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Key indicators

Powder X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.025\text{ \AA}$

R factor = 0.067

wR factor = 0.059

Data-to-parameter ratio = 5.14

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

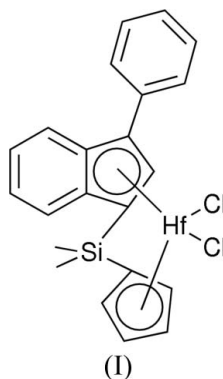
Dichloro[$(\eta^5\text{-cyclopentadienyl})\text{dimethyl-}(\eta^5\text{-3-phenylindenyl})\text{silane}]$ hafnium(IV): a powder study

The title compound, $[\text{Hf}(\text{C}_{22}\text{H}_{20}\text{Si})\text{Cl}_2]$, was solved by simulated annealing from laboratory X-ray powder diffraction data collected at room temperature. The molecular structure comprises a hafnium dichloride centre, coordinated by a $\eta^5\text{-cyclopentadienyl}$ and a $\eta^5\text{-3-phenylindenyl}$ unit, which are connected through a shared dimethylsilicon linkage.

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Comment

For approximately two decades, there has been substantial interest in group 4 metallocenes, driven by their ability, in combination with methylalumoxane, to catalyse the isotactic polymerization of propylene [for a recent review see Resconi *et al.* (2000)] and ethylene [for reviews see Alt & Köppl (2000) and Möhring & Coville (2006)]. For ansa-bridged indenyl-derived molecules, the stereoselectivity and regioselectivity of the propylene monomer are strongly influenced by substitution at the indenyl ring system. Characterization of these molecules through crystallography is clearly desirable in order to elucidate fully the relationship between the structure of the catalyst and both the stereoregularity and the molecular weight of the polymer it produces. For many of these compounds, growth of single crystals suitable for diffraction analysis can be difficult or impossible. Here we employed laboratory X-ray powder diffraction to solve and refine the crystal structure of an Hf-containing cyclopentadienyl–indenyl catalyst, (I), in which the ligand presents heterotopic faces to the active Hf site.



The Hf ion in (I) is linked to two Cl ions at distances of 2.305 (3) and 2.303 (3) Å (this distance was restrained in the Rietveld refinement to be 2.3 Å) (Fig. 1). The coordination of Hf is completed by an $\eta^5\text{-cyclopentadienyl}$ and an $\eta^5\text{-phenylindenyl}$ unit, which are connected through a dimethylsilicon linkage at an angle φ of 100.3 (1)° through the Si atom, which can be compared with 94.6 (1)° in the bisindenyl zirconocene

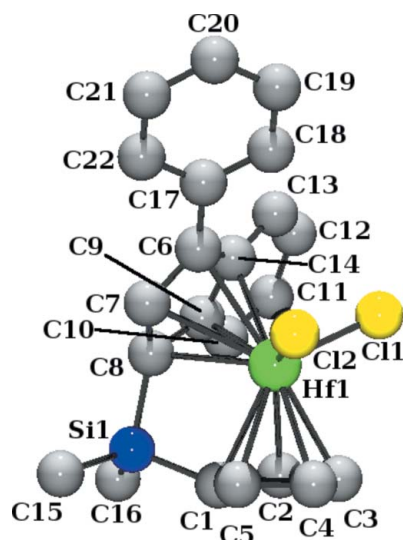


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are not shown for clarity. Hf green, Cl yellow, Si blue and C grey.

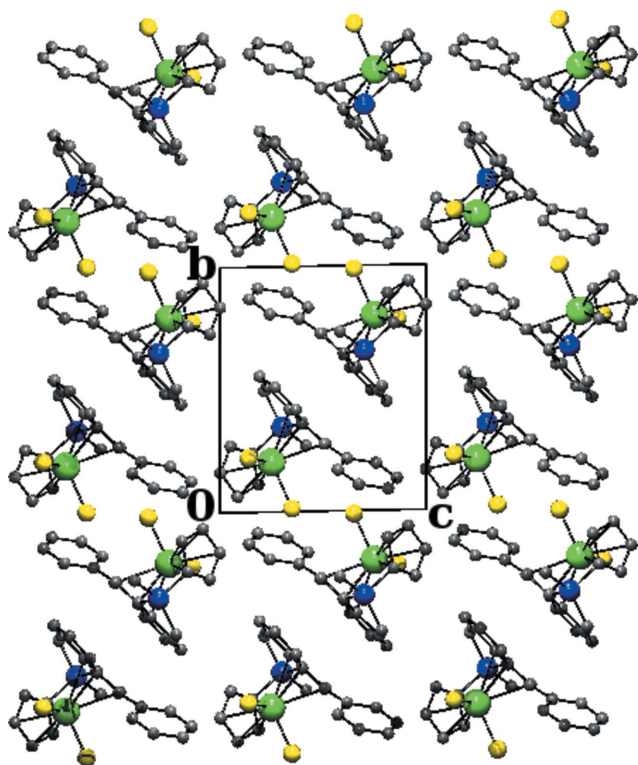


Figure 2
Crystal packing in (I), viewed parallel to the *a* axis. Hf green, Cl yellow, Si blue and C grey. H atoms have been omitted.

analogue. The Si atom is bonded to the indenyl unit in the 1-position. The distances between the Hf and the cyclopentadienyl centroid are 2.26 (3) Å for the indenyl residue and 2.170 (3) Å for the cyclopentadienyl; these distances were not constrained at the refinement stage. The indenyl and cyclopentadienyl rings are tilted at an angle β of 55 (2)° with

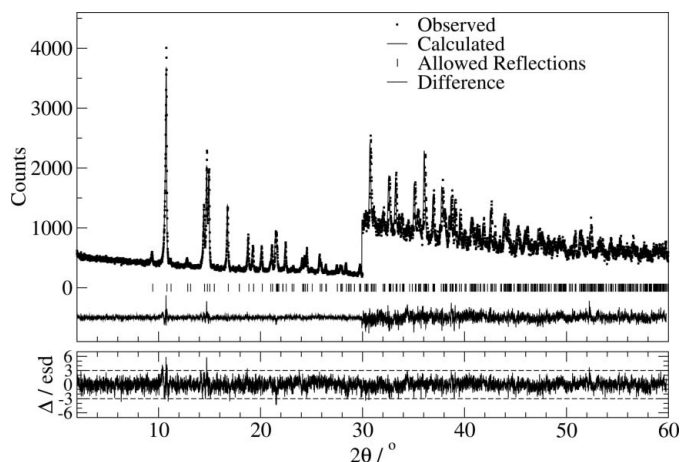


Figure 3
Final observed (points), calculated (line), difference [$(y_{\text{obs}} - y_{\text{calc}})$] and weighted difference [$(y_{\text{obs}} - y_{\text{calc}})/\sigma$] profiles for the Rietveld refinement of (I).

respect to each other, which can be compared with an angle of 61.8° in the bis-indenyl zirconocene analogue (Dang *et al.*, 1999). The angles δ (hafnium–cyclopentadienyl centroid–carbon α to silicon) are 92.4 (2) and 87.3 (2)° for the cyclopentadienyl and indenyl rings, respectively. The phenyl residue is twisted out of plane with respect to the indenyl residue by a torsion angle of 24.1 (2)°.

The molecules pack so that the indenyl rings on neighbouring molecules are parallel and in contact (Fig. 2). Excluding H···H contacts, two short contacts (less than the sum of the van der Waals radii) exist. Between the indenyl ring systems, the C7···C10 distance of 3.37 (3) Å is only slightly shorter than the value of 3.4 Å derived from the sum of the carbon van der Waals radii (Bondi, 1964). There also exists a contact C5···C21 of 3.35 (3) Å between the cyclopentadienyl residue and a phenyl ring on a neighbouring molecule. Both of these contacts are only marginally shorter than expected and it is not clear that they indicate the presence of any strong directional interactions between molecules or that the crystal structure adopted can be rationally based on the close packing of molecules.

Experimental

All manipulations were performed under argon using conventional Schlenk techniques. Solvents were dried and distilled under argon prior to use. 1-Phenylindenyl lithium, cyclopentadienyl lithium and hafnium tetrachloride (zirconium content < 0.5%) are commercial products from <http://www.mcat.de>.

(Cyclopentadienyl)(3-phenylinden-1-yl)dimethylsilane: To a solution of dichlorodimethylsilane (6.80 g, 6.4 ml, 52.68 mmol) in 200 ml of diethyl ether, 1-phenylindenyl lithium (3.48 g, 17.56 mmol) was added at 195 K. The mixture was slowly warmed to ambient temperature and stirred for 1 h. The solvent was removed under vacuum and the oily residue extracted with pentane. The combined extracts were filtered through celite, the solvent removed and the residual oil dried under high vacuum to obtain 17.51 mmol (99.7%) of crude product as a red oil. The crude product was used without further purification in the next step. The red oil was dissolved in

toluene (30 ml) and cyclopentadienyl lithium (1.32 g) was added. After 2 d the reaction was complete (determined by $^1\text{H NMR}$). Water and saturated NH_4Cl were added and the mixture extracted several times with diethyl ether. The combined organic fractions were dried over Na_2SO_4 and the solvent was removed under vacuum. (Cyclopentadienyl)(3-phenylinden-1-yl)dimethylsilane was obtained as a yellow oil as a mixture of isomers which was used directly in the next step.

(η^5 -Cyclopentadienyl)(η^5 -3-phenylindenyl)dimethylsilanehafnium(IV) dichloride: To a solution of (cyclopentadienyl)(3-phenylinden-1-yl)dimethylsilane (4.91 g, 15.61 mmol) in 150 ml of diethyl ether, 2.5 M *n*-butyl lithium (12.5 ml, 31.25 mmol) in hexane was added at 195 K. The mixture was slowly warmed to ambient temperature and stirred overnight. The dark-yellow mixture was then cooled to 195 K and HfCl_4 (5.00 g, 31.25 mmol) was added over a period of 1 h. The mixture was then warmed to ambient temperature and stirred for 1 h. The solvent was removed and the oily residue extracted twice with dichloromethane. The combined extracts were filtered through celite, the solvent removed and the residual oil dried under high vacuum to obtain 14.62 mmol (93.7%) of crude product. Analytically pure product was obtained by recrystallization from toluene/hexane (1:2).

Crystal data

$[\text{Hf}(\text{C}_{22}\text{H}_{20}\text{Si})\text{Cl}_2]$
 $M_r = 561.88$
 Triclinic, $P\bar{1}$
 $a = 10.1894$ (4) Å
 $b = 11.0993$ (4) Å
 $c = 9.6940$ (4) Å
 $\alpha = 91.974$ (2)°
 $\beta = 108.693$ (2)°
 $\gamma = 80.501$ (3)°

$V = 1024.07$ (7) Å³
 $Z = 2$
 $D_x = 1.822$ Mg m⁻³
 Co $K\alpha$ radiation
 $T = 293$ K
 Specimen shape: cylinder
 0.7 × 0.1 mm
 Particle morphology: finely ground powder, yellow

Data collection

Stoe Stadi-P diffractometer
 Specimen mounting: 0.3 mm
 Lindemann glass capillary
 Specimen mounted in transmission mode

Scan method: step
 $2\theta_{\min} = 2.0$, $2\theta_{\max} = 60.0$ °
 Increment in $2\theta = 0.01$ °

Refinement

$R_p = 0.046$
 $R_{wp} = 0.059$
 $R_{\text{exp}} = 0.059$
 $R_B = 0.068$
 $S = 1.04$
 Wavelength of incident radiation:
 1.78892 Å
 Excluded region(s): none
 The *GSAS* profile function number 3 was employed, which utilizes a pseudo-Voigt description of the peak shape which allows for angle-dependent asymmetry. The function is fully documented in the *GSAS* technical manual which is distributed with the software package. Peak tails were ignored when the intensity was

0.1 % of the overall peak.
 Refined parameters were GV (3.996), LX (3.016) and LY (16.261), with S/L and H/L set fixed at 0.013 and 0.035, which are generally suitable values for the diffractometer in question.
 169 parameters
 All H-atom parameters refined subject to stereochemical restraints
 $(\Delta/\sigma)_{\max} = 0.03$
 Preferred orientation correction: March–Dollase AXIS 1 Ratio = 1.08679, $h = 0.000$, $k = 0.000$, $l = 1.000$. Preferred orientation correction range: Min = 0.77904, Max = 1.13297

A powder diffraction pattern was collected using a monochromated Stoe Stadi-P instrument operating in Debye–Scherrer

geometry with the sample contained in a 0.3 mm Lindemann glass capillary which was spun during the measurement to minimize preferred orientation effects. The pattern was indexed using *TREOR* (Werner *et al.*, 1985), employing 18 low-angle reflections. A triclinic unit cell of reasonable volume (assuming $Z = 2$) gave indexing figures of merit $M_{18}=84$, $F_{18}=178$. The crystal structure was solved using the simulated annealing algorithms as implemented in both *PSSP* (Stephens & Huq, 2002) and *DASH* (David *et al.*, 2006). The crystal structure was assumed to be centrosymmetric (space group $P\bar{1}$, $Z' = 1$), and this approach led to a chemically reasonable starting model for Rietveld refinement. For the refinement, suitable restraints were imposed on bond lengths, angles and planar groups, including bonds to H atoms. The CH and CH₃ distances were constrained to be 0.93 and 0.96 Å, respectively. Three independent atomic displacement parameters were employed: one for the Hf, one for the two Cl atoms, one for all C and Si, and one for the H atoms which was set equal to 1.2 times that for the C and Si atoms. Trials were made employing preferred orientation in directions suggested by a basic BFDH calculation of likely crystal morphology, which indicated that a small degree of preferred orientation existed in the sample [refined ratio=1.09 (4)], with plate-like crystallites being preferentially oriented normal to the diffraction plane. Given the air-sensitive nature of the sample, we did not try to confirm this through visual microscopy. The refinement, using the *GSAS* software suite (Larson & Von Dreele, 2000), converged readily to yield acceptable figures of merit of $\chi^2 = 1.08$, $R_{wp} = 0.059$, $R_p = 0.046$, $DWd = 1.43$ and $R_{\text{Bragg}} = 0.068$, and a visually acceptable fit (Fig. 3). Standard deviations are taken from the program employed and represent statistical uncertainties rather than estimates of the absolute error, which are likely to be considerably greater.

Data collection: *WinXpow* (Stoe & Cie, 1999); data reduction: *WinXpow*; program(s) used to solve structure: *DASH* (David *et al.*, 2006) and *PSSP* (Stephens & Huq, 2002); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2000); molecular graphics: *PLATON* (Spek, 2003).

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