

Synthesis of bis(*tert*-butyl)cyclopentadienyl derivatives of titanium and zirconium. NMR spectra and dynamic behaviour of the base-free $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_2]^+$ cation [☆]

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Abstract

Reaction of $\text{Si}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Me}_3$ with MCl_4 ($\text{M} = \text{Ti}, \text{Zr}$) in toluene or hexane at room temperature affords the new trichloromonocyclopentadienyl-type derivatives $[\text{M}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{Cl}_3]$ ($\text{M} = \text{Ti}$ (**2**), Zr (**3**)). Treatment of complexes **2** and **3** with appropriate alkylating reagents in hexane gives the 1,3-di(*tert*-butyl)cyclopentadienyl trialkyl titanium and zirconium complexes $[\text{M}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{R}_3]$ [$\text{M} = \text{Ti}$, $\text{R} = \text{CH}_3$ (**4**), CH_2Ph (**5**); $\text{M} = \text{Zr}$, $\text{R} = \text{CH}_3$ (**6**), CH_2Ph (**7**), $\text{CH}_2\text{CMe}_2\text{Ph}$ (**8**)]. Interestingly, when **2** reacts with 3.1 equivalents of $\text{LiCH}_2\text{CMe}_2\text{Ph}$ in hexane at room temperature the ring-*tert*-butyl-metallated complex $[\text{Ti}(1\text{-}^t\text{Bu}\text{-}3\text{-CMe}_2\text{CH}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ (**9**) was isolated in 90% yield. The cationic mono(1,3-di(*tert*-butyl)cyclopentadienyl) dibenzyl zirconium species $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_2]^+$, generated in situ by reaction of the tribenzyl complex **7** with $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ reagents, is reported and their dynamic NMR behaviour in CD_2Cl_2 solutions at low temperatures is studied.

Keywords: Titanium; Zirconium; Zirconocene cation; Cyclopentadienyl; Base-free cation NMR spectroscopy

1. Introduction

It is now well established that 14-electron cationic di(η^5 -cyclopentadienyl) alkyl Group 4 metal complexes $[\text{MCp}_2\text{R}]^+$ are active species in the homogeneous Ziegler–Natta polymerization of olefins [1], and their chemistry has been extensively developed in the last few years [2]. Although most catalytic studies have been referred to cationic methyl complexes $[\text{MCp}_2(\text{CH}_3)]^+$, the synthesis of benzyl derivatives has received particular attention, as they provide thermally more stable base-free cationic complexes [1d,2c,3]. Similar cationic mono- η^5 -cyclopentadienyl species, which also play an important role in some olefin polymerization processes [2c,4], have been less extensively studied. We report here the synthesis and NMR characterization of di(*tert*-butyl)cyclopentadienyl trichloro- and trialkyl-titanium and zirconium complexes $[\text{M}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{X}_3]$ [$\text{M} = \text{Ti}$, $\text{X} = \text{Cl}$ (**2**), CH_3 (**4**), CH_2Ph (**5**);

$\text{M} = \text{Zr}$, $\text{X} = \text{Cl}$ (**3**), CH_3 (**6**), CH_2Ph (**7**), $\text{CH}_2\text{CMe}_2\text{Ph}$ (**8**)] and the metallated complex $[\text{Ti}(1\text{-}^t\text{Bu}\text{-}3\text{-CMe}_2\text{CH}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ (**9**). We also report the dynamic NMR behaviour at low temperatures of the cationic zirconium species, generated in situ by reaction of the tribenzyl complex **7** with boron $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ reagents.

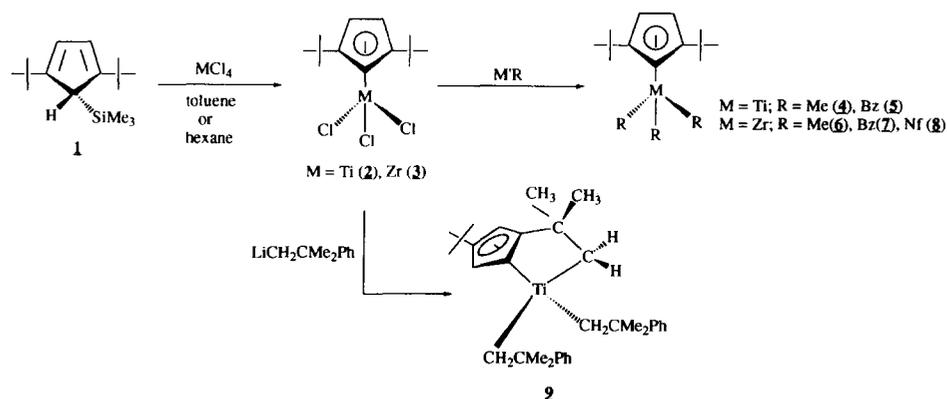
2. Results and discussion

2.1. Trichloro and trialkyl complexes

Following a well known and extensively used method to prepare monocyclopentadienyl-type complexes, the reaction of $\text{Si}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Me}_3$ (**1**) with MCl_4 ($\text{M} = \text{Ti}, \text{Zr}$) in toluene or hexane at room temperature led to the isolation of the trichloro derivatives **2** and **3** as microcrystalline solids. Reduction was not observed when an hexane solution of complex **2** was treated with 3 equivalents of methyl lithium and an almost quantitative yield of the trimethyltitanium complex **4** was isolated after filtration and evaporation of the solvent

[☆] Dedicated to Prof. Dr. Hans-H. Brintzinger on the occasion of his 60th birthday

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Scheme 1.

(Scheme 1). The same reaction took place for complex 3, but a much higher yield (90%) of the trimethylzirconium derivative 6 resulted when 3 was reacted with a diethylether solution of MeMgCl. Both methyl compounds 4 and 6 were isolated as yellow oils at room temperature. Reaction of hexane solutions of 2 and 3 with stoichiometric amounts of $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2 \cdot 2\text{THF}$ afforded the tribenzyl complexes 5 and 7, respectively. Complex 5 was isolated as a microcrystalline red solid whereas 7 was obtained as a yellow oil at room temperature. A similar alkylation of the zirconium complex 3 with the lithium derivative of the bulkier neophyl group led to the trineophyl complex 8, isolated in 90% yield as a yellow oil at room temperature.

However, the expected trineophyltitanium complex could not be obtained by reaction of an hexane solution of complex 2 with 3.1 equivalents of $\text{LiCH}_2\text{CMe}_2\text{Ph}$. Instead, the ring methyl-metallated complex $[\text{Ti}(1\text{-}^t\text{Bu}-3\text{-CMe}_2\text{CH}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ (9) was isolated in 90% yield as a yellow oil at room temperature. Apparently the metallacyclic complex results from the intramolecular activation of one C–H bond of the cyclopentadienyl bonded *tert*-butyl group with elimination of *tert*-butylbenzene.

Complexes 1–9 were characterized by the usual analytical and spectroscopic methods. ^1H NMR spectra of compounds 4–8 show the expected resonances for the alkyl groups bonded to the metal atom (see Section 3). The *tert*-butyl protons appear as a singlet and the cyclopentadienyl ring protons as two sets of pseudo-doublet (2H) and pseudo-triplet (1H) signals, corresponding to an AA'B spin system. The ^1H NMR spectrum for compound 9 shows two singlets (δ 1.05, 1.10) for the methyl protons and two sets of doublets (δ 2.47,

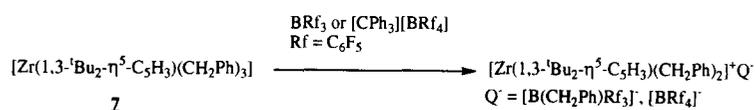
2.89) for the diastereotopic methylene protons of the neophyl groups. The *tert*-butyl protons exhibit one singlet (δ 1.21), whereas two resonances (δ 1.47, 1.51) and two sets of doublets (δ 1.89, 2.92) are observed respectively for the methyl and methylene protons for the *tert*-butyl activated group. The cyclopentadienyl ring protons appear as three pseudo-triplets (δ 5.99, 6.13, 6.31) corresponding to an ABC spin system.

2.2. Cationic zirconium compounds

The reaction of the tribenzylzirconium complex 7 with $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 at 193 K (Scheme 2) took place with an instantaneous change of colour to give red-brown solutions of the cationic zirconium complex.

The formation of $[\text{B}(\text{C}_6\text{F}_5)_3\text{CH}_2\text{Ph}]^-$ in the reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ was proved by the presence of a sharp signal (δ +11) in the ^{11}B NMR spectrum, in the characteristic region for the tetracoordinate borate anion. Similarly, the formation of 1,1,1,2-tetraphenylethane in the reaction with $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was confirmed by ^1H and ^{13}C NMR spectroscopy.

The ^1H NMR spectrum (CD_2Cl_2 , 500 MHz) of the cationic zirconium species $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ at 193 K, shows the Zr- CH_2Ph protons as four broad signals ($\Delta\nu \approx 14$ Hz) at δ 3.8 and 2.4 (δ 3.1 average; $\Delta\delta = 1.4$ ppm) assignable by using the "saturation transfer" technique, [5] to one of the Zr- CH_2Ph groups, and at δ 5.4 and 2.6 (δ 4.0 average; $\Delta\delta = 2.8$ ppm) for the other Zr- CH_2Ph group. This spectrum corresponds, therefore, to two pairs of doublets, indicating that both benzylic CH_2 groups are not equivalent and have diastereotopic protons. These



Scheme 2.

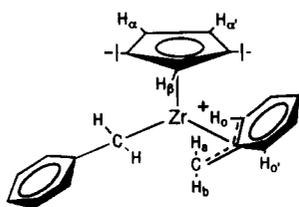


Fig. 1. Structural disposition proposed for the dibenzyl cationic species.

signals are shifted downfield in relation to the neutral complex $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_3]$. The two Ph groups also give two sets of resonances. The first [at 163 K: δ 6.9 (2H), 6.6 (2H), 6.1 (1H)] corresponds to a C_{2v} symmetry free rotating group, whereas the second consists of five multiplets (δ 7.5, 6.8, 6.5, 6.4 and 5.8), suggesting that no symmetry is found for this group. It is important to note that resonances for the *ortho* Ph protons of the second group show very different chemical shifts (δ 7.5 and 5.8; $\Delta\delta$: 1.7 ppm). Two different *tert*-butyl protons (δ 1.2 and 1.3) and three signals for the cyclopentadienyl protons (δ 6.3, 5.3 and 5.2) are also observed. The ^{13}C NMR spectrum at 193 K shows the carbons of the benzylic methylene groups as two resonances at δ 73 ($J_{\text{C-H}} = 120$ Hz), typical for an undistorted η^1 -benzyl ligand, and δ 85 ($J_{\text{C-H}} = 148$ Hz), in agreement with a η^3 -coordinated benzyl group [1d,4,5]. One resonance at δ 31.6 assignable to $(\text{CH}_3)_3\text{C}$ and two resonances at δ 33.9 and 33.0 for the $(\text{CH}_3)_3\text{C}$ *tert*-butyl carbons are also observed. The spectroscopic features give evidence for a pseudotetrahedral chiral arrangement for the metal centre at low temperatures with the positive charge of the cation delocalized into the $\text{Zr-CH}_2\text{-Ph}$ system of the distorted benzyl ligand (Fig. 1), relieving the electron deficiency by η^3 -coordination of the Zr-bound benzyl ligand. The big difference between the two benzylic methylene protons ($\Delta\delta = 2.8$ ppm) and the two *ortho* phenyl protons ($\Delta\delta$: 1.7 ppm) for this benzyl group is due to their different orientation, one proton of each pair being placed in closer proximity to the di-(*tert*-butyl)cyclopentadienyl ring giving an important anisotropic nature.

The ^1H NMR spectrum of the related $[\text{Zr}(\text{C}_5\text{H}_5)(\text{CH}_2\text{Ph})_2]^+ [\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{Ph})]^-$ compound [2c,4], confirms that the cationic unit is stabilized by π -coordination of the phenyl ring of the anion, showing only two doublets of an AB system at δ 1.8 and 2.1 (δ 1.95

average) for the diastereotopic $\text{Zr-CH}_2\text{Ph}$ protons, and one singlet for both *ortho* Ph protons at δ 6.8 in the usual range for normal, undistorted η^1 -benzyl groups [4]. Similar spectral behaviour has been observed by Pellechia et al. [4] for the compound $[\text{Zr}(\text{C}_5\text{Me}_5)(\text{CH}_2\text{Ph})_2]^+ [\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{Ph})]^-$, for which they infer a solvent-separated ion pair and propose a rotational dynamic behaviour at increasing temperatures which is not easily explained.

2.3. Dynamic behaviour of the $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_2]^+$ cation

Variable-temperature ^1H NMR experiments performed in CD_2Cl_2 show broadening of all resonances as the temperature increases between 193 and 263 K, suggesting dynamic behaviour. Coalescences are observed at 228, 238 and 263 K for *tert*-butyl, cyclopentadienyl and benzyl proton resonances, respectively. Above this temperature rapid decomposition occurs, possibly through chlorine abstraction from the solvent, precluding further analysis.

Table 1 shows the kinetic parameters in CD_2Cl_2 , for the dynamic process observed for the cationic species formed in the reaction of **2** with $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, calculated by using D NMR and a complete line-shape analysis of the resonances of the *tert*-butyl protons. These parameters are independent of the nature of the anion, coalescence being observed at the same temperature with the same value of ΔG^\ddagger ($\Delta G^\ddagger(228\text{ K}) = 10.7\text{ Kcal mol}^{-1}$) for species formed in reactions with both $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Superimposable ^1H , ^{13}C , ^{19}F and ^{11}B NMR spectra in the temperature range 173–263 K are obtained for both species, suggesting that coordination of the anion through metal–arene π -bonding is absent. The steric properties of the cyclopentadienyl ligands strongly influence the structure of the intermediate species in the metallocene catalyzed α -olefin polymerization. Recently, Jordan et al. [6] claimed a direct relation between this effect and β -Me and β -H elimination in $[\text{M}(\eta^5\text{-C}_5\text{R}_5)_2(\text{CH}_2\text{CHR}'\text{R}')(\text{L})]^+$ species by analysis of the previous observations by Teuben and coworkers for pentamethylcyclopentadienyl derivatives [7]. Owing to the more crowded cyclopentadienyl ring probably the presence of two bulky *tert*-butyl substituents prevents the coordination of the anion observed by Bochmann

Table 1
Kinetic parameters for the dynamic process of $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_2]^+$

Anion	LgA		$E_a /$ Kcal mol^{-1}	$\Delta H^\ddagger /$ Kcal mol^{-1}		ΔS^\ddagger e.u.	$\Delta G_{298\text{ K}}^\ddagger$ Kcal mol^{-1}
BRf_4	14.3 ± 0.2		12.5 ± 0.4	12.0 ± 0.4		-3.5 ± 1.3	10.9
		$r = 0.999$			$r = 0.997$		
$\text{PhCH}_2\text{BRf}_3$	13.4 ± 0.7		11.6 ± 0.8	11.2 ± 0.8		-1.3 ± 2.0	10.8
		$r = 0.997$			$r = 0.997$		

and coworkers [2c,4] in related cyclopentadienyl and pentamethylcyclopentadienyl derivatives.

The A values measured indicate that the process is an intramolecular transformation through a transition state with a favourable energy. The negligible values of ΔS^\ddagger justify the assumption that no entropy change is required to reach the transition state. Therefore, the dynamic process is related to a typical η^3 -allyl isomerization process in which only one benzyl group is involved.

The η^1 coordination of the other benzyl group would give a highly electron deficient 12-electron compound. Intramolecular coordination of its phenyl ring to give a η^7 -benzyl group [8], leading to a more stable 18-electron complex, cannot be excluded and could be an acceptable proposal to explain the observed behavior during transition state formation in solution.

The monocyclopentadienyl zirconium cationic species generated in situ promotes the ethylene and propylene polymerization in toluene solution of the olefin, at temperatures ranging from -20 to 50 °C and 1 atm pressure.

3. Experimental section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high vacuum line techniques or a VAC glove box Model HE 63P. Solvents were purified by distillation from an appropriate deoxygenated drying agent (sodium for toluene and sodium/potassium alloy for hexane). MeLi (1.6 M diethyl ether solution), MeMgCl (3 M diethyl ether solution), TiCl_4 and ZrCl_4 (Aldrich) were purchased and used without further purification. $\text{Si}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Me}_3$ [9] and $\text{MgBz}_2 \cdot 2\text{THF}$ [10] were prepared according to published procedures. $\text{LiCH}_2\text{-CMe}_2\text{Ph}$ was prepared as a yellow microcrystalline solid by reaction of lithium metal with $\text{ClCH}_2\text{CMe}_2\text{Ph}$ (Aldrich) in hexane under reflux for one week. NMR spectra were recorded on Varian FT-80 and Varian Unity FT-300 instruments (^1H and ^{13}C chemical shifts were referenced to Me_4Si , $\delta = 0$ ppm). Elemental C and H analyses were carried out on a Perkin Elmer 240B microanalyzer.

3.1. Preparation of $[\text{Ti}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{Cl}_3]$ (2)

$\text{Si}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Me}_3$ (1.051 ml, 0.83 g, 3.317 mmol) was added at 0 °C under argon to a solution of TiCl_4 (0.33 ml, 0.57 g, 3.016 mmol) in hexane (100 ml). The reaction mixture was slowly warmed to room temperature and stirred for 24 h to give a red solution. The solvent was evaporated under vacuum to leave a red solid which was recrystallized from toluene/hexane and characterized as **2** (1 g, 97% yield) [11].

Anal. Calc. for $\text{C}_{13}\text{H}_{21}\text{TiCl}_3$: C, 47.06; H, 6.33. Found: C, 46.94; H, 6.47. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.11 (s, 18H, ^tBu), 6.21 (d, 2H, C_5H_3), 6.63 (t, 1H, C_5H_3).

3.2. Preparation of $[\text{Zr}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{Cl}_3]$ (3)

$\text{Si}(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Me}_3$ (0.93 ml, 0.73 g, 2.93 mmol) was added to a suspension of ZrCl_4 (0.61 g, 2.66 mmol) in toluene (100 ml). The reaction mixture was stirred under reflux overnight. The resulting solution was filtered at 70 °C and evaporated in vacuo to give a light brown solid. Recrystallization from toluene/hexane at -78 °C gave a crystalline brown solid which was characterized as **3** (1 g, 90% yield).

Anal. Calc. for $\text{C}_{13}\text{H}_{21}\text{ZrCl}_3$: C, 41.65; H, 5.64. Found: C, 41.53; H, 5.84. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.12 (s, 18H, ^tBu), 5.99 (d, 2H, C_5H_3), 6.44 (t, 1H, C_5H_3). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 30.0 (^tBu), 33.2 ($\text{C}_{\text{ipso}}\text{ }^t\text{Bu}$), 113.80 (br, $\text{C}_1\text{-C}_2$ C_5H_3), 150.6 ($\text{C}_{\text{ipso}}\text{ } \text{C}_5\text{H}_3$).

3.3. Preparation of $[\text{Ti}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_3)_3]$ (4)

A 1.6 M solution of MeLi in diethyl ether (7.16 ml, 3.70 mmol) was added to a hexane (50 ml) solution containing $[\text{Ti}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{Cl}_3]$ (1.22 g, 3.70 mmol) at -40 °C. The reaction mixture was stirred for 30 min and then slowly warmed to room temperature and stirred overnight. After filtration, the solvent was evaporated in vacuo to dryness to give a yellow oil which was characterized as **4** (1 g, 98% yield).

Anal. Calc. for $\text{C}_{16}\text{H}_{30}\text{Ti}$: C, 71.12; H, 11.19. Found: C, 70.98; H, 11.00. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.08 (s, 18H, ^tBu), 1.40 (s, 9H, CH_3), 5.81 (d, 2H, C_5H_3), 5.98 (t, 1H, C_5H_3). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 31.27 (^tBu), 31.6 ($\text{C}_{\text{ipso}}\text{ }^t\text{Bu}$), 62.4 (CH_3), 105.1, 107.3 (C_5H_3), 123.1, 127.0, 128.7, 150.7 ($\text{C}_{\text{para}}, \text{C}_{\text{meta}}, \text{C}_{\text{ortho}}, \text{C}_{\text{ipso}}\text{ Ph}$), 149.5 ($\text{C}_{\text{ipso}}\text{ } \text{C}_5\text{H}_3$).

3.4. Preparation of $[\text{Ti}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)(\text{CH}_2\text{Ph})_3]$ (5)

Solid $\text{MgBz}_2 \cdot 2\text{THF}$ (0.79 g, 2.26 mmol) was added to a solution of $[\text{Ti}(1,3\text{-}^t\text{Bu}_2\text{-}\eta^5\text{-C}_5\text{H}_3)\text{Cl}_3]$ (0.5 g, 1.50 mmol) in hexane (50 ml). The mixture was cooled to 0 °C and stirred for 12 h to give a red solution. After filtration the resulting solution was evaporated to dryness and the residue, recrystallized from hexane at -30 °C, gave a red microcrystalline solid which was characterized as **5** (0.45 g, 60% yield).

Anal. Calc. for $\text{C}_{34}\text{H}_{42}\text{Ti}$: C, 81.90; H, 8.49. Found: C, 81.60; H, 8.00. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.02 (s, 18H, ^tBu), 3.27 (s, 6H, CH_2), 5.77 (d, 2H, C_5H_3), 5.91 (t, 1H, C_5H_3), 6.94, 6.96, 7.16 (*o*-, *p*-, *m*-Ph). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 31.6

(¹Bu), 34.0 (*C*_{ipso} ¹Bu), 95.9 (CH₂), 108.5, 111.3 (C₅H₃), 123.1, 127.0, 128.7, 150.7 (*C*_{para}, *C*_{meta}, *C*_{ortho}, *C*_{ipso} Ph), 149.5 (*C*_{ipso} C₅H₃).

3.5. Preparation of [Zr(1,3-¹Bu₂-η⁵-C₅H₃)(CH₃)₃] (6)

The same procedure described to prepare 4 using [Zr(1,3-¹Bu₂-η⁵-C₅H₃)Cl₃] (1.19 g, 3.18 mmol) and a 3 M solution of MeMgCl in diethyl ether (3.29 ml, 9.88 mmol) gave 6 (1 g, 90% yield).

Anal. Calc. for C₁₆H₃₀Zr: C, 61.43; H, 9.66. Found: C, 61.00; H, 9.30. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.57 (s, 9H, CH₃), 1.14 (s, 18H, ¹Bu), 5.81 (d, 2H, C₅H₃), 6.04 (t, 1H, C₅H₃). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ 31.33 (¹Bu), 31.7 (*C*_{ipso} ¹Bu), 45.6 (CH₃), 102.4, 104.1 (C₁–C₂ C₅H₃), 144.4 (*C*_{ipso} C₅H₃).

3.6. Preparation of [Zr(1,3-¹Bu₂-η⁵-C₅H₃)(CH₂Ph)₃] (7)

The same procedure described to prepare complex 5 using [Zr(1,3-¹Bu₂-η⁵-C₅H₃)Cl₃] (0.5 g, 1.33 mmol) and MgBz₂·2THF (0.79 g, 2.26 mmol) at room temperature gave 7 (0.61 g, 85% yield).

Anal. Calc. for C₃₄H₄₂Zr: C, 75.37; H, 7.81. Found: C, 74.80; H, 7.70. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 1.20 (s, 18H, ¹Bu), 1.94 (s, 6H, CH₂), 5.80 (d, 4H, C₅H₃), 6.66 (t, 2H, C₅H₃), 6.98, 7.00, 7.16 (*o*-, *p*-, *m*-Ph). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.05 (s, 18H, ¹Bu), 2.02 (s, 6H, CH₂), 5.78 (d, 4H, C₅H₃), 5.93 (t, 2H, C₅H₃), 6.78, 6.94, 7.13 (*o*-, *p*-, *m*-Ph). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ 31.7 (¹Bu), 33.2 (*C*_{ipso} ¹Bu), 72.3 (CH₂), 104.9, 108.1 (C₅H₃), 123.3, 127.7, 129.5, 144.3 (*C*_{para}, *C*_{meta}, *C*_{ortho}, *C*_{ipso} Ph), 146.1 (*C*_{ipso} C₅H₃).

3.7. Preparation of [Zr(1,3-¹Bu₂-η⁵-C₅H₃)(CH₂CMe₂-Ph)₃] (8)

Hexane (50 ml) was added to a mixture of [Zr(1,3-¹Bu₂-η⁵-C₅H₃)Cl₃] (0.55 g, 1.49 mmol) and solid Li(CH₂CMe₂Ph) (0.62 g, 4.48 mmol) and stirred at room temperature overnight. After filtration, the resulting solution was evaporated to dryness to give a yellow oil which was characterized as 8 (1 g, 90% yield).

Anal. Calc. for C₄₃H₆₀Zr: C, 77.29; H, 9.05. Found: C, 77.00; H, 8.90. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 1.03 (s, 18H, ¹Bu), 1.26 (s, 6H, CH₂CMe₂Ph), 1.46 (s, 18H, CH₂CMe₂Ph), 5.65 (d, 2H, C₅H₃), 5.92 (t, 1H, C₅H₃), 7.20–7.40 (Ph).

3.8. Preparation of [Ti(1-¹Bu-3-CMe₂CH₂-η⁵-C₅H₃)(CH₂CMe₂Ph)₂] (9)

The same procedure described for the preparation of 8 using [Ti(1,3-¹Bu₂-η⁵-C₅H₃)Cl₃] (0.67 g, 2.03 mmol)

and Li(CH₂CMe₂Ph) (0.88 g, 6.31 mmol) at room temperature gave 9 (1 g, 90% yield).

Anal. Calc. for C₃₃H₄₆Ti: C, 80.78; H, 9.44. Found: C, 79.90; H, 9.30. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.21 (s, 18H, ¹Bu), 1.05 (s, 6H, CH₂CMe₂Ph), 1.10 (s, 6H, CH₂CMe₂Ph), 1.47 (s, 3H, C₅H₃¹Bu(CCH₂Me₂)), 1.51 (s, 3H, C₅H₃¹Bu(CCH₂Me₂)), 1.89 (dd, 1H, C₅H₃¹Bu(CCH₂Me₂)), 2.47 (dd, 2H, CH₂CMe₂Ph), 2.89, (dd, 2H, CH₂CMe₂Ph), 2.92 (dd, 1H, C₅H₃¹Bu(CCH₂Me₂)), 5.99, 6.13, 6.31 (t, 3H, C₅H₃), 7.10, 7.18, 7.40 (*o*-, *p*-, *m*-Ph).

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