Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

DOI: 10.1002/zaac.202000013

ARTICLE

Syntheses and Molecular Structures of $[(thf)_4Li][\{(thf)Li\}M(C_4H_8)_3]$ (M = Zr, Hf) and Their Solution Behavior

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In Memoriam Professor Gerd Becker

Abstract. The reaction of $MCl_4(thf)_2$ (M = Zr, Hf) with 1,4-dilitiobutane in diethyl ether at –25 °C or at 0 °C with a molar ratio of 1 : 3 yields the homoleptic "ate" complexes $[(thf)_4Li]$ $[\{(thf)Li\}M(C_4H_8)_3]$ **1-Zr** (M = Zr) and **1-Hf** (M = Hf). The crystalline compounds form ion lattices with solvent-separated $[(thf)_4Li]^+$ cations and $[\{(thf)Li\}M(C_4H_8)_3]^-$ anions. The NMR spectra at –20 °C show magnetic equivalence of the M–CH_2 and of the β-CH_2 groups of the butane-1,4-diide ligands on the NMR time scale. Analogous reactions of $MCl_4(thf)_2$ with 1,4-dilithiobutane with a molar ratio of 1 : 2 proceed unclear. However, single crystals of $[Li(thf)_4]$ $[HfCl_5(thf)]$ (**2**) can be isolated with the hafnium atom in a distorted octahedral coordination sphere of five chloro and one thf ligand. NMR spectra allow to elucidate the time-dependent degradation of **1-Hf** and **1-Zr** in THF and toluene at 25 °C via THF cleavage. Addition of tmeda to a solution of **1-Zr** allows the isolation of intermediately formed $[\{(tmeda)Li\}_2Zr(nBu)_2(C_4H_8)_2]$ (**3**).

Introduction

Organozirconium compounds are valuable synthons in organic synthesis, hydrozirconation processes and as catalysts in hydrofunctionalization and umpolung reactions[1,2] as well as in zirconium-catalyzed carbomagnesiation reactions.[3] Hafnium-containing organometallics are much more stable and significantly less reactive and therefore, these Hf-based complexes often serve as model compounds to elucidate the reaction mechanisms of catalytic transformations involving group 4 metals.[2] Many of these complexes are based on titanocene, zirconocene and hafnocene substructures because the side-on bound *cyclo*pentadienide ligands shield the inner core and their substitution pattern allows to tune bulkiness and availability of coordination sites at the metal center and in some cases also to introduce stereoselective reactivity.

The formation of metallacycles also stabilizes transition metal complexes because intramolecular hydride elimination processes are hindered. The bifunctional synthon 1,4-dilithiobutane enables the syntheses of metallacycles and metalates with the butane-1,4-diide acting as a chelate base. Crystallographically authenticated homoleptic metalates have been reported for chromium(II),[4] nickel(II),[5] platinum(II),[6] magnesium(II),[7] and zinc(II).[8] In order to study the dependency of the molecular structures on the oxidation state of the metal we also prepared and investigated the yttrium(III) congener.[9] Homoleptic metalates with central metal(IV) atoms are missing as of yet.

A zirconium-based complex of the composition "$Li_2Zr(C_4H_8)_3(THF)_{5.5}$" (**1-Zr**) has been isolated by *Fröhlich* and co-workers.[10] The authors also carboxylated[11] and carbonylated[12] the compound and initiated the living anionic polymerization of 1,3-dienes.[13] However, the molecular structure of this complex remained unknown.

In this investigation we elucidated the crystal structures of **1-Zr** and of the thermally more stable homologous hafnium congener **1-Hf** and studied their behavior in solution and in the presence of a chelating Lewis base.

Results and Discussion

1 Molecular Structures of $[(thf)_4Li][\{(thf)Li\}M(C_4H_8)_3]$ with M = Zr (1-Zr), Hf (1-Hf)

The complex $[(thf)_4Li][\{(thf)Li\}Zr(C_4H_8)_3]$ (**1-Zr**) was synthesized according to the procedure of *Fröhlich* and *Göbel*[10] via the metathesis reaction of $ZrCl_4(thf)_2$ with $Li_2(CH_2)_4$ in the molar ratio of 1:3.1 in diethyl ether at –25 °C (Scheme 1). After recrystallization of the crude product from THF solution colorless and thermally highly sensitive single crystals were isolated allowing the determination of the crystal structure. Molecular structure and numbering scheme of the anion of $[(thf)_4Li][\{(thf)Li\}Zr(C_4H_8)_3]$ (**1-Zr**) are depicted in Figure 1, the whole molecule is shown in the Supporting Information.

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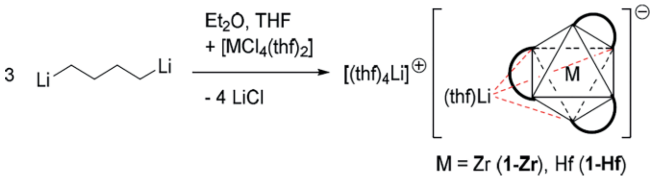
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.202000013** or from the author.



Scheme 1. Synthesis of [(thf)$_4$Li][{(thf)Li}M(C$_4$H$_8$)$_3$] with M = Zr (**1-Zr**) and Hf (**1-Hf**) in diethyl ether and formation of the thf adduct after addition of tetrahydrofuran. The bold semicycles symbolize the butane-1,4-diide ligands at the octahedral coordination spheres of M.

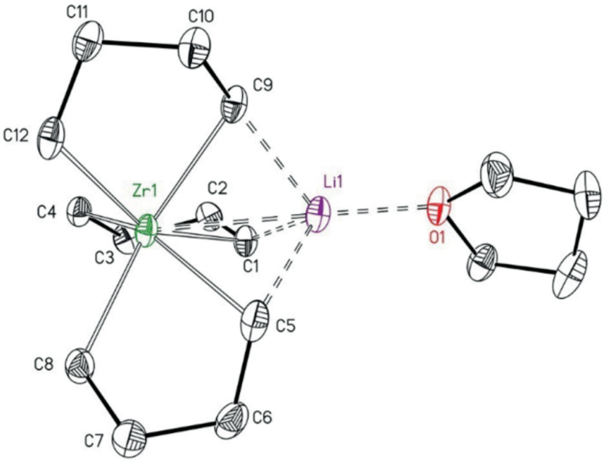


Figure 1. Molecular structure and atom labeling scheme of the anion of [Li(thf)$_4$][Zr(C$_4$H$_8$)$_3${Li(thf)}] (**1-Zr**). The hydrogen atoms are omitted for clarity reasons. The ellipsoids represent a probability of 30 %. Selected bond lengths /pm: Zr1–C1 243.1(4), Zr1–C4 231.6(4), Zr1–C5 241.2(4), Zr1–C8 231.7(5), Zr1–C9 242.7(5), Zr1–C12 233.1(4), Li1–O1 191.2(7), Li1–C1 218.9(7), Li1–C5 221.2(7), Li1–C9 221.2(7); non-bonding interatomic distance/pm: Zr1···Li1 267.7(7); selected bond angles/°: C1–Zr1–C4 73.18(14), C5–Zr1–C8 72.68(17), C9–Zr1–C12 72.40(16), C1–Zr1–C5 88.11(14), C1–Zr1–C9 84.59(14), C4–Zr1–C8 93.86(17), C5–Zr1–C9 85.81(17), C8–Zr1–C12 98.63(18), C4–Zr–C12 97.65(16), O1–Li1–C1 119.8(5), O1–Li1–C5 121.2(5), O1–Li1–C9 123.2(5), C1–Li1–C5 93.8(5), C1–Li1–C9 96.0(5), C1–Li1–C9 96.2(5).

Crystalline **1-Zr** forms a 1–1 ion lattice. The cations are [(thf)$_4$Li]$^+$ ions with a distorted tetrahedral environment of the lithium atoms. In the anion [Zr(C$_4$H$_8$)$_3${Li(thf)}]$^-$ the zirconium(IV) center is in a distorted octahedral coordination sphere of three chelating butane-1,4-diide ligands. In the crystalline state both enantiomers of the octahedral complexes form a racemate of Δ and Λ isomers due to the centrosymmetric space group $P2_1/c$. The bite angles of the hydrocarbyl chelate ligands are significantly smaller than 90° [C–Zr–C of the zirconacycles: 72.40(16)–73.18(14)°]. From each butane-1,4-diide ligand one α-methylene group also binds to the Li1 atom of the Li(thf) unit via Li–C–Zr three-center two-electron bonds. These bridging positions of the methylene groups cause additional distortion of the octahedral environment of Zr1 and elongation of the respective Zr–C bonds by approx. 10 pm compared to the Zr–C bonds without interaction to the lithium atom. The C–Zr–C bond angles between carbanionic methylene groups of the butane-1,4-diide moieties with Li contacts are smaller than 90° [84.59(14)–88.11(14)°] whereas the C–Zr–C values between the carbanionic sites that also bind to lithium are larger than 90° [93.86(17)–98.63(18)°]. The interatomic Zr1···Li1 distance of 267.7(7) pm clearly excludes bonding interactions.

The homologous hafnium(IV) complex [(thf)$_4$Li][{thf)Li}Hf(C$_4$H$_8$)$_3$] (**1-Hf**) was obtained with good yields via the metathetical approach of HfCl$_4$(thf)$_2$ with an ethereal 1,4-dilithiobutane solution in the molar ratio of 1:3.2 at 0 °C in diethyl ether. After removal of precipitated lithium chloride and addition of THF the product crystallized in the centrosymmetric space group $P2_1/n$ as a colorless and thermally moderately sensitive compound. Contrary to **1-Zr**, the asymmetric unit contains two molecules A and B which differ by the orientation of the thf ligands at O1A and O1B; however, the influence on the structural parameters is negligible. The structure of the anion of **1-Hf** and the atom labeling scheme of molecule A are depicted in Figure 2, molecule B and the whole molecule including the cation are shown in the Supporting Information.

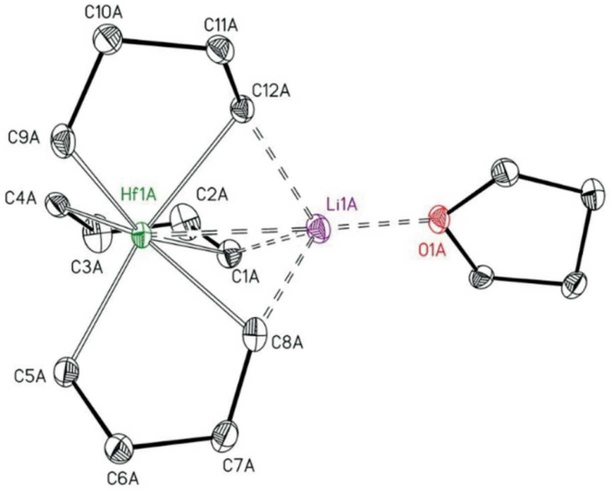


Figure 2. Molecular structure and atom labeling scheme of the anion of molecule A of [Li(thf)$_4$][Hf(C$_4$H$_8$)$_3${Li(thf)}] (**1-Hf**). The hydrogen atoms are neglected for the sake of clarity (see Figure S1, Supporting Information, for molecule B.) Selected bond lengths of molecule A [molecule B]/pm: Hf1–C1 241.4(3) [240.8(3)], Hf1–C4 230.2(3) [229.7(3)], Hf1–C5 230.3(3) [230.0(3)], Hf1–C8 239.4(3) [240.7(3)], Hf1–C9 229.6(3) [229.9(3)], Hf1–C12 240.5(3) [239.1(3)], Li1–O1 190.1(5) [192.1(6)], Li1–C1 220.2(6) [220.5(6)], Li1–C8 222.8(6) [221.8(6)], Li1–C12 221.5(6) [221.5(6)]; non-bonding interatomic distances /pm: Hf1···Li1 265.8(5) [267.0(5)]; selected bond angles/°: C1–Hf1–C4 74.32(11) [73.50(10)], C5–Hf1–C8 73.58(11) [73.83(10)], C9–Hf1–C12 74.32(11) [73.65(12)], C1–Hf1–C5 108.72(12) [112.27(12)], C1–Hf1–C8 84.55(11) [85.11(11)], C1–Hf1–C9 152.92(12) [153.18(12)], C1–Hf1–C12 84.62(11) [85.80(12)], C4–Hf1–C5 93.53(11) [96.44(12)], C4–Hf1–C8 149.98(12) [151.27(12)], C4–Hf1–C9 98.83(12) [97.98(12)], C4–Hf1–C12 110.49(11) [111.80(12)], C5–Hf1–C9 97.71(12) [93.72(12)], C5–Hf1–C12 155.17(11) [150.17(12)], C8–Hf1–C9 109.56(12) [109.41(12)], C8–Hf1–C12 87.55(11) [84.86(11)].

The ion lattice consists of two crystallographically independent units A and B. The ionic radii of Zr^{4+} (86 pm) and Hf^{4+} (85 pm) are very similar due to the lanthanoide contraction of the radii in the 5d row of the Periodic Table of the elements.[14] As a consequence the structural parameters of **1-Zr** and **1-Hf** are very similar with the Hf–C bonds even being slightly shorter by approx. 2 pm. Despite the far-reaching structural similarity between the zirconiate and hafniate anions chemical stability and reactivity differ significantly (see Section 2.2).

Selected structural parameters of homoleptic **1-Zr** and **1-Hf** are compared with heteroleptic complexes LL′MC_4H_8 of the group 4 metals, containing saturated metalla-*cyclo*-pentane fragments. Most commonly these compounds have been prepared via the cyclization reaction of the "LL′M" precursor with two equivalents of ethylene. For the sake of completeness also the very rare structures of titanium complexes containing the titana-*cyclo*-pentane fragment are included.

The Zr–C and Hf–C bond lengths in **1-Zr** and **1-Hf**, respectively, lie at the upper range of metal-carbon single bonds. On the one hand, intramolecular steric repulsion between the ligands plays a significant role. On the other hand, this elongation is effectuated by intramolecular electrostatic repulsion between six carbanions bound at the metal center. The formation of Li–C–M three-center two-electron bonds via coordination of the Li(thf) moiety additionally stretches the M–C bonds. Due to ring strain, the C–M–C bond angles are in all compounds significantly smaller than 90°. The narrowest angles are observed for **1-Zr** and **1-Hf**, which is a consequence of the large Zr–C and Hf–C distances (Table 1).

Table 1. Comparison of M–C bond lengths /pm and C–M–C bond angles /° of metallacycles with saturated MC_4H_8 rings in complexes of the type LL′MC_4H_8 of titanium, zirconium, and hafnium.

M	L/L′ a)	M–C	C–M–C	Reference
Ti	2 × O-C_6H_3-2,6-Ph_2	208.6	85.6	[15]
	Cp/N=P*t*Bu_3	214.3	86.2	[16]
Zr	2 × C_4H_8 (**1-Zr**)	232.1 / 242.3	72.8	This work
	2 × Cp^{Ment}	230.4	82.6	[17]
	Cp′-C_2H_4-Cp′	229.8	84.0	[18]
	2 × C_5H_3-1,3-*t*Bu_2	230.2	81.2	[19]
	Ind-C_2H_4-Ind	229.4	84.8	[20]
	2 × Ind^{R4}	230.1	81.0	[21]
	2 × $(Me_3Si\text{-}N)_2C$-Ph	224.8	76.4	[22]
Hf	2 × C_4H_8 (**1-Hf**)	230.0 / 240.3	73.7	This work
	Cp′-C_2H_4-Cp′	225.7	84.6	[23]

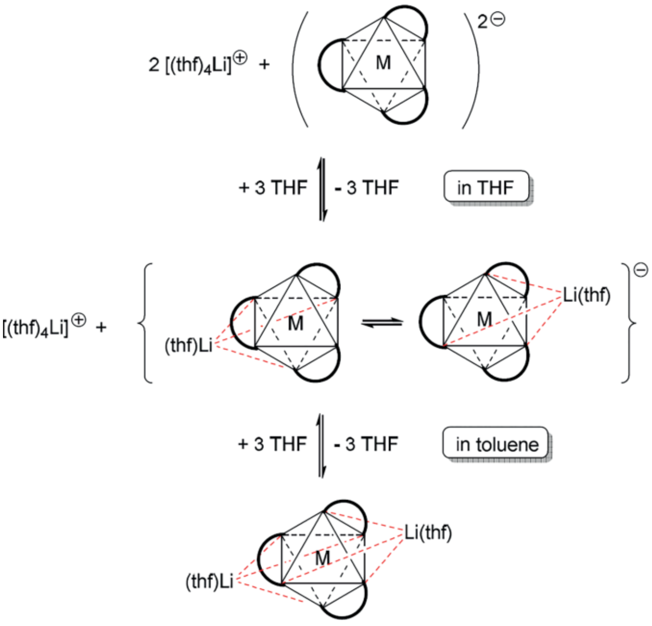
a) Bu = butyl, Cp′ = 4,5,6,7-tetrahydroindenyl, Ind = indenyl, Ment = menthyl, Ph = phenyl.

2 Solution Behavior of [$(thf)_4$Li][{(thf)Li}M$(C_4H_8)_3$] [M = Zr (1-Zr), Hf (1-Hf)]

2.1 Fluxionality in Solution

1-Zr and **1-Hf** are highly soluble at –20 °C in THF and toluene. The excellent solubility in hydrocarbons was not expected based on the ionic composition of both complexes. At temperatures above –20 °C these compounds slowly degrade and the solutions turned increasingly dark brown.

In the ^{1}H and ^{13}C NMR spectra one would expect four resonance sets of equal intensity for the butane-1,4-diide fragments. However, in all these spectra only two signal sets were observed. The assignment succeeded with HSQC experiments. It is noteworthy that in the ^{13}C{^{1}H} NMR spectra the α-carbon atoms were found at lower field than the β-carbon atoms (**1-Zr** in [D_8]THF: α-C 49.9 ppm, β-C 36.2 ppm; in [D_8]toluene: α-C 47.9 ppm, β-C 33.9 ppm; **1-Hf** in [D_8]THF: α-C 56.1 ppm, β-C 36.2 ppm; in [D_8]toluene: α-C 57.2 ppm, β-C 34.9 ppm). Such shifts of the α-carbon atoms to lower field have also been observed earlier for zircona-[17–22] and hafna-*cyclo*-pentane[23] congeners and was explained with the heavy atom effect induced by these metal atoms. The ^{1}H NMR resonances of the butane-1,4-diide ligands lie in the expected ranges (**1-Zr** in [D_8]THF: α-CH_2 0.08 ppm, β-CH_2 1.78 ppm; in [D_8]toluene: α-CH_2 0.83 ppm, β-CH_2 2.76 ppm; **1-Hf** in [D_8]THF: α-CH_2 0.05 ppm, β-CH_2 1.96 ppm; in [D_8]toluene: α-CH_2 0.86 ppm, β-CH_2 2.89 ppm). Obviously these complexes show symmetric structures in solution and/or exchange processes that are fast on the NMR time scale. Hence, the following three possible solution structures are proposed in Scheme 2: solvent-separated ion pairs, contact ion pairs and fast exchange of the Li(thf) unit from one octahedral face to the opposite face. In Scheme 2 the fluxionality in solution is depicted at a Δ isomer; these equilibria are equally operative in the Λ isomers; in addition Δ/Λ enantiomer interconversion is very likely, too.



Scheme 2. Molecular dynamics of **1-Zr** (M = Zr] and **1-Hf** (M = Hf] depending on the polarity of the solvents THF and toluene. The bold hemicycles symbolize the butane-1,4-diide ligands. The metal-bound carbon atoms form a distorted octahedron, which is drawn with thin solid and broken lines. The Li–C bonds are shown with red broken lines.

In the ^{13}C{^{1}H} NMR spectrum of **1-Hf** in [D_8]THF solution at –20 °C the signal of the Hf-bound methylene units is significantly broader than the resonance of the β-CH_2 fragments. At the lower temperature of –50 °C this effect is getting stronger, however, the coalescence could not be realized. The ^{13}C{^{1}H} NMR spectrum of **1-Zr** in [D_8]toluene shows no such effects down to –45 °C. A slight broadening of the Zr-bound methylene group is observed below this temperature and at –50 °C crystallization of **1-Zr** is observed.

If a molar ratio of 1:2 is applied for the metathesis reaction of [$ZrCl_4(thf)_2$] with ethereal 1,4-dilithiobutane a yellow, sticky and thermally very sensitive product formed that contained at least two different zirconium-containing compounds. The NMR spectroscopic data of a [D_8]toluene solution at –40 °C shows two sets of resonances for **1-Zr** and a yet unknown second component [^{1}H NMR: 1.11 ppm (CH_2Zr), 3.20 ppm (β-CH_2); $^{13}C\{^1H\}$ NMR: 16.6 ppm (β-CH_2), 66.0 ppm (CH_2Zr)]. Nevertheless, the reaction proceeded quite unclear and we were unable to solve the reaction mechanism. The use of homologous [$HfCl_4(thf)_2$] allowed the isolation of a hafniate derivative without butane-1,4-diide ligands, namely [$(thf)_4Li$][$HfCl_5(thf)$] (**2**). Molecular structure and atom labeling scheme are depicted in Figure 3. This hafniate ion has already been structurally authenticated with other counter cations.[24]

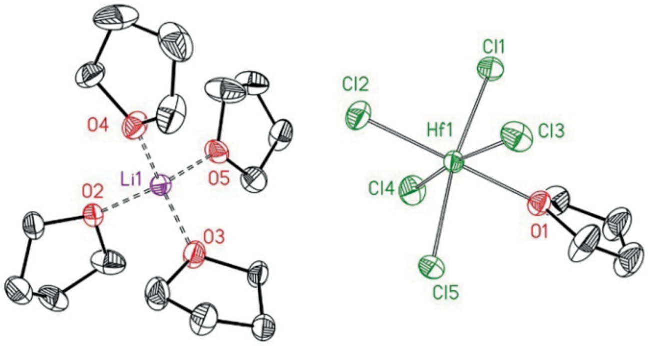


Figure 3. Molecular structure of [$Li(thf)_4$]$^+$[$HfCl_5(thf)$]$^-$ (**2**). Hydrogen atoms are omitted for clarity reasons. The ellipsoids represent a probability of 30 %. Selected bond lengths /pm: Hf1–Cl1 243.11(16), Hf1–Cl2 238.6(2), Hf1–Cl3 242.11(19), Hf1–Cl4 242.0(2), Hf1–Cl5 243.39(16), Hf1–O1 222.1(5), Li1–O2 193.4(12), Li1–O3 190.3(12), Li1–O4 189.2(12), Li1–O5 190.3(12); selected bond angles /°: O1–Hf1–Cl1 85.70(12), O1–Hf1–Cl2 179.87(15), O1–Hf1–Cl3 85.87(14), O1–Hf1–Cl4 85.36(14), O1–Hf1–Cl5 84.89(12), Cl1–Hf–Cl5 170.58(7), Cl3–Hf–Cl4 171.23(8), Cl1–Hf–Cl2 94.31(7), Cl2–Hf–C3 94.26(8), Cl2–Hf–C4 94.51(8), Cl2–Hf–C5 95.11(7).

The hafnium center in **2** has a distorted octahedral coordination sphere. All Cl2–Hf1–Cl bond angles are larger than 90° and the O1–Hf1–Cl values to the *cisoid* chloride ligands are smaller than 90°. This finding is caused by the electrostatic repulsion between the halide anions whereas the oxygen atom is electroneutral. The Hf1–Cl2 bond length is approx. 4 pm smaller than the distances to the *cisoid* chloride atoms. These Hf–Cl distances of the hafniate **2** are in agreement with values of other six-coordinate hafnium derivatives like [*cis*-$HfCl_4(thf)_2$],[25] [Ph_4P]$_2$[$HfCl_6$]·2solv,[26] and [Et_4N]$_2$[$HfCl_6$][27] with increasing number of chloro ligands (see Table S1, Supporting Information). The lithium atom Li1 is in a distorted tetrahedral environment.

The formation of **2** hints toward a side reaction of [$HfCl_4(thf)_2$] with lithium chloride that forms during the metathesis reaction or might already be present in the ethereal solution of starting [$(Et_2O)_4Li$][$Li_{12}(C_4H_8)_6(@Cl)$].[28] This complex **2** can also act as starting material for the metathesis reaction with 1,4-dilithiobutane. The significantly more thermolabile neutral compounds "$M(C_4H_8)_2(thf)_2$" and "$MCl_2(C_4H_8)(thf)_2$" are not accessible via metathetical approaches of [$MCl_4(thf)_2$] with 1,4-dilithiobutane with molar ratios of 1:2 or 1:1.

2.2 Stability of [$(thf)_4Li$][$\{(thf)Li\}M(C_4H_8)_3$] [M = Zr (1-Zr), Hf (1-Hf)] in Solution

In the crystalline state the complexes **1-Zr** and **1-Hf** could be stored at –20 °C. In THF and toluene solutions these complexes already started to slowly degrade already at –20 °C. At room temperature the degradation was significantly accelerated which could be monitored by NMR spectroscopy. The intensity of new signals increased in equal measure as the resonances of **1-Zr** and **1-Hf** vanished. The decomposition process could be observed by ^{1}H NMR experiments (Figure 4). The newly formed hydrocarbons were n-butane and toward the end of the degradation also ethylene was detected. Under these conditions the half-life time of the decomposition of **1-Hf** in [D_8]toluene at 25 °C was approx. 15 hours. If THF was replaced by [D_8]THF (deuteration of 99.5 %) the degradation at room temperature was significantly decelerated and a half-life time of 105 hours was observed. Expectedly, the solution of **1-Zr** in [D_8]THF was much more thermolabile and a half-life time of approx. 2 hours was determined. Due to this finding a reliable time dependency of the very fast degradation of **1-Zr** in toluene could not be elucidated.

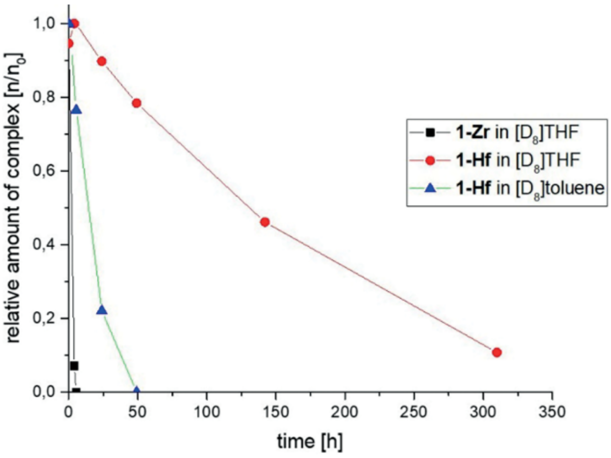
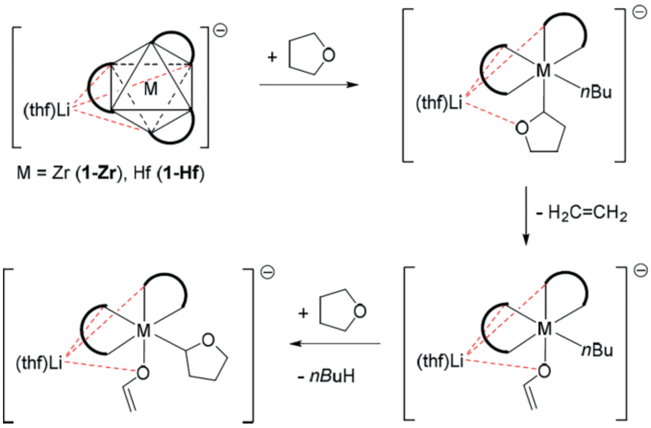


Figure 4. Time depending decomposition of **1-Zr** (black) and **1-Hf** (red and blue) at 25 °C in [D_8]THF and [D_8]toluene solutions.

The fact that **1-Hf** degrades much faster in [D_8]toluene than in [D_8]THF supports a fast ligand exchange of coordinated thf ligands by deuterated THF solvent molecules which were present with large excess during the NMR experiments. Tetrahydrofuran acts as a weak Brønsted base toward the highly nucleophilic butane-1,4-diide.[29] The rate of degradation depends on the deprotonation of the methylene groups CH_2O in [D_8]toluene and CD_2O in [D_8]THF after ligand substitution of the ether bases. The quotient k_D/k_H (kinetic isotope effect of $^2D/^1H$) of this reaction has a value of 7. A similarly stabilizing solvent effect of [D_8]THF has been observed earlier for solutions of related [$\{(thf)_2Li\}_3Y(C_4H_8)_3$].[9] Initially the butane-1,4-diide ions form n-butyl groups. A second deprotonation of THF or [D_8]THF yields *n*-butane (or 1-[D]butane and 1,4-

[D_2]butane) which have been authenticated by NMR spectroscopy. Pure 1,4-[D_2]butane is not accessible due to metalation reactions also with [D_7]THF and THF from the original complex. The decomposition end products of THF are the vinylate as well as ethylene and [D_4]ethylene, which are authenticated by NMR spectroscopy. The vinylate species are only sparingly soluble and hence, trapped in the white precipitate which forms during the decomposition process. This main degradation cascade is depicted in Scheme 3.



Scheme 3. Proposed initial decomposition steps of **1-Zr** and **1-Hf** at room temperature via deprotonation of THF molecules.

This degradation proceeds primarily via deprotonation of THF and [D_7]THF und only secondarily via dedeuteration of [D_8]THF (and [D_7]THF]). In the solution of **1-Hf** in hydrocarbons like toluene the thf ligands are not substituted and hence, they remain in the vicinity of the carbanions. Therefore, degradation of **1-Hf** in toluene is significantly accelerated in comparison to this reaction in [D_8]THF solutions. Expectedly, the solution of the hafnium complex is much more stable than of the zirconium congener due to stronger Hf–C σ-bonds.[30]

According to *Fröhlich* and *Göbel*[10] the ligated thf bases can be substituted by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) ligands yielding "$Li_2Zr(C_4H_8)_3(tmeda)_3$", which should be more stable than the thf adduct. We reinvested the reaction and added 1,4-dilithiobutane to [$ZrCl_4(thf)_2$] with a molar ratio of 1:3.1 in diethyl ether. Thereafter we removed precipitated lithium chloride and added a stoichiometric amount of tmeda. At –40 °C a colorless sticky substance precipitated which was isolated. After recrystallization at –40 °C only a few crystals of [$\{(tmeda)Li\}_2Zr(n\mathrm{Bu})_2(C_4H_8)_2$] (**3**) were obtained. The crystal structure determination verified the proposed composition, however due to poor crystal quality we were only able to refine a structural motif. The molecular structure and atom labeling scheme of C_2 symmetric **3** is depicted in Figure 5.

Despite the substandard data set the molecular structure verifies the formation of a heteroleptic zirconiate complex as contact ion pair. The zirconium center binds to six carbanions. The Li(tmeda) fragments bind to the carbanionic sites of the different butane-1,4-diide ligands leading to a coordination number of four for the lithium atoms and a distorted tetrahedral environment. The shielding of the lithium center by the chelate tmeda ligands prevents coordination to the butyl groups. Isolation of this complex supports the degradation pathway which is discussed above.

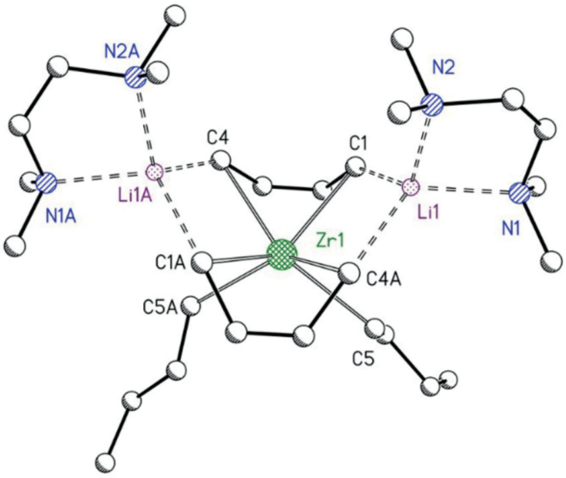


Figure 5. Structural motif and atom labeling scheme of [$\{(tmeda)Li\}_2Zr(n\mathrm{Bu})_2(C_4H_8)_2$] (**3**). Symmetry-related atoms are marked with the letter "A". Hydrogen atoms are omitted for clarity reasons, heavy atoms are drawn with arbitrary radii.

Conclusions

After the structural characterization of homoleptic butane-1,4-diide complexes with metal(II) and metal(III) centers we report here for the first time the structures of metal(IV) derivatives which are accessible via the metathetical approach of [$MCl_4(thf)_2$] (M = Zr, Hf) with 1,4-dilitiobutane with a molar ratio of 1:3.1 in diethyl ether. After addition of THF thermally highly sensitive $Li_2M(C_4H_8)_3(thf)_5$ [M = Zr (**1-Zr**) and Hf (**1-Hf**)] can be isolated that form ion lattices with solvent-separated [$(thf)_4Li$]$^+$ cations and [$\{(thf)Li\}M(C_4H_8)_3$]$^-$ anions. Despite the ionic composition these complexes are highly soluble in ethereal and aromatic hydrocarbon solvents. In THF and toluene solutions these compounds show a dynamic behavior with only two resonances caused by the α-CH_2 and β-CH_2 fragments of the butane-1,4-diide ligands. This finding can be explained by the formation of solvent-separated ions [$(thf)_4Li^+$]$_2$ [$M(C_4H_8)_3$]$^{2-}$ in Lewis donor solvents and by a contact ion pair of the type [$\{(thf)Li\}_2M(C_4H_8)_3$] in hydrocarbons. At room temperature these complexes degrade via α-deprotonation of (ligated) thf molecules followed by the characteristic degradation pathway yielding ethylene and sparingly soluble vinylate species. In the presence of tmeda a complex of the composition of "$Li_2Zr(C_4H_8)_3(tmeda)_3$" forms which slowly decomposes already at –40 °C via ether cleavage with formation of [$\{(tmeda)Li\}_2Zr(n\mathrm{Bu})_2(C_4H_8)_2$] (**3**), which crystallizes as a contact ion pair.

The metathesis reactions with different stoichiometric ratios of 1:2 and 1:1 for [$MCl_4(thf)_2$] and 1,4-dilitiobutane yield different species which cannot be separated and isolated. During these experiments using the substrate [$HfCl_4(thf)_2$] the solvent separated hafniate [$(thf)_4Li$][$HfCl_5(thf)$] (**2**) crystallizes. Complexes of the types $[M(C_4H_8)_2(thf)_2]$ and $[MCl_2(C_4H_8)(thf)_2]$ (or LiCl adducts thereof) are not accessible using this metathetical procedure.

The compounds **1-Zr**, **1-Hf**, and **3** are complexes with six very reactive M–C σ-bonds allowing the application in multilevel syntheses or catalyses.

Experimental Section

General: All manipulations were carried out under anaerobic conditions in an argon atmosphere using standard *Schlenk* techniques. The solvents were dried according to common procedures and distilled in an argon atmosphere; deuterated solvents were dried with sodium, degassed, and saturated with argon. The yields given are not optimized. ^1H and ^{13}C NMR spectra and two dimensional spectra were recorded on Bruker AC 400 and AC 500 spectrometers. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the solvent.[31] Anhydrous zirconium tetrachloride, hafnium tetrachloride, and 1,4-dichlorobutane were supplied by Alfa Aesar. $MCl_4(thf)_2$ with M = Zr, Hf were prepared by recrystallization of MCl_4 from a THF solution.[32] The 1,4-dilithiobutane solution was prepared according to a literature procedure from lithium sand (Ø ≈ 50 µm) and 1,4-dichlorobutane in diethyl ether.[28] The concentration of the solution was determined by acidimetric titrations of an aliquot with N/10 hydrochloric acid against phenolphthalein. **1-Zr** was prepared according to a protocol of *Fröhlich* and *Göbel*.[10] The elemental analyses gave no reliable data due to the enormous reactivity toward moisture and air as well as due to loss of thf ligands during handling, weighing and combustion analyses.

Synthesis of $[(thf)_4Li][\{(thf)Li\}Hf(C_4H_8)_3]$ (1-Hf): $HfCl_4(thf)_2$ (2.52 g, 5.42 mmol) was suspended in 20 mL of diethyl ether at –78 °C. Thereafter 30 mL (17.4 mmol) of a 1,4-dilithiobutane solution in diethyl ether (0.58 M) was added dropwise. The suspension was slowly warmed to 0 °C. At this temperature the stirring was continued for 4 h until all the starting compounds were consumed. The color of the solution turned red and lithium chloride precipitated. The precipitate was removed by filtration with a *Schlenk* frit (G4). Then 5 mL of THF were added to the clear filtrate. At –40 °C white crystals of **1-Hf** grew. Yield of **1-Hf**: 3.49 g (89 % with respect to starting $HfCl_4(thf)_2$). **^1H NMR** (400 MHz, $[D_8]$THF, –30 °C): δ = 0.05 (12 H, br, α-CH_2-Hf), 1.85 (m, 20 H, THF), 1.96 (12 H, br, β-CH_2), 3.69 (m, 20 H, THF). **$^{13}C\{^1H\}$ NMR** (100.6 MHz, $[D_8]$THF, –30 C): δ = 26.4 (THF), 36.2 (β-CH_2), 56.1 (br., α-CH_2-Hf), 68.3 (THF). **^1H NMR** (400 MHz, $[D_8]$toluene, –20 °C): δ = 0.86 (12 H, br, α-CH_2-Hf), 1.31 (m, 20 H, THF), 2.89 (12 H, br, β-CH_2), 3.50 (m, 20 H, THF). **$^{13}C\{^1H\}$ NMR** (100.6 MHz, $[D_8]$toluene, –20 C): δ = 25.3 (THF), 34.9 (β-CH_2), 57.2 (α-CH_2-Hf), 67.6 (THF).

Reaction of $ZrCl_4(thf)_2$ with 1,4-Dilithiobutane in the 1:2 Molar Ratio: $ZrCl_4(thf)_2$ (1.3 g, 3.45 mmol) was suspended in a solvent mixture of 5 mL of diethyl ether and 10 mL of THF. At –78 °C 15 mL of an ethereal 1,4-dilithiobutane solution (7.35 mmol, 0.49 M) was added in small portions. Thereafter the cooling bath was warmed to –40 °C. During this time the fast depositing $ZrCl_4(thf)_2$ disappeared and slowly depositing white lithium chloride formed. At the moment when residual substrate started to combine with the fine precipitate with formation of an creme-colored oil, the reaction mixture was cooled again to –55 °C and additional 5 mL of THF were added. Now the oil dissolved and a yellow solution formed containing a fine white precipitate. The solid was removed by filtration and was collected in a cooled flask and stored overnight at –78 °C. Crystals of $[LiCl(thf)_2]_2$ formed.[33] The mother liquor was decanted and layered with 10 mL of diethyl ether. At –78 °C a yellow sticky substance formed which was isolated by decanting the mother liquor. Then this substance was dried in vacuo. A $[D_8]$THF solution was studied at –40 °C by NMR spectroscopy. This solution is highly temperature sensitive and quickly turned brownish black already at –20 °C. The product is a mixture of **1-Zr** and an unknown organozirconium compound. **1-Zr**: **^1H NMR** (400 MHz, $[D_8]$toluene, –40 °C): δ = 0.71 (12 H, br, α-CH_2-Zr), 1.59 (20 H, br, THF), 2.46 (12 H, br, β-CH_2), 3.46 (20 H, br, THF). **$^{13}C\{^1H\}$ NMR** (100.6 MHz, $[D_8]$toluene, –40 °C): δ = 25.6 (THF), 36.1 (β-C), 50.0 (α-C-Zr), 68,3 (THF). **^1H NMR** (400 MHz, $[D_8]$THF, –40 °C): δ = 0.08 (12 H, br, α-CH_2-Zr), 1.78 (32 H, br, β-CH_2, THF), 3.62 (20 H, br, THF). **$^{13}C\{^1H\}$ NMR** (100.6 MHz, $[D_8]$THF, –40 °C): δ = 25.3 (CH_2, THF), 36.2 (β-C), 50.1 (α-C-Zr), 68.1 (THF). Unknown organozirconium compound: **^1H NMR** (400 MHz, $[D_8]$toluene, –40 °C): δ = 1.11 (α-CH_2Zr), 3.20 (β-CH_2). **$^{13}C\{^1H\}$ NMR** (100.6 MHz, $[D_8]$toluene, –40 °C): δ = 16.6 (β-C), 66.0 (α-C-Zr).

NMR Control of the Solvolysis of 1-Zr and 1-Hf: Approx. 0.1 g of **1-Zr** and **1-Hf** were dissolved at –20 °C in approx. 0.7 mL of $[D_8]$THF or $[D_8]$toluene (approx. 0.2 M solutions) and transferred into NMR tubes. Immediately thereafter the NMR spectra were recorded at 25 °C. The NMR sample remained in the tempered NMR spectrometer and spectra were recorded in regular intervals (^1H NMR of **1-Zr** in $[D_8]$THF: 0 h, 4 h, 5.5 h. ^1H NMR of **1-Hf** in $[D_8]$THF: 0 h, 4 h, 24 h, 49 h, 142 h, 310 h. ^1H NMR of **1-Hf** in $[D_8]$toluene: 0 h, 5.5 h, 24 h, 49 h). The residual solvent signals were used as standard to determine the intensity of the resonances (see Figure 4).

Single Crystal Preparation of $[(thf)_4Li][HfCl_5(thf)]$ (2): $HfCl_4(thf)_2$ (4.04 g, 8.70 mmol) was suspended in 30 mL of diethyl ether and cooled to –40 °C. 1,4-Dilithiobutane (30 mL of a 0.58 M diethyl ether solution, 17.4 mmol) was added to this suspension. The reaction mixture was stirred at this temperature for 4 h. Then the precipitated lithium chloride was removed with a precooled frit covered with diatomaceous earth. At –40 °C THF was slowly added dropwise to the filtrate till the light brown precipitate redissolved again. After filtration the clear filtrate was stored at –78 °C. A brown solid crystallized and was recrystallized several times from THF solution until colorless crystals of $[(thf)_4Li]$ $[HfCl_5(thf)]$ (**2**) were isolated.

Single Crystal Preparation of $[\{(tmeda)Li\}_2(nBu)_2Zr(C_4H_8)_2]$ (3): A solution of 1,4-dilithiobutane (19.0 mL of a 1.5 M diethyl ether solution, 28.5 mmol) was diluted with 50 mL of diethyl ether and cooled to –40 °C. $ZrCl_4(thf)_2$ (3.3 g, 8.75 mmol) were added in small portions. After 2 h of stirring at –40 °C the reaction was finished. The lithium chloride precipitate was removed by filtration with a precooled *Schlenk* frit. Then 3.9 mL of TMEDA (3.0 g, 26.0 mmol) were added dropwise at –40 °C to the stirred solution. During this time a clumpy white precipitate formed, which was collected on a cooled frit and dried in vacuo. The solid was washed from the frit with 60 mL of diethyl ether and this suspension was stirred for 3 h at –50 °C. Remaining solid materials were removed by filtration and the clear filtrate was stored at –40 °C. After 3 d a few slightly orange crystals of $[\{(tmeda)Li\}_2(n\text{Bu})_2Zr(C_4H_8)_2]$ (**3**) precipitated besides an amorphous white solid.

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[34–36] The structures were solved by Direct Methods (SHELXS)[37] and refined by full-matrix least-squares techniques against F_o^2.[38] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[38] The crystal of **3** was extremely thin and of low quality, resulting in a substandard data set; however, the structure is sufficient to show connectivity and geometry despite the high final *R* values. We only publish the conformation of the molecule and the crystallographic data. We will not deposit the data at the Cambridge Crystallographic Data Centre. Crystallographic data as well as structure solution and refinement details are summarized in Table S2 (Supporting Information). XP[39] and POV-Ray[40] were used for the structure representations.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1975946 for 1-Hf, CCDC-1975947 for **1-Zr**, and CCDC-1975948 for 2 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Representation of the complete molecular structures of **1-Zr** and **1-Hf**, crystal and refinement data, NMR spectra.

Acknowledgements

We acknowledge the valuable support of the NMR service platform (www.nmr.uni-jena.de/) of the Faculty of Chemistry and Earth Sciences of the Friedrich Schiller University Jena, Germany.

Keywords: Zirconium; Hafnium; Organohafniate complexes; Organozirconiate complexes; α,ω-Alkanediides

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Received: January 10, 2020