Journal of Organometallic Chemistry, 288 (1985) 69–77
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ansa-METALLOCENE DERIVATIVES

VIII *. SYNTHESES AND CRYSTAL STRUCTURES OF ETHYLENE-BRIDGED TITANOCENE AND ZIRCONOCENE DERIVATIVES WITH PERMETHYLATED RING LIGANDS

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(Received November 14th, 1984)

Summary

Ethylene-bridged titanocene and zirconocene derivatives with permethylated ring ligands, $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$, have been synthesized and their crystal structures determined.

Introduction

The increased stability of peralkylated metallocene derivatives towards loss of cyclopentadienyl ligands or other reactions is well documented [2–9]. Recently we showed that interconnection of both ring ligands by an ethylene bridge also stabilizes the bent metallocene derivatives of Group IV transition metals towards rearrangements of their ring ligands [10,11]. For a study of the separate steps in a number of reactions it would be desirable to have available metallocene derivatives in which alkylation of the ring ligands and their connection to a chelate structure renders the metal–ring skeleton as inert as possible, limiting chemical transformation to the equatorial ligands. In this paper we report the syntheses and molecular structures of the ethylene-bridged, permethyl-titanocene and -zirconocene derivatives, $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ ($en(cp^\star)_2TiCl_2$) and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ ($en(cp^\star)_2ZrCl_2$).

Results and discussion

The ligand required for the preparation of the title compounds, namely bis(2,3,4,5-tetramethyl-1-cyclopentadienyl)ethane, was synthesized by an extension

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* For part VII see ref. 1.

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of the method developed by Threlkel and Bercaw [12] for the synthesis of alkyl- and aryl-tetramethylcyclopentadienes; thus when the diethyl ester of succinic acid was treated with 4 equivalents of 2-lithio-2-butene, 1,1,4,4-tetravinyl-1,4-butandiol was obtained in ca. 85% yield. The cyclization of this intermediate is complicated, since the carbenium ion generated from it by H_2SO_4 (or by toluenesulfonic acid in $CHCl_3$) is much more stable, as judged by the persistence of its dark red colour, than its unbridged analogue [13–15], probably because of some kind of stabilizing interaction between the two halves of the molecule. When the carbenium ion is generated in higher concentrations at or above room temperature, the cyclization is accompanied by substantial rearrangement and polymerization, which give rise to numerous additional signals in the ^1H NMR spectrum of the product mixture. If the cyclization with H_2SO_4 is conducted at about 0°C and the system is quickly quenched with cold aqueous carbonate, 20–30% of the desired bis(tetramethylcyclopentadienyl)ethane is present in the product mixture, as indicated by gas chromatography. The product was purified by chromatography on a silica gel column with CH_2Cl_2/petroleum ether (3/7), and when it was treated with n-butyllithium in n-hexane the dilithium salt was precipitated in an overall yield of ca. 10%, based on the dicarbinol intermediate.

The synthesis of en(cp*)$_2$TiCl$_2$ was achieved by reaction of the dilithium salt of bis(tetramethylcyclopentadienyl)ethane with $TiCl_3 \cdot 3THF$ in THF for three days at the reflux temperature, oxidation of the reaction product with concentrated aqueous HCl, and extraction with $CHCl_3$. Crystallization from $CHCl_3$/petroleum ether gave the desired product as dark red-brown crystals in ca. 15% yield. The compound was identified by elemental analysis and by its mass spectrum, which showed parent ions at *m/e* 386–390 with the expected isotope distribution.

For the synthesis of en(cp*)$_2$ZrCl$_2$, the dilithium salt of bis(tetramethylcyclopentadienyl)ethane was treated with $ZrCl_4$ in glyme, first at −80°C, then for three days at the reflux temperature. Removal of solvent, work-up with aqueous $HCl/CHCl_3$ and crystallization from $CHCl_3$ gave about 20% of en(cp*)$_2$ZrCl$_2$ as light yellow crystals. The compound was characterized by elemental analysis and by

TABLE 1

^1H SPECTRA OF $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ AND $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$, RECORDED IN C_6D_6 SOLUTION AT 250 MHz; ^1H NMR SHIFTS IN ppm RELATIVE TO $\delta = 7.15$ ppm FOR C_6D_5H; ^{13}C NMR SPECTRA RECORDED IN $CDCl_3$ SOLUTION; SHIFTS IN ppm RELATIVE TO $\delta = 75.6$, 77.0 AND 78.4 ppm FOR $CDCl_3$

$C_2H_4(C_5(CH_3)_4)_2TiCl_2$		$C_2H_4(C_5(CH_3)_4)_2ZrCl_2$		Assignment	
Shift	Intensity	Shift	Intensity	H-atoms	C-atoms
2.64	4 (s)	2.64	4 (s)	C_2H_4	
2.06	12 (s)	2.01	12 (s)	CH_3	
1.66	12 (s)	1.73	12 (s)	CH_3	
135.6	91	129.4	252		$C_5(\alpha)$
130.2	72	127.3	123		C_5(bridge-head)
124.5	182	120.1	226		$C_5(\beta)$
28.0	116	27.6	152		C_2H_4
13.4	202	12.3	314		CH_3
13.1	217	12.0	221		CH_3

its mass spectrum, which gave parent ions at m/e 428–436 with the expected isotope distribution.

The ^{1}H NMR data for $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ are shown in Table 1. The signals from the hydrogen of the ethylene bridge, (3.30 and 3.21 ppm in $CDCl_3$, 2.64 ppm in C_6D_6) were close to that from $C_2H_4(C_5H_4)_2TiCl_2$ (3.26 ppm) [16]. The difference in chemical shifts for the α- and β-methyl substituents in $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ is smaller than that between the α and β protons in $C_2H_4(C_5H_4)_2TiCl_2$ [16], but still clearly discernible in C_6D_6 solution (Table 1). In $CDCl_3$ this α,β-splitting is reduced to 0.08 ppm for $C_2H_4(C_5(CH_3)_4)_2TiCl_2$, and to an unresolved signal at δ 1.99 ppm for $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$.

The ^{13}C NMR shifts of the C_5-ring and C_2H_4-bridge carbon atoms in both compounds (Table 1) are similar to corresponding values of 139.7–114.1 ppm and of 30.4 ppm reported for $C_2H_4(C_5H_4)_2TiCl_2$ [16]; the ^{13}C resonances of the methyl as well as the ring carbon atoms are close to the corresponding resonances in $(C_5(CH_3)_5)_2ZrCl_2$ [17], for which we obtained values of 11.9 and 123.6 ppm, respectively in $CDCl_3$ solution.

For a structural characterization of en(cp*)$_2$TiCl$_2$ and en(cp*)$_2$ZrCl$_2$, space groups, cell parameters and X-ray diffraction intensities were determined on a Syntex-P3 four-circle diffractometer at 223 and 216 K, respectively (Mo-K_α, λ 0.71069 Å, graphite monochromator, ω-scan with $1.8 < \dot{\omega} < 29.3°\ \mathrm{min}^{-1}$, $\Delta\omega$ 1° and $1 < 2\theta < 44°$ for en(cp*)$_2$TiCl$_2$ and $2.0 < \dot{\omega} < 29.3°\ \mathrm{min}^{-1}$, $\Delta\omega$ 1° and $1 < 2\theta < 46°$ for en(cp*)$_2$ZrCl$_2$. The crystals of both compounds were monoclinic, space group $C2/c$, with 4 crystallographically equivalent molecules per unit cell. Cell parameters for en(cp*)$_2$TiCl$_2$: a 1679.6(8), b 792.3(3), c 1613.6(7) pm; β 124.69(3)°; V 1766×10^6 pm^3; $d_{\mathrm{calcd.}}$ 1.46 g/cm^3; absorption coefficient μ 8 cm^{-1}. Cell parameters for en(cp*)$_2$ZrCl$_2$: a 1708(2), b 806.7(4), c 1641(1) pm; β 124.42(5)°; V 1865×10^6 pm^3; $d_{\mathrm{calcd.}}$ 1.53 g/cm^3; absorption coefficient μ 8.6 cm^{-1}. For resolving and refining the structures, 991 and 1198 reflections with $F_0 > 2\sigma$ were used, respectively; empirical absorption corrections were applied for both data sets.

The structures were solved by direct methods (SHELXTL) and refined with partially anisotropic models; a weighting scheme based on counting statistics was used in both cases. For the structure of en(cp*)$_2$TiCl$_2$, H atoms were calculated and then rigid-group refined (86 pm from adjacent C atom). For that of en(cp*)$_2$ZrCl$_2$, H atoms were taken from the Fourier difference map but not refined. The refinement converged at $R_1 = 0.036$ and $R_2 = 0.037$, $R_1 = 0.023$, and $R_2 = 0.027$, where $R_1 = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$ and $R_2 = [\Sigma\omega(|F_0| - |F_c|)^2]^{1/2}/[\Sigma\omega|F_0|^2]^{1/2}$. Relevant bond lengths and bond angles for en(cp*)$_2$TiCl$_2$ and en(cp*)$_2$ZrCl$_2$ are listed in Table 4. * Since the molecules are isostructural, only that of the latter compound is shown (Fig. 1).

For both compounds the expected symmetry axis coincides with a crystallographic C_2 axis. C–C distances within the C_5-rings of 139–142 pm, C–CH$_3$ distances for the methyl substituents of 148–151 pm, a CH$_2$–CH$_2$ bond length of 154 pm, CH$_2$–CH$_2$–C(bridge-head) angles of 111 and 113°, and a torsional angle of

(Continued on p. 74)

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* Detailed structural data are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldszentrum 2, under quotation of deposit No. CSD 51352, the authors and the journal reference of this article.

TABLE 2

STRUCTURAL PARAMETERS FOR $C_2H_4(C_5(CH_3)_4)_2TiCl_2$

Fractional coordinates (with e.s.d.'s) and isotropic thermal parameters

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
Ti	0.00000	0.0826(1)	0.75000		C(5)	0.0741(2)	0.2474(5)	0.8997(3)	0.0231(8)
Cl(1)	0.05448(6)	−0.1135(1)	0.68578(7)		C(6)	0.1387(3)	−0.0157(5)	1.0132(3)	0.0313(9)
C(1)	0.1261(2)	0.0953(4)	0.9330(3)	0.0240(8)	C(7)	0.2409(3)	−0.0643(5)	0.9060(3)	0.0333(9)
C(2)	0.1731(2)	0.0751(5)	0.8852(3)	0.0241(8)	C(8)	0.1988(3)	0.2473(5)	0.7686(3)	0.0335(1)
C(3)	0.1528(2)	0.2168(5)	0.8234(3)	0.0241(8)	C(9)	0.0556(3)	0.4934(5)	0.7857(3)	0.0314(9)
C(4)	0.0926(2)	0.3250(4)	0.8336(3)	0.0235(8)	C(10)	0.0241(3)	0.3239(5)	0.9428(3)	0.0325(9)

(b) Anisotropic thermal parameters [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.0244(5)	0.0123(5)	0.0225(5)	0.00000	0.0165(4)	0.00000
Cl(1)	0.0366(5)	0.0218(5)	0.0314(5)	−0.0021(4)	0.0234(4)	0.0049(4)

[a] U, U_{ij} in 10^2 pm^2 refer to $T = \exp(-2\pi^2(U_{11}h^2a^{\star 2} + \ldots 2U_{23}klb^{\star}c^{\star})$

TABLE 3

STRUCTURAL PARAMETERS FOR $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$

(a) Fractional coordinates (with e.s.d.'s)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Zr	0.00000	0.06963(5)	0.75000	C(5)	0.0773(2)	0.2453(4)	0.9021(2)
Cl(1)	0.05740(6)	−0.1280(1)	0.68250(6)	C(6)	0.1412(2)	−0.0159(4)	1.0147(2)
C(1)	0.1291(2)	0.0953(4)	0.9354(2)	C(7)	0.2444(2)	−0.0619(5)	0.9088(3)
C(2)	0.1764(2)	0.0759(4)	0.8884(2)	C(8)	0.1998(2)	0.2460(5)	0.7708(3)
C(3)	0.1556(2)	0.2152(4)	0.8266(2)	C(9)	0.0544(2)	0.4852(4)	0.7851(3)
C(4)	0.0939(2)	0.3208(4)	0.8354(2)	C(10)	0.0256(3)	0.3203(4)	0.9435(3)

(b) Anisotropic thermal parameters [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	0.0244(2)	0.0133(2)	0.0249(2)	0.00000	0.0178(2)	0.00000
Cl(1)	0.0396(5)	0.0249(4)	0.0366(5)	−0.0018(3)	0.0276(4)	0.0054(3)
C(1)	0.028(2)	0.022(2)	0.025(2)	−0.003(1)	0.015(1)	−0.003(1)
C(2)	0.025(2)	0.025(2)	0.030(2)	−0.002(1)	0.015(1)	0.000(1)
C(3)	0.025(2)	0.025(2)	0.030(2)	−0.003(1)	0.017(1)	−0.006(1)
C(4)	0.030(2)	0.017(2)	0.029(2)	−0.004(1)	0.017(1)	−0.007(1)
C(5)	0.030(2)	0.023(2)	0.025(2)	−0.006(1)	0.017(1)	−0.003(1)
C(6)	0.040(2)	0.035(2)	0.031(2)	0.003(2)	0.020(2)	0.001(2)
C(7)	0.035(2)	0.039(2)	0.044(2)	0.003(2)	0.023(2)	0.007(2)
C(8)	0.036(2)	0.044(2)	0.045(2)	−0.002(2)	0.028(2)	−0.007(2)
C(9)	0.045(2)	0.018(2)	0.039(2)	0.001(1)	0.025(2)	−0.003(1)
C(10)	0.044(2)	0.035(2)	0.037(2)	−0.005(2)	0.027(2)	0.002(2)

[a] U, U_{ij} in 10^2 pm^2 refer to $T = \exp(-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)$.

TABLE 4

BOND LENGTHS (in pm) AND BOND ANGLES (in degree) AT Ti ATOM IN $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ AND AT Zr ATOM IN $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ (CR = centroid of C_5 ring; PL = mean plane of C_5 ring)

Ti–Cl	232.5(2)	Cl–Ti–Cl′	96.1(1)	Zr–Cl	244.1(2)	Cl–Zr–Cl′	98.4(1)
Ti–CR	208.8	CR–Ti–CR′	131.0	Zr–CR	221.1	CR–Zr–CR′	127.7
Ti–PL	208.5	PL–PL′	55.9	Zr–PL	220.8	PL–PL′	57.7
Ti–C(4)	235.4(3) br.-hd.			Zr–C(4)	247.0(3) br.-hd.		
Ti–C(3)	237.9(4) α-C			Zr–C(3)	249.9(3) α-C		
Ti–C(5)	238.0(4) α-C			Zr–C(5)	250.1(3) α-C		
Ti–C(2)	244.9(3) β-C			Zr–C(2)	255.0(3) β-C		
Ti–C(1)	246.9(3) β-C			Zr–C(1)	256.4(3) β-C		

32° at the ethylene bridge are all in accord with an essentially undistorted ligand framework.

The α-methyl substituents of en(cp*)$_2$TiCl$_2$ approach each other to a C–C distance of 339 pm; the corresponding distance in en(cp*)$_2$ZrCl$_2$ is 350 pm. This unusually close non-bonded contact would provide an explanation of the ^{1}H NMR splitting between α- and β-methyl substituents in en(cp*)$_2$TiCl$_2$ and en(cp*)$_2$ZrCl$_2$.

The methyl substituents deviate somewhat from coplanarity with the C_5-ring planes, toward the outside of the molecule, by 11–18 pm in en(cp*)$_2$TiCl$_2$ and by 10–15 pm in en(cp*)$_2$ZrCl$_2$. These CH_3 out-of-plane displacements are small, however, in comparison to CH_3 out-of-plane displacements of up to 49 pm reported for $(C_5(CH_3)_5)_2TiCl_2$ [17], in which the innermost CH_3 substituent at one ring ligand approaches two CH_3 groups at the opposite ring to C–C contact distances of 331 and 342 pm. The substantial reduction of steric strain associated with the replacement of two of the innermost CH_3 substituents of (Cp*)$_2$TiCl$_2$ by an

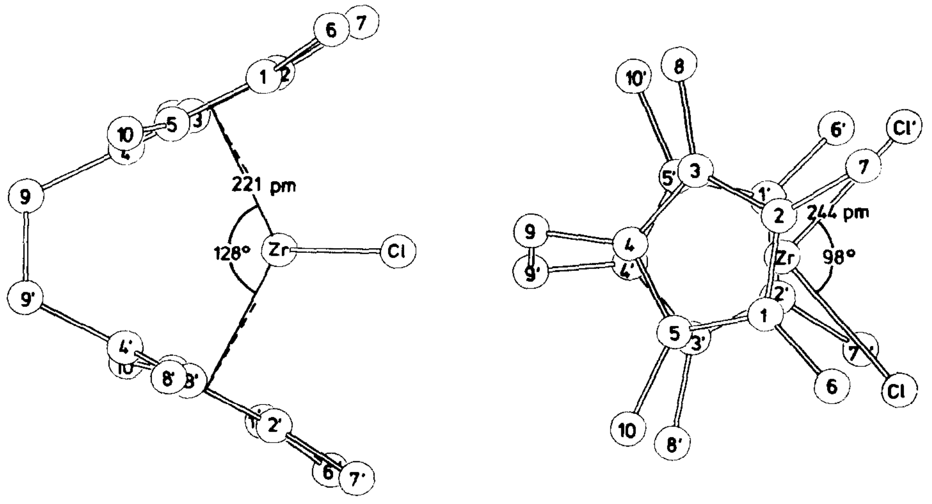

Fig. 1. Molecular structure of $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$. Atoms not otherwise labelled are C atoms of ligand framework. Zr-ring centroid connections indicated by solid, single lines, normals on the ring centroids by dashed lines.

ethylene bridge results in a shortening of the unusually long Ti–Cp* ring centroid distance of 213 to 209 pm and in a reduction of the unusually large Cp* centroid-Ti-centroid angle of 137.4 to 131.0° in en(cp*)$_2$TiCl$_2$, thus making the bonding geometry of the bridged permethyl complex rather close to that of the parent compound Cp$_2$TiCl$_2$, in which the corresponding parameters are 206 pm and 131.0°, respectively [19].

A slight degree of residual mismatch between the rather rigid bridged ligand framework and the coordination requirements of the metal centres is indicated, however, by deviations of 6.9 and 5.4° between the angles spanned by the two mean C$_5$-ring and the corresponding centroid-metal-centroid angles; this places the metal centres closer, by 9–10 pm, to the bridgehead C atoms than to the peripheral (β) C atoms.

The metal–chlorine distances as well as the chlorine–metal–chlorine angles given in Table 4 are rather similar to those reported for related titanocene [16–20] and zirconocene [1,20] dichloride derivatives.

Experimental

All solvents were thoroughly dried, and were stored and transferred under vacuum. TiCl$_3$ · 3THF was prepared as described in ref. 21.

1. Dilithio bis(2,3,4,5-tetramethyl-1-cyclopentadienyl)ethane. To a solution of 1.48 mol of 2-lithio-2-butene in 2.5 l diethyl ether, prepared in situ in a 4 l three-neck flask with stirrer, reflux condenser and dropping funnel, a solution of 58 g (0.333 mol) of diethyl succinate in 60 ml diethyl ether was added at such a rate as to keep the solution boiling. The mixture was kept under reflux for another 2 h, then cooled to room temperature and hydrolysed in several portions, by shaking each portion with about twice its volume of saturated aqueous NH$_4$Cl solution. The aqueous phase was extracted with diethyl ether; the combined organic phase was dried (Na$_2$SO$_4$) and freed from solvent in vacuo. To remove any volatile impurities, the liquid residue was kept for 3 h in vacuo connected to a −196° trap. The oily residue thus obtained consisted of 85 g of satisfactorily pure 1,1,4,4-tetravinyl-1,4-butandiol.

^{1}H NMR in CDCl$_3$ solution (δ relative to δ 7.24 for CHCl$_3$, at 90 MHz): 5.1–5.8 ppm (m, 4, =CH), 2.1–2.7 ppm (m, 4, CH$_2$), 1.4–2.0 ppm (m, 24, CH$_3$). Tetravinyl butanediol (10 ml) was added dropwise with stirring to 45 ml of conc. H$_2$SO$_4$ cooled to −10°C contained in a 100 ml three-neck flask fitted with magnetic stirring bar, dropping funnel, thermometer, and drying tube the rate of addition being such as to keep the temperature below 4°C. The dark red solution thus obtained was then slowly transferred by pipette into a well-stirred solution of 96 g Na$_2$CO$_3$ in 1.5 l of a water/ice mixture. The light yellow emulsion was extracted with n-pentane, and the resulting organic phase was dried (Na$_2$SO$_4$) and freed from solvent in vacuo. The oily residue thus obtained was taken up in a few ml of petroleum ether, poured onto a chromatography column (4 × 40 cm) filled with silica gel (Merck 60, 70–120 mesh) and kept ca. 10°C, elution with a mixture of CH$_2$Cl$_2$ and petroleum ether (3/7) gave the desired product (as indicated by GLC) in the first fractions. These were combined, dried (Na$_2$SO$_4$) and evaporated to dryness, to yield 2.5 g of an oily residue.

For conversion to the dilithium salt, this crude product was dissolved in 50 ml of air-free, anhydrous n-hexane. With exclusion of air, 11.6 ml of 1.6 *M* n-butyllithium in n-hexane were added at 0°C to the well-stirred solution, which was then kept at the reflux temperature for 2 h. The precipitate was collected and washed with n-hexane on a frit under N_2, then dried in vacuo at room temperature, to give 0.7 g of the dilithium salt as colourless crystals.

The product ignites in air, but can be stored under N_2 or Ar for several weeks. Hydrolysis of the dilithium salt yields essentially pure bis(tetramethylcyclopentadienyl)ethane, as indicated by mass spectroscopy and GLC. The identification and checking of the purity of this material by ^1H NMR spectroscopy was complicated by the presence of numerous prototropic isomers; for the following syntheses, the dilithium salt was used without further purification.

2. $C_2H_4(C_5(CH_3)_4)_2TiCl_2$. Under an N_2 atmosphere, 100 ml THF were condensed onto 0.95 g (3.4 mmol) of dilithium bis(tetramethylcyclopentadienyl)ethane; warming to room temperature yielded a red-brown solution. The solution was cooled to −50°C and 1.25 g (3.4 mmol) of solid $TiCl_3 \cdot 3THF$ were added under N_2. Warming to room temperature gave a dark green-brown solution, which was heated under reflux for 3 days, after which it was cooled to −40°C and treated with 16 ml of concentrated aqueous HCl. Stirring at room temperature for ca. 2 h afforded a red-brown solution, to which 100 ml of $CHCl_3$ were added. After 30 min the $CHCl_3$ phase was separated, dried (Na_2SO_4), and evaporated to about 10 ml. Addition of ca. 20 ml of petroleum ether and subsequent partial evaporation yielded about 200 mg of (ca. 15%) of en(cp*)$_2$TiCl$_2$ as dark red-brown crystals. Elemental analysis: Found: C, 61.59; H, 7.50. $C_{20}H_{28}TiCl_2$, calcd.: C, 62.06; H, 7.25%. For further characterization see the Results section.

3. $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$. Under an N_2 atmosphere, 50 ml of air-free, anhydrous dimethoxy ethane (glyme) were condensed onto 0.7 g (2.5 mmol) of the ligand dilithium salt. Warming to room temperature yielded a red-brown solution. This was cooled to −80°C and 0.58 g (2.5 mmol) of solid $ZrCl_4$ were slowly added. The mixture was slowly warmed to room temperature and then kept under reflux for three days. The solvent was then removed in vacuo and the light brown, solid residue was taken up in 15 ml $CHCl_3$ and 5 ml of 6 *M* aqueous HCl. The organic phase was washed with little H_2O and dried (Na_2SO_4). Removal of solvent in vacuo gave light yellow crystals, which were washed with n-pentane to yield 0.22 g (ca. 21%) of en(cp*)$_2$ZrCl$_2$.

Elemental analysis: Found: C, 55.81; H, 6.59; Cl 15.84. $C_{20}H_{28}ZrCl_2$ calcd.: C, 55.81; H, 6.51; Cl, 16.48%. For further characterization see the Results section.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft (grant Bri 510/12-2), by the University of Konstanz, and by the Fonds der Chemischen Industrie.

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