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Ring-Opening Reactions of Tetrahydrofuran versus Alkyne Complexation by Group 4 Metallocene Complexes Leading to General Consequences for Synthesis and Reactions of Metallocene Complexes

Torsten Beweries, Ulrike Jäger-Fiedler, Marc A. Bach, Vladimir V. Burlakov,[§]
Perdita Arndt, Wolfgang Baumann, Anke Spannenberg, and Uwe Rosenthal*

*Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Strasse 29a,
D-18059 Rostock, Germany*

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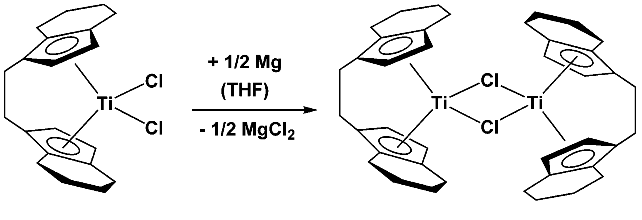
The reduction of certain group 4 metallocene dichlorides by magnesium or lithium in the presence or absence of $Me_3SiC_2SiMe_3$ in THF or toluene was investigated, giving in the case of titanium the dinuclear Ti(III) complex [*rac*-(ebthi)Ti(μ-Cl)]$_2$ (**1**). For zirconium the 1-oxa-2-zirconacyclohexane **2** was formed by ring-opening reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) with THF. As a byproduct from the synthesis of $Cp^*{}_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ starting from $Cp^*{}_2ZrCl_2$ another 1-oxa-2-zirconacyclohexane (**3**) was obtained by ring-opening reaction of THF via the dinuclear complex $Cp^*{}_2Zr(Cl)\text{-}(CH_2)_4O{-}Zr(Cl)Cp^*{}_2$ (**4**). In the case of hafnium the analogous dinuclear complex $Cp^*{}_2Hf(Cl){-}(CH_2)_4O{-}Hf(Cl)Cp^*{}_2$ (**5**) and 1-oxa-2-hafnacyclohexane (**6**) were the main products of the reaction, inhibiting the synthesis of $Cp^*{}_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**). The tendency for ring opening of THF initiated by metallocenes increases in the series Ti, Zr, Hf, thus leading to consequences for the synthesis of metallocene complexes.

Introduction

THF is a very well-suited solvent for organometallic synthesis, but sometimes it does not behave as an inert solvent. This has consequences for the outcome of the desired reaction. Stoichiometric and catalytic ring-opening reactions of THF by group 4 transition metal complexes are well-known reactions, proved by their importance for the catalytic ROP of THF, too.[1] For example Stephan et al. reported on the ring-opening reaction of THF starting from zirconium halides in the presence of PCy_3 resulting in a functionalization of the formed $(CH_2)_4O$ chain with the phosphine to give the complex $ZrCl_4[\mu\text{-}O(CH_2)_4\text{-}PCy_3]_2$.[1e] Moreover Jordan and co-workers found a zirconocene hydride-mediated ring opening of THF to give the complex $(C_5H_4Me)_2Zr(THF)[{-}O(CH_2)_3{-}CH_3]$.[1f] Chirik and co-workers published for isolable η^6,η^5-bis(indenyl)zirconium THF compounds that thermolysis at 85 °C also resulted in C−O bond cleavage to yield the corresponding 1-oxa-2-zirconacyclohexane.[1g] Very recently a number of papers appeared in the literature that described some other unusual products of THF activation and cleavage processes, formed in the coordination sphere of transition metals,[2] e.g., octanediol[2a] and butadiene.[2b]

Very recently we have published that during the synthesis of $Cp^*{}_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$[3] this ring opening of THF becomes a problem, which was never observed before in the often performed synthesis of analogous titanocene and zirconocene bis(trimethylsilyl)acetylene complexes.[4] Nevertheless we were interested to find out to what extent in the series of Ti, Zr, and Hf the ring opening of THF can lower the yields of the alkyne complexes in these reactions. This question could be of general importance for organometallic synthesis of metallocene complexes in THF.

Scheme 1. Preparation of [*rac*-(ebthi)Ti(μ-Cl)]$_2$ (1)



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Results and Discussion

During the established synthesis of certain titanocene and zirconocene bis(trimethylsilyl)acetylene complexes[4] we found under argon as inert gas several byproducts. If in the preparation of *rac*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)[5] starting from *rac*-(ebthi)-$TiCl_2$, $Me_3SiC_2SiMe_3$, and magnesium in THF a shorter reaction time or a wrong stoichiometry was used, a green

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* Corresponding author. E-mail: uwe.rosenthal@catalysis.de.

[§] On leave from the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 117813, Moscow, Russia.

(1) Selected examples: Ti: (a) Covert, K. J.; Mayol, A.-R.; Wolczanski, P. T. *Inorg. Chim. Acta* **1997**, *263*, 263. (b) Delaney, P. A.; Johnstone, R. A. W.; Entwistle, I. D. *J. Chem. Soc., Perkin Trans. 1* **1986**, *11*, 1855. Zr: (c) Polamo, M.; Mutikainen, I.; Leskela, M. *Acta Crystallogr., Sect. C* **1997**, *C53,* 1036. (d) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974. (e) Breen, T. L.; Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4019. (f) Guo, Z. Y.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690. (g) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 16600.

(2) Eisch, J. J.; Gitua, J. N. *Organometallics* **2007**, *26*, 778. (b) Horacek, M; Pinkas, J.; Kubista, J.; Cisarova, I.; Gyepes, R.; Stepnicka, P. *Collect. Czech. Chem. Commun*. **2007**, in press.

(3) Beweries, T.; Burlakov, V. V.; Bach, M. A.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 247.

(4) Rosenthal, U.; Burlakov, V. V. *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: New York, 2002; p 355.

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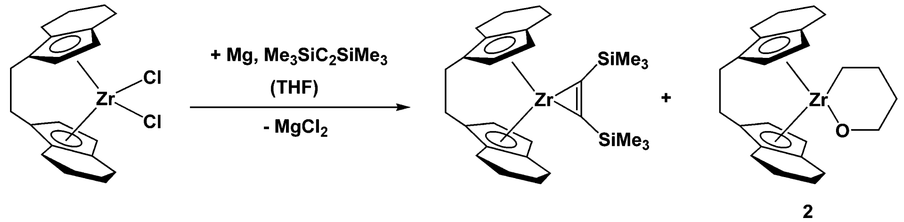
10.1021/om0702173 CCC: $37.00

Scheme 2. Preparation of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) under Formation of the Byproduct 2



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byproduct was isolated. Reaction of this mixture without the alkyne at 60 °C gave the dinuclear complex [*rac*-(ebthi)Ti(μ-Cl)]$_2$ (**1**) (Scheme 1). Complex **1** did not show any further reaction with THF at all. However, the same behavior was described for the mononuclear complex Cp^*_2TiCl.[6a] This is of importance with regard to the considerations of reactions with similar zirconium and hafnium complexes (see below, Schemes 7 and 10).

From NMR measurements it was concluded that complex **1** is paramagnetic. Due to the low isolated yield, no magnetic moment was determined. The molecular structure of **1** displays a dinuclear Ti(III) complex (Figure 1). Similar molecular structures are known for other ligands, too.[6b−d]

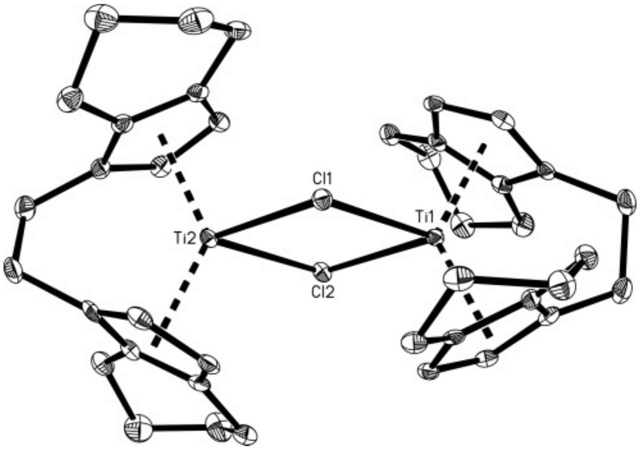


Figure 1. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Ti1−Cl1 2.5228(9), Ti2−Cl1 2.5227(9), Ti1−Cl2 2.5290(9), Ti2−Cl2 2.5362(9); Ti1−Cl1−Ti2 100.95(3), Ti1−Cl2−Ti2 100.41(3), Cl1−Ti1−Cl2 79.39(3), Cl1−Ti2−Cl2 79.25(3).

The Ti1−Cl2 bond distance (2.5290(9) Å) is slightly shorter compared to the Ti2−Cl2 bond (2.5362(9) Å), whereas the angle Ti1−Cl1−Ti2 (100.95(3)°) is slightly larger compared to the Ti1−Cl2−Ti2 angle (100.41(3)°). For this binding mode several examples are known, e.g., [$(C_5Me_2H_3)_2Ti(\mu\text{-}Cl)$]$_2$,[6b] [$Cp_2Ti(\mu\text{-}Cl)$]$_2$,[6e] and [$(C_5MeH_4)_2Ti(\mu\text{-}Cl)$]$_2$.[6f] The structural parameters of the latter one can be very well compared with those of complex **1** [Ti−Cl bond lengths of 2.535(2), 2.566(2), 2.562(2), and 2.526(2) Å; Ti1−Cl−Ti2 angles of 100.74(7)° and 100.88(7)°].

In the case of zirconium we found during our convenient synthesis of the complex *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$)[5] the formation of a byproduct, which was identified as the 1-oxa-2-zirconacyclohexane **2** (Scheme 2).

Recrystallization from benzene-d_6 gave single crystals well suited for an X-ray analysis of **2** (Figure 2).

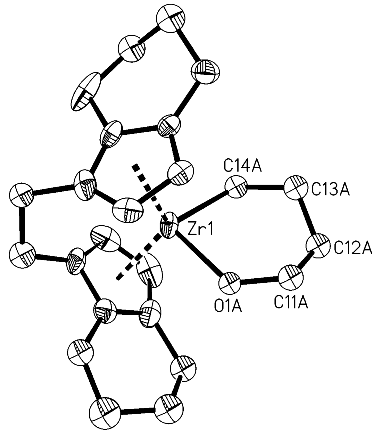
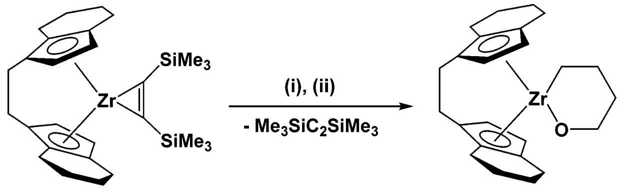


Figure 2. Molecular structure of complex **2**. Hydrogen atoms and one position of the disordered groups are omitted for clarity. Thermal ellipsoids correspond to 30% probability.

For the molecular structure of **2** the connectivity of an 1-oxa-2-zirconacyclohexane is established. Nevertheless, the 1-oxa-2-zirconacyclohexane as the central fragment was found to be disordered. For that reason a detailed discussion of bond distances and angles is not feasible.

If *rac*-(ebthi)$ZrCl_2$ reacts with magnesium in THF without the alkyne, the ^1H NMR spectra indicate the formation of **2** together with several byproducts, which could not be separated and identified. Interestingly **2** is formed starting from *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) and THF in a yield of 98% after a very long reaction time of four weeks at 70 °C (Scheme 3). Using a CEM-Discover microwave in a much shorter reaction time of 1 h a quantitative formation of **2** was found (Scheme 3). An epimerization reaction of the racemic complex **2** to give the corresponding *meso* species has not been observed by NMR.

Scheme 3. Preparation of 2 Starting from *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$)



2

(i) microwave, 200°C, 300 W, 1h, in 3 ml of THF

(ii) 70°C, 4 weeks, in 20 ml of THF

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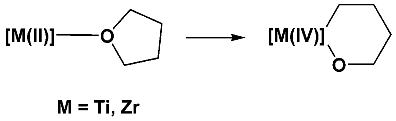
[6] (a) Pattiasina, J. W.; Heeres, H. J.; van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004. (b) Mach, K.; Varga, V.; Schmid, G.; Hiller, J.; Thewalt, U. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1285. (c) Schmid, G.; Thewalt, U.; Sedmera, P.; Hanus, V.; Mach, K. *Collect. Czech. Chem. Commun.* **1998**, *63*, 636. (d) Baum, E.; Matern, E.; Pikies, J.; Robaszkiewicz, A. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1090. (e) Lacroix, F.; Plecnik, C. E.; Liu, S.; Liu, F.; Meyers, E. A.; Shore, S. G. *J. Organomet. Chem.* **2003**, *687*, 69, and references therein. (f) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

Starting from the analogous titanium complex *rac*-(ebthi)-Ti(η^2-$Me_3SiC_2SiMe_3$) we did not observe the same reaction with a ring opening of THF.

The surprising formation of the 1-oxa-2-zirconacyclohexane **2** was a result of the ring-opening reaction of THF, but it is not clear if this happens by an associative or a dissociative mechanism: Coordination of THF and subsequent elimination of the alkyne would give a Zr(II) THF complex as an intermediate. The same species could be formed by dissociation of the alkyne and subsequent coordination of THF. For titanium Mach and co-workers described the formation of certain titanocenes by dissociation of the alkyne from its bis(trimethylsilyl)acetylene complexes.[7] On the other hand the temperature-dependent coordination of THF in zirconocene bis(trimethylsilyl)-acetylene complexes was investigated by us in detail.[8] Obviously for Zr in contrast to Ti an associative process is preferred.[9]

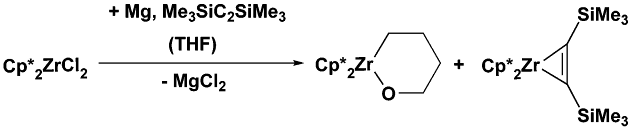
Dehnicke discussed for the ring opening of THF the coordination of THF at Ti(II) followed by an oxidative addition (Scheme 4).[10] For Zr(II) this was investigated in detail by the Chirik group.[1g] There is a higher tendency for the ring opening of THF in the case of zirconium compared to titanium.

Scheme 4. Oxidative Addition of THF at Ti(II) and Zr(II)



The formation of the complex $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with an isolated yield of 56% was first described by Mach et al. by reacting $Cp^*_2ZrCl_2$ with magnesium and the alkyne in THF; however, the formation of byproducts was not reported in this paper.[11] With regard to the above-mentioned results we reinvestigated this reaction under different conditions. During the preparation of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ the corresponding zirconacycle **3** was formed (via complex **4**, see Scheme 7).

Scheme 5. Preparation of the Byproduct 3



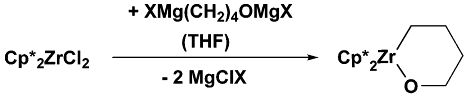
3

This complex was obtained before by the Takaya group using another procedure (Scheme 6).[12] The spectroscopic data are the same as those reported for **3**.

1-Oxa-2-zirconacyclohexanes are very rare complexes and were in most cases obtained by coupling of group 4 metal olefin or alkyne complexes with carbonyl compounds.

To get more information about the formation of **3**, we investigated the reaction of $Cp^*_2ZrCl_2$ and magnesium with and without the alkyne in detail. The reaction conditions such as concentration and temperature influence the ratio of the alkyne complex to the ring-opening product **4**. If the reaction with the alkyne was conducted at higher temperature (50−60 °C) in addition to $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (35% yield), the dinuclear complex $Cp^*_2Zr(Cl)(CH_2)_4OZr(Cl)Cp^*_2$ (**4**) was formed (24% yield) (Scheme 7). Conducting the reaction under the same conditions without the alkyne increased the yield of complex **4** up to 63% (Scheme 7).

Scheme 6. Preparation of 3 Starting from $Cp^*_2ZrCl_2$ and $XMg(CH_2)_4OMgX$



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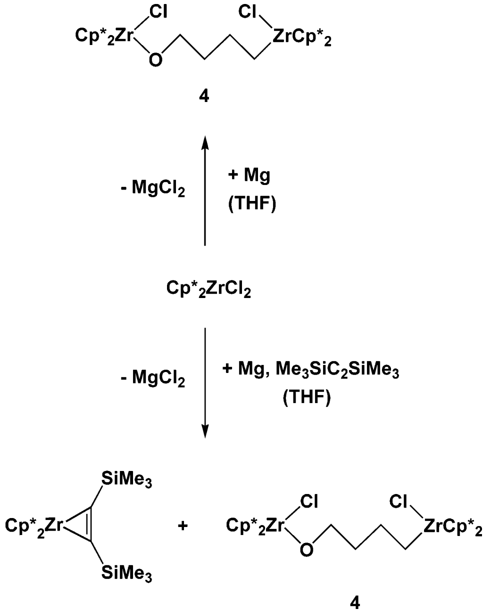
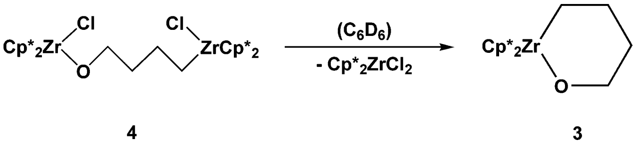
Scheme 7. Preparation of 4 in Reactions of $Cp^*_2ZrCl_2$ with Magnesium with and without the Alkyne



NMR experiments have shown that after dissolving in benzene complex **4** was converted to complex **3** within 3−4 days (Scheme 8).

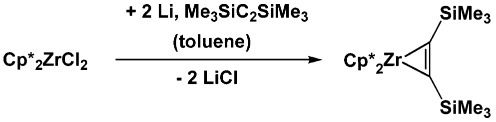
Scheme 8. Formation of 3 from 4



4 3

The best yields of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (56%) in our experiments were obtained by using toluene as solvent and lithium for the reduction instead of THF and magnesium. This was originally described by Mach, giving a yield of 75% (Scheme 9).[11]

Scheme 9. Formation of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ Using Lithium as Reducing Agent and Toluene as Solvent



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(7) Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572.

(8) Peulecke, N.; Ohff, A.; Kosse, P.; Tillack, A.; Spannenberg, A.; Kempe, R.; Baumann, W.; Burlakov, V. V.; Rosenthal, U. *Chem. Eur. J.* **1998**, 1852, and references therein.

(9) (a) Mansel, S.; Thomas, D.; Lefeber, C.; Heller, D.; Kempe, R.; Baumann, W.; Rosenthal, U. *Organometallics* **1997**, *16*, 2886. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884.

(10) Mommertz, A.; Leo, R.; Massa, W.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1647.

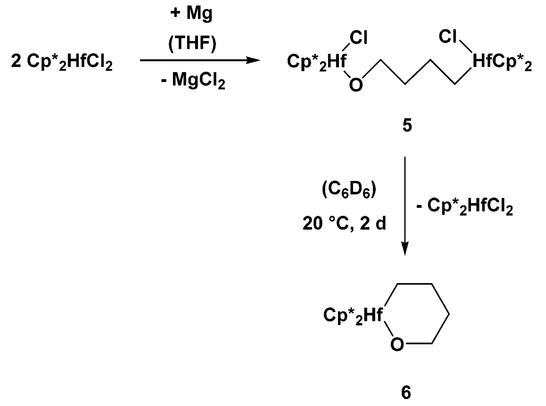
(11) Hiller, J.; Thewalt, U.; Polasek, M.; Petrusova, L.; Varga, V.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 3752.

(12) Mashima, K.; Yamakawa, M.; Takaya, H. *J. Chem. Soc., Dalton Trans.* **1991**, 2851.

It is worth mentioning that in the reaction of $Cp*_2TiCl_2$ with magnesium and the alkyne in THF a higher isolated yield of $Cp*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was obtained (73%) and no byproducts were detected. In this respect zirconium behaves similarly as described very recently for hafnium,[3] and the reaction behavior of these two metals is clearly distinct from that of titanium.

Very recently we reported that in the reactions of $Cp*_2HfCl_2$ with magnesium in THF without added alkyne a ring-opening reaction of THF occurred (Scheme 10), giving the dinuclear complex $Cp*_2Hf(Cl){-}O(CH_2)_4{-}(Cl)HfCp*_2$ (**5**).[3] In benzene solution **5** underwent reaction to $Cp*_2HfCl_2$ and the 1-hafna-2-oxa-cyclohexane **6**, as indicated by NMR. This complex is very similar to the analogous 1-zircona-2-oxa-cyclohexane **3** described above.

Scheme 10. Ring-Opening Reaction of THF Starting from $Cp*_2HfCl_2$



Conclusion

The reactivity difference between the group homologues Ti, Zr, and Hf is highlighted by the synthesis of the alkyne complexes of the type $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ ($Cp'_2 = Cp*_2$, *rac*-(ebthi)). The titanium complex $Cp*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was prepared with magnesium in THF without any byproducts in a high yield. The corresponding zirconium complex $Cp*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was made by the use of magnesium in THF, yielding **3** as a byproduct, whereas the synthesis of the hafnium analogue $Cp*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**) is not possible at all under these conditions in THF. Zr and Hf behave similarly in reactivity toward THF but differ significantly from Ti. This clearly indicates that the alkyne and THF compete to coordinate to the metal. In the case of Ti and Zr the coordination of the alkyne is preferred; for Hf the stronger interaction with THF gives ring opening instead of alkyne complexation. This behavior rationalizes why the synthesis of $Cp*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ completely fails in THF and the alternative procedure using lithium in toluene is to be preferred.

Another aspect to be mentioned is that the stability of the M(III) species $Cp*_2MCl$ as assumed intermediates decreases in the series Ti, Zr, Hf. This can be derived from the fact that the corresponding monochlorides can be isolated only in the case of M = Ti. Such compounds may also exist for Zr and Hf; however, they have not been isolated so far. Nevertheless these M(III) species play an important role in the above-described ring-opening reactions of THF. All this is in agreement with the well-established higher reactivity of hafnocenes[3,13] and of general importance and consequence for the synthesis of organometallic compounds in THF as solvent.

Experimental Section

General Procedures. 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 solvent (C_6D_6) was treated with sodium tetraethylaluminate, distilled, and stored under argon. The starting complexes *rac*-(ebthi)$TiCl_2$, *rac*-(ebthi)$ZrCl_2$, and $Cp*_2ZrCl_2$ are commercially available and were provided by MCAT. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^1H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: C_6D_6 ($\delta_H = 7.16$, $\delta_C = 128.0$). The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of [*rac*-(ebthi)TiCl]$_2$ (1). *rac*-(ebthi)$TiCl_2$ (0.76 g, 1.9 mmol) and finely sliced magnesium (0.25 g, 1.0 mmol) were suspended in 10 mL of THF. The red solution was stirred for 4 h at 60 °C and cooled to room temperature. After 1 day green crystals had formed from the violet solution, which were separated by filtration from the mother liquor, washed with *n*-hexane, and dried in vacuum to give 0.17 g (25%) of complex **1**. Mp: 102 °C (dec) under Ar. Anal. Calcd for $C_{40}H_{48}Ti_2Cl_2$ (695.45 g·mol^{-1}): C, 69.08; H, 6.96. Found: C, 65.80; H, 7.16 (despite repeated recrystallization from THF samples contained small amounts of $MgCl_2$, preventing better analytical data). MS (*m*/*z* 70 eV): 347 $[M - C_{20}H_{28}TiCl]^+$.

Preparation of 2. Method A: *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (1.40 g, 2.66 mmol) was dissolved in 20 mL of THF. The green solution was stirred for 4 weeks at 70 °C, changing its color to olive-green. The volatiles were removed in vacuum, and the residue was found to be complex **2** (yield of 1.10 g; 98%), identified by NMR. Method B: A solution of *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.35 g, 0.45 mmol) in 4 mL of THF was poured into a CEM tube. The tube was closed and placed into a CEM-Discover microwave (program: 200 °C, 300 W, 1 h). The volatiles were removed in vacuum, and the residue was identified as complex **2** by NMR (yield of 0.25 g; 100%). Mp: 111 °C under Ar. Anal. Calcd for $C_{24}H_{32}OZr$ (426.15 g·mol^{-1}): C, 67.28; H, 8.07. Found: C, 67.33; H, 8.00. NMR (400 MHz, 297 K, C_6D_6), ^1H: δ 0.53 (ddd, 1H, ^2J = 12.6 Hz, ^3J = 8.7 and 2.7 Hz, Zr-CH_2), 1.3−2.8 ppm (m, 20H ebthi-CH_2 and 5H oxazirconacyclohexane), 3.93 (ddd, 1H, ^2J = 10.1 Hz, ^3J = 8.5 and 3.6 Hz, O−CH_2), 4.30 (ddd, 1H, ^2J = 10.1 Hz, ^3J = 5.0 and 4.2 Hz, O−CH_2), 5.02 (d, 1H, ^3J = 3.0 Hz, ebthi-CH), 5.50 and 5.53 (2d, 1H each, ^3J = 3.1 Hz, ebthi CH), 6.12 (d, 1H, ^3J = 3.0 Hz, ebthi-CH); ^{13}C: δ 23.0, 23.4, 23.4, 23.7, 23.8, 24.2, 24.3, 24.5, 27.7, 27.8, 28.1, 36.1 (10 × ebthi-CH_2 and 2 × oxazirconacyclohexane-CH_2), 39.9 (Zr-CH_2), 73.4 (O-CH_2), 104.5, 106.7, 107.5, 112.1 (4 × ebthi-CH), 119.4, 120.3, 124.3, 126.6, 126.7 (5 × ebthi-C, sixth signal missing, perhaps covered by solvent signal 128 ppm). MS (*m*/*z* 70 eV): 426 $[M]^+$, 354 $[M - C_4H_8O]^+$.

Formation of 3 from 4. Complex **4** (40−50 mg) was dissolved in 0.6 mL of C_6D_6 under Ar, and the solution was placed into an NMR ampule. ^1H and ^{13}C NMR spectra of this solution were recorded at known time intervals. After 3−4 days only Takaya's[12] complex **4** and $Cp*_2ZrCl_2$ were detected in solution.

Preparation of 4 with Alkyne. $Cp*_2ZrCl_2$ (2.58 g, 5.97 mmol), finely sliced magnesium (0.15 g, 5.96 mmol), and bis(trimethylsilyl)acetylene (1.35 mL, 6.0 mmol) in 20 mL of THF were stirred for 4 h at 55 °C and for 16 h at 20 °C. The resulting blue-green

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[13] (a) Bernskoetter, W. H.; Olmos, A. V.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10696. (b) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem.* **2007**, *119*, 1. (c) Chirik, P. J. *Dalton. Trans.* **2007**, 16, and references therein.

Table 1. Crystallographic Data

	1	**2**
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a [Å]	14.435(3)	10.275(2)
b [Å]	17.642(4)	11.594(2)
c [Å]	14.496(3)	16.695(3)
α [deg]	90.00	90.00
β [deg]	103.01(3)	95.21(3)
γ [deg]	90.00	90.00
V [Å^3]	3596.8(13)	1980.6(6)
Z	8	4
density [g·cm^{-3}]	1.364	1.434
μ(Mo Kα) [mm^{-1}]	0.623	0.565
T [K]	200	200
no. of rflns (measd)	12 599	5735
no. of rflns (indep)	5635	3098
no. of rflns (obsd)	3637	2421
no. of params	424	222
R1 ($I > 2(I)$)	0.033	0.047
wR2 (all data)	0.080	0.124

solution was evaporated to dryness in vacuum, and the residue was extracted with *n*-hexane (3 × 10 mL) at 55 °C. The solution was filtered and concentrated in vacuum to a volume of 5 mL. After standing for 24 h at −78 °C, blue-green crystals of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ had formed, which were separated, washed twice with cooled *n*-hexane, and dried in vacuum (yield of 1.11 g; 35%). Mp: 269−271 °C under Ar. NMR (400 MHz, 297 K, C_6D_6): ^{1}H: δ 0.19 (s, 18H, $SiMe_3$); 1.77 (s, 30H, Cp*). ^{13}C: δ 4.0 ($SiMe_3$); 11.8 ($C_5\mathit{Me}_5$); 118.8 (C_5Me_5); 260.5 (C≡C). The residue of the first extraction with *n*-hexane was dried completely in vacuum and extracted with toluene (4 × 10 mL). The yellow solution was filtered and concentrated in vacuum to a volume of 15 mL. After standing for 24 h at −78 °C, yellow crystals had formed, which were separated, washed twice with cooled toluene, and dried in vacuum. The yield of complex **4** was 0.63 g (24%). Mp: 214−215 °C (dec) under Ar. Anal. Calcd for $C_{44}H_{68}Cl_2OZr_2$: C, 61.00; H, 7.91. Found: C, 60.62; H, 7.71. NMR (400 MHz, 297 K, C_6D_6): ^{1}H: 0.66 (m, 2 H, CH_2), 1.44 (m, 2 H, CH_2), 1.77 (quint, $^3J_{H,H} = 7.4$ Hz, 2 H, CH_2), 1.86 (s, 30 H, $\mathit{Cp}^*{}_2$Zr-O), 1.95 (s, 30 H, $\mathit{Cp}^*{}_2$-Zr), 4.32 (dd, $^3J_{H,H} = 7.3$ Hz, 2 H, CH_2-O); ^{13}C: 11.7 ($^1J_{C,H} = 127$ Hz, $C_5\mathit{Me}_5$-Zr), 11.7 ($^1J_{C,H} = 127$ Hz, $C_5\mathit{Me}_5$-Zr-O), 31.5 (CH_2), 42.5 (CH_2), 55.3 ($^1J_{C,H} = 117$ Hz, CH_2), 72.7 ($^1J_{C,H} = 137$ Hz, CH_2-O), 120.1 (C_5Me_5), 120.8 (C_5Me_5). MS (70 eV, *m*/*z*): 468 $[Cp^*_2Zr(Cl)OC_4H_9]^+$, 394 $[Cp^*_2Zr(Cl) - H]^+$, 333 $[Cp^*Zr(Cl)OC_4H_9]^+$.

Preparation of 4 without Alkyne. $Cp^*_2ZrCl_2$ (1.693 g, 3.91 mmol) and finely sliced magnesium (0.095 g, 3.91 mmol) were stirred in 15 mL of THF at 55 °C under Ar for 2.5 h. The resulting yellow solution was evaporated to dryness in vacuum, and the residue was extracted with toluene (3 × 10 mL) at 55 °C. The solution was filtered and concentrated in vacuum to a volume of 15 mL. After standing for 24 h at −78 °C, yellow crystals had formed, which were separated, washed twice with cooled toluene, and dried in vacuum. The yield of complex **4** was 1.067 g (63%); mp 213−214 °C (dec) under Ar. NMR data of the product are identical with those given above for **4**.

Preparation of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ by Using Lithium as Reducing Agent in Toluene. A mixture of $Cp^*_2ZrCl_2$ (1.740 g, 4.02 mmol), finely cut lithium wire (0.056 g, 8.07 mmol), and bis(trimethylsilyl)acetylene (0.91 mL, 4.05 mmol) in 15 mL of toluene were stirred for 7 days at 60 °C. The resulting green solution was filtered and cooled to −78 °C. After 2 days at this temperature blue-green crystals had formed, which were separated from the mother liquor by decanting, washed with cold toluene, and dried in vacuum to give 1.202 g (56%) of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$, mp 270−272 °C under Ar. NMR data of the product are identical with those given in ref 11.

X-ray data were collected with a STOE-IPDS-diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97[14]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[15]). XP (Bruker AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in cif file format, including bond lengths and angles of compounds **1** and **2** (data). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0702173

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(14) Sheldrick, G. M. *SHELXS-97*, Program of Crystal Structure Solution; University Göttingen: Germany, 1997.

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