Synthesis and structural characterisation of the novel metallasiloxane compound [Cp$_2^*$ ZrOSiPh$_2$OLiOH]$_2$ [1]

Isaac Abrahams, Charlotte Simon, Majid Motevalli, Syed A.A. Shah, Alice C. Sullivan *

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

Abstract

The reactions between Cp$_2$ZrCl$_2$ or Cp$_2^*$ ZrCl$_2$ with in situ generated Ph$_2$Si(OLi)$_2$ gave unexpected dimeric cyclozirconasiloxane products incorporating LiOH within the chelate-bridging unit OSiPh$_2$OLi(OH). The crystal structure of [Cp$_2^*$ ZrOSiPh$_2$OLiOH]$_2$ is reported and the origin of the LiOH discussed.

Keywords: Silicon; Zirconium; Metallasiloxane; Cyclopentadienyl; Metallocene; Crystal structure

1. Introduction

There has been considerable recent interest in the chemistry and applications of metallasiloxane compounds having α,ω-siloxanediolate ligands (see Ref. [1] and references cited therein). In this regard a number of complexes (some showing catalytic activity for olefin polymerisation) containing cyclopentadienyl (η^5-C$_5$H$_5$, Cp, and η^5-C$_5$Me$_5$, Cp*, groups) and α,ω-siloxane-diolate ligands have recently been structurally characterised. A number of these compounds incorporate the diorganosilanediolate dianion R$_2$SiO$_2^{2-}$, and this usually adopts a bridging mode in these compounds; examples include [CpClTiOSiR$_2$O]$_2$ R = ^{t}Bu, Ph, [2] and [Cp$_2$MOSiPh$_2$O]$_2$ M = Zr, Hf [3], with eight-membered dimetallasiloxane rings. The zirconium and hafnium compounds were isolated on treatment of the metallocene dichlorides with the diol Ph$_2$Si(OH)$_2$.

2. Results and discussion

We report here on the outcome of the reactions between Cp$_2$ZrCl$_2$ or Cp$_2^*$ ZrCl$_2$ with in situ generated

Ph$_2$Si(OLi)$_2$. The diolate ligand Ph$_2$SiO$_2^{2-}$ is not always transferred intact to target metal centres and the outcome varies with combination of target metal and diolate reagent used, e.g. [Cp$_2$MOSiPh$_2$O]$_2$ M = Zr, Hf [3] from Cp$_2$ZrCl$_2$ and the diol Ph$_2$Si(OH)$_2$, [Ti(O(SiPh$_2$O)$_4$)$_2$] from Ph$_2$Si(OH)$_2$ and [Ti(OPri)$_4$] [4], or [Ba$_3$(O(SiPh$_2$O)$_2$)$_3$] from Ba–NH$_3$ and Ph$_2$Si(OH)$_2$ [5]. However, we found that changing the reagent from Ph$_2$Si(OH)$_2$ to Ph$_2$Si(OLi)$_2$ affected the outcome of reaction with Cp$_2$ZrCl$_2$ or Cp$_2^*$ ZrCl$_2$ in an unexpected way. In these cases, products incorporating LiOH as a component part of the cyclozirconasiloxane were isolated from the reaction between Cp$_2$ZrCl$_2$ or Cp$_2^*$ ZrCl$_2$ and Ph$_2$Si(OLi)$_2$. A dimeric structure [Cp$_2^*$ ZrOSiPh$_2$OLiOH]$_2$ (Fig. 1) having LiOH as a component part of the cyclozirconasiloxane ring structure was confirmed by X-ray crystallography. The product from the reaction between Cp$_2$ZrCl$_2$ and Ph$_2$Si(OLi)$_2$ is likely to adopt a similar structure [Cp$_2$ZrOSiPh$_2$OLiOH]$_2$, as evidenced by the presence of lithium (flame test) and similarities in the IR spectra; (its elemental analyses also agree with this formulation). The presence of LiOH was an unexpected novel feature. The manner in which the LiOH is formed is not clear. Partial hydrolysis of any of the starting materials Cp*ZrCl$_2$, BuLi or in situ generated Ph$_2$Si(OLi)$_2$ would give hydroxide, but standard precautions were taken to prevent this. The precise nature of species formed when Ph$_2$Si(OH)$_2$ is treated with two equivalents of BuLi is

not known, but we have found that this reaction is invariably accompanied by precipitation of some insoluble (in water as well as hydrocarbons, including ethers) white powders. The IR spectra of this material was indicative of a Ph_2SiO-containing species and the poor solubility suggests oligomers $[Ph_2SiO]n$ with $n > 4$. It may be that this oligomerisation on lithiation of the diol $Ph_2Si(OH)_2$, is accompanied by formation of LiOH.

3. Crystal structure of [Cp$_2^*$ZrOSiPh$_2$OLiOH]$_2$

The structure of (1) is shown in Fig. 1 with selected bond lengths and angles in Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Thus we have a dimeric arrangement of [Cp$_2^*$ZrOSiPh$_2$OLiOH]$_2$ comprising a tricyclic core consisting of two outer six-membered lithiozirconasiloxane rings fused to an inner four-membered lithiooxane ring. The geometry at silicon is close to tetrahedral, while that at zirconium is very distorted tetrahedral and that at lithium distorted trigonal. The atoms in each ring are relatively coplanar (maximum deviation in the six-membered rings is centred on O(3) at 0.3083 Å). The angle between the six-membered rings and the central Li$_2$O$_2$ plane is 5.20°, indicating that the three rings are relatively co-planar. All the bond distances and angles within the six- and four-membered rings are within previously measured ranges. The Si—O distance Si(1)–O(Li) 1.574(4) Å is significantly lower than Si(1)–O(Zr) 1.642(4) Å. The Cp* rings are stag-

gered with respect to one another with Cp*-centroid–Zr(1)–Cp*-centroid 134.84°, which is slightly smaller than the corresponding angles in Cp$_2^*$ZrCl(OH) 137.9° [6] and Cp$_2^*$Zr(OH)$_2$ 137.6° [6] in the solid state structure. Other examples of cyclopentadienyl zirconium hydroxide complexes include Cp$_2^*$ZrCl(OH) [6], Cp$_2^*$Zr(OH)$_2$ [6], [Cp$_2$Zr(μ-OH)(H$_2$O)$_6$]$^{4+}$ [7], [Cp*ZrCl]$_3$O-(OH)$_4$ · 2THF [8] and [CpZr(NO$_3$)$_2$(μ-OH)]$_2$ · 2THF [9]. The hydroxy groups are either terminal or bridging two zirconium atoms in these compounds.

The ^{1}H NMR spectrum of [Cp$_2^*$ZrOSiPh$_2$OLiOH]$_2$ shows a multiplet in the Cp*Me region. The methyl groups would indeed be expected to show magnetic inequivalence if apparent steric constraints (reflected by small Cp*-centroid–Zr(1)–Cp* angles) in the solid state structure of (1) impose some stereochemical rigidity on the structure in solution. It is noteworthy that the related compound [Cp$_2$ZrOSiPh$_2$OLiOH]$_2$ shows a single peak in the ^{1}H NMR spectrum for the cyclopentadienyl protons, indicating stereochemical non-rigidity in that case.

4. Experimental

Standard Schlenk techniques were employed throughout. NMR spectra were recorded on GE 300 and Bruker WH250 spectrometers. IR spectra were recorded on a PE 1720X FT instrument. Microanalyses were obtained from the service at University College London.
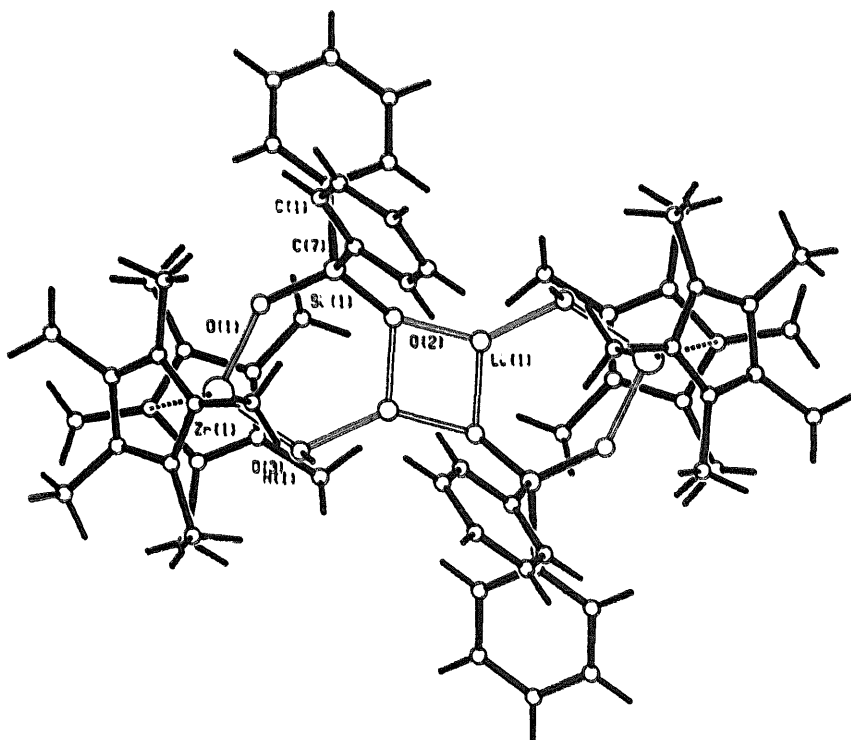

Fig. 1. Molecular structure of [Cp$_2^*$Zr(OSiPh$_2$OLiOH)]$_2$.

4.1. Preparation of [Cp$_2^*$Zr{OSiPh$_2$OLiOH}]$_2$

A stirred solution of diphenylsilanediol (0.36 g, 1.6 mmol) in THF (20 cm^3), was treated at 0°C with *n*-butyllithium (1.23 cm^3 of a 2.7 mol dm^{-3} solution in hexanes; 3.32 mmol), followed by Cp$_2^*$ZrCl$_2$ (0.72 g, 1.66 mmol) in toluene (20 cm^3). The resulting mixture was stirred 12 h, after which the volatile solvents were removed under vacuum and the pale yellow residue treated with toluene (30 cm^3). The filtered toluene solution was concentrated to (ca. 15 cm^3) and colourless crystals (0.3 g, 30%) of (**1**) were deposited on standing at room temperature. M.p. 245°C dec. Found: C, 62.75; H, 6.87. C$_{64}$H$_{82}$Li$_2$O$_6$Si$_2$Zr$_2$. Calc.: C, 64.06; H, 6.88%.

^{1}H NMR (C$_7$D$_8$, 298 K) δ 1.70–1.90(m, 30H, Cp*Me), 7.22(m, 6H, Ph), 7.78(m, 4H, Ph). ^{7}Li NMR (C$_7$D$_8$ 298 K) δ 0.54 (s). IR (cm^{-1}, nujol) 3661w, 3443w, 1591w, 1429m, 1261s, 1115vs, 1018s, 954m,

Table 1
Selected bond lengths (Å) and angles (deg) for [Cp$_2^*$Zr{OSi-Ph$_2$OLiOH}]$_2$

Zr(1)–O(1)	1.994(3)
Zr(1)–O(3)	2.049(4)
Zr(1)–Cp(1) [a]	2.279
Zr(1)–Cp(2)	2.257
Si(1)–O(2)	1.574(4)
Si(1)–O(1)	1.642(4)
Si(1)–C(1)	1.898(3)
Si(1)–C(7)	1.911(4)
O(2)–Li(1)	1.793(10)
O(2)–Li(1')	1.843(9)
O(3)–Li(1')	1.963(10)
O(3)–H(01)	0.79(4)
Li(1)–O(2')	1.843(9)
Li(1)–O(3')	1.963(10)
Li(1)–Li(1')	2.31(2)
O(1)–Zr(1)–O(3)	96.1(2)
Cp(1)–Zr(1)–Cp(2)	134.84
O(2)–Si(1)–O(1)	112.4(2)
O(2)–Si(1)–C(1)	113.7(2)
O(1)–Si(1)–C(1)	106.5(2)
O(2)–Si(1)–C(7)	108.4(2)
O(1)–Si(1)–C(7)	111.4(2)
C(1)–Si(1)–C(7)	104.2(2)
Si(1)–O(1)–Zr(1)	141.0(2)
Si(1)–O(2)–Li(1)	149.6(4)
Si(1)–O(2)–Li(1')	123.7(4)
Li(1)–O(2)–Li(1')	78.8(4)
Li(1')–O(3)–Zr(1)	115.7(3)
Li(1')–O(3)–H(01)	95(3)
Zr(1)–O(3)–H(01)	124(3)
O(2)–Li(1)–O(2')	101.2(4)
O(2)–Li(1)–O(3')	137.5(5)
O(2')–Li(1)–O(3')	117.6(5)

[a] Ring centroid.
Symmetry transformations used to generate equivalent atoms (denoted by primes): − x + 1, y, − z + 1/2.

Table 2
Fractional atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters (Å^2 $\times 10^{-3}$) for [Cp$_2^*$Zr{OSiPh$_2$OLiCH}]$_2$

	x	y	z	U_{eq}
Zr(1)	3860(1)	3578(1)	3625(1)	36(1)
Si(1)	3986(1)	4087(2)	2146(1)	40(1)
O(1)	3716(1)	3944(4)	2750(1)	36(1)
O(2)	4517(1)	3535(5)	2244(2)	51(1)
O(3)	4582(1)	3977(4)	3684(2)	50(1)
Li(1)	5110(3)	3496(12)	2023(4)	46(3)
C(1)	3588(1)	3182(3)	1524(1)	44(2)
C(2)	3090(1)	3257(4)	1472(2)	55(2)
C(3)	2814(1)	2695(5)	976(2)	67(3)
C(4)	3037(2)	2059(5)	532(2)	76(3)
C(5)	3535(2)	1984(5)	584(2)	67(3)
C(6)	3811(1)	2545(4)	1080(2)	58(2)
C(7)	3998(1)	5947(3)	1884(1)	45(2)
C(8)	3590(1)	6684(4)	1661(2)	62(2)
C(9)	3635(2)	8024(4)	1467(2)	65(2)
C(10)	4086(2)	8627(4)	1496(2)	86(3)
C(11)	4493(2)	7890(4)	1719(2)	97(3)
C(12)	4449(1)	6550(4)	1913(2)	68(2)
C(13)	4045(2)	1390(8)	4247(3)	63(2)
C(14)	4276(2)	1256(8)	3785(3)	80(2)
C(15)	3966(3)	1061(7)	3304(3)	87(3)
C(16)	3479(3)	1191(7)	3459(4)	86(3)
C(17)	3541(2)	1444(7)	4064(3)	67(2)
C(18)	4327(4)	1437(11)	4896(4)	175(5)
C(19)	4809(3)	1048(11)	3799(6)	186(6)
C(20)	4018(4)	692(10)	2658(4)	191(5)
C(21)	2999(3)	1004(10)	3088(5)	268(5)
C(22)	3174(3)	1138(10)	4498(4)	164(4)
C(23)	3183(2)	4833(8)	3998(3)	64(3)
C(24)	3354(3)	5744(8)	3621(3)	65(2)
C(25)	3778(2)	6123(7)	3818(3)	60(2)
C(26)	3899(2)	5514(9)	4386(2)	78(3)
C(27)	3516(3)	4726(8)	4497(3)	71(2)
C(28)	2663(3)	4308(11)	3943(6)	163(5)
C(29)	3065(3)	6185(10)	3012(4)	136(4)
C(30)	4096(3)	7157(9)	3544(4)	129(4)
C(31)	4338(3)	5809(12)	4832(4)	201(5)
C(32)	3432(4)	4222(11)	5114(4)	180(4)

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

924s, 890s, 801s, 742m, 702m, 522m, 487m, 390m, 353m, 261w, 227s, 221s, 214m.

4.2. Preparation of [Cp$_2$Zr{OSiPh$_2$OLiOH}]$_2$

A compound with the above suggested formulation was isolated as colourless crystals from a reaction using Cp$_2$ZrCl$_2$ and in situ generated Ph$_2$Si(OLi)$_2$ in the manner described above. M.p. 265°C dec. Found: C, 57.62, H, 4.78. C$_{22}$H$_{21}$LiO$_3$SiZr. Calc.: C, 57.64, H, 4.62%.

^{1}H NMR (C$_7$D$_8$, 298 K) δ 5.98(s, 10H, CpH), 7.24(m, 6H, PhH), 7.78(m, 4H, PhH). IR(cm^{-1}, nujol) 3446w, 1590m, 1429m, 1261s, 1111s, 1017vs, 1004s, 994vs, 967m, 941s, 800m, 742m, 712m, 703m, 514m, 487m, 390m, 261w, 225m.

Table 3
Crystal data and structure refinement

Empirical formula	$C_{64}H_{82}Li_2O_6Si_2Zr_2$
Formula weight	1199.80
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	28.043(6)
b (Å)	9.763(2)
c (Å)	22.531(5)
α (deg)	90
β (deg)	97.13(3)
γ (deg)	90
Volume (Å^2)	6121(2)
Z	4
Density (calculated) (Mg m^{-3})	1.302
Absorption coefficient (mm^{-1})	0.428
$F(000)$	2512
Crystal size (mm^3)	$0.45 \times 0.53 \times 0.30$
Theta range for data collection (deg)	1.46 to 22.97
Index ranges	$-30 \leqslant h \leqslant 30$, $-2 \leqslant k \leqslant 10$, $-24 \leqslant l \leqslant 24$
Reflections collected	8648
Independent reflections	4208 ($R(int) = 0.0973$)
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4205/0/337
Goodness-of-fit on F^2	0.913
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0936$, $wR2 = 0.1666$
R indices (all data)	$R1 = 0.2065$, $wR2 = 0.1965$
Largest diff. peak and hole (e Å^{-3})	0.819 and -0.549

$R_1 = \Sigma \| F_o \| - \| F_c \| / \Sigma \| F_o \| = 0.0936$ (1905 reflections with $I > 2\sigma(I)$). $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

4.3. X-ray crystallography

Data were recorded on a CAD4 diffractometer operating in the ω–2θ scan mode. An empirical absorption correction (ψ-scan) was carried out (minimum trans. 68.13%; maximum trans. 98.26%). The structure was solved by Patterson methods (SHELXS-86) [10]. Refinement was carried out by full-matrix least squares analysis on F^2 (SHELXL-93) [11]. Crystal data are given in Table 3.

X-ray diffraction data were collected in triclinic symmetry. However, a clear relationship to a monoclinic C centred cell ($a = 28.043$, $b = 9.763$, $c = 22.531$ Å, $\beta = 97.13°$) was noted. The structure was solved in the monoclinic space group $C2/c$ (No. 15). On transformation to monoclinic symmetry several systematic absence violations were observed for the $C2/c$ space group, notably $-22\ 0\ 3$, $0\ 0\ -5$, and $0\ 0\ 5$. However, the majority of reflections obeyed the systematic absence criteria for $C2/c$, and the few violations observed may indicate a small degree of pseudo symmetry. The solution obtained in monoclinic $C2/c$ refined satisfactorily, and represents the best model for the average molecular structure. All non-hydrogen atoms were refined anisotropically. The hydroxyl proton was located on the difference map and refined with a fixed O–H distance.

References

[1] M. Motevalli, S.A.A. Shah and A.C. Sullivan, *J. Organomet. Chem.*, *492* (1995) 99 and references cited therein.

[2] F.-Q. Liu, H.-G. Schmidt, M. Noltemeyer, C. Freire-Erdbrugger, G.M. Sheldrick and H.W. Roesky, *Z. Naturforsch. Teil B:*, *47* (1992) 1085.

[3] E. Samuel, J.F. Harrod, M.J. McGlinchey, C. Cabestaing and F. Robert, *Inorg. Chem.*, *33* (1994) 1292; A.M. Piotrowski and E.I. Band, EP 0423 872 A2.

[4] M.B. Hursthouse and M.A. Hossain, *Polyhedron*, *3* (1984) 95.

[5] J. Darr, S.R. Drake, D.J. Williams and A.M.Z. Slawin, *J. Chem. Soc. Chem. Commun.*, (1993) 866.

[6] R. Bartolin, V. Patel, I. Munday, N.J. Taylor and A.J. Carty, *J. Chem. Soc. Chem. Commun.*, (1985) 456.

[7] L.M. Babcock, V.W. Day and W.G. Klemperer, *J. Chem. Soc. Chem. Commun.*, (1988) 5196.

[8] W. Lasser and U. Thewalt, *J. Organomet. Chem.*, *311* (1986) 69.

[9] W. Lasser and U. Thewalt, *J. Organomet. Chem.*, *275* (1984) 63.

[10] G.M. Sheldrick, *Acta Crystallogr. Sect. A:*, *46* (1990) 467.

[11] G.M. Sheldrick, SHELXL93, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.