Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 26 (2007) 406–414

POLYHEDRON

www.elsevier.com/locate/poly

Aqueous chemistry of the five-coordinate zirconocene dichloride $PhP(CH_2CH_2–\eta^5-C_5H_4)_2ZrCl_2$: X-ray structure of the sulfato complex $PhP(CH_2CH_2–\eta^5-C_5H_4)_2Zr(\eta^2-SO_4)$

James R. Butchard, Owen J. Curnow *

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Received 3 April 2006; accepted 28 June 2006
Available online 14 July 2006

Abstract

ES-MS of dilute solutions of (bcep)$ZrCl_2$ (**1**) (bcep = $PhP(CH_2CH_2–\eta^5-C_5H_4)_2$) in acetonitrile–water indicates the presence of three species in solution: $[(bcep)Zr(H_2O)_2]^{2+}$ (**2**), $[\{(bcep)Zr(\mu-OH)\}_2]^{2+}$ (**3**), and the singly deprotonated form of dimer **3**, $[\{(bcep)Zr\}_2(\mu-O)(\mu-OH)]^+$ (**4**). In aqueous solutions, reactivity studies investigated largely by ^{31}P NMR spectroscopy support the presence of **2**, **3** and **4**. One equivalent of fluoride was found to react immediately with **2**, but slowly with **3** and **4**, to give the monofluoro complex $[(bcep)ZrF]^+$ which was isolated as the BPh_4^- salt. Addition of aqueous sodium sulphate gave insoluble crystals of the sulfato complex (bcep)Zr(SO_4) which was characterised by X-ray crystallography. Addition of acids HX (X = Br, NO_3, HSO_4, HCO_3) to aqueous solutions of **1** gave species observed by ES-MS corresponding to $[(bcep)ZrX]^+$.

Keywords: Zirconocene; Phosphine; Sulfato complex; Fluoro complex; Aqueous chemistry

1. Introduction

The chemistry of zirconocene dichlorides is currently one of the most significant areas of research in organometallic chemistry [1]. The area of functionalised bis(cyclopentadienyl) ligands capable of chelation is an active field of organometallic chemistry [2–4]. Notable zirconocenes are the complexes $MeN(CH_2CH_2C_5H_4)_2ZrCl_2$ and $\{C_5H_3N(CH_2C_5H_4)_2-2,6\}ZrCl_2$ in which amine and pyridine coordination, respectively, is proposed on the basis of ^1H NMR spectroscopy and XPS studies [2]. A crystallographically characterized hydrolysis product of $\{C_5H_3N(CH_2C_5H_4)_2-2,6\}ZrCl_2$ is the cationic chloro-aqua complex $[\{C_5H_3N(CH_2C_5H_4)_2-2,6\}ZrCl(H_2O)]^+$ in which the pyridine substituent is coordinated to the metal center [3].

Ansa-metallocenes with a P bridging atom directly bonded to the C_5 ring are known for a number of iron [5] and zirconium [6] complexes. The number of bis(cyclopentadienyl) phosphine ligands capable of chelation is very small [7,8]. The ligand $C_6H_{11}P(CHMe-2-PPh_2C_5H_3^-)_2$ [7] could exhibit phosphine chelation, but this has not yet been demonstrated. We recently communicated the preparation of $PPh(CH_2CH_2C_5H_5)_2$ (bcepH_2) and the synthesis of ferrocene complexes derived from this compound in which the P atom is not coordinated to the Fe center [8]. The P atom can, however, coordinate to a second metal center as in the complex *trans*-$PdCl_2\{(bcep)Fe\}_2$ [8].

The aqueous chemistry of zirconocenes has been investigated by a small number of workers (in contrast to that of the titanocenes [9]) with the identification of species in solution largely dependent upon crystallographic characterisation of the compounds isolated in the solid state. Addition of two equivalents of water to $Cp_2Zr(C_7H_7SO_3)_2$ gives the toluenesulfonatodiaqua cation $[Cp_2Zr(C_7H_7SO_3)(H_2O)_2]^+$ [10], whereas addition of three equivalents of water to the bistriflate complex $Cp_2Zr(CF_3SO_3)_2$ (THF) gives the triaqua dication $[Cp_2Zr(H_2O)_3]^{2+}$ [11] and addition of six

---

* Corresponding author. Tel.: +64 3 364 2819; fax: +64 3 364 2110.
E-mail address: owen.curnow@canterbury.ac.nz (O.J. Curnow).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.06.031

equivalents gives a 30% yield of the dinuclear hydroxo-bridged complex $[Cp_2Zr_2(\mu\text{-}OH)_2(H_2O)_6]^{4+}$ in which one Cp ligand has been hydrolysed from each Zr atom [12]. Other zirconocene dichloride hydrolysis products have been reported by Thewalt and co-workers in which one Cp ligand has been hydrolysed and there are oxo/hydroxo bridges: $\{CpZr(NO_3)_2\}_2(\mu\text{-}OH)_2$ was isolated from nitric acid in chloroform [13] and $[Cp_3Zr_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}PhCOO)_3]^+$ was isolated from sodium benzoate in water/chloroform [14]. Fischer and co-workers obtained the dicationic dinuclear di-μ-hydroxo complex $[\{Cp_2Zr(\mu\text{-}OH)(n\text{-}PrCN)\}_2]^{2+}$ by addition of *n*-PrCN to a mixture they formulated as $[\{Cp_2Zr(H_2O)\}_2O][BPh_4]_2 \cdot pH_2O$ and/or $[Cp_2Zr(OH)(H_2O)_n][BPh_4] \cdot mH_2O$ (this was prepared by addition of $Na[BPh_4]$ to Cp_2ZrCl_2 dissolved in water) [15]. A related neutral dinuclear di-μ-hydroxo complex, $[Cp_2Zr(\mu\text{-}OH)(CF_3COO)]_2$, was obtained by Klima and Thewalt by treatment of Cp_2ZrCl_2 with CF_3COOH in a $CHCl_3/H_2O$ two-phase system [16]. Erker and co-workers reported that treatment of $[Cp_2ZrCH_3(THF)]^+$ with excess water in CH_2Cl_2/THF gave the trinuclear cluster $[(Cp_2Zr)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ in which the cyclopentadienyl ligands are still intact [17]. Using chloride potentiometry, Toney and Marks studied the aqueous chemistry of Cp_2ZrCl_2: the rate of the second chloride loss was found to be 1.31 h^{-1} for 1–3.5 mM solutions with an equilibrium $[Cl^-]$:[Zr] ratio of 1.75 [18]. Thus, significant amounts of $[Cp_2ZrCl(H_2O)_x]^+$ and $[Cp_2Zr(H_2O)_x]^{2+}$ are present in these solutions. Some aqueous polymerisation studies of styrene and methyl methacrylate using Cp_2ZrCl_2 have also been reported [19]. Hillhouse and Bercaw have reported some stoichiometric reactions of bis(pentamethylcyclopentadienyl)-zirconium and -hafnium hydrides to give a variety of hydroxo and oxo complexes [20].

We recently reported the preparation and structure of $(bcep)ZrCl_2$ (**1**) along with some initial chemical investigations [21]: crystals of $[(bcep)ZrCl(H_2O)]Cl$ were isolated by evaporation of a wet methanol solution of **1**; the ES-MS of a CH_3CN/H_2O solution of **1** with added HCl(aq) gave peaks corresponding to the expected species $[(bcep)Zr(OH)]^+$ and $[(bcep)ZrCl]^+$ in addition to species of the formulae $[(bcep)Zr(OH)O]^+$ and $[(bcep)ZrClO]^+$ (no peak corresponding to the crystallographically characterised cation $[(bcep)ZrCl(H_2O)]^+$ has been observed).

In this paper, we detail further aqueous chemistry of complex **1** which has been studied using ^{31}P NMR spectroscopy, ES-MS, and X-ray crystallography.

2. Results and discussion

Positive-ion ES-MS of dilute (ca. 10^{-4} M) solutions of complex **1** in 1:1 acetonitrile–water shows the presence of three species (Fig. 1). The masses are consistent with the hydroxo complex $[(bcep)Zr(OH)]^+$ (**5**) (derived from the diaqua dicationic complex $[(bcep)Zr(H_2O)_2]^{2+}$ (**2**)) and its dimer $[\{(bcep)Zr(\mu\text{-}OH)\}_2]^{2+}$ (**3**), as well as the singly-deprotonated form of **3**, $[\{(bcep)Zr\}_2(\mu\text{-}O)(\mu\text{-}OH)]^+$ (**4**) (Scheme 1). Although the diaqua dication $[(bcep)Zr(H_2O)_2]^{2+}$ (**2**) is not observed directly by ES-MS, this is not surprising: under ES-MS conditions, as the solvent evaporates and the charge density increases, the dication **2** can both lose solvent and reduce charge by the loss of H_3O^+ to give the hydroxo complex **5**. There is no evidence in these dilute solutions for any chloro complexes such as the crystallographically-characterised cation $[(bcep)ZrCl(H_2O)]^+$ [21].

The aqueous chemistry of **1** was investigated with reactivity studies that were followed by ^{31}P NMR spectroscopy. Results are summarised in Table 1. Three major species, in a 14:2:1 ratio, are observed. These are proposed to be the diaqua dication $[(bcep)Zr(H_2O)_2]^{2+}$ (**2**) (δ 32.32), and the dinuclear complexes **3** (δ 33.14) and **4** (δ 34.36). The assignment of the resonance at δ 32.32 as the diaqua dication **2** rather than the mononuclear hydroxo complex **5**, as is observed under ES-MS conditions, or the hydroxo-aqua complex

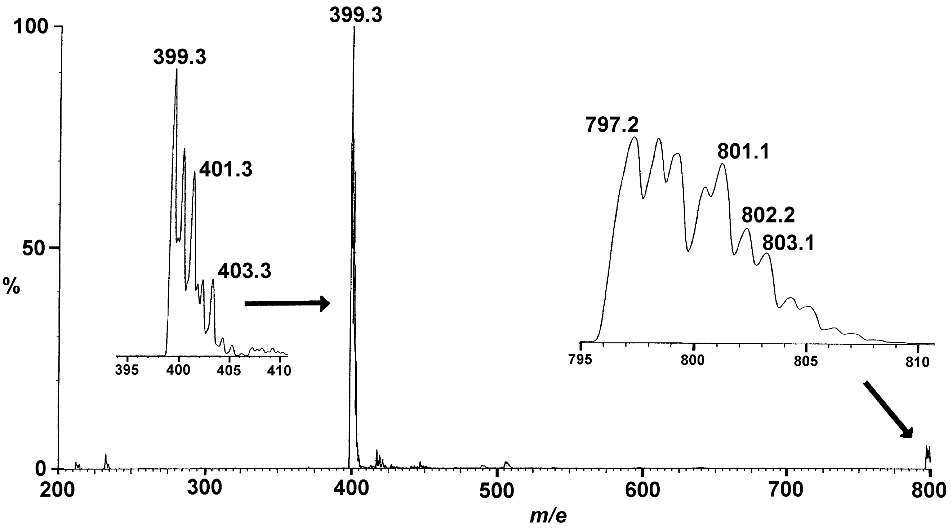
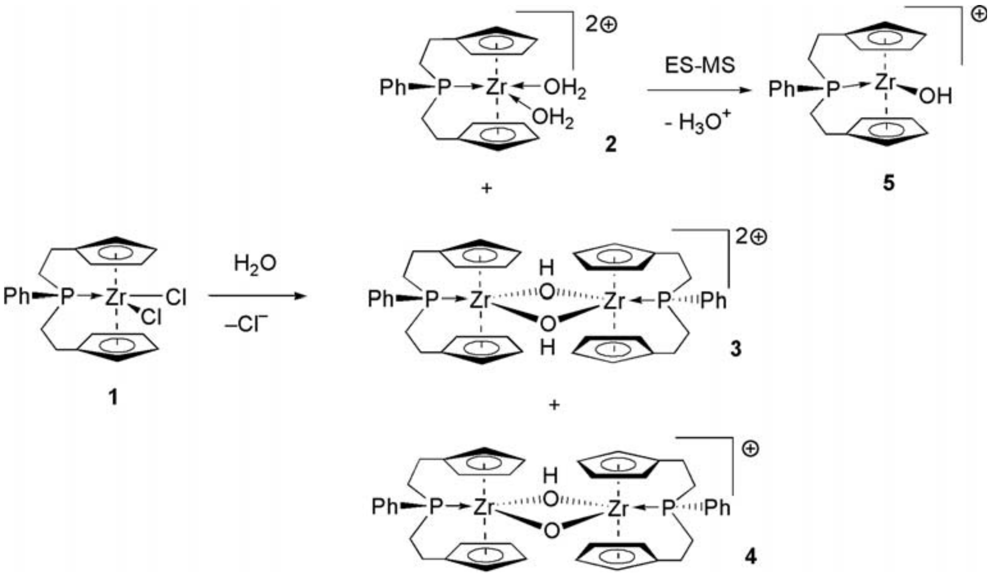


Fig. 1. ES-MS of $(bcep)ZrCl_2$ (**1**) in H_2O/CH_3CN (cone voltage of 20 V).



Scheme 1. (Bcep)ZrCl$_2$ (**1**) in H_2O.

Table 1
^{31}P NMR spectra of aqueous solutions of **1**[a]

Solvent	$[(bcep)_2Zr_2(O)(OH)]^+$	$[\{(bcep)Zr(OH)\}_2]^{2+}$	$[(bcep)Zr(H_2O)_2]^{2+}$
H_2O	34.36 (0.11)	33.14 (0.18)	32.32 (0.71)
D_2O	34.25 (0.10)	33.01 (0.22)	32.46 (0.68)
1:1 H_2O/D_2O	34.34 (0.10)	33.18 (0.05)	32.40 (0.70)
		33.15 (0.05)	
		33.12 (0.05)	
		33.09 (0.05)	
2:1 H_2O/D_2O	34.34 (0.11)	33.18 (0.02)	32.40 (0.71)
		33.15 (0.04)	
		33.12 (0.04)	
		33.09 (0.08)	
25:75 H_2O/CH_3CN	33.16 (0.15)	33.03 (0.22)	29.12 (0.63)
			$w_{1/2} \sim 83$ Hz
50:50 H_2O/CH_3CN	33.11	33.01	31.38
			$w_{1/2} \sim 50$ Hz
65:35 H_2O/CH_3CN	34.10 (0.12)	33.09 (0.22)	32.09 (0.66)
			$w_{1/2} = 23$ Hz
75:25 H_2O/CH_3CN	34.17 (0.11)	33.12 (0.20)	32.15 (0.69)
			$w_{1/2} = 9$ Hz
H_2O + 10HCl (5 min)	34.36 (0.01)	33.14 (0.14)	32.68 (0.85)
H_2O + 10HCl (30 min)			32.68 (1.00)

[a] Chemical shift in ppm, integral given in parentheses.

$[(bcep)Zr(OH)(H_2O)]^+$ (**6**) is based on the following observations: addition of one half equivalent of NaOH(aq) rapidly converts **2** to **3** and **4** (more than one equivalent of hydroxide rapidly leads to hydrolysis of bcep from the complex) whereas addition of aqueous HCl converts **3** and **4** to **2** over several minutes – a possible equilibrium between **3** and its monomer **5** (or a complex such as **6**) would not be affected by addition of acid or base. Balzarek et al. have reported that the monomer/dimer equilibrium between $[Cp_4Mo_2(\mu\text{-}OH)_2]^{2+}$ and $[Cp_2Mo(OH)(H_2O)]^+$ (equivalent to an equilibrium between **3** and **6**) is independent of pH [22]. Dicationic species such as **2** also have precedence in the form of the triaqua complex $[Cp_2Zr(H_2O)_3]^{2+}$ [11]. Dissolving complex **1** in 0.1 M HCl(aq) gives only **2**.

The assignment of the resonance at δ 33.14 to the di-μ-hydroxo complex **3**, with the phosphorus atoms *trans* about the $Zr_2(OH)_2$ core, is supported by its ^{31}P NMR spectrum in 2:1 D_2O/H_2O which shows four peaks in a 4:2:2:1 ratio (Fig. 2). The downfield resonance at 32.94 ppm is assigned to $[\{(bcep)Zr(\mu\text{-}OD)\}_2]^{2+}$, the resonances at 32.91 and 32.88 ppm to the mixed species $[\{(bcep)Zr\}_2(\mu\text{-}OH)(\mu\text{-}OD)]^{2+}$, and the resonance at 32.85 ppm to $[\{(bcep)Zr(\mu\text{-}OH)\}_2]^{2+}$. Complex **4** could also give four peaks in this solvent mixture, but they would be in a 2:2:1:1 ratio. Accidental degeneracy of two of these peaks could give a 1:3:2 pattern, unfortunately, we have been unable to resolve the resonances at ca. 34 ppm sufficiently well to confirm this unambiguously. The resonance due to **2** is essentially

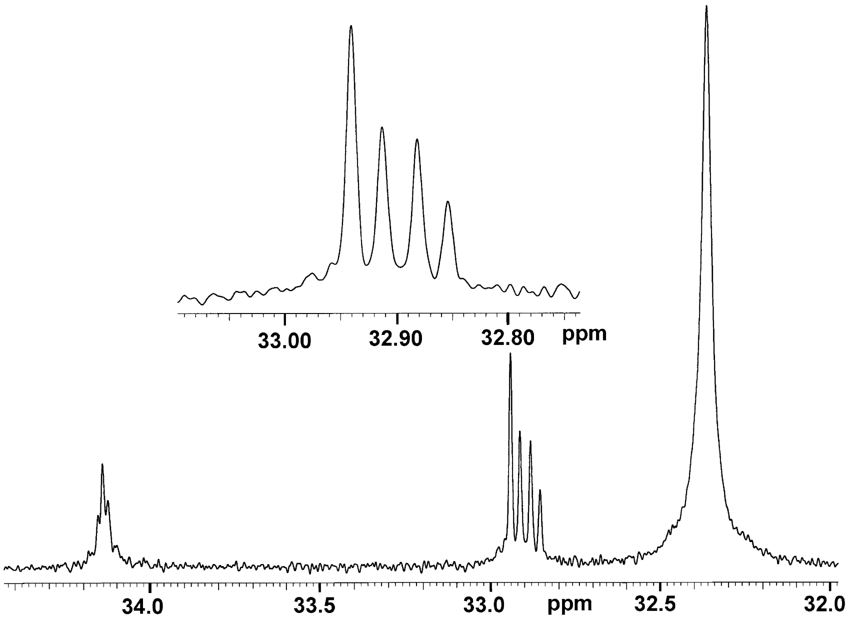


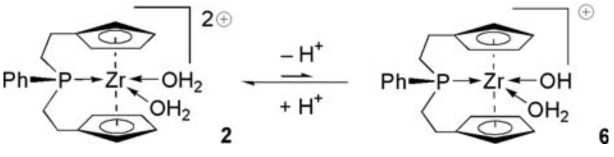
Fig. 2. ^{31}P NMR spectrum of complex **1** dissolved in a 2:1 D_2O/H_2O mixture.

unchanged, as would be expected for rapid proton exchange in this complex. In a 1:1 solvent mixture, both **3** and **4** would have four peaks in a 1:1:1:1 ratio; this is observed for **3** but, again, is unresolved for **4**. The related complex $[\{Cp_2Zr(n\text{-}PrCN)(\mu\text{-}OH)\}_2]^{2+}$, has been crystallographically characterized and also found to have the *n*-PrCN substituents *trans* about the $Zr_2(OH)_2$ core [15]. The observation of this isotope effect deserves some comment. The average isotope effect on the ^{31}P NMR chemical shift is 0.045 ppm per H/D substitution, which is quite significant considering that the substitution is made three bonds away from the P atoms. A comparison can be made with $P(CH_3)_3$ versus $P(CD_3)_3$ in which the chemical shifts are −61.9 and −64.9 ppm, respectively [23]. This is an average isotope effect of 0.33 ppm per H/D exchange, for which the P atom is two bonds from the H/D atoms.

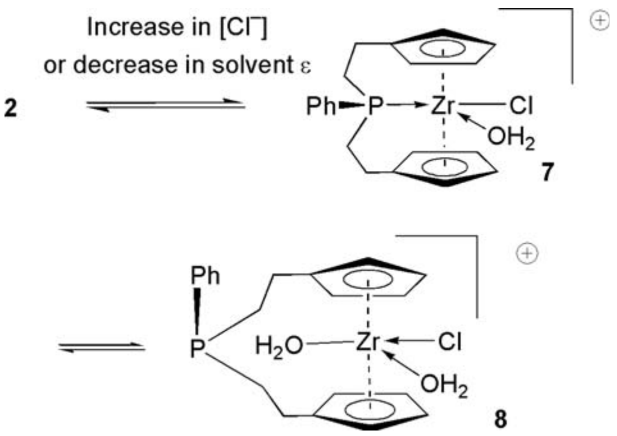
To confirm the absence of chloro complexes, $Ag(NO_3)$(aq) was added to the aqueous solution of **1**. Although the expected precipitate of AgCl rapidly formed, there was no change in the ^{31}P NMR spectrum. Thus, the presence of chloro complexes can be ruled out.

Further evidence in support of the proposed structures for **2**, **3** and **4** is provided by the treatment of aqueous **1** with aqueous $HClO_4$. One equivalent immediately precipitates out only **3** and **4**, as is expected from their larger size and hydrophobic exterior (the Zr_2O_2 cores are sterically shielded by the four cyclopentadienyl rings and two phenyl groups, as evidenced by the slow rate of proton exchange in the mixed D_2O/H_2O solvent systems). The concentration of **2** is unaffected and it seems reasonable to suggest that hydrogen bonding with the solvent keeps this species in solution.

Potentiometry measurements were also carried out to support the proposed mixture of compounds. Complex **1** dissolves in water over several minutes to give an acidic solution for which a stable pH reading can be taken after about 30 min. For a 10^{-3} M solution, the equilibrium pH is 3.3. This is lower than the expected pH calculated using the ^{31}P NMR peak ratios, which gives a pH of 3.7, but is higher than would be expected if **2** was in fact a hydroxo species like **5** or **6**, in which case, the expected pH would be less than 3.0. Similarly, a 10^{-2} M solution gives a pH of 2.2, rather than 2.7. The discrepancy could be accounted for by an equilibrium between **2** and **6**, which would be expected to be rapid and which could also provide a proton exchange mechanism. Attempts to measure the free chloride concentration using a chloride-ion selective electrode were prevented by chronic electrode fouling.



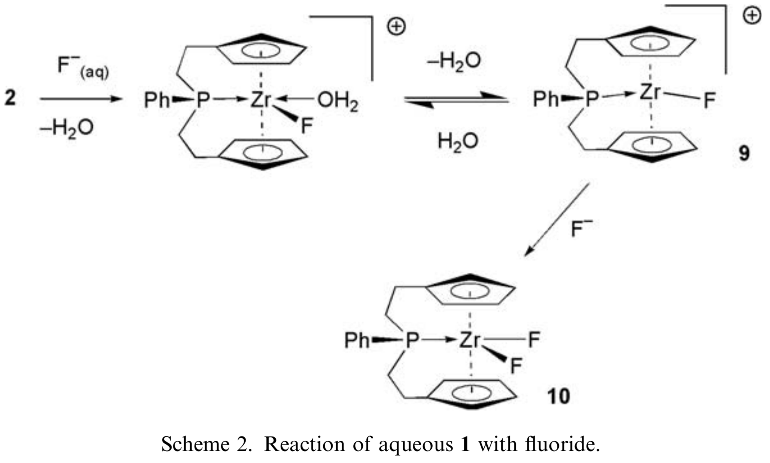
In an attempt to observe a species such as $[(bcep)ZrCl(H_2O)]^+$ (**7**), aqueous NaCl was added to an aqueous solution of **1**. Although no new peaks were observed in the ^{31}P NMR spectrum and the peaks assigned to **3** and **4** remained unchanged, the peak assigned to **2** at ca. 32 ppm broadened from 6 Hz with no added chloride to 60 Hz at 1.2 M chloride. A similar broadening effect was seen upon addition of acetonitrile (Table 1). We believe that this broadening is due to the formation of an equilibrium in which the **7** is in rapid equilibrium with the dication **2**. The chloroaqua cation may also have a largely non-coordinated phosphorus atom as in complex **8** since a non-coordinated P atom would be expected to have a chemical shift considerably upfield of **2** and similar to that of the ferrocene complex (bcep)Fe at −16.8 ppm [8].



Unlike the addition of chloride, the addition of one equivalent of fluoride to aqueous solutions of **1** immediately converts **2** to the monofluoro species $[(\text{bcep})\text{ZrF}(\text{H}_2\text{O})_x]^+$ (**9**) ($x = 0$ or 1), while **3** and **4** react only slowly to give the same product (Scheme 2). Following the reaction by ^{31}P NMR spectroscopy, a doublet is observed for **9** at 27.3 ppm with a P–F coupling constant of 67 Hz. A small doublet of doublets is also observed at 18.3 ppm with coupling constants of 95 and 84 Hz. This compound is assigned as the difluoro complex $\text{PhP}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{ZrF}_2$ (**10**). This compound disappears after several minutes and attempts to isolate a difluoro complex failed: only the oxide of the free ligand is observed in solution and a white precipitate that forms after addition of a second equivalent of fluoride contains no carbon or hydrogen. ES-MS of aqueous **1** with added CsF(aq) gives cation **9** as the major species with the difluoride observed as a Cs^+ adduct, $[\text{PhP}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{ZrF}_2\text{Cs}]^+$ ($m/e = 553$) with a relative intensity of 8%. Significant peaks for hydrolysis products $[\text{PHPh}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_5)_2]^+$ (75%) and $[\text{C}_{20}\text{H}_{22}\text{FPO}]^+$ (50%) are also observed. The chemistry with fluoride contrasts with that of isothiocyanate in which the diisothiocyanato complex readily forms, but the monoisothiocyanato complex cannot be isolated, even with only one equivalent of thiocyanate [21]. This difference in chemistry can be attributed to the π-donor effect of fluoride which disfavours (relative to isothiocyanate) coordination of an additional ligand.

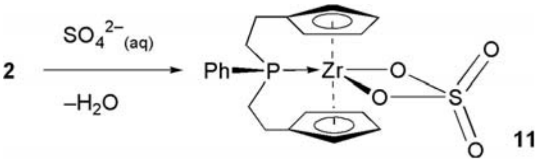
The fluoro complex **9** was precipitated from aqueous solution as the tetraphenylborate salt. It is important to do this reaction in the presence of added acid (as HCl(aq)), otherwise, an increase in pH as F^- substitutes OH^- in **3** and **4** eventually leads to hydrolysis of the zirconocene. Spectroscopic evidence indicates that there is no water coordinated in the solid state: no υ_{OH} in the infrared spectrum or additional proton resonances in the ^{1}H NMR spectrum (CD_3CN solvent) were observed and TGA/DSC shows no changes below 175 °C – above 175 °C, there are significant mass losses (>25%). In solution, however, a weakly coordinated water molecule cannot be ruled out. Fluoride is a much better π-donor ligand than chloride and, thus, electronic factors may disfavour coordination of water. As would be expected for ES-MS conditions, the highest mass ion (401 *m*/*e* (^{90}Zr isotopomer) for $[\text{PhP}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{ZrF}]^+$) does not contain coordinated water.

Treatment of an acidified aqueous solution of (bcep)-ZrCl_2 with sulfate gives a precipitate of $(\text{bcep})\text{Zr}(\text{SO}_4)$ (**11**) that is insoluble in common solvents. Fortunately, the precipitate appears over several minutes and X-ray quality crystals were obtained directly from the reaction mixture. The infrared S=O stretch was observed at 1263 cm^{-1}, similar to other Zr(IV) complexes [24]. Under dilute conditions, complex **11** can be observed by ES-MS at 479 *m*/*e* as a bisulfato complex, $[(\text{bcep})\text{Zr}(\text{SO}_4\text{H})]^+$. A single crystal of **11** was subjected to an X-ray crystallographic analysis. The structure contains one independent molecule in the asymmetric unit. The structure is similar to other mononuclear (bcep)Zr complexes: the zirconium atom is approximately trigonal bipyramidal with the two cyclopentadienyl rings and one oxygen atom of the sulfato ligand occupying the equatorial positions and the axial positions occupied by the phosphorus atom and another sulfato oxygen atom. The sulfato ligand is O,O′ chelated. Fig. 3 shows an ORTEP plot of **11** with the atomic



Scheme 2. Reaction of aqueous **1** with fluoride.

labelling scheme and selected bond distances and angles. Table 2 gives the crystallographic data and structure refinement details.



The Zr–O distances in **11** are very similar with the axial distance of 2.2010(12) Å only very slightly longer than the equatorial distance of 2.1944(12) Å. These distances are similar to those found in other chelated Zr(IV) sulfato complexes, for example, in $[Zr(SO_4)_4]^{4-}$, the Zr–O distances range from 2.180(4) to 2.220(5) Å [25] and in $[\{CpCo(P(OEt)_2O)_3\}Zr(NO_3)_2(SO_4)]^-$, the Zr–$O_{sulfato}$ distances are 2.232(3) and 2.164(4) Å [24]. The Zr–P distance of 2.7793(5) Å is in the middle of the range of distances found in other (bcep)Zr complexes: 2.7810(8), 2.7499(7) and 2.794(2) Å for (bcep)ZrCl$_2$, (bcep)Zr(NCS)$_2$ and [(bcep)ZrCl(H$_2$O)]Cl, respectively [21]. Similarly, the Zr–CNT distances and the CNT–Zr–CNT angle are typical of (bcep)Zr complexes reported to date [21]. The *trans* angle, P–Zr–O2, of 139.54(3)° is small compared to the other (bcep)Zr complexes in which the smallest *trans* angle of 148.55(8)° is found in (bcep)Zr(NCS)$_2$ [11]. However, this is simply due to the chelating nature of the sulfato ligand since the P–Zr–O1 angle of 75.68(3)° is actually larger than the corresponding angle in (bcep)Zr(NCS)$_2$ (71.14(8)°). Notably, the *trans* angles in the five-coordinate di-μ-hydroxo complexes $[Cp_2Zr(CF_3COO)(\mu\text{-}OH)]_2$ [16] and $[\{Cp_2Zr(^nPrCN)(\mu\text{-}OH)\}_2]^{2+}$ [15] are similar (141.9° and 139.5°, respectively) to those found in **11**. The ligand conformation is similar to that found in $[(bcep)ZrCl(H_2O)]^+$ in which $\alpha_x = -69.8°$ and 95.9° (α_x = Cl–Zr–CNT(x)–C(x2), (CNT(x) = centroid of atoms C(x3) to C(x7)) and $\beta = 2.6°$ (β = Cl–Zr–P–C11) [21]. The corresponding angles in **11** are $\alpha_2 = -67.3°$, $\alpha_3 = 98.7°$ and $\beta = -3.1°$. The difference in $|\alpha_x|$ of 31.4° corresponds to staggered cyclopentadienyl rings. The most significant difference is that in $[(bcep)ZrCl(H_2O)]^+$ the phenyl plane lies between the chloro ligand and a cyclopentadienyl ring which forces one ring to be further from the equatorial chloro ligand than the other: CNT–Zr–Cl angles of 120.0° and 111.9°. In **11**, the phenyl ring is approximately perpendicular to the ZrPO$_2$ plane (Zr–P–C(11)–C(12) = −94.7°) and the CNT–Zr–O1 angles are consequently similar to each other (116.44° and 115.42°).

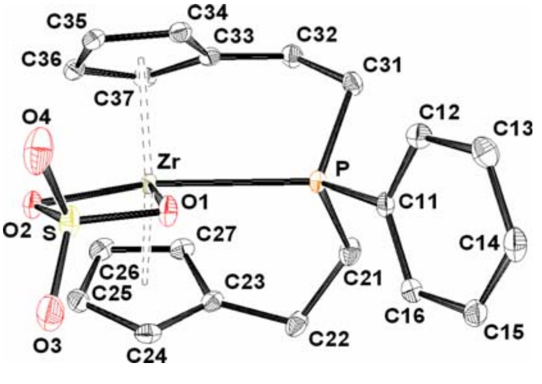


Fig. 3. ORTEP of (bcep)Zr(SO$_4$) (**11**) with 40% thermal ellisoids. Selected bond distances and angles are Zr–O1 = 2.1944(12), Zr–O2 = 2.2010(12), Zr–P = 2.7793(5), Zr–CNT(C23–C27) = 2.225(1), Zr–CNT(C33–C37) = 2.223(1), S–O1 = 1.5341(12), S–O2 = 1.5209(12), S–O3 = 1.4382(15), S–O4 = 1.4412(16) Å, O1–Zr–O2 = 63.87(4)°, O1–Zr–P = 75.68(3)°, O2–Zr–P = 139.54(3)°, Zr–P–C11 = 125.05(5)°, Zr–P–C21 = 105.91(6)°, Zr–P–C31 = 108.57(6)°, CNT–Zr–CNT = 128.13°, CNT(2)–Zr–O1 = 116.44°, CNT(2)–Zr–O2 = 100.24°, CNT(2)–Zr–P = 96.82°, CNT(3)–Zr–O1 = 115.42°, CNT(3)–Zr–O2 = 102.91°, CNT(3)–Zr–P = 94.62°.

Table 2
Crystallographic data and structure refinement parameters for (bcep)Zr(SO$_4$) (**11**)

Empirical formula	$C_{20}H_{21}O_4PSZr$
Formula weight	479.62
Crystal colour	colourless
Crystal size (mm)	0.39 × 0.12 × 0.07
Temperature (K)	93(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.6805(13)
b (Å)	8.9775(13)
c (Å)	17.800(2)
α (°)	90
β (°)	93.110(2)
γ (°)	90
$F(000)$	976
Volume (Å^3)	1863.8(4)
Z	4
D_{calc}	1.709
Absorption coefficient (mm^{-1})	0.812
θ Range (°)	1.75–33.41
Limiting indices	$-15 \leqslant h \leqslant 16$ $-11 \leqslant k \leqslant 13$ $-23 \leqslant l \leqslant 23$
Reflections collected	23474
Independent reflections (>2σ)	4733
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0269$, $wR_2 = 0.0589$
R indices (all data)	$R_1 = 0.0366$, $wR_2 = 0.0656$
Largest difference in peak/hole (e Å^{-3})	0.477/−0.422

2.1. Other electrospray mass spectrometry studies

Addition of acids HX (X = Br, NO$_3$, HSO$_4$, HCO$_3$) to 10^{-4} M CH$_3$CN/H$_2$O solutions of **1** eliminates the peaks due to the dinuclear complexes **3** and **4** and gives only peaks corresponding to **2** and $[(bcep)ZrX]^+$ (Table 3). Since the structure of (bcep)Zr(SO$_4$) contains a chelated sulfato ligand, it seems reasonable that the complexes $[(bcep)Zr(HCO_3)]^+$, $[(bcep)Zr(HSO_4)]^+$, and $[(bcep)Zr(NO_3)]^+$ would also contain chelated ligands to give five-coordinate

Table 3
Summary of ES-MS experiments with H_2O/CH_3CN solutions of **1** at low cone voltage (20 V)

Reagent added	*m*/*e* (rel. int.)	Assignment
None	399(100)	$[\{(bcep)Zr(OH)\}_n]^{n+}$ ($n = 1, 2$)[a]
	797(6)	$[\{(bcep)Zr\}_2(O)(OH)\}]^+$
$CO_2(aq)$	399(10)	$[(bcep)Zr(OH)]^+$
	443(100)	$[(bcep)Zr(CO_3H)]^+$
HBr	399(45)	$[(bcep)Zr(OH)]^+$
	463(100)	$[(bcep)ZrBr]^+$
	479(8)	$[(bcep)ZrOBr]^+$
HBr (after 1 h)	399(13)	$[(bcep)Zr(OH)]^+$
	415(65)	$[(bcep)Zr(OH)O]^+$
	463(10)	$[(bcep)ZrBr]^+$
	479(100)	$[(bcep)ZrBrO]^+$
H_2SO_4	399(35)	$[(bcep)Zr(OH)]^+$
	479(100)	$[(bcep)Zr(SO_4H)]^+$
HNO_3	399(15)	$[(bcep)Zr(OH)]^+$
	444(100)	$[(bcep)Zr(NO_3)]^+$
CsF	553(8)	$[PhP(CH_2CH_2C_5H_4)_2ZrF_2Cs]^+$
	401(100)	$[PhP(CH_2CH_2C_5H_4)_2ZrF]^+$
	328(50)	$[C_{20}H_{22}PFO]^+$
	295(75)	$[PHPh(CH_2CH_2C_5H_5)_2]^+$

[a] Ratio of approximately 1:2 for $n = 1$ and 2, respectively.

zirconocene complexes. After 1 h, the solution containing added HBr has additional peaks corresponding to $[(bcep)ZrOBr]^+$ (479 *m*/*e*, rel. int. = 100) and $[(bcep)ZrO(OH)]^+$ (415 *m*/*e*, rel. int. = 65), which may contain oxidised phosphine, while $[(bcep)ZrOH]^+$ and $[(bcep)ZrBr]^+$ are now much weaker with relative intensities of 13 and 10, respectively. Similar behaviour was observed for solutions containing added HCl [21].

3. Conclusions

In this paper, we have described some aqueous chemistry of the five-coordinate zirconocene dichloride complex **1**. Its speciation in water and water/acetonitrile solvents was investigated by ^{31}P NMR and ES-MS studies and shown to give three species in solution. Some reactivity studies were also carried out: treatment of aqueous solutions of **1** with various acids HX produced cationic complexes $[(bcep)ZrX]^+$ which were observed by ES-MS; addition of fluoride allowed the isolation of the monofluoro complex **9**, but not the difluoro complex **10**; addition of sulphate allowed the isolation of the sulfato complex **11** which was crystallographically characterised. These reactions thus demonstrate the potential to carry out reactions of this zirconocene in aqueous solutions.

4. Experimental

4.1. General considerations

Solvents were distilled prior to use. Complex **1** was prepared by the published procedure [21]. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data were collected on a Varian XL-300 spectrometer operating at 300, 75 and 121 MHz, respectively. Unless otherwise stated, spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H and $^{13}C\{^1H\}$ NMR. $^{31}P\{^1H\}$ NMR chemical shifts are reported relative to external 85% H_3PO_4, positive shifts representing deshielding. ES-MS were collected on a VG Platform MS8 and *m*/*e* are reported for the ^{90}Zr isotopomer. IR spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analyses were done by Campbell Microanalysis Services, University of Otago, Dunedin.

4.2. Speciation of *1* in H_2O, D_2O and CD_3CN solutions by ^{31}P NMR spectroscopy

In a typical NMR experiment, **1** (2.5 mg) was dissolved in the solvent (0.6 mL) to give a 10^{-2} M solution in Zr. H_2O solutions were locked with a D_2O insert. A 10 s delay was used to ensure accurate determination of integrals. The results for a variety of solvent mixtures are given in Table 1.

4.3. Reactions of *1* followed by ^{31}P NMR spectroscopy

(a) Addition of one half equivalent of NaOH(aq) gave only peaks at δ 34.4 and 33.1 in the ratio 1:1.6.
(b) Addition of one equivalent of $AgNO_3(aq)$ immediately gave a white precipitate of AgCl. The ^{31}P resonances were unchanged.
(c) Addition of one equivalent of $HClO_4(aq)$ gave an immediate precipitate with loss of the ^{31}P resonances of the dinuclear complexes while the resonance due to $[(bcep)Zr(H_2O)_2]^{2+}$ was unchanged.
(d) Addition of NaCl broadens the resonance of the diaqua dication while the other resonances are unaffected: $[Zr] = 1.4 \times 10^{-2}$; $[Cl^-]$ ($w_{1/2}$): 2.8×10^{-2} M (6 Hz), 5.4×10^{-2} M (8 Hz), 16.8×10^{-2} M (14 Hz), 60×10^{-2} M (27 Hz), 120×10^{-2} (60 Hz).

4.4. Speciation and reactions of *1* in CH_3CN/H_2O solutions by ES-MS

In a typical experiment, a dilute solution of the reagent was added to 10^{-4} M solutions of **1** in 1:1 CH_3CN/H_2O. The reagents and results are summarised in Table 3.

4.5. Preparation of $[PhP(CH_2CH_2C_5H_4)_2ZrF]BPh_4$ (*9*)

Complex **1** (0.0339 g, 0.0745 mmol) was dissolved in water and HCl(aq) (0.55 mmol) added after the complex had dissolved. One equivalent of NaF (1 mL of a 0.0313 g/10 mL solution, 0.0745 mmol) was slowly added and the solution stirred at ambient temperature for 1 h. $^{31}P\{^1H\}$ NMR (H_2O): δ 27.3 (d, $^2J_{PF} = 62$ Hz) (s). An aqueous solution of $NaBPh_4$ (0.0291 g, 0.0850 mmol) was slowly added to give immediately a white precipitate, this was stirred for 1 h before collection by filtration and drying in air to give 0.050 g (93% yield) of **9**. ^1H NMR (CD_3CN): δ 7.75 (m, 3H, Ph), 7.52 (m, 2H, Ph), 7.27 (m, 8H, BPh_4^-), 6.98 (t, $J = 7.5$ Hz, 8H, BPh_4^-), 6.83 (t, $J = 7.2$ Hz, 4H, BPh_4^-), 6.53 (m, 2H, Cp), 6.20 (m, 2H, Cp), 6.13 (m, 2H, Cp), 5.97 (m, 2H, Cp), 3.2–2.7 (m, 8H, CH_2); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 137.0 (s, BPh_4^-), 133.7 (d, $J_{PC} = 9$ Hz, Ph), 132.3 (s, Ph), 130.1 (d, $J_{PC} = 9$ Hz, Ph), 126.7 (m, BPh_4^-), 123.7 (s, Cp), 122.9 (s, BPh_4^-), 113.0 (s, Cp), 111.9 (s, Cp), 104.3 (s, Cp), 32.7 (d, $^1J_{PC} = 23$ Hz, PCH_2), 25.5 (d, $^2J_{PC} = 11$ Hz, PCH_2CH_2), (*i*-Ph and *i*-Cp not observed); $^{31}P\{^1H\}$ NMR (CD_3CN): δ 24.3 (d, $^2J_{PF} = 55$ Hz). *Anal.* Calc. for $C_{44}H_{41}BFPZr$: C, 73.22; H, 5.73. Found: C, 72.41; H 5.59%.

4.6. Attempted preparation of (bcep)ZrF_2 (**10**)

Complex **1** (0.015 g, 0.033 mmol) was dissolved in D_2O and one equivalent of NaF added (1.4 mg, 0.033 mmol). The ^{31}P resonance at 32.77 ppm, assigned as the dication **2**, rapidly disappeared with the formation of a doublet due to the monofluoro complex **9** and a small doublet of doublets at 18.31 ppm ($^2J_{PF} = 95$ and 84 Hz), assigned as the difluoro complex **10**. This doublet of doublets disappeared after several minutes as the resonances due to the dinuclear complexes **3** and **4** slowly converted to that of **9**. Addition of a second equivalent of NaF rapidly gave an insoluble white precipitate and resonances consistent with the oxide of the free ligand (^{31}P NMR: δ 40.28, 40.12 and 39.96 in a ratio of 1:2:1).

4.7. Preparation of $PhP(CH_2CH_2C_5H_4)_2ZrSO_4$ (**11**)

Complex **1** (0.011 g, 0.024 mmol) was dissolved in aqueous HCl (3 mL of 0.1 M HCl). After 20 min, Na_2SO_4 (0.0034 g, 0.024 mmol) was added. Over several minutes, small colourless plates of the product **11** appeared (0.01 g, 87%). The product was found to be insoluble in common solvents. IR (KBr) (cm^{-1}): 1263 (s), 1155 (s) 935 (s), 918 (s). *Anal.* Calc. for $C_{20}H_{21}O_4PSZr$: C, 50.08; H, 4.41. Found: C, 50.06; H, 4.62%.

4.8. Potentiometry experiments

Dissolution of complex **1** (0.227 g, 0.5 mmol) in H_2O (50 mL) to give a 10^{-2} M solution was followed by pH measurement. Total dissolution occurred within 10 min and a stable pH reading (pH 3.3) was obtained after about 30 min. Neutralisation required two equivalents of NaOH(aq) with a white precipitate forming at this pH (7–8). Attempts to follow the dissolution process or to measure chloride-ion equilibria using a chloride-ion selective electrode were prevented by chronic electrode fouling.

4.9. Crystal structure determination

X-ray crystallographic data for **11** were collected from a single crystal sample which was mounted on a glass fibre. Data were collected using an APEX-II diffractometer equipped with a Bruker SMART CCD area detector (using the program SMART [26]). Processing was carried out by use of the program SAINT [26] which applied Lorentz and polarisation corrections to three-dimensionally integrated diffraction spots. The program SADABS [26] was utilised for the scaling of diffraction data, the application of a decay correction, and empirical absorption correction based on redundant reflections. The structure was solved by the direct methods procedure [27] and refined by least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as riding contributors, at calculated positions with isotropic thermal parameters based on the attached carbon atom. Crystal data and structure refinement parameters are given in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 299554. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web: http://www.ccdc.cam.ac.uk.

Acknowledgements

We thank Professor Brian K. Nicholson, University of Waikato, for assistance with the ES-MS work and Dr. Cees Lensink, Industrial Research Laboratories, Lower Hutt, New Zealand, for the TGA/DSC results.

References

[1] (a) P. Binger, S. Podabrin, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 439 (Chapter 7);
(b) E.J. Ryan, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 465 (Chapter 8);
(c) E.J. Ryan, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 483 (Chapter 9);
(d) E. Hey-Hawkins, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 501 (Chapter 10);
(e) S. Gambarotta, J. Jubb, J. Song, D. Richeson, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 543 (Chapter 11);
(f) A.S. Guran, R.F. Jordan, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier, 1995, p. 589 (Chapter 12).
[2] C. Qian, J. Guo, C. Ye, J. Sun, P. Zheng, J. Chem. Soc. D (1993) 3441.
[3] K.-H. Thiele, Ch. Schliessburg, B. Neumüller, Z. Anorg. Allg. Chem. 621 (1995) 1106.
[4] (a) For examples, see: U. Siemeling, Chem. Rev. 100 (2000) 1495;
(b) D.W. Macomber, W.P. Hart, M.D. Rausch, Adv. Organomet. Chem. 21 (1982) 1;
(c) N.J. Coville, K.E. du Plooy, W. Pickl, Coordin. Chem. Rev. 116 (1992) 1;

(d) P.J. Shapiro, Coordin. Chem. Rev. 231 (2002) 67;
(e) C. Qian, Z. Xie, Y. Huang, J. Organomet. Chem. 323 (1987) 285;
(f) J. Gräper, R.D. Fischer, G. Paolucci, J. Organomet. Chem. 471 (1994) 87;
(g) C. Qian, D. Zhu, J. Chem. Soc. D (1994) 1599;
(h) G. Paolucci, F. Ossola, M. Bettinelli, R. Sessoli, M. Benetollo, G. Bombieri, Organometallics 13 (1994) 1746;
(i) T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, A. Woltermann, Angew. Chem., Int. Ed. Engl. 19 (1980) 328;
(j) T. Kauffmann, J. Ennen, K. Berghus, Tetrahedron Lett. 25 (1984) 1971.
[5] (a) T. Mizuta, T. Yamasaki, H. Nakazawa, K. Miyoshi, Organometallics 15 (1996) 1093;
(b) D. Seyferth, H.P. Withers, Organometallics 1 (1982) 1275;
(c) T. Mizuta, M. Onishi, K. Miyoshi, Organometallics 19 (2000) 5005;
(d) C.H. Honeyman, T.J. Peckham, J.A. Massey, I. Manners, J. Chem. Soc., Chem. Commun. (1996) 2589;
(e) C.H. Honeyman, D.A. Foucher, F.Y. Dahman, R. Rulkens, A.J. Lough, I. Manners, Organometallics 14 (1995) 5503;
(f) H.P. Withers, D. Seyferth, J.D. Fellmann, P.E. Garrou, S. Martin, Organometallics 1 (1982) 1283;
(g) T.J. Peckham, A.J. Lough, I. Manners, Organometallics 18 (1999) 1030;
(h) A.G. Osborne, R.H. Whiteley, R.E. Meads, J. Organomet. Chem. 193 (1980) 345;
(i) H. Stoeckli-Evans, A.G. Osborne, R.H. Whiteley, J. Organomet. Chem. 194 (1980) 91;
(j) I.R. Butler, W.R. Cullen, S.J. Rettig, Organometallics 6 (1987) 872.
[6] (a) J.H. Shin, B.M. Bridgewater, G. Parkin, Organometallics 19 (2000) 5155;
(b) N. Leyser, K. Schmidt, H.-H. Brintzinger, Organometallics 17 (1998) 2155;
(c) J.H. Shin, T. Hascall, G. Parkin, Organometallics 18 (1999) 6;
(d) C.J. Schaverien, R. Ernst, W. Terlouw, P. Schut, O. Sudmerijer, P.H.M. Budzelaar, J. Mol. Catal. A: Chem. 128 (1998) 245;
(e) H.G. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 127;
(f) G.K. Anderson, M. Lin, Organometallics 7 (1988) 2285.
[7] P. Barbaro, A. Togni, Organometallics 14 (1995) 3570.
[8] O.J. Curnow, G. Huttner, S.J. Smail, M.M. Turnbull, J. Organomet. Chem. 524 (1996) 267.
[9] K. Doppert, Naturwissenschaften 77 (1990) 19, and references therein.
[10] W. Lasser, U. Thewalt, J. Organomet. Chem. 302 (1986) 201.
[11] U. Thewalt, W. Lasser, J. Organomet. Chem. 276 (1984) 341.
[12] W. Lasser, U. Thewalt, J. Organomet. Chem. 311 (1986) 69.
[13] W. Lasser, U. Thewalt, J. Organomet. Chem. 275 (1984) 63.
[14] U. Thewalt, K. Döppert, W. Lasser, J. Organomet. Chem. 308 (1986) 303.
[15] H. Aslan, S.H. Eggers, R.D. Fischer, Inorg. Chim. Acta 159 (1989) 55.
[16] S. Klima, U. Thewalt, J. Organomet. Chem. 354 (1988) 77.
[17] M. Niehues, G. Erker, O. Meyer, R. Fröhlich, Organometallics 19 (2000) 2813.
[18] J.H. Toney, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 947.
[19] (a) B.N. Patra, M. Bhattacharjee, J. Poly. Sci., Part A: Poly. Chem. 43 (2005) 3707;
(b) B.N. Patra, M. Bhattacharjee, J. Poly. Sci., Part A: Poly. Chem. 43 (2005) 3797.
[20] G.L. Hillhouse, J.E. Bercaw, J. Am. Chem. Soc. 106 (1984) 5472.
[21] J.R. Butchard, O.J. Curnow, S.J. Smail, J. Organomet. Chem. 541 (1997) 407.
[22] C. Balzarek, T.J.R. Weakley, L.Y. Kuo, D.R. Tyler, Organometallics 19 (2000) 2927.
[23] P.J. Desrosiers, R.S. Shinomoto, T.C. Flood, J. Am. Chem. Soc. 108 (1986) 7964.
[24] Q.-F. Zhang, T.C.H. Lam, X.-Y. Li, E.Y.Y. Chan, W.-Y. Wong, H.H.Y. Sung, I.D. Williams, W.-H. Leung, Chem. Eur. J. 11 (2005) 101.
[25] Y.-L. Fu, Z.-W. Xu, J.-L. Ren, S.W. Ng, Acta Crystallogr. E 61 (2005) 1520.
[26] APEX-II v 2.02, SMART, XPREP, SAINT, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
[27] SHELXTL v 6.12, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.