Carbon–Hydrogen and Metal–Carbon Bond Formation and Breakage in Thermal Reactions of Bis(mesityl)(cyclo-octatetraene)zirconium(IV) Derivatives. Crystal Structures of $[Zr(\eta^8-C_8H_8)(mes)_2]$, $[\{Zr(\eta^8-C_8H_8)[\eta-OC(mes)_2]\}_2]$, $[\{Zr(\eta^8-C_8H_8)(\mu-2,4-Me_2-6-CH_2C_6H_2)\}_2]$, and $[\{Zr(\eta^8-C_8H_8)\}_2(\mu-mes)(\mu-2,4-Me_2-6-CHC_6H_2)]$ (mes = $2,4,6-Me_3C_6H_2$)†

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The reaction of $[Zr(\eta^8-C_8H_8)Cl_2(thf)]$, (**1**), with Mg(mes)Br (thf = tetrahydrofuran, mes = $2,4,6-Me_3C_6H_2$) in Et_2O afforded the very thermally labile complex $[Zr(\eta^8-C_8H_8)(mes)_2]$, (**2**). An *X*-ray analysis on complex (**2**) at 173 K gave insights on the possible stabilization of the hitherto unstable alkyl derivatives of (**1**), showing that the *o*-methyl groups protect the metal centre. The significant lability of the aryl ligand in complex (**2**) is shown by the facile double migration of the mes residue to CO forming $[\{Zr(\eta^8-C_8H_8)[\eta-OC(mes)_2]\}_2]$, (**3**). The carbonylation reaction has to be carried out at 0 °C, since complex (**2**) undergoes thermal decomposition at room temperature, the nature of which depends on the solvent used. In Et_2O complex (**2**) loses mesitylene at room temperature forming $[\{Zr(\eta^8-C_8H_8)(\mu-2,4-Me_2-6-CH_2C_6H_2)\}_2]$, (**7**). Complex (**7**) has a triple-decker type structure in which two allyl units, coplanar with the $\eta^8-C_8H_8$ rings, bridge the two zirconium atoms. Because of the allyl structure the aromaticity of the phenyl ring is lost. More drastic thermal conditions cause a hydrogen migration in (**7**) which rearranges to $[\{Zr(\eta^8-C_8H_8)\}_2(\mu-mes)(\mu-2,4-Me_2-6-CHC_6H_2)]$, (**8**), which contains an alkylidene ligand bridging two zirconium atoms. Complexes (**2**), (**3**), (**7**), and (**8**) were characterized by single-crystal *X*-ray analysis: (**2**), tetragonal, space group $I4_1/a$, $a = b = 26.495(4)$, $c = 13.711(2)$ Å, $Z = 16$, $R = 0.054$ for 2 468 independent observed reflections; (**3**), monoclinic, space group $C2/c$, $a = 25.856(9)$, $b = 12.444(3)$, $c = 15.571(8)$ Å, $\beta = 92.59(3)°$, $Z = 4$, $R = 0.112$ for 1 659 independent observed reflections; (**7**), orthorhombic, space group $Pbca$, $a = 7.831(1)$, $b = 19.368(2)$, $c = 18.177(2)$ Å, $Z = 4$, $R = 0.045$ for 949 independent observed reflections; (**8**), triclinic, space group $P\bar{1}$, $a = 16.469(3)$, $b = 17.452(3)$, $c = 10.373(2)$ Å, $\alpha = 92.35(1)$, $\beta = 103.83(2)$, $\gamma = 103.06(2)°$, $Z = 2$, $R = 0.041$ for 3 792 independent observed reflections.

The chemistry of the Zr–R functionality is largely attributable to the unsaturation at the metal centre,[1] even in compounds such as the 16-valence-electron (v.e.) complexes $[Zr(cp)_2R_2]$ (cp = $\eta^5-C_5H_5$). This unsaturation will determine to an extent the intramolecular reactivity of the alkyl or aryl group bonded to the metal, or the pre-co-ordination of a substrate preceding reaction with the M–C bond. The use of highly unsaturated metal centres enables the C–H functionality in the substituent of the R group to interact, and even to react, with the metal centre.[2] This was the reason for our interest in 14 v.e. zirconium organic derivatives. The C–H bond is susceptible to the attack either by electron-rich or by very electron-poor systems, and the latter is applicable to early transition metals in their highest oxidation state.[2] Special attention has been devoted to the chemistry of 14 v.e. species of the type $[Zr(\eta^8-C_8H_8)R_2]$. Such species have been known for several years, but their isolation and characterization is difficult,[3] mainly due to their high reactivity which leads to decomposition even at low temperature. The effect of the metal unsaturation on the stability of the Zr–R functionality is clearly illustrated by studies on stable $[Zr(\eta^8-C_8H_8)(\eta^5-C_5Me_5)R]$ derivatives.[4] Herein we report the synthesis, intramolecular C–H bond activation, and M–C bond reactivity of $[Zr(\eta^8-C_8H_8)(mes)_2]$ (mes = $2,4,6-Me_3C_6H_2$). Some of this work has been communicated previously.[5,6]

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The compound $[ZrCl_4(thf)_2]$ (thf = tetrahydrofuran) was prepared as reported.[7] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, ^1H n.m.r. spectra using a 200-AC Brucker instrument.

Preparations.—$K_2[C_8H_8]$. Potassium sand (18.14 g, 0.464 mol) was suspended in thf (350 cm^3), then distilled cyclo-octatetraene (21.0 cm^3, 19.3 g, 0.186 mol) was added dropwise in order to keep the temperature a little lower than the boiling point of thf. The resulting yellow-brown solution was cooled to room temperature, filtered, and freed from a small excess of potassium metal.

$[Zr(\eta^8-C_8H_8)(\eta^4-C_8H_8)(thf)]$.[8] The $K_2[C_8H_8]$ solution above was added slowly (2 h) to a thf suspension (150 cm^3) of $[ZrCl_4(thf)_2]$ (34.54 g, 0.093 mol). A red microcrystalline solid formed. The suspension was refluxed overnight, then extracted for 1 week using the mother-liquor. Complex (**1**) was obtained

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Experimental data for the *X*-ray diffraction study of complexes (**2**), (**3**), (**7**), and (**8**)

Complex	(**2**)	(**3**)	(**7**)	(**8**)
Formula	$C_{26}H_{30}Zr\cdot 0.5Et_2O$	$C_{54}H_{60}O_2Zr_2\cdot Et_2O$	$C_{34}H_{36}Zr_2$	$C_{34}H_{36}Zr_2$
M	470.8	997.6	627.1	627.1
Crystal system	Tetragonal	Monoclinic	Orthorhombic	Triclinic
Space group	$I4_1/a$	$C2/c$	$Pbca$	$P\bar{1}$
T/K	173	298	295	295
a/Å	26.495(4)	25.856(9)	7.831(1)	16.469(3)
b/Å	26.495(4)	12.444(3)	19.368(2)	17.452(3)
c/Å	13.711(2)	15.571(8)	18.177(2)	10.373(2)
α/°	90	90	90	92.35(1)
β/°	90	92.59(3)	90	103.83(2)
γ/°	90	90	90	103.06(2)
U/Å^3	9 625(3)	5 005(3)	2 756.9(5)	2 805.8(9)
Z	16	4	4	2
D_c/g cm^{-3}	1.30	1.32	1.511	1.485
F(000)	3 952	2 088	1 280	1 280
Crystal size/mm	0.22 × 0.30 × 0.33	0.05 × 0.25 × 0.30	0.31 × 0.31 × 0.40	0.25 × 0.28 × 0.32
μ/cm^{-1}	40.6	39.6	7.64	7.50
Diffractometer	Nicolet R3m	Nicolet R3m	Philips PW1100	Philips PW1100
Radiation	*a*	*a*	*b*	*b*
2θ range/°	3—110	3—110	6—47	6—47
Unique total data	3 029	2 848	2 028	8 298
Observation criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2.5\sigma(I)$	$I > 3\sigma(I)$
Unique observed data	2 468	1 659	949	3 792
R[c]	0.054	0.112	0.045	0.041
R'	0.063[d]	0.111[e]	0.046[e]	0.039[e]

[a] Nickel-filtered Cu-K_α radiation (λ = 1.541 78 Å). [b] Graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å). [c] $\Sigma|\Delta F|/\Sigma|F_o|$. [d] $\Sigma w|\Delta F|^2/\Sigma w|F_o|^2$. [e] $\Sigma w|\Delta F|/\Sigma(w|F_o|)^{\frac{1}{2}}$.

as a red crystalline solid (24.44 g, *ca.* 71%). ^{1}H N.m.r. (CD_2Cl_2): δ 6.00 (s) at 300, 5.59 (s) at 203 K.

$[Zr(\eta^8\text{-}C_8H_8)Cl_2(thf)]$.[9] To a thf suspension (150 cm^3) of complex (**1**) (48.37 g, 0.130 mol) was added a thf solution (106 cm^3, 2.45 mol dm^{-3}) of HCl freshly prepared at 0 °C. A yellow-orange solid formed. The suspension was refluxed overnight and the solid filtered off and collected (40.90 g, *ca.* 93%). ^{1}H N.m.r. (CD_2Cl_2): δ 6.94 (s).

$[Zr(\eta^8\text{-}C_8H_8)(mes)_2]\cdot 0.5Et_2O$, (**2**). Complex (**1**) (5.33 g, 15.77 mmol) was suspended in Et_2O (600 cm^3) and the suspension cooled at −50 °C. Then a thf solution of Mg(mes)Br (31.5 mmol) was added with vigorous stirring of the suspension. The temperature was then raised to −20 °C, and the suspension stirred overnight. A colour change was observed from yellow-orange to red-orange. The temperature was then increased again to −4 °C for 4 h. The addition of dioxane (5.5 cm^3) led to separation of the magnesium salts, which were removed by filtration at −20 °C. The resulting orange solution was evaporated to 100 cm^3 at −20 °C, then allowed to stand at −78 °C for 15 h. The resulting orange crystalline solid was filtered off at −20 °C, and stored at −30 °C (3.08 g, *ca.* 48.0%). The thermal instability of the solid prevented a microanalytical determination. ^{1}H N.m.r. (C_6D_6): δ 6.54 (s, 4 H), 6.42 (s, 8 H), 2.57 (s, 12 H), and 2.08 (s, 6 H). The room-temperature spectrum had to be recorded within minutes to minimize decomposition.

Reaction of complex (**2**) *with carbon monoxide, synthesis of complex* (**3**). An Et_2O solution (180 cm^3) of complex (**2**) (1.45 g, 3.08 mmol) was treated at 0 °C with carbon monoxide. The solution changed from orange to deep red in a few minutes, and a red crystalline solid formed (0.98 g, *ca.* 64%) (Found: C, 69.00; H, 6.60. Calc. for $[\{Zr(\eta^8\text{-}C_8H_8)[\eta\text{-}\mu\text{-}OC(mes)_2]\}_2]\cdot Et_2O$, $C_{58}H_{70}O_3Zr_2$: C, 69.80; H, 7.05%). ^{1}H N.m.r. (C_6D_6): δ 6.63 (s, 6 H), 6.58 (s, 2 H), 6.00 (s, 16 H), 3.35 (s, 6 H), 2.27 (s, 6 H), 2.19 (s, 6 H), 2.16 (s, 12 H), and 2.04 (s, 6 H).

Thermal decomposition of complex (**2**), *synthesis of complex* (**7**). Complex (**2**) (2.5 g, 5.31 mmol) was suspended in Et_2O (200 cm^3) at room temperature for 2 d. The suspension changed from orange to deep brown in colour producing a deep green crystalline solid (0.93 g, *ca.* 50%). The mother-liquor was found to contain mesitylene (*ca.* 78%) (Found: C, 65.00; H, 5.85. Calc. for $[\{Zr(\eta^8\text{-}C_8H_8)(2,4\text{-}Me_2\text{-}6\text{-}CH_2C_6H_2)\}_2]$, $C_{34}H_{36}Zr_2$: C, 65.10; H, 5.80%). ^{1}H N.m.r. (C_6D_6): δ 6.95 (s, 2 H), 6.43 (s, 2 H), 5.60 (s, 16 H), 2.84 (s, 6 H), 2.67 (d, 2 H, *J* 7.5), 2.31 (s, 6 H), and 2.22 (d, 2 H, *J* 7.5 Hz). Complex (**7**) did not react with carbon monoxide.

Thermal decomposition of complex (**7**), *synthesis of* (**8**). A suspension of complex (**7**) (2.62 g, 4.17 mmol) in benzene (80 cm^3) was refluxed for 3 h with stirring. This on heating gave a brown solution which was concentrated to 20 cm^3, and n-hexane (50 cm^3) was added. The solution on standing at −3 °C gave a brown crystalline solid (1.65 g, *ca.* 63%). (Found: C, 65.90; H, 5.70. Calc. for $[Zr_2(\eta^8\text{-}C_8H_8)_2(\mu\text{-}2,4\text{-}Me_2\text{-}6\text{-}CH\text{-}C_6H_2)]$, $C_{34}H_{36}Zr_2$: C, 65.10; H, 5.80%). ^{1}H N.m.r. (C_6D_6) δ 6.73 (s, 1 H), 6.70 (s, 1 H), 6.50 (s, 1 H), 6.27 (s, 1 H), 5.61 (s, 16 H), 4.62 (s, 1 H), 3.17 (s, 3 H), 2.98 (s, 3 H), and 2.31 (m, 9 H). Complex (**8**) did not react with carbon monoxide.

X-Ray Crystallography.[10]—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data for complex (**2**) were collected at 173 K because of its thermal instability, all the others were collected at room temperature on a single-crystal four-circle diffractometer. Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25—30 carefully centred reflections chosen from diverse region of reciprocal space. Crystal data and details of the parameters associated with data collection and structure refinement are given in Table 1. Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 using SHELX 76. The reduced cells quoted were obtained with use of TRACER.[11] The structure amplitudes were obtained after the usual Lorentz and polarization corrections. Correction for absorption was made for complex (**8**).[12] The function minimized during the full-matrix least-squares refinement was $\Sigma w(\Delta F)^2$. Weights were applied according to the scheme w =

Table 2. Fractional atomic co-ordinates for complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.371 8(1)	0.627 3(1)	0.508 3(1)
C(1)	0.296 6(3)	0.670 3(3)	0.564 6(6)
C(2)	0.311 9(3)	0.694 0(3)	0.475 5(6)
C(3)	0.357 8(4)	0.713 4(3)	0.439 1(5)
C(4)	0.408 0(4)	0.711 8(3)	0.468 2(7)
C(5)	0.432 5(3)	0.691 0(3)	0.553 4(7)
C(6)	0.416 8(3)	0.670 1(3)	0.638 7(6)
C(7)	0.371 4(4)	0.659 0(3)	0.680 9(5)
C(8)	0.320 9(3)	0.657 8(3)	0.650 0(5)
C(9)	0.398 4(2)	0.601 4(2)	0.354 5(4)
C(10)	0.374 8(2)	0.607 7(3)	0.262 8(4)
C(11)	0.400 1(3)	0.597 4(3)	0.175 2(5)
C(12)	0.449 4(3)	0.580 0(3)	0.174 3(5)
C(13)	0.472 3(2)	0.572 4(2)	0.263 3(4)
C(14)	0.448 0(2)	0.581 2(2)	0.350 8(4)
C(15)	0.477 0(2)	0.569 7(3)	0.442 6(4)
C(16)	0.321 5(3)	0.627 1(3)	0.251 6(5)
C(17)	0.476 1(3)	0.570 7(4)	0.079 2(5)
C(18)	0.361 0(2)	0.545 3(2)	0.559 9(4)
C(19)	0.317 7(2)	0.520 4(2)	0.523 1(4)
C(20)	0.303 0(2)	0.473 1(2)	0.553 0(4)
C(21)	0.330 5(3)	0.447 1(2)	0.622 6(4)
C(22)	0.373 1(2)	0.470 1(2)	0.660 8(4)
C(23)	0.388 4(2)	0.517 9(2)	0.630 5(4)
C(24)	0.435 3(2)	0.539 2(3)	0.678 6(5)
C(25)	0.283 9(3)	0.546 5(3)	0.448 7(5)
C(26)	0.313 0(3)	0.396 1(2)	0.658 5(5)
O	0.500 0(—)	0.250 0(—)	0.065 5(4)
C(27)	0.539 6(4)	0.271 6(4)	0.009 2(6)
C(28)	0.573 7(3)	0.301 0(3)	0.071 1(6)

Table 3. Fractional atomic co-ordinates for complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.231 4(1)	0.220 1(1)	0.108 5(1)
O(1)	0.206 0(4)	0.280 9(9)	−0.017 7(9)
C(1)	0.169 1(8)	0.328 3(13)	0.038 2(10)
C(2)	0.163 9(7)	0.450 0(13)	0.023 7(9)
C(3)	0.202 5(7)	0.522 7(12)	0.057 2(9)
C(4)	0.201 3(8)	0.630 4(13)	0.047 8(11)
C(5)	0.163 4(8)	0.677 9(14)	−0.001 1(12)
C(6)	0.123 6(8)	0.611 7(15)	−0.032 8(11)
C(7)	0.123 4(8)	0.500 8(13)	−0.024 1(9)
C(8)	0.078 9(8)	0.439 6(15)	−0.066 2(12)
C(9)	0.247 3(8)	0.480 0(13)	0.108 9(11)
C(10)	0.158 1(9)	0.804 4(12)	−0.013 9(15)
C(11)	0.116 2(7)	0.277 8(14)	0.056 5(9)
C(12)	0.083 7(9)	0.321 1(14)	0.118 7(11)
C(13)	0.040 1(8)	0.269 0(16)	0.138 9(11)
C(14)	0.018 2(8)	0.176 8(17)	0.103 6(13)
C(15)	0.051 2(9)	0.138 8(16)	0.037 0(13)
C(16)	0.094 7(8)	0.185 7(15)	0.009 0(11)
C(17)	0.120 4(7)	0.137 4(14)	−0.066 2(9)
C(18)	0.098 7(8)	0.420 5(15)	0.175 1(11)
C(19)	−0.029 3(8)	0.116 4(18)	0.128 8(16)
C(20)	0.251 0(5)	0.031 3(7)	0.139 7(6)
C(21)	0.296 0(5)	0.078 7(7)	0.177 5(6)
C(22)	0.304 7(5)	0.180 7(7)	0.213 7(6)
C(23)	0.273 8(5)	0.257 7(7)	0.253 2(6)
C(24)	0.220 2(5)	0.273 2(7)	0.261 0(6)
C(25)	0.176 8(5)	0.208 2(7)	0.242 2(6)
C(26)	0.166 2(5)	0.122 1(7)	0.186 3(6)
C(27)	0.197 1(5)	0.043 4(7)	0.149 0(6)
O(2)	0.000 0(—)	0.189 8(31)	0.750 0(—)
C(28)	0.028 3(22)	0.249 3(41)	0.681 3(34)
C(29)	0.062 7(18)	0.164 6(35)	0.672 9(26)

Table 4. Fractional atomic co-ordinates for complex (**7**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.006 30(2)	0.074 20(1)	0.052 90(1)
C(1)	−0.081 10(20)	0.128 90(8)	0.169 80(8)
C(2)	0.050 70(22)	0.083 60(7)	0.188 50(7)
C(3)	0.212 70(20)	0.066 60(7)	0.158 90(8)
C(4)	0.308 20(17)	0.089 80(6)	0.099 10(9)
C(5)	0.279 50(14)	0.136 20(6)	0.041 20(6)
C(6)	0.147 10(16)	0.184 30(6)	0.024 70(7)
C(7)	−0.007 90(20)	0.202 40(5)	0.054 20(7)
C(8)	−0.101 70(16)	0.178 70(7)	0.114 10(8)
C(11)	−0.008 70(17)	−0.048 80(4)	0.076 40(5)
C(12)	−0.130 80(14)	−0.073 60(6)	0.129 90(6)
C(13)	−0.102 70(18)	−0.131 30(6)	0.171 00(7)
C(14)	0.050 70(14)	−0.170 00(6)	0.161 90(7)
C(15)	0.169 50(15)	−0.149 00(6)	0.112 80(6)
C(16)	0.145 00(15)	−0.087 90(5)	0.070 00(6)
C(17)	−0.305 10(15)	−0.038 20(6)	0.140 30(7)
C(18)	0.075 40(20)	−0.237 80(6)	0.205 90(7)
C(19)	0.256 90(14)	−0.069 50(6)	0.009 10(6)

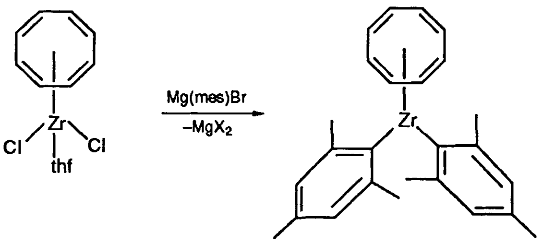
$1/[\sigma^2(F_o) + g(F_o)^2]$. Anomalous scattering corrections were included in all structure-factor calculations.[13b] Scattering factors for neutral atoms were taken from ref. 13*a* for non-hydrogen atoms and from ref. 14 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropically, then anisotropically for all the non-H atoms. During the refinement of complex (**3**) a constraint was applied to the C–C distances of cyclo-octatetraene (C–C 1.40 ± 0.01 Å), and the associated hydrogen atoms were ignored. The other hydrogen atoms either located in difference maps or put in idealized calculated positions were introduced in the refinement as fixed contributors for all complexes [$U = 0.08$ Å^2 for complexes (**7**) and (**8**)]. The final difference maps showed no unusual features, with no significant peak above the general background. Final atomic co-ordinates for non-hydrogen atoms are listed in Tables 2—5, selected bond distances and angles in Tables 6—9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The alkylation of complex (**1**) is very sensitive to a number of factors such as temperature, the solvent used, and the nature of the alkyl groups. It has been shown that isolation is difficult or unsuccessful in a number of cases. In our experience the most successful route is *via*. reaction (1) under the conditions specified



(1)

(**1**) $[Zr(\eta^8-C_8H_8)Cl_2(thf)]$

(**2**) $[Zr(\eta^8-C_8H_8)(mes)_2]$

Table 5. Fractional atomic co-ordinates for complex (**8**)

	Molecule (a)			Molecule (b)		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr(1)	0.252 3(1)	0.605 0(1)	−0.020 4(1)	−0.215 8(1)	0.068 8(1)	0.556 6(1)
Zr(2)	0.189 9(1)	0.432 4(1)	0.070 7(1)	−0.220 5(1)	−0.092 7(1)	0.389 7(1)
C(1)	0.209 9(12)	0.728 8(7)	−0.015 6(25)	−0.116 7(7)	0.198 1(6)	0.629 6(14)
C(2)	0.188 4(8)	0.699 9(8)	−0.151 6(21)	−0.113 0(6)	0.160 6(6)	0.743 4(12)
C(3)	0.232 0(12)	0.664 9(8)	−0.230 0(13)	−0.175 0(8)	0.115 2(6)	0.796 3(9)
C(4)	0.313 3(12)	0.646 3(7)	−0.208 5(14)	−0.264 9(8)	0.087 2(6)	0.760 9(12)
C(5)	0.384 0(9)	0.657 0(7)	−0.098 1(17)	−0.331 4(7)	0.098 5(6)	0.653 0(13)
C(6)	0.405 2(8)	0.690 5(7)	0.030 8(18)	−0.332 3(6)	0.143 1(6)	0.545 9(13)
C(7)	0.362 7(11)	0.724 1(7)	0.105 6(15)	−0.270 9(9)	0.187 2(6)	0.486 6(10)
C(8)	0.284 4(15)	0.740 4(7)	0.088 2(16)	−0.181 1(9)	0.209 6(5)	0.519 7(12)
C(9)	0.258 1(9)	0.318 5(7)	0.079 1(19)	−0.339 5(7)	−0.217 4(6)	0.310 9(16)
C(10)	0.275 8(9)	0.349 7(8)	0.213 1(18)	−0.332 4(8)	−0.178 6(8)	0.197 3(13)
C(11)	0.221 6(11)	0.374 9(8)	0.289 4(12)	−0.263 7(12)	−0.137 7(7)	0.144 7(11)
C(12)	0.136 5(12)	0.383 3(8)	0.263 7(15)	−0.172 5(10)	−0.120 6(6)	0.188 3(12)
C(13)	0.068 5(9)	0.364 2(8)	0.153 4(18)	−0.116 4(7)	−0.141 8(6)	0.293 5(13)
C(14)	0.054 3(8)	0.329 0(7)	0.023 5(15)	−0.122 0(8)	−0.183 2(7)	0.404 9(12)
C(15)	0.104 1(11)	0.303 7(6)	−0.051 6(13)	−0.189 8(9)	−0.219 9(6)	0.455 2(11)
C(16)	0.187 2(12)	0.301 7(6)	−0.030 9(14)	−0.278 1(9)	−0.232 6(6)	0.421 6(13)
C(21)	0.210 6(5)	0.478 5(4)	−0.129 9(8)	−0.212 1(5)	−0.059 2(4)	0.613 5(8)
C(22)	0.124 0(6)	0.488 6(5)	−0.140 2(9)	−0.121 6(5)	−0.030 6(5)	0.614 9(8)
C(23)	0.056 0(5)	0.461 4(5)	−0.257 0(8)	−0.056 1(5)	−0.046 1(5)	0.719 7(8)
C(24)	0.072 3(6)	0.423 6(5)	−0.361 9(8)	−0.078 8(6)	−0.089 1(5)	0.816 4(9)
C(25)	0.157 9(6)	0.415 4(5)	−0.354 9(9)	−0.166 2(6)	−0.118 0(5)	0.818 5(8)
C(26)	0.225 3(6)	0.441 9(5)	−0.245 3(9)	−0.232 0(6)	−0.103 7(5)	0.719 4(8)
C(27)	0.126 6(5)	0.526 6(5)	−0.012 4(8)	−0.117 8(5)	0.012 7(4)	0.501 6(7)
C(28)	0.001 6(7)	0.390 9(6)	−0.488 6(9)	−0.010 4(6)	−0.108 7(6)	0.927 5(10)
C(29)	0.311 6(7)	0.427 4(6)	−0.245 5(9)	−0.324 8(6)	−0.136 0(6)	0.723 1(9)
C(31)	0.305 8(6)	0.547 4(5)	0.196 1(9)	−0.305 8(5)	0.004 8(5)	0.324 0(8)
C(32)	0.284 3(6)	0.587 6(5)	0.301 3(9)	−0.285 5(5)	0.058 9(5)	0.231 2(8)
C(33)	0.247 6(7)	0.620 6(6)	0.417 4(10)	−0.343 7(6)	0.092 4(5)	0.149 8(9)
C(34)	0.433 1(8)	0.613 8(7)	0.436 4(10)	−0.430 4(7)	0.074 8(6)	0.157 8(10)
C(35)	0.452 5(6)	0.574 5(6)	0.333 1(11)	−0.453 2(6)	0.021 6(5)	0.243 7(9)
C(36)	0.391 6(6)	0.541 1(5)	0.217 7(9)	−0.394 6(6)	−0.013 5(5)	0.326 7(8)
C(37)	0.195 5(7)	0.596 5(6)	0.299 9(10)	−0.193 1(6)	0.081 0(5)	0.213 0(9)
C(38)	0.500 1(8)	0.650 0(10)	0.561 8(12)	−0.495 5(7)	0.111 7(6)	0.070 2(11)
C(39)	0.422 9(6)	0.501 1(6)	0.113 5(11)	−0.429 2(5)	−0.072 8(5)	0.412 9(9)

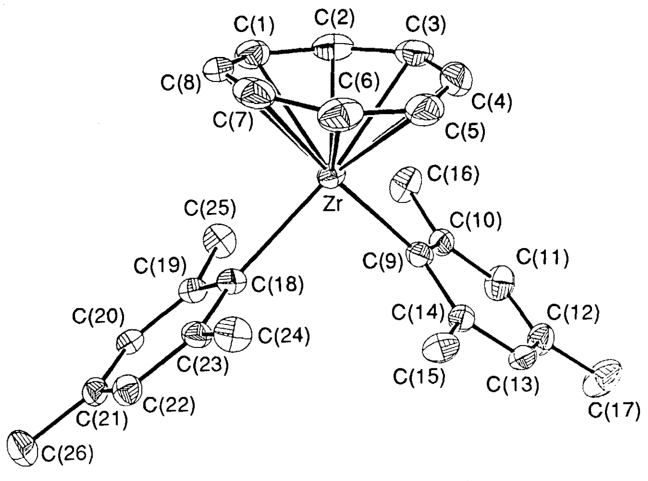


Figure 1. An ORTEP drawing of complex (**2**) [Zr(η^8-C_8H_8)(mes)$_2$]

in the Experimental section. The crucial factors determining the success of reaction (1) are the use of low temperature and of Et_2O as solvent. Use of tetrahydrofuran under the same conditions leads to the uncontrolled decomposition of (**2**) occurring to a large extent. The low solubility of complex (**2**) in Et_2O however prevents large-scale preparations. The relative thermal stability of (**2**) can be attributed to steric hindrance afforded by the *o*-methyl groups providing a sort of cage protecting the unsaturated metal ion. The suspected C–H ··· metal interaction has not been detected in solution with variable-temperature ^{1}H n.m.r. spectroscopy down to 200 K (CD_2Cl_2) not revealing any peculiarity. An ORTEP view of the *X*-ray structure taken at liquid-nitrogen temperature is shown in Figure 1. Selected bond distances and angles are quoted in Table 6. The structure of complex (**2**) consists of discrete monomeric units [Zr(η^8-C_8H_8)(mes)$_2$] and Et_2O solvent molecules in the molar ratio of 2:1. The solvent lies on a two-fold axis running through the oxygen atom. Zirconium co-ordinates a η^8-bonded cyclo-octatetraene ligand and two σ-bonded mesityl groups through a phenyl carbon. The geometry of the Zr(η^8-C_8H_8) fragment is similar to others reported for cyclo-octatetraene derivatives of zirconium,[4,9b,15] the Zr–C distances ranging from 2.412(8) to 2.511(7) Å with a Zr–C_8H_8 (centroid) distance of 1.651(8) Å. The Zr–C(phenyl) bond distances [Zr–C(9) 2.327(6) and Zr–C(18) 2.303(6) Å] compare well with the values found for zirconium–alkyl bonds.[16] The C–C distances within the cyclo-octatetraene and benzene rings are in agreement with the aromaticity of the ligands. The two benzene rings, which are planar and nearly perpendicular to each other [dihedral angle 79.8(2)°], are symmetrically oriented with respect to the approximately planar cyclo-octatetraene ring, forming with it dihedral angles of 37.1(2) and 42.8(1)°. The zirconium atom is 0.374(3) and 0.224(2) Å from the planes through C(9)—C(14) and C(18)—C(23) respectively. The

Table 6. Selected interatomic distances (Å) and angles (°) for complex (**2**)

Zr–C(1)	2.421(8)	Zr–C(9)	2.327(6)
Zr–C(2)	2.417(8)	Zr–C(18)	2.303(6)
Zr–C(3)	2.498(8)	Zr ··· H(152)	2.98
Zr–C(4)	2.497(8)	Zr ··· H(252)	2.94
Zr–C(5)	2.412(8)	Zr ··· C(15)	3.303(7)
Zr–C(6)	2.430(8)	Zr ··· C(25)	3.267(8)
Zr–C(7)	2.511(7)	Zr ··· H(161)	3.20
Zr–C(8)	2.499(7)	Zr ··· H(242)	3.29
C(9)–C(10)	1.414(7)	C(18)–C(19)	1.416(7)
C(9)–C(14)	1.420(7)	C(18)–C(23)	1.411(7)
C(10)–C(11)	1.402(9)	C(19)–C(20)	1.375(7)
C(10)–C(16)	1.511(9)	C(19)–C(25)	1.523(9)
C(11)–C(12)	1.385(11)	C(20)–C(21)	1.384(8)
C(12)–C(13)	1.378(9)	C(21)–C(22)	1.385(8)
C(12)–C(17)	1.504(10)	C(21)–C(26)	1.511(8)
C(13)–C(14)	1.381(7)	C(22)–C(23)	1.393(7)
C(14)–C(15)	1.506(7)	C(23)–C(24)	1.516(8)
C(7)–Zr–C(8)	32.5(3)	C(9)–Zr–C(18)	92.2(2)
C(6)–Zr–C(7)	32.1(3)	Zr–C(9)–C(14)	115.1(4)
C(5)–Zr–C(6)	32.6(3)	Zr–C(9)–C(10)	129.6(4)
C(4)–Zr–C(5)	34.2(3)	C(10)–C(9)–C(14)	115.0(5)
C(3)–Zr–C(4)	32.3(3)	Zr–C(18)–C(23)	129.2(4)
C(2)–Zr–C(3)	33.3(3)	Zr–C(18)–C(19)	115.5(4)
C(2)–Zr–C(1)	34.4(3)	C(19)–C(18)–C(23)	114.9(5)
C(1)–Zr–C(8)	32.4(3)		

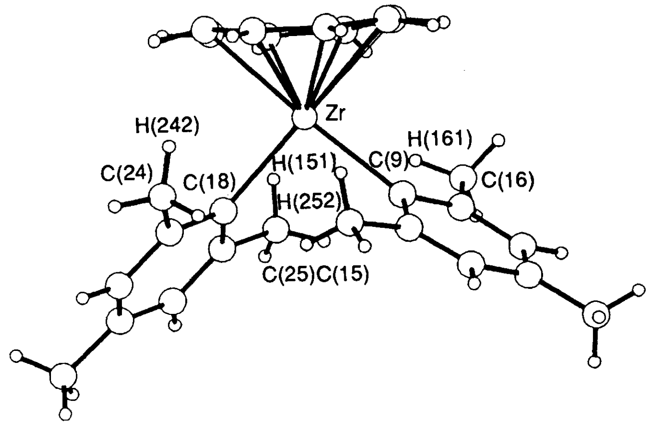
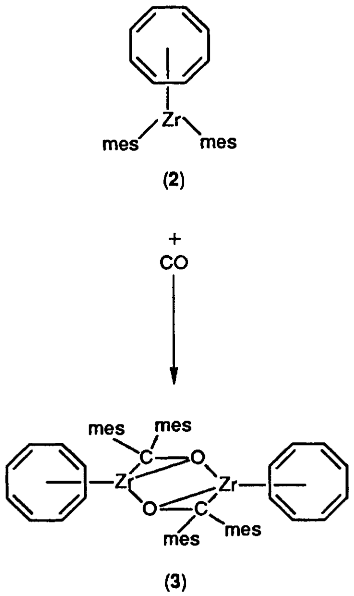


Figure 2. A view of complex (**2**) showing the methyl group of the mesityl ligand providing an environment for the metal atom

methyl groups lie slightly, even if significantly, out of these planes. Figure 2 and the data quoted in Table 6 support the proposal that the *ortho*-methyl carbons provide a cage of hydrogen atoms for the metal atom. Although the distances involved have higher values than those usually considered as bonding interactions, some useful information can be derived from the molecular parameters. If CH(15) and CH(25) are used to label the midpoints of the C(15) ··· H(151) and C(25) ··· H(252) bonds respectively, the following data are obtained: Zr–CH(15) 3.11, Zr–CH(25) 3.07 Å, C(18)–Zr–CH(15) 80.4, C(18)–Zr–CH(25) 55.9, C(9)–Zr–CH(25) 83.6, and C(9)–Zr–CH(15) 55.4°. These angular values are close to those for the C–Zr–C bond angles in complex (7) (see Table 8). The C(9) and C(18) carbon atoms and the CH(15) and CH(25) positions define a plane parallel to the cyclo-octatetraene ring (dihedral angle 2.0°), from which zirconium is displaced by 1.59 Å. Such an arrangement of the ligands seems to precede the formation of the triple-decker sandwich complex (7) (see below). The zirconium atom attains co-ordinative saturation with the formation of the two chelate rings Zr–C(9)–C(14)–C(15)–H(15) and Zr–C(18)–C(19)–C(25)–H(25). Therefore, in spite of the rather high values of the Zr–CH contacts and a large uncertainty in the positions of the hydrogen atoms, these data are consistent with the presence of zirconium carbon–hydrogen interactions, and make the thermal evolution of (**2**) into (**7**) understandable. The relative thermal stability of (**2**) is in agreement with these suggestions.

The chemistry of complex (**2**) is rather intriguing because of the concurrent thermal decomposition. Reactions on (**2**) therefore have to be very fast and to occur at low temperature. A rare example fitting in this class is the reaction with carbon monoxide, to form complex (**3**) in good yield within a few minutes at 0 °C in Et_2O [equation (2)].



(**2**)

(**3**)

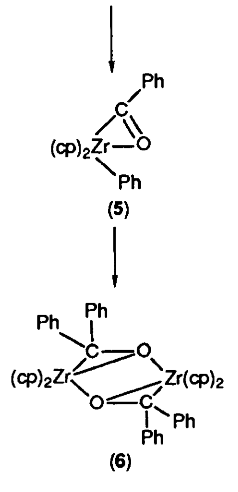
$[\{Zr(\eta^8\text{–}C_8H_8)[\mu\text{–}\eta\text{–}OC(mes)_2]\}_2]$

(2)

The double aryl migration to CO leading to the ketone moiety is a known reaction for zirconium but previously only under rather drastic conditions. A significant example is the carbonylation of $[Zr(cp)_2Ph_2]$ leading in a stepwise process to complex (**6**), a structural analogue of complex (**3**)[17a] [equation (3)].

$[Zr(cp)_2Ph_2]$ + CO

(**4**)



(**5**)

(**6**)

(3)

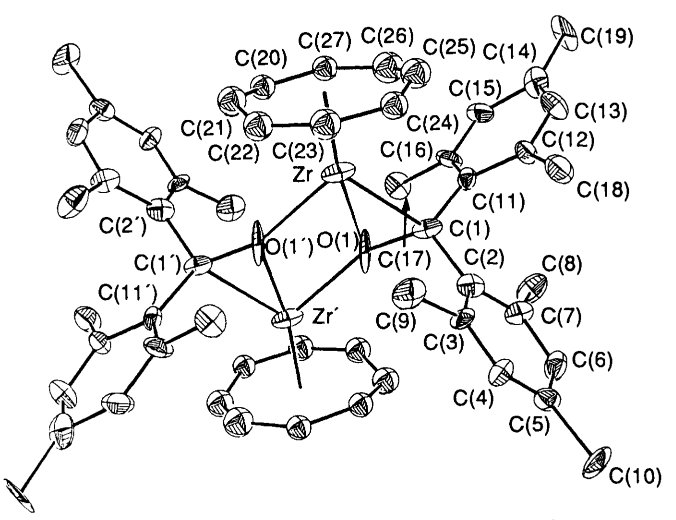


Figure 3. An ORTEP drawing of complex (**3**), $[\{Zr(\eta^8-C_8H_8)[\eta-OC(mes)_2]\}_2]$

Table 7. Selected bond distances (Å) and angles (°) for complex (**3**)*

Zr–C(20)	2.447(9)	Zr–O(1)	2.179(13)
Zr–C(21)	2.623(10)	Zr–O(1′)	2.197(12)
Zr–C(22)	2.497(11)	Zr–C(1)	2.334(18)
Zr–C(23)	2.505(10)	O(1)–C(1)	1.446(22)
Zr–C(24)	2.494(9)	C(1)–C(2)	1.536(22)
Zr–C(25)	2.572(11)	C(1)–C(11)	1.543(26)
Zr–C(26)	2.446(11)		
Zr–C(27)	2.464(9)		
C(2)–C(3)	1.428(23)	C(11)–C(12)	1.417(25)
C(2)–C(7)	1.407(24)	C(11)–C(16)	1.460(24)
C(3)–C(4)	1.348(22)	C(12)–C(13)	1.350(30)
C(3)–C(9)	1.479(25)	C(12)–C(18)	1.556(25)
C(4)–C(5)	1.350(26)	C(13)–C(14)	1.382(28)
C(5)–C(6)	1.391(27)	C(14)–C(15)	1.452(30)
C(5)–C(10)	1.592(23)	C(14)–C(19)	1.507(30)
C(6)–C(7)	1.387(24)	C(15)–C(16)	1.357(30)
C(7)–C(8)	1.505(26)	C(16)–C(17)	1.498(24)
C(26)–Zr–C(27)	33.3(3)	Zr–O(1)–Zr′	112.2(5)
C(25)–Zr–C(26)	32.3(3)	Zr′–O(1)–C(1)	156.2(10)
C(24)–Zr–C(25)	32.1(3)	Zr–O(1)–C(1)	77.2(8)
C(23)–Zr–C(24)	32.8(3)	Zr–C(1)–O(1)	65.6(7)
C(22)–Zr–C(23)	32.7(3)	O(1)–C(1)–C(11)	124.0(13)
C(21)–Zr–C(22)	31.7(3)	O(1)–C(1)–C(2)	111.7(13)
C(20)–Zr–C(27)	33.5(4)	Zr–C(1)–C(11)	106.1(10)
C(20)–Zr–C(21)	32.0(3)	Zr–C(1)–C(2)	133.8(12)
O(1)–Zr–C(1)	37.2(5)	C(2)–C(1)–C(11)	110.9(14)
O(1)–Zr–O(1′)	67.8(4)		

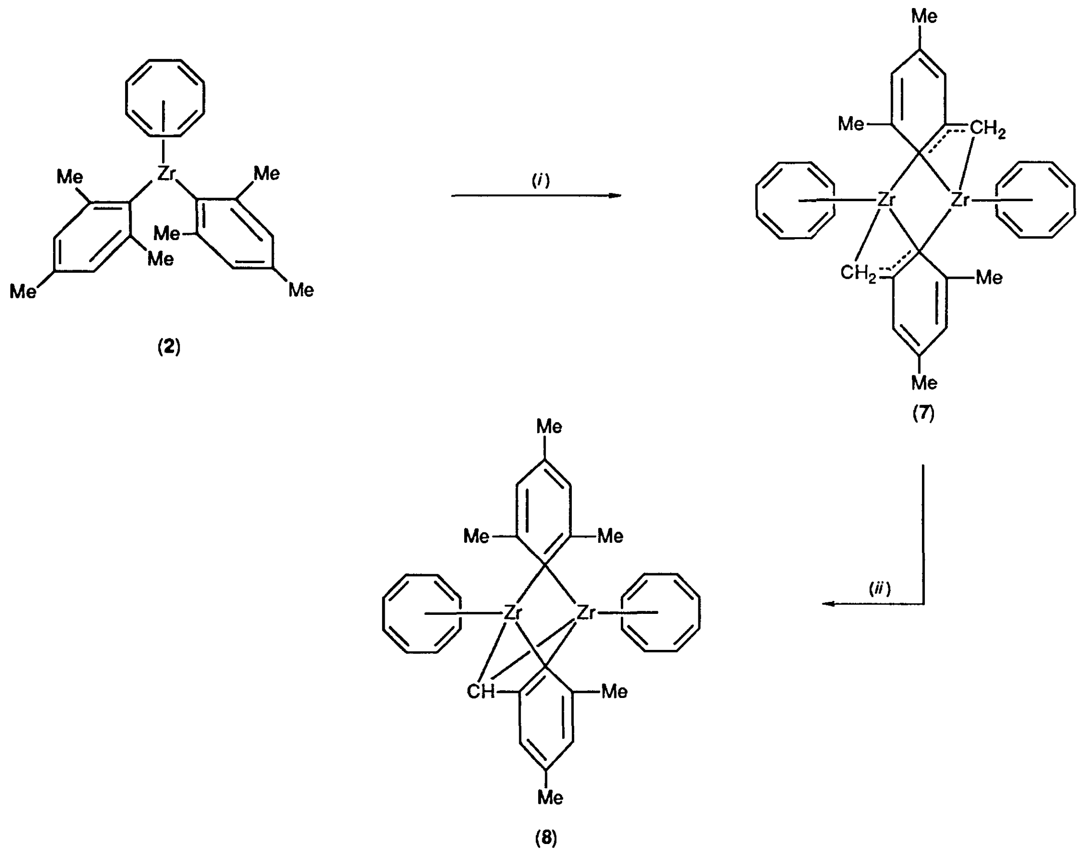
* Primed atoms related to unprimed atoms by symmetry operation $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The major difference between reactions (2) and (3) is the conditions under which the double migration occurs. In case of reaction (2) it was impossible to detect any acyl intermediate. The reaction is as fast as that observed for $[Ti(cp)_2(CH_2Ph)_2]$ leading to $[Ti(cp)_2(CO)_2]$ and $(PhCH_2)_2CO$, by a reductive elimination process.[18] Such a reductive elimination does not occur in the case of zirconium, mainly due to its high oxophilicity.[17b] Complex (**3**) has a good thermal stability in the solid state, while its stability in solution is rather limited. It has been fully characterized by n.m.r. and i.r. spectra. The very strong Zr–O interaction is revealed by a band at 760 cm^{-1}. A view of its structure is shown in Figure 3 and selected bond distances and angles are in Table 7. The structure consists of dimeric centrosymmetric units, $[\{Zr(\eta^8-C_8H_8)[OC(mes)_2]\}_2]$, and Et_2O solvent molecules in the molar ratio of 1:1. The solvent lies on a two-fold axis running through the oxygen atom. Two $Zr(\eta^8-C_8H_8)$ centrosymmetric moieties, each of them η^2-*C,O* bonded to a dimesityl ketone, are linked in the dimers by the bridging oxygen atoms. As a result the cyclo-octatetraene rings are parallel. The zirconium atoms interact with the ketone in an asymmetric manner, the Zr–O(1) bond distance [2.179(13) Å] being significantly shorter than the Zr–C(1) distance [2.334(18) Å]. A similar trend was found in several bis(cyclopentadienyl)zirconaoxirane derivatives.[19] The oxygen atom is symmetrically bonded by the centrosymmetric zirconium atoms, the two Zr–O bond distances not being significantly different [2.179(13) *vs.* 2.197(12) Å]. The C–O bond distance [1.446(22) Å] approximates to a single bond and compares well with that found in η-ketone and η-aldehyde derivatives of $[Zr(\eta^5-C_5H_5)_2]$.[17a,19e–g] The planar Zr,O(1),Zr′,O(1′) fragment forms a dihedral angle of 22.9(6)° with the plane through Zr,O(1),C(1) and a dihedral angle of 76.0(1) with the cyclo-octatetraene ring. The geometry of the $Zr(\eta^8-C_8H_8)$ unit is similar to that of complex (**2**), the zirconium–centroid distance being 1.722(10) Å. All the other bond distances and angles are as expected and the two zirconium atoms in the dimer are separated by 3.632(3) Å. The intramolecular distances show that only the C(9) methyl carbon approaches zirconium [3.260(16) Å] pointing two hydrogens towards the metal [Zr ··· H(91) 2.83, Zr ··· H(93) 2.88 Å]. However the rather poor accuracy of the analysis prevents any significant discussion on this matter.

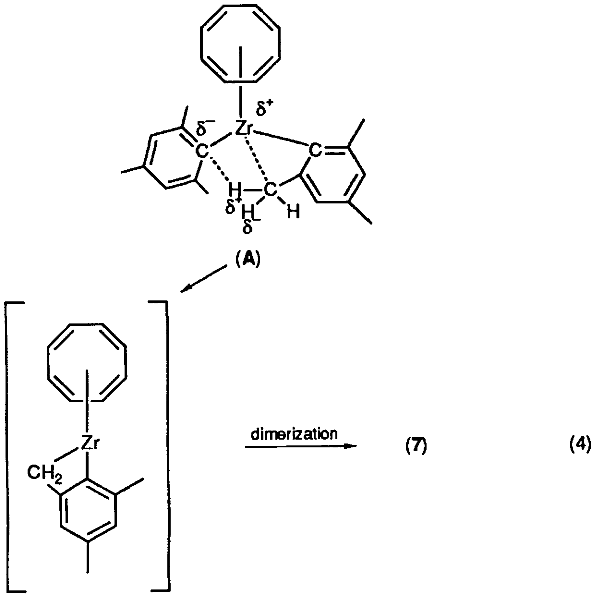
Complex (**2**) undergoes thermal decomposition under fairly mild conditions, the pathway of which was clearly defined by the isolation of the zirconium complex (**7**) and the organic fragment. The reaction occurs spontaneously at room temperature in Et_2O. Higher temperatures, such as in refluxing benzene, caused a rearrangement of complex (**7**) to (**8**) with a formal shift of a hydrogen atom (Scheme).

The high oxophilicity of the zirconium 14 v.e. centre is responsible for the easy cleavage of a C–H bond from a methyl group in close proximity as in complex (**2**).

The early stage of the C–H and H–H bond activation by acidic metals is normally viewed as depicted in (**A**).[20] The metal-assisted protonic hydrogen transfer to the highly polarized Zr–C bond becomes facile in an intramolecular process. The elimination of mesitylene leads to the formation of the monomeric pseudo-allylic complex (**B**), which can dimerize to complex (**7**) [equation (4)]. An intermolecular process seems much more unlikely because of the steric inaccessibility of the metal centre. The spectroscopic characterization of complex (**7**) is in agreement with the bonding mode of the pseudo-allylic form. In particular, the methylene hydrogen appears in the ^1H n.m.r. spectrum as a pair of doublets separated by 0.45 p.p.m. and with *J*(HH) of 7.5 Hz. Confirmation of the bonding mode of the pseudo-allylic ligand comes from the *X*-ray analysis. A view of complex (**7**) is given in Figure 4 and selected bond distances and angles are in Table 8. The structure of complex (**7**) consists of centrosymmetric dimers, where two $Zr(\eta^8-C_8H_8)$ units are bridged by ligands derived from the original mesityl groups. The bridging bonding mode of the mesityl group is responsible for the rather short zirconium–zirconium distance [3.460(3) Å]. The two zirconium atoms are bridged by two coplanar pseudo-allyl ligands. Some interesting features of the structure account for an allylic bonding mode involving C(11), C(16), and C(19): (*i*) the zirconium–carbon bond distances [Zr–C(11′) 2.401(9), Zr–C(19′) 2.351(11), Zr–C(16′) 2.543(11) Å][15a,21] indicate asymmetry in the 3C-fragment–Zr interaction which has also been observed in a related compound $[Zr(\eta^8-C_8H_8)(\eta^3-C_3H_5)(OBu^t)]$,[15a] (*ii*) the loss of the aromaticity of the benzene



Scheme. (*i*) Et_2O, $-2,4,6\text{-}Me_3C_6H_3$, 25 °C; (*ii*) heat, C_6H_6



(4)

Table 8. Selected bond distances (Å) and angles (°) for complex (7)*

Zr–C(1)	2.471(14)	C(1)–C(2)	1.397(22)
Zr–C(2)	2.496(13)	C(1)–C(8)	1.408(20)
Zr–C(3)	2.519(15)	C(2)–C(3)	1.417(22)
Zr–C(4)	2.527(13)	C(3)–C(4)	1.394(21)
Zr–C(5)	2.463(11)	C(4)–C(5)	1.402(18)
Zr–C(6)	2.455(12)	C(5)–C(6)	1.426(16)
Zr–C(7)	2.486(9)	C(6)–C(7)	1.372(19)
Zr–C(8)	2.460(13)	C(7)–C(8)	1.391(19)
Zr–C(11)	2.423(8)	C(12)–C(17)	1.539(16)
Zr–C(11′)	2.401(9)	C(13)–C(14)	1.426(17)
Zr–C(19′)	2.351(11)	C(14)–C(15)	1.352(16)
Zr–C(16′)	2.543(11)	C(14)–C(18)	1.550(17)
C(11)–C(12)	1.446(15)	C(15)–C(16)	1.429(15)
C(11)–C(16)	1.427(16)	C(16)–C(19)	1.456(16)
C(12)–C(13)	1.362(17)		
C(11)–Zr–C(11′)	88.4(3)	Zr′–C(11)–C(12)	126.5(7)
C(11)–Zr–C(19′)	90.2(4)	Zr–C(11)–C(16)	117.8(6)
C(11′)–Zr–C(19′)	62.0(4)	Zr–C(11)–C(12)	118.5(6)
C(11′)–Zr–C(16′)	33.4(4)	C(12)–C(11)–C(16)	115.9(8)
C(16′)–Zr–C(19′)	34.3(4)	C(11)–C(16)–C(19)	116.1(9)
Zr–C(11)–Zr′	91.6(3)	C(11)–C(16)–C(15)	120.6(10)
Zr′–C(11)–C(16)	78.8(6)	C(15)–C(16)–C(19)	122.4(9)
Zr′–C(19)–C(16)	80.1(7)		

* Primed atoms related to unprimed atoms by symmetry operation $-x$, $-y$, $-z$.

ring with C(12)—C(13) and C(14)—C(15) [1.362(17) and 1.352(16) Å] showing significant double-bond character; (*iii*) the shortening of the C(16)–C(19) bond distance [1.456(16) Å] when compared to the other methyl to phenyl distances [C(12)–C(17) 1.539(16) and C(14)–C(18) 1.550(17) Å]; (*iv*) the planarity of the six bridging carbon atoms [C(11), C(16), C(19), and the centrosymmetric ones] which define a plane parallel to cyclo-octatetraene [dihedral angle 2.6(2)°] and nearly parallel to the benzene ring itself [dihedral angle 11.7(3)°]. The compound could be therefore regarded as having a triple-decker structure with zirconium atoms symmetrically sandwiched by

Table 9. Selected bond distances (Å) and angles (°) for complex (**8**)

Molecule	(a)	(b)	Molecule	(a)	(b)
Zr(1)–C(1)	2.418(15)	2.436(9)	Zr(2)–C(9)	2.489(14)	2.531(9)
Zr(1)–C(2)	2.447(16)	2.478(9)	Zr(2)–C(10)	2.523(15)	2.525(11)
Zr(1)–C(3)	2.435(13)	2.466(9)	Zr(2)–C(11)	2.507(12)	2.510(11)
Zr(1)–C(4)	2.462(17)	2.476(13)	Zr(2)–C(12)	2.481(17)	2.471(15)
Zr(1)–C(5)	2.487(16)	2.491(13)	Zr(2)–C(13)	2.445(16)	2.466(13)
Zr(1)–C(6)	2.539(11)	2.532(11)	Zr(2)–C(14)	2.463(11)	2.491(14)
Zr(1)–C(7)	2.503(12)	2.505(12)	Zr(2)–C(15)	2.475(10)	2.472(11)
Zr(1)–C(8)	2.463(12)	2.461(8)	Zr(2)–C(16)	2.460(12)	2.478(10)
Zr(1)–C(21)	2.318(7)	2.344(7)	Zr(2)–C(21)	2.334(8)	2.334(8)
Zr(1)–C(27)	2.231(8)	2.236(9)	Zr(2)–C(27)	2.235(9)	2.252(6)
Zr(1)–C(31)	2.544(9)	2.566(7)	Zr(2)–C(31)	2.496(7)	2.460(9)
C(21)–C(22)	1.456(13)	1.457(11)	C(31)–C(32)	1.429(14)	1.420(12)
C(21)–C(26)	1.430(13)	1.430(12)	C(31)–C(36)	1.407(14)	1.432(13)
C(22)–C(23)	1.418(10)	1.413(11)	C(32)–C(33)	1.393(11)	1.371(12)
C(22)–C(27)	1.445(12)	1.429(11)	C(32)–C(37)	1.502(16)	1.542(13)
C(23)–C(24)	1.361(13)	1.359(13)	C(33)–C(34)	1.407(18)	1.414(15)
C(24)–C(25)	1.434(14)	1.419(13)	C(43)–C(35)	1.387(17)	1.367(14)
C(24)–C(28)	1.522(11)	1.516(13)	C(34)–C(38)	1.497(14)	1.511(15)
C(25)–C(26)	1.364(11)	1.380(12)	C(35)–C(36)	1.372(12)	1.400(13)
C(26)–C(29)	1.499(16)	1.515(13)	C(36)–C(39)	1.513(15)	1.499(12)
C(27)–Zr(1)–C(31)	82.3(3)	82.4(3)	C(27)–Zr(2)–C(31)	83.3(3)	84.5(3)
C(21)–Zr(1)–C(31)	88.9(3)	87.2(3)	C(21)–Zr(2)–C(31)	89.7(3)	89.9(3)
C(21)–Zr(1)–C(27)	61.1(3)	61.1(3)	C(21)–Zr(2)–C(27)	60.8(3)	61.1(3)
C(7)–Zr(1)–C(8)	31.6(5)	32.6(4)	C(15)–Zr(2)–C(16)	31.6(5)	32.3(4)
C(6)–Zr(1)–C(7)	31.2(5)	32.4(4)	C(14)–Zr(2)–C(15)	32.5(4)	32.3(4)
C(5)–Zr(1)–C(6)	31.6(5)	31.9(4)	C(13)–Zr(2)–C(14)	33.2(5)	32.8(4)
C(4)–Zr(1)–C(5)	32.8(5)	33.3(4)	C(12)–Zr(2)–C(13)	32.2(6)	32.3(4)
C(3)–Zr(1)–C(4)	33.6(6)	33.0(4)	C(11)–Zr(2)–C(12)	32.7(6)	33.1(5)
C(2)–Zr(1)–C(3)	33.6(5)	32.5(3)	C(10)–Zr(2)–C(11)	33.5(5)	33.0(4)
C(1)–Zr(1)–C(8)	33.2(6)	33.6(4)	C(9)–Zr(2)–C(16)	32.6(5)	32.8(4)
C(1)–Zr(1)–C(2)	33.7(7)	32.3(4)	C(9)–Zr(2)–C(10)	32.7(6)	32.1(5)
Zr(1)–C(21)–C(26)	135.3(6)	134.7(6)	Zr(2)–C(27)–C(22)	84.4(5)	84.2(5)
Zr(1)–C(21)–C(22)	83.6(5)	81.7(5)	Zr(1)–C(27)–C(22)	87.1(6)	86.4(5)
Zr(2)–C(21)–C(26)	132.8(6)	133.8(6)	Zr(1)–C(27)–Zr(2)	92.0(3)	91.8(3)
Zr(2)–C(21)–C(22)	80.5(5)	80.6(5)	Zr(1)–C(31)–Zr(2)	79.2(3)	79.7(3)
C(22)–C(21)–C(26)	116.9(8)	117.9(8)	Zr(2)–C(31)–C(36)	117.5(6)	119.1(6)
Zr(1)–C(21)–Zr(2)	87.4(3)	87.1(3)	Zr(2)–C(31)–C(32)	114.8(7)	120.8(5)
C(23)–C(22)–C(27)	132.0(9)	131.7(8)	Zr(1)–C(31)–C(36)	113.3(6)	107.7(5)
C(21)–C(22)–C(27)	105.8(8)	107.7(7)	Zr(1)–C(31)–C(32)	108.5(6)	107.2(6)
C(21)–C(22)–C(23)	122.2(8)	120.6(8)	C(32)–C(31)–C(36)	117.1(8)	114.2(8)

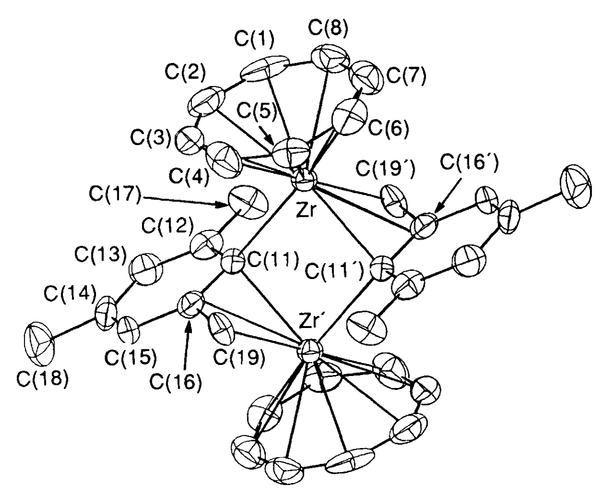


Figure 4. An ORTEP drawing of complex (**7**)

two coplanar allyl ligands. The zirconium-to-plane distances are 1.680(12) and 1.565(2) Å for cyclo-octatetraene and middle plane respectively.[15a,21] The geometry of the Zr(η^8-C_8H_8) unit is very close to that observed in complexes (**2**) and (**3**).

The dimerization of fragment (**B**) to complex (**7**) produces relatively saturated metal centres sterically protected by some rigid bridging ligands. Such structural features along with the absence of metal–carbon σ bonds should explain the absence of reactivity with carbon monoxide. The thermal rearrangement of complex (**7**) requires a hydrogen shift between the two zirconium-bonded methylenes and gives a μ-alkylidene. Such a shift is likely to be mediated by the metal in an intramolecular process, though we do not have any evidence for this. The interesting aspect of such a rearrangement is the rather mild conditions under which conversion of an alkyl into a bridging μ-alkylidene group occurs. Such a reaction, in which the alkylidene bridges two metal centres, may be regarded as a disproportionation [equation (5)].

(5)

Complex (**8**) has some unique characteristics associated with the μ-alkylidene zirconium moiety of which this is the first

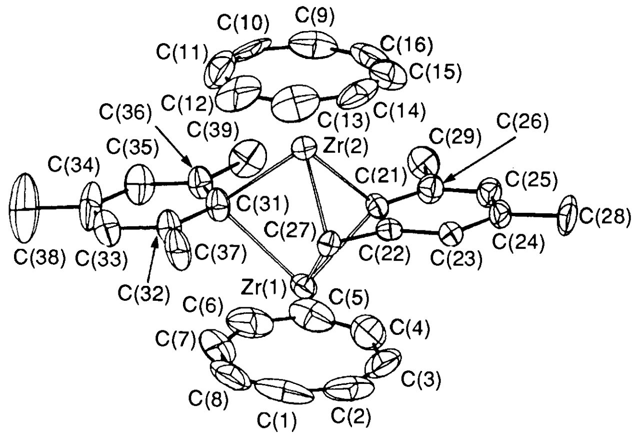


Figure 5. An ORTEP drawing of complex (**8**)

example. An ORTEP view of (**8**) is given in Figure 5 and selected bond distances and angles are in Table 9. Two crystallographically independent molecules (a) and (b) having the same geometry are present in the asymmetric unit (Table 9). Molecule (a) only is presented in Figure 5. The singly bridging mesityl group binds asymmetrically the two zirconium atoms [values for molecule (b) in square brackets] {Zr(1)–C(31) 2.544(9) [2.566(7)], Zr(2)–C(31) 2.496(7) [2.460(9)] Å}. In the multiple bridging mesityl group the two zirconium atoms share at a very short distance two carbons, C(21) and C(27) {Zr(1)–C(21) 2.318(7) [2.344(7)], Zr(1)–C(27) 2.231(8) [2.236(9)], Zr(2)–C(21), 2.334(8) [2.334(8)], Zr(2)–C(27) 2.235(9) [2.252(6)] Å}, while they are significantly further from C(22) {Zr(1)–C(22) 2.595(8) [2.576(9)], Zr(2)–C(22) 2.539(9) [2.542(7)] Å}. The C(21)–C(22)–C(27) fragment, though it binds the metal rather asymmetrically, is very reminiscent of the allylic structure observed in complex (**7**). In addition the C–C bond distance sequence in the phenyl rings is similar to that in (**7**). The double bonds are mainly localized on C(23)–C(24) and C(25)–C(26) {C(23)–C(24) 1.361(13) [1.359(13)], C(25)–C(26) 1.364(11) [1.380(12)], C(24)–C(25) 1.434(14) [1.419(13)] Å}, and the C(22)–C(27) bond distances {1.445(12) [1.429(11)] Å} are significantly shorter than the corresponding ones involving methyl carbons (Table 9). Other features of the structure are similar to those observed in complex (**7**): (*i*) the two cyclo-octatetraene rings are nearly parallel {dihedral angle 7.6(3) [5.4(3)]°}; (*ii*) the cyclo-octatetraene rings are nearly parallel to the plane through the C(21), C(27), and C(31) co-ordinated carbon atoms, the dihedral angle they form being 4.1(3) [3.0(3)]° and 3.4(3) [2.8(3)]° respectively; (*iii*) the phenyl rings are twisted relative to each other by 14.8(3)°. The compound could be therefore regarded as a triple-decker sandwich with the zirconium atoms symmetrically sandwiched between a common central layer and two parallel cyclo-octatetraene rings at each end. The zirconium-to-plane distances are 1.674(2) [1.682(1)], and 1.686(1) [1.694(1)] Å for Zr(1) and Zr(2) from cyclo-octatetraene; and 1.615(2) [1.640(1)] and 1.597(1) [1.581(1)] Å for Zr(1) and Zr(2) respectively from the central plane. The geometry of the Zr(η^8-C_8H_8) unit is very similar to that observed in complexes (**2**), (**3**), and (**7**). The Zr–C(22) distances are in good agreement with respect to the corresponding distances observed in complex (**7**). Comparison with other alkylidene complexes of zirconium is limited to the work of Schwarz and co-workers,[22] for which no structural information is available.

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