Zirconium and Hafnium Complexes with (Allylsilyl)(η-amidosilyl)-η^5-cyclopentadienyl Ligands: Synthesis, Structure and Reactivity

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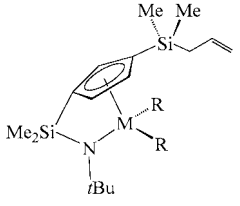
The disubstituted cyclopentadiene $C_5H_4(SiMe_2Cl)[SiMe_2(CH_2CH=CH_2)]$ was isolated by reaction of the lithium salt $[Li\{C_5H_4SiMe_2(CH_2CH=CH_2)\}]$ with $SiMe_2Cl_2$. It was then treated with NH_2tBu and $LiNH(2,6\text{-}Me_2C_6H_3)$ to give the (aminosilyl)cyclopentadienes $C_5H_4[SiMe_2(CH_2CH=CH_2)][SiMe_2(NHR)]$, which were further deprotonated to their dilithium salts $[Li_2\{1\text{-}SiMe_2NR\text{-}3\text{-}SiMe_2(CH_2CH=CH_2)C_5H_3\}]$ (R = *t*Bu, 2,6-$Me_2C_6H_3$). Reactions of the metal halides $ZrCl_4(THF)_2$ and $HfCl_4$ with these dilithium salts, followed by alkylation of the resulting dichloro complexes, afforded the (η^1-amidosilyl)-η^5-cyclopentadienyl complexes $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NR)[SiMe_2(CH_2CH=CH_2)]\}X_2]$ (R = *t*Bu, 2,6-$Me_2C_6H_3$; X = Cl, Me, CH_2Ph; M = Zr, Hf). Only the bis(iminoacyl) complexes $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}Nt\text{Bu})[SiMe_2(CH_2CH=CH_2)]\}\{\eta^2\text{-}CR=N(2,6\text{-}Me_2C_6H_3)\}_2]$ (M = Zr, Hf; R = Me, CH_2Ph) could be isolated when the dialkylzirconium and -hafnium complexes were treated with CN(2,6-$Me_2C_6H_3$); these were slowly transformed into the C–C-coupled diazametallacyclopentene compounds $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}Nt\text{Bu})[SiMe_2(CH_2CH=CH_2)]\}\{\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)\text{-}CR=CR\text{-}\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)\}]$ (R = Me, CH_2Ph, M = Zr; R = Me, M = Hf) when their toluene solutions were heated to 70 °C–80 °C for long periods (2–4 d). The structural characterisation of all of the new compounds is described and the molecular structure of the dimeric dichlorozirconocene $[ZrCl(\mu\text{-}Cl)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}Nt\text{Bu})[SiMe_2(CH_2CH=CH_2)]\}]_2$, was determined by X-ray diffraction methods.

Introduction

Many reports[1–9] have described the dynamics of the ion pairs formed by activation of a precursor metallocene with various Lewis acids, which are assumed to be the species responsible for the metallocene-catalysed alkene polymerisation[5,10–15] and considered to be the cornerstone of its efficiency and stereocontrol. Several strategies have been used to stabilize the intermediate cationic alkyl alkene metallocene[10,16–21] and (η^1-amidosilyl)-η^5-cyclopentadienyl[3,22–30] d^0 group-4 metal complexes. We have reported[31,32] the formation of alkyl alkene metallocene cations through η^2-coordination of the alkene moiety of an allylsilyl group tethered to the cyclopentadienyl ring. In order to study the formation and reactivity of the corresponding (η^1-amidosilyl)-η^5-cyclopentadienyl cationic compounds reported elsewhere, we synthesised and characterised disubstituted (allylsilyl)(amidosilyl)cyclopentadienyl group 4 metal complexes of the type represented in Scheme 1. These compounds are described in this paper, along with the insertion reactions of isocyanides into their metal–alkyl bonds and C–C coupling reactions of the resulting iminoacyl derivatives.



Scheme 1.

Results and Discussion

Successful synthesis of the disubstituted cyclopentadiene containing the two required aminosilyl $[SiMe_2(NHt\text{Bu})]$ and allylsilyl $[SiMe_2(CH_2CH=CH_2)]$ functionalities was achieved by first introducing the allylsilyl group[33] followed by metallation and reaction of the resulting lithium (allylsilyl)cyclopentadienide salt[31,32] with $SiMe_2Cl_2$ to give the disilylated cyclopentadiene $C_5H_4(SiMe_2Cl)[SiMe_2(CH_2CH=CH_2)]$ (**1**, Scheme 2), which was isolated as a yellow liquid.

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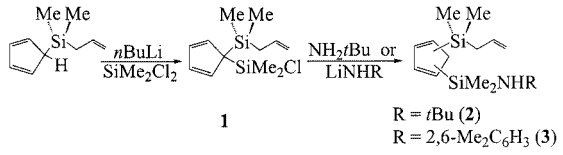


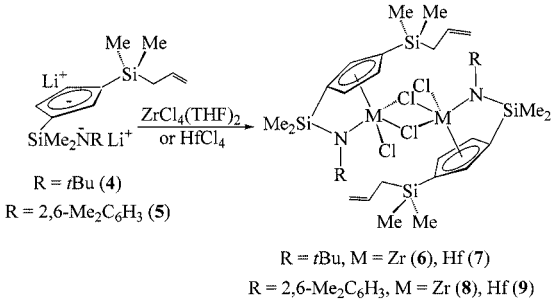
Scheme 2.

Further aminolysis of the chorosilyl derivative **1** by reaction with the primary amine NH_2tBu or metathesis with $LiNH(2,6\text{-}Me_2C_6H_3)$ afforded the disilylated cyclopentadienes $C_5H_4[SiMe_2(CH_2CH{=}CH_2)][SiMe_2(NHR)]$ (R = *t*Bu **2**, 2,6-$Me_2C_6H_3$ **3**), which were isolated as oily yellow and orange liquids, respectively. The chlorosilyl derivative **1** was identified by ^1H NMR spectroscopy as a unique 1,1-isomer. However, formation of the 1,3-isomer is favoured for the aminosilyl compounds **2** and **3** due to the presence of the sterically more demanding amino substituents (see Exp. Sect.).

The mixture of isomers of the disilylcyclopentadienes **2** and **3** was metallated by treatment with 2 equiv. of *n*BuLi to give the dilithium salts, which were isolated as white solids containing one single component and were identified by ^1H NMR spectroscopy as the 1,3-isomer $[Li_2\{1\text{-}SiMe_2NR\text{-}3\text{-}SiMe_2(CH_2CH{=}CH_2)C_5H_3\}]$ (R = *t*Bu **4**, 2,6-$Me_2C_6H_3$ **5**). Their ^1H NMR spectra show the three ring-proton signals expected for an asymmetric molecule, whereas the diastereotopic methyl groups of both silyl fragments and the diastereotopic methylene protons of the allylsilyl fragment are observed as two singlets (see Exp. Sect.).

A direct synthesis based on halide metathesis, when the metal tetrahalides were treated with 1 equiv. of the dilithium salts **4** and **5**, was used to transfer the (amidosilyl)cyclopentadienyl ligand, as shown in Scheme 3. Reaction of **4** with $ZrCl_4(THF)_2$ or $HfCl_4$ in toluene at room temperature yielded the "constrained-geometry" complexes $[MCl(\mu\text{-}Cl)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}]_2$ (M = Zr **6**, Hf **7**), which were isolated in high yield as a yellow crystalline solid (**6**) and an oily orange solid (**7**) and characterised by elemental analysis (**6**), NMR spectroscopy and X-ray diffraction methods (**6**). Analogous reactions using the dilithium salt of the corresponding (2,6-dimethylphenyl) amido ligand **5** were carried out in the hope of obtaining improved crystallinity of the resulting metal compounds.[34] However, the new dichloro complexes $[MCl(\mu\text{-}Cl)\{\eta^5\text{-}C_5H_3[SiMe_2\text{-}\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)][SiMe_2(CH_2CH{=}CH_2)]\}]_2$ (M = Zr **8**, Hf **9**) were always obtained as oily orange and white solid products, respectively, which easily decomposed with elimination of free amine; consequently, they were difficult to purify, giving rather low yields (lower than 30%) after purification. These compounds were not studied further.

The ^1H and ^{13}C NMR spectra of the silylamido derivatives **6**–**9** show three multiplets (^1H) and five resonances (^{13}C) for the Cp ring protons and carbon atoms and four singlets (^1H and ^{13}C) for the two diastereotopic silylmethyl groups; two of the multiplets were occasionally observed as overlapped signals in the ^1H NMR spectrum. The ^1H NMR



Scheme 3.

spectra of all the complexes show the typical pattern of the allyl substituent, which consists of one high-field multiplet for the $SiCH_2$ protons at δ = 1.7–1.8 ppm, one multiplet at δ = 5.6–5.8 ppm for the internal olefinic proton and one multiplet for the two external olefinic protons at δ = 4.8–4.9 ppm. The ring C_{ipso} resonance for compounds **6**–**9** appears at higher field than those of the other carbon atoms, consistent with the (amidosilyl)cyclopentadienyl ligands adopting a chelate coordination mode with the metal centre.[35] This NMR behaviour may suggest the presence of mononuclear structures of the silylamido derivatives **6**–**9** in solution, for which the enantiotopic 1,3-disilylcyclopentadienyl ring faces are responsible for the asymmetry of these molecules. However, it could also be consistent with a centrosymmetric dimeric diastereoisomer with two equivalent Cp-silylamido systems, which is formed by two mononuclear units held together by a pair of bridging chloro ligands. Both mono- and dinuclear structures exhibit two non-equivalent chloro ligands, one of which is localised under the allyldimethylsilyl substituent of the cyclopentadienyl ligand in the mononuclear structure or is the terminal ligand in the dinuclear compound.

The dimeric structure of complex **6** in the solid state was determined by X-ray diffraction methods on a single crystal obtained from a hexane solution cooled to –35 °C. The same dimeric structure may be tentatively assigned to all of the other complexes **7**–**9** in the solid state, as shown in Scheme 3. Typical signals due to coordinated THF were observed in the ^1H and ^{13}C NMR spectra of the more electron-deficient complex **8** containing the less basic amido ligand.

A view of the molecular structure of complex **6**, together with the atomic labelling scheme, is shown in Figure 1. Selected bond lengths and angles are given in Table 1. The crystal structure consists of discrete chloro-bridged centrosymmetric dimeric molecules of $[ZrCl(\mu\text{-}Cl)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2CH_2CH{=}CH_2]\}]_2$. Each zirconium atom is bound to the cyclopentadienyl ring in a slightly asymmetric fashion [Zr–C bond lengths are in the range 2.441(6)–2.557(7) Å, while the Zr–CT distance is 2.187(8) Å, where CT is the centroid of the ring], to the nitrogen atom of the silylamido moiety [Zr–N = 2.042(6) Å], to a terminal chlorine atom [Zr–Cl2 = 2.457(2) Å] and to two bridging chlorine atoms [Zr–Cl1 = 2.645(2) and Zr–Cl1′ = 2.653(2) Å]. The Zr atom is in a

four-legged piano-stool arrangement if the centroid of the cyclopentadienyl ring is taken into consideration. The value of the Zr–N bond length is consistent with double-bond character and falls in the range (2.034–2.088 Å) retrieved from the Cambridge Structural Database files for pentacoordinate Zr complexes containing the ZrClCpSiN(amido) moiety.[36–45] The almost equal bridging Zr–Cl distances are significantly longer than the terminal Zr–Cl distance, and this last bond length again falls in the range 2.432–2.529 Å retrieved from the CSD files for similar complexes. To the best of our knowledge, the only chloro-bridged dimeric zirconium complex found in the literature containing a (amidosilyl)cyclopentadienyl moiety is (*R*,*R*)-[ZrCl(μ-Cl)]{η^5:η^1-$C_5Me_4SiMe_2NCH(Me)(Ph)$}$_2$,[39] where the Zr–Cl bridging bond lengths are significantly different. The *trans* influence of the amido nitrogen and chlorine coordinating atoms seem similar in **6**, and the bridging Zr–Cl bond lengths are not significantly different.

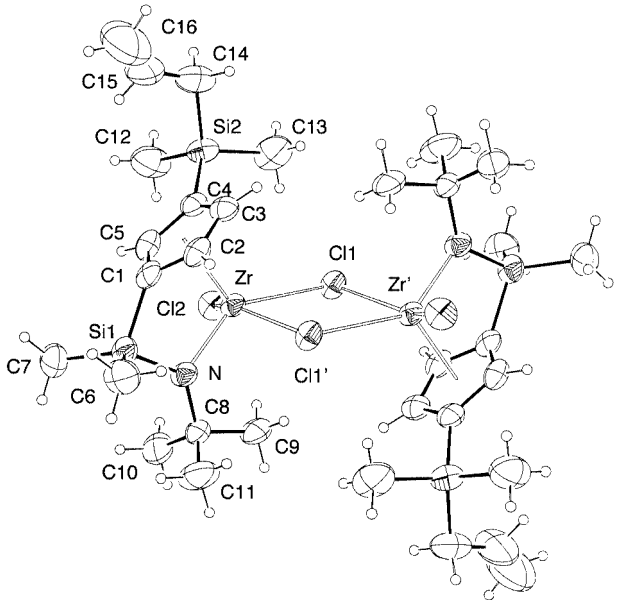
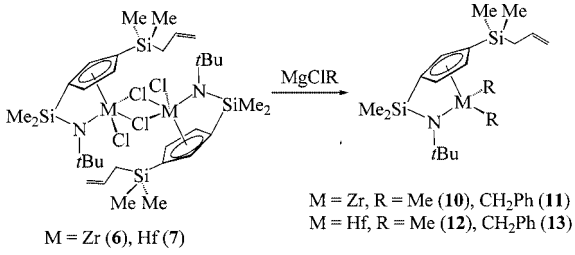


Figure 1. ORTEP drawing of the molecular structure of **6** in the solid state; thermal ellipsoids are drawn at the 30% probability level.

The C1 atom that bears the amidosilyl arm is pyramidally distorted, as shown by the sum of bond angles (350.8°) as in the other chloro(amidosilyl)cyclopentadienyl complexes,[36–45] and in the doubly silylamido-bridged cyclopentadienyltitanium complex,[46] while the C4 atom that bears the allylsilyl arm is weakly pyramidally distorted (the sum of the bond angles is 359.3°). The Si1 and Si2 atoms are out of the Cp plane by –0.845(2) and 0.250(3) Å, respectively.

In spite of having non-equivalent chloro ligands, none of these zirconium and hafnium complexes showed selective reactions when they were treated with alkylating agents. As shown in Scheme 4, reactions of complexes **6** and **7** with 2 equiv. of MgClR (R = Me, CH_2Ph) in hexane at room temperature gave the dialkyl complexes [M{η^5-$C_5H_3(SiMe_2$-η^1-N*t*Bu)[$SiMe_2(CH_2CH{=}CH_2)$]}R_2] (M = Zr, R = Me **10**, CH_2Ph **11**; M = Hf, R = Me **12**, CH_2Ph **13**), which were isolated as brown and orange oily solids, respectively, and identified by elemental analysis and NMR spectroscopy. In addition to the same features discussed above for the precursor dichloro complexes, the non-equivalency of the two alkyl groups of these asymmetric molecules is easily demonstrated by their ^{1}H and ^{13}C NMR spectra. The spectra of the methyl complexes **10** and **12** show two singlets (^{1}H) and two resonances (^{13}C) for the two non-equivalent, metal-bonded methyl groups, whereas four doublets (^{1}H) for the two diastereotopic methylene protons and two resonances (^{13}C) for the methylene carbon atom are observed for each non-equivalent, metal-bonded benzyl group of the benzyl derivatives **11** and **13**.



Scheme 4.

Insertion of isocyanide into one of the two non-equivalent metal–alkyl bonds of these dialkyl compounds may afford mixtures of two diastereomers, unless for diastereoselective reactions.[47] However, when 1 equiv. of CN(2,6-$Me_2C_6H_3$) was added to the toluene solutions of the dialkyl(amidosilyl)cyclopentadienyl compounds **10**–**13**, the initially formed 16-electron iminoacyl compounds could not be detected by NMR spectroscopy because they react very easily to give the bis(iminoacyl) complexes by further insertion into the second metal–alkyl bond. This behaviour is in contrast to that observed for metallocene-type complexes for which the monoiminoacyl complexes are 18-electron species, which do not undergo further insertion into the second metal–alkyl bond.

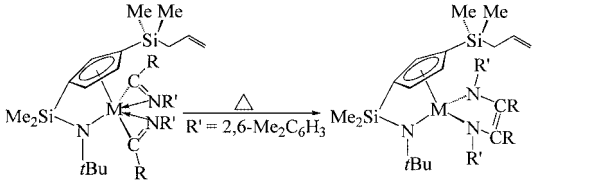
Table 1. Selected bond lengths [Å] and angles [°] for compound **6**.

Zr–Cl(1)	2.645(2)	C(4)–C(5)	1.447(10)
Zr–Cl(1)′	2.653(2)	C(1)–C(5)	1.393(10)
Zr–Cl(2)	2.457(2)	C(1)–Si(1)	1.872(9)
Zr–N	2.042(6)	Si(1)–N	1.743(5)
Zr–CT	2.187(8)	N–C(8)	1.492(9)
C(1)–C(2)	1.418(10)	C(4)–Si(2)	1.890(9)
C(2)–C(3)	1.416(10)	Si(2)–C(14)	1.894(10)
C(3)–C(4)	1.411(10)		
Cl(1)–Zr–Cl(1)′	72.26(7)	N–Zr–Cl(2)	96.6(2)
Cl(2)–Zr–Cl(1)	80.76(7)	N–Zr–Cl(1)	138.2(2)
Cl(2)–Zr–Cl(1)′	145.37(7)	N–Zr–Cl(1)′	89.6(2)
Cl(1)–Zr–CT[a]	120.4(2)	N–Zr–CT	100.3(3)
Cl(2)–Zr–CT[a]	107.9(2)	CT–Zr–Cl(1)′	104.4(2)
Si(1)–N–Zr	108.1(3)	C(8)–N–Zr	123.0(4)
C(8)–N–Si(1)	128.9(5)		

[a] CT is the centroid of the C(1)···C(5) cyclopentadienyl ring. Symmetry transformation used to generate equivalent atoms: –*x*, –*y*, –*z* + 2.

Therefore these insertion reactions were complete when toluene solutions of the dialkyl complexes **10**–**13** were treated with two equivalents of 2,6-xylyl isocyanide at room temperature to give the corresponding bis(iminoacyl) compounds[48] [M{η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$(CH_2CH=CH_2)]}{η^2-CR=N(2,6-$Me_2C_6H_3$)}$_2$] (M = Zr, R = Me **14**, CH_2Ph **15**; M = Hf, R = Me **16**, CH_2Ph **17**) which were isolated as red and orange oily products and identified by elemental analysis and NMR and infrared spectroscopy.

As shown in Scheme 5 the bis(iminoacyl) complexes **14**–**16** were slowly converted into the C–C-coupled compounds.[49] This transformation was complete when their toluene solutions were heated at 70 °C–80 °C for long periods (2 d for **18** and **19** and 4 d for **20**) in sealed tubes to give the diazametallacyclopentene complexes [M{η^5-C_5H_3($SiMe_2$-η-N*t*Bu)[$SiMe_2$(CH_2CH=CH_2)]}-{η-N(2,6-$Me_2C_6H_3$)CR=CR-η-N(2,6-$Me_2C_6H_3$)] (R = Me, M = Zr **18**, Hf **19**; R = CH_2Ph, M = Zr **20**). Complexes **18**–**20** were isolated as red (**18**) and brown (**19**, **20**) oily products and identified by NMR and IR spectroscopy. The ^{1}H and ^{13}C NMR spectra of all of these iminoacyl (**14**–**17**) and enediamido (**18**–**20**) compounds correspond to the asymmetric molecules expected from the enantiotopic character of the disilylcyclopentadienyl ligand (see Exp. Sect.). The presence of four methyl resonances (occasionally overlapped) for the [(2,6-dimethylphenyl)imino]acyl groups indicates that rotation around the N–aryl bond is avoided.



M = Zr, R = Me (**14**), CH_2Ph (**15**)
M = Hf, R = Me (**16**), CH_2Ph (**17**)

M = Zr, R = Me (**18**), CH_2Ph (**19**)
M = Hf, R = Me (**20**)

Scheme 5.

Compounds **14**–**17** contain the iminoacyl ligand η^2-coordinated to the metal centre as shown by their spectroscopic data. The signals observed in the ^{1}H NMR spectra for the alkyl and methylene(benzyl) groups migrated to the inserted aryl isocyanide are shifted downfield (by about 2 ppm) with respect to the values observed for the metal-bonded groups of the precursor dialkyl complexes. In contrast, the ^{13}C NMR resonance of the alkyl carbon atom is shifted to higher field (by about 10 ppm for Zr and 20 ppm Hf) on insertion. The most remarkable feature observed in the NMR spectra of these complexes is the chemical shift of the resonance due to the iminoacyl carbon atoms, which is shifted downfield at δ = 250–268 ppm. Another important spectroscopic feature that allows the assignment of the iminoacyl coordination mode in solution is the stretching ν(C=N) frequency of the iminoacyl bond observed in the IR spectra at 1540–1555 cm^{-1}, which corresponds to the η^2-coordinated iminoacyl ligands.[50] The ^{1}H NMR resonances due to the migrated alkyl groups in the C–C coupled enediamido complexes **18**–**20** are shifted downfield with respect to those observed for the starting bis(iminoacyl) compounds, whereas the ^{13}C NMR signals due to the enediamido sp^2-carbon atoms are observed at δ = 111–112 ppm.

Conclusions

Dichloro- and dialkyl(amidosilyl)cyclopentadienyl zirconium and -hafnium complexes of the type [M{η^5-C_5H_3[$SiMe_2$(CH_2CH=CH_2)]($SiMe_2$-η-NR)}X_2] with the allyldimethylsilyl-substituted cyclopentadienyl ligand have been isolated in high yields by conventional synthetic methods and characterised by NMR spectroscopy and X-ray diffraction methods.

The two non-equivalent chloro and alkyl ligands of these asymmetric molecules do not show diastereoselective reactions, so that alkylation of the dichloro complexes only gives dialkyl derivatives, and insertion of CN(2,6-$Me_2C_6H_3$) into the metal–alkyl bonds only afforded bis(iminoacyl) compounds. Formation of monoalkyl and monoiminoacyl complexes could not be detected in any of these reactions. NMR spectroscopic studies revealed that the iminoacyl ligand is η^2-coordinated in all of these compounds with the nitrogen atom always occupying the internal coordination site. C–C coupling reactions between the two iminoacyl ligands are very slow processes that give quantitative yields of the diazametallacyclopentene complexes after heating the toluene solutions of the bis(iminoacyl) complexes at 70–80 °C for 2–4 d.

Experimental Section

General Considerations: All manipulations were performed under argon using standard Schlenk and high-vacuum line techniques or a glovebox model MO40-2. Solvents were pre-dried and purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium/potassium alloy for hexane and sodium/benzophenone for diethyl ether and THF) before use. Deuterated solvents were stored over activated molecular sieves (4 Å) in Teflon-valved flasks and previously degassed by several freeze-pump-thaw cycles. NH_2tBu (Aldrich) was dried with sodium and distilled prior to use. $SiMe_2$(CH_2CH=CH_2)Cl (Aldrich), $SiMe_2Cl_2$ (Aldrich), *n*BuLi (Aldrich), $HfCl_4$ (Merck), MgClMe (Aldrich) and MgCl(CH_2Ph) (Aldrich) were purchased from commercial sources and used without further purification. C_5H_5[$SiMe_2$(CH_2CH=CH_2)],[51] [Li{$C_5H_4SiMe_2$(CH_2CH=CH_2)}],[51] and $ZrCl_4(THF)_2$[52] were prepared according to literature procedures. C, H and N microanalyses were performed with a Perkin–Elmer 240B. Unreliable elemental analytical data are not given for some highly soluble and air-sensitive compounds which could not be crystallised and were isolated as spectroscopically pure oily products. NMR spectra, measured at 25 °C, were recorded with a Varian Unity 300 (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ units relative to TMS standard.

Synthesis of C_5H_4($SiMe_2$Cl)[$SiMe_2$(CH_2CH=CH_2)] (1): $SiMe_2Cl_2$ (5.7 mL, 47 mmol) was added to a THF (100 mL) solution of [Li{η^5-$C_5H_4SiMe_2$(CH_2CH=CH_2)}] (8.0 g, 47 mmol), cooled to –78 °C and the mixture was stirred at room temperature for 16 h. The solvent was then removed under vacuum and the residue was

extracted into hexane (2 × 50 mL). After filtration and evaporation of the solvent under reduced pressure, compound **1** was isolated as a yellow liquid (9.81 g, 38.18 mmol, 82% yield). $C_{12}H_{21}ClSi_2$ (256.92): calcd. C 56.10, H 8.24; found C 55.88, H 8.36. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.05 (s, 6 H, SiMe_2), 0.23 (s, 6 H, SiMe_2), 1.47 (d, J = 8.1 Hz, 2 H, SiCH_2), 4.86 (m, 2 H, CH=CH_2), 5.65 (m, 1 H, CH=CH_2), 6.57 (m, 2 H, C_5H_4), 6.81 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = –2.9 (SiMe_2), 1.5 (SiMe_2), 22.8 (SiCH_2), 58.3 (C_5H_4, C_{ipso}), 113.9 (CH=CH_2), 133.1 (C_5H_4), 134.6 (C_5H_4), 134.9 (CH=CH_2) ppm. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.04 (s, 6 H, SiMe_2), 0.10 (s, 6 H, SiMe_2), 1.47 (d, J = 8.1 Hz, 2 H, SiCH_2), 4.86 (m, 2 H, CH=CH_2), 5.63 (m, 1 H, CH=CH_2), 6.40 (m, 2 H, C_5H_4), 6.64 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.9 (SiMe_2), 1.7 (SiMe_2), 22.6 (SiCH_2), 58.0 (C_5H_4, C_{ipso}), 113.6 (CH=CH_2), 132.8 (C_5H_4), 134.3 (C_5H_4), 134.7 (CH=CH_2) ppm.

Synthesis of C_5H_4[SiMe$_2$(CH$_2$CH=CH$_2$)][SiMe$_2$(NH*t*Bu)] (2): NH_2tBu (11.5 mL, 109 mmol) was added to a solution of **1** (14 g, 54.5 mmol) in THF at –78 °C. The mixture was slowly warmed to room temperature and stirred for 15 h. After removal of the solvent under vacuum, the residue was extracted into hexane and the ammonium chloride salt was removed by filtration. Product **2** was obtained as a yellow liquid (12.48 g, 42,51 mmol, 78% yield). $C_{16}H_{31}NSi_2$ (293.60): calcd. C 65.46 H, 10.64, N 4.77; found C 64.44, H 10.68, N 4.48. Major isomer: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = –0.14 (s, 3 H, SiMe_2), –0.01 (s, 3 H, SiMe_2), 0.26 (s, 3 H, SiMe_2), 0.36 (s, 3 H, SiMe_2), 0.60 (br. s, 1 H, NH), 1.08 (s, 9 H, CMe_3), 1.45 (m, 2 H, SiCH_2), 3.23 (br. s, 1 H, C_5H_4), 4.93 (m, 2 H, CH=CH_2), 5.69 (m, 1 H, CH=CH_2), 6.60, 6.81, 6.89 (m, 3 H, C_5H_4) ppm. Minor isomer: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.05 (s, 6 H, SiMe_2), 0.07 (s, 6 H, SiMe_2), 0.66 (br. s, 1 H, NH), 1.15 (s, 9 H, CMe_3), 1.74 (m, J = 8.1 Hz, 2 H, SiCH_2), 4.93 (m, 2 H, CH=CH_2), 5.88 (m, 1 H, CH=CH_2), 6.46, 6.72 (m, 3 H, C_5H_4) ppm.

Synthesis of C_5H_4[SiMe$_2$(CH$_2$CH=CH$_2$)][SiMe$_2$NH(2,6-Me$_2$C$_6$H$_3$)] (3): Compound **1** (13 g, 53 mmol) was added at room temperature to a suspension of LiNH(2,6-$Me_2C_6H_3$) (6.7 g, 53 mmol) in hexane (100 ml) and the mixture was stirred for 16 h. LiCl was filtered off and the solvent was removed from the resulting solution to give an orange oil which was identified as **3** (14.5 g, 42.4 mmol, 80% yield). Major isomer: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = –0.20 (s, 3 H, SiMe_2), 0.01 (s, 3 H, SiMe_2), 0.14 (s, 3 H, SiMe_2), 0.34 (s, 3 H, SiMe_2), 1.39 (m, 2 H, SiCH_2), 2.15 (s, 6 H, C_6H_3 Me_2), 2.54 (br. s, 1 H, NH), 3.07 (br. s, 1 H, C_5H_4), 4.92 (m, 2 H, CH=CH_2), 5.68 (m, 1 H, CH=CH_2), 6.40–7.00 (m, C_5H_4 + C_6H_3) ppm. Minor isomer: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.05 (s, 3 H, SiMe_2), 0.10 (s, 3 H, SiMe_2), 0.23 (s, 3 H, SiMe_2), 0.28 (s, 3 H, SiMe_2), 1.70 (m, 2 H, SiCH_2), 2.22 (s, 6 H, C_6H_3 Me_2), 2.54 (br. s, 1 H, NH), 2.92 (br. s, 1 H, C_5H_4), 4.92 (m, 2 H, CH=CH_2), 5.68 (m, 1 H, CH=CH_2), 6.40–700 (m, C_5H_4 + C_6H_3) ppm.

Synthesis of [Li$_2${1-SiMe$_2$N*t*Bu-3-SiMe$_2$(CH$_2$CH=CH$_2$)C$_5$H$_3$}] (4): A 1.6 M solution of *n*BuLi in hexane (17 ml, 28 mmol) was added dropwise to a solution of **3** (4 g, 14 mmol) in diethyl ether at –78 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The solvent was removed under reduced pressure to yield a solid, which was washed with hexane. The yellow solid was dried under vacuum and was characterised as **3** (3.85 g, 12.6 mmol, 90% yield). $C_{16}H_{29}Li_2NSi_2$ (305.47): calcd. C 62.91, H 9.57, N 4.59; found C 62.19, H 9.78, N 4.04. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.30 (s, 6 H, SiMe_2), 0.46 (s, 6 H, SiMe_2), 1.18 (s, 9 H, CMe_3), 1.83 (m, 2 H, SiCH_2), 4.89 (m, 2 H, CH=CH_2), 6.04 (m, 1 H, CH=CH_2), 6.65 (m, 1 H, C_5H_3), 6.80 (m, 1 H, C_5H_3), 6.90 (m, 1 H, C_5H_3) ppm.

Synthesis of [Li$_2${1-SiMe$_2$N(2,6-Me$_2$C$_6$H$_3$)-3-SiMe$_2$(CH$_2$CH=CH$_2$)-C$_5$H$_3$}] (5): A suspension of **3** (14 g, 41 mmol) in diethyl ether was treated at –78 °C with a 1.6 M hexane solution of *n*BuLi (51 mL, 82 mmol). The mixture was stirred at room temperature for 4 h and the solvent was then removed under vacuum to give a yellow solid which, after being washed with hexane (2 × 50 mL) and dried under vacuum, was identified as the dilithium salt **5** (13 g, 36.9 mmol, 90% yield). $C_{20}H_{29}Li_2NSi_2$ (353.51): calcd. C 67.95, H 8.27, N 3.96; found C 67.18, H 8.02, N 3.95. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.32 (s, 6 H, SiMe_2), 0.57 (s, 6 H, SiMe_2), 1.85 (m, 2 H, SiCH_2), 2.75 (s, 6 H, C_6H_3 Me_2), 4.90 (m, 2 H, CH=CH_2), 6.05 (m, 1 H, CH=CH_2), 6.75–7.45 (m, C_5H_3 + C_6H_3) ppm.

Synthesis of [Zr{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}Cl$_2$] (6): Toluene at –78 °C was added to a mixture of **4** (3 g, 9.8 mmol) and $ZrCl_4(THF)_2$ (3.7 g, 9.8 mmol) also cooled to –78 °C. The reaction mixture was warmed to room temperature and was stirred for 16 h. The toluene was removed under vacuum and the residue was extracted into hexane. The solvent volume was reduced and the solution was cooled to –40 °C to give yellow crystals which were isolated by filtration (2.67 g, 5.89 mmol, 60% yield). $C_{16}H_{29}Cl_2NSi_2Zr$ (453.71): calcd. C 42.36, H 6.44, N 3.09; found C 42.90, H 6.42, N 3.05. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.33 (s, 6 H, SiMe_2), 0.55 (s, 6 H, SiMe_2), 1.37 (s, 9 H, CMe_3), 1.77 (m, 2 H, SiCH_2), 4.86 (m, 2 H, CH=CH_2), 5.74 (m, 1 H, CH=CH_2), 6.44 (t, 1 H, C_5H_3), 6.58 (t, 1 H, C_5H_3), 7.02 (t, 1 H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = –3.6 (SiMe_2), –3.3 (SiMe_2), 0.5 (SiMe_2), 0.9 (SiMe_2), 23.7 (SiCH_2), 32.5 (CMe_3), 57.1 (CMe$_3$), 111.9 (C_5H_3, C_{ipso}), 113.7 (CH=CH_2), 126.1 (C_5H_3), 127.1 (C_5H_3), 132.9 (C_5H_3, C_{ipso}), 133.5 (CH=CH_2) ppm.

Synthesis of [Hf{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}Cl$_2$] (7): Toluene cooled to –78 °C was added to a mixture of **4** (1.5 g, 4.9 mmol) and $HfCl_4$ (1.6 g, 4.9 mmol) also at –78 °C. The reaction mixture was stirred while it was warmed to room temperature. After the solution had been stirred overnight, the toluene was removed under reduced pressure and the residue was extracted into hexane. The solution was filtered and the solvent was removed to give **7** as an orange oil (1.59 g, 2.95 mmol, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.32 (s, 3 H, SiMe_2), 0.33 (s, 3 H, SiMe_2), 0.56 (s, 6 H, SiMe_2), 1.31 (s, 9 H, CMe_3), 1.77 (m, 2 H, SiCH$_2$), 4.89 (m, 2 H, CH=CH_2), 5.77 (m, 1 H, CH=CH_2), 6.35 (t, 1 H, C_5H_3), 6.49 (t, 1 H, C_5H_3), 6.97 (t, 1 H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = –3.6 (SiMe_2), –3.3 (SiMe_2), 0.8 (SiMe_2), 1.2 (SiMe_2), 23.7 (SiCH_2), 33.2 (CMe_3), 55.6 (CMe$_3$), 111.8 (C_5H_3, C_{ipso}), 113.7 (CH=CH_2), 124.5 (C_5H_3), 125.6 (C_5H_3), 126.0 (C_5H_3), 131.6 (C_5H_3, C_{ipso}), 133.5 (CH=CH_2) ppm.

Synthesis of [Zr{η^5-C$_5$H$_3$[SiMe$_2$-η^1-N(2,6-Me$_2$C$_6$H$_3$)][SiMe$_2$(CH$_2$-CH=CH$_2$)]}Cl$_2$] (8): Toluene (100 mL) was added at –78 °C to a mixture of solid dilithium salt **5** (2 g, 5.66 mmol) and $ZrCl_4$·2THF (2.13 g; 5.66 mmol) and the mixture was then stirred at room temperature for 16 h. After filtration of the resulting LiCl, the solvent was removed under vacuum and the residue was extracted into hexane (2 × 50 mL). The solution was concentrated by evaporation of the solvent under reduced pressure and cooled to –35 °C to give compound **8** as an orange oily solid (0.91 g, 1.70 mmol, 30% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.04 (s, 3 H, SiMe_2), 0.12 (s, 3 H, SiMe_2), 0.38 (s, 3 H, SiMe_2), 0.39 (s, 3 H, SiMe_2), 1.52 (m, 2 H, SiCH_2), 1.80 (t, 4 H, C_2H_4), 2.10 (s, 3 H, C_6H_3 Me_2), 2.24 (s, 3 H, C_6H_3 Me_2), 3.70 (t, 4 H, OC_2H_4), 4.78 (m, 2 H, CH=CH_2), 5.61 (m, 1 H, CH=CH_2), 6.50 (t, 1 H, C_5H_3), 6.77 (t, 1 H, C_5H_3), 6.83 (t, 1 H, C_5H_3), 6.70–7.00 (m, 3 H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = –2.7 (SiMe_2), –2.6 (SiMe_2), –0.4 (SiMe_2), 0.2 (SiMe_2), 20.3 (C_6H_3 Me_2), 20.6 (C_6H_3 Me_2), 24.8

($SiCH_2$), 25.3 (C_2H_4), 68.5 (OC_2H_4), 113.2 (CH=CH_2), 116.7 (C_5H_3, C_{ipso}), 122.4 (C_5H_3), 124.2 (C_5H_3), 127.8 (C_5H_3), 127.8, 129.8, 130.0, 130.7, 132.4 (C_6H_3), 134.2 (C_5H_3, C_{ipso}), 134.9 (CH=CH_2), 151.2 (C_6H_3, C_{ipso}) ppm.

Synthesis of [Hf{η^5-C_5H_3[$SiMe_2$-η^1-N(2,6-$Me_2C_6H_3$)][$SiMe_2$(CH_2-CH=CH_2)]}Cl_2] (9): Toluene (100 mL) was added at room temperature to a mixture of **5** (2 g, 5.66 mmol) and $HfCl_4$ (1.81 g, 5.66 mmol). The mixture was stirred for 16 h and the solvent was then removed under reduced pressure to give a residue which was extracted into hexane (2 × 50 mL) to separate the LiCl formed. The resulting solution was concentrated and cooled to –35 °C overnight to give a colourless solid identified as **9** (1.0 g, 1.7 mmol, 30% yield). $C_{20}H_{29}Cl_2HfNSi_2$ (589.02): calcd. C 40.78, H 4.96, N 2.38; found C 40.77, H 5.09, N 2.23. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.36 (s, 3 H, SiMe_2), 0.39 (s, 3 H, SiMe_2), 0.51 (s, 3 H, SiMe_2), 0.55 (s, 3 H, SiMe_2), 1.80 (m, 2 H, SiCH_2), 2.11 (s, 3 H, C_6H_3 Me_2), 2.14 (s, 3 H, C_6H_3 Me_2), 4.88 (m, 2 H, CH=CH_2), 5.77 (m, 1 H, CH=CH_2), 6.64 (t, 1 H, C_5H_3), 6.80 (t, 1 H, C_5H_3), 7.07 (t, 1 H, C_5H_3), 6.82–7.02 (m, 3 H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = –3.0 (SiMe_2), –2.7 (SiMe_2), 0.1 (SiMe_2), 0.3 (SiMe_2), 19.6 (C_6H_3 Me_2), 19.7 (C_6H_3 Me_2), 24.2 (SiCH_2), 114.3 (CH=CH_2), 117.9 (C_5H_3, C_{ipso}), 123.9 (C_5H_3), 125.6 (C_5H_3), 125.8 (C_5H_3), 126.6–128.6 (C_6H_3), 133.7 (CH=CH_2), 142.5 (C_6H_3, C_{ipso}) ppm.

Synthesis of [Zr{η^5-C_5H_3[$SiMe_2$-η^1-N*t*Bu][$SiMe_2$(CH_2CH=CH_2)]}-Me_2] (10): A solution of MgClMe in THF (3.3 mL, 10 mmol) was added to a solution of **6** (2.3 g, 5.1 mmol) in hexane cooled to –78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for 16 h. The solution was filtered and the solvent was removed under reduced pressure to give **10** as a brown oil (1.3 g, 3.1 mmol, 60% yield). $C_{18}H_{35}NSi_2Zr$ (412.87): calcd. C 52.37, H 8.54, N 3.39; found C 52.74, H 9.13, N 3.04. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.15 (s, 3 H, ZrMe_2), 0.17 (s, 3 H, ZrMe_2), 0.26 (s, 3 H, SiMe_2), 0.27 (s, 3 H, SiMe_2), 0.35 (s, 6 H, SiMe_2), 1.36 (s, 9 H, CMe_3), 1.70 (m, 2 H, SiCH_2), 4.92 (m, 2 H, CH=CH_2), 5.80 (m, 1 H, CH=CH_2), 6.27 (t, 1 H, C_5H_3), 6.36 (t, 1 H, C_5H_3), 6.72 (t, 1 H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.9 (SiMe_2), –2.7 (SiMe_2), 1.5 (SiMe_2), 2.0 (SiMe_2), 24.9 (SiCH_2), 34.2 (CMe_3), 35.1 (ZrMe_2), 35.7 (ZrMe_2), 55.5 (CMe$_3$, C_{ipso}), 107.1 (C_5H_3, C_{ipso}), 113.9 (CH=CH_2), 122.8 (C_5H_3), 124.8 (C_5H_3), 125.2 (C_5H_3), 126.8 (C_5H_3, C_{ipso}), 134.6 (CH=CH_2) ppm.

Synthesis of [Zr{η^5-C_5H_3[$SiMe_2$-η^1-N*t*Bu][$SiMe_2$(CH_2CH=CH_2)]}-(CH_2Ph)$_2$] (11): A 2 M THF solution of MgClBz (5 mL, 10 mmol) was added at –78 °C to a hexane solution of the dichloro complex **6** (2.3 g, 5.1 mmol). The mixture was stirred for 16 h while it was warmed to room temp. After filtration to separate $MgCl_2$, the solvent was removed under vacuum to give **11** as a brown oil (1.73 g, 3.06 mmol, 60% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.22 (s, 3 H, SiMe_2), 0.24 (s, 3 H, SiMe_2), 0.34 (s, 3 H, SiMe_2), 0.36 (s, 3 H, SiMe_2), 1.11 (s, 9 H, CMe_3), 1.60 (m, 2 H, SiCH_2), 1.50 (d, J = 11.0 Hz, 1 H, CH_2Ph), 1.71 (d, J = 10.3 Hz, 1 H, CH_2Ph), 2.10 (d, J = 11.2 Hz, 1 H, CH_2Ph), 2.15 (d, J = 10.1 Hz, 1 H, CH_2Ph), 4.92 (m, 2 H, CH=CH_2), 5.72 (m, 1 H, CH=CH_2), 6.18 (t, 1 H, C_5H_3), 6.25 (t, 1 H, C_5H_3), 6.52 (t, 1 H, C_5H_3), 6.86–7.18 (m, 10 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.7 (SiMe_2), –2.4 (SiMe_2), 1.5 (SiMe_2), 2.1 (SiMe_2), 25.3 (SiCH_2), 33.7 (CMe_3), 54.4 (ZrCH_2), 54.7 (CMe$_3$, C_{ipso}), 57.6 (ZrCH_2), 109.7 (C_5H_3, C_{ipso}), 114.0 (CH=CH_2), 122.4, 124.1, 125.4 (C_5H_3), 126.8, 127.7, 128. 3, 129.6, 129.7 (C_6H_5), 134.4 (CH=CH_2), 145.5, 145.9 (C_6H_5, C_{ipso}) ppm.

Synthesis of [Hf{η^5-C_5H_3[$SiMe_2$-η^1-N*t*Bu][$SiMe_2$(CH_2CH=CH_2)]}-Me_2] (12): A 3 M THF solution of MgClMe (2.9 mL, 8.8 mmol) was added at –78 °C to a solution of the dichloro complex **7** (2.4 g, 4.4 mmol) in hexane. The reaction mixture was stirred for 16 h while it was warmed slowly to room temp. The solution was filtered and the solvent removed under reduced pressure to give complex **12** as an orange oil (1.32 g, 2.64 mmol, 60% yield). $C_{18}H_{35}HfNSi_2$ (500.14): calcd. C 43.23, H 7.05, N 2.80; found C 43.09, H 7.51, N 2.67. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.00 (s, 3 H, HfMe_2), 0.03 (s, 3 H, HfMe_2), 0.24 (s, 3 H, SiMe_2), 0.26 (s, 3 H, SiMe_2), 0.38 (s, 6 H, SiMe_2), 1.32 (s, 9 H, CMe_3), 1.68 (m, 2 H, SiCH_2), 4.91 (m, 2 H, CH=CH_2), 5.78 (m, 1 H, CH=CH_2), 6.20 (t, 1 H, C_5H_3), 6.27 (t, 1 H, C_5H_3), 6.67 (t, 1 H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.6 (SiMe_2), –2.4 (SiMe_2), 2.0 (SiMe_2), 2.4 (SiMe_2), 25.2 (SiCH_2), 35.1 (CMe_3), 47.1 (HfMe_2), 48.0 (HfMe_2), 55.0 (CMe$_3$, C_{ipso}), 107.9 (C_5H_3, C_{ipso}), 114.3 (CH=CH_2), 122.9 (C_5H_3), 125.2 (C_5H_3), 125.7 (C_5H_3), 126.9 (C_5H_3, C_{ipso}), 134.9 (CH=CH_2) ppm.

Synthesis of [Hf{η^5-C_5H_3[$SiMe_2$-η^1-N*t*Bu][$SiMe_2$(CH_2CH=CH_2)]}-(CH_2Ph)$_2$] (13): The same procedure described to prepare **11** was applied using a 2 M THF solution of MgClBz (4.4 mL, 8.8 mmol) and **7** (2.4 g, 4.4 mmol) to give **13** as an orange oil (1.72 g, 2.64 mmol, 60% yield). $C_{30}H_{43}HfNSi_2$ (652.34): calcd. C 55.24, H 6.64, N 2.15; found C 55.23, H 5.99, N 2.28. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.22 (s, 3 H, SiMe_2), 0.24 (s, 3 H, SiMe_2), 0.38 (s, 3 H, SiMe_2), 0.41 (s, 3 H, SiMe_2), 1.19 (s, 9 H, CMe_3), 1.40 (d, J = 12.5 Hz, 1 H, CH_2Ph), 1.47 (d, J = 11.5 Hz, 1 H, CH_2Ph), 1.63 (m, 2 H, SiCH_2), 1.84 (d, J = 12.5 Hz, 1 H, CH_2Ph), 1.96 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.83 (m, 2 H, CH=CH_2), 5.69 (m, 1 H, CH=CH_2), 5.91 (t, 1 H, C_5H_3), 6.19 (t, 1 H, C_5H_3), 6.28 (t, 1 H, C_5H_3), 6.77–7.20 (m, 10 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.8 (SiMe_2), –2.6 (SiMe_2), 1.4 (SiMe_2), 2.0 (SiMe_2), 25.0 (SiCH_2), 34.5 (CMe_3), 56.4 (CMe$_3$, C_{ipso}), 71.2 (HfCH_2), 73.5 (HfCH_2), 109.2 (C_5H_3, C_{ipso}), 114.0 (CH=CH_2), 122.0, 122.5, 125.3 (C_5H_3), 126.5, 126.7, 128. 2, 128.7, 128.8 (C_6H_5), 134.4 (CH=CH_2), 147.0, 147.3 (C_6H_5, C_{ipso}) ppm.

Synthesis of [Zr{η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$(CH_2CH=CH_2)]}-{η^2-CMe=N(2,6-$Me_2C_6H_3$)}$_2$] (14): A solution of **10** (1.0 g, 2.42 mmol) in toluene (50 mL) was treated with a toluene (20 mL) solution of CN(2,6-$Me_2C_6H_3$) (0.63 g, 4.84 mmol) at room temperature. The mixture was stirred for 3 h and the solvent was then removed under vacuum. The residue was extracted into pentane (40 mL) and the solution was filtered and concentrated under reduced pressure to give a red oily product identified as compound **14** (1.31 g, 1.94 mmol, 80% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.11 (s, 3 H, SiMe_2), 0.25 (s, 3 H, SiMe_2), 0.70 (s, 6 H, SiMe_2), 1.11 (s, 9 H, CMe_3), 1.62 (m, 2 H, SiCH_2), 1.89 (s, 3 H, N$Me_2C_6H_3$), 1.93 (s, 6 H, N$Me_2C_6H_3$), 1.96 (s, 3 H, N$Me_2C_6H_3$), 2.05 (s, 3 H, CMe_2), 2.12 (s, 3 H, CMe_2), 4.90 (m, 2 H, CH=CH_2), 5.76 (m, 1 H, CH=CH_2), 6.33 (t, 1 H, C_5H_3), 6.53 (t, 1 H, C_5H_3), 6.61 (t, 1 H, C_5H_3), 6.90–7.00 (m, 6 H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.7 (SiMe_2), –2.5 (SiMe_2), 3.9 (SiMe_2), 4.6 (SiMe_2), 18.4, 18.7, 18.9, 19.6 (N$Me_2C_6H_3$), 24.2 (SiCH_2), 25.5, 25.6 (CMe_2), 35.3 (CMe_3), 55.8 (CMe$_3$, C_{ipso}), 113.4 (CH=CH_2), 114.5 (C_5H_3, C_{ipso}), 119.2, 121.4, 121.7 (C_5H_3), 125.3–129.9 (C_6H_3), 135.1 (CH=CH_2), 146.9, 147.4 (NC), 253.0, 257.1 (CMe$_2$) ppm.

Synthesis of [Zr{η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$(CH_2CH=CH_2)]}-{η^2-C(CH_2Ph)=N(2,6-$Me_2C_6H_3$)}$_2$] (15): A toluene (10 mL) solution of CN(2,6-$Me_2C_6H_3$) (0.37 g, 2.83 mmol) was added to a solution of **11** (0.80 g, 1.42 mmol) in toluene (40 mL) and the mixture was stirred at room temperature overnight. The solvent was re-

moved under vacuum and the resulting residue was extracted into pentane (40 mL). The solution was filtered and the solvent was removed under vacuum to give an orange oil identified as compound **15** (0.76 g, 0.92 mmol, 65% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.07 (s, 3 H, SiMe_2), 0.08 (s, 3 H, SiMe_2), 0.64 (s, 3 H, SiMe_2), 0.74 (s, 3 H, SiMe_2), 1.12 (s, 9 H, CMe_3), 1.45 (m, 2 H, SiCH_2), 1.65 (s, 3 H, NMeC$_6$H$_3$), 1.87 (s, 3 H, NMeC$_6$H$_3$), 1.97 (s, 3 H, NMeC$_6$H$_3$), 2.12 (s, 3 H, NMeC$_6$H$_3$), 3.47 (d, J = 14.3 Hz, 1 H, CH_2Ph), 3.60 (d, J = 17.3 Hz, 1 H, CH_2Ph), 3.64 (d, J = 14.6 Hz, 1 H, CH_2Ph), 3.80 (d, J = 17.3 Hz, 1 H, CH_2Ph), 4.85 (m, 2 H, CH=CH_2), 5.63 (m, 1 H, CH=CH$_2$), 6.10 (t, 1 H, C$_5H_3$), 6.21 (t, 1 H, C$_5H_3$), 6.84 (t, 1 H, C$_5H_3$), 6.50–7.40 (m, C$_6H_3$, C$_6H_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.1 (SiMe_2), –1.9 (SiMe_2), 4.2 (SiMe_2), 4.6 (SiMe_2), 18.8, 19.0, 20.1, 20.3 (NMeC$_6$H$_3$), 26.2 (SiCH$_2$), 36.1 (CMe_3), 45.7, 46.1 (CH$_2$Ph), 56.4 (CMe$_3$, C$_{ipso}$), 113.6 (CH=CH$_2$), 115.4 (C_5H_3, C$_{ipso}$), 117.1, 121.2, 123.0 (C_5H$_3$), 125.5–130.7 (C_6H$_5$, C_6H$_3$), 135.4 (CH=CH$_2$), 137.7, 137.8, 147.5, 148.3 (C_6H$_5$, C_6H$_3$, C$_{ipso}$), 253.0, 257.1 [C(CH$_2$Ph)$_2$] ppm.

Synthesis of [Hf{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}{η^2-CMe=N(2,6-Me$_2$C$_6$H$_3$)}$_2$] (16): A toluene solution (60 mL) of CN(2,6-Me$_2$C$_6$H$_3$) (0.47 g, 3.60 mmol) and **12** (0.90 g, 1.80 mmol) was stirred at room temperature overnight. The solvent was removed under vacuum and the residue was extracted into pentane (40 mL). After filtration and elimination of the solvent under vacuum, compound **16** was obtained as a red oily product (1.37 g, 1.1 mmol, 80% yield). $C_{36}H_{53}HfN_3Si_2$ (762.50): calcd. C 56.71, H 7.01, N 5.51; found C 56.42, H 7.02, N 5.52. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.09 (s, 3 H, SiMe_2), 0.25 (s, 3 H, SiMe_2), 0.67 (s, 3 H, *Si*Me_2), 0.70 (s, 3 H, SiMe_2), 1.08 (s, 9 H, CMe_3), 1.59 (m, 2 H, SiCH$_2$), 1.95 (s, 3 H, NMeC$_6$H$_3$), 1.96 (s, 6 H, NMe_2C$_6$H$_3$), 1.98 (s, 3 H, NMeC$_6$H$_3$), 2.10 (s, 3 H, CMe), 2.19 (s, 3 H, CMe), 4.86 (m, 2 H, CH=CH_2), 5.72 (m, 1 H, CH=CH$_2$), 6.27 (t, 1 H, C$_5H_3$), 6.46 (t, 2 H, C$_5H_3$), 6.95–7.00 (m, 6 H, C$_6H_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.8 (SiMe_2), –2.5 (SiMe_2), 4.1 (SiMe_2), 4.6 (SiMe_2), 18.5, 18.6, 18.8, 19.8 (NMeC$_6$H$_3$), 24.6 (SiCH$_2$), 25.7, 25.9 (CMe_2), 35.5 (CMe_3), 55.5 (CMe$_3$, C$_{ipso}$), 113.4 (CH=CH$_2$), 114.1 (C_5H$_3$, C$_{ipso}$), 118.3, 120.3, 120.7 (C_5H$_3$), 125.3–129.5 (C_6H$_3$), 135.1 (CH=CH$_2$), 146.3, 146.8 (NC), 262.3, 268.6 (CMe$_2$) ppm.

Synthesis of [Hf{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}{η^2-C(CH$_2$Ph)=N(2,6-Me$_2$C$_6$H$_3$)}$_2$] (17): A toluene (50 mL) solution containing **13** (0.80 g, 1.23 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) (0.32 g, 2.46 mmol) was stirred at room temperature for 2 d. The solvent was removed under reduced pressure and the residue was extracted into pentane (40 mL). After filtration, the solvent was removed under vacuum to give an orange oil identified as compound **17** (0.79 g, 0.86 mmol, 70% yield). $C_{48}H_{61}HfN_3Si_2$ (914.69): calcd. C 63.03, H 6.72, N 4.59; found C 63.00, H 6.55, N 4.50. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.06 (s, 3 H, SiMe_2), 0.09 (s, 3 H, SiMe_2), 0.64 (s, 3 H, SiMe_2), 0.71 (s, 3 H, SiMe_2), 1.11 (s, 9 H, CMe_3), 1.44 (m, 2 H, SiCH_2), 1.72 (s, 3 H, NMeC$_6$H$_3$), 1.89 (s, 3 H, NMeC$_6$H$_3$), 2.00 (s, 3 H, NMeC$_6$H$_3$), 2.11 (s, 3 H, NMeC$_6$H$_3$), 3.54 (d, J = 14.5 Hz, 1 H, CH_2Ph), 3.69 (d, J = 16.8 Hz, 1 H, CH_2Ph), 3.72 (d, J = 14.5 Hz, 1 H, CH_2Ph), 3.86 (d, J = 17.0 Hz, 1 H, CH_2Ph), 4.83 (m, 2 H, CH=CH_2), 5.62 (m, 1 H, CH=CH$_2$), 6.09 (t, 1 H, C$_5H_3$), 6.21 (t, 1 H, C$_5H_3$), 6.72 (t, 1 H, C$_5H_3$), 6.55–7.35 (m, C$_6H_3$, C$_6H_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –2.5 (SiMe_2), –2.3 (SiMe_2), 3.9 (SiMe_2), 4.5 (SiMe_2), 18.6, 19.7, 20.0 (NMeC$_6$H$_3$), 25.9 (SiCH$_2$), 36.0 (CMe_3), 45.8, 46.2 (CH$_2$Ph), 55.7 (CMe$_3$, C$_{ipso}$), 113.3 (CH=CH$_2$), 115.8 (C_5H$_3$, C$_{ipso}$), 120.2, 125.4, 126.7 (C_5H$_3$), 128.5–130.4 (C_6H$_5$, C_6H$_3$), 135.1 (CH=CH$_2$), 137.4, 137.5, 147.0, 147.5 (C_6H$_5$, C_6H$_3$, C$_{ipso}$), 261.2, 265.4 [C(CH$_2$Ph)$_2$] ppm.

Synthesis of [Zr{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}{η-N(2,6-Me$_2$C$_6$H$_3$)CMe=CMe-η-N(2,6-Me$_2$C$_6$H$_3$)}] (18): A toluene (50 mL) solution of **14** (0.63 g, 0.93 mmol) was heated at 70 °C for 2 d in a Teflon-valved Schlenk vessel. The solvent was then removed under vacuum and the residue was extracted into pentane (40 mL). After removal of the solvent under vacuum, compound **18** was isolated as a red oil (0.63 g, 0.93 mmol, 100% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = –0.25 (s, 3 H, SiMe_2), –0.12 (s, 3 H, SiMe_2), 0.64 (s, 3 H, SiMe_2), 0.66 (s, 3 H, SiMe_2), 1.10 (s, 9 H, CMe_3), 1.23 (m, 2 H, SiCH_2), 1.59 (s, 3 H, NMeC$_6$H$_3$), 1.62 (s, 3 H, NMeC$_6$H$_3$), 2.04 (s, 3 H, NMeC$_6$H$_3$), 2.09 (s, 3 H, NMeC$_6$H$_3$), 2.45 (s, 3 H, CMe_2), 2.52 (s, 3 H, CMe_2), 4.74 (m, 2 H, CH=CH_2), 5.50 (m, 1 H, CH=CH$_2$), 6.16 (t, 1 H, C$_5H_3$), 6.35 (t, 1 H, C$_5H_3$), 6.53 (t, 1 H, C$_5H_3$), 6.90–7.10 (m, 6 H, C$_6H_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –4.4 (SiMe_2), –3.5 (SiMe_2), 3.4 (SiMe_2), 3.6 (SiMe_2), 16.9, 17.9, 19.8, 19.9 (NMeC$_6$H$_3$), 21.2, 21.7 (CMe_2), 24.5 (SiCH$_2$), 35.7 (CMe_3), 55.5 (CMe$_3$, C$_{ipso}$), 110.8, 111.2 (NC=CN), 113.3 (CH=CH$_2$), 114.5 (C_5H$_3$, C$_{ipso}$), 122.7, 123.4, 124.5 (C_5H$_3$), 125.3–129.5 (C_6H$_3$), 132.3, 133.2, 133.3, 133.8 (C_6H$_3$, C$_{ipso}$), 134.8 (CH=CH$_2$), 149.9, 150.1 (NC) ppm.

Synthesis of [Hf{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}{η-N(2,6-Me$_2$C$_6$H$_3$)CMe=CMe-η-N(2,6-Me$_2$C$_6$H$_3$)}] (19): A toluene (50 mL) solution of **15** (0.60 g, 0.79 mmol) was heated at 80 °C for 2 d in a Teflon-valved Schlenk vessel and the solvent was then removed under vacuum. The residue was extracted into pentane (40 mL) and the solvent was removed under vacuum to give compound **19** as a brown oil. (0.60 g, 0.79 mmol, 100% yield). $C_{36}H_{53}HfN_3Si_2$ (762.50): calcd. C 56.71, H 7.01, N 5.51; found C 56.42, H 7.02, N 5.52. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = –0.22 (s, 3 H, SiMe_2), –0.12 (s, 3 H, SiMe_2), 0.65 (s, 3 H, SiMe_2), 0.68 (s, 3 H, SiMe_2), 1.08 (s, 9 H, CMe_3), 1.29 (m, 2 H, SiCH_2), 1.60 (s, 3 H, NMeC$_6$H$_3$), 1.61 (s, 3 H, NMeC$_6$H$_3$), 1.99 (s, 3 H, NMeC$_6$H$_3$), 2.06 (s, 3 H, NMeC$_6$H$_3$), 2.41 (s, 3 H, CMe_2), 2.49 (s, 3 H, CMe_2), 4.79 (m, 2 H, CH=CH_2), 5.53 (m, 1 H, CH=CH$_2$), 6.14 (t, 1 H, C$_5H_3$), 6.46 (t, 1 H, C$_5H_3$), 6.65 (t, 1 H, C$_5H_3$), 6.91–7.08 (m, 6 H, C$_6H_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –4.0 (SiMe_2), –3.3 (SiMe_2), 3.9 (SiMe_2), 4.0 (SiMe_2), 17.0, 18.5, 20.0, 20.2 (NMe_2C$_6$H$_3$), 21.4, 22.6 (CMe_2), 24.7 (SiCH$_2$), 35.6 (CMe_3), 55.7 (CMe$_3$, C$_{ipso}$), 112.0, 112.1 (NC=CN), 113.3 (CH=CH$_2$), 114.9 (C_5H$_3$, C$_{ipso}$), 123.3, 123.4, 124.6 (C_5H$_3$), 125.4–129.5 (C_6H$_3$), 132.0, 132.5, 132.8, 133.2 (C_6H$_3$, C$_{ipso}$), 134.8 (CH=CH$_2$), 149.8, 149.9 (NC) ppm.

Synthesis of [Zr{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH=CH$_2$)]}{η-N(2,6-Me$_2$C$_6$H$_3$)C(CH$_2$Ph)=C(CH$_2$Ph)-η-N(2,6-Me$_2$C$_6$H$_3$)}] (20): A toluene (50 mL) solution of **16** (0.80 g, 0.97 mmol) was heated at 80 °C for 4 d and the solvent was then removed under vacuum. The residue was extracted into pentane (40 mL) and the solvent was removed under vacuum to give a brown oil identified as compound **20** (0.80 g, 0.97 mmol, 100% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = –0.29 (s, 3 H, SiMe_2), –0.15 (s, 3 H, SiMe_2), 0.63 (s, 3 H, SiMe_2), 0.65 (s, 3 H, SiMe_2), 1.01 (s, 9 H, CMe_3), 1.18 (m, 2 H, SiCH_2), 1.77 (s, 3 H, NMeC$_6$H$_3$), 1.98 (s, 3 H, NMeC$_6$H$_3$), 2.47 (s, 3 H, NMeC$_6$H$_3$), 2.50 (s, 3 H, NMeC$_6$H$_3$), 3.21 (d, J = 15.2 Hz, 1 H, CH_2Ph), 3.61 (d, J = 14.3 Hz, 1 H, CH_2Ph), 3.87 (d, J = 14.5 Hz, 1 H, CH_2Ph), 4.35 (d, J = 15.4 Hz, 1 H, CH_2Ph), 4.76 (m, 2 H, CH=CH_2), 5.50 (m, 1 H, CH=CH$_2$), 6.11 (t, 1 H, C$_5H_3$), 6.20 (t, 1 H, C$_5H_3$), 6.59 (t, 1 H, C$_5H_3$), 6.65–7.15 (m, C$_6H_5$, C$_6H_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ = –4.7 (SiMe_2), –3.7 (SiMe_2), 3.1 (SiMe_2), 3.9 (SiMe_2), 20.2, 20.3, 21.5, 22.0 (NMeC$_6$H$_3$), 24.5 (SiCH$_2$), 35.6 (CMe_3), 38.3,

39.2 (CH_2Ph), 55.5 (CMe_3, C_{ipso}), 112.8 (N*C*=*C*N), 113.2 (CH=*C*H_2), 117.3, 119.4 (C_5H_3, C_{ipso}), 123.3, 123.8, 124.8 (C_5H_3), 125.8–129.4 (C_6H_3, C_6H_5), 134.7 (*C*H=CH_2), 138.6, 139.1, 149.4, 149.8 (C_6H_3, C_6H_5, C_{ipso}) ppm.

X-ray Structure Determination of [ZrCl(μ-Cl){η⁵-C_5H_3($SiMe_2$-η¹-N*t*Bu)[$SiMe_2$($CH_2CH=CH_2$)]}]₂ (6): Crystals of compound **6** were obtained by crystallisation from hexane, and a suitably sized crystal in a Lindemann tube was mounted on a Philips PW 1100 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarised in Table 2. No decay was observed during the data collection. A semi-empirical method of absorption correction was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.665).[53] The structure was solved by direct methods (SIR97)[54] and refined by least squares against F_o^2 (SHELXL-97).[55] All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. The programs PARST[56] ad ORTEP[57] were also used. CCDC-273336 (**6**) contains 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.

Table 2. Crystal data and structure refinement for **6**.

Empirical formula	$C_{32}H_{58}Cl_4N_2Si_4Zr_2$
Formula mass	907.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/a$
Unit cell dimensions	a = 14.412(9) Å b = 12.300(6) Å, β = 92.29(2)° c = 12.784(6) Å
Volume	2264(2) Å^3
Z, calculated density	2, 1.331 Mg m^{-3}
Absorption coefficient	0.825 mm^{-1}
F(000)	936
Crystal size	0.45 × 0.25 × 0.20 mm
Theta range for data collection	3.19–24.00°
Limiting indices	$-16 \le h \le 16$, $0 \le k \le 14$, $0 \le l \le 14$
Reflections collected/unique	3729/3563 [R(int) = 0.0971]
Completeness to θ = 24.00	99.8%
Absorption correction	empirical
Max./min. transmission	1.000/0.665
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	3563/0/199
Goodness-of-fit on F^2	0.857
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0514, wR_2 = 0.1102
R indices (all data)	R_1 = 0.1346, wR_2 = 0.1372
Largest diff. peak and hole	0.444 and –0.503 e Å^{-3}

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[1] X. M. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625.
[2] M. Bochmann, S. J. Lancaster, M. B. Hursthouse, K. M. A. Malik, *Organometallics* **1994**, *13*, 2235–2243.
[3] X. M. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031.
[4] S. Beck, M. H. Prosenc, H. H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A: Chem.* **1996**, *111*, 67–79.
[5] E. Y. X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.
[6] S. Beck, S. Lieber, F. Schaper, A. Geyer, H. H. Brintzinger, *J. Am. Chem. Soc.* **2001**, *123*, 1483–1489.
[7] S. Döring, V. V. Kotov, G. Erker, G. Kehr, K. Bergander, O. Kataeva, R. Fröhlich, *Eur. J. Inorg. Chem.* **2003**, 1599–1607.
[8] T. Beringhelli, G. D'Alfonso, D. Maggioni, P. Mercandelli, A. Sironi, *Chem. Eur. J.* **2005**, *11*, 650–661.
[9] D. Maggioni, T. Beringhelli, G. D'Alfonso, L. Resconi, *J. Organomet. Chem.* **2005**, *690*, 640–646.
[10] C. P. Casey, D. W. Carpenetti, H. Sakurai, *J. Am. Chem. Soc.* **1999**, *121*, 9483–9484.
[11] R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325–387.
[12] T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57–65.
[13] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170.
[14] M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1996**, 255–270.
[15] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253–1345.
[16] Z. Wu, R. F. Jordan, J. L. Petersen, *J. Am. Chem. Soc.* **1995**, *117*, 5867–5868.
[17] C. P. Casey, D. W. Carpenetti, *Organometallics* **2000**, *19*, 3970–3977.
[18] C. P. Casey, S. L. Hallenbeck, D. W. Pollock, C. R. Landis, *J. Am. Chem. Soc.* **1995**, *117*, 9770–9771.
[19] J. F. Carpentier, V. P. Maryin, J. Luci, R. F. Jordan, *J. Am. Chem. Soc.* **2001**, *123*, 898–909.
[20] J. F. Carpentier, Z. Wu, C. W. Lee, S. Stromberg, J. N. Christopher, R. F. Jordan, *J. Am. Chem. Soc.* **2000**, *122*, 7750–7767.
[21] E. J. Stoebenau III, R. F. Jordan, *J. Am. Chem. Soc.* **2003**, *125*, 3222–3223.
[22] Z. T. Xu, K. Vanka, T. Ziegler, *Organometallics* **2004**, *23*, 104–116.
[23] K. Kunz, G. Erker, G. Kehr, R. Fröhlich, H. Jacobsen, H. Berke, O. Blacque, *J. Am. Chem. Soc.* **2002**, *124*, 3316–3326.
[24] G. Lanza, I. L. Fragala, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 12764–12777.
[25] K. Vanka, M. S. W. Chan, C. C. Pye, T. Ziegler, *Organometallics* **2000**, *19*, 1841–1849.
[26] A. T. Rappe, W. M. Skiff, C. J. Casewit, *Chem. Rev.* **2000**, *100*, 1435–1456.
[27] M. S. W. Chan, K. Vanka, C. C. Pye, T. Ziegler, *Organometallics* **1999**, *18*, 4624–4636.
[28] L. T. Li, T. J. Marks, *Organometallics* **1998**, *17*, 3996–4003.
[29] L. Jia, X. M. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 842–857.
[30] P. A. Deck, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 6128–6129.
[31] J. Cano, P. Gómez-Sal, G. Heinz, G. Martínez, P. Royo, *Inorg. Chim. Acta* **2003**, *345*, 15–26.
[32] M. V. Galakhov, G. Heinz, P. Royo, *Chem. Commun.* **1998**, 17–18.
[33] T. Cuenca, P. Royo, *Coord. Chem. Rev.* **1999**, *195*, 447–498.
[34] M. J. Humphries, M. L. H. Green, R. E. Douthwaite, L. H. Rees, *J. Chem. Soc., Dalton Trans.* **2000**, 4555–4562.
[35] S. Ciruelos, T. Cuenca, R. Gomez, P. Gómez-Sal, A. Manzanero, P. Royo, *Organometallics* **1996**, *15*, 5577–5585.
[36] S. Ciruelos, A. Sebastian, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, *J. Organomet. Chem.* **2000**, *604*, 103–115.
[37] H. G. Alt, K. Föttinger, W. Milius, *J. Organomet. Chem.* **1998**, *564*, 115–123.
[38] H. G. Alt, K. Föttinger, W. Milius, *J. Organomet. Chem.* **1999**, *572*, 21–30.
[39] W. P. Leung, F. Q. Song, Z. Y. Zhou, F. Xue, T. C. W. Mak, *J. Organomet. Chem.* **1999**, *575*, 232–241.
[40] A. Razavi, U. Thewalt, *J. Organomet. Chem.* **2001**, *621*, 267–276.
[41] Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko, *Can. J. Chem.* **1996**, *74*, 1696–1703.

[42] J. Okuda, T. Eberle, T. P. Spaniol, V. Piquet-Faure, *J. Organomet. Chem.* **1999**, *591*, 127–137.
[43] P. Doufou, K. A. Abboud, J. M. Boncella, *J. Organomet. Chem.* **2000**, *603*, 213–219.
[44] K. E. Duplooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* **1995**, *14*, 3129–3131.
[45] D. W. Carpenetti, L. Kloppenburg, J. T. Kupec, J. L. Petersen, *Organometallics* **1996**, *15*, 1572–1581.
[46] J. Cano, P. Royo, M. Lanfranchi, M. A. Pellinghelli, A. Tiripicchio, *Angew. Chem. Int. Ed.* **2001**, *40*, 2495.
[47] A. Sebastian, P. Royo, P. Gómez-Sal, C. Ramírez de Arellano, *Eur. J. Inorg. Chem.* **2004**, 3814–3821.
[48] L. Kloppenburg, J. L. Petersen, *Organometallics* **1997**, *16*, 3548–3556.
[49] L. D. Durfee, I. P. Rothwell, *Chem. Rev.* **1988**, *88*, 1059–1079.
[50] L. R. Chamberlain, L. D. Durfee, P. E. Fanwick, L. Kobriger, S. L. Latesky, A. K. McMullen, I. P. Rothwell, K. Folting, J. C. Huffman, W. E. Streib, R. Wang, *J. Am. Chem. Soc.* **1987**, *109*, 390–402.
[51] P. Nicolas, P. Royo, M. V. Galakhov, O. Blacque, H. Jacobsen, H. Berke, *Dalton Trans.* **2004**, 2943–2951.
[52] L. E. Manzer, *Inorg. Synth.* **1982**, *21*, 135–140.
[53] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.
[54] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
[55] G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, Universität Göttingen, Göttingen, Germany, **1997**.
[56] M. Nardelli, *Comput. Chem.* **1983**, *7*, 95–98.
[57] L. Zsolnai, H. Pritzkow, *ZORTEP – ORTEP* original program modified for PC, Universität Heidelberg, Heidelberg, **1994**.

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