Fourteen Electron Monoalkyl and Monohydrido Derivatives of Cyclooctatetraenezirconium: Reduction of Carbon Monoxide to Formaldehyde

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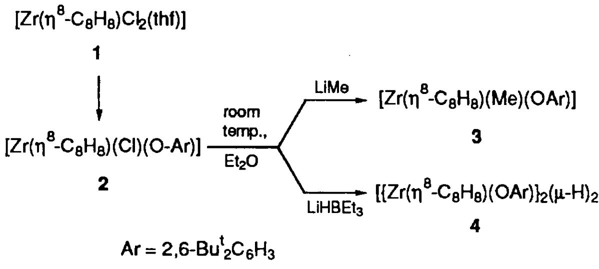
[Zr(η^8-C_8H_8)(OAr)(Cl)] (Ar = 2,6-Bu^t_2-C_6H_3) **2** was transformed into the corresponding methyl, [Zr(η^8-C_8H_8)(Me)(OAr)] **3** and dimeric hydrido, [{Zr(η^8-C_8H_8)(OAr)}$_2$(μ-H)$_2$] **4** derivatives; the latter complex reduced CO to formaldehyde to produce the dimeric [{Zr(η^8-C_8H_8)(OAr)}$_2$(μ-CH_2O)] **5**, isostructural to **4**.

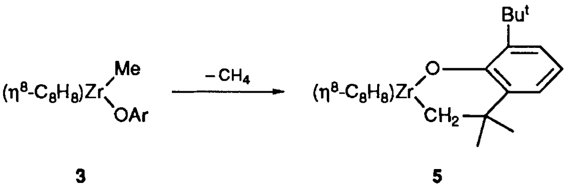
Despite the fact that some cyclooctatetraene derivatives of zirconium have been known for several years,[1] the Zr(η^8-C_8H_8) fragment has been scarcely used in orgamometallic chemistry,[2–4] though its high unsaturation is responsible for easy intramolecular C–H bond activation.[4]

In this context [Zr(η^8-C_8H_8)Cl_2(thf)] **1**[2b] (thf = tetrahydrofuran) was converted into the aryloxo compound [Zr(η^8-C_8H_8)(Cl)($OC_6H_3Bu^t_2$-2,6) **2**,† having the reactive Zr–Cl functionality protected in a sort of cavity by the sterically hindered 2,6-$Bu^t_2C_6H_3O^-$ anion. According to reaction (1), complex **2** was converted at room temperature in diethyl ether into the crystalline derivatives **3**† and **4**.†‡ They are thermally rather labile and very reactive. Complex **3** forms the metallacycle **5**† by loss of CH_4 at reflux in hexane [reaction (2)].

Complex **4** is a remarkably reactive monohydrido derivative of zirconium(IV), which is soluble in organic solvents, unlike the polymeric form of [Zr(η^5-C_5H_5)(H)(Cl)].[5] Its structure is shown in Fig. 1, with some relevant structural parameters. A relatively limited number of hydrido derivatives of Zr^{IV} has so far been structurally characterized, namely [{Zr(η^5-C_5H_4Me)(H)}$_2$(μ-H)$_2$] **6**[6a] and [Zr(η^8-C_8H_8)(η^5-C_5H_5)(H)] **7**.[3b] The structural parameters for the [Zr(μ-H)$_2$Zr] core are close to those in **6**, except for the differences in the Zr–H bond distances. There are major differences, however, in terms of reactivity between the 18, 16 and 14 electron hydrido derivatives, the degree of reactivity being parallel to the metal unsaturation.[7] Complex **1** shows poor reactivity.[3b] The phenoxo group in complex **4** provides, in addition to steric protection, some electronic stabilization to the M–H functionality due to the existence of multiple Zr–O bonding (see caption of Fig. 1). Complex **4** reacts at room temperature and atmospheric pressure with carbon monoxide to produce the formaldehyde complex **8**.†



(1)



(2)

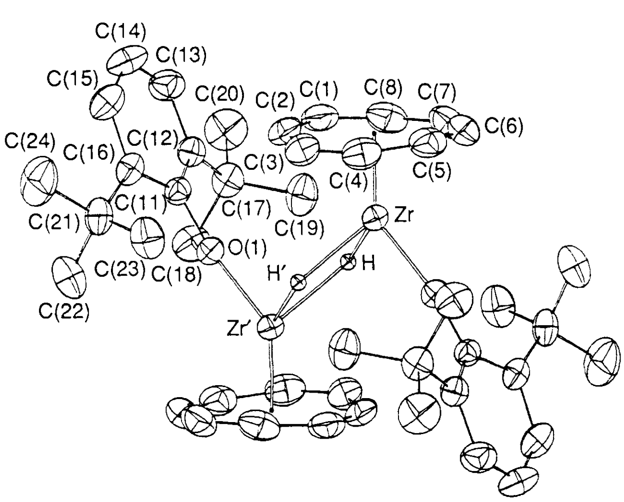


Fig. 1 An ORTEP view of the dimer in complex **4** (30% probability ellipsoids). Prime denotes a transformation of $-x$, $-y$, $-z$. Interatomic distances (Å): Zr–O(1), 1.983(2); Zr–Cp(centroid), 1.702(4); Zr–H, 1.85(3); Zr–H′, 2.03(3); Zr · · · Zr′, 3.482(1). Bond angles (°): H–Zr–H′, 52.4(13); O(1)–Zr–Cp, 134.6(1); Cp–Zr–H′, 129.0(9); Cp–Zr–H 129.1(10); O(1)–Zr–H′, 90.7(9); O(1)–Zr–H, 90.7(10), Zr–H–Zr′, 127.6(16).

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† Satisfactory analytical and ^{1}H NMR data have been obtained for **2**, **3**, **4**, **5** and **8**. ^{1}H NMR (CD_2Cl_2, δ): complex **2**, 7.12 (s, 8 H), 7.04 (d, *J* 7.8 Hz, 2 H), 6.68 (t, *J* 7.8 Hz, 1 H) and 1.31 (s, 18 H); complex **3**, 7.01 (d, *J* 8.0 Hz, 2 H), 6.92 (s, 8 H), 6.61 (t, *J* 8.0 Hz, 1 H), 1.28 (s, 18 H) and −1.03 (s, 3 H); complex **4**, 7.21 (d, *J* 8.0 Hz, 2 H), 6.81 (t, *J* 8.0 Hz, 1 H), 6.17 (s, 8 H), 4.38 (s, 1 H) and 1.46 (s, 18 H); complex **5**, 6.98 (s, 8 H), 6.94–6.87 (m, 2 H), 6.56 (t, *J* 8.0 Hz, 1 H), 1.26 (s, 9 H), 0.94 (s, 6 H) and 0.09 (s, 2 H); complex **8**, 7.18 (d, *J* 8.0 Hz, 2 H), 6.76 (t, *J* 8.0 Hz, 1 H), 6.19 (s, 8 H), 1.99 (s, 1 H), and 1.38 (s, 18 H); preliminary X-ray analysis is available for **5**.

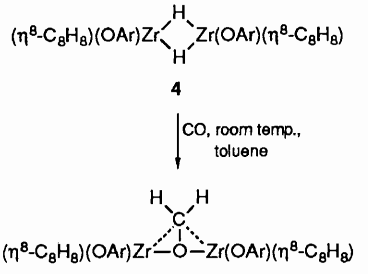
‡ *Crystal data*: complex (**4**), $C_{44}H_{60}O_2Zr_2$, M = 803.4, monoclinic, space group $P2_1/n$, a = 18.687(1), b = 11.603(1), c = 9.098(1) Å, β = 97.40(1)°, U = 1956.3(3) Å^3, Z = 2, D_c = 1.364 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 5.57 cm^{-1}, crystal dimensions 0.25 × 0.32 × 0.40 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 2640 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range 6 < 2θ < 50°, the R value is 0.028. Complex **8**, $C_{45}H_{60}O_3Zr_2$, M = 831.4, monoclinic, space group $P2_1/n$, a = 19.031(4), b = 11.525(2), c = 9.086(1) Å, β = 95.19(1), U = 1984.7(6) Å^3, Z = 2, D_c = 1.391 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 5.53 cm^{-1}, crystal dimensions 0.35 × 0.48 × 0.55 mm. The structure was solved and refined as above. For 2898 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range 6 < 2θ < 54°, the R value is 0.050. The oxygen atom of formaldehyde was found to lie on a centre of symmetry requiring a statistical distribution of the CH_2 group. As a consequence the C(25) carbon atom was given site occupation factor of 0.5. All calculations were carried out using SHELX76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$[\{Zr(\eta^5\text{-}C_5H_4Me)(H)^2\}_2(\mu\text{-}H)_2]$

6

$[Zr(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)(H)]$

7



4

8

(3)

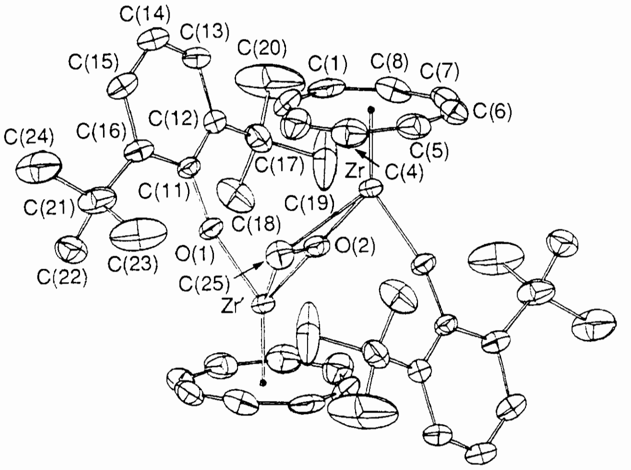


Fig. 2 An ORTEP view of the dimer in complex **8** (20% probability ellipsoids). Prime denotes a transformation $-x$, $1 - y$, $-z$. Interatomic distances (Å): Zr–O(1), 1.983(4); Zr–Cp(centroid), 1.690(7); Zr–O(2), 2.094(1); Zr–C(25), 2.574(14); Zr'–C(25), 2.366(14); O(2)–C(25), 1.313(14); Zr · · · Zr', 4.189(1). Bond angles (°): O(2)–Zr–C(25), 30.5(3); O(1)–Zr–Cp, 134.5(3); Cp–Zr–C(25), 128.8(4); Cp–Zr–O(2), 135.9(3); O(1)–Zr–C(25), 88.6(4); O(1)–Zr–O(2), 89.7(1), Zr–O(2)–Zr', 180.0; Zr–C(25)–Zr', 115.9(6).

The isostructurality of complexes **4** and **8** (Fig. 2) shows that the hydrogenation of CO occurs with the dimeric structure remaining almost intact.

The monomeric fragment $\{Zr(\eta^8\text{-}C_8H_8)(OAr)\}$ has the same characteristics in both complexes **4** and **8**, which are centrosymmetric and isostructural. In complex **4** the centre of symmetry is located between the two hydrogens.‡ In complex **8** the oxygen lies on the centre of symmetry and this implies a statistical distribution of C(25) in two equivalent positions around the linear Zr–O–Zr' bond. The $Zr(\mu\text{-}H)_2Zr$ unit undergoes significant changes upon carbonylation, the Zr · · · Zr separation increasing from 3.482(1) Å to 4.189(1) Å and the H–Zr–H' angle [52.4(13)°] to Zr–O(2)–Zr (180°) and Zr–C(25)–Zr' [115.9(6)°]. The bridging bonding mode is similar to that in $[\{(C_5H_5)_2ZrCl\}_2(\mu\text{-}CH_2O)]$,[8a] though in **8** the Zr–C bond distances [2.574(14) and 2.366(14) Å] are much longer than the Zr–O[2.094(1) Å] and the C–O significantly shorter than in the few other formaldehyde complexes known.[8] The chemistry of **3** and **4** is currently being explored.

We thank the Fonds National Suisse de la Recherche Scientifique (Grant. No. 20-26245-89) and Ciba-Geigy A. G. (Basel) for financial support.

Received, 25th September 1990: Com. 0/04337C

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