ELSEVIER

Journal of Organometallic Chemistry 535 (1997) 155–168

Journal of Organometallic Chemistry

Neutral and cationic di(*tert*-butyl)cyclopentadienyl titanium, zirconium and hafnium complexes. Dynamic NMR study of the ligand-free cations $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)(CH_3)]^+$ (M = Zr, Hf)

José Ignacio Amor, Tomás Cuenca, Mikhail Galakhov, Pilar Gómez-Sal [1], A. Manzanero [1], Pascual Royo *

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain

Received 31 October 1996; revised 12 December 1996

Abstract

Group 4 metal complexes containing the di(*tert*-butyl)cyclopentadienyl ligand ($1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3$) have been synthesized. The reaction of a mixture of 1,3- and 1,4-di(*tert*-butyl)cyclopentadiene isomers with KH in THF at −78 °C gives the salt $K^+[(1,3\text{-}^tBu_2C_5H_3)]^-(THF)_{1-3}$ **2** as a white solid. Treatment of **2** with chlorotrimethylsilane in a 1:1 molar ratio gives the air-stable trimethylsilylcyclopentadienyl derivative $Si(1,3\text{-}^tBu_2C_5H_3)(CH_3)_3$ **3**. The silyl derivative **3** is an excellent precursor for monocyclopentadienyl trichlorotitanium and zirconium compounds $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl_3$ [M = Ti (**4**), Zr (**5**)]. Addition of a stoichiometric amount of water in the presence of NEt_3 to a toluene solution of **4** affords the oxo trimer compound $[Ti(1,3\text{-}^tBu_2\text{-}\eta^5 - C_5H_3)Cl(\mu\text{-}O)]_3$ **6**. The reaction of **4** with 2 equiv. of LiMe affords the chloro dimethyl derivative $Ti(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl(CH_3)_2$ **7**. The mixed dicyclopentadienyl compounds $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)Cl_2$ [M = Ti (**8**); Zr (**9**)] were prepared by reaction of complexes **4** and **5** respectively with $Tl(C_5H_5)$. Treatment of complexes (**8**) and (**9**) with the appropriate alkylating reagent and molar ratio, in hexane at −78 °C, gives the chloro alkyl derivatives $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)ClR$ [M = Ti, R = Me (**10**); M = Zr, R = Me (**11**), Bz (**12**)] or the dialkyl complexes $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)R_2$ [M = Ti, R = Me (**13**); M = Zr, R = Me (**14**), Bz (**15**), Nf (**16**)]. When **8** reacts with 2 equiv. of $MgBz_2(THF)_2$ or $LiCH_2CMe_2Ph$ the metallacyclic complexes $Ti(1\text{-}^tBu\text{-}3\text{-}CMe_2CH_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)R$ [R = Bz (**17**); Nf (**18**)] were isolated as red oils at room temperature, with the elimination of toluene or *tert*-butyl benzene respectively. The previously reported cationic mono 1,3-di(*tert*-butyl)cyclopentadienyl dibenzyl zirconium species $[Zr(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(CH_2Ph)_2]^+$ (**19**) can be stabilized by reaction with ^{t}BuNC or PMe_3, in CD_2Cl_2 at −78 °C, and the formation of the new cationic species $[Zr(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(L)(CH_2Ph)_2]^+$ [L = ^{t}BuNC (**20**); PMe_3 (**21**)] was identified by NMR spectroscopy. The reaction of $B(C_6F_5)_3$ with the monocyclopentadienyl trimethyl derivatives $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(CH_3)_3$ [M = Ti (**22**), Zr (**23**)], in the presence of PMe_3, gives the cationic species $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(PMe_3)_2(CH_3)_2]^+$ [M = Ti (**24**); Zr (**25**)], obtained as orange-yellow solids, stable at room temperature. The reaction of $B(C_6F_5)_3$ with the metallocene dimethyl derivatives $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)(CH_3)_2$ [M = Zr (**14**); Hf (**26**)], in a 1:1 molar ratio and in hydrocarbon solvents gives the cationic derivatives $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)(CH_3)]^+[(CH_3)B(C_6F_5)_3]^-$ [M = Zr (**27**); Hf (**28**)] as yellow oils which can be stored for weeks under an inert atmosphere. When the same reactions of (**14**) and (**26**) with $B(C_6F_5)_3$ are carried out in a 2:1 molar ratio at room temperature, the complexes $\{[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)Me]_2(\mu\text{-}Me)\}[MeB(C_6F_5)_3]$ [M = Zr (**29**), Hf (**30**)] can be obtained as a mixture of syn- and anti-isomers as shown by NMR spectroscopic observations. The formation of (**29**) and (**30**) implies the stabilization of the 14-electron cationic intermediate by interaction with one methyl group of the neutral complexes (**14**) and (**26**). Complexes (**27**) and (**28**) undergo heterolytic dissociation of the Metal–$MeB(C_6F_5)_3$ bonds, leading to the formation of the free $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)(CH_3)]^+$ 14-electron species, verified by ^{1}H DNMR spectroscopy. When compound (**27**) was heated at 50 °C the metallacyclic cation $[Zr(1\text{-}^tBu\text{-}3\text{-}CMe_2CH_2\text{-}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5H_5)]^+$ (**31**) was formed. The alkyl derivatives synthesized and reported herein, activated with

* Corresponding author.

[1] X-ray diffraction studies.

PII S0022-328X(97)00034-X

MAO, $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$, polymerize ethylene with very low activity. The molecular structure of $[Ti(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl(\mu\text{-}O)]_3$ **6** has been determined by X-ray diffraction methods. © 1997 Elsevier Science S.A.

Keywords: Titanium; Zirconium; Hafnium; Cyclopentadienyl derivatives; Cationic derivatives

1. Introduction

Group 4 metallocene derivatives have been widely used in recent years as homogeneous catalysts for olefin polymerization [1]. It is now widely accepted that the active intermediates in this process are coordinatively unsaturated 14-electron cationic alkyl species $[MCp_2R]^+$ (M = Ti, Zr; Cp = substituted or unsubstituted η^5-cyclopentadienyl ligand; R = alkyl group) [2]. These complexes can be generated in situ in the presence of the olefin, resulting in polymerization, or stabilized either by coordination of a donor ligand [3] or through cation–anion contact interactions [4]. Nevertheless, to the best of our knowledge, these compounds have seldom been directly observed as pure 14-electron base-free species [5].

Investigations have subsequently revealed a direct dependence of the activity and stereoselectivity of the polymerization process on the coordination geometry of the metal center of a particular catalyst. Particularly interesting is the effect of the substituents in the cyclopentadienyl ligands [6], which has stimulated considerable efforts to develop catalysts able to produce polymers with special properties and to find models to study the different steps of the olefin polymerization process.

Less saturated and sterically less hindered monocyclopentadienyl complexes have not been so extensively studied, although they also behave as useful catalysts particularly for styrene polymerization [7]. 1,3-Di(*tert*-butyl)cyclopentadienyl is a convenient bulky ligand to obtain scarcely active titanocene and zirconocene complexes which can be used to carry out NMR studies of polymerization intermediates.

In this paper we report the preparation of the reagents $K^+[(1,3\text{-}^tBu_2C_5H_3)]^-(THF)_{1-3}$ **2** and $Si(1,3\text{-}^tBu_2C_5H_3)(CH_3)_3$ **3** used to transfer the di(*tert*-butyl)cyclopentadienyl ligand for the synthesis of neutral and cationic titanium, zirconium and hafnium complexes. We herein describe the synthesis of monocyclopentadienyl trichloro, dioxo-chloro and dimethyl-chloro titanium derivatives, and the mixed dicyclopentadienyl chloro-alkyl, dialkyl and metallacyclic titanium and zirconium complexes, along with the synthesis of cationic titanium, zirconium and hafnium derivatives.

2. Results and discussion

2.1. Neutral complexes

The reaction of a THF solution containing a mixture of 1,3- and 1,4-di(*tert*-butyl)cyclopentadiene [8] **1** with KH at −78 °C gave the $K^+(1,3\text{-}^tBu_2C_5H_3)^-(THF)_{1-3}$ **2** salt as a white solid. When a hexane suspension of **2** was treated with chlorotrimethylsilane in a 1:1 molar ratio, the air-stable trimethyl[2,5-di(*tert*-butyl)cyclopentadienyl]silane derivative **3** was obtained as a yellow oil soluble in hexane (Scheme 1).

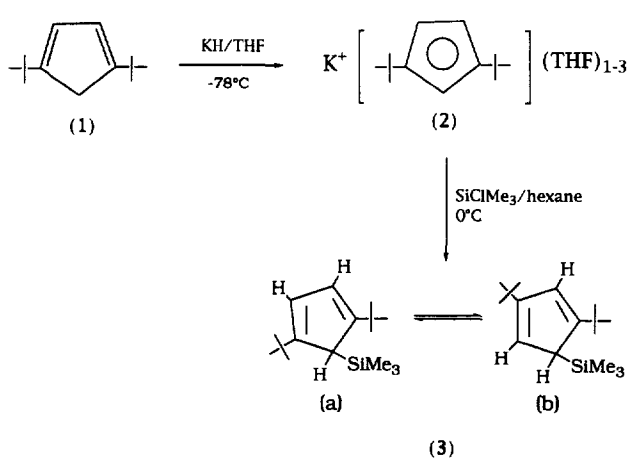
The ^1H NMR spectrum of **2** in d_5-pyridine indicates the coordination of three molecules of THF which were partially eliminated when the solid was maintained overnight under vacuum.

The ^1H NMR spectrum of **3** is temperature dependent and shows the expected sigmatropic rearrangement [9] leading to the interconversion of isomers (a) and (b) in the NMR time scale (Scheme 1). At −50 °C (500 MHz) the ^1H NMR spectrum in toluene-d_8 shows two signals for the *tert*-butyl protons, one singlet for the methyl–silyl groups along with one singlet and one AB spin system ($^4J_{H-H}$ = 1.5 Hz) for the ring protons, which corresponds to isomer (b) (> 90%), whereas at room temperature only one singlet (18H) for the *tert*-butyl protons, two very broad and one broad signals for the ring protons are observed.

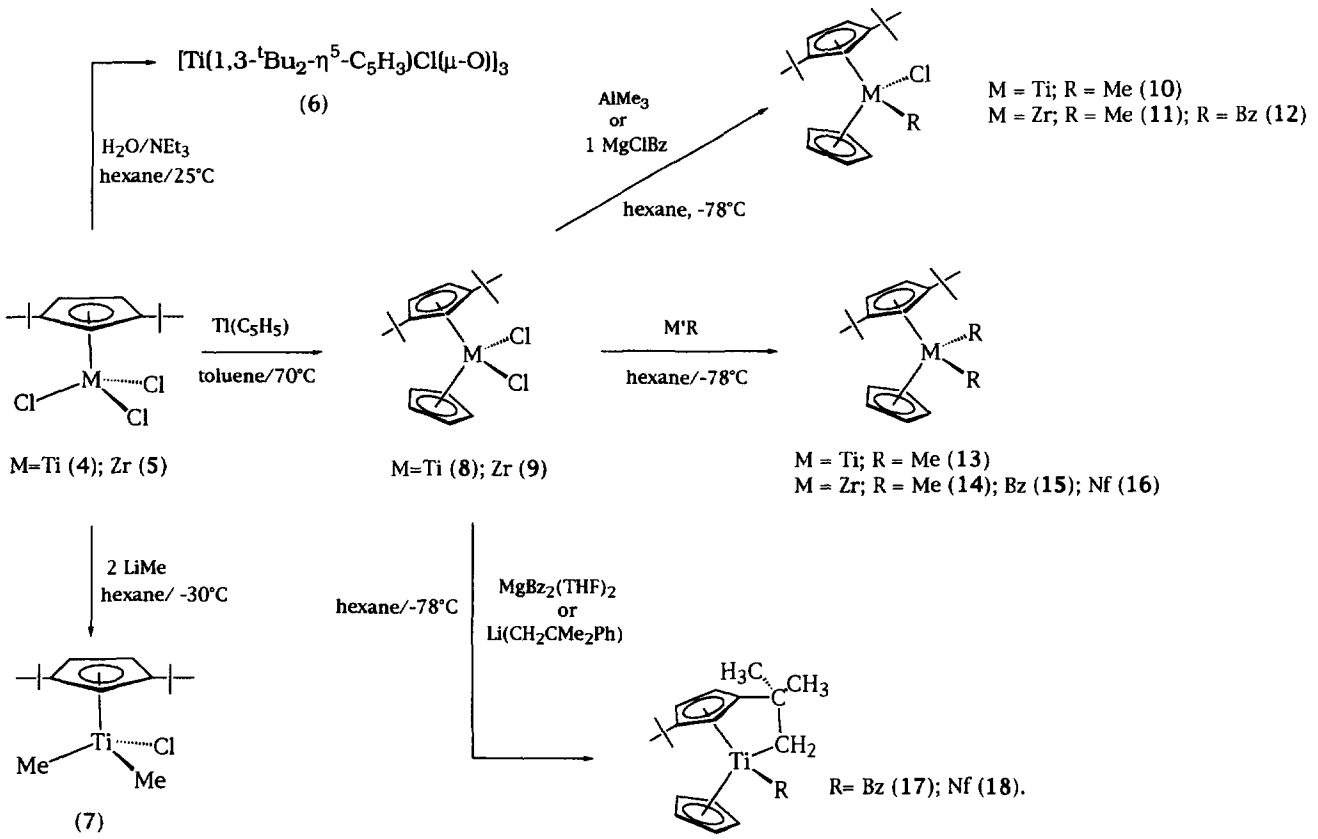
Reaction of **3** with MCl_4 in toluene or hexane at room temperature provides a route to the monocyclopentadienyl trichlorometal complexes $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl_3$ [M = Ti (**4**), Zr (**5**)] [10].

Addition of a stoichiometric amount of water, in the presence of NEt_3, to a toluene solution of **4** afforded the μ-oxo trimer $[Ti(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl(\mu\text{-}O)]_3$ **6** in a diastereoselective way (Scheme 2). Attempts to hydrolyze the remaining Ti–Cl bonds by further addition of water were unsuccessful, indicating that the bulky *tert*-butyl substituents hinder the approach of the reagent.

The ^1H NMR spectrum of **6** at room temperature in



Scheme 1.



Scheme 2.

C_6D_6 shows the presence of three singlets for the *tert*-butyl protons along with one ABC and one ABB' spin system (1:2 ratio) for the cyclopentadienyl ring protons, in agreement with the meso structural disposition shown in Fig. 1(A) containing two inequivalent types of cyclopentadienyl ring, with a structure similar to those previously reported for $[Ti(C_5H_{5-n}Me_n)X(\mu\text{-}O)]_3$ (X = Cl [11], Br [12] and Me [13]). The cyclopentadienyl ligand located in anti position gives one singlet for both equivalent *tert*-butyl groups (18H) and one ABB' spin system for the ring protons (Fig. 1(B)), whereas the two equivalent enantiotopic cyclopentadienyl groups occupying syn positions and bonded to chiral titanium centers show two inequivalent *tert*-butyl groups and ring protons corresponding to an ABC spin system (Fig. 1(C)).

When a hexane solution of **4** was treated at −30 °C, with 2 equiv. of LiMe, the chloro dimethyl complex $Ti(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl(CH_3)_2$ **7** was isolated as an orange oil, after filtration and evaporation of the solvent. The same reaction with MgClMe or MgClBz produced a mixture of compounds which could not be resolved. The mixed dicyclopentadienyl compounds $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)Cl_2$ [M = Ti (**8**); Zr (**9**)] were obtained by reaction of complexes **4** and **5** with $Tl(C_5H_5)$. Reactions of **8** and **9** with 1 equiv. of $AlMe_3$ or MgClR in hexane at −78 °C afforded the chloro alkyl derivatives $M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)ClR$ [M

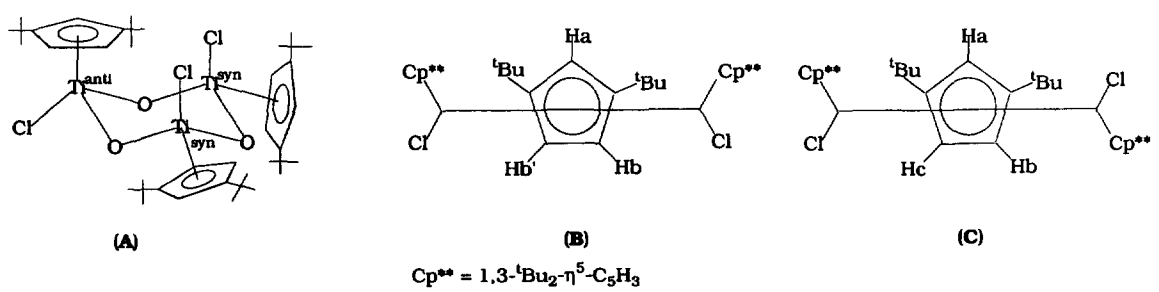
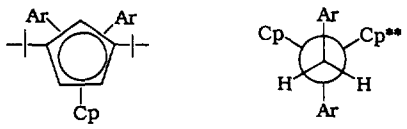


Fig. 1. (A) Structural disposition for compound **6**. (B) Viewed along the Ti–(1,3-$^tBu_2$-η^5-C_5H_3) centroid anti bond. (C) Viewed along the Ti–(1,3-$^tBu_2$-η^5-C_5H_3) centroid syn bond.



Ar = Bz, Nf
Cp = η^5-C_5H_5
Cp** = 1,3-^{t}Bu$_2$-η^5-C_5H_3

Fig. 2. Prochiral arrangement of the metal center in compounds **15** and **16**. (A) Viewed along the Zr–C(Bz) bond. (B) Viewed along the Zr–(1,3-^{t}Bu$_2$-η^5-C_5H_3) centroid bond.

= Ti, R = Me (**10**); M = Zr, R = Me (**11**), Bz (**12**)]. The use of other alkylating agents led to intractable mixtures even at low temperatures, as confirmed by NMR spectroscopy. When the same reaction in hexane at −78 °C was carried out with 2 equiv. of the corresponding alkylating agent, the dialkyl complexes M(1,3-^{t}Bu$_2$-η^5-C_5H_3)(C_5H_5)R_2 [M = Ti, R = Me (**13**); Zr, R = Me (**14**), Bz (**15**), Nf (**16**)] were obtained (Scheme 2).

Complexes **7–16** were characterized by their analytical composition and NMR spectroscopy. The ^{1}H NMR spectra of compounds **7–9** and **13–16** show one singlet for the *tert*-butyl protons, one signal for the C_5H_5 protons and one AA'B spin system [one pseudo-doublet (2H) and one pseudo-triplet (1H)] for the cyclopentadienyl ring protons (Fig. 2(A)). The expected resonances for the alkyl groups bonded to the metal center are also observed (see Section 3). The methylene protons of the benzyl and neophyl groups appear as an AB spin system at $\delta_{av.}$ = 2.02 (^2J = 6.4 Hz) in complex **15** and at δ = 0.66 and 1.56 (^2J = 12.4 Hz) in complex **16** (Fig. 2(B)). The ^{13}C–^{1}H NMR spectrum of **16** shows two signals (δ 35.3 and 35.6) for the methyl carbons of the neophyl ligand.

The chiral character of the metal center in compounds **10–12** makes both *tert*-butyl groups and the cyclopentadienyl protons of the 1,3-^{t}Bu$_2$-η^5-C_5H_3 ligand inequivalent, their ^{1}H NMR spectra showing two singlets and one ABC spin system respectively. The presence of an AB spin system at $\delta_{av.}$ = 2.46 for the methylene protons in compound **12** also indicates its chiral character.

Whereas compounds **13–16** can be obtained as pure samples in the solid state and characterized by analytical methods, the related dibenzyl and dineophyl titanium derivatives could not be obtained by treatment of **8** with 2 equiv. of $MgBz_2(THF)_2$ or $LiCH_2CMe_2Ph$. Instead, the formation of toluene or *tert*-butyl benzene was observed and the ring methyl-metallated complexes Ti(1-^{t}Bu-3-CH_2CMe_2-η^5-C_5H_3)(C_5H_5)R [R = Bz (**17**); Nf (**18**)] were isolated as red oils at room temperature (Scheme 2). The metallacyclic complexes result from the intramolecular activation of one of the cyclopentadienyl-bonded *tert*-butyl groups with elimination of the corresponding hydrocarbon [14]. This behavior is consistent with the higher steric requirement of the bulkier benzyl and neophyl substituents bonded to the smaller titanium centre. Complexes **17** and **18** exhibit a high-field shifted AB spin system in the ^{1}H NMR for the diastereotopic metallacyclic methylene protons [δ −2.05, −0.57 (J_{H-H} = 9.9 Hz) (**17**) and −2.21, −0.46 (J_{H-H} = 9.6 Hz) (**18**)]

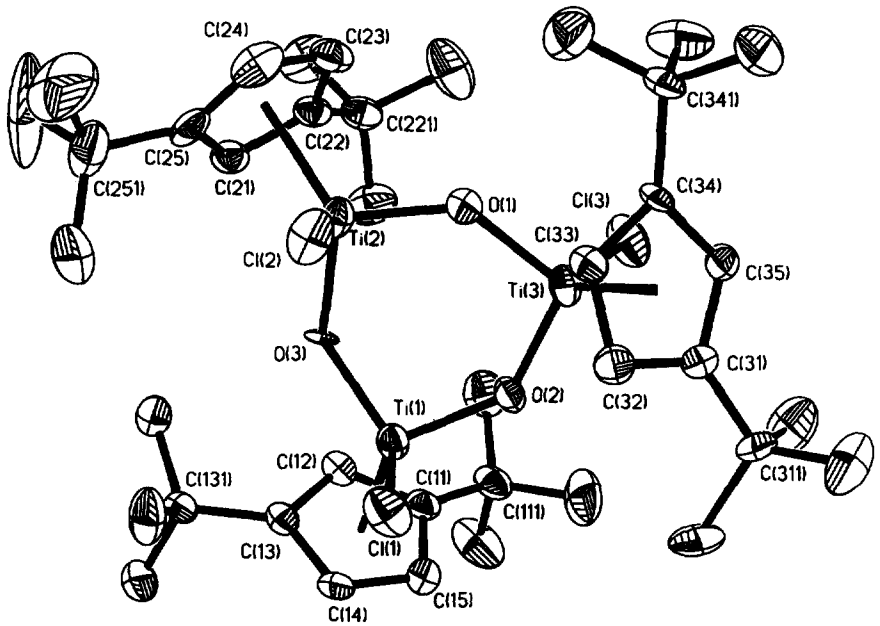


Fig. 3. ORTEP drawing view of the molecular structure of compound **6** along with the atomic labeling scheme.

Table 1
Selected bond lengths (Å) and angles (deg) for compound **6**

Ti(1)–O(3)	1.806(4)	Ti(1)–O(2)	1.813(3)
Ti(1)–Cl(1)	2.288(2)	Ti(1)–C(14)	2.363(6)
Ti(1)–C(12)	2.367(5)	Ti(1)–C(15)	2.382(6)
Ti(1)–C(13)	2.387(5)	Ti(1)–C(11)	2.425(5)
Ti(2)–O(1)	1.818(3)	Ti(2)–O(3)	1.835(5)
Ti(2)–Cl(2)	2.284(2)	Ti(2)–C(23)	2.364(7)
Ti(2)–C(21)	2.372(5)	Ti(2)–C(22)	2.378(5)
Ti(2)–C(24)	2.385(7)	Ti(2)–C(25)	2.438(5)
Ti(3)–O(1)	1.819(3)	Ti(3)–O(2)	1.824(4)
Ti(3)–Cl(3)	2.257(2)	Ti(3)–C(33)	2.333(5)
Ti(3)–C(32)	2.343(5)	Ti(3)–C(35)	2.395(5)
Ti(3)–C(34)	2.401(7)	Ti(3)–C(31)	2.409(6)
Ti(1)–Cp1	2.057	Ti(2)–Cp2	2.065
Ti(3)–Cp3	2.052		
O(3)–Ti(1)–O(2)	103.0(2)	O(3)–Ti(1)–Cl(1)	103.4(1)
O(2)–Ti(1)–Cl(1)	99.1(1)	O(1)–Ti(2)–O(3)	101.1(2)
O(1)–Ti(2)–Cl(2)	101.4(1)	O(3)–Ti(2)–Cl(2)	101.9(1)
O(1)–Ti(3)–O(2)	101.5(2)	O(1)–Ti(3)–Cl(3)	104.0(1)
O(2)–Ti(3)–Cl(3)	102.1(1)	Ti(2)–O(1)–Ti(3)	137.1(2)
Ti(1)–O(2)–Ti(3)	135.2(2)	Ti(1)–O(3)–Ti(2)	134.2(2)
O(2)–Ti(1)–Cp1	118	O(3)–Ti(1)–Cp1	117
Cl(1)–Ti(1)–Cp1	113	Cl(2)–Ti(2)–Cp2	112
O(3)–Ti(2)–Cp2	122	O(1)–Ti(2)–Cp2	114
Cl(3)–Ti(3)–Cp3	115	O(2)–Ti(3)–Cp3	117
O(1)–Ti(3)–Cp3	114		

Cp1 is the centroid of C(11)...C(15); Cp2 is the centroid of C(21)...C(25); Cp3 is the centroid of C(31)...C(35).

2.2. Crystal structure of complex [Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)Cl(μ-O)]$_3$ 6

The molecular structure of complex **6** was determined by X-ray diffraction methods. Fig. 3 shows an ORTEP drawing of the molecular structure along with the atomic labeling scheme used. Selected bond distances and bond angles are listed in Table 1.

The molecular structure shows a cyclic trinuclear system consisting of three 'Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)Cl' units bonded by oxygen bridges. Each titanium shows a three-legged piano stool coordination, where the legs are formed by the chlorine and the two oxygen atoms. With respect to the central ring, two (1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$) rings are located above and the other one below the mean plane, with the opposite disposition for the chlorine atoms. These structural features are similar to those previously reported for the complexes [TiCp*ClO]$_3$ [11], [TiCp*BrO]$_3$ [12] or [TiCp*MeO]$_3$ [13] (Cp* = C$_5$H$_{5-n}$Me$_n$), but in contrast, the central ring for compound **6** shows a 'chair' configuration (Fig. 3), instead of the 'boat ' or 'semi-boat' disposition found in the other cases [11,12].

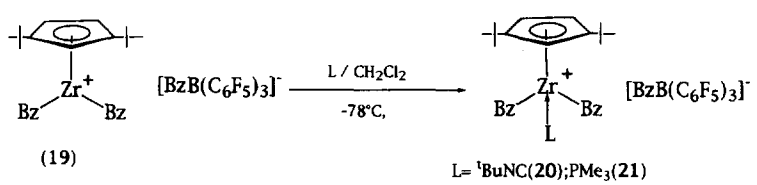
The Cp–centroid, Ti–O, Ti–C and C–C distances and the corresponding angles are unexceptional.

If we consider the plane defined by Ti(1), Ti(2), O(1) and O(2), the O(3) atom is located 0.317 Å above it and Ti(3) is 0.274 Å below in order to minimize the interactions between the bulky Cp rings and the central ring. Also related to this feature are the deviations of the central carbon of the *tert*-butyl groups from the Cp ring plane observed in compound **6**. In all the cases these carbon atoms are above this plane with distances ranging from 0.111 Å to 0.254 Å. The greatest distance corresponds to C(111), for which one of the carbon atoms of its methyl groups is located 3.278 Å from O(2).

2.3. Cationic complexes

Following a well known and extensively used method, the cationic mono 1,3-di(*tert*-butyl)cyclopentadienyl dibenzyl zirconium species [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_2$]$^+$ (**19**) was obtained in situ by reacting the tribenzyl derivative Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_3$ with B(C$_6$F$_5$)$_3$ or [CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, and its dynamic NMR behaviour in CD_2Cl_2 solutions at low temperatures has been reported [10] to be a typical η^3-benzallylic isomerization of one of the benzyl groups. When ^{t}BuNC or PMe_3 was added to a solution of **19** in CD_2Cl_2 at −78 °C an instantaneous change to a yellow-orange colour was observed and the formation of the new cationic complexes [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(L)(CH$_2$Ph)$_2$]$^+$ [L = ^{t}BuNC (**20**); PMe_3 (**21**)] (Scheme 3) was shown by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectra of complexes **20** and **21** show the presence of two equivalent *tert*-butyl groups, the expected AA'B spin system for the ring protons and two equivalent benzyl ligands with methylene groups containing diastereotopic protons (see Section 3 for details). The related reaction of M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_3$)$_3$ [M = Ti (**22**); Zr (**23**)] [10] with B(C$_6$F$_5$)$_3$ did not give identifiable materials. However, by addition of PMe_3 to this reaction mixture, the ligand coordinated cationic adducts [M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(PMe$_3$)$_2$(CH$_3$)$_2$]$^+$ [M = Ti (**24**); Zr (**25**)] can be obtained as orange-yellow solids stable at room temperature.



(19)

L= ^{t}BuNC(**20**);PMe$_3$(**21**)

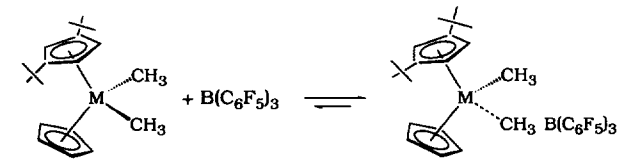
Scheme 3.

The ^1H NMR spectra of both compounds show equivalent methyl metal bonded groups as one triplet at δ 0.91 ($^3J_{H-P} = 9.0$ Hz) (**24**) and 0.86 ($^3J_{H-P} = 5.4$ Hz) (**25**). The $^{13}C\{^1H\}$ NMR spectrum for compound **24** shows one triplet at δ 74.9 ($^2J_{C-P} = 9.9$ Hz) for the titanium methyl bonded groups due to coupling with two equivalent cis ^{31}P nuclei. These data are in agreement with a pseudo-square pyramidal arrangement with the cyclopentadienyl ring occupying the axial position and the two methyl groups and two phosphine ligands located in the square base with a trans configuration (Scheme 4).

Complexes **20** and **21** are formally 12-electron systems, whereas **24** and **25** are 14-electron species. Several $[M(C_5H_{5-n}Me_n)(R)_2(L)_n]^+$ complexes have been reported [15–18], showing different structural dispositions. The 14-electron complex $[Zr(C_5Me_5)(CH_3)_2(THF)_2]^+$ adopts the same four-legged piano-stool structure with cis CH_3 groups, whereas the 16-electron compound $[Zr(C_5Me_5)(CH_3)_2(dmpe)(THF)]^+$ has a distorted octahedral structure with equatorial/axial coordination of the dmpe ligand trans to the phosphine ligand and the C_5Me_5 ring, and the two mutually trans CH_3 groups occupy the other two equatorial positions [15]. Similar $[M(C_5Me_5)(CH_3)_2(PMe_3)_2]^+$ (M = Ti, Zr, Hf) cations have only been spectroscopically identified [18], showing the same spectroscopic features observed for **24** and **25**. When R is benzyl, formally 12- and 14-electron THF complexes, $[Zr(C_5Me_5)(CH_2Ph)_2(THF)]^+$ [15], and $[Zr(C_5R_5)(CH_2Ph)_2(THF)_2]^+$ (R = H, Me) [17] have been reported, for which η^n interactions of the benzyl ligand with the zirconium atom have been proposed.

The related dicyclopentadienyl-type cationic complexes were prepared by reaction in toluene at room temperature of the dimethyl derivatives M(1,3-^{t}Bu$_2$-η^5-C_5H_3)(C_5H_5)(CH_3)$_2$ (M = Zr (**14**); Hf (**26**) [19]) with $B(C_6F_5)_3$ in a 1:1 molar ratio, leading to the complexes $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)(CH_3)]^+[(CH_3)B(C_6F_5)_3]^-$ [M = Zr (**27**); Hf (**28**)], obtained as yellow oils which can be stored for weeks in an inert atmosphere (Scheme 5). In contrast, the benzyl and neophyl derivatives **15** and **16** did not react with the boron reagent.

The ^1H NMR spectra of **27** and **28** in toluene-d_8 at room temperature show one singlet for the unsubstituted



M = Zr (**14**); Hf (**26**) M = Zr (**27**); Hf (**28**)

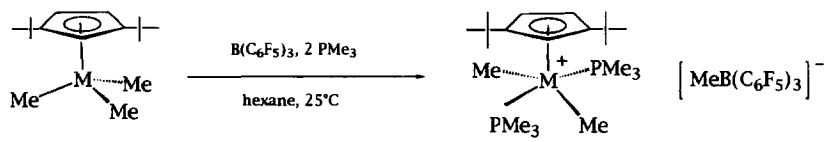
Scheme 5.

cyclopentadienyl ring protons, one singlet for the metal-bonded methyl protons, one broad signal for the boron-bonded methyl group and one singlet for both equivalent *tert*-butyl protons of the substituted cyclopentadienyl ligand. The ring protons of this ligand appear as one resolved triplet and one broad signal (1:2 ratio) for **27** and one triplet and two broad signals in a 1:1:1 ratio for **28** (see Section 3 for details). Variable-temperature ^1H NMR spectra, between 223 and 323 K, performed in $CD_3C_6D_5$ show a broadening of the resonances which suggests dynamic behaviour. Collapse points are observed at 253 K (**27**) and 278 K (**28**) for *tert*-butyl protons, 263 K (**27**) and 304 K (**28**) for the H_b protons of the cyclopentadienyl ligand. For complex (**28**) the coalescence for the methyl groups bonded to the metal center is also observed. The ^1H NMR spectra at 223 K show two signals for *tert*-butyl and three resolved multiplets for the ring protons.

These data are in agreement with the chiral character for the metal center at low temperature and dynamic behavior consistent with the loss of this chiral character at high temperature. A possible explanation of these features could be a typical intramolecular exchange between two sites of the same population. Table 2 summarizes the kinetic parameters for these exchange processes obtained by temperature dependence of life time values τ, calculated by using line shape analysis (DNMR5 program).

The obtained Arrhenius and Eyring plots are characterized by a reliable correlation parameters ($r > 0.999$) for nine experimental points in all cases. However, these kinetic data are not consistent with any exchange between two positions, since both ^{t}Bu groups and the H_b protons of the substituted $C_3H_5{}^tBu_2$ ring should reflect the same process, and must be characterized by the same values of kinetic parameters.

According to the DNMR theory [14] one of the probable explanations for the observed dynamic be-



M = Ti(**22**); Zr(**23**) M = Ti(**24**); Zr(**25**)

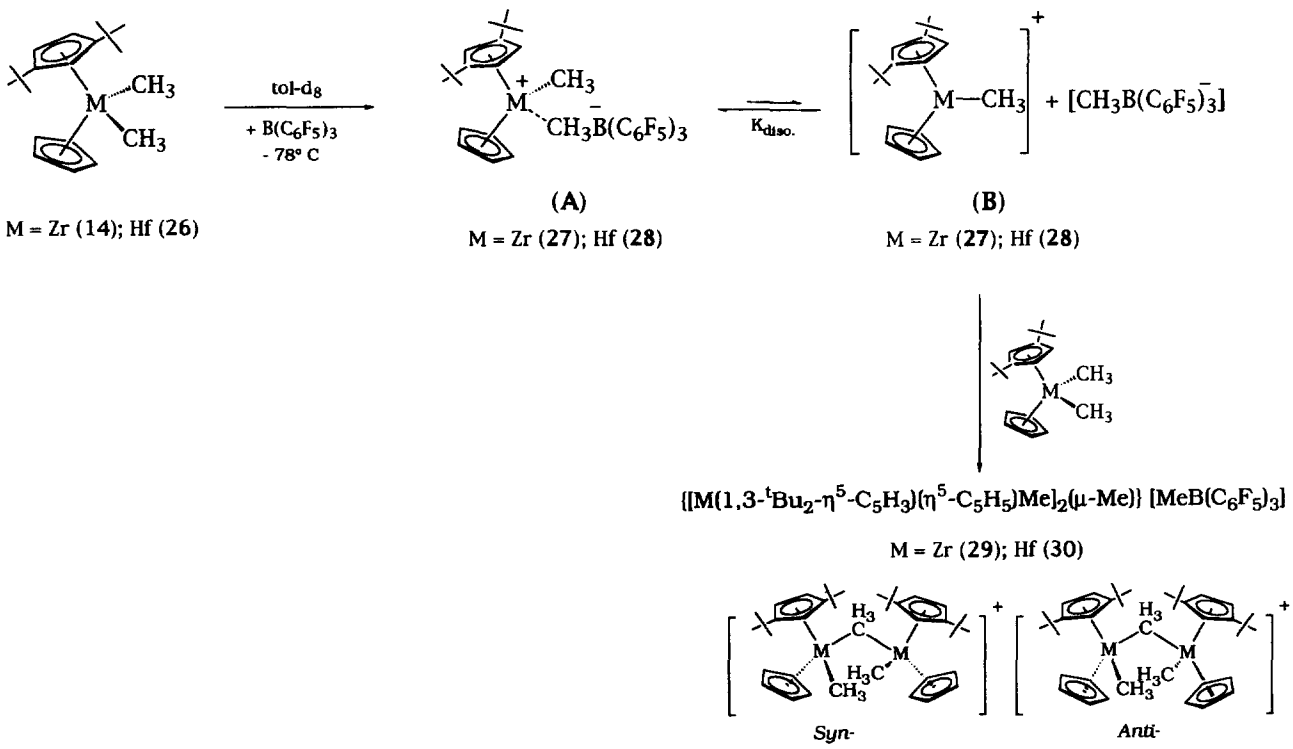
Scheme 4.

Table 2
Kinetic parameters of two sites mutual exchange between ^{t}Bu groups and H_b protons for complexes (**27**) and (**28**) in $CD_3C_6D_5$ solution (n is the number of experimental points, r is the correlation coefficient, τ is the life time values)

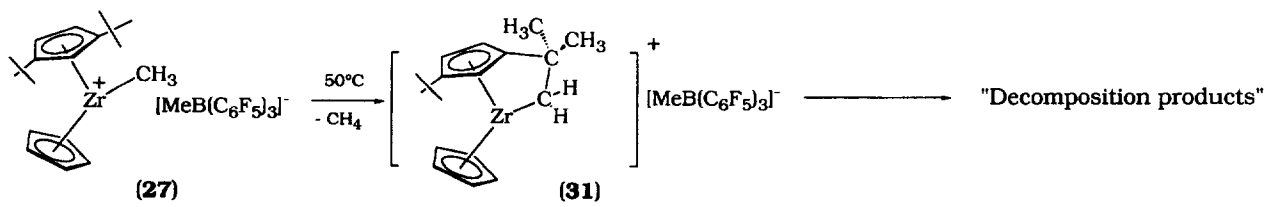
Complex	Signal	Interval t (°C)	Interval τ (s)	log A	E_a (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (e.u.)	$\Delta G^{\#298}$ (kcal mol^{-1})
(**27**)	^{t}Bu	−40 to +40 (n = 9)	0.044–0.0004	9.30 ± 0.07	8.4 ± 0.07 (r = 0.9997)	7.9 ± 0.07	−17.8 ± 0.3 (r = 0.9997)	13.2
[M = Zr]	H_b	−30 to +50 (n = 9)	0.042–0.000037	13.8 ± 0.3	13.9 ± 0.4 (r = 0.9973)	13.4 ± 0.4	+2.8 ± 1.3 (r = 0.9972)	12.6
(**28**)	^{t}Bu	−20 to +30 (n = 9)	0.0650–0.00145	11.1 ± 0.3	11.5 ± 0.35 (r = 0.997)	11.0 ± 0.3	−9.4 ± 1.2 (r = 0.997)	13.8
[M = Hf]	H_b	−5 to +50 (n = 9)	0.0320–0.000017	14.8 ± 0.3	16.4 ± 0.5 (r = 0.997)	15.8 ± 0.5	+7.4 ± 1.7 (r = 0.997)	13.6

haviour may be the exchange of three NMR sites with the third position characterized by a very low population. We have studied theoretically by DNMR5 program the exchange between two nonequivalent *tert*-butyl groups in (**27**) and (**28**) with the equivalent *tert*-butyl groups in a third system with 3% population. These computer-simulated experiments showed very good agreement between the theoretical and experimentally observed spectra. Moreover, the results of this calculation show a very large line width at the third position, including in the slow exchange region, making impossible the direct observation of the corresponding signal in the NMR spectra, when the reaction is carried out in a 1:1 molar ratio. This third NMR position could be considered as the complexes (**14**) and (**26**), involving a B–C bond homolytic dissociation or the base-free 14-electron species $[M(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)(C_5H_5)(CH_3)]^+$ generated by heterolytic dissociation of the M–C bond [20,21].

To check these possibilities, the reactions of $B(C_6F_5)_3$ with an excess of the complexes (**14**) and (**26**) were carried out. The presence of (**14**), (**27**) and (**26**), (**28**) was not observed in the ^{1}H NMR spectra of the final product of such reactions. The ^{1}H NMR spectra in toluene-d_8 at −50 °C show the formation of new cationic dimer species (**29**) and (**30**), characterized by the presence of two chiral metal centers in the same molecule with two syn- and anti-isomers (Scheme 6). The resonances for the methyl groups bridging both metal atoms at high field, the terminal methyl and the



Scheme 6.



Scheme 7.

methyl bonded to boron were detected (see Section 3) in the ^{1}H NMR spectra in toluene-d_8 at −50 °C.

Complexes (**29**) and (**30**) can be considered as containing a 14-electron cationic fragment [M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(C$_5$H$_5$)(CH$_3$)]$^+$ stabilized by adduct formation with one molecule of the neutral dimethyl metallocene complexes M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(C$_5$H$_5$)(CH$_3$)$_2$ as ligands [22].

The structural behavior observed can be explained by the reactions shown in Scheme 6.

The reactions of complexes (**14**) and (**26**) with B(C$_6$F$_5$)$_3$ led to the contact ion pair disposition (**A**) for (**27**) and (**28**) in which the metal–MeB(C$_6$F$_5$)$_3$ bond dissociates heterolytically, giving the base-free 14-electron cations [M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(C$_5$H$_5$)(CH$_3$)]$^+$ shown for (**B**), which are stabilized by interaction with one methyl group of the neutral complexes (**14**) and (**26**).

These results agree with the formation of a base-free [MCp$_2$R]$^+$ 14-electron species [5], which is believed to be the active species in homogeneous Ziegler–Natta polymerization of α-olefins. The base-free complex [Zr(F$_6$-acen)(CH$_2$CMe$_3$)]$^+$ has been recently reported [23]. These chemical data also confirm the dynamic behaviour observed in the DNMR spectroscopic studies.

Compound (**27**) decomposes when heated at 50 °C via the formation of the ring methyl-metallated cation [Zr(1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)]$^+$ (**31**) (Scheme 7).

Apparently, the metallacyclic complex results from the intramolecular activation of one C–H bond of the cyclopentadienyl-bonded *tert*-butyl group with elimination of methane [14]. Formation of (**31**) was shown by the presence of two doublets at δ −0.11 and −1.67 (J_{H-H} = 12 Hz) in the ^{1}H NMR spectrum in C$_6$D$_6$, assignable to the AB spin system corresponding to the methylene protons of the metallacyclic ring. The protons of the normal *tert*-butyl group appear as one singlet at δ 0.62 whereas the methyl protons in the activated *tert*-butyl group give two singlets at δ 0.85 and 1.30. One singlet at δ 5.59 for the η^5-C$_5$H$_5$ ring and the ABC spin system of the substituted *tert*-butyl ring are observed. The presence of methane was detected in the ^{1}H NMR spectrum. A similar C–H activation process was also observed at 50 °C for the hafnium compound (**28**) followed by its decomposition to give unidentifiable products.

The alkyl derivatives reported here polymerize ethylene, in the presence of MAO, B(C$_6$F$_5$)$_3$ or [Ph$_3$C][B(C$_6$F$_5$)$_4$], with very low activity, probably due to the steric hindrance produced by the presence of two bulky ^{t}Bu substituents in the cyclopentadienyl ring, blocking the coordination sphere of the metal. The benzyl and neophyl complexes M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(C$_5$H$_5$)R$_2$ (**15** and **16**) did not react with B(C$_6$F$_5$)$_3$ or [Ph$_3$C][B(C$_6$F$_5$)$_4$].

3. Experimental section

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium amalgam for hexane and sodium–benzophenone for diethyl ether). KH, PMe$_3$ (1 M toluene solution), AlMe$_3$ (2 M toluene solution), MgClMe (3 M tetrahydrofuran solution) and MgCl(CH$_2$Ph) (3 M tetrahydrofuran solution) (Aldrich), ^{t}BuNC and LiMe (1.6 M diethyl ether solution) (Fluka) and NEt$_3$ (Panreac) were obtained commercially. Li(CH$_2$CMe$_2$Ph) was prepared in hexane (in almost quantitative yield) as a free solvent solid from Li and ClCH$_2$CMe$_2$Ph. M(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)X$_3$ (M = Ti, Zr; X = Cl, CH$_3$; **4**, **22**, **5** and **23**) [10], Hf(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5 − C$_5$H$_5$)(CH$_3$)$_2$ **26** [19], ^{t}Bu$_2$(C$_5$H$_4$) [24], Mg(CH$_2$Ph)$_2$(THF)$_2$ [25], Tl(C$_5$H$_5$) [26], B(C$_6$F$_5$)$_3$ [27] were prepared as described in the literature. Electron impact (EI) mass spectra were recorded at 70 eV on a Hewlett-Packard 5890 spectrometer, only selected MS are reported. NMR spectra were recorded on a Varian Unity 300 and Varian Unity 500-Plus spectrometers. ^{1}H and ^{13}C chemical shifts are reported in δ units relative to TMS standard, ^{31}P chemical shift was referenced to 85% H$_3$PO$_4$. C and H microanalyses were performed on a Perkin–Elmer 240B microanalyzer. (The chloro alkyl derivatives **10**–**12**, the compound **18** and the cationic complexes were slightly impure even after several recrystallizations. None of them could be correctly characterized by elemental analysis.)

3.1. Synthesis of K(1,3-^{t}Bu$_2$C$_5$H$_3$)(THF)$_2$ 2

H^{t}Bu$_2$C$_5$H$_3$ **1** (24.11 ml, 113.58 mmol) was added at −78 °C under argon to a suspension of KH (5 g,

124.65 mmol) in THF (400 ml). The reaction mixture was slowly warmed to room temperature and stirred for 24 h to give a white suspension. The solution was filtered leaving a white solid which was washed with dry hexane (3 × 100 ml) and characterized as **2** (22.3 g, 90% yield). Anal. Calc. for $C_{25}H_{45}KO_3$: C, 69.39; H, 10.48. Found: C, 69.20; H, 10.60. ^{1}H NMR (300 MHz, pyridine-d_5, 25 °C): δ 1.54 (s, 18H, ^{t}Bu); 4.95 (m, 2H, C_5H_3); 6.09 (m, 1H, C_5H_3); 1.59, 3.63 (m, 24H, THF).

3.2. Synthesis of Si(^{t}Bu$_2$C$_5$H$_3$)Me$_3$ 3

$SiClMe_3$ (21.52 ml, 0.17 mol) was added at 0 °C under argon to a suspension of K(1,3-^{t}Bu$_2$C$_5$H$_3$)(THF)$_2$, **2**, (24.57 g, 113.58 mmol) in hexane (300 ml). The reaction mixture was stirred for 2 h and then slowly warmed to room temperature. After filtration, the solvent was evaporated under reduced pressure to give a yellow oil which was characterized as **3** (32 ml, 90% yield). Anal. Calc. for $C_{16}H_{30}Si$: C, 76.72; H, 12.07. Found: C, 76.99; H, 12.44. ^{1}H NMR (300 MHz, toluene-d_8, 25 °C): δ 0.04 (s, 9H, Si–CH_3); 1.22 (s, 18H, ^{t}Bu); 3.40 (br, 1H, C_5H_3); 5.90 (br, 1H, C_5H_3); 6.50 (s, 1H, C_5H_3). ^{1}H NMR (500 MHz, toluene-d_8, −50 °C): δ 0.18 (s, 9H, Si–CH_3); 1.32 (s, 9H, ^{t}Bu); 1.36 (s, 9H, ^{t}Bu); 3.46 (s, 1H, C_5H_3); 6.03 (d, 1H, J = 1.5 Hz, C_5H_3); 6.58 (d, 1H, C_5H_3).

3.3. Synthesis of [Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)ClO]$_3$ 6

0.2 ml (11 mmol) of H_2O and 1.67 ml (12.12 mmol) of NEt_3 were added to a solution of Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)Cl_3, **4**, (2 g, 6.06 mmol) in 30 ml of CH_2Cl_2, at room temperature, by syringe. The solution was stirred for 24 h, filtered, and the solvent was evaporated under vacuum to leave a yellow solid which was characterized as **6** (1.31 g, 80% yield). Anal. Calc. for $C_{39}H_{63}Cl_3O_3Ti_3$: C, 56.44; H, 7.65. Found: C, 56.65; H, 7.57. ^{1}H NMR (500 MHz, benzene-d_6, 25 °C): δ 1.34 (s, 18H, ^{t}Bu$_{trans}$); 1.35 (s, 18H, ^{t}Bu$_{cis}$); 1.40 (s, 18H, ^{t}Bu$_{cis}$); 6.22 (dd, 2H, J = 2.5, 3.5 Hz, C_5H_{3cis}); 6.42 (t, 2H, J = 2.5 Hz, C_5H_{3cis}); 6.59 (dd, 2H, J = 2.5, 3.5 Hz, C_5H_{3cis}); 6.57 (t, 2H, J = 2.5 Hz, C_5H_{3trans}); 6.85 (d, 2H, J = 2.5 Hz, C_5H_{3trans}). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 25 °C): δ 31.3, 31.3, 31.4 [C(CH_3)$_3$]; 31.6, 31.6, 31.7 [C(CH$_3$)$_3$]; 112.8, 113.8, 115.3, 115.6, 116.8, 147.6, 147.9, 148.7 (C_5H_3).

3.4. Synthesis of Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)ClMe$_2$ 7

A 1.6 M solution of LiMe in diethyl ether (2.42 ml, 3.88 mmol) was added to a hexane (30 ml) solution containing Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)Cl_3, **4**, (0.65 g, 1.95 mmol) at −40 °C. The reaction mixture was stirred for 4 h and warmed to room temperature to give an orange solution. After filtration, the solvent was evaporated under vacuum to leave an orange oil which was characterized as **7** (0.45 g, 80% yield). Anal. Calc. for $C_{15}H_{27}ClTi$: C, 61.97; H, 9.36. Found: C, 62.15; H, 10.10. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.79 (s, 6H, Ti–Me); 1.28 (s, 18H, ^{t}Bu); 5.99 (d, 2H, J = 2.25 Hz, C_5H_3); 6.36 (t, 1H, C_5H_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 31.3 [C(CH$_3$)$_3$]; 31.4 [C(CH_3)$_3$]; 53.4 (Ti–Me); 107.7, 107.9 (C_5H_3); 143.6 (C_{ipso}, C_5H_3).

3.5. Synthesis of Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)Cl$_2$ 8

TlCp (1.62 g, 6.03 mmol) was added to a solution containing Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)Cl_3, **4**, (2 g, 6.03 mmol) in toluene (100 ml). The reaction mixture was stirred under reflux overnight to give a red solution. After filtration, the solvent was removed in vacuo to give a red solid which was characterized as **8** (1.96 g, 90% yield). Anal. Calc. for $C_{18}H_{26}Cl_2Ti$: C, 59.85; H, 7.25. Found: C, 59.09; H, 7.26. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.15 (s, 18H, ^{t}Bu); 5.86 (d, 2H, J = 2.3 Hz, C_5H_3); 6.14 (s, 5H, C_5H_5); 6.40 (t, 1H, J = 2.3 Hz, C_5H_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 30.9 [C(CH_3)$_3$]; 34.9 [C(CH$_3$)$_3$]; 115.5, 117.3 (C_5H_3); 120 (C_5H_5); 150.3 (C_{ipso}, C_5H_3). EI/MS (70 eV) m/z [assignment, rel. int. (%)]: 361.1 [M^+, 1.48], 295 [$M^+ - C_5H_5$, 27.64].

3.6. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)Cl$_2$ 9

The same procedure described for the preparation of **8** using TlCp (2.79 g, 10.35 mmol) and Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)Cl_3, **5**, (3.88 g, 10.35 mmol) in toluene (100 ml) gave **9** (3.71 g, 88% yield). Anal. Calc. for $C_{18}H_{26}Cl_2Zr$: C, 53.44; H, 6.40. Found: C, 53.18; H, 6.47. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.90 (s, 18H, ^{t}Bu); 5.92 (d, 2H, J = 2.1 Hz, C_5H_3); 6.10 (s, 5H, C_5H_5); 6.16 (t, 1H, J = 2.1 Hz, C_5H_3). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 31.3 [C(CH_3)$_3$]; 33.8 [C(CH$_3$)$_3$]; 111.7, 111.8 (C_5H_3); 115.9 (C_5H_5); 143.4 (C_{ipso}, C_5H_3). EI/MS (70 eV) m/z [assignment, rel. int. (%)]: 404.2 [M^+, 23.92], 385 [$M^+ - CH_3$, 29.6].

3.7. Synthesis of Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)ClMe 10

A 2 M solution of $AlMe_3$ in toluene (0.49 ml, 1.47 mmol) was added to a solution containing Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl_2, **8**, (0.3 g, 0.83 mmol) in dichloromethane (30 ml), at 0 °C. The reaction mixture was stirred for 2 h and was then slowly warmed to room temperature and stirred for 30 min. The solvent was removed in vacuo and the residue recrystallized from dichloromethane–diethyl ether at −30 °C, to give a red microcrystalline solid which was characterized as **10** (0.24 g, 85% yield). ^{1}H NMR (300 MHz, benzene-d_6,

25 °C): δ 0.92 (s, 9H, ^{t}Bu); 1.06 (s, 3H, Ti–Me); 1.10 (s, 9H, ^{t}Bu); 5.47 (m, 1H, C_5H_3); 6.04 (s, 5H, C_5H_5); 6.43 (m, 1H, C_5H_3); 6.54 (m, 1H, C_5H_3). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 25 °C): δ 31.2 [C(CH_3)$_3$]; 31.4 [C(CH_3)$_3$]; 33.6 [C(CH$_3$)$_3$]; 49.1 (Ti–Me); 116.1 (C_5H_5); 106.7, 118.3, 119 (C_5H_3); 140.5 (C_{ipso}, C_5H_3); 141.3 (C_{ipso}, C_5H_3).

3.8. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)ClMe 11

The same procedure described to prepare **10** using Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **9** (0.25 g, 0.61 mmol) and a 2 M solution of AlMe$_3$ in toluene (0.37 ml, 0.74 mmol), gave **11**. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.01 (s, 9H, ^{t}Bu); 1.06 (s, 3H, Zr–Me); 1.15 (s, 9H, ^{t}Bu); 5.60 (m, 1H, C_5H_3); 6.02 (s, 5H, C_5H_5); 6.09 (m, 1H, C_5H_3); 6.22 (m, 1H, C_5H_3).

3.9. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl(CH_2Ph) 12

A 2 M solution of MgClBz in THF (1.35 ml, 2.71 mmol) was added to a solution containing Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **9**, (1 g, 2.47 mmol) in hexane (50 ml), at −40 °C. The reaction mixture was stirred for 3 h and then slowly warmed to room temperature. After filtration, the solvent was removed in vacuo to give an orange solid. Recrystallization from hexane at −30 °C gave an orange solid which was characterized as **12** (0.90 g, 80% yield). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.00 (s, 9H, ^{t}Bu); 1.11 (s, 9H, ^{t}Bu); 2.46 (AB, 2H, J = 2.41 Hz, CH_2Ph); 5.54 (m, 1H, C_5H_3); 5.89 (s, 5H, C_5H_5); 6.02 (m, 1H, C_5H_3); 6.16 (m, 1H, C_5H_3); 6.94 (m, 1H, CH_2Ph_{para}); 7.20 (m, 2H, CH_2Ph_{meta}); 7.29 (m, 2H, CH_2Ph_{ortho}). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 25 °C): δ 31.5 [C(CH_3)$_3$]; 31.6 [C(CH_3)$_3$]; 31.7 [C(CH$_3$)$_3$]; 32 (C_{ipso}, ^{t}Bu); 61.0 (CH_2Ph); 113.9 (C_5H_5); 104.3, 117.2, 121.7 (C_5H_3); 138.7 (C_{ipso}, C_5H_3); 140.1 (C_{ipso}, C_5H_3).

3.10. Synthesis of Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ 13

A 1.6 M solution of LiMe in diethyl ether (1.08 ml, 1.74 mmol) was added to a solution containing Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **8**, (0.3 g, 0.83 mmol) in hexane (30 ml), at −78 °C. The reaction mixture was stirred for 4 h and warmed to room temperature to give a red solution. After filtration, the solvent was removed under vacuum to leave a red oil which was characterized as **13** (0.21 g, 80% yield). Anal. Calc. for $C_{20}H_{32}Ti$: C, 74.96; H, 10.06. Found: C, 74.25; H, 10.29. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.21 (s, 6H, Ti–Me); 0.90 (s, 18 H, ^{t}Bu); 4.78 (t, 1H, J = 2.1 Hz, C_5H_3); 5.94 (s, 5H, C_5H_5); 6.84 (d, 2H, J = 2.1 Hz, C_5H_3). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 25 °C): δ 31.6 [C(CH_3)$_3$]; 33 [C(CH$_3$)$_3$]; 47.2 (Ti–Me); 113.9 (C_5H_5); 102.8, 117.8 (C_5H_3); 136.7 (C_{ipso}, C_5H_3).

3.11. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ 14

The same procedure described for the preparation of **13** using Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **9**, (1 g, 2.47 mmol) and 1.6 M solution of LiMe in diethyl ether (2.47 ml, 3.95 mmol) gave a white solid which was characterized as **14**. (0.89 g, 100% yield). Anal. Calc. for $C_{20}H_{32}Zr$: 66.05; H, 8.86. Found: C, 65.71; H, 8.87. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.05 (s, 6H, Zr–Me); 1.03 (s, 18 H, ^{t}Bu); 5.15 (t, 1H, J = 2.5 Hz, C_5H_3); 5.95 (s, 5H, C_5H_5); 6.34 (d, 2H, J = 2.5 Hz, C_5H_3). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 25 °C): δ 31.9 [C(CH_3)$_3$]; 32.7 (Zr–Me); 111 (C_5H_5); 100.4, 111.9 (C_5H_3); 136.8 (C_{ipso}, C_5H_3). EI/MS (70 eV) m/z [assignment, rel. int. (%)]: 363.20 [M$^+$, 9.54], 348.15 [M$^+$ − CH_3, 10.30].

3.12. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)(CH_2Ph)$_2$ 15

0.38 g of MgBz$_2$ · 2THF (1.08 mmol) was added to a solution of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **9**, (0.44 g, 1.08 mmol) in hexane (50 ml) at −78 °C. The reaction mixture was stirred for 4 h and then slowly warmed to room temperature. After filtration, the solvent was removed in vacuo to dryness, to give an orange solid which was characterized as **15**. (0.49 g, 90% yield). Anal. Calc. for $C_{32}H_{40}Zr$: C, 74.50; H, 7.81. Found: C, 74.20; H, 8.00. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.99 (s, 18H, ^{t}Bu); 2.02 (av.) (AB, 4H, J = 6.4 Hz, CH_2Ph); 5.22 (t, 1H, J = 2.4 Hz, C_5H_3); 5.75 (s, 5H, C_5H_5), 6.08 (d, 2H, J = 2.4 Hz, C_5H_3); 6.93 (m, 1H, CH_2Ph_{para}); 7.03 (m, 2H, CH_2Ph_{ortho}); 7.25 (m, 2H, CH_2Ph_{meta}). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 25 °C): δ 31.9 [C(CH_3)$_3$]; 33 [C(CH$_3$)$_3$]; 63.8 (t, J = 120 Hz, Zr–CH_2Ph); 112.3 (C_5H_5); 102.5, 113.9 (C_5H_3); 121.3 (CH_2Ph_{para}); 126.1 (CH_2Ph_{ortho}); 128.4 (CH_2Ph_{meta}); 154.3 (C_{ipso}, C_5H_3). EI/MS (70 eV) m/z [assignment, rel. int. (%)]: 424.3 [M$^+$ − C_7H_7, 14.96].

3.13. Synthesis of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)(CH_2CMe_2Ph)$_2$ 16

The same procedure described for the preparation of **15** using Li(CH_2CMe_2Ph) (0.50 g, 3.56 mmol) and Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Cl$_2$, **9**, (0.68 g, 1.69 mmol) in hexane (30 ml) at −78 °C, gave **16** as a yellow solid. (0.91 g, 90% yield). Anal. Calc. for $C_{38}H_{52}Zr$: C, 76.06; H, 8.73. Found: C, 75.80; H, 8.51.

^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 0.66, 1.56 (AB, 4H, J = 12.4 Hz, CH_2CMe$_2$Ph), 1.10 (s, 18H, ^{t}Bu); 1.48 (s, 12H, CH$_2$CMe_2Ph); 5.57 (t, 1H, J = 2.1 Hz, C$_5$H$_3$); 5.61 (s, 5H, C$_5$H$_5$), 5.91 (d, 2H, J = 2.1 Hz, C$_5$H$_3$); 7.12 (m, 2H, CH$_2$CMe$_2$$Ph_{para}$); 7.28 (m, 4H, CH$_2CMe_2$$Ph_{ortho}$); 7.48 (m, 4H, CH$_2CMe_2$$Ph_{meta}$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 32 [C(CH_3)$_3$]; 33.3 [C(CH$_3$)$_3$]; 35.3, 35.6 (CH$_2$CMe_2Ph); 43.3 (CH$_2$$CMe_2$Ph); 74.6 ($CH_2CMe_2$Ph); 109.4 (C$_5H_5$); 106.1, 110.7 (C$_5H_3$); 125.4 (CH$_2CMe_2$$Ph_{para}$); 126.5 (CH$_2CMe_2$$Ph_{ortho}$); 128.3 (CH$_2CMe_2$$Ph_{meta}$); 137.5 (C$_{ipso}$, C$_5H_3$); 153.6 (CH$_2CMe_2$$Ph_{ipso}$). EI/MS (70 eV) m/z [assignment, rel. int. (%)]: 332.04 [M$^+$ − C$_{20}$H$_{30}$, 76.15].

3.14. Synthesis of Ti(1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$)(η^5 − C$_5$H$_5$)(CH$_2$Ph) 17

0.34 g of MgBz$_2$(THF)$_2$ (0.99 mmol) was added to a hexane (30 ml) solution containing 0.3 g (0.83 mmol) of Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)Cl$_2$, **8**, at −80 °C. The reaction mixture was then slowly warmed to room temperature and stirred overnight. After filtration, the resulting solution was evaporated to dryness to give a yellow oil which was characterized as **17** (0.22 g, 70% yield). Anal. Calc. for C$_{25}$H$_{32}$Ti: C, 78.93; H, 8.47. Found: C, 78.86; H, 8.63. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ −0.25, −0.57 [AB, 2H, J = 9.9 Hz, (1-^{t}Bu-3-CMe$_2$CH_2-η^5-C$_5$H$_3$)]; 0.58, 2.29 (AB, 2H, J = 10.5 Hz, CH_2Ph); 1.05 (s, 9H, ^{t}Bu); 1.49 and 1.50 [6H, (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$)]; 4.38, 4.67, 6.79 [t, 1H, J = 2.4 Hz, (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$$H_3$)]; 5.57 (s, 5H, C$_5H_5$); 6.60 (m, 2H, CH$_2$$Ph_{ortho}$); 6.93 (m, 1H, CH$_2$$Ph_{para}$); 7.21 (m, CH$_2$$Ph_{meta}$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 28.4 (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$); 30.1 (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$); 31.7 (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$); 32.7 (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$), 33.3 [C(CH$_3$)$_3$], 48.8 [t, J = 134.6 Hz, (1-^{t}Bu-3-CMe$_2$$CH_2$-η^5-C$_5H_3$)]; 66.9 (Ti–$CH_2$Ph), 113.5 (C$_5H_5$), 105.9, 106.9, 114.2 (C$_5$H$_3$); 117.8, 143.3 (C$_{ipso}$, C$_5$H$_3$); 121.1 (CH$_2$$Ph_{para}$), 126.2 (CH$_2$$Ph_{ortho}$); 128.1 (CH$_2$$Ph_{meta}$), 155.4 (CH$_2$$Ph_{ipso}$).

3.15. Synthesis of Ti(1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)(CH$_2$CMe$_2$Ph) 18

The same procedure described for the preparation of **17** using Ti(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(η^5-C$_5$H$_5$)Cl$_2$, **8**, (0.3 g, 0.83 mmol) and LiNf (2.44 g, 1.74 mmol) at −80 °C gave **18** as a red oil (0.24 g, 70% yield). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ −2.21, −0.46 [AB, 2H, J = 9.6 Hz, (1-^{t}Bu-3-CMe$_2$CH_2-η^5-C$_5$H$_3$)]; 0.18, 1.61 (AB, 2H, J = 13.2 Hz, CH_2CMe$_2$Ph); 1.15 [s, 9H, (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$)]; 1.22, 1.27 [2s, 6H, (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$)]; 1.39, 1.46 (2s, 6H, CH$_2$CMe_2Ph); 4.33, 4.63, 6.69 [t, 1H, J = 2.4 Hz, (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$$H_3$)]; 5.60 (s, 5H, C$_5H_5$); 7.21 (m, 2H, CH$_2CMe_2$$Ph_{ortho}$); 7.26 (m, 1H, CH$_2CMe_2$$Ph_{para}$); 7.38 (m, 2H, CH$_2CMe_2$$Ph_{meta}$). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 25 °C): δ 28.6 (CH$_2$CMe_2Ph); 30.0 (CH$_2$CMe_2Ph); 31.3 (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$); 31.9 (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$); 32.2 (1-^{t}Bu-3-CMe$_2$CH$_2$-η^5-C$_5$H$_3$); 32.6 (1-^{t}Bu-3-CMe_2CH$_2$-η^5-C$_5$H$_3$); 32.8 [C(CH$_3$)$_3$]; 34.6 (CH$_2$$CMe_2$Ph); 39.2 (1-^{t}Bu-3-CMe$_2$$CH_2$-η^5-C$_5H_3$); 76.5 ($CH_2CMe_2$Ph); 111.5 (C$_5H_5$); 105.3, 106.5, 116.8 (C$_5$H$_3$); 115.2, 143.2 (C$_{ipso}$, C$_5$H$_3$).

3.16. Synthesis of [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_2$(^{t}BuNC)]$^+$[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]$^-$ 20

17 μl of ^{t}BuNC (0.15 mmol) was added, at −78 °C, to a solution of [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_2$]$^+$[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]$^-$, **19**, (0.15 g, 0.15 mmol) in dichloromethane (10 ml). The reaction mixture was stirred at −78 °C for 2 h and then slowly warmed to room temperature. The solvent was evaporated under vacuum to leave an orange oil which was solidified at −110 °C. The resulting solid was washed with 3 × 10 ml of hexane at −78 °C, the solid was dried in vacuo to give **20** as an orange oil at room temperature. (0.13 g, 80% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 1.22 (s, 18H, ^{t}Bu); 1.25 (s, 9H, ^{t}BuNC); 1.58 and 3.00 (2d, 4H, J = 9.0 Hz; CH_2Ph); 2.84 (br, 2H, B–CH_2Ph); 5.72 (d, 2H, J = 2.1 Hz, C$_5$$H_3$); 6.49 (t, 1H, J = 2.4 Hz, C$_5$$H_3$); 6.77 (m, 4H, CH$_2$$Ph_{ortho}$); 6.85 (m, 1H, B–CH$_2$$Ph_{para}$); 6.98 (m, 2H, CH$_2$$Ph_{para}$); 7.15 (m, 2H, B–CH$_2$$Ph_{meta}$); 7.23 (m, 4H, CH$_2$$Ph_{meta}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 28.8 (C$_{ipso}$ ^{t}BuNC); 29.2 (^{t}BuNC); 31.6 (^{t}Bu); 33.5 [C(CH$_3$)$_3$]; 68.2 (CH$_2$Ph); 69.4 (CH$_2$Ph); 105.3, 107.5 (C$_5$H$_3$); 126.7 (CH$_2$$Ph_{meta}$); 128 (B–CH$_2$$Ph_{para}$); 128.5 (CH$_2$$Ph_{para}$); 128.6 (B–CH$_2$$Ph_{meta}$); 130.8 (B–CH$_2$$Ph_{ortho}$); 132.1 (CH$_2$$Ph_{ortho}$); 143.5 (C$_{ipso}$ C$_5$H$_3$).

3.17. Synthesis of [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_2$(PMe$_3$)]$^+$[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]$^-$ 21

The same procedure described for the preparation of **20** using [Zr(1,3-^{t}Bu$_2$-η^5-C$_5$H$_3$)(CH$_2$Ph)$_2$]$^+$[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]$^-$, **19**, (0.15 g, 0.15 mmol) and PMe$_3$ (0.15 ml, 0.15 mmol) at −78 °C, gave **21** as an orange oil at room temperature (0.11 g, 70% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 0.75 (d, 9H, $^2J_{H-P}$ = 7 Hz, Zr–PMe$_3$); 1.25 (s, 18H, ^{t}Bu); 1.53, 2.81 (AB, 4H, J = 10 Hz; CH_2Ph); 2.91 (br, 2H, B–CH_2Ph); 6.01 (d, 2H, C$_5$$H_3$); 6.53 (2H, B–CH$_2$$Ph_{ortho}$); 6.77 (1H, C$_5$$H_3$); 6.82 (4H, CH$_2$$Ph_{meta}$); 6.94 (2H, CH$_2$$Ph_{para}$); 7.01 (2H, B–CH$_2$$Ph_{meta}$); 7.47 (4H, CH$_2$$Ph_{ortho}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 31.1 (d, $^1J_{C-P}$ = 25 Hz, PMe_3); 31.3

[C(CH_3)$_3$]; 33.4 [C(CH$_3$)$_3$]; 69.7 (CH_2Ph); 124.3, 125.3 (C_5H_3). $^{31}P\{^1H\}$ NMR: δ −3.58.

3.18. Synthesis of [Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)Me$_2$-(PMe$_3$)$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ 24

0.74 g of B(C_6F_5)$_3$ (1.44 mmol) were added to a solution containing 0.39 g of Ti(1,3-^{t}Bu$_2$-η^5-C_5H_3)Me$_3$, **22**, (1.44 mmol) and 2.89 mmol of PMe$_3$ (2.89 ml of a 1 M toluene solution) in a mixture of hexane–toluene (20 ml–20 ml), at −78 °C. The reaction mixture was stirred for 2 h and then slowly warmed to room temperature to give a red oil. After filtration, the oil was solidified at −110 °C to give a red solid which was washed with hexane (3 × 10 ml) at −78 °C, and obtained as an oil at room temperature which was characterized as **24**. (0.87 g, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.51 (br, 3H, B–CH$_3$); 0.91 (t, 6H, J_{H-P} = 9.0 Hz, Ti–Me); 1.13 (s, 18H, ^{t}Bu); 1.43 (d, 18H, J = 6.5 Hz, PMe$_3$); 6.12 (d, 2H, C_5H_3); 6.52 (t, 1H, C_5H_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 10 (B–Me); 16.1 (d, $^1J_{C-P}$ = 18.7 Hz, PMe$_3$); 30.8 [C(CH_3)$_3$]; 34.8 [C(CH$_3$)$_3$]; 74.9 (t, $^2J_{C-P}$ = 9.9 Hz, Ti–Me); 110.6, 11.6 (C_5H_3); 150.9 (C_{ipso} C_5H_3).

3.19. Synthesis of [Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)Me$_2$(PMe$_3$)$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ 25

The same procedure described for the preparation of **24** using 0.25 g (0.80 mmol) of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)Me$_3$, **23**, 0.40 g (0.80 mmol) of B(C_6F_5)$_3$ and 1.6 ml of 1 M solution of PMe$_3$ in toluene (1.6 mmol) at −78 °C gave **25** as an orange oil (0.39 g, 50% yield). Anal. Calc. for $C_{40}H_{48}BF_{15}P_2Zr$: C, 49.10; H, 4.95. Found: C, 49.69; H, 4.27. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.06 (br, 3H, B–CH$_3$); 0.86 (m, 6H, Zr–Me); 1.25 (d, 18H, $^2J_{H-P}$ = 11.7 Hz, PMe$_3$); 1.35 (s, 18H, ^{t}Bu); 6.40 (d, 2H, C_5H_3); 6.55 (t, 1H, C_5H_3).

3.20. Reaction of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ (14) with B(C_6F_5)$_3$ in molar ratio 1:1 (27)

20 mg (0.55 mmol) of [Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$, **14**, and 28 mg (0.55 mmol) of B(C_6F_5)$_3$ were transferred to an NMR tube containing toluene-d_8 and cooled at −30 °C. ^{1}H NMR spectroscopic analysis revealed the formation of the cationic species [Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me]$^+$[(Me)B(C_6F_5)$_3$]$^-$ (**27**). ^{1}H NMR (500 MHz, toluene-d_8, 25 °C): δ 0.37 (br, 3H, B–CH$_3$–Zr); 0.55 (s, 3H, Zr–CH$_3$); 0.68 (s, 18H, ^{t}Bu); 5.40 (t, 1H, J = 2.3 Hz, C_5H_3); 5.81 (s, 5H, C_5H_5); 6.10 (br, 2H, C_5H_3). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8, −25 °C): δ 22.5 (B–CH$_3$–Zr); 31.4 [C(CH_3)$_3$], 33.5 [C(CH$_3$)$_3$]; 43.8 (Zr–Me); 106.8, 115.7 (C_5H_3); 114.8 (C_5H_5).

3.21. Reaction of Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ (26) with B(C_6F_5)$_3$ in molar ratio 1:1 (28)

A 30 mg (0.66 mmol) sample of Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$, **26**, and 33 mg (0.66 mmol) of B(C_6F_5)$_3$ were transferred to an NMR tube containing toluene-d_8 and cooled at −30 °C. ^{1}H NMR spectroscopic analysis revealed the formation of the cationic species [Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me][(Me)B(C_6F_5)$_3$] (**28**). ^{1}H NMR (500 MHz, toluene-d_8, 25 °C): δ 0.31 (s, 3H, Hf–CH$_3$); 0.66 (br, 3H, B–CH$_3$–Hf); 0.73 (s, 18H, ^{t}Bu); 5.38 (t, 1H, J = 2.5 Hz, C_5H_3); 5.70, 6.10 (br, 2H, C_5H_3); 5.73 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8, −25 °C): δ 20 (B–CH$_3$–Hf); 31.2 [C(CH_3)$_3$]; 33.2 [C(CH$_3$)$_3$]; 42.3 (Hf–Me); 107.1, 112.6, 116.8 (C_5H_3); 113.6 (C_5H_5); 140.3 (C_{ipso} C_5H_3).

3.22. Reaction of Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ (14) with B(C_6F_5)$_3$ in molar ratio 2:1 (29)

A 25 mg (0.06 mmol) sample of Zr(1-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$, **14**, and 14 mg (0.03 mmol) of B(C_6F_5)$_3$ were transferred to an NMR tube containing toluene-d_8 and cooled at −30 °C. NMR spectroscopic analysis revealed the formation of the cationic species {[Zr(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me]$_2$(μ-Me)}[MeB(C_6F_5)$_3$] (**29**). ^{1}H NMR (500 MHz, toluene-d_8, 25 °C): δ −0.91 (br, 3H, Zr–CH$_3$–Zr); 0.07, 0.09 (s, 6H, Zr–CH$_3$); 0.74, 0.79 (s, 36H, ^{t}Bu); 1.12 (br, 3H, B–CH$_3$); 5.32, 6.35 (2m, 4H, C_5H_3); 5.66, 5.82 (2m, 2H, C_5H_3); 5.75, 5.76 (2s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8, −30 °C): δ 22 (B–CH$_3$); 26.2 (Zr–CH$_3$–Zr); 31, 31.2 [C(CH_3)$_3$]; 33.2. 32.6 [C(CH$_3$)$_3$]; 40.1, 40.5 (Zr–Me); 103.9, 104.4, 115.4 (C_5H_3); 113.4 and 113.7 (C_5H_5); 140.7 and 141 (C_{ipso} C_5H_3).

3.23. Reaction of Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$ (26) with B(C_6F_5)$_3$ molar ratio 2:1 (30)

25 mg (0.056 mmol) of [Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me$_2$], **26**, and 14 mg (0.028 mmol) of B(C_6F_5)$_3$ were transferred to an NMR tube containing toluene-d_8 and cooled at −30 °C. NMR spectroscopic analysis revealed the formation of the cationic species {[Hf(1,3-^{t}Bu$_2$-η^5-C_5H_3)(η^5-C_5H_5)Me]$_2$(μ-Me)}[MeB(C_6F_5)$_3$] (**30**). ^{1}H NMR (500 MHz, toluene-d_8, 25 °C): δ −0.95 (br, 3H, Hf–CH$_3$–Hf); −0.15, −0.17 (s, 6H, Hf–CH$_3$); 0.73, 0.79 (s, 36H, ^{t}Bu); 1.06 (br, 3H, B–CH$_3$); 5.28 (m, 2H, C_5H_3); 5.42, 5.75, 6.18, 6.14 (m, 4H, C_5H_3); 5.63, 5.65 (2s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8, −30 °C): δ 20 (B–CH$_3$); 25.0, 26.3 (Hf–CH$_3$–Hf); 31.2 [C(CH_3)$_3$]; 32.6, 33.1 [C(CH$_3$)$_3$]; 42.7 (br, Hf–Me); 104.7, 104.4, 114.2 (C_5H_3); 112.3 (C_5H_5); 147.9 and 149.9 (C_{ipso} C_5H_3).

Table 3
Crystal data and structure refinement for compound **6**

Empirical formula	$Ti_3O_3Cl_3C_{39}H_{63}$
Crystal size (mm^3)	$0.05\times0.05\times0.3$
Color	Red
Crystal habit	Prismatic
Formula weight	829.94
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.112(2)
b (Å)	15.309(7)
c (Å)	25.931(7)
β (deg)	99.35(1)
Volume (Å^3)	4353(2)
Z	4
Density (calc.) ($g\,cm^{-3}$)	1.267
Absorption coefficient (cm^{-1})	7.54
$F(000)$	1752
θ range for data collection (deg)	2.0 to 25.0
Index ranges	$0<h<13$, $0<k<18$, $-30<l<30$
Reflections collected	5029
Independent reflections	4472 ($R_{int}=0.0573$)
Refl. observed with $I>2\sigma(I)$	2870
Absorption correction	N/A
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4455/0/433
Goodness-of-fit on F^2	1.110
Final R indices [$I>2\sigma(I)$][a]	$R1=0.0397$, $wR2=0.0882$
R indices (all data)	$R1=0.1136$, $wR2=0.1377$
Largest diff. peak and hole (e^- Å^{-3})	0.348 and −0.220

Weighting scheme: calc $w^{-1}=1/[\sigma^2(F_o^2)+(0.0494P)^2+2.5787P]$ where $P=(F_o^2+2F_c^2)/3$.
[a] $R1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$. $wR2=\{[\Sigma\omega(F_o^2-F_c^2)]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

3.24. Crystal structure determination of $[Ti(1,3\text{-}^tBu_2\text{-}\eta^5\text{-}C_5H_3)Cl(\mu\text{-}O)]_3$ 6

A suitably sized yellow crystal of **6** was obtained by crystallization from hexane. The crystal was mounted in an Enraf–Nonius Cad-4 automatic four circle diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å). Crystallographic and experimental details are summarized in Table 3. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXS 90) [28] and refined by least squares against F^2 (SHELXL 93) [29]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the carbon to which they are bonded. Calculations were carried out on an Alpha AXP(Digital) workstation.

4. Supplementary material

The supplementary material available includes a complete list of bond distances and angles, anisotropic thermal factors, the calculated fractional coordinates of the hydrogen atoms, and a list of observed and calculated structure factors and DNMR study data about the cationic species.

Acknowledgements

Financial support for this research by DGICYT (Project PB92-0178C) is gratefully acknowledged. J.I.A. acknowledges Repsol Petróleo S.A. for a fellowship. A.M. is grateful to Consejería Educación (CAM) for a fellowship.

References

[1] (a) W. Kamynsky and H. Sinn (Eds.), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, New York, 1988. (b) J.E. Ewen, M.J. Elder, R.L. Jones, S. Curtis and H.N. Cheng, in T. Keii and K. Soga (Eds.), *Catalytic Olefin Polymerization*, Kodansha and Elsevier, Amsterdam, 1990. (c) A. Zambelli, C. Pellecchia and L. Oliva, *Makromol. Chem. Makromol. Symp., 48–49* (1991) 297.
[2] (a) F.S. Dyachkovskii, in J.C.W. Chien (Ed.), *Coordination Polymerization*, Academic Press, New York, 1975. (b) R.F. Jordan, P.K. Bradley, R.E. LaPointe and D.F. Taylor, *New. J. Chem., 14* (1990) 499. (c) T.J. Marks, *Acc. Chem. Res., 25* (1992) 57 and references cited therein. (d) M. Bochmann, *Nachr. Chem. Lab. Techn., 41* (1993) 1220. (e) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R.M. Waymouth, *Angew. Chem. Int. Ed. Engl., 34* (1995) 1143.
[3] R.F. Jordan, *Adv. Organomet. Chem., 32* (1991) 325.
[4] (a) M. Bochmann, A.J. Jaggar and J.C. Nichols, *Angew. Chem. Int. Ed. Engl., 29* (1990) 780. (b) X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc., 113* (1991) 3623. (c) R.B. Grossmann, R.A. Doyle and S.L. Buchwald, *Organometallics, 10* (1991) 1501. (d) A.D. Horton and J.H. Frijns, *Angew. Chem. Int. Ed. Engl., 30* (1991) 1152. (e) A.D. Horton and A.G. Orpen, *Organometallics, 10* (1991) 3910. (f) A.D. Horton, *J. Chem. Soc. Chem. Commun.*, (1992) 185. (g) M. Bochmann and A.J. Jaggar, *J. Organomet. Chem., 424* (1992) C5. (h) M. Bochmann and S.J. Lancaster, *J. Organomet. Chem., 434* (1992) C1. (i) M. Bochmann and S.J. Lancaster, *Organometallics, 12* (1993) 633. (j) O. Robinson, S.J. Lancaster, M. Bochmann, S.J. Coles and M.B. Hursthouse, *Organometallics, 14* (1995) 2456 and references cited therein.
[5] L. Jia, X. Yang, A. Ishihara and T.J. Marks, *Organometallics, 14* (1995) 3135.
[6] P.C. Möhring and N.J. Coville, *J. Organomet. Chem., 479* (1994) 1.
[7] (a) N. Ishihara and M. Kuramoto, *Macromolecules, 21* (1988) 3356. (b) A. Zambelli, L. Oliva and C. Pellechia, *Macromolecules, 22* (1989) 2129. (c) C. Pellechia, P. Longo, L. Oliva and A. Zambelli, *Makromol. Chem., 192* (1991) 233. (d) A. Proto and A. Zambelli, *Macromolecules, 22* (1989) 2126. (e) C. Pellechia, P. Longo, A. Grassi and A. Zambelli, *Makromol. Chem. Rapid Commun., 11* (1990) 519. (f) C. Pellechia, A.

Grassi and A. Zambelli, *J. Chem. Soc. Chem. Commun.*, (1993) 947. (g) C. Pellechia, A. Immirzi and A. Peluso, *Organometallics, 13* (1994) 3773. (h) C. Pellechia, A. Immirzi and A. Zambelli, *J. Organomet. Chem., 479* (1994) C9. (i) C. Pellechia, A. Grassi and A. Zambelli, *Organometallics, 13* (1994) 298. (j) C. Pellechia, P. Longo, A. Proto and A. Zambelli, *Makromol. Chem. Rapid Commun., 13* (1992) 265.

[8] (a) Riemschneider, *Naturforscher, 18* (1963) 641. (b) S. Schonholzer and M. Slongo, *Makromol. Chem., 1181* (1980) 37. (c) G. Clifford, E. Vernier and W. Casserly, *J. Am. Chem. Soc., 112* (1990) 2808.

[9] (a) P. Jutzi, *J. Organomet. Chem., 169* (1979) 373. (b) P. Jutzi, *Chem. Rev., 86* (1986) 983.

[10] J.I. Amor, T. Cuenca, M. Galakhov and P. Royo, *J. Organomet. Chem., 497* (1995) 127.

[11] T. Carofligio, C. Floriani, A. Sgamellotti, M. Rosi, A. Chiesi-Villa and C.J. Rizzole, *J. Chem. Soc. Dalton Trans.*, (1992) 1081.

[12] S.I. Troyanov, V. Varga and K. Mach, *J. Organomet. Chem., 402* (1991) 201.

[13] S.G. Blanco, M.P. Gómez-Sal, S. Carrera, M. Mena, R. Serrano and P. Royo, *J. Chem. Soc. Chem. Commun.*, (1986) 1572.

[14] L.M. Jackman and F.A. Cotton, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1975, p. 51.

[15] D.J. Crowther, R.F. Jordan, N.C. Baenzinger and A. Verma, *Organometallics, 9* (1990) 2574.

[16] (a) M. Bochmann, K. Karger and A.J. Jaggar, *J. Chem. Soc. Chem. Commun.*, (1990) 1038. (b) R. Quyoum, Q. Wang, M.-J. Tudoret and M.C. Baird, *J. Am. Chem. Soc., 116* (1994) 6435. (c) S.J. Lancaster, O.B. Robinson, M. Bochmann, *Organometallics, 14* (1995) 2456. (d) F. Barsan and M.C. Baird, *J. Chem. Soc. Chem. Commun.*, (1995) 1065 and references cited therein.

[17] C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics, 12* (1993) 4473.

[18] D.J. Gillis, M.-J. Tudoret and M.C. Baird, *J. Am. Chem. Soc., 115* (1993) 2543.

[19] T. Cuenca, C. Montejano and P. Royo, *J. Organomet. Chem., 514* (1996) 93.

[20] X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc., 116* (1994) 10015.

[21] P.A. Deck and T.J. Marks, *J. Am. Chem. Soc., 117* (1995) 6128.

[22] M. Bochmann and S.J. Lancaster, *Angew. Chem. Int. Ed. Engl., 33* (1994) 1634.

[23] D.C. Swenson, E.B. Tjaden and R.F. Jordan, *Organometallics, 14* (1995) 371.

[24] G. Clifford, E. Vernier and W. Casserly, *J. Am. Chem. Soc., 12* (1990) 2808.

[25] R.R. Schrock, *J. Organomet. Chem., 122* (1976) 209.

[26] H.G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Vol. III, Erke, Stuttgart, 1981.

[27] A.G. Massey and A.J. Park, *J. Organomet. Chem., 2* (1964) 245.

[28] G.M. Sheldrick, *Acta Crystallogr. Sect. A:, 46* (1990) 67.

[29] G.M. Sheldrick, SHELXL 93, University of Göttingen, 1993.