Lipophilic Halogenozirconocene(III) Complexes: $[\{Zr[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2]$, $[NBu^n_4][Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$†

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Treatment of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ with Na–Hg in tetrahydrofuran (THF) affords the blue (X = Cl **2a** or Br) or green (X = I) crystalline complexes $[\{Zr[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}X)\}_2]$, with characteristic Zr^{III} ESR spectra (PhMe, 300 K) and exceptionally long (3.86–4.17 Å) Zr···Zr contacts; **2a** is susceptible to facile $Zr(\mu\text{-}Cl)_2Zr$ bridge-cleavage upon reaction with either a neutral (*e.g.* THF) or an anionic (*e.g.* Cl^-) nucleophile, as in its conversion into $[NBu^n_4][Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$.

We report the following novel contributions to zirconium(III) chemistry. (*i*) Crystalline, paramagnetic, dinuclear zirconocene(III) complexes $[\{Zr[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}X)\}_2]$ (X = Cl **2a**, Br **2b** or I **2c**) have been synthesised from $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ precursors (*e.g.* X = Cl **1**)[1] (i in Scheme 1). (*ii*) Nucleophilic bridge-cleavage addition reactions of **2a** have been demonstrated, including that (ii in Scheme 1) with Cl^- to generate the crystalline, paramagnetic zirconocenate(III) complex $[NBu^n_4][Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ **3**. (*iii*) The X-ray structures‡ of **1** (Fig. 1) and **2a** (Fig. 2) (with an exceptionally long ZrZr distance, but shorter than in **2b** or **2c**) are compared in the context of those of related compounds (Table 1); for each of complexes **1**, **2a** and **3** the metal centre has the same four ligands in its inner coordination sphere. (*iv*) Electron spin resonance (ESR) spectra of **2a**, **2b**, **2c** and **3** are compared with literature data (Table 2).

The +4 oxidation state is dominant for organic compounds of zirconium, although complexes in some lower states are also known; evidence for elusive paramagnetic Zr^{III} complexes has, until recently, rested largely on cyclic voltammetry and ESR spectroscopic data.[2] X-Ray structures appear to have been limited to two neutral mononuclear (1989), $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl]$[3] and $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)]$,[4] and twelve diamagnetic dinuclear[5] complexes.

$$[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2] \xrightarrow{\text{i}} [\{Zr[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2]$$

1; X = Cl (ref. 1)

2a; X = Cl, 50%, blue, m.p. 135–137 °C
2b; X = Br, 50%, blue, m.p. 175–176 °C
2c; X = I, 60%, green, m.p. 163–165 °C

$$\xrightarrow[X = Cl]{\text{ii}} [NBu_4][Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$$

3; 55%, brown, m.p. 146–147 °C

Scheme 1 *Reagents and conditions*: i, Na–Hg, THF, 0 to 20 °C, 1 to 3 h; then removal of THF and crystallisation from PhMe; ii, excess of $[NBu_4]Cl$, PhMe, 0 °C, 2 h. *Characterisation*: **1**, **2a**, **2b**, **2c**, and **3** are crystalline (satisfactory microanalytical results); for the X-ray structures of **1** and **2a**, see Figs. 1 and 2; for ESR data see Table 2.

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† No reprints available.

‡ *Crystal data* for **1**: $C_{22}H_{42}Cl_2Si_4Zr$, $M = 581.1$, orthorhombic, space group *Pbcn*, $a = 17.929(7)$, $b = 9.132(3)$, $c = 18.647(2)$ Å, $U = 3053.1$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $F(000) = 1216$, μ(Mo-Kα) = 6.9 cm^{-1}.

For **2a**: $C_{44}H_{84}Cl_2Si_8Zr_2$, $M = 1091.2$, triclinic, space group $P\bar{1}$(no. 2), $a = 13.400(3)$, $b = 14.553(6)$, $c = 16.631(7)$ Å, $\alpha = 75.82(3)$, $\beta = 81.32(3)$, $\gamma = 71.88(3)°$, $U = 2978.7$ Å^3, $Z = 2$, $D_c = 1.22$ g cm^{-3}, $F(000) = 1148$, μ(Mo-Kα) = 6.2 cm^{-1}.

Data were measured on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα-radiation, $\lambda = 0.71069$ Å. Intensities were measured for unique reflections with $2 < \theta < 25°$ **1** and $2 < \theta < 22°$ **2a**. Out of the 3056 **1** and 7287 **2a** unique reflections measured, 1697 **1** and 4674 **2a** reflections with $|F^2| > 2\sigma(F^2)$ for **1** and $|F^2| > 3\sigma(F^2)$ for **2a** were used in the refinement. The structures were solved by routine heavy atom methods and refined by full-matrix least-squares analysis with anisotropic temperatures for **1** and **2a**. Hydrogen atoms were held fixed at calculated positions. The weighting scheme was $w = 1/\sigma^2(F)$ and final residuals were $R = 0.055$, $R' = 0.066$ **1** and $R = 0.051$, $R' = 0.065$ **2a**. All calculations were carried out using an Enraf-Nonius SDP-plus program system.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

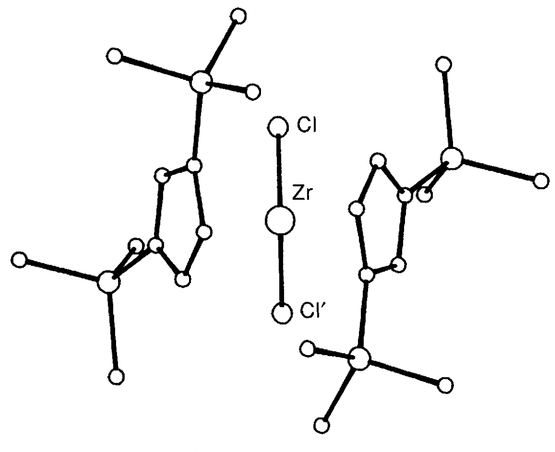

Fig. 1 X-Ray structure of $[Zr\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2Cl_2]$ **1**, with atom numbering scheme. Selected intramolecular bond angles (°) (see also Table 1): cent–Zr–cent 130.8, cent–Zr–Cl 104.5, cent–Zr–Cl′ 107.0 (cent = centroid of the cyclopentadienyl ring).

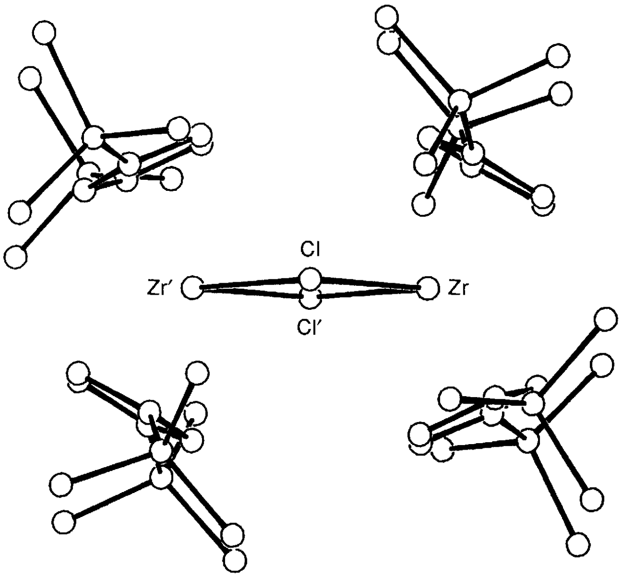

Fig. 2 X-Ray structure of $[\{Zr[\eta-C_5H_3(SiMe_3)_2-1,3]_2(\mu-Cl)\}_2]$ **2a**, with atom numbering scheme. Selected intramolecular bond lengths (Å) and angles (°) (see also Table 1): Zr(1)–Cl(1) 2.598(2), Zr(1)–Cl(1′) 2.596(2), Zr(1)–cent(1) 2.195, Zr(1)–cent(2) 2.216, Zr(2)–Cl(2) 2.609(2), Zr(2)–Cl(2″) 2.606(2), Zr(2)–cent(3) 2.202, Zr(2)–cent(4) 2.201; Cl(1)–Zr(1)–Cl(1′) 83.87(6), cent(1)–Zr(1)–cent(2) 131.0, Cl(2)–Zr(2)–Cl(2″) 81.67(6), cent(3)–Zr(2)–cent(4) 130.9.

The majority of the known Zr_2 complexes have had a $Zr(\mu-Cl)_2Zr$ core; alternative bridges have been $(\mu-PMe_2)_2$,[5c] $(\mu-Cl)(\mu-PMe_2)$,[5c] $(\mu-I)_2$,[5e,f] $(\mu-I)(\mu-\eta,\eta-C_5H_4-C_5H_4)$,[5f] $(\mu-SPh)(\mu-\eta,\eta-C_5H_4-C_5H_4)$[5g] and $(\mu-Cl)[\mu-P(CH_2CH_2-PMe_2)_2]$.[5h] Their $(d^1)_2$ electronic configuration provides one of the simplest models for study of the metal–metal bond (for MO calculations, see ref. 6). Single bonding was postulated for six cases (d_{ZrZr} 3.10 to 3.36 Å);[5a,b,d,h] in the remainder (d_{ZrZr} 3.42 to 3.67 Å), antiferromagnetic exchange or ligand-mediated superexchange was invoked to account for their diamagnetism. The paramagnetism of **2a** is attributed to its exceptionally long average d_{ZrZr}, 3.90 Å.

Sodium-amalgam reduction of $[Zr\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2Cl_2]$ **1** in tetrahydrofuran (THF) gave a red solution. Upon concentration, this became blue. Recrystallisation of the THF-free blue solid from toluene yielded $[\{Zr[\eta-C_5H_3(SiMe_3)_2-1,3]_2(\mu-Cl)\}_2]$ **2a**. Addition of THF to **2a** caused the red solution to be reformed. Likewise, addition of PMe_3 to **2a** produced a yellow solution, which upon concentration reverted to **2a**. These findings, together with ESR spectroscopic data (Table 2),[7] are attributed to the equilibrium in eqn. (1). The Zr–O and Zr–P bonds in the adducts **4** (L = THF) and **5** (L = PMe_3) are evidently quite weak, as further demonstrated by variable temperature ESR spectroscopic studies.

Table 1 Selected X-ray diffraction data on zirconocene dichlorides

Compound	Zr–Cl/Å	Cl–Zr–Cl/°	Ref.
1	2.426	98.50	This work
2a[a,b]	2.597	83.87	This work
	2.608	81.67	
3	2.56	85	[c]
$[Zr(\eta-C_5H_5)_2Cl_2]$	2.44	97	9
$[\{Zr(\eta-C_5H_5)_2\}_2(\mu-Cl)(\mu-PMe_2)]$	2.591	(95.5)[d]	5*c*
$[\{Zr(\eta-C_5H_5)(\mu-Cl)\}_2(\mu-\eta,\eta-C_5H_4-C_5H_4)]$[e]	2.578	100.00	5*b*

[a] The unit cell contains two independent dimers, both of which lie on an inversion centre; Zr···Zr 3.86 and 3.94 Å. [b] The unit cell of the corresponding bromide and iodide contains only one dimer: Zr···Zr 4.101(1) and 4.171(2) Å, respectively; *cf.* Zr···Zr in $[\{Zr(\eta-C_5H_5)_2(\mu-I)\}_2]$ 3.669(2) Å;[5e] Zr–Br–Zr 96.13(3); Zr–I–Zr 91.92(6). [c] Preliminary data. [d] This is Cl–Zr–P. [e] Zr–Zr 3.233 Å, Zr–Cl–Zr 77.6°.

Table 2 Anisotropic ESR spectra data on complexes **2a**, **2b**, **2c** and **3** in PhMe at 300 K and **4**, **5** and **6** in THF at 300 K

Compound	g_{ave}	$a(^{91}Zr)/G$	Ref.
2a	1.9506	22	This work
4	1.9775	23	7
5	1.9780(d)[a]	33	7
3[c]	1.9856	17	This work
2b	1.9448	45	This work
2c	1.9339	47	This work
6	1.9794(t)[b]		This work

[a] $a(^{31}P)$ 9 G. [b] $a(^{31}P)$ 17 G. [c] A complex assigned as containing the ion $[Zr\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2Cl_2]^-$, obtained by *in situ* electrolysis at 233 K in the cavity of an ESR spectrometer of the neutral Zr^{IV} precursor **1** in THF (0.5 mol dm^{-3} $[NBu_4][BF_4]$ as supporting electrolyte) had g_{ave} 1.976 and $a(^{91}Zr)$ 25.9 G.[10]

$$[\{Zr[\eta-C_5H_3(SiMe_3)_2-1,3]_2(\mu-Cl)\}_2] + 2L \rightleftharpoons 2\,[Zr\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2(Cl)(L)] \quad (1)$$

Complexes **2** have a potentially rich derivative chemistry, giving rise not only to adducts such as **4** or **5**, but also to substitution products. An example of the latter is in the reaction between **2a** and $[Li(THF)_n][C_6H_4\{P(SiMe_3)\}_2-1,2]$[8] to yield a complex believed to contain the anion $[\overline{Zr\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2[P}(SiMe_3)]_2C_6H_4-1,2\}]$ **6**, evidence for which rests on ESR data (Table 2). A further point of interest regarding complexes **2** is their kinetic stability, which contrasts with the propensity of less sterically hindered compounds such as $[\{Zr(\eta-C_5H_5)_2(\mu-X)\}_2]$ (X = Cl, Br or I) or $[\{Zr(\eta-C_5H_4Me)_2(\mu-Cl)\}_2]$ to disproportionate to the appropriate zirconocene(IV) halide and an unidentified (Zr^{II}?) coproduct.[5f]

The bond angles at the metal in the $Zr[\eta-C_5H_3(SiMe_3)_2-1,3]_2Cl_2$ unit of the three crystalline complexes **1**, **2a** and **3** (preliminary data) are essentially similar, with the two $[\eta-C_5H_3(SiMe_3)_2-1,3]$ rings being staggered rather than eclipsed, even in the dimer **2a**. The mean Zr–Cl bond length is significantly longer in the Zr^{III} complexes **2a** and **3** than in **1**. The mean Zr–Cl bond length of 2.426 Å in **1** may also be compared with the 2.423(3) Å for $[Zr(\eta-C_5H_3Bu^t_2-1,3)_2Cl]$ claimed as being the shortest Zr–Cl bond length;[3] although terminal Zr–Cl bond lengths of *ca.* 2.42 Å appear in the complexes $[Zr_2Cl_6L_4]$ [L = PR_3 or L_2 = ethylenebis(diphenylphosphine (dppe)].[5d] Details of the X-ray structures of **2b**, **2c** and **3** [as well as variable temperature magnetic measurements (with N. M. Edelstein, which are in progress)] will be published later.

We thank the SERC for the award of a studentship for E. J. R., IFP for providing leave of absence for H. O. and the SERC and the Leverhulme Trust for support.

Received, 18th November 1991; Com. 1/05851G

References

1 A. Antiñolo, M. F. Lappert, A. Singh, D. J. W. Winterborn, L. M. Engelhardt, C. L. Raston, A. H. White, A. J. Carty and N. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1987, 1463.

2 *Cf.* D. J. Cardin, M. F. Lappert and C. L. Raston, *Chemistry of Organo-zirconium and -hafnium Compounds,* Ellis Horwood, Chichester, 1986.

3 I. F. Urazowski, V. I. Ponomaryev, I. E. Nifant'ev and D. A. Lemenovskii, *J. Organomet. Chem.*, 1989, **368**, 287.

4 R. D. Rogers and J. H. Teuben, *J. Organomet. Chem.*, 1989, **359**, 41.

5 (*a*) J. H. Wengrovius, R. R. Schrock and C. S. Day, *Inorg. Chem.*, 1981, **20**, 1844; (*b*) S. Gambarotta and M. Y. Chiang, *Organometallics*, 1987, **6**, 897; (*c*) M. Y. Chiang, S. Gambarotta and F. van Bolhuis, *Organometallics*, 1988, **7**, 1864; (*d*) F. A. Cotton, M. P. Diebold and P. A. Kibala, *Inorg. Chem.*, 1988, **27**, 799; (*e*) Y. Wielstra, S. Gambarotta, A. Meetsma and J. L. de Boer, *Organometallics*, 1989, **8**, 250; (*f*) Y. Wielstra, S. Gambarotta, A. Meetsma and A. L. Spek, *Organometallics*, 1989, **8**, 2948; (*g*) Y. Wielstra, S. Gambarotta, A. Meetsma, A. L. Spek and W. J. Smeets, *Organometallics*, 1990, **9**, 2142; (*h*) P. G. Edwards, J. A. K. Howard, J. S. Parry and A-R. Al-Soudani, *J. Chem. Soc., Chem. Commun.*, 1991, 1385.

6 M.-M. Rohmer and M. Bénard, *Organometallics*, 1991, **10**, 157.

7 A. Antiñolo, M. F. Lappert, G. A. Lawless and H. Olivier, *Polyhedron*, 1989, **8**, 1882.

8 K. Issleib, H. Schmidt and E. Leissring, *J. Organomet. Chem.*, 1990, **382**, 53; Yin Ping, DPhil Thesis, University of Sussex, 1991.

9 K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290.

10 G. K. Campbell, M. F. Lappert and D. J. W. Winterborn, unpublished work cited in ref. 2, p. 282.