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Journal of Organometallic Chemistry 682 (2003) 8–13
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis, characterization and structures of zirconocene complexes of sterically demanding pentaphenylcyclopentadienyl and tetraphenyl-*m*-tolyl cyclopentadienyl ligands

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Received 15 May 2003; received in revised form 7 July 2003; accepted 8 July 2003

Abstract

The synthesis, characterization and catalytic activity of zirconium complexes containing bulky pentaarylcyclopentadienyl ligands are reported. The monocyclopentadienyl 12-electron complex, trichloropentaphenylcyclopentadienylzirconium(IV), $C_5Ph_5ZrCl_3$ (**I**), has an unusual monomeric structure in the solid state and has short Zr–ligand distances suggesting that the complex has significant Lewis acidity. The phenyl rings adopt a propeller arrangement in the solid state; VT ^{1}H-NMR measurements of the analogous trichloro(tetraphenyl-*m*-tolylcyclopentadienyl)zirconium(IV) (**II**) indicate that there is rapid rotational motion of the phenyl rings. The Lewis acidity of this complex is manifested in its ability to catalyze the [4+2] cycloadditions of acrolein and methyl acrylate to cyclopentadiene. The sandwich complex, $C_5Ph_5CpZrCl_2$ (**III**), has more typical Zr–ligand distances, but has a more parallel arrangement of the two cyclopentadienyl rings and does not display the reactivity shown by **I** and **II**.

Keywords: Zirconocene; Pentaphenylcyclopentadienyl; X-ray structure; Monocyclopentadienyl; Lewis

1. Introduction

The development of catalysts for promoting stereoselective organic transformations is an important goal [1]. One method that has enjoyed considerable success is the development of asymmetric catalysts for the desired transformations [2–11]. Our work is directed towards developing chiral half sandwich or piano stool Lewis acid complexes to promote C–C bond formation reactions like [4+2] cycloaddition among other reactions. Half sandwich complexes offer great potential as chiral catalysts as recently summarized [12]. In this paper, the synthesis and characterization of complexes containing the pentaphenylcyclopentadienide ligand (C_5Ph_5) with zirconium(IV), $C_5Ph_5ZrCl_3$ (**I**), an analogue, *m*-tolyltetraphenylcyclopentadienyltrichlorozirconium(IV) (**II**) and prochiral $C_5Ph_5CpZrCl_2$ (**III**), are reported. The syntheses and structures of **I** and **III**, a ^{1}H VT-NMR study of **II** and results of the study of [4+2] cycloaddition reactivity of **I** and **II** are reported.

2. Results and discussion

We have previously reported the preparation and characterization of two complexes of zirconium with C_5Ph_5 [13]. Our routes to the piano stool complex, **I**, (Fig. 1) and the bent sandwich complex, **III**, (Fig. 2) are shown below along with their ORTEP diagrams.

Complex **I**, $C_5(C_6H_5)_5ZrCl_3$, is obtained by refluxing a mixture of lithium pentaphenylcyclopentadienide and zirconium tetrachloride in toluene for 2 days. Removal of the solvent and extraction of the solids with refluxing xylenes gives **I** in 88.4% yield. The pale yellow solid **I** often crystallizes from the xylenes upon cooling. The structure shows that the phenyl rings in **I** adopt a

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doi:10.1016/S0022-328X(03)00637-5

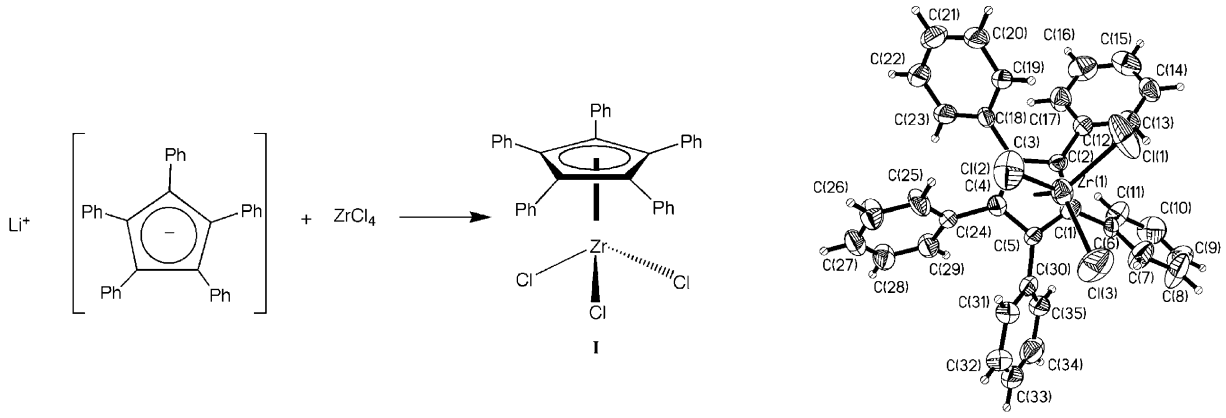

Fig. 1. Synthesis and structure of **I**.

propellor arrangement to reduce steric contacts. The ^{1}H-NMR of **I** (C_6D_6) shows a complex multiplet centered at δ 7.05 for the phenyl protons. The ^{13}C-NMR show one resonance for the *ortho* and *meta* carbons, suggesting that there is a process that renders these atoms equivalent on the NMR time scale or that they have coincidental chemical shifts. Chirality due to static left or right handed propeller orientations of the phenyl groups would lead to diastereomers upon substitution of chiral ligands for the chloride ligands of **I**. If the phenyl rings had facile rotation about the *ipso*-carbon-cyclopentadienyl carbon-bond, then interconversion between right-handed and left-handed propellers would be rapid.

In order to investigate the dynamic behavior of this five bladed propeller we prepared trichloro-(*meta*-tolyltetraphenylcyclopentadienyl)zirconium(IV) (**II**) through methods similar to those used to synthesize **I**. This modification installs a spectroscopic flag, the methyl group (a singlet at δ 2.08 and increases the solubility of **II** over that of **I**. The *meta*-tolyl group is expected to have similar steric bulk to a phenyl group since the methyl group is relatively remote and should not cause significant changes in the rotational barrier, compared to an *ortho* substitution. The ^{1}H-NMR spectra obtained in CD_2Cl_2 at ambient temperature and $-90\,^{\circ}C$ were virtually identical, confirming the presence of a facile rotation of the rings, perhaps through mechanisms analogous to that proposed for the ring rotations in tri-aryl boranes [14] and more recently for polyphenylcyclopentadienes [15].

Metathesis of **I** with lithiumcyclopentadienide in dichloromethane for 24 h gives a pale yellow suspension. Removal of the solvent and extraction of the residue with dichloromethane gives the pale yellow–green product $CpC_5Ph_5ZrCl_2$ (**III**) in 95.1% yield. Analytically pure yellow–green crystalline material is obtained by Soxhlet extraction of the crude with refluxing xylenes resulting in a final yield of 77%. Complex **III** is sparingly soluble in toluene and benzene and more soluble in polar organic solvents such as chloroform and dichloromethane. In the ^{1}H-NMR (CD_2Cl_2), a singlet is observed for the C_5H_5 at δ 6.60, and the phenyl ring protons are observed as multiplets centered at δ 6.98 and 7.09 ppm. The $^{13}C\{^1H\}$-NMR is also consistent with the given formulation.

The structure of $C_5Ph_5ZrCl_3$ (Fig. 1, Tables 1 and 2) is unusual for two reasons. It is a monomeric piano stool, not undergoing the oligomerization observed in the solid state in other $Cp'ZrCl_3$ complexes [16] and has short Zr–ligand bond distances. The monomeric structure is likely due to the steric demands of the C_5Ph_5 ligand; changes in geometry have been observed upon substitu-

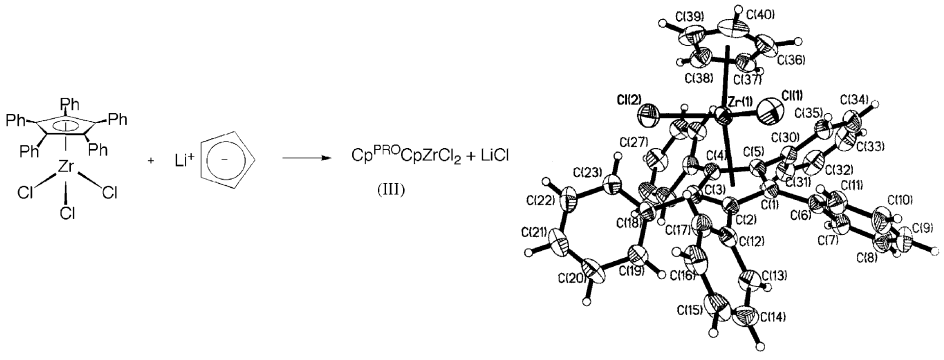

Fig. 2. Synthesis and structure of **III**.

Table 1
Summary of structural parameters for **I** and **III** with comparison values

Compound	(cnt)Zr(cnt) (°)	Zr–Cp(cnt) (Å)	Cl–Zr–Cl (°)	Zr–Cl (Å)	Reference
$C_5Ph_5ZrCl_3$	n/a	2.222	101.2	2.34	This work
$(CpZrCl_3)_n$ (pseudo-octahedral)	n/a	2.196	n/a	2.419 (non-bridging)	[18]
$C_5Ph_5CpZrCl_2$	132.9	2.211 (Cp) 2.302 (C_5Ph_5)	96.9	2.42	This work
$(CH_2)_3(\eta^5\text{-}C_5H_4)_2ZrCl_2$	129.5	2.193	96.92	2.441	[27]
$(\eta^5\text{-}C_5H_4\text{-}CH_3)_2ZrCl_2$	128.9			2.442	[19]
$Me_2Si(\eta^5\text{-}C_5H_4)_2ZrCl_2$	125.4	2.197	97.98	2.435	[19]
$((SiMe_3)_3C_5H_2)_2ZrCl_2$	135.41	2.246	96.2	2.429	[20]

Table 2
X-ray collection data for **I** and **III**

Compound	**I**	**III**
Empirical formula	$C_{35}H_{25}Cl_3Zr$	$C_{40}H_{30}Cl_2Zr$
Formula weight	643.12	672.76
Crystal size (mm)	$0.4 \times 0.4 \times 0.1$	$0.50 \times 0.59 \times 0.50$
Space group	$Pna2_1$	$P2_1/c$
Cell constants		
a (Å)	16.680(3)	12.4266(6)
b (Å)	10.1308(15)	14.0366(7)
c (Å)	17.835(3)	17.7939(9)
β (°)	n/a	92.9590(10)
V (Å^3)	3013.8(8)	3099.6(3)
Z	4	4
Diffractometer used	SMART CCD area detector	SMART CCD area detector
Radiation	Mo	Mo
R_1 ($3422F > 4\sigma_F$)	0.0387	0.0579
R_1 (7153 all)	0.1284	0.1335
wR_2	0.0499	0.1130 0.1593

tion of a C_5Ph_5 ligand for a Cp ligand [17]. Also, complex **I** is formally a 12-electron complex; the electron deficiency is reflected in the shorter metal–cyclopentadienide and metal–chloride bonds. The C_5Ph_5 centroid and the chloride ligands in **I** are about 8 pm closer to the Zr atom than in the 16-electron complex **III**. Comparison of Zr–ligand distances with oligomeric $CpZrCl_3$ finds that the Zr–Cp^{+PRO} centroid is 2.6 pm longer even though the Zr–Cl (unbridged) distance is 8.0 pm shorter in **I** [18]. These differences may reflect either donor strength or steric differences between the two cyclopentadienyl ligands.

The X-ray crystal structural data for **III** (Fig. 2, Tables 1 and 2) shows a systematic variation of the Zr–C distances; the average Zr–C distance to the pentaphenylcyclopentadienyl ligand (260.4 pm) are all longer than that to the cyclopentadienyl group (251.2 pm). The Zr–Cp(cnt) distance (221.1 pm) is about 9 pm shorter than the Zr–C_5Ph_5(cnt) distance (230.2 pm). In addition, the distances to each ring show significant variation, with those Zr–C distances above the 'pocket' (C1, C2 and C3)being longer than those away from the 'pocket' by about 5 pm. The centroid–Zr–centroid angle of 132.9° is larger than that of $(Me\text{–}Cp)_2ZrCl_2$ (128.9°) [19] but not as open as the 135.4° in hexakis(trimethylsilyl)zirconocene dichloride [20]. The distances to the chloride ligands (242 pm) are somewhat smaller than those for zirconocene dichloride (244.3 pm) [19] as is the Cl1–Zr–Cl2 angle of (96.69°) when compared to that of other zirconocene dichlorides (98°). The structural similarities between the C_5Ph_5 complex and the severely hindered hexakis(trimethylsilyl)zirconocenedichloride [20] complexes reflect like steric effects; however, the lack of a second bulky ligand in **III** should result in greater reactivity by allowing attack from the side of the less bulky Cp ligand.

As 12-electron complexes, **I** and **II** are expected to display Lewis acidity as observed in other such low-electron count complexes [11,21–24]. Both complexes **I** and **II** accelerate the [4+2] cyclization reaction of acrolein and methyl acrylate with cyclopentadiene and also change the selectivity towards *endo* and *exo* isomers compared to the control reactions. A wide variety of conditions (different temperatures, orders of addition, rate of addition and diene:dienophile ratio) were explored to optimize yields of the different isomers and to gain some insight to the mechanism of the reaction. The selectivity and yields reported below represent a minimum of three runs each.

For the reactive dienophile, acrolein, the catalyzed reaction proceeds to completion in about an hour and the control proceeds to $>95\%$ conversion at room temperature. The *endo*:*exo* ratio for the uncatalyzed reaction of acrolein and cyclopentadiene at 294 K is about 4.3 ± 0.02. At loadings of 1.0 mol.% **I** or **II**, *endo*:*exo* ratios of about 2.0 were obtained when cyclopentadiene is added to a solution containing the catalyst and acrolein (**I**; 2.05 ± 0.05: **II**; 2.09 ± 0.08). Reaction at -85 °C for 25 h with 1.0 mol.% loading of **II** gives *endo*:*exo* ratios of 2.43 ± 0.47 with 62% conversion and the uncatalyzed control has an *endo*:*exo* ratio of 3.36 ± 0.23 with only 13% conversion.

Methyl acrylate cycloaddition shows different selectivity. At room temperature, the control reaction runs nearly to completion in 2 h, with an *endo*:*exo* ratio

4.15±0.03. However, the presence of **I** or **II** *increases* the *endo*:*exo* ratio. Best results in our hands came from adding cyclopentadiene to a solution containing the dienophile and catalyst. At 1.0 mol.% **II**, *endo*:*exo* ratios of 17.71.±0.06 were obtained, with lower ratios of 10.59±0.87 for **I**. The selectivities decrease with lower catalyst loading. Optimal conditions appear to be at lower temperature; at −15 °C and 1 mol.% **II**, *endo*:*exo* ratios of 24.7±1.1 were obtained with complete consumption of methyl acrylate in 18 h. Catalyst **I** gave *endo:exo* ratio of 22.0±0.4 with 88.2% conversion and the uncatalyzed reaction mixture had an *endo*:*exo* ratio of 4.85±0.13 with only 15% consumption of methyl acrylate at −15 °C after 18 h. The *endo*:*exo* ratio obtained with **II** is higher than that reported for a cationic zirconocene catalyst reported by Hong et al., which had *endo*:*exo* ratios of 22 at even lower temperatures with lower conversion [6].

Current efforts are directed at understanding the root of the different selectivity observed for the two dienophiles by computational methods as well as investigating the versatility of these achiral precursors. We are investigating the coordination chemistry of **I** and **II** with the methacrolein and methyl acrylate by NMR methods and pursuing the synthesis of chiral derivatives of **I** and **II** by the substitution of chloride ligands with chiral alkoxides.

3. Experimental

3.1. General considerations

Most of the compounds described were air sensitive and were prepared with use of either Schlenk or high-vacuum techniques. Solid compounds were manipulated in a Vacuum Atmospheres Corp. (VAC) HE-43 Dri-Lab with an HE-63P Pedatrol pressure regulator and HE-393 Dri Train. The inert gas used in the glovebox and Schlenk and vacuum lines was either nitrogen or argon, which was further purified by passage through activated Chemalog R3-11 catalyst and activated 4 Å molecular sieves. Solvents were all reagent grade or better and were further purified by standard techniques [25]. Pentaphenylcyclopentadiene and the lithium salt were prepared as previously described [26] with minor modifications.

3.2. Physical measurements

^{1}H- and ^{13}C-NMR spectra were obtained with Bruker AM-400 or AM-300 spectrometers. Proton NMR spectra were referenced by either the residual proton resonance or internal tetramethylsilane. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

3.3. $C_5(C_6H_5)_5ZrCl_3$ (*I*)

Pentaphenylcyclopentadienyltrichlorozirconium **(I)** was prepared by refluxing 3.462 g of lithium pentaphenylcyclopentadienide with 2.651 g of zirconium tetrachloride for ∼24 h in 50 ml dry xylene. The solvent was removed in vacuo and the reddish brown solid was then extracted with 50 ml of dry xylene for 24 h in a Soxhlet type extractor. The solvent was removed in vacuo to give a yellow solid and the remaining residue extracted for an additional 24 h. The total product obtained from two successive extractions was 4.35 g with an 88.4% yield. Analytically pure crystalline material may be obtained by slow cooling of the xylenes solution. ^{1}H-NMR ($CDCl_3$): overlapping multiplets centered at δ 7.2. ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): $C_5(C_6H_5)$, δ 128.0; $C_5(C_6H_5)$, *ipso-C*, δ 133.8; *o*-C δ 131.7; *m*-C, δ 132.0; *p*-C, δ 127.8. Anal. Found (Calc.): C, 65.25(65.36); H, 4.10(3.92)%.

3.4. X-ray structure of *I*

The sample crystallized as yellow hexagonal plates from a slowly cooled, hot xylenes solution. One plate of ca. 0.4 × 0.4 × 0.1 mm was sampled by X-ray diffraction with graphite monochromated Mo–K_α radiation up to $\theta = 28.28^\circ$ by a Bruker SMART CCD area detector mounted on a three-circle goniostat. The diffraction pattern of the crystal was consistent with a $Pna2_1$ orthorhombic space group with cell dimensions of $a =$ 16.680(3), $b = 10.1308(15)$, and $c = 17.835(3)$ Å. 31 756 observations were measured and averaged with their symmetry-related reflections to form 7153 unique reflections. Of the unique reflections, 3422 reflections had an intensity $I > 2\sigma_I$. $R_{\text{int}} = 0.0982$. The structure was solved by Patterson methods and subsequently refined to convergence with the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were isotropically refined from initial ideal positions. The final agreement statistic of 3422 structure factor amplitudes having $F > 4\sigma_F$ were $R_1 =$ 3.87% based on F, and $wR_2 = 4.99\%$ based on **I**. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 132703.

3.5. $((m\text{-}CH_3\text{–}C_6H_4)(C_6H_5)_4C_5)OH$

Under an atmosphere of nitrogen, 10.0 g tetraphenylcyclopentadienone is dissolved with stirring in 150 ml of freshly distilled toluene. Next, *m*-tolylmagnesium chloride (3.0 M in ether) is added dropwise until the purple solution turns golden yellow (17.3 ml of the Grignard added over 1–2 min). The solution is then placed over an ice bath and quenched dropwise using 100 ml H_2SO_4 (1 M degassed with N_2). The organic

layer is separated, washed three times with 75 ml H_2O, and dried over $MgSO_4$. Next, the toluene is removed in vacuo providing a tan/brown residue. The residue is placed over a sintered glass filter and washed several times with heptane to provide a golden yellow solid. Recrystallization from heptanes provided the analytical sample as yellow nodules 88% yield m.p. 167–170 °C. The residue provided before recrystalization was of sufficient quality to be used, as is, for further synthesis (m.p. 160–165). ^{1}H-NMR ($CDCl_3$): δ 2.27 (s, CH_3, 3H); δ 2.44 (s, O*H*, 1H); δ 7.02 (m, Ph); δ 7.10 (m, Ph). δ 7.23 (s(br), Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 21.73 *C*H_3; δ 90.16 C-1: δ 147.93, 142.37, 137.86, 135.11, 133.90, 130.39, 129.91, 129.54, 128.35, 127.85, 127.70, 127.28, 127.01, 126.93, 125.84, 125.72, 122.09 Ph and sp^2 cyclopentadiene carbons. Anal. Found (Calc.): C, 90.72(90.65); H, 5.92(6.04)%.

3.6. *((m-CH$_3$–C$_6$H$_4$)(C$_6$H$_5$)$_4$C$_5$)H*

A 4.78 g sample of ((*m*-*C*H$_3$–C$_6$H$_4$)(C$_6$H$_5$)$_4$C$_5$)OH is dissolved in 100 ml glacial acetic acid with heating. An aliquot of 5.0 ml conc. HCl is added and the solution refluxed for 1 h. Next, 2.72 g Zn powder is added along with 20 ml more glacial acetic acid. The mixture is left to reflux. After 24 h the reaction mixture is gravity filtered hot and to the filtrate is added 300 ml of water. The precipitate is collected on a Buchner funnel and washed with ample water providing a pale yellow powder. Recrystallization from dry toluene provided the analytical sample in (yellow faceted crystals m.p. 207–210 °C) with 95% yield. The powder provided before recrystallization was of sufficient quality to be used, as is, for further synthesis (m.p. 189–199 °C).

The synthetic procedure results in a statistical mixture of the three isomers, 1:2:2 of 1-*m*-tolyltetraphenylcyclopentadiene, 2-*m*-tolyltetraphenylcyclopentadiene and 3-*m*-tolyltetraphenylcyclopentadiene, respectively. ^{1}H-NMR ($CDCl_3$): δ 2.08, 2.15, 2.23 (s; C*H*$_3$; 3H, 2:2:1 intensities, respectively): δ 5.05, 5.09 (s; Cp ring C*H*; 1 H, 1:4 intensities, respectively): δ 6.8 (m; Ph); δ 7.0 (m; Ph); δ 7.2 (m, Ph) (total Ph; 24H). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 21.48 (1C); 21.35 (2C); 21.29 (2C) *C*H_3; δ 62.56 C-1: δ 146.67, 146.44, 146.21, 144.13, 144.01, 143.88, 143.84, 138.20, 138.16, 137.81, 137.24, 136.91, 136.23, 136.19, 135.98, 135.83, 135.62, 130.78, 130.09, 129.78, 129.51, 129.18, 129.03, 128.99, 128.93, 128.52, 128.50, 128.43, 128.32, 127.82, 1237.78, 127.64, 127.49, 127.39, 127.14, 127.09, 126.62, 126.47, 126.54, 126.12, 125.49, Ph and C$_5$. Anal. Found (Calc.): C, 93.87(93.41); H, 6.13(6.00)%.

3.7. *((m-CH$_3$–C$_6$H$_4$)(C$_6$H$_5$)$_4$C$_5$)ZrCl$_3$ (**II**)*

Under an atmosphere of nitrogen, 2.00 g of the lithium dienide (prepared by deprotonation of ((*m*-CH$_3$–C$_6$H$_4$)(C$_6$H$_5$)$_4$C$_5$)H with *n*-butyllithium) is placed along with 1.00 g zirconium(IV) tetrachloride in 40 ml of dry toluene. The purple suspension is left to reflux 48 h. The toluene is then removed under vacuum and the residue transferred to a continuous extraction apparatus. The dark tan solids are continuously extracted for 24 h with toluene. The product crystallizes from the extraction liquors to provide 2.06 g yellow to tan granular crystals (73% yield). ^{1}H-NMR ($CDCl_3$): δ 2.07 (s, C*H*$_3$, 3H); δ 6.8, 7.12 (m, Ph, 24H).$^{13}C\{^1H\}$-NMR ($CDCl_3$): ((*m*-*C*H$_3$–C$_6$H$_4$)(C$_6$H$_5$)$_4$C$_5$)ZrCl$_3$ δ 21.3 *C*H$_3$; δ 137.23: 133.7, 132.7, 132.0, 131.72, 131.69, 131.41, 129.06, 128.70, 127.98, 127.73, 127.67, 127.55, Ph and C$_5$ Anal. Found (Calc.): C, 65.79(65.87); H, 4.14(4.62); Cl, 16.18(16.05)%.

3.8. *CpC$_5$Ph$_5$ZrCl$_2$ (**III**)*

Cyclopentadienyl(pentaphenylcylopentadienyl)dichlorozirconium **III**, was prepared by stirring 4.120 g of pentaphenylcyclopentadienyltrichlorozirconium and 0.451 g of lithium cyclopentadienide in 30 ml of dry dichloromethane for 24 h at room temperature. Removal of the solvent in vacuo gave a yellow brown solid. The solid was then Soxhlet extracted with 60 ml of dry dichloromethane to yield 4.021 g of **II** as a pale yellow powder in a 95.1% yield. Analytically pure crystalline material may be obtained by slow cooling of a hot xylenes solution of **II**. ^{1}H-NMR ($CDCl_3$): C$_5$*H*$_5$, δ 6.55 (s); C$_5$(C$_6$*H*$_5$)$_5$ δ 7.10 (m),δ 6.94. $^{13}C\{^1H\}$-NMR ($CDCl_3$): *C*$_5$H$_5$, δ 118.6; C$_5$(*C*$_6$H$_5$), *ipso*-C δ 133.5; *m*-C δ 132.0; *p*-C δ 127.5; *o*-C δ 127.3; *C*$_5$(C$_6$H$_5$) δ 129.9. Anal. Found (Calc.): C, 71.40(71.41); H, 4.49(4.49)%.

3.9. *X-ray structure of **III***

The sample crystallized as dark green violet prisms from a slowly cooled hot xylenes solution. One prism of ca. $0.5 \times 0.5 \times 0.5$ mm was sampled by X-ray diffraction with graphite monochromated Mo–K_α radiation up to $\theta = 28.28°$ by a Bruker SMART CCD area detector mounted on a three-circle goniostat. The diffraction pattern of the crystal was consistent with a $P2_1/c$ monoclinic space group with cell dimensions of $a =$ 12.4266(6), $b = 14.0366(7)$, and $c = 17.7939(9)$ Å, and with $\beta = 92.9590(10)°$. 30 932 observations were measured and averaged with their symmetry-related reflections to form 7076 unique reflections. Of the unique reflections, 4562 reflections had an intensity $I > 4\sigma_I$. $R_{int} = 0.1192$ before correction factors were refined for absorption and decay, and $R_{int} = 0.0456$ after correction. The structure was solved by Patterson methods and subsequently refined to convergence with the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were isotropically refined from initial ideal positions. The

final agreement statistics of 4562 structure factor amplitudes having $F > 4\sigma_F$ were $R_1 = 5.79\%$ based on F, and $wR_2 = 13.35\%$ based on **I**. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 132704.

4. Cycloaddition studies

The required amount of catalyst was placed in a Schlenk flask, evacuated and filled with N_2. The solid was then dissolved at room temperature in 20 ml of dry CH_2Cl_2 and 1 ml of dry toluene using a stirrer bar. The dienophile (0.0298 mol) was filtered through a hydroquinone and monomethyl ether hydroquinone inhibitor remover and then added by syringe to the reaction flask followed by the injection of pre-distilled cyclopentadiene (0.0596 mol) and reaction time was started. The reaction mixture was stirred for 15 h.

For slow addition reactions the dienophile (diluted in 3 ml of dry CH_2Cl_2) is added slowly to the reaction flask (containing the dissolved catalyst and cyclopentadiene) and a syringe pump (KD Scientific model 100) was used and set to the desired rate of injection.

Cold temperature runs ($-85\,^{\circ}C$) were performed by submerging the flasks in a liquid N_2/toluene slush bath. For $-15\,^{\circ}C$ reactions, flasks were sealed and stored in a Fisher Scientific *Isotemp* freezer.

All reactions were monitored with GC by direct injection of a 0.4 μl initial and final sample for each reaction, where toluene was the internal standard. Gas chromatographic analysis of the reaction products was performed with a SRI model 8610C instrument fitted with a Phenomenex ZB-5 (5% phenyl polysiloxane) 60 m × 0.53 mm × 1.5 μm column and thermal conductivity detector. Injection temperature is $30\,^{\circ}C$ and the temperature is ramped at $10\,^{\circ}C\ min^{-1}$ up to $200\,^{\circ}C$.

Acknowledgements

The purchase of the Bruker AM-400 NMR Spectrometer was supported in part by PHS grant RR-08101 from the NIH-MBRS program, NSF Grant DMB-8503839 and grants from the W.M. Keck Foundation and the Camille and Henry Dreyfus Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and to the National Institutes of Health MARC Program Grant T34 GM 08228 (MB) for support of this research.

References

[1] J. Marsh, Advanced Organic Chemistry, fourth ed., Wiley, New York, 1992.
[2] S. Collins, B.A. Kuntz, Y. Hong, J. Org. Chem. 54 (1989) 4154.
[3] S. Collins, Y. Hong, N.J. Taylor, Organometallics 9 (1990) 2695.
[4] I.-M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115.
[5] S. Collins, D.G. Ward, J. Am. Chem. Soc. 114 (1992) 5460.
[6] Y. Hong, B.A. Kuntz, S. Collins, Organometallics 12 (1993) 964.
[7] L. Cavallo, P. Corradini, G. Guerra, L. Resconi, Organometallics 15 (1996) 2254.
[8] R.L. Halterman, D. Combs, J.G. Kihega, M.A. Khan, J. Organomet. Chem. 520 (1996) 163.
[9] R.L. Halterman, T.M. Ramsey, J. Organomet. Chem. 530 (1997) 225.
[10] S.Q. Lin, G.V. Bondar, C.J. Levy, S. Collins, J. Org. Chem. 63 (1998) 1885.
[11] J.B. Jaquith, C.J. Levy, G.V. Bondar, S.T. Wang, S. Collins, Organometallics 17 (1998) 914.
[12] C. Ganter, Chem. Soc. Rev. 32 (2003) 130.
[13] D.L. Greene, O.A. Villalta, D.M. Macias, A. Gonzalez, W. Tikkanen, B. Schick, K. Kantardgief, Inorg. Chem. Commun. 2 (1999) 311.
[14] J.F. Blount, P. Finocchiaro, D. Gust, K. Mislow, J. Am.Chem. Soc. 95 (1973) 7019.
[15] S. Brydges, M.J. McGlinchey, J. Org. Chem. 67 (2002) 7688.
[16] G. Poli, Chem. Rev. 1991 (1991) 509.
[17] C. Janiak, H. Schumann, C. Stader, B. Wrackmeyer, J.J. Zucker1man, Chem. Ber. 121 (1988) 1745.
[18] L.M. Engelhardt, R.I. Papasergio, C.L. Raston, A.H. White, Organometallics 4 (1984) 18.
[19] C.S. Bajgur, W. Tikkanen, J.L. Petersen, Inorg. Chem. 24 (1985) 2539.
[20] R. Choukroun, F. Dahan, Organometallics 13 (1994) 2097.
[21] G. Erker, C. Sarter, M. Albrecht, S. Dehnicke, C. Krüger, E. Raabe, R. Schlund, R. Benn, A. Rufińska, R. Mynott, J. Organomet. Chem. 382 (1990) 89.
[22] R.O. Duthaler, A. Hafner, P.L. Alsters, S.P. Rothe, G. Rihs, Pure Appl. Chem. 64 (1992) 1897.
[23] P. Wipf, H. Jahn, Tetrahedron 52 (1996) 12853.
[24] T.K. Hollis, N.P. Robinson, B. Bosnich, Organometallics 11 (1992) 2745.
[25] A.J. Gordon, R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques and References, Wiley, New York, 1972.
[26] J.W. Chambers, A.J. Baskar, S.G. Bott, J.L. Atwood, M.D. Rausch, Organometallics 5 (1986) 1635.
[27] C.H. Saldarriaga-Molina, A. Clearfield, I. Bernal, Inorg. Chem. 13 (1974) 2880.