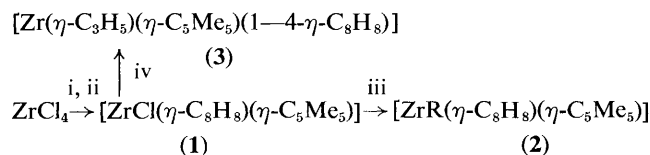


The Relative Stability of Cyclo-octatetraene Complexes of Zirconium(II) and Zirconium(IV); X-Ray Crystal Structure of $[\text{Zr}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(1\text{-}4\text{-}\eta\text{-C}_8\text{H}_8)]$

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Reaction of $[\text{ZrCl}(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)]$ (1) with MR (M = MgCl or Li; R = n-alkyl, aryl, vinyl, acetylide, and substituted allyl) affords the yellow zirconium(IV) species $[\text{ZrR}(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)]$ (2) whereas Mg(Cl)-(CH₂-CH=CH₂) gives the purple-black complex (3) shown by X-ray crystallography to be $[\text{Zr}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_3\text{Me}_5)(1\text{-}4\text{-}\eta\text{-C}_8\text{H}_8)]$, formally a derivative of zirconium(II).

Catalytically active transition-metal systems generally exhibit a facile interchange between oxidation states, and also a variable co-ordination number (or electron count). This behaviour is exemplified by certain of the platinum-group metals to which the group 4 elements Ti, Zr, and Hf show a superficial resemblance in their tendency to form 16-electron complexes.¹ However, examples of easy interchange between oxidation states are rare in group 4, particularly in the case of the much studied bis(cyclopentadienyl) complexes for which the +4 state is preferred. With the intention of creating a system delicately balanced between Zr^{II} and Zr^{IV} we have investigated complexes of the electronically ambivalent ligand cyclo-octatetraene which effects an implicit intramolecular oxidation-reduction on changing its co-ordination mode from the planar 1-8- η to, for instance, the commonly observed 1-4- η form.² We report here a series of apparently similar complexes which includes an example of 18-electron Zr^{IV} and an example of 16-electron Zr^{II}, indicating that the energy difference between them may be small.



Scheme 1. Reagents: i, K₂C₈H₈; ii, LiC₅Me₅; iii, MR (M = MgCl or Li; R = n-alkyl, aryl, vinyl, acetylide, and substituted allyl, e.g. Me, Et, Ph, 4-MeC₆H₄, CMe=CHMe, C=CMe, and C=CPh); iv, Mg(Cl)(CH₂CH=CH₂) in Et₂O.

Reaction of (1)³ (Scheme 1) with n-alkyl, aryl, vinyl, or acetylide Grignard or lithium reagents affords the corresponding derivative (2) in good yield (>60%). Complexes (2) are bright yellow, thermally stable crystalline materials for which an 18-electron configuration with planar $\eta\text{-C}_8\text{H}_8$ is proposed on the following grounds: (i) singlet resonances (¹H n.m.r., [²H₈]benzene or [²H₈]toluene) ascribed to co-ordinated C₈H₈ are observed in the range δ 5.72–5.96, downfield from free C₈H₈ measured under the same conditions (δ 5.63), thus implying increased aromaticity on co-ordination; (ii) 1-6- η - and 1-4- η -C₈H₈ complexes exhibit bands in the i.r. spectrum in the regions 1 660–1 680 and 1 500–1 575 cm⁻¹ respectively,^{3,4} attributed to the stretching of the unco-

ordinated C=C. No such bands are observed in complexes (2) which cannot be reasonably ascribed to the R group (e.g. R = aryl); and (iii) Zr^{IV} complexes of carbocyclic ligands are generally pale in colour, e.g. $[\text{ZrCl}_2(\text{C}_5\text{H}_5)_2]$ ¹ and $[\text{ZrCl}_2(\eta\text{-C}_8\text{H}_8)(\text{thf})]$,³ whereas those of Zr^{II} tend to be highly coloured, e.g. $[\text{Zr}(\text{dmpe})(\text{C}_8\text{H}_8)_2]$ ⁵ and $[\text{Zr}(\eta\text{-C}_8\text{H}_8)(1\text{-}4\text{-}\eta\text{-C}_8\text{H}_8)(\text{thf})]$ (thf = tetrahydrofuran; dmpe = 1,2-bisdimethylphosphinoethane).³ Thus the complexes (2) may be regarded as complexes of C₈H₈²⁻ and Zr^{IV}.

Similarly, the substituted allyl derivatives (2; R = CH₂CH=CHMe, CH₂CH=CHPh, and CH₂CMe=CH₂) share the same properties, and the spectroscopic evidence clearly favours a σ bonding mode for the allyl ligand {e.g. (2; R = CH₂CMe=CH₂), ν (C=C) 1 588 cm⁻¹; ¹H n.m.r., [²H₈]toluene, -80 °C δ 5.76 (s, 8H, C₈H₈), 4.84 and 4.58 (br ss, 2H, =CH₂), 1.84 (s, 3H, Me), 1.40 (s, 15H, C₅Me₅), and 0.88 (br s, 2H, Zr-CH₂). At 50 °C signals corresponding to a dynamic $\sigma\text{-C}_3\text{H}_4\text{Me}$ group are observed}.

In contrast, addition of Mg(Cl)(CH₂CH=CH₂) to (1) in diethyl ether gave a dark solution from which purple-black crystals of (3) were obtained. An intense absorption in the i.r. spectrum of (3) at 1 524 cm⁻¹ is indicative of an $\eta\text{-C}_3\text{H}_5$ group⁶ and a weaker absorption at 1 509 cm⁻¹ is assigned to the stretching of free double bonds of C₈H₈. Above -50 °C the ¹H n.m.r. pattern of the C₃H₅ group (AX₂) is typical of an η -allyl undergoing rapid *syn-anti* exchange {[²H₈]toluene, 30 °C, δ 6.67 (quintet, 1H, CH, J_{HH} 11 Hz), 5.52 (s, 8H, C₈H₈), $Z = 8$, $D_c = 1.40$ g cm⁻³, $F(000) = 1 552$, $\mu(\text{Mo-K}\alpha) = 6.08$ cm⁻¹. The structure was solved by heavy-atom methods from data collected at 210 K to $2\theta = 56^\circ$ on a Nicolet P3m diffractometer with monochromatised Mo-K α X-radiation. For the 2 303 observed reflections [$I \geq 2.5 \sigma(I)$], and with anisotropic thermal parameters for all non-hydrogen atoms, $R = 0.042$, $R' = 0.036$.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data for (3): C₂₁H₂₈Zr, $M = 371.7$, monoclinic, space group $A2/a$ (non-standard setting $C2/c$ No. 15), $a = 13.537(5)$, $b = 9.831(4)$, $c = 28.954(12)$ Å, $\beta = 113.78(3)^\circ$, $U = 3 526(3)$ Å³, $Z = 8$, $D_c = 1.40$ g cm⁻³, $F(000) = 1 552$, $\mu(\text{Mo-K}\alpha) = 6.08$ cm⁻¹. The structure was solved by heavy-atom methods from data collected at 210 K to $2\theta = 56^\circ$ on a Nicolet P3m diffractometer with monochromatised Mo-K α X-radiation. For the 2 303 observed reflections [$I \geq 2.5 \sigma(I)$], and with anisotropic thermal parameters for all non-hydrogen atoms, $R = 0.042$, $R' = 0.036$.

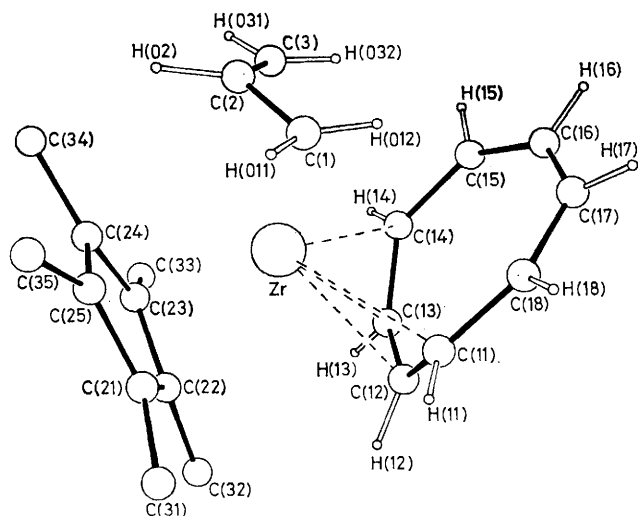


Figure 1. Molecular structure of $[\text{Zr}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(1\text{-}4\text{-}\eta\text{-C}_8\text{H}_8)]$. Methyl hydrogens have been omitted for clarity. Selected bond lengths (Å) are: Zr–C(11) 2.521(4), Zr–C(12) 2.386(5), Zr–C(13) 2.382(6), Zr–C(14) 2.540(6), C(11)–C(12) 1.404(7), C(12)–C(13) 1.401(7), C(13)–C(14) 1.418(6), C(14)–C(15) 1.444(6), C(15)–C(16) 1.360(8), C(16)–C(17) 1.413(8), C(17)–C(18) 1.372(7), C(18)–C(11) 1.441(6). Atoms C(15) and C(18) are >3.25 Å from the metal. The atom sequences C(11)–C(14) and C(14)–C(18), C(11) are each approximately coplanar and make an interplanar angle of *ca.* 150° .

The structure of (3) is illustrated in Figure 1, together with the atomic numbering system. The molecule has approximate (non-crystallographic) mirror symmetry with atoms Zr, C(2), C(22), and C(32) lying on the pseudo-mirror plane which also

bisects the bonds C(12)–C(13), C(16)–C(17), and C(24)–C(25). The metal is equivalently bonded to all three allyl carbon atoms [Zr–C(1) 2.467(6); Zr–C(2) 2.485(5); Zr–C(3) 2.488(5) Å] with allyl bond lengths of C(1)–C(2) 1.380(7) and C(2)–C(3) 1.388(9) Å. The pentamethylcyclopentadienyl ligand shows no significant deviation from idealized pentagonal geometry [mean C–C 1.418(7); mean C–Zr 2.510(5) Å]. The cyclo-octatetraene ligand is 1–4- η co-ordinated to the metal resulting in an overall 16-electron configuration for Zr. Atoms C(11) to C(14), co-ordinated to Zr, are separated by bonds of equal length, whereas the bonds between the unco-ordinated atoms of the C_8 ring are as expected for a free butadiene fragment.⁷

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