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Formation of novel P-functionalized ligands by insertion reactions into the Zr—P bond of $Cp^{\circ}_2ZrCl(PHCy)$ ($Cp^{\circ} = \eta^5$-C_5EtMe_4, Cy = cyclohexyl)

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Abstract—$Cp^{\circ}_2ZrCl_2$ ($Cp^{\circ} = \eta^5$-C_5EtMe_4) reacts with LiPHCy (Cy = cyclohexyl) with the formation of $Cp^{\circ}_2ZrCl(PHCy)$ (**1**). Compound **1** undergoes insertion of CS_2 or PhNCS into the Zr—P bond, yielding $Cp^{\circ}_2ZrCl(\eta^2$-$S_2CPHCy)$ (**2**) and $Cp^{\circ}_2ZrCl\{\eta^2$-$SC(PHCy)NPh\}$ (**3**). Compounds **1–3** were characterized spectroscopically (IR, NMR, MS) and crystal structure determinations were carried out on **1** and **3**, showing an η^2-bonding mode of the SC(PHCy)NPh (S, N) ligand in the latter. © 1997 Elsevier Science Ltd

Keywords: zirconocene monophosphanido complex; insertion reaction; phosphinodithioformato ligand; N-phenylthiophosphinoamidato ligand.

Although the first dinuclear zirconocene phosphanido complexes were prepared as early as 1966 [1], these complexes remained largely unexplored until 1983, when Baker *et al.* [2] prepared the first zirconocene(IV) complex with terminal dialkyl- or diarylphosphanido ligands. To date, several group 4 complexes with dialkyl- or diarylphosphanido ligands are known; however, complexes of this type with P-functionalized phosphanido ligands are still rare [3].

For some time we have been interested in the preparation of zirconocene phosphanido complexes with P-functionalized ligands. While zirconocene complexes with terminal $P(SiMe_3)_2$ are easily accessible [4,5], zirconocene complexes with terminal primary phosphanido ligands PHR are only obtained with certain combinations of substituted cyclopentadienyl ligand and P—R substituent. Thus, P—H-functionalized zirconocene complexes of general formula $Cp^Z_2ZrCl(PHR)$ and $Cp^Z_2Zr(PHR)_2$ (Cp^Z = substituted cyclopentadienyl ligand) were only obtained from reactions of Cp_2ZrCl_2 with $LiPH(2,4,6\text{-}R'_3C_6H_2)$ (R′ = Me [6], Pr^i [7], Bu^t [8]), i.e. sterically less demanding ligand at Zr, bulky substituent at phosphorus, or from $Cp^*_2MX_2$ and LiPHR ($Cp^* = \eta^5$-C_5Me_5; M = Zr, X = Cl, R = Cy (cyclohexyl); M = Hf, X = I, Cl, R = Cy, X = I, R = Ph) [9], i.e. sterically less demanding substituent at phosphorus and bulky substituent at Zr or Hf. However, for the latter combination only monophosphanido complexes were obtained.

The insertion of polar multiple-bond systems such as CS_2 [10], diazoalkanes [11], phenylacetylene [12], carbodiimides [13,14] or isonitriles [14] into the Zr—P bond of the P-functionalized zirconocene monophosphanido complexes $Cp^Z_2ZrCl\{P(SiMe_3)_2\}$ ($Cp^Z = \eta^5$-C_5H_5, η^5-C_5H_4Me) allowed the synthesis within the coordination sphere of zirconium of novel P-functionalized phosphino ligands which are either difficult to synthesize or inaccessible by other routes [12,15]. Only a few insertion reactions of the dialkyl- or diarylphosphanido complexes $Cp^*HfCl_2(PBu^t_2)$ with CO [16] or of $Cp^*_2HfH(PPh_2)$ with CO_2 [9] have been reported. Up to now, insertion reactions with the corresponding primary phosphanido complexes, $Cp^Z_2ZrCl(PHR)$, are rare [6].

We now report the synthesis of a P—H functionalized zirconocene monophosphanido complex

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with a sterically less demanding alkyl substituent at phosphorus, $Cp^{\circ}_2ZrCl(PHCy)$ (**1**) ($Cp^{\circ} = \eta^5$-C_5EtMe_4) and its reactions with CS_2 and PhNCS to give $Cp^{\circ}_2ZrCl(\eta^2$-$S_2CPHCy)$ (**2**) and $Cp^{\circ}_2ZrCl\{\eta^2$-$SC(PHCy)NPh\}$ (**3**).

RESULTS AND DISCUSSION

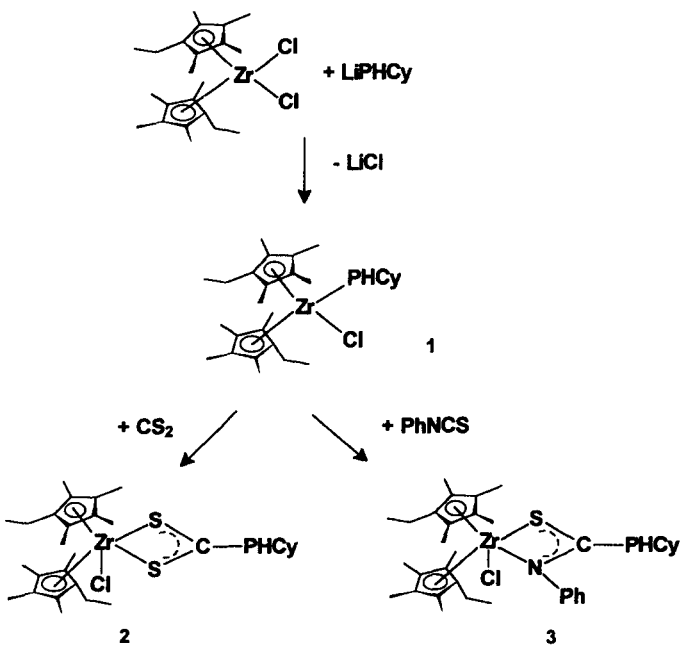
Synthesis and properties of 1–3

While Cp_2ZrCl_2 reacts with LiPHCy with the formation of the triphosphane-1,3-diyl complex $Cp_2Zr(PCy—PCy—PCy)$ as the major product [17], the reaction with PH_2Cy in the presence of Mg turnings yields the Zr^{III} complex $[Cp_2Zr(\mu$-$PHCy)]_2$ [18,19]. The latter is also obtained from zirconocene (prepared by the Negishi method [20]) or Cp_2ZrHCl and cyclohexylphosphine [19]. However, when $Cp^{\circ}_2ZrCl_2$ is reacted with LiPHCy, the orange-red monophosphanido complex $Cp^{\circ}_2ZrCl(PHCy)$ (**1**) is formed as the major product in 38% yield (Scheme 1). Similarly, $Cp^{*}_2MX_2$ and LiPHR are reported to give the products $Cp^{*}_2MX(PHR)$ (M = Zr, X = Cl, R = Cy; M = Hf, X = I, Cl, R = Cy, X = I, R = Ph) [9]. Besides **1**, the diphosphene complex $Cp^{\circ}_2Zr(PCy—PCy)$ and the triphosphane-1,3-diyl complex $Cp^{\circ}_2Zr(PCy—PCy—PCy)$ are also formed (as shown by the ^{31}P NMR spectrum of the reaction mixture); however, no attempts were made to isolate these compounds.

The spectroscopic data (NMR, IR) of **1** are similar to those of $Cp^{*}_2ZrCl(PHCy)$ [9]. Like comparable complexes [6–9], **1** shows a doublet [71.7 ppm, $^1J(PH) = 209$ Hz] in the proton-coupled ^{31}P NMR spectrum, which is shifted to low field compared with the resonance of Li(thf)PHCy (−135.4 ppm) [21], and the PH stretching vibration of **1** (2311 cm^{-1}) is shifted to higher wave numbers compared with the lithium reagent [Li(thf)PHCy: ν(PH)2286 cm^{-1}] [21].

Complex **1** readily inserts CS_2 or the ambident nucleophile PhNCS yielding $Cp^{\circ}_2ZrCl(\eta^2$-$S_2CPHCy)$ (**2**) (S, S′) and $Cp^{\circ}_2ZrCl\{\eta^2$-$SC(PHCy)NPh\}$ (**3**) (S, N; Scheme 1). Whereas **1** undergoes insertion of multiply bonded systems into the Zr—P bond, for $Cp(CO)_2M{=}PR^1R^2$ (M = Mo, W, R^1 = Ph, R^2 = Tol) [2+2] cycloaddition is observed, the reaction with RNCO (R = Et, Ph) affording the four-membered metallacyclic compounds $Cp(CO)_2M—PR^1R^2—C(O)—NR$ with high diasteroselectivity [22].

The insertion products **2** and **3** exhibit doublets in the proton-coupled ^{31}P NMR spectrum, which are shifted to high field and have a larger PH coupling constant compared with **1** [**2**: 29.0, $^1J(PH) = 225.1$ Hz, **3**: −16.1, $^1J(PH) = 226.9$ Hz]. The phosphinodithioformato ligand in **2** and the *N*-phenylthiophosphinoamidato ligand in **3** are expected to show a bidentate (S, S′ or S, N) coordination mode, similar to the comparable complexes $Cp'_2ZrCl[\eta^2$-$NPhC\{P(SiMe_3)_2\}NPh]$ [13] ($Cp' = \eta^5$-C_5H_4Me) (N, N′ coordination) and $Cp_2ZrCl\{\eta^2$-$S_2CP(SiMe_3)_2\}$ [10] (S, S′ coordination), which were obtained by insertion of carbodiimide or CS_2. In the IR spectrum of $Cp'_2ZrCl[\eta^2$-$NPhC\{P(SiMe_3)_2\}NPh]$, two strong absorptions at 1485 and 1431 cm^{-1} indicate the bidentate bonding mode [13]. For Cp_2ZrCl



Scheme 1.

$\{\eta^2$-$S_2CP(SiMe_3)_2\}$, the corresponding absorptions occur at 978 and 923 cm^{-1} [10]. In **2**, two strong absorptions at 960 and 896 cm^{-1} can tentatively be assigned to the CS vibrations. In **3**, new strong absorptions at 1488 and 1022 cm^{-1} and a medium absorption at 1198 cm^{-1} are observed compared with **1** and PhNCS [23]. The first two can be assigned to ν(CN) (1488 cm^{-1}) and ν(CS) (1022 cm^{-1}) by comparison with the products of carbodiimide- and CS_2-insertion mentioned above.

Insertion reactions of isothiocyanates into metal–nitrogen (amide) bonds are known [24]. However, $[Ti(NMe_2)_3]_2$, $M(NMe_2)_4$ (M = Ti, Zr) and Me_3SnNMe_2 react with RNCS to give $Ti\{SC(NMe_2)NPh\}_3$ [25], $M\{SC(NMe_2)NR\}_4$ (M = Ti, R = Ph; M = Zr, R = Me) [26] and $Me_3Sn\{SC(NMe_2)NEt\}$ [27], respectively, in which the ligand has an η^1 (S) bonding mode, while $RZnNR'_2$ undergoes R″NCS insertion to give $RZn\{NR''CS(NR'_2)\}$ [28] (R = Et, R′ = R″ = Ph; R = R′ = Et, R″ = Ph; R = R′ = R″ = Ph; R = Et, R′ = Ph, R″ = Me), with an η^1 (N) bonding mode. The related zirconium complexes $CpZr(\eta^2$-NRCR′S)R'_2 (R = benzyl or 1-phenylethyl, R′ = tolyl) have been obtained by insertion of isothiocyanate into a Zr–aryl bond [29]. The η^2 coordination (N, S) of the *N*-alkylthiobenzamidato ligand was suggested by IR data [29]. However, to our knowledge none of these insertion products has been structurally characterized.

Molecular structure of **1** *and* **3**

Both complexes **1** and **3** crystallize triclinic in the space group $P\bar{1}$ (no. 2) with two formula units in the unit cell.

In **1**, the zirconium atom is coordinated in a distorted tetrahedral fashion by two Cp° rings, one chloro ligand and the P atom of the cyclohexylphosphanido ligand (Fig. 1, Table 1). The overall geometry of **1**, with a Zr—P bond length of 2.6539(9) Å and a sum of bond angles at P of 308(2)°, is comparable to that of $Cp'_2ZrCl\{PH(2,4,6\text{-}Pr^i_3C_6H_2)\}$ [Zr—P 2.6381(8) Å, sum of bond angles at P 328.6°] [7]. In both complexes, the phosphanido group has a pyramidal geometry, suggesting that the PHR ligands act as one-electron donors.

In **3**, the zirconium atom is coordinated by two Cp° rings, one chloro ligand and the S and N atom of the *N*-phenylthiophosphinoamidato ligand, thus achieving a coordination number of five (Fig. 2, Table 2). The overall structure is comparable to those of the phosphaguanidino complex $Cp'_2ZrCl[\eta^2$-NPhC$\{P(SiMe_3)_2\}$NPh] [13] (N, N′ coordination) and the CS_2 insertion product $Cp_2ZrCl\{\eta^2$-$S_2CP(SiMe_3)_2\}$ [10] (S, S′ coordination). While both the guanidino ligand and the phosphinodithioformato ligand are bonded to the zirconium atom almost symmetrically in a bidentate fashion [phosphaguanidino ligand: Zr—N 2.309(5), 2.348(5) Å [13], phosphinodithioformato ligand: Zr—S 2.733(7), 2.640(8) Å] [10], the N, S coordination in **3** is unsymmetrical, with the Zr—N [2.361(4) Å] and Zr—S [2.769(1) Å] bond lengths comparable to the N, N′ and S, S′ bonded ligands. However, in all three complexes, delocalization of the π-electrons of the N_2C, S_2C and NCS fragment can be assumed, as the C—N and C—S bonds are shorter than expected for single bonds, and the N and C atoms of the N_2C [C—N 1.331(7), 1.323(7) Å] [13], S_2C [C—S 1.68(3), 1.64(3) Å] [10] and NCS fragments [N—C(23) 1.296(6), S—C(23) 1.718(5) Å] are coordinated in a trigonal planar fashion.

In **3**, the chlorine atom and the ZrSCN fragment are coplanar. The P atom of the pyramidal PHCy group deviates from this plane by 0.37 Å. Of the two possible coordination modes of the ligand, the only one observed is that in which the NPh group is adjacent to the Zr—Cl bond (Fig. 2).

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 spectrum 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. Cp'_2ZrCl_2 [30] and LiPHCy [21] were prepared by literature procedures. CS_2 and PhNCS are commercially available and were kept over molecular sieve prior to use.

Synthesis of $Cp'_2ZrCl(PHCy)$ (**1**) [31]

With a canula a solution of LiPHCy (4.1 g, 33.6 mmol) in 50 cm^3 THF (cooled to −70 °C) was added dropwise to a solution of Cp'_2ZrCl_2 (14.9 g, 31.9 mmol) in 50 cm^3 THF, which was also cooled to −70 °C. A colour change from pale yellow to orange–brown was observed. The solution was kept at −70 °C for 4 h, then at room temperature for 30 h. Then the solvent was pumped off to dryness and the purple–red residue was dissolved in 50 cm^3 toluene. LiCl was filtered off and washed with 10 cm^3 toluene. The red–brown mother liquor was concentrated. At room temperature, first a small amount of **1** containing Cp'_2ZrCl_2 as impurity is obtained. Removal of the solid and concentration of the mother liquor then gave large red crystals of **1** at room temperature over night (4.1 g, 24%). By concentrating and cooling the mother liquor to −20 °C the yield of **1** can be increased to a maximum of 38%.

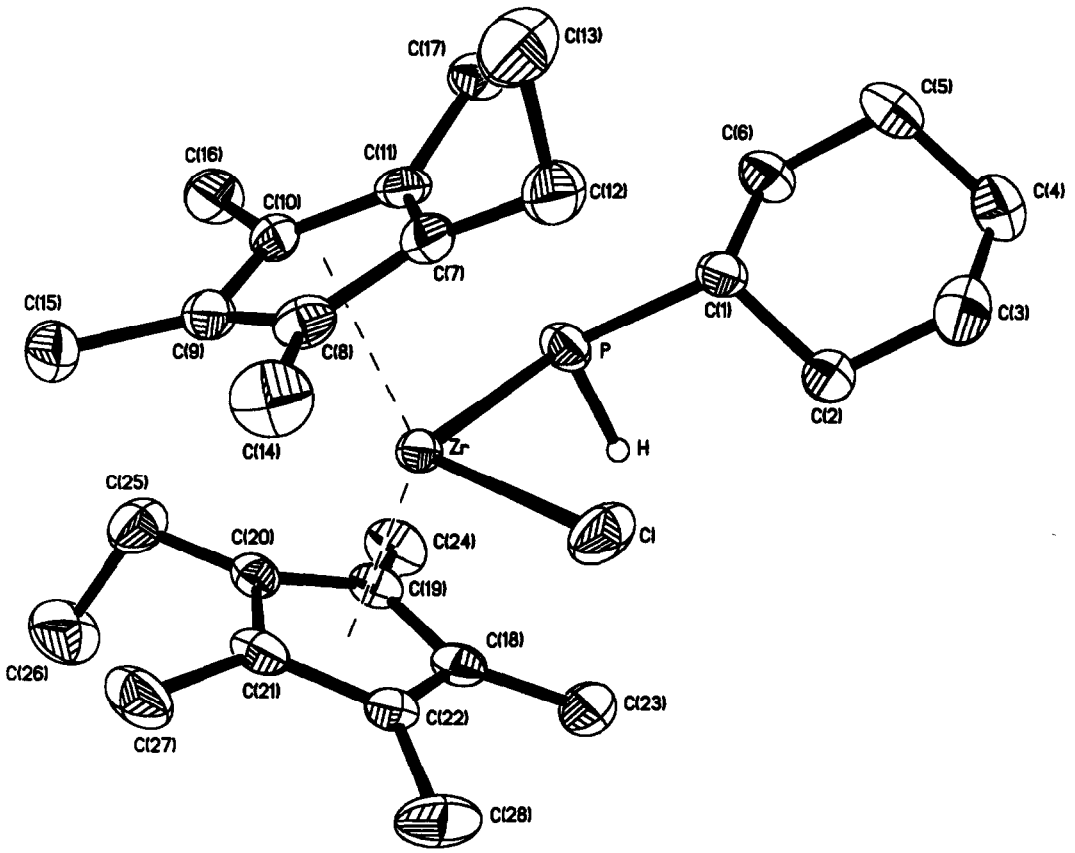


Fig. 1. Molecular structure of $Cp^{\circ}_2ZrCl(PHCy)$ (**1**), showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP) [34]. Hydrogen atoms (other than P—H) are omitted for clarity.

M.pt 77–81°C. ^{1}H NMR (C_6D_6, ppm): 0.91 t [6 H, CH_2CH_3, ^3J(HH) = 7.5 Hz]; *ca* 1.2–1.85 m, broad (11 H, Cy), 1.88 s (12 H, C_5Me_4Et), 1.90 s (6 H, C_5Me_4Et), 1.95 s (6 H, C_5Me_4Et), 2.48 q [4 H, CH_2CH_3, ^3J(HH) = 7.5 Hz], 3.49 dd [1 H, P*H*, ^1J(PH) = 204 Hz, ^2J(PH) = 6.8 Hz]. ^{13}C NMR (C_6D_6, ppm): 12.49 s, 12.54 s, 12.62 s, 12.67 s, 12.76 s, 12.83 s, 12.85 s, 12.91 s [eight s for $C_5(CH_3)_4Et$]; 15.34 s [$C_5Me_4(CH_2CH_3)$]; 21.07 s, 21.04 s [$C_5Me_4(CH_2CH_3)$]; 27.50 s [C4 of Cy], 29.97 d [C3 and C5 of Cy, ^3J(PC) = 7.2 Hz], 37.67 d [C2 and C6 of Cy, ^2J(PC) = 15.7 Hz], 39.53 d [C1 of Cy, ^1J(PC) = 3.6 Hz]; 119.97 s, 120.64 s, 121.71 s, 122.31 s [four s for $C_4(CH_3)_4CEt$]; 126.83 s [$C_4(CH_3)_4CEt$]. Assignment by comparison with $Cp^{\circ}_2ZrCl_2$ (ref. [32]) and according to ref. [33]. ^{31}P NMR (C_6D_6, ppm): 71.7 d [^1J(PH) = 209 Hz]. IR (KBr, cm^{-1}): ν = 2982 st, 2963 st, 2948 st, 2914 vst, 2841 st, 2720 w, 2311 st, 1485 m, 1457 st, 1442 st, 1427 st, 1379 st, 1367 st, 1329 w, 1309 w, 1290 w, 1260 m, 1252 w, 1190 w, 1171 w, 1113 w, 1073 w, 1050 m, 1024 st, 996 st, 965 w, 946 w, 912 w, 877 w, 840 w, 764 w, 610 vw, 591 w, 550 w, 457 w, 393 w, 370 st (ν ZrCl). MS, *m/z* (%): 538 (23) [M^+], 424 (100) [$M^+ - PHCy = Cp^{\circ}_2ZrCl^+$], 116 (6) [$PH_2Cy^+$], and fragmentation products thereof. Found: C, 61.5; H, 8.4. Calc. for $C_{28}H_{46}ClPZr$: Calc. C, 62.2; H, 8.6%.

A ^{31}P NMR spectrum of the reaction mixture showed the presence of **1** as the major product as well as of $Cp^{\circ}_2Zr(PCy—PCy)$ (219.6 ppm, s) and $Cp^{\circ}_2Zr(PCy—PCy—PCy)$ [−143.5 t, 106.1 d, ^1J(PP) = 300 Hz] [31]. When the reaction is carried out in the stoichiometry 1:2, $Cp^{\circ}_2ZrCl_2$ (9.65 g, 20.9 mmol) and LiPHCy (4.87 g, 41.9 mmol) in 70 cm^3 THF (both solutions at −70°C), $Cp^{\circ}_2Zr(PCy—PCy)$ (219.6 ppm, s) and $Cp^{\circ}_2Zr(PHCy)_2$ [146.2 ppm, d, ^1J(PH) = 249 Hz] are the major products, shown by ^{31}P NMR spectroscopy [31].

Synthesis of $Cp^{\circ}_2ZrCl(\eta^2\text{-}S_2CPHCy)$ (**2**)

Using a pipette, carbon disulfide (0.18 cm^3, 3.0 mmol) was added to a solution of $Cp^{\circ}_2ZrCl(PHCy)$ (**1**; 1.60 g, 3.0 mmol) in 20 cm^3 toluene and the reaction mixture was stirred at room temperature. After a few minutes the colour changed from wine-red to dark green. The solution was stirred overnight. Concentrating and cooling of the mother liquor to −20°C

Table 1. Selected bond lengths (Å) and bond angles (°) for **1**

Zr(1)—P(1)	2.6539(9)	Zr(1)—Cl(1)	2.4442(9)
Zr—C(Cp°)	2.531(3) to 2.592(3)	P(1)—C(1)	1.889(4)
P(1)—H(1)	1.34(6)	Zr—Centre (Cp°)	2.258, 2.256
C(1)—C(2)	1.527(5)	C(1)—C(6)	1.538(5)
C(2)—C(3)	1.539(7)	C(3)—C(4)	1.521(8)
C(4)—C(5)	1.513(7)	C(5)—C(6)	1.517(6)
C(7)—C(11)	1.418(5)	C(7)—C(8)	1.420(5)
C(7)—C(12)	1.507(5)	C(8)—C(9)	1.420(5)
C(8)—C(14)	1.517(5)	C(9)—C(10)	1.424(4)
C(9)—C(15)	1.505(5)	C(10)—C(11)	1.432(5)
C(10)—C(16)	1.491(5)	C(11)—C(17)	1.498(5)
C(12)—C(13)	1.521(6)	C(18)—C(22)	1.406(5)
C(18)—C(19)	1.427(5)	C(18)—C(23)	1.489(5)
C(19)—C(20)	1.428(5)	C(19)—C(24)	1.499(5)
C(20)—C(21)	1.431(5)	C(20)—C(25)	1.503(5)
C(21)—C(22)	1.421(5)	C(21)—C(27)	1.505(5)
C(22)—C(28)	1.499(5)	C(25)—C(26)	1.527(6)

Cl(1)—Zr(1)—P(1)	99.79(4)	C(1)—P(1)—H(1)	96(3)
C(1)—P(1)—Zr(1)	110.79(12)	Centre(Cp°)—Zr(1)—Centre(Cp°)	137.4
Zr(1)—P(1)—H(1)	102(3)	C(2)—C(1)—C(6)	109.5(3)
C(2)—C(1)—P(1)	113.4(2)	C(6)—C(1)—P(1)	109.9(3)
C(1)—C(2)—C(3)	110.9(4)	C(4)—C(3)—C(2)	111.1(5)
C(5)—C(4)—C(3)	111.7(4)	C(4)—C(5)—C(6)	111.5(4)
C(5)—C(6)—C(1)	111.8(4)	C(11)—C(7)—C(8)	107.7(3)
C(11)—C(7)—C(12)	125.4(3)	C(8)—C(7)—C(12)	126.0(3)
C(7)—C(8)—C(9)	108.5(3)	C(7)—C(8)—C(14)	126.0(4)
C(9)—C(8)—C(14)	125.1(4)	C(8)—C(9)—C(10)	107.8(3)
C(8)—C(9)—C(15)	124.9(3)	C(10)—C(9)—C(15)	125.2(3)
C(9)—C(10)—C(11)	107.5(3)	C(9)—C(10)—C(16)	126.8(3)
C(11)—C(10)—C(16)	124.7(3)	C(7)—C(11)—C(10)	108.2(3)
C(7)—C(11)—C(17)	126.9(3)	C(10)—C(11)—C(17)	123.2(3)
C(7)—C(12)—C(13)	111.3(3)	C(22)—C(18)—C(19)	108.4(3)
C(22)—C(18)—C(23)	124.4(3)	C(19)—C(18)—C(23)	126.9(3)
C(18)—C(19)—C(20)	107.7(3)	C(18)—C(19)—C(24)	126.7(3)
C(20)—C(19)—C(24)	124.4(3)	C(19)—C(20)—C(21)	107.6(3)
C(19)—C(20)—C(25)	123.7(3)	C(21)—C(20)—C(25)	127.1(3)
C(22)—C(21)—C(20)	107.8(3)	C(22)—C(21)—C(27)	123.6(4)
C(20)—C(21)—C(27)	127.1(4)	C(18)—C(22)—C(21)	108.5(3)
C(18)—C(22)—C(28)	126.6(4)	C(21)—C(22)—C(28)	124.2(4)
C(20)—C(25)—C(26)	111.3(4)		

gave green–yellow crystals of **2**. Yield: 1.83 g (98%), m.pt 125°C. ^{1}H NMR (C_6D_6, ppm): 0.85 t [3 H, CH_2CH_3, ^3J(HH) = 7.5 Hz], 0.86 t, [3 H, CH_2CH_3, ^3J(HH) = 7.5 Hz], *ca* 1.0–1.7 m, broad (11 H, Cy), 1.85 s (6 H, C_5Me_4Et), 1.86 s (6 H, C_5Me_4Et), 1.88 s (6 H, C_5Me_4Et), 1.89 s (6 H, C_5Me_4Et), 2.37 q [2 H, CH_2CH_3, ^3J(HH) = 7.5], 2.38 q [2 H, CH_2CH_3, ^3J(HH) = 7.5], 4.85 dd [1 H, P*H*, ^1J(PH) = 225.6 Hz, ^2J(PH) = 6.9 Hz]. ^{31}P NMR (C_6D_6, ppm): 29.0 d [^1J(PH) = 225.1 Hz]. IR (KBr, cm^{-1}): ν = 2288 s (ν PH), 1551 w*, 1488 m, 1448 st*, 1324 m, 1312 w, 1268 w, 1152 w, 1102 w, 1024 m, 1004 st, 960 st* (ν_{as} CS), 904 w, 896 st* (ν_s CS), 832 m, 816 w, 752 m*, 672 m*, 592 w, 516 w, 448 m, 390 sh, 350 vst (ν ZrCl); peaks marked * are new compared with **1**. MS, *m/z* (%): 614 (5) [M$^+$], 578 (8) [M$^+$ − Cl], 500 (1) [M$^+$ − PHCy], 465 (50) [M$^+$ − Cl − PHCy], 422 (100) [M$^+$ − S_2CPHCy = $Cp^\circ_2ZrCl^+$], 115 (8) [PHCy$^+$], and fragmentation products thereof. Found: C, 56.7; H, 6.7; Cl, 5.9. Calc. for $C_{29}H_{46}ClPS_2Zr$: C, 56.5; H, 7.5; Cl, 5.7%.

Synthesis of $Cp^\circ_2ZrCl\{\eta^2$-SC(PHCy)NPh$\}$ (**3**)

Using a pipette, phenyl isothiocyanate (0.31 cm^3, 3.0 mmol) was added to a solution of 1.60 g (3.0 mmol) $Cp^\circ_2ZrCl(PHCy)$ (**1**) in 25 cm^3 toluene and the reaction mixture was stirred at room temperature. After a few minutes a colour change from wine–red to green was observed. The solution was stirred overnight. Concentrating and cooling of the mother liquor

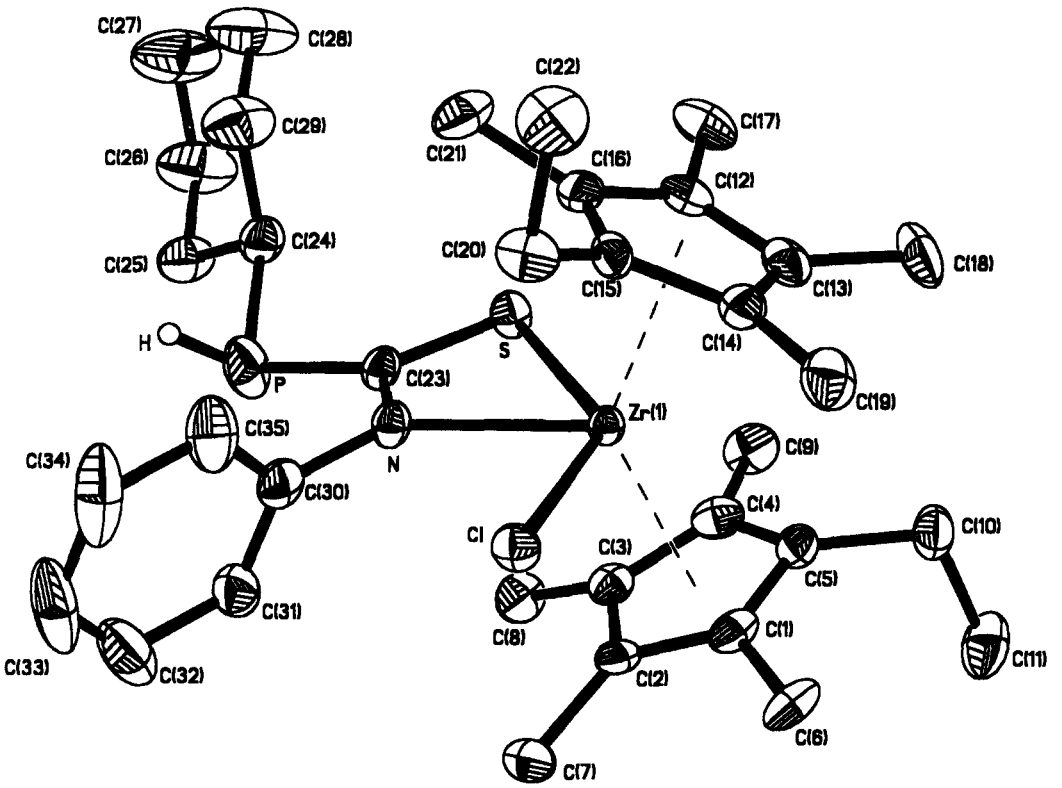


Fig. 2. Molecular structure of $Cp^{\circ}_2ZrCl\{\eta^2\text{-}SC(PHCy)NPh\}$ (**3**) showing the atom-numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP) [34]. Hydrogen atoms (other than P—H) are omitted for clarity.

to −20°C for several weeks gave yellow crystals of **3**. Yield: *ca* 0.4 g (*ca* 20%), m.pt 63–67°C. ^{1}H NMR (C_6D_6, ppm): 0.91 t [6 H, CH_2CH_3, ^3J(HH) = 7.5 Hz], *ca* 0.9–1.6 m, broad (11 H, Cy), 1.94 s (12 H, C_5Me_4Et), 1.98 s (12 H, C_5Me_4Et), 2.45 q [4 H, CH_2CH_3, ^3J(HH) = 7 Hz], 3.86 dd [1 H, P*H*, ^1J(PH) = 226 Hz, ^2J(PH) = 6.8 Hz], 6.96–7.02 m and 7.12–7.15 m (5 H, Ph). ^{13}C NMR (C_6D_6, ppm): 13.28–13.49 [several (overlapping) s for $C_5(CH_3)_4Et$], 15.30 s and 15.32 s [$C_5Me_4(CH_2CH_3)$], 21.39 s and 21.42 s [$C_5Me_4(CH_2CH_3)$], 26.74 s [C4 of Cy], 28.15 d [C3 and C5 of Cy, ^3J(PC) = *ca* 3 Hz], 34.46 d [C2 and C6 of Cy, ^2J(PC) = 9.2 Hz], 35.62 d [C1 of Cy, ^1J(PC) = 2.8 Hz], 120.14 s, 120.42 s, 120.68 s, 120.90 s, 122.10 s, 122.17 s, 122.21 s, 122.29 s [$C_4(CH_3)_4CEt$], 125.62 s and 125.76 s [$C_4(CH_3)_4CEt$], 126.33 s (Ph, other signals for Ph group are obscured by solvent), 204.11 d [S*C*(PHCy)N, ^1J(PC) = 51.1 Hz]. ^{31}P NMR (C_6D_6, ppm): −16.1 d [^1J(PH) = 226.9 Hz]. IR (KBr, cm^{-1}): ν = 3083 w, 3053 w, 2953 st, 2923 vst, 2847 vst, 2718 m, 2297 m (ν PH), 1590 m* (Ph), 1488 vst*, 1453 vst, 1375 st, 1364 st, 1265 m, 1198 m*, 1175 w, 1165 w, 1116 w, 1070 m, 1044 m, 1022 vst*, 998 st, 948 m, 921 w, 896 m, 834 m, 769 st* (Ph), 731 st* (Ph), 695 vst* (Ph), 643 w, 604 m, 528 m*, 508 w*, 490 m*, 465 m*, 447 w (peaks marked * are new compared with **1**). MS, *m/z* (%): 424 (73) [$M^+ - SC(PHCy)NPh = Cp^{\circ}_2ZrCl^+$], 135 (82) [PhNCS$^+$] 116 (12) [$PH_2Cy^+$], 77 (37) [$Ph^+$], and fragmentation products thereof. The molecular ion peak is not observed, signal of highest *m/z* is at 526 corresponding to [$M^+ - Cp^{\circ} = Cp^{\circ}ZrCl\{SC(PHCy)NPh\}^+$]. Found: C, 61.1; H, 7.6; N, 2.4; Cl, 5.1. Calc. for $C_{35}H_{51}ClNPSZr$: C, 62.2; H, 7.6; N, 2.1; Cl, 5.2%.

Data collection and structural refinement of **1** *and* **3**

Crystallographic details are given in Table 3. Data (Mo-K_α = 0.71073 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit-cell parameters (8090 for **1**, 8687 for **3**). Empirical absorption correction with SADABS [35]. The structures were solved by direct methods (SHELXTL PLUS [34]). Restrictions for **1**: Zr, Cl, P and C atoms anisotropic, H atoms located by difference maps and refined isotropically. Restrictions for **3**: Zr, Cl, P, N, S and C atoms anisotropic, H atoms (except P—H) located by difference maps and refined isotropically; the P—H proton was refined isotropically in a calculated position. One molecule of toluene (disordered, only C atoms located and refined isotropically) per unit cell is present in **3**. Anisotropic atomic parameters and full lists of bond lengths and angles have been deposited as

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**

Zr(1)—Cl	2.5231(10)	Zr(1)—N	2.361(4)
Zr(1)—S	2.769(1)	Zr(1)—Centre (Cp^1)	2.292, 2.286
Zr(1)···C(23)	2.999	Zr(1)—C(Cp^2)	2.563(4) to 2.620(4)
S—C(23)	1.718(5)	N—C(23)	1.296(6)
N—C(30)	1.443(6)	P—C(24)	1.839(5)
P—C(23)	1.842(4)	P—H	1.258(2)
C(1)—C(5)	1.418(7)	C(1)—C(2)	1.422(7)
C(1)—C(6)	1.514(7)	C(2)—C(3)	1.407(6)
C(2)—C(7)	1.493(6)	C(3)—C(4)	1.432(7)
C(3)—C(8)	1.505(6)	C(4)—C(5)	1.422(7)
C(4)—C(9)	1.503(7)	C(5)—C(10)	1.490(7)
C(10)—C(11)	1.550(7)	C(12)—C(13)	1.407(7)
C(12)—C(16)	1.413(6)	C(12)—C(17)	1.516(7)
C(13)—C(14)	1.431(6)	C(13)—C(18)	1.482(7)
C(14)—C(15)	1.433(6)	C(14)—C(19)	1.501(7)
C(15)—C(16)	1.403(6)	C(15)—C(20)	1.509(6)
C(16)—C(21)	1.498(7)	C(20)—C(22)	1.531(7)
C(24)—C(29)	1.517(8)	C(24)—C(25)	1.534(7)
C(25)—C(26)	1.525(8)	C(26)—C(27)	1.499(12)
C(27)—C(28)	1.523(11)	C(28)—C(29)	1.550(10)
C(30)—C(35)	1.382(8)	C(30)—C(31)	1.399(8)
C(31)—C(32)	1.389(8)	C(32)—C(33)	1.380(11)
C(33)—C(34)	1.326(12)	C(34)—C(35)	1.368(9)
N—Zr(1)—S	58.8(1)	N—Zr(1)—Cl	77.14(9)
C(23)—S—Zr(1)	80.18(14)	C(23)—N—C(30)	118.6(4)
C(23)—N—Zr(1)	106.5(3)	C(30)—N—Zr(1)	134.4(3)
C(24)—P—C(23)	105.4(2)	C(24)—P—H	102.1(2)
C(23)—P—H	99.5(2)	C(5)—C(1)—C(2)	108.3(4)
C(5)—C(1)—C(6)	125.5(5)	C(2)—C(1)—C(6)	125.4(5)
C(3)—C(2)—C(1)	108.3(4)	C(3)—C(2)—C(7)	126.0(4)
C(1)—C(2)—C(7)	125.1(4)	C(2)—C(3)—C(4)	107.7(4)
C(2)—C(3)—C(8)	124.9(4)	C(4)—C(3)—C(8)	126.3(4)
C(5)—C(4)—C(3)	108.1(4)	C(5)—C(4)—C(9)	124.9(5)
C(3)—C(4)—C(9)	126.1(5)	C(1)—C(5)—C(4)	107.5(4)
C(1)—C(5)—C(10)	123.9(4)	C(4)—C(5)—C(10)	125.2(4)
C(5)—C(10)—C(11)	108.5(4)	C(13)—C(12)—C(16)	108.9(4)
C(13)—C(12)—C(17)	122.8(5)	C(16)—C(12)—C(17)	127.3(5)
C(12)—C(13)—C(14)	107.4(4)	C(12)—C(13)—C(18)	124.4(5)
C(14)—C(13)—C(18)	125.8(5)	C(13)—C(14)—C(15)	107.5(4)
C(13)—C(14)—C(19)	125.8(4)	C(15)—C(14)—C(19)	125.9(4)
C(16)—C(15)—C(14)	107.8(4)	C(16)—C(15)—C(20)	126.3(4)
C(14)—C(15)—C(20)	125.3(4)	C(15)—C(16)—C(12)	108.3(4)
C(15)—C(16)—C(21)	124.9(4)	C(12)—C(16)—C(21)	125.8(4)
C(15)—C(20)—C(22)	111.8(4)	N—C(23)—S	114.4(3)
N—C(23)—P	123.8(3)	S—C(23)—P	121.2(3)
C(29)—C(24)—C(25)	111.0(4)	C(29)—C(24)—P	115.6(4)
C(25)—C(24)—P	108.0(4)	C(26)—C(25)—C(24)	111.7(5)
C(27)—C(26)—C(25)	112.7(7)	C(26)—C(27)—C(28)	110.2(7)
C(27)—C(28)—C(29)	111.5(7)	C(24)—C(29)—C(28)	110.1(6)
C(35)—C(30)—C(31)	119.1(5)	C(35)—C(30)—N	121.5(5)
C(31)—C(30)—N	119.4(4)	C(32)—C(31)—C(30)	118.8(6)
C(33)—C(32)—C(31)	121.0(7)	C(34)—C(33)—C(32)	119.6(6)
C(33)—C(34)—C(35)	120.6(7)	C(34)—C(35)—C(30)	121.0(7)

Table 3. Crystal data and structure refinement for **1** and **3**

	1	**3** · 1/2toluene
Formula	$C_{28}H_{46}ClPZr$	$C_{35}H_{51}ClNPSZr \cdot 1/2C_7H_8$
Molecular weight	540.29	675.47 (+46.04)
Temperature (K)	243(2)	213(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Cell constants:		
a (Å)	9.4411(5)	10.2399(5)
b (Å)	10.7758(6)	11.2407(5)
c (Å)	14.4387(8)	16.5619(8)
α (°)	106.165(1)	103.246(1)
β (°)	99.972(1)	96.222(1)
γ (°)	91.233(1)	95.786(1)
V (Å^3)	1385.8(1)	1829.1(2)
Z	2	2
d_{calc} (g cm^{-3})	1.295	1.226
2Θ range (°)	3–56	4–52
h (min., max.)	−12/9	−12/7
k (min., max.)	−14/10	−12/14
l (min., max.)	−15/18	−19/19
Total reflections	8090	8687
Independent reflections	5791 (R_{int} = 0.0501)	6439 (R_{int} = 0.0483)
F(000)	572	748
Parameters	465	616
Absorption coefficient (μ mm^{-1})	0.564	0.501
Largest difference peak/hole (e Å^{-3})	0.818/−0.745	1.425/−0.878
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0443	R_1 = 0.0482
	wR_2 = 0.1600	wR_2 = 0.1559
R indices (all data)	R_1 = 0.0508	R_1 = 0.0615
	wR_2 = 0.1736	wR_2 = 0.1941
Goodness-of-fit	1.092	1.082

supplementary material with the Cambridge Crystallographic Data Centre.

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