Supporting Information

Anionic hafnium species: an active catalytic intermediate for the coupling of epoxides with CO_2?†

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General procedures. All experiments were performed under argon with rigorous exclusion of air and moisture, using standard Schlenk, high-vacuum and glovebox techniques (MB Braun MB200B-G; < 1 ppm O_2, < 1 ppm H_2O). Dichloromethane, chloroform and diethyl ether were dried over CaH_2, toluene, pentane and hexane were purified over a sodium mirror and THF was distilled from sodium benzophenone ketyl (pre-purified over Grubbs columns: MB Braun Solvent Purification System 800). All solvents were vacuum distilled, degassed prior to use. Benzene-d_6 dichloromethane-d_2 and chloroform-*d* were obtained from Aldrich, dried over sodium or CaH_2, vacuum distilled, degassed and filtered prior to use. All other chemicals were purchased from Sigma-Aldrich and used as received. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) was recrystallized from dichloromethane and hexane, dried several hours at 80 °C under vacuum.[1] $Hf(OiPr)_4$ was purchased from Sigma-Aldrich and stored at -30 °C in a glovebox. The 1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl) imidazolidinium chloride salt[2] was prepared according to slightly modified literature procedures. Chlorotrimethylsilane (TMSCl) and cyclohexene oxide (CHO), propylene oxide (PO), styrene oxide (SO) and 1,3-cyclohexadiene oxide (1,3-CHDO) and cyclopentene oxide (CPO) were purchased from Sigma-Aldrich, distilled from CaH_2 under vacuum following three freeze-pump-thaw cycles and stored at -30 °C in a glovebox. CO_2 was purchased from Praxair (purity grade: 99.9995%, H_2O < 0.5 ppm).

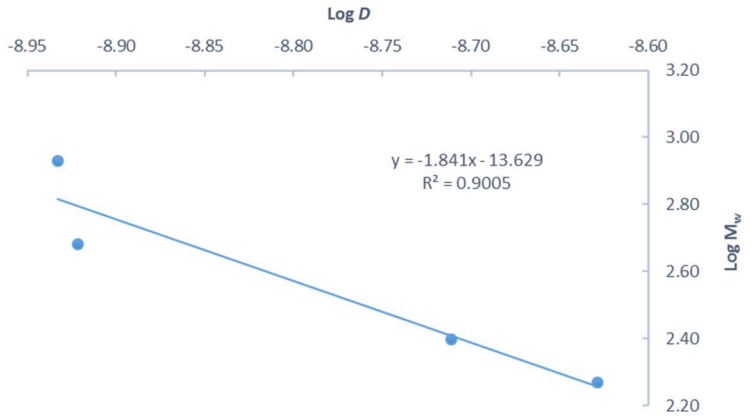
The NMR spectra of air and moisture sensitive compounds were recorded using J. Young valve NMR tubes at 298 K on Bruker AVANCE DMX400 spectrometer (5 mm Broadband observe probehead (BBO), ^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz), Bruker BioSpin AVANCE AV500 (5 mm BBO, ^{1}H: 500.13 MHz; ^{13}C: 125.77 MHz) and Bruker 850 MHz AVANCE III HD NMR (5 mm triple resonance CryoProbe, ^{1}H: 850.13 MHz; ^{13}C: 213.77 MHz). Chemical shifts are referenced to the residual proton solvent signals (^{1}H (δ): chloroform-*d*, 7.26; dichloromethane-d_2, 5.32, benzene-d_6 : 7.16) and solvent ^{13}C signals (^{13}C (δ): chloroform-*d*, 77.16; dichloromethane-d_2, 53.84, benzene-d_6: 128.06) and reported in *parts per million* (ppm) relative to tetramethylsilane.[3]

The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed at 298 K, on the Bruker 850 MHz AVANCE III HD NMR spectrometer spectrometer which have a maximum gradient of 59.1 G/cm. The DOSY data was acquired using the pulse sequence ledbpgp2s with 16 scans, 64k points, a spectral width of 10 ppm centered at 4.5 ppm, and with a relaxation delay of 1 s. The diffusion time was set to 13 ms while the bipolar gradient pulses were 1400 µs. The two spoil gradients were 600 µs long. The bipolar gradient strengths were increased linearly from 2% to 95% in 25 steps. The data was processed and analyzed with TopSpin 3.6. The DOSY calibration[4] curve was established by using a set of organometallic compounds and ligand as external standards with different molecular weights (Table S1): ferrocene (Cp_2Fe: 186.03 g mol^{-1}); titanocene dichloride (Cp_2TiCl_2: 248.96 g mol^{-1}); 1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl) imidazolidinium salt[2] ($(NHC)H_3$: 479.73 g mol^{-1}) and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)

(tricyclohexylphosphine)ruthenium (Grubbs catalyst GII: 848.97 g mol^{-1}). From each external standard a diffusion coefficient (*D*) was measured, and by plotting log *D* vs log M_w a calibration curve was obtained (Graph S1) allowing to determine the diffusion coefficient via DOSY analysis and calculate the estimated M_w of an unknown species in solution.

Table S1. Diffusion coefficient of standards *versus* their molecular weights in CD_2Cl_2.

Compound	Log *D* (m^2 sec^{-1})	M_w (g mol^{-1})	log M_w (g mol^{-1})
Cp_2Fe	-8.629±0.003	186.03	2.270
Cp_2TiCl_2	-8.711±0.001	248.96	2.396
(NHC)H$_3$I	-8.921±0.003	479.73	2.681
Grubbs catalyst GII	-8.933±0.004	848.97	2.929



Graph S1. Plot of log *D* (total summed diffusion) *versus* log M_w for a set of standards in CD_2Cl_2.

IR spectra were recorded on a Nicolet FT-IR Protégé 460 spectrometer with a DRIFT collector. The spectra were averaged over 64 scans; the resolution was ±4 cm^{-1}. Elemental analyses of C, H and N were performed on an Elementar Vario EL III instrument.

The molecular weights (M_n and M_w) and PDIs were determined by GPC-SEC from Viscotek. Polystyrene PS-99K (M_w = 99 kg mol^{-1}, IV = 0.477) calibration standard for molecular weight calibration were obtained from Malvern Panalytical (TDS3000). Chromatographic separation of polycarbonates samples was performed at a column temperature of 30 °C with a flow-rate of 1 mL min^{-1}. SEC was performed with a pump supplied by Viscotek (GPCmax), employing two ViscoGelTM columns (GMHHR-H columns (300 (L) x 7.8 mm (I.D.), 10 µm particle size, 100 Å pore size). Signals were detected by means of a triple detection array (TDA 302) and calibrated against polystyrene standards (M_w/M_n < 1.15, from 1-900 kg mol^{-1}) from Malvern Panalytical (UCS3000). The NMR conversion and microstructure of the polycarbonates were determined by means of ^{1}H and ^{13}C NMR spectroscopy using chloroform-*d* as solvent.

({κ^3-*O,C,O*}-NHC)Hf(O*i*Pr)(Cl)(THF) (1). In a glovebox, to precooled THF solution (30 mL) at - 30 °C of 1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl) imidazolidinium chloride salt (300 mg, 0.58 mmol) was added dropwise over 15 min a THF solution (10 mL) of Hf(O*i*Pr)$_4$ (241 mg, 0.58 mmol) cooled to - 30 °C. The solution was stirred for 18 h at room temperature and the initial colorless solution slowly turned pale yellow. All volatile were completely removed under vacuum. The solid was then washed

with a mixture of toluene:hexane (1:4 v/v, 3 times) and evaporated to dryness under vacuum to afford compound **1** as a colorless powder (400 mg, 83% yield). The compound **1** was crystallized as colorless crystals in a saturated solution of benzene:hexane (1:2 v/v) at room temperature. Anal. Calcd for $C_{38}H_{59}ClHfN_2O_4$: C, 55.54; H, 7.24; N, 3.41. Found: C, 55.94; H, 7.21; N, 3.35. DRIFT (ν/cm^{-1}): 2959s, 2901m, 2866w, 1475vs, 1448s, 1386w, 1360w, 1322s, 1251w, 1169m, 1028m, 852m, 761vw, 667vw, 553w. ^{1}H NMR (500.13 MHz, benzene-d_6): δ 7.53 (d, J_{HH} = 2 Hz, 2H, Ar-*H*), 6.74 (d, J_{HH} = 2 Hz, 2H, Ar-*H*), 4.62 (sept, J_{HH} = 6 Hz, 1H, O-C*H*$(CH_3)_2$), 3.68 (m, 4H, THF), 3.23 (s, 4H, NC*H*$_2$), 2.0 (s, 18H, *t*Bu), 1.89 (s, 18H, *t*Bu), 1.42 (d, J_{HH} = 6 Hz, 6H, O-CH(C*H*$_3)_2$), 1.05 (m, 4H, THF) ppm. ^{13}C{^{1}H}-ATP NMR (125.77 MHz, benzene-d_6): δ, 204.4 (N*C*N), 150.1 (C_q, Ar), 139.5 (C_q, Ar), 139.1 (C_q, Ar), 130.8 (C_q, Ar), 120.0 (*C*H-Ar), 112.3 (*C*H-Ar), 73.2 (O-*C*H$(CH_3)_2$), 71.2 (THF), 47.4 (N*C*H$_2$), 36.2 (C_q, *t*Bu), 34.7 (C_q, *t*Bu), 32.1 (*C*H, *t*Bu), 30.6 (*C*H, *t*Bu), 27.2 (O-CH(*C*H$_3)_2$), 25.0 (THF) ppm.

({κ^3-*O,C,O*}-NHC)Hf(Cl)$_2$(THF) (2). Synthesis of compound **2** was carried out by adapting the literature procedure and from the isolated compound **1** as starting material.[5] To a toluene solution (8 mL) of **1** (320 mg, 0.39 mmol) in glass pressure tube was added an excess of TMSCl (99 µL, 0.78 mmol). The reaction mixture was stirred at 100 °C for 3 days. The yellow-green solution was then evaporated under vacuum and washed with a mixture of toluene:hexane (1:4 v/v 3times). The solid was washed with hexane until disappearance of the greenish color in the washings and dried to afford compound **2** as a yellow powder (280 mg, 90% yield). Suitable single crystals for X-ray analysis of **2** were obtained from Et_2O:toluene (1:1 v/v) at room temperature. Anal. Calcd for $C_{35}H_{52}Cl_2HfN_2O_3$: C, 52.67; H, 6.57; N, 3.51. Found: C, 53.06; H, 6.61; N, 3.45. ^{1}H NMR (850.13 MHz, dichloromethane-d_2): δ 7.30 (d, J_{HH} = 2 Hz, 2H, Ar-*H*), 7.05 (d, J_{HH} = 2 Hz, 2H, Ar-*H*), 4.41 (m, 4H, NC*H*$_2$), 3.81 (m, 4H, THF), 1.75 (m, 4H, THF), 1.59 (s, 18H, *t*Bu), 1.38 (s, 18H, *t*Bu) ppm. The ^{1}H and ^{13}C NMR data and X-ray structure matched those reported in the literature.[5]

[PPN][({κ^3-*O,C,O*}-NHC)Hf(Cl)$_3$] (3). To a mixture of **2** (150 mg, 0.188 mmol) and [PPN]Cl (108 mg, 0.188 mmol) was added dichloromethane (8 mL), and the mixture was stirred at room temperature for 18 h. The reaction mixture was then centrifuged, filtered, dried under vacuum, washed with toluene and then dried under vacuum to yield compound **3** as a pale yellow powder (180 mg, 73% yield). Large block of single crystals of **3** were obtained by mixing 2 mL of THF to a saturated solution of **3** in dichloromethane (ca 0.6 mL) at room temperature. Anal. Calcd for $C_{67}H_{74}Cl_3HfN_3O_2P_2.0.5C_7H_8$: C, 62.90; H, 5.84; N, 3.12. Found: C, 63.29; H, 5.92; N, 3.05. DRIFT (ν/cm^{-1}): 2951s, 2901m, 2866w, 1474vs, 1447s, 1438vs, 1322s, 1299m, 1285m, 1265m, 1254m, 1115m, 854vw, 723m, 694m, 549m, 534m, 499w. ^{1}H NMR (850.13 MHz, dichloromethane-d_2): δ7.67-7.62 (m, 6H, *p*-Ar-*H*, PPN), 7.50-7.45 (m, 24H, *o,m*-Ar-*H*, PPN), 7.21 (d, J_{HH} = 1.6 Hz, 2H, Ar-*H*), 6.98 (d, J_{HH} = 1.6 Hz, 2H, Ar-*H*), 4.28 (s, 4H, NC*H*$_2$), 1.56 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (213.77 MHz, dichloromethane-d_2): δ 202.2 (N*C*N), 149.3 (C_q, Ar), 139.8 (C_q, Ar), 138.8 (C_q, Ar), 134.3 (m, *p*-*C*H, PPN), 132.7 (m, *o*-*C*H, PPN), 131.4 (C_q, Ar), 130.1 (m, *m*-*C*H, PPN), 127.6 (dd, J_{PC} = 108 Hz, 2 Hz, *ipso*-*C*, PPN), 119.2 (*C*H, Ar), 112.6 (*C*H, Ar), 48.1 (N*C*H$_2$), 36.0 (C_q, *t*Bu), 34.9 (C_q, *t*Bu), 32.1 (*C*H$_3$, *t*Bu), 30.4 (*C*H$_3$, *t*Bu) ppm.

({κ^3-*O,C,O*}-NHC)Hf(OC$_6$H$_{10}$Cl)$_2$(CHO) (4). The mixture of **2** (46 mg, 0.058 mmol) and CHO (28.2 mg, 0.29 mmol) in toluene (4 mL) was stirred at room temperature for 48 h. All volatile were removed under vacuum, and washed with hexane to give a colorless powder after drying. Anal. Calcd. for $C_{49}H_{74}Cl_2HfN_2O_5$.1.5CHO: C, 59.66; H, 7.68; N, 2.40. Found: C, 61.00; H, 7.31; N, 2.14 (attempts to remove residual CHO either under vacuum or by washing the complex revealed to be extremely tedious due to the high boiling point of CHO). DRIFT (ν/cm^{-1}): 2936s, 2859m, 1475s, 1448s, 1317s, 1170m, 1090m. ^{1}H NMR (500.13 MHz, dichloromethane-d_2): δ, 7.17 (d, $J_{H\text{-}H}$ = 2.2 Hz, 2H, H$_{Ar}$), 6.91 (d, $J_{H\text{-}H}$ = 2.2 Hz, 2H, H$_{Ar}$), 4.25 (s, 4H, NC*H*$_2$) 3.97 (br s, 2H, OC*H*), 3.71 (br s, 2H,ClC*H*), 3.35 (br s, 2H, CHO), 2.07- 1.08 (m, 24 H, -C*H*$_2$-), 1.60 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (125.77 MHz, , benzene-d_6): δ, 208.0 (N*C*N), 151.0 (C_q, Ar), 138.9 (C_q, Ar), 138.4 (C_q, Ar), 131.2 (C_q, Ar), 119.4 (*C*H-Ar), 112.1 (*C*H-Ar), 80.5 (O-*C*H-), 67.2 (Cl-*C*H), 57.1 (*C*H of CHO), 47.6 (N*C*H$_2$), 36.2 (C_q, *t*Bu), 34.8 (-*C*H$_2$-, CHO), 34.6 (C_q, *t*Bu), 33.4 (-*C*H$_2$-, CHO), 32.1 (*C*H, *t*Bu), 30.5 (*C*H, *t*Bu), 24.2, 23.6, 22.9, 19.1 (-*C*H$_2$-, OC$_6$H$_{10}$Cl).

Typical procedure for epoxide-CO_2 copolymerization (run 1, table 1). In a glovebox, to a reaction tube for low-pressure reactions equipped with a magnetic stirring bar, a solution of the [PPN]Cl cocatalyst (8 µmol) in dichloromethane (1 mL) was added under vigorous stirring to a solution of Hf complex (8 µmol) in dichloromethane (1 mL). After 30 min, the solvent was removed and dried for 2 h under vacuum. The resulting solid was then dissolved in a pre-cooled solution of CHO (1250 equiv, 10 mmol) at -30 °C. Without cocatalyst, the epoxide was directly added to the Hf complex. The reactor was then pressurized at one bar of CO_2 and the reaction mixture was stirred at 60 °C. After 24 h, the reaction was cooled down to room temperature and the pressure was released. An aliquot of the solution was taken for characterization of crude material by ^{1}H NMR spectroscopy in chloroform-*d*. Then the reaction mixture was quenched with 1 mL of 5% methanolic HCl, precipitated with methanol and dried overnight at 80 °C. The yield was determined gravimetrically after washing the polymer with methanol and dried until constant weight.

X-ray crystallography and crystal structure determination. Suitable crystals for diffraction experiments were selected in a glovebox and mounted in a minimum of Parabar 10312 oil (Hampton Research) in a nylon loop and then mounted under a nitrogen cold stream from an Oxford Cryosystems 700 series open-flow cryostat. Data collection was done on a Bruker AXS TXS rotating anode system with an APEXII Pt^{135} CCD detector using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Data collection and data processing were done using APEX2[6], SAINT[7], and SADABS[8] version 2012/1,whereas structure solution and final model refinement were done using SHELXT[9] version 2014/4 and SHELXL[10] version 2014/7. CCDC reference codes 1908218, 1908219 and 1908220 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

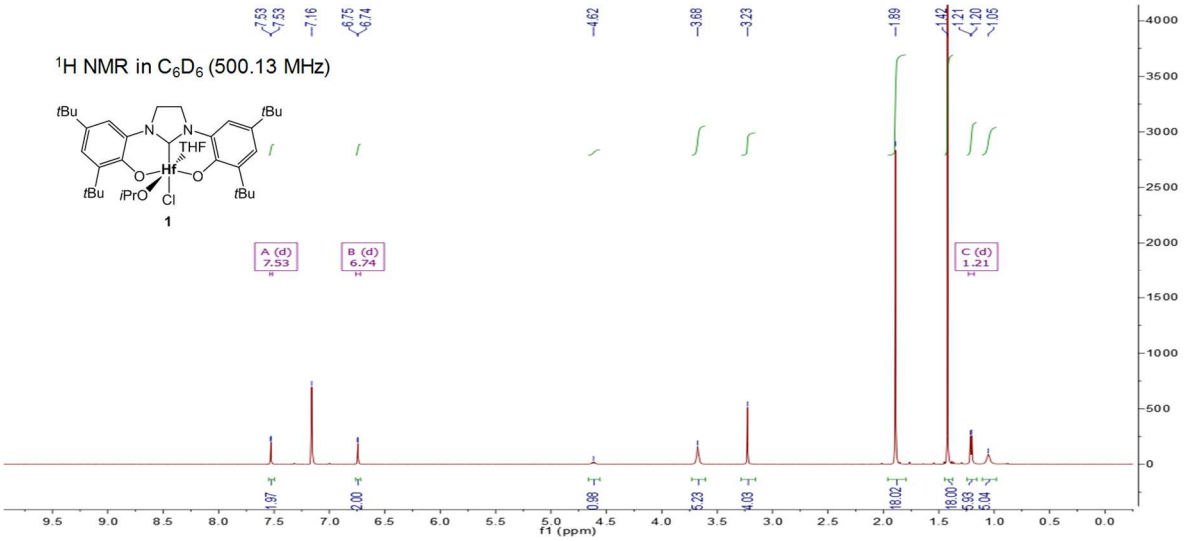


Figure S1. ^{1}H NMR spectrum of complex **1**.

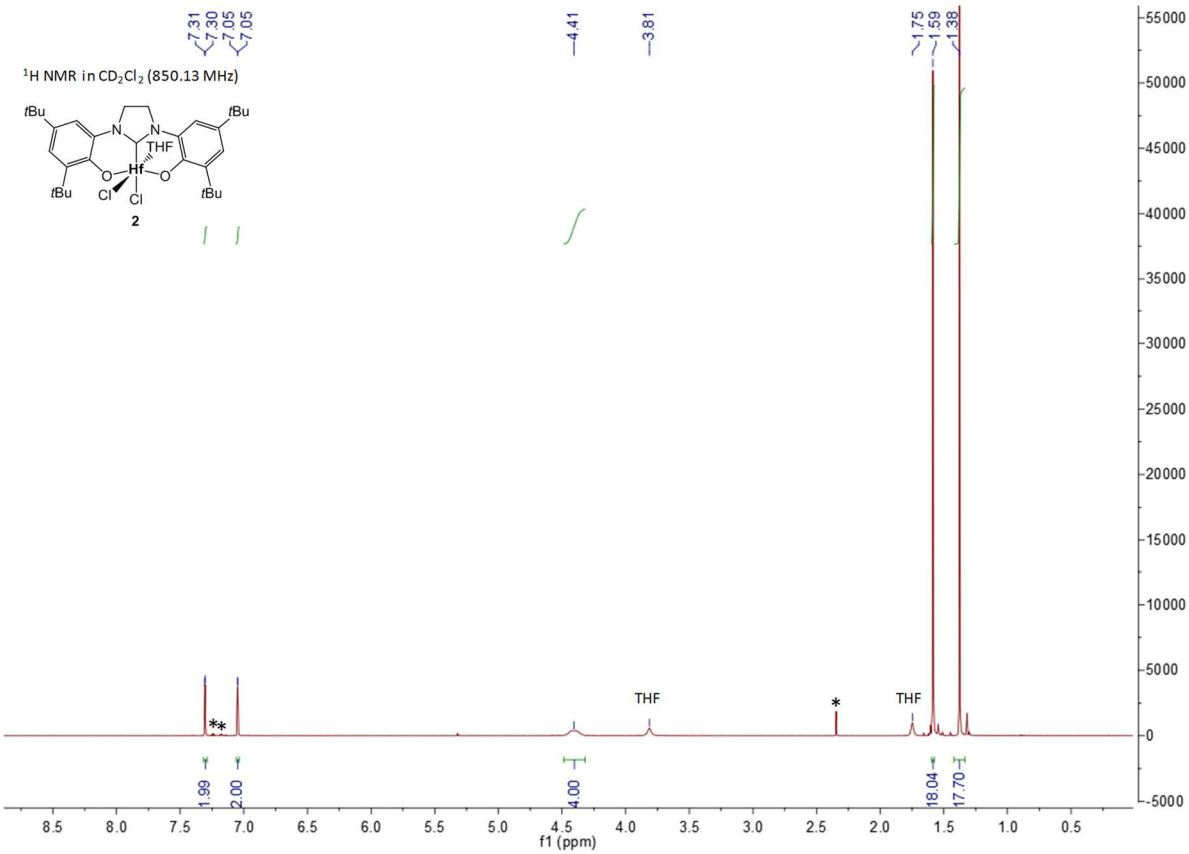


Figure S2. ^{1}H NMR spectrum of complex **2** (residual solvent: * = toluene).

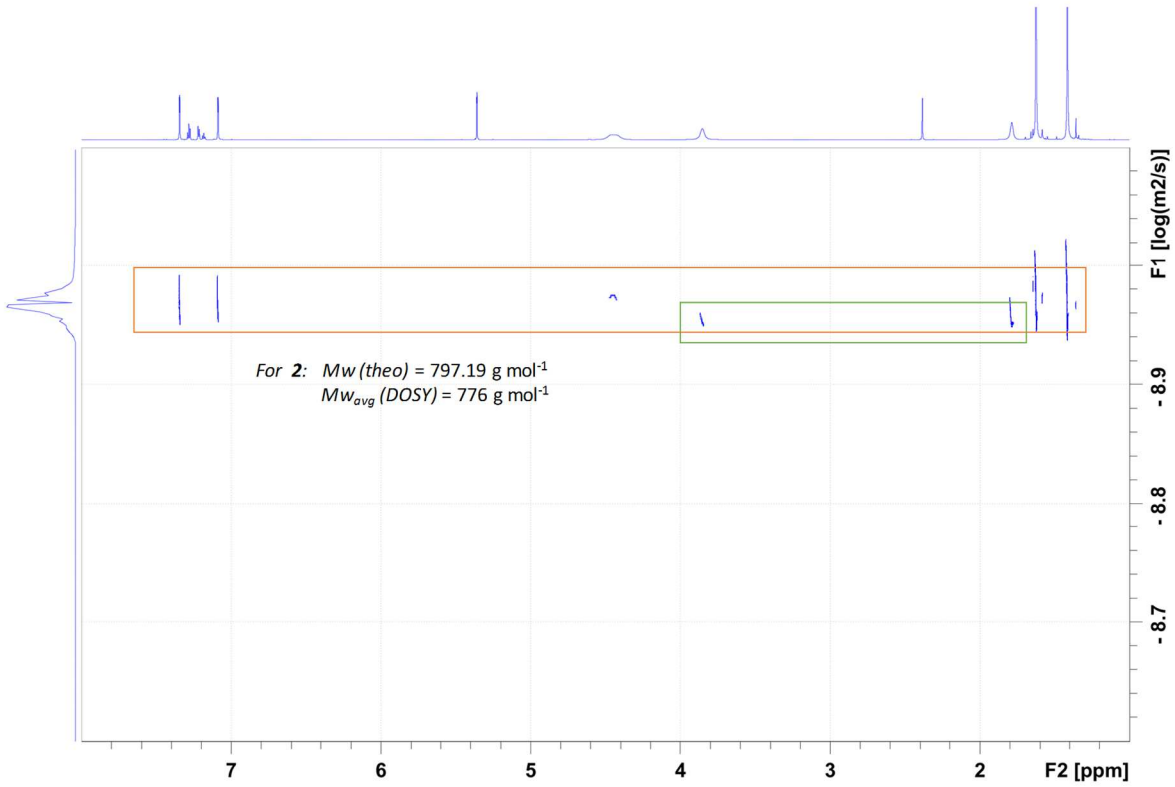


Figure S3. DOSY NMR spectra of **2** in CD_2Cl_2 at 298 K. The DOSY NMR spectrum of **2** displayed one set of resonances with diffusion coefficients log D_{avg}≈-8.973±0.001 (orange box) and another one with diffusion coefficients log D_{avg}≈-8.959±0.005 (green box). The signals in the orange box belongs to **2**, and the estimated molecular weight from the calibration curve indicate the presence of species with an average molecular weight close to 776 g mol^{-1}, which fits very well with monomeric **2**. The two signals in the green box originate from the THF moiety of **2**, and the diffusion coefficient corresponds to a species with molecular weight of 736 g mol^{-1}. The reason for the slightly lower diffusion coefficient of the THF moiety can be that a fraction of the time is dissociated from the complex. The two signals are also broadened, corroborating a fluxional dissociation/association of THF from monomeric complex **2** on the ms time scale.

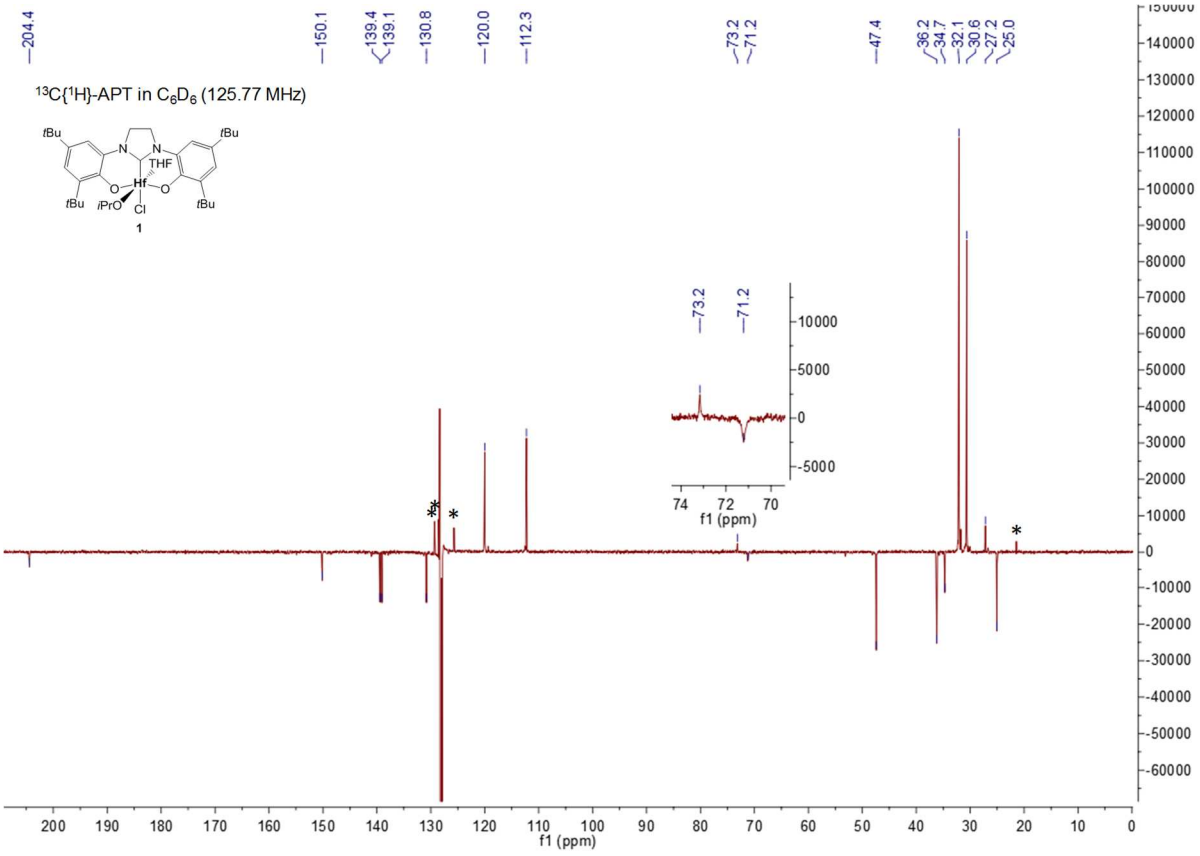


Figure S4. $^{13}C\{^{1}H\}$-ATP NMR spectrum of complex **1** (residual solvent: * = toluene).

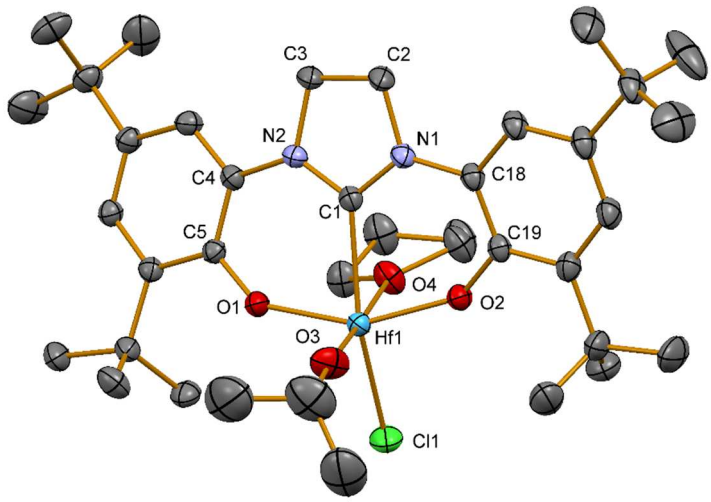


Figure S5. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Hf1-C1 = 2.333(3), Hf1-Cl1 = 2.4614(9), Hf1-O1 = 1.986(2), Hf1-O2 = 1.975(2), Hf1-O3 = 2.014(3), Ti1-O4 = 2.309(2), N1-C1 = 1.343(4), N2-C1 = 1.348(4). Selected angles (°): O1-Hf1-O2 = 154.71 (8), C1-Hf1-Cl1 = 157.57(7), O3-Hf1-O4. = 178.33(10), C1-Hf1-O4 = 76.82(9), Cl1-Hf1-O4 = 80.89(7), C1-Hf1-O3 = 102.15(10), O1-Hf1-O3 = 93.95(10), O1-Hf1-O4 = 84.56(9), O2-Hf1-O4 = 84.40(8).

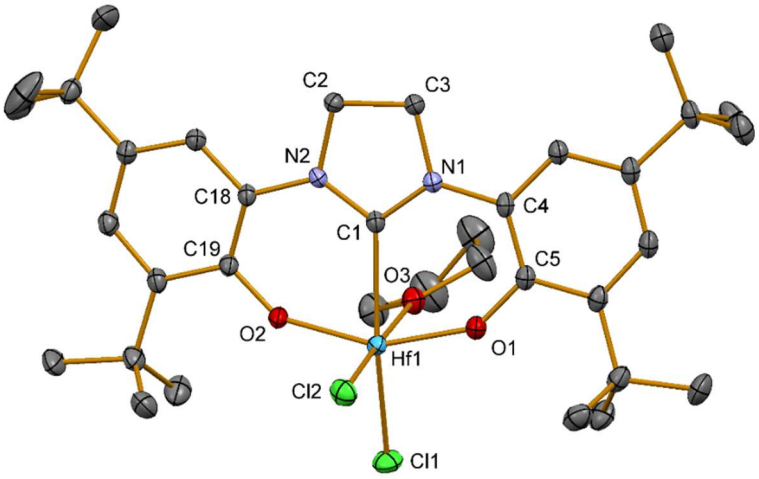


Figure S6. Crystal structure of **2**. Hydrogen atoms and solvent Et_2O molecule are omitted for clarity. Hf1-C1 = 2.334(3), Hf1-Cl1 = 2.4466(7), Hf1-Cl2 = 2.4046(7), Hf1-O1 = 1.965(2), Hf1-O2 = 1.9595(19), Hf1-O3 = 2.260(2), N1-C1 = 1.356(3), N2-C1 = 1.351(3). Selected angles (°): O1-Hf1-O2 = 155.12(8), C1-Hf1-Cl1 = 163.32(7), O3-Hf1-Cl2 = 177.54(6), C1-Hf1-Cl2 = 99.97(7), O1-Hf1-Cl2 = 91.35(6).

Table S2. Crystal Structure and Refinement Data for **1**, **2** and **3**.

Compound	**1**	**2.Et_2O**	**3.2THF**
Chemical formula	$C_{38}H_{59}ClHfN_2O_4$	$C_{39}H_{62}Cl_2HfN_2O_3$	$C_{75}H_{90}Cl_3HfN_3O_4P_2$
Formula weight	821.81	872.29	1444.27
Temperature/K	153(2)	103(2)	103(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	P-1 (No.2)
a/ Å	15.7324(16)	16.5953(6)	15.0310(12)
b/ Å	13.8338(14)	14.0285(5)	15.1732(12)
c/ Å	19.0436(19)	17.4961(7)	20.3432(17)
α/ °	90	90	109.7190(10)
β/ °	110.6910(10)	96.2400(10)	93.3830(10)
γ/ °	90	90	116.0500(10)
V/ Å^3	3877.3(7)	4049.1(3)	3804.3(5)
Z	4	4	2
ρ_{calcd}/ g cm^{-3}	1.408	1.431	1.261
Absorption coeff./ mm^{-1}	2.798	2.748	1.565
F(000)	1688	1792	1492
Crystal size/ mm^3	0.35 x 0.20 x 0.13	0.202 x 0.108 x 0.054	0.163 x 0.089 x 0.087
colour/habit	Colorless/'long prism'	Colorless/thin plate	Colorless/prism
Θ Range for data collection/ °	1.864 to 31.037	1.906 to 30.049	1.614 to 27.877
Reflections collected	48754	67447	55516
Independent reflections	12382 [R_{int} =0.0688]	11853 [R_{int} =0.0634]	18138 [R_{int} = 0.0637]
Completeness to Θ/ %	100	100	100.0
Data/restraints/parameters	12382/499/466	11853/426/447	18138/744/806
Goodness-of-fit on F^2	1.079	1.071	1.048
Final R_1 indices [$I>2\sigma(I)$]	0.0378	0.0352	0.0531
wR_2 (all data)	0.1006	0.0950	0.1461
Largest diff. peak; hole/e Å^{-3}	3.080; -0.798	3.521; -0.866	4.278; -1. 962

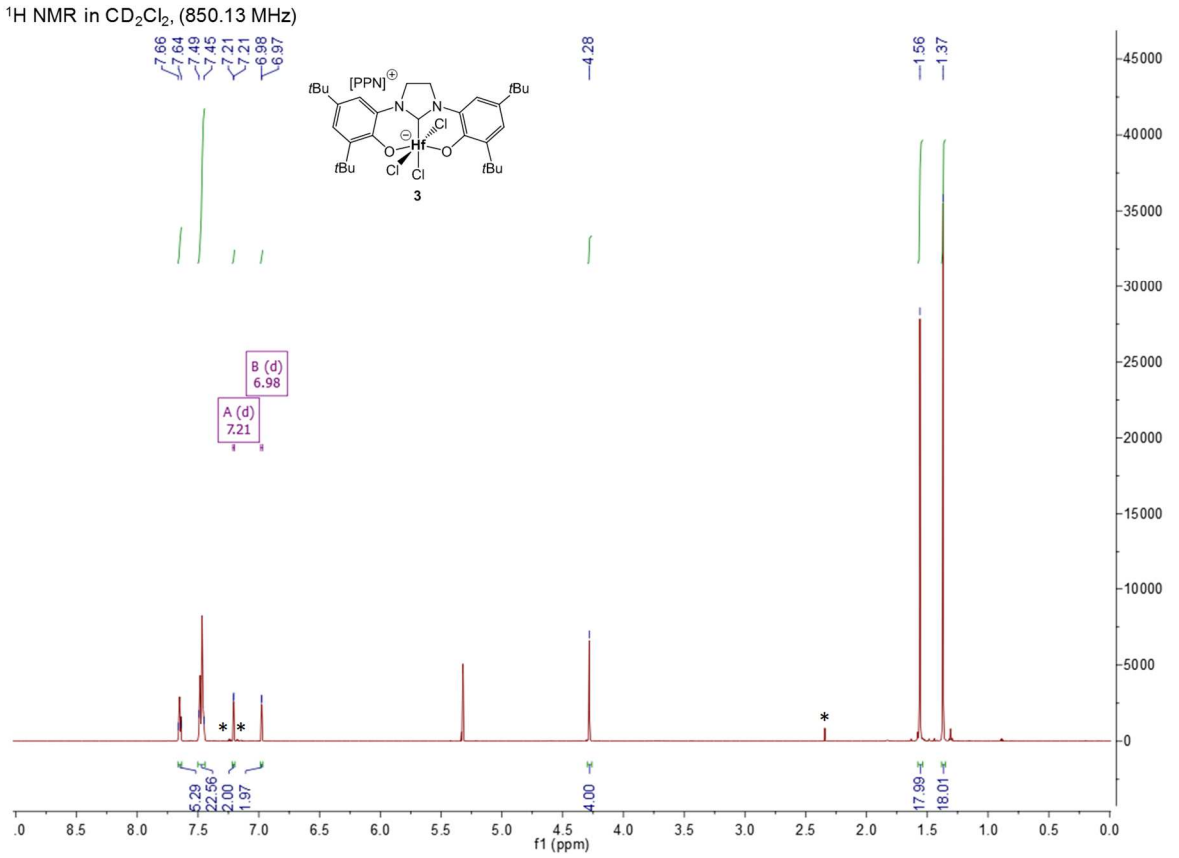


Figure S7. ^{1}H NMR spectrum of complex **3** (residual solvent: * = toluene)

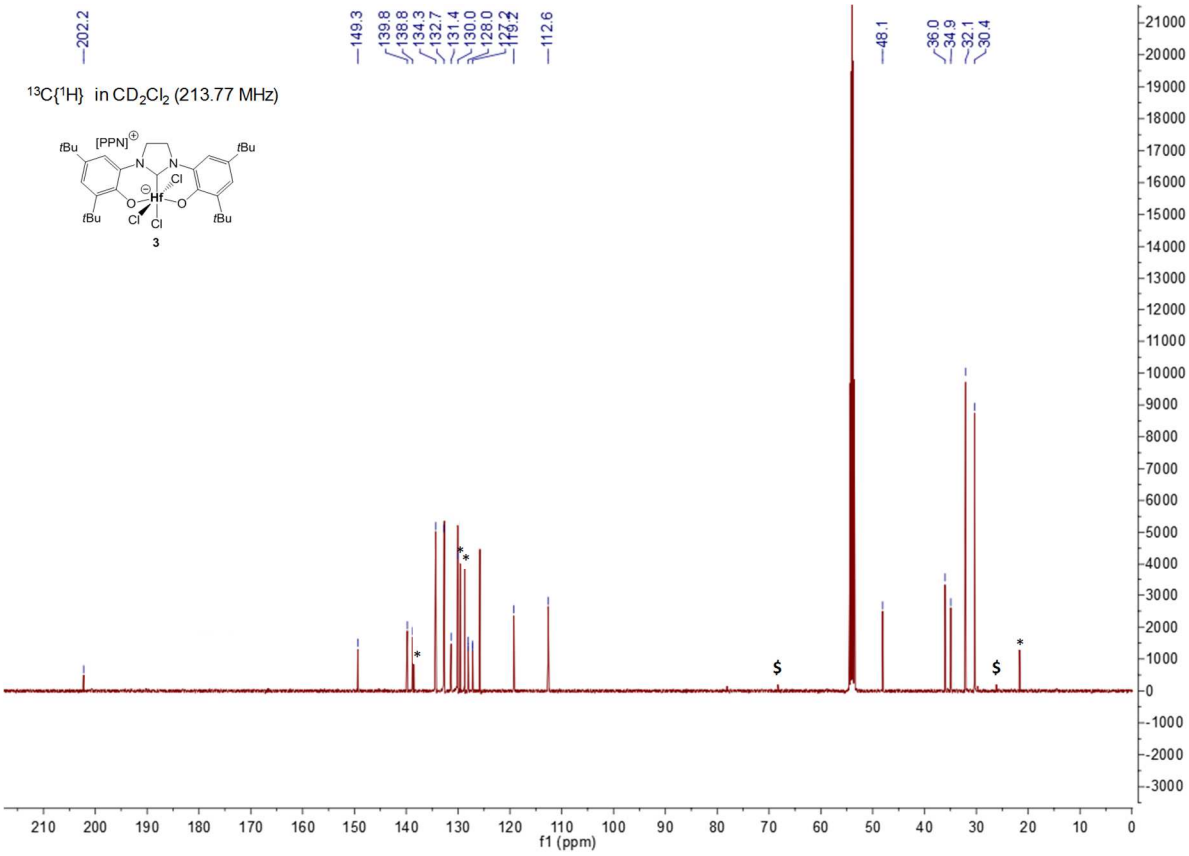


Figure S8. ^{13}C{^{1}H} NMR spectrum of complex **3** (residual solvents: * = toluene and $ = THF)

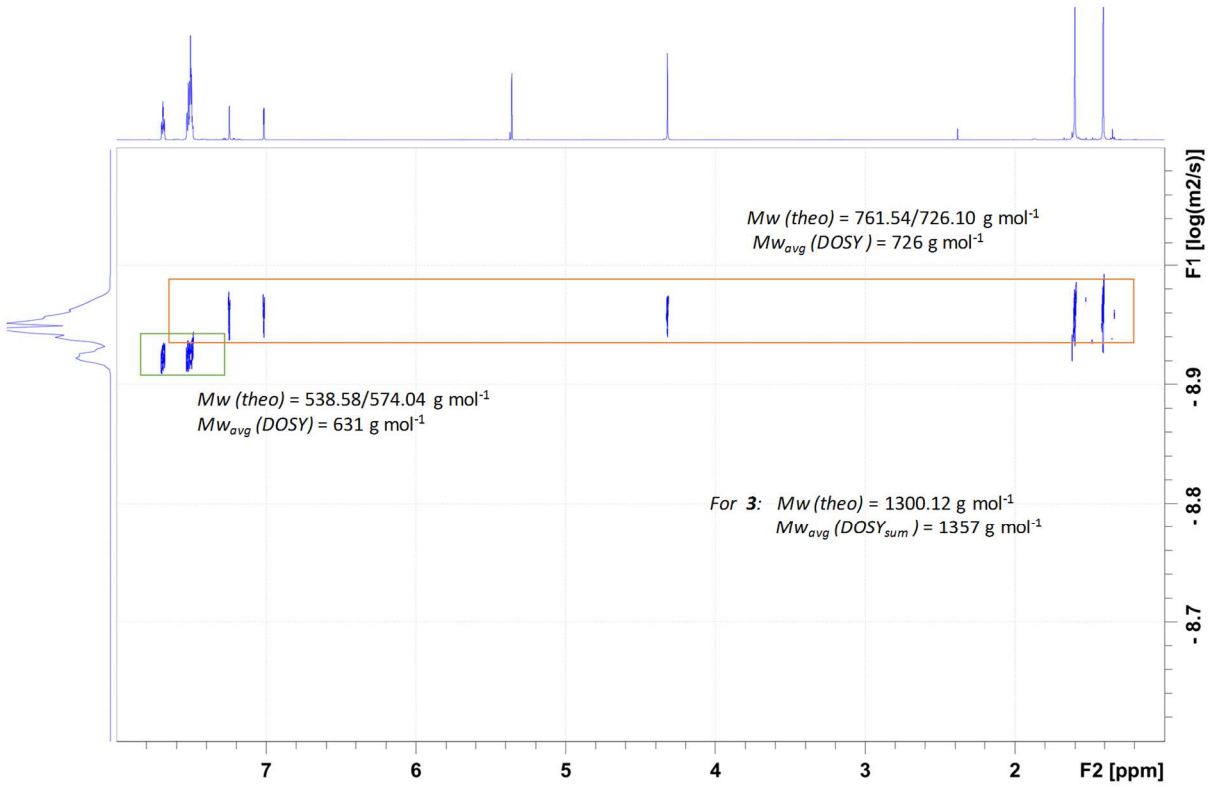


Figure S9. DOSY NMR spectra of **3** in CD_2Cl_2 at 298 K. The DOSY NMR spectrum of **3** displayed two sets of resonances with different diffusion coefficients (log *D* = -8.924±0.003 and -8.957±0.002). The estimated molecular weights determined from the calibration curve indicate molecular weights of 631 and 726 g mol^{-1}, respectively .These values are consistent with the presence of two species in solution, *i.e.* a cationic $[PPN]^+$ (538.58 g mol^{-1}) and an anionic $[(\{\kappa^3\text{-}O,C,O\}\text{-NHC})Hf(Cl)_3]^-$ (761.54 g mol^{-1}) species, although the dissociation of Cl atom from Hf forming [PPN]Cl salt (574.04 g mol^{-1}) and a neutral $\{\kappa^3\text{-}O,C,O\}$-NHC)$Hf(Cl)_2$ species (726.10 g mol^{-1}) cannot be excluded from this DOSY NMR experiment. The data show no indication of ion association or dimerization.

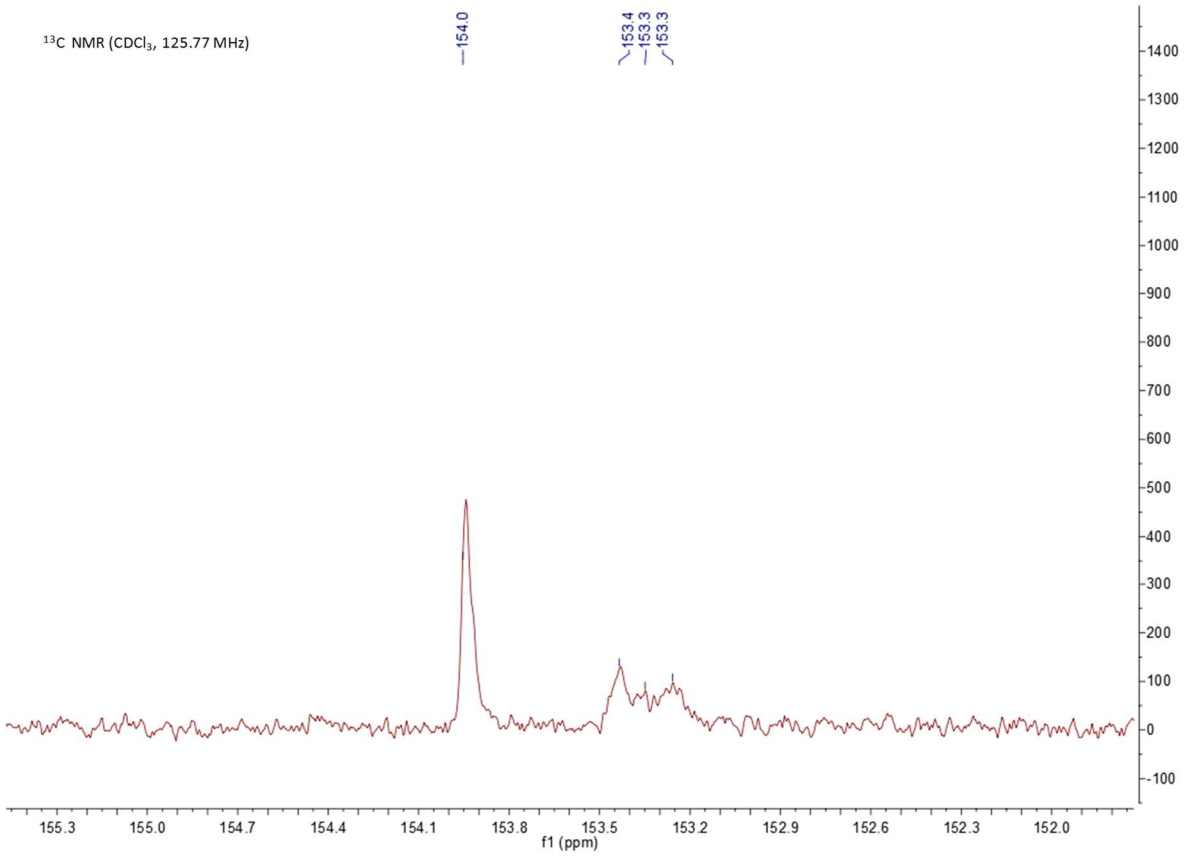


Figure S10. ^{13}C NMR spectrum of PCHC (Table 1, run 1)**.** The chemical resonances at δ 154.0 and 153.3 ppm are corresponding to the syndiotactic and isotactic diads, respectively, and characteristic of atactic PCHC.[11]

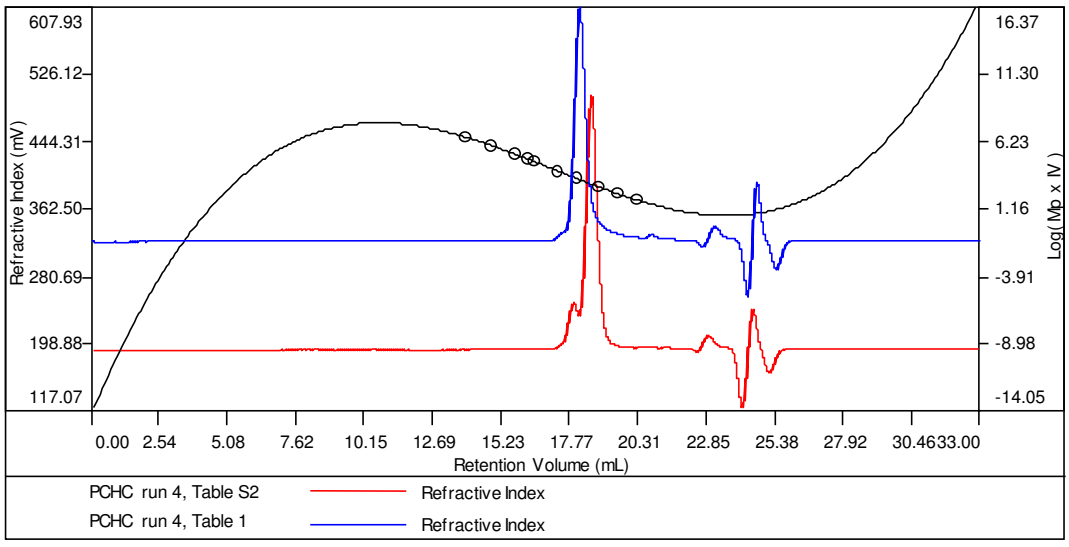


Figure S11. GPC-SEC profile of PCHC.

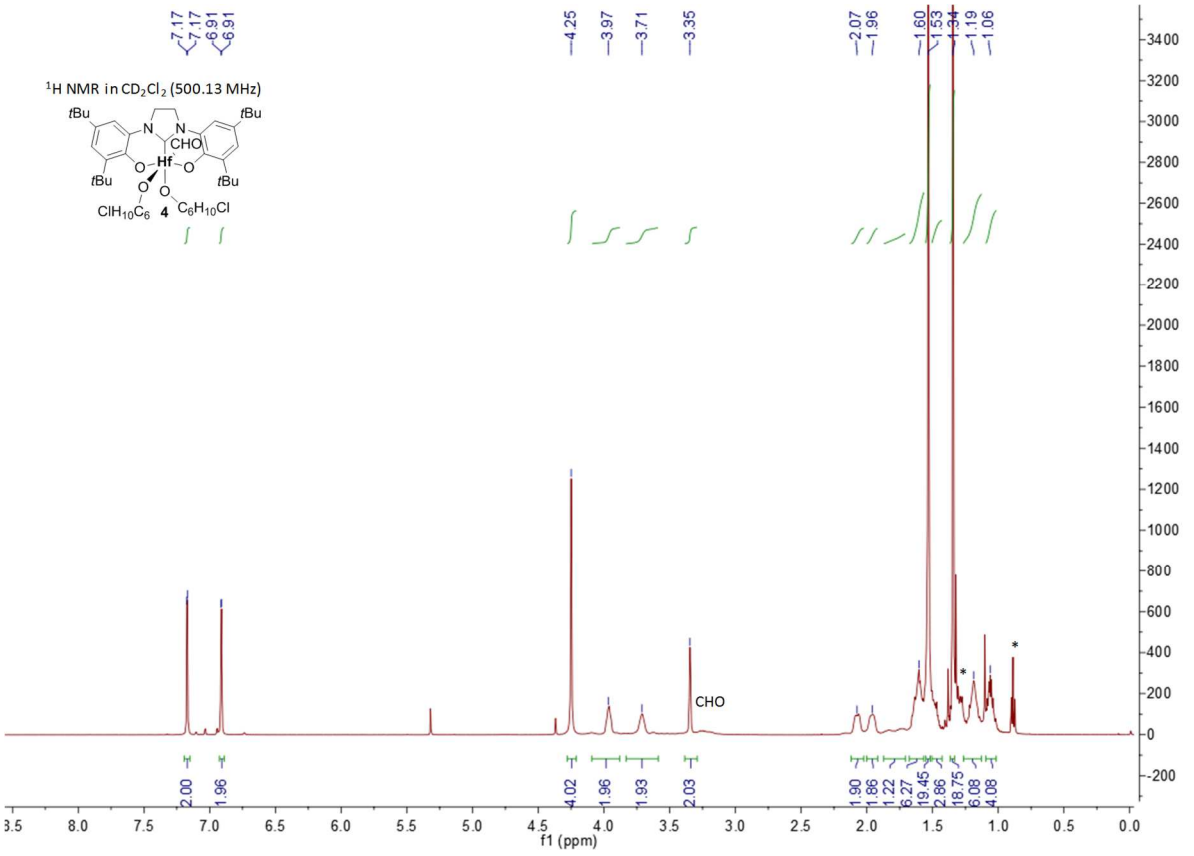


Figure S12. ^{1}H NMR spectrum of complex **4** (residual solvent:* = hexane).

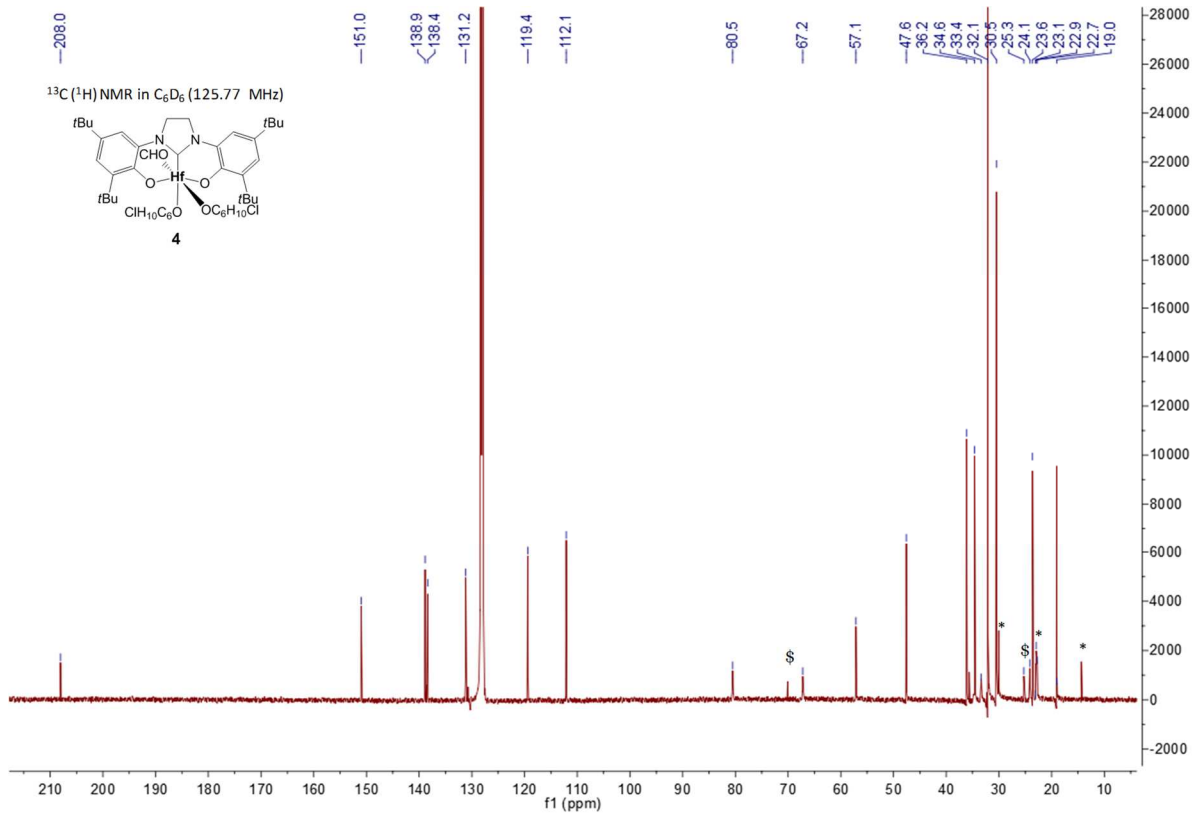


Figure S13. ^{13}C{^{1}H} NMR spectrum of complex **4** (residual solvents: * = hexane and $ = THF)

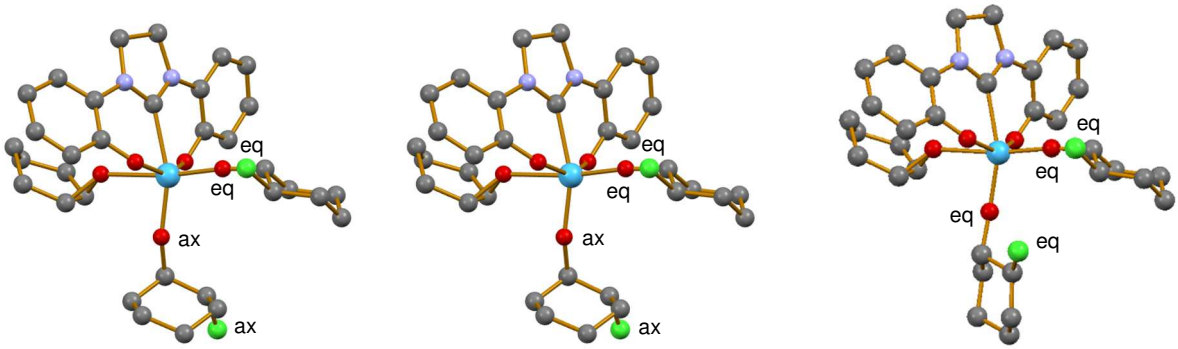


Figure S14. Connectivity for complex **4** deduced from X-ray crystallography. Hydrogen atoms and *t*Bu groups are omitted for clarity (blue, Hf; red, O; purple, N; green, Cl; grey, C). In the crystal structure three geometric isomers of the $OC_6H_{10}Cl$ group located *trans* to the $NHC_{carbene}$ are co-crystallized. The disorder involves the position of the Cl atom in the cyclohexyl ring in a ratio 0.34:0.34:0.32 (left: (NHC)Hf(*S*,*S*-α-$OC_6H_{10}Cl$)(*R*,*R*-β-$OC_6H_{10}Cl$)(CHO)); middle: (NHC)Hf(*R*,*R*-α-$OC_6H_{10}Cl$)(*R*,*R*-β-$OC_6H_{10}Cl$)(CHO); right: (NHC)Hf(*S*,*S*-β-$OC_6H_{10}Cl$)(*R*,*R*-β-$OC_6H_{10}Cl$)(CHO) as well as the orientation of the ring itself. Note: whilst the cyclohexyl ring *cis* to the $NHC_{carbene}$ with both substituents (O and Cl atoms) in an equatorial position the substituents on two (left and middle above) of the cyclohexyl ring *trans* to the $NHC_{carbene}$ ligand assume the axial positions rather than the commonly favored equatorial positions, again assumed by the third *trans* isomer. The relative orientation of the three isomers clearly seem strongly governed by intramolecular steric interactions.

Table S3. Copolymerization of CHO with CO_2 catalyzed by hafnium complexes.[a]

Run	Complex/co-catalyst (equiv.)[b]	Ratio (CHO:Hf)	Time (h)	Conv.[c] (%)	Carbonate linkage/ Selectivity in PC[c] (%)	Homopolymer[c] (%)	TOF[d] (h^{-1})	M_n[e] (kg mol^{-1})	$Đ$[e]
1	**2**/-	1250	24	63	0/-	99	32	15.0	1.8
2	**4**/[PPN]Cl (1)	1250	18	50	≥99/99	-	35	10.2	1.7
3	**1**/[PPN]Cl (1)	1250	4	18	≥99/99	-	56	9.6	1.2
4	**2**/[PPN]Cl (1)	1250	4	24	≥99/99	-	75	9.4	1.2

[a] Polymerization conditions: 0.08 $mol\%_{Hf}$, P_{CO2} = 1 bar at 60 °C. [b] Catalyst pre-formation: addition of [PPN]Cl: 30 min in CH_2Cl_2 at 30 °C and dried 2 h under vacuum. [c] Measured by ^{1}H NMR spectroscopy in chloroform-*d* on the crude product, PC = polycarbonate, CC = cyclic carbonate. [d] Turnover frequency (in $mol_{prod.}$ mol_{Hf}^{-1} h^{-1}). [e] Determined by GPC-SEC in THF at 30 °C against polystyrene standards.

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