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Formation of novel P-functionalised ligands by insertion of CyNC into the Zr–P bonds of [Cp°_2ZrCl(PHCy)] ($Cp^{\circ} = \eta^5$-C_5EtMe_4, Cy = cyclohexyl) and [Cp'_2ZrCl(PHTipp)] ($Cp' = \eta^5$-C_5H_4Me, Tipp = 2,4,6-$Pr^i_3C_6H_2$). Molecular structures of [Cp°_2ZrCl{η^2-NCyC(PHCy)}] and [Cp'_2Zr(Cl){η^2-NCyC(PHTipp)}]

Ulrike Segerer, Steffen Blaurock, Joachim Sieler, Evamarie Hey-Hawkins *

Institut für Anorganische Chemie der Universität, Johannisallee 29, D-04103 Leipzig, Germany

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Abstract

[Cp'_2ZrCl(PHTipp)] (**1**) ($Cp' = \eta^5$-C_5H_4Me, Tipp = 2,4,6-$Pr^i_3C_6H_2$) and [Cp°_2ZrCl(PHCy)] (**2**) ($Cp^{\circ} = \eta^5$-C_5EtMe_4, Cy = cyclohexyl) readily insert CyNC to give [Cp'_2ZrCl{η^2-NCyC(PHTipp)}] (**3**) and [Cp°_2ZrCl{η^2-NCyC(PHCy)}] (**4**). **3** and **4** were characterised spectroscopically (IR, NMR, MS) and by crystal structure determination, which showed an η^2 bonding mode (C,N) of the NCyC(PHR) ligands. Of the two possible coordination modes of the ligand, **3** is obtained exclusively as the *exo* isomer, in which the NCy group is adjacent to the Zr–Cl bond, while for **4**, both isomers (*exo* and *endo*) are formed [1:1.5 (**4a**:**4b**)], whereby the *endo* isomer is favoured. The *exo* isomer **4a** was structurally characterised.

Keywords: Zirconocene phosphanido complexes; Insertion reaction; Isonitriles; Molecular structure

1. Introduction

For some time we have been interested in the preparation of zirconocene phosphanido complexes with P-functionalised ligands [1,2]. While zirconocene complexes with terminal $P(SiMe_3)_2$ ligands are easily accessible [3,4], zirconocene complexes with terminal primary phosphanido groups of general formula [Cp^Z_2ZrCl(PHR)] are only obtained with certain combinations of substituted cyclopentadienyl ligand and P–*R* substituent. Thus, P–H-functionalised zirconocene complexes were obtained from reactions of [Cp_2ZrCl_2] or [Cp'_2ZrCl_2] ($Cp' = \eta^5$-C_5H_4Me) with LiPH(2,4,6-$R'_3C_6H_2$) ($R' =$ Me [5], Pr^i [6], Bu^t [7]), i.e. sterically less demanding ligand at Zr, bulky substituent at phosphorus ('small/large'), or from [$Cp^Z_2MX_2$] and LiPHR [$Cp^Z = Cp^* = \eta^5$-C_5Me_5; M = Zr, X = Cl, R = Cy (cyclohexyl); M = Hf, X = I, Cl, R = Cy, X = I, R = Ph [8]; and $Cp^Z = Cp^{\circ} = \eta^5$-$C_5EtMe_4$; M = Zr, X = Cl, R = Cy] [2], i.e. bulky substituent at Zr or Hf and sterically less demanding substituent at phosphorus ('large/small') [9].

The insertion of polar multiple-bond systems into the Zr–P bond of the P-functionalised zirconocene monophosphanido complexes allows the synthesis within the coordination sphere of zirconium of novel P-functionalised phosphino ligands which are either difficult to synthesise or inaccessible by other routes [9–11]. Thus, CS_2 [12], diazoalkanes [13], phenylacetylene [10], or carbodiimides [14,15] are readily inserted into the Zr–P bond of the P-functionalised zirconocene monophosphanido complexes [Cp^Z_2ZrCl{$P(SiMe_3)_2$}] [$Cp^Z = Cp, Cp'$]. The insertion reaction of isonitriles into Zr–P [15,16] and Hf–As bonds [17] of P–Si- or As–Si-functionalised complexes has also been observed. Only a few insertion reactions of the dialkyl- or diarylphosphanido complexes [Cp*$HfCl_2(PBu^t_2)$]

* Corresponding author. Fax: +49-341-9739319.
E-mail address: hey@rz.uni-leipzig.de (E. Hey-Hawkins).

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with CO [18] or of [$Cp^*_2HfH(PPh_2)$] with CO_2 [8] have been reported. Up to now, insertion reactions of CS_2, PhNCS [2], MeCN [19] and RNCX [20] (R = Ph, Cy, X = O, S) with [$Cp'_2ZrCl(PHTipp)$] (**1**) (Tipp = 2,4,6-$Pr^i_3C_6H_2$) and [$Cp^\circ_2ZrCl(PHCy)$] (**2**) have been described. A systematic study of the influence of the steric and electronic factors of Cp^Z and R on the course of the insertion reaction was undertaken for the RNCX insertion reaction [20].

We now report the insertion reactions of CyNC into the Zr–P bond of [$Cp'_2ZrCl(PHTipp)$] (**1**) and [$Cp^\circ_2ZrCl(PHCy)$] (**2**) to give [$Cp'_2ZrCl\{\eta^2$-NCyC(PHTipp)$\}$] (**3**) and [$Cp^\circ_2ZrCl\{\eta^2$-NCyC(PHCy)$\}$] (**4**).

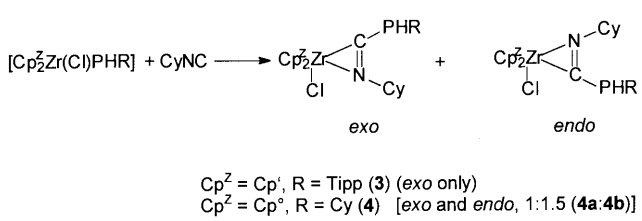
2. Results and discussion

2.1. Synthesis and characterisation

The insertion of isonitriles RNC into M–X bonds, especially M–C bonds [21], has been reported for several transition metal complexes, and the mechanism of this reaction has been studied [22]. Besides the insertion of one isonitrile molecule, insertion of two or more isonitrile molecules into different M–X bonds was observed, depending on electronic and steric factors [23]. The η^2-bonded iminoacyl ligands can undergo intramolecular coupling reactions on thermolysis [24].

[$Cp'_2ZrCl(PHTipp)$] (**1**) and [$Cp^\circ_2ZrCl(PHCy)$] (**2**) readily insert CyNC to give [$Cp'_2ZrCl\{\eta^2$-NCyC(PHTipp)$\}$] (**3**) and [$Cp^\circ_2ZrCl\{\eta^2$-NCyC(PHCy)$\}$] (**4**) (Scheme 1).

While a ^{31}P-NMR spectrum of the reaction mixture of **3** showed only one signal at −83.2 ppm (d, $^1J_{PH}$ = 259.8 Hz) for the *exo* isomer (shown by X-ray structure determination, vide infra), two signals were observed for **4** at −25.4 ppm (d, $^1J_{PH}$ = 254.3, *exo* isomer **4a**) and −31.7 ppm (d, $^1J_{PH}$ = 207.3 Hz, *endo* isomer **4b**) in the ratio 1:1.5. Work up yielded the less favoured *exo* isomer **4a** as yellow needles (X-ray structure determination); **4b** was not obtained in pure form. The signals are shifted to high field and have a larger PH coupling constant compared to **1** (−4.6 ppm, $^1J_{PH}$ = 230.0 Hz) [6] and **2** (71.7 ppm, $^1J_{PH}$ = 209.0 Hz) [2]. The ^{1}H-NMR spectrum of **3** exhibits a doublet for the P–H proton at 5.83 ppm ($^1J_{PH}$ = 259.9 Hz); for **4a**, this signal is observed at 4.55 ppm ($^1J_{PH}$ = 253.7 Hz). The signals of the P–H groups are shifted to low field by ca. 1 ppm relative to **1** (4.86 ppm) [6] and **2** (3.49 ppm) [2], and the P–H coupling constant increased by almost 44 Hz.



Cp^Z = Cp′, R = Tipp (**3**) (*exo* only)
Cp^Z = Cp°, R = Cy (**4**) [*exo* and *endo*, 1:1.5 (**4a**:**4b**)]

Scheme 1.

In the ^{13}C-NMR spectrum, the C atom of the iminoacyl group (C=N) gives rise to a doublet at 237.76 ppm ($^1J_{PC}$ = 106.4 Hz) for **3** and at 243.02 ppm ($^1J_{PC}$ = 97.6 Hz) for **4a**. This is in the range reported for other iminoacyl complexes, such as [$Cp_2ZrCl\{\eta^2$-N(Bz)C(C[$SiMe_3$]=CHPh)$\}$] (238.0 ppm) [21d], [$Cp_2Zr(SR')(\eta^2$-NRCMe)] (R = xylyl, SR′ = 4,6-dimethylpyrimidine-2-thiolate) (241.8 ppm) [21d] and [{(C_5Me_4)$SiMe_2$-(NBu^t)}ZrMe(η^2-NBu^{t}CMe)] (247.9 ppm) [23d].

The phosphinoiminoacyl ligands in **3** and **4** are expected to show a bidentate (C,N) coordination mode, as was observed previously for related iminoacyl complexes [15,17,21d,23c]. In the IR spectrum of **3** and **4a**, the absorptions at 1596 and 1580 cm^{-1}, respectively, were assigned to the ν(C=N) vibration. These values are in the range usually observed for η^2-bonded iminoacyl groups (cf. [$Cp'_2ZrCl\{\eta^2$-NPhC(P[$SiMe_3$]$_2$)$\}$] (1540–1560 cm^{-1}) [15], [$Cp_2ZrCl\{\eta^2$-N(Bz)C(C[$SiMe_3$]=CHPh)$\}$] [21d] (1616 cm^{-1}), [(Bu^tCH_2)$_3$Zr$\{\eta^2$-NRC(Si[$SiMe_3$]$_3$)$\}$] (R = 2,6-dimethylphenyl) [23c] (1579 cm^{-1}), and [$Cp'_2HfCl\{\eta^2$-NPhCAs($SiMe_3$)$_2\}$] (1536 cm^{-1}) [17]). For CyNC, the CN stretching band is observed at 2136 cm^{-1}.

The ν(PH) vibration in **3** (2339 cm^{-1}) and **4b** (2324 cm^{-1}) is shifted to higher wavenumber compared with **1** (2322 cm^{-1}) [6] and **2** (2311 cm^{-1}) [2].

2.2. Molecular structures

Large colourless crystals of **3** were obtained from a concentrated pentane solution at room temperature. **3** crystallises monoclinic in the space group $P2_1/c$ with four formula units in the unit cell. **4a** was obtained as yellow needles on recrystallisation from toluene. **4a**

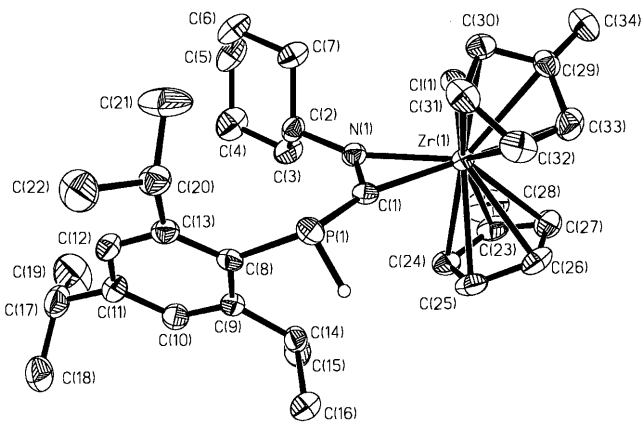


Fig. 1. Molecular structure of **3** showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP) [27]. Hydrogen atoms (other than P–H) are omitted for clarity.

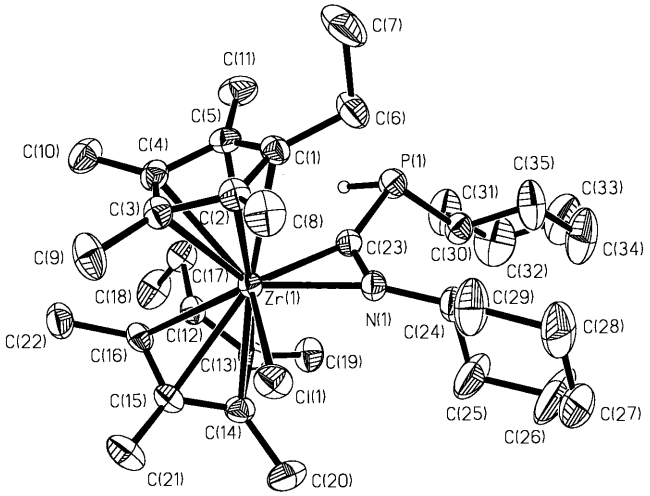


Fig. 2. Molecular structure of **4a** showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP) [27]. Hydrogen atoms (other than P–H) are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) of **3** and **4a**

	3 [a]	**4a** [b]
Zr(1)–N(1)	2.212(2)	2.238(2)
Zr(1)–Cl(1)	2.5434(5)	2.5608(6)
Zr(1)–C(′)	2.247(2)	2.267(2)
P(1)–H(1P)	1.29(2)	1.33(3)
P(1)–C(′)	1.803(2)	1.821(2)
P(1)–C(*)	1.851(2)	1.877(3)
N(1)–C(′)	1.272(2)	1.280(3)
N(1)–C(″)	1.472(2)	1.482(3)
N(1)–Zr(1)–C(′)	33.15(6)	33.00(7)
N(1)–Zr(1)–Cl(1)	83.71(4)	84.21(5)
C(′)–Zr(1)–Cl(1)	116.80(5)	117.22(6)

[a] **3**: C(′) = C(1), C(″) = C(2), C(*) = C(8).
[b] **4a**: C(′) = C(23), C(″) = C(24), C(*) = C(30).

crystallises triclinic in the space group $P\bar{1}$ with two formula units in the unit cell. There is one disordered toluene molecule present in the unit cell.

In **3** and **4a**, the zirconium atom is coordinated by two Cp′ or Cp° rings, one chloro ligand and the C and N atoms of the iminoacyl ligand, thus achieving a coordination number of five (Figs. 1 and 2, Table 1). The iminoacyl ligands are bonded to the zirconium atom almost symmetrically in a bidentate fashion [**3**: Zr–N 2.212(2), Zr–C 2.247(2) Å; **4a**: Zr–N 2.238(2), Zr–C 2.267(2) Å]. Of the two possible coordination modes of the ligand, in **3** only the *exo* isomer, in which the NCy group is adjacent to the Zr–Cl bond, is observed. The C–N bond lengths of 1.272(2) (**3**) and 1.280(3) Å (**4a**) are in agreement with the mean C–N double bond lengths observed for organic azomethines (1.279 Å) [25]. Similar Zr–N and Zr–C bond lengths were observed for other isonitrile insertion products, such as $[Cp_2Zr(SR')(\eta^2\text{-NRCMe})]$ (R = xylyl, SR′ = 4,6-dimethylpyrimidine-2-thiolate) [21b] [N–C 1.268(5) Å, Zr–N 2.271(3) Å, Zr–C 2.206(4) Å], and $[Cp_2ZrCl\{\eta^2\text{-N(Bz)C(C[SiMe}_3\text{]=CHPh)}\}]$ [21d] [N–C 1.267(5) Å, Zr–N 2.200(3) Å, Zr–C 2.250(4) Å].

The chlorine atom and the ZrCN fragments of **3** and **4a** are coplanar. The P atom of the pyramidal PHR group deviates only slightly from this plane by 0.263(4) (**3**) and 0.259(5) Å (**4a**).

3. Summary and conclusion

$[Cp'_2ZrCl(PHTipp)]$ (**1**) and $[Cp°_2ZrCl(PHCy)]$ (**2**) readily insert CyNC to give $[Cp'_2ZrCl\{\eta^2\text{-NCyC(PHTipp)}\}]$ (**3**) and $[Cp°_2Zr(Cl)\{\eta^2\text{-NCyC(PHCy)}\}]$ (**4**). The η^2 bonding mode (C,N) of the NCyC(PHR) ligands was shown by crystal structure determination. Of the two possible coordination modes of the ligand, **3** is obtained as the *exo* isomer exclusively, while for **4**, both isomers (*exo* and *endo*) are formed [1:1.5 (**4a**:**4b**)], whereby the *endo* isomer is favoured. Apparently, the bulky cyclopentadienyl ligand Cp° favours the formation of the *endo* isomer, in which the steric interaction between the Cp° ligands and the C(PHR) group is smallest, while the less bulky Cp′ ligands favour the *exo* isomer, in which the Cl–C(PHR) interaction is minimised. This result is in agreement with the selectivity observed for the insertion of RNCX (R = Ph, Cy, X = O, S) into **1** and **2** [20].

4. Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. NMR spectra: Avance DRX 400 (Bruker), standards: ^{1}H-NMR (400 MHz): trace amounts of protonated solvent, C_6D_6, ^{13}C-NMR (100.6 MHz): internal solvent, ^{31}P-NMR (162 MHz): external 85% H_3PO_4. The IR spectra were recorded as KBr mulls on a Perkin–Elmer FT-IR spectrometer System 2000 in the range 350–4000 cm^{-1}. The mass spectra were recorded with a Sektorfeldgerät AMD 402 (AMD Intectra GmbH) (EI, 70 eV). The melting points were determined in sealed capillaries under argon and are uncorrected. **1** [2] and **2** [6] were prepared by literature procedures. CyNC is commercially available and was kept over molecular sieves prior to use.

4.1. Preparation of $[Cp'_2Zr(Cl)\{\eta^2\text{-NCyC(PHTipp)}\}]$ (3)

Compound **1** (1.34 g, 2.57 mmol) was suspended in 50 ml pentane and 0.35 ml (2.85 mmol) CyNC was added dropwise with a pipette. An immediate colour

change from red to yellow was observed. After 2 min, **1** had dissolved completely, and a clear yellow solution had formed. The solution was stirred at room temperature (r.t.) for 9 h. A ^{31}P-NMR spectrum of the reaction mixture (C_6D_6) showed only one signal at -83.2 ppm (d, $^1J_{PH} = 259.8$ Hz). On concentrating the reaction mixture, 1.1 g of **3** was obtained as a white powder. Colourless crystals were obtained from a concentrated pentane solution at r.t. Yield: 1.1 g (67%). M.p. 105°C. The signals in the ^{13}C-NMR spectrum of **3** were assigned by means of a 2D NMR spectrum (^{1}H/^{13}C). ^{1}H-NMR (C_6D_6): $\delta = 0.6$–1.7 (br, m, 11H, Cy), 1.14 (d, 6H, *p*-Me_2CH, $^3J_{HH} = 7.0$ Hz), 1.25 (d, 6H, *o*-Me_2CH, $^3J_{HH} = 6.7$ Hz), 1.29 (d, 6H, *o*-Me_2CH, $^3J_{HH} = 6.7$ Hz), 2.17 (s, 3H, C_5H_4Me), 2.25 (s, 3H, C_5H_4Me), 2.72 (sept, 1H, *p*-Me_2CH, $^3J_{HH} = 6.8$ Hz), 3.42 (sept, br, 1H, *o*-Me_2CH), 3.72 (sept, br, 1H, *o*-Me_2CH), 5.57 (m, br, 4H, C_5H_4Me), 5.62 (m, br, 2H, C_5H_4Me), 5.71 and 5.73 (m, br, 2H, C_5H_4Me), 5.83 (d, 1H, P–H, $^1J_{PH} = 259.9$ Hz), 7.10 (s, 2H, *m*-H in 2,4,6-$Pr^i_3C_6H_2$). ^{13}C-NMR (C_6D_6): $\delta = 16.20$ (s, C_5H_4Me), 16.30 (s, C_5H_4Me), 24.48 (s, Me_2CH and C4 of Cy), 25.04 (s, Me_2CH), 25.63 (s, C3/C5 of Cy), 25.75 (s, Me_2CH), 32.34 (s, C2 or C6 of Cy), 32.63 (s, C2 or C6 of Cy), 34.22 (s, Me_2CH), 34.36 (s, Me_2CH), 35.26 (s, Me_2CH), 64.95 (d, $^1J_{PC} = 11.6$ Hz, C1 of Cy), 105.79, 107.17, 108.00, 109.82, 111.41, 112.52 and 113.35 (each s, C_5H_4Me), 122.28 (d, C3/C5 of 2,4,6-$Pr^i_3C_6H_2$, $^3J_{PC} = 4.3$ Hz), 152.88 (s, C4 of 2,4,6-$Pr^i_3C_6H_2$), 154.77 (d, C1 of 2,4,6-$Pr^i_3C_6H_2$, $^1J_{PC} = 12.5$ Hz), 237.76 (d, N*C*P, $^1J_{PC} = 106.4$ Hz). Signals for C2 and C6 of 2,4,6-$Pr^i_3C_6H_2$ are obscured by C_6D_6. ^{31}P-NMR (C_6D_6): $\delta = -83.2$ (d, $^1J_{PH} = 259.8$ Hz). EI MS: *m*/*z* 592 (1%, $M^+ - Cl$), 544 (1%, $M^+ - Cy$), 492 (1%, $[Cp'_2Zr(Cl)(NCyCPHC_2Pr^i)]^+$), 470 (2%, $[Zr(Cl)(NCyCPHTipp)]^+$), 425 (1%, $[Cp'_2Zr(Cl)(NCyCPH)]^+$), 391 (13%, $[Cp'_2Zr(Cl)(NCyC)]^+$), 345 (1%, $[CyNCPHTipp]^+$), 283 (70%, $[Cp'_2ZrCl]^+$), 247 (15%, $[CPHTipp]^+$ oder $[Zr(Cl)NCy]^+$), 236 (32%, PH_2Tipp^+), 203 (100%, $Tipp^+$), 193 (16%, $PC_6H_2Pr^{i+}_2$), 176 (8%, $[PC_6H_2Pr^iCHCH_3]^+$), 160 (13%, $C_6H_2Pr^{i+}_2$), 132 (10%, $[ZrNCHCH_2]^+$), 109 (11%, $CyNC^+$), 91 (19%, Zr^+), 81 (18%, Cy-2H$^+$), 42 (66%, Pr^{i+}) and fragmentation products thereof (molecular ion peak was not observed). IR (cm^{-1}, KBr): 3082 w, 3044 vw, 2958 vs, 2932 vs, 2856 s, 2339 m, 1596 m, 1548 m, 1499 m, 1460 m, 1426 m, 1385 m, 1362 m, 1348 m, 1311 w, 1261 m, 1246 m, 1152 m, 1104 m, 1061 m, 1053 m, 1039 m, 1028 m, 959 m, 946 m, 918 m, 894 m, 880 m, 859 m, 835 m, 810 vs, 779 m, 734 s, 651 w, 615 m, 553 w, 522 w, 455 m, 425 w, 391 m, 369 m. Elemental analysis of $C_{34}H_{49}ClNPZr$ (629.38). Calc.: C, 59.0; H, 7.3; N, 2.7. Found: C, 58.9; H, 7.1; N, 2.5%.

4.2. Preparation of [$Cp^\circ_2Zr(Cl)\{\eta^2$-NCyC(PHCy)$\}$] (4)

At r.t. 0.47 ml (3.8 mmol) CyNC was added to a solution of 2.05 g (3.8 mmol) **2** in 20 ml toluene. The colour of the reaction mixture turned orange over 3 min. The mixture was stirred for 12 h. A ^{31}P-NMR spectrum of the solution (C_6D_6) showed two signals at -25.4 (d, $^1J_{PH} = 254.3$, *exo* isomer, **4a**) and -31.7 ppm (d, $^1J_{PH} = 207.3$ Hz, *endo* isomer, **4b**) in the ratio 1:1.5. The solution was concentrated to half its volume. The red solid that formed over-night was isolated. Recrystallisation from toluene yielded yellow needles of **4a** (yield: 0.57g, 23.1%). M.p. 72°C. **4b** was not obtained in pure form. ^{1}H-NMR (C_6D_6): $\delta = 0.94$ (t, br, 6H, CH_2CH_3), 1.1–1.9 (m, br, 22H, Cy of PHCy and CyNC), 1.91 (s, 12H, C_5Me_4Et), 1.94 and 1.95 (s, each 3H, C_5Me_4Et), 1.98 (s, 6H, C_5Me_4Et), 2.40 (q, br, 2H, CH_2CH_3), 2.48 (q, br, 2H, CH_2CH_3), 4.55 (d, 1H, P–H, $^1J_{PH} = 253.7$ Hz). ^{13}C-NMR (C_6D_6): $\delta = 12.22$, 12.36, 12.47, 12.61, 12.83, 12.84, and 13.10 (each s, C_5Me_4Et), 15.35 (s, $C_5Me_4CH_2CH_3$), 20.93 and 21.08 (s, $C_5Me_4CH_2CH_3$), 21.87–35.85 (N–Cy and C2–C6 of P–Cy), 70.20 (d, C1 of P–Cy, $^1J_{PC} = 16.6$ Hz), 116.35, 117.22, 117.44, 117.98, 118.23, 118.72, 118.73 and 119.32 (each s, C_4Me_4CEt), 122.96 and 123.79 (each s, C_4Me_4CEt), 243.02 (d, NCP, $^1J_{PC} = 97.6$ Hz). ^{31}P-NMR (C_6D_6): $\delta = -25.8$ (d, $^1J_{PH} = 250.3$ Hz). EI MS: *m*/*z* 613 (0.04%, $M^+ - Cl$), 565 (0.1%, $M^+ - Cy$), 533 (22%, $M^+ - Cy - PH$), 498 (3%, $M^+ - Cy - PH - Cl$), 459 (5%, $[Cp^\circ CpMe_4ZrNCy]^+$), 423 (100%, $Cp^\circ_2ZrCl^+$), 383 (4%, $M^+ - Cy - PH_2 - Cp^\circ$), 149 (5%, $Cp^{\circ+}$), 133 (10%, $C_5EtMe^+_3$), and fragments thereof. IR (cm^{-1}, KBr): 3010 m, 2924 vs, 2854 vs, 2720 m, 2324 m, 2137 vw, 1929 vw, 1580 m, 1489 m, 1446 vs, 1376 m, 1366 m, 1346 m, 1305 m, 1260 m, 1243 w, 1175 m, 1150 m, 1074 m, 1055 m, 1027 s, 996 m, 960 m, 899 m, 890 m, 846 m, 807 m, 756 w, 734 s, 697 m, 593 w, 546 w, 505 vw, 466 m, 374 s. Elemental analysis of $C_{35}H_{57}ClNPZr$ (649.49). Calc.: C, 64.7; H, 8.8; N, 2.1. Found: C, 64.0; H, 8.7; N, 2.1%.

4.3. Data collection and structural refinement of 3 and 4a

Crystallographic details are given in Table 2. Data (Mo–$K_\alpha = 0.71073$ Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters (19 011 for **3**, 15 416 for **4a**). Empirical absorption correction with SADABS [26]. The structures were solved by direct methods (SHELXTL PLUS [27]). Restrictions for **3** and **4a**: Zr, Cl, P, N, and C atoms anisotropic, H atoms located by difference maps and refined isotropically. **4a** crystallises with one disordered toluene molecule per unit cell. The toluene molecule is located above a crystallographic inversion centre where five independent C atoms generate the remaining part of the

Table 2
Crystal data and structure refinement for **3** and **4a**

	3	**4a**
Emperical formula	$C_{34}H_{49}ClNPZr$	$C_{35}H_{57}ClNPZr \cdot 1/2$ toluene
Formula weight	629.38	649.49 + 46.07
Temperature (K)	213(2)	220(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	18.015(1)	9.956(1)
b (Å)	9.526(1)	10.711(1)
c (Å)	19.512(1)	18.445(1)
α (°)	90	77.45(1)
β (°)	95.014(1)	78.00(1)
γ (°)	90	83.32(1)
V (Å^3)	3335.6(1)	1872.7(1)
Z	4	2
$D_{calc.}$ (Mg m^{-3})	1.253	1.225
$F(000)$	1328	734
Crystal size (mm)	0.30 × 0.20 × 0.20	0.50 × 0.30 × 0.20
Absorption coefficient (mm^{-1})	0.480	0.433
$2\Theta_{max}$ (°)	2.2–56.4	2.3–55.8
Reflections collected	19 011	15 416
Independent reflections	7403	7904
R_{int}	0.0671	0.0400
Parameters	540	457
R ($I > 2\sigma(I)$)	0.0323	0.0370
wR_2 (all data)	0.0678	0.1061
Largest difference peak and hole (e Å^{-3})	0.584 and −0.906	0.467 and −0.709

disordered molecule and the methyl group coincides with an aromatic CH group. Therefore, no H atoms of the disordered toluene were included in the refinement.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (**3**: CCDC 142354, **4a**: CCDC 142353). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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