Summary

Introduction.

Since initial studies on scandium catalysts the success of η^5-cyclopentadienylsilyl-η^1-amido group 4 metal complexes as efficient catalysts for olefin polymerization has motivated numerous studies and applications.[1-4] The active species of these homogeneous Ziegler-Natta catalysts is a cationic coordinatively unsaturated 12-electron d^0 alkyl compound. Alkene coordination to the metal alkyl cation followed by alkyl migration to the coordinated alkene is the generally accepted mechanism of propagation.[5,6]

Several strategies have been used to stabilize the intermediate cationic (alkylalkene) η^5-ciclopentadienylsilyl-η^1-amido d^0 group-4 metal complexes.[7-14] We have described the formation of catalytically active group 4 metal cationic species stabilized by coordination of the silylallyl olefinic moiety of η^5-ciclopentadienylsilyl-η^1-amido and metallocene compounds.[15-17]

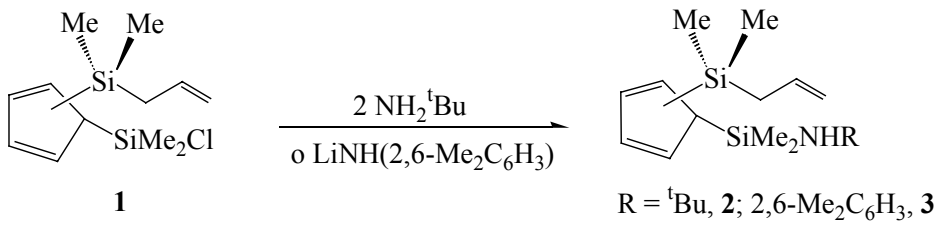
Over the past few years there has been a growing interest in developing precatalysts containing only one such group which can be active for olefin polymerization.[18-21] We have developed the synthesis of new η^1-amidosilylmetalocene derivatives, their behaviour in reactions with $B(C_6F_5)_3$ and as catalysts for olefin polymerization processes.

Metal alkyl compounds are convenient models not only for olefin polymerization but also for insertion reactions.[22-32] We have synthesised and characterised the insertion reactions of isocyanides into metal-alkyl bonds of dialkyl (allylsilyl)(amidosilyl)cyclopentadienyl group 4 metal complexes and C-C coupling reactions of the resulting iminoacyl derivatives.

Results and Discussion.

Synthesis of chloro complexes.

The disubstituted cyclopentadiene $C_5H_4(SiMe_2Cl)[SiMe_2(CH_2CH{=}CH_2)]$ **1** was isolated by reaction of the lithium salt $Li[C_5H_4SiMe_2(CH_2CH{=}CH_2)]$[15,16] with $SiMe_2Cl_2$ followed by reaction with $NH_2{}^tBu$ and $LiNH(2,6\text{-}Me_2C_6H_3)$ to give the aminosilyl cyclopentadienes $C_5H_4[SiMe_2(CH_2CH{=}CH_2)][SiMe_2(NHR)]$ (R = ^tBu **2**, 2,6-$Me_2C_6H_3$ **3**), (Scheme 1).



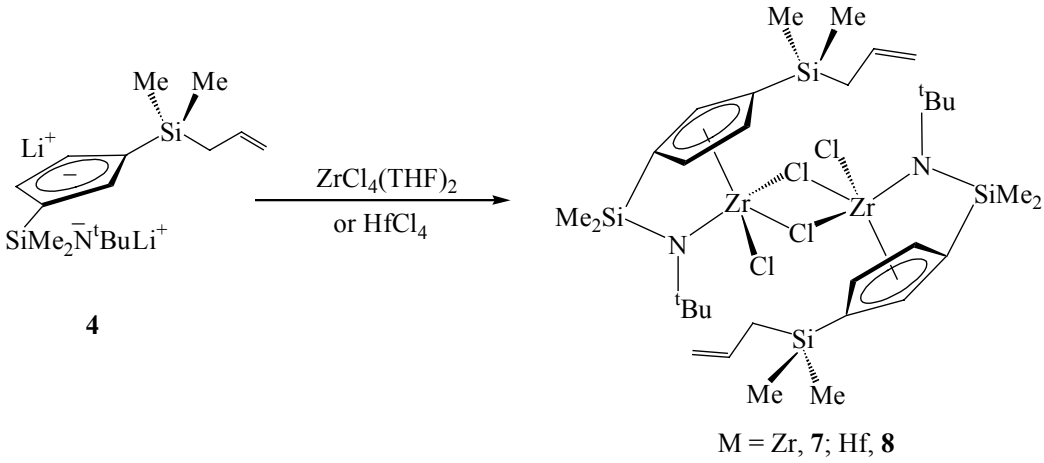
Scheme 1

The chlorosilyl derivative **1** was identified by ^1H NMR spectroscopy as the 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 more sterically demanding amino substituents.

The mixture of isomers of the disilylcyclopentadienes **2** and **3** were metallated by reaction with 2 equivalents of ^nBuLi to give the dilithium salts, isolated as white solids containing one single component 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 = ^tBu **4**, 2,6-$Me_2C_6H_3$ **5**).

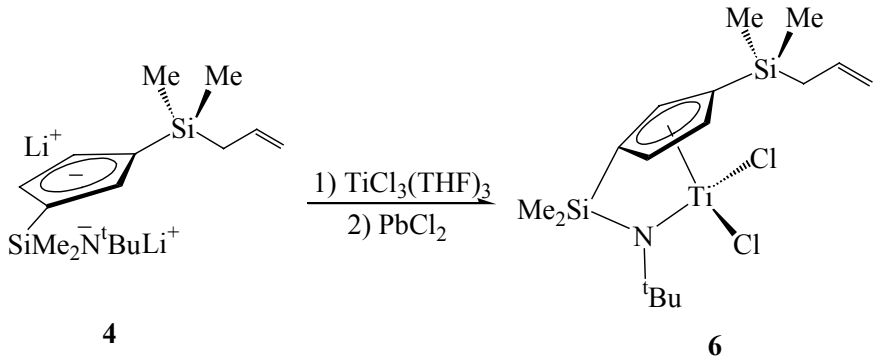
Direct synthesis based on halide metathesis,[33,34] when the metal tetrahalides were treated with 1 equiv of the dilithium salts **4** and **5,** was used to transfer the cyclopentadienyl-silyl-amido ligand, as shown in Scheme 2. Reaction of **4** with $ZrCl_4(THF)_2$ and $HfCl_4$ in toluene at room

temperature yielded the "constrained geometry" complexes [MCl(μ-Cl){η^5-C_5H_3($SiMe_2$-η^1-N^tBu) [$SiMe_2(CH_2CH{=}CH_2)$]}]$_2$ (M = Zr **7**, Hf **8**), which were isolated in high yield as crystalline solid **7** and an oily solid **8**.



Scheme 2

However similar reaction with $TiCl_4$ led to a mixture containing reduction products from which the desired compound could be isolated in very low yields.[1] The most convenient method was the direct access to the titanium(III) complex by reaction of the dilithium salt **4** with $TiCl_3(THF)_3$ and further oxidation with $PbCl_2$[35] to give the complex [Ti{η^5-C_5H_3($SiMe_2$-η^1-N^tBu)[$SiMe_2(CH_2CH{=}CH_2)$]}Cl_2] **6** as a dark oil in high yield.



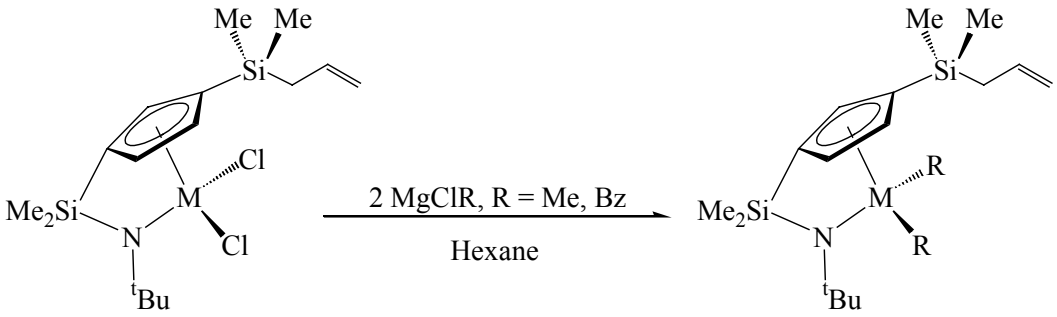
Scheme 3

Analogous reactions using the dilithium salt of the corresponding 2,6-dimethylphenylamido ligand **5** were carried out in the hope of obtaining improved crystallinity[36] of the resulting metal compounds. However the new dichloro-complexes [Ti{η^5-C_5H_3[$SiMe_2$-η^1-N(2,6-$Me_2C_6H_3$)][$SiMe_2$(CH_2CH=CH_2)]}Cl_2] **9** and [MCl(μ-Cl){η^5-C_5H_3[$SiMe_2$-η^1-N(2,6-$Me_2C_6H_3$)][$SiMe_2$(CH_2CH= CH_2)]}]$_2$ (M = Zr **10**, Hf **11**) 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 further studied.

All compounds were identified by elemental analysis and NMR spectroscopy. The dimeric structure of complex **7** in the solid state and the monomeric structure of compound **9** were determined by X-ray diffraction methods on single crystals obtained from hexane solutions cooled at -35 ºC. The same dimeric structure may be tentatively assigned to all of the other **8**, **10** y **11** complexes in the solid state, as represented in Scheme 2.

Synthesis of alkyl complexes.

As shown in Scheme 4, reactions of complexes **6-8** with 2 equiv of MgClR (R = Me, CH_2Ph)[37-43] in hexane at room temperature gave the dialkyl complexes [M{η^5-C_5H_3($SiMe_2$-η^1-N^tBu)[$SiMe_2$(CH_2CH=CH_2)]}Me_2] (M = Ti **12**, M = Zr **13**, M = Hf **14**) and [M{η^5-C_5H_3($SiMe_2$-η^1-N^tBu)[$SiMe_2$(CH_2CH=CH_2)]}(CH_2Ph)$_2$] (M = Ti **15**, M = Zr **16**, M = Hf **17**) which were isolated as oily solids, and identified by elemental analysis and NMR spectroscopy.

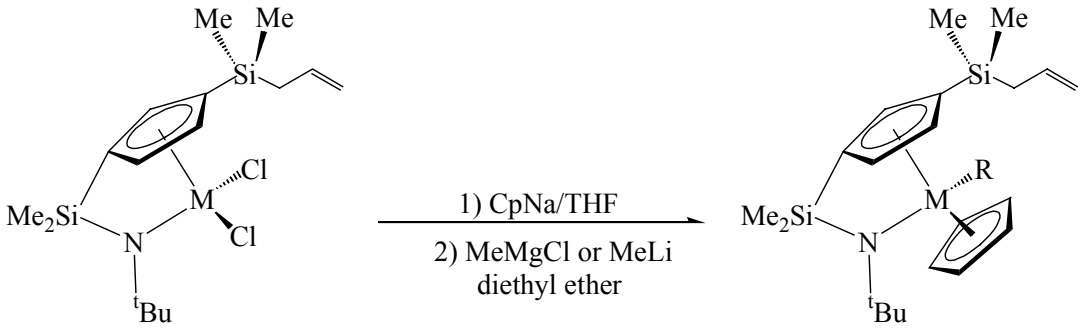


M = Ti, **6**, Zr, **7**; Hf, **8**

R = Me
M = Ti, **12**, Zr, **13**; Hf, **14**
R = Bz
M = Ti, **15**, Zr, **16**; Hf, **17**

Scheme 4

Complexes **18-20** were prepared from the reaction of sodium cyclopentadienide in THF with the corresponding dichloride precursors obtained as solids in high yields.[19,44] Reaction of complexes **18-19** with MeMgCl and MeLi, respectively, in diethyl ether produced the monomethyl derivates **21** and **22**.



M = Ti, **6**, Zr, **7**; Hf, **8**

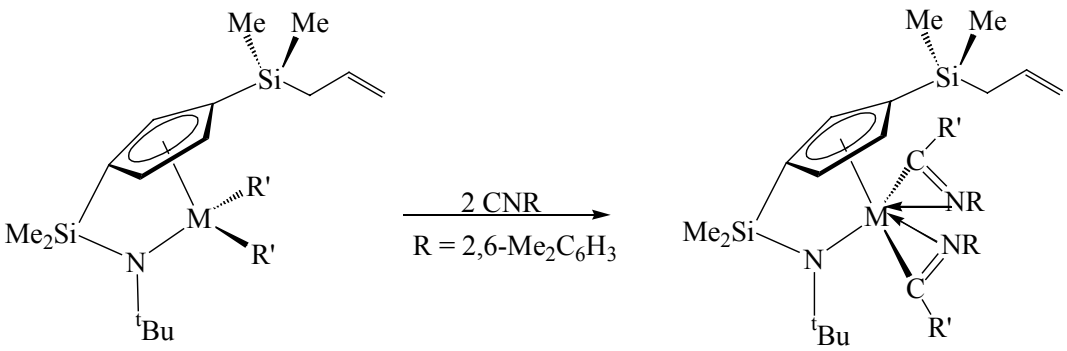
R = Cl
M = Ti, **18**, Zr, **19**; Hf, **20**
R = Me
M = Ti, **21**, Zr, **22**

Scheme 5

All compounds have been characterized spectroscopically and analytically and complex **19** and **20** have also been characterized crystallographically.

Synthesis of iminoacyl complexes.

When 1 equiv of CN(2,6-$Me_2C_6H_3$) was added to the toluene solutions of the cyclopentadienylsilyl-η-amido dimethyl compounds **13**, **14** and cyclopentadienylsilyl-η-amido dibenzyl compounds **16**, **17**, the initially formed 16-e iminoacyl derivates 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. Therefore these insertion reactions were complete when toluene solutions of the dialkyl complexes **13**, **14** and **16**, **17**, were treated with 2 equiv of 2,6-xylyl isocyanide at room temperature to give the corresponding bis(iminoacyl)[45,46] compounds [M{η^5-C_5H_3($SiMe_2$-η^1-N^tBu)[$SiMe_2$(CH_2CH=CH_2)]}{η^2-CR=N(2,6-$Me_2C_6H_3$)}$_2$] (M = Zr, R = Me **23**, CH_2Ph **24**; M = Hf, R = Me **25**, CH_2Ph **26**) which were isolated as oily products and identified by elemental analysis, NMR and infrared spectroscopy.

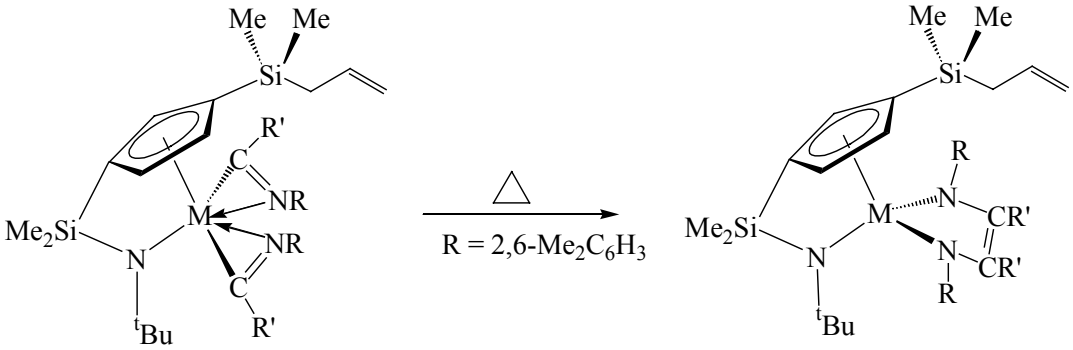


M = Zr, R '= Me (**13**), CH_2Ph (**16**)
M = Hf, R' = Me (**14**), CH_2Ph (**17**)

M = Zr, R' = Me (**23**), CH_2Ph (**24**)
M = Hf, R' = Me (**25**), CH_2Ph (**26**)

Scheme 6

As shown in Scheme 7 the bis(iminoacyl) complexes **23-25** were slowly converted into the C-C coupled compounds.[25] This transformation was complete when their toluene solutions were heated at 70ºC – 80ºC for long periods (2 d. for **27**, **28** and 4 d. for **29**) 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 **27**, Hf **28**; R = CH_2Ph, M = Zr **29**). Complexes **27-29** were isolated as oily solids and identified by elemental analysis, NMR and IR spectroscopy.



M = Zr, R' = Me (**23**), CH_2Ph (**24**)
M = Hf, R' = Me (**25**)

M = Zr, R' = Me (**27**), CH_2Ph (**28**)
M = Hf, R' = Me (**29**)

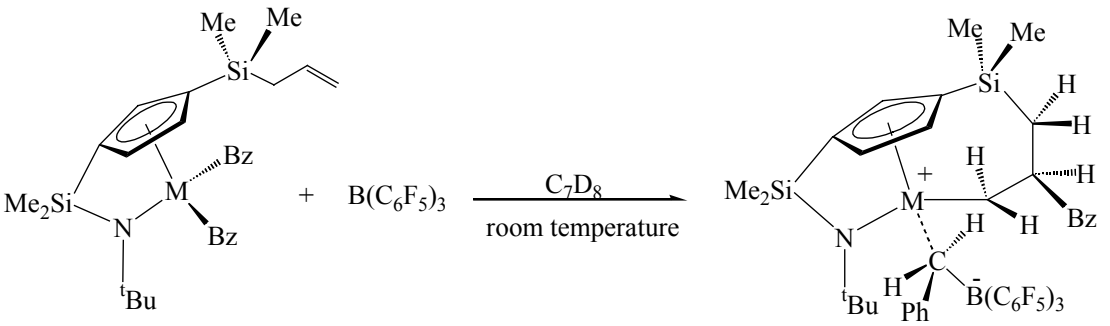
Scheme 7

Reaction of the complex **22** with 1 equiv of CN(2,6-$Me_2C_6H_3$) at 85ºC gave the corresponding iminoacyl compound [Zr{η^5-C_5H_3($SiMe_2$-η^1-N^tBu)[$SiMe_2$($CH_2CH{=}CH_2$)]}{(η^1-CMe=N(2,6-$Me_2C_6H_3$)(η^5-C_5H_5)}] **30** which was isolated as an oil an characterized by elemental analysis and NMR and IR spectroscopy.

Preparation of cationic species.

Reaction of the dibenzyl compounds **16** and **17** with the Lewis acid tris(pentafluorophenyl)boron, $B(C_6F_5)_3$, were carried out in C_7D_8 using a

Teflon-valved NMR tube, to give the salts $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)[SiMe_2\text{-}\eta^1\text{-}CH_2CH(CH_2Ph)CH_2]\}]^+[(CH_2Ph)B(C_6F_5)_3]^-$ (M = Zr **31**, Hf **32**). The complexes **31** and **32** exhibited two stereogenic centers at metal and at the benzyl-bound tertiary carbon atom and were characterized by ^1H, ^{13}C, ^{19}F, TOCSY-1D, NOESY-1D and HMQC-2D NMR techniques as unique *endo*-isomers, resulting from the migratory insertion of the alkene into the metal-benzyl bond.[17] A slight stabilization by a weak interaction of this coordinatively unsaturated cation with the benzylborate anion is consistent with the ^{19}F NMR spectrum, which shows a difference of $\Delta\delta = \delta_{para}\text{-}\delta_{meta}$ = 4,2 (**31**), 4,1 (**32**).[47]



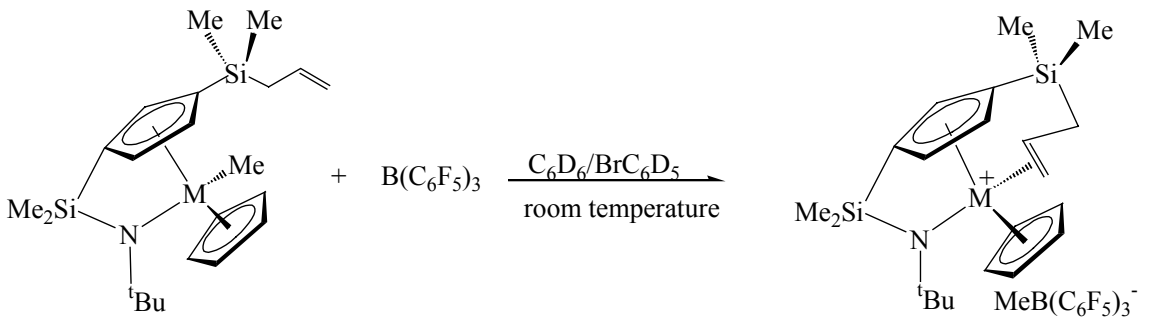
M= Zr, **16**; Hf, **17**

M= Zr, **31**; Hf, **32**

Scheme 8

When C_6D_6/C_6D_5Br solutions of complexes **21** and **22** into a Teflon-valved NMR tube were treated with 1 equiv of $B(C_6F_5)_3$ formation of the salts $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)[SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]\}(\eta^5\text{-}C_5H_5)]^+[(CH_2Ph)B(C_6F_5)_3]^-$ (M = Ti **33**, Zr **34**) were immediately observed. These salts contain the 18-electron cation and the presence of the free methylborate anion is demonstrated by the small $\Delta\delta = \delta_{para}\text{-}\delta_{meta}$ = 2,5 (**31**), 2,7 (**32**)[47] observed in the ^{19}F NMR spectrum in spite of the broad boron-methyl signals shifted lowfield at δ = 1,27 (**33**); 1,15 (**34**) observed in the ^1H-NMR spectra which could suggest the presence of the metal-coordinate anion. These cationic species are stabilized by asymmetrical coordination

of the olefin to the metal centre[15,16] and have been characterized by ^{1}H, ^{13}C, ^{19}F, TOCSY-1D, NOESY-1D and HMQC-2D NMR techniques as unique *exo*-isomers.



M= Ti, **21** Zr, **22**

M= Ti, **33**; Zr, **34**

Scheme 9

Polymerization.

The dichloro **6-8** and the monochloro **18-20** complexes were studied as catalysts for polymerization of different olefins. These catalysts were tested for ethylene polymerization upon activation with MAO and $B(C_6F_5)_3$ in toluene for different times, pressures and temperatures. The activities exhibited for the **18-19** complexes are markedly higher than the **6-7** complexes.[18,19,48]

The titanium complexes **6** and **18** were also studied as ethylene/1-hexene copolymerization catalysts and the catalytic activities measured were higher than those observed for the polymerization of ethylene due to the known comonomer effect.[49,50] Complex **6** exhibited an activity lower than at obtained with complex **18**. Both complexes show low catalytic activities for styrene and the PS samples obtained were atactic polymers.[51,52]

General methods.

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 4 Å molecular sieves in teflon-valved flasks and previously degassed by several freeze-pump-thaw cycles. C, H and N microanalyses were performed on a Perkin-Elmer 240B. NMR spectra, measured at 25 ºC, were recorded on a Varian Unity 300 (^{1}H-NMR at 300 MHZ, ^{13}C-NMR at 75 MHZ and ^{19}F-NMR at 188) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ units relative to internal TMS standard or external $CFCl_3$ for ^{19}F chemical shifts. IR spectra were performed in nujol mulls on a Perkin-Elmer 883 spectrophotometer. The thermal properties of the polymers samples were studied using a Perkin-Elmer DSC 6 or Perkin-Elmer Pyris-I DSC instruments calibrated by measuring the melting point of indium and the applied scanning rate was 10ºC/min. The molecular weights and molecular weight distributions were measured at 145ºC by gel-permeation chromatography, using 1,2,4-trichlorobenzen as solvent.

Conclusions.

Dichloro and dialkyl Cp-silyl-η-amido complexes of the type $[M\{\eta^5\text{-}C_5H_3[SiMe_2(CH_2CH{=}CH_2)](SiMe_2\text{-}\eta\text{-}N^tBu)\}X_2]$ (X = Cl, Me, Bz) and the η-amidosilylmetalocene $[M\{\eta^5\text{-}C_5H_3[SiMe_2(CH_2CH{=}CH_2)](SiMe_2\text{-}\eta\text{-}N^tBu)\}(\eta^5\text{-}C_5H_5)X]$ (X = Cl, Me) group 4 metal compounds with the allyldimethylsilyl-substituted cyclopentadienyl ligand have been isolated in high yields by conventional synthetic methods and characterized by elemental analysis, 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 gave 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 N always occupying the internal coordination site. C-C coupling reactions between the two iminoacyl ligands are very slow processes that gave quantitative yields of the diazametallacyclopentene complexes after heating the toluene solutions of the bis(iminoacyl) complexes.

The dibenzyl zirconium and hafnium complexes react with the Lewis acid $B(C_6F_5)_3$ to generate the cationic species $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)[SiMe_2\text{-}\eta^1\text{-}CH_2CH(CH_2Ph)CH_2]\}][(CH_2Ph)B(C_6F_5)_3]$ by migratory insertion of the alkene into the metal-benzyl bond, in which the benzyl group adopts an *endo* orientation. Both cationic species were stabilized by interactions contact with the $[(CH_2Ph)B(C_6F_5)_3]^-$ anion.

The η-amidosilylmetalocene monomethyl titanium and zirconium complexes were treated with $B(C_6F_5)_3$ to give the cationic species $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)(SiMe_2\text{-}\eta^2\text{-}CH_2CH{=}CH_2)\}(\eta^5\text{-}C_5H_5)][MeB(C_6F_5)_3]$, which contain the allylic olefin coordinated to the metal in an *exo* orientation. All cationic compounds were characterized by NMR techniques.

The $[M(\eta^5\text{-}C_5Me_4SiMe_2\text{-}\eta^1\text{-}N^tBu)Cl_2]$ and $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)[SiMe_2(CH_2CH{=}CH_2)]\}(\eta^5\text{-}C_5H_5)Cl]$ group 4 metal complexes, activated with a large excess methylalumoxane (MAO), were used as catalyst precursors for polymerization of ethylene and copolymerization of ethylene/1-hexene. The activities exhibited for the η-amidosilylmetalocene complexes are higher than those observed for the dialkyl Cp-silyl-η-amido complexes.

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