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New zirconium complexes supported by *N*-heterocyclic carbene (NHC) ligands: Synthesis and assessment of hydroamination catalytic properties

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ABSTRACT

Reactions of 2-(bromomethyl)-4,6-di-*tert*-butylphenol or 2-(bromomethyl)-4,6-bis(2-phenylpropan-2-yl)phenol with 1*H*-imidazole led to syntheses of *N*,*N*-disubstituted imidazolium bromides presenting two methylene-bis(2,4-di-*tert*-butylphenol) ($[H_2L^1]Br$) or methylene-bis(2,4-di-*tert*-butylphenol) ($[H_2L^2]Br$) appended groups. Treatment of $Zr(NMe_2)_4$ with $[H_2L^1]Br$ or $[H_2L^2]Br$ gave tethered NHC zirconium complexes of general formula $[ZrL(NMe_2)(THF)Br]$ ($L = L^1$, **7**; L^2, **8**). The bonding of the tridentate ligands to the metal adopts S-shape conformation. In solution a fluxional process between the left- and right-handed forms of the ligand is observed for both complexes. In agreement with the NMR spectra, the optimised structure obtained by DFT revealed octahedral geometry around zirconium with mutually *trans* Br and $C_{carbene}$ donors. Complexes **7** and **8** react with 2,2-diphenylpent-4-en-1-amine in a 1:1 ratio to give the hydroamination product 2-methyl-4,4-diphenylpyrrolidine. In catalytic conditions, the systems deactivate and catalytic conversions are not observed.

1. Introduction

N-Heterocyclic carbenes (NHCs) derived from imidazolium salts [1,2] have been widely used as supporting ligands for transition metals with important applications in catalysis [3,4]. The good donor properties, their chemical robustness and the possibility to modulate either electronic or stereochemical properties are important features of NHC ligands that are responsible for their extensive late transition metal chemistry. On the contrary, the stabilization of early transition metals NHC complexes revealed in many cases critical and therefore significant applications of these compounds are by far less developed. A usual strategy to overcome those problems requires the functionalization of the NHC nitrogen atoms with appended moieties that provide additional binding points to the metals. The incorporation of one or two O- or N-based anionic fragments, which form strong bonds with high oxidation state early metals, proved to stabilize the carbene coordination and yielded robust NHC-based high-oxidation-state metal complexes [5–9]. This methodology, which strongly depends on experimental issues as the metal precursors and the NHC scaffolds, as well as the stability of the anionic NHC ligand precursors [10–13] is currently the most convenient entry into NHC early metals chemistry originating a growing number of complexes with interest in catalysis [5,14–17].

As part of our interest in the chemistry of early transition metals and lanthanides we explored multidentate ligands where cyclic or tripodal amine frames were combined with ariloxide donors [18–24]. The bonding of the phenolate moieties guaranteed the stabilization of low and high oxidation state metal complexes with diverse structures and reactivity, which were investigated in radical reactions [18,19], olefin polymerization [20] as well as in epoxidation and sulfoxidation catalysis [21,22]. Furthermore, we studied Zr complexes anchored by cyclam diamido–diamine ligands and reported the first example of an intramolecular hydroamination catalysts supported by a macrocyclic scaffold [25]. In view of recent reports on the catalytic activity of Group 4 NHC complexes in the intramolecular hydroamination of aminoalkenes [14,15b,26] we report here new tridentate bis-ariloxide NHC zirconium complexes and their evaluation as intramolecular hydroamination catalysts.

2. Results and discussion

The ligand precursors $[H_3L^1]Br$ (**3**) and $[H_3L^2]Br$ (**4**) were prepared by alkylation of 1*H*-imidazole using 2-(bromomethyl)-4,6-di-

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tert-butylphenol (**1**) and 2-(bromomethyl)-4,6-bis(2-phenylpropan-2-yl)phenol (**2**), respectively (Scheme 1, top). Compound **1** was obtained as described in the literature [27] by reaction of 2-(bromomethyl)-4,6-di-*tert*-butylphenol, paraformaldehyde and HBr, and compound **2** was prepared using an adaptation of that procedure. The reaction of 1 equiv. of either **1** or **2** with imidazole, described in the literature [28] gave, in our hands, mixtures of mono- and disubstituted products (**5** + **3** and **6** + **4** in Scheme 1, bottom) but one pot dialkylation of imidazole, using 2 equiv. of **1** or **2**, led cleanly to imidazolium salts $[H_3L^1]Br$ (**3**) and $[H_3L^2]Br$ (**4**), respectively, in good yields. ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** and **4** are consistent with C_2-symmetry and in accordance with their formulation. The resonances for the NC*H*N protons show up at δ 9.48 and 9.94 ppm, respectively, while the resonances for the NCHN carbons are observed at δ 137.4 and 136.6 ppm, respectively. The NMR data of **3** are in accordance with those reported in the literature [28].

Crystals of monoalkylated imidazole **6** suitable for X-ray diffraction precipitated from a THF solution of a mixture of **6** and **4** at −20 °C. Although the data obtained are of poor quality the structure could be unequivocally determined. This data can be found in Supporting information.

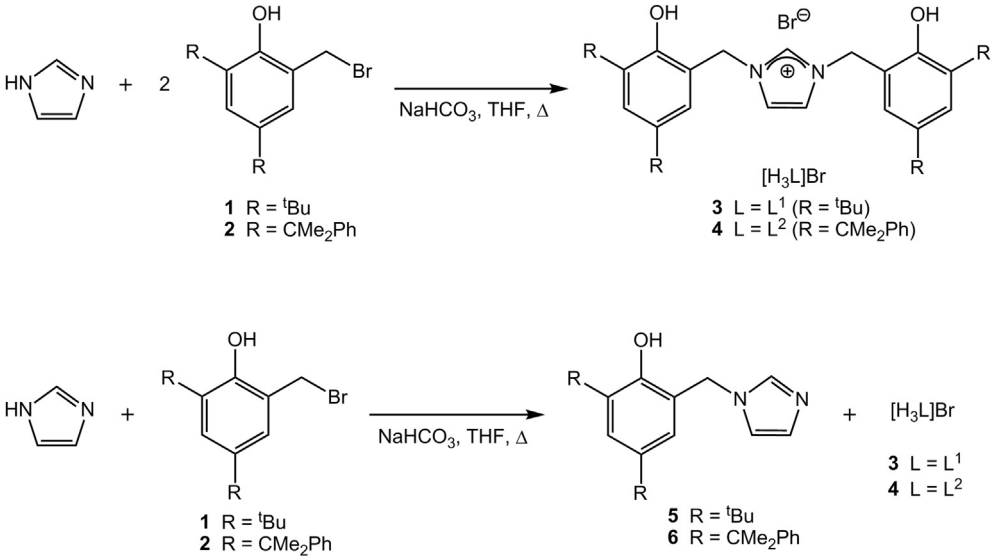
Crystals of $[H_3L^2]Br$ (**4**) suitable for X-ray diffraction were also obtained from a THF solution at −20 °C. $[H_3L^2]Br$ crystallizes in the S shape conformation (Fig. 1, right) with hydrogen bonds between the imidazolium cations and the Br anions with a O2−H2···Br1 length of 2.43 Å (Fig. 1, left). The phenolate rings are almost parallel to each other with an angle of 22.0(3)° between the planes containing the rings.

Treatment of $Zr(NMe_2)_4$ with 1 equiv. of $[H_3L]Br$ (L = L^1, **3**; L^2, **4**) in THF at room temperature afforded complexes $[ZrL(NMe_2)(THF)Br]$ (L = L^1, **7**; L^2, **8**) that were obtained as yellow solids in 62 and 64% yield, respectively (Scheme 2). The reaction proceeds with $HNMe_2$ elimination and thus avoids the use of thermally unstable alkali metal salts of the proligands [28].

The k^3-C,O_2 bonding of the bis(phenolate) NHC ligand might in principle define a U or an S shape. In the first case the two aromatic rings are directed to the same side and in the latter they are oriented to opposite sides in relation to the plane containing the two oxygens, the carbene carbon and the zirconium. The S configuration was observed in analogous titanium and zirconium derived from L^1 [7], and in $[H_3L^2]Br$, **4**, which were characterized by X-ray diffraction. DFT calculation presented below also point out that S shape configuration is more stable and no U shape compounds have been identified yet. Thus, it seems plausible to assume that in complexes **7** and **8** the ligand assumes an S shape that originates an asymmetric zirconium centre, as observed by NMR at low temperature (see below).

The ^1H NMR spectra of **7** and **8** at room temperature display broad resonances that denote a fluxional process in solution. The proton and carbon NMR patterns of the two compounds are essentially the same with exception of the resonances assigned to the *tert*-butyl or dimethylphenyl substituents of the phenolate rings. The *tert*-butyl groups of the phenolate rings of **7** give rise to two broad signals and the dimethylphenyl groups of **8** originate three broad resonances for the methyl groups (integrating 6H, 6H and 12H, respectively) in addition to several aromatic resonances due to the phenyl groups. In common the proton NMR spectra of **7** and **8** reveal two aromatic peaks corresponding to the phenolate groups, two broad AX spin systems for the CH_2 protons, one resonance for the NMe_2 ligand, two broad apparent singlets for the THF and one resonance for the CH protons of the NHC core. In both ^1H NMR spectra of **7** and **8** the proton attached to the carbon atom of the NCN fragment is absent (at δ 9.48 and 9.94 ppm in the ligand precursors, respectively), which is an evidence of the Zr−$C_{carbene}$ bond. In each AX system one of the protons is shifted to low field ($\delta \sim 5$ ppm) and very deshielded in comparison with their geminal protons ($\delta \sim 3.6$ ppm). This difference indicates that the chemical environments of the methylenic protons are very different and reflect the influence of the NMe_2 and THF ligands in complexes **7** and **8** (see DFT discussion below). The carbon NMR spectra are in agreement with the proton data described and the most significant resonances are those assigned to the carbene that are observed at δ 186.8 and 186.0 ppm for **7** and **8**, respectively. The two AX systems in both complexes and the resonances of the Me groups of the CMe_2Ph substituents in **8** observed at room temperature in the NMR spectra reveal *pseudo*-C_2-symmetric species with *trans*-phenolate coordination.

Aiming to attain further information about the structures of **7** and **8** 2D NMR experiments were performed. The NOESY NMR spectra disclosed that the NMe_2 and THF ligands are *trans* to each other, as no cross peaks between the two ligands were identified, but they are mutually *cis* to the phenolate moieties with which they present spatial interactions. Thus, in the NMR time scale, the



Scheme 1.

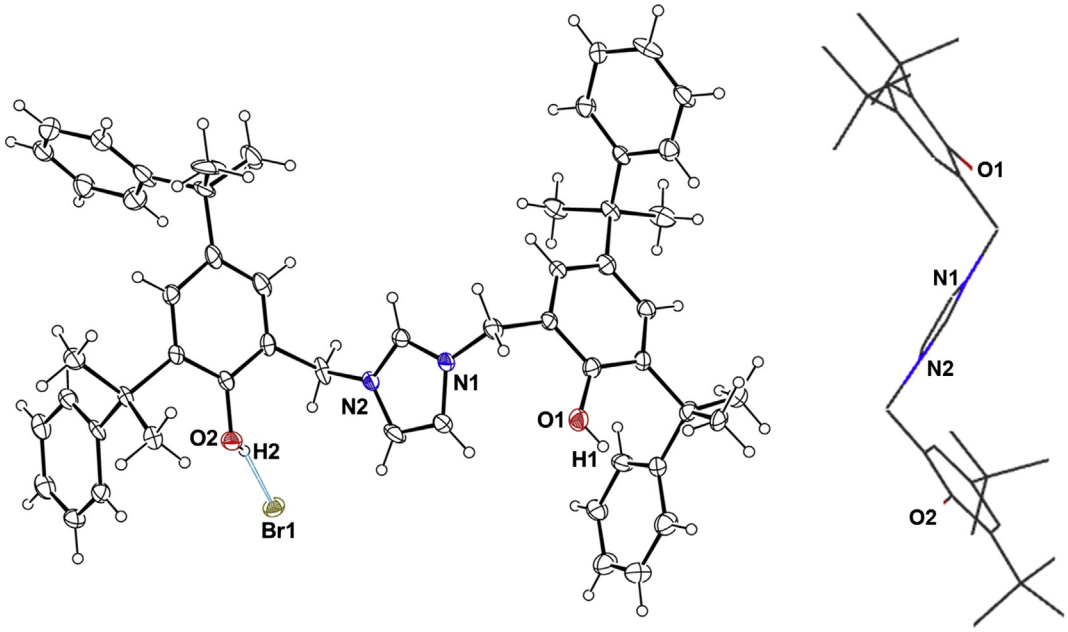
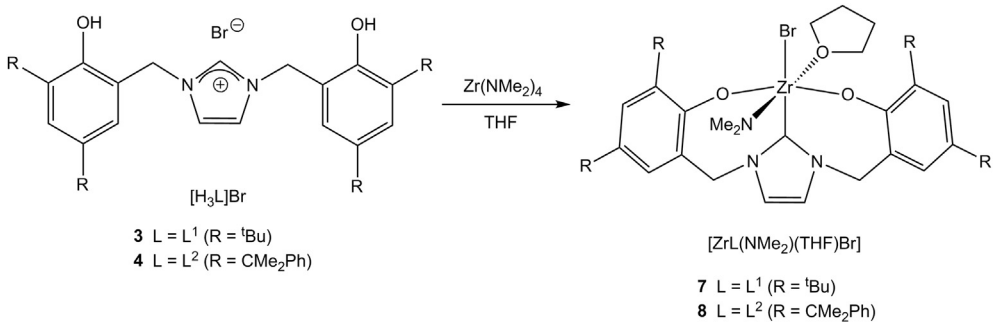


Fig. 1. ORTEP diagram of $[H_3L^2]Br$ (4) (left) using 30% probability level ellipsoids. The hydrogen bond is represented by a dashed light-blue line. Mercury wireframe diagram (right) showing the S shape adopted by the molecule in the solid state. Hydrogen atoms and phenyl groups of the CMe_2Ph substituents of the phenolates are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 2.

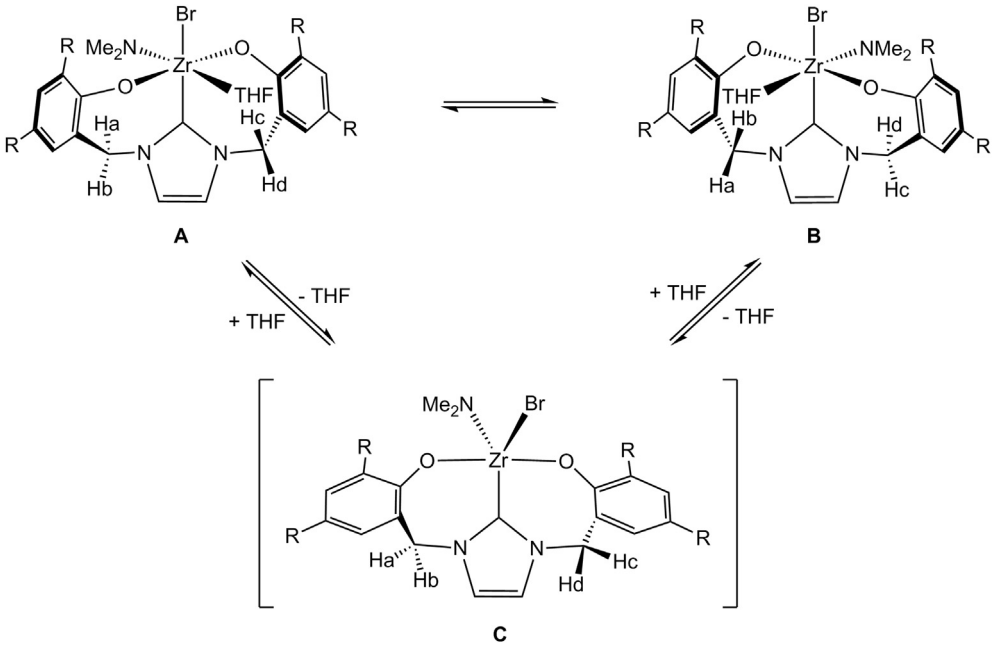
bromide ligand is coordinated *trans* to the carbene. This result excluded an isomer presenting *cis*-phenolate bonding, which would force the NMe_2 and THF ligands to be *cis*. Moreover, the two AX spin systems corresponding to CH_2 protons display conformational exchange peaks in the NOESY NMR spectra.

Variable-temperature ^1H NMR studies of **7** confirmed the occurrence of a fluxional process that was stopped in toluene-d_8 solution at −30 °C, to show the presence of a species with C_1 symmetry. Both splitting and sharpening of all except the THF resonances were observed. The two NC*HCH*N protons of the carbene ligand, which appeared superimposed at room temperature, split in two resonances and the two signals corresponding to the *tert*-butyl groups gave rise to four different resonances. The aromatic protons of the phenolate rings split in four non-equivalent signals as well as the proton resonances assigned to NMe_2 that originate two singlets. The four signals due to the AX system only suffer a small displacement with cooling. The two THF resonances remain broad even at −30 °C.

The changes observed in the $^{13}C\{^1H\}$ NMR spectra at −30 °C are slight but the splitting observed for the *tert*-butyl carbons are significant and in accordance with an unsymmetrical species. The unchanging carbene resonance, in particular, indicates that the carbene remains coordinated to the metal during the process.

The dynamic process observed in the NMR at room temperature may be assigned to the interconversion of the left- and right-handed twisted forms of the ligand (**A** and **B** in Scheme 3). The dissociation of THF promotes the interconversion between the two S-shaped forms in **A** and **B** that involves a pentacoordinated intermediate (**C** in Scheme 3). Thus, at room temperature the fast exchange process originates a *pseudo*-C_2-symmetric pattern on the ^1H NMR time scale with broad peaks for all protons with exception of the CH_2 protons that remain asymmetric due to the non-planarity of the 7-atoms ring formed by $Zr{-}C_{carbene}{-}N{-}CH_2{-}C_{phenolate}{-}C_{phenolate}{-}O_{phenolate}$. The exchange between **A** and **B** generates the magnetic equivalence of protons H_a, H_b, H_c and H_d in **A** with H_d, H_c, H_b and H_a in **B**, respectively.

Several attempts to obtain suitable crystals for X-ray diffraction failed. All off-white crystals obtained from diethyl ether or toluene solutions had very weak diffraction power that did not allow structure determination and hence Density functional theory calculations [29] (GAUSSIAN 03/PBE1PBE [30], see Computational details) were performed to confirm the coordination mode of complexes **7** and **8**. The structures of the three possible



Scheme 3.

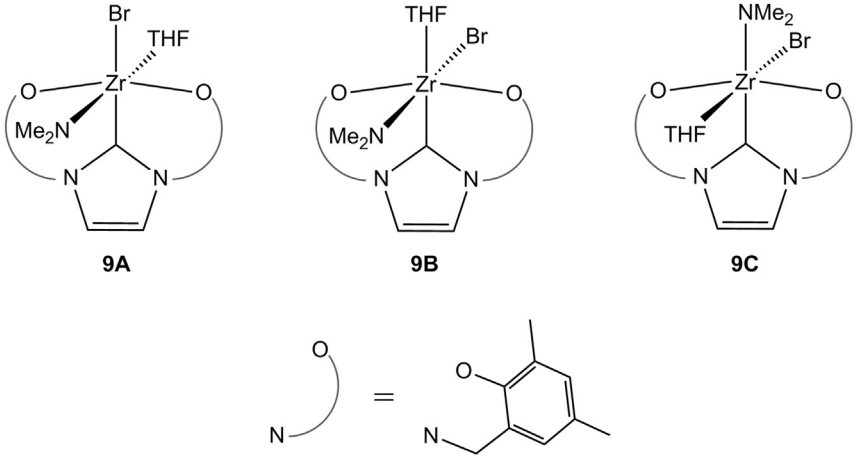
coordination isomers of a model complex of **7** and **8**, in which the R substituents in the phenolate groups were replaced by methyls (**9**), were fully optimized (Scheme 4). Isomer **9A**, with a bromide ligand *trans* to the carbene, is more stable than **9B** and **C** by 2.01 and 1.63 kcal mol^{-1}, respectively. These differences, although consistent with the formulation of complexes **7** and **8** described above are very small and do not exclude the formation of any of the isomers. However, they are in agreement with the NOESY information and may be taken as a further evidence for the preferential formation **9A**.

The optimized geometry of **9A**, depicted in Fig. 2, shows that there is a significant proximity between proton Ha and atom N3 of the NMe_2 moiety (2.62 Å) and between proton Hc and atom O3 of the THF molecule (2.38 Å). Such proximity is responsible for the significant deshielding observed for those protons in the ^{1}H NMR spectra that, as already mentioned, appear close to δ 5 ppm whereas their geminal protons show up at $\delta \sim$3.6 ppm.

NHC complexes of Zr and Hf were reported as intramolecular hydroamination catalysts of unactivated olefins [14,15b,26]. Complexes **7** and **8** might be good candidates to catalyse intramolecular hydroamination reactions because they have one dimethylamido ligand that may be replaced by an aminoalkene (either to give an amido or an imido ligand) and a labile THF molecule that may provide a coordination position for the C=C moiety.

Preliminary catalytic hydroamination studies were carried out with complexes **7** and **8** using 2,2-diphenylpent-4-en-1-amine (Scheme 5). The reactions were performed in toluene-d_8 solution, in an NMR tube equipped with a J-young valve, at 100 °C using 5 mol % precatalyst loading (aminoalkene:Zr = 20:1), for 72 h. The ^{1}H NMR spectra of the reaction mixtures revealed only the aminoalkene resonances and no signals corresponding to the hydroamination product, 2-methyl-4,4-diphenylpyrrolidine.

The 1:1 reaction of **7** with 2,2-diphenylpent-4-en-1-amine was also performed in toluene, at 100 °C, during 48 h. The analysis of the reaction products by ^{1}H NMR revealed no signals due to the aminoalkene and the appearance of a set of new resonances at δ 3.41 (CH_2, C5), 3.15 (CH, C2), 2.36 (CH_2, C3) and 1.04 (CH_3) ppm that are



Scheme 4.

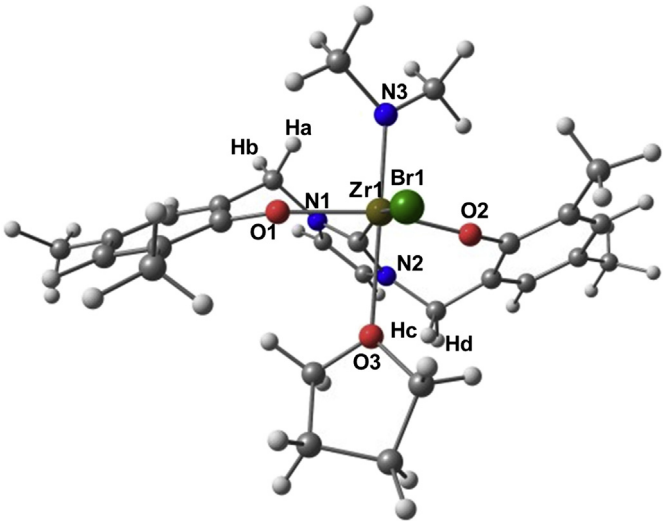
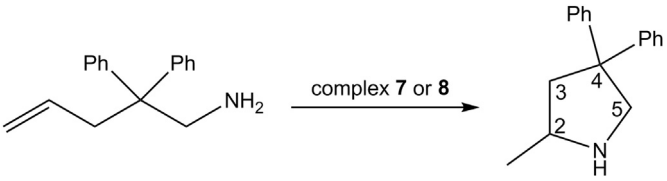


Fig. 2. DFT optimized geometry of **9A**.



Scheme 5.

characteristic of 2-methyl-4,4-diphenylpyrrolidine. Several resonances between 1.15 and 1.90 ppm, possibly due to *tert*-butyl groups resulting from complex decomposition, are also observed.

These results suggest that the critical step in the system behaviour is catalyst regeneration: complexes **7** and **8** react with 2,2-diphenylpent-4-en-1-amine to perform the cyclization reaction but they are not active under catalytic conditions.

3. Experimental

3.1. General procedures

All preparations and subsequent manipulations of air/moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk line and dry box techniques. THF, toluene and Et_2O were dried by standard methods and distilled prior to use. C_6D_6 was dried over Na and distilled under reduced pressure. Toluene-d_8 and $CDCl_3$ were dried with 4 Å molecular sieves and degassed by freeze–pump–thaw method. Unless stated otherwise, all reagents were purchased from commercial suppliers and used as received. 2-(Bromomethyl)-4,6-di-*tert*-butylphenol (**1**) [27] and 2,2-diphenylpent-4-en-1-amine [31] were prepared as described in the literature. 1D and 2D (COSY, NOESY, HSQC) NMR spectra were recorded on a Bruker Advance II+ 300 MHz (UltraShield Magnet) instrument at ambient temperature, unless stated otherwise. ^1H and ^{13}C chemical shifts (δ) are expressed in ppm relative to Me_4Si. The NMR-tube scale reactions were prepared in an N_2-filled glove box. The NMR-tubes were equipped with a Teflon screw cap (J-Young). Carbon, hydrogen and nitrogen analyses were performed in-house using an EA110 CE Instruments automatic analyser. The results presented are, in general, the average of two independent determinations.

3.2. Synthetic procedures

3.2.1. Synthesis of 2-(bromomethyl)-4,6-bis(2-phenylpropan-2-yl) phenol (**2**)

This compound was prepared using an adaptation of a procedure described in the literature [27]. To a solution of 2,4-bis(2-phenylpropan-2-yl)phenol (13.94 g, 42.17 mmol) in acetic glacial acid (c.a. 25 mL) was added paraformaldehyde (1.40 g, 46.62 mmol) and the mixture was stirred for 2 h at room temperature. A solution of HBr 33% in acetic acid (22.1 mL, 126.51 mmol, 3 equiv.) was then added dropwise and the resulting yellow solution was stirred for 30 min. The solvent was evaporated under vacuum and the orange viscous oil obtained was stored at −20 °C for 16 h. An off-white solid that precipitate out of solution was separated from the orange oil, washed with a small amount of diethyl ether and dried in vacuum to yield 12.5 g (70% yield) of an off-white powder. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.37–7.25 (m, 9H CH_{Ph} + 1H CH_{Ar}), 7.22–7.18 (m, 1H, CH_{Ph}), 7.14 (d, $^4J_{HH}$ = 2.2 Hz, 1H, CH_{Ar}), 4.60 (br, 1H, OH), 4.45 (s, 2H, CH_2), 1.75 (s, 6H, $C(CH_3)_2Ph$), 1.63 (s, 6H, $C(CH_3)_2Ph$). ^{13}C-{^1H} NMR (75 MHz, $CDCl_3$, ppm): δ 150.8, 150.3, 147.9, 142.7 and 135.4 (C_{ipso} Ar + Ph), 129.5 and 128.2 (CH_{Ph}), 127.8 and 127.5 (CH_{Ar}), 126.9, 126.2, 126.1 and 125.9 (CH_{Ph}), 125.4 (C_{ipso} Ar or Ph), 42.8 and 42.1 ($C(CH_3)_2Ph$), 31.2 ($C(CH_3)_2Ph$), 30.5 (CH_2), 29.8 ($C(CH_3)_2Ph$). EA calculated for $C_{25}H_{27}BrO$: C, 70.92; H, 6.43. Found: C, 70.86; H, 6.68.

3.2.2. Synthesis of $[H_3L^1]Br$ (**3**)

$[H_3L^1]Br$ was prepared using an adaptation of a procedure described in the literature [28]. Imidazole (1.02 g, 15 mmol) and anhydrous sodium bicarbonate (1.26 g, 15 mmol) were poured in a round-bottom flask under nitrogen. THF (50 mL) was added and the mixture was refluxed. A solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (6.19 g, 30 mmol) in THF (30 mL) was slowly added to the suspension with a dropping funnel and the mixture was stirred for 12 h. After cooling to room temperature, the solution was filtered off and the solvent evaporated to dryness leading to a viscous oil that was sequentially washed with toluene and *n*-hexane and then dried in vacuum to give 6.20 g (70% yield) of a white powder. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 9.48 (s, 1H, NCHN), 7.33 (s, 2H, CH_{Ar}), 7.19 (s, 2H, NCHCHN), 5.55 (s, 4H, CH_2), 1.37 (s, 6H, $C(CH_3)_3$), 1.25 (s, 6H, $C(CH_3)_3$). ^{13}C-{^1H} NMR (75 MHz, $CDCl_3$, ppm): δ 151.9, 143.8 and 139.6 (C_{ipso} Ar), 137.4 (NCHN), 126.0 and 125.7 (CH_{Ar}), 121.8 (NCHCHN), 121.7 (C_{ipso} Ar), 51.3 (CH_2), 35.2 and 34.5 ($C(CH_3)_3$), 30.4 and 30.3 ($C(CH_3)_3$).

3.2.3. Synthesis of $[H_3L^2]Br$ (**4**)

$[H_3L^2]Br$ was prepared using the procedure described for $[H_3L^1]Br$, using 2-(bromomethyl)-4,6-bis(2-phenylpropan-2-yl)phenol: Imidazole (0.90 g, 13.2 mmol); anhydrous sodium bicarbonate (1.11 g, 13.2 mmol); 2-(bromomethyl)-4,6-bis(2-phenylpropan-2-yl)phenol (10.16 g, 24 mmol). The compound was obtained as a white powder (7.20 g, 72% yield). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 9.94 (s, 1H, NCHN), 7.34–7.14 (m, 20H CH_{Ph} + 2H CH_{Ar}), 7.00 (d, $^4J_{HH}$ = 1.8 Hz, 1H, CH_{Ar} or CH_{Ph}), 5.26 (s, 4H, CH_2), 1.70 (s, 6H, $C(CH_3)_2Ph$), 1.54 (s, 6H, $C(CH_3)_2Ph$). ^{13}C-{^1H} NMR (75 MHz, $CDCl_3$, ppm): δ 150.5, 150.2, 147.6 and 143.8 (C_{ipso} Ar + Ph), 136.6 (NCHN), 136.1 (C_{ipso} Ar or Ph), 129.5, 128.2, 128.1, 127.5, 127.2, 126.8, 126.0, 121.5 and 125.8 (CH_{Ar} + CH_{Ph}), 121.2 (C_{ipso} Ar or Ph), 49.6 (CH_2), 42.8 and 42.0 ($C(CH_3)_2Ph$), 31.1 and 29.7 ($C(CH_3)_2Ph$). EA calculated for $C_{53}H_{57}BrN_2O_2$: C, 76.33; H, 6.89; N, 3.36. Found: C, 75.88; H, 6.78; N, 3.52.

3.2.4. Synthesis of $[ZrL^1(NMe_2)(THF)Br]$ (**7**)

A THF solution of $[H_3L^1]Br$ (0.586 g, 1 mmol) was slowly added to a THF solution of $Zr(NMe_2)_4$ (0.267 g, 1 mmol) at room temperature. The mixture was stirred for 16 h and a yellow solution formed. The

solvent was evaporated to dryness under reduced pressure to give a yellow crystalline powder (0.451 g, 62% yield). ^{1}H NMR (300 MHz, C_6D_6, ppm, room temperature): δ 7.65 (br, 2H, *para*-CH_{Ar}), 7.08 (br, 2H, *ortho*-CH_{Ar}), 6.15 (s, 2H, NCHCHN), 5.37 (br, 1H, CH_2), 4.93 (br, 1H, CH_2), 3.85 (br, 2H, CH_2), 3.55 (s, 4H, THF), 2.98 (s, 6H, NMe_2), 1.89 (s, 18H, $C(CH_3)_3$), 1.38 (s, 18H, $C(CH_3)_3$), 1.25 (br, 4H, THF). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, ppm, room temperature): δ 186.8 (C, carbene), 160.5, 138.9 (C_{ipso} Ar), 125.3 (CH_{Ar}), 119.5 (NCHCHN), 69.2 (THF), 52.8 (CH_2), 45.3 (NMe_2), 36.2 and 34.4 ($C(CH_3)_3$), 32.0 and 30.8 ($C(CH_3)_3$), 25.7 (THF). ^{1}H NMR (300 MHz, toluene-d_8, ppm, −30 °C): δ 7.65 (d, 2H, $^4J_{HH}$ = 7.4 Hz, *para*-CH_{Ar}), 7.15 (d, 2H, 8.1 Hz, *ortho*-CH_{Ar}), 6.27 (s, 1H, NCHCHN), 6.21 (s, 1H, NCHCHN), 5.33 (d, 1H, $^2J_{HH}$ = 13.4 Hz, CH_2), 4.87 (d, 1H, $^2J_{HH}$ = 13.4 Hz, CH_2), 3.89 (d, 1H, $^2J_{HH}$ = 12.3 Hz, CH_2), 3.85 (d, 1H, $^2J_{HH}$ = 12.9 Hz, CH_2), 3.60 (br, 4H, THF), 3.38 (br, 3H, NMe_2), 2.61 (br, 3H, NMe_2), 1.93 (s, 9H, ^{t}Bu), 1.88 (s, 9H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu), 1.29 (br, 4H, THF). ^{13}C-{^{1}H} NMR (75 MHz, toluene-d_8, ppm, −30 °C): δ 186.4 (C, carbene), 160.9, 160.7, 140.2, 139.8, 138.8 and 138.7 (C_{ipso} Ar), 125.7 (CH_{Ar}), 124.5 (C_{ipso} Ar), 120.1 (NCHCHN), 66.4 (THF), 52.7 (CH_2), 45.8 (NMe_2), 36.6, 36.4 and 34.7 ($C(CH_3)_3$), 32.3, 31.0 and 30.8 ($C(CH_3)_3$), 25.7 (THF). EA calculated for $C_{39}H_{60}BrN_3O_3Zr$: C, 59.29; H, 7.65; N, 5.32. Found: C, 58.96; H, 7.41; N, 4.94.

3.2.5. Synthesis of [ZrL^2(NMe$_2$)(THF)Br] (**8**)

[ZrL^2(NMe$_2$)(THF)Br] was prepared using the procedure described above to [ZrL^1(NMe$_2$)(THF)Br] using [H_3L^2]Br: [H_3L^2]Br (0.754 g, 1 mmol); $Zr(NMe_2)_4$ (0.267 g, 1 mmol). The compound was obtained as a yellow crystalline powder (0.662 g, 64% yield). ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 7.85–7.63 (m, 4H, CH_{Ph}), 7.48 (s, 2H, *para*-CH_{Ar}), 7.37–7.21 (m, 8H, CH_{Ph}), 7.14–7.00 (m, 8H, CH_{Ph}), 6.86 (s, 2H, *para*-CH_{Ar}), 5.86 (br, 2H, NCHCHN), 5.18 (br, 1H, CH_2), 4.67 (br, 1H, CH_2), 3.60 (br, 1H, CH_2), 3.55 (br, 1H, CH_2), 3.50 (s, 4H, THF), 2.69 (s, 6H, NMe_2), 2.26 (br, 6H, $C(CH_3)_2Ph$), 2.11 (br, 6H, $C(CH_3)_2Ph$), 1.62 (br, 12H, $C(CH_3)_2Ph$), 1.35 (br, 4H, THF). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, ppm): δ 186.0 (C, carbene), 151.5, 138.4 (C_{ipso} Ar), 128.3 (CH_{Ar}), 127.6 and 127.4 (CH_{Ph}), 127.2 (CH_{Ar}), 125.5 (CH_{Ph}), 119.3 (NCHCHN), 68.3 (THF), 52.4 (CH_2), 44.7 (NMe_2), 44.7 and 42.8 ($C(CH_3)_2Ph$), 31.4 ($C(CH_3)_2Ph$), 25.7 (THF). EA calculated for $C_{59}H_{68}BrN_3O_3Zr$: C, 68.25; H, 6.60; N, 4.05. Found: C, 67.89; H, 6.50; N, 4.01.

3.2.6. General procedure for NMR-tube scale hydroamination tests

2,2-Diphenylpent-4-en-1-amine (0.5 mmol), the internal standard (1,3,5-trimethoxybenzene, 0.5 mmol) and the complex (**7** or **8**, 0.025 mmol) were dissolved in toluene-d_8. The NMR tube was closed and heated at 100 °C for 72 h. The mixture was monitored by ^{1}H NMR.

3.2.7. NMR-tube scale stoichiometric reactions of 2,2-diphenylpent-4-en-1-amine with **7** and **8**

The 2,2-diphenylpent-4-en-1-amine (5.9 mg, 0.025 mmol) and the complex (**7**: 20 mg, 0.025 mmol; **8**: 26 mg, 0.025 mmol) were dissolved in toluene-d_8. The tube was heated to 100 °C for 48 h. The products were analysed by ^{1}H NMR. After 48 h the signals of 2,2-diphenylpent-4-en-1-amine disappear and the signals of the 2-methyl-4,4-diphenylpyrrolidine appear. Signals of 2,2-diphenylpent-4-en-1-amine before reaction: ^{1}H NMR (300 MHz, toluene-d_8, ppm): δ 7.28–6.91 (m, CH_{Ph}), 5.55–5.27 (m, CH_2), 5.14–4.74 (dd, =CH_2), 3.17 (s, CH_2), 2.85 (d, CH_2), 0.45 (NH_2). Signals of 2-methyl-4,4-diphenylpyrrolidine after reaction: ^{1}H NMR (300 MHz, toluene-d_8, ppm): δ 3.41 (dd, CH_2), 3.19–3.11 (m, CH), 2.36 (dd, CH_2). The signal of the NH is not observed in the spectra and one of the diasteriomeric protons bonded to C3 that may be hindered by the solvent.

3.3. General procedures for X-ray crystallography

Crystals of **4** and **6** suitable for single-crystal X-ray analysis were obtained from THF solutions at −30 °C. The data were collected using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS [32]. The structures were solved and refined using direct methods with programs SIR2004 [33] or SHELXS-97 [34] using WINGX-Version 1.80.01 [35] SHELXL [36] system of programs. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. The molecular diagrams were drawn with ORTEP-3 for Windows [37] or Mercury 1.4.2 [38] included in the software package. For crystallographic experimental data and structure refinement parameters see Table 1.

3.4. Computational details

DFT [29] calculations for **9A**, **B** and **C** were performed using the GAUSSIAN 03 software package [30] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including a 25% mixture of Hartree–Fock [39] exchange with DFT [29] exchange correlation, given by the Perdew, Burke, and Ernzerhof functional (PBE) [40]. The optimized geometries were obtained with the LanL2DZ [41] basis set augmented with an f-polarization function [42] for Zr and a standard 6-31G(d,p) [43] for the remaining elements (basis b1). Single point energy calculations were performed using an improved basis set (basis b2) and the geometries optimized at the PBE1BPE/b1 level. Basis b2 consisted of the Stuttgart/Dresden ECP with valence triple-ζ (SDD) [44] and an added f-polarization function [42] for Zr and standard 6-311++G(d,p) [45] basis sets for the remaining elements. Three-dimensional structures were obtained with Chemcraft [46].

Table 1
Selected crystallographic experimental data and structure refinement parameters for **4** and **6**.

	4	**6**
Empirical formula	$C_{35}H_{57}N_2O_2Br$	$C_{28}H_{30}N_2O$
Formula weight	833.92	410.54
Temperature (K)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
V (Å^3)	10119.7(14)	5357.7(10)
a (Å)	54.983(4)	34.217(4)
b (Å)	11.5230(9)	8.7210(10)
c (Å)	16.1810(14)	20.987(2)
α (°)	90	90
β (°)	99.206(6)	121.185(5)
γ (°)	90	90
Z, ρ_{calc} (gcm^{-3})	8, 1.095	8, 1.018
μ (mm^{-1})	0.850	0.062
Crystal size	0.25 × 0.18 × 0.05	0.40 × 0.10 × 0.10
Crystal colour	Colourless	Colourless
Crystal shape	Plate	Needle
Refl. collected	22,150	14,879
Unique refl. [*R*(int)]	5231 [0.0570]	2105 [0.0787]
*R*1 [$I > 2\sigma(I)$]	0.0984	0.2088
*wR*2 [$I > 2\sigma(I)$]	0.2735	0.5279
GooF	1.080	1.718

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Appendix A. Supplementary material

CCDC 963630–963631 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.11.041.

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