 6H, –xylylCH_3), 2.26 (s, 6H, –*p*-Ar_{Mes}–CH_3), 2.38 (s, 6H, –*o*-Ar_{Mes}–CH_3), 2.39 (s, 6H, –*o*-Ar_{Mes}–CH_3), 2.47 (s, 3H, –η^2-XyNCCH_3), 3.10 (m, 2H, –N_{Ar}CH_2), 3.43 (m, 2H, –N_{Ar}CH_2), 3.56 (sept, $J = 7$ Hz, 1H, –C*H*(CH_3)$_2$), 3.69 (m, 2H, –N_{imid}CH_2), 3.88 (m, 2H, –N_{imid}CH_2), 6.01 (s, 2H, –imid*H*), 6.89 (s, 2H, –Ar_{Mes}*H*), 6.95 (s, 2H, –Ar_{Mes}*H*), 6.97–7.04 (m, 3H, –Ar_{xylyl}*H*). ^{13}C NMR (C_6D_6): δ 18.5 (–C*C*H_3), 18.7 (–C*C*H_3), 20.3 (–CH(*C*H_3)$_2$), 20.7 (–Ar *C*H_3), 20.9 (–Ar*C*H_3), 26.0 (–Ar*C*H_3), 50.3 (–N*C*H), 52.6 (–N_{Ar}*C*H_2), 56.5 (–N_{imid}*C*H_2), 118.7 (–imid*C*), 124.3 (–Ar *C*), 128.9 (–Ar*C*), 129.4 (–Ar*C*), 130.2 (–Ar*C*), 134.7 (–Ar*C*), 135.8 (–Ar*C*), 148.9 (–Ar*C*), 157.4 (–Ar*C*), 195.1 (–Hf*C*$_{carbene}$), 262.4 (–Hf*C*$_{iminoacyl}$), 264.1 (–Hf*C*$_{iminoacyl}$). IR(nujol): ν(C=N) 1558, 1570 cm^{-1}. Anal. Calc. for $C_{40}H_{54}HfN_6$: C, 60.25; H, 6.83; N, 10.54. Found: C, 60.01; H, 6.82; N, 10.36%.

4.15. ^{Mes}[NCN]Hf(OC(CH$_3$)=C(CH$_3$)NXy) (**18**)

A toluene (10 mL) solution of **14** (102 mg, 0.14 mmol) was freeze–pumped–thawed with 1 atm CO several times and left to stand for 1 day. The solvent was removed in vacuo and the yellow powder was washed with hexane (5 mL). The yellow solid was recrystallized from Et_2O at −30 °C to give crystals suitable for X-ray diffraction (88 mg, 83%). ^{1}H NMR (C_6D_6, 298 K): δ 1.37 (s, 3H, –NCCH_3), 1.59 (s, 3H, –OCCH_3), 2.21 (s, 6H,), 2.37 (s, 6H,), 3.01 (m, 4H, –N_{Ar}CH_2), 3.51 (m, 2H, –N_{imid}CH_2), 3.77 (m, 2H, –N_{imid}CH_2), 5.81 (s, 2H, –imid*H*), 6.90–6.96 (m, 5H, –Ar*H*), 7.07–7.09 (m, 2H, –Ar*H*). ^{1}H NMR ($CD_3C_6D_5$, 223 K): δ 1.31 (s, 3H, –NCCH_3), 1.60 (s, 3H, –OCCH_3), 1.98 (s, 6H, –ArC*H*3), 2.24 (s, 6H, –ArC*H*3), 2.38 (s, 6H, –ArC*H*3), 2.69 (s, 6H, –ArC*H*3), 2.94 (m, 4H, –NCH_2), 3.47 (m, 2H, –NCH_2), 3.73 (m, 2H, –NCH_2), 5.74 (s, 2H, –imid*H*), 6.81 (s, 2H, –Ar_{Mes}*H*),

6.99 (m, 3H, –Ar$_{xy}$*H*), 7.08 (s, 2H, –Ar$_{Mes}$*H*). ^{13}C NMR (C_6D_6, 298 K): δ 15.2 (–NC*C*H$_3$), 17.4 (–Ar*C*H$_3$), 19.0 (-OC*C*H$_3$), 19.4 (–Ar*C*H$_3$), 20.9 (–Ar*C*H$_3$), 52.9 (–N$_{Ar}$*C*H$_2$), 57.3 (–N$_{imid}$*C*H$_2$), 116.2 (–*C*N), 118.7 (–imid*C*), 123.1 (–Ar*C*), 129.6 (–Ar*C*), 131.5 (–Ar*C*), 133.0 (–Ar*C*), 136.0 (–Ar*C*), 137.0 (–*C*O), 147.9 (–Ar*C*), 149.6 (–Ar*C*), 196.7 (–Hf*C*$_{carbene}$). Anal. Calc. for $C_{37}H_{47}HfN_5O$: C, 58.76; H, 6.26; N, 9.26. Found: C, 58.29; H, 6.05; N, 9.33%.

4.16. ^{Mes}[NCN]Hf(η^2-C(O)CH$_3$)(CH$_3$) (**19**) and (^{13}C-**19**)

The product was identified in situ by NMR and IR spectroscopy. A C_6D_6 solution of **8** was freeze–pumped–thawed three times with CO, and the solution left at 1 atm. The solution was left to stand for 6 h and the solvent removed in vacuo to yield a pale yellow solid. The product was contaminated with ~5% **8**. ^{1}H NMR (C_6D_6): δ 0.56 (s, 3H, –HfC*H*$_3$), 1.62 (s, 3H, –HfC(O)C*H*$_3$), 2.11 (s, 6H, –*p*-ArC*H*$_3$), 2.34 (s, 6H, –*o*-ArC*H*$_3$), 2.44 (s, 6H, –*o*-ArC*H*$_3$), 2.92 (m, 2H, –C*H*$_2$), 3.20 (m, 2H, –C*H*$_2$), 3.65 (m, 2H, –C*H*$_2$), 3.96 (m, 2H, –C*H*$_2$), 6.01 (s, 2H, –imid*H*), 6.76 (s, 2H, –Ar*H*), 6.86 (s, 2H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 19.7 (–Ar*C*H$_3$), 19.8 (–Ar*C*H$_3$), 20.8 (–Ar*C*H$_3$), 31.1 (–HfC(O)*C*H$_3$), 34.7 (–Hf*C*H$_2$), 53.7 (–N$_{Ar}$*C*H$_2$), 55.9 (–N$_{imid}$*C*H$_2$), 119.1 (–imid*C*), 128.8 (–Ar*C*), 129.5 (–Ar*C*), 130.0 (–Ar*C*), 132.1 (–Ar*C*), 134.9 (–Ar*C*), 135.5 (–Ar*C*), 151.5 (–Ar*C*), 153.0 (–Ar*C*), 195.6 (–Hf*C*$_{carbene}$), 339.6 (–Hf*C*$_{acyl}$). ν(C=O) 1540 cm^{-1}.

^{13}C-**19**: ^{1}H and ^{13}C NMR spectra identical to **19** except 1.62 (d, $J = 7$ Hz, 3H, –HfC(O)C*H*$_3$).

4.17. ^{Mes}[NCN]Hf(OCH=CH$_2$)(CH$_3$) (**20**) and (^{13}C-**20**)

A benzene solution of **8**(250 mg, 0.42 mmol) was freeze–pumped–thawed three times with CO, and the solution left to stir under 1 atm for three days. The solvent was removed and the residue recrystallized with Et_2O/hexanes at –30 °C (162 mg, 62%). ^{1}H NMR (C_6D_6): δ 0.37 (s, 3H, –HfC*H*$_3$), 2.21 (s, 6H, –*p*-ArC*H*$_3$), 2.34 (s, 6H, –*o*-ArC*H*$_3$), 2.62 (s, 6H, –*o*-ArC*H*$_3$), 2.92 (m, 2H, –N$_{Ar}$C*H*$_2$), 3.15 (m, 2H, –N$_{Ar}$C*H*$_2$), 3.47 (d, $J = 14$Hz, –C*H*), 3.54 (d, $J = 6$Hz, –C*H*), 3.74 (m, 2H, –N$_{imid}$C*H*$_2$), 3.96 (m, 2H, –N$_{imid}$C*H*$_2$), 5.75 (dd, $J = 6$,14 Hz, 1H, –C*H*), 5.94 (s, 2H, –imid*H*), 6.95 (s, 2H, –Ar*H*), 7.01 (s, 2H, –Ar*H*).

^{13}C NMR (C_6D_6): δ19.5 (–*o*-*C*H$_3$), 20.9 (–*p*-*C*H$_3$), 38.4 (–Hf*C*H$_3$), 52.1 (–N$_{Ar}$*C*H$_2$), 55.1 (–N$_{imid}$*C*H$_2$), 117.4 (–imid*C*), 120.2 (–HfOCH=*C*H$_2$), 129.4 (–Ar*C*), 130.4 (–Ar*C*), 133.7 (–Ar*C*), 139.0 (–HfO*C*H=CH$_2$), 145.3 (–Ar*C*), 196.2 (–Hf*C*$_{carbene}$).

Anal. Calc. for $C_{28}H_{38}HfN_4O$: C, 53.80; H, 6.13; N, 8.96. Found: C, 53.53; H, 5.89; N, 8.61%.

^{13}C-**20**. ^{1}H NMR resonances are identical except δ 5.75 (ddd, $J = 6$, 14, 145 Hz, 2H, –HfO^{13}C*H*=CH$_2$).

4.18. In situ generation of ^{Mes}[NCN]Hf(η^2-CO(^{i}Bu))(^{i}Bu) (**21** and ^{13}C-**21**)

A C_6D_6 solution of **12** was freeze–pumped–thawed three times with CO. The reaction was followed by ^{1}H NMR spectroscopy and upon complete conversion to the monoacyl complex, a ^{13}C NMR spectroscopy experiment was performed. ^{1}H NMR (C_6D_6): δ 0.66 (d, $J = 7$ Hz, 6H, –CH(C*H*$_3$)$_2$), 1.06 (d, $J = 7$ Hz, 2H, –HfC*H*$_2$), 1.40 (d, $J = 7$ Hz, 6H, –C(O)CH(C*H*$_3$)$_2$), 1.68 (d, $J = 7$ Hz, 2H, –HfC(O)C*H*$_2$), 1.80 (sept, $J = 7$ Hz, 1H, –C*H*(CH$_3$)$_2$), 2.18 (–ArC*H*$_3$), 2.34 (–ArC*H*$_3$), 2.38 (–ArC*H*$_3$), 2.75 (sept, $J = 7$ Hz, 1H, –C(O)C*H*(CH$_3$)$_2$), 3.07 (m, 2H, –NC*H*), 3.28 (m, 2H, –NC*H*), 3.51 (m, 2H, –NC*H*), 4.00 (m, 2H, –NC*H*), 6.01 (s, 2H, –imid*H*), 6.78 (s, 2H, –Ar*H*), 6.85 (s, 2H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 19.8 (–Ar*C*H$_3$), 20.0 (–Ar*C*H$_3$), 21.2 (–Ar*C*H$_3$), 32.3 (–HfC(O)*C*H$_2$), 36.4 (–Hf*C*H$_2$), 54.2 (–N$_{Ar}$*C*H$_2$), 55.6 (–N$_{imid}$*C*H$_2$), 118.4 (–imid*C*), 128.4 (–Ar*C*), 128.6 (–Ar*C*), 129.2 (–Ar*C*), 130.4 (–Ar*C*), 131.2 (–Ar*C*), 132.4 (–Ar*C*), 149.8 (–Ar*C*), 153.2 (–Ar*C*), 196.1 (–Hf*C*$_{carbene}$), 338.4 (–Hf*C*$_{acyl}$).

^{13}C-**21**: ^{1}H NMR resonances are identical except δ 1.68 (dd, $J = 4.7$ Hz, 2H, –Hf^{13}C(O)C*H*$_2$).

4.19. In situ generation of ^{Mes}[NCN]Hf(OC(^{i}Bu)=C(^{i}Bu)-O) (**22** and ^{13}C-**22**)

The same procedure was followed as described in the synthesis of **21**; however, the reaction was further monitored by ^{1}H NMR spectroscopy after conversion to the monoacyl complex. Within 1 day, the presence of **23** (see below) could be observed. ^{1}H NMR (C_6D_6): δ 1.06 (d, $J = 8$ Hz, 12H, –CH(C*H*$_3$)$_2$), 1.99 (n, $J = 8$ Hz, 2H, –CH$_2$C*H*(CH$_3$)$_2$), 2.02 (d, $J = 8$ Hz, 4H, –OCC*H*$_2$), 2.22 (s, 6H, –*p*-ArC*H*$_3$), 2.40 (s, 12H, –*o*-ArC*H*$_3$), 3.41(m, 4H, –NC*H*$_2$), 3.61 (m, 4H, –NC*H*$_2$), 5.89 (s, 2H, –imid*H*), 6.92 (s, 4H, –Ar*H*). ^{13}C NMR (C_6D_6): δ 15.5 (–CH(*C*H$_3$)$_2$), 19.0 (–*o*-CH$_3$), 21.2 (–*p*-CH$_3$), 33.8 (–*C*H(CH$_3$)$_2$), 38.3 (–C*C*H$_2$), 49.4 (–N$_{Ar}$*C*H$_2$), 52.1 (–N$_{imid}$*C*H$_2$), 120.4 (–imid*C*), 129.2 (–Ar*C*), 132.1 (–Ar*C*), 134.3 (–Ar*C*), 140.6 (–*C*=*C*), 153.5 (–Ar*C*), 198.5 (–Hf*C*$_{carbene}$).

^{13}C-**22**: ^{13}C NMR resonances are identical except δ 140.6 (d, $J = 30$ Hz, –*C*=*C*).

4.20. Isolation of (^{Mes}[NCN]Hf)$_2$(OC(^{i}Bu)=C(^{i}Bu)O)$_2$ (**23** and ^{13}C-**23**)

A benzene solution of **12** (115 mg, 0.17 mmol) was freeze–pumped–thawed three times with CO, and the solution left to stand under 1 atm CO for five days. Colourless crystalline material began to precipitate after three days. The solution was filtered and the crystalline material was washed with pentane (82 mg, 66%). ^{1}H NMR (C_6D_6): δ 0.79 (d, $J = 8$ Hz, 6H, –CH(C*H*$_3$)$_2$), 0.87 (d, $J = 8$ Hz, 6H, –CH(C*H*$_3$)$_2$), 1.09 (m, 2H, –CC*H*$_2$CH), 1.51 (m, 2H, –CC*H*$_2$CH), 2.21 (s, 6H, –ArC*H*$_3$), 2.33 (s, 6H, –ArC*H*$_3$), 2.74 (s, 6H, –ArC*H*$_3$), 3.40 (m, 4H, –NC*H*$_2$), 3.55 (m,

2H, –NCH_2), 4.16 (m, 2H, –NCH_2), 6.01 (s, 2H, –imid$H$), 6.96 (s, 2H, –ArH), 7.05 (s, 2H, –ArH) (multiplet from –$CH_2CH(CH_3)_2$ obscured by aryl resonances). ^{13}C NMR (C_6D_6): δ 14.6 (–CH(CH_3)$_2$), 14.8 (–CH(CH_3)$_2$), 19.6 (–ArCH_3), 19.7 (–ArCH_3), 20.4 (–ArCH_3), 34.3 (–CH(CH_3)$_2$), 34.6 (–CH(CH_3)$_2$), 39.4 (–CCH_2), 39.6 (–CCH_2), 51.3 (–$N_{Ar}CH_2$), 54.4 (–$N_{imid}CH_2$), 119.8 (–imid$C$), 130.4 (–ArC), 131.6 (–ArC), 131.8 (–ArC), 133.4 (–ArC), 134.1 (–ArC), 140.0 (–C=C), 149.4 (–ArC), 153.2 (–ArC), 195.4 (–Hf$C_{carbene}$).

^{13}C-**23**: ^{13}C NMR resonances are identical except δ 140.0 (d, $J = 30$ Hz, –C=C).

Anal. Calc. for $C_{70}H_{100}Hf_2N_8O_4$: C, 57.02; H, 6.84; N, 7.60. Found: C, 56,72; H, 6.59; N, 7.43%.

4.21. [^{Mes}[NCN]M(CH$_3$)][B(C$_6$F$_5$)$_4$] (M = Zr (**24**), Hf (**25**))

The following procedure is representative of the synthesis of **24** and **25**. To a cooled solution of **7** (35 mg, 0.069 mmol) in CD_2Cl_2 (0.5 mL) was added a cooled CD_2Cl_2 (0.5 mL) solution of [Ph_3C][$B(C_6F_5)_4$] (64 mg, 0.069 mmol). The pale orange solution was immediately transferred to an NMR tube and then frozen in liquid N_2. The NMR was taken immediately after warming the solution to −10 °C. **24**: ^{1}H NMR (CD_2Cl_2): δ 0.50 (s, 3H, –ZrCH_3), 2.10 (br s, 12H, –o-ArCH_3), 2.15 (s, 6H, –p-ArCH_3), 3.45 (m, 2H, –$N_{Ar}CH_2$), 3.94 (m, 2H, –$N_{Ar}CH_2$), 4.14 (m, 2H, –$N_{imid}CH_2$), 4.29 (m, 2H, –$N_{imid}CH_2$), 6.85 (br s, 4H, –ArH), 7.04 (s, 2H, –imid$H$). **25**: ^{1}H NMR (CD_2Cl_2): δ 0.26 (s, 3H, –HfCH_3), 2.15 (br s, 12H, –o-ArCH_3), 2.20 (s, 6H, –p-ArCH_3), 3.70 (m, 2H, –$N_{Ar}CH_2$), 4.05 (m, 2H, –$N_{Ar}CH_2$), 4.28 (m, 2H, –$N_{imid}CH_2$), 4.60 (m, 2H, –$N_{imid}CH_2$), 6.99 (br s, 4H, –ArH), 7.15 (s, 2H, –imid H).

4.22. ^{Mes}[NCN]Hf(OTf)(CH$_3$) (**26**)

To a cooled ethereal solution of **8** (200 mg, 0.33 mmol) was added an ethereal solution of CF_3SO_3H (48 mg, 0.32 mmol). The solution was gradually allowed to warm to room temperature and stirred overnight. The solvent was removed and the residue recrystallized from Et_2O/hexane at −30 °C to give a colourless solid. ^{1}H NMR (CD_2Cl_2): δ 0.19 (s, 3H, –HfCH_3), 2.19 (br s, 12H, –o-ArCH_3), 2.21 (s, 6H, –p-ArCH_3), 3.34 (m, 2H, –$N_{Ar}CH_2$), 4.00 (m, 2H, –$N_{Ar}CH_2$), 4.13 (m, 2H, –$N_{imid}CH_2$), 4.55 (m, 2H, –$N_{imid}CH_2$), 6.87 (br s, 4H, –ArH), 7.09 (s, 2H, –imid H). Anal. Calc. for $C_{27}H_{35}F_3HfN_4O_3S$: C, 44.35; H, 4.83; N, 7.66. Found: C, 43.85; H, 4.61; N, 7.09%.

4.23. Polymerization protocols

(a) Ethylene polymerization: A 100 mL Schlenk flask was charged with 50 mL toluene inside a glove box and attached to a vacuum line. The toluene was degassed with ethylene for 30 min at room temperature, whereby a toluene (5 mL) solution of [Ph_3C][$B(C_6F_5)_4$] was syringed into the flask. The orange solution was stirred for 5 min under ethylene. A toluene (5 mL) solution of the catalyst was quickly added and the opaque solution stirred for 15 min. The experiment was stopped by venting the ethylene and quenching the reaction with 10% methanolic HCl. The resulting polyethylene was filtered and washed with 10% methanolic HCl and methanol and air-dried overnight.

(b) 1-Hexene polymerization: The cation was generated in chlorobenzene by the method described in **24**, and 1-hexene added immediately (~500 equivalents). The solution was stirred for 1 h and quenched with 10% methanolic HCl. The solvents were removed, the residue dissolved in pentane, and filtered through silica gel. The solvents were removed in vacuo to yield a minor amount of a viscous gel.

Acknowledgements

The authors thank NSERC of Canada for funding (Discovery Grant to M.D.F. and an NSERC PGS-B Scholarship to L.P.S.). We also thank Mr. Jonah Chang for help with compound preparation.

Appendix A. Supplementary data

Complete experimental details, information on X-ray data collection and processing for **12**, **14**, **15**, **17**, and **22**, and X-ray crystallographic data for **12**, **14**, **15**, **17**, and **22** (CIF). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.121.

References

[1] (a) W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290;
(b) D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.
[2] (a) M. Regitz, Angew. Chem. Int. Ed. 35 (1996) 725;
(b) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. 36 (1997) 2162;
(c) A.J. Arduengo III, R. Krafczyk, Chem. Z. 32 (1998) 6;
(d) J.E.L. Dullins, P.A.Z. Suarez, S. Einloft, R.F. de Souza, J. Dupont, J. Fischer, A. De Cian, Organometallics 17 (1998) 815;
(e) A.J. Arduengo III, Acc. Chem. Res. 32 (1999) 913.
[3] (a) S. Gründemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, J. Am. Chem. Soc. 124 (2002) 10473;
(b) A.A. Danopoulos, N. Tsoureas, J.C. Green, M.B. Hursthouse, Chem. Commun. (2003) 756.
[4] P.L. Arnold, S.A. Mungur, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 42 (2003) 5981.
[5] L.P. Spencer, S. Winston, M.D. Fryzuk, Organometallics 23 (2004) 3372.
[6] M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, J. Organomet. Chem. 663 (2002) 192.
[7] (a) Y. Schrodi, R.R. Schrock, P.J. Bonitatebus Jr., Organometallics 20 (2001) 3560;
(b) R.R. Schrock, P.J. Bonitatebus Jr., Y. Schrodi, Organometallics 20 (2001) 1056.
[8] H.G. Alt, C.E. Denner, W. Milius, Inorg. Chim. Acta 357 (2004) 1682.
[9] L.D. Durfee, I.P. Rothwell, Chem. Rev. 88 (1988) 1059, and the references therein.

[10] L.R. Chamberlain, L.D. Durfee, P.E. Fanwick, L.M. Kobriger, S.L. Latesky, A.K. McMullen, B.D. Steffey, I.P. Rothwell, K. Folting, J.C. Huffman, J. Am. Chem. Soc. 109 (1987) 6068.
[11] F.J. Berg, J.L. Petersen, Tetrahedron 48 (1992) 4749.
[12] L.R. Chamberlain, L.D. Durfee, P.E. Fanwick, L.M. Kobriger, S.L. Latesky, A.K. McMullen, I.P. Rothwell, K. Folting, J.C. Huffman, W.E. Streib, J. Am. Chem. Soc. 109 (1987) 390.
[13] M.F. Lappert, N.T. Luong-Thi, C.R. Milne, J. Organomet. Chem. 174 (1979) C35.
[14] A.K. McMullen, I.P. Rothwell, J.C. Huffman, J. Am. Chem. Soc. 107 (1985) 1072.
[15] S.L. Latesky, A.K. McMullen, I.P. Rothwell, J.C. Huffman, Organometallics 4 (1985) 1986.
[16] L.R. Chamberlain, I.P. Rothwell, J.C. Huffman, J. Chem. Soc., Chem. Commun. (1986) 1203.
[17] G. Erker, K. Engel, C. Kruger, G. Muller, Organometallics 3 (1984) 128.
[18] G.S. Bristow, M.F. Lappert, T.R. Martin, J.L. Atwood, W.F. Hunter, J. Chem. Soc., Dalton Trans. 107 (1985) 5981.
[19] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 100 (1978) 2716.
[20] P.T. Wolczanski, J.E. Bercaw, Acc. Chem. Res. 12 (1980) 121.
[21] R. Choukoun, B. Douziech, F. Soleil, J. Chem. Soc., Chem. Commun. (1995) 2017.
[22] D.C. Sonnenberger, E.A. Mintz, T.J. Marks, J. Am. Chem. Soc. 106 (1984) 3484.
[23] T.J. Marks, Science 217 (1982) 989, and the references therein.
[24] J.M. Manriquez, P.J. Fagan, T.J. Marks, C.S. Day, V.W. Day, J. Am. Chem. Soc. 100 (1978) 7112.
[25] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Am. Chem. Soc. 105 (1983) 1690.
[26] G. Erker, R. Noe, J. Chem. Soc., Dalton Trans. (1991) 685.
[27] (a) G. Erker, K. Engel, J.L. Atwood, W.E. Hunter, Angew. Chem. Int. Ed. 22 (1983) 494;
(b) G. Erker, R. Petrenz, J. Chem. Soc., Chem. Commun. 8 (1989) 450;
(c) G. Erker, F. Sosna, R. Zwettler, C. Kruger, Organometallics 8 (1989) 450.
[28] T.Y. Meyer, L.R. Garner, N.C. Baenziger, L. Messerle, Inorg. Chem. 29 (1990) 4045.
[29] (a) D.H. McConville, J.J. Vittal, Organometallics 16 (1997) 1491;
(b) R.J. Keaton, K.C. Jayaratne, J.C. Fettinger, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 12909;
(c) E.Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, Organometallics 21 (2002) 662;
(d) J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134;
(e) Y.-M. Jeon, S.J. Park, J. Heo, K. Kim, Organometallics 17 (1998) 3161;
(f) C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664;
(g) K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, Organometallics 14 (1995) 2633;
(h) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 3327.
[30] (a) G.W. Coates, P.D. Hustad, S. Reinartz, Angew. Chem. Int. Ed. 41 (2002) 2236;
(b) R.R. Schrock, J. Adamchuck, K. Ruhland, L.P.H. Lopez, Organometallics 24 (2005) 857.
[31] S.J. Skoog, C. Mateo, G.G. Lavoie, F.J. Hollander, R.G. Bergman, Organometallics 19 (2000) 1406.
[32] T. Asakura, M. Demura, Y. Nishiyama, Macromolecules 24 (1991) 2334.
[33] T.J. Reilly, J. Chem. Educ. 76 (1999) 1557.
[34] R. Bird, A.C. Knipe, C.J.M. Stirling, J. Chem. Soc., Perkin Trans. 29 (1973) 1215.
[35] G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.