ELSEVIER

Journal of Organometallic Chemistry 645 (2002) 112–117

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Dinuclear zirconium complexes containing the fulvalene ligand. Synthesis and reactivity

Marta González-Maupoey, Gema Rodríguez, Tomás Cuenca *

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

Received 16 July 2001; accepted 3 October 2001

Abstract

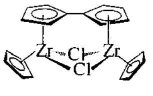
Reduction of $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2$ with 1.5 equiv of 10% sodium amalgam in toluene affords the zirconium(III) derivative $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**1**) which reacts with chlorine or chlorinated solvents to give the zirconium(IV) compound $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**2**). When the tetrachloro fulvalene $[ZrCp'Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ ($Cp' = \eta^5\text{-}C_5H_5$ (Herrmann et al., Angew. Chem. Int. Ed. Engl. 26 (1987) 697); $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$ (**2**)) compounds were treated with four equivalents of LiR (R = Me, Ph) in toluene at −78 °C the tetraalkyl derivatives $[ZrCp'R_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ ($Cp' = \eta^5\text{-}C_5H_5$, R = Me, Ph (**3**); $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$, R = Me (**4**)) were obtained. Compound **4** reacts with a stoichiometric amount of water with hydrolysis of the Zr–methyl bond to give the μ-oxo complex $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(CH_3)]_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**8**). The zirconium alkoxide $[Zr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}O_2SiPh_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**5**) and the iminoacyl complexes $[Zr(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}CR{=}N(2,6\text{-}Me_2C_6H_3)\}R]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (R = Me (**6**), Ph (**7**)) were prepared by reaction of the tetraalkyl complexes with either the alcohol $Ph_2Si(OH)_2$ or isocyanide $CN(2,6\text{-}Me_2C_6H_3)$, respectively. Two diastereoisomers of compounds **6** and **7** were obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium; Fulvalene

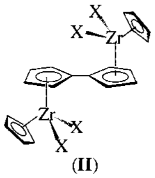
1. Introduction

The study of early transition metal chemistry has been dominated by complexes with ancillary cyclopentadienyl ligands [1]. Mono- and dicyclopentadienyl titanium, zirconium and hafnium compounds have proved to be useful organometallic materials, with considerable interest shown in Group 4 metallocenes as homogeneous catalysts in α-olefin polymerisation [2]. The choice of the ancillary ligand set has been shown to be an important factor in the stabilisation of the active catalyst species. The stability, solubility and reactivity of these metallocene derivatives are dramatically influenced by modifications in the cyclopentadienyl ligands [3].

There has been considerable and increasing attention given to homobimetallic and heterobimetallic complexes in recent years because the cooperative reactivities of their two metal centres has stimulated the study of their properties and reactivity in relation to the analogous mononuclear cyclopentadienyl compound [4]. The fulvalene ligand is particularly interesting as it permits dinuclear complexes with a short inter-metallic distance to be formed, and it may even promote a slight metal–metal interaction as in compound **I**. Free rotation of the rings around the C–C bond in relation to the fulvalene plane makes it possible for two conformations of the metal fragments, *cis* and *trans* (**I**, **II**), a factor that depends mainly on electronic and steric factors. This ligand can be considered as a cyclopentadienyl group substituted with another identical group. It makes the metal more electron-deficient and secondary reactions such as activation of ring C–H bonds are reduced because of the rigid system that generates the fulvalene.



(I)



(II)

---

* Corresponding author. Tel.: +34-91-885-4655; fax: +34-91-885-4683.

E-mail address: tomas.cuenca@uah.es (T. Cuenca).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)01345-6

Since complex **I** was first reported in 1986 [5], this zirconium(III) substance has been the initial compound used to generate a range of interesting complexes with different properties [6]. In recent years, the synthesis and reactivity of dinuclear zirconium organometallic compounds containing the fulvalene ligand have been the subject of our research focus [7], and the study of fundamental chemical reactions with a variety of new fulvalene derivatives has been published [8]. In this paper, we report the formation of new fulvalene complexes containing unsubstituted and substituted additional cyclopentadienyl ligands.

2. Results and discussion

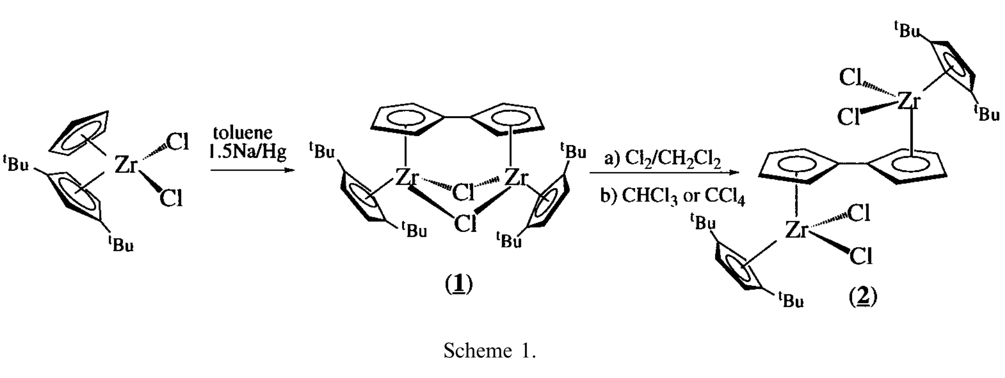
Following the well-known method used to prepare the zirconium(III) compound $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [5a], the dichlorozirconocene $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2$ [9] was reduced with 1.5 equiv of 10% sodium amalgam in toluene at room temperature followed by reflux for 2 h to give a red–purple solution from which a crystalline compound can be isolated in 80% yield and characterised as $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**1**). When a solution of **1** is treated by dropwise addition of a solution of chlorine in dichloromethane, the colour changes immediately to yellow with the formation of a yellow precipitate which is very insoluble in most common organic solvents. After being repeatedly washed, the solid obtained in 21% yield was identified as $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**2**). The reaction of **1** with chlorinated solvents such as $CHCl_3$ or CCl_4 is an alternative method to obtain **2** (Scheme 1).

The formation of **1** by reduction of the mixed dicyclopentadienyl $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2$ revealed that selective C–H activation occurred in the unsubstituted cyclopentadienyl ring and the reductive C–C coupling process afforded the '$C_{10}H_8$' fulvalene system. This result contrasts with that observed for reduction of the dialkyl derivatives $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)R_2$, which afforded an alkane and the ring methyl-metallated complexes $Zr(\eta^5\text{-}C_5H_5)(1\text{-}{}^tBu\text{-}3\text{-}CH_2CMe_2\text{-}\eta^5\text{-}C_5H_3)R$ via intramolecular activation of one of the cyclopentadienyl bonded *tert*-butyl groups with elimination of the corresponding hydrocarbon [10].

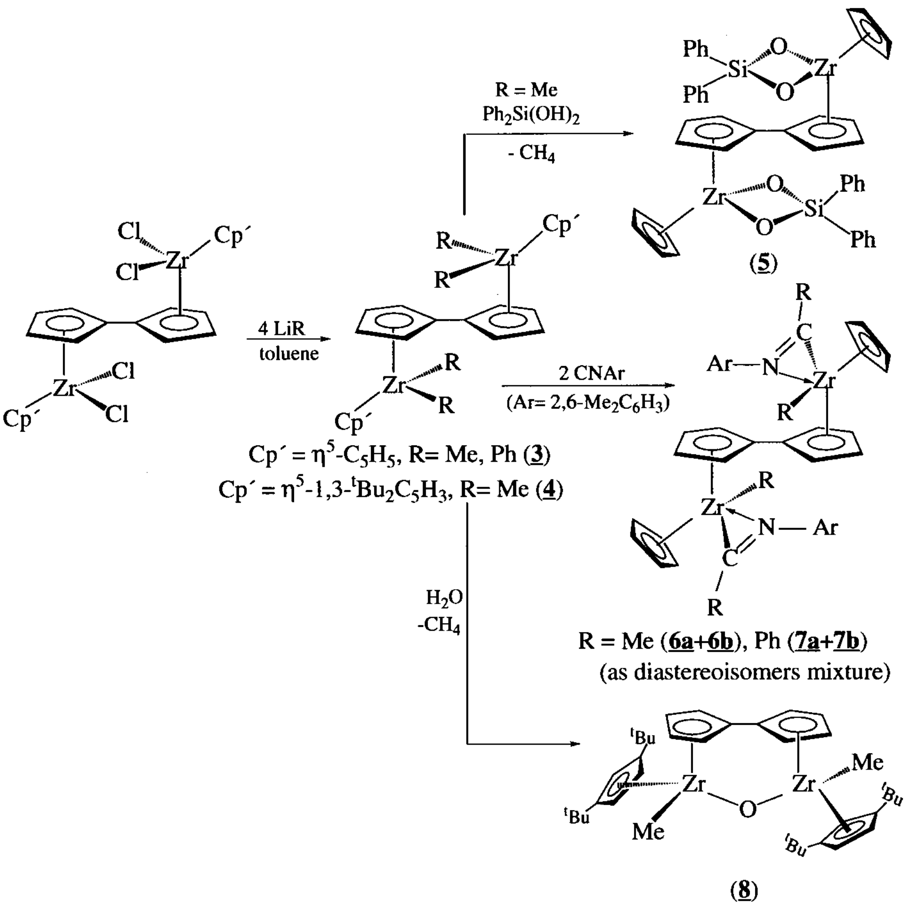
The addition of four equiv of LiR (R = Me, Ph) to a suspension of the compounds $[ZrCp'Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ ($Cp' = \eta^5\text{-}C_5H_5$ [6c]; $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$ (**2**)) in toluene at −78 °C gave a solution from which the crystalline alkyl derivatives $[ZrCp'R_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ ($Cp' = \eta^5\text{-}C_5H_5$, R = Me [6c], Ph (**3**); $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$, R = Me (**4**)) were obtained in good yield (Scheme 2).

The zirconium alkoxide derivative $[Zr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}O_2SiPh_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**5**) was prepared by reaction of the corresponding tetramethyl compound with the alcohol $Ph_2Si(OH)_2$ in toluene at room temperature. The tetraalkyl compounds react with isocyanide to give the corresponding iminoacyl-complexes as shown in Scheme 2. Reaction of the dimethyl and diphenyl zirconium compounds $[Zr(\eta^5\text{-}C_5H_5)R_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ with one equivalent of $CN(2,6\text{-}Me_2C_6H_3)$ in toluene at room temperature afforded the complexes $[Zr(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}CR{=}N(2,6\text{-}Me_2C_6H_3)\}R]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (R = Me (**6**), Ph (**7**)), which did not react when heated with a further addition of isocyanide, as expected for an 18-electron zirconium centre containing the η^2-coordinated iminoacyl group. Compounds **6** and **7** were isolated as a mixture of two diastereoisomers since there are two chiral zirconium centres present in the molecule. The mixture was resolved for **6** by repeated recrystallisation from toluene–hexane solutions, but separation was not possible for the mixture of **7**. Compound **4** reacts in solution with a stoichiometric amount of water with hydrolysis of the zirconium–methyl bond to give the μ-oxo complex $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(CH_3)]_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**8**) and simultaneous formation of methane.

Complex **1** is very air sensitive and **3**–**8** remain air stable (in the solid state) for days, but should be stored under argon or dinitrogen. They were characterised by elemental analysis, IR and NMR spectroscopy. Their mass spectra confirm their dimeric nature and the analytical composition exactly fits the proposed formulation. Attempts to obtain crystals suitable for X-ray



Scheme 1.



Scheme 2.

crystallographic studies were unsuccessful, making solid-state confirmation of the proposed structures impossible. The synthesised compounds are soluble in toluene, benzene, THF, dichloromethane and chloroform, but insoluble in pentane or hexane. Being insoluble in all organic solvents, **2** cannot be characterised by NMR spectroscopy. The lack of solubility of **2** is similar to that known for the similar titanium and zirconium derivatives $[M(\eta^5\text{-}C_5H_5)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [6c,7c]. However, the analogous pentamethylcyclopentadienyl zirconium complex is more soluble and its ^{1}H-NMR spectrum can be recorded [9]. Very clean ^{1}H- and ^{13}C-NMR spectra were obtained for compound **3** but correct elemental analysis data could not be obtained. It indicates the compound contains an impurity (probably LiCl) which could not be removed even after several attempts of recrystallisation.

The ^{1}H-NMR spectra of **1** and **4** in benzene-d_6 at room temperature show AA′BB′ spin systems (two pseudotriplets) for the fulvalene ligand, two signals (one triplet and one doublet) corresponding to an AA′B spin system for the substituted cyclopentadienyl protons and one singlet for the *tert*-butyl group protons. The ^{1}H-NMR spectrum of complex **8**, in C_6D_6, shows one ABCD spin system (four multiplets) for the fulvalene ligand, three multiplets corresponding to an ABC spin system assignable to the substituted cyclopentadienyl protons and two singlets for the *tert*-butyl group protons. These data are in agreement with the chiral character of the two metal centres in **8**, although only one possible stereoisomer was observed in the reaction. The methyl protons in compounds **4** and **8** appear as singlets at δ 0.08 and 0.15, respectively.

Complexes **3** and **5** show the NMR behaviour expected for C_s symmetrical molecules with equivalent cyclopentadienyl rings. This is consistent with a dinuclear structure in which the two metal fragments are located in *trans* positions, bound to each ring of a planar fulvalene group and with a plane of symmetry that contains the two metal atoms and the two fulvalene C_{ipso} atoms. A probable structure with two bridging ‘Ph_2SiO_2’ ligands connecting both zirconium atoms cannot be ruled out. Consequently, their ^{1}H-NMR spectra ($CDCl_3$, room temperature) show two signals characteristic of a fulvalene AA′BB′ spin system, one singlet due to the cyclopentadienyl ring protons and the expected resonances for the phenyl group protons. Compound **5** shows signals for two non-equivalent phenyl groups, consistent with tetrahedral coordination around the silicon atom, which locates one phenyl ligand up and the other down with respect to the bent metallocene wedge. Each zirconium coordination site is occupied by two oxygen atoms from the alkoxide ligands, with the silicon atoms located in this σ-ligand plane.

The presence of the iminoacyl ligand in compounds **6** and **7**, which must locate the nitrogen atom in the more common 'inside' coordination, generates a molecule with two chiral metal centres. As a result the distal and proximal proton of the fulvalene bridging ligand form diastereotopic pairs which produce an ABCD spin system, giving four multiplets in their ^{1}H-NMR spectra. However, both zirconium centres maintain the same ligand arrangements and one signal for the cyclopentadienyl ring protons is observed. The resonances due to the migrated alkyl groups are shifted down-field with respect to the values observed for the metal bonded ligands. The spectra show two resonances due to the non-equivalent methyl protons having equivalent 2,6-$Me_2C_6H_3NC$ ligands, indicating that there must be hindered rotation around *N*-aryl bonds, probably restricted by the fulvalene system. The iminoacyl carbon was not observed in the ^{13}C-NMR spectrum due to the poor solubility of the sample. The presence of two diastereoisomers is observed in the NMR spectra for both iminoacyl complexes **6** and **7**. For **6** both isomers were separated by recrystallisations from toluene–hexane and identified by analytical and spectroscopic methods. Attempts to separate the isomers of **7** were unsuccessful and the spectral data does not allow **7a** to be distinguished from **7b**. The iminoacyl complexes show the ν(CN) absorption band around 1500 cm^{-1} in the IR spectra. For all of these compounds, similar structural features to those described from the ^{1}H-NMR spectroscopy can be deduced from the ^{13}C-NMR spectra.

3. Conclusions

The use of the fulvalene ligand as a bridging system between two metal fragments is a valuable strategy to design new dinuclear zirconium derivatives and to study their chemical and structural behaviour. Neutral dinuclear zirconium(IV) complexes containing one fulvalene and one unsubstituted or substituted cyclopentadienyl ring can be generated by oxidative addition of chorine to the easily accessible zirconium(III) complexes $(ZrCp')_2(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$). Further treatment with various reagents permits the synthesis of new derivatives.

4. Experimental

All manipulations were performed under Ar using Schlenk and high-vacuum line techniques or a glovebox model HE-63. The solvents were purified by distillation under Ar before use by employing the appropriate drying/deoxygenated agent. Deuteriated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. MgClMe, $Ph_2Si(OH)_2$ and 1,6-dimethylisocyanide (Aldrich) were purchased from commercial sources and used without further purification. $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [5a], $[Zr(\eta^5\text{-}C_5H_5)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [6c], $[Zr(\eta^5\text{-}C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [6c], $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2$ [9] and LiC_6H_5 [11] were prepared by known procedures. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyser. IR spectra were recorded on a Perkin–Elmer Spectrum 2000 spectrophotometer using CsI pellets; only selected IR data are reported. NMR spectra, measured at 25 °C, were recorded on a Varian Unity 500 Plus spectrometer and chemical shifts are referenced to residual protons and carbon signals of the solvent.

4.1. Synthesis of $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**1**)

A mixture of 2.00 g (4.9 mmol) of $Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2$ and 10% sodium (0.17 g, 7.3 mmol) amalgam was stirred in toluene (100 ml) at room temperature (r.t) for 12 h. Then, the reaction mixture was heated under reflux for 2 h. A red–purple solution was obtained. After cooling to r.t., the solution was filtered and the residue washed with toluene until the washing solution was colourless. All of the extracts were collected and combined and the resulting solution concentrated to 10 ml. By cooling to −30 °C, 1.50 g (83.2% yield) of **1** was obtained as red–purple crystals. The compound was recrystallised from toluene. Anal. Calc. for $C_{36}H_{50}Cl_2Zr_2$: C, 58.74, H, 6.84. Found: C, 58.11, H, 7.12%. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): δ 6.11, 5.22 (AA′B spin system, 2H + 4H, C_5H_3); 5.37, 4.01 (AA′BB′ spin system, 2 × 4H, $C_{10}H_8$); 1.29 [s, 36H, $C(CH_3)$]. ^{13}C-NMR (125 MHz, C_6D_6, 25 °C): δ 108.2, 101.4 (C_5H_3), 102.9, 101.0 ($C_{10}H_8$), 33.0 [$C(CH_3)$].

4.2. Synthesis of $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**2**)

A solution of 1.00 g (1.34 mmol) of $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**1**) in toluene (50 ml) was treated at r.t. with an excess of chlorine dissolved in CH_2Cl_2 (10 ml). The red–purple solution turned yellow and a solid of the same colour was formed. The reaction mixture was stirred for 1 h. The solvent was evaporated under vacuum and the resulting residue was washed in order with $CHCl_3$ (2 × 50 ml), THF (2 × 50 ml), hexane (2 × 50 ml) and acetone (2 × 50 ml) to give 0.23 g (21% yield) of compound **2**. Anal. Calc. for $C_{36}H_{50}Cl_4Zr_2$: C, 53.58, H, 6.20. Found: C, 53.21, H, 6.17%. NMR study could not be carried out because of the lack of solubility of the compound in all organic solvents.

4.3. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)Ph_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (3)

A 1.8 M solution of LiPh (3.92 ml, 7.05 mmol) in THF was added at − 78 °C to a suspension of 1.00 g (1.72 mmol) of $[Zr(\eta^5\text{-}C_5H_5)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ in toluene (75 ml). The reaction mixture was slowly warmed to r.t. and stirred over 12 h. After filtration, the resulting solution was concentrated to 10 ml and cooled to − 30 °C overnight to give compound **3** as a yellow solid. The compound was recrystallised from toluene–hexane (0.90 g, 70% yield). Anal. Calc. for $C_{44}H_{38}Zr_2$: C, 70.54, H, 5.11%. The isolated yellow solid consisted mainly of **3**, but it also contained an impurity that could not be removed (probably LiCl) preventing correct elemental analysis and only very clean ^{1}H- and ^{13}C-NMR spectra were obtained. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.20–7.00 (Ph), 5.99 (C_5H_5), 6.14, 5.81 (AA′BB′ spin system, 2 × 4H, $C_{10}H_8$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ 183.0 (C_{ipso} Ph); 135.4, 126.3, 125.1 (Ph), 111.6 (C_{ipso} $C_{10}H_8$); 111.1, 110.0 ($C_{10}H_8$), 112.8 (C_5H_5).

4.4. Synthesis of $[Zr(\eta^5\text{-}1,3\text{-}^tBu_2C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (4)

A 3 M solution of MgClMe (0.50 ml, 1.50 mmol) in THF was added at − 78 °C to a suspension of 0.30 g (0.37 mmol) of $[Zr(\eta^5\text{-}1,3\text{-}^tBu_2C_5H_3)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**2**) in toluene (50 ml). The reaction mixture was slowly warmed to r.t. and stirred for 12 h. After filtration, the resulting solution was concentrated to 10 ml and cooled to − 30 °C overnight to give compound **4** as a yellow solid. The compound was recrystallised from toluene–hexane (0.17 g, 63% yield). Anal. Calc. for $C_{40}H_{62}Zr_2$: C, 66.24, H, 8.62. Found: C, 66.33, H, 8.74%. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): δ 6.33, 5.30 (AA′B spin system, 4H + 2H, C_5H_3), 6.46, 5.65 (AA′BB′ spin system, 2 × 4H, $C_{10}H_8$), 1.08 [s, 36H, $C(CH_3)_3$], 0.08 (s, 12H, Zr–CH_3). ^{13}C-NMR (125 MHz, C_6D_6, 25 °C): δ 136.6 (C_{ipso} C_5H_3), 123.9 (C_{ipso} $C_{10}H_8$), 110.9, 100.7 (C_5H_3), 110.2, 105.5 ($C_{10}H_8$), 33.1 (Zr–CH_3), 31.7 [$C(CH_3)_3$].

4.5. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}O_2SiPh_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (5)

$Ph_2Si(OH)_2$ (0.86 g, 4.0 mmol) was added to a solution of $[Zr(\eta^5\text{-}C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (1.00 g, 2.0 mmol) in toluene (40 ml) at r.t. The reaction mixture was stirred for 16 h and methane release was observed. The solvent was removed and a light brown powder was obtained which was washed with diethyl-ether and hexane. Recrystallisation from toluene–hexane gave a yellow–brown microcrystalline solid which was characterised as **5**. Elemental analysis calculated for $C_{44}H_{38}Zr_2Si_2O_4$: C 60.79, H 4.37. Found: C 60.67, H 4.69%. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.70–7.10 (20H, Ph), 6.26 (s, 10H, C_5H_5), 6.16, 6.13 (AA′BB′ spin systems, $C_{10}H_8$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ 139.9, 139.2 (*ipso*-Ph), 134.3, 134.0 (*o*-Ph), 129.1, 128.7 (*p*-Ph), 127.8, 127.4 (*m*-Ph), 113.4 (C_5H_5), 121.1 (C_{ipso}, $C_{10}H_8$), 116.9, 106.2 ($C_{10}H_8$).

4.6. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}CMe{=}N(2,6\text{-}Me_2C_6H_3)\}Me]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (6a + 6b)

2,6-Dimethylisocyanide (0.52 g, 4.0 mmol) was added to a solution of $[Zr(\eta^5\text{-}C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (1.00 g, 2.0 mmol) in toluene (50 ml) at r.t. The reaction mixture was stirred overnight at r.t. The solvent was removed and a light yellow powder was obtained which was washed with diethyl-ether and hexane to yield a mixture of the two diastereoisomers **6a** and **6b**. Repeated recrystallisation from toluene–hexane at − 20 °C gave a yellow microcrystalline solid as a precipitate which was characterised as **6a**. When all of the solvent was removed from the resulting solution under vacuum a mixture of **6a** and **6b** was obtained. Elemental analysis calculated for $C_{42}H_{48}Zr_2N_2$: C 66.10, H 6.34, N 3.67. Found: C 66.57, H 6.46, N 3.62%. Compound **6a**: ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.95 (m, 6H, Ph), 5.51 (s, 10H, C_5H_5); 5.85, 5.81, 5.67, 5.66 (m, 4 × 2H, ABCD spin system, $C_{10}H_8$), 2.24 (s, 6H, NC–CH_3), 1.94, 1.87 (s, 2 × 6H, 2,6-$Me_2C_6H_3$), − 0.26 (s, 6H, Zr–CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ 129, 128, 125 (*m*, *p*, *o*-Ph), 107.4 (C_5H_5), 108.4, 106.0, 104.6, 101.8, ($C_{10}H_8$), 23.9 (NC–CH_3), 18.9, 18.7 (2,6-$Me_2C_6H_3$), 11.5 (Zr–CH_3), (NC–CH_3) not observed. Compound **6b**: ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.90 (m, 6H, Ph), 5.52 (s, 10H, C_5H_5), 5.90, 5.72, 5.68, 5.65 (m, 4 × 2H, ABCD spin system, $C_{10}H_8$), 2.20 (s, 6H, NC–CH_3), 1.96, 1.80 (s, 2 × 6H, 2,6-$Me_2C_6H_3$), − 0.24 (s, 6H, Zr–CH_3).

4.7. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}CPh{=}N(2,6\text{-}Me_2C_6H_3)\}Ph]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (7a + 7b)

2,6-Dimethylisocyanide (0.35 g, 2.67 mmol) was added to a solution of $[Zr(\eta^5\text{-}C_5H_5)Ph_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**3**) (1.00 g, 1.33 mmol) in toluene (50 ml) at r.t. The reaction mixture was stirred overnight at r.t. The solvent was removed and a light yellow powder was obtained which was washed with diethyl-ether and hexane to yield a mixture of the two diastereoisomers **7a** and **7b**. These two isomers could not be separated by repeated recrystallisation from toluene–hexane. Elemental analysis calculated for $C_{62}H_{56}Zr_2N_2$: C 73.63, H 5.58, N 2.77. Found: C 73.90, H 5.92, N 2.33%. IR (KBr, cm^{-1}): ν(CN) 1465. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): **7a**: δ 7.4–6.8 (m, 26H, Ph), 5.62 (s, 10H, C_5H_5), 6.08, 5.91, 5.80, 5.72 (m, 4×2H, ABCD spin system, $C_{10}H_8$), 1.82, 1.75 (s, 2×6H, 2,6-$Me_2C_6H_3$); **7b**: δ 7.5–6.5 (m, 26H, Ph), 5.64 (s, 10H, C_5H_5), 6.04, 5.87, 5.73, 5.71 (m, 4×2H, ABCD spin system, $C_{10}H_8$), 1.86, 1.68 (s, 2×6H, 2,6-$Me_2C_6H_3$).

4.8. Synthesis of $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(CH_3)]_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (8)

A solution containing 0.5 g (6.9 mmol) of $[Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**4**) in wet toluene (25 ml) was stirred for 12 h. A yellow precipitate was formed. The solvent was evaporated and the solid obtained was washed with hexane. Recrystallisation from toluene–hexane at −20 °C gave compound **8** as a yellow solid (0.2 g, 40% yield). Anal. Calc. for $C_{38}H_{56}Zr_2O$: C, 64.17, H, 7.90. Found: C, 63.98, H, 7.54%. ^{1}H-NMR (500 MHz, C_6D_6, 25 °C): δ 6.67, 6.37, 5.77, 5.51 (ABCD spin system, 4×2H, $C_{10}H_8$), 5.99, 5.85, 5.75 (ABC spin system, 3×2H, C_5H_3), 1.26, 1.18 [s, 2×9H, $C(CH_3)_3$], 0.15 (s, 6H, Zr–CH_3).

Acknowledgements

Financial support by DGICYT (Project PB97-0776) is gratefully acknowledged. M.G.-M. acknowledges Comunidad de Madrid (CAM) for the award of a Fellowship.

References

[1] (a) P.C. Wailes, R.S.P. Coates, H. Weigold, Organometallic Chemistry of Titanium, Zirconium and Hafnium, Academic Press, New York, 1974;
(b) D.J. Cardin, M.F. Lappert, C.L. Raston, P.I. Riley, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982;
(c) D.J. Cardin, M.F. Lappert, C.L. Raston, in: Chemistry of Organo-Zirconium and -Hafnium Compounds, Wiley, New York, 1986;
(d) in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II. A Review of the Literature (1982–1994), vol. 4, Pergamon, Oxford, 1994.

[2] (a) W. Kaminsky, 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, H.N. Cheng, in: T. Keli, K. Soga (Eds.), Catalytic Olefin Polymerization, Kodansha and Elsevier, Amsterdam, 1990;
(c) A. Zambelli, C. Pellecchia, L. Oliva, Makromol. Chem. Makromol. Symp. 48/49 (1991) 297;
(d) M. Bochmann, S.J. Lancaster, Organometallics 12 (1993) 633 (and references therein);
(e) R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325;
(f) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255;
(g) T.J. Marks, J. Acc. Chem. Res. 25 (1992) 57;
(h) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(i) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255.

[3] (a) J. Okuda, Comments Inorg. Chem. 16 (1994) 185;
(b) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1;
(c) P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175 (and references);
(d) V. Varga, J. Hiller, R. Gyepes, M. Polásek, P. Sedmera, U. Thewalt, K. Mach, J. Organomet. Chem. 538 (1997) 63.

[4] (a) W.-q. Weng, A.M. Arif, R.D. Ernst, Organometallics 17 (1998) 4240;
(b) Y.K. Kang, K.S. Shin, S.-G. Lee, I.S. Lee, Y.K. Chung, Organometallics 18 (1999) 180 (and references cited therein);
(c) C. Elschenbroich, O. Schiemann, O. Burghaus, K. Harms, J. Pebler, Organometallics 18 (1999) 3273.

[5] (a) T.V. Ashworth, T. Cuenca, E. Herdtweck, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 25 (1986) 289;
(b) S. Gambarotta, M.Y. Chiang, Organometallics 6 (1987) 897.

[6] (a) T. Cuenca, W.A. Herrmann, T.V. Ashworth, Organometallics 5 (1986) 2514;
(b) W.A. Herrmann, T. Cuenca, U. Küsthardt, J. Organomet. Chem. 309 (1986) C15;
(c) W.A. Herrmann, T. Cuenca, B. Menjón, E. Herdtweck, Angew. Chem. Int. Ed. Engl. 26 (1987) 697;
(d) M.M. Rohmer, M. Benard, Organometallics 10 (1991) 157;
(e) Y. Wielstra, S. Gambarotta, A. Meetsma, J.L. de Boer, Organometallics 8 (1989) 250;
(f) Y. Wielstra, S. Gambarotta, A. Meetsma, A.L. Spek, Organometallics 8 (1989) 2948;
(g) Y. Wielstra, A. Meetsma, S. Gambarotta, S. Khan, Organometallics 9 (1990) 876;
(h) Y. Wielstra, S. Gambarotta, A.L. Spek, W.J.J. Smeets, Organometallics 9 (1990) 2142;
(i) W.A. Herrmann, B. Menjón, E. Herdtweck, Organometallics 10 (1991) 2134.

[7] (a) T. Cuenca, R. Gómez, P. Gómez-Sal, G.M. Rodríguez, P. Royo, Organometallics 11 (1992) 1229;
(b) L.M. Alvaro, J.C. Flores, T. Cuenca, P. Royo, M.A. Pellinghelli, A. Tiripicchio, Organometallics 11 (1992) 3301;
(c) A. Cano, T. Cuenca, G. Rodríguez, P. Royo, C. Cardin, D.J. Wilcok, J. Organomet. Chem. 447 (1993) 51;
(d) A. Cano, T. Cuenca, M. Galakhov, G.M. Rodríguez, P. Royo, C. Cardin, M.A. Convery, J. Organomet. Chem. 439 (1995) 17.

[8] (a) M. Bochmann, T. Cuenca, D.T. Hardy, J. Organomet. Chem. 484 (1994) C10;
(b) T. Cuenca, M. Galakhov, G. Jiménez, E. Royo, P. Royo, J. Organomet. Chem. 543 (1997) 209;
(c) E. Royo, M. Galakhov, P. Royo, T. Cuenca, Organometallics 19 (2000) 3347;
(d) E. Royo, M. Galakhov, P. Royo, T. Cuenca, Organometallics 19 (2000) 5559.

[9] (a) C.J. Curtis, R.C. Haltiwanger, Organometallics 10 (1991) 3220;
(b) W.C. Spink, M.D. Rausch, J. Organomet. Chem. 308 (1986) C1.

[10] J.I. Amor, T. Cuenca, M. Galakhov, P. Gómez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 535 (1997) 155.

[11] G. Brauer, Handbuch der Präparativen Anorganischen Chemie. Bd. II. 3 Auflage, Ferdinand Enke Verlag, Stuttgart, 1978, pp. 968.