

Generation and Structural Characterization of an [(Imidazol-2-ylidene)HfCl₅]-Anion/Imidazolium Cation Salt

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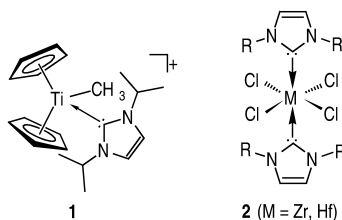
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The reaction of 1,3-diisopropylimidazolium chloride (**3**) with benzylpotassium in d₅-bromobenzene generates the stable carbene 1,3-diisopropylimidazol-2-ylidene that is trapped by hafnium tetrachloride. A chloride anion is subsequently added to the Hf atom of the resulting intermediate to yield the salt [(1,3-diisopropylimidazol-2-ylidene)HfCl₅[−]][1,3-diisopropylimidazolium⁺] **6** that was characterized by an X-ray crystal structure analysis.

Key words: Stable Carbenes, Imidazol-2-ylidene, Hafnium Complex

Introduction

Following the pioneering work of Öfele and Wanzlick [1] and of Arduengo *et al.* [2] imidazol-2-ylidenes and related compounds have become of great interest as stabilizing ligands in transition metal chemistry and as controlling ligands in catalysis [3]. Imidazol-2-ylidene complexes have become known for a great variety of d-block elements. However, among them the number of group 4 metal complexes is still rather small [4–6]. Among the first examples that were structurally characterized by X-ray diffraction was the cationic titanocene complex **1** [5], which exhibits by a conformational “in-plane” orientation of the heterocyclic carbene ligand with the metallocene σ-ligand plane. Shortly thereafter, we have described the structural features of a series of differently substituted bis(imidazol-2-ylidene)MCl₄ complexes of zirconium and hafnium (**2**), together with a theoretical analysis of the specific bonding features of these complexes [6]. They all exhibit pseudo-octahedral coordination geometries of the central metal atoms with the carbene ligands oriented trans to each other. The carbene ligand pairs adopt a conformational orientation in the solid state where the five-membered heterocycles are arranged coplanar and bisecting the Cl–M–Cl angles.



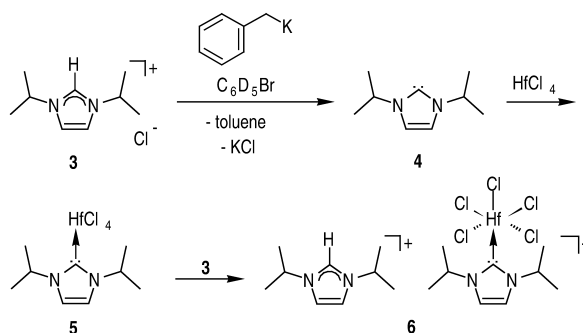
Scheme 1.

The complexes **2** were usually prepared by treatment of the respective MCl₄(THF)₂ reagent (M = Zr or Hf) with the preformed stable “Arduengo-carbene”. It must be assumed that the reaction sequence proceeds stepwise, *i. e.* that one THF ligand at a time is replaced by the incoming stable carbene ligand. Formation of an intermediate mono-carbene complex [(imidazol-2-ylidene)MCl₄(THF)] is likely, although we have not observed this species so far in our experiments [6]. We have now carried out the reaction between HfCl₄ and the Arduengo carbene ligand 1,3-diisopropylimidazol-2-ylidene under slightly different conditions and were able to characterize a charged mono-imidazol-2-ylidene complex that was formed under these specific reaction conditions.

Results and Discussion

1,3-Diisopropylimidazolium chloride (**3**) [7] was used as the starting material for the *in situ* generation of 1,3-diisopropylimidazol-2-ylidene. For that purpose a mixture of the imidazolium salt **3** was treated with 0.5 molar equivalents of each

* X-ray crystal structure analysis.



Scheme 2.

benzylpotassium and of HfCl₄ in d₅-bromobenzene. After a reaction time of 1 h the conversion was complete as judged by NMR spectroscopy and the products characterized spectroscopically. Single crystals that were obtained from this d₅-bromobenzene reaction mixture were used for the characterization of the obtained product by X-ray diffraction. The structural and spectroscopic analysis revealed that the salt [1,3-diisopropylimidazolium⁺][(1,3-diisopropylimidazol-2-ylidene)HfCl₅[−]] (**6**) had been formed. Apparently, in the polar reaction mixture the benzylpotassium reagent has served as a base to abstract a proton from carbon atom C-2 of the imidazolium salt (**3**) to *in situ* generate the stable heterocyclic carbene **4**. This in turn then added to HfCl₄ to probably generate the reactive intermediate [(1,3-diisopropylimidazol-2-ylidene)HfCl₄] (**5**). Under the applied reaction conditions this coordinatively unsaturated complex then was apparently rapidly stabilized by chloride addition to form the observed product **6** (see Scheme 2).

In solution, the [(1,3-diisopropylimidazol-2-ylidene)HfCl₅]-anion shows a ¹H NMR singlet at δ = 6.61 corresponding to the ring protons 4-H, 5-H in addition to the typical isopropyl resonances [septet at δ = 6.08 (2H), doublet at 1.09 (12H, ³J = 6.6 Hz)]. The corresponding ¹H NMR signals of the heterocyclic cation framework appear at δ = 7.13 (4-H, 5-H) and 6.79 (2-H). Most characteristic is the ¹³C NMR spectrum of **6** featuring the imidazol-2-ylidene C-2 resonance of the complex anion at δ = 187.5, whereas the C-2 ¹³C NMR signal of the corresponding cation of **6** appears at δ = 139.9.

The X-ray crystal structure analysis of the salt **6** shows well separated anion and cation moieties. The anion of **6** shows the presence of a pseudo-octahedrally coordinated hafnium center. The imidazol-2-ylidene

Table 1. A comparison of typical bond lengths (Å) found in (1,3-diisopropylimidazol-2-ylidene)Hf complexes and corresponding 1,3-diisopropylimidazolium cations^[a].

	2a	6 (anion)	6 (cation)	7
Hf-C2	2.401(2)	2.406(6)		
N1-C2	1.359(3)	1.375(8)	1.328(10)	1.324(2)
N3-C2	1.361(3)	1.356(8)	1.317(10)	1.324(2)
N3-C31	1.473(4)	1.485(9)	1.499(11)	1.488(2)
N1-C11	1.471(4)	1.478(9)	1.482(9)	1.488(2)
N1-C5	1.376(4)	1.387(9)	1.382(9)	1.379(2)
N3-C4	1.369(4)	1.369(9)	1.380(10)	1.379(2)
C4-C5	1.327(5)	1.340(10)	1.355(11)	1.350(4)
ref.	[5]	b	b	[6]

[a] See Fig. 1 for the principal atom numbering scheme used;

[b] this work.

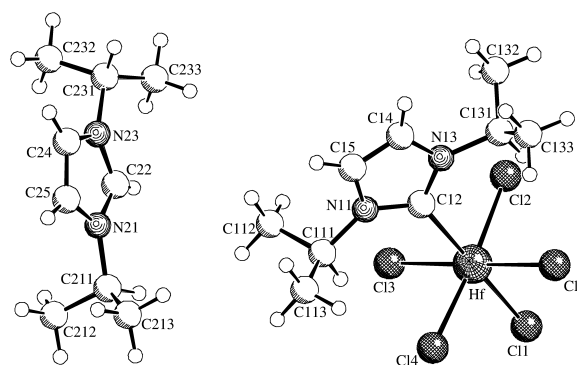


Fig. 1. A view of the molecular structure of the salt [1,3-diisopropylimidazol-2-ylidene)HfCl₅][−][1,3-diisopropylimidazolium⁺] (**6**). Selected bond lengths (Å) and angles (°): Hf-C2 2.406(6), Hf-C11 2.461(2), Hf-C12 2.427(2), Hf-C13 2.461(2), Hf-C14 2.433(2), Hf-C15 2.430(2); C2-Hf-C11 178.8(2), C2-Hf-C12 87.3(2), C2-Hf-C13 90.7(2), C2-Hf-C14 88.0(2), C2-Hf-C15 89.4(2), C11-Hf-C12 93.2(1), C11-Hf-C13 90.4(1), C11-Hf-C14 91.5(1), C11-Hf-C15 89.4(1), C12-Hf-C13 88.2(1), C12-Hf-C14 175.0(1), C12-Hf-C15 91.9(1), C13-Hf-C14 90.3(1), C13-Hf-C15 179.8(1), C14-Hf-C15 89.7(1). For additional values see Table 1.

ligand is bonded to Hf through the carbon atom C2. The Hf-C2 bond (2.406(6) Å) is in a typical range (see Table 1); it is almost identical to the Hf-C2 bond length found in the respective bis(imidazol-2-ylidene)HfCl₄ complex **2a** (R = isopropyl, M = Hf: Hf-C2: 2.401(2) Å). The plane of the carbene ligand in the anion **6** is bisecting the adjacent Cl-Hf-Cl angles. The C2-N1/N3 bonds in the anion of **6** (1.375(8) Å, 1.356(8) Å) are slightly longer than the corresponding C2-N1/N3 distances in the corresponding imidazolium cation of **6** (1.328(10) and 1.317(10) Å). The Hf-C11

bond in **6**(anion) (trans-oriented to the carbene ligand) is found at 2.461(2) Å, which is slightly longer than the cis Hf-(Cl12 to Cl15) linkages which range between 2.427(2) and 2.461(2) Å. The bond angles around Hf deviate only marginally from ideally octahedral (see legend of Fig. 1). Figure 1 shows a view of the cation and the anion parts of **6**. Table 1 lists characteristic bond lengths of **6**(anion) and **6**(cation) with typical systems for comparison {**2a**, R = isopropyl, M = Hf, see Scheme 1; [1,3-diisopropylimidazolium⁺][BPh₄[−]] (**7**), obtained by treatment of **3** with NaBPh₄}.

Experimental Section

Reactions involving metal-containing compounds were carried out under argon using Schlenk-type glassware or in a glove box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. X-ray crystal structure analyses: The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **276**, 307 (1997), absorption correction SORTAV (R.H. Blessing, *Acta Crystallogr.* **A51**, 33 (1995); R.H. Blessing, *J. Appl. Crystallogr.* **30**, 421 (1997), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 213 595. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Formation of the salt 6: The formation of complex **6** was only carried out in an NMR tube experiment. From this solution the single crystals were obtained that were used for the X-ray crystal structure analysis of **6**. Complex **6** was neither prepared nor isolated on a preparative scale.

A solution containing 1,3-diisopropylimidazolium chloride **3** (20 mg, 0.11 mmol), benzylpotassium (8 mg, 0.05 mmol) and hafnium tetrachloride (17 mg, 0.05 mmol) in 0.5 ml d₅-bromobenzene was stirred for 1 h at ambient

temperature. The spectroscopic analysis revealed the practically quantitative formation of **6**. Crystallization from the C₆D₅Br solution at −20 °C gave single crystals of **6** for the X-ray crystal structure analysis. ¹H NMR (400.1 MHz, d₅-bromobenzene, 300 K): anion: δ = 6.61 (s, 2H, 4-H, 5-H), 6.08 (sept. ³J_{HH} = 6.6 Hz, 2H, NCH), 1.09 (d, ³J_{HH} = 6.6 Hz, 12H, NCH(CH₃)₂); cation: δ = 7.13 (s, 2H, 4-H, 5-H), 6.79 (s, 1H, 2-H), 4.27 (broad sept., 2H, NCH), 1.09 (d, ³J_{HH} = 6.6 Hz, 12H, NCH(CH₃)₂). −¹³C{¹H} NMR (100.6 MHz, d₅-bromobenzene, 300 K): anion: δ = 187.5 (C2), 115.3 (C4, C5), 49.9 (NCH), 21.6 (NCH(CH₃)₂); cation: δ = 139.9 (C2), 126.5 (C4, C5), 49.9 (NCH), 21.6 (NCH(CH₃)₂). −GCOSY (400.1 MHz / 400.1 MHz, d₅-bromobenzene, 300 K): anion: δ¹H / δ¹H = 6.08 / 1.09 (NCH / NCH(CH₃)₂), 1.09 / 6.08 (NCH(CH₃)₂ / NCH); cation: δ = 4.27 / 1.09 (NCH / NCH(CH₃)₂), 1.09 / 4.27 (NCH(CH₃)₂ / NCH). −GHSQC (100.6 MHz / 400.1 MHz, d₅-bromobenzene, 300 K): anion: δ¹³C / δ¹H = 115.3 / 6.61 (C4, C5; 4-H, 5-H), 49.9 / 6.08 (NCH / NCH), 21.6 / 1.09 (NCH(CH₃)₂ / NCH(CH₃)₂); cation: 139.9 / 6.79 (C2 / 2-H), 126.5 / 7.13 (C4, C5 / 4-H, 5-H), 49.9 / 4.27 (NCH / NCH), 21.6 / 1.09 (NCH(CH₃)₂ / NCH(CH₃)₂). −GHMBC (100.6 MHz / 400.1 MHz, d₅-bromobenzene, 300 K): anion: δ¹³C / δ¹H = 187.5 / 6.61 (C2 / 4-H, 5-H), 49.9 / 1.09 (NCH / NCH(CH₃)₂), 21.6 / 6.08, 1.09 (NCH(CH₃)₂ / NCH, NCH(CH₃)₂); cation: 49.9 / 1.09 (NCH / NCH(CH₃)₂), 21.6 / 1.09 (NCH(CH₃)₂ / NCH(CH₃)₂).

X-ray crystal structure analysis of 6: formula C₉H₁₆N₂Cl₅Hf⁺C₉H₁₇N₂, *M* = 661.22, colourless crystal 0.30 × 0.15 × 0.10 mm, *a* = 14.331(1), *b* = 12.126(1), *c* = 16.370(1) Å, β = 113.07(1)°, *V* = 2617.2(3) Å³, ρ_{calc} = 1.678 g cm^{−3}, μ = 45.08 cm^{−1}, empirical absorption correction (0.345 ≤ *T* ≤ 0.661), *Z* = 4, monoclinic, space group *P*2₁/*n* (No. 14), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 8913 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{−1}, 5311 independent (*R*_{int} = 0.046) and 4147 observed reflections [*I* ≥ 2σ(*I*)], 265 refined parameters, *R* = 0.048, *wR*² = 0.127, max. residual electron density 3.97 (−1.88) e Å^{−3} close to Hf, hydrogens calculated and refined as riding atoms.

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