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Journal of Organometallic Chemistry 583 (1999) 86–93

Journal of Organometallic Chemistry

Synthesis and reactivity of new mixed dicyclopentadienyl Group 4 metal complexes with the doubly bridged bis(dimethylsilanediyl)-cyclopentadiene-(η^5-cyclopentadienyl) ligand☆

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Received 8 July 1998; received in revised form 7 October 1998

Abstract

The monocyclopentadienyl titanium complex [Ti{$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$} Cl_3] **3** and the dichloro mixed dicyclopentadienyl Group 4 metal complexes [M(η^5-C_5R_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$} Cl_2] (R = H; M = Ti **4**, Zr **5**, Hf **6**; R = Me; M = Ti **7**) containing the doubly bridged bis(dimethylsilanediyl)-cyclopentadiene-(η^5-cyclopentadienyl) ligand were prepared in high yields by reaction of the monolithium salt Li[$(C_5H_4)(SiMe_2)_2(C_5H_3)$] **2** with equimolar amounts of $TiCl_4$ or the monocyclopentadienyl complexes [Cp′MCl_3], respectively. Reactions of the chloro complexes with various alkylating agents afforded the chloroalkyl [M(η^5-C_5H_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}ClR] (M = Ti; R = Me **8**, Et **9**; M = Zr, R = Me **10**, Et **11**, CH_2Ph **12**; M = Hf, R = CH_2Ph **13**) and dialkyl [M(η^5-C_5R_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}$Me_2$] (M = Ti; R = H **14**, Me **15**; M = Zr; R = H **16**, compounds. Formation of the heterodinuclear complex [Zr(η^5-C_5H_5)Cl_2(η^5-C_5H_3)$(SiMe_2)_2(\eta^5$-C_5H_3)Ti$(NMe_2)_3$] **17** with amine elimination was observed by ^{1}H-NMR spectroscopy when complex **5** was reacted with Ti$(NMe_2)_4$. The catalytic activity of compounds **3**–**5** for ethylene polymerization has been studied using MAO as cocatalyst. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Hafnium; Dicyclopentadienyl complexes; Polyethylene

1. Introduction

Cyclopentadienyl ligands constitute one of the various bridging systems that can be used to obtain homo- and hetero-dinuclear complexes. Many dinuclear compounds containing bridging η^5–η^1 cyclopentadienyl rings and η^5–η^5-fulvalene systems, resulting from ring C–H activation in dicyclopentadienyl derivatives, have been reported [1,11]. However di-η^5–cyclopentadienyl ligands singly bridged by various alkyl [2–5] and silyl [6–14] groups are among the most frequently used systems to bridge dinuclear metal compounds. We have recently reported the use of the 1,1′-2,2′-(dimethylsilanediyl)dicyclopentadienyl ligand to synthesize *ansa*-dicyclopentadienyl and bridged homodinuclear mono- and di-cyclopentadienyl complexes of the Group 4 and 6 metals [15–20]. This and related doubly silyl-bridged ligands have also been used [14,21] to isolate mononuclear and dinuclear Group 4 metal compounds. The use of this ligand to bridge two different metal atoms as those recently reported [22] demands the earlier isolation of monocyclopentadienyl-type compounds containing only one of the rings η^5-coordinated to the metal. This was the aim of the work presented here, which includes the isolation and structural characterization of complexes of the following types: [Ti{η^5-C_5H_3-$(SiMe_2)C_5H_4$} Cl_3], [M(η^5-C_5R_5){η^5-$C_5H_3(SiMe_2)C_5H_4$}-Cl_2] (M = Ti, Zr, Hf; R = H; M = Ti; R = Me), [M(η^5-

☆ Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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0022-328X/99/$ - see front matter
PII: S0022-328X(99)00111-4

C_5H_5){η^5-$C_5H_3(SiMe_2)C_5H_4$}ClR] (M = Ti, Zr; R = Me, Et, Bz) and [M(η^5-C_5R_5){η^5-$C_5H_3(SiMe_2)C_5H_4$}Me_2] (M = Ti, Zr; R = H, Me).

2. Results and discussion

2.1. Chloro-complexes

The starting 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene **1** was isolated using the alternative method reported [14] to prepare various related silanes. As shown in Scheme 1, reaction of the dilithium salt of the mono-silyl-bridged dicyclopentadiene with $SiCl_2Me_2$ provided a more direct method to prepare **1** (as a mixture of *cis*- and *trans*-isomers) in higher yield (54%) than reported methods [23]. The monolithium salt Li[$(C_5H_4)(SiMe_2)_2(C_5H_3)$] **2** was prepared by the reported [23] deprotonation of **1** with one equivalent of BuLi at room temperature using hexane instead of THF as solvent.

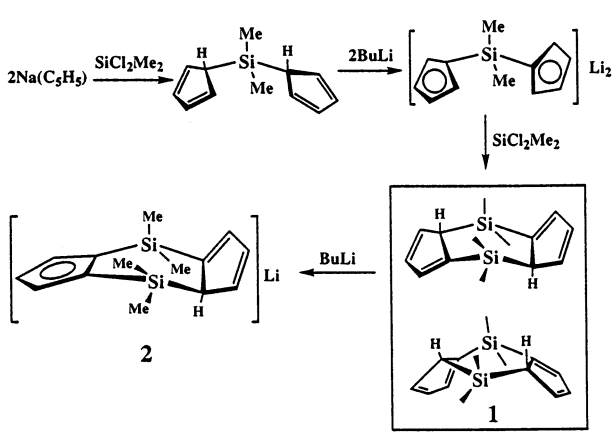
Reaction of $TiCl_4$ with a suspension of one equivalent of the lithium salt **2** in refluxing toluene gave a brown solid, which after purification, provided the trichloro complex [Ti{$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}$Cl_3$] **3** as a brown yellowish solid in rather low yield (22%). Similar yields were also obtained using various solvents at different reaction temperatures. Following the method reported [21] for related compounds, when THF suspensions of the monolithium salt **2** were reacted with THF solutions of [Ti(η^5-C_5R_5)Cl_3] (R = H, Me) and THF suspensions of [M(η^5-C_5H_5)Cl_3 · DME] (M = Zr, Hf), the mixed dicyclopentadienyl complexes [M(η^5-C_5R_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}$Cl_2$] (R = H; M = Ti **4**, Zr **5**, Hf **6**; R = Me; M = Ti **7**) were isolated in high yields (Scheme 2).

All of these chloro complexes are air sensitive and soluble in all of the usual organic solvents. They were characterized by elemental analyses and ^{1}H- and ^{13}C-NMR spectroscopy. The lack of symmetry due to the chiral sp^3 carbon of the non-coordinated cyclopentadiene ring makes all of the seven protons of both rings non equivalent, appearing as seven multiplets in the ^{1}H spectrum whereas the ^{13}C spectra show six signals due to the C_β and C_γ atoms, one signal displaced to high field (δ 55.8–56.4) for the sp^3 carbon and three lower intensity signals always displaced to low field for the other three C_α atoms directly bonded to silicon, although only two were observed for **5**–**7**. The four methyl groups bonded to silicon are also non-equivalent although two signals are overlapped in the titanium derivatives being observed as a unique resonance, whereas four singlets, two of them with very similar chemical shifts, are observed for the zirconium and hafnium derivatives. The ^{13}C spectra confirm the presence of four signals for all compounds. In addition one singlet due to the unsubstituted cyclopentadienyl ring protons or methyl groups is present in complexes **4**–**7**.

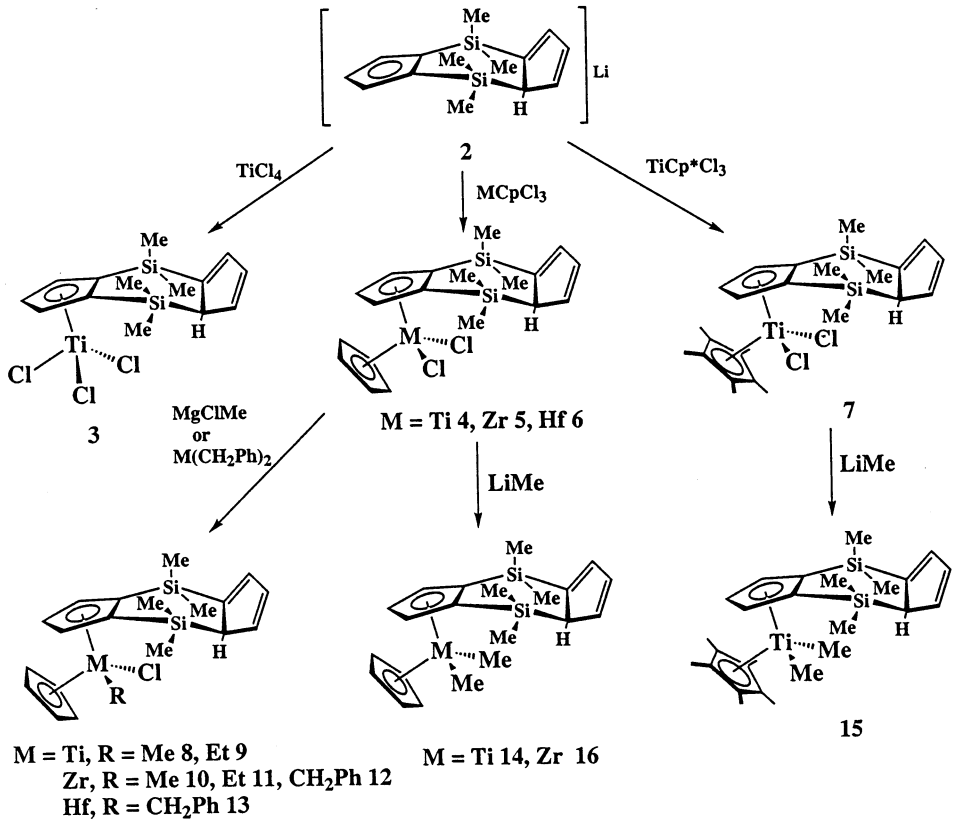
2.2. Alkylation reactions

Monoalkylated titanium and zirconium complexes [M(η^5-C_5H_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}ClR] (M = Ti; R = Me **8**, Et **9**; M = Zr, R = Me **10**, Et **11**) were easily isolated by stirring THF solutions of the dichloro complexes **4** and **5** at room temperature with one equivalent of MgClR (R = Me, Et). Formation of similar chloro-methyl and chloro-ethyl compounds by alkylation of complexes **6** and **7** could be detected by ^{1}H-NMR spectroscopy but the high solubility of the resulting products prevented their purification and suitable characterization in the solid state. The reaction of complexes **5** and **6** with equimolar amounts or excess $Mg(CH_2Ph)_2$ · 2THF afforded only the corresponding chloro-benzyl compounds [M(η^5-C_5H_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$}$Cl(CH_2Ph)$] (M = Zr **12**, Hf **13**), whereas similar reactions of complexes **4** and **7** with $Mg(CH_2Ph)_2$ · 2THF in various solvents, at various temperatures and in different molar ratios, always led to unidentified products.

Although further alkylation of the chloro-methyl complexes took place using two equivalents of MgClMe, better yields of the dimethyl compounds [M(η^5-C_5R_5){$(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)$} Me_2] (M = Ti; R = H **14**, Me **15**; M = Zr; R = H **16**), resulted from direct reactions of the dichloro-complexes with two equivalents of LiMe in hexane. Reduction of the titanium compound was not observed despite the greater reducing capacity of the alkylating agent. It is noteworthy that titanium benzyl complexes could not be isolated and the reaction of complexes **5** and **6** with $Mg(CH_2Ph)_2$ · 2THF always gave monoalkyl complexes, even when a large excess of the alkylating agent was used, probably due to the steric requirements of the bulkier benzyl group. Complexes derived from further



Scheme 1.



Scheme 2.

alkylation of **9** and **11** with MgClEt could not be isolated because β-elimination of the resulting dialkyl compounds takes place spontaneously even at low temperature (− 78°C) to give unidentified decomposition products.

All of the chloro-alkyl and dialkyl complexes **8**–**16** are air and moisture sensitive but can be stored without decomposition under an inert atmosphere at room temperature. Thermal decomposition of complexes **9** and **11** was observed at 40°C in THF with elimination of ethane to give the corresponding dichloro complexes and other unidentified products, whereas no decomposition was observed at 70–80°C in non-polar solvents.

All of the dialkyl compounds were characterized by elemental analyses and NMR spectroscopy. The ^{1}H- and ^{13}C-NMR spectra for the dimethyl complexes **14**–**16** are similar to those described above for the dichloro complexes, with all signals slightly displaced to higher field, and show additional signals due to the metal-bonded diastereotopic methyl groups.

In contrast, the chloro-alkyl complexes have two chiral centres, the sp^3 carbon of the non-coordinated cyclopentadiene ring and the metal, providing a mixture of two diastereomeric components in different molar ratios. Each diastereomer shows the same ^{1}H- and ^{13}C-NMR spectrum as those described above leading, therefore, to two sets of signals of different intensity with some of the signals overlapped (see Section 3). In fact, the non-equivalent methylenic protons of the benzyl derivatives **12** and **13** appear as two doublets ($^{1}J_{C-H} = 12$ Hz) each containing the overlapped signals due to both diastereomers. A similar observation was made for the characteristic methylene multiplets of the ethyl derivatives **9** and **11** whose methyl groups were also overlapped giving a signal observed as a multiplet. The molar ratio of the diastereomers for each chloro-alkyl complex, calculated from the signals of the $SiMe_2$ bridges in the ^{1}H-NMR spectra, were 1:2 for the chloro-methyl and chloro-ethyl compounds and 1:6 for the chloro-benzyl compounds [see detailed assignments to major (**M**) and minor (**m**) components in Section 3].

Table 1
Catalytic polymerization of ethylene[a]

Catalyst	[Catalyst] /[MAO]	T (h)	a (10^5 g l mol^{-1} h^{-1} atm^{-1})
$ZrCp_2Cl_2$	1/1000	0.5	7.32
	1/2000	1.0	4.41
4	1/1000	1.0	0.09
	1/2000	1.0	1.41
5	1/2000	1.0	0.73
6	1/2000	1.0	0.02

[a] [Catalyst] = 4.4×10^{-6} mol l^{-1}; T = 21°C.

The behaviour, observed for reactions with alkylating agents, demonstrates that selective alkylation of the M–Cl bonds instead of deprotonation of the uncoordinated ring occurred, favoured by the formation of LiCl. Consequently, deprotonation of the acidic Csp^3 bonded hydrogen (observed between δ 4.82 and 5.08 in the ^{1}H-NMR spectrum of all the chloro complexes) of the non-coordinated cyclopentadiene ring by basic alkylating agents, does not occur in these dichloro compounds. All attempts made to deprotonate this ring in dialkyl derivatives only led to unidentified products, thus preventing use of the uncoordinated ring to obtain heterodinuclear compounds. However, effective deprotonation was observed when the reaction of complex **5** with $Ti(NMe_2)_4$ was monitored by ^{1}H-NMR in a sealed tube. This reaction, which has been successfully used [24–27] for related *ansa*-metallocene complexes, gave the titanium–zirconium complex [$Zr(\eta^5$-$C_5H_5)Cl_2(\eta^5$-$C_5H_3)(SiMe_2)_2(\eta^5$-$C_5H_3)Ti(NMe_2)_3$] **17**, with two η^5-coordinated cyclopentadienyl rings, as the unique reaction product and is consistent with the observed ^{1}H-NMR spectrum. This dinuclear Ti–Zr complex has C_s symmetry and the expected two singlets due to the bridging methyl–silicon groups and two doublets and two triplets due to the AA′B spin system of the two non-equivalent cyclopentadienyl rings were observed. In addition, the spectrum shows two singlets that can be easily assigned to the unsubstituted cyclopentadienyl ring and the nitrogen-bonded methyl groups. Solutions of complex **17** in polar and non-polar solvents decomposed rapidly at room temperature to give a mixture of unidentified products and for this reason when this reaction was carried out at a preparative level it was not possible to isolate the desired heterodinuclear compound.

2.3. Catalytic polymerization of ethylene

The catalytic activity of the dichloro titanium, zirconium and hafnium complexes for the polymerization of ethylene was studied using MAO as cocatalyst. When ethylene was bubbled through stirring toluene solutions containing the mixed dicyclopentadienyl complexes **4**–**6** and excess MAO under rigorously anhydrous and anaerobic conditions, solid polyethylene precipitated. The activity was determined by quenching the reaction after a measured time interval and weighing the dried polymer (Table 1). All three compounds show rather low activities, that of the zirconium derivative being about eight times higher than that of the titanium complex and 30 times higher than that of the hafnium derivative. The characteristics of the resulting polymers were not studied further.

3. Experimental

3.1. General methods

All reactions were carried out in dried Schlenk tubes under argon and the manipulations were carried out using cannulas through Subaseals. Solvents were dried and distilled under argon; THF from sodium benzophenone ketyl; hexane from sodium and potassium amalgam; toluene from sodium; dichloromethane from P_2O_5. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $Ti(NMe_2)_4$ was synthesized according to the reported method [24].The ^{1}H- and ^{13}C-NMR spectra were recorded at 299.95 and 75.43 MHz, respectively, on a Varian Unity 300 spectrometer; chemical shifts, in ppm, are positive down field relative to external $SiMe_4$, and coupling constants are in Hz. C, H analyses were performed with a Perkin–Elmer 240-B instrument.

3.2. Synthesis of $[(C_5H_4)_2(SiMe_2)_2]$ *1*

Me_2SiCl_2 (32.14 ml; 0.26 mol) was added to a cooled (0°C) solution of CpNa (87.90 g; 0.53 mol) in pentane (400 ml). The mixture was warmed to room temperature and stirred overnight. The solution was filtered and the solvent was removed in vacuo to obtain the monobridged cyclopentadienyl compound $[(C_5H_5)_2(SiMe_2)]$ as a pale yellow liquid (43 ml; 84%).

BuLi (277 ml; 0.44 mol) was added to a cooled (0°C) solution of $[(C_5H_5)_2(SiMe_2)]$ (43 ml; 0.22 mol). The mixture was warmed to room temperature and stirred for 20 h. A solution of Me_2SiCl_2 (26.7 ml; 0.22 mol) in THF (40 ml) was added dropwise to the resulting suspension cooled to 0°C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue was extracted into hexane (400 ml). Compound **1** was then obtained by crystallization as pale yellow crystals (35 g; 54% with respect to starting CpNa).

The lithium salt $Li[(C_5H_4)(SiMe_2)_2(C_5H_3)]$ **2** was prepared in hexane by the reported method [23].

3.3. Synthesis of $[Ti\{(C_5H_4)(SiMe_2)_2(\eta^5$-$C_5H_3)\}Cl_3]$ *3*

A solution of $TiCl_4$ (0.61 ml; 5.59 mmol) in toluene (30 ml) was added at room temperature to a suspension of the lithium salt **2** (1.40 g; 5.59 mmol) in toluene (30 ml). The reaction mixture was refluxed for 5 h and then the solvent was removed in vacuo to give a brown solid. Complex **3** was extracted into hexane (5×20 ml) and the solution was cooled at -35°C overnight to isolate complex **3** as a brown yellowish solid (0.5 g, 22%). Anal. Calc. for $C_{14}H_{19}C_{13}Si_2Ti$: C, 42.28; H, 4.82. Found: C, 42.29; H, 5.03. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.59 (s, 3H, $SiMe_2$ bridges); 0.45 (s, 3H, $SiMe_2$

bridges); 0.47 (s, 3H, $SiMe_2$ bridges); 0.64 (s, 3H, $SiMe_2$ bridges); 4.66 (s, 1H, H allylic-C_5H_4); 6.84 (m, 1H, C_5H_4–C_5H_3); 6.93 (m, 1H, C_5H_4–C_5H_3); 7.06 (m, 2H, C_5H_4–C_5H_3); 7.30 (m, 1H, C_5H_4–C_5H_3); 7.59 (m, 1H, C_5H_4–C_5H_3). ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.72 (s, 3H, $SiMe_2$ bridges); 0.17 (s, 3H, $SiMe_2$ bridges); 0.43 (s, 3H, $SiMe_2$ bridges); 0.46 (s, 3H, $SiMe_2$ bridges); 4.71 (s, 1H, H allylic-C_5H_4); 6.22 (m, 1H, C_5H_4–C_5H_3); 6.62 (m, 1H, C_5H_4–C_5H_3); 6.70 (m, 2H, C_5H_4–C_5H_3); 6.89 (m, 1H, C_5H_4–C_5H_3); 6.95 (m, 1H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ −6.3, −1.8, −1.6, 1.4 ($SiMe_2$ bridges); 54.7 (Csp^3-C_5H_4); 130.8, 131.0, 132.6, 133.1, 139.0, 142.1 (C_β, C_γ to the $SiMe_2$ bridges); 132.4, 133.0, 140.1 (C_α to the $SiMe_2$ bridges).

3.4. Synthesis of [M(η^5-C_5H_5){(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}Cl_2] (M = Ti **4**, Zr **5**, Hf **6**) and [Ti(η^5-C_5-Me_5){(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}Cl_2] **7**

The same procedure was used to prepare these compounds. A suspension of the lithium salt **2** (2.95 g; 11.7 mmol) in THF (40 ml) was added dropwise to a cooled (−78°C) solution of $CpTiCl_3$ or $CpMCl_3 \cdot DME$ (M = Zr, Hf) (11.7 mmol) in THF (60 ml). The reaction mixture was warmed to room temperature and stirred overnight. After removing the solvent, the residue was extracted into CH_2Cl_2 (3 × 30 ml). The solvent was removed in vacuo and the solid was washed with pentane (30 ml) to give red **4** (3.8 g; 77.5%), pale yellow **5** (3.3 g; 75%), pale yellow **6** (2.5 g; 75%) and dark red **7** (2.3 g; 76%).

3.4.1. Complex **4**

Anal. Calc. for $C_{19}H_{24}Si_2TiCl_2$: C, 53.4; H, 5.66. Found: C, 52.93; H, 5.73. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.69 (s, 3H, $SiMe_2$ bridges); 0.38 (s, 6H, $SiMe_2$ bridges); 0.53 (s, 3H, $SiMe_2$ bridges); 4.82 (s, 1H, H allylic-C_5H_4); 6.54 (s, 5H, C_5H_5); 6.34 (m, 1H, C_5H_4–C_5H_3); 6.77 (m, 1H, C_5H_4–C_5H_3); 6.91 (m, 1H, C_5H_4–C_5H_3); 6.97 (m, 1H, C_5H_4–C_5H_3); 7.00 (m, 1H, C_5H_4–C_5H_3); 7.12 (m, 1H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ −5.3, −1.0, −0.7, 1.5 ($SiMe_2$ bridges); 56.2 (Csp^3-C_5H_4); 119.9 (C_5H_5); 115.1, 131.7, 132.0, 132.7, 139.8, 140.7 (C_β, C_γ to the $SiMe_2$ bridges); 140.5, 141.7, 144.7 (C_α to the $SiMe_2$ bridges).

3.4.2. Complex **5**

Anal. Calc. for $C_{19}H_{24}Si_2ZrCl_2$: C, 48.48; H, 5.14. Found: C, 48.44; H, 5.04. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.57 (s, 3H, $SiMe_2$ bridges); 0.33 (s, 3H, $SiMe_2$ bridges); 0.55 (s, 3H, $SiMe_2$ bridges); 0.56 (s, 3H, $SiMe_2$ bridges); 5.08 (m, 1H, H allylic-C_5H_4); 5.63 (m, 1H, C_5H_4–C_5H_3); 5.97 (s, 5H, C_5H_5); 6.37 (m, 1H, C_5H_3–C_5H_4); 6.49 (m, 1H, C_5H_4–C_5H_3); 6.81 (m, 1H, C_5H_4–C_5H_3); 6.86 (m, 1H, C_5H_4–C_5H_3); 7.01 (m, 1H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR (Tol-d_8, 75 MHz): δ −5.2, −1.0, −0.6, 1.5 ($SiMe_2$ bridges); 55.8 (Csp^3-C_5H_4); 114.2, 115.6, 129.5, 132.0, 139.4, 140.6 (C_β, C_γ to the $SiMe_2$ bridges); 137.2, 142.1 (C_α to the $SiMe_2$ bridges).

3.4.3. Complex **6**

Anal. Calc. for $C_{19}H_{24}Si_2HfCl_2$: C, 40.90, H, 4.34. Found: C, 40.73, H, 4.17. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.57 (s, 3H, $SiMe_2$ bridges); 0.34 (s, 3H, $SiMe_2$ bridges); 0.54 (s, 3H, $SiMe_2$ bridges); 0.56 (s, 3H, $SiMe_2$ bridges); 5.00 (s, 1H, H allylic-C_5H_4); 5.56 (m, 1H, C_5H_4–C_5H_3); 5.89 (s, 5H, C_5H_5); 6.30 (m, 1H, C_5H_4–C_5H_3); 6.42 (m, 1H, C_5H_4–C_5H_3); 6.81 (m, 1H, C_5H_4–C_5H_3); 6.85 (m, 1H, C_5H_4–C_5H_3); 7.01 (m, 1H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ −5.1, −1.0, −0.5, 1.5 ($SiMe_2$ bridges); 55.8 (Csp^3-C_5H_4); 114.5 (C_5H_5); 112.5, 128.3, 132.0, 139.4, 140.7 (C_β, C_γ to the $SiMe_2$ bridges); 135.6, 142.0 (C_α to the $SiMe_2$ bridges).

3.4.4. Complex **7**

Anal. Calc. for $C_{24}H_{34}Si_2TiCl_2$: C, 57.94; H, 6.89. Found: C, 57.18; H, 6.62. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.73 (s, 3H, $SiMe_2$ bridges); 0.36 (s, 6H, $SiMe_2$ bridges); 0.45 (s, 3H, $SiMe_2$ bridges); 2.04 (s, 15H, C_5Me_5); 4.83 (s, 1H, H allylic-C_5H_4); 6.08 (m,1H, C_5H_3–C_5H_4); 6.43 (m, 1H, C_5H_4–C_5H_3); 6.67 (m, 1H, C_5H_4–C_5H_3); 6.75 (m, 1H, C_5H_4–C_5H_3); 6.87 (m, 1H, C_5H_4–C_5H_3); 6.92 (m, 1H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ −5.2, −0.7, −0.3, 2.2 ($SiMe_2$ bridges); 13.5 (C_5Me_5); 56.4 (Csp^3-C_5H_4); 117.6, 128.2, 132.1, 132.8, 139.5 (C_β, C_γ to the $SiMe_2$ bridges); 140.1, 143.0 (C_α to the $SiMe_2$ bridges).

3.5. Synthesis of [Ti(η^5-C_5H_5){(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}ClMe] **8**

A 3 M THF solution of MgClMe (0.74 ml; 2.22 mmol) was added at low temperature (−78°C) to a solution of **4** in THF (30 ml). The solution was warmed to room temperature and stirred for 2 h. The solvent was removed in vacuo and the residue was extracted into pentane (3 × 15 ml). After removing the solvent in vacuo, complex **8** was isolated as a red solid (0.87 g, 96%). Anal. Calc. for $C_{20}H_{27}Si_2TiCl$: C, 59.03; H, 6.69. Found: C, 59.63; H, 7.03. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.41, 0.10, 039, 0.76, 0.89 (**M**, s, 3H, $SiMe_2$ bridges and Ti–Me); −0.47, 0.11, 0.51, 0.76, 0.89 (**m**, s, 3H, $SiMe_2$ bridges and Ti–Me); 4.81 (**M**, m, 1H, H allylic-C_5H_2); 4.93 (**m**, m, 1H, H allylic-C_5H_4); 4.97 (**m**, m, 1H, C_5H_4–C_5H_3); 5.18 (**m**, m, 1H, C_5H_4–C_5H_3); 5.21 (**M**, m, 1H, C_5H_4–C_5H_3); 5.38 (**M**, m, 1H, C_5H_4–C_5H_3); 5.81 (**m** + **M**, s, 10H, C_5H_5); 6.85, 6.92, 6.96, 7.00, 7.09 (**m** + **M**, m, 8H, C_5H_4–C_5H_3). ^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ −4.9, −1.2, −1.0, 1.7 (**M**, $SiMe_2$ bridges); −5.5, −0.8, 0.1, 1.0 (**m**, $SiMe_2$ bridges); 48.9

(**M**, Ti–Me); 49.2 (**m**, Ti–Me); 56.3 (**m** + **M**, Csp^3-C_5H_4); 116.2 (**M**, C_5H_5); 115.8 (**m**, C_5H_5); 114.5, 115.5, 119.2, 131.8, 134.0, 138.9 (**M**, C_β, C_γ to the $SiMe_2$ bridges); 114.9, 117.5, 119.8, 132.0, 134.3, 138.9 (**m**, C_β, C_γ to the $SiMe_2$ bridges); 138.6, 141.9, 142.4 (**M**, C_α to the $SiMe_2$ bridges); not observed (**m**, C_α to the $SiMe_2$ bridges).

3.6. Synthesis of $[Ti(\eta^5\text{-}C_5H_5)\{(C_5H_4)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}ClEt]$ **9**

A 2 M ethyl ether solution of MgClEt (0.53 ml; 1.07 mmol) was added to a cooled solution of complex **4** (0.4 g, 1.07 mmol) in THF (30 ml). The mixture was warmed to 0°C and stirred for 2 h. Then the solvent was removed in vacuo and the residue was extracted into hexane (3 × 15 ml). The solvent was removed in vacuo to give **9** as a brown reddish solid (0.35 g, 77%). Anal. Calc. for $C_{21}H_{29}Si_2TiCl$: C, 59.92, H, 6.94, Found: C, 59.81, H, 7.10. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.47 (**m**, s, 3H, $SiMe_2$ bridges), 0.07 (**m**, s, 3H, $SiMe_2$ bridges), 0.53 (**m**, s, 3H, $SiMe_2$ bridges), 0.77 (**m**, s, 3H, $SiMe_2$ bridges); −0.39 (**M**, s, 3H, $SiMe_2$ bridges), 0.04 (**M**, s, 3H, $SiMe_2$ bridges), 0.38 (**M**, s, 3H, $SiMe_2$ bridges), 0.77 (**M**, s, 3H, $SiMe_2$ bridges); 1.16 (**M**, t, $^1J_{C-H} = 7.3$ Hz, 3H, $-CH_2CH_3$); 1.23 (**m**, t, $^1J_{C-H} = 7.3$ Hz, 3H, $-CH_2-CH_3$); 1.51 (**m** + **M**, m, 2H, $-CH_2CH_3$); 2.26 (**m** + **M**, m, 2H, $-CH_2CH_3$); 4.89 (**M**, m, 1H, H allylic-C_5H_4); 4.92 (**m**, m, 1H, H allylic-C_5H_4); 5.02 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.12 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.18 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.32 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.86 (**m** + **M**, s, 10H, C_5H_5); 6.84, 6.93, 7.05, 7.19 (**m** + **M**, m, 8H, $C_5H_4-C_5H_3$). $^{13}C\{^1H\}$-NMR (C_6D_6, 50 MHz): δ −4.9, −1.3, −1.2, 1.4 (**M**, $SiMe_2$ bridges); 21.7 (**M**, $-CH_2CH_3$); 56.2 (**M**, Csp^3-C_5H_4); 63.9 (**M**, $-CH_2CH_3$); 114.4, 119.5, 131.8, 133.9, 139.8, 140.1 (**M**, C_β, C_γ to the $SiMe_2$ bridges); 115.9 (**M**, C_5H_5); 134.9, 139.8, 141.9 (C_α to the $SiMe_2$ bridges).

3.7. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)\{(C_5H_4)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}ClMe]$ **10**

A 3 M THF solution of MgClMe (0.31 ml, 0.93 mmol) was added to a cooled (−78°C) solution of **5** (0.43 ml, 0.93 mmol) in THF (30 ml). The mixture was warmed to room temperature and stirred for 4 h. After removing the solvent in vacuo the residue was extracted into hexane (3 × 30 ml). The solvent was removed in vacuo to give complex **10** as a pale yellow solid (0.33 g; 78%). Anal. Calc. for $C_{20}H_{27}Si_2ZrCl$: C, 53.35; H, 6.04. Found: C, 53.36; H, 6.49. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.49, 0.28, 0.39, 0.51, 0.69 (**M**, s, 3H, $SiMe_2$ bridges and Zr–Me); −0.52, 0.30, 0.42, 0.51, 0.69 (**m**, s, 3H, $SiMe_2$ bridges and Zr–Me); 4.94 (**m**, m, 1H, H allylic-C_5H_4); 5.12 (**M**, m, 1H, H allylic-C_5H_4); 5.20 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.23 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.47 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.66 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.81 (**m** + **M**, m, 10H, C_5H_5); 6.82, 6.88, 7.04 (**m** + **M**, m, 8H, $C_5H_4-C_5H_3$). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ −4.9, −1.1, −0.2, 1.4 (**M**, $SiMe_2$ bridges); 31.8 (**M**, Zr–Me); 55.8 (**M**, Csp^3-C_5H_4); 110.7 (**M**, C_5H_5); 113.7, 119.2, 121.6, 132.2, 138.9, 140.8 (**M**, C_β, C_γ to the $SiMe_2$ bridges); 139.9, 140.5, 142.6 (**M**, C_a to the $SiMe_2$ bridges).

3.8. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)\{(C_5H_4)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}ClEt]$ **11**

A 2 M ethyl ether solution of MgClEt (0.44 ml; 0.89 mmol) was added to a cooled solution of complex **5** (0.42 g; 0.89 mmol) in THF (30 ml). The procedure described for **9** was used to isolate complex **11** as a pale yellow solid (0.32 g, 78%). Anal. Calc. for $C_{21}H_{29}Si_2ZrCl$: C, 54.32; H, 6.30. Found: C, 53.80; H, 6.26. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.49 (**m**, s, 3H, $SiMe_2$ bridges); 0.26 (**m**, s, 3H, $SiMe_2$ bridges); 0.42 (**m**, s, 3H, $SiMe_2$ bridges); 0.70 (**m**, s, 3H, $SiMe_2$ bridges); −0.49 (**M**, s, 3H, $SiMe_2$ bridges); 0.24 (**M**, s, 3H, $SiMe_2$ bridges); 0.39 (**M**, s, 3H, $SiMe_2$ bridges); 0.70 (**M**, s, 3H, $SiMe_2$ bridges); 1.00 (**m** + **M**, m, 2H, $-CH_2CH_3$); 1.40 (**m** + **M**, m, 6H, $-CH_2CH_3$); 1.49 (**m** + **M**, m, 2H, $-CH_2CH_3$); 4.95 (**m**, m, 1H, H allylic-C_5H_4); 5.10 (**M**, m, 1H, H allylic-C_5H_4); 5.25 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.29 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.42 (**m**, m, 1H, $C_5H_4-C_5H_3$); 5.62 (**M**, m, 1H, $C_5H_4-C_5H_3$); 5.84 (**m** + **M**, s, 10H, C_5H_5); 6.83, 6.88, 7.04 (**m** + **M**, m, 8H, $C_5H_4-C_5H_3$). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ −4.9, −1.2, 0.2, 1.1 (**M**, $SiMe_2$ bridges); 20.2 (**M**, $-CH_2CH_3$); 47.2 (**M**, $-CH_2CH_3$); 55.7 (**M**, Csp^3-C_5H_4); 110.5 (**M**, C_5H_5); 113.6, 121.9, 132.0, 134.9, 140.9, 141.8 (**M**, C_β, C_γ to the $SiMe_2$ bridges); 135.7, 138.9, 142.0 (C_α to the $SiMe_2$ bridges).

3.9. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)\{(C_5H_4)(SiMe_2)_2(\eta^5\text{-}C_5H_3)\}Cl(CH_2Ph)]$ **12**

Cooled (−30°C) THF (30 ml) was added to a mixture of **5** (0.5 g; 1.06 mmol) and $Mg(CH_2Ph)_2 \cdot 2THF$ (0.37 g; 1.06 mmol). The mixture was warmed to room temperature and stirred for 3 h. The solvent was removed in vacuo and the residue was extracted into pentane (3 × 15 ml). The solution was concentrated by evaporation of the solvent to half volume and kept at −35°C overnight to give complex **12** as an orange solid (0.42 g, 75%). Anal. Calc. for $C_{26}H_{31}Si_2ZrCl$: C, 59.33; H, 5.94. Found: C, 58.70; H, 6.26. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.50 (**M**, s, 3H, $SiMe_2$ bridges); 0.21 (**M**, s, 3H, $SiMe_2$ bridges); 0.37 (**M**, s, 3H, $SiMe_2$ bridges); 0.73 (**M**, s, 3H, $SiMe_2$ bridges); −0.50 (**m**, s, 3H, $SiMe_2$ bridges); 0.22 (**m**, s, 3H, $SiMe_2$ bridges); 0.42 (**m**, s, 3H, $SiMe_2$ bridges); 0.79 (**m**, s, 3H, $SiMe_2$ bridges); 2.01

(**m** + **M**, d, $^1J_{C-H}$ = 12 Hz, 2H, –CH_2Ph); 2.74 (**m** + **M**, d, $^1J_{C-H}$ = 12 Hz, 2H, –CH_2Ph); 4.91 (**m**, m, 1H, H allylic-C_5H_4); 5.14 (**M**, m, 1H, H allylic-C_5H_4); 5.27 (**M**, m, 1H, C_5H_4–C_5H_3); 5.31 (**m**, m, 1H, C_5H_4–C_5H_3); 5.48 (**m**, m, 1H, C_5H_4–C_5H_3); 5.65 (**m**, s, 5H, C_5H_5); 5.66 (**M**, s, 5H, C_5H_5); 5.72 (**M**, m, 1H, C_5H_4–C_5H_3); 6.63, 6.68, 6.84, 6.93, 7.04, 7.10, 7.27 (**m** + **M**, 18H, C_5H_4–C_5H_3, –CH_2Ph). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): −5.1, −1.1, −0.8, 2.2 (**M**, $SiMe_2$ bridges); 55.9 (**M**, Csp^3-C_5H_4); 59.9 (**M**, –CH$_2$Ph); 113.8 (**M**, C_5H_5); 113–152 (**M** + **m**, ten signals C_5H_4–C_5H_3, –CH_2Ph).

3.10. Synthesis of [Hf(η^5-C_5H_5){(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}Cl(CH_2Ph)] **13**

Cooled (−30°C) THF (30 ml) was added to a mixture of **6** (0.3 g; 0.53 mmol) and Mg(CH_2Ph)$_2$ · 2THF (0.18 g; 0.53 mmol). The mixture was warmed to room temperature and stirred for 5 h. The procedure described for **12** was used to obtain complex **13** as a pale yellow solid (0.22 g; 69%). Anal. Calc. for $C_{26}H_{31}Si_2HfCl$: C, 50.89; H, 5.09. Found: C, 51.23; H, 5.38. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.52 (**M**, s, 3H, $SiMe_2$ bridges); 0.24 (**M**, s, 3H, $SiMe_2$ bridges); 0.38 (**M**, s, 3H, $SiMe_2$ bridges); 0.72 (**M**, s, 3H, $SiMe_2$ bridges); −0.52 (**m**, s, 3H, $SiMe_2$ bridges); 0.24 (**m**, s, 3H, $SiMe_2$ bridges); 0.40 (**m**, s, 3H, $SiMe_2$ bridges); 0.79 (**m**, s, 3H, $SiMe_2$ bridges); 1.60 (**m** + **M**, d, $^1J_{C-H}$ = 12 Hz, 2H, –CH_2Ph); 2.58 (**m** + **M**, d, $^1J_{C-H}$ = 12 Hz, 2H, –CH_2Ph); 4.84 (**m**, m, 1H, H allylic-C_5H_4); 5.06 (**M**, m, 1H, H allylic-C_5H_4); 5.17 (**M**, m, 1H, C_5H_4–C_5H_3); 5.22 (**m**, m, 1H, C_5H_4–C_5H_3); 5.54 (**m**, m, 1H, C_5H_4–C_5H_3); 5.61 (**m** + **M**, s, 10H, C_5H_5); 5.77 (**M**, m, 1H, C_5H_4–C_5H_3); 6.55 (**M**, m, 1H, C_5H_4–C_5H_3); 6.61 (**m**, m, 1H, C_5H_4–C_5H_3), 6.84, 6.94, 7.04, 7.09, 7.12, 7.30, 7.32 (**m** + **M**, 16H, C_5H_4–C_5H_3, –CH_2Ph). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): −4.9, −1.2, −0.8, 2.2 (**M**, $SiMe_2$ bridges); 55.9 (**M**, Csp^3-C_5H_4); 60.8 (**M**, –CH$_2$Ph); 112.8 (**M**, C_5H_5); 114.5–151.9 (**M** + **m**, ten signals C_5H_4–C_5H_3, –CH_2Ph).

3.11. Synthesis of [M(η^5-C_5H_5){(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}Me_2] (M = Ti **14**, Zr **16**) and [Ti(η^5-C_5Me_5)-{(C_5H_4)($SiMe_2$)$_2$(η^5-C_5H_3)}Me_2] **15**

The same procedure was used to prepare these compounds. A 1.6 M ethyl ether solution of LiMe (1.65 ml; 2.8 mmol) was added to a cooled solution (−78°C) of complexes **4**, **5** or **6** (1.4 mmol) in hexane (30 ml). The mixture was warmed to room temperature and stirred for 2 h (**14**, **15**) or 4 h (**16**). The solvent was removed in vacuo and the residue was extracted into hexane (3 × 20 ml). After removing the solvent in vacuo, orange oily solid **14** (0.38 g, 71%), pale yellow solid **5** (0.46 g; 77%) and yellow oily solid **16** (0.26 g; 70%) were isolated.

3.11.1. Complex **14**

Anal. Calc. for $C_{21}H_{30}Si_2Ti$: C, 65.26, H, 7.82. Found: C, 64.97, H, 7.53. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.38 (s, 3H, $SiMe_2$ bridges), 0.22 (s,br, 6H, $TiMe_2$), 0.25 (s, 3H, $SiMe_2$ bridges), 0.32 (s, 3H, $SiMe_2$ bridges), 0.47 (s, 3H, $SiMe_2$ bridges); 4.29 (s, 1H, H allylic-C_5H_4); 5.77 (s, 5H, C_5H_5); 5.08 (m, 1H, C_5H_4–C_5H_3); 5.92 (m, 1H, C_5H_4–C_5H_3); 6.00 (m, 1H, C_5H_4–C_5H_3); 6.85 (m, 2H, C_5H_4–C_5H_3); 7.09 (m, 1H, C_5H_4–C_5H_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ −4.9, −1.4, 0.3, 1.0 ($SiMe_2$ bridges); 47.0, 47.1 (Ti–Me); 56.0 (Csp^3-C_5H_4); 113.9 (C_5H_5); 114.2, 123.0, 124.5, 132.2, 139.1, 140.8 (C_β, C_γ to the $SiMe_2$ bridges); 137.2, 140.3, 142.7 (C_α to the $SiMe_2$ bridges).

3.11.2. Complex **15**

Anal. Calc. for $C_{21}H_{40}Si_2Ti$: C, 68.39; H, 8.83. Found: C, 68.01; H, 8.41. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.33 (s, 3H, $SiMe_2$ bridges), −0.08 (s, 3H, $TiMe_2$), −0.06 (s, 3H, $TiMe_2$), 0.36 (s, 3H, $SiMe_2$ bridges), 0.40 (s, 3H, $SiMe_2$ bridges), 0.58 (s, 3H, $SiMe_2$ bridges); 1.66 (s, 15H, C_5Me_5); 4.46 (s, 1H, H allylic-C_5H_4); 5.08 (m, 1H, C_5H_4–C_5H_3); 5.84 (m, 1H, C_5H_4–C_5H_3); 6.09 (m, 1H, C_5H_4–C_5H_3); 6.89 (m, 3H, C_5H_4–C_5H_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ −4.7, −0.5, 0.4, 1.7 ($SiMe_2$ bridges); 12.4 (C_5Me_5); 47.2 (Ti–Me); 56.4 (Csp^3-C_5H_4); 116.0, 120.5, 121.4, 125.4, 132.2, 139.8 (C_β, C_γ to the $SiMe_2$ bridges); 132.4, 134.1, 143.3 (C_α to the $SiMe_2$ bridges).

3.11.3. Complex **16**

Anal. Calc. for $C_{21}H_{30}Si_2Zr$: C, 58.68; H, 7.03. Found: C, 59.01; H, 6.87. ^{1}H-NMR (C_6D_6, 300 MHz): δ −0.47 (s, 3H, $SiMe_2$ bridges), 0.00 (s, br, 6H, $ZrMe_2$), 0.31 (s, 3H, $SiMe_2$ bridges), 0.34 (s, 3H, $SiMe_2$ bridges), 0.41 (s, 3H, $SiMe_2$ bridges); 4.31 (s, 1H, H allylic-C_5H_4); 5.51 (m, 1H, C_5H_4–C_5H_3); 5.78 (s, 5H, C_5H_5); 5.93 (m, 1H, C_5H_4–C_5H_3); 6.12 (m, 1H, C_5H_4–C_5H_3); 6.83 (m, 2H, C_5H_4–C_5H_3); 7.04 (m, 1H, C_5H_4–C_5H_3). $^{13}C\{^1H\}$-NMR (C_6D_6): δ −4.9, −1.1, 0.2, 1.4 ($SiMe_2$ bridges); 31.8, 32.3 (Zr–Me); 55.8 (Csp^3-C_5H_4); 110.7 (C_5H_5); 113.7, 119.2, 121.6, 132.2, 138.9, 140.8 (C_β, C_γ to the $SiMe_2$ bridges); 139.9, 140.4, 142.6 (C_α to the $SiMe_2$ bridges).

3.12. Reaction of complex **5** with Ti(NMe_2)$_4$

Ti(NMe_2)$_4$ (0.023 g; 0.109 mmol) was added at room temperature to a C_6D_6 solution of complex **5** (0.048 g; 0.109 mmol) in a valved NMR tube. After 2 h, the reaction was complete as observed from the ^{1}H-NMR spectrum, which showed the signals expected for complex **17**. ^{1}H-NMR (C_6D_6, 300 MHz): δ 0.45 (s, 6H, $SiMe_2$ bridges); 0.71 (s, 6H, $SiMe_2$ bridges); 2.93 (s, 18H, Ti–NMe_2); 5.84 (t, $^1J_{C-H}$ = 3Hz, 1H, C_5H_3); 5.99 (s, 5H, C_5H_5); 6.33 (t, $^1J_{C-H}$ = 3Hz, 1H, C_5H_3); 6.39 (d,

$^1J_{C-H} = 3Hz$, 2H, C_5H_3); 6.74 (d, $^1J_{C-H} = 3Hz$, 2H, C_5H_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ 2.0, 4.0 ($SiMe_2$ bridges); 50.3 (Ti–NMe_2); 113.8 (C_γ to the $SiMe_2$ bridges); 115.7 (C_5H_5); 116.4 (C_γ to the $SiMe_2$ bridges); 120.6 (C_β to the $SiMe_2$ bridges); 125.0 (C_α to the $SiMe_2$ bridges); 130.2 (C_β to the $SiMe_2$ bridges); 134.5 (C_α to the $SiMe_2$ bridges).

Acknowledgements

The authors acknowledge DGICYT (PB97-0776) and CAM (I + D0033/94) for financial support. R.G-G acknowledges CAM for a fellowship.

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