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Metallaoxirane-Supported Hydrido Group 4 Metallocene Cations

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The (η^2-diaryl ketone)zirconocene dimers **17a** and **17b** (aryl = phenyl or *p*-tolyl) react with the group 4 metallocene dihydride complexes [^{R}Cp$_2$MH$_2$] (^{R}Cp$_2$M = Cp$_2$Zr, (MeCp)$_2$Zr, or Cp$_2$Hf) to yield the dimetallic compounds [(μ-η^1-O:η^2-C,O-Ar$_2$CO)ZrCp$_2$/H$_2$M^{R}Cp$_2$] **18a**−**f**. These systems contain a dimetallabicyclic framework in which the two metal centers are bridged by the η^2-diaryl ketone ligand oxygen atom and a μ-hydride ligand. The remaining hydride ligand is trans-oriented to the μ-H moiety at the M^{R}Cp$_2$ unit. The complexes **18a**−**c** were characterized by X-ray diffraction. Treatment of the complexes **18** with B(C$_6$F$_5$)$_3$ results in the selective abstraction of the terminal hydride ligand to form the dimetallic cation complexes [(μ-η^1-O:η^2-C,O-Ar$_2$CO)ZrCp$_2$(μ-H)M^{R}Cp$_2$]$^+$ **19a**−**f** (with HB(C$_6$F$_5$)$_3^-$ anion). The complexes **19** contain the intact (η^2-diaryl ketone)ZrCp$_2$ unit to which a (H−M^{R}Cp$_2$)$^+$ cation is formally attached. They exhibit a planar dimetallabicyclic framework, in which the two group 4 metal centers are connected by means of the η^2-ketone oxygen atom and the μ-hydride ligand. The complexes **19a**,**b** and **e** were characterized by X-ray crystal structure analyses. The complexes **19** behave chemically as adducts of the highly reactive (^{R}Cp$_2$M−H)$^+$ cations with a metallaoxirane matrix. Ethene is polymerized by the systems **19** with high catalyst activities.

Introduction

The hydrozirconation reaction of alkenes probably represents the first significant usage of a molecular organometallic zirconium compound in organic synthesis.[1] Electrophilic hydridozirconium complexes have, therefore, been thought of as important intermediates in carbon−carbon coupling sequences. [^{R}Cp$_2$ZrH$^+$] complexes **1** may be regarded as the archetypes of strongly electrophilic hydrozirconation reagents that instantaneously react with almost any alkene. Hydridozirconocene complexes of the type **1** had been regarded as the effective chain transfer intermediates in homogeneous metallocene Ziegler catalysis; but theoretical and experimental evidence has rapidly accumulated indicating that more complex intermediates are involved that may contain the respective [^{R}Cp$_2$ZrH$^+$] building block or just mimic its function.[2]

In view of its catalytic relevance, the organometallic functional group [Zr$^+$]−H has been in the center of a comparatively small number of detailed experimental studies. This may be due to the elusive nature of the parent [Cp$_2$Zr−H$^+$] monomer and the many difficulties encountered in generating it in a suitable stabilizing environment. Most examples, such as those listed in Scheme 1, were prepared by using a hydrogenation route, i.e., by treating the respective stabilized [^{R}Cp$_2$-Zr−CH$_2$R(L)$^+$] cation systems with dihydrogen under suitable reaction conditions.[3] It appears that the [Cp*$_2$-ZrH$^+$] system was prepared by a common anion abstraction route (here H$^-$ abstraction effected by B(C$_6$F$_5$)$_3$) from the Cp*$_2$ZrH$_2$ precursor, but again the free [Zr$^+$]−

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† X-ray crystal structure analyses.

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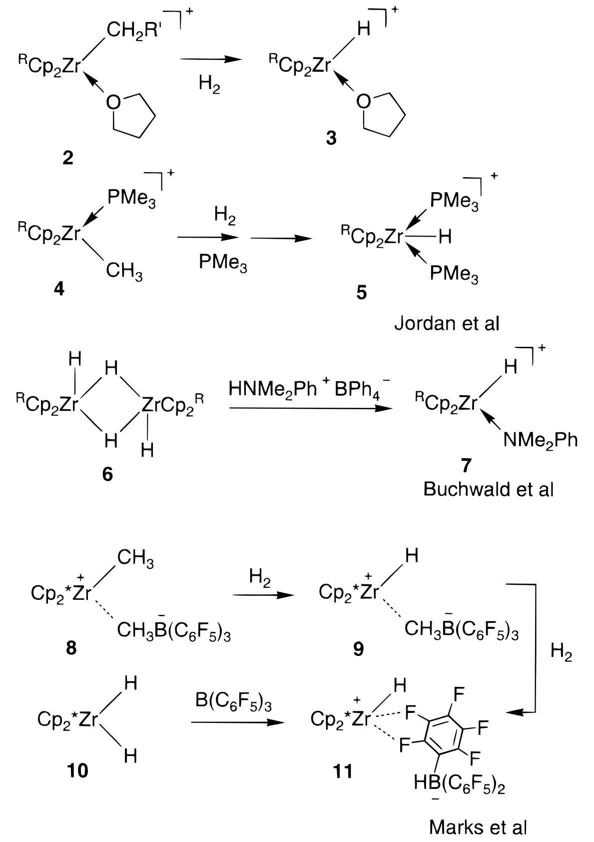
Scheme 1



H species is not obtained but rather its stabilized tight ion pair (see Scheme 1).[4]

These examples show that stabilizing the reactive [$^RCp_2Zr{-}H^+$] building block has predominantly relied on decreasing the electron deficiency at the metal center. However, we know from the chemistry of many neutral $^RCp_2ZrH_2$ complexes that dimerization or oligomerization is often a preferred mode of stabilization, making use of the formation of thermodynamically favorable (μ-H)Zr_2 bridges.[5] Increasing the knowledge about the chemical properties of the [Zr^+]$-$H functionality could therefore possibly profit from the synthetic availability of groups of compounds that contain, for example, the [$^RCp_2Zr{-}H^+$] moiety **1** linked to and stabilized by an organometallic template that may take care of stabilizing both the electrophilic group 4 metal center in **1** and its nucleophilic hydride ligand. We[6] and others[7] had previously shown that neutral oxazirconacycles of ring sizes three, four, or five all contain a strongly electrophilic metal center (mostly because of the effective inductive electron-withdrawing properties of the σ-bonded oxygen atom) and a rather nucleophilic $-$OR group that does not share its lone-pair electron density with the adjacent metal center because of strain effects in a metallacycle of this ring size.[8,9] Especially the three-membered ring systems, the respective metallaoxiranes, show this dichotomy of the coordination properties at the [Zr]$-$O$-$ unit very strongly.[10-12] Consequently, the group 4 metallaoxiranes should serve as suitable templates to bind the bis(cyclopentadienyl)(hydrido)zirconium cation by stabilizing both the metallocene moiety and the hydrido ligand by a favorable coordinative interaction as schematically depicted by the general structure **12** in formula 1. We have prepared a first series of such compounds using the (η^2-diaryl ketone)-zirconocene metallaoxiranes as suitable templates and describe their preparation, characterization, and some scouting experiments about their potential catalytic properties in this article.

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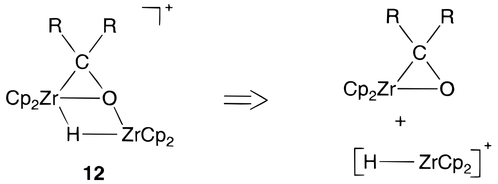


12 (1)

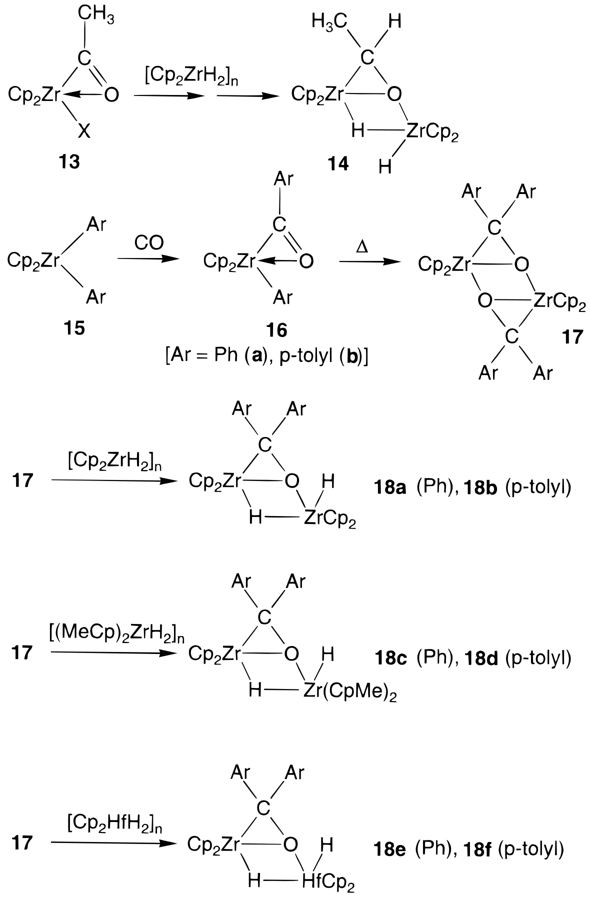
Results and Discussion

Template-Supported Group 4 Metallocene Dihydride Complexes. (η^2-Aldehyde)- and (η^2-ketone)zirconocene complexes can readily be prepared by carbonylation routes starting from alkyl- and arylzirconocene complexes. We had previously shown that treatment of (η^2-acetyl)zirconocene halide complexes (**13**) with (hydrido)zirconocene complexes such as $[Cp_2Zr(H)Cl]_n$ or $[Cp_2ZrH_2]_n$[13] gives rise to the formation of dinuclear metallocene complexes (**14**) that contain a monomeric Cp_2ZrH_2 unit that is bonded to the (η^2-acetaldehyde)$ZrCp_2$ metallaoxirane template.[10a] Bridging is effected by the metallaoxirane oxygen atom and by one of the hydrides of the Cp_2ZrH_2 moiety. In the case of **14** the bridging and terminal hydride ligands are cis-oriented at the bent metallocene unit in the "southeast position" of the homodimetallic complex framework (see Scheme 2). This was shown by X-ray diffraction and by ^1H NMR spectroscopy ($^2J_{HH} \approx 14$ Hz).

For this study we have decided to use (η^2-benzophenone)- and (η^2-di-*p*-tolyl ketone)zirconocene as the metallaoxirane templates. The (η^2-diaryl ketone)$ZrCp_2$ complexes (**17a** and **17b**) were prepared starting from the respective bis(aryl)zirconocenes **15a**,**b**. Carbonylation gave the (η^2-aroyl)arylmetallocene complexes **16a** and **16b**.[14] Subsequent thermolysis resulted in migration of the remaining σ-aryl ligand from zirconium to the electrophilic acylcarbon center to give the respective metallaoxiranes[15] that were isolated as the dimetallatricyclic dimers **17a** (Ar = Ph) and **17b** (Ar = *p*-tolyl) (see Scheme 2).

The (η^2-diaryl ketone)MCp_2 dimers were then treated with a suitable $^RCp_2MH_2$ reagent (M = Zr or Hf).[13] In a typical experiment the (η^2-benzophenone)zirconocene dimer **17a** was stirred with an equimolar quantity of the oligomeric $[Cp_2ZrH_2]_n$ metallocene dihydride in benzene or toluene solution for a time period of ca. 2 days. During this time thermally induced cleavage of both associated reagents does occur with a sufficient rate, and eventually the cross-coupling of their respective monomeric building blocks, the $(\eta^2\text{-}Ph_2\overline{CO})ZrCp_2$ metallaoxirane and the di(hydrido)metallocene Cp_2ZrH_2, takes place effectively. The corresponding metallaoxirane-template-supported zirconocene dihydride complex **18a** was isolated from the reaction mixture in close to 90% yield.

Scheme 2



The [(η^2-di-*p*-tolyl ketone)$ZrCp_2$/Cp_2ZrH_2] adduct **18b** was obtained analogously. Both the complexes **18a** and **18b** exhibit typical spectroscopic properties. There are two $\tilde{\nu}$(M−H) features at 1504 and 1308 cm^{-1} (for **18b**) that indicate bridging and terminal hydride ligands at a zirconocene moiety.[13a] Consequently, two ^1H NMR metal hydride resonances are observed (see Table 1) that are in the typical range of bridging (**18a**: δ −1.44 ppm) and terminal (**18a**: δ 5.04) zirconocene hydride ligands.[13] There is strong evidence in the whole series of complexes **18** (see below and Table 1) that the hydride ligands are oriented trans (i.e., both oriented in lateral positions[16]) at the southeast $ZrCp_2$ unit with the bridging metallaoxirane oxygen atom between them. This is evident from the consistently small $^2J_{HH}$ coupling constant (ca. 7 Hz) that is quite different from that observed for the cis-dihydride complex **14** (ca. 14 Hz, see Scheme 2), and this interpretation is also supported by the X-ray crystal structure analyses carried out in this study (see below). The metallaoxirane framework inside the dimetallic system of **18a** shows a typical *C*Ph$_2$ ^{13}C NMR resonance at δ 83.6 ppm. As expected for the adduct structure, we observe the ^1H and ^{13}C NMR resonances of two chemically inequivalent Cp_2Zr units in both **18a** and **18b**.

Both the complexes **18a** and **18b** were characterized by X-ray crystal structure analyses. They show a very

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Table 1. Selected Spectroscopic Parameters of the Dimetallic Metallocene Dihydrides 18 and the Dimetallic Hydridometallocene Cation Complexes 19

	18a[a]	**18b**[a]	**18c**[a]	**18d**[a]	**18e**[a]	**18f**[a]	**19a**[b]	**19b**[b]	**19c**[b]	**19d**[b]	**19e**[b]	**19f**[b]
M^1	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr
M^2	Cp_2Zr	Cp_2Zr	$MeCp_2Zr$	$MeCp_2Zr$	Cp_2Hf	Cp_2Hf	Cp_2Zr	Cp_2Zr	$MeCp_2Zr$	$MeCp_2Zr$	Cp_2Hf	Cp_2Hf
Ar	Ph	*p*-tolyl	Ph	*p*-tolyl	Ph	*p*-tolyl	Ph	*p*-tolyl	Ph	*p*-tolyl	Ph	*p*-tolyl
$\delta(\mu\text{-H})$	−1.44	−1.46	−1.36	−1.38	−0.81	−0.84	−1.87	−1.91	−1.67	−1.88	0.63	0.61
$\delta(M^2\text{–H})$	5.04	5.01	5.38	5.34	8.19	8.13	(4.3)[e]	(4.3)[e]	(4.3)[e]	(4.3)[e]	(4.3)[e]	(4.3)[e]
$^2J_{HH}$ (Hz)	7.4	7.4	6.9	7.0	7.8	7.7						
$\delta(CAr_2)$	83.6	83.3	83.4	83.5	82.1	81.6	89.6	*f*	*f*	*f*	*f*	*f*
$\Delta G^{\ddagger}{}_{rot}{}^{c}$	11.8	11.4	11.0	11.2	11.6	11.5	9.9	9.2	9.7	9.7	10.1	10.3
T_{coal} (K)	258	248	238	238	250	243	228	213	223	223	223	233
$\tilde{\nu}(MH)^d$	1488 1313	1504 1308	*f* 1322	*f* 1314	1538 1319	1553 1314	*f*	*f*	*f*	*f*	*f*	*f*

[a] NMR in THF-d_8. [b] NMR in bromobenzene-d_5. [c] C-aryl rotational barrier in kcal mol^{-1} at T_{coal}. [d] IR in KBr (cm^{-1}). [e] ^{1}H NMR $HB(C_6F_5)_3^-$ resonance. [f] Not located.

Table 2. Selected Structural Parameters of the Dimetallic Neutral Metallocene Dihydrides 18 and Their Related Cationic Monohydride Complexes 19

	18a	**18b**	**18c**	**19a**[c]	**19b**[c]	**19e**
M^1	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr	Cp_2Zr
M^2	Cp_2Zr	Cp_2Zr	$MeCp_2Zr$	Cp_2Zr	Cp_2Zr	Cp_2Hf
Ar	Ph	*p*-tolyl	Ph	Ph	*p*-tolyl	Ph
Zr1–O	2.119(3)	2.116(4)	2.110(6)	2.252(3)	2.255(5)	2.259(5)
Zr2–O	2.146(3)	2.146(4)	2.150(7)	2.027(3)	2.021(5)	2.004(5)[d]
Zr1–C1	2.330(5)	2.328(6)	2.320(10)	2.349(5)	2.349(8)	2.358(8)
C1–O	1.419(5)	1.410(7)	1.426(12)	1.429(6)	1.433(9)	1.435(9)
Zr1–μH	1.95(5)	1.78(5)	*b*	2.01(4)	2.20(6)	*b*
Zr2–μH	2.24(5)	2.10(5)	*b*	2.07(4)	1.97(6)	*b*
Zr1–C1–O	63.5(2)	63.5(3)	63.4(4)	68.3(2)	68.4(3)	68.1(4)
C1–Zr1–O	36.8(1)	36.6(2)	37.2(3)	36.1(1)	36.2(2)	36.1(2)
C1–O–Zr1	79.7(2)	79.9(3)	79.5(5)	75.7(2)	75.5(4)	75.7(4)
C1–O–Zr2	171.0(3)	169.7(4)	170.8(6)	178.2(3)	177.1(5)	177.0(5)[d]
Zr1–O–Zr2	109.2(2)	109.4(2)	109.7(3)	102.9(1)	103.2(2)	102.6(2)[d]

[a] Bond lengths in Å, angles in deg. [b] Not located. [c] Averaged values from two crystallographically independent molecules. [d] Bond to hafnium.

similar structural pattern (see Table 2). Complex **18a** (see also Figure 1) exhibits a dimetallic framework that contains a metallaoxirane ring system. Both the Zr1–O (2.119(3) Å) and the Zr1–C1 (2.330(5) Å) bonds inside the metallacyclic three-membered ring system are in the typical range of such σ-bonds at the bent metallocene framework.[10,17] The corresponding C1–O bond is 1.419(5) Å.

The metallaoxirane oxygen atom in **18a** is also strongly coordinated to the second Cp_2Zr unit. The Zr2–O bond length is 2.146(3) Å, which is only slightly longer than the Cp_2Zr1–O linkage. The Zr_2CO framework of **18a** is planar. The Zr1–O–Zr2 angle is 109.2(1)°, and the C1–O–Zr2 angle at the bridging planar-tricoordinate oxygen is nearly linear, at 171.0(3)°.

The planar central complex framework of **18a** is completed by a μ-H ligand that is unsymmetrically bridging between Zr1 and Zr2. Even within the uncertainty that is involved with hydrogen atom location by X-ray diffraction methods, it appears that the μ-H atom is located closer to Zr1 (1.95(5) Å) than to Zr2 (2.24(5) Å). The in-plane hydrogen bridge between Zr1 and Zr2 is bent (calculated Zr1···H···Zr2 angle 112(2)°). In the structure of **18a** we have located electron density at Zr2 in the σ-ligand plane[16] in a trans-orientation to the μ-H ligand. This feature may indicate the position of the terminal hydride at this zirconium atom as it was already characterized by the ^{1}H NMR analysis. Due to the problematic nature of determining the exact location of a singly metal bonded hydride by X-ray diffraction, further details about the hydride bonding parameters

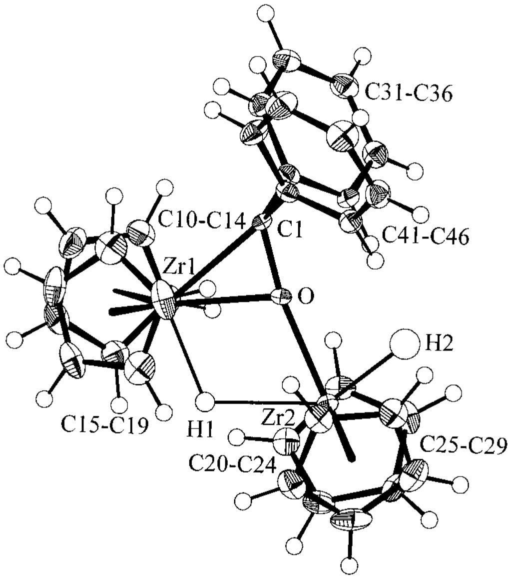

Figure 1. View of the molecular structure of the [Cp_2Zr-(η^2-Ph_2CO)/Cp_2ZrH_2] addition product **18a**. Selected bond lengths (Å) and angles (deg): Zr1–O 2.119(3), Zr2–O 2.146(3), Zr1–C1 2.330(5), Zr1–H1 1.95(5), Zr2–H1 2.24(5), Zr2–H2 1.79(6), O–C1 1.419(5), C1–C31 1.502(6), C1–C41 1.502(6); Zr1–O–Zr2 109.2(1), Zr1–O–C1 79.7(1), Zr1–H1–Zr2 112(2), Zr2–O–C1 171.0(3), C1–Zr1–O 36.8(1), Zr1–C1–O 63.5(2), Zr1–C1–C31 124.1(3), Zr1–C1–C41 122.8(3), O–C1–C31 112.4(4), O–C1–C41 112.1(4), C31–C1–C41 110.4(4).

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[17] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

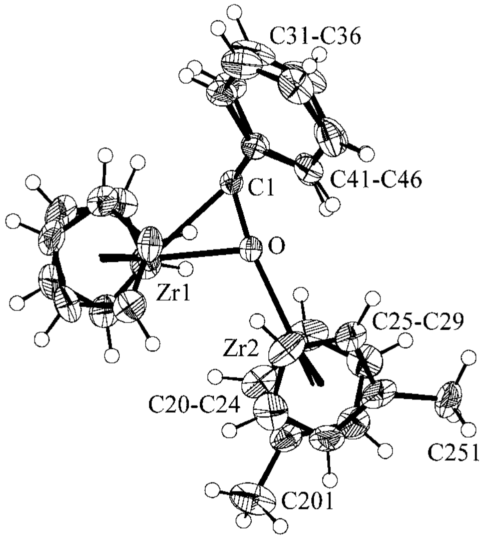

Figure 2. View of the framework of the molecular structure of complex **18c** (the two hydride ligands were not located). Selected bond lengths (Å) and angles (deg): Zr1−O 2.110(6), Zr2−O 2.150(7), Zr1−C1 2.320(10), O−C1 1.426(12), C1−C31 1.512(14), C1−C41 1.514(14); Zr1−O−Zr2 109.7(3), Zr1−O−C1 79.5(5), Zr2−O−C1 170.8(6), C1−Zr1−O 37.2(3), Zr1−C1−O 63.4(4), Zr1−C1−C31 125.0(7), Zr1−C1−C41 122.7(6), O−C1−C31 112.5(8), O−C1−C41 111.4(8), C31−C1−C41 110.0(8).

will not be discussed. The [$Cp_2Zr(\eta^2$-di-*p*-tolyl ketone)/Cp_2ZrH_2] adduct **18b** shows very similar bonding features (see Table 2). Details are, therefore, provided only with the Experimental Section and the Supporting Information.

Dimetallic complexes that contain (μ-η^1-O:η^2-C,O-$R^1R^2CO)[ZrCp_2]_2$-type frameworks can in principle undergo a degenerate rearrangement[18,19] that can be described as a dyotropic rearrangement. Using suitable molecular markers, we were able to show that for the (diaryl ketone)$ZrCp_2$-derived systems this reorganization process is so slow that under the applied reaction conditions and the temperatures at which the spectroscopic analyses were carried out it does not complicate the [$Cp_2Zr(Ar_2CO)/{}^RCp_2MH_2$] chemistry. In all cases investigated, adducts were obtained that exhibited regioisomeric orientations corresponding to the substituent (or metal) patterns directly as introduced in the reaction.

Thus, treatment of the (η^2-benzophenone)$ZrCp_2$ dimer (**17a**) with $[(MeCp)_2ZrH_2]_2$[5] gave rise to the clean formation of a single regioisomeric adduct [$Cp_2Zr(Ph_2CO)/(MeCp)_2ZrH_2$], **18c**. The X-ray crystal structure analysis showed that the methyl-Cp-substituted bent metallocene unit occupies the "southeast" corner of the dimetallic framework. The parent Cp_2Zr unit is part of the metallacyclic three-membered ring system (see Figure 2). The spectroscopic features of **18c** and its [(di-*p*-tolyl ketone)zirconocene/$(MeCp)_2ZrH_2$] analogue **18d** are very similar to those of the parent complexes **18a** and **18b** (see Table 1).

(η^2-Benzophenone)zirconocene dimer (**17a**) also reacts cleanly with $[Cp_2HfH_2]_n$ to give a single regioisomeric product (**18e**), isolated in ca. 70% yield. The ^1H NMR chemical shifts of the hydride ligands in the "mixed" Zr,-Hf-containing adduct are characteristically different from those of the respective Zr,Zr-containing addition products **18a**−**d** (**18e**, μ-H resonance at δ −0.81, M−H signal at δ 8.19; **18a**, −1.44, 5.04). This indicates that the hafnium center in **18e** is bonded to both hydride ligands. Their arrangement at Hf is trans ($^2J_{HH} = 7.8$ Hz). The [$Cp_2Zr(Ph_2CO)/Cp_2HfH_2$] adduct **18f** shows similar features (see Table 1).

All the complexes **18a**−**f** exhibit dynamic NMR spectra. This is due to a structurally located dynamic behavior that only affects the ortho- and meta-C−H resonances of the metallaoxirane aryl substituents. For example, the 600 MHz ^1H NMR spectrum of **18a** shows three phenyl multiplets at δ 6.83 (para-H), 7.15 (2 meta-hydrogens), and 7.60 (2 ortho-H atoms) in THF-d_8 at 298 K. Lowering the monitoring temperature rapidly leads to selective line broadening of only the latter two resonances (all other ^1H NMR signals of **18a** remain sharp within the examined temperature range). Eventually splitting of the meta- and ortho-phenyl resonances into four separate signals is observed (^1H NMR Ph resonances of **18a** at 213K: δ 7.73, 7.52, 7.21, 7.16, and 6.85 ppm). This selective dynamic behavior is due to freezing of the metallaoxirane C1-aryl rotation on the NMR time scale. For the coalescence temperature a Gibbs activation energy of $\Delta G^\ddagger$ (258 K) $\approx 11.8 \pm 0.3$ kcal mol^{-1} was determined from the dynamic ^1H NMR spectra of **18a** for this conformational equilibration process. Very similar activation energies around ca. 11.5 kcal mol^{-1} have been obtained for the metallaoxirane C1-aryl rotation of the other members (**18b**−**f**) of this series of complexes (see Table 1).

Template-Supported (Hydrido)metallocene Cations. The organometallic Lewis acid tris(pentafluorophenyl)borane[20] was employed as the reagent to convert the dihydridometallocene complexes **18** into the respective monohydridometallocene cations.[21] In a first (and representative) experiment the [$Cp_2Zr(Ph_2CO)/Cp_2ZrH_2$] adduct **18a** was treated with an equimolar amount of $B(C_6F_5)_3$ at ambient temperature in bromobenzene. Within minutes the educts were consumed with formation of a dark violet colored solution. Diffusion of pentane vapor into this solution resulted in the precipitation of the organometallic salt **19a** as very dark brown-black colored crystals (isolated in 85% yield) that were suited for a X-ray crystal structure analysis.

The structural analysis shows that $B(C_6F_5)_3$ has abstracted one of the hydride ligands from **18a** to form a dimetallic cation [$Cp_2Zr(Ph_2CO)/Cp_2ZrH^+$] and an independent [$HB(C_6F_5)_3^-$] anion. The overall framework of the cation of **19a** is similar to that of the neutral starting material **18a**, although several structural details are noticeably different. However, the overall dimetallabicyclic structure of the system has been retained. We observe the presence of a metallaoxirane

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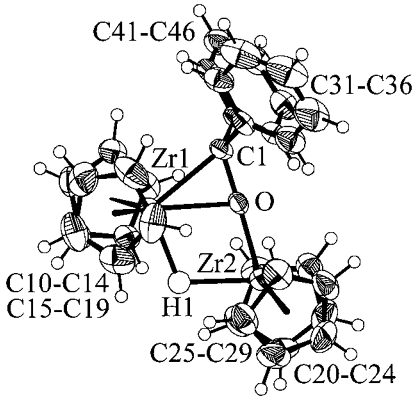
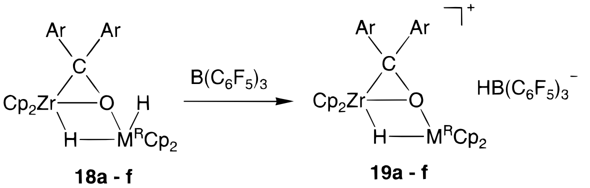


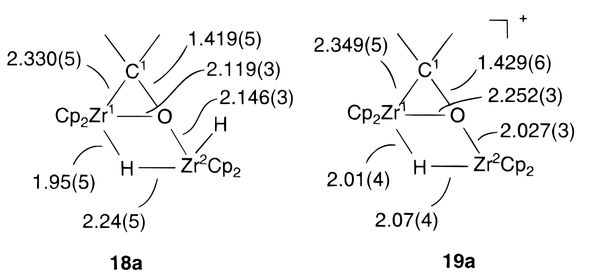
Figure 3. Molecular structure of **19a** (only the cation is depicted) with selected bond lengths (Å) and angles (deg) of the two independent molecules found in the crystal. Zr1a−O1a 2.254(3), Zr1b−O1b 2.250(3), Zr2a−O1a 2.025(3), Zr2b−O1b 2.028(3), Zr1a−C1a 2.356(5), Zr1b−C1b 2.341(5), Zr1a−H1a 2.02(4), Zr1b−H1b 2.00(4), Zr2a−H1a 2.07(4), Zr2b−H1b 2.07(4), O1a−C1a 1.429(6), O1b−C1b 1.429(5), C1a−C31a 1.516(7), C1b−C31b 1.498(7), C1a−C41a 1.506(7), C1b−C41b 1.517(6), Zr1a−O1a−Zr2a 102.4(1), Zr1b−O1b−Zr2b 103.3(1), Zr1a−O1a−C1a 75.9(2), Zr1b−O1b−C1b 75.4(2), Zr1a−H1a−Zr2a 110(2), Zr1b−H1b−Zr2b 111(2), Zr2a−O1a−C1a 178.2(3), Zr2b−O1b−C1b 178.2(3), C1a−Zr1a−O1a 36.0(1), C1b−Zr1b−O1b 36.2(1), Zr1a−C1a−O1a 68.1(2), Zr1b−C1b−O1b 68.4(2), Zr1a−C1a−C31a 124.0(3), Zr1b−C1b−C31b 121.3(3), Zr1a−C1a−C41a 121.4(3), Zr1b−C1b−C41b 126.2(3), O1a−C1a−C31a 112.3(4), O1b−C1b−C31b 112.3(4), O1a−C1a−C41a 112.0(4), O1b−C1b−C41b 112.1(4), C31a−C1a−C41a 110.2(4), C31b−C1b−C41b 108.3(4).

Scheme 3[a]



[a] See Table 1 for substituent and metal combinations used.

Scheme 4[a]



[a] Bond lengths in Å.

ring, whose Zr1−C1 (2.349(5) Å) and C1−O (1.429(6) Å) bond lengths are very similar to the values typically observed for the precursors **18**. To this template the remaining Cp_2Zr-H^+ unit is coordinated in **19a** in such a way that the metallaoxirane template oxygen binds strongly to Zr2 and the remaining single hydride ligand is found bridging between the two zirconium atoms.

A close inspection of the bond lengths and angles of the central planar framework of **19a** and a comparison with **18a** (see Table 2 and Scheme 4) reveal a variety of systematic differences in structural detail between these two classes of compounds. The bonding of the template oxygen in **19a** is markedly stronger than in **18a**. This is as expected since Zr2 in the monocation is much more electron deficient and needs stabilizing electron density from the electron-rich template heteroatom. This has resulted in making the Zr2−O bond considerably shorter (**19a**, 2.027(3) Å; **18a**, 2.146(3) Å). The C1−O−Zr2 angle increases (178.2(3)°) and the Zr1−O−Zr2 angle becomes smaller (102.9(1)°) in **19a**. The altered electron distribution in the **19a** framework shows up in the position of the bridging hydride ligand and brings the μ-H atom closer to Zr2 (see Scheme 4). The electron attraction of the $[Zr2]^+$ center in **19a** even shows up in the Zr1−O bond length, which is increased to 2.252(3) Å in **19a** relative to **18a** (Zr1−O: 2.119(3) Å).

Thus it appears that the metallaoxirane subunits in **18a** and **19a** are not just mere sterically favored templates but serve as electronically active components in stabilizing the added metal hydride component. The crystallographic data demonstrate that the molecular and electronic structure of the (η^2-diaryl ketone)$ZrCp_2$ moiety responds to the increased electron deficiency of the cationic metallocene hydride fragment. The metallaoxirane seems to act as a structurally active bifunctional template, which will probably make it a very useful tool for stabilizing a large variety of other reactive reagents in the future.

As expected, the (η^2-di-*p*-tolyl ketone)zirconocene template behaves the same way. Treatment of **18b** with an equimolar quantity of $B(C_6F_5)_3$ gives rise to the formation of the respective monohydrido zirconocene cation adduct **19b**. Its X-ray crystal structure analysis has revealed quite analogous structural properties (see Table 2). An illustrative projection of the cation of **19b** is given in Figure 4.

The formation of the dimetallic (μ-hydrido)(μ-η^1-O:η^2-C,O-benzophenone)bis(zirconocene) cation complex **19a** by treatment of **18a** with $B(C_6F_5)_3$ is also evident from the spectroscopic features of the product. A new pair of ^1H NMR Cp singlets of **19a**, each representing 10 hydrogen atoms, is observed at δ 6.29 and 5.64 ppm (in bromobenzene-d_5). The μ-H signal appears at δ −1.87 ppm, and the ^{13}C NMR resonance of the quaternary metallaoxirane carbon atom (C1) is found at δ 89.6 ppm. The $HB(C_6F_5)_3^-$ anion formation is evident from the occurrence of a broad ^1H NMR resonance at δ 4.3 ppm representing the single hydrogen atom, which is complemented by a ^{11}B NMR doublet at δ −24.9 ppm with a typical $^1J_{BH}$ coupling constant of 85 Hz. Complex **19b** exhibits similar spectroscopic features.

Treatment of the "mixed" metallocene complexes **18c** and **18d** with $B(C_6F_5)_3$ proceeds analogously to yield the respective mono(hydrido)bis(metallocene) cations **19c** and **19d**, respectively. The introduction of the $(MeCp)_2Zr$ unit in the southeast corner of the framework in both the starting material (i.e., **18c**,**d**) and the product (**19c**,**d**) is structurally diagnostic in several ways.

In each case a single cationic reaction product is obtained. This indicates that the hydride abstraction takes place at the intact dimetallic starting material and takes a strictly intramolecular course, within the limits of the NMR analysis. Also, the symmetry label at the $(MeCp_2)Zr$ unit allows us to determine spectroscopically by means of symmetry arguments (i.e., independent of

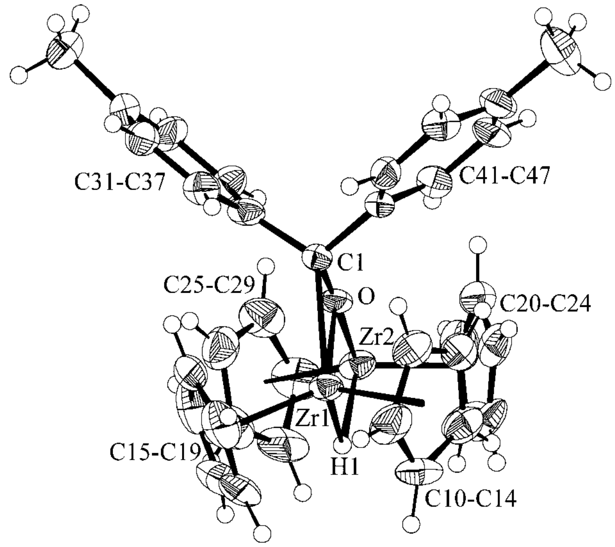


Figure 4. Projection of **19b** (cation only). Selected bond lengths (Å) and angles (deg) of the two independent molecules: Zr1a−O1a 2.252(5), Zr1b−O1b 2.257(5), Zr2a−O1a 2.018(5), Zr2b−O1b 2.024(5), Zr1a−C1a 2.352(7), Zr1b−C1b 2.345(8), Zr1a−H1a 2.21(6), Zr1b−H1b 2.18(5), Zr2a−H1a 1.96(6), Zr2b−H1b 1.98(5), O1a−C1a 1.448(8), O1b−C1b 1.417(9), C1a−C31a 1.503(10), C1b−C31b 1.535(11), C1a−C41a 1.502(10), C1b−C41b 1.493(11); Zr1a−O1a−Zr2a 102.9(2), Zr1b−O1b−Zr2b 103.5(2), Zr1a−O1a−C1a 75.5(4), Zr1b−O1b−C1b 75.5(4), Zr1a−H1a−Zr2a 106(2), Zr1b−H1b−Zr2b 108(2), Zr2a−O1a−C1a 177.0(4), Zr2b−O1b−C1b 177.1(5), C1a−Zr1a−O1a 36.6(2), C1b−Zr1b−O1b 35.8(2), Zr1a−C1a−O1a 68.0(3), Zr1b−C1b−O1b 68.7(3), Zr1a−C1a−C31a 127.4(5), Zr1b−C1b−C31b 120.1(5), Zr1a−C1a−C41a 120.6(5), Zr1b−C1b−C41b 127.3(6), O1a−C1a−C31a 111.1(6), O1b−C1b−C31b 110.7(7), O1a−C1a−C41a 111.9(6), O1b−C1b−C41b 113.0(7), C31a−C1a−C41a 108.5(6), C31b−C1b−C41b 108.5(6).

chemical shift interpretations) that the southeast zirconium center contains two inequivalent ligands bonded to it in the σ-ligand plane; here these are the bridging metallaoxirane oxygen atom and the bridging hydrogen ligand. This follows clearly from, for example, the observation of four equal intensity MeCp methine ^{1}H NMR resonances of the cation complex **19c** at δ 6.40, 6.33, 6.26, and 5.82 (corresponding ^{13}C NMR signals at δ 119.5, 118.0, 116.3, 115.6 ppm) in bromobenzene-d_5. Also the frameworks of the complexes **19c** and **19d** do not undergo any rapid skeletal rearrangement under the applied conditions; the $(MeCp)_2Zr$ group stays in its specific position during and after the hydride transfer process.

This is also true for the hydride abstraction products derived from the mixed metal complex adducts **18e** and **18f** of the compositions $[Cp_2Zr(Ar_2CO)/Cp_2HfH_2]$ (Ar = Ph or *p*-tolyl). In each case the H$^-$ abstraction with $B(C_6F_5)_3$ leads to the formation of a single cation product, **19e** and **19f**, respectively. The characteristic chemical shift of the μ-hydride NMR resonance (see Table 1) indicates its bonding to both zirconium and hafnium. Complex **19e** was, in addition, characterized by an X-ray crystal structure analysis. It shows a framework analogous to that previously found for its cation complex relatives **19a** and **19b**. Therefore, the reader is referred to a respective plot of the structure in the Supporting Information. A set of selected typical structural parameters of complex **19e** is listed in Table 2 for comparison.

The cationic complexes **19** also exhibit temperature-dependent dynamic NMR spectra that arise from a hindered rotation of the metallaoxirane aryl substituents. In all these dinuclear metallocene cations **19** the rotational barriers are by ca. 1.5 kcal mol^{-1} lower as compared to their neutral precursors **18** (e.g., $\Delta G^{\ddagger}_{rot}$(**18a**), 11.8 kcal mol^{-1}; $\Delta G^{\ddagger}_{rot}$(**19a**), 9.9 kcal mol^{-1}). This probably indicates a sterically more encumbered situation around the aryl substituents in the neutral metal dihydrides **18** than in the cationic complexes **19**. Thus, some relief of steric strain of the framework and around the four Cp groups and two aryl substituents arranged normal to it (see Figure 4) might have assisted in the clean and favorable formation of the cationic monohydride bis(metallocene) complexes **19** from **18** by treatment with $B(C_6F_5)_3$.

We carried out a few scouting ethene polymerization reactions using the cationic monohydride bis(metallocene) complexes **19c**−**f** as catalysts. The reactions (for details see the Experimental Section) were performed in a toluene suspension in the presence of triisobutylaluminum as a moisture scavenger. Under these conditions the systems **19** exhibited high ethene polymerization activities, although control experiments have shown that the catalyst performance and the actual polymerization activity values were somewhat dependent on the specific reaction conditions chosen. Typically, polyethylene was formed at the complexes **19** with maximum activities of ca. 4000−7000 g/mmol **19**·bar·h).

Our study has shown that group 4 metallaoxiranes can serve as structurally and electronically flexible organometallic templates for binding and stabilizing very reactive group 4 metallocene hydrido cation entities. The resulting template-supported $[^RCp_2M-H]^+$ species show a high ethene polymerization activity, as might be expected from them. Of course, we do not know so far whether the template-supported dimetallic system as such exhibits an intrinsic ethene activating property or if dissociation of an active Cp_2M-H^+ monomer is causing the observed catalytic activity. Also we do not know at present if the three-membered $Cp_2Zr(OCAr_2)$ unit remains unchanged in the course of the polymerization process, and thereby might have the potential to interact with subsequently formed reactive intermediates of the polymerization process, or whether the metallaoxirane is itself consumed by, for example, ethene insertion. The development of a simple synthetic route to the dimetallic hydrido group 4 metallocene cations **19** should open up experimentally viable pathways toward answering such questions and learning more about ways to initiate and moderate homogeneously catalyzed polymerization processes at reactive organometallic catalyst systems by selectively employing structurally and electronically active bifunctional organometallic template systems such as the metallaoxiranes used in this study. Such experimental work is in progress in our laboratory.

Experimental Section

All reactions involving organometallic reagents or substrates were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC 200, Bruker ARX 300, and Varian Unity Plus 600 NMR spectrometers; Nicolet 5 DXC FT-IR spectrometer; DSC 2010 (TA Instruments). Elemental analyses: Foss-Heraeus CHN-O-Rapid. X-ray crystal structure analyses: All data sets were collected with an Enraf Nonius CAD4 or MACH3 diffractometer, equipped with sealed tube or rotating anode generators. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics DIAMOND and SCHAKAL-92. Tris(pentafluorophenyl)borane,[20] diphenylzirconocene, **15a**, di-*p*-tolylzirconocene,[22] **15b**, $[Cp_2ZrH_2]_n$,[13a] $[(MeCp)_2ZrH_2]_2$,[5a] and $[Cp_2HfH_2]_n$[5c] were prepared according to literature procedures. The barriers for aryl group rotation ($\Delta G^{\ddagger}_{rot}$) were determined from the temperature-dependent NMR spectra using the Gutowsky-Holm approximation.[23]

Preparation of (η^2-Benzophenone)zirconocene, 17a. In a modified literature procedure,[15,24] a solution of diphenylzirconocene **15a** (9.50 g, 25.3 mmol) in 100 mL of dichloromethane was stirred for 2 h at room temperature under an atmosphere of carbon monoxide, during which 540 mL (24.1 mmol) of carbon monoxide was consumed. After removing the solvent in vacuo and washing with 30 mL of pentane the orange-yellow powder **16a** was briefly dried in vacuo. The solid was then suspended in heptane (250 mL) and stirred for 5 h at 70 °C. The yellow precipitate was isolated by filtration, washed twice with pentane (150 mL), and dried in vacuo. Complex **17a** was used without any further purification. Yield: 8.9 g (87%).

Preparation of (η^2-*p*-Tolyl ketone)zirconocene, 17b. In a modified literature procedure[15,24] a solution of di-*p*-tolylzirconocene, **15b** (8.00 g, 19.8 mmol), in 100 mL of dichloromethane was exposed to carbon monoxide with rapid stirring for 2 h at room temperature (CO-uptake: 401 mL, 17.9 mmol). After removing the solvent in vacuo and washing with 30 mL of pentane the orange-yellow powder of **16b** was briefly dried in vacuo. The solid was then suspended in heptane (200 mL) and stirred for 5 h at 70 °C. The yellow precipitate was isolated by filtration, washed twice with pentane (50 mL), and dried in vacuo. **17b** was used without any further purification. Yield: 7.1 g (83%).

Preparation of μ-(η^1-O:η^2-C,O-Benzophenone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium], 18a. According to a literature procedure,[15] 4.70 g (11.7 mmol) of dimeric (η^2-benzophenone)zirconocene (**17a**) and 2.60 g (11.6 mmol) of dihydridozirconocene were weighed together in a Schlenk tube. After adding 150 mL of benzene, the resulting suspension was stirred for 48 h at room temperature. After isolating by filtration, the ivory-colored precipitate was dried in vacuo. The product contains 0.5 equiv of benzene. Yield: 6.5 g (89%). IR (KBr): 1488, 1312 cm^{-1} ($\tilde{\nu}_{M-H}$, this assignment was controlled by a deuterium substitution experiment using Cp_2ZrD_2 as a starting material). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 7.60 (psd, 4H, 2′-H), 7.15 (pst, 4H, 3′-H), 6.83 (pst, 2H, 4′-H), 5.95, 5.41 (each s, each 10H, Cp), 5.04 (d, $^2J_{HH}$ = 7.4 Hz, 1H, Zr−H$_{term.}$), −1.44 (d, $^2J_{HH}$ = 7.4 Hz, 1H, μ-H) ppm. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 213 K): δ 7.73 (psd, 2H, 2′-H), 7.52 (psd, 2H, 2″-H), 7.21 (pst, 2H, 3′-H), 7.16 (pst, 2H, 3″-H), 6.85 (pst, 2H, 4′-H), 5.99, 5.43 (each s, each 10H, Cp), 4.92 (d, $^2J_{HH}$ = 7.4 Hz, 1H, Zr−H$_{term.}$), −1.56 (d, $^2J_{HH}$ = 7.4 Hz, 1H, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 154.6 (C1′), 127.6 (C3′), 127.0 (br, C2′), 123.4 (C4′), 107.1 (Cp), 105.8 (Cp) ppm, C1 resonance not observed. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 213 K): δ 154.7 (C1′), 128.9 (C2′), 128.0 (C3′), 127.6 (C3″), 124.1 (C2″), 123.3 (C4′), 107.2 (Cp), 106.0 (Cp), 83.6 (C1) ppm. $\Delta G^{\ddagger}$ for phenyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C = 258 K), 11.8 ± 0.3 kcal/mol ($\Delta\nu$ = 127 Hz); from 3′-H coalescence (T_C = 243 K), 11.8 ± 0.3 kcal/mol ($\Delta\nu$ = 29.4 Hz).

X-ray Crystal Structure Analysis of 18a. Single crystals were obtained from a saturated solution of **18a** in 2 mL of tetrahydrofuran, after standing for 2 days at room temperature: formula $C_{33}H_{32}OZr_2\cdot C_4H_8O$, M = 699.13, 0.4 × 0.2 × 0.1 mm, a = 15.341(2) Å, b = 9.054(2) Å, c = 22.060(4) Å, β = 91.45(1)°, V = 3063.1(10) Å^3, ρ_{calc} = 1.516 g cm^{-3}, μ = 7.12 cm^{-1}, empirical absorption correction via ψ scan data (0.962 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 173 K, $\omega/2\theta$ scans, 6362 reflections collected (±h, +k, +l), [(sin θ)/λ] = 0.62 Å^{-1}, 6190 independent and 4577 observed reflections [$I \geq 2\,\sigma(I)$], 405 refined parameters, R = 0.048, wR^2 = 0.114, max. residual electron density 1.37 (−0.69) e Å^{-3} close to the disordered solvent molecule (THF), hydrido hydrogens from difference Fourier, others calculated and all refined riding.

Preparation of μ-(η^1-O:η^2-C,O-Di-*p*-tolyl ketone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium], 18b. A 4.00 g (4.63 mmol) sample of dimeric (η^2-di-*p*-tolyl ketone)zirconocene (**17b**) and 2.07 g (9.26 mmol) of dihydridozirconocene were weighed together in a Schlenk tube. After adding 150 mL of toluene the slurry was stirred for 48 h at room temperature. After isolating by filtration, the ivory-colored precipitate was dried in vacuo. The product contains 0.5 equiv of toluene. Yield: 5.38 g (83%). Mp: 180 °C (decomp) (DSC). Anal. Calcd for $C_{35}H_{36}OZr_2\cdot 0.5C_7H_8$ (701.2): C, 65.95; H, 5.75. Found: C, 66.48; H, 5.93. IR (KBr): 1504; 1308 cm^{-1} ($\tilde{\nu}_{M-H}$). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 7.46 (psd, 4H, 2′-H), 6.96 (psd, 4H, 3′-H), 5.93, 5.40 (each s, each 10H, Cp), 5.01 (d, $^2J_{HH}$ = 7.4 Hz, 1H, Zr−H$_{term.}$), 2.19 (s, 6H, 4′-Me), −1.46 (d, $^2J_{HH}$ = 7.4 Hz, 1H, μ-H) ppm. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 193 K): δ = 7.58 (psd, 2H, 2′-H), 7.40 (psd, 2H, 2″-H), 7.02 (psd, 2H, 3′-H), 6.97 (psd, 2H, 3″-H), 5.99, 5.43 (each s, each 10H, Cp), 4.85 (d, $^2J_{HH}$ = 7.4 Hz, 1H, Zr−H$_{term.}$), 2.20 (s, 6H, 4′-Me), −1.61 (d, $^2J_{HH}$ = 7.4 Hz, 1H, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 152.0 (C1′), 132.4 (C4′), 128.3 (C3′), 126.6 (br, C2′), 107.1 (Cp), 105.9 (Cp), 84.1 (C1), 21.0 (4′-Me) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 193 K): δ 152.1 (C1′), 132.0 (C4′), 128.8 (C2′), 128.7 (C3′), 128.1 (C3″), 124.0 (C2″), 107.2 (Cp), 105.9 (Cp), 83.3 (C1), 21.2 (4′-Me) ppm. $\Delta G^{\ddagger}$ for *p*-tolyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C = 248 K), 11.4 ± 0.3 kcal/mol ($\Delta\nu$ = 107 Hz); from 3′-H coalescence (T_C = 233 K), 11.3 ± 0.3 kcal/mol ($\Delta\nu$ = 28.7 Hz).

X-ray Crystal Structure Analysis of 18b. Single crystals were obtained from a saturated solution of **18b** in 2 mL of tetrahydrofuran, after standing for 2 days at room temperature: formula $C_{35}H_{36}OZr_2\cdot 3C_4H_8O$, M = 871.39, 0.3 × 0.1 × 0.1 mm, a = 13.016(1) Å, b = 18.764(4) Å, c = 17.676(3) Å, β = 105.26(1)°, V = 4164.8(12) Å^3, ρ_{calc} = 1.390 g cm^{-3}, μ = 5.42 cm^{-1}, empirical absorption correction via ψ scan data (0.911 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1$/c (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 7682 reflections collected (+h, +k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 7338 independent and 3223 observed reflections [$I \geq 2\,\sigma(I)$], 486 refined parameters, R = 0.056, wR^2 = 0.119, max. residual electron density 0.59 (−0.54) e Å^{-3}, hydrido hydrogens from difference Fourier, others calculated and all refined riding.

Preparation of μ-(η^1-O:η^2-C,O-Benzophenone)-μ-hydrido-[bis(η^5-methylcyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium], 18c. A 1.50 g (3.72 mmol) sample of dimeric (η^2-benzophenone)zirconocene (**17a**) and 0.93 g (3.72 mmol) of dimeric bis(η^5-methylcyclopentadienyl)dihydridozirconium were weighed together in a Schlenk tube, 30

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(24) Kropp, K. Doctoral Dissertation, Ruhr-Universität Bochum, 1981.

mL of toluene was added, and the resulting yellow suspension was stirred at room temperature. After 24 h a clear, slightly red solution was obtained. The solvent was evaporated in vacuo, and the resulting oil formed a powder suspension after stirring in 10 mL of pentane. The solid was isolated by filtration, washed with 5 mL of pentane, 10 mL of a 10:1 mixture of pentane/toluene, and finally again with 5 mL of pentane, and dried in vacuo. Yield: 1.9 g (76%). Mp 146 °C (decomp) (DSC). Anal. Calcd for $C_{35}H_{36}OZr_2$ (655.1): C, 64.17; H, 5.54. Found: C, 63.78; H, 5.62. IR (KBr): 1322 cm^{-1} (second $\tilde{\nu}_{M-H}$ band not located). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 7.62 (psd, 4H, 2′-H), 7.15 (pst, 4H, 3′-H), 6.83 (pst, 2H, 4′-H), 5.93, 5.67, 5.62, 5.53 (each m, each 2H, $C_5H_4CH_3$), 5.40 (s, 10H, Cp), 2.50 (s, 6H, Cp*Me*), −1.36 (d, 1H, $^2J_{HH}$ = 6.9 Hz, μ-H) ppm, resonance of the terminal Zr-hydride at δ 5.38 ppm under Cp signal. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 203 K): δ 7.72 (psd, 2H, 2′-H), 7.57 (psd, 2H, 2″-H), 7.21 (pst, 2H, 3′-H), 7.16 (pst, 2H, 3″-H), 6.86 (pst, 2H, 4′-H), 5.94, 5.68, 5.67, 5.63 (each m, each 2H, $C_5H_4CH_3$), 5.43 (s, 10H, Cp), 5.38 (d, 1H, $^2J_{HH}$ = 6.9 Hz, Zr−$H_{term.}$), 2.49 (s, 6H, Cp*Me*), −1.52 (d, 1H, $^2J_{HH}$ = 6.9 Hz, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 153.8 (C1′), 126.6 (C3′), 125.7 (br, C2′), 122.5 (C4′), 121.3 (quart. (CpMe)), 108.6, 108.1, 107.1 ($C_4H_4CCH_3$), 106.2 (Cp), 101.2 ($C_4H_4CCH_3$), 83.4 (C1), 16.1 (Cp*Me*) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 203 K): δ = 154.9 (C1′), 128.9 (C2′), 128.0 (C3′), 127.5 (C3″), 124.3 (C2″), 123.4 (C4′), 121.9 (quart. (CpMe)), 109.4, 109.1, 108.7 ($C_4H_4CCH_3$), 107.3 (Cp), 101.5 ($C_4H_4CCH_3$), 17.3 (Cp*Me*) ppm, resonance of C1 not found. $\Delta G^{\ddagger}$ for phenyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C 238 K), 11.0 ± 0.3 kcal/mol ($\Delta\nu$ = 88.9 Hz); from 3′-H coalescence (T_C 228 K), 11.0 ± 0.3 kcal/mol ($\Delta\nu$ = 27.9 Hz).

X-ray Crystal Structure Analysis of 18c. Single crystals were obtained from a suspension of **18c** in 5 mL of toluene after standing for two weeks at 4 °C: formula $C_{35}H_{36}OZr_2$, M = 655.08, 0.5 × 0.2 × 0.05 mm, a = 10.253(2) Å, b = 16.307(2) Å, c = 17.245(4) Å, V = 2883.3(9) Å^3, ρ_{calc} = 1.509 g cm^{-3}, μ = 7.49 cm^{-1}, empirical absorption correction via ψ scan data (0.902 ≤ C ≤ 0.999), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 3285 reflections collected (+h, -k, -l), [(sin θ)/λ] = 0.62 Å^{-1}, 3285 independent and 2459 observed reflections [$I \geq 2\ \sigma(I)$], 345 refined parameters, R = 0.052, wR^2 = 0.136, max. residual electron density 0.85 (−0.78) e Å^{-3}, Flack parameter 0.1(1), hydrido hydrogens not located, others calculated and refined riding.

Preparation of μ-(η¹-O:η²-C,O-Di-*p*-tolyl ketone)-μ-hydrido-[bis(η⁵-methylcyclopentadienyl)hydridozirconium]-[bis(η⁵-cyclopentadienyl)zirconium], 18d. A 1.00 g (2.32 mmol) sample of dimeric (η²-*p*-tolyl ketone)zirconocene (**17b**) and 583 mg (2.32 mmol) of dimeric bis(η⁵-methylcyclopentadienyl)hydridozirconium were mixed in a Schlenk tube. After addition of 30 mL of toluene, the resulting suspension was stirred for 24 h at room temperature. A clear, slightly reddish solution was obtained. The solvent was removed in vacuo and the oily residue solidified by stirring it with 10 mL of pentane. The ivory-colored solid was isolated by filtration, washed with 5 mL of pentane, 10 mL of a 10:1 mixture of pentane/toluene and finally again with 5 mL of pentane, and dried in vacuo. Yield: 1.2 g (73%). Mp: 150 °C (decomp) (DSC). Anal. Calcd for $C_{37}H_{40}OZr_2$ (683.2): C, 65.05; H, 5.90. Found: C, 64.58; H, 5.94. IR (KBr): 1314 cm^{-1} (second $\tilde{\nu}_{M-H}$ band not located). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 7.48 (psd, 4H, 2′-H), 6.96 (psd, 4H, 3′-H), 5.92, 5.65, 5.58, 5.52 (each m, each 2H, $C_5H_4CH_3$), 5.39 (s, 10H, Cp), 5.34 (d, 1H, $^2J_{HH}$ = 7.0 Hz, Zr−$H_{term.}$) 2.50 (s, 6H, Cp*Me*), 2.19 (s, 3H, 4′-Me), −1.38 (d, 1H, $^2J_{HH}$ = 6.9 Hz, μ-H) ppm. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 203 K): δ 7.56 (psd, 2H, 2′-H), 7.46 (psd, 2H, 2″-H), 7.01 (psd, 2H, 3′-H), 6.97 (psd, 2H, 3″-H), 5.97, 5.63, 5.62, 5.60 (each m, each 2H, $C_5H_4CH_3$), 5.42 (s, 10H, Cp), 5.18 (d, 1H, $^2J_{HH}$ = 6.9 Hz, Zr−$H_{term.}$), 2.49 (s, 6H, Cp*Me*), 2.20 (s, 6H, 4′-Me), −1.54 (d, 1H, $^2J_{HH}$ = 6.9 Hz, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 151.2 (C1′), 131.3 (C4′), 127.2 (C3′), 125.6 (br, C2′), 121.3 (quart. (CpMe)), 108.5, 108.0, 107.1 ($C_4H_4CCH_3$), 106.1 (Cp), 101.1 ($C_4H_4CCH_3$), 83.3 (C1), 20.0 (4′-Me), 16.1 (Cp*Me*) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 203 K): δ 152.3 (C1′), 132.1 (C4′), 128.8 (C2′), 128.7 (C3′), 128.0 (C3″), 124.1 (C2″), 122.0 (quart. (CpMe)), 109.2, 108.9, 108.8 ($C_4H_4CCH_3$), 107.1 (Cp), 101.4 ($C_4H_4CCH_3$), 83.5 (C1), 21.2 (4′-Me), 17.4 (Cp*Me*) ppm. $\Delta G^{\ddagger}$ for *p*-tolyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C = 238 K), 11.2 ± 0.3 kcal/mol ($\Delta\nu$ = 61.3 Hz); from 3′-H coalescence (T_C = 228 K), 11.1 ± 0.3 kcal/mol ($\Delta\nu$ = 24.4 Hz).

Preparation of μ-(η¹-O:η²-C,O-Benzophenone)-μ-hydrido-[bis(η⁵-cyclopentadienyl)hydridohafnium][bis(η⁵-cyclopentadienyl)zirconium], 18e. According to a literature procedure,[15] 1.25 g (3.10 mmol) of dimeric (η²-benzophenone)-zirconocene (**17a**) was weighed together with 0.95 g (3.10 mmol) of dihydridohafnocene in a Schlenk tube. A 30 mL portion of benzene was added and the resulting suspension stirred for 24 h at room temperature. The suspension was filtered, and the ivory-colored precipitate was washed twice with 10 mL of benzene and dried in vacuo. **18e** still contains 0.5 equiv of benzene. Yield: 1.5 g (68%). IR (KBr): 1538, 1319 cm^{-1} ($\tilde{\nu}_{M-H}$). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 8.19 (d, 1H, $^2J_{HH}$ = 7.8 Hz, Hf−$H_{term.}$), 7.63 (psd, 4H, 2′-H), 7.15 (pst, 4H, 3′-H), 6.83 (pst, 2H, 4′-H), 5.89, 5.43 (each s, each 10H, Cp), −0.81 (d, $^2J_{HH}$ = 7.8 Hz, 1H, μ-H) ppm. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 213 K): δ 7.97 (d, $^2J_{HH}$ = 7.4 Hz, 1H, Hf−$H_{term.}$), 7.72 (psd, 2H, 2′-H), 7.58 (psd, 2H, 2″-H), 7.20 (pst, 2H, 3′-H), 7.17 (pst, 2H, 3″-H), 6.85 (pst, 2H, 4′-H), 5.94, 5.46 (each s, each 10H, Cp), −0.95 (d, $^2J_{HH}$ = 7.4 Hz, 1H, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 154.5 (C1′), 127.7 (C3′), 126.7 (br, C2′), 123.6 (C4′), 107.5 (Cp), 105.1 (Cp), 82.8 (C1) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 213 K): δ 154.5 (C1′), 128.9 (C2′), 128.0 (C3′), 127.6 (C3″), 124.2 (C2″), 123.4 (C4′), 107.5 (Cp), 105.1 (Cp), 82.1 (C1) ppm. $\Delta G^{\ddagger}$ for phenyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C = 250 K), 11.6 ± 0.3 kcal/mol ($\Delta\nu$ = 83.1 Hz); from 3′-H coalescence (T_C = 238 K), 11.7 ± 0.3 kcal/mol ($\Delta\nu$ = 20.0 Hz).

Preparation of μ-(η¹-O:η²-C,O-Di-*p*-tolyl ketone)-μ-hydrido-[bis(η⁵-cyclopentadienyl)hydridohafnium][bis(η⁵-cyclopentadienyl)zirconium], 18f. A Schlenk tube was charged with 1.30 g (3.01 mmol) of dimeric (η²-di-*p*-tolyl ketone)zirconocene (**17b**) and 0.93 g (3.01 mmol) of dihydridohafnocene. A 30 mL portion of benzene was added and the suspension stirred for 24 h at room temperature. The ivory-colored precipitate was then isolated by filtration, washed twice with 10 mL of toluene, and dried in vacuo. **18f** contains 0.5 equiv of benzene. Yield: 1.7 g (73%). Mp: 178 °C (decomp) (DSC). Anal. Calcd for $C_{35}H_{36}HfOZr \cdot 0.5C_6H_6$ (781.4): C, 58.41; H, 5.03. Found: C, 58.20; H, 5.19. IR (KBr): 1553, 1314 cm^{-1} ($\tilde{\nu}_{M-H}$). ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 298 K): δ 8.13 (d, $^2J_{HH}$ = 7.7 Hz, 1H, Hf−$H_{term.}$), 7.49 (psd, 4H, 2′-H), 6.96 (psd, 4H, 3′-H), 5.87, 5.42 (each s, each 10H, Cp), 2.18 (s, 6H, 4′-Me), −0.84 (d, $^2J_{HH}$ = 7.7 Hz, 1H, μ-H) ppm. ^{1}H NMR (tetrahydrofuran-d_8, 599.9 MHz, 213 K): δ = 7.91 (d, $^2J_{HH}$ = 7.7 Hz, 1H, Hf−$H_{term.}$), 7.56 (psd, 2H, 2′-H), 7.46 (psd, 2H, 2″-H), 7.00 (psd, 2H, 3′-H), 6.97 (psd, 2H, 3″-H), 5.91, 5.45 (each s, each 10H, Cp), 2.19 (s, 6H, 4′-Me), −0.97 (d, $^2J_{HH}$ = 7.7 Hz, 1H, μ-H) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 298 K): δ 150.8 (C1′), 131.4 (C4′), 127.3 (C3′), 125.6 (br, C2′), 106.3 (Cp), 104.1 (Cp), 81.6 (C1), 20.0 (4′-Me) ppm. ^{13}C NMR (tetrahydrofuran-d_8, 150.8 MHz, 213 K): δ 151.8 (C1′), 132.2 (C4′), 128.8 (C2′), 128.6 (C3′), 128.1 (C3″), 124.1 (C2″), 107.4 (Cp), 105.1 (Cp), 81.9 (C1), 21.1 (4′-Me) ppm. $\Delta G^{\ddagger}$ for *p*-tolyl group rotation (in tetrahydrofuran-d_8): from 2′-H coalescence (T_C = 243 K), 11.5 ± 0.3 kcal/mol ($\Delta\nu$ = 58.6 Hz); from 3′-H coalescence (T_C = 233 K), 11.4 ± 0.3 kcal/mol ($\Delta\nu$ = 21.6 Hz).

Reaction of μ-(η^1-O:η^2-C,O-Benzophenone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] (18a) with Tris(pentafluorophenyl)borane: Formation of 19a. A 200 mg (0.30 mmol) sample of **18a** and 154 mg (0.30 mmol) of $B(C_6F_5)_3$ were mixed in a Schlenk tube. A 10 mL portion of bromobenzene was added at room temperature. Within 1 min the compounds had dissolved, forming a deep dark violet solution. Brown-black needles of **19a** were obtained within a day by allowing pentane to diffuse into this solution. The needles were isolated by decanting the solvent and were then dried in vacuo. Yield: 290 mg (85%). Mp: 155 °C (decomp) (DSC). Anal. Calcd for $C_{51}H_{32}BOF_{15}Zr_2$ (1139.0): C, 53.78; H, 2.83. Found: C, 53.49; H, 2.98. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 7.17 (pst, 4H, 3′-H), 6.97 (pst, 2H, 4′-H), 6.83 (psd, 4H, 2′-H), 6.29, 5.64 (each s, each 10H, Cp), 4.3 (br, 1H, B−*H*), −1.87 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 150.2 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 128.1 (C3′), 125.9 (C4′), 122.9 (br, C2′), 116.5, 110.5 (Cp), 89.6 (C1) ppm, resonance of *ipso*-$B(C_6F_5)_3$ not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH}$ = 85 Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^{\ddagger}$ for phenyl group rotation (in dichloromethane-d_2): from 2′-H coalescence (T_C = 228 K), 9.9 ± 0.3 kcal/mol ($\Delta\nu$ = 360 Hz); from 3′-H coalescence (T_C = 218 K), 10.2 ± 0.3 kcal/mol ($\Delta\nu$ = 67 Hz).

X-ray Crystal Structure Analysis of 19a. Single crystals of **19a** obtained in the preparative scale reaction were suitable for X-ray structure analysis: formula $C_{51}H_{32}BOF_{15}Zr_2$, M = 1139.02, 0.5 × 0.25 × 0.2 mm, a = 15.399(1) Å, b = 15.581(1) Å, c = 21.105(3) Å, α = 85.94(1)°, β = 79.91(1)°, γ = 64.45(1)°, V = 4497.9(8) Å^3, ρ_{calc} = 1.682 g cm^{-3}, μ = 5.65 cm^{-1}, empirical absorption correction via ψ scan data (0.982 ≤ C ≤ 0.999), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 233 K, $\omega/2\theta$ scans, 15837 reflections collected (-*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.59 Å^{-1}, 15202 independent and 8996 observed reflections [$I \geq 2\ \sigma(I)$], 1269 refined parameters, R = 0.049, wR^2 = 0.124, max. residual electron density 1.02 (−0.67) e Å^{-3}, two nearly identical cations and anions, hydrido hydrogens from difference Fourier, others calculated and all refined riding.

Reaction of μ-(η^1-O:η^2-C,O-*p*-Tolyl ketone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] (18b) with Tris(pentafluorophenyl)borane: Formation of 19b. A 200 mg (0.285 mmol) sample of **18b** and 146 mg (0.285 mmol) of $B(C_6F_5)_3$ were added to a Schlenk tube. Bromobenzene (10 mL) was added at room temperature, and within 1 min the compounds dissolved, forming a deep dark violet solution. Brown-black needles of **19b** were obtained within 1 day by allowing pentane to diffuse into this solution. The needles were isolated by decanting the solvent and were then dried in vacuo. Yield: 270 mg (84%). Mp: 137 °C (decomp) (DSC). Anal. Calcd for $C_{53}H_{36}BOF_{15}Zr_2$ (1167.1): C, 54.54; H, 3.11. Found: C, 53.77; H, 3.12. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 7.00 (psd, 4H, 3′-H), 6.76 (psd, 4H, 2′-H), 6.30, 5.66 (each s, each 10H, Cp), 4.3 (br, 1H, B−*H*), 2.19 (s, 6H, 4′-Me), −1.91 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 147.7 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 135.2 (C4′), 128.7 (C3′), 122.9 (br, C2′), 116.5 (Cp), 110.5 (Cp), 20.8 (4′-Me) ppm, *ipso*-$B(C_6F_5)_3$ and C1 resonances not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH}$ = 85 Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^{\ddagger}$ for *p*-tolyl group rotation (in dichloromethane-d_2): from 2′-H coalescence (T_C = 213 K), 9.2 ± 0.3 kcal/mol ($\Delta\nu$ = 352 Hz); from 3′-H coalescence (T_C = 208 K), 9.6 ± 0.3 kcal/mol ($\Delta\nu$ = 71 Hz).

X-ray Crystal Structure Analysis of 19b. Single crystals of **19b** obtained in the preparative scale reaction were suitable for X-ray structure analysis: formula $C_{53}H_{36}BOF_{15}Zr_2$, M = 1167.07, 0.4 × 0.2 × 0.1 mm, a = 15.394(4) Å, b = 15.465(6) Å, c = 22.396(4) Å, α = 86.22(3)°, β = 75.63(2)°, γ = 64.41(3)°, V = 4653(2) Å^3, ρ_{calc} = 1.666 g cm^{-3}, μ = 5.49 cm^{-1}, empirical absorption correction via ψ scan data (0.838 ≤ C ≤ 0.999), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 19348 reflections collected (±*h*, ±*k*, -*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 18 844 independent and 8137 observed reflections [$I \geq 2\ \sigma(I)$], 1309 refined parameters, R = 0.074, wR^2 = 0.185, max. residual electron density 0.97 (−1.31) e Å^{-3}, two nearly identical cations and anions, hydrido hydrogens from difference Fourier, others calculated and all refined riding.

Reaction of μ-(η^1-O:η^2-C,O-Benzophenone)-μ-hydrido-[bis(η^5-methylcyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] (18c) with Tris(pentafluorophenyl)borane: Formation of 19c. A 200 mg (0.305 mmol) sample of **18c** and 156 mg (0.305 mmol) of $B(C_6F_5)_3$ were mixed together in a Schlenk tube and were then dissolved in 5 mL of toluene. Within a few seconds, a red-violet oil precipitated. The solution was decanted and the oil washed with 2 mL of toluene and two times further with the same amount of pentane and dried in vacuo. **19c** was obtained as a purple-red powder. Yield: 288 mg (81%). Mp: 91 °C (decomp) (DSC). Anal. Calcd for $C_{53}H_{36}BOF_{15}Zr_2$ (1167.1): C, 54.54; H, 3.11. Found: C, 53.08; H, 3.10. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 7.15 (pst, 4H, 3′-H), 6.9 (m, 6H, 2′-H/4′-H), 6.40, 6.33, 6.26, 5.82 (each m, each 2H, each $C_5H_4CH_3$), 5.68 (Cp), 4.3 (br, 1H, B−*H*), 2.03 (s, 6H, Cp*Me*), −1.67 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 150.6 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 128.1 (C3′), 125.8 (C4′), 123.3 (C2′), 122.9 (br, *ipso*-$B(C_6F_5)_3$), 119.5, 118.0, 116.3, 115.6 ($C_4H_4CCH_3$), 110.4 (Cp), 14.9 (Cp*Me*) ppm, quat. (CpMe) and C1 resonances not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH}$ = 85 Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^{\ddagger}$ for phenyl group rotation (in dichloromethane-d_2): from 2′-H coalescence (T_C = 223 K), 9.7 ± 0.3 kcal/mol ($\Delta\nu$ = 362 Hz); from 3′-H coalescence (T_C = 213 K), 9.9 ± 0.3 kcal/mol ($\Delta\nu$ = 72.4 Hz).

Reaction of μ-(η^1-O:η^2-C,O-*p*-Tolyl ketone)-μ-hydrido-[bis(η^5-methylcyclopentadienyl)hydridozirconium][bis(η^5-cyclopentadienyl)zirconium] (18d) with Tris(pentafluorophenyl)borane: Formation of 19d. A 5 mL sample of toluene was added to a flask containing 200 mg (0.293 mmol) of **18d** and 150 mg (0.293 mmol) of $B(C_6F_5)_3$. The two compounds dissolved, and within a few seconds a red-violet oil precipitated. The solution was decanted and the oil washed with 2 mL of toluene and twice further with the same amount of pentane and dried in vacuo. **19d** was obtained as a purple-red powder. Yield: 256 mg (73%). Mp: 77 °C (decomp) (DSC). Anal. Calcd for $C_{53}H_{36}BOF_{15}Zr_2$ (1195.2): C, 55.27; H, 3.37. Found: C, 55.23; H, 3.74. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 6.85 (psd, 4H, 3′-H), 6.65 (psd, 4H, 2′-H), 6.26, 6.25, 6.15, 5.69 (each m, each 2H, each $C_5H_4CH_3$), 5.55 (s, 10H, Cp), 4.3 (br, 1H, B−*H*), 2.02 (s, 6H, Cp*Me*), 1.89 (s, 6H, 4′-Me), −1.88 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 148.0 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF}$ = 240 Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 135.1 (C4′), 128.7 (C3′), 123.2 (C2′), 122.9 (br, *ipso*-$B(C_6F_5)_3$), 119.4, 117.9, 116.2, 115.5 ($C_4H_4CCH_3$), 110.3 (Cp), 20.8 (4′-Me), 14.9 (Cp*Me*) ppm, quat. (CpMe) and C1 resonances not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH}$ = 85 Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^{\ddagger}$ for *p*-tolyl group rotation (in dichloromethane-d_2): from 2′-H coalescence (T_C = 223 K), 9.7 ± 0.3 kcal/mol ($\Delta\nu$ = 334 Hz); from 3′-H coalescence (T_C = 208 K), 9.5 ± 0.3 kcal/mol ($\Delta\nu$ = 115 Hz).

Reaction of μ-(η^1-O:η^2-C,O-Benzophenone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridohafnium][bis(η^5-cyclo-

pentadienyl)zirconium] (18e) with Tris(pentafluorophenyl)borane: Formation of 19e. A 200 mg (0.265 mmol) sample of **18e** and 136 mg (0.265 mmol) of $B(C_6F_5)_3$ were loaded into a Schlenk tube. A 5 mL portion of bromobenzene was added and the compounds dissolved within 1 min to give a deep dark red solution. Allowing pentane to diffuse through the gas phase into this solution, dark red crystals of **19e** were obtained within 2 days. The solution was decanted, and the crystals were isolated and dried in vacuo. Yield: 231 mg (71%). Mp: 144 °C (decomp) (DSC). Anal. Calcd for $C_{51}H_{32}BOF_{15}ZrHf$ (1226.3): C, 49.95; H, 2.63. Found: C, 49.41; H, 2.91. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 7.17 (pst, 4H, 3′-H), 6.97 (pst, 2H, 4′-H), 6.83 (psd, 4H, 2′-H), 6.20, 5.68 (each s, each 10H, Cp), 4.35 (br, 1H, B−*H*), 0.63 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 150.0 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF} = 240$ Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 128.3 (C3′), 125.9 (C4′), 123.3 (C2′), 122.9 (br, *ipso*-$B(C_6F_5)_3$), 114.9, 110.9 (Cp) ppm, C1 resonance not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH} = 85$ Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^\ddagger$ for phenyl group rotation (in dichloromethane-d_2): from 2′-H coalescence ($T_C = 233$ K), 10.1 ± 0.3 kcal/mol ($\Delta\nu = 351$ Hz); from 3′-H coalescence ($T_C = 223$ K), 10.5 ± 0.3 kcal/mol ($\Delta\nu = 57.1$ Hz).

X-ray Crystal Structure Analysis of 19e. Single crystals of **19e** obtained in the preparative scale reaction were suitable for X-ray structure analysis: formula $C_{51}H_{32}BOF_{15}ZrHf$, $M = 1226.29$, 0.4 × 0.1 × 0.1 mm, $a = 15.367(2)$ Å, $b = 21.120(4)$ Å, $c = 15.412(1)$ Å, $\beta = 115.42(1)°$, $V = 4517.7(11)$ Å^3, $\rho_{calc} = 1.803$ g cm^{-3}, $\mu = 26.29$ cm^{-1}, empirical absorption correction via ψ scan data ($0.487 \le C \le 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 8254 reflections collected ($\pm h$, $+k$, $+l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 7942 independent and 4462 observed reflections [$I \ge 2\,\sigma(I)$], 631 refined parameters, $R = 0.050$, $wR^2 = 0.118$, max. residual electron density 1.53 (−1.76) e Å^{-3} close to Hf2, hydrido hydrogen not located, others calculated and refined riding.

Reaction of μ-(η^1-O:η^2-C,O-*p*-Tolyl ketone)-μ-hydrido-[bis(η^5-cyclopentadienyl)hydridohafnium][bis(η^5-cyclopentadienyl)zirconium] (18f) with Tris(pentafluorophenyl)borane: Formation of 19f. A Schlenk tube was charged with 200 mg (0.260 mmol) of **18f** and 131 mg (0.260 mmol) of $B(C_6F_5)_3$. A 5 mL portion of bromobenzene was added, and the compounds dissolved within 1 min to give a deep dark red solution. Allowing pentane to diffuse through the gas phase into this solution, a dark red powder formed within 2 days. After decanting the solvent, the powder **19f** was dried in vacuo. Yield: 199 mg (61%). Mp: 132 °C (decomp) (DSC). Anal. Calcd for $C_{53}H_{36}BOF_{15}ZrHf$ (1254.4): C, 50.75; H, 2.89. Found: C, 50.61; H, 3.16. ^{1}H NMR (bromobenzene-d_5, 599.9 MHz, 298 K): δ 7.00 (psd, 4H, 3′-H), 6.74 (psd, 4H, 2′-H), 6.21, 5.70 (each s, each 10H, Cp), 4.3 (br, 1H, B−*H*), 2.18 (s, 6H, 4′-Me), 0.61 (s, 1H, μ-H) ppm. ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K): δ 148.4 (C1′), 148.5, 138.9, 136.8 (each d, each $^1J_{CF} = 240$ Hz, *o*, *p*, *m*-$B(C_6F_5)_3$), 136.1 (C4′), 129.6 (C3′), 124.2 (C2′), 123.7 (br, *ipso*-$B(C_6F_5)_3$), 115.7 (Cp), 111.7 (Cp), 21.6 (4′-Me) ppm, C1 resonance not located. ^{11}B NMR (bromobenzene-d_5, 64.2 MHz, 298 K): δ −24.9 (d, $^1J_{BH} = 85$ Hz) ppm. ^{19}F NMR (bromobenzene-d_5, 282.4 MHz, 298 K): δ −132.0, −162.8, −165.7 (*o*, *p*, *m*-$B(C_6F_5)_3$) ppm. $\Delta G^\ddagger$ for *p*-tolyl group rotation (in dichloromethane-d_2): from 2′-H coalescence ($T_C = 233$ K), 10.3 ± 0.3 kcal/mol ($\Delta\nu = 269$ Hz); from 3′-H coalescence ($T_C = 223$ K), 11.1 ± 0.3 kcal/mol ($\Delta\nu = 15.3$ Hz).

Table 3. Ethene Polymerization Reactions Catalyzed by Complexes 19

catalyst (mg/μmol)	T^a	PE (g)	mp (°C)	act^b
19c (15.1/12.9)	60	12.7	129	5900
19d (15.4/12.9)	50	16.7	129	7700
19e (16.9/13.8)	40	15.8	128	5600
19f (15.9/12.7)	40	11.1	129	4100

[a] Final temperature (°C) reached under nonisothermal conditions. [b] Catalyst activity in g polymer/(mmol [catalyst]·bar·h).

Ethene Polymerization Reactions. A thermostated Büchi glass autoclave (25 °C) was charged with 300 mL of toluene and 0.5 mL of triisobutylaluminum. Ethene was introduced at a pressure of 2.0 bar. After 0.5 h, a solution of catalyst **19** in 3 mL of bromobenzene, which was loaded into a syringe within a glovebox, was added and the polymerization reaction allowed to proceed. After 5 min the system was vented and its contents were quenched by treatment with 20 mL of a 1:1 volume mixture of methanol and 2 N aqueous hydrochloric acid. The polymer was collected by filtration, extracted with toluene, and then washed 3 times consecutively with half concentrated HCl, H_2O, and then acetone. The resulting polyethylene samples were then dried for 12 h under vacuo. Details of the respective polymerization experiments carried out according to this general procedure are compiled in Table 3.

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Supporting Information Available: Additional NMR data of the complexes **18** and **19**. Details on the X-ray crystal structure determinations of the complexes **18a−c** and **19a**,**b** and **e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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