Bond Activation

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Hafnium: Stepping into the Limelight!

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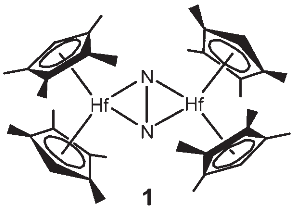
In the periodic table, just as in real life, not all the protagonists play leading roles. Depending on their abilities some elements are more prominent than others. Frequently, one group in the periodic table hosts one or two outstanding characters, while the other elements appear as pale epigones. For example, titanium and zirconium dominate Group 4. Both are leading actors which are akin as can be expected for close relatives but possess enough individuality to play their roles with equal billing. Next to these two elements hafnium, the third member of Group 4, appears strangely insignificant. Hafnium's position as a latecomer is apparent even historically. While titanium and zirconium were discovered in the 18th century, proof of the existence of hafnium was achieved only in 1923. The reason for this delay in entering "the stage" of elements is the close resemblance of hafnium and zirconium. As a consequence of the lanthanide contraction both metals have practically identical metal and ionic radii. Hafnium, which accompanies zirconium in its minerals, therefore remained undiscovered. If the chemistry of hafnium and zirconium are compared it seems that the heavier hafnium, similar to the situation with the siblings palladium/platinum, imitates zirconium in a sluggish way. Some researchers have exploited this property to study mechanistic peculiarities of zirconium chemistry in detail.[1]

However, very recently a number of publications have shown that hafnium compounds can favorably compete with their zirconium counterparts in the highly competitive fields of C–H and N_2 activation. A subtle difference between zirconocene and hafnocene fragments is their preference for the formation of σ and π bonds.[2] The bonding behavior probably reflects the stability of the free metallocenes. Hafnium's stronger participation in σ-bonding can be exploited advantageously. A more pronounced σ-bonding is characterized by a stronger degree of backbonding. Such bonding changes the character of the ligand and can be interpreted as a formal reduction. This behavior is beneficial for the activation of dinitrogen. In compound **1** the strong backbonding decreases the bond order of the side-on coordinated N_2 ligand. The N–N distance of 1.098 Å in molecular dinitrogen is extended to 1.432(11) Å. The amidic character of the ligand can thus be used to allow reactions of the otherwise inert nitrogen with electrophiles.[3]



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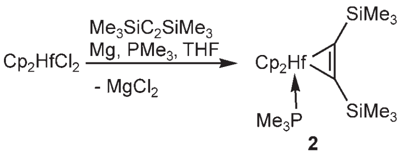
The remarkable achievements of the research groups of P. Chirik and M. Fryzuk in this area have been recognized recently also in this journal.[4] The group of U. Rosenthal in Rostock has also been involved in Group 4 metallocene chemistry for several years, and their studies on the bis(trimethylsilyl)acetylene adducts have revealed a very rich and exciting chemistry.[5] A closer look at the studies from Rostock reveals an almost complete absence of hafnium chemistry. The focus on titanium and zirconium is even more peculiar, since the metallocene variations of these two metals were studied in a very systematic way. The reason for the lack of analogous hafnium compounds was the inaccessibility of the hafnocene bis(trimethylsilyl)acetylene adducts. The method of reducing the metallocene dichloride with magnesium in THF in the presence of the respective alkyne works well for titanium and zirconium; however, for hafnocene this reaction leads to the formation of a number of unidentifiable products. This seems to be a result of the interaction of the strong Lewis acids hafnocene and hafnocene monochloride with THF. This problem may actually be responsible for the rarity of hafnocene alkyne complexes in general.[7]

Quite recently Rosenthal and co-workers reported important progress on the synthesis of hafnocene alkyne complexes. In the presence of a stoichiometric amount of trimethylphosphane, the long-sought conversion of hafnocene dichloride with magnesium in THF proceeded to give the phosphane adduct of the desired compound **2** [Eq. (1)].[6]



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(1)

The use of the stronger reducing agent lithium and the exchange of THF for toluene led to the formation of the already known bimetallic hafnocene alkyne complex **3** [Eq. (2)].[6]

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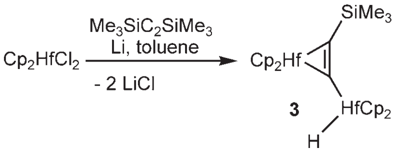
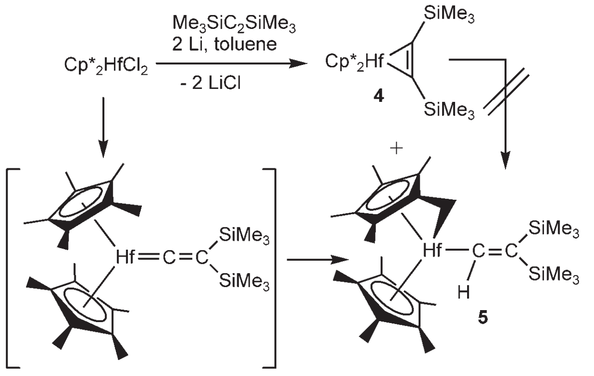


(2)

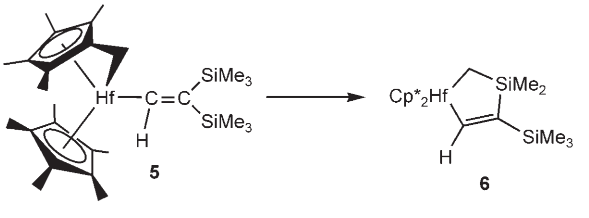
The change to the sterically more demanding Cp^*_2Hf system ($Cp^* = C_5Me_5$) subsequently allowed access to the donor-free bis(trimethylsilyl)acetylene adduct **4** (Scheme 1).



Scheme 1.

More interesting than the formation of **4** proved to be the observation of an alternative reaction path by which compound **5** was isolated as a side product.[8] According to the authors its formation proceeds via oxidative addition of the hafnocene fragment across the Si–C bond and subsequent rearrangement to the vinylidene complex, which stabilizes itself by oxidative addition into a methyl group of a Cp* ligand. Similar reaction patterns have been observed in the chemistry of Chirik's dinitrogen complexes.[4b]

The formation of **5** is independent of **4**. Following the argumentation of the authors, the free hafnocene can either coordinate to the alkyne triple bond thus forming **4** or alternatively to the Si–C bond. The stronger backbonding ability of hafnium leads to the oxidative addition of this bond. The silyl group migration, which is required for the formation of **5**, can be interpreted as the insertion of the alkyne into the Si–Hf bond. Compound **5** eventually selectively reacts to give the hafnasilacyclopentene **6** [Eq. (3)].



(3)

The latter can be regarded as the product of oxidative addition of the mentioned vinylidene complex into the C–H bond of a trimethylsilyl group. DFT calculations by Jemmis, Pathak, and Bach suggest that **5** and **6** are the kinetic and thermodynamic products of the stabilization of the vinylidene complex through C–H activation. The structural type of **6** is already known from insertion reactions into silene complexes of zirconocene.[9]

The formation of **3** and **5** are examples of the above-mentioned superior reactivity of hafnocene compared to zirconocene. The observed activation of the Si–C bond of the silylalkyne is without precedent for zirconocene. The competition of coordination modes is nonetheless also known for zirconocene. A similar effect was studied by Rosenthal and co-workers using the zirconocene adducts of hydrosilylalkynes.[10] Considering the ability of Group 4 metallocenes for σ-bond metathesis of Si–H and Si–Si bonds,[11] this was probably not completely unexpected.

As a result of the studies of Rosenthal and Chirik, a new player has entered the stage of transition-metal chemistry. Hafnium is on the track to loose its image as a pale "zirconium-clone". While it may not exhibit substantially different chemistry in the oxidation state +4, it seems to bear a rich reactivity spectrum in its lower oxidation states. These unusual qualities are so far only apparent in the described stoichiometric examples. Possible catalytic properties connected to this are eagerly anticipated.

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[1] Interestingly, the physical properties of zirconium and hafnium are sometimes markedly different. The neutron absorption of hafnium is about 600 times higher than that of zirconium. For this reason hafnium-free zirconium is used as fuel rod cladding, while zirconium-free hafnium is employed as neutron catcher.

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