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Preliminary communication

Cationic mono(pentamethylcyclopentadienyl)(2-methallyl) complexes of hafnium

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Abstract

Two new cationic mono(pentamethylcyclopentadienyl) organohafnium complexes with η^3-2-methallyl ligands, $[(C_5Me_5)Hf(\eta^3\text{-}2\text{-}C_4H_7)Me][MeB(C_6F_5)_3]$ (**5**) and $[(C_5Me_5)Hf(\eta^3\text{-}2\text{-}C_4H_7)_2][B(C_6F_5)_4]$ (**6**), have been prepared. The former readily polymerises ethene, but is not active towards propene. The latter, with the weakly coordinating $[B(C_6F_5)_4]$ anion, oligomerises propene to atactic oligomers. In contrast with metallocene systems, the oligomerisation of α-olefins like propene is apparently readily initiated on the 2-methallyl groups in this complex.

Keywords: Allyl; Catalysis; Cyclopentadienyl

The success of cationic metallocene alkyl species as highly active olefin polymerisation catalysts (for recent reviews see Ref. [1]) has also spawned a substantial research effort into the chemistry of non-metallocene early transition-metal alkyl systems to determine the general potential of cationic Group 4 metal alkyl species in olefin polymerisation catalysis. One obvious choice is to look for cationic monocyclopentadienyl metal alkyl systems. Various additional ancillary ligands can be used in such half-sandwich complexes, like the η-benzamidinate ligand in the recently reported $(C_5R_5)Zr[\eta\text{-}CPh(NSiMe_3)_2]X_2$ (X = halide, hydrocarbyl) complexes and their derivatives [2]. The η^3-allyl group is a monoanionic 3-electron hydrocarbon ligand that, due to the nucleophilicity of the terminal carbon atoms, is more reactive than a cyclopentadienyl group but expected to be more inert towards olefins than metal–alkyl moieties. In this communication we describe the use of the η^3-bound 2-methallyl (2-methylpropenyl) group as ancillary and as reactive ligand in cationic 12- and 14-electron mono(pentamethylcyclopentadienyl) hafnium species of the type $[Cp^*Hf(\eta^3\text{-}2\text{-methallyl})R]^+$ (R = Me, 2-methallyl; $Cp^* = \eta^5\text{-}C_5Me_5$) and the reactivity of these species towards ethene and propene.

Neutral precursors to these cationic species can be prepared in relatively straightforward fashion. The tris-2-methallyl complex $Cp^*Hf(2\text{-}C_4H_7)_3$ (**1**, $2\text{-}C_4H_7$ = 2-methallyl) can be obtained by reaction of Cp^*HfCl_3 with 3 equivalents of $(2\text{-}C_4H_7)MgCl$, in similar fashion to $Cp^*Hf(1\text{-}C_4H_7)_3$ [3] and $CpZr(C_3H_5)_3$ [4–6]. The bis-2-methallyl complex $Cp^*Hf(2\text{-}C_4H_7)_2Cl$ (**2**) is obtained similarly with 2 equivalents of the Grignard reagent. As reported previously for the 1-methallyl derivatives [7] and for the unsubstituted Cp–Zr–allyl system [4,5], the mono-2-methallyl complex $Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Cl_2$ (**3**) can be most conveniently obtained by comproportionation of the tris-2-methallyl complex **1** with Cp^*HfCl_3 (Scheme 1). The dichloride **3** is readily methylated with 2 equivalents of MeLi to give the dimethyl derivative $Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Me_2$ (**4**).

4: ^{1}H NMR (300 MHz, C_6D_6): δ 2.62 (s, 4H, $=CH_2$), 1.81 (s, 15H, Cp^*), 1.65 (s, 3H, allyl Me), −0.10 (s, 6H, Hf–Me). ^{13}C NMR (75.4 MHz, C_6D_{12}): δ 155.78 (s, allyl C), 117.92 (s, Cp^*-ring), 78.86 (t, 150.1, allyl CH_2), 45.27 (q, 113.6, Hf–Me), 27.04 (overlap with solvent resonance, allyl Me), 11.63 (q, 126.5, Cp^*–Me).

Methylation of the monochloride **2** with MeLi leads only to $Cp^*Hf(2\text{-}C_4H_7)_2Me$ as a transient (observed by NMR), as it subsequently disproportionates to **1** and **4**. In all complexes the allyl ligand is fluxional (down to −60 °C, by NMR), equivalencing the allyl methylene

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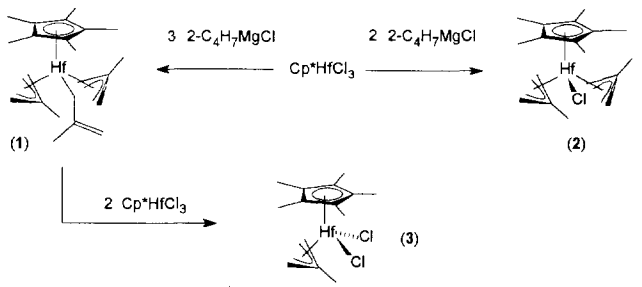
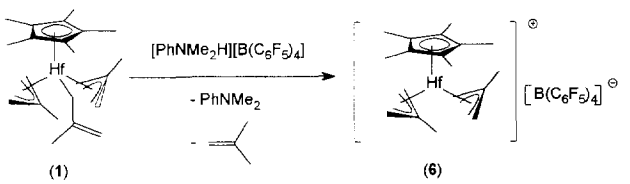


Scheme 1.



Scheme 3.

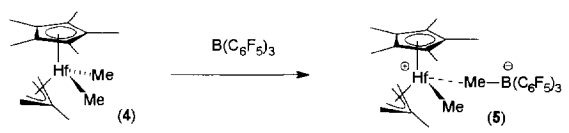
syn and *anti* protons via an η^3,σ,η^3-process. It suggests that in the $Cp^*Hf(2\text{-}C_4H_7)X_2$ species the allyl π,σ-interconversion is significantly faster than in the unsubstituted Zr derivatives $CpZr(C_3H_5)X_2$ [5]. Compounds **1**, **2** and **4** are all thermally labile at ambient temperature, and need to be stored in a refrigerator.

The dimethyl complex **4** reacts with the Lewis acid $B(C_6F_5)_3$ to give the complex $[Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Me][MeB(C_6F_5)_3]$ (**5**, Scheme 2), which can be isolated as pale needles of its pentane solvate by precipitation from pentane. The compound is thermally labile at ambient temperature, decomposing in benzene solution in a few hours liberating methane. In this case, at low temperature (−60 °C) the fluxionality in the complex can be frozen out, and its ^1H NMR spectrum shows four non-equivalent methallyl methylene protons.

5: ^1H NMR (300 MHz, CD_2Cl_2, −63 °C): δ 3.77 (m, 1H, *syn*-=CH_2), 3.02 (m, 1H, *syn*-=CH_2), 1.95 (3H + 15H, Cp^* and allyl Me), 1.17 (m, 1H, *anti*-=CH_2), 1.14 (br, 3H, B–Me), 0.34 (m, 1H, *anti*-=CH_2), 0.00 (s, 3H, Hf–Me). ^{19}F NMR (188 MHz, CD_2Cl_2, 25 °C): δ −133.63 (*o*-F), −161.0 (*p*-F), 165.5 (*m*-F).

The $MeB(C_6F_5)_3$ anion appears to show significant interaction with the metal centre [8], as seen for example from the B–Me ^1H NMR resonance at δ 1.19 ppm (free anion in CD_2Cl_2 around δ 0.55 ppm) and the relatively large $\Delta\delta$[(*m*-F) − (*p*-F)] of 4.5 ppm (in the free anion 2.7 ppm [9]). The complex **5** reacts with 1 equivalent of PMe_3 through displacement of the $MeB(C_6F_5)_3$ anion, giving the adduct $[Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Me(PMe_3)][MeB(C_6F_5)_3]$.

In contrast, reaction of **4** with the electrophiles $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ proceeds through attack on the nucleophilic allyl methylene groups rather than on the Hf–Me moiety, thus rendering 12-electron cations $[Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Me]^+$ with the



Scheme 2.

$[B(C_6F_5)_4]$ anion inaccessible via this route. However, reaction of the tris-2-methallyl complex **1** with $[PhNMe_2H][B(C_6F_5)_4]$ proceeds smoothly to give the 14-electron species $[Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)_2][B(C_6F_5)_4]$ (**6**, Scheme 3) and free $PhNMe_2$. The compound **6** is again thermolabile, decomposing at ambient temperatures in a few hours, but can be stored in a dry-box at −40 °C for weeks. Low-temperature NMR data suggest the complex has two η^3-bound 2-methallyl ligands.

6: ^1H NMR (400 MHz, C_6D_5Br, −30 °C): δ 3.02 (br, 4H, *syn*-CH_2), 2.27 (br, 4H, *anti*-CH_2), 1.64 (s, 15H, Cp^*), 1.28 (s, 6H, Me). ^{13}C NMR (100.5 MHz, C_6D_5Br, −30 °C): δ 163.75 (s, allyl C), 148.6 (d, J_{CF} = 237, *o*-CF), 138.5 (d, J_{CF} = 243, *p*-CF), 136.7 (d, J_{CF} = 246, *m*-CF), 124.5 (br, C_6F_5 *ipso* C), 120.09 (s, Cp^*-ring), 79.67 (dd, 144, 161, ill resolved, CH_2), 27.83 (q, 127.5, allyl Me), 12.14 (q, 127.4, Cp^*–Me). ^{19}F NMR (188 MHz, C_6D_5Br): δ −133.8 (*o*-F), −162.9 (*p*-F), −167.0 (*m*-F).

By ^1H NMR the methallyl methylene *syn*- and *anti*-protons can be seen to exchange at 25 °C, but the exchange is frozen out at −30 °C.

The complex $[Cp^*Hf(\eta^3\text{-}2\text{-}C_4H_7)Me][MeB(C_6F_5)_3]$ (**5**) readily polymerises ethene in either dichloromethane or toluene solvent at ambient temperature and pressure. Brief (1 min) runs with 8.2 μmol of catalyst in 12 ml of solvent yielded productivities of 5.1 kg PE $(g\,Hf^{-1})h^{-1}$ and 3.7 kg PE $(g\,Hf^{-1})h^{-1}$ in CH_2Cl_2 and toluene respectively. In contrast, catalytic activity of **5** towards propene is negligible. However, the cationic bis-allyl complex $[Cp^*Hf(2\text{-}C_4H_7)_2][B(C_6F_5)_4]$ (**6**) reacts readily with propene (benzene solvent, ambient temperature, 5 bar propene) to produce oligomers with M_n = 2676, M_w = 4921 (M_w/M_n = 1.84, by GPC). A 30 min run with 17.2 μmol of catalyst yielded 2.23 g of oligomer, corresponding to a productivity of 1.4 kg $(g\,Hf^{-1})h^{-1}$ or 6160 t.o. $Hf^{-1}\,h^{-1}$. By NMR, the product was found to be fully atactic, with only vinylidene-type olefinic end-groups.

These results show that the (formally 12-electron) $Cp^*Hf(\eta^3\text{-}2\text{-methallyl})(alkyl)$ cation is able to catalyse the polymerisation of olefins, but that the reactivity of this sterically unencumbered system is very sensitive to the nature of the anion. It seems the affinity of the $MeB(C_6F_5)_3$ anion for the metal centre is too great to allow ready insertion of propene into the metal–carbon bond of **5**. This impediment is absent in **6** with the

weakly coordinating $B(C_6F_5)_4$ anion. Apparently in this system the η^3-2-methallyl group is sufficiently reactive to initiate the oligomerisation of propene. This is an interesting contrast with the more sterically hindered metallocene cations (such as the decamethyl–metallocene systems), where η^3-allyl species usually show little reactivity towards α-olefins and where their formation has been associated with catalyst deactivation [10].

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