# Synthesis, Structure and Reactivity of a Zirconocene Dichloride with $(Me_3Si)_2NSiMe_2$ Side-Chains

**Alexander Rau,*[a] Hans-Peter Dornik,[a] Helmut Paulus,[b] and Gerhard Luft[a]**

**Keywords:** Metallocenes / Zirconium / N ligands / Structure elucidation / Cyclopentadienyl ligands

The new zirconocene $[(\eta^5\text{-}C_5H_4SiMe_2N(SiMe_3)_2]_2ZrCl_2$ (**1**) has been prepared in a convenient three-step synthesis. A crystal structure determination of **1** shows two molecules in the unit cell, one in which the $(Me_3Si)_2NSiMe_2$ groups are accommodated in a nearly synperiplanar conformation directly above and below the $ZrCl_2$ group, and one in which these groups exhibit a synclinal conformation. The reaction of **1** with a mixture of $SOCl_2/SO_2Cl_2$ leads to the formation of $[(\eta^5\text{-}C_5H_4SiMe_2Cl]_2ZrCl_2$ (**2**).

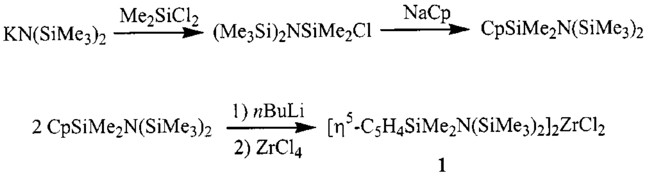
## Introduction

Group 4 metallocene complexes bearing side-chains that can modify the steric and electronic properties of the metal centre have attracted growing interest in recent years due to their potential catalytic applications. The influence of alkyl groups attached to the cyclopentadienyl (Cp) unit on the structure-reactivity relation of metallocene catalysts has been intensively studied.[1−3] Metallocenes with side-chains containing $NR_2$, $PR_2$, OR and SR functions are found to have interesting catalytic properties due to intra- or intermolecular donor acceptor interactions.[4,5] Furthermore, ROSi[6−8] and ClSi[8] functions can be used for anchoring metallocene pre-catalysts *covalently* on solid surfaces.

In this paper we describe the synthesis of the new zirconocene $[(\eta^5\text{-}C_5H_4SiMe_2N(SiMe_3)_2]_2ZrCl_2$ (**1**). The influence of the bulky group attached to the Cp fragment on the molecular structure is discussed. In addition, we report on the conversion of complex **1** into $[(\eta^5\text{-}C_5H_4SiMe_2Cl]_2ZrCl_2$ (**2**).

## Results and Discussion

$[(\eta^5\text{-}C_5H_4SiMe_2N(SiMe_3)_2]_2ZrCl_2$ (**1**) was prepared on a large scale by the synthetic route depicted in Scheme 1. All the synthetic steps were performed at room temperature. In the first step, potassium bis(trimethylsilyl)amide was reacted with an excess of $Me_2SiCl_2$ to give $(Me_3Si)_2NSiMe_2Cl$, which was obtained as a colourless oil after distillation. Reaction of $(Me_3Si)_2NSiMe_2Cl$ with CpNa in THF resulted in the new cyclopentadiene $(Me_3Si)_2NSiMe_2Cp$, which was isolated as a mixture of three isomers after distillation.[9] The target complex **1** was synthesized by deprotonation of $(Me_3Si)_2NSiMe_2Cp$ with *n*BuLi and a subsequent salt metathesis reaction of the resulting lithium cyclopentadienyl compound with $ZrCl_4$.



$$KN(SiMe_3)_2 \xrightarrow{Me_2SiCl_2} (Me_3Si)_2NSiMe_2Cl \xrightarrow{NaCp} CpSiMe_2N(SiMe_3)_2$$

$$2\ CpSiMe_2N(SiMe_3)_2 \xrightarrow[2)\ ZrCl_4]{1)\ nBuLi} \underset{\mathbf{1}}{[\eta^5\text{-}C_5H_4SiMe_2N(SiMe_3)_2]_2ZrCl_2}$$

Scheme 1

Due to the lipophilic trimethylsilyl groups,[10,11] complex **1** is highly soluble in hydrocarbons, which made necessary two successive low-temperature crystallisations from the mother liquor to obtain a 58% yield of **1** as colourless crystals. The NMR spectra of **1** recorded at room temperature give no indication of a hindered rotation of the Cp moieties, as is known for related metallocenes with sterically demanding cyclopentadienyl ligands.[12] In the $^1H$ NMR spectrum, the Cp hydrogens appear as two multiplets centred at $\delta = 6.67$ and 6.37, and the trimethyl silyl groups appear as two sharp singlets at $\delta = 0.04$ and 0.48.

Single crystals of **1** suitable for X-ray diffraction were obtained by slow cooling of toluene solutions. Figure 1 shows the two molecular structures of **1** that are found in the unit cell in a 1:1 ratio. Both molecular structures show the expected pseudo-tetrahedral coordination of the zirconium atom. As shown in Figure 2 and listed in Table 1, the molecular structures of $(RC_5H_4)_2ZrCl_2$ compounds with bulky R groups can be divided into three distinct types with different conformations of the cyclopentadiene moieties.[10,13−15] According to the data in Table 1, the size and the degree of rotational freedom of the R groups seem to determine what type of structure is formed: compounds that contain bulky substituent groups with a fixed geometry adopt structure type I, whereas the other compounds prefer the structure types II or III. Remarkably, single crystals of complex **1** contain the structure types II and III, whereas

---

[a] Institut für Chemische Technologie der Technischen Universität Darmstadt,
Petersenstraße 20, 64287 Darmstadt, Germany
Fax: (internat.) + 49-6151/16-4214
E-mail: alex@bodo.ct.chemie.tu-darmstadt.de
[b] Material und Geowissenschaften der Technischen Universität Darmstadt,
Petersenstraße 23, 64287 Darmstadt, Germany

1434−1948/01/0707−1785 $ 17.50+.50/0

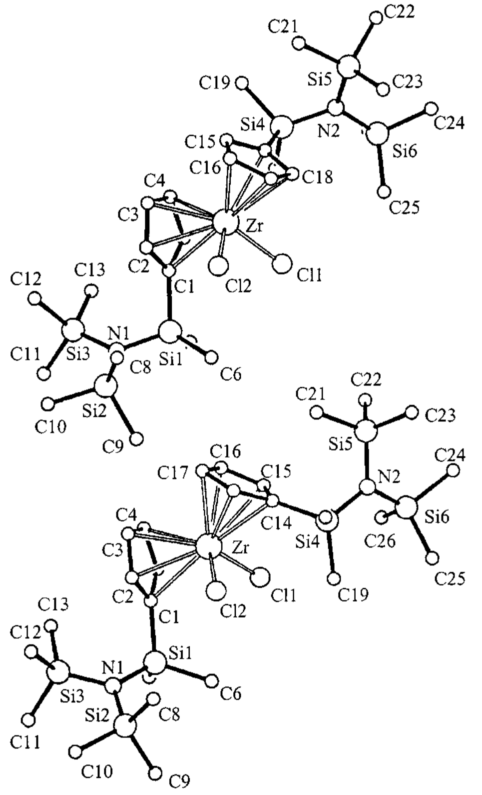


Figure 1. Molecular structures of 1 together with atomic labelling scheme

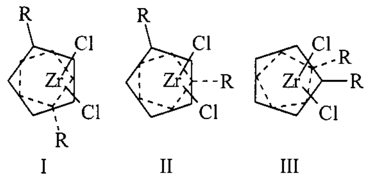


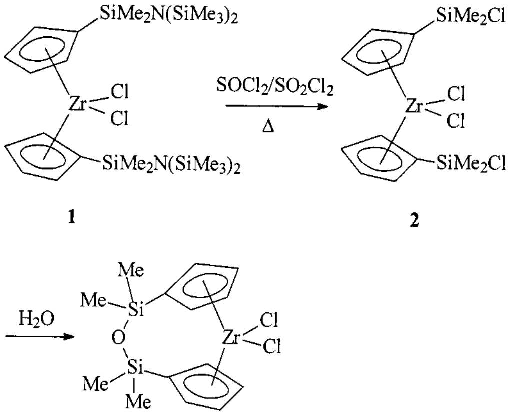
Figure 2. Structure types of ($\eta^5$-$RC_5H_4$)$_2$$ZrCl_2$ compounds

the unit cells of the other compounds contain only one single molecular structure.

As displayed in Table 1, the (Cp centroid)−Zr−(Cp centroid) bond angles and the Zr−(Cp centroid) bond lengths of complex **1** are in the range of other ($RC_5H_4$)$_2$$ZrCl_2$ compounds, whereas the Cl−Zr−Cl bond angles of **1** are increased relative to those of related compounds. In particular, the structure type III of **1** shows a widened Cl−Zr−Cl bond angle (105.7°). This is probably due to the steric bulk of the Cp ligands. The same trend concerning the Cl−Zr−Cl bond angle was found with ($R_2C_5H_3$)$_2$$ZrX_2$ metallocenes.[10]

Attempts to prepare the mono-cyclopentadienyl complex [($\eta^5$-$C_5H_4SiMe_2N(SiMe_3)_2$]$ZrCl_3$ by reaction of [$(Me_3Si)_2NSiMe_2C_5H_4$]Li with one equivalent $ZrCl_4$ failed. Even if the reaction was performed with a large excess of $ZrCl_4$, only the sandwich complex **1** could be isolated. This must be due to ligand redistribution reactions of the zirconium trichloride leading to complex **1** and $ZrCl_4$, as has already been reported by Lappert and co-workers for ($\eta^5$-$C_5H_4Bu$*t*)$_2$$ZrCl_2$ in the presence of THF.[11] Apart from some exceptions, such as [($\eta^5$-$C_5H_3(SiMe_3)_2$]$_2$$ZrCl_2$, they observed that in the absence of THF, in toluene as solvent, the redistribution reaction of ($\eta^5$-$C_5H_{5-n}R_n$)$ZrCl_2$ with $ZrCl_4$ can be directed to the monocyclopentadienyl zirconium trichlorides. However, we observed no reaction of complex **1** with $ZrCl_4$ in toluene at room temperature.

Another method for the preparation of mono-cyclopentadienyl complexes from the corresponding dichlorides has been described by Garg and co-workers.[16] They refluxed $Cp_2TiCl_2$ with a mixture of $SOCl_2/SO_2Cl_2$ to produce $CpTiCl_3$ in more than 90% yield. However, we found that the reaction of [($\eta^5$-$C_5H_4SiMe_2N(SiMe_3)_2$]$_2$$ZrCl_2$ (**1**) in refluxing $SOCl_2/SO_2Cl_2$ leads to ($\eta^5$-$C_5H_4SiMe_2Cl$)$_2$$ZrCl_2$ (**2**). No trichloride products were found (Scheme 2). Complex **2** is extremely sensitive to moisture and reacts on addition of a stoichiometric amount of water to form the bridged complex [($\eta^5$-$C_5H_4$)$SiMe_2OSiMe_2$($\eta^5$-$C_5H_4$)]$ZrCl_2$,



Scheme 2

Table 1. Structural parameters for some ($\eta^5$-$RC_5H_4$)$_2$$ZrCl_2$ compounds

| Metallocene | Structure type | Cp(z)−Zr−Cp(z)[a] [°] | Zr−Cp(z) [Å] | Cl−Zr−Cl [°] | ref. |
|---|---|---|---|---|---|
| ($C_6H_5CH_2C_5H_4$)$_2$$ZrCl_2$ | III | 126 | 2.16 | 94.4 | [13] |
| (Methylestratrienyl-$C_5H_4$)$_2$$ZrCl_2$ | II | 128.7 | 2.2 | 95.2 | [14] |
| (*t*Bu$C_5H_4$)$_2$$ZrCl_2$ | I | 128.6 | 2.2 | 94.3 | [15] |
| ($Me_3SiC_5H_4$)$_2$$ZrCl_2$ | I | 129.1 | 2.2 | 94 | [10] |
| [$(Me_3Si)_2NSiMe_2C_5H_4$]$_2$$ZrCl_2$ (**1**) | III | 126 | 2.2 | 105.7 | |
| | II | 126 | 2.2 | 99.5 | |

[a] Cp(z) = centroid of cyclopentadienyl rings.

as already described by Royo and co-workers for the analogous Ti and Hf complexes of **2**.[17]

Group 4 metallocenes bearing reactive groups like $Me_3OSi$ or $ClSiMe_2$ cannot be produced by the classic salt metathesis reaction of alkali metal cyclopentadienyl compounds with transition metal chlorides.[6] Instead of this synthetic pathway, the central metal has to be introduced by the reaction of the cyclopentadiene compounds with metal amides,[6] or, if groups attached to the cyclopentadiene ring increase its acidity, by refluxing the cyclopentadiene compound in the presence of metal tetrachlorides and triethylamine.[17] As we have shown, the $(Me_3Si)_2NSiMe_2$ group is not sensitive to strong bases like *n*BuLi and, in complex **1**, is easily transformed to the $ClSiMe_2$ group, which opens up the classic synthetic pathway to zirconocenes with the $ClSiMe_2$ function.

## Conclusion

The new metallocene complex $[(Me_3Si)_2NSiMe_2C_5H_4]_2ZrCl_2$ (**1**) bearing bulky, functionalized side-chains was prepared on a large scale in a convenient three-step synthesis. The X-ray analysis of **1** shows that the unit cell contains two different molecular structures in a 1:1 ratio. The structures differ from the conformation of the cyclopentadiene rings. In one of these conformations, the side-chains are positioned in a nearly synperiplanar conformation at the open side of the sandwich complex. When the molecular structures of **1** and related $(RCp)_2ZrCl_2$ compounds with bulky R groups are compared, it can be concluded that this conformation requires R groups with a certain degree of rotational freedom, which allows less steric congestion in this conformation.

The reaction of complex **1** with $SOCl_2/SO_2Cl_2$ leads to $(\eta^5\text{-}C_5H_4SiMe_2Cl)_2ZrCl_2$ (**2**) in good yields. Group 4 metallocenes with reactive side-chains containing $ClSiMe_2$ functions are interesting precursors for heterogeneous catalysts. Because of the reactive group these metallocenes cannot be produced by the classic reaction of metal chloride salts with the alkali metal derivatives of the ligand system. In one example, we have shown that the $(Me_3Si)_2NSiMe_2$ group can be used as a protecting group of the $ClSiMe_2$ function in zirconocene synthesis, which opens up the classic synthetic pathway to zirconocenes bearing the $ClSiMe_2$ group.

## Experimental Section

**General:** All experiments with air-sensitive materials were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were dried over Na-K alloy (THF, hexane, toluene, diethyl ether) or calcium hydride (dichloromethane), followed by distillation and storage under argon. $^1H$ (300 MHz) and $^{13}C$ (75 MHz) NMR spectra were recorded on either a Bruker ARX 300 or a Bruker AC 300 spectrometer. The mass spectra were determined using a Varian MAT 311A instrument. The elemental analyses were obtained using a Perkin−Elmer CHN 240B instrument.

**$(Me_3Si)_2NSiMe_2Cl$:** $KN(SiMe_3)_2$ (100.82 g, 0.505 mol) and 500 mL of toluene were added to a three-necked flask equipped with a stirring device. Then, $Me_2SiCl_2$ (400 mL, 3.298 mol) was added dropwise within 2 h. The resulting mixture was stirred for 4 days. The volatiles were then removed in vacuo. The resulting suspension was filtered, and the residue was washed three times with 75 mL of hexane. The volatiles of the filtrate were removed in vacuo and the residue was distilled at $10^{-2}$ mbar. The fraction between 99 and 101 °C yielded 108.39 g (0.427 mol, 84.5%) of $(Me_3Si)_2NSiMe_2Cl$ as a colourless oil. − $^1H$ NMR ($CDCl_3$): $\delta = 0.25$ (s, 18 H, $SiMe_3$), 0.55 (s, 6 H, $SiMe_2$). − MS (FI): $m/z = 254$ $[M]^+$, 219 $[M - Cl]^+$.

**$(Me_3Si)_2NSiMe_2Cp$:** $(Me_3Si)_2NSiMe_2Cl$ (107.95 g, 0.425 mol) and 100 mL of THF were placed in a flask, and then 232 mL of NaCp solution (0.464 mol, 2 M in THF) were added dropwise. The resulting mixture was stirred for 2 days. Most of the solvent was removed in vacuo and then 200 mL of hexane was added. The resulting suspension was filtered and the brown residue was washed three times with 50 mL hexane. The volatiles of the filtrate were removed in vacuo to give 106.74 g (0.376 mol) of the crude product as a brown oil, which was further purified by distillation at $10^{-2}$ mbar. The fraction between 148 and 150 °C yielded $(Me_3Si)_2NSiMe_2Cp$ (54.59 g, 0.193 mol, 45%) as a pale yellow oil (mixture of three isomers 10:10:1 by $^1H$ NMR spectroscopy). − $^1H$ NMR of all isomers ($CDCl_3$): $\delta = -0.01$ (s, 6 H, $SiMe_2$), 0.13 (s, 18 H, $SiMe_3$), 0.14 (s, 6 H, $SiMe_2$), 0.23 (s, 18 H, $SiMe_3$), 0.29 (s, 18 H, $SiMe_3$), 0.30 (s, 6 H, $SiMe_2$), 2.99 (br. s, 2 H, $CH_2$, both main isomers), 3.64 (br. s, 1 H, CH saturated), 6.41−6.77 (m, CH, unsaturated, all isomers). − MS (FD): $m/z = 283$ $[M]^+$, 218 $[M - C_5H_5]^+$. − $C_{13}H_{29}NSi_3$ (283.64): calcd. C 55.05, H 10.31, N 4.94; found C 54.78, H 10.55, N 4.69.

**$[(Me_3Si)_2NSiMe_2C_5H_4]_2ZrCl_2$ (1):** $(Me_3Si)_2NSiMe_2Cp$ (22.08 g, 0.078 mol), 200 mL of hexane and 200 mL of toluene were placed into a flask, and then 50 mL of *n*BuLi (0.080 mol, 1.6 M in hexane) were added dropwise. The resulting solution was stirred for 18 h and then added to a suspension of $ZrCl_4$ (9.32 g, 0.040 mol) in 200 mL of toluene. Next, 150 mL of THF were slowly added dropwise to the suspension and the resulting mixture was stirred for 2 days. After sedimentation of the solids, the liquid phase was removed with a cannula, and the residue was washed with 100 mL of hexane and filtered. The resulting liquids were combined, and the volatiles were removed in vacuo to produce a brown solid residue. Crystallisation from hexane/toluene at low temperatures gave colourless crystals of **1** (22.89 g, 0.031 mol, 39.7%). From two successive crystallisations of the mother liquor, further 10.45 g (0.014 mol, 17.9%) of **1** could be isolated. − $^1H$ NMR ($CDCl_3$): $\delta = 0.08$ (s, 36 H, $SiMe_3$), 0.52 (s, 18 H, $SiMe_2$), 6.41 ("t", 4 H, Cp), 6.71 ("t", 4 H, Cp). − $^{13}C$ NMR ($CDCl_3$): $\delta = 5.38$ ($SiMe_2$), 5.67 ($SiMe_3$), 114.42 (CH), 127.99 ($C_q$), 129.06 (CH). − MS (FD): $m/z = 727$ $[M^+]$. − $C_{26}H_{56}Cl_2N_2Si_6Zr$ (727.38): calcd. C 42.93, H 7.76, N 3.85; found C 42.63, H 7.86, N 3.91.

### X-ray Crystal Structure Analysis of 1

**Crystal Data and Refinement Details:** Formula $C_{26}H_{56}Cl_2N_2Si_6Zr$, $M_r = 727.38$, $0.35 \times 0.22 \times 0.18$ mm, $a = 15.032(5)$ Å, $b = 17.443(6)$ Å, $c = 17.962(6)$ Å, $\alpha = 61.49(1)°$, $\beta = 74.48(1)°$, $\gamma = 74.93(1)°$, $V = 3938.7(2)$ Å$^3$, $Z = 4$, $d = 1.23\ g\,cm^{-3}$, triclinic, space group $P\bar{1}$, diffractometer Stoe-Stadi4, $\lambda = 0.71069$ Å (Mo-$K_\alpha$), graphite, data collection mode $2\Theta/\omega = 1:1$, range $3 < 2\Theta < 45$, $-16 \le h \le 16$, $-18 \le k \le 18$, $-19 \le l \le 19$, reflections measured 20561, reflections observed 7302, $I > 2\sigma(I)$, $5.99\ cm^{-1}$, $\psi$-scan, $T_{min}$ 0.787, $T_{max}$ 0.893. Structural analysis SHELXS-86, refinement on $F^2$, hydrogen positions geom., $R_1 = 0.0370$ and $wR_2 = 0.0815$. Programs used SHELXS-86 and SHELXL-93.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152331. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

**$(ClMe_2SiC_5H_4)_2ZrCl_2$ (2):** Compound **1** (3.40 g, 4.68 mmol) was placed in a flask and a solution of $SO_2Cl_2$ (5 mL, 62.24 mmol) and $SOCl_2$ (14 mL, 191.93 mmol) was added dropwise. The resulting mixture was refluxed for 2 h and then filtered. The volatiles of the filtrate were removed in vacuo to produce a light brown residue. Recrystallisation from toluene/hexane yielded **2** (1.10 g, 2.30 mmol; 50%). − $^1H$ NMR ($CDCl_3$): $\delta = 0.72$ (s, 12 H, $SiMe_2Cl$), 6.57 (m, 4 H, $C_5H_4$), 6.78 (m, 4 H, $C_5H_4$). − $^{13}C$ NMR ($CDCl_3$): $\delta = 3.2$ ($SiMe_2$), 116.7 ($C_{ipso}$ ($C_5H_4$), 122.5, 126.3 [CH of ($C_5H_4$)]. − MS (EI): $m/z$ = 478 $[M]^+$, 320 $[M - C_5H_4SiClMe_2]^+$, 122 $[C_5H_4SiMe_2]^+$. − $C_{14}H_{20}Cl_4Si_2Zr$ (477.52): calcd. C 35.21, H 4.22; found C 35.48, H 4.35.

**$[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_5)]ZrCl_2$:** Water (35 µL) was added to a solution of **2** (810 mg, 1.69 mmol) in 25 mL of toluene. The resulting solution was stirred for 12 h at room temperature, and then the volatiles were removed in vacuo. Recrystallisation of the residue from toluene/hexane yielded $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_5)]ZrCl_2$ (574 mg, 1.36 mmol; 80%) as pale yellow crystals. − $^1H$ NMR ($CDCl_3$): $\delta = 0.36$ (s, 12 H, $SiMe_2$), 6.53 ("tr", 4 H, $C_5H_4$), 6.84 ("tr", 4 H, $C_5H_4$). − $^{13}C$ NMR ($CDCl_3$): $\delta = 0.9$ ($SiMe_2$), 117.2 [($C_{ipso}$ ($C_5H_4$)], 122.4, 125.7 [CH ($C_5H_4$)]. − MS (EI): $m/z$ = 422 $[M]^+$, 407 $[M - CH_3]$. − $C_{14}H_{20}Cl_2OSi_2Zr$ (422.61): calcd. C 39.79, H 4.77, found C 39.76, H 5.92.

## Acknowledgments

The authors wish to thank the Bundesministerium für Bildung und Forschung and the BASF AG for financial support.

---

[1] P. C. Möhring, N. J. Coville, *J. Mol. Catal.* **1992**, *77*, 41−50.
[2] P. Burger, K. Hortmann, H.-H. Brintziger, *Makromol. Chem. Macromol. Sym.* **1993**, *66*, 127−140.
[3] C. Janiak, K. C. H. Lange, U. Versteeg, D. Lentz, P. H. M. Budzelaar, *Chem. Ber.* **1996**, *129*, 1517−1529.
[4] For a recent review, see: C. Müller, D. Vos, P. Jutzi, *J. Organomet. Chem.* **2000**, *600*, 127−143 and references therein.
[5] A. Rau, T. Wieczorek, A. Dyroff, H.-P. Dornik, G. Luft, *J. Mol. Catal.* submitted.
[6] M. Galan-Fereres, T. Koch, E. Hey-Hawkins, M. S. Eisen, *J. Organomet. Chem.* **1999**, *580*, 145−155.
[7] H. Juvaste, T. T. Pakkanen, E. I. Iiskola, *J. Organomet. Chem.* **2000**, *606*, 169−175.
[8] P. Jutzi, T. Heidemann, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1995**, *472*, 27−38.
[9] For isomers and fluxionality of Cp compounds, see: P. Jutzi, *Chem. Rev.* **1986**, *86*, 983−996.
[10] A. Antinolo, M. F. Lappert, A. Singh, D. J. W. Winterborn, L. M. Engelhardt, C. L. Raston, A. H. White, A. J. Carty, N. J. Taylor, *J. Chem. Soc., Dalton Trans.* **1987**, 1463−1472.
[11] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, E. Ryan, *Polyhedron* **1995**, *14*, 2745−2752.
[12] J. Okuda, *Top. Curr. Chem.* **1991**, *160*, 97−145.
[13] Y. Dusausoy, J. Protas, P. Reaut, B. Gautheron, G. Tainturier, *J. Organomet. Chem.* **1978**, *157*, 167−172.
[14] G. Erker, C. Mollenkopf, M. Grehl, B. Schönecker, *Chem. Ber.* **1994**, *127*, 2341−2345.
[15] R. A. Howie, G. P. McQuillan, D. W. Thompson, G. A. Lock, *J. Organomet. Chem.* **1986**, *303*, 213−220.
[16] K. Chandra, R. K. Sharma, N. Kumar, B. S. Garg, *Chem. and Ind.* **1980**, 288.
[17] S. Ciruelos, A. Sebastián, T. Cuenca, P. Gomez-Sal, A. Manzanero, P. Royo, *J. Organomet. Chem.* **2000**, *604*, 103−115.

Received December 14, 2000
[I00471]