Synthesis and X-ray structures of the five-coordinate zirconocene complexes PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$ZrCl$_2$, [PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$ZrCl(H$_2$O)]Cl and PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Zr(NCS)$_2$ [1]

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Abstract

The five-coordinate zirconocene dichloride PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$ZrCl$_2$ (**3**), containing a tethered bis(cyclopentadienyl)-phosphine ligand, was prepared by treating a tetrahydrofuran solution of ZrCl$_4$(thf)$_2$ with Li$_2$[PhP(CH$_2$CH$_2$C$_5$H$_4$)$_2$]. An X-ray crystal structure analysis confirmed the phosphorus atom to be coordinated to the zirconium metal center. Dissolution of **3** in wet methanol followed by evaporation of the solvent yielded the crystallographically characterized cationic chloroaqua complex [PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$ZrCl(H$_2$O)]$^+$ as the chloride salt (**4**). Treatment of an aqueous solution of **3** with excess thiocyanate gave a good yield of the bis(isothiocyanato) complex PhP(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Zr(NCS)$_2$ (**7**), the structure of which was confirmed by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Zirconium; Metallocenes; Crystal structure; Phosphine; Thiocyanate

1. Introduction

There are now a large number of complexes containing functionalized cyclopentadienyl ligands, of which the bis(cyclopentadienyl) ligands can be considered a sub-class [1]. The number of functionalized bis(cyclopentadienyl) ligands capable of a tridentate binding mode, however, is still quite small [2,3]. Prior to our work, the only examples of bis(cyclopentadienyl)-phosphine ligands were RP(C$_5$H$_4^-$)$_2$ (R = Cl, alkyl, aryl) [3,4] and C$_6$H$_{11}$P(CHMe-2-PPh$_2$C$_5$H$_3^-$)$_2$ [5], although the latter is only known for coordination of the cyclopentadienyl groups to Fe. To date, the only zirconocene complexes containing a functionalized bis(cyclopentadienyl) ligand bound in a tridentate fashion are MeN(CH$_2$CH$_2$C$_5$H$_4$)ZrCl$_2$ [6], C$_5$H$_3$N-2,6-(CH$_2$C$_5$H$_4$)$_2$ZrCl$_2$ (**1**) [6] and the chloroaqua cationic complex [C$_5$H$_3$N-2,6-(CH$_2$C$_5$H$_4$)$_2$ZrCl(H$_2$O)]$^+$ (**2**)

[7], of which the latter has been structurally characterized.
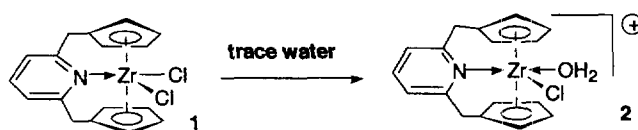
We recently described the preparation of bis(2-cyclopentadienylethyl)phenylphosphine (bcepH$_2$) in which the phosphine contains a phenyl substituent and the P atom is tethered to two cyclopentadienyl rings via ethylene bridges. Although the ferrocene complex (bcep)Fe, derived from this compound, does not have the P atom coordinated to the Fe center, the P atom can coordinate to a second metal center as in the complex *trans*-PdCl$_2$\{PPh(CH$_2$CH$_2$-η^5-C$_5$H$_4$)$_2$Fe\}$_2$ [8]. To further the chemistry of this ligand, we sought to prepare complexes in which the ligand acts as a tridentate ligand with both cyclopentadienyl rings as well as the P atom coordinated to the one metal center. In this paper we

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[1] Dedicated to Professor Dr. Gottfried Huttner on the occasion of his 60th birthday.

report the X-ray structures of three five-coordinate zirconocene complexes containing the ligand $PPh(CH_2CH_2C_5H_4^-)_2$ ($bcep^{2-}$) bound in a tridentate fashion.

2. Results and discussion

2.1. Synthesis and spectroscopy

The novel zirconocene complex $(bcep)ZrCl_2$ (3) was prepared by treatment of a tetrahydrofuran solution of $ZrCl_4(thf)_2$ with a solution of $Li_2(bcep)$ in tetrahydrofuran. After filtration to remove LiCl, the solvent was removed in vacuo to give a white solid from which the product was extracted with hot tetrahydrofuran. Solubility in solvents with which 3 does not react, even tetrahydrofuran, is very limited. Colorless needles of complex 3 were obtained in 22% yield.
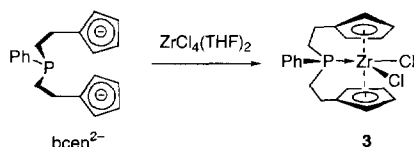
The ^1H- and ^{13}C-NMR spectra of 3 in $CDCl_3$ are consistent with equivalent cyclopentadienyl rings and the presence of a mirror plane through the Ph group and the P, Zr, and Cl atoms; there is one ABCD pattern for the cyclopentadienyl ring protons (δ 6.78, 6.25, 6.11, 5.67) and four resonances for the secondary cyclopentadienyl ring carbons (δ 129.08, 112.5, 108.49, 103.01). The phosphorus chemical shift in $CDCl_3$ (17.5 ppm relative to 85% H_3PO_4) is 39.9 ppm downfield of that found for the free ligand [8]. This is consistent with the coordination of the P atom to the Zr center.

Dissolution of 3 in wet methanol followed by evaporation of the solvent under a stream of dinitrogen gave colorless crystals of $[(bcep)ZrCl(H_2O)]Cl$ (4). The isolation of this compound from methanol was somewhat surprising; electrospray mass spectroscopy (ES-MS) of 3 dissolved in methanol shows only $[(bcep)Zr(OMe)]^+$ (5) ($m/e = 413$) at low cone voltages (20 V). At higher cone voltages (60 V), loss of MeOH occurs to give a compound which can reasonably be formulated as [1,2-

$C_6H_4P(CH_2CH_2C_5H_4)_2Zr]^+$ (6) ($m/e = 381$) with a cyclometallated phenyl group.
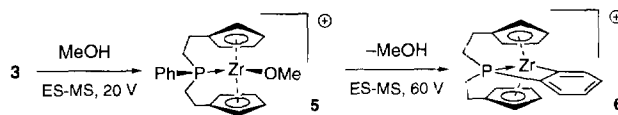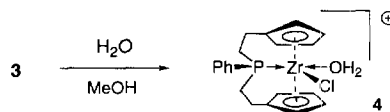
Attempts to observe the cation of 4 in aqueous solution have not given definitive results. Characterization of aqueous solutions of 3 by ES-MS and ^{31}P NMR spectroscopy indicates the presence of three major species: $[(bcep)Zr(H_2O)_2]^{2+}$, $[\{(bcep)Zr(\mu\text{-}OH)\}_2]^{2+}$, and $[(bcep)_2Zr_2(\mu\text{-}OH)(\mu\text{-}O)]^+$ [9]. Addition of HCl(aq) (10 equiv.) to this mixture gives a ^{31}P NMR spectrum after 30 min containing only $[(bcep)Zr(H_2O)_2]^{2+}$. We now report that under ES-MS conditions, a mixture of products is observed, even at low cone voltages (17 V): m/e for the ^{90}Zr isotopomer (relative intensity, assignment): 399 (65, $[(bcep)Zr(H_2O)_2]^{2+} - H_3O^+$), 415 (25, $[(bcep)Zr(OH)O]^+$), 417 (40, $[(bcep)ZrCl]^+$), 433 (100, $[(bcep)ZrClO]^+$). At higher cone voltages, or several minutes after the addition of acid, the amount of $[(bcep)ZrCl]^+$ increases at the expense of $[(bcep)ZrClO]^+$. The compounds with m/e 415 and 433 may be the phosphine oxide adducts of $[(bcep)ZrOH]^+$ and $[(bcep)ZrCl]^+$ respectively. Simulation of the isotopic pattern for $[(bcep)ZrClO]^+$ (Fig. 1) indicates that there is no intensity attributable to a compound of the formula $[(bcep)ZrCl(H_2O)]^+$.
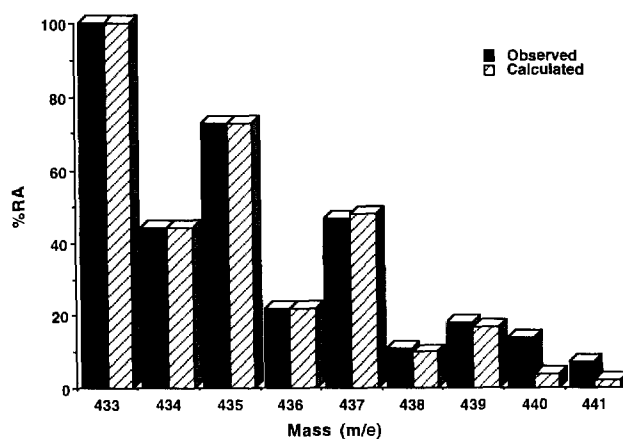

Fig. 1. Calculated and observed isotopic pattern for $[(bcep)ZrClO]^+$.

The bis(isothiocyanato) complex (bcep)Zr(NCS)$_2$ (7) was prepared by treatment of an aqueous solution of 3 with a small excess of thiocyanate and overnight extraction with a chloroform–acetonitrile mixed solvent. As with 3, a single ABCD pattern for the cyclopentadienyl ring protons in the ^{1}H NMR spectrum (δ 6.39, 6.24, 6.11, 6.01) and four resonances for the secondary cyclopentadienyl carbons in the ^{13}C NMR spectrum (δ 125.01, 110.8, 110.0, 102.7) indicates equivalent cyclopentadienyl rings and the presence of a mirror plane through the phenyl group, the P and Zr atoms, and the isothiocyanato ligands. A phosphorus chemical shift of 32.1 ppm is also consistent with coordination of the P atom to the metal center. The solution infrared spectrum in acetonitrile confirms that there are two isothiocyanato ligands. There are two ν_{CN} at 2075(s) and 2046(m) cm^{-1}

Table 1
Selected bond lengths (Å) and angles (deg) for 3, 4, and 7 [a]

(bcep)ZrCl$_2$ (3)		[(bcep)ZrCl(H$_2$O)]Cl (4)		(bcep)Zr(NCS)$_2$ (7)	
CNT(2)–Zr	2.252(3)	CNT(2)–Zr	2.222(2)	CNT(2)–Zr	2.220(1)
CNT(3)–Zr	2.234(3)	CNT(3)–Zr	2.220(2)	CNT(3)–Zr	2.243(1)
Zr–P	2.7810(8)	Zr–P	2.794(2)	Zr–P	2.7499(7)
Zr–Cl2	2.6219(8)	Zr–Cl1	2.488(2)	Zr–N1	2.248(2)
Zr–Cl1	2.5512(8)	Zr–O	2.282(5)	Zr–N2	2.237(2)
Zr–C23	2.616(3)	Zr–C23	2.562(7)	Zr–C23	2.580(3)
Zr–C24	2.596(3)	Zr–C24	2.541(7)	Zr–C24	2.544(2)
Zr–C25	2.541(3)	Zr–C25	2.500(7)	Zr–C25	2.510(3)
Zr–C26	2.464(3)	Zr–C26	2.472(7)	Zr–C26	2.464(3)
Zr–C27	2.527(3)	Zr–C27	2.530(6)	Zr–C27	2.514(3)
Zr–C33	2.557(3)	Zr–C33	2.551(6)	Zr–C33	2.590(2)
Zr–C34	2.541(3)	Zr–C34	2.554(7)	Zr–C34	2.577(2)
Zr–C35	2.542(4)	Zr–C35	2.527(8)	Zr–C35	2.530(2)
Zr–C36	2.517(3)	Zr–C36	2.459(7)	Zr–C36	2.480(2)
Zr–C37	2.499(3)	Zr–C37	2.476(7)	Zr–C37	2.532(2)
P–C11	1.829(3)	P–C11	1.818(7)	P–C11	1.823(3)
P–C21	1.829(3)	P–C21	1.816(7)	P–C21	1.821(3)
P–C31	1.850(4)	P–C31	1.830(7)	P–C31	1.826(2)
C21–C22	1.522(5)	C21–C22	1.515(9)	C21–C22	1.530(4)
C22–C23	1.512(5)	C22–C23	1.515(10)	C22–C23	1.505(4)
C31–C32	1.506(6)	C31–C32	1.519(9)	C31–C32	1.531(4)
C32–C33	1.493(5)	C32–C33	1.507(9)	C32–C33	1.503(3)
				N1–C1	1.166(3)
				S1–C1	1.613(3)
				N2–C2	1.164(3)
				S2–C2	1.619(3)
CNT(2)–Zr–CNT(3)	127.2(1)	CNT(2)–Zr–CNT(3)	128.0(2)	CNT(2)–Zr–CNT(3)	129.2(1)
CNT(2)–Zr–P	92.9(1)	CNT(2)–Zr–P	92.4(2)	CNT(2)–Zr–P	94.1(1)
CNT(2)–Zr–Cl2	97.5(1)	CNT(2)–Zr–O	96.1(2)	CNT(2)–Zr–N1	148.5(1)
CNT(2)–Zr–Cl1	122.9(1)	CNT(2)–Zr–Cl1	120.1(2)	CNT(2)–Zr–N2	109.3(1)
CNT(3)–Zr–P	92.4(1)	CNT(3)–Zr–P	95.3(2)	CNT(3)–Zr–P	94.4(1)
CNT(3)–Zr–Cl2	100.0(1)	CNT(3)–Zr–O	99.6(2)	CNT(3)–Zr–N1	98.3(1)
CNT(3)–Zr–Cl1	109.2(1)	CNT(3)–Zr–Cl1	111.9(2)	CNT(3)–Zr–N2	121.1(1)
Cl2–Zr–P	154.04(3)	O–Zr–P	152.80(12)	N1–Zr–P	148.55(8)
Cl1–Zr–Cl2	78.90(3)	Cl1–Zr–O	75.58(14)	N2–Zr–N1	75.66(8)
Cl1–Zr–P	75.49(3)	Cl1–Zr–P	77.61(10)	N2–Zr–P	71.14(8)
C11–P–Zr	126.19(11)	C11–P–Zr	122.5(2)	C11–P–Zr	124.45(8)
C21–P–Zr	105.35(12)	C21–P–Zr	110.9(2)	C21–P–Zr	109.36(9)
C31–P–Zr	109.61(12)	C31–P–Zr	106.2(2)	C31–P–Zr	104.20(8)
C21–P–C11	101.0(2)	C21–P–C11	105.0(3)	C21–P–C11	107.35(12)
C21–P–C31	104.4(2)	C21–P–C31	104.7(3)	C21–P–C31	105.82(12)
C11–P–C31	107.8(2)	C11–P–C31	106.1(3)	C11–P–C31	104.12(11)
C22–C21–P	105.6(2)	C22–C21–P	106.9(5)	C22–C21–P	106.7(2)
C23–C22–C21	112.8(3)	C23–C22–C21	111.4(6)	C23–C22–C21	112.3(2)
C32–C31–P	110.4(2)	C32–C31–P	106.6(5)	C32–C31–P	106.8(2)
C33–C32–C31	113.0(3)	C33–C32–C31	111.6(6)	C33–C32–C31	113.3(2)
				C1–N1–Zr	173.2(2)
				N1–C1–S1	179.4(2)
				C2–N2–Zr	166.8(2)
				N2–C2–S2	179.1(2)

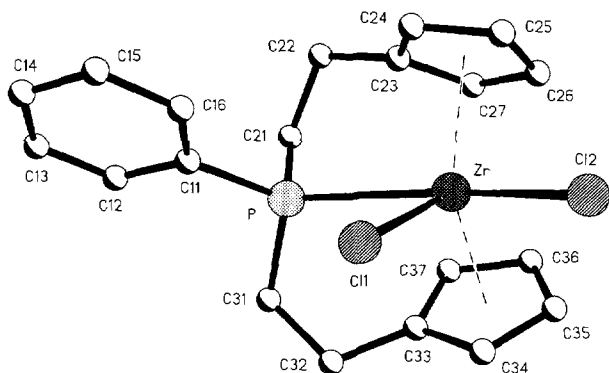[a] CNT(2) = centroid of C23 to C27; CNT(3) = centroid of C33 to C37.

Fig. 2. Plot showing the solid state structure of complex **3** and the atomic labeling scheme.

and one weak broad ν_{CS} at 822 cm^{-1}. These are consistent with N-bonded thiocyanato ligands. In $Cp_2Zr(NCS)_2$, the ν_{CN} stretches occur at lower energy, 2041 and 2003 cm^{-1} [10]. Using the Cotton–Kraihanzel method [11], the angle between the isothiocyanato ligands in **7** is calculated to be 75°. This is in excellent agreement with the N–Zr–N angle, found by an X-ray crystallographic analysis (see below) to be 75.66(8)°, and further confirms coordination of the P atom to the metal center in solution. For $Cp_2Zr(NCS)_2$, the angle between the isothiocyanato ligands in solution is calculated, from the relative intensities of the ν_{CN} infrared bands above, to be 108°. This is somewhat larger than that expected for a d^0 Cp_2ML_2 complex (94–97°) [12].

$$3 \xrightarrow[H_2O]{2SCN^-} Ph\!-\!P\!-\!Zr\!-\!NCS \quad \substack{NCS} \quad 7$$
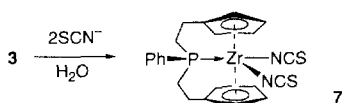
Addition of KSCN(aq) (ca. 0.5 equiv.) to an aqueous solution of **3** gives an ES-MS spectrum containing peaks corresponding to the mono(isothiocyanato) complex [(bcep)Zr(NCS)]$^+$ (m/e 440) and the bis(isothiocyanato) complex **7** which is observed as the potassium ion adduct [(bcep)Zr(NCS)$_2$K]$^+$ (m/e 537) in

which the potassium ion is presumably coordinated by the isothiocyanato sulfur atoms. Given the five-coordinate geometry of **4**, it is reasonable that the mono(isothiocyanato) complex may contain a coordinated water molecule in solution; however, this would be readily lost under ES-MS conditions. Unlike the successful preparation and isolation of the monofluoro complex [(bcep)ZrF][BPh$_4$] [9], attempts to isolate the monoisothiocyanto complex, by addition of 1 equiv. of KSCN(aq) to an aqueous solution of **3**, have yielded only the bis(isothiocyanato) complex **7**.

2.2. Structural analyses

A single crystal of **3** was obtained by slowly cooling a tetrahydrofuran solution of **3** to $-35\,^\circ$C. An X-ray crystallographic analysis shows the Zr center to be approximately trigonal bipyramidal with two cyclopentadienyl rings and one chloro ligand occupying the equatorial sites, while the axial sites are occupied by a P atom and another chloro ligand. The tetrahedral P atom has a phenyl substituent and is tethered to each cyclopentadienyl ring by an ethylene bridge. The ethylene backbones have differing conformations which result in staggered cyclopentadienyl rings and a phenyl group twisted out of the ZrPCl$_2$ plane (Cl1–Zr–P–C11 = 47.9(3)°) to lie between the central chloro ligand and cyclopentadienyl ring 2 (C23–C27). Fig. 2 shows a plot of **3** with the atomic labeling scheme and Table 1 gives selected bond distances and angles.

The most remarkable features of the solid state structure are the large trans-P–Zr–Cl2 angle and the long Zr–Cl distances. The trans-P–Zr–Cl2 angle of 154.04(3)° is larger than that found in any other Cp_2ZrL_3 complex. For example, the corresponding angles in $[Cp_2Zr(H_2O)_3]^{2+}$ [13] and $[Cp_2Zr(SO_3C_7H_7)(H_2O)_2]^+$ [14] are 145.2° and 148.0° respectively, whereas in the complex $Cp_2ZrCl(S_2CNEt_2)$, which contains a chelating dithiocarbamate ligand, the trans angle is 137.5(1)° [15]. This large trans angle in **3** is attributed to steric factors; no other Cp_2ZrL_3 complex has been reported in which the three donor atoms come from different lig-
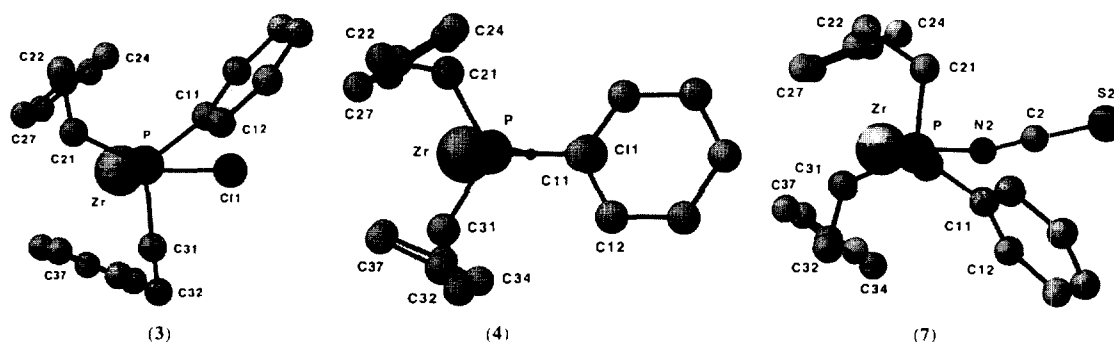

Fig. 3. Plots showing the adopted conformers for the bcep ligand in, from left to right, the complexes **3**, **4**, and **7**.

ands and are from the second period. The Cl–Zr–Cl angle of 78.90(3)° is much smaller than that found in other d^0 metallocene dichlorides in which the angles are generally in the range 94–97° [16].

The outer Zr–Cl2 distance of 2.6219(8) Å is somewhat longer than the central Zr–Cl1 distance of 2.5512(8) Å. A similar difference was observed in the structure of $[Cp_2Zr(H_2O)_3]^{2+}$ where the corresponding distances were 2.25 Å (average) and 2.195(7) Å respectively [13]. This difference can be attributed to a combination of greater s-character in the equatorial bonds and a lower bond order for the axial bonds. These Zr–Cl distances are significantly longer than those found in other zirconocene dichlorides in which the distances lie in the range 2.43–2.46 Å [17] and, to date, only $Cp_2ZrCl(\mu\text{-}CH_2)_2P(NEt_2)_2$ has a longer Zr^{IV}–Cl bond distance (2.643(1) Å) [18]. Indeed, these Zr–Cl distances are comparable to those found in chloro-bridged complexes such as $Cp_2ZrCl(ClAlCl_3)$ (Zr–ClAlCl$_3$ = 2.605(2) Å) [19]. The Zr–P distance of 2.7810(8) Å, in contrast, is not exceptional. It falls within a wide range of Zr–P distances (2.6–2.9 Å) that vary due to differences in ligand environment, phosphine cone angle, Lewis π acidity, and chelate ring-strain effects [20].

The view down the P–Cl2 vector (Fig. 3) illustrates the conformation adopted by the chelating ligand. When the P atom of the bcep ligand is chelated to a metal center, only three torsion angles are necessary to define the ligand conformation. Two of these correspond to rotation of the cyclopentadienyl rings, measured by the Cl1–Zr–CNT(x)–Cx2 torsion angles α_x where CNT(x) = centroid of atoms Cx3–Cx7 and x = 2 or 3, and the other corresponds to rotation about the Zr–P bond, measured by the Cl1–Zr–P–Cl1 dihedral angle β. If the two ethylene backbones have identical conformations, β will be zero and $|\alpha_2|$ will equal $|\alpha_3|$. In complex 3, these torsion angles are 41.9°, −83.1° and 47.9° respectively. Thus, the phenyl group lies between the ZrPCl$_2$ plane and cyclopentadienyl ring 2 (C23–C27) and the cyclopentadienyl rings are staggered; $|\alpha_2|$ − $|\alpha_3|$ = 35.2°. Also, the phenyl ring is oriented about the P–C11 axis such that H16 lies between the chloro ligand Cl1 and ring 2. The disposition of the phenyl group has a significant steric effect on ring 2 which is pushed away from the ZrPCl$_2$ plane (Cl1–Zr–CNT(2) = 122.9(1)° whereas Cl1–Zr–CNT(3) = 109.2(1)°) and is noticeably tilted (Zr–CNT(2) = 2.252 Å vs. 2.247 Å for Zr–(ring 2 plane)) compared to ring 3 (Zr–CNT(3) = 2.234 Å vs. 2.234 Å for Zr–(ring 3 plane)). The Zr–C distances also vary by 0.152 Å for ring 2 but by only 0.058 Å for ring 3. Remarkably, the CNT(2)–Zr–CNT(3) angle of 127.2(1)° is similar to that found in Cp$_2$ZrCl$_2$ (126°) [16].

A single crystal of $[(bcep)ZrCl(H_2O)]Cl$ (4) was obtained by slow evaporation of a wet methanol solution of 3. An X-ray crystal structure analysis shows the
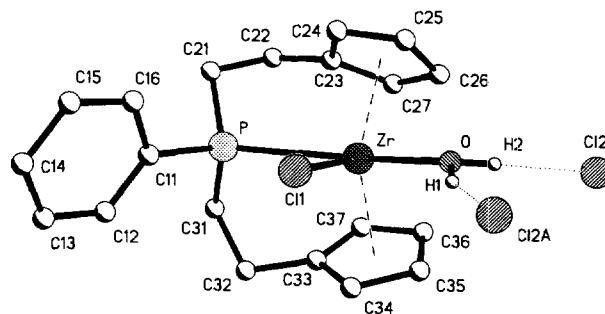

Fig. 4. Plot showing the solid state structure of complex 4, the symmetry-related chloride anion Cl2A, and the atomic labeling scheme.

cation of 4 to have a similar structure to that of 3; the Zr atom is approximately trigonal bipyramidal with two cyclopentadienyl rings and a chloro ligand occupying the equatorial sites while the axial sites are occupied by a water O atom, rather than another chloro ligand, in addition to the phosphine P atom. The H atoms of the water molecule were located from the difference Fourier map but were refined with a fixed O–H distance of 0.89 Å. The O atom is approximately trigonal planar (the sum of angles is 354.1°) and is hydrogen-bonded to two symmetry-related chloride counterions (O–Cl2 = 3.075 Å and O–Cl2A = 3.078 Å) thus forming a crystal lattice of the hydrogen-bonded dimer unit $[(bcep)ZrCl(OH_2Cl)]_2$. Hydrogen bonding was also observed in the closely related chloroaqua complex 2 which has $[ZrCl_6]^{2-}$ counterions [7]. In 2, O–Cl = 3.053(4) Å and 3.026(4) Å. Fig. 4 shows a plot of 4 with the additional symmetry-related chloride anion Cl2A. Table 1 gives selected atomic distances and bond angles.

As with the solid state structure of 3, the most remarkable features of the cation of 4 are the large trans-P–Zr–O angle and long Zr–O and Zr–Cl distances. The trans-P–Zr–O angle of 152.80(12)° is only exceeded by the P–Zr–Cl angle of 154.04(3)° in 3. In 2, the N–Zr–O angle is 148.66°.

The equatorial Zr–Cl distance of 2.488(2) Å is markedly shorter than the corresponding distances in 3 (2.5512(8) Å) and 2 (2.558(2) Å), whereas the axial Zr–O distance of 2.282(5) Å is similar to that in 2 (2.265(4) Å) and the axial Zr–P distance of 2.794(2) Å is similar to that in 3 (2.7810(8) Å). Other five-coordinate cationic zirconocene complexes with axial aqua ligands also have similar Zr–O distances: 2.276(5) Å and 2.242(5) Å in $[Cp_2Zr(C_7H_7SO_3)(H_2O)_2]^+$ [14] and 2.25 Å in $[Cp_2Zr(H_2O)_3]^{2+}$ [13].

The view down the P–O vector of 4 (Fig. 3) illustrates the conformer adopted by the bcep ligand. The conformer torsion angles are β = −2.6°, α_2 = −95.9° and α_3 = 69.8°. Thus, as with 3, the cyclopentadienyl rings are staggered: $|\alpha_2|$ − $|\alpha_3|$ = 26.1°. Although C11

of the phenyl group lies in the ZrPClO plane, the phenyl ring is oriented about the P–C11 axis such that H16 lies similarly between the chloro ligand and cyclopentadienyl ring 2. As with **3**, ring 2 is pushed away from the ZrPClO plane: Cl1–Zr–CNT(2) = 120.0° whereas Cl1–Zr–CNT(3) = 111.9°. Other metrical parameters for the two rings are quite similar, especially when compared to **3**: both rings are tilted only slightly (Zr–CNT(2) = 2.220 Å vs. 2.219 Å for Zr–(ring 2 plane) and Zr–CNT(3) = 2.216 Å vs. 2.213 Å for Zr–(ring 3 plane) (cf. 2.252/2.247 Å and 2.234/2.234 Å respectively for **3**) and the Zr–C distances vary by 0.090 Å for ring 2 and 0.095 Å for ring 3 (cf. 0.152 Å and 0.058 Å respectively for **3**). The smaller differences between the two rings in **4**, compared to the large differences in **3**, can be attributed to a smaller influence of the phenyl ring in **4**; the Zr–H16 distance in **4** is 4.29 Å compared to 3.79 Å in **3**. The CNT(2)–Zr–CNT(3) angle of 128.0(2)°, however, is similar to that found in both **3** (127.2°) and Cp_2ZrCl_2 (126°) [16].

A single crystal of **7** was obtained by slow evaporation of a chloroform solution and an X-ray crystallographic analysis carried out. As with **3** and **4**, the Zr atom is approximately trigonal bipyramidal. The equatorial sites are taken up by the cyclopentadienyl rings and one of the isothiocyanato ligands while the axial sites are taken up by the P atom and the other isothiocyanato ligand. Fig. 5 shows a thermal ellipsoid plot of **10** with the atomic labeling scheme, and Table 1 gives selected atomic distances and bond angles.

The trans-N1–Zr–P angle of 148.55(8)° is smaller than the corresponding angles in **3** and **4** but is very similar to that in **2** (148.66°). The variation in this trans angle correlates well with the number of second-row donor atoms. Thus, for **7** (PN_2) and **2** (NClO), with one second-row donor atom each, the angle is less than that in **4** (PClO) with two, which is less than that in **3** (PCl_2) with three. As expected, the axial Zr–N distance, 2.248(2) Å, is longer than the equatorial distance, 2.237(2) Å. These distances are slightly longer than that found in (bipy)$_2$Zr(NCS)$_4$ of 2.182(2) Å [21]. The difference between the axial and equatorial distances of
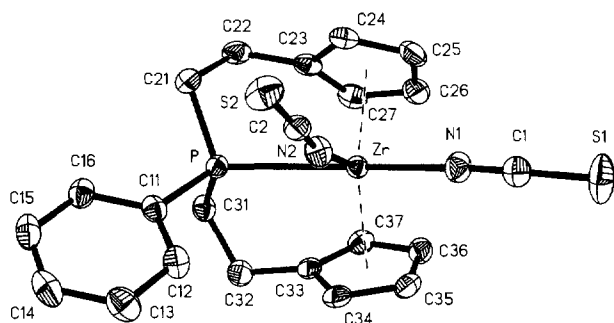
0.011 Å is not as great as in the dichloro complex **3** (0.071 Å) and the trisaqua complex $[Cp_2Zr(H_2O)_3]^{2+}$ (0.055 Å). Comparison with the Zr–O distances in this latter complex (2.25 Å for the axial ligands and 2.195 Å for the equatorial ligand) suggests that it is the axial Zr–N distance that is shorter than expected. This may be due to an increased π-donor contribution because of the trans π-acceptor phosphine ligand. The Zr–P distance of 2.7499(7) Å is also noticeably shorter than those found in **3** (2.7810(8) Å) and **4** (2.794(2) Å).

The view down the P–N1 vector (Fig. 3) illustrates the conformation adopted by the chelating ligand. In this complex, β = – 39.7°, α_2 = – 75.9° and α_3 = 84.0°. **7** has a similar $|\beta|$ angle to **3** (41.9°), with the phenyl ring lying between the ZrPN$_2$ plane and, in this case, ring 3. The $|\alpha|$ angles in **7** are quite similar and so give an eclipsed conformation of the cyclopentadienyl rings: $|\alpha_3| - |\alpha_2| = 8.1°$. Both **3** and **4**, in contrast, have staggered cyclopentadienyl rings. Like **3** and **4**, the phenyl group is twisted about the P–C11 axis such that H12 lies between N2 and ring 3 and, similarly, ring 3 is pushed away from the ZrPN$_2$ plane (N2–Zr–CNT(3) = 121.1° whereas N2–Zr–CNT(2) = 109.3°). As with **4**, most of the metrical parameters for the two rings are quite similar, especially when compared to **3** in which the two rings are quite different. The rings are tilted only slightly (Zr–CNT(2) = 2.220 Å vs. 2.218 Å for Zr–(ring 2 plane) and Zr–CNT(3) = 2.243 Å vs. 2.240 Å for Zr–(ring 3 plane)) and the Zr–C distances vary by 0.116 Å for ring 2 and 0.110 Å for ring 3. The major difference is the slightly larger Zr–CNT(3) distance compared to Zr–CNT(2). As with **4**, the smaller differences between the two rings in **7** compared to the differences in the rings of **3** can be attributed to a smaller influence of the phenyl ring; although the Zr–H12 distance at 3.68 Å is shorter than the corresponding distances in both **3** and **4** (3.79 Å and 4.29 Å respectively), steric strain is relieved by the smaller N atom which has a van der Waals' radius approximately 0.3 Å smaller than a Cl atom. Another consequence of the smaller N atom is that the CNT(2)–Zr–CNT(3) angle of 129.2(1)° is larger than those found in **3** (127.2°), **4** (128.0(2)°), and Cp_2ZrCl_2 (126°) [16]. One other steric effect of the phenyl group is that the equatorial isothiocyanato ligand is bent away from ring 3: the Zr–N2–C2 angle is 166.8° compared to 173.2° for Zr–N1–C1 and S2 lies 0.60 Å out of the plane defined by the Zr, P, N1, and N2 atoms towards ring 2, whereas S1 lies 0.30 Å out of this plane towards ring 3.

3. Conclusions

We have described the synthesis and structures of three novel zirconocene compounds that display a new

Fig. 5. Plot showing the solid state structure of complex **7** and the atomic labeling scheme.

tripodal bonding mode for the bis(cyclopentadienyl)phosphine ligand bcep. The variety of conformers observed in the three structures described here, along with that of the palladium–ferrocene complex *trans*-PdCl$_2${(bcep)Fe}$_2$ described in an earlier paper [8], illustrates the great flexibility of this ligand. Molecular modeling studies are in progress.

4. Experimental

The synthesis of **3** was carried out under an inert atmosphere by use of standard Schlenk line techniques. Tetrahydrofuran was dried and distilled prior to use from Na–benzophenone; Li$_2$[bcep] [8] was prepared by the published procedure. All other reagents were purchased from Aldrich Chemical Company. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR data were collected on a Varian XL-300 spectrometer operating at 300 MHz, 75 MHz and 121 MHz respectively. Unless otherwise stated, spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^{1}H- and ^{13}C{^{1}H}-NMR. ^{31}P{^{1}H} NMR chemical shifts are reported relative to external 85% H$_3$PO$_4$, positive shifts representing deshielding. ES-MS spectra were collected on a VG Platform II mass spectrometer and m/e are reported for the ^{90}Zr isotopomer. Infrared spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analyses were done by Campbell Microanalysis Services, Otago University, Dunedin.

4.1. Preparation of PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$ZrCl$_2$ (3)

Li$_2$[bcep] (9.2 g, 30 mmol) in thf (150 ml) was added to a solution of ZrCl$_4$(thf)$_2$ (11.5 g, 30.5 mmol) in thf (250 ml) at −78 °C. The solution was allowed to warm to ambient temperature whereupon it was stirred for 3 days to give a red solution. Subsequent heating to reflux for 6 h gave a pale yellow solution with a fine precipitate of LiCl which was removed by filtration through Celite. The volume was reduced to 80 ml and the solution cooled to −35 °C to give a colorless precipitate. This solid was then extracted with refluxing thf (800 ml), the volume reduced to one-half, and cooled to −35 °C to yield crystallographic-quality crystals of **3** (3.02 g, 22% yield). M.p. 255 °C dec.; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 7.81 (m, 2H, Ph), 7.46 (m, 3H, Ph), 6.78 (m, 2H, Cp), 6.25 (m, 2H, Cp), 6.11 (m, 2H, Cp), 5.67 (m, 2H, Cp), 3.0 (m, 2H, CH$_2$), 2.7 (m, 4H, CH$_2$), 2.6 (m, 2H, CH$_2$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, TMS): δ 132.80 (d, ^3J(P,C) = 7.3 Hz, *m*-Ph), 130,61 (d, ^4J(P,C) = 3.1 Hz, *p*-Ph), 129.08 (s, Cp), 128.73 (d, ^2J(P,C) = 8.3 Hz, *o*-Ph), 112.50 (s, Cp), 108.49 (s, Cp), 103.01 (s, Cp), 31.87 (d, ^1J(P,C) = 18.8 Hz, PCH$_2$), 24.09 (d, ^2J(P,C) = 12.0 Hz, PCH$_2$CH$_2$), (*i*-Ph and *i*-Cp not observed); ^{31}P{^{1}H}

NMR (121 MHz, CDCl$_3$, 85% H$_3$PO$_4$): δ 17.50 (s); Anal. Calcd. for C$_{20}$H$_{21}$Cl$_2$PZr: C, 52.85; H, 4.67. Found: C, 52.41; H, 4.57.

4.2. Addition of HCl(aq) to aqueous solutions of 3

Addition of dilute HCl(aq) to a CH$_3$CN–H$_2$O solution of **3** (ca. 10^{-4} M) gives the following ES-MS spectra: 17 V cone voltage, m/e (rel. int., assignment): 399 (64, [(bcep)ZrOH]$^+$), 415 (27, [(bcep)Zr(O)OH]$^+$), 417 (45, [(bcep)ZrCl]$^+$), 433 (100, [(bcep)ZrClO]$^+$); 100 V cone voltage, m/e (rel. int., assignment): 381 (20, [C$_6$H$_4$(CH$_2$CH$_2$C$_5$H$_4$)$_2$Zr]$^+$), 399 (60, [(bcep)ZrOH]$^+$), 415 (33, [(bcep)Zr(O)OH]$^+$), 417 (100, [(bcep)ZrCl]$^+$), 433 (48, [(bcep)ZrClO]$^+$).

4.3. ES-MS of 3 in methanol

A methanol solution of **3** (ca. 10^{-4} M) gives the following spectra: 20 V cone voltage, m/e 413 [(bcep)ZrOMe]$^+$, no other peaks with relative intensity greater than 1% were observed; 60 V cone voltage, m/e 381 (42%) for [C$_6$H$_4$P(CH$_2$CH$_2$C$_5$H$_4$)$_2$Zr]$^+$, m/e 413 for [(bcep)ZrOMe]$^+$.

4.4. Preparation of [PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$ZrCl(H$_2$O)]Cl (4)

Compound **3** (0.050 g, 0.11 mmol) was dissolved in wet methanol (15 ml) and stirred for 30 min at ambient temperature. Evaporation to dryness under a stream of dinitrogen gave a white crystalline solid from which a crystal of **4** was isolated.

4.5. Preparation of PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$Zr(NCS)$_2$ (7)

Compound **3** (0.050 g, 0.11 mmol) and KSCN (0.135 g, 1.39 mmol) were dissolved in distilled water (10 ml) to give a cloudy solution. Addition of chloroform (20 ml) and acetonitrile (5 ml) followed by stirring overnight gave two colorless layers. The organic layer was separated, dried over magnesium sulfate, and evaporated to dryness under a stream of nitrogen to give a white crystalline powder of **7** (0.044 g, 80% yield). M.p. 260–270 °C. ^{1}H NMR (acetone-d_6): δ 7.72 (m, 2H, Ph), 7.53 (m, 3H, Ph), 6.39 (m, 2H, CpH), 6.24 (m, 2H, CpH), 6.11 (m, 2H, CpH), 6.01 (m, 2H, CpH), 3.1–2.9 (m, 2H, CH$_2$), 2.9–2.6 (m, 6H, CH$_2$). ^{13}C NMR (acetone-d_6): δ 133.0 (d, J = 8.3 Hz, Ph), 131.3 (d, J = 3.1 Hz, Ph), 130.0 (d, J = 8.3 Hz, Ph), 125.01 (s, Cp), 110.8 (s, Cp), 110.0 (s, Cp), 102.7 (s, Cp), 32.7 (d, J = 20.7 Hz, CH$_2$), 25.0 (d, J = 10.4 Hz, CH$_2$), the quaternary C atoms were not observed due to the low solubility of the complex. ^{31}P NMR (acetone-d_6): 32.1 (s). IR (CH$_3$CN): ν_{CN} 2075(10), 2046(5.8); ν_{CS} 822 (0.5, br) cm^{-1}. Anal. Calcd. for C$_{22}$H$_{21}$N$_2$PS$_2$Zr: C,

52.87; H, 4.24; N, 5.61. Found: C, 52.63; H, 4.25; N, 5.71.

Addition of approximately 0.5 equiv. of KSCN(aq) to a ca. 10^{-4} M $CH_3CN–H_2O$ solution of **3** gave the following ES-MS spectrum, m/z (rel. int.): 537 (100) [(bcep)Zr(NCS)$_2$K]$^+$, 440 (25) [(bcep)ZrNCS]$^+$, 399 (15) [(bcep)ZrOH]$^+$.

4.6. X-ray structure of PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$ZrCl$_2$ (3)

A crystallographic-quality crystal of **3** was obtained by cooling a thf solution of **3** to $-35\,°C$. A colorless rod was mounted on a glass capillary. The unit cell parameters were obtained by least squares refinement of the setting angles of 26 reflections with $5.147 < 2\theta < 12.455°$ from a Siemens P4 diffractometer. Refinement was full-matrix least squares on $|F^2|$ [22] after correction for absorption using the ψ-scan method. The intensities of three standard reflections, measured every 497 reflections throughout the data collection, showed only 3.68% decay. The structure was solved by direct methods [23]. All hydrogen atoms were refined in their calculated positions with isotropic thermal parameters

1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [24]. Table 1 contains selected bond distances and angles, Table 2 contains the crystallographic data, and Table 3 contains the atomic coordinates and equivalent isotropic displacement parameters.

4.7. X-ray structure of [PPh(CH$_2$CH$_2$C$_5$H$_4$)$_2$ZrCl(H$_2$O)]Cl (4)

Single crystals of **4** were obtained by slow evaporation of a wet methanol solution of **3** under a stream of dinitrogen gas. A colorless plate was mounted on a glass capillary. The unit cell parameters were obtained by least squares refinement of the setting angles of 25 reflections with $3.123 < 2\theta < 12.428°$ from a Siemens P4 diffractometer. Data were refined on F^2 using the full-matrix least squares method [22] after being corrected for absorption by using the ψ-scan method. The intensities of three standard reflections, measured every

Table 2
Crystallographic data [a] and structure refinement for **3**, **4**, and **7**

Compound	3	4	7
Formula	C$_{20}$H$_{21}$Cl$_2$PZr	C$_{20}$H$_{23}$Cl$_2$OPZr	C$_{22}$H$_{21}$N$_2$PS$_2$Zr
FW	454.46	472.47	499.72
Crystal color	colorless	colorless	colorless
Crystal size (mm^3)	0.70 × 0.22 × 0.20	0.42 × 0.22 × 0.10	0.7 × 0.46 × 0.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	11.9230(10)	9.511(4)	8.8970(10)
b (Å)	13.4120(10)	15.060(3)	14.955(4)
c (Å)	11.9490(10)	13.680(4)	15.988(3)
β (deg)	103.473(4)	104.86(2)	99.260(10)
$F(000)$	920	960	1016
V (Å^3)	1858.2(3)	1893.9(10)	2099.6(7)
Z	4	4	4
d_{calc} (Mg m^{-3})	1.624	1.657	1.581
Abs. coeff. (mm^{-1})	0.964	0.953	0.810
T (K)	168(2)	188(2)	173(2)
Scan type	ω scans	ω scans	ω scans
Abs. correction	ψ-scans	ψ-scans	Semi-empirical
Max. and min. trans.	0.316 and 0.292	0.329 and 0.292	0.94088 and 0.70384
Refl. collected	4846	3591	4844
Independent refl.	3654 ($R_{int} = 0.0207$)	2975 ($R_{int} = 0.0491$)	3698 ($R_{int} = 0.0174$)
θ range (deg)	2.17 to 26.00	2.05 to 23.99	2.47 to 25.00
Range of h, k and l	−14:3; 0:16; −14:14	−10:2; 0:17; −15:15	−10:2; 0:17; −19:18
Data/restraints/parameters	3654/0/217	2975/2/232	3698/0/253
Gof on F^2	1.052	1.016	1.069
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$	$R_1 = 0.0537$	$R_1 = 0.0279$
	$wR_2 = 0.0683$	$wR_2 = 0.0890$	$wR_2 = 0.0630$
R indices (all data)	$R_1 = 0.0500$	$R_1 = 0.1032$	$R_1 = 0.0366$
	$wR_2 = 0.0741$	$wR_2 = 0.1069$	$wR_2 = 0.0660$
Largest diff. peak/hole (e$^-$ Å^{-3})	1.040/−0.509	0.468/−0.536	0.434/−0.267

[a] Conditions: Siemens P4, Mo Kα radiation ($\lambda = 0.71073$ Å), fine-focus sealed tube, graphite monochromator.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **3**

	x	y	z	U_{eq} [a]
Zr	2370(1)	1069(1)	1608(1)	17(1)
P	3256(1)	1744(1)	−211(1)	22(1)
Cl1	2488(1)	−488(1)	415(1)	24(1)
Cl2	1425(1)	−263(1)	2707(1)	28(1)
C11	2772(3)	1370(3)	−1719(3)	28(1)
C12	3383(4)	1696(4)	−2500(3)	56(1)
C13	3004(5)	1478(4)	−3656(4)	68(2)
C14	2018(4)	930(3)	−4048(3)	47(1)
C15	1397(3)	600(3)	−3284(3)	35(1)
C16	1784(3)	817(3)	−2116(3)	29(1)
C21	2948(3)	3082(2)	−313(3)	27(1)
C22	1657(3)	3174(3)	−413(3)	35(1)
C23	1251(3)	2584(2)	496(3)	24(1)
C24	481(3)	1756(3)	293(3)	28(1)
C25	243(3)	1479(3)	1333(3)	30(1)
C26	888(3)	2088(3)	2200(3)	29(1)
C27	1497(3)	2779(2)	1678(3)	25(1)
C31	4848(3)	1667(3)	185(3)	37(1)
C32	5244(3)	1019(4)	1232(3)	43(1)
C33	4571(3)	1187(3)	2125(3)	30(1)
C34	4271(3)	431(3)	2828(4)	38(1)
C35	3702(3)	868(3)	3592(3)	39(1)
C36	3607(3)	1874(3)	3372(3)	33(1)
C37	4116(3)	2086(3)	2460(3)	25(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **4**

Atom	x	y	z	U_{eq} [a]
Zr	1064(1)	1058(1)	3201(1)	16(1)
P	−1819(2)	1102(1)	2042(1)	18(1)
Cl1	240(2)	−491(1)	3354(1)	25(1)
Cl2	5830(2)	1455(1)	4986(2)	31(1)
O	2969(6)	405(3)	4333(4)	33(1)
C11	−2977(8)	123(5)	1832(6)	23(2)
C12	−3401(8)	−303(5)	893(6)	29(2)
C13	−4281(8)	−1043(6)	770(7)	40(2)
C14	−4777(9)	−1354(5)	1562(8)	47(3)
C15	−4337(8)	−960(5)	2509(7)	39(2)
C16	−3431(8)	−226(5)	2634(6)	31(2)
C21	−2852(8)	1940(5)	2513(6)	26(2)
C22	−1812(8)	2692(5)	2927(6)	28(2)
C23	−420(8)	2351(5)	3634(5)	21(2)
C24	−330(9)	1687(5)	4399(5)	28(2)
C25	1121(8)	1616(5)	4931(5)	26(2)
C26	1955(8)	2197(5)	4516(5)	25(2)
C27	989(8)	2663(4)	3731(5)	21(2)
C31	−1764(8)	1498(5)	788(5)	25(2)
C32	−525(7)	1008(5)	511(5)	27(2)
C33	887(7)	1123(5)	1309(5)	19(2)
C34	1898(8)	453(5)	1698(5)	27(2)
C35	3108(8)	838(6)	2353(6)	35(2)
C36	2829(9)	1747(6)	2397(6)	37(2)
C37	1458(9)	1917(5)	1750(5)	27(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

97 reflections throughout the data collection, showed no variation within experimental error. The structure was solved by direct methods [23]. H1 and H2 were located from the difference Fourier map and refined with fixed O–H distances of 0.90 Å and isotropic thermal parameters 1.2 times that of the O atom. All other hydrogen atoms were refined in their calculated positions with isotropic thermal parameters 1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [24]. Table 1 contains selected bond distances and angles, Table 2 contains the crystallographic data, and Table 4 contains the atomic coordinates and equivalent isotropic displacement parameters.

4.8. X-ray structure of $PPh(CH_2CH_2C_5H_4)_2Zr(NCS)_2$ (7)

Single crystals of **7** were obtained by slow evaporation of a $CHCl_3$ solution under a stream of dinitrogen gas. A colorless plate was mounted on a glass capillary. The unit cell parameters were obtained by least squares

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **7**

Atom	x	y	z	U_{eq} [a]
Zr	1619(1)	5236(1)	3055(1)	19(1)
P	3739(1)	5836(1)	2110(1)	21(1)
N1	−24(2)	4164(2)	3304(1)	31(1)
N2	1590(2)	4278(1)	1978(1)	27(1)
S1	−1971(1)	2898(1)	3820(1)	50(1)
S2	1045(1)	3334(1)	460(1)	35(1)
C1	−847(3)	3635(2)	3517(2)	28(1)
C2	1352(3)	3887(2)	1341(2)	24(1)
C11	5016(3)	5113(2)	1632(2)	24(1)
C12	5273(3)	4239(2)	1904(2)	31(1)
C13	6354(3)	3719(2)	1600(2)	36(1)
C14	7146(3)	4059(2)	997(2)	36(1)
C15	6869(3)	4919(2)	704(2)	34(1)
C16	5819(3)	5451(2)	1022(2)	29(1)
C21	2821(3)	6584(2)	1284(2)	29(1)
C22	1794(3)	7205(2)	1702(2)	31(1)
C23	854(3)	6704(2)	2251(2)	27(1)
C24	−266(3)	6055(2)	1952(2)	28(1)
C25	−1032(3)	5828(2)	2622(2)	32(1)
C26	−359(3)	6291(2)	3350(2)	34(1)
C27	799(3)	6840(2)	3115(2)	30(1)
C31	5016(3)	6536(2)	2843(2)	26(1)
C32	5552(3)	5968(2)	3632(2)	31(1)
C33	4277(3)	5488(2)	3955(1)	24(1)
C34	4022(3)	4547(2)	3933(2)	27(1)
C35	2798(3)	4363(2)	4351(2)	28(1)
C36	2253(3)	5179(2)	4623(2)	29(1)
C37	3182(3)	5866(2)	4388(2)	26(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

refinement of the setting angles of 23 reflections with $4.822 < 2\theta < 12.5055°$ from a Siemens P4 diffractometer. Data were refined on F^2 using the full-matrix least squares method [22] after a semi-empirical absorption correction. The intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed no variation within experimental error. The structure was solved by direct methods [23]. Hydrogen atoms were fixed in idealized positions with isotropic thermal parameters 1.2 times that of the attached atom. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [24]. Table 1 contains selected bond distances and angles, Table 2 contains the crystallographic data, and Table 5 contains the atomic coordinates and equivalent isotropic displacement parameters.

5. Supplementary material

Text of crystallographic data, crystal and data refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for $(bcep)ZrCl_2$ (3), $[(bcep)ZrCl(H_2O)Cl]Cl$ (4), and $(bcep)Zr(NCS)_2$ (7) are available.

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