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Mixed-sandwich complexes of zirconium(III) and hafnium(III): Potential analogues of [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-Cp*)] for cyclooligomerisation of CO☆

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ABSTRACT

Reaction of $ZrCl_4$ or $HfCl_4$ with 2 equivalents of K_2(COT\{Si^iPr_3-1,4\}$_2$), followed by *in situ* treatment of the resultant sandwich complexes M(COT\{Si^iPr_3-1,4\}$_2$) with a further equivalent of MCl_4 affords the mono-COT chloro-bridged dimers [M(η-COT\{Si^iPr_3-1,4\}$_2$)(μ-Cl)Cl]$_2$, M = Zr (**1**); M = Hf (**4**). Further reaction of the latter with 2 equivalents of KCp* yields the crystallographically characterised M(IV) mixed-sandwich complexes [M(η-COT\{Si^iPr_3-1,4\}$_2$)(η-Cp*)Cl], M = Zr (**2**); M = Hf (**5**). Reduction of **2** with KC_8 in toluene affords the monomeric Zr(III) mixed-sandwich complex [Zr(η-COT\{Si^iPr_3-1,4\}$_2$)(η-Cp*)], whereas the analogous reaction with **5** results in coupling of the COT rings to give dimeric [Hf(η-Cp*)]$_2$(μ-η^7,η^7-(C_8H_6\{Si^iPr_3-3,6\}$_2C_8H_6$\{Si^iPr_3-3,6\}$_2$)); both **2** and **5** have been structurally characterised.

1. Introduction

We have recently reported the reductive cyclooligomerisation of CO by mixed-sandwich U(III) complexes of the type [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-Cp^R)(thf)] (Cp^R = Cp* or C_5Me_4H) to form the deltate and squarate complexes, [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-Cp*)]$_2$(μ-η^1:η^2-C_3O_3) and [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-C_5Me_4H)]$_2$(μ-η^2:η^2-C_4O_4), and the stoichiometric dimerisation of CO to afford the linear yne diolate complex [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-C_5Me_4H)]$_2$(μ-C_2O_2) [1–3]. [U(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-Cp^R)(thf)] complexes also effect the reductive disproportionation of CO_2 [4].

In terms of potential transition metals analogues of these highly reducing U(III) systems, electron counting and oxidation state considerations suggest that the 17-electron Zr(III) or Hf(III) complexes [M(η-C_8H_6\{Si^iPr_3-1,4\}$_2$)(η-Cp^R)] would be the most likely to display comparable reactivity to small molecules; the latter would also be expected to have M(III)/M(IV) redox potentials [5,6] comparable to the uranium systems. The mixed-sandwich Zr(III) complex [Zr(η-COT)(η-Cp*)] has previously been described and structurally characterised, although the hafnium equivalent remained elusive [7–9]. Here, tri-isopropylsilyl-substituted COT has been employed in an effort to stabilise the M(III) complexes for both Zr and Hf, which may be candidates for reductive activation of carbon oxides.

☆ In kind memory of Herbert Schumann, one of the pioneers of organo-f-element chemistry.

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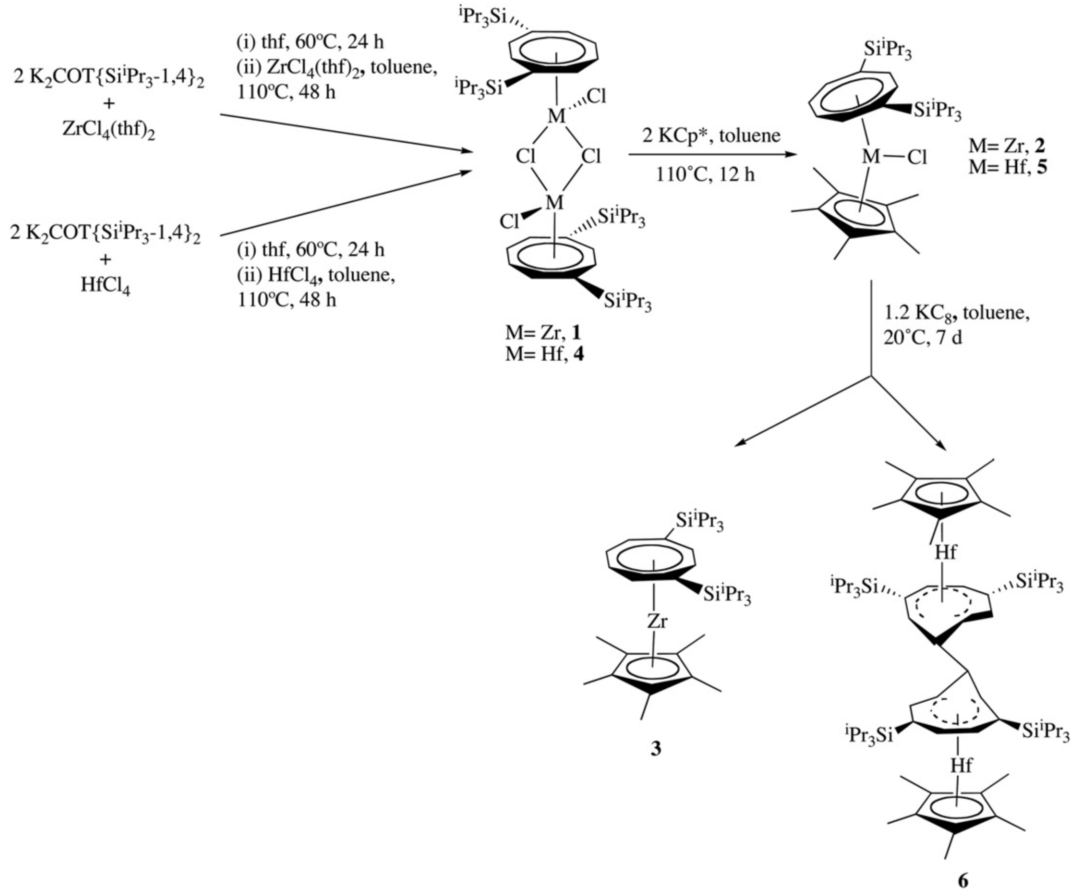
2. Results and discussion

The synthetic strategies to the target mixed-sandwich Zr and Hf complexes are shown in Scheme 1. We have previously described the synthesis of bis(COT\{$SiMe_3$-1,4\}$_2$) complexes of the Group IV elements [10], and the chloro-bridged dimer [Zr(η^8-COT\{$SiMe_3$-1,4\}$_2$)Cl_2]$_2$ has also been reported [11]. Accordingly, $ZrCl_4(thf)_2$ in thf was treated with 2 equivalents of K_2(COT\{Si^iPr_3-1,4\}$_2$) to afford [Zr(COT\{Si^iPr_3-1,4\}$_2$)$_2$]; the latter was not isolated, but subjected to a ligand redistribution reaction by treatment with a further equivalent of $ZrCl_4(thf)_2$ in toluene and 48 h reflux, giving [Zr(η^8-COT\{Si^iPr_3-1,4\}$_2$)Cl_2]$_2$ **1** as a pale brown solid in a moderate yield (51% w.r.t. $ZrCl_4(thf)_2$) after work-up. Slow addition of KCp* to a toluene solution of **1** followed by reflux for 16 h yielded [Zr(η^8-COT\{Si^iPr_3-1,4\}$_2$)(η-Cp*)Cl] **2** as a yellow crystalline solid in moderate yield (55% w.r.t. **1**) after recrystallisation from pentane. Essentially identical procedures, using $HfCl_4$, afforded [Hf(η^8-COT\{Si^iPr_3-1,4\}$_2$)Cl_2]$_2$ **4** as a pale yellow solid in 60% yield, and hence [Hf(η^8-COT\{Si^iPr_3-1,4\}$_2$)(η-Cp*)Cl] **5** as a bright yellow crystalline solid in 74% yield.

The X-ray crystal structures of **2** and **5** have been determined and are shown in Figs. 1 and 2, respectively, together with selected bond distances and angles. Both **2** and **5** display the expected bent sandwich structures and, given the extremely similar sizes of Zr(IV) and Hf(IV), important bond distances and angles are essentially identical (within esds): *i.e.* the ring centroid–metal-ring centroid angles of 145.56(7) and 145.9(19)°, the COT(centroid)–metal distances of 1.730(2) and 1.72(4) Å, the Cp*(centroid) distances of 2.254(2) and 2.23(4) Å, and the metal–chloride distances of 2.5584



Scheme 1.

(5) and 2.4968(10) Å, respectively. [Zr(η^8-COT)(η-Cp*)Cl] has been reported but not structurally characterised [8], and other analogues of **2** (or indeed **5**) have not been described.

Attempts to reduce **2** using activated magnesium in thf (as used for the reduction of Zr(IV) in the synthesis of [Zr(η^8-COT)(η-Cp*)]) [7], or potassium metal in thf were unsuccessful and led to an intractable mixture of products. Clean reduction of **2** was finally achieved by stirring with 1.2 equivalents of KC_8 in toluene at room temperature over a seven-day period. Pentane extraction of the dried reaction mixture, filtration and crystallisation at −80 °C afforded dark red crystals of [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)] **3** in 76% yield. **3** is extremely soluble in aliphatic and aromatic solvents, and displays a very broad ^{1}H NMR spectrum in solution, as expected for a paramagnetic Zr(III) centre.

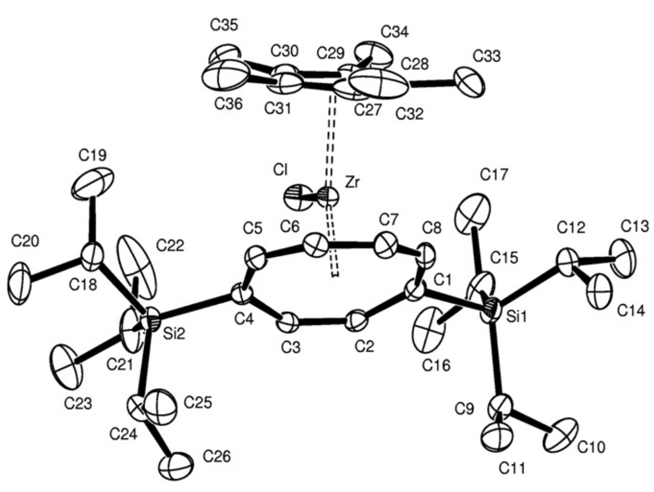


Fig. 1. Molecular structure of **2**. Thermal ellipsoids at 50%. Selected bond distances (Å) and angles (°): Zr–M(1) 1.730(2), Zr–M(2) 2.254(2), Zr–Cl 2.5584(5); M(1)–Zr–M(2) 145.56(7). M(1) and M(2) are the centroids of the COT and Cp* rings, respectively

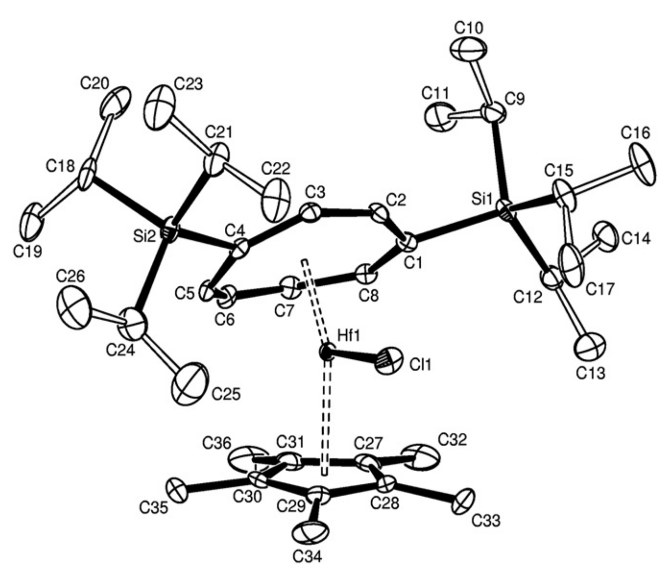


Fig. 2. Molecular structure of **5**. Thermal ellipsoids at 50%. Selected bond distances (Å) and angles (°): Hf(1)–M(1) 1.72(4), Hf(1)–M(2) 2.23(4), Hf(1)–Cl(1) 2.4968(10); M(1)–Hf(1)–M(2) 145.9(19). M(1) and M(2) are the centroids of the COT and Cp* rings, respectively.

The X-ray crystal structure of **3** has been determined and is shown in Fig. 3, together with selected bond distances and angles.

3 displays a slightly bent sandwich structure, with a COT(centroid)–Zr–Cp*(centroid) angle of 170.64(16)° which is slightly more acute than that of 173.8° found in the unsubstituted analogue [Zr(η^8-COT)(η-Cp*)] [9], attributable to the steric influence of the bulky Si^{i}Pr$_3$ substituents in **3**. Similarly, the COT(centroid)–Zr and Cp*(centroid)–Zr distances in **3** (1.688(3) and 2.206(3) Å, respectively) are slightly longer than those (1.59 and 2.17 Å, respectively) in [Zr(η^8-COT)(η-Cp*)] [9].

A similar reduction of **5** using 1.1 equivalents of KC_8 in toluene followed by pentane extraction yielded **6** as dark red crystals in low, 18% yield. Once isolated, crystalline **6** was found to have very poor solubility in a variety of solvents. Some material partially dissolved in boiling toluene, but not to the extent that any meaningful NMR spectra could be obtained. The mass spectrum of **6** displayed an envelope of peaks at *m*/*z* 1455–1465 consistent with the dimeric formulation [Hf(COT{Si^{i}Pr$_3$}$_2$)(Cp*)]$_2$, and strong peaks for monomeric [Hf(COT{Si^{i}Pr$_3$}$_2$)(Cp*)]. The X-ray crystal structure of **6** is shown in Fig. 3, together with selected bond distances and angles (Fig. 4).

The structure shows a binuclear complex in which two [Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)] moieties have dimerised *via* formation of a C–C bond and coupling of the COT rings to form an η^7,η^7-(C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$) bridging ligand; each 8-membered ring thus behaves as a cyclooctatrienyl ligand. The regiochemistry of this C–C bond (C(6)-C(6)′) linking the two rings in **6** is presumably dictated by the positions of the bulky Si^{i}Pr$_3$ substituents. The structure of the related, but unsubstituted vanadium complex [V(η-C$_5$H$_5$)$_2$(μ-"η^7,η^7-{C$_8$H$_8$}$_2$)] has been reported [12]. The C(6)–C(6)′ bond distance of 1.525(6) Å is identical to that (1.523(2) Å) of the analogous bond in the vanadium complex, although the angles around the sp^3 carbon C6 (C(7)–C(6)–C(6)′117.4(4), C(6)′–C(6)–C(5) 114.7(4), C(7)–C(6)–C(5) 105.0(3) Å) are all somewhat larger than their vanadium counterparts (113.2(1), 114.1(1) and 101.3(1), respectively).

The structurally characterised cycloheptatrienyl-pentamethylcyclopentadienyl hafnium complex [Hf(η^7-C$_7$H$_7$)(η-Cp*)] [13] also provides a useful comparison with **6**. The centroid(Cp*)–Hf–"centroid"(C$_7$ part of COT ring) angle of 162.8(3)° in **6** is somewhat more acute than that (172.2°) in [Hf(η^7-C$_7$H$_7$)(η-Cp*)], again likely due to the steric effects of the ring Si^{i}Pr$_3$ substituents in **6**. Nonetheless, both the centroid(Cp*)-Hf and "centroid" (C$_7$ part of COT ring) distances

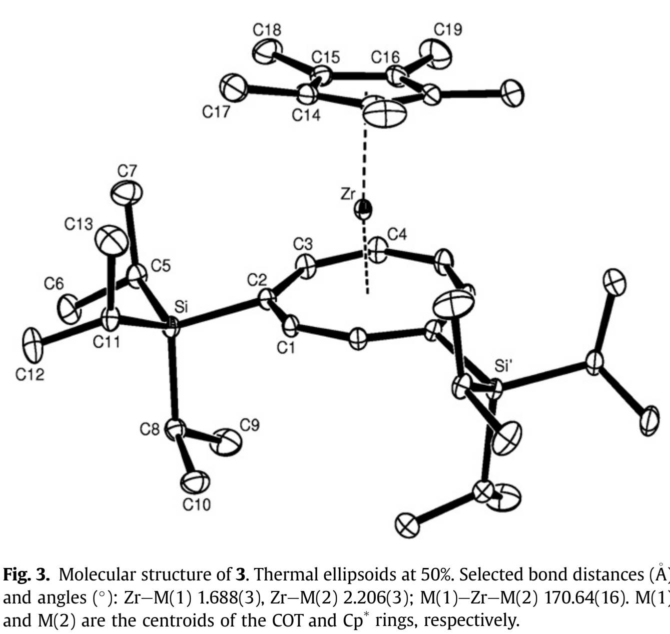


Fig. 3. Molecular structure of **3**. Thermal ellipsoids at 50%. Selected bond distances (Å) and angles (°): Zr–M(1) 1.688(3), Zr–M(2) 2.206(3); M(1)–Zr–M(2) 170.64(16). M(1) and M(2) are the centroids of the COT and Cp* rings, respectively.

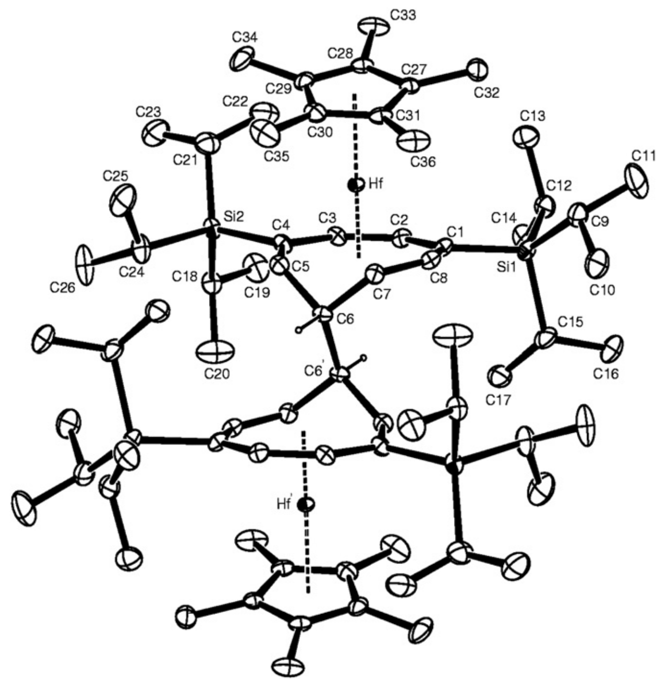


Fig. 4. Molecular structure of **6**. Thermal ellipsoids at 50%. Selected bond distances (Å) and angles (°): C(6)–C(6)′ 1.525(6), Hf–M(1) 2.183(5), Hf–M(2) 1.602(5); C(7)–C(6)–C(6)′117.4(4), C(6)′–C(6)–C(5) 114.7(4), C(7)–C(6)–C(5) 105.0(3), M(1)–Hf–M(2) 162.8(3). M(1) is the centroid of the Cp* ring and M(2) is the 'centroid' of the C5, C4, C3, C2, C1, C8, C7 part of the COT ring

(2.183(5) and 1.602(5) Å, respectively) in **6** are comparable to those in [Hf(η^7-C$_7$H$_7$)(η-Cp*)] (2.13 and 1.62 Å, esds not reported).

Photoelectron spectroscopy and theoretical studies have shown that, in early transition metal complexes containing the η^7-cycloheptratienyl ligand, the latter is most realistically described as behaving as a trianionic ligand [14], *i.e.* as a $10\pi C_7H_7^{3-}$ aromatic system; recent experimental results and structural studies on compounds of the type [(η^7-C$_7$H$_7$)M(η^5-C$_5$H$_5$)] (M = Ti, Zr, Hf) also support this assignment [15,16]. We therefore suggest that the cyclooctatrienyl ligands in **6** act similarly, thus leading to each hafnium centre being 16-electron Hf(IV).

3. Concluding remarks

The monomeric 17-electron Zr(III) mixed-sandwich complex [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)] **3** has been prepared by potassium-graphite reduction of [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)Cl] **2**. The analogous reduction of the hafnium complex [Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)Cl] **5** affords dimeric [Hf(η-Cp*)]$_2$(μ-η^7,η^7-(C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$)) **6**, in which two cyclooctatetraene rings have been linked together. We ascribe the formation of the latter to the higher reducing power of Hf(III) compared to that of Zr(III), leading to significant unpaired electron density on the COT ring in the putative monomer [Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(η-Cp*)] which consequently dimerises.

Studies on the reactions of **2** with small molecules, in particular CO and CO_2, are in progress.

4. Experimental section

4.1. General procedures

Manipulations of air-sensitive compounds were conducted in an atmosphere of catalytically dried and deoxygenated argon using standard Schlenk line techniques, or under catalytically dried and deoxygenated nitrogen in an MBraun glove box (<1 ppm H_2O, <1 ppm O_2). Solvents were purified by standard procedures and degassed prior to use. NMR solvents were dried over molten potassium and vacuum distilled.

NMR spectra were obtained using a Varian Direct Drive 400 MHz spectrometer. Single crystal X-ray diffraction analysis was carried out on a Nonius Kappa CCD diffractometer.

Elemental Analyses were carried out at the Elemental Analysis Service, London Metropolitan University. Mass spectra were recorded using a VG Autospec Fisons instrument (electron impact ionisation at 70 eV).

K_2(COT{Si^{i}Pr$_3$-1,4}$_2$)] [2], Cp*H (deprotonated using KN(TMS)$_2$ in toluene to give KCp*) [17], $ZrCl_4$(thf)$_2$ [18], and KC_8 [19] were prepared according to published procedures. $HfCl_4$ (Strem) was used as supplied.

4.2. [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$]$_2$ (1)

A red-green thf (80 mL) solution of K_2(COT{Si^{i}Pr$_3$-1,4}$_2$) (5.04 g, 10.21 mmol) was added at room temperature, dropwise, over 40 min to a white suspension of $ZrCl_4$(thf)$_2$ (1.92 g, 5.11 mmol) in thf (40 mL). The mixture darkened immediately on addition to a deep red colour before heating to reflux at 65 °C for 16 h after which time a pale precipitate was observed. Volatiles were removed under vacuum and the solids extracted with petroleum–ether and filtered on a frit through dry Celite®. Subsequent solvent removal yielded a sticky dark red matrix. This was taken up in toluene (120 mL) and a further equivalent of $ZrCl_4$(thf) added dropwise in toluene (20 mL) over 20 min. This was allowed to reflux at 120 °C for 48 h before removing volatiles to give pale brown solids. Washing in cold pentane yielded **1** as a pale orange solid (3.00 g, 51%). ^{1}H NMR (thf-d_8 303 K): δ 7.04 (s, 4H, COT–H), 7.02 (m, 4H, COT–H), 6.92 (m, 4H, COT–H), 1.73 (m, 12H, ^{i}Pr–CH), 1.26 (d, ^3J(H,H) = 2.40 Hz, 36H, CH_3), 1.24 (d, ^3J(H,H) = 2.46 Hz, 36H, CH_3); ^{13}C{^{1}H} NMR (thf-d_8 303 K): δ 107.96 (COT–*C*H), 105.33 (COT–*C*H), 104.00 (COT–*C*H), 101.49 (COT–*C*Si), 19.67 (^{i}Pr–*C*H$_3$), 19.59 (^{i}Pr–*C*H), 13.18 (^{i}Pr–*C*H$_3$); ^{29}Si NMR (thf-d_8 303 K): δ 11.60 (Si–^{i}Pr); MS (EI) *m/z* 1156 (2% M$^+$), 1121 (28% M$^+$ – Cl), 578 (24% M$^+$ – Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$), 535 (100% M$^+$ – Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$, –Cl).

4.3. Synthesis of [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(Cp*)Cl] (2)

A white toluene (30 mL) suspension of KCp* (0.33 g, 1.89 mmol) was added dropwise over 5 min to an orange toluene (50 mL) suspension of **1** (1.08 g, 0.93 mmol). The mixture turned bright yellow within 10 min of addition and was allowed to reflux at 120 °C for 16 h after which a dark yellow precipitate was observed. The mixture was filtered on a frit through dry Celite® before stripping to dryness to yield a bright yellow polycrystalline solid. Recrystallisation of **2** from pentane at –50 °C yielded yellow rectangular crystals (0.70 g, 55%). ^{1}H NMR (benzene-d_6 303 K): δ 6.88 (s, 2H, COT–H), 5.85 (m, 2H, COT–H), 5.60 (m, 2H, COT–H), 1.73 (s, 15H, Cp–CH_3), 1.56 (septet, ^3J(H,H) = 7.43 Hz, 6H, ^{i}Pr–CH), 1.34 (d, ^3J(H,H) = 7.43 Hz, 18H, ^{i}Pr–CH_3), 1.22 (d, ^3J(H,H) = 7.43 Hz, 18H, ^{i}Pr–CH_3); ^{13}C NMR (benzene-d_6 303 K): δ 119.67 (Cp–*C*CH$_3$), 113.32 (COT–*C*H), 101.03 (COT–*C*H), 98.62 (COT–*C*Si), 94.85 (COT–*C*H), 19.72 (^{i}Pr–*C*H$_3$), 13.06 (^{i}Pr–*C*H), 12.56 (Cp–*C*H$_3$); ^{29}Si NMR (benzene-d_6 303 K): δ 10.73 (s, Si^{i}Pr$_3$); MS (EI) *m/z* 677 (2% M$^+$), 633 (2% M$^+$ – ^{i}Pr), 541 (69% M$^+$ – Cp*).

4.4. Synthesis of [Zr(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(Cp*)] (3)

An ampoule was charged with **2** (0.68 g, 1.00 mmol), KC_8 (0.16 g, 1.22 mmol) and toluene (30 mL) added to yield a bronze-coloured suspension that was allowed to stir for 7 days to give a dark red solution with black solids. Removal of volatiles under vacuum yielded sticky dark solids that were extracted with pentane and filtered. The solution was concentrated and on cooling to –80 °C yielded **3** as rectangular dark red crystals (0.49 g, 76%). Due to the paramagnetic nature of **3**, NMR analysis was not possible. MS (EI) *m/z* 641 (50% M$^+$), 541 (64% M$^+$ – CH_3, –^{i}Pr, –^{i}Pr).

4.5. [Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$]$_2$ (4)

This was prepared in an analogous manner to **1** from K_2(COT{Si^{i}Pr$_3$-1,4}$_2$) (5.12 g, 10.36 mmol) and $HfCl_4$ (1.65 g, 5.19 mmol) before further addition of $HfCl_4$ (1.58 g, 4.98 mmol) to yield **4** as a pale yellow solid (4.01 g, 60%). ^{1}H NMR (thf-d_8 303 K): δ 6.94 (s, 4H, COT–H), 6.90 (m, 4H, COT–H), 6.80 (m, 4H, COT–H), 1.68 (m, 12H, ^{i}Pr–CH), 1.22 (d, ^3J(H,H) = 1.48 Hz, 36H, ^{i}Pr–CH_3), 1.20 (d, ^3J(H,H) = 1.76 Hz, 36H, ^{i}Pr–CH_3); ^{13}C{^{1}H} NMR (thf-d_8 303 K): δ 104.10 (COT–*C*H), 101.46 (COT–*C*H), 98.76 (COT–*C*H), 97.29 (COT–*C*Si), 18.45 (^{i}Pr–*C*H$_3$), 18.37 (^{i}Pr–*C*H$_3$), 12.04 (^{i}Pr–*C*H); ^{29}Si NMR (thf-d_8 303 K): δ 13.29 (Si–^{i}Pr); MS (EI) *m/z* 666 (25% M$^+$ – (Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$)), 623 (95% M$^+$ – (Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)Cl$_2$), –^{i}Pr).

4.6. Synthesis of [Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(Cp*)Cl] (5)

This was prepared in an analogous manner to **2** from **4** (2.02 g, 1.52 mmol) and KCp* (0.53 g, 3.04 mmol) to yield bright yellow rectangular crystals from pentane (1.72 g, 74%). ^{1}H NMR (benzene-d_6 303 K): δ 6.88 (s, 2H, COT–H), 5.78 (m, 2H, COT–H), 5.57 (m, 2H, COT–H), 1.80 (s, 15H, Cp–CH_3), 1.57 (septet, ^3J(H,H) = 7.39 Hz, 6H, ^{i}Pr–CH), 1.35 (d, ^3J(H,H) = 7.37 Hz, 18H, ^{i}Pr–CH_3), 1.22 (d, ^3J(H,H) = 7.10 Hz, 18H, ^{i}Pr–CH_3); ^{13}C NMR (benzene-d_6 303 K): δ 117.82 (Cp–*C*CH$_3$), 112.65 (COT–*C*H), 99.27 (COT–*C*H), 96.29 (COT–*C*Si), 90.83 (COT–*C*H), 19.83 (^{i}Pr–*C*H$_3$), 12.87 (^{i}Pr–*C*H), 12.21 (Cp–*C*H$_3$); ^{29}Si NMR (benzene-d_6 303 K): δ 10.20 (s, Si^{i}Pr$_3$); MS (EI) *m/z* 766 (14% M$^+$), 723 (4% M$^+$ – ^{i}Pr), 631 (100% M$^+$ – Cp*).

4.7. Synthesis of [Hf(η-Cp*)]$_2$(μ-η^7,η^7-(C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$C$_8$H$_6${Si^{i}Pr$_3$-3,6}$_2$)) (6)

An ampoule was charged with **5** (1.66 g, 2.17 mmol), KC_8 (0.33 g, 2.41 mmol) and toluene (50 mL) added to yield a bronze-coloured suspension that was allowed to stir for 7 days to give a dark brown solution with black solids. Removal of volatiles under vacuum yielded sticky dark solids that were extracted with pentane and filtered as a yellow-brown solution. This solution was concentrated and cooled to –50 °C to yield **6** as large, rectangular dark red crystals (0.25 g, 18%). Due to the highly insoluble nature of **6**, NMR analysis was not possible. MS (EI) *m/z* 1458 (1% M$^+$), 731 (63% M$^+$ – Hf(η^8-COT{Si^{i}Pr$_3$-1,4}$_2$)(Cp*)); elemental analysis calcd (%) for $C_{72}H_{126}Hf_2Si_4$: C 59.18, H 8.69; found: C 59.30, H 8.77.

4.8. X-ray diffraction

The data for crystals **2**, **3**, **5**, **6** were collected at 173 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was handled using Kappa CCD software, final cell parameter calculations performed using program package WinGX. The data were corrected for absorption using the MULTISCAN program. Refinement was performed using SHELXL-97, and the thermal ellipsoid plots drawn using Shelxtl-XP. SADI restraints, isotropic C atoms, ^{i}Pr groups and H atoms omitted, except where specified.

Crystal data for **2**. Yellow air-sensitive prism 0.25 × 0.20 × 0.05 mm^3, $C_{36}H_{63}ClSi_2Zr$, a = 8.5410(2), b = 13.0372(2), c = 18.6994(4) Å, α = 69.615(1)°, β = 88.160(1)°, γ = 71.287(1)°, U = 1841.16(6) Å^3, triclinic, $P\bar{1}$ (No. 2), Z = 2, total reflections 29 392, independent reflections 7200, $R_{int} = 0044$, $\theta_{max} = 26.02$, R_1 $[I > 2\sigma(I)] = 0.032$, $wR^2 = 0.073$ and 378 parameters.

Crystal data for **3**. Dark red air-sensitive block 0.30 × 0.20 × 0.12 mm^3, $C_{36}H_{63}Si_2Zr$, $a = 8.7791(1)$, $b = 22.2176(4)$, $c = 9.5499(2)$ Å, $\beta = 100.616(1)^\circ$, $U = 1830.83(5)$ $Å^3$, monoclinic, $P\,2_1/m$ (No. 11), $Z = 2$, total reflections 31 486, independent reflections 4285, $R_{int} = 0.052$, $\theta_{max} = 27.48$, R_1 $[I > 2\sigma(I)] = 0.028$, $wR^2 = 0.068$ and 184 parameters.

Crystal data for **5**. Yellow air-sensitive rhombohedra, 0.18 × 0.14 × 0.10 mm^3, $C_{36}H_{63}ClHfSi_2$, $a = 11.7530(2)$, $b = 16.8027(3)$, $c = 19.6881(3)$ Å, $\alpha = 99.778(1)^\circ$, $\beta = 107.251(1)^\circ$, $\gamma = 90.039(1)^\circ$, $U = 3653.82(11)$ $Å^3$, triclinic, $P\bar{1}$ (No. 2), $Z = 4$, total reflections 56 162, independent reflections 14 702, $R_{int} = 0.061$, $\theta_{max} = 26.73$, R_1 $[I > 2\sigma(I)] = 0.034$, $wR^2 = 0.069$, 741 parameters.

Crystal data for **6**. Red air-sensitive prism, 0.24 × 0.20 × 0.13 mm^3, $C_{72}H_{126}Hf_2Si_4$, $a = 14.0891(2)$, $b = 18.3487(4)$, $c = 15.8885(3)$ Å, $\beta = 120.090(1)^\circ$, $U = 3553.92(11)$ $Å^3$, monoclinic, $P\,2_1/c$ (No. 14), $Z = 2$, total reflections 53 709, independent reflections 8327, $R_{int} = 0.062$, $\theta_{max} = 27.89$, R_1 $[I > 2\sigma(I)] = 0.032$, $wR^2 = 0.071$ and 357 parameters.

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