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A comparative study of the reactivity of Zr(IV), Hf(IV) and Th(IV) metallocene complexes: Thorium is not a Group IV metal after all

Kimberly C. Jantunen, Brian L. Scott, Jaqueline L. Kiplinger*

Los Alamos National Laboratory, Mail Stop J514, Los Alamos, NM 87545, USA

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Abstract

Thorium(IV) is often considered to show similar chemistry to Group IV transition metals. However, studies in our laboratory have shown that this generalization is incorrect. This report presents direct comparisons where the Th(IV) metallocene complexes $(C_5Me_5)_2ThR_2$ ($R = CH_3$, Ph, CH_2Ph) undergo unique chemical reactivity with pyridine, 2-picoline, pyridine N-oxide, 2-picoline N-oxide, and benzonitrile, while the Group IV metal analogues $(C_5R_5)_2M(CH_3)_2$ ($R = H$, CH_3; $M = Zr$, Hf) do not. We also report revised high-yield syntheses for the zirconium and hafnium starting materials, $(C_5H_5)_2MR_2$ ($M = Zr$, Hf; $R = CH_3$, Ph, CH_2Ph), using Grignard reagents for alkylation in addition to the X-ray crystal structures of $(C_5H_5)_2Hf(Ph)_2$ and $(C_5H_5)_2Hf(CH_2Ph)_2$.

Keywords: Thorium; Zirconium; Hafnium; Group IV metals; Grignard alkylating reagents

1. Introduction

Thorium(IV) and Group IV transition metal complexes show some similarities in their reaction chemistry such as the ability to form metallocene complexes $(C_5Me_5)_2MR_2$ ($M = Ti$, Zr, Hf, or Th; $R =$ alkyl or aryl) [1], activate CO [2], and form complexes containing bridging hydride ligands [3]. However, there are significant differences in the electronic structure and reactivity of the Group IV metals and thorium. With a nominal ground state electronic configuration $[Rn]6d^27s^25f^0$, thorium has accessible 5f and 6d orbitals that may be available to accept electron density from bonding ligands. Furthermore, the ionic radius of Th(IV) is 0.94 Å, which is considerably larger than Zr(IV) (0.72 Å) and Hf(IV) (0.71 Å) [4]. Together, the larger ionic radius of Th(IV) and the potential accessibility of the 5f orbitals can lead to chemical behaviors that cannot be exhibited by transition metal complexes.

Whereas the 18-electron rule can be used to predict the stability of transition metal complexes, no such rule exists for the actinides. Thus, coordination numbers for actinides are largely determined by steric factors, rather than crystal field effects. For instance, the solid-state molecular structure of the bis(cyclooctatetraenyl) Th(IV) complex, $Th(C_8H_8)_2$, has both ligands bound in a planar η^8-C_8H_8 fashion to the Th(IV) center rendering the complex a 20-electron system [5]. In contrast, the Group IV analogues, $M(C_8H_8)_2$ ($M = Ti$, Zr, Hf) adopt an asymmetric structure in which one of the two C_8H_8 rings coordinates η^8 while the other is bound η^4 for a total electron count of 16 for the metal complexes [6]. Similarly, thorium can accommodate up to four η^5-C_5H_5 ligands around its metal center [7], but zirconium and hafnium can only accept a maximum of three η^5-C_5H_5 ligands [8].

More striking contrasts come from molecular chemistry. For example, whereas the Group IV metals can readily form alkylidene [9], carbonyl [10], and alkyne [11] complexes, these systems are as yet noticeably absent for thorium. These differences have in part been attributed to the lower propensity of thorium to form covalent bonds compared to hafnium and zirconium. Recently, we discovered that the thorium metallocene complexes $(C_5Me_5)_2ThR_2$ ($R = Me$, Ph, CH_2Ph) undergo unique chemical reactivity with pyridine ring systems and either activate the sp^2 and sp^3 hybridized C–H bonds in pyridine N-oxide and lutidine N-oxide to give cyclometalated N-oxide complexes [12], or mediate the ring-opening and dearomatization of the pyridine ring in pyridine N-oxide under ambient conditions (forming thorium η^2-(O,N) oximate complexes) [13].

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* Corresponding author. Tel.: +1 505 665 9553; fax: +1 505 667 9905.
E-mail address: kiplinger@lanl.gov (J.L. Kiplinger).

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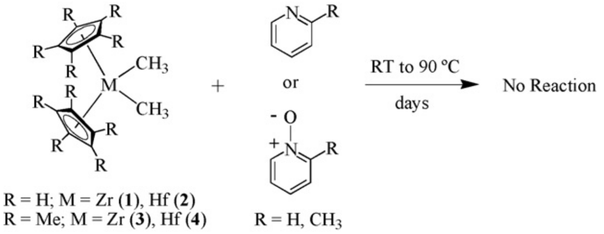
Given the anticipated conformity in behavior of Group IV metals and Th(IV), contrasted by these exceptional modes of reactivity exhibited for thorium, we were interested to see if the related hafnocene and zirconocene alkyl and aryl complexes would perform analogous chemistry. Herein, we describe detailed studies which show that significant differences exist between the chemical reactivities of Th(IV) and Group (IV) complexes, and that the generalization that complexes of these elements behave similarly is incorrect.

2. Results and discussion

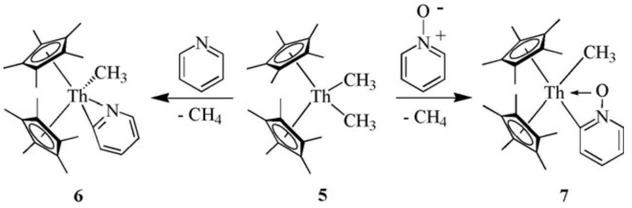
2.1. Reactivity of Group IV and thorium(IV) metallocenes

As depicted in Eq. (1), reaction of $(C_5H_5)_2M(CH_3)_2$ (M = Zr (**1**), Hf (**2**)) or $(C_5Me_5)_2M(CH_3)_2$ (M = Zr (**3**), Hf (**4**)) with either pyridine, 2-picoline, pyridine N-oxide, or 2-picoline N-oxide (1 or 2 equiv.) in toluene-d_8 resulted in no reaction despite heating to 90 °C for 7 days (Eq. (1)).



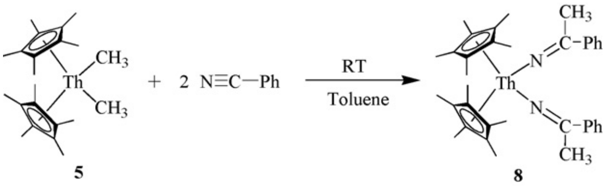
(1)

This is in contrast to the chemistry displayed by the isostructural thorium complex, $(C_5Me_5)_2Th(CH_3)_2$ (**5**), which readily reacts with the aromatic sp^2-hybridized *ortho* C–H bond in both pyridine and pyridine N-oxide, with loss of methane and formation the corresponding η^2-(N,C)-pyridyl complex (**6**) and the cyclometalated pyridine N-oxide complex (**7**), respectively (Eq. (2)) [14].

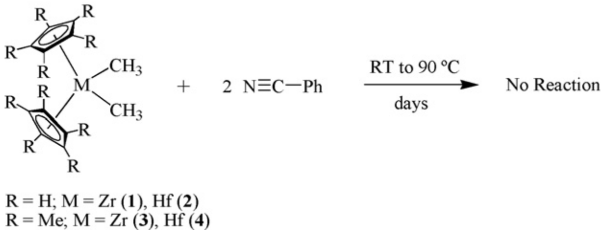


(2)

Another example of variant behavior is provided by reaction chemistry with benzonitrile. Although benzonitrile rapidly inserts into the Th–CH_3 bonds of complex **5** to give the bis(ketimide) complex $(C_5Me_5)_2Th[–N{=}C(CH_3)(Ph)]_2$ (**8**) (Eq. (3)) [15], there is no reaction observed between complexes **1**–**4** and 2 equiv. benzonitrile in toluene-d_8. Likewise, heating these mixtures at 90 °C for 5 days does not initiate reactivity (Eq. (4)).



(3)



(4)

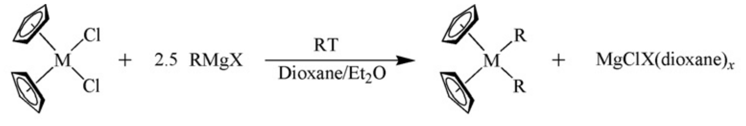
Preparation of Group IV ketimide complexes involving nitrile insertion has been observed for compounds possessing M–H and M–Si bonds. For example, nitrile insertion into a Zr–H bond was observed for the reaction of $(C_5Me_5)_2ZrH_2$ with 1 equiv. 4-methylbenzonitrile forming $(C_5Me_5)_2Zr(H)[–N{=}C(H)(C_6H_4Me)]$ [16], reaction of $[(C_5H_5)_2Zr(H)(THF)][BPh_4]$ with excess acetonitrile affording $[(C_5H_5)_2Zr\{–N{=}C(H)(CH_3)\}(N{\equiv}CCH_3)][BPh_4]$ [17], and reaction of $(C_5H_5)_2Zr(H)(Cl)$ with either benzonitrile or acetonitrile giving $(C_5H_5)_2Zr(Cl)[–N{=}C(H)(R)]$ (where R = Me, Ph) [18]. The Zr–Si bond in $(C_5H_5)(C_5Me_5)Zr[Si(SiMe_3)_3](Me)$ also reacts with acetonitrile, acrylonitrile, and benzonitrile to produce the corresponding ketimide complexes $(C_5H_5)(C_5Me_5)Zr[–N{=}Si(R)(SiMe_3)_3](Me)$ (where R = Me, $CH{=}CH_2$, Ph) [19].

It is important to point out that the titanium and zirconium bis(ketimide) complexes $(C_5Me_5)_2M[–N{=}C(Ph)_2]_2$ (M = Ti (**9**), Zr (**10**)) have been prepared by salt metathesis reactions between metal halides and alkali metal ketimide compounds or by reductive cleavage of azines [20]. As such, steric factors cannot account for the lack of reactivity between complexes **1**–**4** and benzonitrile. However, the smaller ionic radii of Ti(IV) and Zr(IV) have been invoked to explain the observation that the Ti(IV) and Zr(IV) systems have M-N-C ketimide angles of 160.8(2)° and 161.0(2)° (**9**) and 164.1(2)° and 173.7(2)° (**10**); whereas the thorium(IV) analogue, $(C_5Me_5)_2Th[–N{=}C(Ph)_2]_2$ (**11**), displays nearly linear Th-N-C angles (174.0(4) and 179.4(5)°).

In total, the observed lack of reactivity between the Group IV bis(alkyl) compounds **1**–**4** and pyridine, 2-picoline, pyridine N-oxide, 2-picoline N-oxide, and benzonitrile in comparison to the modes of reactivity observed for the analogous Th(IV) system with the same substrates provides dramatic evidence of marked differences between thorium and the Group IV metals.

2.2. *Revised syntheses of $(C_5H_5)_2M(R)_2$ (M = Zr, Hf; R = CH_3, Ph, CH_2Ph)*

During the course of our studies it was necessary to improve the syntheses of the Group IV metallocene alkyl and aryl complexes $(C_5H_5)_2MR_2$ (M = Zr, R = CH_3 (**1**), Ph (**14**), CH_2Ph (**15**); M = Hf, R = CH_3 (**2**), Ph (**16**), CH_2Ph (**17**)). While syntheses for complexes **1**, **2**, **14**, and **16** have been previously reported using lithium reagents to alkylate the metal centers [21], the reported yields were considerably lower compared to the following revised syntheses. As shown in Eq. (5), treatment of a diethyl ether slurry of $(C_5H_5)_2ZrCl_2$ (**12**) or $(C_5H_5)_2HfCl_2$ (**13**) with either MeMgBr, PhMgBr, or $PhCH_2MgBr$ (2.5 equiv.) and dioxane affords the corresponding bis(alkyl) or bis(aryl) complexes, $(C_5H_5)_2MR_2$ (M = Zr, R = CH_3 (**1**), Ph (**14**), CH_2Ph (**15**); M = Hf, R = CH_3 (**2**), Ph (**16**), CH_2Ph (**17**)). Following workup the isolated yields for these complexes are 85–95%.



M = Zr (**12**), Hf (**13**)

M = Zr; R = CH_3 (**1**), Ph (**14**), CH_2Ph (**15**)
M = Hf; R = CH_3 (**2**), Ph (**16**), CH_2Ph (**17**)

(5)

Some precedence exists in Group IV chemistry for using Grignard reagents for alkylation. For example, $(C_5H_5)_2Zr(CH_2Ph)_2$ (**15**) [22] and $(C_5H_5)_2Hf(CH_2Ph)_2$ (**17**) [23] have been prepared by reacting **12** and **13** with 2 equiv. $PhCH_2MgCl$, respectively. Similarly, $(C_5Me_5)Hf(CH_2Ph)_3$ (**18**) was prepared by reacting $(C_5Me_5)HfCl_3$ with 3 equiv. $PhCH_2MgCl$ [24]. However, these compounds were obtained in low to moderate yields (∼60% (**15**), 65% (**17**), 36% (**18**)), which may be attributed to the omission of dioxane from these synthetic procedures. Addition of dioxane permits the facile removal of precipitated $MgX_2(\text{dioxane})_x$ adducts from solution and allows for the straightforward workup and high-yield syntheses of compounds **1**, **2**, and **14**–**17** [25].

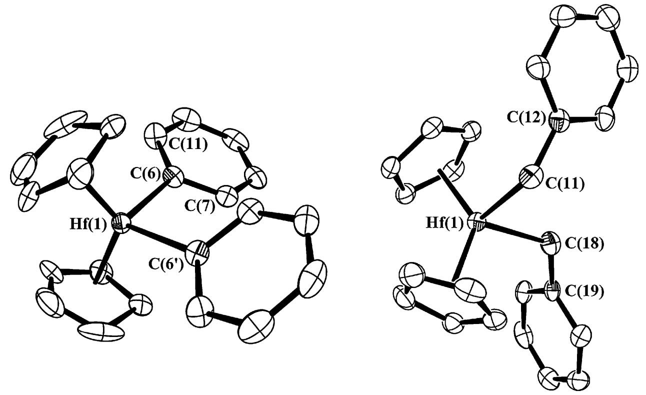


Fig. 1. Molecular structure of complexes **16** (left) and **17** (right) with thermal ellipsoids at the 33% probability level. Selected bond distances (Å) and angles (degree) for complex **16**: Hf(1)-C(6) 2.268(6), C(6)-Hf(1)-C(6′) 101.6(3), Hf(1)-C(6)-C(7) 117.4(4), Hf(1)-C(6)-C(11) 128.4(4), C(7)-C(6)-C(11) 114.0(5). For complex **17**: Hf(1)-C(11) 2.291(7), Hf(1)-C(18) 2.294(7), C(11)-Hf(1)-C(18) 93.7(3), C(12)-C(11)-Hf(1) 120.1(5), C(19)-C(18)-Hf(1) 123.3(5).

2.3. *Crystallographic characterization of complexes 16 and 17*

The molecular structures for complexes **16** and **17** have not been previously reported and are shown in Fig. 1. Complex **16** displays a bent metallocene framework with a distorted tetrahedral geometry about the hafnium metal center. The two phenyl ligands lie within the metallocene wedge with the Hf–C_{ipso} bond lengths being 2.268(6) Å and the C_{ipso}-Hf-C_{ipso} angle being 101.6(3)°. The C(7)-C(6)-C(11) angle of 114.0(5)° at C_{ipso} in the phenyl ring is slightly distorted from regular hexagonal geometry (120°) which is typical for σ-aryl complexes [26]. The selected metrical parameters for complex **16** compare well with those reported for the two other structurally characterized hafnium phenyl compounds, $[N(SiMe_2CH_2PMe_2)_2]Hf(Ph)(\eta^4\text{-}C_4H_6)$ (Hf-C_{ipso} = 2.290(6) Å, C-C_{ipso}-C = 112.7(6)°) [26a] and $[NBu_4][Hf(C_6Cl_5)_3Cl_2]$ (Hf-C_{ipso} = 2.259(13), 2.297(13), 2.306(13) Å, C-C_{ipso}-C = 112.3(12), 114.2(12), 115.0(12)°) [26b].

Compound **17** also possesses a distorted tetrahedral coordination environment about the hafnium center with the two benzyl ligands situated in the metallocene wedge. The Hf(1)-C(11) (2.291(7) Å) and Hf(1)-C(18) (2.294(7) Å) bond lengths fall within the range typically observed for a hafnium-benzyl linkage (2.214(7)-2.374(9) Å) [24,27]. For example, the tris(benzyl) complexes, $(C_5H_5B\text{-}CH_2Ph)Hf(CH_2Ph)_3$ and $(C_5Me_5)Hf(CH_2Ph)_3$, have Hf–CH_2 bond distances of 2.234(3), 2.249(3), and 2.271(3) Å [27d] and 2.240(5), 2.26(3), and 2.282(6) Å [24], respectively. The benzyl ligands are bound to the metal center in an η^1-fashion (Hf(1)-C(12) = 3.338 Å, Hf(1)-C(11)-C(12) = 120.1(5)°; Hf(1)-C(19) = 3.304 Å, Hf(1)-C(1)-C(19) = 123.3(5)°) and display no secondary interactions between the arene ring and the hafnium metal center.

3. Conclusion

We have demonstrated significant differences in the chemical reactivity between Th(IV) and Group (IV) compounds. Although the Th(IV) metallocene complexes $(C_5Me_5)_2ThR_2$ (R = CH_3, Ph, CH_2Ph) undergo unique chemical reactivity with pyridine, 2-picoline, pyridine N-oxide, 2-picoline N-oxide, and benzonitrile, the structurally similar Group IV complexes $(C_5R_5)_2M(CH_3)_2$ (R = H, CH_3; M = Zr, Hf) do not. The breakdown in the analogy for the Zr(IV), Hf(IV), and Th(IV) complexes with the same substrates provides clear-cut evidence that thorium is not merely a bigger member of the Group(IV) metals, and ultimately leads to neglect of some very rich and interesting actinide-specific reaction chemistry.

4. Experimental

4.1. Methods and materials

Reactions and manipulations were performed at 21 °C in a recirculating Vacuum Atmospheres inert atmosphere (He) drybox with a MO-40-2 Dri-Train. Glassware was dried overnight at 150 °C before use. NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Chemical shifts were referenced to the protio solvent impurity in benzene-d_6 at δ 7.15 ppm (^{1}H) and δ 128.39 ppm (^{13}C{^{1}H}) or toluene-d_8 at δ 2.09 ppm (^{1}H). Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), pentane (Aldrich), diethyl ether (Aldrich), dioxane (Aldrich), benzonitrile (Aldrich), pyridine (Aldrich), and 2-picoline (Aldrich) were passed through a column of activated alumina under nitrogen and stored over activated 4 Å molecular sieves prior to use. Deuterated solvents were dried by storage over activated 4 Å molecular sieves. Pyridine N-oxide (Acros) and 2-picoline N-oxide (Aldrich) were dissolved in toluene and passed through a column of activated alumina and recrystallized (from toluene at −30 °C) prior to use. $(C_5Me_5)_2Zr(CH_3)_2$ (**3**) [1a] and $(C_5Me_5)_2Hf(CH_3)_2$ (**4**) [1e] were prepared according to the literature procedures. $(C_5H_5)_2Zr(CH_3)_2$ (**1**) [21], $(C_5H_5)_2Hf(CH_3)_2$ (**2**) [21], $(C_5H_5)_2Zr(Ph)_2$ (**14**) [21], $(C_5H_5)_2Hf(Ph)_2$ (**16**) [21], $(C_5H_5)_2Zr(CH_2Ph)_2$ (**15**) [22], $(C_5H_5)_2Hf(CH_2Ph)_2$ (**17**) [23] were prepared using modifications to the literature procedures which are detailed below.

4.2. Preparation of $(C_5H_5)_2Zr(CH_3)_2$ (*1*)

A 125 mL side-arm flask equipped with a stir bar was charged with $(C_5H_5)_2ZrCl_2$ (**12**) (0.761 g, 2.60 mmol) and diethyl ether (60 mL). To the resulting colorless slurry was added methyl magnesium bromide (3.0 M soln/Et_2O, 2.17 mL, 6.51 mmol) with stirring. The reaction mixture immediately became clear and colorless. After 45 min of stirring at room temperature, dioxane (1.33 mL, 15.62 mmol) was added to the reaction mixture giving rise to an immediate white precipitate. After 1 h of continued stirring the volatiles were removed under reduced pressure to afford a white solid. The solid was extracted with toluene (60 mL) and filtered through a Celite-padded coarse frit. The filtrate was collected and the toluene was removed under reduced pressure. The resultant product was triturated with pentane (20 mL) and the volatiles were removed under reduced pressure to give **1** as a white powder (0.614 g, 2.44 mmol, 94%). ^{1}H NMR (C_6D_6, 297 K): δ 5.70 (s, 10H, C_5H_5), −0.14 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 110.72 (s, C_5H_5), 30.62 (s, CH_3).

4.3. Preparation of $(C_5H_5)_2Hf(CH_3)_2$ (*2*)

The synthesis of **2** was performed in an analogous manner to **1**. Reaction of $(C_5H_5)_2HfCl_2$ (**13**) (0.752 g, 1.98 mmol) with methyl magnesium bromide (3.0 M soln/Et_2O, 1.65 mL, 4.95 mmol) and dioxane (1.01 mL, 11.87 mmol) gave **2** as a white powder (0.633 g, 1.87 mmol, 94%). ^{1}H NMR (C_6D_6, 298 K): δ 5.63 (s, 10H, C_5H_5), −0.32 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 299 K): δ 110.22 (s, C_5H_5), 36.84 (s, CH_3).

4.4. Preparation of $(C_5H_5)_2Zr(Ph)_2$ (*14*)

A 125 mL side-arm flask equipped with a stir bar was charged with $(C_5H_5)_2ZrCl_2$ (**12**) (0.749 g, 2.56 mmol) and diethyl ether (60 mL). To the resulting colorless slurry was added phenyl magnesium bromide (3.0 M soln/Et_2O, 2.14 mL, 6.41 mmol) with stirring. The reaction mixture immediately became clear and pale yellow in color. After 10 min of stirring dioxane (1.31 mL, 15.37 mmol) was added to the reaction mixture immediately forming a white precipitate. After 15 h of continued stirring the volatiles were removed under reduced pressure to give a pale pink solid. The solid was extracted with toluene (60 mL) and filtered through a Celite-padded coarse frit. The filtrate was collected and the toluene was removed under reduced pressure to give **14** as an orange powder (0.957 g, 2.55 mmol, 95%). ^{1}H NMR (C_6D_6, 298 K): δ 7.25 (m, 8H, Ar *H*), 7.11 (t, 2H, para *H*), 5.76 (s, 10H, C_5H_5). ^{13}C{^{1}H} NMR (C_6D_6, 299 K): δ 183.58 (s, quat Ar *C*), 136.29 (Ar *C*), 127.30 (Ar *C*), 126.02 (Ar *C*), 112.64 (s, C_5H_5).

4.5. Preparation of $(C_5H_5)_2Hf(Ph)_2$ (*16*)

The synthesis of **16** was performed in an analogous manner to **14**. Reaction of $(C_5H_5)_2HfCl_2$ (**13**) (0.757 g, 1.99 mmol) with phenyl magnesium bromide (3.0 M soln/Et_2O, 1.66 mL, 4.99 mmol) and dioxane (1.02 mL, 11.97 mmol) gave **16** as a white powder (0.835 g, 1.80 mmol, 91%). Crystals suitable for X-ray crystallographic analysis were obtained overnight from cooling a 1:1 toluene:pentane solution of **16** at −30 °C. ^{1}H NMR (C_6D_6, 298 K): δ 7.32 (m, 8H, Ar *H*), 7.10 (t, 2H, para *H*), 5.73 (s, 10H, C_5H_5). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 192.32 (s, quat Ar *C*), 138.13 (Ar *C*), 127.62 (Ar *C*), 125.77 (Ar *C*), 112.32 (s, C_5H_5).

4.6. Preparation of $(C_5H_5)_2Zr(CH_2Ph)_2$ (*15*)

A 125 mL side-arm flask equipped with a stir bar was charged with $(C_5H_5)_2ZrCl_2$ (**12**) (0.745 g, 2.55 mmol) and diethyl ether (60 mL). To the resulting colorless slurry was added benzyl magnesium chloride (1.0 M soln/Et_2O, 6.37 mL, 6.37 mmol) with stirring. The reaction mixture immediately became clear and yellow in color. After 10 min of stirring dioxane (1.30 mL, 15.29 mmol) was added to the reaction solution immediately forming a precipitate. After 2 h of continued stirring the volatiles were removed under reduced pressure to give a yellow solid. The solid was extracted with toluene (60 mL) and filtered through a Celite-padded coarse frit. The filtrate was collected and the toluene was removed under reduced pressure to give **15** as a yellow powder (0.880 g, 2.18 mmol, 86%). ^{1}H NMR (C_6D_6, 299 K): δ 7.22 (m, 4H, Ar *H*), 6.91 (m, 6H, Ar *H*), 5.51 (s, 10H, C_5H_5), 1.82 (s, 4H, CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ 152.68 (s, quat Ar *C*) 128.87 (Ar *C*), 126.41 (Ar *C*), 121.64 (Ar *C*), 112.59 (s, C_5H_5), 61.15 (s, CH_2Ph).

4.7. Preparation of $(C_5H_5)_2Hf(CH_2Ph)_2$ (*17*)

The synthesis of **17** was performed in an analogous manner to **15**. Reaction of $(C_5H_5)_2HfCl_2$ (**13**) (0.757 g, 1.99 mmol) with benzyl magnesium chloride (1.0 M soln/Et_2O, 4.99 mL, 4.99 mmol) and dioxane (1.02 mL, 11.97 mmol) gave **17** as a yellow powder (0.920 g, 1.87 mmol, 94%). Crystals suitable for X-ray crystallographic analysis were obtained overnight from cooling a 1:1 toluene:pentane solution of **17** at −30 °C. ^{1}H NMR (C_6D_6, 298 K): δ 7.27 (m, 4H, Ar *H*), 6.89 (m, 6H, Ar *H*), 5.47 (s, 10H, C_5H_5), 1.54 (s, 4H, CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 152.58 (s, quat Ar *C*) 128.65 (Ar *C*), 127.01 (Ar *C*), 121.97 (Ar *C*), 111.85 (s, C_5H_5), 64.97 (s, CH_2Ph).

4.8. Crystal structure determination

Crystal data for **16** ($C_{22}H_{20}Hf$): $M = 462.87$, orthorhombic, space group *Aba*2, $a = 8.256(3)$ Å, $b = 16.470(5)$ Å, $c = 12.813(4)$ Å, $V = 1742.2(10)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.765\ \mathrm{g\,cm^{-3}}$, $T = 203(2)$ K, θ range 2.47–27.29°, μ(Mo Kα) = 5.984 mm^{-1}, 4584 reflections collected, 1333 reflections with $I > 2\sigma(I)$. $R = 0.0175$ (obs. data), $wR_2 = 0.0430$ (all data), GOF = 1.186 (F^2).

Crystal data for **17** ($C_{24}H_{24}Hf$): $M = 490.92$, orthorhombic, space group *pbca*, $a = 11.477(3)$ Å, $b = 15.912(5)$ Å, $c = 21.013(6)$ Å, $V = 3837.4(19)$ Å^3, $Z = 8$, $D_{\mathrm{calc}} = 1.699\ \mathrm{g\,cm^{-3}}$, $T = 203(2)$ K, θ range 1.94–27.49°, μ(Mo Kα) = 5.439 mm^{-1}, 32456 reflections collected, 3338 reflections with $I > 2\sigma(I)$. $R = 0.0427$ (obs. data), $wR_2 = 0.0931$ (all data), GOF = 1.189 (F^2).

Single crystals of **16** (0.30 mm × 0.25 mm × 0.10 mm) and **17** (0.38 mm × 0.38 mm × 0.10 mm) were mounted from Paratone-N oil under argon gas flow onto a glass fiber and placed on a Bruker P4/CCD diffractometer, equipped with a Bruker LT-2 temperature device. A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. The instrument was equipped with graphite monochromatized Mo Kα X-ray source ($\lambda = 0.71073$ Å). Data collection and initial indexing and cell refinement were handled using SMART software [28]. Frame integration and final cell parameter calculations were carried out using SAINT software [29]. The data were corrected for absorption using the SADABS program [30]. Decay of reflection data was monitored by analysis of redundant frames.

Both structures were solved using direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix lest-squares procedures. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. For **16**, three disordered carbon atoms in the cyclopentadienyl ligand were refined as three one-half occupancy positions (C(1) through C(3) and C(1′) through C(3′)). Additionally, C(1) was restrained during the refinement to approximate isotropic behavior using the ISOR SHELXTL command. Hydrogen atom positions were not included on disordered carbon atoms. Structure solution, refinement, and creation of publication materials were performed using SHELX-TL [31].

5. Supplementary information

CCDC-615039 and CCDC-615040 contain the supplementary crystallographic data for complexes **16** and **17**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Database Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] See for example:
(a) J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 100 (1978) 2716–2724;
(b) P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6650–6667;
(c) H.S. Tung, C.H. Brubaker Jr., Inorg. Chim. Acta 52 (1981) 197–204;
(d) L.E. Schock, C.P. Brock, T.J. Marks, Organometallics 6 (1987) 232–241;
(e) L.E. Schock, T.J. Marks, J. Am. Chem. Soc. 110 (1988) 7701–7715.

[2] See for example:
(a) J.M. Manriquez, P.J. Fagan, T.J. Marks, C.S. Day, V.W. Day, J. Am. Chem. Soc. 100 (1978) 7112–7114;
(b) P.T. Wolczanski, J.E. Bercaw, Acc. Chem. Res. 13 (1980) 121–127;
(c) S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Am. Chem. Soc. 105 (1983) 1690;
(d) D.C. Sonnenberger, E.A. Mintz, T.J. Marks, J. Am. Chem. Soc. 106 (1984) 3484–3491;
(e) K.G. Moloy, T.J. Marks, J. Am. Chem. Soc. 106 (1984) 7051–7064;
(f) P. Hofmann, M. Frede, P. Stauffert, W. Lasser, U. Thewalt, Angew. Chem. Int. Ed. Engl. 24 (1985) 712–713.

[3] See for example:
(a) R.W. Broach, A.J. Schultz, J.M. Williams, G.M. Brown, J.M. Manriquez, P.J. Fagan, T.J. Marks, Science 203 (1979) 172–174;
(b) C.M. Fendrick, L.D. Schertz, V.W. Day, T.J. Marks, Organometallics 7 (1988) 1828–1838;
(c) J.E. Gozum, G.S. Girolami, J. Am. Chem. Soc. 113 (1991) 3829–3837;
(d) J.B. Love, H.C.S. Clark, F.G.N. Cloke, J.C. Green, P.B. Hitchcock, J. Am. Chem. Soc. 121 (1999) 6843–6849;
(e) J.R. Hagadorn, M.J. McNevin, G. Wiedenfeld, R. Shoemaker, Organometallics 22 (2003) 4818–4824;
(f) T. Matsuo, H. Kawaguchi, Organometallics 22 (2003) 5379–5381.

[4] R.D. Shannon, Acta Crystallogr. A32 (1976) 751–767.

[5] A. Avdeef, K.N. Raymond, K.O. Hodgson, A. Zalkin, Inorg. Chem. 11 (1972) 1083–1088.

[6] (a) H. Dietrich, M. Soltwisch, Angew. Chem. Int. Ed. Engl. 8 (1969) 765;
(b) D.M. Rogers, S.R. Wilson, G.S. Girolami, Organometallics 10 (1991) 2419–2424;
(c) P. Berno, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Chem. Soc. Dalton Trans. (1991) 3085–3091;
(d) F.G.N. Cloke, J.C. Green, P.B. Hitchcock, S.C.P. Joseph, P. Mountford, N. Kaltsoyannis, A. McCamley, J. Chem. Soc. Dalton Trans. (1994) 2867–2874.

[7] R. Maier, B. Kanellakopulos, C. Apostolidis, D. Meyer, J. Rebizant, J. Alloys Compd. 190 (1993) 269–271.

[8] See for example:
(a) R.D. Rogers, R.V. Bynum, J.L. Atwood, J. Am. Chem. Soc. 100 (1978) 5238–5239;
(b) H. Jacobsen, H. Berke, T. Brackemeyer, T. Eisenblätter, G. Erker, R. Fröhlich, O. Meyer, K. Bergander, Helv. Chim. Acta 81 (1998) 1692–1709;
(c) W.W. Lukens, R.A. Andersen, Organometallics 14 (1995) 3435–3439;
(d) T. Brackemeyer, G. Erker, R. Fröhlich, Organometallics 16 (1997) 531–536;
(e) B.L. Edelbach, A.K.F. Rahman, R.J. Lachicotte, W.D. Jones, Organometallics 18 (1999) 3170–3177;
(f) G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, Chem. Eur. J. 6 (2000) 258–266.

[9] See for example:
(a) M.D. Fryzuk, P.B. Duval, S.S.H. Mao, M.J. Zaworotko, L.R. MacGillivray, J. Am. Chem. Soc. 121 (1999) 2478–2487;
(b) M.D. Fryzuk, S.S.H. Mao, M.J. Zaworotko, L.R. MacGillivray, J. Am. Chem. Soc. 115 (1993) 5336–5337;
(c) M.D. Fryzuk, P.B. Duval, B.O. Patrick, S.J. Rettig, Organometallics 20 (2001) 1608–1613;
(d) R.R. Schrock, Chem. Rev. 102 (2002) 145–179;
(e) B.C. Bailey, J.C. Huffman, D.J. Mindiola, W. Weng, O.V. Ozerov, Organometallics 24 (2005) 1390–1393.

[10] See for example:
(a) D.J. Sikora, M.D. Rausch, R.D. Rogers, J.L. Atwood, J. Am. Chem. Soc. 101 (1979) 5079–5081;
(b) J.L. Atwood, R.D. Rogers, W.E. Hunter, C. Floriani, G. Fachinetti, A. Chiesi-Villa, Inorg. Chem. 19 (1980) 3812–3817;
(c) D.J. Sikora, M.D. Rausch, R.D. Rogers, J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 1265–1267;
(d) B.H. Edwards, R.D. Rogers, D.J. Sikora, J.L. Atwood, M.D. Rausch, J. Am. Chem. Soc. 105 (1983) 416–426;
(e) Y. Wielstra, S. Gambarotta, J.B. Roedelof, Organometallics 7 (1988) 2177–2182.

[11] (a) U. Rosenthal, V.V. Burlakov, in: I. Marek (Ed.), Titanium and Zirconium in Organic Synthesis, Wiley–VCH, Weinheim, Germany, 2002;
(b) T. Beweries, V.V. Burlakov, M.A. Bach, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, Organometallics 26 (2007) 247–249.

[12] J.A. Pool, B.L. Scott, J.L. Kiplinger, J. Am. Chem. Soc. 127 (2005) 1338–1339.

[13] J.A. Pool, B.L. Scott, J.L. Kiplinger, Chem. Commun. (2005) 2591–2593.

[14] J.A. Pool, B.L. Scott, J.L. Kiplinger, J. Alloys Compd. 418 (2006) 178–183.

[15] (a) K.C. Jantunen, C.J. Burns, I. Castro-Rodriguez, R.E. Da Re, J.T. Golden, D.E. Morris, B.L. Scott, F.L. Taw, J.L. Kiplinger, Organometallics 23 (2004) 4682–4692;
(b) E.J. Schelter, D.E. Morris, B.L. Scott, J.L. Kiplinger, Chem. Commun. (2007) 1029–1031.

[16] J.E. Bercaw, D.L. Davies, P.T. Wolczanski, Organometallics 5 (1986) 443–450.

[17] R.F. Jordan, C.S. Bajgur, W.E. Dasher, A.L. Rheingold, Organometallics 6 (1987) 1041–1051.

[18] G. Erker, W. Frömberg, J.L. Atwood, W.E. Hunter, Angew. Chem. Int. Ed. Engl. 23 (1984) 68–69.

[19] H.G. Woo, T.D. Tilley, J. Organomet. Chem. 393 (1990) C6–C9.

[20] (a) G. Erker, W. Frömberg, C. Krüger, E. Raabe, J. Am. Chem. Soc. 110 (1988) 2400–2405;

(b) T. Zippel, P. Arndt, A. Ohff, A. Spannenberg, R. Kempe, U. Rosenthal, Organometallics 17 (1998) 4429–4437.

[21] (a) E. Samuel, M.D. Rausch, J. Am. Chem. Soc. 95 (1973) 6263–6267;
(b) W.E. Hunter, D.C. Hrncir, R.V. Bynum, R.A. Penttila, J.L. Atwood, Organometallics 2 (1983) 750–755.

[22] G. Fachinetti, C. Floriani, J. Chem. Soc., Chem. Commun. (1972) 654–655.

[23] B. Demerseman, G. Bouquet, M. Bigorgne, J. Organomet. Chem. 93 (1975) 199–204.

[24] D.C. Swenson, Z. Guo, D.J. Crowther, N.C. Baenziger, R.F. Jordan, Acta Cryst. C56 (2000) e313–e314.

[25] G.S. Silverman, P.E. Rakita (Eds.), Handbook of Grignard Reagents, Marcel Dekker, New York, 1996.

[26] (a) M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 8 (1989) 1723–1732;
(b) I. Ara, J. Forniés, M. García-Monforte, A. Martín, B. Menjón, Chem. Eur. J. 10 (2004) 4186–4197.

[27] See for example:
(a) A.R. Bulls, W.P. Schaefer, M. Serfas, J.E. Bercaw, Organometallics 6 (1987) 1219–1226;
(b) P. Giorgio Cozzi, E. Gallo, C. Floriani, Organometallics 14 (1995) 4994–4996;
(c) M.J. Scott, S.J. Lippard, Inorg. Chim. Acta 263 (1997) 287–299;
(d) M.A. Putzer, J.S. Rogers, G.C. Bazan, J. Am. Chem. Soc. 121 (1999) 8112–8113;
(e) E.Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, Organometallics 21 (2002) 662–670;
(f) T.R. Boussie, G.M. Diamond, C. Goh, K.A. Hall, A.M. LaPointe, M. Leclerc, C. Lund, V. Murphy, J.A.W. Shoemaker, U. Tracht, H. Turner, J. Zhang, T. Uno, R.K. Rosen, J.C. Stevens, J. Am. Chem. Soc. 125 (2003) 4306–4317;
(g) I. Westmoreland, I.J. Munslow, A.J. Clarke, G. Clarkson, P. Scott, Organometallics 23 (2004) 5066–5074;
(h) S.C. Cole, M.P. Coles, P.B. Hitchcock, Organometallics 24 (2005) 3279–3289.

[28] SMART-NT 4, Bruker Analytical X-ray Instruments, Inc., Madison, WI 53719, 1996.

[29] SAINT-NT 5.050, Data Collection Software, Bruker Analytical X-ray Instruments, Inc., Madison, WI 53719, 1998.

[30] G. Sheldrick, SADABS, Empirical Absorption Correction Program, Version 2.03, University of Göttingen, Germany, 2001.

[31] SHELXTL, Version 5.10, Bruker Analytical X-ray Instruments, Inc., Madison, WI 53719, 1997.