JACS ARTICLES

Published on Web 03/10/2009

Combination of Spectroscopic Methods: *In Situ* NMR and UV/Vis Measurements To Understand the Formation of Group 4 Metallacyclopentanes from the Corresponding Metallacyclopropenes

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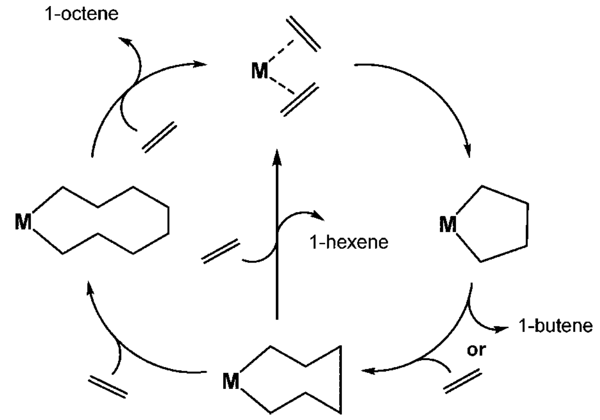
Abstract: By reaction of the dichloride *rac*-(ebthi)HfCl$_2$ [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] with lithium in the presence of bis(trimethylsilyl)acetylene, the hafnacyclopropene *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Hf**) was obtained. The reaction of the blue-green complex **1-Hf** with an excess of ethylene at room temperature leads by insertion of the olefin to the yellow-green hafnacyclopentene **2-Hf** which is only stable in solution and eliminates the alkyne at 100 °C under ethylene to form the corresponding yellow hafnacyclopentane **3-Hf**, which was characterized by X-ray crystal structure analysis. The reaction of **1-Hf** to give stepwise via **2-Hf** the complex **3-Hf** was investigated in detail and compared to the formation and stability of the corresponding zirconacyclopropene **1-Zr**, zirconacyclopentene **2-Zr**, and zirconacyclopentane **3-Zr**. Moreover, the reaction of the titanocene alkyne complex **1-Ti** with ethylene was studied. For investigating the reaction behavior of the alkyne complexes **1-M**, NMR spectroscopy was used and the results were compared with UV/vis spectroscopy, suggesting the existence of a bis-π-complex prior to the formation of the hafnacyclopentene **2-Hf**.

1. Introduction

Saturated metallacycles such as metallacyclopentanes or metallacycloheptanes are believed to play an important role in the oligomerization of ethylene to give linear α-olefins (LAOs). Upon insertion of ethylene into an existing metal olefin complex followed by further insertions of ethylene into the M−Cα bond, the corresponding metallacycles are formed which can then selectively eliminate the product olefins (i.e., 1-butene for metallacyclopentanes, 1-hexene for metallacycloheptanes, and 1-octene for metallacyclononanes, Scheme 1).[1] Metallacycles of group 4 metals can serve as model complexes for active catalysts for this reaction.

Scheme 1. Mechanism for the Oligomerization of Ethylene with Metallacycles as Key Intermediates



The complexes *rac*-(ebthi)M(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Ti**: M = Ti; **1-Zr**: M = Zr)[2] are excellent starting materials, which eliminate the alkyne upon reaction with a variety of unsaturated substrates.[3] Being relevant to the polymerization of olefins,[4] the zirconacyclopropene *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Zr**) was found to react by elimination of the alkyne with different olefins, e.g., ethylene, propylene, styrene, vinylpyridine, nor-

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10.1021/ja809368s CCC: $40.75

bornadiene, acrylates, and isoprene to well-defined differently substituted zirconacyclopentanes.[5] These zirconacycles are proven to be intermediates in coupling reactions of unsaturated hydrocarbons with zirconocene complex fragments.[6a,b] This chemistry was studied and reviewed extensively by the groups of Negishi and Takahashi.[6c,d] Moreover the relationship to other zirconacycles, i.e., zirconacyclopentenes and zirconacyclopentadienes has been pointed out.[6c,e] However, only a few zirconacyclopentanes, being relevant as model complexes for the above-mentioned oligomerization of ethylene, have been isolated and structurally characterized.[5,7] For example, Takahashi and co-workers reported the isolation and structural characterization of the stable zirconacyclopentane (t-$Bu_2C_5H_3)_2Zr(C_4H_8)$,[7a] and the structure of the complex *rac*-(ebi)Zr(C_4H_8)[7c] (ebi = 1,2-ethylene-1,1′-bis(η^5-indenyl)) also was briefly mentioned. The corresponding hafnacyclopentanes have also been reported before;[8] their reactivity, e.g., in reactions with alkynes, and their role in the polymerization of ethylene were studied in detail by Erker and co-workers.[8a,d] To the best of our knowledge there is only one example for a structural characterization of a stable hafnacyclopentane, which was also published by this group.[9]

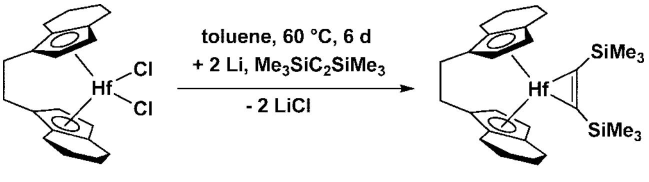
In the past we investigated the reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1-Zr**) with ethylene, giving an insertion to the corresponding zirconacyclopentene **2-Zr** at low temperature. At room temperature the zirconacyclopentane *rac*-(ebthi)Zr(C_4H_8) (**3-Zr**), which was isolated as stable yellow crystals and characterized by X-ray analysis, is formed. Complex **2-Zr** was assumed to be the intermediate for the formation of **3-Zr**.[5a,10]

In this paper we report on the synthesis of *rac*-(ebthi)Hf(η^2-$Me_3SiC_2SiMe_3$) (**1-Hf**) and its reaction with an excess of ethylene at room temperature to the hafnacyclopentene **2-Hf**. In the presence of ethylene, this species eliminates the alkyne at higher temperature to form the corresponding hafnacyclopentane *rac*-(ebthi)Hf(C_4H_8) (**3-Hf**). We were interested to compare the reaction and stability of these hafnium metallacycles **1-Hf**, **2-Hf**, and **3-Hf** to those of the corresponding titanacyclopropene **1-Ti**, zirconacyclopropene **1-Zr**, zirconacyclopentene **2-Zr**, and zirconacyclopentane **3-Zr**. This was solely possible on the basis of the recently established synthetic procedure using lithium in toluene for the reduction of the corresponding dichlorides Cp'_2HfCl_2 (Cp′ = *rac*-(ebthi) or Cp*)[11] and by the combination of *in situ* NMR and UV/vis techniques.

2. Results and Discussion

The hafnacyclopropene *rac*-(ebthi)Hf(η^2-$Me_3SiC_2SiMe_3$) (**1-Hf**) was obtained by the reaction of *rac*-(ebthi)$HfCl_2$ with lithium in toluene in the presence of $Me_3SiC_2SiMe_3$ in a good yield of 65% (Scheme 2). **1-Hf** is an air and moisture sensitive blue-green solid, which melts under decomposition at 101−103 °C.

Scheme 2. Formation of the Hafnocene Alkyne Complex **1-Hf**



1-Hf

In complex **1-Hf** the alkyne is coordinated symmetrically to the metal. The most important property of this compound is the strong interaction of the alkyne with the hafnium which can be derived from the spectroscopic and structural data. The observed wavenumber ν (C≡C) of 1439 cm^{-1} for complex **1-Hf** is indicative of the strong complexation of the alkyne to the metal center resulting in the hafnacyclopropene structure (**1-Ti**: 1594; **1-Zr**: 1534 cm^{-1}).[2] The ^{13}C NMR signal for the carbon atoms of the complexed alkyne at 281.2 ppm is shifted far downfield compared to the analogous titanium and zirconium complexes *rac*-(ebthi)M(η^2-$Me_3SiC_2SiMe_3$) (**1-Ti**: 244.5; **1-Zr**: 259.7 ppm).[2] The same trend was observed recently in the series of complexes $Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti: 1563/1596 cm^{-1}, 248.5 ppm;[12] Zr: 1516 cm^{-1}, 260.5 ppm;[13] Hf: 1470 cm^{-1}, 283.4 ppm[11a]).

Nevertheless, the reaction of the blue-green complex **1-Hf** with an excess of ethylene at ambient temperature leads by insertion of the olefin to the yellow-green hafnacyclopentene **2-Hf**, which is only stable in solution and could not be isolated. Upon removal of the ethylene atmosphere, complex **1-Hf** can be regained (Scheme 3).

^{13}C NMR investigations of **2-Hf** clearly show the incorporated alkene, giving signals at 28.4 (C3) and 47.2 ppm (C4).

Complex **2-Hf** eliminates the alkyne at 100 °C under an ethylene atmosphere to form the corresponding hafnacyclopentane **3-Hf**. This complex was isolated as stable yellow crystals in a yield of 70% and characterized by X-ray crystal structure analysis (Scheme 4).

NMR measurements show the resonances for the Cp protons at 4.79 and 6.20 ppm. Compared to the corresponding Zr complex **3-Zr**, this is in the same range (4.92 and 6.32 ppm).

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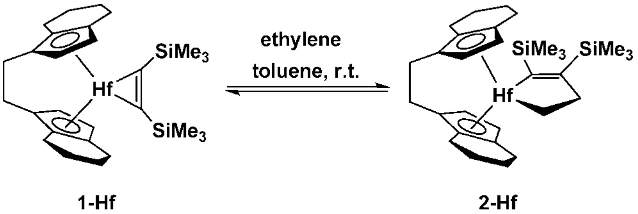
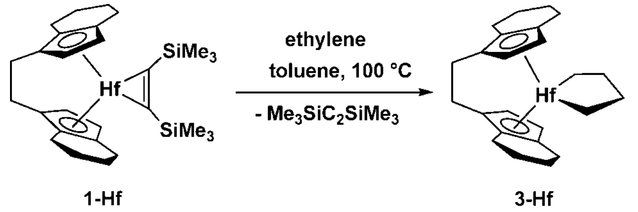
Scheme 3. Reaction of **1-Hf** with Ethylene To Give the Hafnacyclopentene **2-Hf**



Scheme 4. Formation of the Hafnacyclopentane **3-Hf**



Moreover the difference of the chemical shifts of the Cp protons in **3-Hf** becomes smaller compared to the alkyne complex **1-Hf** (4.44 and 7.28 ppm). This observation was made before for similar titanium and zirconium complexes.

The molecular structure of complex **3-Hf** is depicted in Figure 1. The characteristic data of the hafnacycle **3-Hf** (Hf−Cα 2.258(3) and 2.256(3), C*β*−C*β*′ 1.493(5) Å; Cα−Hf−Cα 84.58(1)°) correspond very well to those of Erker's hafnacyclopentane[9] (Hf−Cα 2.258(5) and 2.282(5), C*β*−C*β*′ 1.511(8) Å; Cα−Hf−Cα 86.2(2)°). Moreover, these data are within the range established for the isostructural complex **3-Zr** (Zr−Cα 2.289(4) and 2.307(4), C*β*−C*β*′ 1.451(9) Å[14]; Cα−Zr−Cα 84.0(2)°).

Reaction of the complex **3-Hf** with $B(C_6F_5)_3$ results in the formation of an active system for ethylene polymerization (T = 40 °C, activity: 204 kg of polymer·mol^{-1}·h^{-1}·bar^{-1}). Most probably the five-membered ring is opened by interaction with the Lewis acid under generation of a zwitterionic species.[15] The latter should consist of a hafnocenium center and a boranate unit linked by the C_4 chain of the hafnacyclopentane. However it was not possible to isolate the assumed active species.

3. Mechanistic Considerations

The formation of metallacyclopentanes starting from alkyne complexes is rather unusual. In many cases exchange reactions of olefins by alkynes are observed.[7a,8d] However, this pathway becomes possible due to the special feature of the bis(trimethylsilyl)acetylene ligand, which is reluctant to undergo coupling reactions,[16] giving the reason why the bis(trimethylsilyl)acetylene ligand, in contrast to other alkynes, can even be removed by ethylene. However, for hafnocene alkyne complexes the described reaction with ethylene is the first example for a substitution of the alkyne by a substrate, as it was observed before for similar titanium and zirconium compounds.

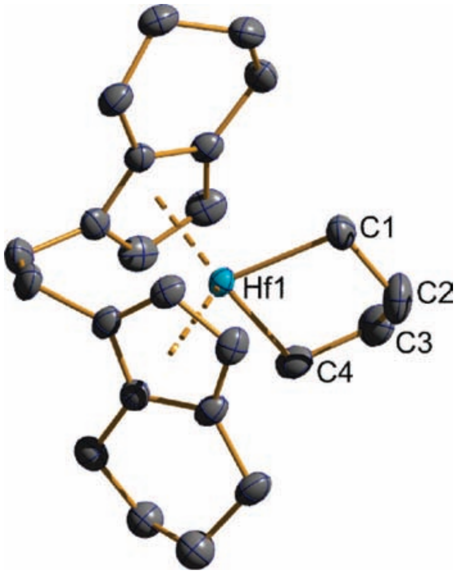


Figure 1. Molecular structure of complex **3-Hf**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 50% probability. Selected bond lengths [Å] and angles [deg]: Hf1−C1 2.258(3), C1−C2 1.553(5), C2−C3 1.493(5), C3−C4 1.513(5), Hf1−C4 2.256(3); Hf1−C1−C2 100.48(19), C1−C2−C3 112.6(3), C2−C3−C4 111.9(3), C3−C4−Hf1 103.0(2), C4−Hf1−C1 84.58(11).

Several groups described the reaction of hafnacyclopentanes with alkynes and observed the totally reverse reaction from hafnacyclopentanes via hafnacyclopentenes to the hafnium alkyne complexes,[8] in the same manner as described for zirconium metallacycles, too. The formation of **2-Hf** from **1-Hf** and ethylene is reversible. Moreover the hafnacyclopentane **3-Hf** is formed at higher temperature by formal coupling of two molecules of ethylene at the hafnium center. Most probably this reaction proceeds via the hafnacyclopentene **2-Hf**, which is indicated by the fact that **2-Hf** is formed at ambient temperature and gives **3-Hf** upon heating in an ethylene atmosphere. These observations prove that the reaction of the alkyne complex with ethylene proceeds rather in an *associative* than in a *dissociative* manner. This is contradictory to the expected behavior of metallocene alkyne complexes which in general act as metallocene generators. In the herein described case an addition, i.e., coordination, followed by subsequent insertion of the substrate to complex **1-Hf** with formation of **2-Hf** followed by an elimination or substitution of the alkyne to give **3-Hf** was evident.

In principle the here established reaction sequence for the formation of the hafnium complexes **2-Hf** and **3-Hf** is similar to the one described for the corresponding zirconium complexes. However, the activation barrier for the olefin insertion is higher for **1-Hf**, as can be derived from the reaction temperature of the formation of the five-membered metallacycles. With regard to the above-discussed stronger complexation of the alkyne with hafnium compared to zirconium, we were interested in what consequences this effect has on the exchange of the alkyne by ethylene. Moreover it was interesting to study the reaction of the corresponding titanocene alkyne complex **1-Ti** with ethylene, which has not been reported before. For these investigations

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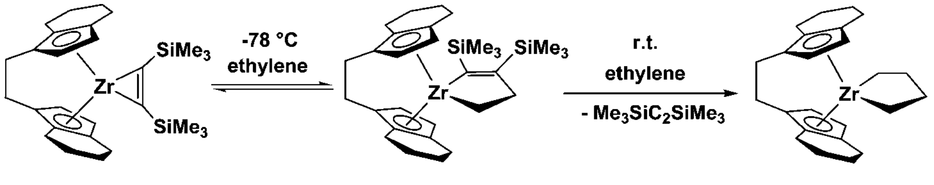
(14) The shorter C*β*−C*β*′ distance in this zirconacyclopentane is a result of a conformational disorder which could not be resolved.

(15) This assumption was made according to the results from the reaction of 1-metallacyclopent-3-ynes with $B(C_6F_5)_3$. The ring opening products have been characterized by X-ray crystallography and used in the polymerization of ethylene. (a) Bach, M. A.; Beweries, T.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Bonrath, W. *Organometallics* **2005**, *24*, 5916. (b) Beweries, T.; Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 241.

Scheme 5. Reaction of **1-Zr** with Ethylene



1-Zr **2-Zr** **3-Zr**

we compared the results of NMR measurements with those of (stopped-flow) UV/vis spectroscopy.

3.1. Reaction of 1-Ti with Ethylene. 3.1.1. NMR. At room temperature, no reaction was found to take place between **1-Ti** and an excess of ethylene in toluene-d_8. However, upon heating to 100 °C, large amounts of butene (identified by ^{1}H NMR[17]) were formed, whereas most of **1-Ti** remained unchanged. No other complex species could be characterized. Attempts to identify a reactive intermediate, for example, an alkyne-olefin π-complex, at −78 °C failed, showing only the alkyne complex **1-Ti**. Most likely, at higher temperature, alkyne dissociation takes place, which is followed by a coupling of two molecules of ethylene at the titanocene fragment and elimination of butene under reconstitution of the alkyne complex (see the olefin oligomerization mechanism in Scheme 1).

3.1.2. UV/Vis Spectroscopy. When complex **1-Ti** was dissolved in a saturated solution of ethylene in toluene, no reaction with the olefin was found to take place. Instead, the spectra show a decrease of the extinction, indicating that **1-Ti** is not stable in solution. Most likely, bis(trimethylsilyl)acetylene dissociates from the complex to give a small amount of free titanocene "*rac*-(ebthi)Ti". This observation is in agreement with the fact that in NMR experiments with pure **1-Ti** (and other titanocene alkyne complexes) free alkyne was found. Such a dissociation finds additional support in the investigations of Mach et al. who reported that the complex $[\eta^5\text{-}C_5Me_4(SiMe)_3]_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ gives, after dissociation of the alkyne, the stable, free titanocene $[\eta^5\text{-}C_5Me_4(SiMe)_3]_2Ti$.[18]

3.2. Reaction of 1-Zr with Ethylene. 3.2.1. NMR. At low temperature (−78 °C), the alkyne complex **1-Zr** reacts with ethylene to give the zirconacyclopentene **2-Zr**, whereas, at ambient temperature, **1-Zr** reacts with ethylene to give the zirconacyclopentane **3-Zr** (Scheme 5). The first reaction is very fast, and **2-Zr** cannot be observed by NMR methods at room temperature. However, at −63 °C **2-Zr** can be detected and disproportionates upon warming to room temperature to give **1-Zr** and **3-Zr** in a 1:1 ratio.[5a] Remarkably, during this reaction 0.5 equiv of bis(trimethylsilyl)acetylene but no ethylene is released. This suggests that the alkyne is a weaker ligand than ethylene.

3.2.2. UV/Vis Spectroscopy. Compound **2-Zr** is unstable at room temperature. Therefore, the reaction of **1-Zr** with 2 equiv of ethylene to give **3-Zr** should be observed. If the concentration of the olefin is in excess and therefore in principle constant, due to the instability of **2-Zr**, the expected consecutive reaction (according to Scheme 5) should give a pseudo-first-order reaction.

In the case of tracing this reaction by UV/vis spectroscopy typical isosbestic points should be found, indicating that only two species are present in solution. Thus, it should be a kinetically uniform reaction.

Under consideration of the fact that the extinction should not exceed a value of 1 considerably with a given solubility of ethylene in toluene,[19] the cell thickness and the concentration of **1-Zr** have to be optimized. Thus, ratios of **1-Zr**/ethylene of 1:10 to 1:35 are realizable, which can be regarded as pseudo conditions.[20]

In Figure 2 reaction spectra are shown for the ratio **1-Zr**/ethylene of 1:22.5. As expected, one isosbestic point is observed. The extinction diagrams (see Supporting Information) confirm the nature of a pseudo-first-order reaction.[21] With the values from Figure 2 a nonlinear curve fit for the chosen wavelength was processed for the pseudo-first-order reaction; a comparison of spectroscopic and fitted values is shown in the Supporting Information (Figure S3). The plotting of those pseudo constants against the ethylene concentration is shown in Figure 3. From the slope of this curve for 25 °C a rate constant of 0.35 s^{-1} can be determined.

3.3. Reaction of 1-Hf with Ethylene. 3.3.1. NMR. The hafnocene alkyne complex **1-Hf** reacts only slightly different with ethylene. At room temperature, only the hafnacylopentene **2-Hf** is observed. This is a reversible reaction because the metallacyclopentene is labile. Exchange between free and incorporated ethylene is observable on the NMR time scale; under reduced ethylene concentration **1-Hf** is regenerated. Conversion of hafnacylopentene **2-Hf** to the hafnacylopentane **3-Hf** requires heating to 100 °C. The overall behavior resembles that observed with **1-Zr**, but the reaction sequence needs higher temperatures to be driven to completion.

3.3.2. UV/Vis Spectroscopy. The formation of **3-Hf** from **2-Hf** is not observed at room temperature. Therefore a simple pseudo-

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(16) This behaviour was observed in numerous reactions in our group before. Moreover Fagan and Nugent and Livinghouse published similar results. (a) Rosenthal, U.; Burlakov, V. V. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; WILEY-VCH: Weinheim, 2002; p *355*. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Spannenberg, A.; Baumann, W. *Organometallics* **2003**, *22*, 884. (c) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (d) Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.

(17) 1-Butene, olefinic protons at 5.71, 5.39, and 5.29 ppm, CH_2 hidden under signals of **1-Ti**, CH_3 0.84 ppm. Besides that, considerable amounts of *cis-* and *trans*-2-butene were generated (5.29 and 1.51 ppm, 5.39 and 1.45 ppm, respectively), as titanocene derivatives are known to catalyze alkene isomerization: Ohff, A.; Burlakov, V. V.; Rosenthal, U. *J. Mol. Catal. A: Chem.* **1996**, *105*, 103.

(18) (a) Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572. (b) Lukesova, L.; Horacek, M.; Stepnicka, P.; Fejrova, K.; Gyepes, R.; Cisarova, I.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2002**, *663*, 134.

(19) Waters, J. A.; Clements, H. E. *J. Chem. Eng. Data* **1970**, *15*, 174.

(20) Creation of pseudo-conditions is a common method in kinetics to allow for an easier description of more complex reactions. This method is described in the literature; e.g., see ref 21b.

(21) (a) Preetz, A.; Drexler, H.-J.; Fischer, C.; Dai, Z.; Börner, A.; Baumann, W.; Spannenberg, A.; Thede, R.; Heller, D. *Chem. Eur. J.* **2008**, *14*, 1445. (b) Connors, K. A. *Chemical Kinetics: the Study of Reaction Rates in Solution*; VCH Publishers, Inc.: New York, 1990; p 445. (c) Mauser, H. *Formale Kinetik*; Bertelsmann Universitätsverlag: 1974.

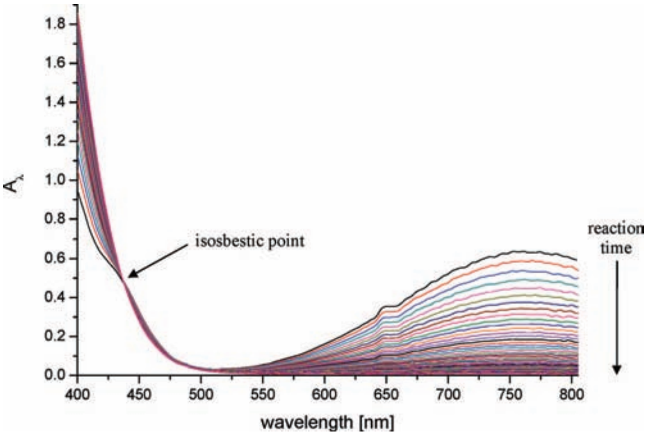

Figure 2. Reaction spectra of **1-Zr** with ethylene (0.0051 mol·L^{-1} **1-Zr**, 0.1168 mol·L^{-1} ethylene; ratio **1-Zr**/ethylene of 1:22.5) in toluene at room temperature.

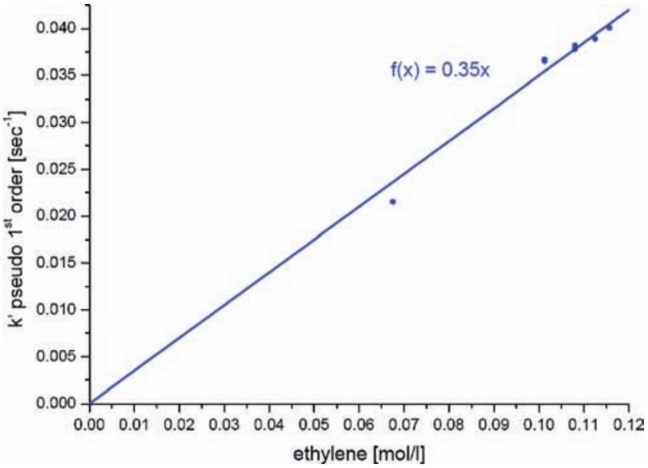

Figure 3. Pseudo rate constants of the reaction of **1-Zr** with ethylene as a function of the ethylene concentration.

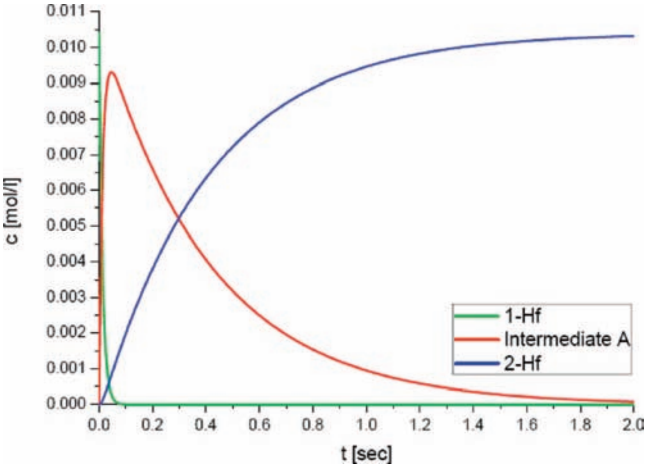

Figure 4. Concentration profile for the reaction of **1-Hf** with ethylene (calculated as consecutive reaction with Specfit from the original data).

first-order reaction should be observed for the conversion of **1-Hf** into **2-Hf** at an excess concentration of ethylene, which is characterized by at least one isosbestic point. Similar to the zirconium case, **1-Hf**/ethylene ratios of 1:10 to 1:30 were realized. The spectra of **1-Hf** resemble those of its zirconium analogue; however, they are slightly shifted to smaller wavelengths.

Surprisingly, we found no isosbestic point, which is valid for the full reaction time (see Supporting Information, Figure S4). Moreover the time dependence is not consistent with a first-order reaction. In fact the experimental results can be interpreted as a simple consecutive reaction with the first step being much faster than the second step (Figure 4). The corresponding extinction diagram can be found in the Supporting Information (Figure S5). Surprisingly, the plotting of the experimental rate constants of the consecutive reaction determined with the program Specfit shows that both constants depend on the concentration of ethylene; the rate constants are directly proportional to the concentration of ethylene (see Supporting Information, Figures S6 and S7). Thus, **1-Hf** seems to react very fast with ethylene to give an unknown intermediate **A**, which then gives in another reaction the hafnacyclopentene **2-Hf**. Most likely this unknown species equals a bis-π-complex of bis(trimethylsilyl)acetylene and ethylene which then forms **2-Hf** by coupling of the alkyne and the olefin (Scheme 6). Such precoordinations have been observed before and are well-known for other group 4 metallocene alkyne complexes. For example, the alkyne complex $Cp_2Zr(acetone)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ equilibrates with the cyclic acetone insertion product $Cp_2Zr[-C(SiMe_3)=C(SiMe_3)-C(CH_3)_2-O-]$.[22]

4. Conclusion

Complex **1-Hf** displays a strong coordination of the alkyne at the metal center, which has been observed before for other hafnocene alkyne complexes.[11] The pattern of the reaction of **1-Hf** with ethylene to give the hafnacyclopentene **2-Hf** at ambient temperature and the hafnacyclopentane **3-Hf** at higher temperature has been observed before for analogous zirconium complexes. However for the hafnium complex these reactions take place at much higher temperatures. This shift is indicative of the higher stability of Hf−C σ-bonds compared to Zr−C σ-bonds, which has been described before.[23]

The increasing stability of M−C σ-bonds when going down group 4 in the Periodic Table is also evident from further observations described herein: Neither metallacyclopentene nor metallacyclopentane were isolated for Ti; the decomposition products (butenes) were found instead. Stepping over via Zr to Hf results in a gradually better access to these intermediates in olefin dimerization.

UV/vis measurements have shown that the reaction of **1-Zr** with ethylene follows pseudo-first-order kinetics; i.e., the reaction equates the simple conversion of **1-Zr** and ethylene to **3-Zr**. The formation of **2-Zr** is not observed at room temperature. In contrast the hafnocene alkyne complex **1-Hf** reacts with ethylene to give the hafnacyclopentene **2-Hf**. Most interestingly, the formation of this complex can be regarded as a simple consecutive reaction: in a first step, **1-Hf** reacts with ethylene to give an intermediate **A** which has not been characterized so far. Presumably this species consists of a hafnium center which is π-coordinated with bis(trimethylsilyl)acetylene and ethylene. In a second step this intermediate reacts to the hafnacyclopentene **2-Hf**. The assumed π-complex has

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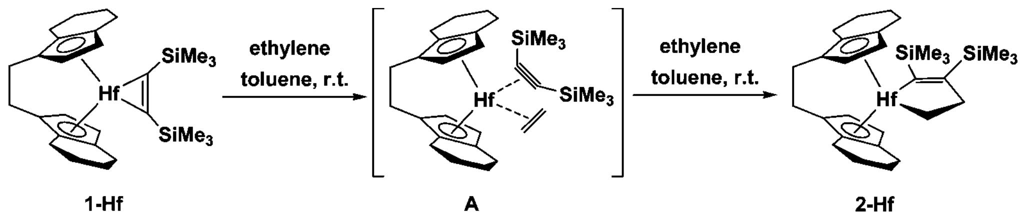
(22) (a) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *J. Organomet. Chem.* **1994**, *484*, 203. (b) Baumann, W.; Ohff, A.; Ebener, M. *Helv. Chim. Acta* **1996**, *79*, 454. *Helv. Chim. Acta* **1996**, *79*, 1239.

(23) (a) Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

Scheme 6. Reaction of **1-Hf** with Ethylene To Give the Hafnacyclopentene **2-Hf** with Presumed Previous Formation of the Intermediate **A**



not been observed before by common NMR methods, and first hints for the existence of such a complex were found by UV/vis spectroscopy. These findings should be encouraging to complement NMR spectroscopic studies with faster techniques such as the herein described UV/vis methods.

In summary we have found a significant gradation in reactivity in the reaction of the alkyne complexes **1-M** with ethylene: whereas the titanium compound **1-Ti** seems to form a highly reactive titanacyclopentane at 100 °C, which eliminates 1-butene, the corresponding zirconium and hafnium complexes **1-Zr** and **1-Hf** form stable metallacyclopentanes. However, compared to **3-Zr**, the formation of **3-Hf** proceeds at different temperatures, indicating the stronger complexation of the alkyne and the lower reactivity of the hafnocene alkyne complex **1-Hf**.

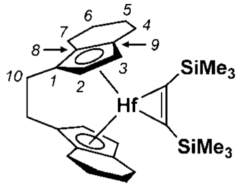
5. Experimental Section

5.1. General. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents (benzene-d_6 and toluene-d_8) were treated with sodium tetraethylaluminate, distilled, and stored under argon. The starting material *rac*-(ebthi)HfCl$_2$ was purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. The following spectrometers were used: Mass spectra: MAT 95-XP. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^{1}H, ^{13}C) are given relative to SiMe$_4$ and are referenced to signals of the used solvent: benzene-d_6 ($\delta_H = 7.16$, $\delta_C = 128.0$), toluene-d_8 ($\delta_H = 2.03$, $\delta_C = 20.4$). The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

For UV/vis experiments a stopped-flow device (BioLogic μSFM-20) was used to mix the complex solution and the saturated ethylene solution (both in toluene). UV/vis spectra were recorded with a J&M MMS/100-1 with CLD/F. The spectra were analyzed with the program Specfit.[24]

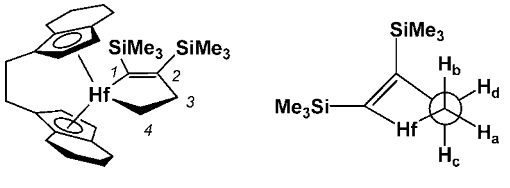
5.2. Preparation of the Hafnacyclopropene *rac*-(ebthi)-Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (1-Hf). A suspension of *rac*-(ebthi)HfCl$_2$ (1.147 g, 2.23 mmol), a finely cut lithium wire (0.063 g, 8.93 mmol), and bis(trimethylsilyl)acetylene (0.506 mL, 2.23 mmol) in 20 mL of toluene was stirred for 6 days at 60 °C, followed by removal of all volatiles in vacuum. The residue was extracted with 3 × 15 mL of *n*-hexane at 55 °C. The resulting blue-green solution was filtered and evaporated to dryness in vacuum. Recrystallization from THF gave blue-green crystals which were separated, washed with cold *n*-hexane, and dried in vacuum to give complex **1-Hf**: yield 0.883 g (1.44 mmol, 65%); mp 101−103 °C under Ar. Anal. Calcd for C$_{28}$H$_{42}$HfSi$_2$ (613.29 g·mol^{-1}): C, 54.83; H, 6.90. Found: C, 54.89; H, 6.78. IR (nujol mull, cm^{-1}): 1439 (ν C≡C). NMR: (297 K, benzene-d_6), ^{1}H: δ 0.23 (s, 18H, SiMe$_3$), 1.04 (ddd, $^2J = 15.8$ Hz, $^3J = 7.5$ and 5.3 Hz, 2H, CH$_2$−H*7*), 1.28−1.47 (m, 4H, CH$_2$−H*6*), 1.54−1.72 (m, 4H, CH$_2$−H*5*), 2.09 (ddd, $^2J = 15.8$ Hz, $^3J = 6.5$ and 5.5 Hz, 2H, CH$_2$−H*7*), 2.24 (half AA′BB′, 2H, CH$_2$−H*10*), 2.39 (half AA′BB′, 2H, CH$_2$−H*10*), 2.86 (dt, $^2J = 15.5$ Hz, $^3J = 6.5$ Hz, 2H, CH$_2$−H*4*), 3.06 (dt, $^2J = 15.5$ Hz, $^3J = 6.3$ Hz, 2H, CH$_2$−H*4*), 4.44 (d, 2H, $^3J = 3.2$ Hz, H*2*), 7.28 (d, 2H, $^3J = 3.2$ Hz, H*3*). ^{13}C: δ 3.4 (SiMe$_3$), 23.0 (CH$_2$−C*7*), 23.2 (CH$_2$−C*6*), 24.3 (CH$_2$−C*5*), 24.7 (CH$_2$−C*4*), 26.3 (CH$_2$−C*10*), 107.8 (Cp−C*3*), 108.7 (Cp−C*2*), 122.0 (Cp−C*9*), 122.5, (Cp−C*1*) 122.7 (Cp−C*8*) 281.2 (s, C≡C). ^{29}Si: δ −0.2 (SiMe$_3$). MS: *m/z* (EI, 70 eV) 613 [M]$^+$, 267 [*rac*-(ebthi)]$^+$.

Numbering scheme for complex **1-Hf**:



5.3. Preparation of the Hafnacyclopentene 2-Hf. The complex *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Hf**) (ca. 0.03 g) was dissolved in an NMR Young tube in 0.7 mL of toluene-d_8. Argon was removed carefully in vacuum and substituted by ethylene. The color of the solution changed very fast from blue-green to yellow-green, and the tube was used for room temperature NMR characterization of complex **2-Hf**: (297 K, toluene-d_8), ^{1}H: δ 0.19 (s, 9H, SiMe$_3$), 0.19 (s, 9H, SiMe$_3$), 0.47 (ddd, 1H, $^2J_{a,b} = 12.5$ Hz, $^3J_{a,c} = 4.7$ Hz, $^3J_{a,d} = 3.3$ Hz, H$_a$), 0.84 (ddd, 1H, $^3J_{b,c} = 11.8$ Hz, $^3J_{b,d} = 6.4$ Hz, H$_b$), 2.34 (ddd, 1H, $^2J_{c,d} = 17.9$ Hz, H$_c$), 3.19 (ddd, 1H, H$_d$), 1.30−1.70 (m, 8H, β-CH$_{2\ \mathrm{ebthi}}$), 2.1−2.9 (5 m, 12H, CH$_{2\ \mathrm{ebthi}}$), 4.64 (d, 1H, $^3J_{H,H} = 3.1$ Hz, CH$_{\mathrm{ebthi}}$), 5.14 (d, 1H, $^3J_{H,H} = 2.9$ Hz, CH$_{\mathrm{ebthi}}$), 6.21 (d, 1H, $^3J_{H,H} = 3.1$ Hz, CH$_{\mathrm{ebthi}}$), 6.35 (d, 1H, $^3J_{H,H} = 2.8$ Hz, CH$_{\mathrm{ebthi}}$). ^{13}C: δ 2.2 (SiMe$_3$), 5.3 (SiMe$_3$), 22.8, 23.0, 23.0, 23.2, 23.3, 23.8, 24.4, 24.5, 26.0, 26.1 (CH$_{2\ \mathrm{ebthi}}$), 28.4 (C*3*), 47.2 (C*4*), 103.4, 104.4, 107.9, 115.6 (CH$_{\mathrm{ebthi}}$), 120.8, 122.1, 122.3, 122.7, 124.3, 126.0 (C$_{\mathrm{ebthi}}$) 174.3 (C*2*), 223.4 (C*1*). ^{29}Si: $\delta = -19.0$, -11.4 (SiMe$_3$).

Numbering scheme for complex **2-Hf**:



5.4. Preparation of the Hafnacyclopentane 3-Hf. 5.4.1. NMR Experiment. The complex *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Hf**) (ca. 0.03 g) was dissolved in an NMR Young tube in 0.7 mL of toluene-d_8. Argon was removed carefully in vacuum and substituted by ethylene. The color of the solution changed very fast from blue-green to yellow-green. The solution was heated for 1 h at 100 °C, giving a dark yellow solution which was subsequently used for room temperature NMR measurements.

5.4.2. Isolation. The complex *rac*-(ebthi)Hf(η^2-Me$_3$SiC$_2$SiMe$_3$) (**1-Hf**) (0.350 g, 0.57 mmol) was dissolved in 10 mL of toluene. Argon was removed in vacuum, and ethylene was bubbled into

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[24] Specfit is a tool for fitting complex models of emission lines, absorption lines, and continua to one-dimensional spectra and was developed by G. Kriss (Department of Physics and Astronomy, Johns Hopkins University).

the blue-green solution. The color of the solution changed immediately to yellow-green. The solution was heated for 2 h at 100 °C and evaporated to dryness in vacuum. The yellow residue was dissolved in *n*-hexane giving after 2 days at −78 °C yellow crystals which were separated, washed with cold *n*-hexane, and dried in vacuum to give complex **3-Hf**. Yield: 0.198 g (0.40 mmol, 70%); mp 106 °C (dec.) under Ar. Anal. Calcd for $C_{24}H_{32}Hf$ (499.00 $g \cdot mol^{-1}$): C, 57.77; H, 6.46. Found: C, 57.71; H, 6.51. NMR: (297 K, toluene-d_8), ^1H: δ 0.32 (m, 2H, C_{α}−H), 1.08 (m, 2H, C_{α}−H), 1.96 (m, 2H, C_{β}−H), 2.16 (m, 2H, C_{β}−H), 1.70, 2.18, 2.75, 3.05 (4 m, 8H, α-$CH_{2\ \mathrm{ebthi}}$), 1.31, 1.53 (2 m, 8H, β-$CH_{2\ \mathrm{ebthi}}$), 2.37 (AA′BB′, 4H, bridge-$CH_{2\ \mathrm{ebthi}}$), 4.79 (d, 2H, $^3J_{H,H} = 3.0$ Hz, CH_{ebthi}), 6.20 (d, 2H, $^3J_{H,H} = 3.0$ Hz, CH_{ebthi}). ^{13}C: δ 23.3, 23.3, 23.7, 24.7, 27.8 ($CH_{2\ \mathrm{ebthi}}$), 27.1 (C_{β}), 48.8 (ZrC_{α}), 106.8, 111.9 (CH_{ebthi}), 119.5, 123.1, 125.3 (C_{ebthi}). MS: *m/z* (CI, isobutane) 499 $[M]^+$.

5.5. Crystallographic Details of 3-Hf. $C_{24}H_{32}Hf$, $M_r = 498.99$, yellow crystal, 0.35 × 0.25 × 0.12 mm^3, monoclinic, space group $P2_1/n$, $a = 9.7076(4)$ Å, $b = 16.4786(7)$ Å, $c = 12.0871(6)$ Å, $\beta = 101.802(4)°$, $V = 1892.67(15)$ $Å^3$, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.751$ $g \cdot cm^{-3}$, $T = 200$ K, $\mu = 5.515$ mm^{-1}, numerical absorption correction (max. and min. transmission: 0.4941 and 0.1442), 28 515 reflections collected, 4014 independent reflections ($R_{\mathrm{int}} = 0.0337$), 3489 reflections observed [$I > 2\sigma(I)$], 225 refined parameters, final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.0170$, $wR_2 = 0.0384$, *R* indices (all data): $R_1 = 0.0227$, $wR_2 = 0.0393$. Diffraction data were collected on a STOE IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS-97[25]) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[25]). DIAMOND[26] was used for graphical representation. Non-hydrogen atoms were refined anisotropically except C21 and C22, which were disordered over two sites with occupancies 0.697:0.303. Hydrogen atoms were included at calculated positions and refined using a riding model.

Acknowledgment. We thank our technical staff in particular Regina Jesse, Petra Bartels, and Cornelia Pribbenow for assistance. Support by the Deutsche Forschungsgemeinschaft (GRK 1213) and the Russian Foundation for Basic Research (Project Code 09-03-00503) is acknowledged.

Supporting Information Available: Crystallographic data in cif file format of compound **3-Hf** (data) and UV/vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JA809368S

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(26) Brandenburg, K. *DIAMOND*, version 3.1e; Crystal Impact Gbr: Bonn, Germany, 2007.