

## Facile Formation of a Bridging Cyclooctatrieneyne Ligand; Synthesis and Molecular Structure of $[\{\eta\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\}\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}\{\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\}\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}]$

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The reaction between the bridging chloride dimer  $[\{\text{Zr}(\eta\text{-COT}^m)\text{Cl}_2\}_2]$  [ $\text{COT}^m = 1,4\text{-bis}(\text{trimethylsilyl})\text{cyclooctatetraene}$ ] and  $[\text{LiCH}(\text{SiMe}_3)_2]$  affords the title complex, whose X-ray structure reveals a bridging cyclooctatrieneyne ligand resulting from double hydrogen abstraction from a COT ring.

We have been interested in preparing early transition metal and *f*-element complexes that incorporate the substituted cyclooctatetraene ligand, 1,4-bis(trimethylsilyl)cyclooctatetraene ( $\text{COT}^m$ ) since preliminary studies have shown that inclusion of the bulky  $\text{SiMe}_3$  groups affords complexes of high solubility and low nuclearity as well as providing products with unusual solid-state structures.<sup>1,2</sup> The synthesis of the dimer  $[\{\text{Zr}(\text{COT}^m)\text{Cl}_2\}_2]$ , which was independently reported during the course of this work,<sup>3</sup> has allowed us to investigate the chemistry of half-sandwich  $\text{Zr}^{\text{IV}}$  compounds that contain the  $[\text{Zr}(\text{COT}^m)]$  moiety, some of which may prove to be viable alternatives to the ubiquitous bis(cyclopentadienyl) systems of Group IV in, for example, olefin polymerisation.

Concerted hydrogen atom abstraction reactions from, for example, coordinated pentamethylcyclopentadienyl, alkyl or aryl groups to afford fulvene,<sup>4</sup> alkylidene or aryne complexes<sup>5</sup> is well established. However, the formation of a cyclooctatrieneyne ligand by hydrogen abstraction from coordinated cyclooctatetraene has only very recently been observed, *via* the thermolysis of  $[\text{Zr}(\text{COT}^m)(\text{C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)]$  at elevated temperatures.<sup>6</sup>

Herein, we report the synthesis and structural characterisation of a binuclear zirconium complex containing a cyclooctatrieneyne ligand formed *via* double C-H activation of a coordinated  $\text{COT}^m$  ligand under extremely mild conditions.

Treatment of  $[\{\text{Zr}(\text{COT}^m)\text{Cl}_2\}_2]$  with 4 equiv. of  $[\text{LiCH}(\text{SiMe}_3)_2]$  in diethyl ether at  $-78^\circ\text{C}$  afforded a red-orange solution; rapid room-temperature work-up and recrystallisation from pentane at  $-30^\circ\text{C}$  afforded dark red air-sensitive crystals of  $[\{\eta\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\}\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}\{\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\}\text{Zr}\{\text{CH}(\text{SiMe}_3)_2\}]$  **1** in 60% yield (Scheme 1).<sup>†</sup> Complex **1** is somewhat unstable in solution at room temperature, and decomposes to a mixture (by NMR) of, as yet, unidentified products.

Solution NMR studies<sup>‡</sup> confirm the existence of a bridging cyclooctatrieneyne ligand in **1**. The  $^1\text{H}$  NMR spectrum shows the presence of a coordinated planar  $\eta^8\text{-COT}^m$  ring as indicated by two multiplets and a singlet at  $\delta$  6.7–7.1, characteristic of the AA'BB'X<sub>2</sub> splitting pattern for  $\text{COT}^m$ . For the  $[\text{C}_8\text{H}_4(\text{SiMe}_3)_2]$  ring the two inequivalent pairs of ring protons are separated by the  $\text{SiMe}_3$  ring substituents and appear in the  $^1\text{H}$  NMR spectrum as two singlets at  $\delta$  7.3 and 7.6. The upfield region of the proton NMR spectrum shows the expected four singlets assigned to the  $\text{SiMe}_3$  substituents in the ratio of 1:1:1:1; this is also apparent in the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum which shows four resonances between  $\delta$  9.46 and  $-9.36$ . In the  $^{13}\text{C}$  NMR spectrum a low field resonance at  $\delta$  197.1 confirms the presence of an alkyne carbon. The substantial chemical shift difference (43 ppm) between the

resonances for the  $\alpha$ -carbons in the two  $\text{CH}(\text{SiMe}_3)_2$  ligands is also noteworthy. The latter may be due to differing charge densities on  $\text{Zr}(1)$  and  $\text{Zr}(2)$  arising from differences in formal oxidation states and/or formal charges.  $J_{\text{CH}}$  of 94 Hz for the  $\alpha$  carbons of the  $\text{CH}(\text{SiMe}_3)_2$  groups is in the normal range for a carbon bearing electropositive substituents, and mitigates against any agostic interactions in solution.

Crystals of **1** suitable for an X-ray structure determination<sup>¶</sup> were grown from a saturated pentane solution at  $-30^\circ\text{C}$  overnight, and the structure, together with selected bond distances and angles, is shown in Fig. 1. The two zirconium centres [ $\text{Zr}(1)$  and  $\text{Zr}(2)$ ] are bridged *via* a bis(trimethylsilyl)cyclooctatrieneyne ligand, which is coordinated through carbon atoms C(6) and C(7) to  $\text{Zr}(2)$  but through all eight carbon atoms C(1)–C(8) to  $\text{Zr}(1)$ . The bond distance C(6)–C(7) [1.398(8) Å] for the coordinated alkyne fragment is slightly shorter than the other C–C distances, except C(3)–C(4) [1.403(9) Å], in this bridging ring. The existence of a cycloalkyne ligand in **1** is comparable with those found in  $[\text{Zr}(\text{C}_5\text{H}_5)_2(\eta^2\text{-C}_6\text{H}_4)(\text{PMe}_3)]$ ,<sup>7</sup>  $[\text{Ni}(\eta^2\text{-C}_6\text{H}_4)\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}]$ ,<sup>8</sup>  $[\text{Ta}(\text{C}_5\text{Me}_5)(\eta^2\text{-C}_6\text{H}_4)\text{Me}_2]$ <sup>9</sup> and  $[\text{Re}(\eta^2\text{-C}_6\text{H}_3\text{Me}_2)(\text{C}_6\text{H}_4\text{Me}_2)_2(\text{PMe}_3)_2][\text{I}_5]$ .<sup>10</sup> In the recently published structure of  $[\text{Zr}(\text{C}_5\text{Me}_5)(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{Zr}(\text{C}_5\text{Me}_5)(\eta^4\text{-C}_8\text{H}_8)]$  a C–C bond length of 1.39(1) Å was observed for the coordinated alkyne, although the latter was not the shortest C–C distance in the ring; however, crystallographic disorder

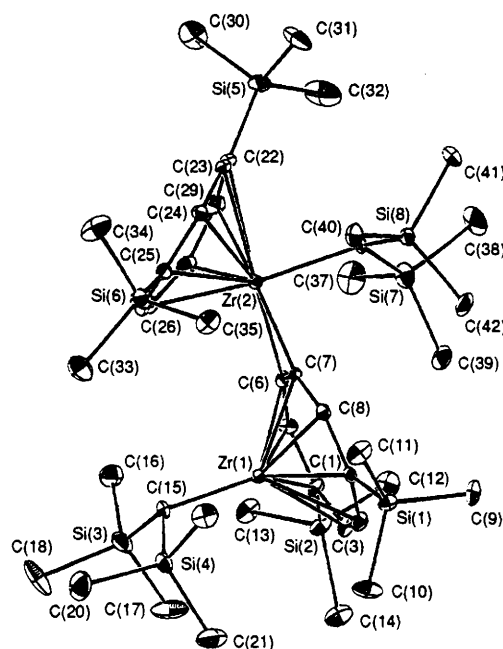
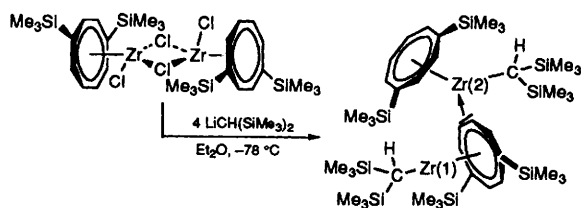


Fig. 1 ORTEP drawing of **1** (non-H atoms as 20% thermal vibration ellipsoids). Selected bond distances (Å) and angles ( $^\circ$ ):  $\text{Zr}(1)\text{---Cen}(1)$  1.449,  $\text{Zr}(2)\text{---Cen}(2)$  1.751,  $\text{Zr}(1)\text{---C}(15)$  2.219(7),  $\text{Zr}(2)\text{---C}(36)$  2.354(6),  $\text{Zr}(1)\text{---C}(6)$  2.297(6),  $\text{Zr}(1)\text{---C}(7)$  2.303(5), av.  $\text{Zr}(1)\text{---C}$  in  $\text{Cen}(1)$  2.355,  $\text{Zr}(2)\text{---C}(6)$  2.207(6),  $\text{Zr}(2)\text{---C}(7)$  2.192(6), av.  $\text{Zr}(2)\text{---C}$  in  $\text{Cen}(2)$  2.539, C(6)–C(7) 1.398(8), av. C–C in  $\text{Cen}(1)$  1.422(9), av. C–C in  $\text{Cen}(2)$  1.409(10), C(6)–Zr–C(7) 37.1(2), C(15)–Zr(1)–Cen(1) 176.4, C(36)–Zr(2)–C(6) 90.5(2). Cen(1) and Cen(2) are the centroids of C(1)–C(8) and C(22)–C(29) respectively.



Scheme 1

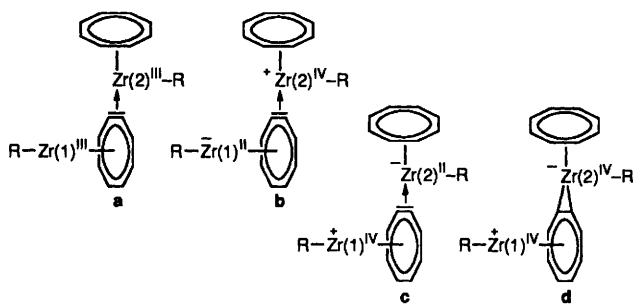


Fig. 2 Bonding models for **1** [ring SiMe<sub>3</sub> groups omitted for clarity; R = CH(SiMe<sub>3</sub>)<sub>2</sub>]

problems prevented a detailed discussion of the bonding of the cycloalkyne ring. A comparison of the angle C(6)–Zr(2)–C(7) of 37.1(2)° in **1** with that found in [Zr(C<sub>5</sub>Me<sub>5</sub>)(μ-η<sup>8</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>6</sub>)Zr(C<sub>5</sub>Me<sub>5</sub>)(η<sup>4</sup>-C<sub>8</sub>H<sub>8</sub>)]<sup>6</sup> [36.8(3)°] shows little difference and the bond distances of Zr(2) to C(6) and C(7), 2.207(6) and 2.192(6) Å respectively, are also comparable with those for the analogous fragment in [Zr(C<sub>5</sub>Me<sub>5</sub>)(μ-η<sup>8</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>6</sub>)Zr(C<sub>5</sub>Me<sub>5</sub>)(η<sup>4</sup>-C<sub>8</sub>H<sub>8</sub>)] [2.203(8) and 2.206(7) Å]. The Zr(1)–Cen(1) and Zr(2)–Cen(2) distances in **1** are strikingly different: the Zr(1)–Cen(1) distance of 1.449 Å is appreciably shorter than that for Zr(2)–Cen(2) (1.751 Å). Similarly, the two Zr–CH(SiMe<sub>3</sub>)<sub>2</sub> bond lengths differ: Zr(1)–C(15) [2.219(7) Å] is considerably shorter than Zr(2)–C(36) [2.354(6) Å]. The CH(SiMe<sub>3</sub>)<sub>2</sub> group bound to Zr(2) is orientated so as to minimise steric interactions, reflected in the angles C(36)–Zr(2)–Cen(2) and C(36)–Zr(2)–C(6) which are 127.1 and 90.5(2)° respectively. Similar factors dictate the angle C(15)–Zr(1)–Cen(1) (176.4°). The hydrogen atoms on the α carbons of the CH(SiMe<sub>3</sub>)<sub>2</sub> substituents were located and show no evidence of agostic interactions.

Fig. 2 shows the four most reasonable possibilities for describing the bonding of the cycloalkyne ligand and assignment of formal oxidation states in **1**.

The observed diamagnetism of **1** is readily accounted for by the zwitterionic nature of structures **b**, **c** and **d**; structure **a** would require spin pairing of the two Zr<sup>III</sup> centres through the bridging ligand. The significantly longer ligand–metal bonds for Zr(2) compared with those for Zr(1) would argue strongly in favour of structure **c** in which Zr(1) is a cationic Zr<sup>IV</sup> centre whilst Zr(2) is anionic and Zr<sup>II</sup>, or structure **d** in which Zr(1) is again cationic Zr<sup>IV</sup> and Zr(2) is anionic and also Zr<sup>IV</sup>. Indeed, the difference between the ring centroid–metal distances for Zr(1) and Zr(2) (0.302 Å) is greater than the difference between the ionic radii for Zr<sup>IV</sup> and Zr<sup>II</sup> (0.22 Å),<sup>11</sup> which lends credence to structure **c**. Furthermore, the slightly short ring C–C bond in the μ-η<sup>8</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring associated with Zr(2) may be indicative of an alkyne-type unit rather than part of a metallacycle. The latter, metallacyclic structure has been proposed for [Zr(C<sub>5</sub>Me<sub>5</sub>)(μ-η<sup>8</sup>:η<sup>2</sup>-C<sub>8</sub>H<sub>6</sub>)Zr(C<sub>5</sub>Me<sub>5</sub>)(η<sup>4</sup>-C<sub>8</sub>H<sub>8</sub>)]<sup>6</sup>, but, on balance, we feel that our structural and NMR evidence favours a structure of type **c** for **1**.

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## Footnotes

† Satisfactory microanalytical and mass spectral data for **1** have been obtained.

‡ NMR data for **1**: spectra were recorded at probe temperature on a

Bruker AMX 500 instrument. For <sup>1</sup>H and <sup>13</sup>C δ is relative to internal solvent (<sup>2</sup>H<sub>6</sub> benzene), and for <sup>29</sup>Si δ is relative to external SiMe<sub>4</sub>.

<sup>1</sup>H NMR: δ 7.69 [2H, s, C<sub>8</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring], 7.31 [2H, s, C<sub>8</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring], 7.11 [2H, m, C<sub>8</sub>H<sub>6</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring], 7.08 [2H, s, C<sub>8</sub>H<sub>6</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring], 6.72 [2H, m, C<sub>8</sub>H<sub>6</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring], 0.72 [18H, s, C<sub>8</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>], 0.44 [18H, s, C<sub>8</sub>H<sub>6</sub>(SiMe<sub>3</sub>)<sub>2</sub>], 0.12 [1H, s, CH(SiMe<sub>3</sub>)<sub>2</sub>], –0.11 [18H, s, CH(SiMe<sub>3</sub>)<sub>2</sub>], –0.21 [1H, s, CH(SiMe<sub>3</sub>)<sub>2</sub>], –0.23 [18H, s, CH(SiMe<sub>3</sub>)<sub>2</sub>].

<sup>13</sup>C{<sup>1</sup>H} NMR: δ 197.1 (s, CH ring), 120.0 (s, CH ring), 107.7 (s, CH ring), 107.4 (s, CH ring), 100.9 (s, CH ring), 99.1 (s, CH ring), 96.9 (s, CH ring), 84.4 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>], 41.5 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>], 5.5 (s, SiMe<sub>3</sub> ring), 4.5 (s, SiMe<sub>3</sub> ring), 1.4 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>], 0.4 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>].

<sup>29</sup>Si{<sup>1</sup>H} NMR: δ 9.46 (s, SiMe<sub>3</sub>), 6.52 (s, SiMe<sub>3</sub>), –5.74 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>], –9.36 [s, CH(SiMe<sub>3</sub>)<sub>2</sub>].

¶ Crystal data for C<sub>42</sub>H<sub>84</sub>Si<sub>8</sub>Zr<sub>2</sub>: *M* = 996.3, orthorhombic, *Pna*2<sub>1</sub> (no. 33), *a* = 24.784(7), *b* = 12.301(3), *c* = 18.250(4) Å, α = β = γ = 90°, *V* = 5564 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.19 g cm<sup>–3</sup>, λ(Mo-Kα) = 0.71069 Å, μ = 5.7 cm<sup>–1</sup>, *F*(000) = 2112, *T* = 173 K. Dark red, air sensitive hexagonal rods.

Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode, using a crystal of dimensions ca. 0.35 × 0.35 × 0.4 mm mounted under Nujol oil and held at 173 K in a stream of cooled nitrogen gas. A total of 5443 unique reflections were measured for 2 < θ < 25° and +*h*, +*k*, +*l*, and 4397 reflections with |*F*<sup>2</sup>| > 2σ(*F*<sup>2</sup>) were used in the refinement where σ(*F*<sup>2</sup>) = [σ<sup>2</sup>(*I*) + (0.04)*I*]<sup>1/2</sup>/Lρ (Lρ = Lorentz polarisation). A correction (*T*<sub>max</sub> 0.999, *T*<sub>min</sub> 0.953) from ψ scans was applied for absorption after isotopic refinement. No decay correction was applied.

The structure was solved *via* direct methods using SHELXS-86 with non-H atoms refined anisotropically by full-matrix least squares. Hydrogen atoms were held at fixed calculated positions with *U*<sub>iso</sub> = 1.3*U*<sub>eq</sub> for the parent atom except for H(15) and H(36) which were freely refined isotropic. With a weighting scheme of *w* = 1/σ<sup>2</sup>(*F*) the final residues were *R* = 0.0402 and *R*' = 0.0432 with a ratio of observations to variables of 9.24:1, and *S* = 1.17. The opposite absolute structure gave *R* = 0.0407, *R*' = 0.0438 and *S* = 1.19. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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