

Behind the Scenes of Group IV Metallocene Catalysis: Examination of the Metal–Carbon Bond

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Metallocene – zirconium – hafnium – group IV chemistry – bond strength – bond compressibility – electron density – lanthanide contraction – ionic character – covalent character – enthalpy – entropy – polyolefin catalysis – propene polymerization – polypropylene – high melting transition – stereoselectivity

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1. Synthesis – Procedures

rac-Dimethylsilanediylbis[4-(3',5'-dimethylphenyl)-7-methoxy-2-methylindenyl]zirconium dichloride (**2-Zr**)

0.86 g (1.47 mmol, 1.00 eq.) of bis[4-(3',5'-dimethylphenyl)-7-methoxy-2-methylindenyl]dimethyl silane were dissolved in 40 mL dry toluene, cooled down to $-78\text{ }^{\circ}\text{C}$ and 1.73 mL (2.94 mmol, 2.00 eq.) 1.7 M tBuLi solution in pentane were added dropwise. After maintaining the temperature for one hour the reaction mixture was stirred for additional 3 h at room temperature. The yellow suspension was cooled down to $0\text{ }^{\circ}\text{C}$ and subsequently transferred *via cannulae* to a suspension of 343 mg (1.47 mmol, 1.00 eq.) ZrCl_4 in 20 mL dry toluene at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to unfreeze overnight resulting in an orange to red suspension. The suspension was filtered, the solvent of the filtrate was distilled off and the residue was washed with dry pentane ($2 \times 65\text{ mL}$) and a 1:2 toluene/pentane-mixture (150 mL). After recrystallization in a toluene/ pentane mixture 160 mg (15 %) of orange crystalline powder were obtained containing the pure *rac*-isomer. Anal. Calcd for $\text{C}_{40}\text{H}_{42}\text{Cl}_2\text{O}_2\text{SiZr}$: C, 64.49; H, 5.68. Found: C, 64.62; H, 5.78. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ (ppm) = 7.30 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 7.26 (s, 4H, H-Ar'), 6.96 (m, 4H, H-Ar', $-\text{CH}=\text{}$), 6.42 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 3.90 (s, 6H, $-\text{OCH}_3$), 2.32 (s, 12H, Ar'- CH_3), 2.16 (s, 6H, $-\text{CH}_3$), 1.21 (s, 6H, Si- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2) δ 156.0, 140.0, 138.6, 135.5, 133.6, 131.3, 129.3, 127.9, 126.8, 123.9, 121.8, 103.7, 84.4, 21.6, 17.9, 6.2.

rac-Dimethylsilanediylbis[4-(3',5'-dimethylphenyl)-7-methoxy-2-methylindenyl]dimethyl zirconium (**3-Zr**)

41.1 mg (55.2 μmol , 1.00 eq.) of **2-Zr** were dissolved in 5.0 mL dry benzene and 46.0 μL (138 μmol , 2.50 eq.) 3.0 M MeMgBr solution in diethyl ether were added. After stirring the yellow reaction mixture for 6 h at $40\text{ }^{\circ}\text{C}$ the filtrate was isolated and the solvent was removed *in vacuo*. After recrystallization in a dry toluene/*n*-pentane mixture 25.3 mg (65%) of yellow crystalline solid **3-Zr** were isolated. Crystals suitable for high resolution X-ray diffraction analysis were obtained by diffusion of *n*-pentane into a saturated benzene solution at $6\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{O}_2\text{SiZr}$: C, 71.64; H, 6.87. Found: C, 71.62; H, 6.79. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ (ppm) = 7.23 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 7.20 (s, 4H, H-Ar'), 6.97 (s, 2H, $-\text{CH}=\text{}$), 6.96 (s, 2H, H-Ar'), 6.36 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 3.83 (s, 6H, $-\text{OCH}_3$), 2.32 (s, 12H, Ar'- CH_3), 1.99 (s, 6H, $-\text{CH}_3$), 1.01 (s, 6H, Si- CH_3), -1.17 (s, 6H, Zr- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2) δ 156.2, 140.9, 138.5, 134.7, 130.9, 130.1, 129.0, 126.7, 125.6, 121.3, 116.7, 102.1, 79.2, 34.2, 21.7, 17.4, 6.2.

rac-Dimethylsilanediylbis[4-(3',5'-dimethylphenyl)-7-methoxy-2-methylindenyl]dimethyl hafnium (**3-Hf**)

90.0 mg (108 μmol , 1.00 eq.) of **2-Hf** were dissolved in 10 mL dry benzene and 180 μL (540 μmol , 5.00 eq.) 3.0 M MeMgBr solution in diethyl ether were added. After stirring the reaction mixture for 18 h at $50\text{ }^{\circ}\text{C}$ the slightly yellow solution was separated from the brownish residue and the solvent of the filtrate was removed *in vacuo*. After recrystallization in a dry toluene/*n*-pentane mixture 47.9 mg (56%) of yellow crystalline solid **3-Hf** were isolated. Crystals suitable for high resolution X-ray diffraction analysis were obtained by diffusion of *n*-pentane into a saturated benzene solution at $6\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{O}_2\text{SiHf}$: C, 63.74; H, 6.11. Found: C, 63.83; H, 6.10. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ (ppm) = 7.22 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 7.20 (s, 4H, H-Ar'), 6.96 (s, 2H, H-Ar'), 6.89 (s, 2H, $-\text{CH}=\text{}$), 6.36 (d, $^3J = 7.8\text{ Hz}$, 2H, H-Ar), 3.85 (s, 6H, $-\text{OCH}_3$), 2.32 (s, 12H, Ar'- CH_3), 2.05 (s, 6H, $-\text{CH}_3$), 1.03 (s, 6H, Si- CH_3), -1.35 (s, 6H, Zr- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2) δ 156.2, 141.0, 138.5, 133.2, 130.6, 130.0, 128.9, 126.7, 125.8, 120.9, 115.8, 101.9, 81.3, 40.0, 21.7, 17.3, 6.2.

2. Synthesis – ^1H NMR and ^{13}C NMR spectra

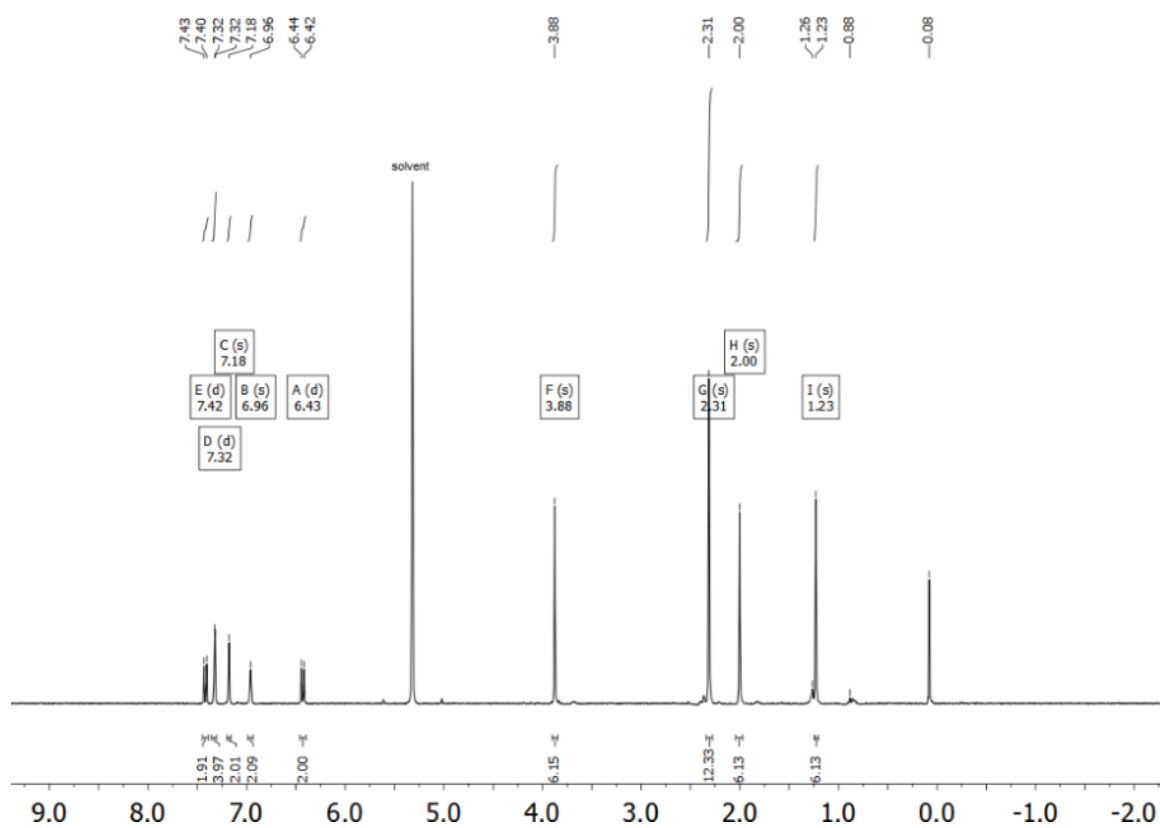


Figure S1. ^1H NMR spectrum (400 MHz) of **2-Ti** in CD_2Cl_2 . Traces of *n*-hexane and grease are visible.¹

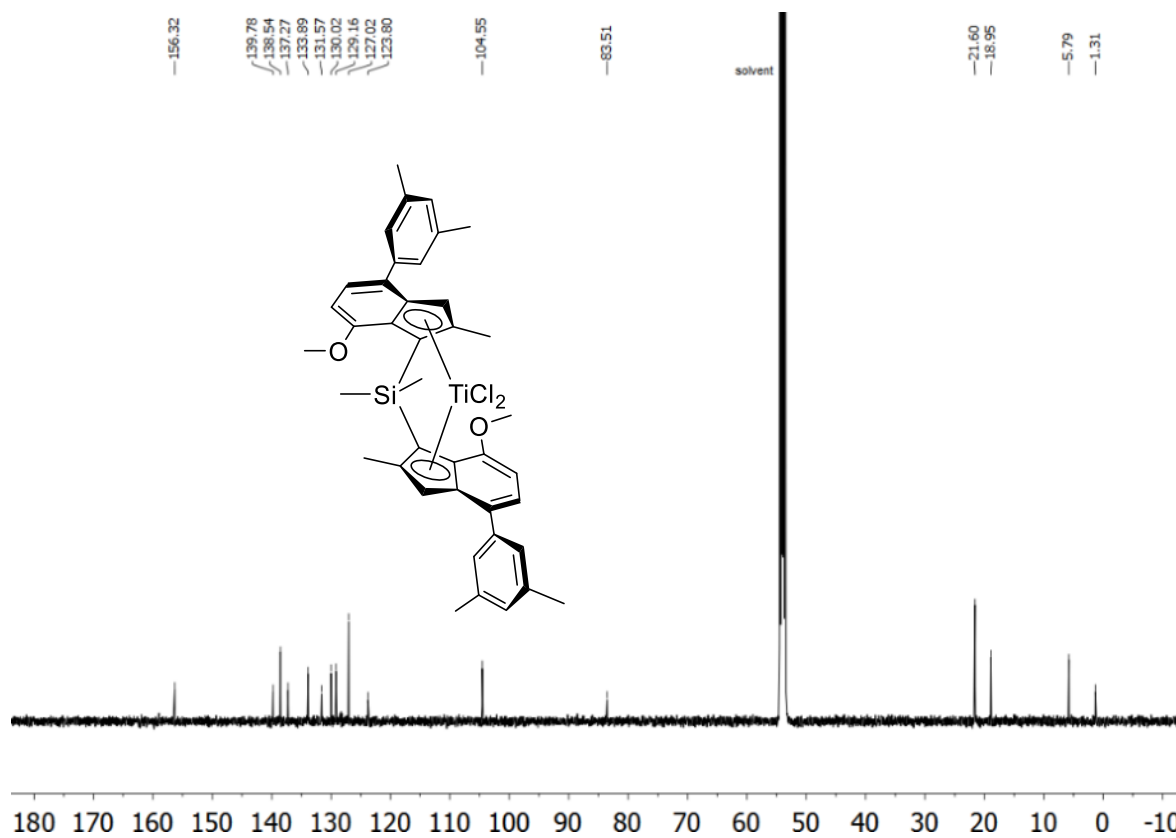


Figure S2. ^{13}C $\{^1\text{H}\}$ NMR spectrum (100 MHz) of **2-Ti** in CD_2Cl_2 . Traces of grease are visible.¹

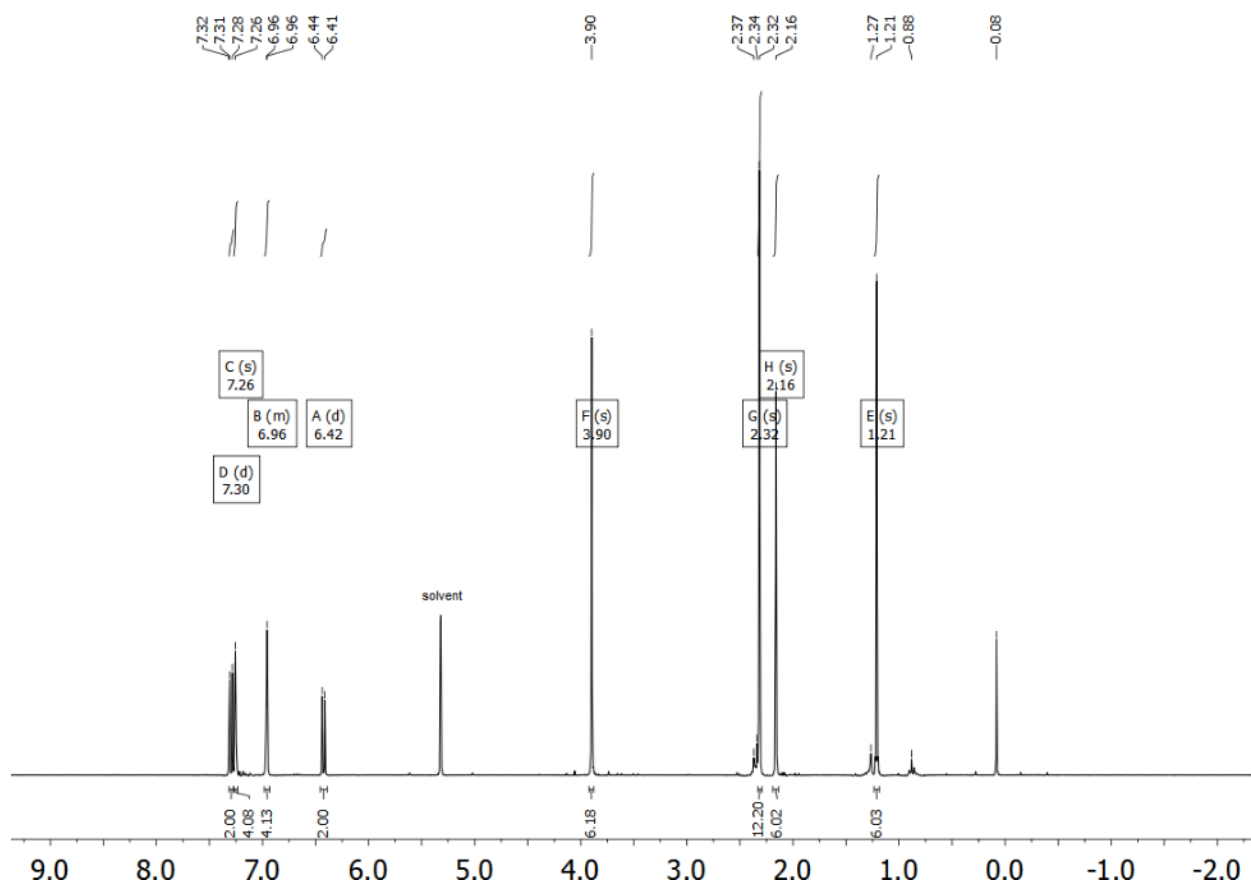


Figure S3. ¹H NMR spectrum (400 MHz) of **2-Zr** in CD₂Cl₂. Traces of *n*-pentane and grease are visible.

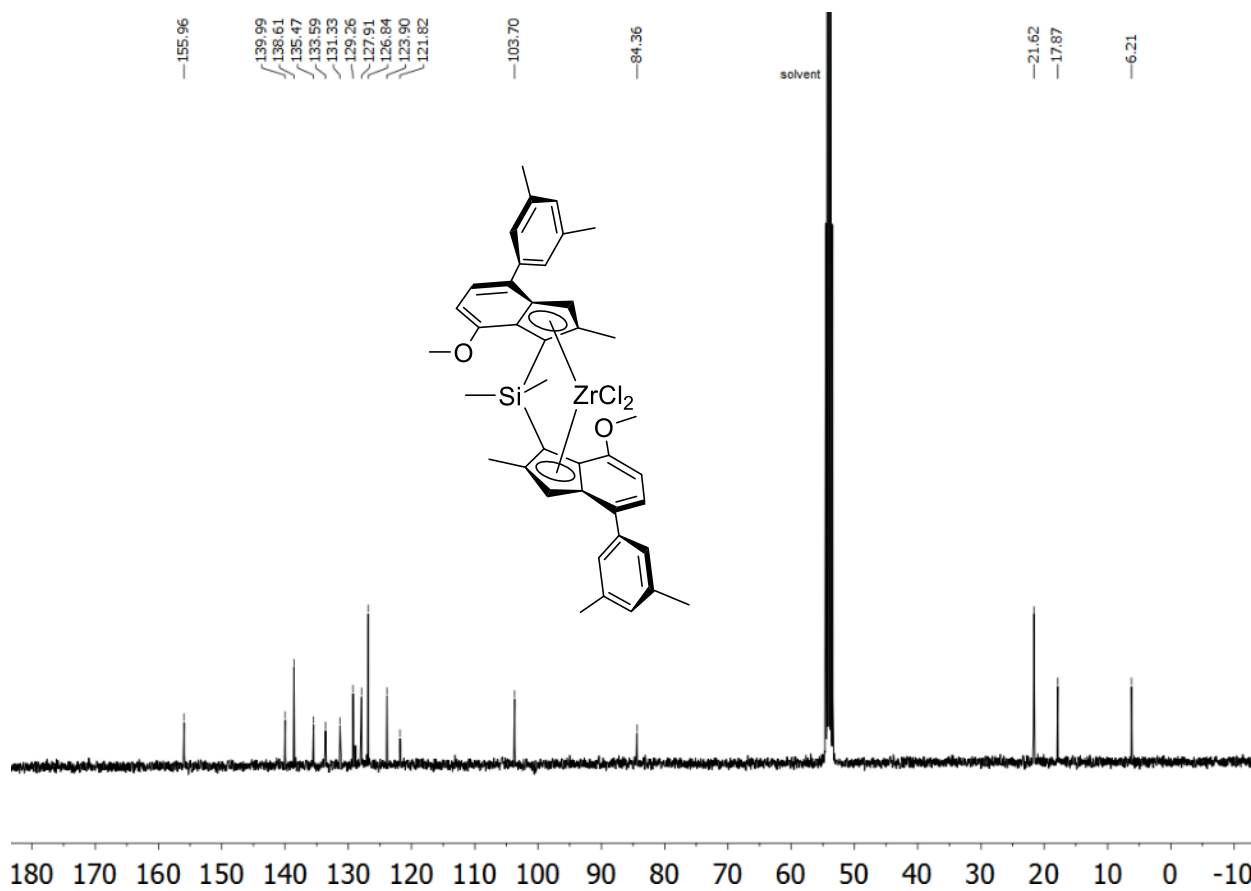


Figure S4. ¹³C {¹H} NMR spectrum (100 MHz) of **2-Zr** in CD₂Cl₂.

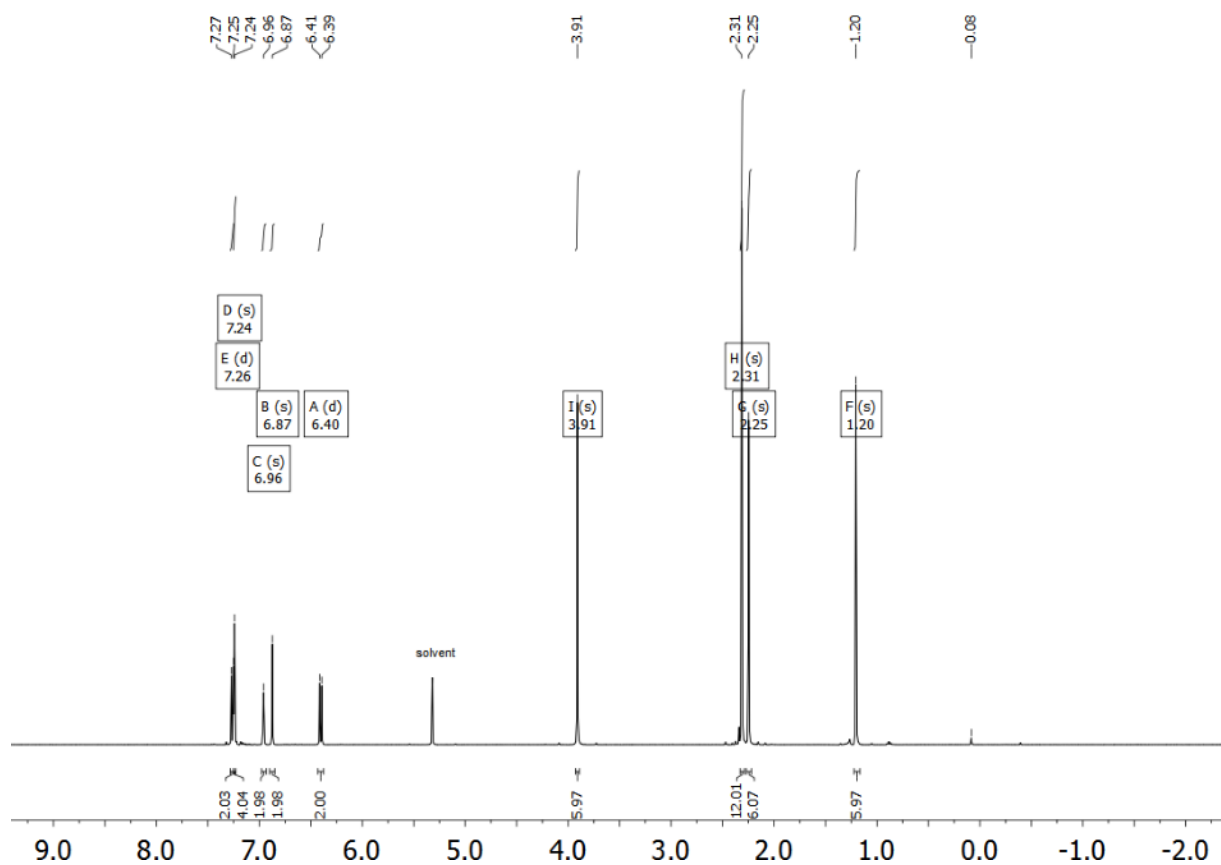


Figure S5. ^1H NMR spectrum (400 MHz) spectrum of **2-Hf** in CD_2Cl_2 . Traces of grease are visible.²

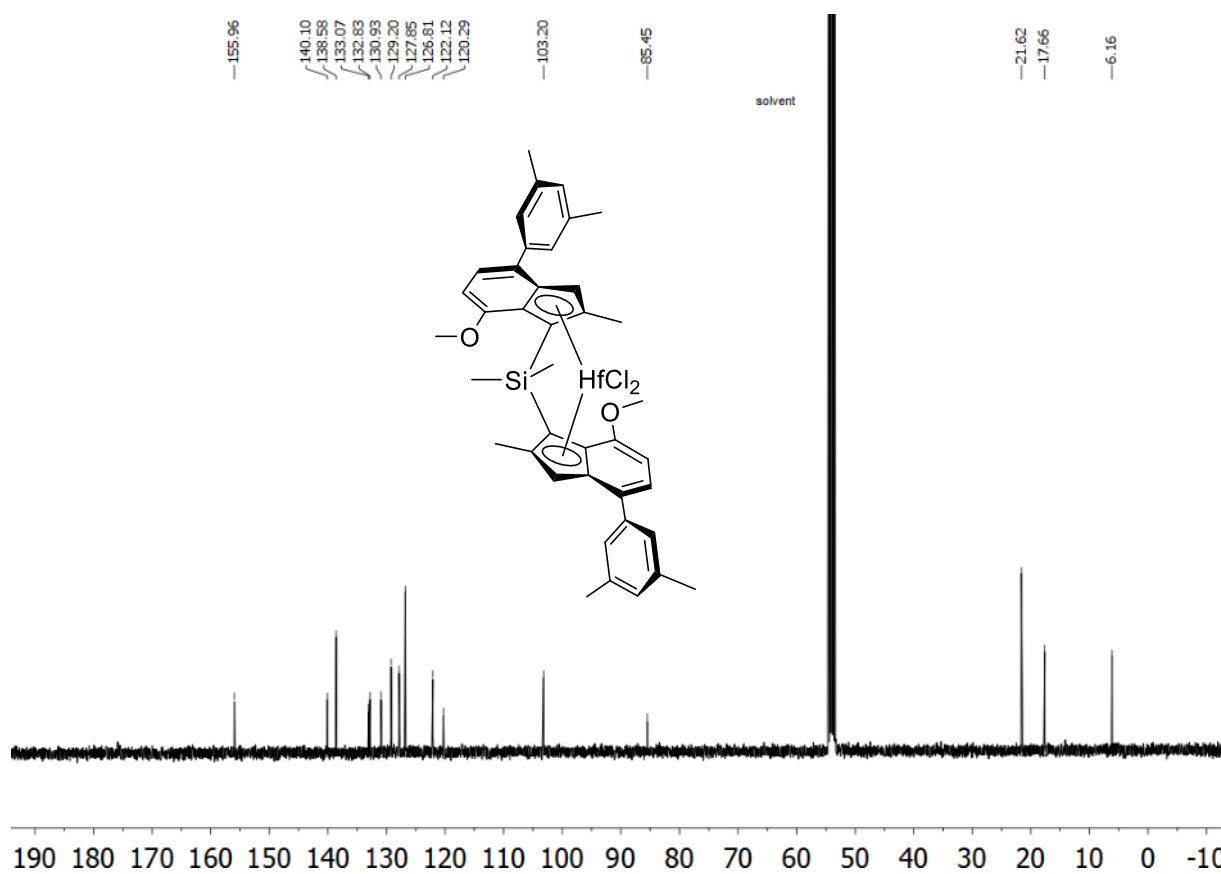


Figure S6. ^{13}C $\{^1\text{H}\}$ NMR spectrum (100 MHz) of **2-Hf** in CD_2Cl_2 .²

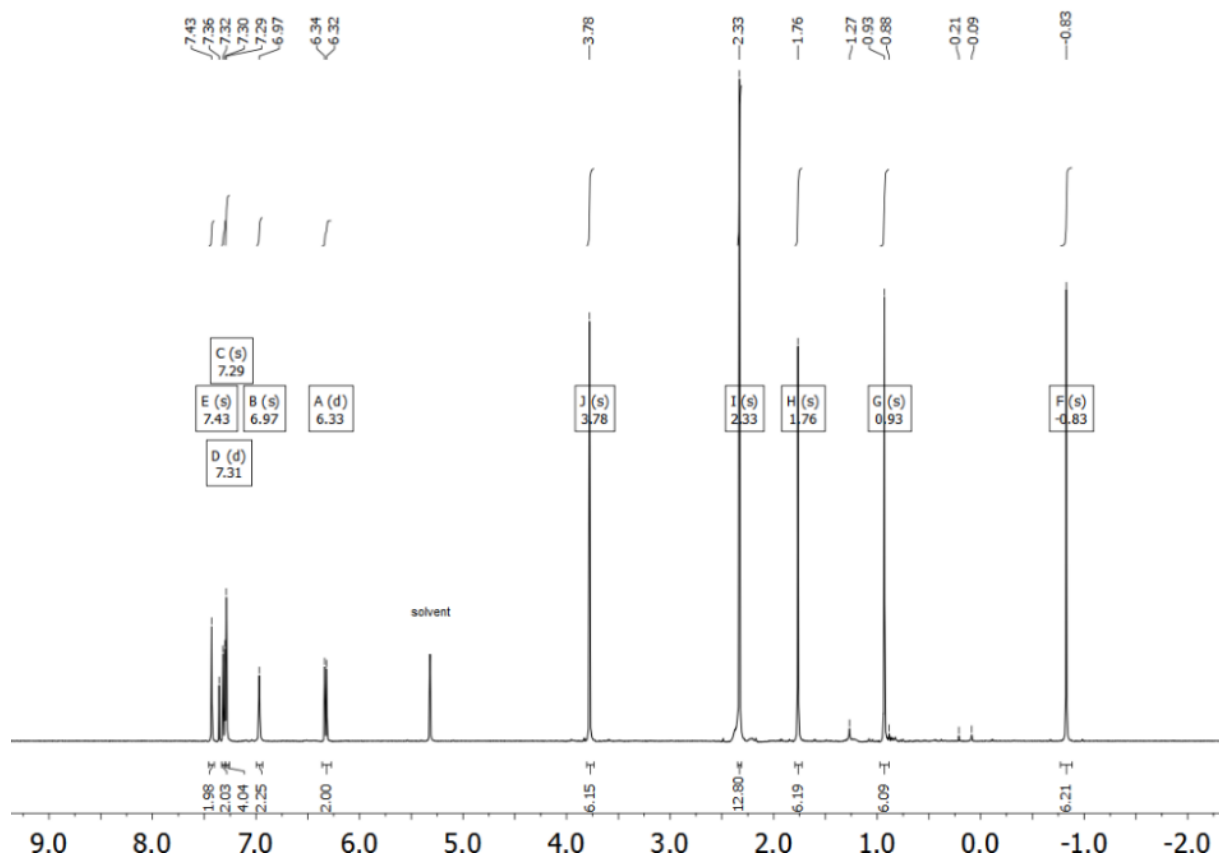


Figure S7. ^1H NMR spectrum (400 MHz) of **3-Ti** in CD_2Cl_2 . Traces of benzene, *n*-pentane and grease are visible.¹

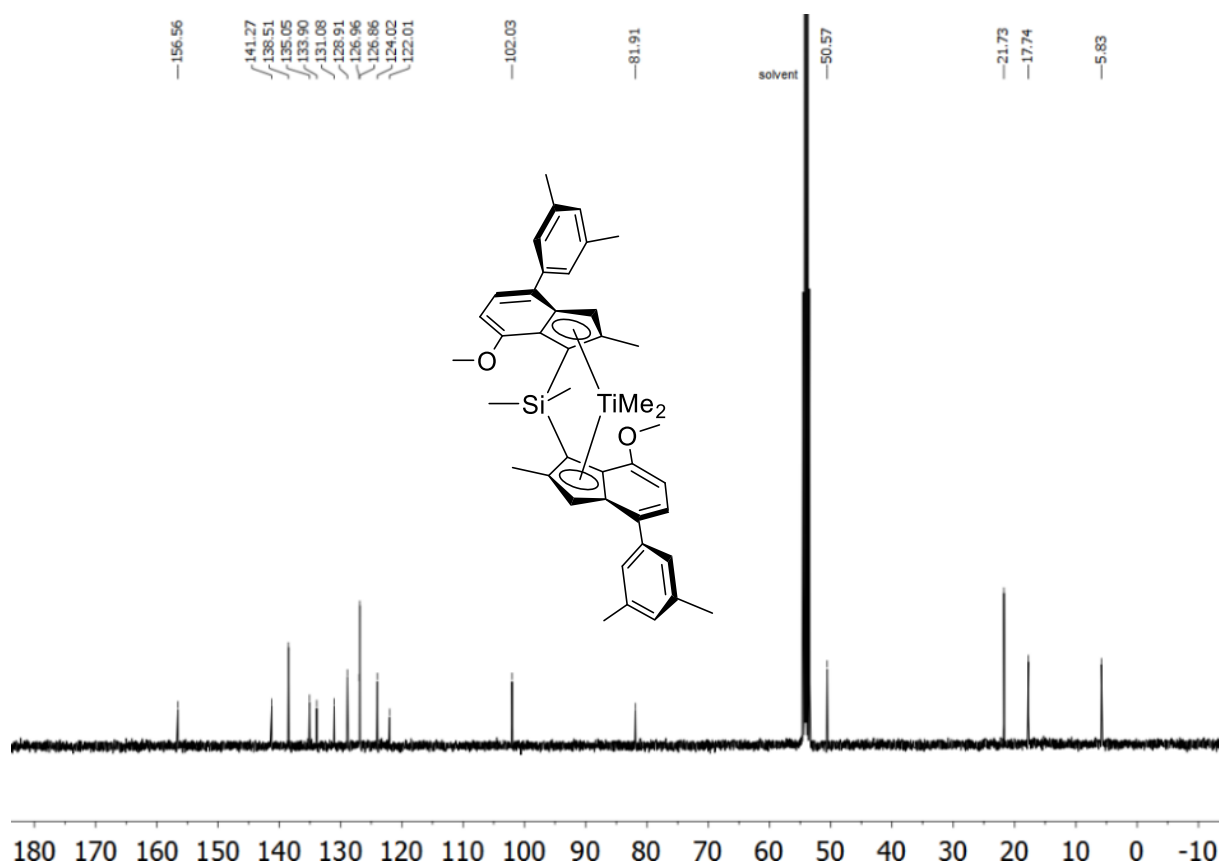


Figure S8. ^{13}C $\{^1\text{H}\}$ NMR spectrum (100 MHz) of **3-Ti** in CD_2Cl_2 .¹

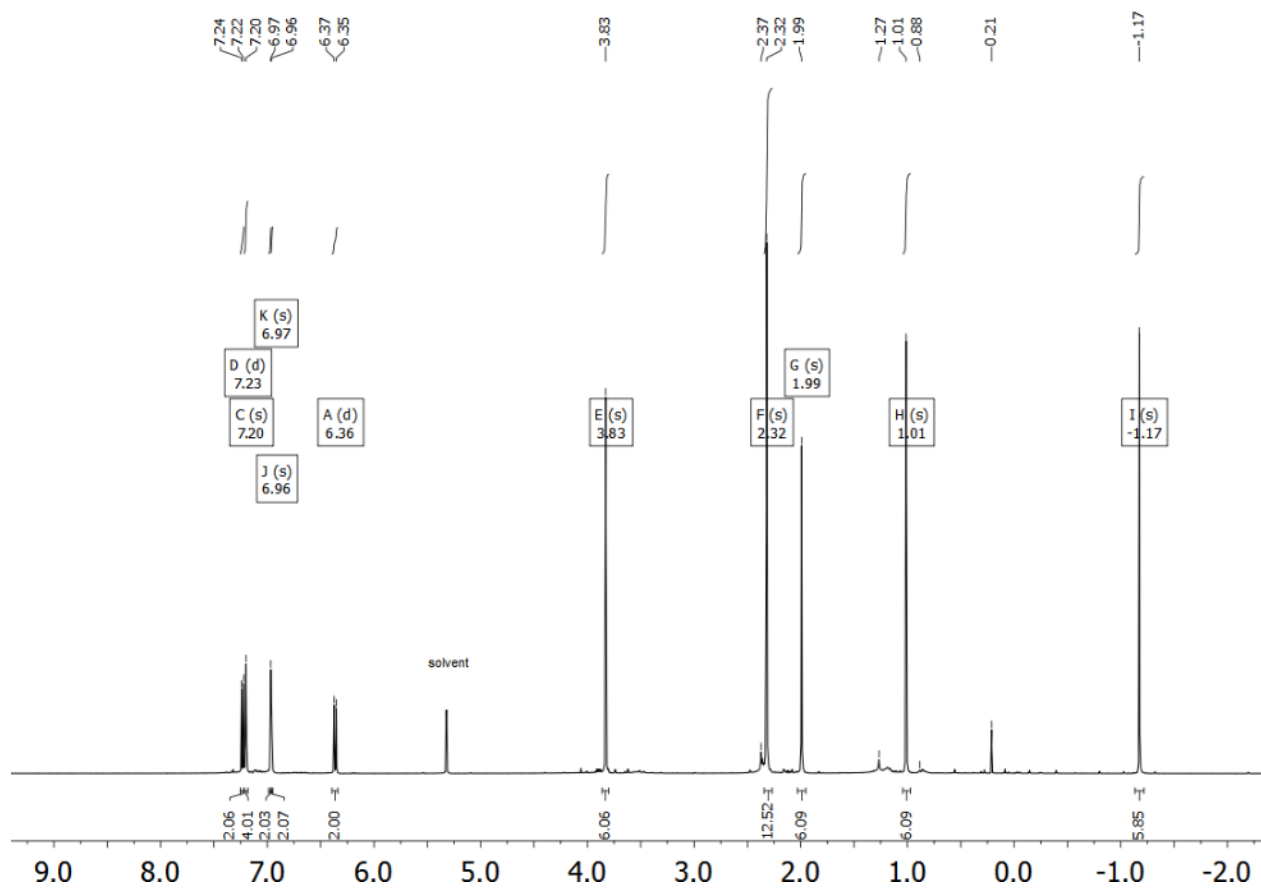


Figure S9. ^1H NMR spectrum (400 MHz) of **3-Zr** in CD_2Cl_2 . Traces of *n*-pentane and toluene are visible.

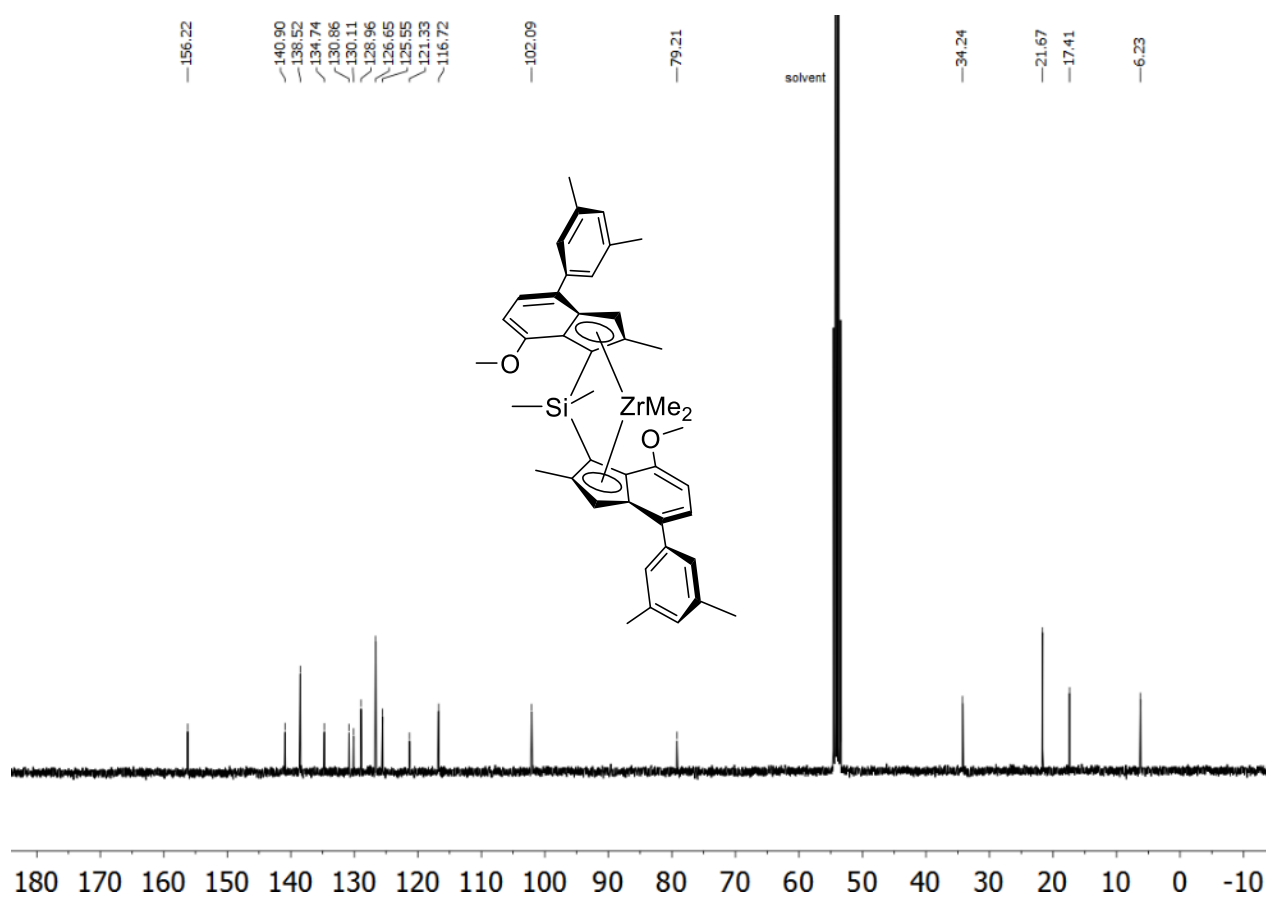


Figure S10. ^{13}C $\{^1\text{H}\}$ NMR spectrum (100 MHz) of **3-Zr** in CD_2Cl_2 .

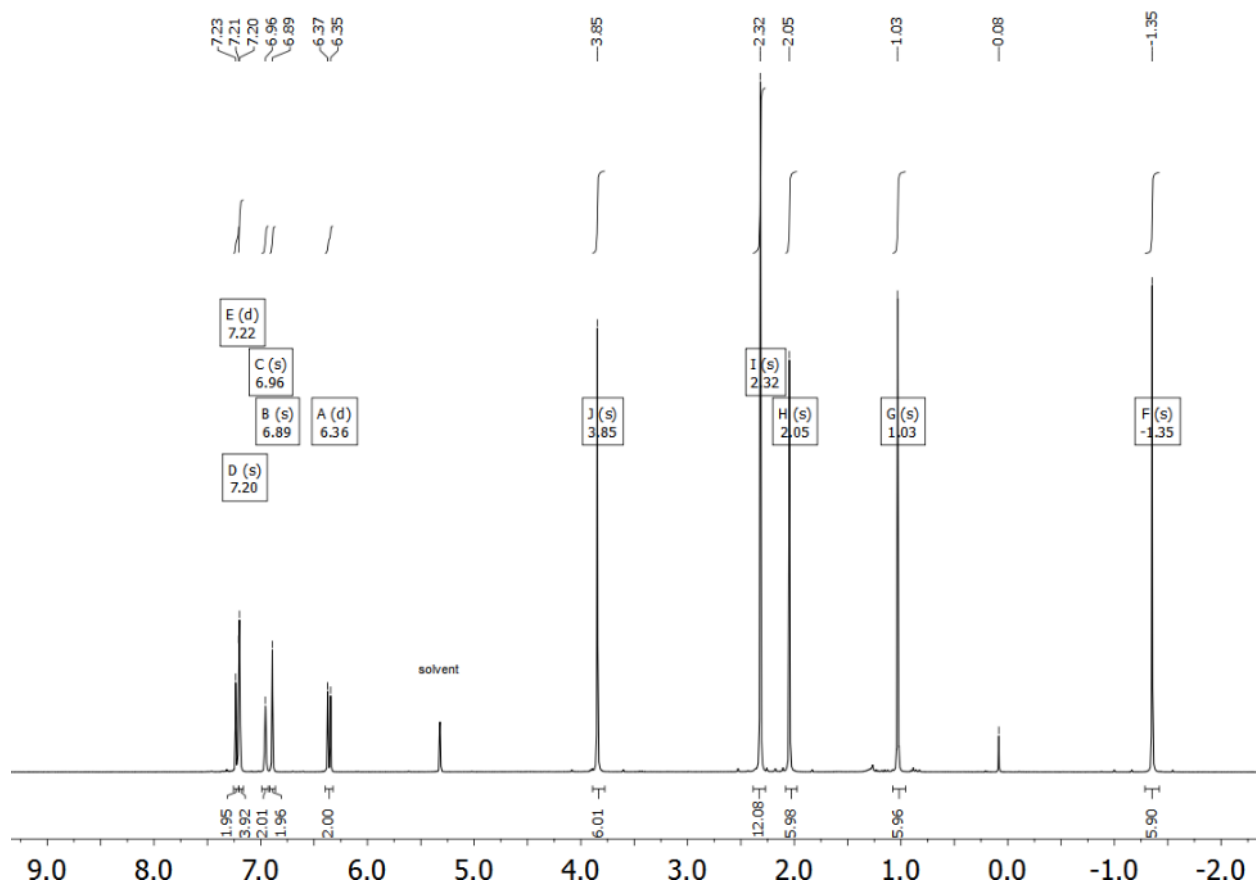


Figure S11. ¹H NMR spectrum (400 MHz) of **3-Hf** in CD₂Cl₂. Traces of *n*-pentane and grease are visible.

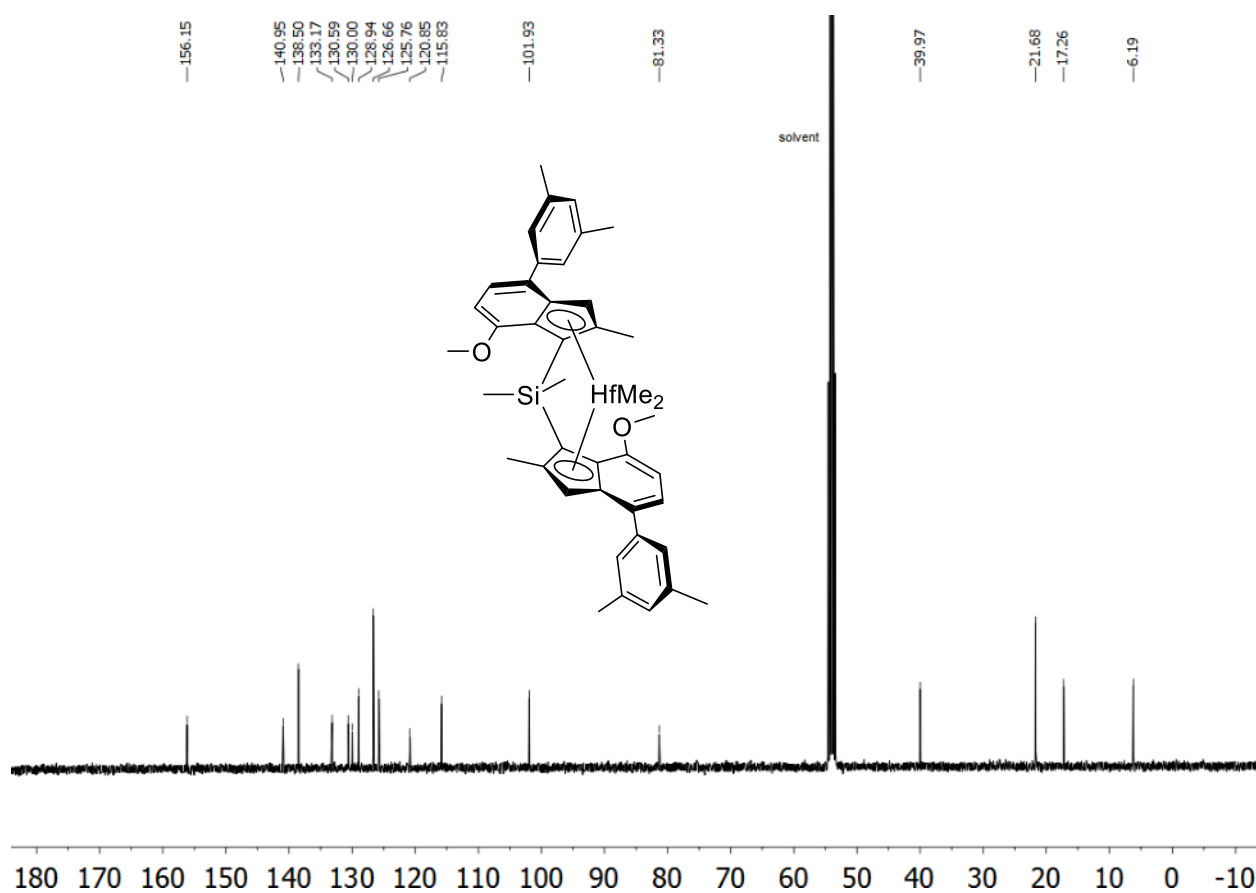


Figure S12. ¹³C {¹H} NMR spectrum (100 MHz) of **3-Hf** in CD₂Cl₂.

3. Kinetic measurements

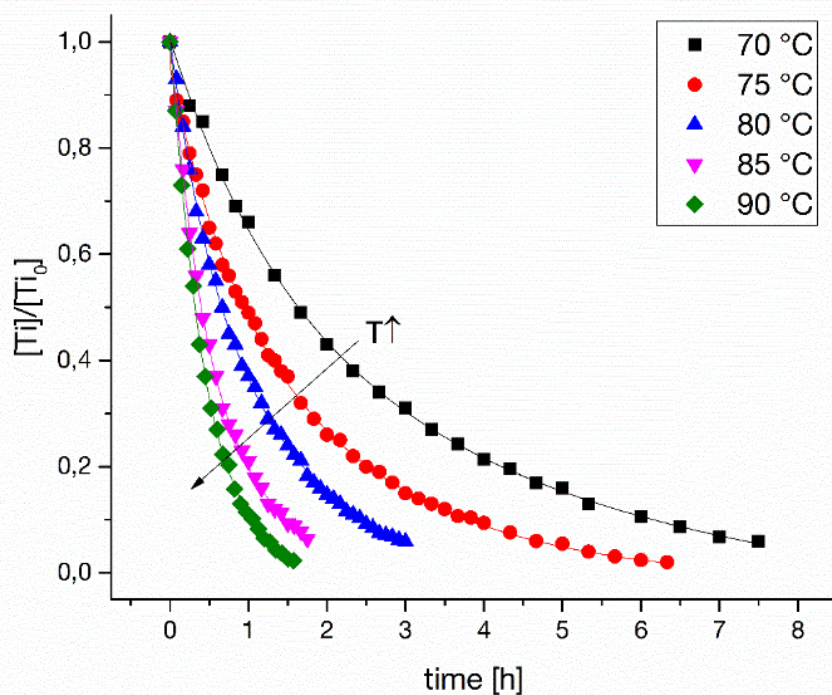


Figure S13. Decay of the $\text{Ti}(\text{CH}_3)_2$ signal in a reaction pseudo first order with 100 eq. $t\text{BuOH}$ at elevated temperatures monitored *via* ^1H NMR spectroscopy.

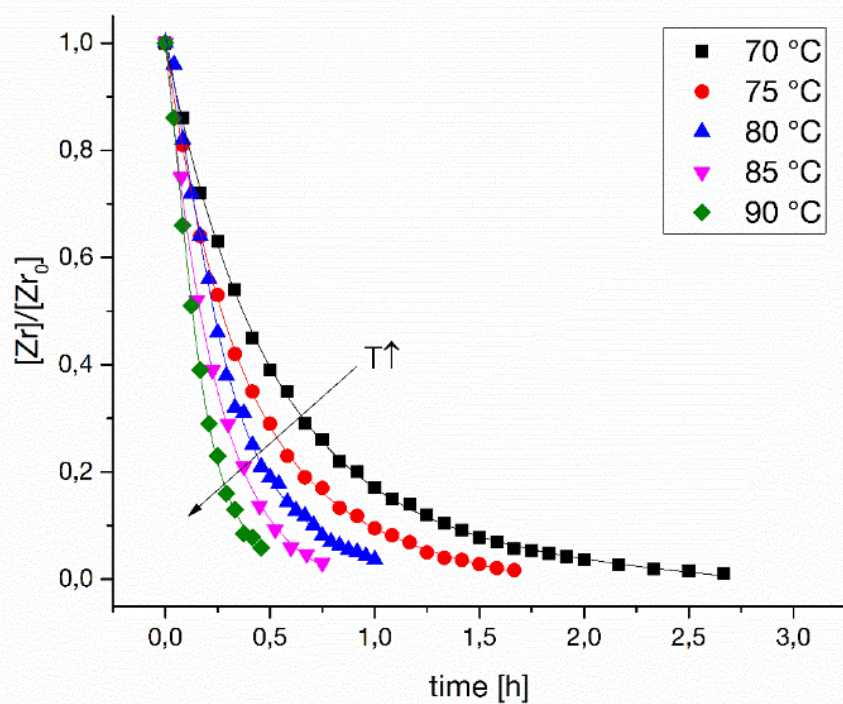


Figure S14. Decay of the $\text{Zr}(\text{CH}_3)_2$ signal in a reaction pseudo first order with 100 eq. $t\text{BuOH}$ at elevated temperatures monitored *via* ^1H NMR spectroscopy.

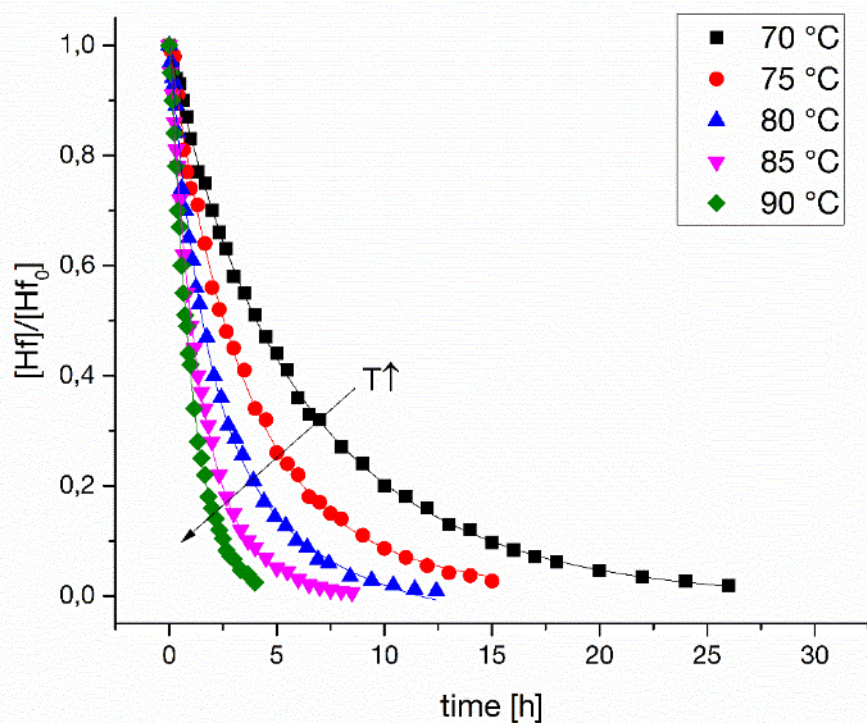


Figure S15. Decay of the $\text{Hf}(\text{CH}_3)_2$ signal in a reaction pseudo first order with 100 eq. $t\text{BuOH}$ at elevated temperatures monitored *via* ^1H NMR spectroscopy.

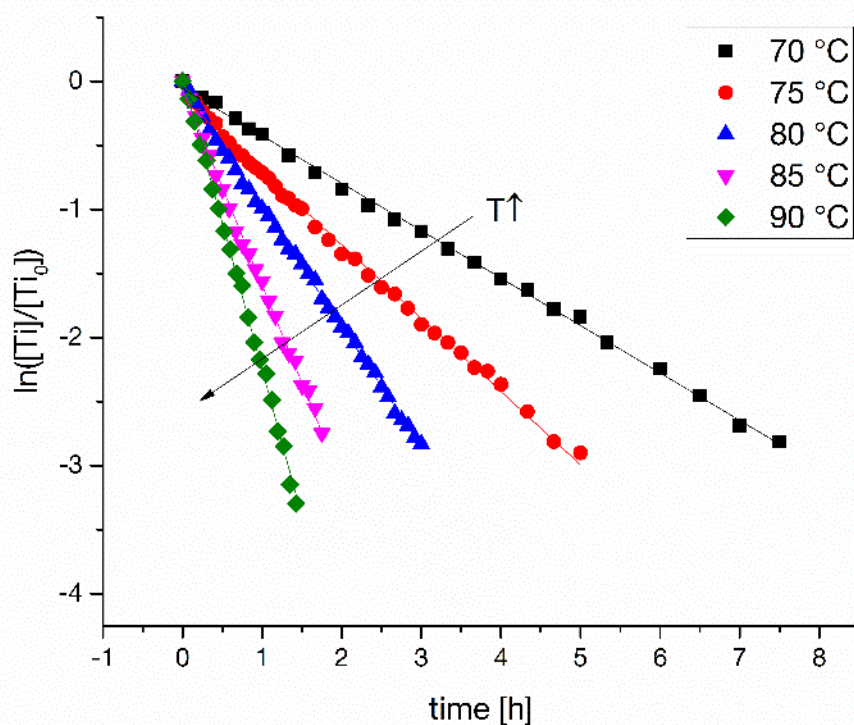


Figure S16. Logarithmic plot of the $\text{Ti}(\text{CH}_3)_2$ signal as a function of reaction time.

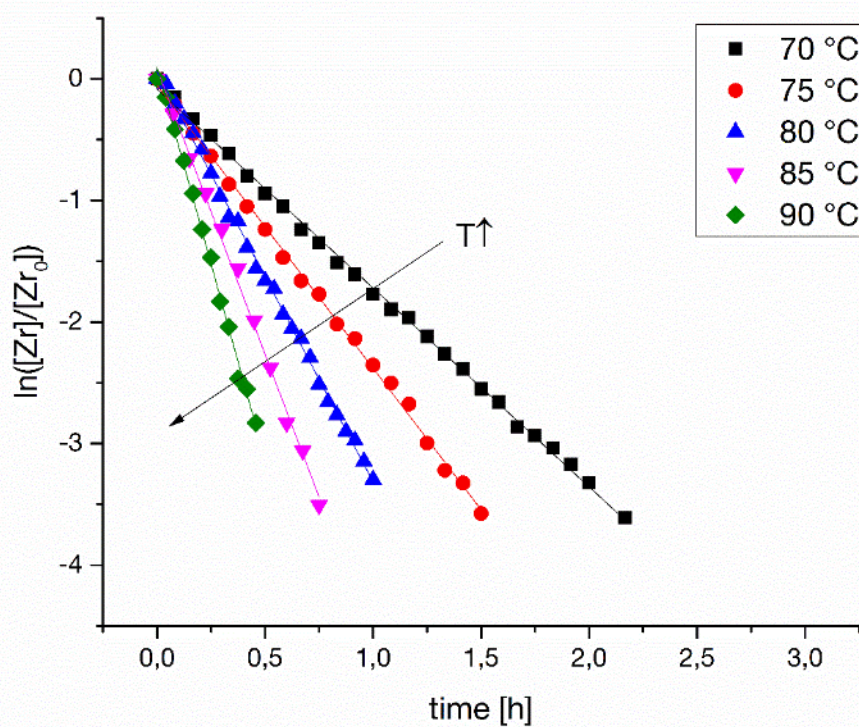


Figure S17. Logarithmic plot of the $\text{Zr}(\text{CH}_3)_2$ signal as a function of reaction time.

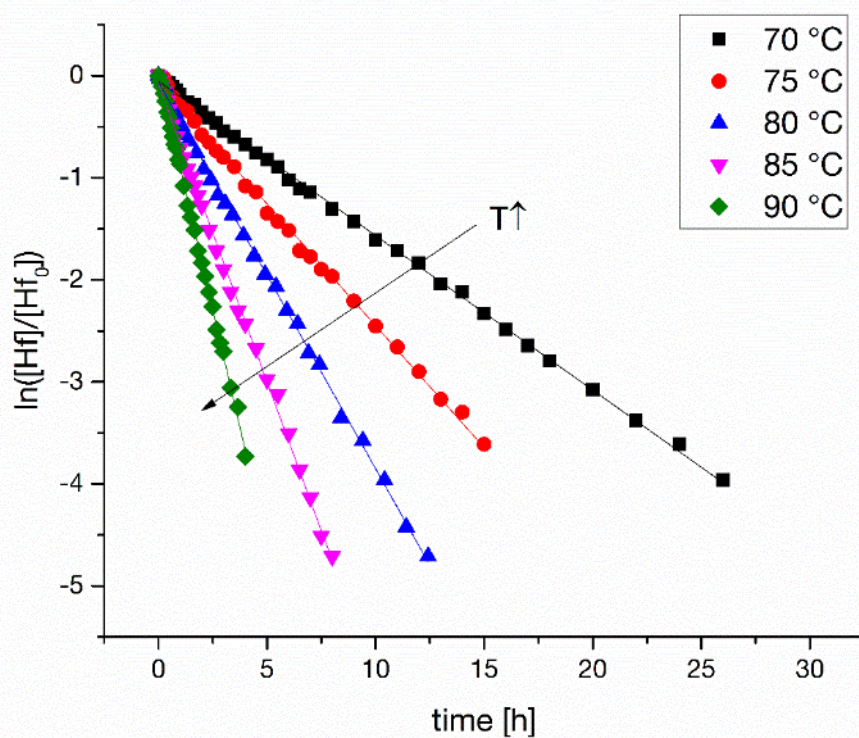


Figure S18. Logarithmic plot of the $\text{Hf}(\text{CH}_3)_2$ signal as a function of reaction time.

Table S1. Determined rate constants of the logarithmic plots.

<i>Complex</i>	<i>Temperature [°C]</i>	<i>Rate constant^a [s⁻¹]</i>	<i>Deviation^b [s⁻¹]</i>
3-Ti	70	1.03 E-4	8.72 E-7
3-Ti	75	1.63 E-4	1.29 E-6
3-Ti	80	2.59 E-4	2.49 E-6
3-Ti	85	4.24 E-4	5.01 E-6
3-Ti	90	6.54 E-4	8.67 E-6
3-Zr	70	4.56 E-4	2.98 E-6
3-Zr	75	6.58 E-4	6.95 E-6
3-Zr	80	9.41 E-4	8.60 E-6
3-Zr	85	1.30 E-3	2.56 E-5
3-Zr	90	1.79 E-3	3.55 E-5
3-Hf	70	4.21 E-5	2.18 E-7
3-Hf	75	6.64 E-5	5.85 E-7
3-Hf	80	1.05 E-4	6.97 E-7
3-Hf	85	1.63 E-4	1.23 E-6
3-Hf	90	2.57 E-4	1.75E-6

^aSlope of the logarithmic plots. ^bDetermined by the square root of reduced chi square.

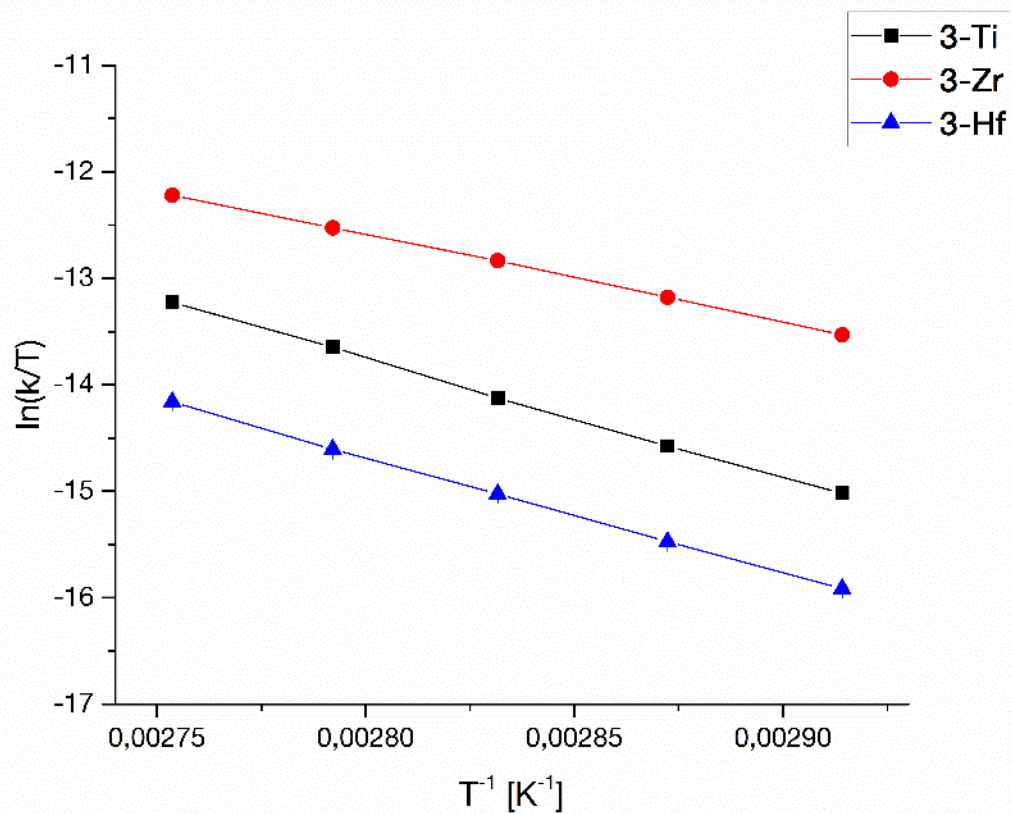


Figure S19. Eyring plots of the reaction of **3-Ti**, **3-Zr** and **3-Hf** with ^tBuOH between 70 °C and 90 °C.

Table S2. Enthalpy and entropy of activation determined by the Eyring equation.

<i>Complex</i>	<i>Enthalpy [kJ·mol⁻¹]</i>	<i>Entropy [J·(mol·K)⁻¹]</i>
3-Ti	93.3 ± 1.3	-50.7 ± 3.7
3-Zr	67.9 ± 0.7	-112 ± 1.9
3-Hf	90.5 ± 0.7	-66.3 ± 2.0

4. UV VIS spectra for the prealkylation of complexes **2** with 200 eq. of TIBA

UV VIS spectra were recorded using a Varian Cary 50 spectrophotometer with a sealed UV quartz cuvette (1 mm). A $8.0 \cdot 10^{-4}$ M complex solution (**2**) was measured first. Subsequently 200 eq. 1.1 M TIBA solution in toluene were added. The reaction of **2-Zr** and **2-Hf** with TIBA is monitored at 60 °C for one hour *via* UV Vis spectroscopy. In both cases the initial absorbance maxima is significantly shifted to lower wavelength indicating an increase of the HOMO-LUMO gap. This observation suggests a substitution reaction between chloride and alkyl substituents (Figure S20-S21).

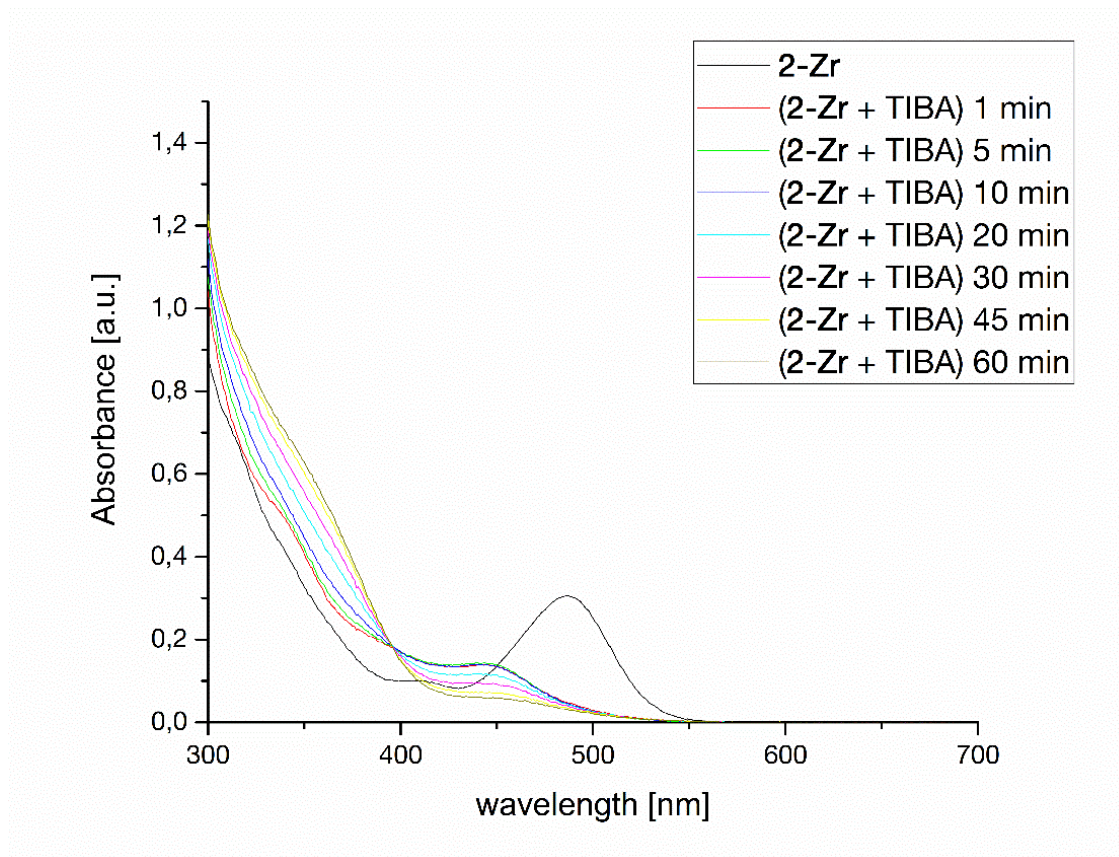


Figure S20. UV VIS spectra of the *in situ* alkylation of **2-Zr** with 200 eq. TIBA at 60 °C.

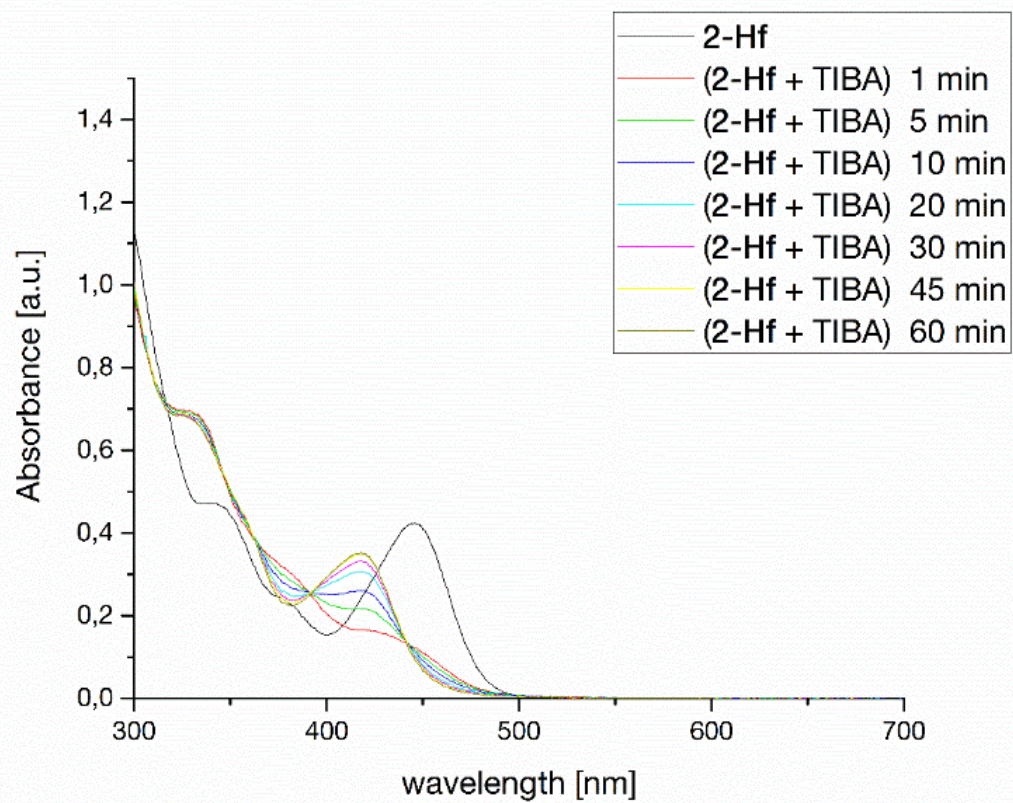


Figure S21. UV VIS spectra of the *in situ* alkylation of **2-Hf** with 200 eq. TIBA at 60 °C.²

5. Olefinic end group analysis *via* ^1H NMR spectroscopy

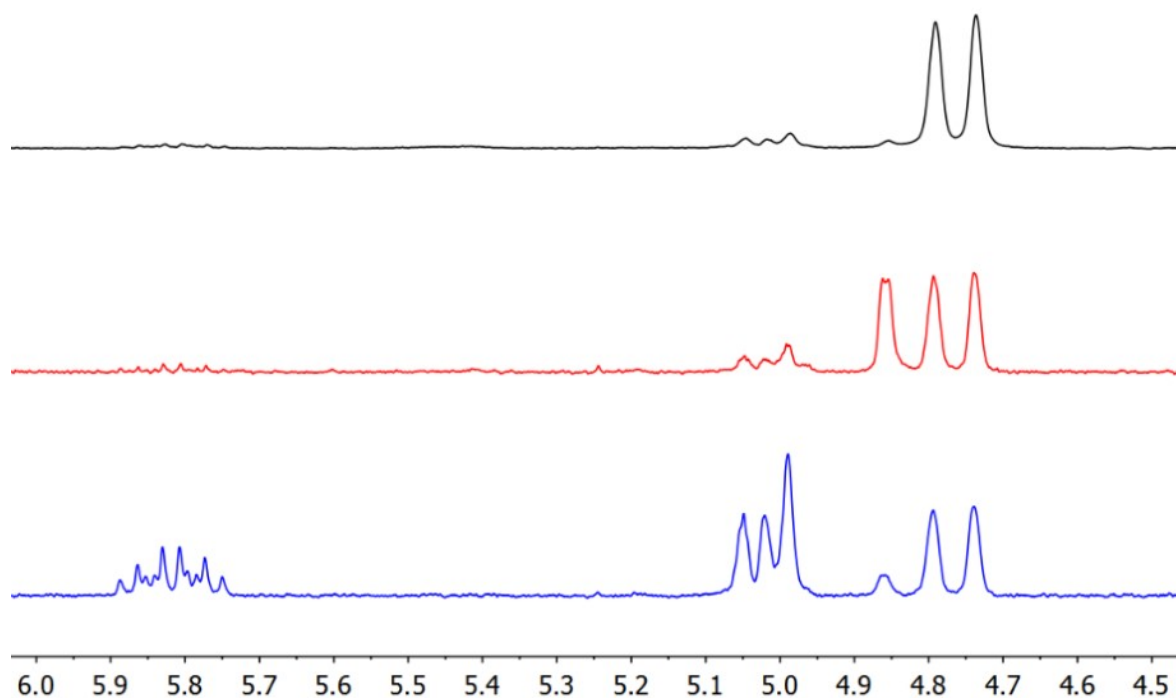


Figure S22. ^1H NMR spectrum (300 MHz) of the polymers produced at 90 °C (entry 5 (black), 11 (red), 17 (blue)) in $\text{C}_6\text{D}_5\text{Br}$ at 140 °C.

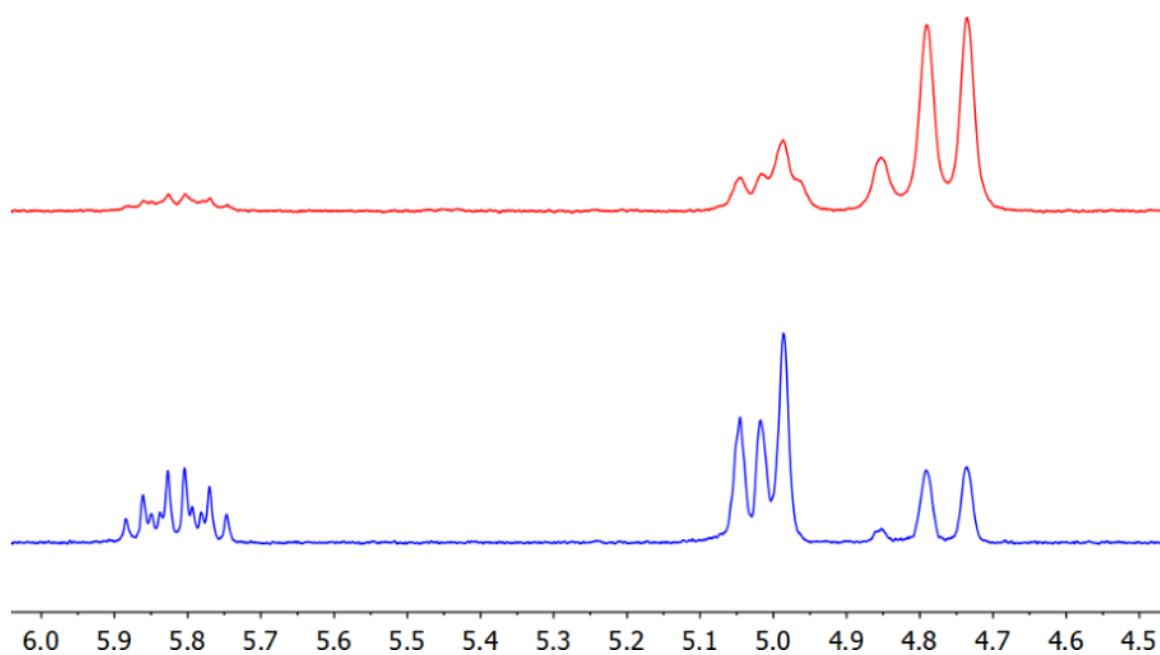


Figure S23. ^1H NMR spectrum (300 MHz) of the polymers produced at 110 °C (11 (red), 17 (blue)) in $\text{C}_6\text{D}_5\text{Br}$ at 140 °C.

6. Tacticity determination *via* ^{13}C $\{^1\text{H}\}$ NMR spectroscopy

All ^{13}C $\{^1\text{H}\}$ NMR measurements were conducted in $\text{C}_6\text{D}_5\text{Br}$ at 140 °C. All chemical shifts are internally referenced on the methyl signal of the isotactic pentad *mmmm* at 21.85 ppm. The tacticity distribution was quantified *via* integration of the methyl region between 22.0 – 19.7 ppm. The relative content of isotactic *mmmm* pentad is reported as mole fraction (in percentage) with respect to all steric pentads.

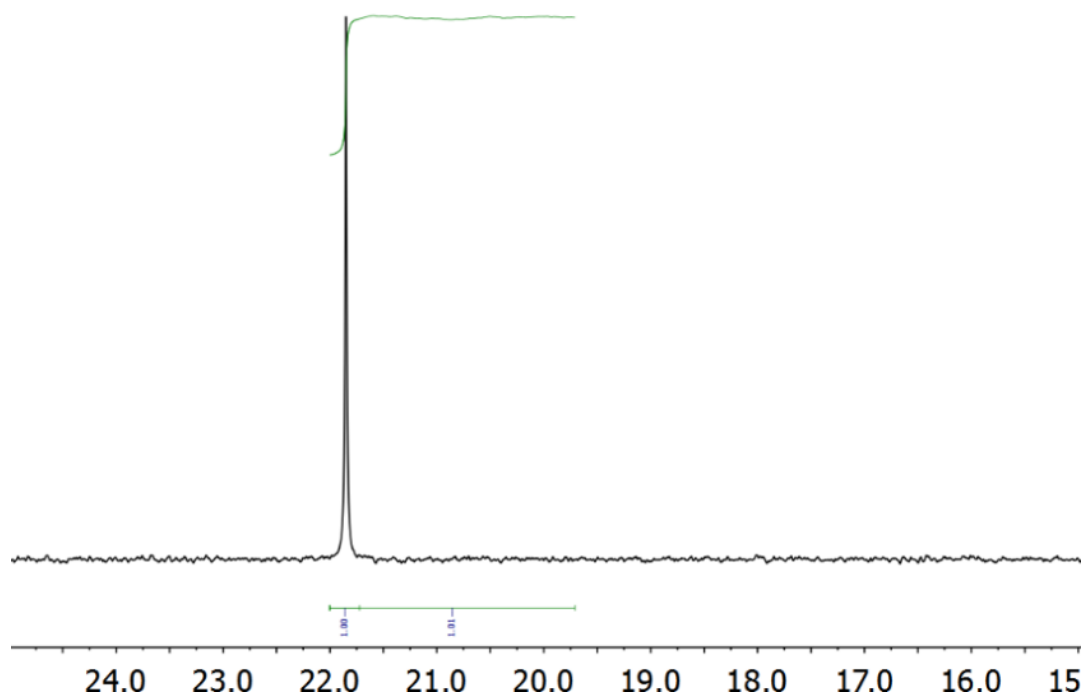


Figure S24. Pentad distribution of entry 3 in the ^{13}C $\{^1\text{H}\}$ NMR spectrum (75 MHz).

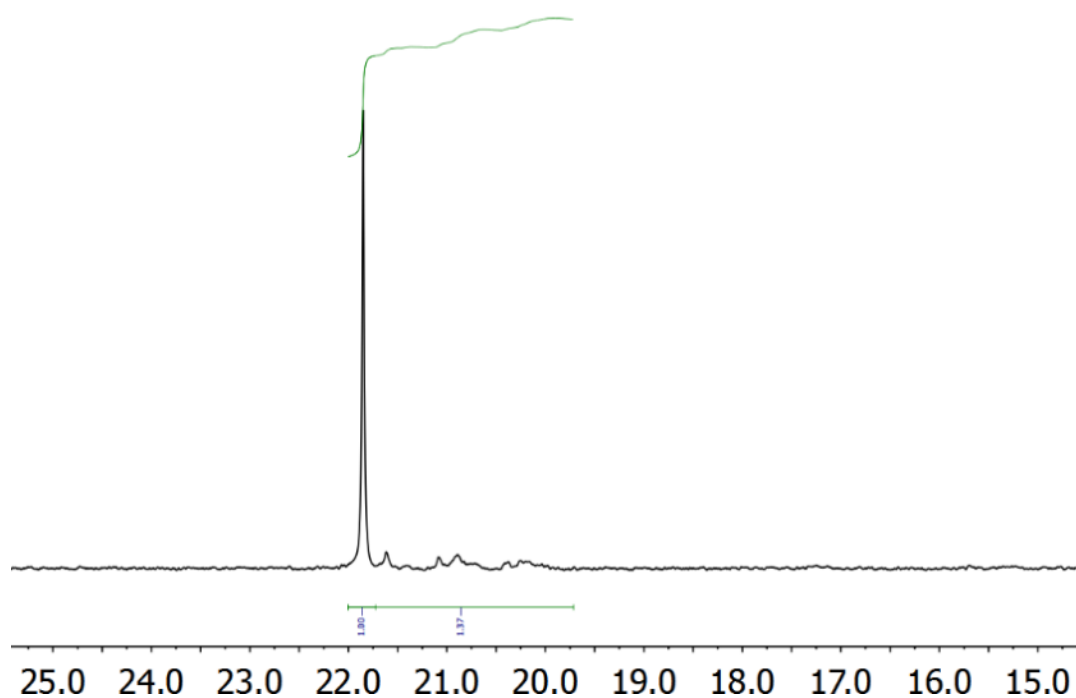


Figure S25. Pentad distribution of entry 4 in the ^{13}C $\{^1\text{H}\}$ NMR spectrum (75 MHz).

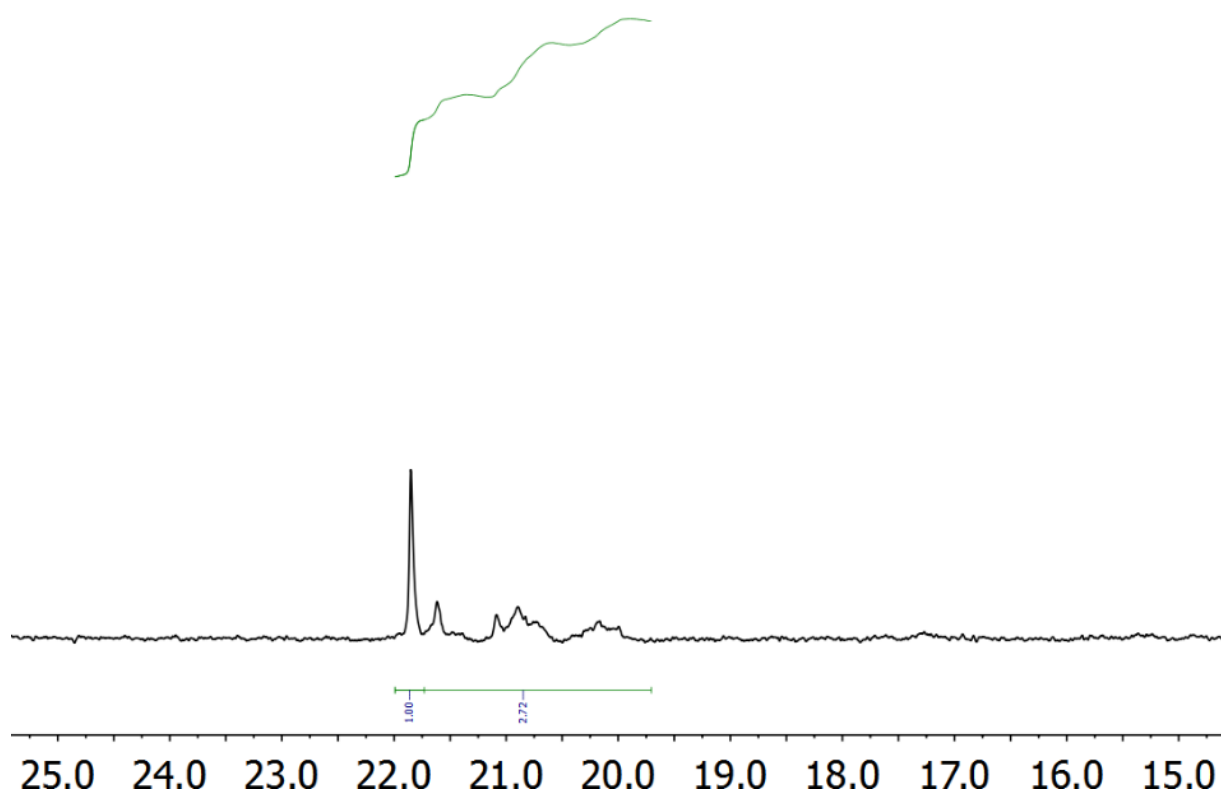


Figure S26. Pentad distribution of entry 5 in the ^{13}C $\{^1\text{H}\}$ NMR spectrum (75 MHz).

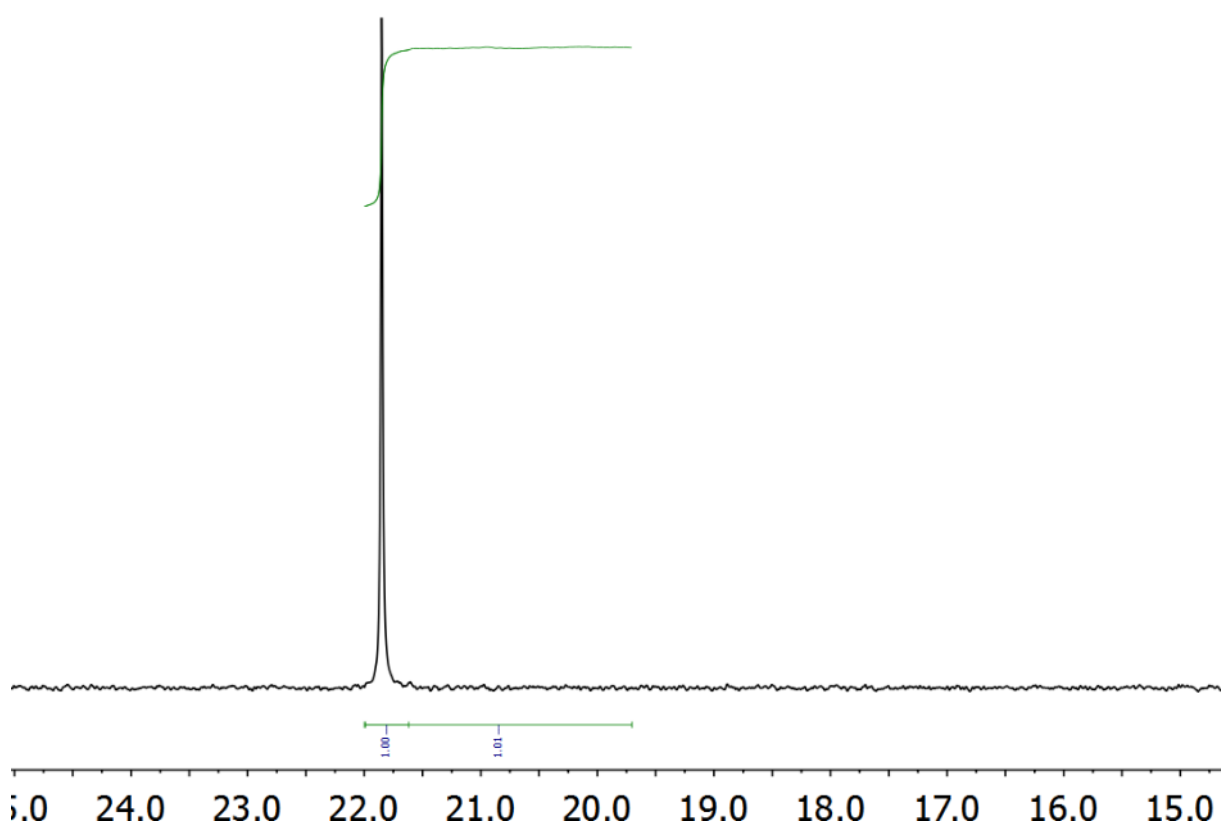


Figure S27. Pentad distribution of entry 9 in the ^{13}C $\{^1\text{H}\}$ NMR spectrum (75 MHz).

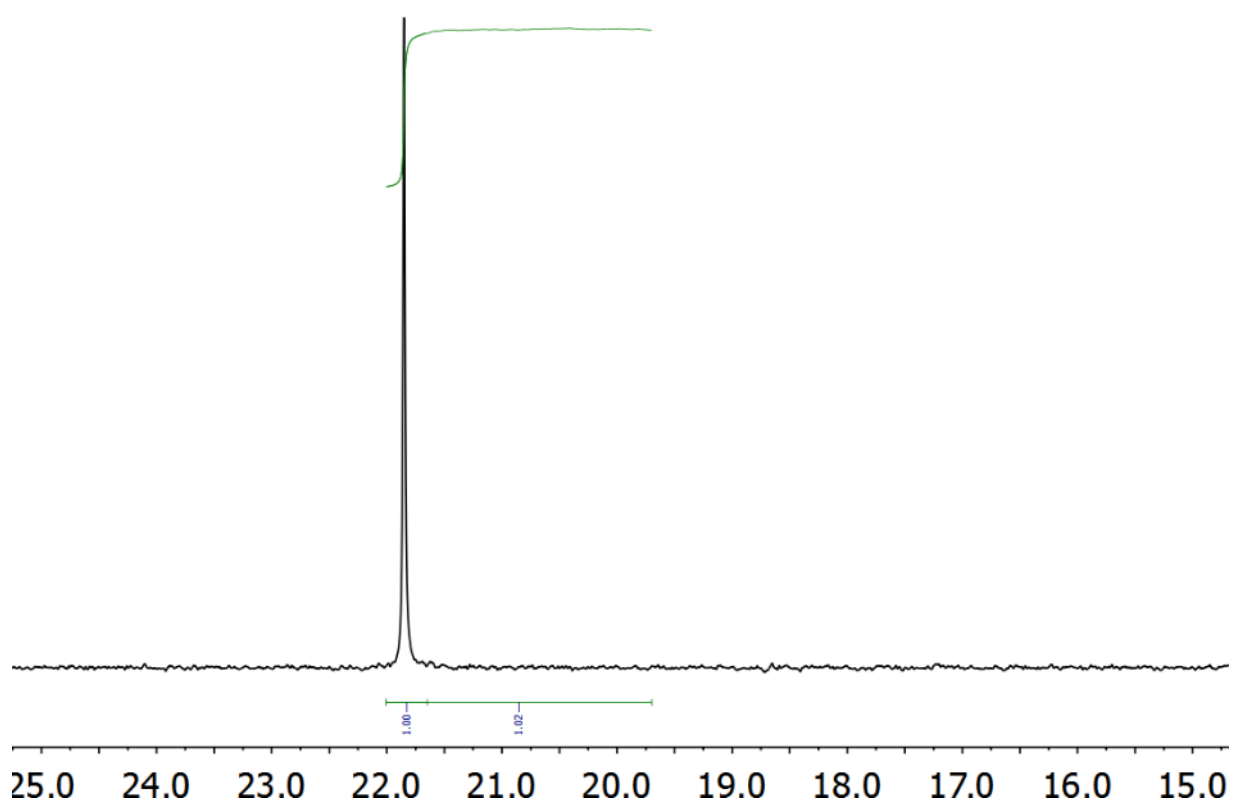


Figure S28. Pentad distribution of entry 10 in the $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (75 MHz).

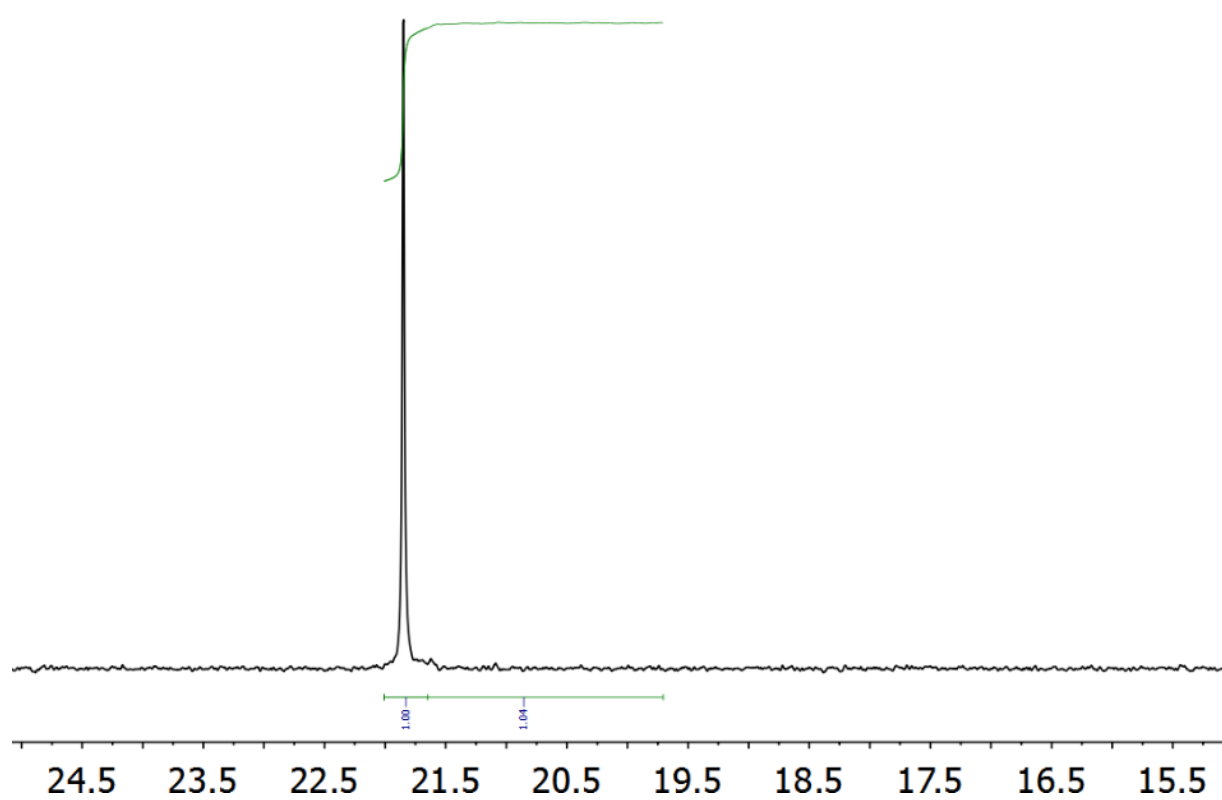


Figure S29. Pentad distribution of entry 11 in the $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (75 MHz).

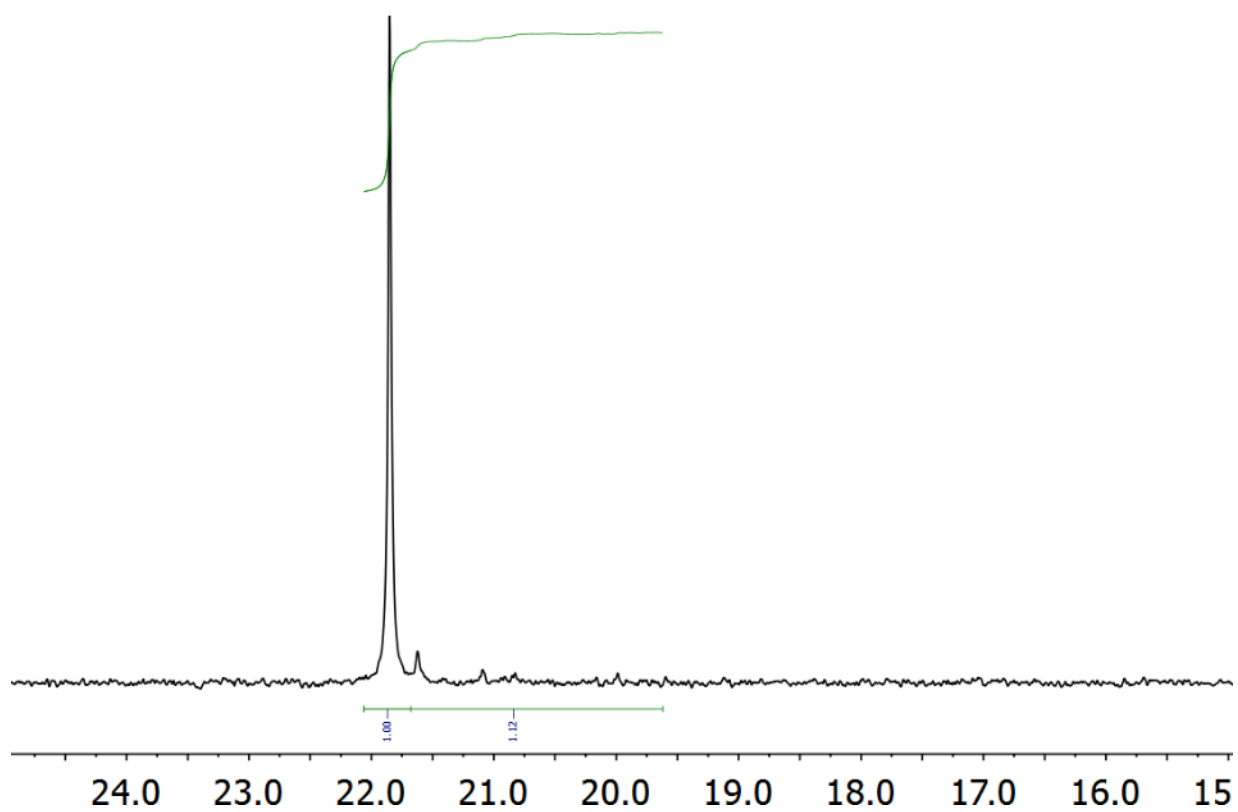


Figure S30. Pentad distribution of entry 12 in the $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (75 MHz).

7. ORTEP representations of 3-Zr, 2-Zr, 3-Ti and 3-Hf

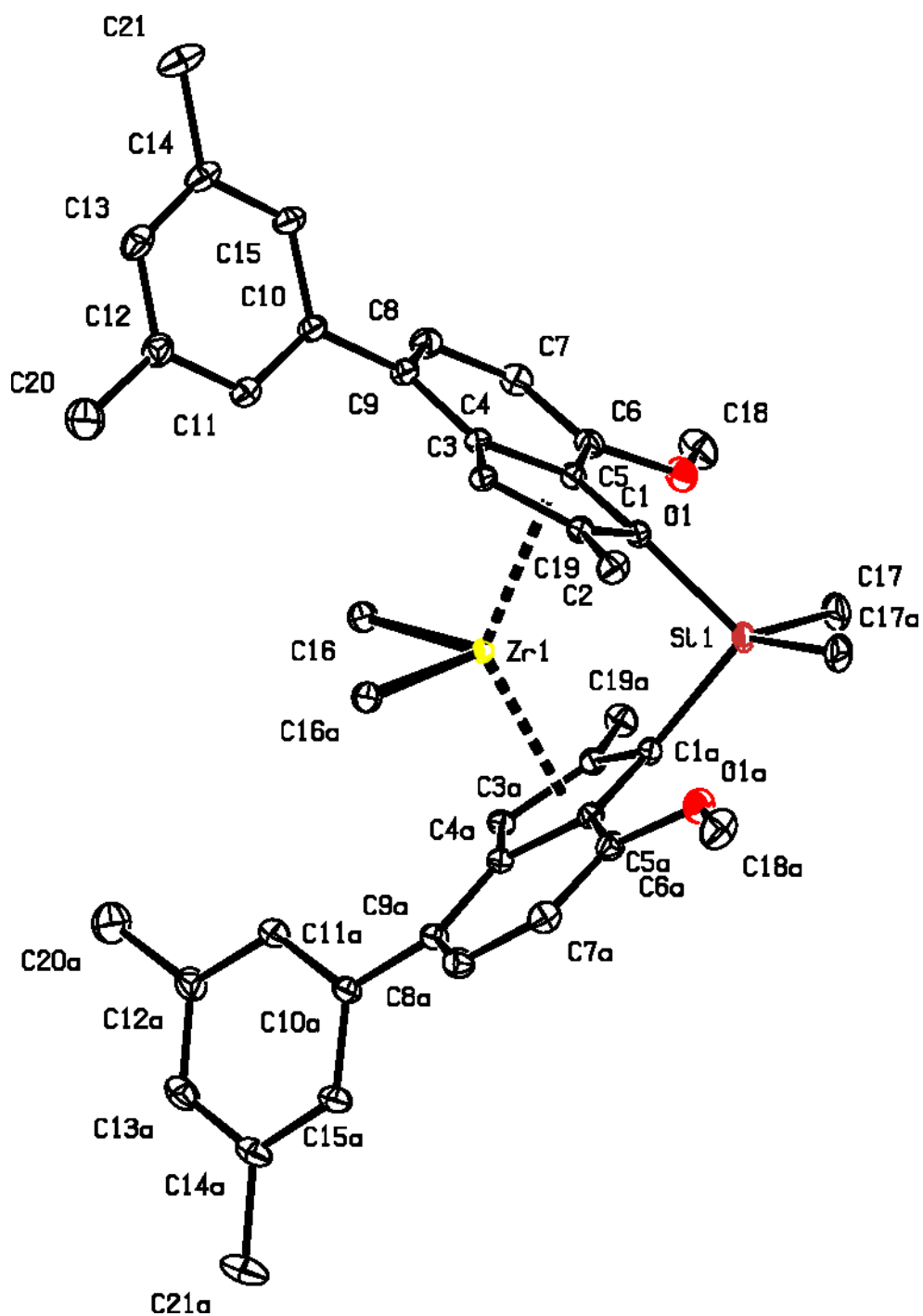


Figure S31. ORTEP style representation of **3-Zr** with ellipsoids drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

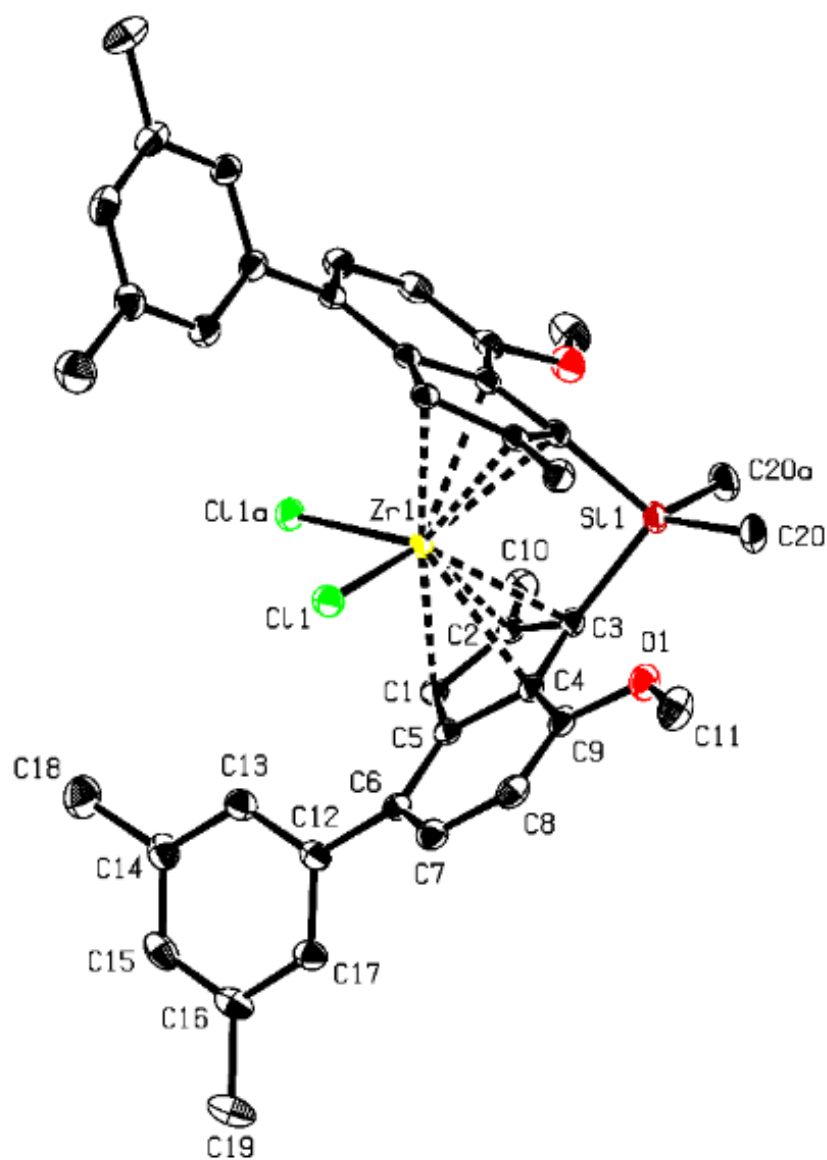


Figure S32. ORTEP style representation of **2-Zr** with ellipsoids drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

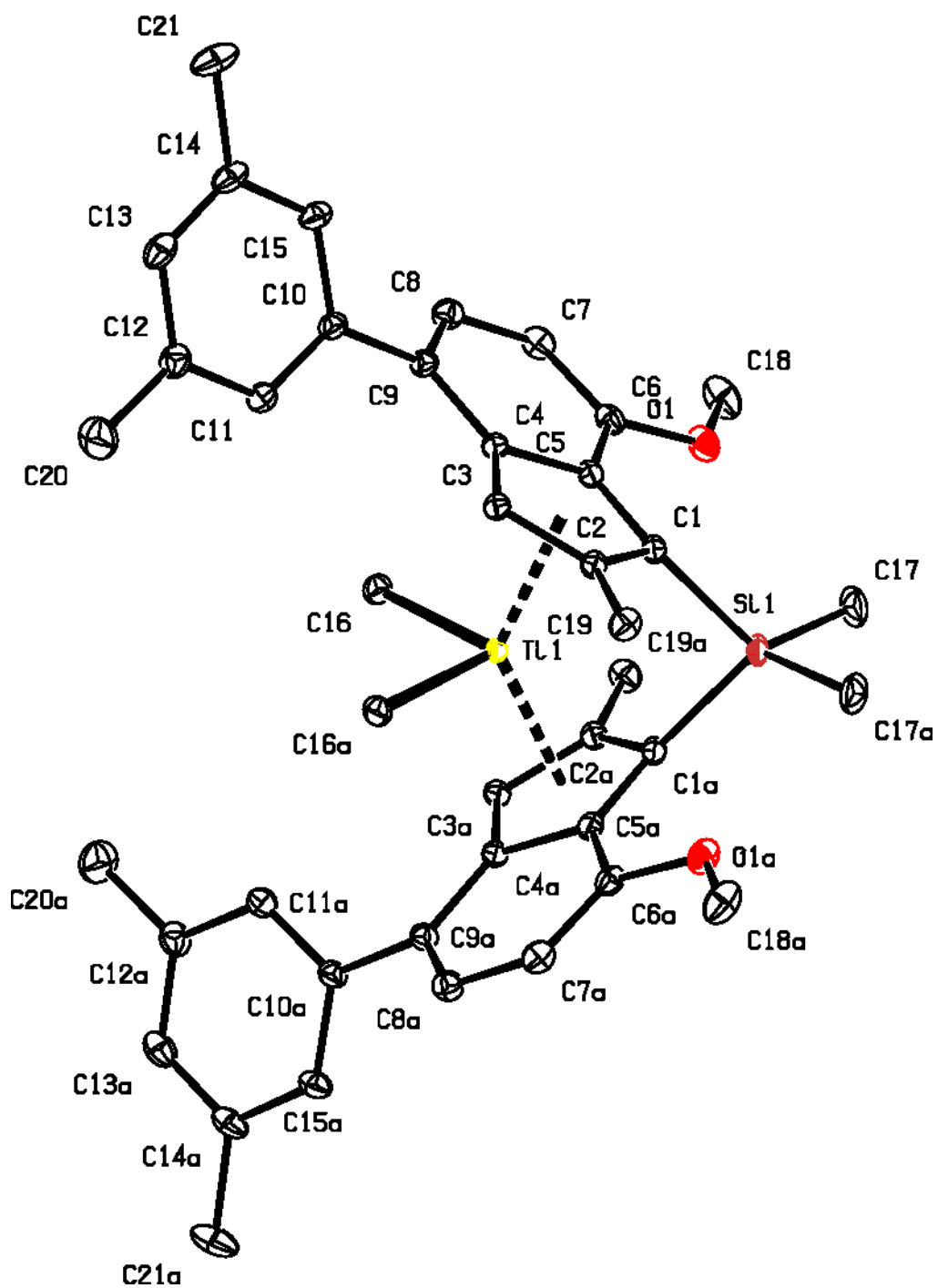


Figure S33. ORTEP style representation of 3-Ti with ellipsoids drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

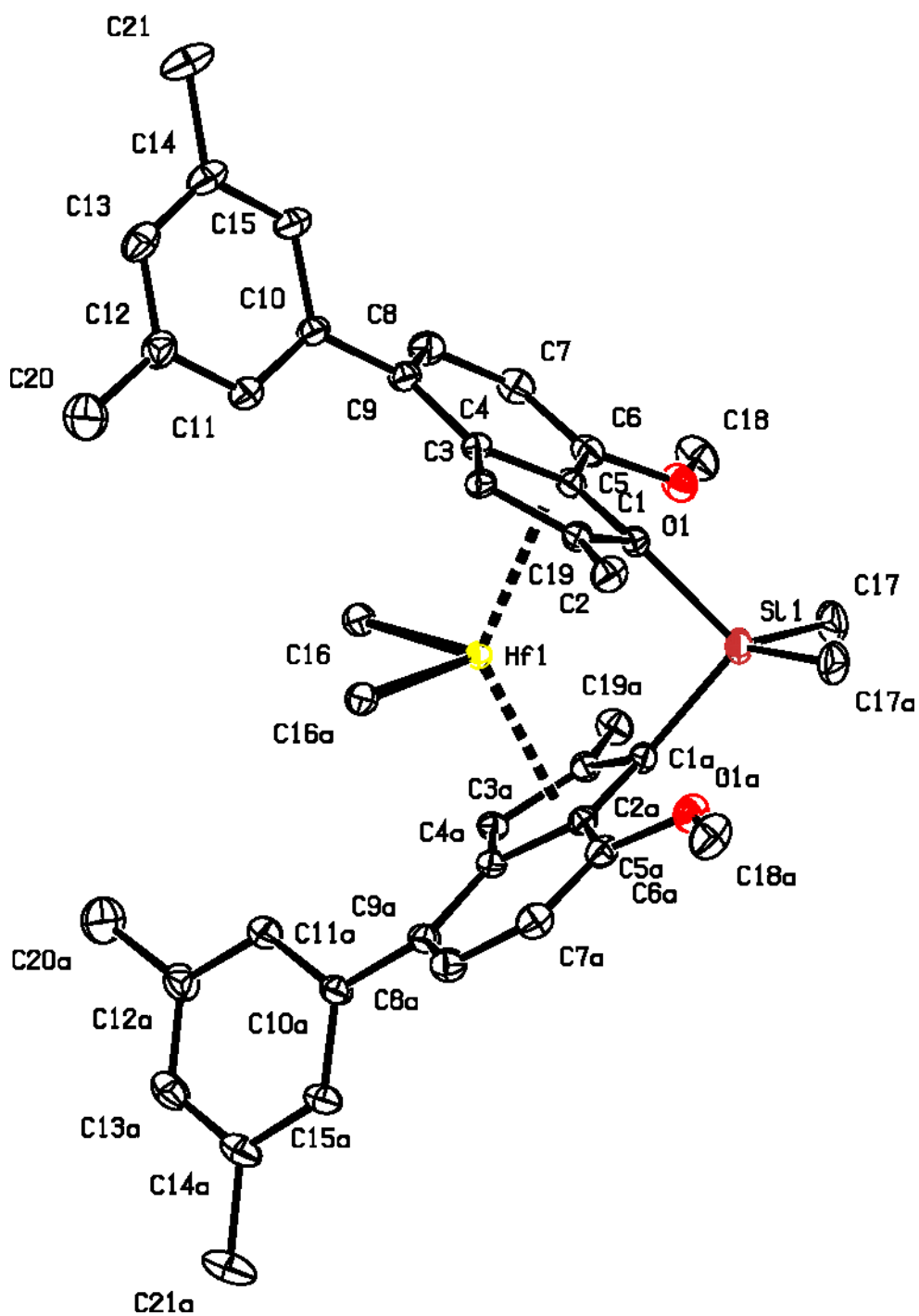


Figure S34. ORTEP style representation of 3-Hf with ellipsoids drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

8. Theoretical estimation of M–C force constants of 3-Ti, 3-Zr and 3-Hf

Theoretical isolated force constants k_{is} of the *M*-C bond have been calculated with ADF using the same level of theory and basis set. The potential energy surface has been sampled by 21 single point calculations around the ground state geometry by simply moving one of the methyl groups along the *M*-C vector. The maximum displacements were 0.02 Å. The *M*-C(Me) bond length was varied without imposing any symmetry constraints (C_1 symmetry; Table S6). The force constants were finally determined by fitting the 21 data points with a polynomial of the 2nd order and successive curve analysis to determine the individual *M*-C force constants in the framework of a harmonic oscillator model.

Table S3. *M*-C force constants.

	k_{is} [N/m]
3-Ti	150.3
3-Zr	149.4
3-Hf	168.0

9. Crystallographic Studies of **3** under High-Pressure (HP)

High-Pressure Preparation: A requirement for collecting diffraction data at elevated pressures is a hydrostatic and inert pressure-transmitting medium (PTM). Therefore, single crystals of **3-Ti**, **3-Zr** and **3-Hf** were tested concerning the reactivity or dissolution in the two nonpolar PTM of choice with a reasonably high hydrostatic limit: 1:1 volume mixture of iso-pentane: *n*-pentane (limit: 7 GPa) and Daphne 7575 (limit: 3.9-4 GPa).^{3,4} Due to the air-sensitivity of **3** all testing steps and the actual loading of the single crystals into the diamond anvils (DAC) were performed in an Ar-glovebox. The behavior of the **3-Zr** and **3-Hf** crystals were similar, showing no hints of reaction with Daphne 7575 but a rougher surface after being in contact with isopentane: *n*-pentane is indicating a slight modification of the surface. The **3-Ti** crystals reacted differently and showed instantaneously the similar optical changes after being in contact with both PTM: A darkening of the color and creation of a few tiny cracks in the crystals. Nevertheless, single crystals of **3-Ti** were loaded subsequently with both PTMs in a DAC and intensity diffraction data was collected. For both PTMs the obtained diffraction data was of exceptionally low quality including insufficient scattering power and multiple domains. Finally, perfluoro-2-butyltetrahydrofuran (FC-75) was tested as PTM, which has a hydrostatic limit of 1.2 GPa.⁵ However, the obtained intensity data from a crystal surrounded by this PTM contained the same diffraction issues. We like to note that the low diffraction quality of the single crystals being in contact with these PTM has not necessarily to be related to a severe reaction of **3-Ti** with these PTMs. The diminished crystal quality might be also based on the light sensitivity of **3-Ti** combined with the loading procedure of the pressure chamber. Accordingly, no data collection of **3-Ti** at high pressures were feasible. In case of **3-Zr** and **3-Hf** Daphne 7575 served as PTM.

X-ray data collection: In order to generate the high pressures two different types of DACs were employed. In case of **3-Zr** a Boehler-Plate DAC was used and for **3-Hf** a modified Merrill-Bassett DAC with tungsten carbide seats was applied.⁶⁻⁹ In both cases, the culet diameter of the conical (Boehler-Almax) anvils was 0.6 mm.⁸ For both compounds, the stainless steel gasket was pre-indented from initially 250 μm to 80 μm . The diameter of the borehole was 270 and 280 μm for **3-Zr** and **3-Hf**, respectively. The pressure chamber were loaded in an Ar-filled glovebox with a single crystal, three ruby spheres for the pressure determination via the ruby fluorescence method, and Daphne 7575 as PTM. The size of the clear, yellowish and trapezoidally shaped single crystals were 140 x 110 x 40 μm^3 (**3-Zr**) and 130 x 120 x 40 μm^3 (**3-Hf**).

The pressure was determined with an estimated precision of ± 0.1 GPa by the ruby fluorescence method.¹⁰ In case of **3-Hf** the combination of a diode pumped solid-state laser (CNI MGL-FN_532nm-50mW) and a fiber optic spectrometer (Ocean Optics HR2000+) was employed. For **3-Zr** an *Almax eaysLab* Optiprex PLS photoluminescence system was used.

Intensity diffraction data of **3-Hf** were collected with a *Bruker* SMART-APEX diffractometer with a D8 goniometer and an APEX II CCD detector using mirror optics monochromated Ag $K\alpha$ radiation ($\lambda = 0.56087$ Å; Incoatec I μ S 1.0). The data collections were based on ω scans with 0.5° steps with a fixed sample detector distance of 6 cm. The theta dependent exposure times varied between 15 s ($2\theta = 0^\circ$), 30 s ($2\theta = \pm 14^\circ$) and 60 s ($2\theta = \pm 28^\circ$).

To compensate for the reduced scattering power of **3-Zr** the higher brilliance of the synchrotron beam at the X04SA Material Science-beamline of the Paul Scherrer Institute, Switzerland, was employed.¹¹⁻¹³ A photon

energy of 25 keV for the monochromated beam (square of $200 \times 200 \mu\text{m}^2$) was used corresponding to a precise wavelength of $\lambda = 0.49616 \text{ \AA}$, which was verified by the refinement of the lattice parameters of NIST SRM 660a LaB6 powder standard in a capillary. A Dectris Pilatus 6M single-photon counting detector was employed for the collection of the intensity diffraction data during the single crystal experiment.¹³ The distance between the sample and detector was fixed to 200.15 mm. The alignment of the entire setup was verified by a standard single crystal diffraction experiment on NIST SRM 1990 ruby single-crystal standard.¹⁴

The precise alignment of the DAC to the primary beam was achieved by centering the hole of the gasket to the centre of the beam with a *xyz*-motor equipped on the cradle's ϕ -circle.^{12,13,15} The modified single-crystal high pressure setup on the beamline allowed only ϕ -scans. In order to increase the redundancy and completeness the circular shaped Boehler-Plate DAC was mounted for each pressure point on two different positions, which were approximately 120° separated. This 120° rotation of the DAC mimics a χ rotation. However, for each rotation the DAC had to be detached from the cradle's ϕ -circle and centered again after the rotation to the primary beam. Therefore, the orientation matrix *UB* of the single crystal was not only rotated about 120° in χ between these two mounting positions but also slight deviations in ϕ due to slight inaccuracies during the alignment are expected. This led to an individual data reduction of each mounting position. For each mounting position two ϕ -scans separated by 0.2° in ϕ with a step size of 0.5° were performed. The exposure time per frame was 5 s.

The collected frames were imported into *CrysAlis^{Pro}* software.¹⁶ Obvious diamond reflections were rejected before the integration, data reduction and empirical absorption correction of the imported diffraction data were performed. Typically, the data reduction contained 2200 frames for **3-Hf** and 290 frames per mounting position for **3-Zr**. In case of **3-Zr** the data sets of different mounting positions but same pressure were finally merged via Sortav applying a single scale factor for each individual reduced data set.^{17,18}

The more accurately determined cell parameters in terms of standard uncertainties of the two mounting positions were used for the merged datasets. The space group of the compounds (Int. Tables No. 15) allows different choices regarding the cell setting. In case of the DAC experiments with the limitations of the restricted reciprocal space the choice of the conventional *I2/a* cell setting produces slightly more accurate cell parameters than the more often applied unconventional cell setting *C2/c* for these compounds.^{1,2,19,20} Therefore, the conventional setting *I2/a* with the shorter translation vectors in the *ac*-plane and a monoclinic angle β closer to 90° for the cell at $P = 0.0001 \text{ GPa}$ is applied during the high-pressure studies. In order to trace the pressure dependency of the cell parameters the rough alignment of the orientation matrix of the single-crystal was remained and adapted to the elevated pressure points and the different alignment. The pressure evolution of the cell parameters and the fixed principal direction of the translation vectors yield minor crystallographic issues like acute monoclinic angle, *i.e.* $\beta < 90^\circ$, for $a > c$ which were however ignored to keep the cell setting identical for all diffraction data sets.

The crystal structures were solved with SHELXS-2014 using the structure expansion method and refined by SHELXL-2014.^{21,22} The anomalous dispersion coefficients f' and f'' for the applied wavelength $\lambda = 0.49616 \text{ \AA}$ at the PSI were calculated by the FPRIME code in the XDISP module of the WINGX-suite.^{18,23} To obtain a better match with the absorption coefficient μ estimated by *CrysAlis^{Pro}* software the photon interaction cross-sections were derived from the Henke tables via the *Computational Crystallography Toolbox* implemented in the *Olex2*-suite.^{16,24–26}

For consistency, the same labelling scheme for all non-hydrogen atoms was applied for **3-Zr** and **3-Hf** (see Fig. SXb). In case of **3-Zr** anisotropic displacement parameters (ADP) were used for all non-hydrogen atoms. For **3-Hf** the aromatic carbon atoms of the ansa-bridging cyclopentadienyl (Cp) and phenyl (Ph) groups are treated isotropically. The remaining non-hydrogen atoms were refined anisotropically. However, the ADPs of the carbons in the remaining Ph rings as well as the terminal carbons connected to Si or O were restrained by the enhanced ‘rigid-bond’ instruction RIGU.²⁷ For both compound, measured reflections with too (i) low or (ii) high intensity compared to the model and an unambiguous relation of this intensity difference due to position of the reflections on the frames, i.e. (i) in a partially shaded area or (ii) close to a tail of a diamond reflection, were finally omitted from the refinement.

All H atom positions were restricted geometrically with a riding model with isotropic displacement parameters equal to 1.5 times U_{eq} of the corresponding C atom for terminal CH₃ groups or 1.2 times U_{eq} of the attached C in the Cp- and Ph-rings. The terminal methyl groups were allowed to rotate along the C—Hf/Zr/Si/O/C axis during the least-square refinement to achieve the best possible position of the restrained hydrogen atoms.

In order to track the evolution of the intermolecular distances a Hirshfeld surface analysis is applied employing *CrystalExplorer17*.^{28,29} On the Hirshfeld surfaces, the normalized contact distances d_{norm} are mapped indicating longer or shorter intermolecular distances than the sum of the van der Waals radii of the participating atoms in the neighbouring molecules in the crystal.^{28,30}

Key parameters of the data reduction and refinement for the high-pressure studies on **3-Zr** and **3-Hf** are summarized in Table S7 and Table S8, respectively. The evolution of the cell parameters with increasing pressure is shown in Figure S36. The pressure dependency of the volume is described by a least square fit of a 3rd order Vinet equation of state (EoS) applying the EoSFit7-GUI suite.^{31–34} The obtained fitting parameters are listed in Table S13. The pressure dependency of selected bond distances and angles following the labeling scheme (Figure S35) are briefly summarized in Table S9 to Table S12 and depicted in Figure S37 to Figure S39, respectively. Figure S40 indicates the packing of the molecules in the crystal system. Figure S41 to Figure S43 show the evolution of the Hirshfeld surfaces of **3-Zr** and **3-Hf** with increasing pressure.

10. Crystallographic Studies of **3** under HP: Crystal Data and Selected Bond Distances and Angles

Table S4: Crystallographic data and parameters from the X-ray data reduction and refinement of the **3-Zr** structure at the four different pressure points between 0 and 3.0(1) GPa collected at the PSI.

<i>Crystal Parameters</i>				
Formula, FW [g mol ⁻¹]	C ₄₂ H ₄₈ O ₂ ZrSi, 704.11,			
F000	1480.0			
Crystal system,	Monoclinic,			
space group, Z:	<i>I</i> 2/ <i>a</i> , 4			
P [GPa]	0	1.2(1)	1.8(1)	3.0(1)
<i>a</i> [Å]	18.503(3)	18.026(2)	17.887(2)	17.685(2)
<i>b</i> [Å]	9.85906(12)	9.56487(7)	9.49549(8)	9.41697(9)
<i>c</i> [Å]	18.7642(3)	18.1779(2)	17.9728(2)	17.6556(3)
β [°]	90.492(3)	89.158(3)	88.701(3)	87.902(3)
<i>V</i> [Å ³]	3423.0(6)	3133.9(4)	3051.8(4)	2938.4(4)
Reflections (cell)	4888	5584	5321	4794
λ [Å]	0.49616			
ρ_{calc} [g cm ⁻³]	1.366	1.492	1.533	1.592
μ [mm ⁻¹]	0.744	0.813	0.835	0.867
<i>T</i> _{min} , <i>T</i> _{max}	0.93719, 1.000	0.95308, 1.000	0.95463, 1.000	0.94473, 1.000
θ range [°]	1.629-22.425 -8 ≤ <i>h</i> ≤ 10	1.683-22.431 -8 ≤ <i>h</i> ≤ 9	1.693-22.436 -8 ≤ <i>h</i> ≤ 9	1.711-22.437 -8 ≤ <i>h</i> ≤ 10
Index ranges	-15 ≤ <i>k</i> ≤ 15	-14 ≤ <i>k</i> ≤ 14	-14 ≤ <i>k</i> ≤ 14	-14 ≤ <i>k</i> ≤ 14
	-28 ≤ <i>l</i> ≤ 28	-27 ≤ <i>l</i> ≤ 27	-27 ≤ <i>l</i> ≤ 27	-27 ≤ <i>l</i> ≤ 27
Reflections	19013	17242	17211	16375
Coverage to 0.65 Å [%]	41.2	39.1	39.3	41.3
<i>I</i> /σ(<i>I</i>)	34.6	44.4	46.5	47.6
Average redundancy	7.2	7.4	7.5	7.1
<i>R</i> _{int}	0.0549	0.0508	0.0483	0.0446
<i>R</i> _{sigma}	0.0288	0.0225	0.0215	0.0210
Unique reflections	2690	2338	2291	2313
Reflections <i>I</i> > 2 σ(<i>I</i>)	2513	2247	2184	2185
Parameters (restraints)	215 (0)	215 (0)	215 (0)	215 (0)
Goodness-of-Fit on <i>F</i> ²	1.061	1.081	1.062	1.094
<i>R</i> ₁ [<i>I</i> > 2 σ(<i>I</i>)],	0.0293	0.0277	0.0267	0.0311
(<i>R</i> ₁ all data)	0.0317	0.0288	0.0282	0.0332
<i>wR</i> ₂ [<i>I</i> > 2 σ(<i>I</i>)],	0.0762	0.0731	0.0698	0.0796
(<i>wR</i> ₂ all data)	0.0778	0.0736	0.0708	0.0806
Largest diff. peak and hole [e Å ⁻³]	0.179 and -0.297	0.209 and -0.222	0.266 and -0.244	0.271 and -0.416
CCDC number	1832118	1832119	1832120	1832121

Table S5: Crystallographic data and parameters from the X-ray data reduction and refinement of the **3-Hf** structure at the five different pressure points between 0 and 4.0(1) GPa collected with I μ S system.

<i>Crystal Parameters:</i>						
Formula, FW [g mol ⁻¹]	C ₄₂ H ₄₈ O ₂ HfSi, 791.38,					
F000	1608.0					
Crystal system, space group, Z:	Monoclinic, I2/a, 4					
P [GPa]	0	1.1(1)	2.1(1)	3.3(1)	4.0(1)	
<i>a</i> [Å]	18.499(8)	18.117(9)	17.830(7)	17.636(8)	17.492(8)	
<i>b</i> [Å]	9.8948(3)	9.6368(3)	9.4989(3)	9.4100(3)	9.3924(3)	
<i>c</i> [Å]	18.7755(6)	18.2893(7)	17.9061(6)	17.5509(6)	17.3845(6)	
β [°]	90.731(7)	89.649(8)	88.708(7)	87.700(9)	87.215(10)	
<i>V</i> [Å ³]	3436.5(14)	3193.0(15)	3032.0(12)	2910.3(14)	2825.7(14)	
Reflections (cell)	19690	18299	17462	15778	15491	
λ [Å]	0.56087					
ρ_{calc} [g cm ⁻³]	1.530	1.646	1.734	1.806	1.843	
μ [mm ⁻¹]	1.680	1.808	1.904	1.984	2.024	
<i>T</i> _{min} , <i>T</i> _{max}	0.94307, 1.000	0.89082, 1.000	0.95137, 1.000	0.88856, 1.000	0.89803, 1.000	
θ range [°]	1.712–21.979 -7 ≤ <i>h</i> ≤ 7	1.757–22.033 -7 ≤ <i>h</i> ≤ 7	1.795–21.977 -7 ≤ <i>h</i> ≤ 7	1.833–22.028 -7 ≤ <i>h</i> ≤ 7	1.851–21.995 -7 ≤ <i>h</i> ≤ 7	
Index ranges	-13 ≤ <i>k</i> ≤ 13 -25 ≤ <i>l</i> ≤ 25	-12 ≤ <i>k</i> ≤ 12 -24 ≤ <i>l</i> ≤ 24	-12 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 23	-12 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 23	-12 ≤ <i>k</i> ≤ 12 -23 ≤ <i>l</i> ≤ 23	
Reflections	26623	24561	23389	22219	21960	
Coverage to 0.75 Å [%]	37.0	37.2	37.5	37.4	37.1	
<i>I</i> /σ(<i>I</i>)	42.6	45.5	56.5	52.1	55.6	
Average redundancy	16.5	16.2	16.3	15.9	16.3	
<i>R</i> _{int}	0.0611	0.0601	0.0499	0.0528	0.0507	
<i>R</i> _{sigma}	0.0235	0.0220	0.0177	0.0192	0.0180	
Unique reflections	1583	1489	1411	1366	1320	
Reflections <i>I</i> > 2 σ(<i>I</i>)	1451	1419	1326	1234	1194	
Parameters (restraints)	170 (42)	170 (42)	170 (42)	170 (42)	170 (42)	
Goodness-of-Fit on <i>F</i> ²	1.068	1.131	1.080	1.121	1.095	
<i>R</i> ₁ [<i>I</i> > 2 σ(<i>I</i>)],	0.0248	0.0213	0.0210	0.0215	0.0219	
(<i>R</i> ₁ all data)	0.0311	0.0239	0.0245	0.0271	0.0273	
<i>wR</i> ₂ [<i>I</i> > 2 σ(<i>I</i>)],	0.0501	0.0455	0.0460	0.0448	0.0474	
(<i>wR</i> ₂ all data)	0.0519	0.0462	0.0472	0.0467	0.0490	
Largest diff. peak and hole [e Å ⁻³]	0.321 and -0.314	0.295 and -0.309	0.317 and -0.261	0.289 and -0.234	0.363 and -0.224	
CCDC number	1832122	1832123	1832124	1832125	1832126	

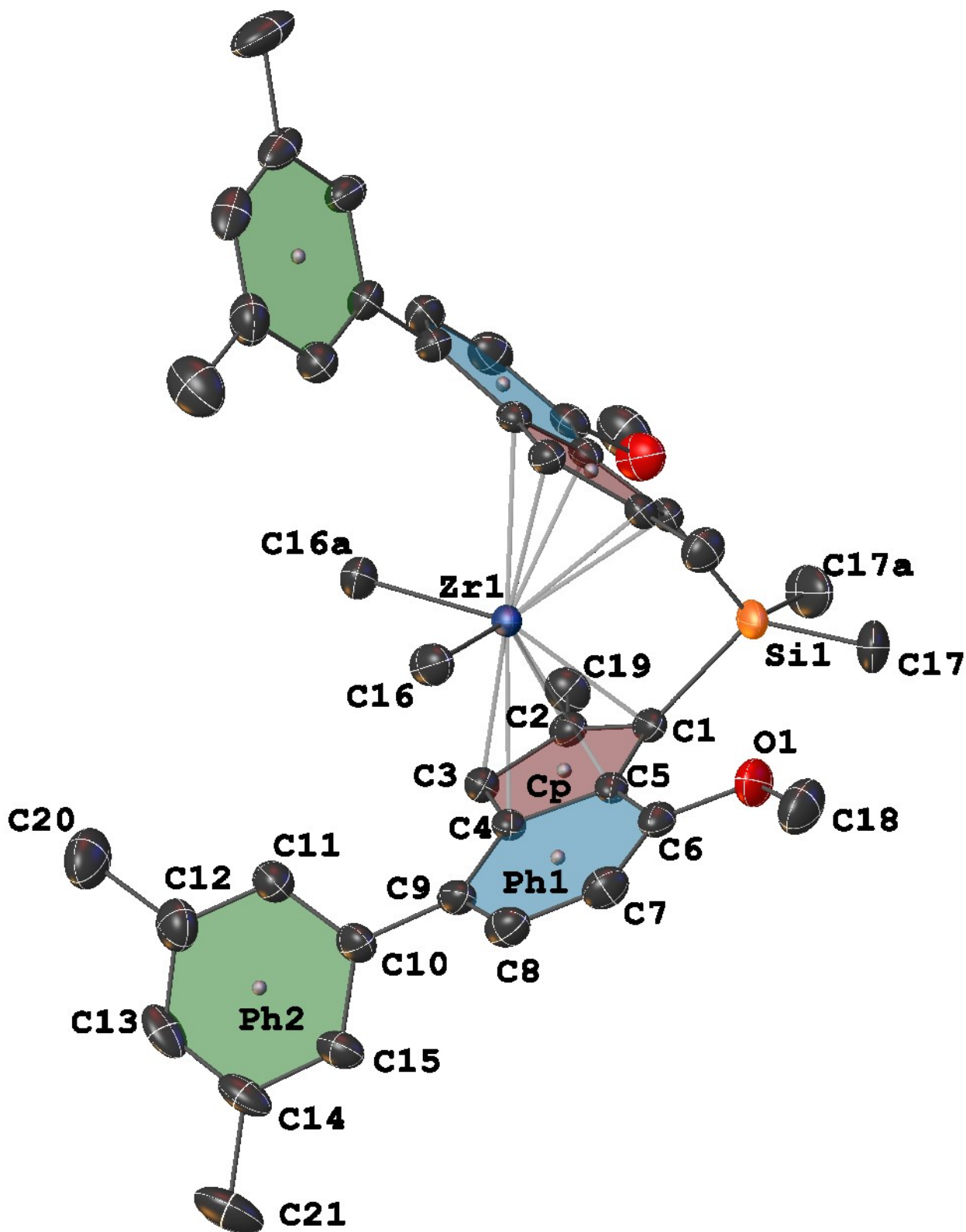


Figure S35: Labeling scheme of the unconstrained refined atoms. Atomic displacement ellipsoids are drawn at 50 % probability level. Cp, Ph1 and Ph2 are the calculated centroids by Olex2 of mean plane spanned by the Cp- and Ph-rings of the Shelxl-14 refined C1 to C5, C4 to C9 and C10 to C15 atoms, respectively.²⁶ The structural model is from **3-Zr** at $P = 1.2(1)$ GPa.

Table S6: Pressure dependency of selected heteroatomic bond distances of **3-Zr** with estimated standard uncertainties (esd).

Distances [Å]				
P [GPa]	0	1.2(1)	1.8(1)	3.0(1)
Zr1—C16	2.272(3)	2.260(3)	2.264(3)	2.255(4)
Zr1—Cp	2.2670(15)	2.2430(15)	2.2335(16)	2.2213(18)
Zr1—C1	2.495(2)	2.483(2)	2.481(2)	2.474(3)
Zr1—C2	2.533(4)	2.526(4)	2.530(4)	2.527(5)
Zr1—C3	2.601(5)	2.576(5)	2.561(5)	2.567(6)
Zr1—C4	2.669(3)	2.634(3)	2.618(3)	2.595(3)
Zr1—C5	2.5713(18)	2.5400(17)	2.5253(17)	2.503(2)
Si1—C1	1.909(3)	1.897(3)	1.896(3)	1.890(3)
Si1—C17	1.881(4)	1.876(4)	1.875(4)	1.870(5)
O1—C6	1.364(4)	1.353(4)	1.350(4)	1.351(5)
O1—Cl8	1.423(7)	1.436(7)	1.429(7)	1.423(7)

Table S7: Pressure dependency of selected heteroatomic bond distances of **3-Hf** with esds.

Distances [Å]					
P [GPa]	0	1.1(1)	2.1(1)	3.3(1)	4.0(1)
Hf1—C16	2.262(8)	2.253(7)	2.239(6)	2.226(7)	2.219(7)
Hf1—Cp	2.254(4)	2.236(3)	2.228(4)	2.214(4)	2.205(4)
Hf1—C1	2.494(6)	2.487(5)	2.485(5)	2.481(5)	2.479(6)
Hf1—C2	2.508(9)	2.514(9)	2.515(9)	2.519(9)	2.520(10)
Hf1—C3	2.581(11)	2.563(10)	2.555(11)	2.546(11)	2.538(12)
Hf1—C4	2.656(7)	2.629(6)	2.611(6)	2.587(7)	2.573(7)
Hf1—C5	2.568(4)	2.539(4)	2.521(4)	2.495(4)	2.479(4)
Si1—C1	1.906(7)	1.902(6)	1.904(6)	1.903(6)	1.898(7)
Si1—C17	1.878(9)	1.880(8)	1.880(8)	1.866(8)	1.866(9)
O1—C6	1.358(9)	1.357(8)	1.352(8)	1.356(9)	1.359(9)
O1—Cl8	1.441(14)	1.433(12)	1.414(12)	1.421(13)	1.413(13)

Table S8: Pressure dependency of selected bond angles of **3-Zr** with esds.

Angle [°]				
<i>P</i> [GPa]	0	1.2(1)	1.8(1)	3.0(1)
bite	59.2(2)	57.9(2)	57.1(2)	56.9(2)
Cp—Zr1—Cpa	129.46(5)	129.68(5)	129.70(5)	129.73(6)
C16—Zr1—C16a	97.13(17)	96.91(17)	96.63(16)	95.78(19)
C1—Si1—C1a	96.85(14)	96.53(15)	96.63(15)	96.25(18)
Cp—Si1—Cpa	82.32(5)	81.67(5)	81.43(5)	81.05(6)
Si1—C1—Cp	161.4(2)	161.0(2)	160.6(2)	160.6(2)
Twist: Ph1—Ph2	46.8(2)	47.0(2)	46.8(2)	46.9(2)

Table S9: Pressure dependency of selected bond angles of **3-Hf** with esds.

Angle [°]					
<i>P</i> [GPa]	0	1.1(1)	2.1(1)	3.3(1)	4.0(1)
bite	58.7(5)	57.6(4)	56.7(4)	55.9(5)	55.6(5)
Cp—Hf1—Cpa	129.39(12)	129.63(11)	129.78(11)	129.74(11)	129.46(12)
C16—Hf1—C16a	96.7(4)	96.6(3)	96.1(3)	94.8(3)	94.2(4)
C1—Si1—C1a	96.8(4)	96.5(3)	96.7(3)	96.7(4)	96.3(4)
Cp—Si1—Cpa	81.89(13)	81.30(11)	81.08(12)	80.72(12)	80.32(13)
Si1—C1—Cp	161.0(4)	160.7(4)	160.1(4)	159.7(4)	159.7(4)
Twist: Ph1—Ph2	46.2(3)	46.5(3)	46.6(3)	46.7(3)	46.7(3)

11. Overview of the Structural Changes in **3** with increasing Pressure

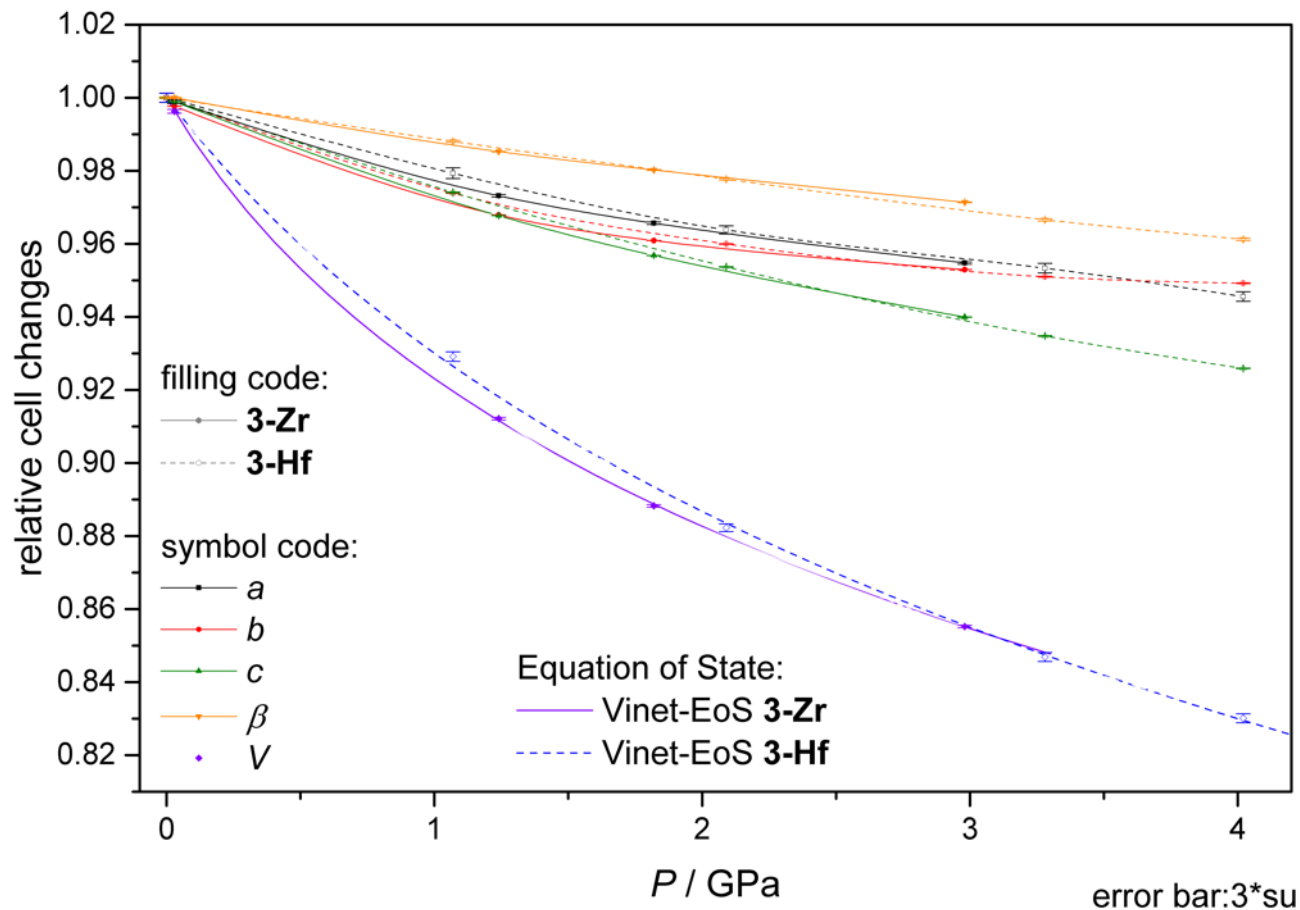


Figure S36: Evolution of the lattice parameters with increasing pressure normalized to the values at 0.0(1) GPa. The error bars, which represent three times the estimated standard uncertainty, are roughly of the size of the symbols. For the volume the pressure dependency is fitted by the 3rd order Vinet equation of state (EoS) applying the EoSFit7-GUI suite.^{31–34}

Table S10: Obtained parameters from fitting of the 3rd order Vinet-EoS to the experimental $P - V$ -data. V_0 is the initial volume, K_0 is the Bulk modulus at $P = 0$ GPa and K'_0 is the first partial derivative of K_0 with respect to P .

Parameter	3-Zr	3-Hf
$V_0 / \text{\AA}$	3436 (14)	3436.5 (15)
K_0 / GPa	8.0 (16)	10.3 (12)
K'_0	11 (3)	8.1 (14)

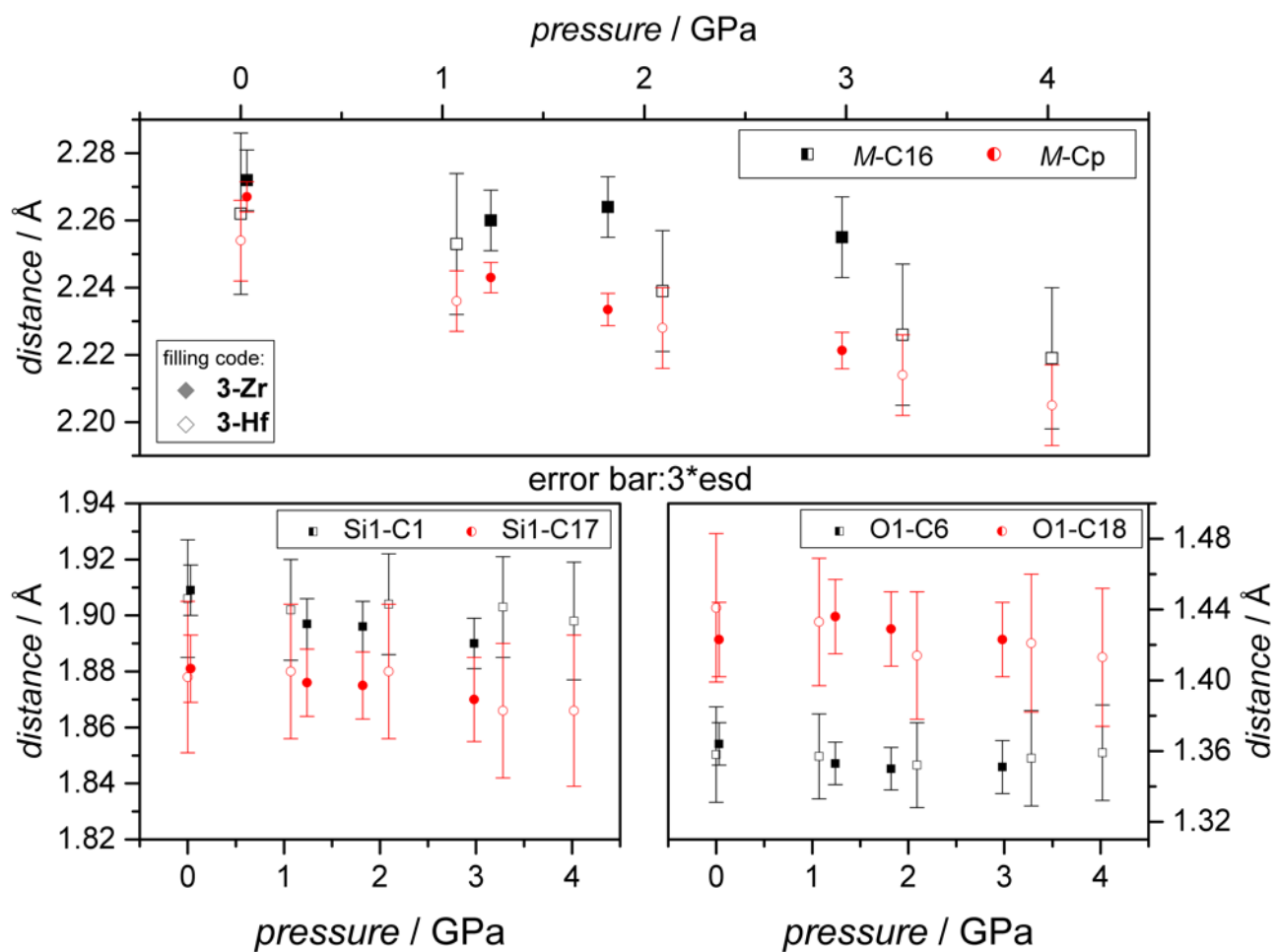


Figure S37: Evolution of the M—C16, M—Cp, Si1—C1, Si1—C17, O1—C6 and O1—C18 bond distances with increasing pressure. The error bars represent 3 times the esd of the structure refinement.

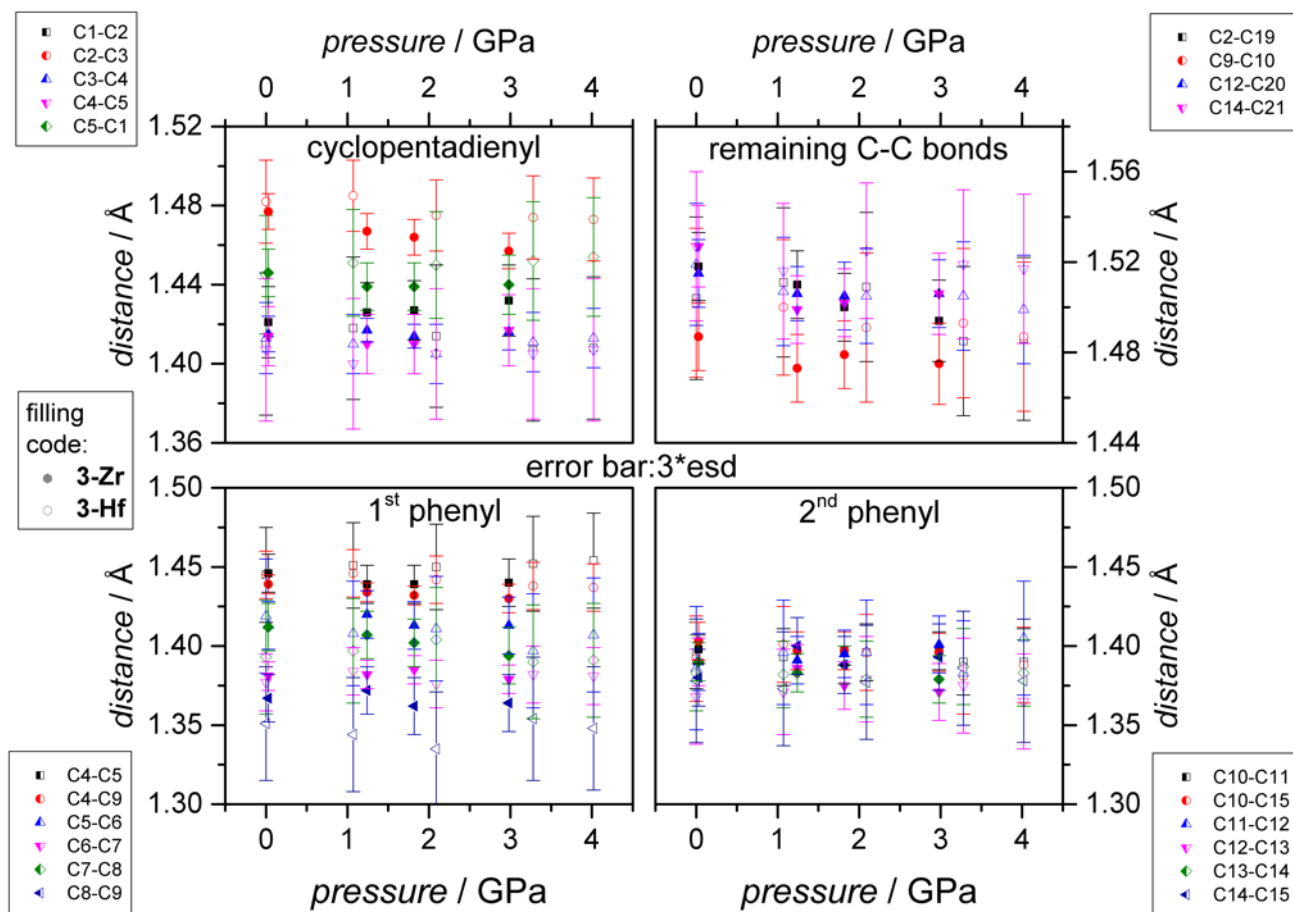


Figure S38: Evolution of the C—C bond distances in with increasing pressure. The error bars represent 3 times the esd of the structure refinement.

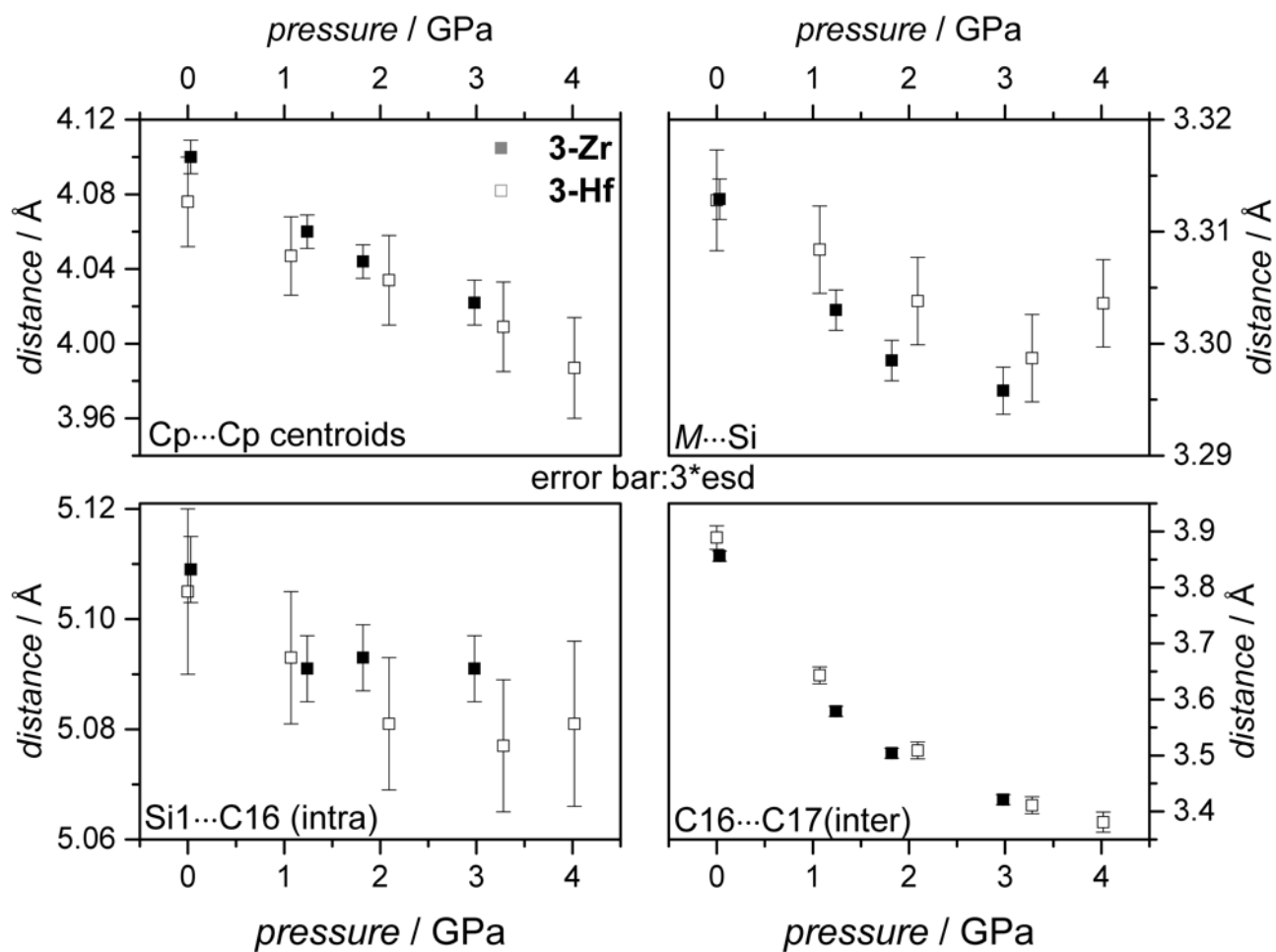


Figure S39: Evolution of the Cp...Cp, M...Si1, Si1...C16 and C16...C17 distances with increasing pressure. The error bars represent 3 times the esd of the structure refinement.

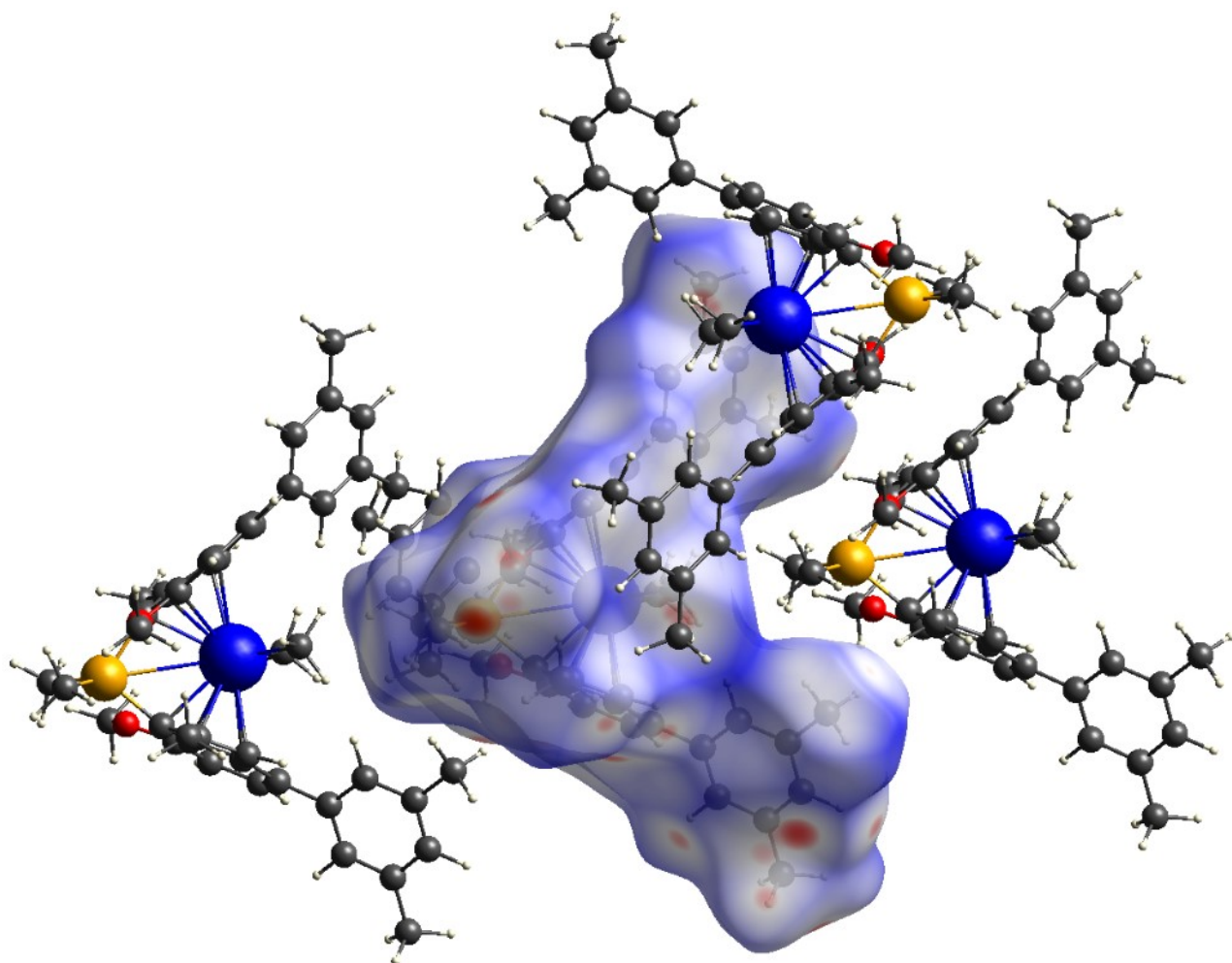
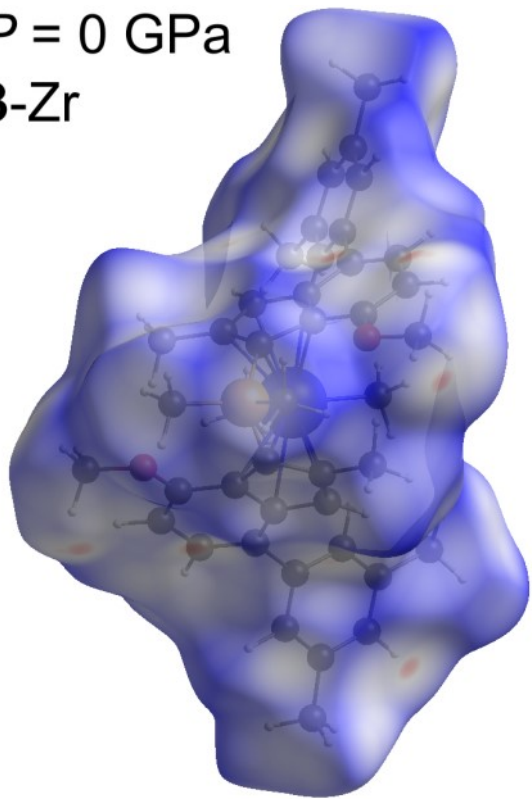
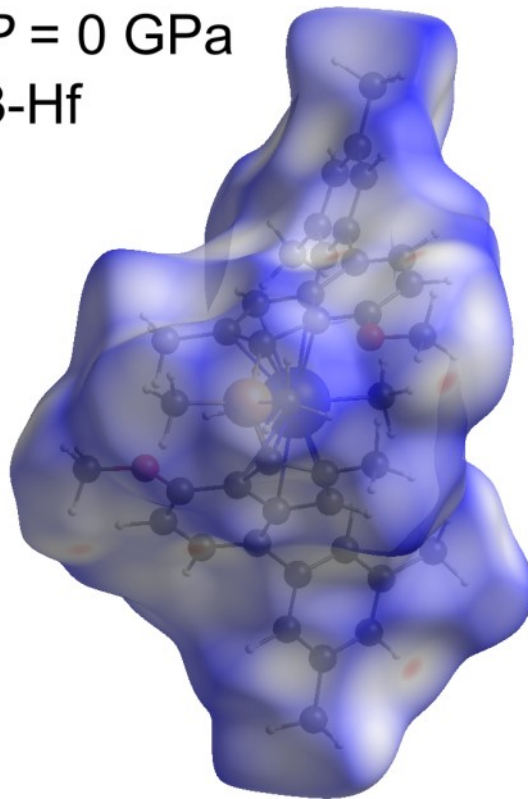


Figure S40: Section of the crystal packing. The V-shaped molecules are stacked along the b -axis. For the molecule in the middle the Hirshfeld surface is plotted.^{28,29}

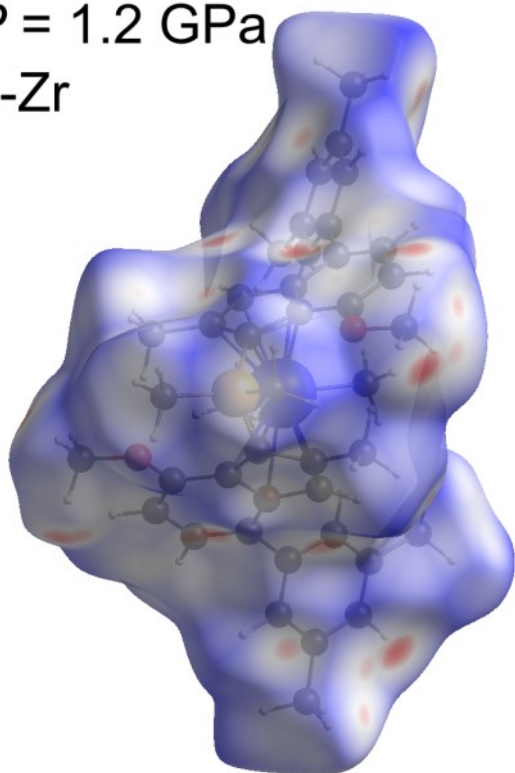
$P = 0$ GPa
3-Zr



$P = 0$ GPa
3-Hf



$P = 1.2$ GPa
3-Zr



$P = 1.1$ GPa
3-Hf

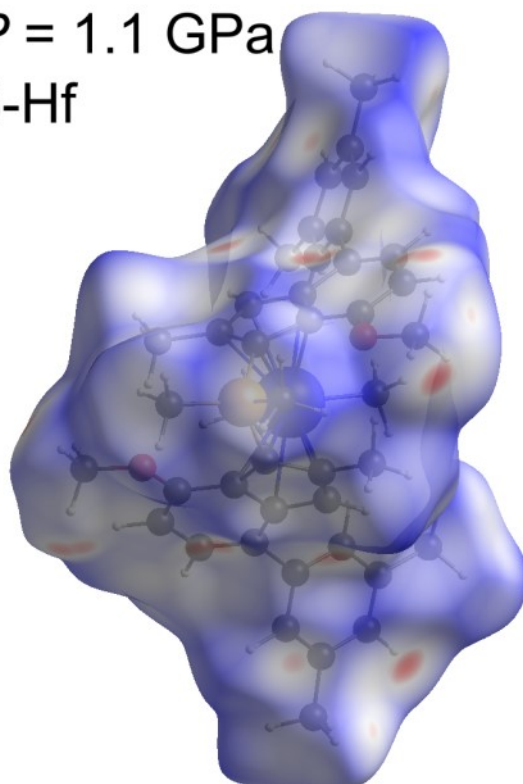
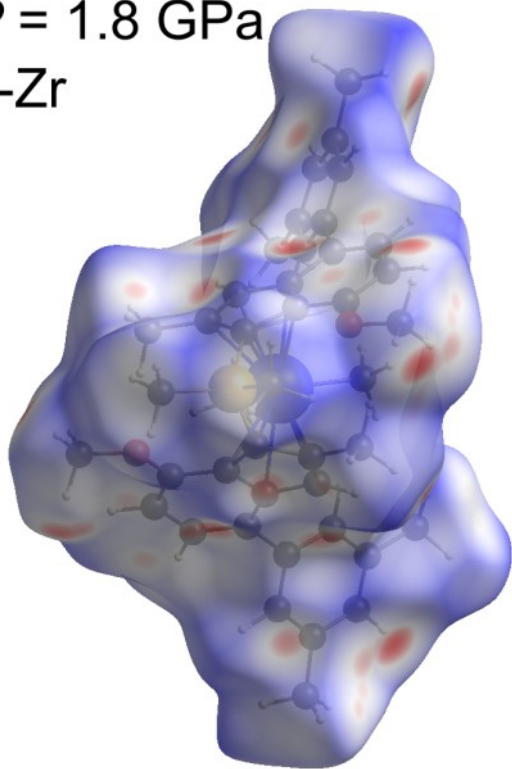
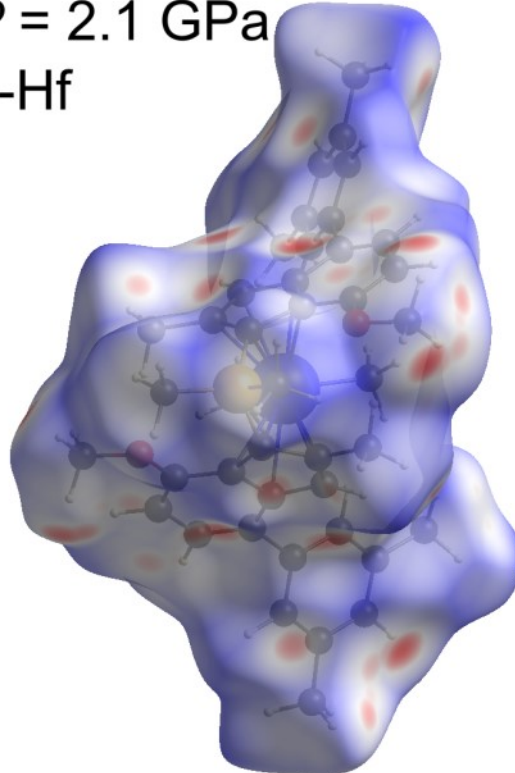


Figure S41: Evolution of the Hirshfeld surfaces with increasing pressure. The normalized contact distance d_{norm} is mapped on the surface.^{28,30} Color coding ranges from blue over white to red.^{28,30} Blue color indicates longer intermolecular distances than the sum of the van der Waals radii (vdW). Red color represents a shorter distance than the sum of the vdW-radii. Pressure range: 0-1.2 GPa

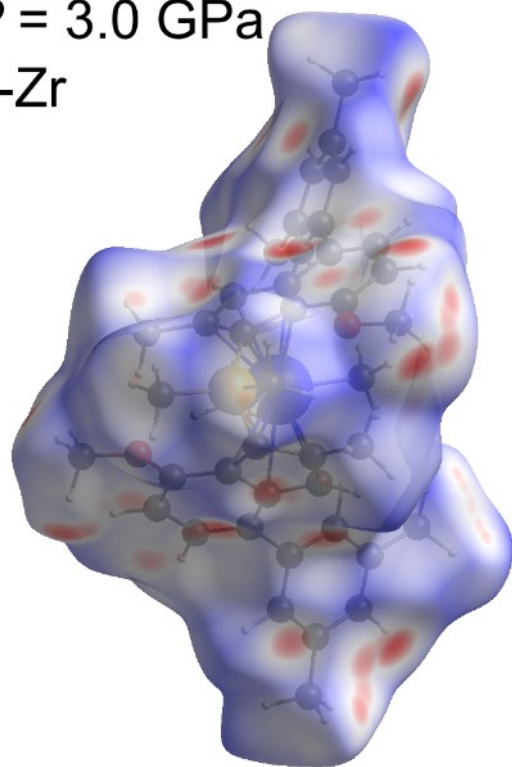
$P = 1.8$ GPa
3-Zr



$P = 2.1$ GPa
3-Hf



$P = 3.0$ GPa
3-Zr



$P = 3.3$ GPa
3-Hf

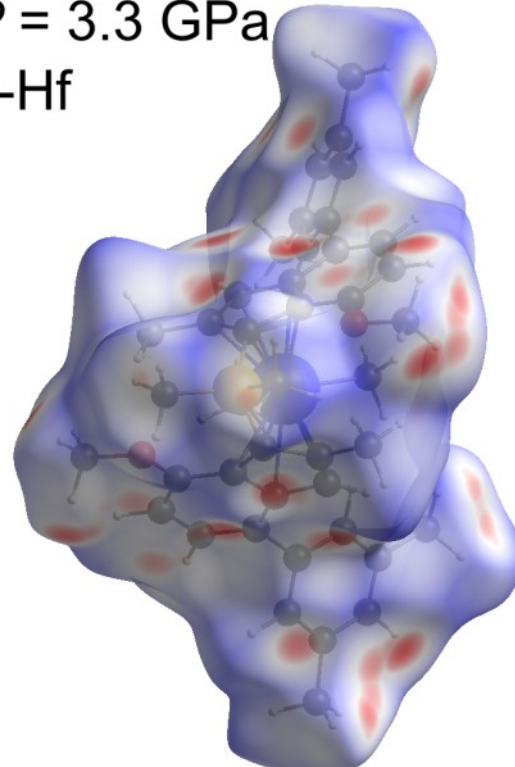


Figure S42: Evolution of the Hirshfeld surfaces with increasing pressure. The normalized contact distance d_{norm} is mapped on the surface.^{28,30} Color coding ranges from blue over white to red.^{28,30} Blue color indicates longer intermolecular distances than the sum of the van der Waals radii (vdW). Red color represents a shorter distance than the sum of the vdW-radii. Pressure range: 1.8-3.3 GPa

$P = 4.0$ GPa
3-Hf

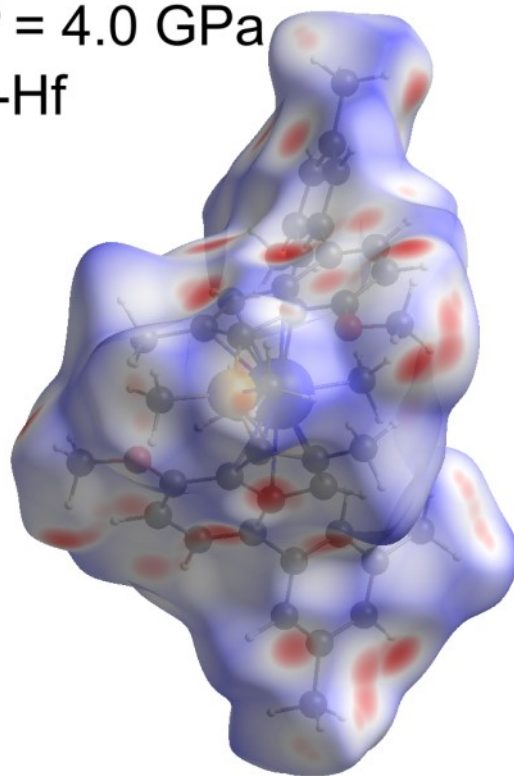


Figure S43: Hirshfeld surface of **3-Hf** at $P = 4$ GPa. The normalized contact distance d_{norm} is mapped on the surface.^{28,30} Color coding ranges from blue over white to red.^{28,30} Blue color indicates longer intermolecular distances than the sum of the van der Waals radii (vdW). Red color represents a shorter distance than the sum of the vdW-radii.

12. High resolution charge density refinement details of **3-Ti**, **3-Zr** and **3-Hf**

First, an independent atom model (IAM) refinement for **3-Ti** [**3-Zr**] [**3-Hf**] was carried out using SHELXL^{21,22}. Anisotropic thermal parameters were introduced to describe the thermal motion of all non-hydrogen atoms. The refinement finally converged at $R_1 = 2.67$ [2.16] {1.77}%, $wR_2 = 8.81$ [6.52] {4.40} and $Goof = 1.065$ [1.052] {1.101} for all reflections $F_o > 4\sigma(F_o)$ and 215 [215] {215} parameters. Analyzing the residual electron density $\Delta\rho(r)$, the deepest holes were -0.355 [-0.385] {-0.973} and the highest peaks were 0.728 [1.276] {4.226}. A multipole model was then adopted to describe the aspherical charge density deformation of $\rho(\mathbf{r})$.

According to a method proposed by Stewart,³⁵ the electron density $\rho(\mathbf{r})$ in a crystal is described by a sum of aspherical pseudoatoms at the nuclear positions $\{\mathbf{R}_j\}$.

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{R}_j)$$

Based on the Hansen-Coppens formalism,³⁶ the pseudoatom density ρ_{at} is expressed in terms of multipoles:

$$\rho_{at}(\mathbf{r}) = P_c \rho_{core}(r) + P_v \kappa^3 \rho_{valence}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^l P_{lm\pm} d_{lm\pm}(\theta, \phi)$$

In the refinement of our best model the multipole expansion was truncated at the hexadecapole level ($l_{max} = 4$) for M and Si and at the octupolar level ($l_{max} = 3$) for carbon and oxygen. A bond-directed dipole and quadrupole ($l_{max} = 2$) was introduced for all hydrogen atoms. Core and spherical valence densities were constructed using relativistic wave functions, which are expanded over Slater-type basis functions, as implemented in the databank-file of Volkov and Macchi (VM) provided by the XD2006 suite of programs.³⁷ Single- ξ functions were also taken from the VM databank. The valence configuration of the central M atoms were selected based on the refinements of theoretical structure factors and its extracted QTAIM charges in comparison with the ones obtained directly from the wavefunction.

The atomic coordinates and thermal displacement parameters of all non-hydrogen atoms were optimized along with all multipolar parameters using all data with $\sin\theta/\lambda < 1.0543$ [1.0925] {1.1137} Å⁻¹. During the multipolar refinements the hydrogen positions were restrained with fixed C-H bond distances $r(C-H) = 1.10$ Å for hydrogen atoms bonded to sp³ hybridized carbons atoms and $r(C-H) = 1.08$ Å for hydrogen atoms bonded to sp² hybridized carbon atoms, and their isotropic thermal parameters were related to 1.5 x $U_{eq}(C)$ for methyl (sp³) groups and 1.2 x $U_{eq}(C)$ for all other (sp²) groups.

To reduce the number of independently populated multipole parameters a chemically constrained model was employed. For all Me groups a local C_{3v} pseudo symmetry was imposed and for the oxygen atom as well as C(6)-C(9) a local C_s symmetry was assumed. Furthermore, the dimethylphenyl group was assumed to be C_{2v}-symmetric and all parameters breaking that symmetry have not been refined (with zero occupancies) or constrained to be the same if symmetry related. In contrast to that, all five carbon atoms that are part of the indenyl group and coordinated to the central metal atom were kept fully flexible in order to take the electronic effects due to M-C interactions into account.

In addition, after a multipole model had been applied for all atoms, the thermal motion of the M and Si atoms for **3-Zr** and **3-Hf** were described by an anharmonic model, using the Gram-Charlier expansion³⁸ up to the fourth order. First, all multipolar parameters were kept fixed, and only the positional and thermal parameters of these atoms were refined, to avoid correlation between multipole- and anharmonic thermal parameters. In the next step both multipolar parameters as well as all thermal displacement parameters (also

anharmonic parameters) were refined simultaneously. The validity of the thermal displacement parameters was carefully checked for negative probability density regions in a cube of 2 Å base length around the respective atom using the XDPDF routine. For **3-Zr** and Zr(1) no negative region was found whereas for Si(1) a small fraction of 0.020% of the integrated volume was negative. For **3-Hf** no negative region was found, despite the higher degree of anharmonic motion.

Individual sets radial scaling parameters (κ , κ') were adopted for the M, Si and O atoms, the C atoms of methyl ligands, the C atoms of the methyl group at the Si atom, the C atoms of the remaining methyl groups and finally one set for all the remaining C atoms (7 sets in total) to adjust the spherical atomic density as well as deformation density contributions. The κ - and κ' -values for the hydrogen atoms was kept fixed at the default value of 1.20 and 1.20 at all times, respectively. The total charge of the asymmetric unit was constrained to zero during all refinements.

In order to obtain reference parameters for the multipolar refinements, simplified model systems have been calculated based on the experimental structural parameters for, where the 4-(3',5'-dimethylphenyl)-7-methoxy-2-methylindenyl structural fragment has been replaced by a simple cyclopentadienyl fragment. Hydrogen positions were pre-optimized using Gaussian09 Rev. C³⁹ at the B3LYP/6-311G++(2d,2p) level of theory. For the metal atoms the LANL2TZ(f) basis including effective core potentials (ECP) were used.⁴⁰ The resulting coordinates were then used for an all-electron calculations with ADF at the PBE/QZ4P level of theory for consistency reasons with the VM database as employed in the XD2006 suite of programs. The theoretical structure factors have been calculated with DENPROP using a similar strategy as described elsewhere.^{41,42}

Comparing selected multipolar populations of the Ti-atom in **3-Ti** between experiment and theory shows very good agreement (i.e. H42+ = -0.123(7) and -0.119(1) or H40 = -0.100(8) and -0.096(1) for experiment and theory, respectively, justifying the use of theoretically obtained parameters of the multipolar model in cases where a refinement on the experimental data is hindered by anharmonic motion.

For **3-Zr**, the κ -, and κ' -parameter were taken from the refinement of the theoretical structure factors of the simplified model system.

Due to the high extent of anharmonic motion in **3-Hf** which caused a severe correlation between the multipolar and anharmonic motion parameters all multipolar parameters (charge, populations, κ -, and κ' -parameters) of the Hf atom were fixed and their values taken from the refinement of the theoretical structure factors of the simplified model system. Furthermore the κ' parameter of the Si atom was kept at the default value of 1.0.

The final agreement factors were $R_1 = 1.91$ [1.50] {1.42}% and $wR_2 = 3.25$ [2.37] {2.26}% for 14917 [16879] {18591} reflections ($F_o > 3\sigma(F_o)$) and 461 [486] {473} parameters ($N_{\text{ref}} / N_{\text{var}} = 32.4$ [34.7] {39.3}). The final multipole population parameters, the local coordinate system, fractional coordinates, bond distances, angles and dihedral angles are given in the crystallographic information file (CIF). The residual electron density distribution was almost featureless with the minimum and maximum values of +0.212/-0.200 [+0.268/-0.188] {+0.907/-0.424} e/Å³ throughout the unit cell using a 0.025Å grid using the XDFFT routine ($\sin(\theta/\lambda) < 0.8$ Å⁻¹). The residual electron density values at full data resolution are +0.502/-0.270 [+0.771/-0.307] {+1.606/-1.868}. These values are somewhat higher compared to the ones at lower resolution ($\sin(\theta/\lambda) < 0.8$ Å⁻¹), especially for **3-Zr** and **3-Hf** due to anharmonic motion.

All refinements were carried out with the full-matrix least-square program XDLSM of the XD2006 suite of programs, the quantity minimized was $\varepsilon = \sum w_1 (|F_o| - k|F_c|)^2$, where k is a scale factor, based on all reflections with $F_o > 3\sigma(F_o)$. Weights were taken as $w_1 = 1/\sigma^2(F_o)$ and $w_2 = 1/\sigma^2(F_o^2)$. For sufficient convergence, the all κ -parameters were fixed in the final refinement. Convergence was assumed when a maximal shift/esd $< 10^{-11}$ was achieved. For the topological analysis, critical points of the electron density were searched by using the XDPROP module of the XD2006 suite of programs, which was also employed to calculate the bond paths.

CCDC 1832106 [1832107] { 1832108 } contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif

13. Experimental d-orbital populations at the metal center of **3-Ti**, **3-Zr** and **3-Hf**

Table S11: d-orbital populations derived from refined multipole populations at the metal center.

3-Ti	3-Zr	3-Hf
$z^2 = 0.26143 (0.00649)$	$z^2 = 0.38030 (0.01057)$	$z^2 = 0.36587 (0.00000)$
$xz = 0.30655 (0.00657)$	$xz = 0.36569 (0.01060)$	$xz = 0.41839 (0.00000)$
$yz = 0.66097 (0.00662)$	$yz = 0.64711 (0.01079)$	$yz = 0.70021 (0.00000)$
$x^2-y^2 = 0.34364 (0.00660)$	$x^2-y^2 = 0.21959 (0.01086)$	$x^2-y^2 = 0.44990 (0.00000)$
$xy = 0.33672 (0.00660)$	$xy = 0.40371 (0.01085)$	$xy = 0.45555 (0.00000)$

14. Residual electron density maps of **3-Ti**, **3-Zr** and **3-Hf**

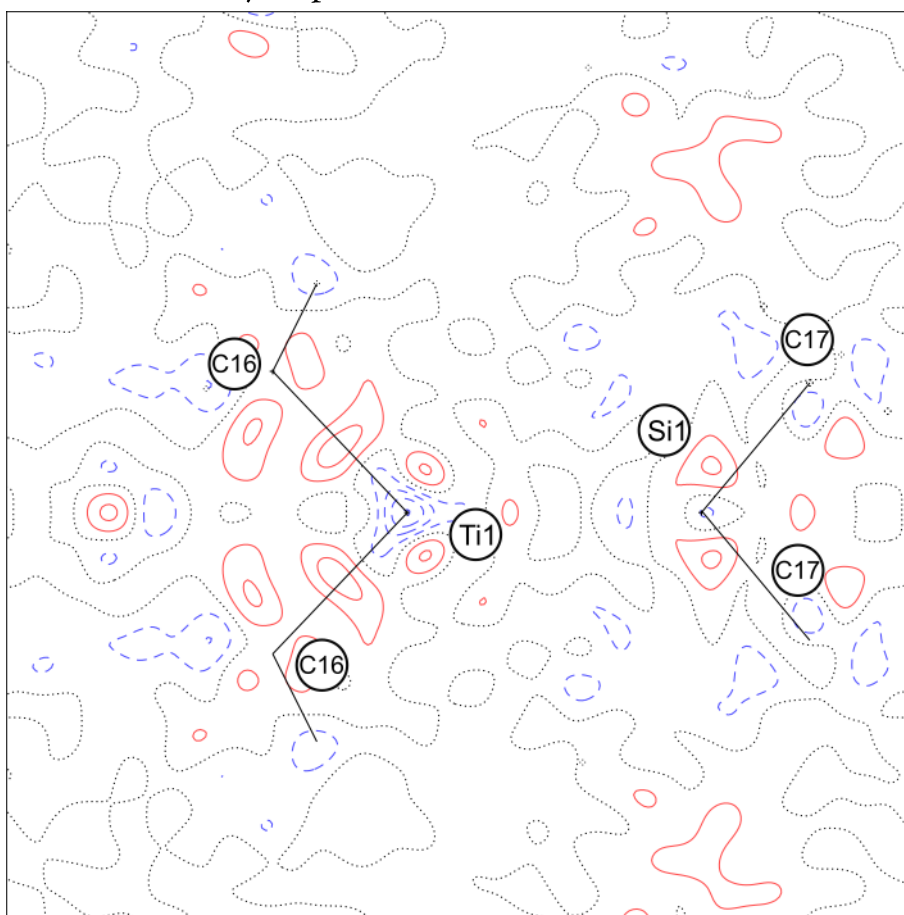


Figure S44: Residual density map of **3-Ti** (data cut-off at $\sin\theta/\lambda = 0.8 \text{ \AA}^{-1}$; contour level intervals = $\pm 0.05 \text{ e/\AA}^3$, positive red, negative blue) in the Ti(1), Si(1), C(16) plane.

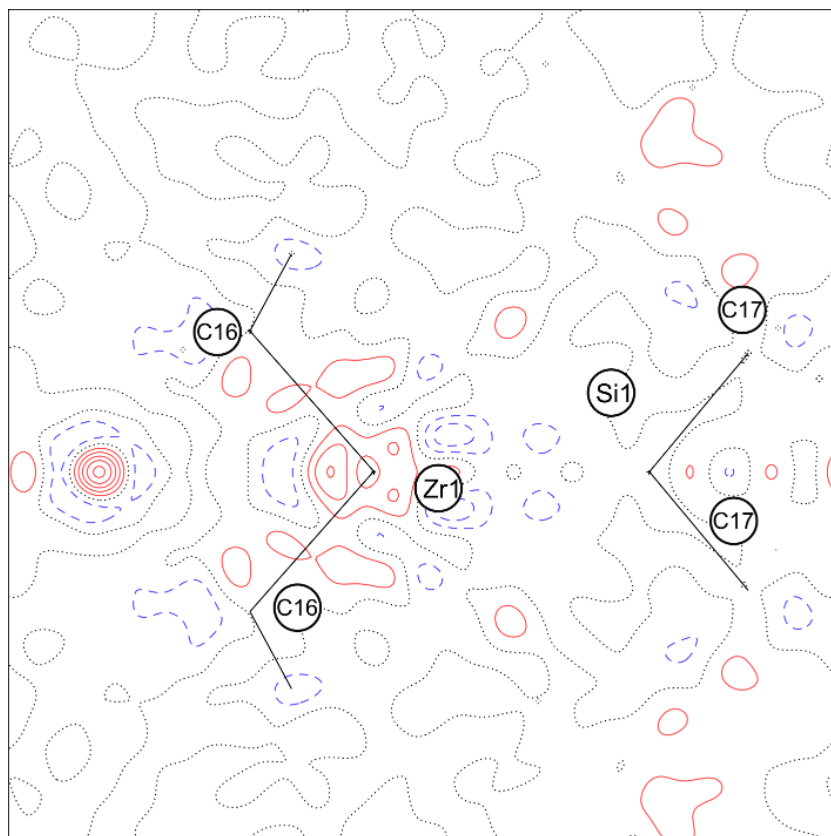


Figure S45: Residual density map of **3-Zr** (data cut-off at $\sin\theta/\lambda = 0.8 \text{ \AA}^{-1}$; contour level intervals = $\pm 0.05 \text{ e/\AA}^3$, positive red, negative blue) in the Zr(1), Si(1), C(16) plane.

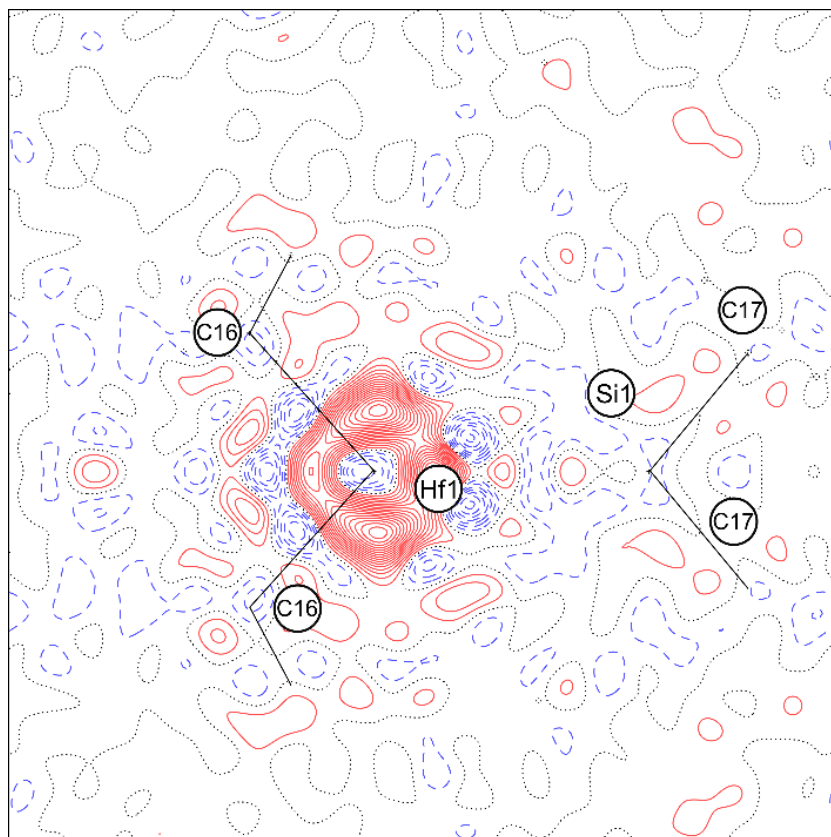


Figure S46: Residual density map of **3-Hf** (data cut-off at $\sin\theta/\lambda = 0.8 \text{ \AA}^{-1}$; contour level intervals = $\pm 0.05 \text{ e/\AA}^3$, positive red, negative blue) in the Ti(1), Si(1), C(16) plane.

15. Scaling and drk plots of 3-Ti, 3-Zr and 3-Hf

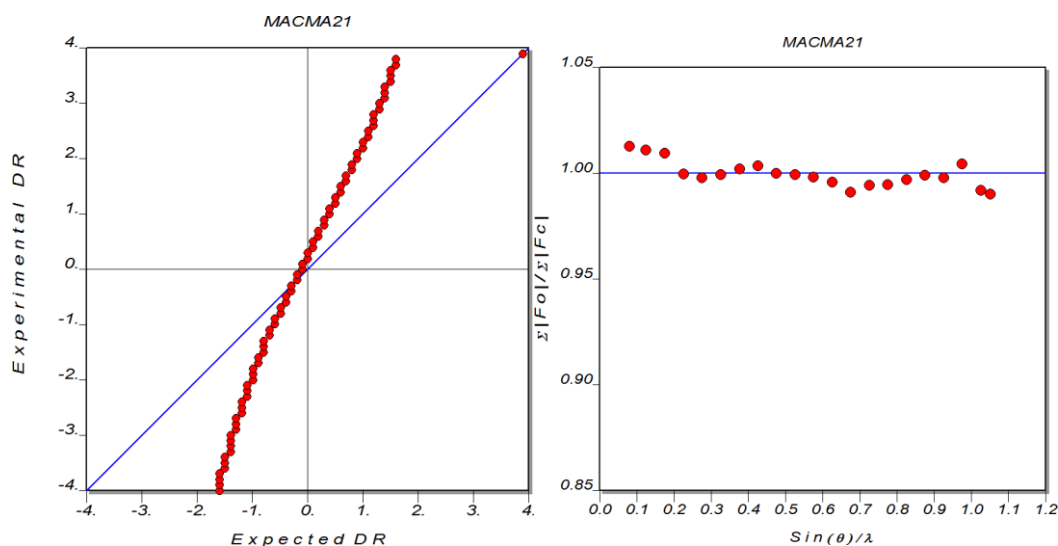


Figure S47: DRK-plot (left) and scaling-plot (right) of 3-Ti.

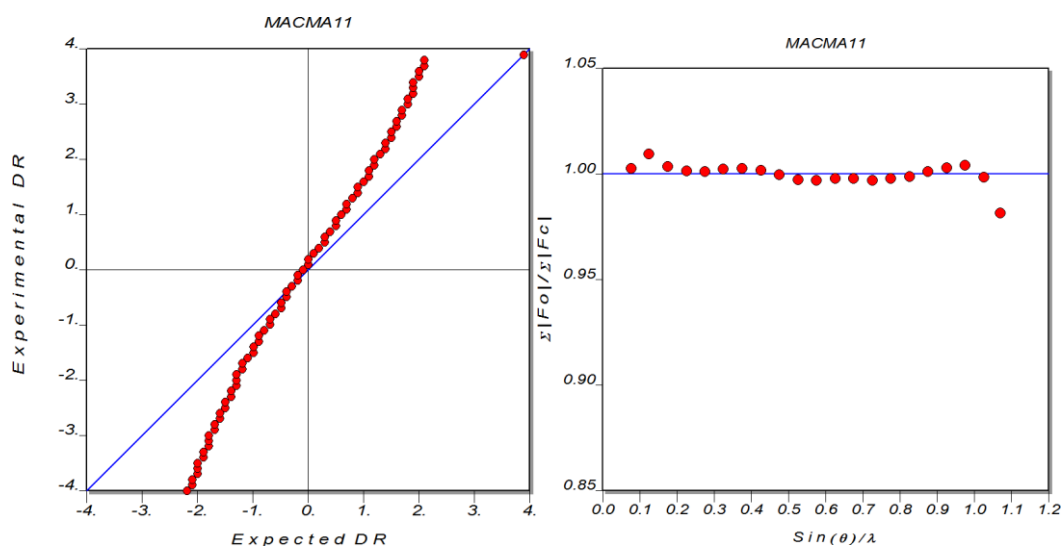


Figure S48: DRK-plot (left) and scaling-plot (right) of 3-Zr.

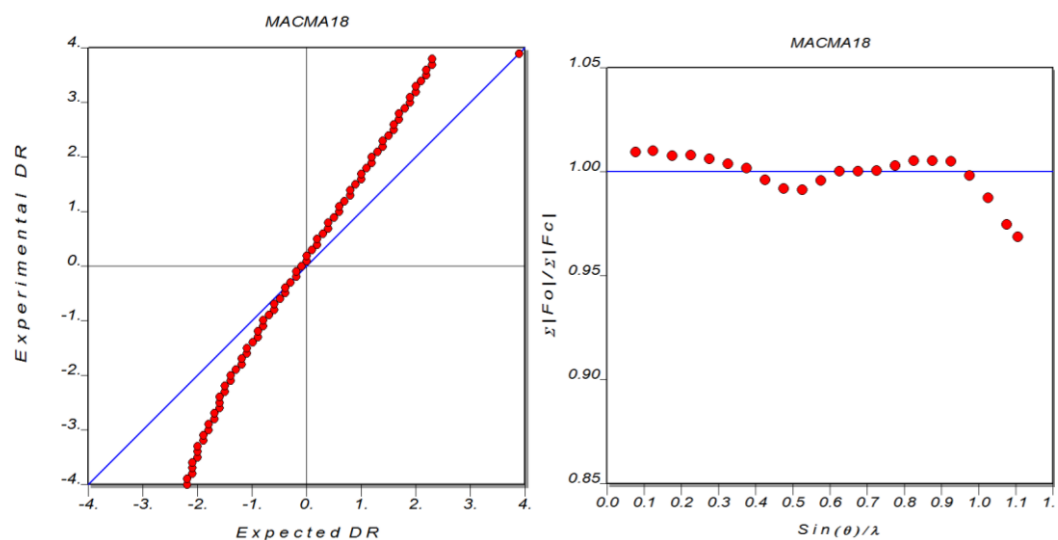


Figure S49: DRK-plot (left) and scaling-plot (right) of 3-Hf.

16. Topological parameters of selected bonds of selected atoms of 3-Ti, 3-Zr and 3-Hf

Table S12: Topological parameters of selected bonds in **3-Ti** in experiment and theory (ADF).

Bond	Method	Distance [Å]	$\rho(\mathbf{r}_c)$ [$e/\text{\AA}^3$]	$\nabla^2\rho(\mathbf{r}_c)$ [$e/\text{\AA}^5$]	r_1 [Å]	r_2 [Å]	ε
Ti(1)-C(16)	Exp.	2.1527(3)	0.531(3)	5.470(3)	1.0696	1.0831	0.06
	DFT ^a	2.1454	0.662	1.110	1.0895	1.0559	0.048
Si(1)-C(1)	Exp.	1.8908(4)	0.807(8)	-0.844(27)	0.7994	1.0922	0.11
	DFT ^a	1.9002	0.778	2.088	0.7507	1.1507	0.098
Si(1)-C(17)	Exp.	1.8730(4)	0.930(8)	-3.604(26)	0.8118	1.0636	0.06
	DFT ^a	1.8864	0.825	1.359	0.7471	1.1400	0.011
C(1)-C(2)	Exp.	1.4438(4)	1.849(7)	-12.076(18)	0.7002	0.7441	0.22
	DFT ^a	1.4474	1.850	-14.878	0.7152	0.7325	0.187
C(2)-C(3)	Exp.	1.4074(4)	2.063(8)	-17.136(18)	0.7099	0.6979	0.25
	DFT ^a	1.4105	2.019	-18.236	0.7071	0.7036	0.220
C(3)-C(4)	Exp.	1.4178(4)	2.031(8)	-17.113(19)	0.7048	0.7137	0.22
	DFT ^a	1.4212	1.974	-17.803	0.7044	0.7171	0.167
C(4)-C(5)	Exp.	1.4415(4)	1.939(7)	-14.964(17)	0.7146	0.7271	0.22
	DFT ^a	1.4511	1.875	-15.915	0.7232	0.7281	0.150
C(5)-C(1)	Exp.	1.4527(4)	1.806(8)	-11.614(20)	0.7769	0.6771	0.20
	DFT ^a	1.4520	1.825	-14.787	0.7400	0.7122	0.156

Table S13: Topological parameters of selected bonds in **3-Zr** in experiment and theory (ADF).

Bond	Method	Distance [Å]	$\rho(\mathbf{r}_c)$ [$e/\text{\AA}^3$]	$\nabla^2\rho(\mathbf{r}_c)$ [$e/\text{\AA}^5$]	r_1 [Å]	r_2 [Å]	ε
Zr(1)-C(16)	Exp.	2.2654(3)	0.584(4)	4.166(4)	1.1762	1.0904	0.12
	DFT ^a	2.2724	0.629	1.481	1.1841	1.0883	0.020
Si(1)-C(1)	Exp.	1.8999(4)	0.834(8)	-0.351(28)	0.7784	1.1217	0.05
	DFT ^a	1.9091	0.767	1.894	0.7538	1.1561	0.100
Si(1)-C(17) 133	Exp.	1.8725(3)	0.922(9)	-0.855(31)	0.7637	1.1097	0.23
	DFT ^a	1.8866	0.825	1.344	0.7472	1.1401	0.015
C(1)-C(2)	Exp.	1.4473(4)	1.892(8)	-13.955(20)	0.7072	0.7405	0.17
	DFT ^a	1.4501	1.839	-14.682	0.7155	0.7347	0.191
C(2)-C(3)	Exp.	1.4095(4)	2.082(9)	-18.200(21)	0.7071	0.7026	0.27
	DFT ^a	1.4111	2.015	-18.101	0.7085	0.7028	0.227
C(3)-C(4)	Exp.	1.4217(3)	2.027(9)	-17.553(21)	0.7169	0.7058	0.23
	DFT ^a	1.4245	1.958	-17.457	0.7053	0.7195	0.173
C(4)-C(5)	Exp.	1.4439(4)	1.928(8)	-15.691(20)	0.7220	0.7224	0.17
	DFT ^a	1.4528	1.865	-15.685	0.7242	0.7288	0.158
C(5)-C(1)	Exp.	1.4576(4)	1.814(8)	-12.801(20)	0.7658	0.6925	0.19
	DFT ^a	1.4570	1.805	-14.364	0.7432	0.7140	0.163

Table S14: Topological parameters of selected bonds in **3-Hf** in experiment and theory (ADF).

Bond	Method	Distance [$\text{\AA}$]	$\rho(\mathbf{r}_c)$ [$\text{e}/\text{\AA}^3$]	$\nabla^2\rho(\mathbf{r}_c)$ [$\text{e}/\text{\AA}^5$]	r_1 [$\text{\AA}$]	r_2 [$\text{\AA}$]	ε
Hf(1)-C(16)	Exp.	2.2443(5)	0.680(6)	4.383(6)	1.1623	1.0820	0.09
	DFT ^a	2.2430	0.665	2.018	1.1733	1.0697	0.036
Si(1)-C(1)	Exp.	1.8988(6)	0.787(15)	2.227(53)	0.7668	1.1329	0.15
	DFT ^a	1.9075	0.769	1.912	0.7532	1.1552	0.088
Si(1)-C(17)	Exp.	1.8725(8)	0.919(16)	-0.265(58)	0.7628	1.1098	0.02
	DFT ^a	1.8873	0.824	1.326	0.7474	1.1406	0.014
C(1)-C(2)	Exp.	1.4455(6)	1.921(14)	-16.117(34)	0.6651	0.7813	0.15
	DFT ^a	1.4493	1.840	-14.679	0.7151	0.7344	0.194
C(2)-C(3)	Exp.	1.4119(7)	2.012(14)	-18.280(32)	0.6803	0.7323	0.30
	DFT ^a	1.4135	2.004	-17.902	0.7097	0.7040	0.226
C(3)-C(4)	Exp.	1.4201(6)	2.023(15)	-19.516(32)	0.6851	0.7361	0.20
	DFT ^a	1.4237	1.959	-17.474	0.7050	0.7191	0.175
C(4)-C(5)	Exp.	1.4444(7)	1.880(14)	-15.738(30)	0.7294	0.7151	0.21
	DFT ^a	1.4531	1.864	-15.677	0.7243	0.7289	0.157
C(5)-C(1)	Exp.	1.4576(6)	1.826(14)	-14.509(32)	0.7798	0.6783	0.16
	DFT ^a	1.4559	1.808	-14.426	0.7425	0.7136	0.163

17. Integrated AIM charges of selected atoms of **3-Ti**, **3-Zr** and **3-Hf**

List of the QTAIM-charges Q given in [e] and $L(\Omega)$: $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ integrated over the atomic basins in [a.u.]; experimental values based on the multipolar refinements of the electron density; theoretical values based on DFT optimized structures.

Table S15. Theoretical (ADF) and experimental QTAIM charges of **3-Ti**, **3-Zr** and **3-Hf**.

Basin		Q	$L(\Omega)$	Q	$L(\Omega)$	Q	$L(\Omega)$
		<i>3-Ti</i>		<i>3-Zr</i>		<i>3-Hf</i>	
M(1)	Exp.	1.648	<0.001	1.746	0.004	1.636	0.003
	DFT ^a	1.649	-0.010	1.939	-0.002	2.024	0.001
Si(1)	Exp.	2.349	-0.006	2.433	-0.008	2.454	-0.010
	DFT ^a	2.663	-0.003	2.652	-0.003	2.649	-0.004
C(16)	Exp.	-0.773	0.002	-1.189	0.008	-1.223	0.002
	DFT ^a	-0.324	-0.020	-0.385	-0.004	-0.406	-0.006
H(16A)	Exp.	0.192	<0.001	0.264	<0.001	0.321	<0.001
	DFT ^a	-0.051	0.006	-0.053	-0.001	-0.049	<0.001
H(16B)	Exp.	0.192	<0.001	0.266	<0.001	0.322	<0.001
	DFT ^a	-0.031	0.007	-0.037	0.006	-0.034	0.007
H(16C)	Exp.	0.194	<0.001	0.270	<0.001	0.324	<0.001
	DFT ^a	-0.031	0.007	-0.031	-0.001	-0.031	<0.001
C(17)	Exp.	-1.135	0.004	-1.093	0.003	-1.417	<0.001
	DFT ^a	-0.607	-0.006	-0.600	-0.003	-0.600	-0.002
H(17A)	Exp.	0.124	<0.001	0.181	<0.001	0.182	0.001
	DFT ^a	0.002	-0.001	0.003	<0.001	0.002	-0.001
H(17B)	Exp.	0.121	<0.001	0.176	<0.001	0.171	<0.001
	DFT ^a	-0.015	0.006	-0.017	0.005	-0.017	<0.001
H(17C)	Exp.	0.122	<0.001	0.179	<0.001	0.170	<0.001
	DFT ^a	-0.015	0.001	-0.018	-0.001	-0.017	0.005
C(1)	Exp.	-0.485	0.003	-0.684	0.005	-0.707	0.003
	DFT ^a	-0.779	-0.002	-0.793	-0.003	-0.794	-0.004
C(2)	Exp.	-0.101	<0.001	-0.130	<0.001	-0.218	<0.001
	DFT ^a	-0.123	<0.001	-0.121	-0.001	-0.129	0.002
C(3)	Exp.	-0.222	<0.001	-0.319	<0.001	-0.258	<0.001
	DFT ^a	-0.128	0.006	-0.152	0.004	-0.152	-0.001
C(4)	Exp.	-0.002	0.001	-0.072	<0.001	-0.088	0.001
	DFT ^a	-0.062	0.003	-0.087	0.003	-0.089	0.004
C(5)	Exp.	-0.227	-0.002	-0.146	-0.001	-0.213	0.001
	DFT ^a	-0.095	<0.001	-0.114	-0.001	-0.118	-0.001

18. Critical points of the Laplacian of the electron density of selected atoms of **3-Ti**, **3-Zr** and **3-Hf**

Table S16: Critical points of the Laplacian of the electron density and their distance to the nuclei for 3-Ti, 3-Zr and 3-Hf in experiment and theory (ADF).

		3-Ti		3-Zr		3-Hf	
		$\nabla^2\rho$	r	$\nabla^2\rho$	r	$\nabla^2\rho$	r
<i>trans</i> -LICC (CC1)	Exp.	-287.64	0.4066	-30.77	0.6009	-	-
	DFT ^a	-299.77	0.4026	-32.21	0.5924	-	-
BCC (CC2)	Exp.	-258.00	0.4079	-25.71	0.6013	-	-
	DFT ^a	-234.54	0.4087	-16.01	0.5989	-	-
<i>trans</i> -LICC(Cp) (CC3)	Exp.	-201.37	0.4109	-16.13	0.6029	-	-
	DFT ^a	-246.49	0.4067	-25.31	0.5927	-	-
BCC(Me) (CC4)	Exp.	-26.84	0.4940	-27.00	0.4965	-33.21	0.4913
	DFT ^a	-17.91	0.4920	-18.32	0.4903	-19.36	0.4886

Table S17: Selected angles of the charge concentrations with respect to the metal center.

		3-Ti	3-Zr	3-Hf
$\angle C-M-C$	Exp.	92.79(1)	97.24(1)	96.00(2)
(reference)	DFT ^a	95.69	100.05	98.12
$\angle CC1-M-CC1$	Exp.	91.20	87.84	-
	DFT ^a	95.96	100.28	-
$\angle CC2-M-CC2$	Exp.	88.08	85.11	-
	DFT ^a	80.25	64.80	-
$\angle CC3-M-CC3$	Exp.	172.81	176.88	-
	DFT ^a	153.37	143.53	-

19. Critical points of the ELI-D of the outer shell of selected atoms **3-Ti**, **3-Zr** and **3-Hf**

Table S18. Critical points of the ELI-D in the valence shell and their distance to the metals centers for **3-Ti**, **3-Zr** and **3-Hf** in theory (ADF).

		3-Ti		3-Zr		3-Hf	
		ELI-D	<i>r</i>	ELI-D	<i>r</i>	ELI-D	<i>r</i>
<i>trans</i> -LICC (ELI-D)	DFT ^a	1.676	0.5381	1.526	0.7168	1.229	0.7491
BCC (ELI-D)	DFT ^a	1.563	0.5263	-	-	-	-
<i>trans</i> -LICC(Cp) (ELI-D)	DFT ^a	1.574	0.5334	1.483	0.7063	1.185	0.7227
LICC(Me) (CC4) (ELI-D)	DFT ^a	1.772	0.7477	1.779	0.7417	1.780	0.7296

Table S19. Selected angles of the critical points in the ELI-D with respect to the metal center.

∠CC1-M-CC1 (ELI-D)	DFT ^a	96.59	101.71	99.90
∠CC2-M-CC2 (ELI-D)	DFT ^a	83.75	-	-
∠CC3-M-CC3 (ELI-D)	DFT ^a	153.67	140.20	140.53

20. Experimental and theoretical Laplacian maps of **3-Zr** and **3-Hf**

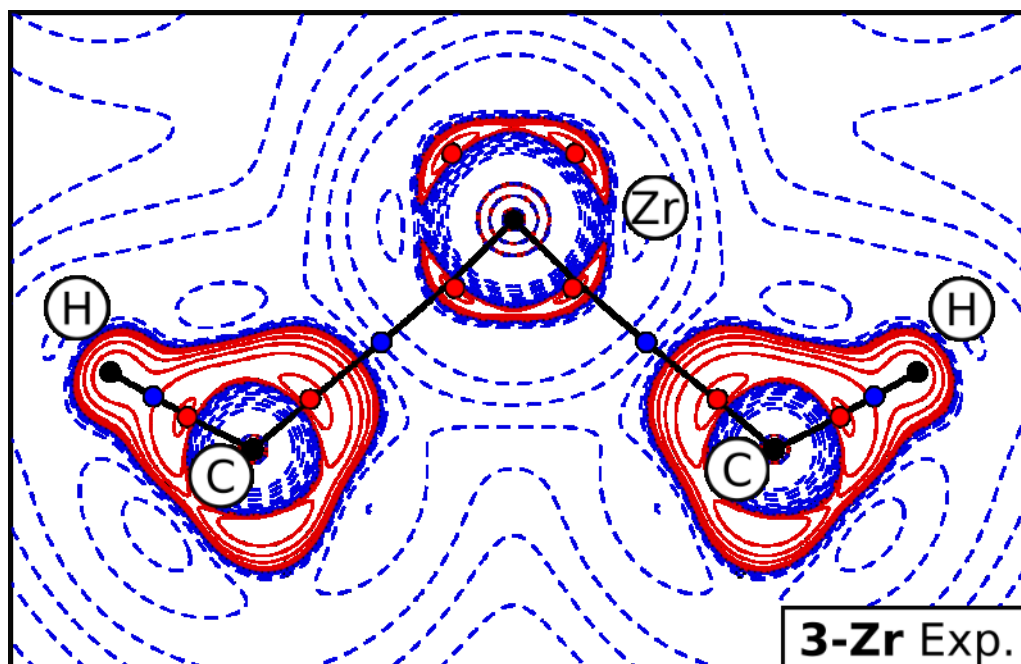


Figure S50: Experimental $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ map of **3-Zr** in the plane defined by *M* and the two methyl ligands; positive (red, solid) and negative (blue, dashed). $L(\mathbf{r})$ contour lines were drawn at $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n$ e/Å⁵ with $n = \pm 2, \pm 1, 0$. Bond paths are displayed as black solid lines. Bond critical points and charge concentrations are drawn as blue and red filled circles, respectively.

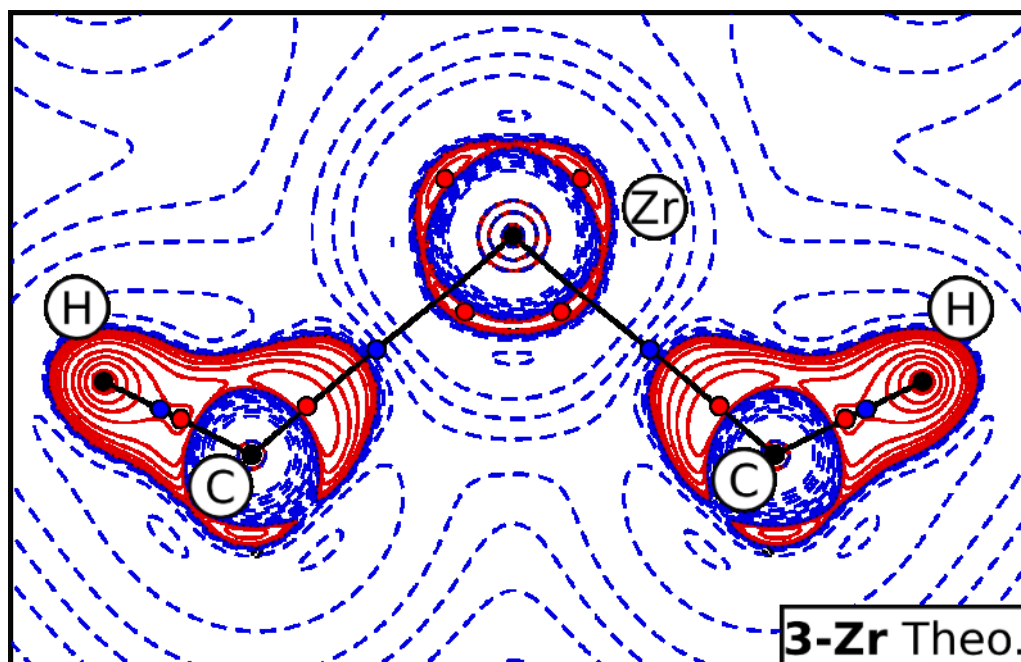


Figure S51: Theoretical (ADF) $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ map of **3-Zr** in the plane defined by *M* and the two methyl ligands; positive (red, solid) and negative (blue, dashed). $L(\mathbf{r})$ contour lines were drawn at $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n$ e/Å⁵ with $n = \pm 2, \pm 1, 0$. Bond paths are displayed as black solid lines. Bond critical points and charge concentrations are drawn as blue and red filled circles, respectively.

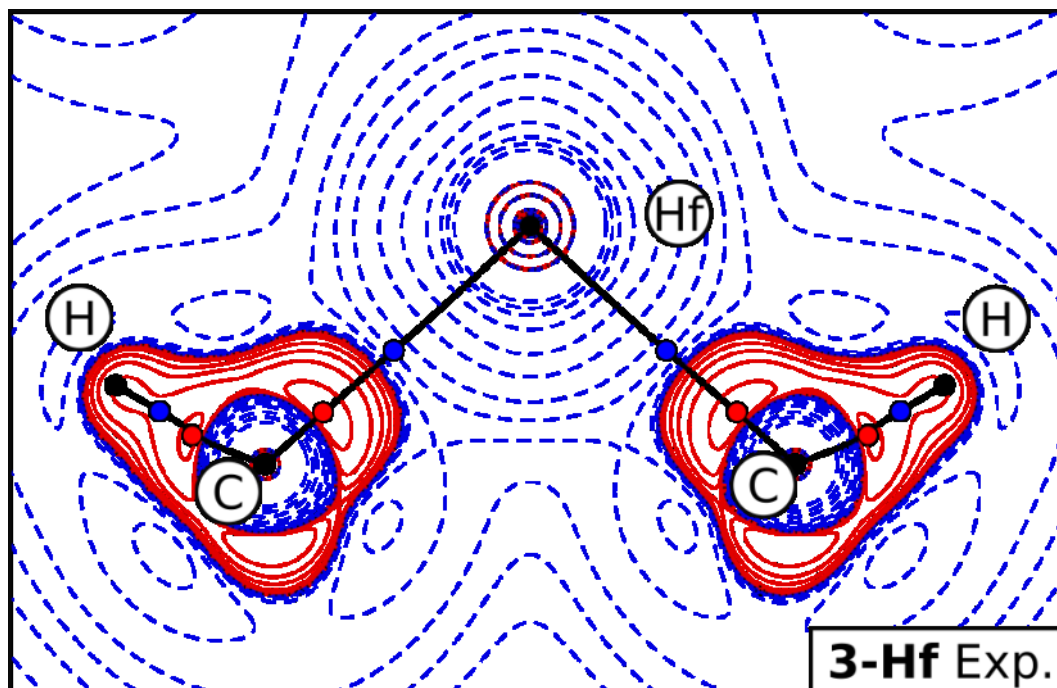


Figure S52: Experimental $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ map of **3-Hf** in the plane defined by *M* and the two methyl ligands; positive (red, solid) and negative (blue, dashed). $L(\mathbf{r})$ contour lines were drawn at $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n$ e/Å⁵ with $n = \pm 2, \pm 1, 0$. Bond paths are displayed as black solid lines. Bond critical points and charge concentrations are drawn as blue and red filled circles, respectively.

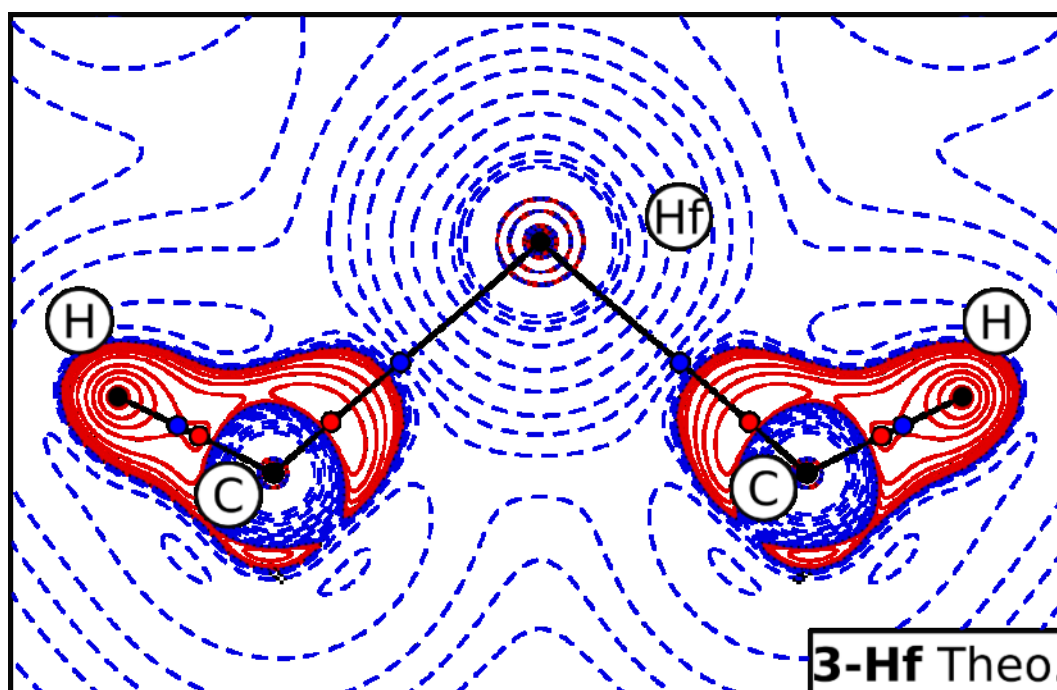


Figure S53: Theoretical (ADF) $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ map of **3-Zr** in the plane defined by *M* and the two methyl ligands; positive (red, solid) and negative (blue, dashed). $L(\mathbf{r})$ contour lines were drawn at $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n$ e/Å⁵ with $n = \pm 2, \pm 1, 0$. Bond paths are displayed as black solid lines. Bond critical points and charge concentrations are drawn as blue and red filled circles, respectively.

21. Experimental and theoretical Laplacian 3D-isosurface plot of **3-Ti** and **3-Zr**

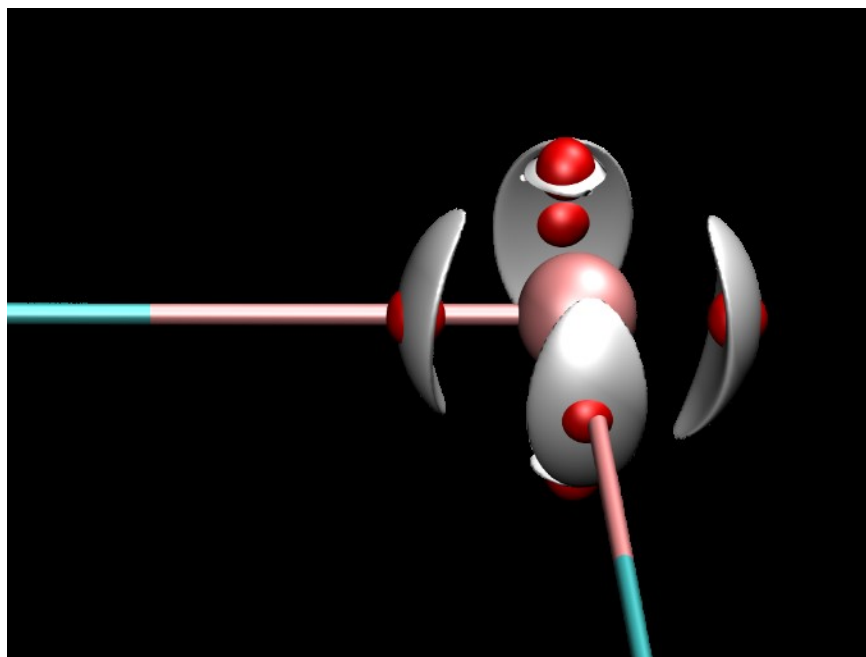


Figure S54: Experimental 3D isosurface plot of the Laplacian ($\nabla^2\rho = -192\text{e}/\text{\AA}^5$) of **3-Ti** at the metal atom. Ti-Me bonds are shown as sticks. The position of valence shell charge concentration maxima are shown as red spheres.

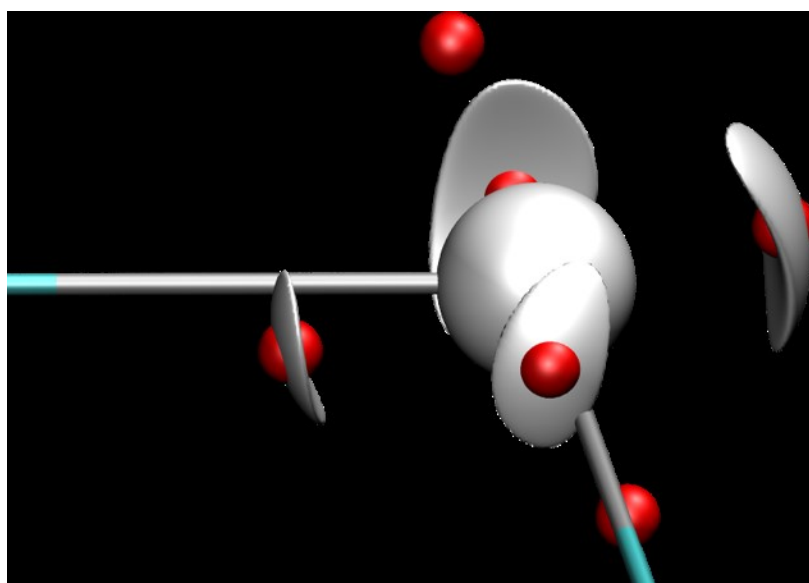


Figure S55: Experimental 3D isosurface plot of the Laplacian ($\nabla^2\rho = -14.94\text{e}/\text{\AA}^5$) of **3-Zr** at the metal atom. Zr-Me bonds are shown as sticks. The position of valence shell charge concentration maxima are shown as red spheres.

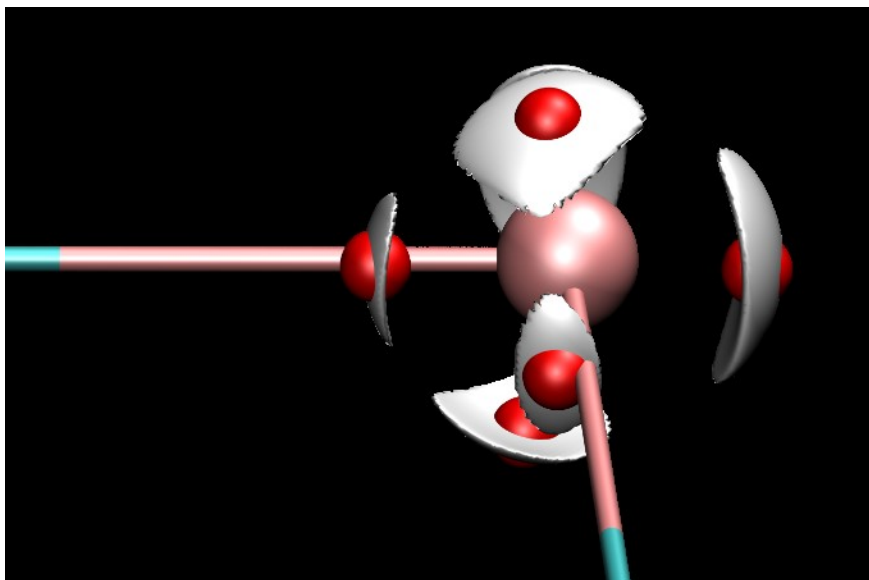


Figure S56: Theoretical 3D isosurface plot of the Laplacian ($\nabla^2\rho = -214e/\text{\AA}^3$) of **3-Ti** at the metal atom. Ti-Me bonds are shown as sticks. The position of valence shell charge concentration maxima are shown as red spheres.

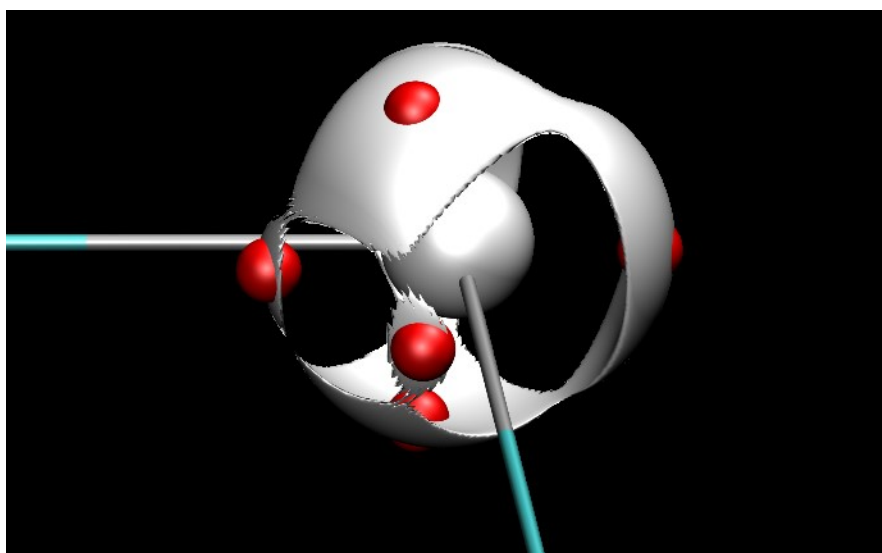


Figure S57: Theoretical 3D isosurface plot of the Laplacian of **3-Zr** at the metal atom. Zr-Me bonds are shown as sticks. The position of valence shell charge concentration maxima are shown as red spheres.

22. Theoretical ELI-D 3D-isosurface plots of **3-Ti**, **3-Zr** and **3-Hf**

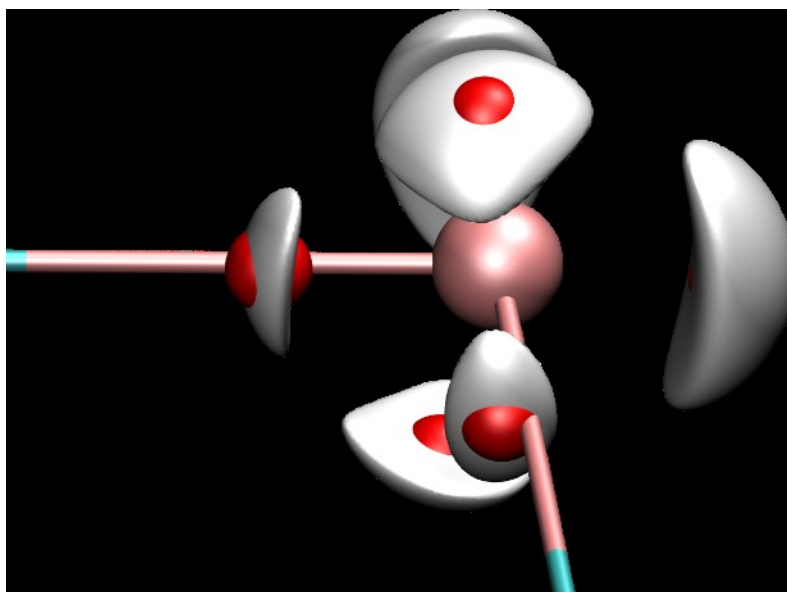


Figure S58: Theoretical 3D isosurface plot of the ELI-D (value: 1.52) of **3-Ti** at the metal atom. Ti-Me bonds shown as sticks. The position of valence shell maxima are shown as red spheres.

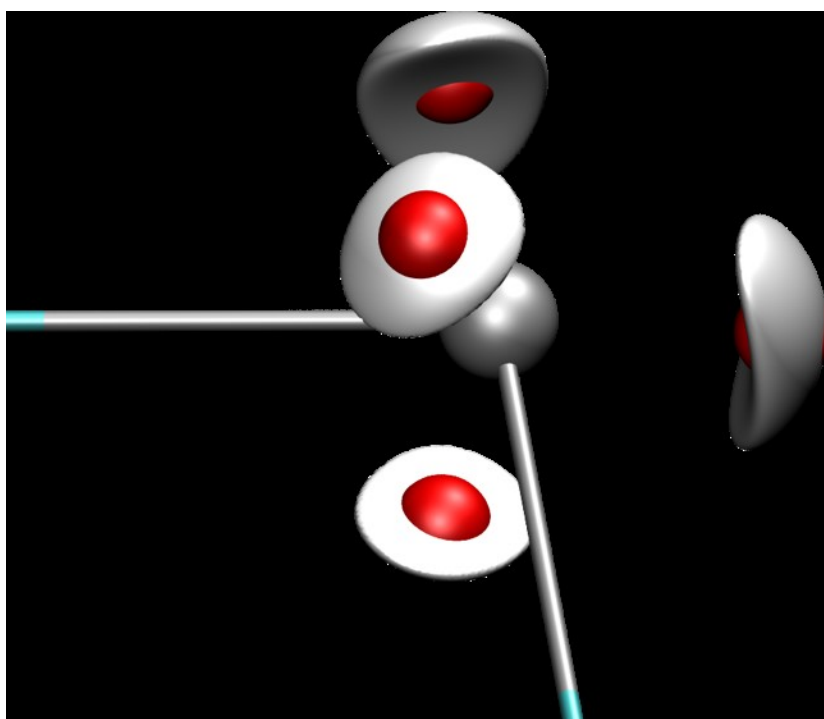


Figure S59: Theoretical 3D isosurface plot of the ELI-D (value: 1.45) of **3-Zr** at the metal atom. Zr-Me bonds shown as sticks. The position of valence shell maxima are shown as red spheres.

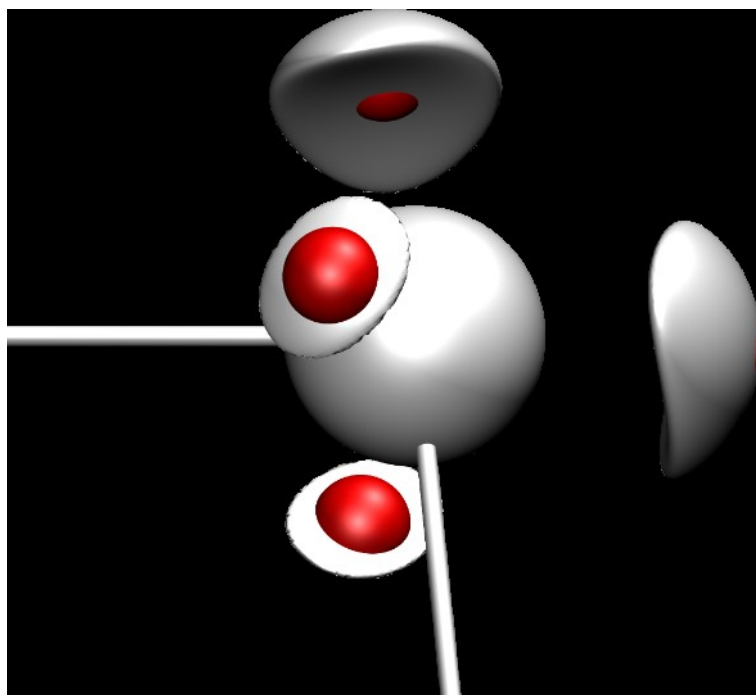
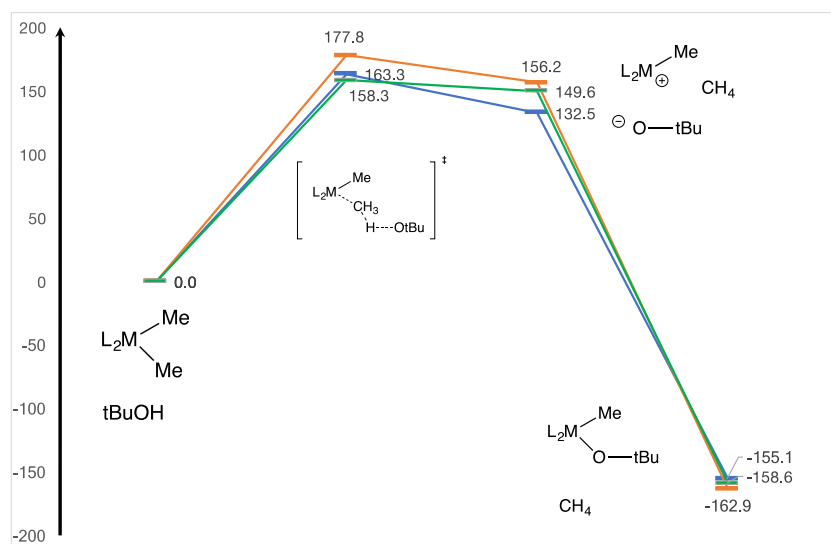


Figure S60: Theoretical 3D isosurface plot of the ELI-D (value: 1.18) of 3-Hf at the metal atom. Hf-Me bonds shown as sticks. The position of valence shell maxima are shown as red spheres.

23. Kinetic measurements – theoretical study



Scheme S1. Calculated free energies ΔG (kJ/mol) in solution along the proposed pathway (green: $M=\text{Ti}$; blue: $M=\text{Zr}$; orange: $M=\text{Hf}$). Note: The 4-aryl groups on each of the sandwich rings have been replaced by methyl for saving computing time and resources.

Molecular representation and absolute energies (E, H, G) for each species:

Methane

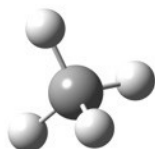


Figure S61. Molecular representation of methane.

Table S20. Calculated values of methane.

HF=	-40.5316364 / NImag=0	
Sum of electronic and thermal Enthalpies=		-40.484428
Sum of electronic and thermal Free Energies=		-40.505587

^tBu-OH

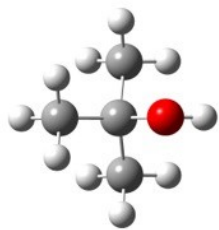


Figure S62. Molecular representation of ^tBuOH.

Table S21. Calculated values of ^tBuOH.

HF= -233.7745988 / NImag=0	
Sum of electronic and thermal Enthalpies=	-233.635642
Sum of electronic and thermal Free Energies=	-233.672636

^tBuO⁻

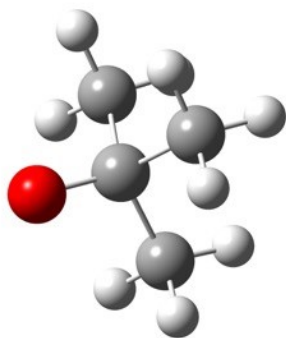


Figure S63. Molecular representation of ^tBuO⁻.

Table S22. Calculated values of ^tBuO⁻.

HF= -233.2497064 / NImag=0	
Sum of electronic and thermal Enthalpies=	-233.125392
Sum of electronic and thermal Free Energies=	-233.161595

3-Hf (4-Aryl $\leftrightarrow$ Me)

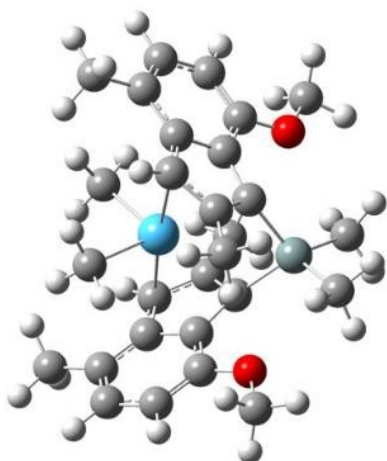


Figure S64. Molecular representation of **3-Hf**.

Table S23. Calculated values of **3-Hf**.

HF=-1578.2383043 / NImag=0	
Sum of electronic and thermal Enthalpies=	-1577.654785
Sum of electronic and thermal Free Energies=	-1577.755477

3-Zr (4-Aryl $\leftrightarrow$ Me)

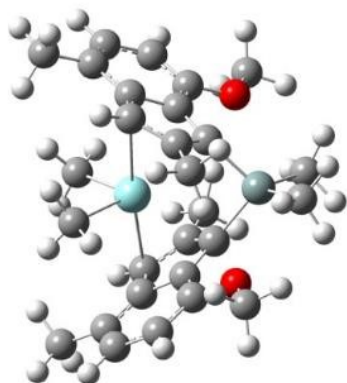


Figure S65. Molecular representation of **3-Zr**.

Table S24. Calculated values of **3-Zr**.

HF=-1575.9089236 / NImag=0	
Sum of electronic and thermal Enthalpies=	-1575.325709
Sum of electronic and thermal Free Energies=	-1575.426397

3-Ti (4-Aryl ↔ Me)

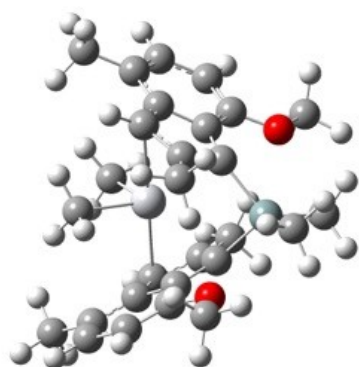


Figure S66. Molecular representation of **3-Ti**.

Table S25. Calculated values of **3-Ti**.

HF=-2378.837271 / NImag=0	
Sum of electronic and thermal Enthalpies=	-2378.252721
Sum of electronic and thermal Free Energies=	-2378.352156

3-Hf⁺ cation (4-Aryl ↔ Me)

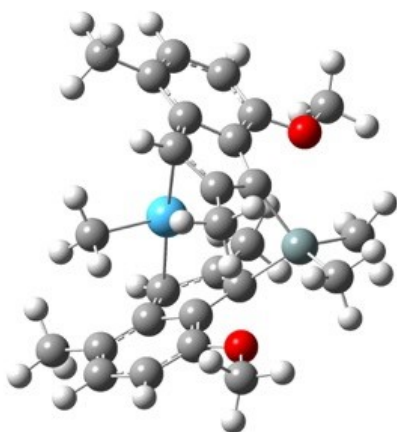


Figure S67. Molecular representation of **3-Hf⁺ cation**.

Table S26. Calculated values of **3-Hf⁺ cation**.

HF=-1538.1536482 / NImag=0	
Sum of electronic and thermal Enthalpies=	-1537.605478
Sum of electronic and thermal Free Energies=	-1537.701444

3-Zr⁺ cation (4-Aryl ↔ Me)

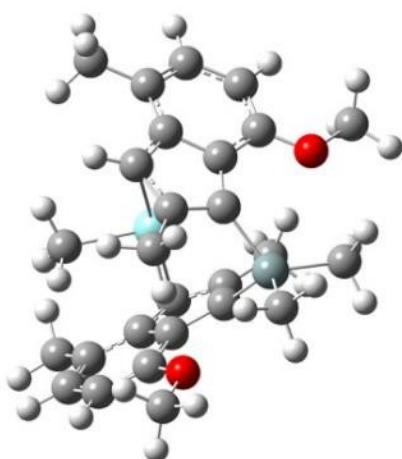


Figure S68. Molecular representation of **3-Zr⁺** cation.

Table S27. Calculated values of **3-Zr⁺** cation.

HF=-1535.8341356 / NImag=0	
Sum of electronic and thermal Enthalpies=	-1535.286000
Sum of electronic and thermal Free Energies=	-1535.381372

3-Ti⁺ cation (4-Aryl ↔ Me)

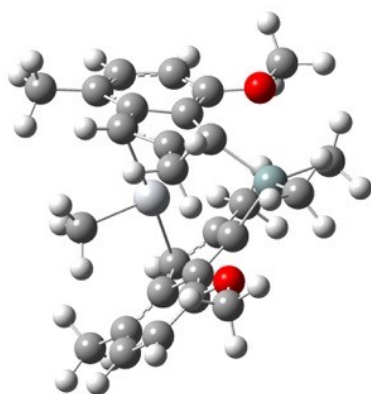


Figure S69. Molecular representation of **3-Ti⁺** cation.

Table S28. Calculated values of **3-Ti⁺** cation.

HF= -2338.7553392 / NImag=0	
Sum of electronic and thermal Enthalpies=	-2338.206367
Sum of electronic and thermal Free Energies=	-2338.300619

3-Hf⁺ – ^tBuO⁻ ion pair

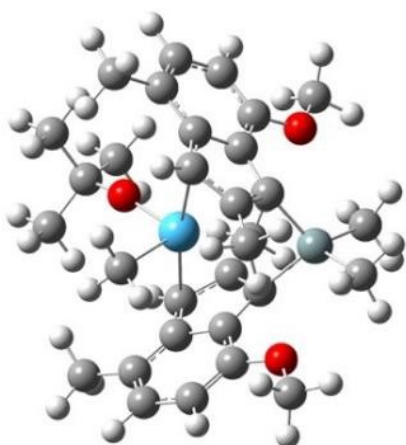


Figure S70. Molecular representation of the **3-Hf⁺ – ^tBuO⁻** ion pair.

Table S29. Calculated values of the **3-Hf⁺ – ^tBuO⁻** ion pair.

HF=-1771.5478942 / NImag=0	
Sum of electronic and thermal Enthalpies=	-1770.871818
Sum of electronic and thermal Free Energies=	-1770.984579

3-Zr⁺ – ^tBuO⁻ ion pair

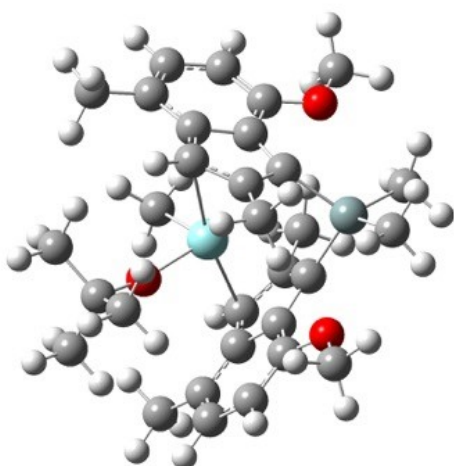


Figure S71. Molecular representation of the **3-Zr⁺ – ^tBuO⁻** ion pair.

Table S30. Calculated values of the **3-Zr⁺ – ^tBuO⁻** ion pair.

HF=	-1769.2167771 / NImag=0	
Sum of electronic and thermal Enthalpies=		-1768.540769
Sum of electronic and thermal Free Energies=		-1768.652525

3-Ti⁺ – ^tBuO⁻ ion pair

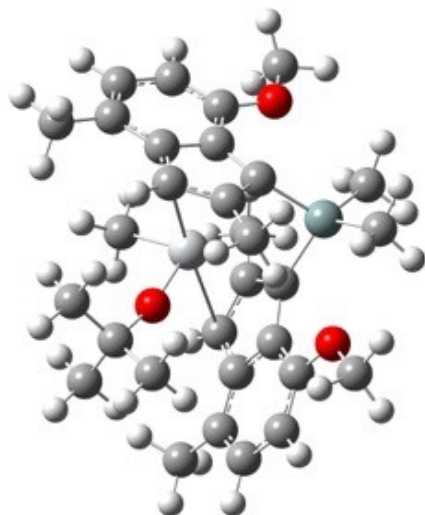


Figure S72. Molecular representation of the **3-Ti⁺ – ^tBuO⁻** ion pair.

Table S31. Calculated values of the **3-Ti⁺ – ^tBuO⁻** ion pair.

HF=	-2572.1420675 / NImag=0	
Sum of electronic and thermal Enthalpies=		-2571.465965
Sum of electronic and thermal Free Energies=		-2571.579595

Transition state (3-Hf): H-transfer to methyl group

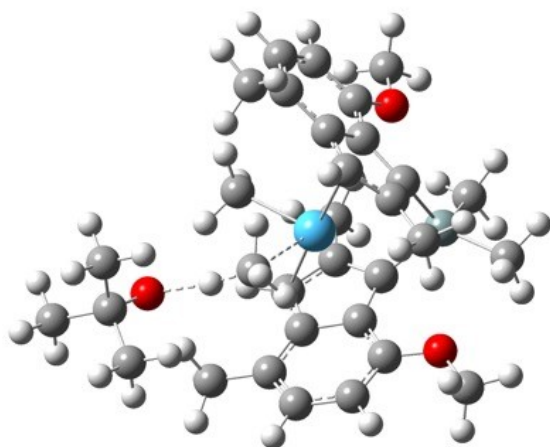


Figure S73. Molecular representation of the transition state (3-Hf): H-transfer to methyl group.

Table S32. Calculated values of the transition state (3-Hf): H-transfer to methyl group.

HF=	-1811.9627347	/	NImag=1	(-79.9630 cm ⁻¹)	
Sum of electronic and thermal Enthalpies=					-1811.241180
Sum of electronic and thermal Free Energies=					-1811.360399

Transition state (**3-Zr**): H-transfer to methyl group

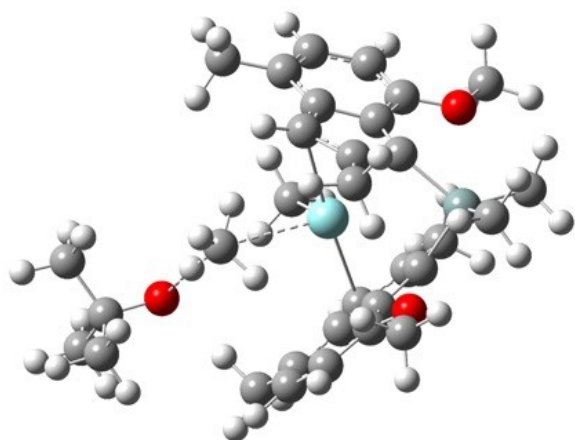


Figure S74. Molecular representation of the transition state (**3-Zr**): H-transfer to methyl group.

Table S33. Calculated values of the transition state (**3-Zr**): H-transfer to methyl group.

HF=	-1809.6403007	/	NImag=1	(-47.9336 cm ⁻¹)	
Sum of electronic and thermal Enthalpies=					-1808.918957
Sum of electronic and thermal Free Energies=					-1809.036851

Transition state (3-Ti): H-transfer to methyl group

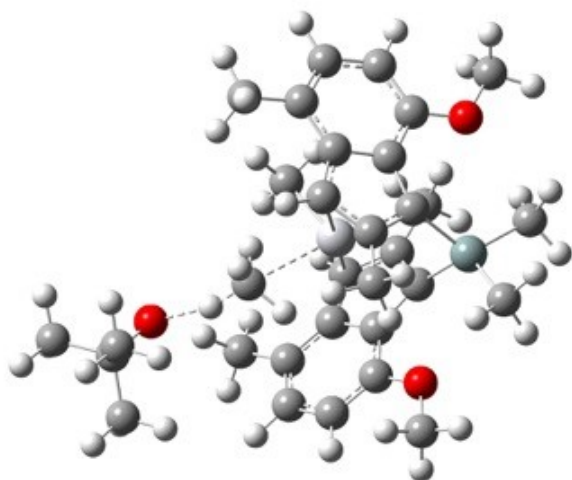


Figure S75. Molecular representation of the transition state (3-Ti): H-transfer to methyl group.

Table S34. Calculated values of the transition state (3-Ti): H-transfer to methyl group.

HF=	-2612.5716875	/	NImag=1	(-45.0558 cm ⁻¹)	
Sum of electronic and thermal Enthalpies=					-2611.848659
Sum of electronic and thermal Free Energies=					-2611.964497

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