Carbon–Hydrogen Bond Activation by an Electron Deficient Bis(aryl)(cyclo-octatetraene)zirconium(IV) Complex: Stepwise Thermal Rearrangement of Bis(σ-mesityl)(η^8-cyclo-octatetraene)zirconium(IV) to a Complex containing a Bridging Mesityl, then a Bridging Alkylidene

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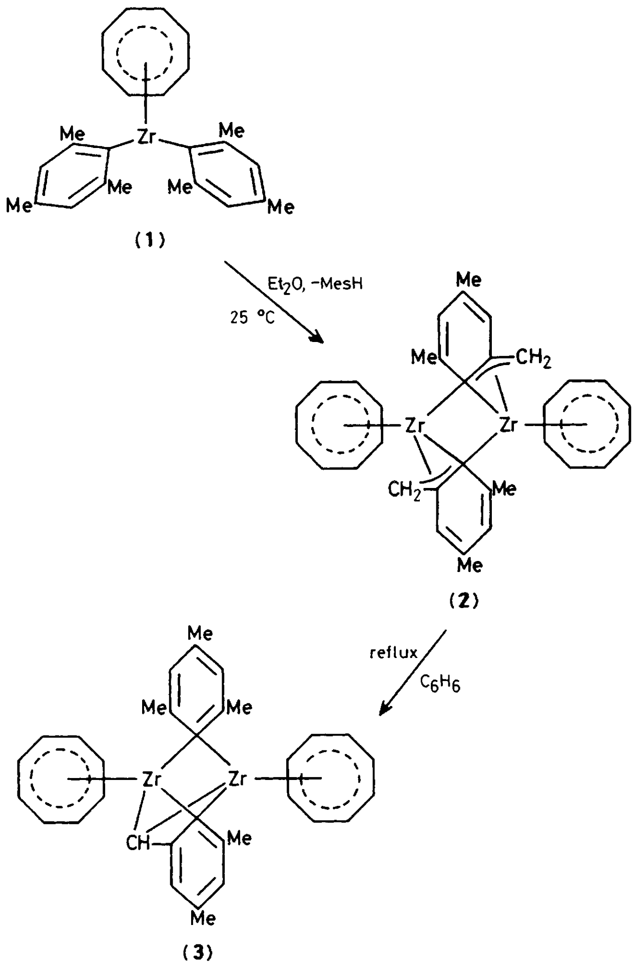
A stepwise thermal rearrangement of [(η^8-C_8H_8)Zr(Mes)$_2$] (Mes = 2,4,6-$Me_3C_6H_2$) led to the loss of mesitylene and to a dinuclear complex, [(η^8-C_8H_8)$_2$Zr(μ-2,4-Me_2-6$CH_2C_6H_2$)$_2$], containing two bridging η^3-benzylic groups, which further rearranged to a complex containing a bridging mesityl and a bridging alkylidene ligand, as shown by the *X*-ray analysis on both complexes.

Although few examples are so far available, it seems that highly unsaturated 'electrophilic' systems are particularly efficient in promoting the C–H bond activation either by an intra- or inter-molecular process.[1] In this context we report a fourteen electron complex of zirconium(IV) which may be the prototype of a new class of early transition metal compounds in high oxidation states suitable for C–H bond activation.

We succeeded in the preparation of a thermally labile bis(σ-mesityl)(η^8-cyclo-octatetraene)zirconium(IV) derivative, [(η^8-C_8H_8)Zr(Mes)$_2$] (Mes = 2,4,6-$Me_3C_6H_2$), which was fully characterized including *X*-ray analysis.[2–4] Complex (**1**), which is only stable for a long period at −20 °C either in the solid state or in solution, undergoes a stepwise thermal rearrangement which is particularly significant for the activation of C–H by an electrophilic electron-deficient metal. The thermal rearrangement of (**1**) is shown in Scheme 1. The transformation of (**1**) into (**2**) was achieved by keeping a Et_2O solution of (**1**) at room temperature for two days. Complex (**2**)



Scheme 1

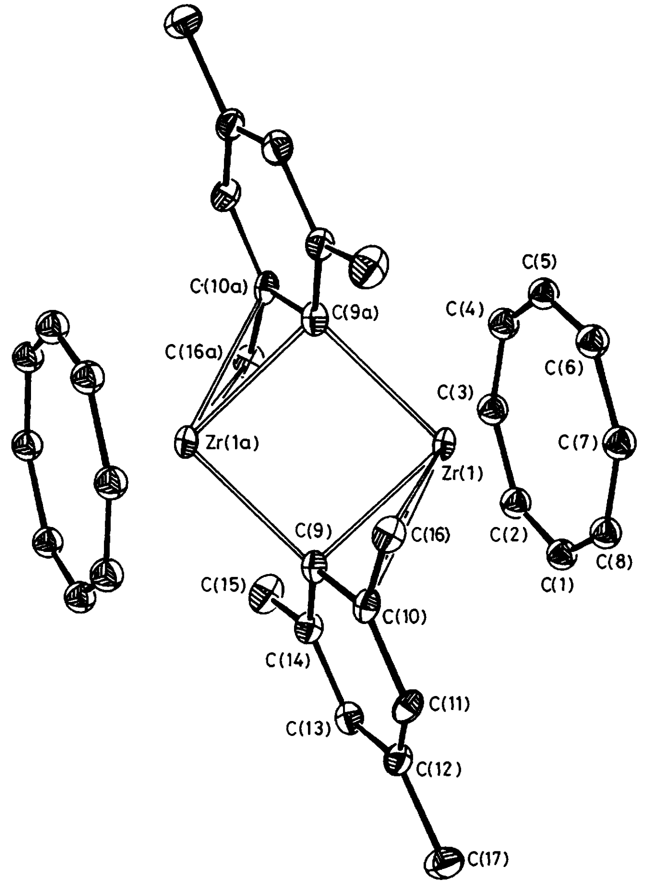


Figure 1. An ORTEP view of the dimer (**2**). Bond distances and angles are for molecule (1) in the unit cell. Bond distances (Å): Zr–C (C_8H_8) range from 2.460(8) to 2.503(11); Zr–C_8H_8 (centroid), 1.681(8); Zr(1)–C(16), 2.362(8); Zr(1)–C(10), 2.537(8), Zr(1)–C(9), 2.414(7); Zr(1)–C(9a), 2.433(6); C(9)–C(10), 1.452(8); C(10)–C(11), 1.416(10); C(11)–C(12), 1.352(10); C(12)–C(13), 1.402(9); C(13)–C(14), 1.383(10); C(9)–C(14), 1.414(9); C(10)–C(16), 1.442(9); C(12)–C(17), 1.519(12); C(14)–C(15), 1.518(9); Zr(1) · · · Zr(1a), 3.476(1). Bond angles (°): C(9)–Zr(1)–C(9a), 88.4(2); Zr(1)–C(9)–Zr(1a), 91.6(2).

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formed as green crystals (*ca.* 46%), and mesitylene was identified. The Zr–C (phenyl) bond undergoes an intramolecular metathesis reaction with the C–H bond of an ortho-methyl group of the other mesityl residue. The resulting monomeric unit dimerizes to the stable form (**2**). A related reaction is the thermolysis of $[cp_2Zr(Ph)_2]$ (cp = η^5-C_5H_5) leading to aryne complexes.[5] While (**2**) was stable at room temperature in the solid state and, even, in air, it undergoes a slow thermal rearrangement in refluxing benzene. Complex (**2**) rearranges in almost quantitative yield into complex (**3**) (*ca.* 60%), which crystallizes as brown crystals. Such a rearrangement requires a hydrogen shift between the two zirconium-bonded methylenes and gives a μ_2-alkylidene. An intramolecular hydrogen shift is very likely, though not yet proven. The structures of (**2**) and (**3**), which are in agreement with the analytical and ^{1}H and ^{13}C n.m.r. data,‡ were fully elucidated by an *X*-ray analysis.§ ORTEP drawings of complexes (**2**) and (**3**) are shown in Figures 1 and 2, respectively, with some selected bond distances and angles. Both compounds have a similar dimeric structure, where two (η^8-C_8H_8)Zr units are bridged by ligands derived from the original mesityl groups. The bridging bonding modes of the mesityl groups are responsible for the short zirconium–zirconium distances [Zr(1)Zr(1a), 3.476(1) Å in complex (**2**) and Zr(1)–Zr(2), 3.220(1) Å in complex (**3**)].[6] The Zr–C_8H_8 (centroid) distances are very close in both structures and similar to others reported for cyclo-octatetraene derivatives of zirconium.[3,7] The phenyl rings of the bridging ligands are almost parallel to the C_8H_8 mean plane in both compounds. The two zirconium atoms are bridged in the centrosymmetric structure of (**2**) by two pseudo-allyl ligands [C(9)–C(10)–C(16)] in a rather unusual bonding mode. The two C–C bond distances within the allyl ligands are very close [C(9)–C(10), 1.452(8); C(10)–C(16), 1.442(9) Å], while the sequence in the Zr–C bond distances is Zr(1)–C(9), 2.414(7); Zr(1)–C(10), 2.537(8); Zr(1)–C(16), 2.362(8) Å]. The bridging phenyl carbon is shared by the two zirconium atoms at almost the same distance [Zr(1)–C(9a), 2.433(6) Å]. The allyl bonding mode of the C(9), C(10), C(16) fragment accounts for the loss of aromaticity of the phenyl ring (see the C–C bond distances within the ring), and for the significant shortening of the C(10)–C(16) [1.442(9) Å] bond distance, compared with C(14)–C(15) [1.518(9) Å] and C(12)–C(17) [1.519(12) Å]. Compound (**2**) rearranges to (**3**) maintaining the same bonding mode of both phenyl rings. The singly bridging mesityl group binds zirconium at significantly longer distances [Zr(1)–C(26), 2.551(5) and Zr(2)–C(26), 2.465(7) Å] than the other mesityl group [Zr(1)–C(17), 2.332(6) and Zr(2)–C(17), 2.340(6) Å] because of its doubly bridging mode. The bridging alkylidene ligand binds zirconium at distances [Zr(1)–C(24), 2.226(5) and Zr(2)–C(24), 2.238(4) Å] which are significantly shorter than those of normal zirconium–alkyl bonds.[8] The only other well characterized μ_2-alkylidenes of zirconium are

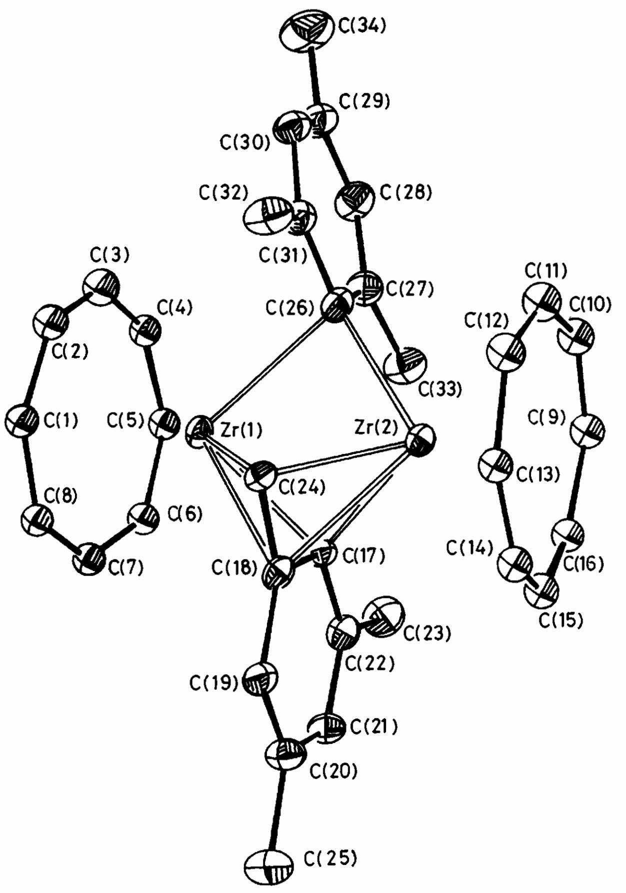

Figure 2. An ORTEP view of the dimer (**3**). Bond distances and angles are for molecule (1) in the unit cell. Bond distances (Å): Zr(1)–Zr(2), 3.220(1); Zr(1)–C(26), 2.551(5); Zr(2)–C(26), 2.465(7); Zr(1)–C(17), 2.332(6); Zr(2)–C(17), 2.340(6); Zr(1)–C(24), 2.226(5); Zr(2)–C(24), 2.238(4); Zr(1)–C(18), 2.546(6); Zr(2)–C(18), 2.535(5); C(18)–C(24), 1.427(8); Zr(1)–C_8H_8(centroid), 1.671(5); Zr(2)–C_8H_8(centroid), 1.679(5). Bond angles (°): Zr(1)–C(26)–Zr(2), 79.2(2); Zr(1)–C(24)–Zr(2), 92.3(1); Zr(1)–C(17)–Zr(2), 87.2(2); Zr(1)–C(18)–Zr(2), 78.7(2).

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‡ Complex (**2**): ^{1}H n.m.r. (δ, C_6D_6) 6.95 (s, 2H, Ph), 6.43 (s, 2H, Ph), 5.60 (s, 16H, C_8H_8), 2.84 (s, 6H, Me), 2.67 (d, 2H, CH_2, J_{CH} 7.5 Hz), 2.31 (s, 6H, Me), 2.22 (d, 2H, CH_2).

Complex (**3**): ^{1}H n.m.r. (δ, C_6D_6) 6.73 (s, 1H), 6.70 (s, 1H), 6.50 (s, 1H), 6.27 (s, 1H), 5.61 (s, 16H), 4.62 (s, 1H), 3.17 (s, 3H), 2.98 (s, 3H), 2.31 (m, 9H); ^{13}C-n.m.r. (δ, C_6D_6) 183.1 (CH), 128.3—117.6 (phenyl rings), 95.0 (C_8H_8), 31.3 (1Me), 27.9 (1Me), 24.2 (1Me), 22.5 (1Me), 21.7 (1Me).

Temperature variable spectra did not show any agostic interactions.

§ *Crystal data:* complex (**2**): $C_{34}H_{36}Zr_2$, M = 627.1, triclinic, space group $P\bar{1}$, a = 9.245(2), b = 10.311(2), c = 15.840(3) Å, α = 94.28(2), β = 106.40(1), γ = 109.97(2)°, U = 1336.6(5) Å^3, Z = 2, D_c = 1.56 g cm^{-3}, F(000) = 640, μ(Cu-K_α) = 75.09 cm^{-1} (λ = 1.54178 Å), crystal dimensions 0.13 × 0.39 × 0.36 mm. Intensities of 3343 reflections were measured at 298 K on a Nicolet R3m diffractometer using Cu-K_α radiation resulting in 2909 independent reflections. The structure was solved by the heavy atom method and refined by full-matrix least squares. All calculations were carried out using the SHELX-TL program. For 2907 unique observed reflections [$I > 2\sigma(I)$] the final R value is 0.046 (R_w = 0.055). There are two half-dimers in the asymmetric unit. The η^8-C_8H_8 ring in the first half-dimer is disordered, *i.e.* the site occupancy factor is 73.85% for C(1)–C(8), and 26.15% for C(1′)–C(8′). Structural data are referred to only one of two independent half-dimers, since the two have very close parameters.

Complex (**3**): $C_{34}H_{36}Zr_2$, M = 627.1, triclinic, space group $P\bar{1}$, a = 10.356(2), b = 16.444(3), c = 17.430(3) Å, α = 103.04(1), β = 92.29(1), γ = 103.84(1)°; U = 2793.8(8) Å^3, Z = 4, D_c = 1.49 g cm^{-3}, F(000) = 1280, μ(Cu-K_α) = 75.09 cm^{-1} (λ = 1.54178 Å), crystal dimensions 0.14 × 0.28 × 0.33 mm. Intensities of 7848 reflections were measured at 298 K on a Nicolet R3m diffractometer using Cu-K_α radiation resulting in 7528 independent reflections. The structure was solved by the heavy atom method and refined by full-matrix least squares. All calculations were carried out using the SHELX-TL program. For 5404 unique observed reflections [$I > 2\sigma(I)$] the final R value is 0.039 (R_w = 0.0484). There are two dimers in the asymmetric unit. Structural data are referred to only one of the two independent dimers, since the two have very close parameters.

Absorption corrections were applied for neither complex (**2**) nor (**3**). 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.

from the work of Schwartz *et al.*,[9] for which no structural information is available. Some additional significant distances in complex (**3**) are those between zirconium atoms and C(18) [Zr(1)–C(18), 2.546(6) and Zr(2)–C(18), 2.535(5) Å], which are close to those observed in the pseudo-allylic form for Zr–C(10) in complex (**2**). Such a proximity, in contrast with complex (**2**), does not affect the C–C bond distances in the phenyl ring.

These results emphasize the very promising organometallic chemistry of the highly unsaturated system derived from the (η^8-C_8H_8)M fragment.

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