Coupling Reactions of a [1-(Dialkylboryl)butadiene]hafnocene Complex with Carbonyl Compounds

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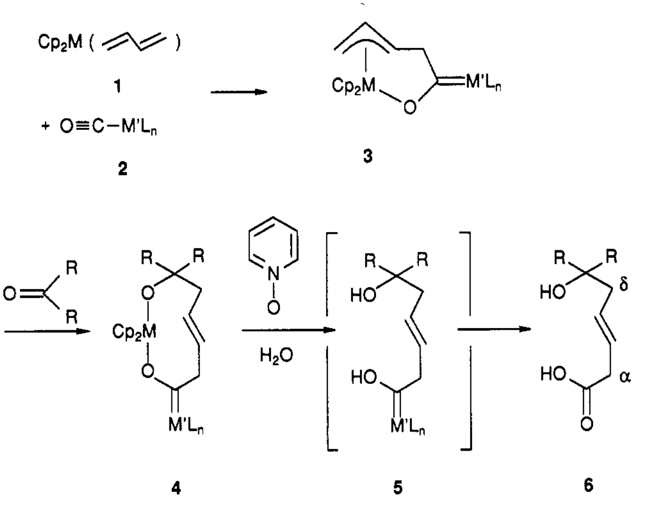
[η^4-*s-cis*-1-(9-BBN)butadiene]hafnocene (*s-cis*-**7**) is readily available by the C–H activation reaction of (butadiene)hafnocene with 9-borabicyclo[3.3.1]nonane. Photolysis generates *s-trans*-**7**, which regioselectively adds ketones with formation of oxametallacycloheptene ring systems (**9**) bearing the bulky 9-BBN substituent at the carbon atom adjacent to hafnium. The structure of the benzophenone addition product (**9b**) to [1-(9-BBN)butadiene]hafnocene was determined by X-ray diffraction. Hexacarbonyltungsten also adds regioselectively to **7** with C–C coupling at the less substituted (9-BBN)butadiene terminus to yield a 4:1 mixture of the isomeric (π-allylmetaloxy)- and seven-membered (σ-allylmetaloxy)carbene complexes **10a** and **10b**. These react with acetone chemo- and stereoselectively to give a single nine-membered metallacyclic δ-boryl-substituted (metaloxy)carbene tungsten complex (**11**) under kinetic control which contains a *trans*-C=C double bond inside the medium-sized ring system. Subsequent thermally induced equilibration leads to *cis-/trans*-isomer formation (**12**:**11** = 3:1 under thermodynamic control). The allylborane functionality which is part of the product **11** adds 1 equiv of acetone with allyl inversion and oxygen–boron bond formation. Thus, the use of a boryl-substituted butadiene ligand allows for the formation of selectively substituted and functionalized products in the sequential C–C coupling reaction between carbonyl building blocks and a conjugated diene at the group 4 bent metallocene template.

We recently developed a useful template synthesis of β,γ-unsaturated ϵ-hydroxy carboxylic acids.[1] This is achieved by the sequential coupling of butadiene with a metal carbonyl complex and an organic carbonyl compound at the Cp$_2$M moiety (M = Zr, Hf). We have isolated many examples of the resulting metallacycles (**4**).[2] They can be regarded as protected Fischer carbene complexes. The (metaloxy)carbene complexes are stable toward oxidizing reagents such as pyridine *N*-oxide which usually cleave ordinary Fischer carbene complexes. Subsequent addition of water hydrolyzes the (metaloxy)carbene complex to generate a zirconium- (or hafnium-) free hydroxycarbene complex (**5**), which then is instantaneously converted to the corresponding carboxylic acid (**6**) in this oxidizing environment (see Scheme I).

Scheme I



We have prepared a variety of β,γ-unsaturated ϵ-hydroxy carboxylic acids (**6**) by this route employing the isolated complex **4a** [M = Zr, M'L$_n$ = W(CO)$_5$] as a reagent.[1] For a variety of applications of this synthesis it would be desirable to have easy access to ways of introducing functional groups or side chains at the positions α and δ to the carboxylic terminus of the chain. The problem of α-derivatization has principally been solved by making use of the facile deprotonation at the stage of the organometallic intermediate **4** to generate a stabilized carbanionic system that is stereoselectively attacked by a variety of electrophiles.[3] At the δ-position groups cannot be introduced as easily. They have to be brought into the

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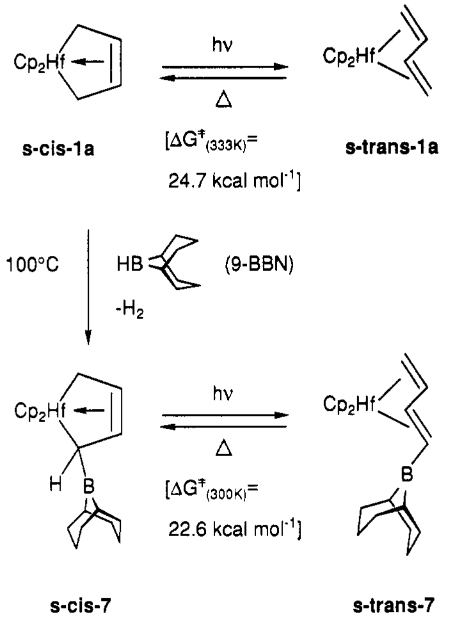
Scheme II



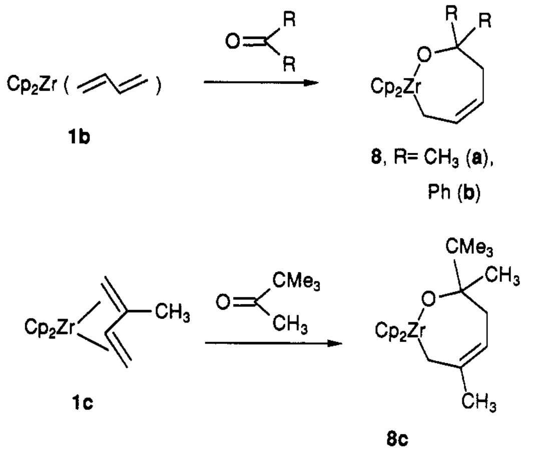
system already attached to the butadiene building block, and then a regioselectivity problem may arise. We have found some indication of how this general synthetic question can be tackled and describe the highly regioselective coupling of the (η^4-1-boryl-1,3-butadiene)hafnocene reagent **7** with organic and organometallic carbonyl compounds.

Results and Discussion

The Addition of Ketones. We recently showed that (η^4-butadiene)hafnocene reacts with 9-borabicyclo[3.3.1]-nonane (9-BBN) at elevated temperature by C–H activation to yield [η^4-*s-cis*-1-(9′-borabicyclo[3.3.1]non-9′-yl)butadiene]hafnocene (*s-cis*-**7**). Photolysis at a temperature below 0 °C rapidly converts the (η^4-*s-cis*-borylbutadiene)$HfCp_2$ complex into the [η^4-*s-trans*-(9-BBN)butadiene]metallocene isomer (*s-trans*-**7**). This in turn is reconverted to the thermodynamically favored (*s-cis*-diene)$HfCp_2$ complex at temperatures above 0 °C. The activation energy of the thermally induced *s-trans*-**7** to *s-cis*-**7** isomerization has been determined [$\Delta G^{\ddagger}(300\ K) = 22.6 \pm 0.5$ kcal mol^{-1}].[4] (See Scheme II.)

It is well established that the (*s-trans*-1,3-diene)-metallocenes react with ketones to give seven-membered metallacyclic (σ-allyl)metallocene complexes **8**.[5] The (*s-trans*-η^4-diene)metallocenes[6] undergo this reaction much faster than their (*s-cis*-η^4-diene)MCp_2 isomers. Reactions with suitably substituted examples indicate that such C–C coupling reactions often take place regioselectively. Thus, (*s-trans*-η^4-isoprene)zirconocene adds pinacolone predominantly at the less substituted conjugated diene double bond to give the metallacycle **8c**.[7] (See Scheme III).

Scheme III



We have generated [η^4-*s-trans*-(9-BBN)butadiene]-hafnocene (*s-trans*-**7**) from the stable *s-cis*-**7** isomer[8] by photolysis (HPK 125, Pyrex filter) in toluene solution in the temperature range −10 to 0 °C in the presence of acetone. Under these conditions, in situ generated *s-trans*-**7** is rapidly trapped by the reaction with the ketone. Workup gives the seven-membered metallacyclic (σ-allyl)-metallocene addition product **9a** in moderate yield (~40%). The NMR analysis (for details see Experimental Section) has revealed that a single isomer of the product is obtained. This contains a chiral center as part of the ring perimeter [–CH(9-BBN)–] and thus gives rise to the

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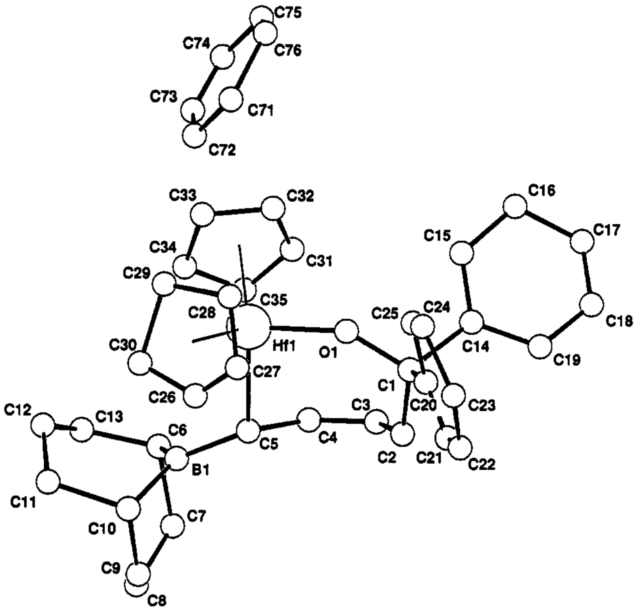
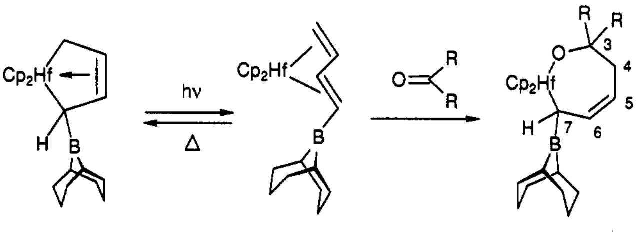


Figure 1. View of the molecular geometry of complex **9b** (with unsystematic atom-numbering scheme) in the crystal (only one of the independent molecule is shown; the unit cell contains two benzene molecules).

Scheme IV



s-cis-7 s-trans-7 9, R= CH$_3$ (a) Ph (b)

occurrence of pairs of diastereotopic Cp ligands at hafnium (^{1}H/^{13}C NMR singlets at δ 5.83, 5.78/109.8, 108.2), methyl substituents at C-3 (δ 1.15, 0.87/31.8, 29.8), and hydrogen atoms at C-4 (δ 1.79 and 1.43). The reaction of [(9-BBN)-butadiene]hafnocene with benzophenone proceeds analogously. A single isomer of the corresponding seven-membered metallacyclic addition product is isolated (**9b**). We conclude that the addition of these ketones to [(9-BBN)butadiene]hafnocene (**7**) has taken place with very high regioselectivity: only the products of coupling between the unsubstituted conjugated diene terminus with the carbonyl electrophile have been observed. In the isolated 1:1 addition products the bulky 9-BBN substituent is preferentially bonded at a carbon in a position which is directly adjacent to the metallocene moiety. (See Scheme IV.)

Table I. Selected Bond Lengths (Å) and Angles (deg) for 9b[a]

mol 1		mol 2	
Hf(1)–O(1)	1.927(4)	Hf(2)–O(2)	1.942(4)
Hf(1)–C(5)	2.269(6)	Hf(2)–C(40)	2.409(6)
O(1)–C(1)	1.439(6)	O(2)–C(36)	1.392(7)
C(1)–C(2)	1.488(9)	C(36)–C(37)	1.612(8)
C(1)–C(14)	1.616(8)	C(36)–C(49)	1.417(8)
C(1)–C(20)	1.489(8)	C(36)–C(55)	1.590(8)
C(2)–C(3)	1.503(9)	C(37)–C(38)	1.497(9)
C(3)–C(4)	1.338(9)	C(38)–C(39)	1.339(9)
C(4)–C(5)	1.467(8)	C(39)–C(40)	1.503(9)
C(5)–B(1)	1.601(9)	C(40)–B(2)	1.41(1)

mol 1		mol 2	
D(2)–Hf(1)–D(1)	132.1(1)	D(4)–Hf(2)–D(3)	120.4(1)
C(5)–Hf(1)–O(1)	94.2(2)	C(40)–Hf(2)–O(2)	93.6(2)
C(1)–O(1)–Hf(1)	151.0(3)	C(36)–O(2)–Hf(2)	156.3(4)
C(2)–C(1)–O(1)	106.3(4)	C(37)–C(36)–O(2)	105.7(4)
C(3)–C(2)–C(1)	114.8(5)	C(38)–C(37)–C(36)	115.4(5)
C(4)–C(3)–C(2)	124.0(6)	C(39)–C(38)–C(37)	124.8(6)
C(5)–C(4)–C(3)	128.3(6)	C(40)–C(39)–C(38)	130.6(6)
B(1)–C(5)–C(4)	120.1(5)	B(2)–C(40)–C(39)	119.9(6)
B(1)–C(5)–Hf(1)	118.7(4)	B(2)–C(40)–Hf(2)	118.0(5)

[a] D denotes the center of a Cp ring.

This interpretation of the regiochemical outcome of the ketone addition to [(9-BBN)butadiene]hafnocene is supported by the results of the X-ray crystal structure analysis of complex **9b**. It crystallizes in the space group $P1$ with cell parameters a = 8.295(1) Å, b = 10.831(1) Å, c = 18.926(2) Å, α = 93.60(1)°, β = 99.55(1)°, γ = 90.42(1)°. The crystal structure contains two independent molecules of the metallacycle which are chemically equivalent and two molecules of benzene. Complex **9b** exhibits a seven-membered metallacyclic framework containing five carbon atoms, an oxygen atom, and hafnium. Very typically, the oxametallacycloheptene **9b** adopts a folded boat-shaped ring conformation in the solid state similar to that previously observed for **8b**.[5a] To a first approximation the atoms C(5)–Hf(1)–O(1)–C(1)–C(2) (molecule 1) [and C(40)–Hf(2)–O(2)–C(36)–C(37) of molecule 2, respectively] are arranged coplanarly (maximum deviation ± 0.10 Å); carbon atoms C(5)–C(4)–C(3)–C(2) (of molecule 1) [molecule 2: C(40)–C(39)–C(38)–C(37)] are also arranged nearly in one plane. The angle between these two planes is 73.9° (molecule 1) [molecule 2: 68.1°]. Much of the rigidity of the cyclic seven-membered framework in **9b** is due to the large angle at the ring oxygen atom [C(1)–O(1)–Hf(1) = 151.0(3)° (molecule 1); angle in complex **8b** is very similar at 150.5(4)° [5a]]. This indicates some oxygen to hafnium electron π-donation which may serve to decrease the electron deficiency at the Lewis acidic metal center.[9] Consequently, the hafnium–oxygen linkage in **9b** is rather short [Hf(1)–O(1) = 1.927(4) Å (molecule 1); Hf(2)–O(2) = 1.942(4) Å (molecule 2)].

Both independent molecules found in the crystal bear the bulky 9-borabicyclo[3.3.1]non-9-yl-substituents at the carbon center adjacent to hafnium. The 9-BBN group is arranged in a pseudoequatorial position at the boat-shaped oxametallacycloheptene framework [dihedral angles O(1)–Hf(1)–C(5)–B(1) = 180.0° and O(2)–Hf(2)–C(40)–B(2) = 178.2°]. The bulky substituent thus occupies the available space at the lateral sector of the bent metallocene moiety.

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Table II. Atomic Coordinates of 9b

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Hf(1)	0.1683(1)	0.1208(1)	0.2462(1)	C(41)	0.5362(9)	0.7256(7)	0.9022(4)
Hf(2)	0.8319(1)	0.8795(1)	0.7536(1)	C(42)	0.454(1)	0.7686(9)	0.9610(5)
O(1)	0.1897(5)	–0.0472(3)	0.2738(2)	C(43)	0.556(1)	0.7606(7)	1.0325(5)
O(2)	0.8054(5)	1.0497(4)	0.7279(2)	C(44)	0.728(1)	0.8285(7)	1.0392(4)
C(1)	0.2136(7)	–0.1765(5)	0.2570(3)	C(45)	0.8167(8)	0.7655(6)	0.9711(4)
C(2)	0.3005(8)	–0.1831(5)	0.1942(3)	C(46)	0.8467(9)	0.6358(7)	0.9771(4)
C(3)	0.4439(8)	–0.0953(6)	0.2004(3)	C(47)	0.725(1)	0.5502(8)	0.9581(5)
C(4)	0.4328(7)	0.0211(6)	0.1805(3)	C(48)	0.586(1)	0.5829(7)	0.9002(4)
C(5)	0.2871(7)	0.0852(5)	0.1474(3)	C(49)	0.6742(7)	1.2228(5)	0.6783(3)
C(6)	0.4705(8)	0.2756(7)	0.1071(4)	C(50)	0.638(1)	1.1570(6)	0.6130(4)
C(7)	0.538(1)	0.2176(8)	0.0363(5)	C(51)	0.540(1)	1.2087(8)	0.5596(4)
C(8)	0.420(1)	0.2154(8)	–0.0348(4)	C(52)	0.4859(9)	1.3205(8)	0.5568(4)
C(9)	0.256(1)	0.1798(6)	–0.0275(4)	C(53)	0.5256(9)	1.3965(6)	0.6243(4)
C(10)	0.1781(9)	0.2196(5)	0.0312(4)	C(54)	0.6215(8)	1.3416(7)	0.6831(3)
C(11)	0.139(1)	0.3662(8)	0.0309(5)	C(55)	0.9477(7)	1.2421(5)	0.7496(3)
C(12)	0.264(2)	0.4401(7)	0.0864(5)	C(56)	0.9850(7)	1.3466(5)	0.8047(3)
C(13)	0.439(1)	0.4116(8)	0.0980(5)	C(57)	1.135(1)	1.4057(6)	0.8080(4)
C(14)	0.3284(7)	–0.2278(5)	0.3261(3)	C(58)	1.2470(9)	1.3655(7)	0.7627(5)
C(15)	0.3598(9)	–0.1596(7)	0.3908(4)	C(59)	1.189(1)	1.2865(8)	0.7177(5)
C(16)	0.446(1)	–0.2029(7)	0.4556(3)	C(60)	1.0543(8)	1.2188(6)	0.7066(4)
C(17)	0.5112(9)	–0.3269(7)	0.4443(4)	C(61)	1.082(1)	0.858(2)	0.8498(4)
C(18)	0.4787(8)	–0.3912(6)	0.3849(4)	C(62)	1.113(1)	0.9375(8)	0.7934(9)
C(19)	0.3908(7)	–0.3480(5)	0.3254(4)	C(63)	1.120(1)	0.859(2)	0.7382(7)
C(20)	0.0581(7)	–0.2497(5)	0.2471(3)	C(64)	1.099(1)	0.758(1)	0.758(1)
C(21)	0.0072(9)	–0.3338(6)	0.1988(4)	C(65)	1.054(1)	0.749(1)	0.806(1)
C(22)	–0.1408(9)	–0.3982(6)	0.1905(4)	C(66)	0.567(1)	0.833(1)	0.6797(6)
C(23)	–0.2384(9)	–0.3771(7)	0.2368(4)	C(67)	0.671(1)	0.8203(8)	0.6339(5)
C(24)	–0.2098(8)	–0.2726(6)	0.2946(4)	C(68)	0.776(1)	0.7236(8)	0.6486(4)
C(25)	–0.0478(9)	–0.2148(6)	0.2981(4)	C(69)	0.733(1)	0.6696(7)	0.6985(5)
C(26)	–0.0877(9)	0.1102(9)	0.1566(5)	C(70)	0.601(1)	0.722(1)	0.7226(5)
C(27)	–0.1274(7)	0.0452(7)	0.1967(4)	C(71)	0.848(3)	0.457(2)	0.476(2)
C(28)	–0.1195(8)	0.1046(8)	0.2636(4)	C(72)	0.937(4)	0.519(2)	0.432(1)
C(29)	–0.080(1)	0.237(1)	0.2556(7)	C(73)	1.085(2)	0.573(2)	0.458(1)
C(30)	–0.065(1)	0.2323(8)	0.1710(5)	C(74)	1.147(3)	0.569(2)	0.520(1)
C(31)	0.4343(9)	0.1575(8)	0.3415(4)	C(75)	1.084(3)	0.509(2)	0.569(1)
C(32)	0.301(1)	0.1845(9)	0.3725(4)	C(76)	0.938(3)	0.459(2)	0.552(2)
C(33)	0.238(1)	0.290(1)	0.3422(8)	C(77)	1.074(3)	0.910(2)	0.532(1)
C(34)	0.345(1)	0.3130(8)	0.2878(5)	C(78)	0.917(3)	0.888(2)	0.485(1)
C(35)	0.456(1)	0.2204(9)	0.2866(4)	C(79)	0.836(3)	0.992(3)	0.455(1)
C(36)	0.7735(7)	1.1749(5)	0.7383(3)	C(80)	0.900(3)	1.105(2)	0.478(1)
C(37)	0.6933(8)	1.1880(5)	0.8103(3)	C(81)	1.039(3)	1.120(2)	0.511(1)
C(38)	0.7962(8)	1.1438(5)	0.8762(3)	C(82)	1.136(2)	1.029(2)	0.5369(8)
C(39)	0.8042(8)	1.0261(6)	0.8939(3)	B(1)	0.3050(9)	0.1972(6)	0.0978(4)
C(40)	0.7090(7)	0.9132(6)	0.8597(3)	B(2)	0.6919(9)	0.8109(7)	0.9008(4)

Such spatial arrangement of large substituents at the α-positions of metallacyclic compounds of the group 4 bent metallocenes is very favorable and has been observed with other examples as well.[10] One of the phenyl substituents at the seven-membered ring is oriented pseudoequatorially [dihedral angle Hf(1)–O(1)–C(1)–C(14) = 141.8° (molecule 1); Hf(2)–O(2)–C(36)–C(49) = –137.7° (molecule 2)], whereas the other Ph group is bonded in a pseudoaxial position [dihedral angle Hf(1)–O(1)–C(1)–C(20) = –102.4° (molecule 1); Hf(2)–O(2)–C(36)–C(55) = 104.3° (molecule 2)].

Formation of Metaloxycarbene Complexes. (Butadiene)zirconocene reacts with a variety of metal carbonyls with formation of metallacyclic (π-allyl)zirconoxycarbene complexes.[11] Typical examples are the complexes **3a–e**.[12] The analogous addition reaction starting from (butadiene)hafnocene often produces a mixture of the metallacyclic (π-allyl)metaloxycarbene complex and its seven-membered (σ-allyl)metallocene isomer.[12a] In both cases the C–C-coupling reaction between coordinated butadiene and the metal carbonyl seems to occur predominantly via the (s-*trans*-butadiene)metallocene isomer.

We have thus generated [η^4-*s-trans*-(9-BBN)butadiene]hafnocene (*s-trans*-**7**) by low-temperature photolysis of the stable *s-cis*-**7** isomer and then added hexacarbonyltungsten. Workup at ambient temperature gave a 4:1 mixture of two metallacyclic metaloxycarbene complexes which were formed by a 1:1 addition reaction between the employed organometallic reagents. From their characteristic NMR data (see Table III and the Experimental Section) these have been identified as the isomeric carbene complexes **10a** and **10b**. The major component of this product mixture is the metallacyclic (π-allyl)metaloxycarbene tungsten complex **10a**. (See Scheme V.) The respective isomers are readily distinguished by their

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[10] Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276. Sabade, M. B.; Farona, M. F.; Zarate, E. A.; Youngs, W. J. *J. Organomet. Chem.* **1988**, *338*, 347. Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. Erker, G.; Zwettler, R.; Krüger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524. Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. *J. Am. Chem. Soc.* **1990**, *112*, 9620. Erker, G.; Zwettler, R. *J. Organomet. Chem.* **1991**, *409*, 179.

[11] Erker, G. *Polyhedron* **1988**, *7*, 2451. Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. Erker, G.; Sosna, F.; Hoffmann, U. *J. Organomet. Chem.* **1989**, *372*, 41. Erker, G.; Aulbach, M.; Mena, M.; Pfaff, R.; Sosna, F. *Chem. Scr.* **1989**, *29*, 451.

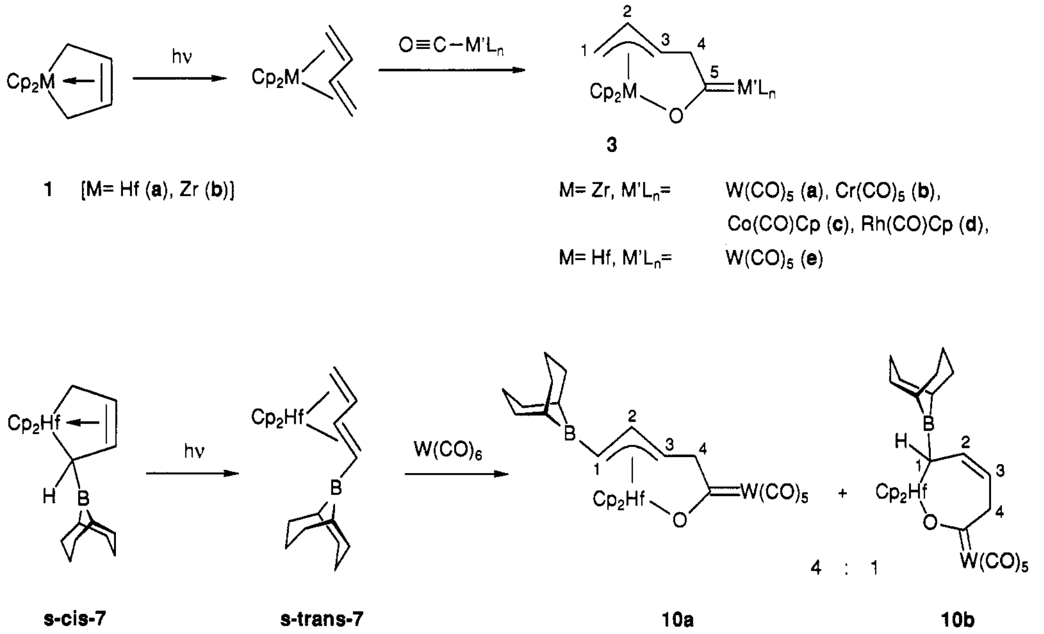
[12] (a) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. (b) Erker, G.; Lecht, R.; Petersen, J. L.; Bönnemann, H. *Organometallics* **1987**, *6*, 1962. (c) Erker, G.; Lecht, R.; Tsay, Y.-H.; Krüger, C. *Chem. Ber.* **1987**, *120*, 1763. (d) Erker, G.; Lecht, R.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem.* **1987**, *99*, 708; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 666.

Table III. Comparison of Characteristic ^{1}H NMR Data of Metallacyclic (σ- and π-Allyl)metallocene Complexes[a]

cmpd	7-H	6-H	5-H	4-H, 4-H′	J(7-H/6-H)	J(6-H/5-H)	J(5-H/4-H)	J(5-H/4-H′)	J(4-H/4-H′)	ref
9a	2.91	6.42	4.98	1.79, 1.43	10.8	10.8	7.5	10.0	12.5	*b*
9b	3.20	6.41	4.93	2.98, 2.15	11.0	11.0	6.9	9.5	12.8	*b*
cmpd	1-H	2-H	3-H	4-H, 4-H′	J(1-H/2-H)	J(2-H/3-H)	J(3-H/4-H)	J(3-H/4-H′)	J(4-H/4-H′)	ref
10b	2.58	6.00	4.45	4.81, 1.46	10.9	10.3	6.9	8.6	12.6	*b*
10a	2.78	5.55	4.97	4.03, 2.37	15.2	15.8	4.5	10.0	17.9	*b*
3a	1.51	4.94	4.56	4.01, 2.42	14.0	16.0	4.8	9.9	17.7	12a
3b	1.50	4.91	4.53	4.20, 2.66	13.5	15.9	4.7	9.8	17.4	12a
3c	1.63	4.92	4.56	3.82, 2.28	14.4	15.4	4.8	10.5	15.6	12b
3d	1.58	4.99	4.59	3.80, 2.45	14.4	16.0	4.9	10.5	16.0	12c
3e	1.31	4.92	4.50	4.18, 2.63	14.1	16.1	4.9	9.6	17.5	12a

[a] ^{1}H NMR spectra in benzene-d_6, chemical shifts relative to TMS, δ scale, coupling constants in Hz. [b] This work.

Scheme V



characteristic sets of proton–proton coupling constants (see Table III).

The metaloxycarbene complexes **10a** and **10b** are expected to react with organic carbonyl compounds at the allyl terminus with formation of nine-membered metallacycles.[2,13] We have realized this by treating the **10a**/**10b** mixture with acetone at −78 °C. Warming the mixture to room temperature and then stirring it for some time resulted in the formation of the nine-membered metallacyclic addition product **11**. Under these reaction conditions a single metallacyclic product is obtained. It contains a *trans*-configurated C═C double bond (^3J(4-H, 5-H) = 14.7 Hz) and thus exhibits a chiral medium-size metallacyclic framework. The boryl substituent is attached to the carbon center C(3). Addition of acetone to the metaloxycarbene complexes **10a,b** has thus formed a product containing two chirality elements and could, therefore, have yielded two diastereomers. However, only a single set of ^{1}H/^{13}C NMR signals is observed [e.g. δ: 5.91, 5.81/112.1, 111.7 (Cp); 1.11, 0.90/34.0, 28.5 (methyl at C-2)], indicating that this coupling reaction has taken place regioselectively, with high stereoselectivity. Which of the two diastereoisomers is actually obtained [(3R*)(4,5,6-pS*) or (3R*)(4,5,6-pR*)] is not known at present. Probably the solution of this question must await the result of an X-ray crystal structure analysis of the product obtained in this experiment.

Complex **11** is formed from acetone and the (allyl)metaloxycarbene complexes **10a,b** under kinetic control. Upon thermolysis in benzene solution, part of **11** isomerizes to **12**, which is distinguished from **11** by exhibiting a *cis*-configurated C═C double bond [^3J(4-H, 5-H) = 11.1 Hz] inside the nine-membered metallacyclic ring system.[14] Equilibrium, containing **12** and **11** in a 3:1 ratio, is reached after ca. 2 h at 60 °C. (See Scheme VI.)

Complex **11** contains an allylborane moiety, part of which is incorporated into the nine-membered metallacyclic ring system. It is expected that the allyl-9-BBN functionality should react with ketones in the typical way, namely undergo C–C coupling with the carbonyl electrophile with allyl inversion and addition of the boron atom to the former carbonyl oxygen.[15] This reaction is observed when the mixture of the (allyl)metaloxycarbene complexes **10a**/**10b** is treated with an excess of acetone (3 molar equiv) in toluene at room temperature. In this experiment, the nine-membered metallacyclic metaloxycarbene/allylborane

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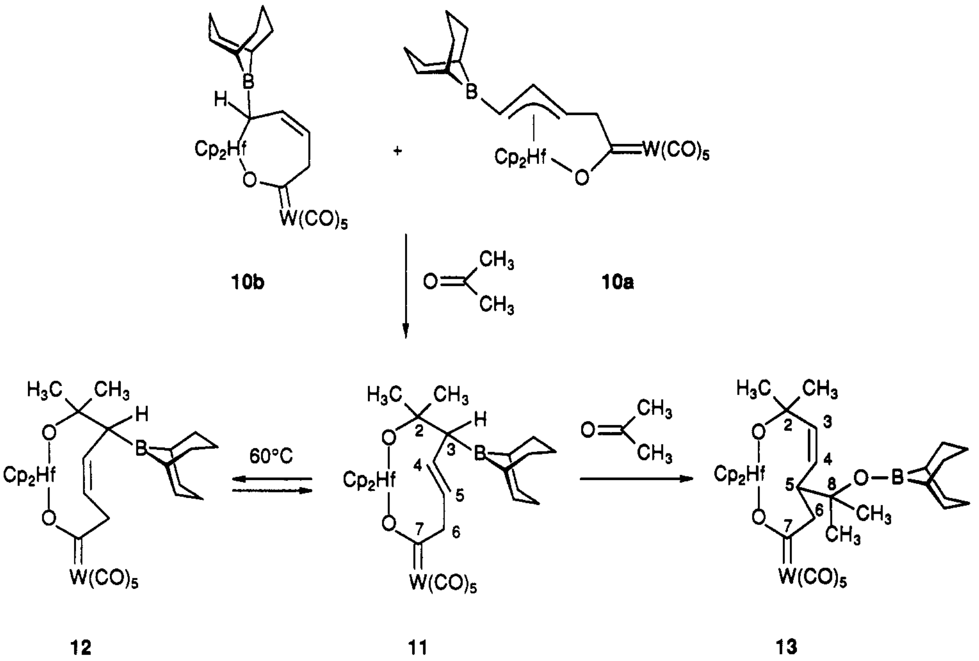
(13) For related examples see: Yasuda, H.; Okamoto, T.; Matsuoka, Y.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1989**, *8*, 1139. Erker, G.; Humphrey, M. G.; *J. Organomet. Chem.* **1989**, *378*, 163. Erker, G.; Pfaff, R.; Krüger, C.; Nolte, M.; Goddard, R. *Chem. Ber.* **1992**, *125*, 1669.

(14) Analogous mixtures of *cis*- and *trans*-dioxametallacyclononene ring systems have previously been obtained upon treatment of complexes **3** with aldehydes; see ref 2a.

(15) Hoffmann, R. W. *Angew. Chem.* **1982**, *94*, 569; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.

Scheme VI



complex 11 is formed in situ and then trapped by the excess ketone present in the solution. We have isolated a single isomer of the acetone addition product (13) to the allylborane function in 75% yield. Complex 13 contains a *cis*-C═C double bond inside the metallacyclic framework [^3J(3-H, 4-H) = 11.6 Hz].

Conclusion

[1-(9-BBN)butadiene]hafnocene (7) is readily available by a C–H activation route reacting (butadiene)hafnocene (1a) with 9-borabicyclo[3.3.1]nonane.[4] The functionalized (diene)metallocene reagent (7) reacts readily and with a very high regioselectivity with organic and organometallic carbonyl groups. In the 1:1 addition products the bulky 9-BBN substituent usually ends up in a terminal position at the carbon center adjacent to the bent metallocene unit. Despite the presence of the bulky 9-BBN substituent, its attached carbon center still undergoes nucleophilic addition to a ketone, of course assisted by thermodynamically favored hafnium–oxygen bond formation[16] taking place simultaneously. At this stage, the regiochemistry is fixed by the substitution pattern at the C_5 chain resulting from the previous reaction step. However, there could have been the alternative choice of complexes 10 acting as allylborane (rather than allylhafnium) reagents. The formation of the single observed reaction product 11 is, therefore, not only very remarkable in view of the high stereoselectivity of the C–C coupling process—this reaction has also occurred with a pronounced chemoselectivity. Eventually, the allylborane functionality contained in the nine-membered metallacyclic template coupling product 11 can be used for further C–C bond formation with an organic carbonyl electrophile, as expected. With this series of reactions it has been demonstrated for the first time that each of the carbon atoms of the butadiene building block introduced and coupled in the course of our template reaction can selectively be substituted or functionalized. This should greatly increase the overall synthetic applicability of the easily performed sequential coupling of two carbonyls and a conjugated diene at the group 4 bent metallocene template.

Experimental Section

All reactions were carried out in an argon atmosphere using Schlenk type glassware or a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterization: Bruker AC 200 P NMR spectrometer (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz; ^{11}B, 64.2 MHz), Bruker ARX 300 NMR spectrometer (^{13}C, 75.0 MHz), Nicolet 5 DXC FT IR spectrometer, Du Pont 910 DSC and Gallenkamp melting point apparatus for melting point, and Voss-Heraeus CHNO-Rapid elemental analyzer. The [1-(9-BBN)butadiene]hafnocene reagent 7 was prepared according to a literature procedure.[4]

7-(9′-Borabicyclo[3.3.1]nonane-9′-yl)-1,1-bis(η-cyclopentadienyl)-3,3-dimethyl-2-oxahafnacyclohept-4-ene (9a). A solution of [1-(9-BBN)butadiene]hafnocene (200 mg, 0.41 mmol) in 20 mL of toluene is treated with 40 μL of acetone (0.54 mmol), and the mixture is irradiated at −10 to 0 °C for 2 h. The solution is concentrated and the residue washed with pentane to yield 90 mg (41%) of **9a**. ^{1}H NMR (benzene-d_6): δ 6.42 (dt, 1 H, 6-H), 5.83, 5.78 (each s, 5 H, Cp), 4.98 (m, 1 H, 5-H), 2.91 (dd, 1 H, 7-H), 2.15–1.9 (br, 12 H, CH_2 of 9-BBN), 1.79 (dd, 1 H, 4-H), 1.43 (dd, 1 H, 4-H′), 1.35–1.2 (br, 2 H, CH of 9-BBN), 1.15, 0.87 (each s, 3 H, CH_3). Coupling constants (Hz): ^2J = 12.5 (4-H, 4-H′), ^3J = 7.5 (4-H, 5-H), 10.0 (4-H′, 5-H), 10.8 (5-H, 6-H), 10.8 (6-H, 7-H), ^4J = 1.3 (4-H′, 6-H), 1.0 (5-H, 7-H). ^{13}C NMR (benzene-d_6, 75.0 MHz); δ 136.7 (C-6), 114.1 (C-5), 109.8, 108.2 (Cp), 89.8 (C-3), 67.4 (C-7), 41.2 (C-4), 31.8, 29.8 (CH_3), 34.1, 33.9, 33.6, 24.1, 23.6 (CH_2 of 9-BBN), 26.9 (CH of 9-BBN). IR (KBr): $\tilde{\nu}$ 3117, 2998, 2961, 2909, 2883, 2856, 2835, 1597 (C═C), 1237, 1023, 802 cm^{-1}.

7-(9′-Borabicyclo[3.3.1]nonane-9′-yl)-1,1-bis(η-cyclopentadienyl)-3,3-diphenyl-2-oxahafnacyclohept-4-ene (9b). A mixture of [1-(9-BBN)butadiene]hafnocene (500 mg, 1.04 mmol) and benzophenone (190 mg, 1.04 mmol) is dissolved in 40 mL of toluene, and the mixture is irradiated at −10 to 0 °C for 2h. The solution is concentrated and filtered. Crystallization at −30 °C gives 220 mg (32%) of **9b** as a yellow microcrystalline material, mp 220 °C, dec. Crystals suitable for an X-ray diffraction study

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[16] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990.

were obtained from hot benzene. Anal. Calcd for $C_{35}H_{39}OBHf$ (M_r = 665.0): C, 63.22; H, 5.91. Found: C, 63.35; H, 6.07. ^{1}H NMR (benzene-d_6): δ 7.4–7.0 (m, 10 H, Ph), 6.41 (dt, 1 H, 6-H), 5.81, 5.79 (each s, 5 H, Cp), 4.93 (m, 1 H, 5-H), 3.20 (d, 1 H, 7-H), 2.98 (dd, 1 H, 4-H), 2.15 (ddd, 1 H, 4-H′), 2.05–1.9 (br, 12 H, CH_2 of 9-BBN), 1.4–1.15 (br, 2 H, CH of 9-BBN). Coupling constants (Hz): ^2J = 12.8 (4-H, 4-H′), ^3J = 6.9 (4-H, 5-H), 9.5 (4-H′, 5-H), 11.0 (5-H, 6-H), 11.0 (6-H, 7-H), ^4J = 1.0 (6-H, 4-H′), 0.8 (5-H, 7-H). ^{13}C NMR (APT, benzene-d_6, 50.3 MHz): δ 150.5, 148.1 (C_{ipso}), 137.0 (C-6), 128.2, 127.8, 127.1, 126.72, 126.66, 126.4 (Ph), 114.2 (C-5), 110.2, 108.9 (Cp), 97.6 (C-3), 68.6 (C-7), 39.2 (C-4), 34.1, 33.5, 24.2 (CH_2 of 9-BBN); CH of 9-BBN is not observed. ^{11}B (benzene-d_6, 64.2 MHz): δ 65 ($\omega_{1/2}$ = 15 ppm). IR (KBr): $\tilde{\nu}$ 2904, 2877, 2833, 1599 (C=C), 1443, 1060, 1016, 806, 702 cm^{-1}. X-ray crystal structure analysis: $C_{35}H_{39}BHfO \cdot C_6H_6$; 0.16 × 0.36 × 0.41 mm, M_r = 743.1; cell constants $a = 8.295(1)$ Å, $b = 10.831(1)$ Å, $c = 18.926(2)$ Å, $\alpha = 93.60(1)°$, $\beta = 99.55(1)°$, $\gamma = 90.42(1)°$, and $V = 1673.2$ Å^3; $D_{calcd} = 1.47$ g cm^{-3}; $\mu = 31.18$ cm^{-1}; $F(000)$ = 752 e; $Z = 2$ (2 independent molecules in asymmetric unit); space group $P1$ (No. 1); Enraf-Nonius CAD4 diffractometer; λ = 0.710 69 Å; graphite monochromator; 7858 reflections collected ($\pm h, \pm k, +l$); $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}; ψ-scan, min/max absorption correction 0.807/1.000; 7858 independent and 7270 observed reflections $[I > 2\sigma(I)]$; 793 refined parameters; $R = 0.027$, R_w = 0.024; maximum residual electron density 0.89 e Å^{-3}. The structure was solved by the heavy-atom method, and H atom positions were calculated and kept fixed in the final refinement stage.

Bis(cyclopentadienyl)[μ-[(1.2.3-η:5-η)-1-(9′-borabicyclo[3.3.1]non-9′-yl)-5-oxo-2-pentene-1,5-diyl-*O*]](pentacarbonyltungsten)hafnium (10a). A solution of [1-(9-BBN)butadiene]hafnocene (630 mg, 1.31 mmol) in 50 mL of toluene is irradiated at −78 °C for 5 h. At this temperature hexacarbonyltungsten (600 mg, 1.70 mmol) is added and the resulting suspension stirred at −23 °C. The reaction mixture is allowed to warm to +15 °C within 16 h. The surplus of hexacarbonyltungsten is crystallized at −30 °C, and the solution is stripped in vacuo. The residue is washed three times with pentane to yield 530 mg (49%) of a yellow powder, which might be recrystallized from toluene. We obtained a 4:1 mixture of the (π-allyl)metaloxycarbene complex **10a** and its σ-allyl isomer **10b**, mp 142 °C (DSC). Anal. Calcd for $C_{28}H_{29}O_6BHfW$ (M_r = 834.7): C, 40.29; H, 3.50. Found: C, 39.57; H, 3.51. ^{1}H NMR (benzene-d_6) for **10a**: δ 5.55 (d, 1 H, 2-H), 5.37, 5.34 (each s, 5 H, Cp), 4.97 (m, 1 H, 3-H), 4.03 (ddd, 1 H, 4-H), 2.78 (d, 1 H, 1-H), 2.37 (dd, 1 H, 4-H′), 2.1–1.6 [br, 12 H, CH_2 of 9-BBN (**10a** and **10b**)], 1.5–1.35 [br, 2 H, CH of 9-BBN (**10a** and **10b**)]. Coupling constants (Hz): ^2J = 17.9 (4-H, 4-H′), ^3J = 15.2 (1-H, 2-H), 15.8 (2-H, 3-H), 4.5 (3-H, 4-H), 10.0 (3-H, 4-H′), ^4J = 0.6 (1-H, 3-H), 0.7 (2-H, 4-H), 0.5 (2-H, 4-H′). ^{1}H NMR (benzene-d_6) for **10b**: δ 6.00 (m, 1 H, 2-H), 5.63, 5.61 (each s, 5 H, Cp), 4.81 (dd, 1 H, 4-H), 4.45 (m, 1 H, 3-H), 2.58 (d, 1 H, 1-H), ~1.46 (m, 1 H, 4-H′). Coupling constants (Hz): ^2J = 12.6 (4-H, 4-H′), ^3J = 10.9 (1-H, 2-H), 10.3 (2-H, 3-H), 6.9 (3-H, 4-H), 8.6 (3-H, 4-H′), ^4J = 0.6 (1-H, 3-H), 1.5 (2-H, 4-H′). ^{13}C NMR (benzene-d_6, 50.3 MHz): **10a** δ 340.4 (C-5), 205.6 (CO_{trans}), 200.4 (CO_{cis}), 132.9 (C-2), 114.4 (C-3), 108.8, 107.5 (Cp), 69.8 (C-4), 61.0 (C-1), 33.7, 23.8 (br, CH_2 of 9-BBN), 29.5 (br, CH of 9-BBN); **10b** δ 134.0 (C-2), 111.2, 109.3 (Cp), 66.6 (C-4). ^{11}B NMR (benzene-d_6, 64.2 MHz): δ 70 ($\omega_{1/2}$ = 25 ppm). IR (KBr): $\tilde{\nu}$ 3118, 1438, 1015, 818 (Cp), 1971, 1918, 1914 (CO), 2908, 2878, 2839, 1418, 1401, 596, 576 cm^{-1}.

***trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-3-(9′-borabicyclo[3.3.1]non-9′-yl)-2,2-dimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)hafnium (11).** The tungsten carbene complex **10** (480 mg, 0.58 mmol) is dissolved in 50 mL of toluene, and the solution is cooled to −78 °C. Under stirring 40 μL of acetone (0.55 mmol) is added. After the mixture is stirred at −20 °C for 2.5 h, the solvent is removed and the residue washed with 15 mL of pentane to isolate 450 mg (92%) of **11** as a yellow solid, mp 155 °C dec. Anal. Calcd for $C_{31}H_{35}O_7BHfW$ (M_r = 892.8): C, 41.71; H, 3.95. Found: C, 41.25; H, 4.06. ^{1}H NMR (benzene-d_6): δ 5.91, 5.81, (each s, 5 H, Cp), 4.88 (d, 1 H, 4-H), 4.45 (m, 1 H, 6-H), 4.32 (m, 1 H, 5-H), 2.63 (ddd, 1 H, 6-H′), 1.99 (d, 1 H, 3-H), 2.1–1.65 (br, 12 H, CH_2 of 9-BBN), 1.4–1.2 (br, 2 H, CH of 9-BBN), 1.11, 0.90 (each s, 3 H, CH_3). Coupling constants (Hz): ^2J = 17.5 (6-H, 6-H′), ^3J = 11.3 (3-H, 4-H), 14.7 (4-H, 5-H), 4.0 (5-H, 6-H), 9.6 (5-H, 6-H′), ^4J = 0.6 (3-H, 5-H), 1.0 (4-H, 6-H), 1.0 (4-H, 6-H′). ^{13}C NMR (benzene-d_6, 50.3 MHz): δ 334.3 (C-7), 204.9 (CO_{trans}), 200.1 (CO_{cis}), 137.3 (C-4), 124.3 (C-5), 112.1, 111.7 (Cp), 83.8 (C-2), 72.1 (C-6), 59.7 (C-3), 34.0 (CH_3), 33.8, 33.6, 23.8 (CH_2 of 9-BBN), 28.5 (CH_3); CH of 9-BBN not observed. ^{11}B NMR (benzene-d_6, 64.2 MHz); δ 90 ($\omega_{1/2}$ = 25 ppm). IR (KBr): $\tilde{\nu}$ 3111, 1015, 809 (Cp), 2059, 1967, 1909 (CO), 2967, 2912, 2889, 2841, 1421, 1390, 596, 577 cm^{-1}.

***cis*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-3-(9′-borabicyclo[3.3.1]non-9′-yl)-2,2-dimethyl-7-*oxo*-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)hafnium (12).** A sealed NMR tube containing 50 mg of **11** dissolved in 0.5 mL of benzene-d_6 is heated for 2 h at 60 °C to obtain the thermodynamic 3:1 mixture of **12**:**11**. ^{1}H NMR of **12** (benzene-d_6): δ 5.90, 5.84 (each s, 5 H, Cp), 5.44 (dt, 1 H, 4-H), 5.14 (dt, 1 H, 5-H), 4.67 (ddd, 1 H, 6-H), 2.45 (dt, 1 H, 6-H′), 2.20 (d, 1 H, 3-H), 2.1–1.6 (br, 12 H, CH_2 of 9-BBN), 1.35–1.2 (br, 2 H, CH of 9-BBN), 1.04, 0.96 (each s, 3 H, CH_3). Coupling constants (Hz): ^2J = 11.9 (6-H, 6-H′), ^3J = 11.7 (3-H, 4-H), 11.1 (4-H, 5-H), 4.0 (5-H, 6-H), 11.3 (5-H, 6-H′), ^4J = 0.5 (3-H, 5-H), 1.6 (4-H, 6-H), 0.5 (4-H, 6-H′). ^{13}C NMR of **12** (benzene-d_6, 50.3 MHz): δ 338.9 (C-7), 205.5 (CO_{trans}), 199.9 (CO_{cis}), 131.0 (C-4), 121.1 (C-5), 111.9, 111.7 (Cp), 83.8 (C-2), 67.0 (C-6), 52.7 (C-3), 34.2 (CH_3), 33.9, 33.1, 23.3 (CH_2 of 9-BBN), 26.9 (CH_3); CH of 9-BBN not observed.

***cis*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2,2-dimethyl-5-(1-methyl-1-(oxo-9′-borabicyclo[3.3.1]non-9′-yl)ethyl)-7-oxo-1-oxa-3-heptene-1,7-diyl-*O*-]](pentacarbonyltungsten)hafnium (13).** The tungsten carbene complex **11** (400 mg, 0.48 mmol) is dissolved in 50 mL of toluene, and the solution is treated with 106 μL of acetone (1.44 mmol). After 2 h of stirring the slightly turbid solution is filtered, solvent is removed, and the oily residue is solidified with the aid of a small amount of pentane to yield 350 mg (75%) of **13** as an orange powder, mp 167 °C dec. Anal. Calcd for $C_{34}H_{41}O_8BHfW$ (M_r = 950.8): C, 42.95; H, 4.35. Found: C, 42.80; H, 4.73. ^{1}H NMR (benzene-d_6): δ 5.96, 5.87 (each s, 5 H, Cp), 5.34 (t, 1 H, 4-H), 5.09 (d, 1 H, 3-H), 4.82 (dd, 1 H, 6-H), 3.10 (ddd, 1 H, 5-H), 2.1–1.8 (br, 12 H, CH_2 of 9-BBN), 1.56 (dd, 1 H, 6-H′), 1.5–1.35 (br, 2 H, CH of 9-BBN), 1.40, 1.28, 1.17, 0.96 (each s, 3 H, CH_3). Coupling constants (Hz): ^2J = 16.9 (6-H, 6-H′), ^3J = 11.6 (3 H, 4-H), 11.3 (4-H, 5-H), 7.2 (5-H, 6-H), 1.9 (5-H, 6-H′). ^{13}C NMR (benzene-d_6, 50.3 MHz); δ 341.2 (C-7), 205.0 (CO_{trans}), 200.2 (CO_{cis}), 134.7, 131.0 (C-3 and C-4), 112.3, 112.0 (Cp), 81.2 (C-2), 77.5 (C-8), 73.3 (C-4), 46.3 (C-6), 33.6, 23.5 (CH_2 of 9-BBN), 33.1, 31.5, 28.9, 27.4 (CH_3), 27.1 (CH of 9-BBN). ^{11}B NMR (benzene-d_6, 64.2 MHz): δ 55.5 ($\omega_{1/2}$ = 20 ppm). IR (KBr): $\tilde{\nu}$ 3110, 1029, 807 (Cp), 2058, 1966, 1920 (CO), 2967, 2921, 2889, 2839, 1402, 1387, 1161, 596, 575 cm^{-1}.

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Supplementary Material Available: Drawings of molecules 1 and 2 and tables giving the details of the X-ray crystal structure analysis, anisotropic thermal parameters, and bond lengths and angles for **9b** (8 pages). Ordering information is given on any current masthead page.

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