The Synthesis and *X*-Ray Structure of cp$Zr^{II}Cl(dmpe)_2$ [cp = Cyclopentadienyl, dmpe = Bis(dimethylphosphino)ethane] *via* the Reduction of cp$ZrCl_3$

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The Na reduction of cp$ZrCl_3$ (cp = cyclopentadienyl) in the presence of a slight excess of dmpe [dmpe = bis(dimethylphosphino)ethane] and a catalytic amount of naphthalene leads to the formation of cp$ZrCl(dmpe)_2$ (45% yield) whose structure has been determined by *X*-ray analysis.

The interest in the synthesis of bivalent zirconium derivatives has been stimulated by several surprising features (N_2 fixation,[1] oxidative addition reactions,[2] CO splitting,[3] olefin dimerization,[4] catalytic performances[5]) which are shown by Zr^{II} organometallic derivatives. Apart from the bis-cyclopentadienyl systems,[6] in which the absence of stabilizing ligands inevitably leads to involvement of the ligand in the reactivity of the metal centre,[7] the chemistry of low-valent zirconium is poorly known. In fact only a few Zr^{II} compounds are easily accessible[3,5,8] and this has been a serious handicap in developing the chemistry of these compounds.

Our interest in the synthetic aspects and in the reactivity of low-valent Zr led us to test the possibility of reducing cp$ZrCl_3$ (cp = cyclopentadienyl) in an attempt to find a general synthetic pathway to new Zr^{II} complexes. In a preliminary approach we have conveniently used a strongly electron-donating phosphine like bis(dimethylphosphino)ethane (dmpe) because of its well-known ability to stabilize the lowest oxidation states.[9]

$$\text{cpZrCl}_3 + 2\ \text{dmpe} + 2\ \text{Na} \xrightarrow{\text{Naphthalene}} \underset{(\mathbf{1})}{\text{cpZrCl(dmpe)}_2} \qquad (1)$$

According to reaction (1), a thf (tetrahydrofuran) solution of cp$ZrCl_3$ reacts with two equiv. of Na sand in the presence of a slight excess of dmpe and a catalytic amount of naphthalene, leading to the formation of (**1**) as light-brown, air sensitive crystals.† The structural analysis reveals that the crystal is composed of discrete monomeric molecules of cp$ZrCl(dmpe)_2$ (Figure 1).‡

The co-ordination around the metal can be described as slightly distorted octahedral with the cp ring centroid occupying the vertex *trans* to the chlorine atom. The Zr–cp centroid distance [2.177(9) Å] falls in the range expected for this moiety. The halide-metal distance [2.629(2) Å] is normal and no significant deviations from the linearity are observed for the vector Cl–Zr–cp centroid. The two chelating phosphines occupy the four equatorial positions of the octahedron. The Zr is above the plane individuated by the phosphorus atoms and its distance from the plane centre is 0.649(2) Å. The carbon atoms of the two dmpe ethylenic chains lie on the opposite sides of the P–Zr–P plane; C(9) and C(15) are above the plane [torsion angles P(1)–Zr–P(2)–C(9) 12.5(6)° and P(4)–Zr–P(3)–C(15) −9.4(3)°] and C(8) and C(14) below [torsion angles P(3)–Zr–P(4)–C(14) −16.5(3)° and P(2)–Zr–P(1)–C(8) 15.0(6)°]. Conformational disorder has been observed for the C(8) and C(9) atoms of one dmpe ligand. In fact, inverting their relative positions with respect to the P(1)–Zr–P(2) plane C(8) and C(9) can be transformed into C(8′) and C(9′) (33.1% occurrence probability), generating a new conformation in which two dmpe molecules are staggered. The new torsion angles are P(1)–Zr–P(2)–C(9′) −19.4(1)° and P(2)–Zr–P(1)–C(8′) −6.2(1)°. All the other bond lengths and angles are as expected.

The spectroscopic and analytical data are consistent with the solid state structure.§ The ^1H n.m.r. spectrum shows an

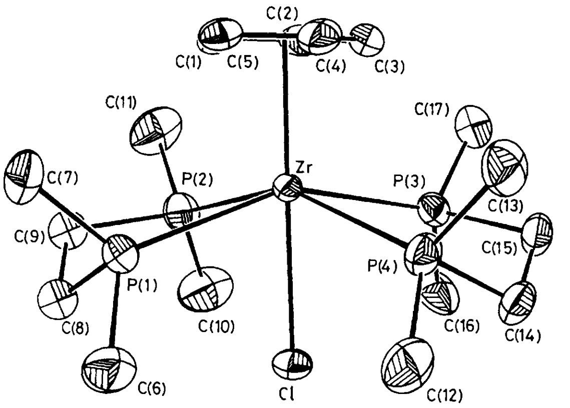

Figure 1. ORTEP view of complex (**1**). Selected bond distances (Å) and angles (°): Zr–P(1) 2.728(3), Zr–P(2) 2.692(3), Zr–P(3) 2.701(3), Zr–P(4) 2.710(3); P(1)–Zr–P(2) 74.9(1), P(3)–Zr–P(4) 74.7(1) (see ref. 10).

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† In a standard experiment, a colourless solution of 2.90 g of cp$ZrCl_3(thf)_2$ and 1 ml of neat dmpe in thf (100 ml), was stirred with 0.17 g of Na sand, in the presence of a catalytic amount of naphthalene. The resulting brown–reddish solution was filtered and concentrated to small volume (~20 ml). After addition of 50 ml of diethyl ether and standing two days at −30 °C, orange–brown crystals of (**1**) separated (45% yield). Another crop of crystals can be obtained from the mother liquor after further concentration and freezing.

‡ *Crystal data* for (**1**): $C_{17}H_{37}P_4ClZr$, $M = 492.05$, monoclinic, space group $P2_1/n$, $a = 10.284(5)$, $b = 13.922(5)$, $c = 17.260(6)$ Å, $\beta = 98.23(3)°$, $U = 446(2)$ Å^3, $Z = 4$, $D_c = 1.34$ g cm^{-3}. $F(000) = 1024$. Data were measured ($2\theta_{\text{max.}} = 114°$) on a Nicolet R3m diffractometer using Cu radiation ($\lambda = 1.54178$ Å) and scan ω. 2183 Independent reflections with [$I > 3\sigma(I)$] were used in the refinement corrected for the absorption [$\mu_{\text{calc.}} = 73.1$ cm^{-1}]. The structure was solved by a heavy-atom method and refined by least-squares methods. All atoms were located and refined anisotropically except C(8), C(9), which were refined isotropically. All the hydrogen atoms positions were calculated and refined isotropically. The final R value is 0.053 (R_w = 0.062), G.O.F. = 1.622. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ ^1H N.m.r. 90 MHz [$^2H_8$]toluene, 4.27 (5H, t, C_5H_5, J_{P-H} 1.8 Hz), 1.64—1.33 (8H, m, 4 × CH_2), 1.38 [12H, d, J_{P-H}, 1 Hz, 4 × Me, C(6)C(10)C(12)C(16)] 0.96 [12H, d, J_{P-H} 1 Hz, 4 × Me, C(7)C(11)C(13)C(17)]; electron impact mass spectrum, *m/z* 490 with the expected isotopic distribution pattern; i.r. (KBr, Nujol mull, cm^{-1}) 1460(m), 1420(s), 1492(s), 1270(s), 1105(m), 995(s), 938(vs), 920(vs), 882(s), 791(s), 718(s), 707(s), 688(s), 625(vs); satisfactory elemental (C, H, P, Zr) analyses were obtained.

unusual splitting of the H(cp) signal probably as a result of coupling with phosphorus (J_{P-H} 1.8 Hz) [H(cp)–P distance 2.881—3.163 Å]. This suggests that no rapid dissociation of dmpe occurs in solution.

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References

1 R. D. Senners, J. M. Manriquez, R. E. Marsch, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351 and references therein.
2 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, 1981, ch. 23.3, p. 610.
3 J. Blenkers, H. J. de Liefde Meijer, and J. H. Teuben, *Organometallics*, 1983, **2**, 1483.
4 S. Datta, M. B. Fisher, and S. S. Wreford, *J. Organomet. Chem.*, 1980, **188**, 352.
5 S. Datta, S. S. Wreford, R. P. Beatty, and T. J. McNeese, *J. Am. Chem. Soc.*, 1979, **101**, 1053; M. B. Fisher, E. J. Jones, T. J. McNeese, S. C. Nyburg, B. Posin, W. Wong-Ng, and S. S. Wreford, *ibid.*, 1980, **102**, 4941.
6 K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 2687; D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *ibid.*, 1981, **103**, 1265; A. Antinolo, M. F. Lappert, and D. J. W. Winterborn, *J. Organomet. Chem.*, 1984, **272**, C37.
7 H. H. Britzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1970, **92**, 6182; J. W. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Britzinger, *ibid.*, 1972, **94**, 1219.
8 H. O. van Oven, C. J. Groenenboom, and H. J. de Liefde Meijer, *J. Organomet. Chem.*, 1974, **81**, 379; G. N. Cloke, K. P. Cox, M. L. H. Green, J. Bashkin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1981, 117; G. Erker, K. Berg, C. Kruger, G. Müller, K. Angermund, R. Benn, and G. Schroth, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 455; L. Stahl, J. P. Hutchinson, D. R. Wilson, and R. D. Ernst, *J. Am. Chem. Soc.*, 1985, **107**, 5016.
9 B. M. Foxman, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, 1978, **17**, 2311.
10 J. O. Albright, S. Datta, B. Dezube, J. Kouba, D. Marynick, S. S. Wreford, and B. M. Foxman, *J. Am. Chem. Soc.*, 1979, **101**, 611.