Improved Synthesis and Structure of Solvated and Unsolvated Forms of Cyclooctatetraene-zirconium and -hafnium Dichloride†

Pietro Berno,[a] **Carlo Floriani,***[,a] **Angiola Chiesi-Villa**[b] **and Corrado Rizzoli**[b]
[a] *Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland*
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy*

An improved synthesis for $[M(\eta^8\text{-}C_8H_8)Cl_2(thf)]$ (M = Zr or Hf) and their unsolvated forms $[M(\eta^8\text{-}C_8H_8)Cl_2]$ has been developed based on a ligand redistribution reaction between $[M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ and $[MCl_4(thf)_2]$ (thf = tetrahydrofuran). This reaction was proven to be valuable also in the case of substituted cyclooctatetraenes, as shown in the synthesis of $[\{Zr[\eta^8\text{-}C_8H_6(SiMe_3)_2]Cl\}_2(\mu\text{-}Cl)_2]$. Crystallographic details: $[Hf(\eta^8\text{-}C_8H_8)Cl_2(thf)]$, space group *Cmca*, $a = 12.308(1)$, $b = 12.005(1)$, $c = 17.470(2)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$, and $R = 0.032$ for 771 independent observed reflections; $[\{Zr[\eta^8\text{-}C_8H_6(SiMe_3)_2]Cl\}_2(\mu\text{-}Cl)_2]$, space group $C222_1$, $a = 10.498(1)$, $b = 23.253(2)$, $c = 15.830(1)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$ and $R = 0.048$ for 3121 independent observed reflections.

The half-sandwich monocyclooctatetraene 14-valence electron derivatives $[M(\eta^8\text{-}C_8H_8)Cl_2]$ (M = Zr or Hf) should be considered a very interesting alternative option to the well known $M(\eta^5\text{-}C_5H_5)_2X_2$ for studying organic transformations induced by zirconium and hafnium.[1] Additional advantages over the well known cyclopentadienyl analogues are their electronic and co-ordinative unsaturation.[2] However, a major obstacle preventing more frequent use of $[M(\eta^8\text{-}C_8H_8)Cl_2]$ complexes has been the lack in the literature of a reliable, inexpensive direct synthesis.[3] We report here high-yield syntheses of these compounds by a very convenient ligand redistribution reaction,‡ and their full characterization including X-ray analysis.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The synthesis of $[M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$[3,6] [M = Zr(thf) (thf = tetrahydrofuran), **3**; or Hf, **4**] $[Zr\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}]$[6] **9** and $[MCl_4(thf)_2]$[7] (M = Zr, **1**; or Hf, **2**) were carried out as reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer and ^1H NMR spectra on a 200-AC Bruker instrument.

Preparations.—$[Zr(\eta^8\text{-}C_8H_8)Cl_2(thf)]$ **5**. Complex **3** (24.31 g, 65.41 mmol) and $[ZrCl_4(thf)_2]$ **1** (24.68 g, 65.40 mmol) were suspended in freshly distilled thf (350 cm^3). The suspension was refluxed overnight during which time the colour changed from red to yellow-orange. The orange microcrystalline solid (39.41 g, 89%) was filtered off and washed with thf (2 × 50 cm^3) (Found: C, 42.60; H, 4.75. $C_{12}H_{16}Cl_2OZr$ requires C, 42.60; H, 4.75%). Proton NMR in CD_2Cl_2: δ 6.94 (s, 8 H, C_8H_8), 3.78 (m, 4 H, thf) and 1.82 (m, 4 H, thf).

$[Hf(\eta^8\text{-}C_8H_8)Cl_2(thf)]$ **6**. Complex **4** (8.632 g, 22.32 mmol) and $[HfCl_4(thf)_2]$ **2** (10.37 g, 22.32 mmol) were suspended in thf (100 cm^3) and refluxed for 48 h during which time the colour changed from red to yellow. The product (11.38 g, 60%) was filtered off and washed with diethyl ether (3 × 50 cm^3) (Found: C, 33.45; H, 3.45. $C_{12}H_{16}Cl_2HfO$ requires C, 32.85; H, 3.80%). Proton NMR in CD_2Cl_2: δ 6.86 (s, 8 H, C_8H_8), 3.81 (m, 4 H, thf) and 1.83 (m, 4 H, thf).

$[Zr(\eta^8\text{-}C_8H_8)Cl_2]$ **7**. Complex **5** (3.50 g, 10.3 mmol) was heated at 120 °C for 1 h (10^{-2} Torr, *ca.* 1.33 Pa). The resulting pink powder was suspended in xylene (250 cm^3) and extracted overnight with the mother-liquor. The product was obtained as a pink microcrystalline powder in quantitative yield (2.75 g) (Found: C, 36.05; H, 3.15. $C_8H_8Cl_2Zr$ requires C, 36.10; H, 3.05%). Its insolubility prevented the recording of an NMR spectrum.

$[Hf(\eta^8\text{-}C_8H_8)Cl_2]$ **8**. Complex **6** (4.37 g, 10.26 mmol) was suspended in toluene (150 cm^3) and the solid was extracted for 36 h with the mother-liquor resulting in a yellow microcrystalline powder (2.92 g, 80.5%) (Found: C, 27.00; H, 2.25. $C_8H_8Cl_2Hf$ requires C, 27.20; H, 2.30%). Proton NMR in CD_2Cl_2: δ 6.87 (s).

$[\{Zr[\eta^8\text{-}C_8H_6(SiMe_3)_2]Cl\}(\mu\text{-}Cl)_2]$ **10**. Compound **9**[6] (5.47 g, 9.30 mmol) and $[ZrCl_4(thf)_2]$ (3.51 g, 9.30 mmol) were refluxed overnight in toluene (100 cm^3) during which time the colour changed from violet to yellow-green. The orange microcrystalline product (4.44 g, 68%) was obtained after the reaction mixture had been concentrated to 20 cm^3 and heptane (30 cm^3) added. Crystals suitable for structure determination were obtained when the filtrate was allowed to stand at room temperature for several days (Found: C, 40.80; H, 6.55. $C_{28}H_{48}Cl_4Si_4Zr_2$ requires C, 40.95; H, 5.90%). Proton NMR in CD_2Cl_2: δ 7.07 (s, 2 H), 6.96–6.54 (m, 4 H) and 0.51 (s, 18 H).

Crystal Structure Determination of Complexes **6** *and* **10**.—Crystal data and details of the data collection and refinement are in Table 1. The crystal quality was tested by ψ scan showing that crystal absorption effects could be neglected for complex **6**.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

‡ Such a reaction was successfully employed previously only once, but the compound $[Zr(\eta^8\text{-}C_8H_8)Cl_2]$ was not isolated and was used *in situ* mixed with the KCl formed during the synthesis.[4] The various aspects of the C_8H_8 redistribution reaction have recently been discussed in connection with the synthesis of $[U(C_8H_8)X_2]$ derivatives.[5]

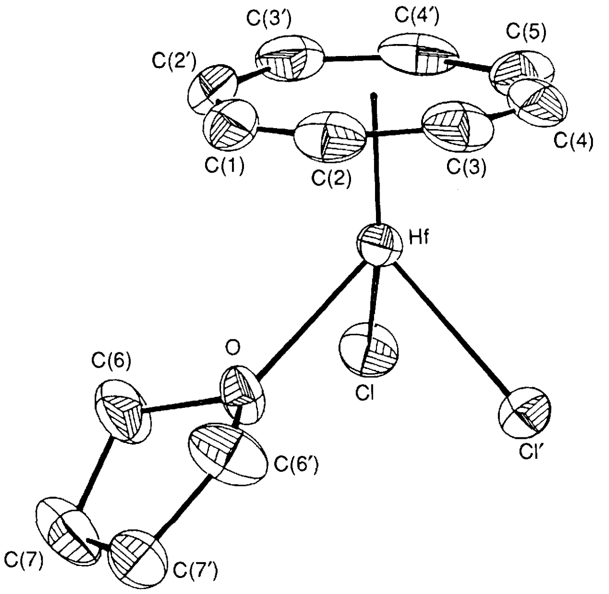

Fig. 1 An ORTEP view of complex **6**. Primes indicate the transformation $-x, y, z$

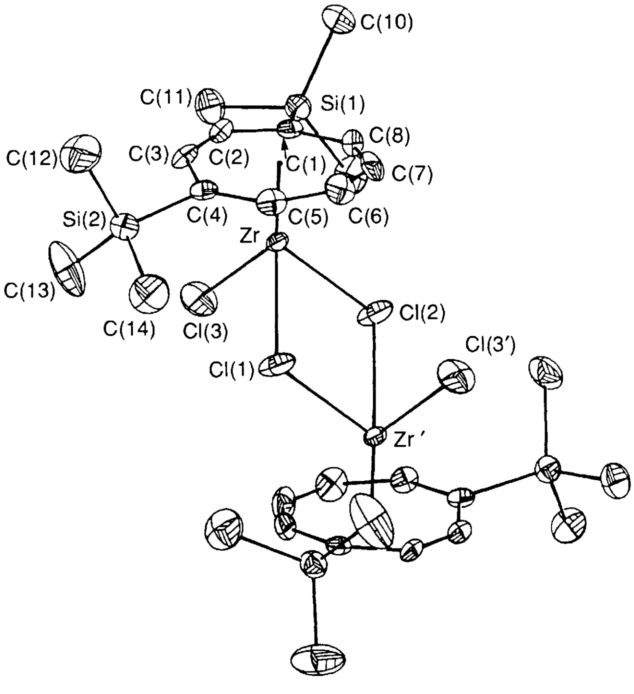

Fig. 2 An ORTEP view of complex **10**. Primes indicate the transformation $-x, y, \frac{3}{2} - z$

These data were then corrected for absorption following a semiempirical method. The structures were solved using SHELX 86.[8] For both complexes all the non-H atoms were isotropically, then anisotropically refined. All H atoms were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic U values of 0.08 Å^2.

Final atomic coordinates are listed in Tables 2 and 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Experimental data for the X-ray diffraction studies of complexes **6** and **10**[a]

Complex	**6**	**10**
Formula	$C_{12}H_{16}Cl_2HfO$	$C_{28}H_{48}Cl_4Si_4Zr_2$
M	425.7	821.3
Space group	*Cmca*	$C222_1$
Cell parameters at 295 K[b]		
a/Å	12.308(1)	10.498(1)
b/Å	12.005(1)	23.253(2)
c/Å	17.470(2)	15.830(1)
U/Å^3	2581.3(4)	3864.3(6)
Z	8	4
D_c/g cm^{-3}	2.191	1.412
F(000)	1616	1680
μ/cm^{-1}	84.08	9.49
Crystal dimension/mm	0.08 × 0.43 × 0.32	0.28 × 0.32 × 0.35
2θ range/°	6–50	6–54
Unique total data	1204	4397
Unique observed data	771	3121
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.032	0.048
$R' = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.031	0.049
Goodness of fit[c]	0.55	0.64

[a] Details pertaining to both complexes: Philips PW 1100 diffractometer; ω scan type; monochromated Mo-Kα radiation (λ = 0.710 69 Å); criterion for observation $I > 2\sigma(I)$, crystal system, orthorhombic. [b] Obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $\Sigma w\lvert\Delta F\rvert^2/(N_o - N_v)$ where N_o, N_v = numbers of observations and variables; $w = 1/[\sigma^2 F_o + gF_o^2]$.

Results and Discussion

$$[MCl_4(thf)_2] + 2K_2C_8H_8 \xrightarrow[-KCl]{thf} [M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)] \quad (1)$$
$$M = Zr\ \mathbf{1}\ \text{or Hf}\ \mathbf{2} \qquad M = Zr(thf)\ \mathbf{3}\ \text{or Hf}\ \mathbf{4}$$

$$[M(\eta^8\text{-}C_8H_8)[(\eta^4\text{-}C_8H_8)] \xrightarrow{HCl} [M(\eta^8\text{-}C_8H_8)Cl_2(thf)] \quad (2)$$
$$M = Zr\ \mathbf{5}\ \text{or Hf}\ \mathbf{6}$$

The previous synthesis of compounds **5** and **6** was carried out in two steps, as exemplified in reactions (1) and (2).[3,4] The main disadvantages of reaction (2) are (*i*) the 50% consumption of the difficult-to-prepare C_8H_8 ligand, and (*ii*) the use of dry HCl which is difficult to control stoichiometrically. We found, however, that reaction (2) can be replaced by the ligand redistribution reaction (3),[4] which doubles the yield of **5** and **6**, without any loss of cyclooctatetraene.

$$[M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)] + [MCl_4(thf)_2] \xrightarrow[-KCl]{thf} [M(\eta^8\text{-}C_8H_8)Cl_2(thf)] \quad (3)$$
$$M = Zr\ \mathbf{5}\ \text{or Hf}\ \mathbf{6}$$

Exchange of C_8H_8 was achieved by refluxing a thf suspension of complexes **3** and **4** with **1** and **2** respectively (see Experimental section). Complexes **5** and **6** have been known for several years,[3] though their use in organometallic chemistry is still very limited.[2–4] They are isostructural.[9] The knowledge of the ligand redistribution reaction (3) suggests that the synthesis of **5** and **6** should be possible in a single step using a 1:1 MCl_4:$K_2C_8H_8$ molar ratio.[4] Although this is possible in principle using the conditions specified in the Experimental section for reaction (3), the separation of KCl from **5** and **6** was unsuccessful.

Therefore, we suggest the most convenient method for the preparation of **5** and **6** involves the two steps shown in reactions (1) and (3). A full account of reaction (1) is reported in the preceding paper.[6] The presence of thf in complexes **5** and **6** may be inconvenient in the preparation of very reactive organometallic and hydrido derivatives, and may be lost by heating followed by an extraction with an aromatic hydrocarbon such as toluene or xylene [equation (4)].

Table 2 Fractional atomic coordinates (× 10^4) for complex **6**

Atom	*X/a*	*Y/b*	*Z/c*
Hf	0(–)	1209.6(4)	1774.4(3)
C(1)	1383(2)	–273(2)	1561(2)
O	0(–)	1016(7)	2745(5)
C(1)	0(–)	3137(10)	1900(10)
C(2)	–1049(9)	2949(8)	1634(7)
C(3)	–1491(7)	2412(10)	998(8)
C(4)	–1056(8)	1817(9)	373(7)
C(5)	0(–)	1555(10)	116(8)
C(6)	–934(8)	1180(10)	3245(7)
C(7)	–614(9)	807(10)	4019(7)

Table 3 Fractional atomic coordinates (× 10^4) for complex **10**

Atom	*X/a*	*Y/b*	*Z/c*
Zr	1757(1)	2376(0)	6926(0)
Cl(1)	0(0)	3084(1)	7500(0)
Cl(2)	0(0)	1672(1)	7500(0)
Cl(3)	502(2)	2354(1)	5627(1)
Si(1)	3220(2)	973(1)	5922(1)
Si(2)	3045(2)	3925(1)	6377(1)
C(1)	3360(6)	1670(3)	6526(4)
C(2)	3605(6)	2168(3)	6049(4)
C(3)	3549(6)	2766(3)	6135(4)
C(4)	3261(6)	3166(3)	6791(4)
C(5)	3073(7)	3070(3)	7676(4)
C(6)	3055(7)	2587(4)	8200(4)
C(7)	3067(7)	2001(3)	8091(4)
C(8)	3156(8)	1615(3)	7400(4)
C(9)	1695(10)	604(3)	6195(6)
C(10)	4629(9)	528(4)	6194(6)
C(11)	3199(10)	1116(3)	4756(5)
C(12)	4616(11)	4217(5)	6158(10)
C(13)	2120(14)	3914(4)	5415(7)
C(14)	2180(11)	4376(4)	7157(7)

$$[\mathrm{M}(\eta^8\text{-}\mathrm{C_8H_8})\mathrm{Cl_2(thf)}] \xrightarrow{-\mathrm{thf}} [\mathrm{M}(\eta^8\text{-}\mathrm{C_8H_8})\mathrm{Cl_2}] \quad (4)$$

$$\mathrm{M} = \mathrm{Zr}\ \mathbf{7}\ \text{or}\ \mathrm{Hf}\ \mathbf{8}$$

The ^{1}H NMR spectra of complexes **6** and **8** do not show any difference between the solvated and unsolvated form in methylene chloride solution, in addition thf appears as a free solvent. This probably implies the existence in solution of an unsolvated form, if solvation by CH_2Cl_2 is neglected. This form could be either monomeric or dimeric. Complexes **7** and **8** should have, however, a dimeric structure in the solid state. Such a characteristic was confirmed indirectly by X-ray analysis on complex **10**.

$$\underset{\mathbf{9}}{[\mathrm{Zr}\{\eta^8\text{-}\mathrm{C_8H_6(SiMe_3)_2}\}\{\eta^4\text{-}\mathrm{C_8H_6(SiMe_3)_2}\}]} + [\mathrm{ZrCl_4(thf)_2}] \;\; \Big\downarrow{\scriptstyle \text{toluene}\ \Delta} \;\; \underset{\mathbf{10}}{[\{\mathrm{Zr}[\eta^8\text{-}\mathrm{C_8H_6(SiMe_3)_2}]\mathrm{Cl}\}_2(\mu\text{-}\mathrm{Cl})_2]} \quad (5)$$

Table 4 Bond distances (Å) and angles (°) for complex **6**

Hf–C_T(1)	1.629(12)	C_T(1)–Hf–Cl	130.8(4)
Hf–Cl	2.468(2)	C_T(1)–Hf–O	126.3(4)
Hf–O	2.233(9)	Cl–Hf–O	82.2(1)
		Cl–Hf–Cl′	87.2(1)

C_T(1) refers to the centroid of the C_8H_8 ring.

Table 5 Bond distances (Å) and angles (°) for complex **10**

Zr–C_T(1)	1.610(6)	Zr–Cl(2)	2.628(2)
Zr–Cl(1)	2.634(2)	Zr–Cl(3)	2.442(2)
C_T(1)–Zr–Cl(1)	128.5(2)	Zr–Cl(2)–Zr′	102.97(2)
C_T(1)–Zr–Cl(2)	129.3(2)	Cl(2)–Zr–Cl(3)	84.23(5)
C_T(1)–Zr–Cl(3)	133.0(2)	Cl(1)–Zr–Cl(3)	85.73(5)
Zr–Cl(1)–Zr′	102.64(2)	Cl(1)–Zr–Cl(2)	77.20(2)

C_T(1) refers to the centroid of the C_8H_8 ring.

Reaction (5) confirms that the redistribution reaction works even in the case of substituted cyclooctatetraenes. In addition, if the redistribution reaction is carried out in toluene the unsolvated form is obtained.

The structure of complex **6**, shown in Fig. 1, possesses a plane of symmetry bisecting the two chlorines. The (C_8H_8)-(centroid)–Hf distance is close to that found in the bis(cyclooctatetraene) derivatives.[6] The dimeric structure of **10** is shown in Fig. 2. The two zirconium atoms of the dimer are doubly bridged by two chlorine atoms lying on a two-fold axis parallel to [010], so the dimer possesses C_2 symmetry. The $ZrCl_2$ ring is, as required by the symmetry, strictly planar. The two C_8H_8 rings are parallel, with a dihedral angle of 1.1(2)°, and they have an *anti* arrangement with respect to the Zr_2Cl_2 ring. The dihedral angle between the C_8H_8 plane and the Zr_2Cl_2 plane is 54.1°.

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