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Preliminary communication

CYCLOPENTADIENYLHAFNIUM TRICHLORIDE, ITS SYNTHESIS AND USE TO PREPARE A CHIRAL HAFNIUM COMPOUND

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Summary

The preparation and characterisation of the new hafnium compound (η^5-C_5H_5)$HfCl_3$,2THF is reported; it has been used to prepare the first chiral complex of hafnium.

Considerable effort has recently gone into preparation of compounds containing chiral metal centers [1,2,3]. We described already the preparation of chiral dicyclopentadienylzirconium(IV) compounds [4], and we now report the synthesis of $CpHfCl_3$,2THF (I) and its use to prepare chiral dicyclopentadienylhafnium(IV) compounds.

Reaction between dicyclopentadienylmagnesium [5] and the metal tetrachloride MCl_4 in xylene which is satisfactory for preparing $CpMCl_3$ when M = Zr, [6], gives poor results when M = Hf. However it gives yields of up to 25% at higher temperature in decalin. Cyclopentadienylhafnium trichloride is separated from the dichloride Cp_2HfCl_2 by using the low solubility of the adduct I in THF.

Analytical data for I are given below; the NMR spectrum of I clearly shows, in addition to the signal of THF, only one singlet (6.33 ppm, C_6D_6, TMS) which is downfield compared to that of Cp_2HfCl_2 (5.82 ppm). The mass spectrum of I is in agreement with the structure*.

Condensation of I with suitable anions affords the corresponding prochiral dichlorides II and III. The product III reacts with $C_6H_5CH_2MgCl$ to give the first known chiral compound of hafnium IV which is characterised by magnetic non-equivalence of diastereotopic groups.

NMR, mass and analytical data

I. (η^5-C_5H_5)$HfCl_3$,2THF: M.p. 125°C (decomp.) (capill/N_2). Found: C, 30.31;

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*Recently Chandrasekaran et al. [7] mentioned the color of $CpHfCl_3$ but gave no details.

H, 4.25; Cl, 21.66. $C_{13}H_{21}Cl_3O_2Hf$ calcd.: C, 31.59; H, 4.28; Cl, 21.52%. Mass spectrum*: (M adduct)$^+$ absent; 350 $(CpHfCl_3)^+$ 5%; 315 $(M - Cl)^+$ 100%; 289 $(M - C_2H_2 - Cl)^+$ 28%; 66 $(C_5H_6)^+$ 52%; 65 $(C_5H_5)^+$ 60%. NMR (C_6D_6, TMS): C_5H_5, 6.33s (5); OCH_2, 3.85m (8); CH_2, 1.37m (8).

II. $[\eta^5\text{-}(CH_3)_2CHC_5H_4](\eta^5\text{-}C_5H_5)HfCl_2 = \eta^5\text{-}Cp'\text{-}\eta^5\text{-}CpHfCl_2$: M.p. 105°C (Kofler). Found: C, 37.20; H, 3.85; Cl, 16.96. $C_{13}H_{16}HfCl_2$ calcd.: C, 37.03; H, 3.82; Cl, 16.82%. Mass spectrum* 422 M^+ 5%; 386 $(M - HCl)^+$ 36%; 371 $(M - HCl - CH_3)^+$ 15%; 357 $(M - C_5H_5)^+$ 6%; 315 $(M - Cp')^+$ 38%. NMR ($CDCl_3$, TMS): CH_3, 1.21d (6); CH, 3.13hp (1); Cp' 6.05—6.30m (4); Cp, 6.34s (5).

III. $[\eta^5\text{-}C_6H_5C(CH_3)_2C_5H_4](\eta^5\text{-}C_5H_5)HfCl_2 = \eta^5\text{-}Cp'\text{-}\eta^5\text{-}CpHfCl_2$: M.p. 152°C (Kofler). Found: C, 45.54; H, 3.91; Cl, 14.27. $C_{19}H_{20}HfCl_2$ calcd.: C, 45.85; H, 4.05; Cl, 14.25%. Mass spectrum*: M^+ absent: 433 $(M - Cp)^+$ 100%; 315 $(M - Cp')^+$ 22%. NMR ($CDCl_3$, TMS): CH_3, 1.77s (6); Cp, 6.14s (5); Cp', 6.20—6.30d (2), 6.30—6.40d (2); C_6H_5, 7.25s (5).

IV$[\eta^5\text{-}C_6H_5C(CH_3)_2C_5H_4](\eta^5\text{-}C_5H_5)HfClCH_2C_6H_5 = \eta^5\text{-}Cp'\text{-}\eta^5\text{-}CpHfClCH_2C_6H_5$ yellow oil. $C_{26}H_{27}HfCl$. Mass spectrum*: M^+ absent; 463 $(M - CH_2C_6H_5)^+$ 100%; 91 $(CH_2C_6H_5)^+$ 5%. NMR ($CDCl_3$, TMS): CH_3, 1.68s (3), 1.75s (3); CH_2, 2.03d.d (2); Cp, 5.74s (5); Cp', 5.40—5.60m (1), 5.70—5.90m (1), 6.20—6.40m (2); $C_6H_5CH_2$, 6.70—7.35m (5); C_6H_5C, 7.24s (5).

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*We report only m/e values corresponding to ^{180}Hf et ^{35}Cl.