Sequential π-Ligand Exchange from Metallacyclopentanes: Synthesis and Structure of 1,1-Bis(cyclopentadienyl)-2,3-diphenyl-1-hafnacyclopent-2-ene

Gerhard Erker,†,§ Ulrich Dorf,† and Arnold L. Rheingold*‡

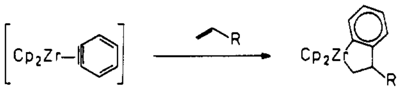
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr, Germany, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

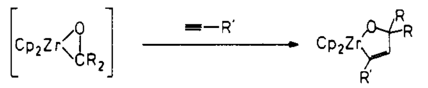
Received April 17, 1987

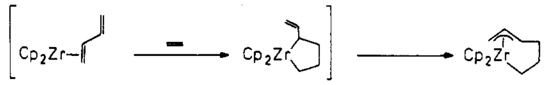
Bis(cyclopentadienyl)hafnacyclopentane was prepared by reaction of Cp_2HfCl_2 and 1,4-dilithiobutane. Thermolysis of the five-membered metallacycle at 80 °C with butadiene results in liberation of 1 equiv of ethylene and formation of an (ethylene)hafnocene/butadiene (1:1) addition product: (1-3:6-η-2-hexenediyl)hafnocene. Similarly, the hafnacyclopentane reacted with diphenylacetylene under suitable controlled reaction conditions at 80 °C in benzene to give a 36% yield of the title compound. 1,1-Bis(cyclopentadienyl)-2,3-diphenyl-1-hafnacyclopent-2-ene crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 8.901$ (2) Å, $b = 9.871$ (2) Å, $c = 13.199$ (3) Å, $\alpha = 78.19$ (2)°, $\beta = 72.49$ (2)°, $\gamma = 65.62$ (2)°, $V = 1003.0$ (4) Å^3, $Z = 2$, and $R(F) = 2.76\%$. The four ring carbons are nearly planar. Bond distances within the metallacyclic five-membered ring system are Hf–C(1) = 2.255 (7), C(1)–C(2) = 1.529 (7), C(2)–C(3) = 1.513 (8), C(3)–C(4) = 1.337 (8), and C(4)–Hf = 2.268 (4) Å. Though the ring system is somewhat strained (bond angles C(1)–C(2)–C(3) = 115.6 (5)° and Hf–C(4)–C(3) = 110.6 (3)°), the strong hafnium to carbon σ-bonds protect it from rapidly reacting further with additional diphenylacetylene to give the very stable metallacycle $Cp_2\overline{Hf(\text{-}CPh{=}CPhCPh{=}C}Ph)$.

Five-membered metallacycles of the transition elements are important organometallic substrates. They may serve as useful reagents in the synthesis of organic compounds. Several complexes of this type have been regarded as being intermediates in metal-catalyzed transformations of organic π-systems.[1] Simple metallacyclopentanes are abundant.[2] They are easily prepared either by treating metal halides with 1,4-butane dianion equivalents[3] or via coupling of two olefinic moieties at a prereduced metal complex fragment.[4] The thermal stability of metallacyclopentanes relative to their open-chain equivalents seems to originate from unfavorable stereoelectronic features of the (usually envelope-shaped) metallacyclic systems with regard to intramolecular β-hydride elimination pathways.[5] Those thermally induced reactions of metallacyclopentane systems which are observed often start with β-CC bond fission to give bis(olefin)metal complexes that may then react further via elimination of an organic π-ligand.

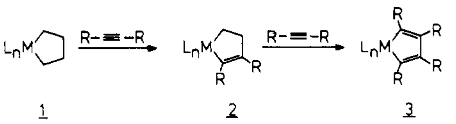
It is this facile reaction that often makes the formation of five-membered metallacycles other than the "symmetrical" metallacyclopentanes very unfavorable. Notable exceptions in the early-transition-metal series are systems like (1)–(3), where facile cleavage of the metallacyclic rings, once they are formed, is precluded by special thermodynamic features or consecutive stabilizing reactions.[6-8]


(1)


(2)


(3)

We have now observed that even in the absence of such additional stabilizing effects it is possible to prepare a metallacyclopent-2-ene complex and prevent it from reacting to give the often preferentially formed "symmetrical" product of disproportionation or from further reacting with the added organic π-ligand.[9]



(4)

---

† Max-Planck-Institut für Kohlenforschung.

‡ University of Delaware.

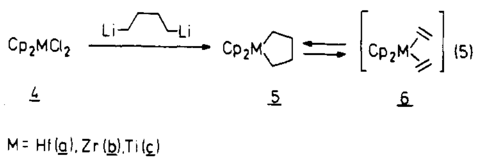
§ Present address: Institut für Organische Chemie der Universität, Am Hubland, D-8700 Würzburg, Germany.

(1) See, e.g.: Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. Bönnemann, *Angew. Chem.* **1978**, *90*, 517. Hong, P.; Yamazaki, H. *Tetrahedron Lett.* **1977**, 1333; *Synthesis* **1977**, 50. Weissberger, E.; Page, G. *J. Am. Chem. Soc.* **1977**, *99*, 147. Weissberger, E.; Laszlo, P. *Acc. Chem. Res.* **1976**, *9*, 209. Schrauzer, G. N. *Adv. Catal.* **1968**, *18*, 373. Frazer, A. R.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1979**, *95*, 253. Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376. Blackborow, J. R.; Feldhoff, U.; Grevels, F.-W.; Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1979**, *173*, 253. Binger, P. *Angew. Chem.* **1972**, *84*, 352; *Synthesis* **1973**, 427. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416. Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515, 6366. For many additional examples see: *Houben-Weyl, Methoden der organischen Chemie*; Falbe, J., Ed.; Thieme Verlag: Stuttgart, 1986; Vol. E. 18/part 2.

0276-7333/88/2307-0138$01.50/0

We describe here the formation of a bis(cyclopentadienyl)hafnacyclopent-2-ene from **1** ((L_nM = Cp_2Hf) and diphenylethyne. The corresponding product has been isolated and thoroughly characterized, including an X-ray crystal structure determination.

Preparation and Spectroscopic Characterization of the Hafnacyclopent-2-ene Product. Hafnacyclopentane **5a** has been shown to be an easily available precursor for the thermal generation of the elusive bis(cyclopentadienyl)(η^2-ethylene)hafnium complex that has found many interesting uses as a versatile organometallic building block.[10] In contrast to the metallacyclopentanes derived from Cp_2Ti and Cp_2Zr,[2a,b] the Cp_2Hf analogue **5a** is of sufficient thermal stability to be handled easily at ambient temperature. It has been prepared by coupling 2 equiv of ethylene at the Cp_2Hf unit.[11] However, it is more conveniently prepared by addition of 1,4-dilithiobutane (obtained from 1,4-dichlorobutane and lithium powder containing 2% sodium) to bis(cyclopentadienyl)hafnium dichloride in ether at low temperature. After conventional workup at ambient temperature bis(cyclopentadienyl)hafnacyclopentane **5a** is obtained in good yield. In contrast to the thermally sensitive bis(cyclopentadienyl)titanacyclopentane and -zirconacyclopentane analogues, the metallacyclic hafnium complex is thermally quite stable. While the former complexes can only be handled in the presence of additional ethylene in solution at room temperature without decomposition, the hafnium complex **5a** does not decompose even in the absence of the kinetically stabilizing olefinic ligand.



(5)

The metallacyclopentane **5a** was characterized spectroscopically, by elemental analysis and chemical degradation. Hydrolysis with aqueous acid yielded the organic product *n*-butane. Treatment of **5a** with a stoichiometric amount of bromine in benzene-d_6 led to the formation of 1,4-dibromobutane and hafnocene dibromide.

In the ^{13}C NMR spectrum (benzene-d_6) $Cp_2Hf(c\text{-}C_4H_8)$ (**5a**) exhibits three signals at δ 109.2 (d, $^1J(CH)$ = 178 Hz, Cp), 43.1 (t, $^1J(CH)$ = 119 Hz, CH_2), and 26.3 (t, $^1J(CH)$ = 125 Hz, CH_2). At δ 5.80 a singlet representing 10 Cp hydrogens appears in the ^1H NMR spectrum (benzene-d_6, relative TMS). Methylene hydrogens give rise to multiplet absorption signals at δ 2.23 (4 H) and 0.89 (4 H). A comparison with NMR spectra of the analogous titanium and zirconium complexes **5c** and **5b**, respectively, as well as metallacyclopentane ring systems derived from other transition-metal complex fragments (see Table I), revealed a considerable variation of the relative chemical shift of α- vs β-methylene resonances with the specific nature of the metal center.

A correct a priori assignment of the observed methylene NMR signals to metallacyclopentane α- and β-CH_2 moieties appeared, therefore, quite uncertain. From the fol-

---

(2) (a) Dorf, U.; Engel, K.; Erker, G. *Angew. Chem.* **1982**, *94*, 916. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (c) Manriquez, J. M.; McAllister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (d) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zucchi, M. *J. Chem. Soc. Dalton Trans.* **1983**, 967. (e) Mayer, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157. (f) For additional examples see: Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551. Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1978**, *161*, 371. Bond, A.; Lewis, B.; Green, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1109. Grevels, F.-W.; Feldhoff, U.; Leitich, J.; Krüger, C. *J. Organomet. Chem.* **1976**, *118*, 79. Grevels, F.-W.; Schulz, D.; Koerner von Gustorf, E. *Angew. Chem.* **1974**, *86*, 558. Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1978**, *154*, C16. Smith, G.; McLain, S. J.; Schrock, R. R. *J. Organomet. Chem.* **1980**, *202*, 269. Green, M.; Howard, J. A. K.; Mitrprachachon, P.; Pfeffer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1979**, 306. Diversi, P.; Ingrosso, G.; Lucherini, A.; Murtas, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1633. Ingrosso, G.; Immirzi, A.; Porri, L. *J. Organomet. Chem.* **1973**, *60*, C35. Diversi, P.; Ingrosso, G.; Immirzi, A.; Porzio, W.; Zucchi, M. *J. Organomet. Chem.* **1977**, *125*, 253.

(3) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. Grubbs, R. H.; Miyashita, A.; Liu, M.-I. M.; Burk, P. *J. Am. Chem. Soc.* **1977**, *99*, 3863. Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1977**, 52. Diversi, P.; Ingrosso, G.; Lucherini, A.; Martinelli, P.; Benetti, M.; Pucci, S. *J. Organomet. Chem.* **1979**, *165*, 253. (b) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 238; **1981**, 319. Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1980**, 476. Lappert, M. F.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1980**, 1284. Engelhardt, L. M.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 893. Leung, W.-P.; Raston, C. L. *J. Organomet. Chem.* **1982**, *240*, C1.

(4) (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) Related examples: Caddy, P.; Green, M.; O'Brian, E.; Smart, L. E.; Woodward, P. *Angew. Chem.* **1977**, *89*, 671. Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. Erker, G.; Lecht R. *J. Organomet. Chem.* **1986**, *311*, 45 and references cited therein.

(5) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808. Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1473.

(6) (a) Structures: McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697. Bennett, M. A.; Hambley, T.-W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Reactions: Dvorak, J.; O'Brien, R. J.; Santo, W. *J. Chem. Soc. D* **1970**, 411. Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750. Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. Berkovich, E. G.; Shur, V. B.; Vol'pin, Me. E.; Lorenz, B.; Rummel, S.; Wahren, M. *Chem. Ber.* **1980**, *113*, 70. Shur, V. B.; Berkovich, E. G.; Vol'pin, M. E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36. Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246. Chamberlain, L. R.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665. Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572. Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310. de Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F.; Erker, G.; Czisch, P.; Mynott, R.; Wallis, J. M.; Krüger, C. *Angew. Chem.* **1986**, *98*, 641.

(7) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921; *Inorg. Chem.* **1978**, *17*, 2995. Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29. Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050. Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462. Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. Choukroun, R.; Dahan, F.; Gervais, D. *J. Organomet. Chem.* **1984**, *266*, C33. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385.

(8) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300. Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71. Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462. Yasuda, H.; Kajihara, A.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945. Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1984**, *268*, C7.

(9) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123. Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962. Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006 (loc. cit.)

(10) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059.

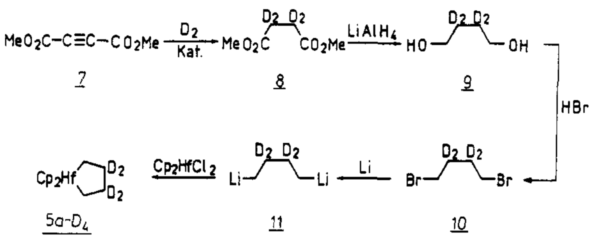
(11) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1982**, *94*, 915.

Table I. Selected NMR Data for Metallacyclopentane Complexes $L_nM-CH_2CH_2CH_2CH_2$ (1)[a]

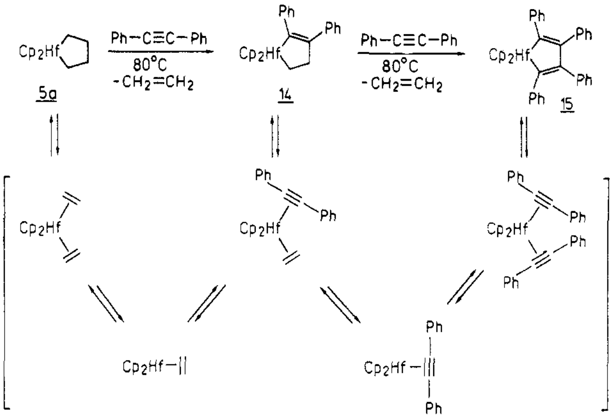
	^{1}H NMR			^{13}C NMR			
L_nM	Cp	H1	H2	Cp	C1	C2	ref
Cp_2Hf^b	5.85	0.89	2.23	109.2	43.1 (119)	26.2 (125)	*e*
Cp_2Zr^c	6.31	0.89	1.66	110.7	39.2 (124)	28.1 (125)	2a
Cp_2Ti^c	6.31	1.14	1.52	114.1	56.6 (124)	33.2 (124)	2a,b
$Cp_2{}^*Zr^b$		0.50	1.95		49.5 (119)	29.8 (124)	2c
Cp_2Mo^b	4.14	1.80^d		88.3	14.5	37.3	2d
$Cp^*(C_4H_6)Ta^b$	2.15/3.10		0.33		54.9 (118)	36.7 (124)	2e

[a] δ scale, relative TMS; ^1J(CH) in Hz; position 1, terminal, position 2, internal CH_2; relative assignments as given in the corresponding reference. [b] Benzene-d_6 at ambient temperature. [c] $CDCl_3$ at −50 °C. [d] Not resolved. [e] This work.

Scheme I



Scheme II

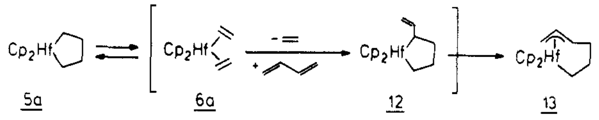


lowing deuterium-labeling study, a correct a posteriori assignment of the high-field ^{1}H NMR signal belonging to the α-methylene group of **5a** could be achieved.

The selectively deuteriated organic halide 1,4-dibromo-2,2,3,3-tetradeuteriobutane was synthesized via the reaction sequence outlined in Scheme I in analogy to a literature procedure.[12] Treatment of the 1,4-dibromide **10** with lithium produced the corresponding 1,4-dilithiobutane reagent, albeit in much poorer yield and purity as compared to those of the analogous reaction starting from the 1,4-dichlorobutane reagent. However, it was possible to obtain a small quantity of 1,1-bis(cyclopentadienyl)-3,3,4,4-tetradeuteriohafnacyclopentane (**5a**-d_4) after treatment with Cp_2HfCl_2. Compound **5a**-d_4 exhibited a singlet at δ 5.80 (s, 10 H, Cp) and a broad signal centered at δ 0.9 representing four hydrogen atoms.

Thermolysis of **5a**-d_4 in benzene-d_6 solution changed the appearance of the ^{1}H NMR spectrum. The intensity of the δ 0.9 signal decreased. A new broad signal at δ 2.2 appeared. NMR spectra were taken at different times at 80 °C giving an approximate half-life of $\tau_{1/2} \approx 40$ min for **5a**-d_4 with regard to the observed equilibration process, eventually leading to equal intensities (representing two hydrogens each) of the methylene ^{1}H signals. Analogous to similar observations reported for other metallacyclopentane complexes metallacyclic ring opening (to give a metallocene bis(olefin) complex) followed by ethylene ligand rotation and ring closure would represent a simple explanation for the deuterium scrambling.[13]

Independent experiments indeed have revealed that the C(2)–C(3) bond of the metallacyclopentane **5a** is readily cleaved at temperatures above 80 °C. Thermolysis of a toluene solution of the hafnacyclopentane in the presence of excess butadiene at 90 °C (2 h) results in liberation of 1 equiv of ethylene from the metallacycle. The formally resulting reactive intermediate (η^2-ethylene)hafnocene is not stable under the reaction conditions. It takes up 1 equiv of the conjugated diene. Subsequent carbon carbon coupling would yield a 2-vinylmetallacyclopentane **12**. However, this (σ-allyl)metallocene complex is not stable under the reaction conditions applied.[11] We consequently have isolated the corresponding isomeric metallacyclic (π-allyl)hafnocene complex **13**.



(6)

There is a similar reaction taking place upon thermolyzing **5a** in benzene solution in the presence of tolane. Prolonged heating of the metallacycle with excess of the diphenylacetylene reagent not unexpectedly led to a clean formation of the known metallacycle[14] 1,1-bis(cyclopentadienyl)-2,3,4,5-tetraphenyl-1-hafnacyclopentadiene (**15**). This very stable reaction product is formally derived from **5a** by extrusion of two ethylene units and incorporation and CC coupling of two acetylene moieties (see Scheme II). It was likely that this reaction occurred stepwise. We were able to demonstrate this in fact experimentally by isolating an intermediate of this exchange process. When the reaction conditions were adjusted carefully (see Experimental Section), 1,1-bis(cyclopentadienyl)-2,3-diphenyl-1-hafnacyclopentene (**14**) was isolated in a 36% yield from the reaction of bis(cyclopentadienyl)hafnacyclopentane with tolane (equimolar in benzene at 80 °C). The metallacyclopentene **14** is completely stable at ambient temperature in an inert atmosphere. It is characterized by ^{13}C NMR signals at δ 191.9 [s, C(1)], 150.8 [s, C(2)], 31.7 [t, ^1J(CH) = 125 Hz, C(3)], 44.9 [t, ^1J(CH) = 122 Hz, C(4)], and 111.2 [d, ^1J(CH) = 173 Hz, Cp] in addition to typical absorptions due to two chemically different phenyl groups. In the ^{1}H NMR spectrum, we find signals at δ 7.1–6.6 (m, 10 H, Ph), 5.83

---

(12) Buschweller, C. H.; Bhat, G.; Lefendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

(13) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300.

(14) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

Table II. Crystal Parameter, Data Collection, and Refinement of [(η^5-C_5H_5)$_2$Hf($CH_2CH_2CPh{=}CPh$)] (14)

formula	$C_{26}H_{24}Hf$	V, Å^3	1003.0 (4)
cryst system	triclinic	Z	2
space group	$P\bar{1}$	$F(000)$	504
a, Å	8.901 (2)	ρ(calcd), g cm^{-3}	1.705
b, Å	9.871 (2)	color	yellow
c, Å	13.199 (3)	cryst dimens, mm	0.31 × 0.33 × 0.36
α, deg	78.19 (2)	μ, cm^{-1}	54.8
β, deg	72.49 (2)	transmissn (max/min)	0.132/0.068
γ, deg	65.62 (2)	T, K	294
diffractometer	Nicolet R3	std rflns	3 stds/197 rflns (17% decay)
radiation	Mo Kα (λ = 0.71073 Å)	rflns collctd	3764
monochromator	graphite	unique rflns	3534
scan technique	ω (full profile)	unique rflns ($F_o \geq 3\sigma(F_o)$)	3317
scan speed, deg min^{-1}	var 3–20	octants collected	$\pm h,\pm k,+l$
scan range, deg	$4 \leq 2\theta \leq 50$		
R(int), %	1.50	g^a	0.005
R_F, %	2.76	mean Δ/σ, last cycle	0.083
R_{wF}, %	2.83	highest peak, final diff map, e Å^{-3}	1.1 (0.89 Å Hf)
GOF	1.63		

$^a w = \sigma^2(F_o) + gF_o^2$.

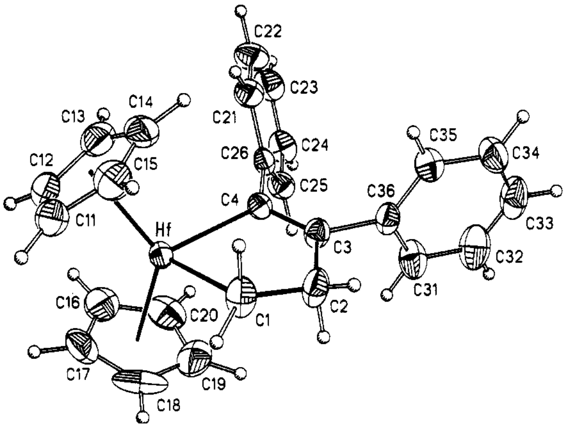


Figure 1. Molecular structure and labeling scheme for $Cp_2Hf(CH_2CH_2CPh{=}CPh)$ drawn with 45% thermal ellipsoids. Hydrogen atoms are drawn with arbitrary radii.

(s, 10 H, Cp), 3.03 (m, 2 H, internal CH_2[15]), and 1.21 (m, 2 H, $HfCH_2$–). With additional tolane 14 reacts at 80 °C to give the "symmetrical" metallacycle 15 plus ethylene.

X-ray Crystal Structure Analysis of the Hafnacyclopentene 14. $Cp_2Hf(CH_2CH_2CPh{=}CPh)$ (14) crystallizes as discrete unassociated molecules (Figure 1). The Hf coordination geometry is distorted tetrahedral (Table II). The (ring centroid)–Hf–(ring centroid) angle is expanded by steric effects to 130.82 (2)°, while the C(1)–Hf–C(4) angle is reduced to 80.2 (2)°; the average angle about Hf is 107.6°.[16] The most prominent feature of the structure is the presence of the hafnacyclopentene ring system. The four ring carbon atoms are nearly planar (maximum deviation at C(3), 0.059 Å);[17] Hf is displaced 0.52 Å from the [C(1),C(2),C(3),C(4)] plane. The ring C–C distances clearly reveal the presence of localized multiple bonding between C(3) and C(4): C(1)–C(2) = 1.529 (7) Å and C(2)–C(3) = 1.513 (8) Å as compared to C(3)–C(4) = 1.337 (8) Å. The two Hf–C distances are very similar, suggesting little difference in the mode of bonding in the organometallic linkages in spite of the different hybridizations of C(1) and C(4): C(1)–Hf = 2.255 (1) Å and C(4)–Hf = 2.268 (4) Å. The C(4)–C(26) bond is, within experimental error, in the metallacyclic plane whereas the C(3)–C(36) bond is inclined 8.30° from the plane in a direction opposite to the Hf atom deviation.

The bonding features of 14 should be compared with those of the tetraphenylhafnacyclopentadiene 15[14] and the structurally closely related titanacycle $Cp_2TiOCMe_2C(Ph){=}C(Ph)$ (16).[18] The latter shows an even more flattened, distorted, envelope-shaped five-membered metallacyclic framework with the metal being oriented away from the C_3O plane by only 0.12 Å. This leads to characteristically small values of the endocyclic angles of the five-membered metallacycle for 16 (e.g. Ti–C–C = 110.1 (3)°). This effect is smaller for the hafnacyclopentadiene 15. Average values of 114° and 117° have been found for the Hf–C(sp^2)–C(sp^2) and C(sp^2)–C(sp^2)–C(sp^2) angles in the planar metallacyclic ring.[14] The remaining C(sp^2)–Hf–C(sp^2) angle is 78.7 (8)° and thus only marginally different from the corresponding value observed for 14. Metallacyclopentene 14 seems to be somewhat more strained, though, as compared to 15. This becomes evident by a comparison of the corresponding Hf–C(sp^2) bond lengths. Complex 14 exhibits a longer bond distance between the metal atom and the adjacent carbon center bearing the phenyl substituent than the metallole 15. An increased ring strain of 14 is also reflected in the respective bond angles. The C(1)–Hf–C(4), C(2)–C(3)–C(4) (122.3 (4)°), and Hf–C(1)–C(2) (106.7 (4)°) angles are not deviating much from normal, while the bond angles C(1)–C(2)–C(3) (115.6 (5) Å) and Hf–C(4)–C(3) (110.6 (3)°) are considerably different from expected values of sp^3- and sp^2-hybridized carbon centers.

---

(15) Tentative relative assignment analogous to 5a-d_4, see above.

(16) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium Compounds*; Wiley: New York, 1986.

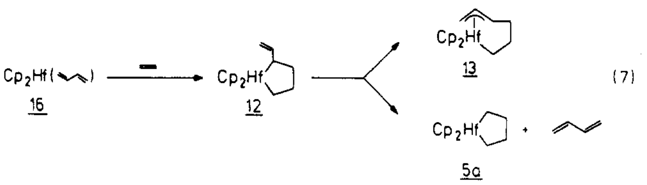
(17) See for a comparison: Biefeld, C. G.; Grubbs, R. H.; Eick, H. A. *Inorg. Chem.* **1973**, *12*, 2166. Schubert, U.; Rengstl, A. *J. Organomet. Chem.* **1979**, *166*, 323. Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6462. Jolly, P. W.; Krüger, C.; Salz, R.; Sekutowski, J. C. *J. Organomet. Chem.* **1979**, *165*, C39. Binger, P.; Doyle, M. J.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch.* **1979**, *34b*, 1289. Legon, A. C. *Chem. Rev.* **1980**, *80*, 231. Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zucchi, M. *J. Chem. Soc., Dalton Trans.* **1983**, 967. Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129 (loc. cit.).

(18) Shur, V. B.; Burlakov, U. V.; Yanovsky, A. I.; Petrovsky, P. V.; Struchkov, Y. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1985**, *297*, 51.

Conclusions

Not unexpectedly, it has been demonstrated by our experiment that the exchange of ethylene units from bis(cyclopentadienyl)hafnacyclopentane **5a** occurs in a stepwise fashion; i.e., one C_2H_4 unit is cleaved off at a time. This feature makes **5a** a reliable (η^2-ethylene)metallocene source that is easy to prepare and handle.

Rather surprising to us was the observation that product **14**, derived from the hafnacyclopentane system by exchange of only one ethylene unit, could be isolated. In fact, this metallacyclopentene system turned out to be rather stable although its further reaction with tolane to give **15** has been shown to be thermodynamically very favorable. We have previously found another example of such rather unusual resting of a potentially doubly exchanging system at an intermediate stage. A five-membered metallacyclic σ-allyl metallocene complex **12** was identified spectroscopically in the reaction of (butadiene)$HfCp_2$ with ethylene, albeit isolation was precluded by its thermal lability.[11]



In the example presented here, the monoexchange product **14** is much more stable and can be isolated. We think that the successful isolation of an intermediate stage of the olefin/alkylene ligand exchange reaction sequence (Scheme II) may be attributed to the higher stability of the hafnium to carbon σ-bond as compared to that of its zirconium or titanium analogues.[19] This prominent feature manifests itself rather drastically in the substantially different thermal stabilities of the bis(cyclopentadienyl)-metallacyclopentane starting materials. As we see now, it also helps to create energy wells which under suitable conditions protect intermediates in sequential reaction schemes from reacting further.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} under argon prior to use. Deuteriated solvents benzene-d_6 and toluene-d_8 were treated with sodium/potassium alloy, $CDCl_3$, and CD_2Cl_2 with P_4O_{10} (Sikapent/Merck), distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 80 FT (^1H, 80 MHz, variable temperature), Bruker WM 300 FT (^{13}C, 75.5 MHz), and Bruker WH 400 FT (^1H, 400 MHz; ^{13}C, 100.6 MHz); IR, Nicolet 7199 FT IR spectrometer; MS, Finnegan 311 A (70 eV), m/e values given correspond to isotopes of highest natural abundance. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. Melting points are uncorrected.

Bis(cyclopentadienyl)hafnium Dichloride. The synthesis of hafnocene dichloride was carried out in close analogy to a literature procedure.[20] Starting from 96 g (0.30 mol) of hafnium tetrachloride (purchased from Alfa Ventron), we obtained 73 g (64%) of pure crystalline Cp_2HfCl_2. ^1H NMR (benzene-d_6): δ 5.85 (s, Cp).

1,4-Dilithiobutane was prepared according to a published procedures.[2b,3a] A solution of 30 g (0.24 mol) of 1,4-dichlorobutane in 100 mL of ether was added dropwise over a period of 2 h at 0 °C to a stirred suspension of 8 g (1.15 mol) of lithium powder (containing 2% sodium, purchased from Metallgesellschaft) in 150 mL of ether. The resulting mixture was stirred at 0 °C for an additional 24 h and then filtered to give a 0.75 M solution (250 mL, 79% yield) of 1,4-dilithiobutane in ether.

1,1-Bis(cyclopentadienyl)-1-hafnacyclopentane. A. A NMR sample of (3:6-η-1-hexenediyl)hafnocene (**12**) was prepared from 30 mg (0.08 mmol) of (*s-trans*-η^4-butadiene)hafnocene and ethylene in 0.6 mL of toluene-d_8. At 60 °C this was reacted with additional ethylene in a sealed NMR tube. ^1H NMR control of the reaction at various times revealed an almost quantitative formation of the hafnacyclopentane **5a** under these conditions.

B. To a suspension of 10 g (26.3 mmol) of hafnocene dichloride in 150 mL of ether at −78 °C was added 35 mL of a 0.75 M ethereal solution of 1,4-dilithiobutane (26.3 mmol). The reaction mixture was warmed to −30 °C, stirred at that temperature for 2 h, and then allowed to warm up to room temperature. Solvent was removed in vacuo. The residue was extracted with 400 mL of pentane. The pentane solution was filtered and evaporated to dryness to give 6.85 g (71%) of analytically pure amorphous bis(cyclopentadienyl)hafnacyclopentane. A solution of 6.85 g of **5a** in 20 mL of dichloromethane was cooled to −50 °C to give 3.2 g (33% from Cp_2HfCl_2) of crystalline $Cp_2Hf(C_4H_8)$ (**5a**), mp 126 °C dec. Anal. Calcd for $C_{14}H_{18}Hf$ (3664.79); C, 46.10; H, 4.97. Found: C, 46.27; H, 4.79. ^1H NMR (benzene-d_6): δ 5.80 (s, 10 H, Cp), 2.23 (m, 4 H, β-CH_2), 0.89 (m, 4 H, α-CH_2); ^{13}C NMR (benzene-d_6): δ 109.2 (d, 178 Hz, Cp), 43.1 (t, 119 Hz, CH_2), 26.3 (t, 125 Hz, CH_2).

Synthesis and Thermolysis of 1,1-Bis(cyclopentadienyl)-3,3,4,4-tetradeuterio-1-hafnacyclopentane. The preparation of $Cp_2Hf(C_4H_4D_4)$ (**5a**-d_4) was carried out according to the procedure of the undeuteriated hafnacyclopentane as described above. Instead of 1,4-dichlorobutane specifically labeled 1,4-dibromo-2,2,3,3-tetradeuteriobutane (prepared according to a literature procedure[13]) was employed as starting material for the preparation of the 1,4-dilithiobutane reagent. The formation of this reagent starting from the 1,4-dibromobutane substrate turned out to proceed far less cleanly as with use of 1,4-dichlorobutane. This effect had been noted in the literature before.[2b,3a] The deuteriated hafnacyclopentane **5a**-d_4 was, therefore, not obtained in a pure form. For purification 0.5 g of the crude material was recrystallized from 1 mL of dichloromethane. At −70 °C ca. 5 mg of pure **5a**-d_4 (as judged by ^1H NMR) was obtained. The material was dissolved in 0.5 mL of benzene-d_6 and thermolyzed at 80 °C. ^1H NMR spectra were monitored at intervals of 10 min. ^1H NMR (benzene-d_6, before thermolysis): δ 5.80 (s, 10 H, Cp), 0.90 (br s, 4 H, α-CH_2). ^1H NMR (benzene-d_6, after thermolysis): δ 5.80 (s, 10 H, Cp), 2.20 (m, 2 H, β-CH_2), 0.9 (m, 2 H, α-CH_2).

(1-3:6-η-2-Hexenediyl)hafnocene (13). A solution of 6.6 g (18.1 mmol) of bis(cyclopentadienyl)hafnacyclopentane (**5a**) and 10 mL of liquid butadiene (110.0 mmol) in 100 mL of toluene was thermolyzed in a sealed glass vessel at 90 °C for 2 h. The solution was cooled to room temperature. Solvent and excess butadiene were removed in vacuo to give 5.5 g (78%) of a rather pure yellow amorphous **13**. A sample of 1 g of the crude reaction product was recrystallized from 30 mL of benzene (reflux) to give pure crystalline **13**, mp 159 °C. Anal. Calcd for $C_{16}H_{20}Hf$ (390.82): C, 49.17; H, 5.16. Found: C, 49.33; H 5.08. ^1H NMR (benzene-d_6, ambient temperature): δ 5.11, 5.17 (s, 5 H each, Cp), 4.67 (m, 1 H, H2), 4.49 (m, 1 H, H3), 3.42 (m, 1 H, H5-c), 2.68 (m, 1 H, H5-t), 2.22 (m, 1 H, H4-c), 1.56 (m, 2 H, H1-syn plus H4-t), 1.09 (m, 1 H, H1-anti), 0.76 (m, 1 H, H6-c), 0.47 (m, 1 H, H6-t). ^1H NMR (toluene-d_8, +96 °C): δ 5.20 (s, 10 H, Cp), 4.70 (m, 1 H, H2), 4.50 (m, 1 H, H3), 3.00 (m, 2 H, H5), 1.95 (m, 2 H, H4), 1.30 (m, 2 H, H1), 0.65 (m, 2 H, H6) Automerization barrier (derived from the Cp coalescence): $\Delta G^{\ddagger}$ (50 °C) = 17.6 ± 0.3 kcal/mol. ^{13}C NMR (benzene-d_6): δ 118.5, 119.0 (d each, 147 Hz, C2, C3), 104.0, 104.7 (d each, 178 Hz, Cp), 51.0 (t, 124 Hz, C4), 34.5 (dd, 146/152 Hz, C1, and t, 127 Hz, C5), 32.9 (t, 116 Hz, C6).

---

(19) Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C.; *J. Organomet. Chem.* **1981**, *204*, 67. Hunter, W. E.; Hrncir, D. C.; VannBynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *3*, 215.

(20) Rausch, M. D.; Gordon, H. B.; Samuel, E. *J. Coord. Chem.* **1971**, *1*, 141.

Table III. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³)

atom	*x*	*y*	*z*	U_{iso}[a]
Hf	2309.5 (2)	2091.9 (2)	2681.9 (1)	37 (1)
C(1)	437 (7)	975 (6)	2984 (6)	60 (3)
C(2)	−1334 (7)	2214 (6)	3159 (6)	60 (3)
C(3)	−1396 (6)	3768 (5)	2703 (4)	43 (2)
C(4)	1 (6)	4097 (5)	2358 (4)	37 (2)
C(11)	4928 (8)	248 (8)	1632 (5)	73 (3)
C(12)	5228 (8)	1530 (9)	1518 (5)	72 (3)
C(13)	4152 (8)	2629 ((8)	949 (5)	70 (3)
C(14)	3147 (8)	2040 (8)	701 (5)	67 (3)
C(15)	3662 (9)	562 (8)	1116 (5)	73 (3)
C(16)	3581 (9)	2840 (9)	3803 (5)	73 (4)
C(17)	3935 (9)	1361 (10)	4076 (5)	86 (4)
C(18)	2423 (13)	1159 (9)	4568 (5)	95 (5)
C(19)	1118 (10)	2612 (11)	4605 (5)	87 (4)
C(20)	1898 (10)	3593 (8)	4139 (5)	73 (4)
C(21)	516 (7)	6024 (6)	891 (4)	52 (2)
C(22)	462 (9)	7466 (7)	526 (5)	66 (3)
C(23)	−222 (8)	8553 (6)	1226 (5)	65 (3)
C(24)	−814 (8)	8194 (6)	2282 (5)	58 (3)
C(25)	−770 (7)	6766 (5)	2651 (4)	48 (2)
C(26)	−104 (6)	5645 (5)	1971 (4)	39 (2)
C(31)	−4135 (7)	5651 (7)	3617 (6)	69 (3)
C(32)	−5788 (9)	6662 (9)	3650 (7)	87 (4)
C(33)	−6484 (8)	6908 (7)	2827 (7)	80 (3)
C(34)	−5556 (8)	6177 (8)	1940 (6)	77 (3)
C(35)	−3903 (7)	5170 (7)	1886 (5)	66 (3)
C(36)	−3166 (6)	4893 (5)	2723 (4)	47 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_5)_2\overline{Hf(CH_2CH_2CPh{=}CPh)}]$

(a) Bond Distances

Hf–C(1)	2.255 (7)	C(1)–C(2)	1.529 (7)
Hf–C(4)	2.268 (4)	C(2)–C(3)	1.513 (8)
Hf–CNT(1)[a]	2.201 (4)	C(3)–C(4)	1.337 (8)
Hf–CNT(2)	2.206 (4)		

(b) Bond Angles

CNT(1)–Hf–CNT(2)	130.8 (2)	C(1)–Hf–C(4)	80.2 (2)
CNT(1)–Hf–C(1)	108.8 (2)	Hf–C(1)–C(2)	106.7 (4)
CNT(2)–Hf–C(1)	110.8 (2)	C(1)–C(2)–C(3)	115.6 (5)
CNT(1)–Hf–C(4)	108.1 (2)	C(2)–C(3)–C(4)	122.3 (4)
CNT(2)–Hf–C(4)	106.6 (2)		

[a] CNT(1) = centroid of C(11)–C(15) ring; CNT(2) = centroid of C(16)–C(20) ring.

Electrophilic Cleavage of Bis(cyclopentadienyl)hafnacyclopentane (5a). A. A solution of 50 mg (0.14 mmol) of hafnacyclopentane **5a** in 0.5 mL of benzene-d_6 was exposed to an atmosphere containing gaseous elemental bromine. Bis(cyclopentadienyl)hafnium dibromide was formed which partially precipitated. The 1,4-dibromobutane formed was identified by a comparison of the ^{1}H NMR spectrum with authentic material. ^{1}H NMR (benzene-d_6): δ 6.0 (s, Cp_2HfBr_2), 3.0, 1.6 (m, $C_4H_8Br_2$).

B. To a solution of 110 mg (0.3 mmol) of hafnacyclopentane **5a** in 2 mL of benzene was added 50 mg of dry silica gel and 0.25 mL of saturated aqueous ammonium chloride solution. The mixture was stirred for 2 h at ambient temperature. Volatile reaction products were then transferred in vacuo with the solvent. Gas chromatic analysis of the condensate (dimethylsulfolane, 4 m, T_s = 30 °C) revealed that *n*-butane (t_R = 2.4 min) was the major hydrolysis product in addition to cyclopentadiene.

1,1-Bis(cyclopentadienyl)-2,3-diphenyl-1-hafnacyclopent-2-ene (14). A solution of 0.9 g (5.1 mmol) of diphenylacetylene in 20 mL of benzene was added dropwise over a period of 3 h to a solution of 1.9 g (5.2 mmol) of bis(cyclopentadienyl)hafnacyclopentane (**5a**) in 30 mL of benzene at reflux temperature. The resulting solution is cooled to room temperature and concentrated in vacuo to a volume of 20 mL. Pentane (50 mL) was added and the solution cooled to −30 °C. After 12 h at −30 °C yellow crystals of the product **14** are obtained. Filtration at low temperature yields 0.95 g (36%) of **14**. A sample of 0.9 g of this material was recrystallized from 20 mL of methylene chloride at −30 °C (48 h). Crystalline material (mp 176 °C) was obtained which was used in the X-ray crystal structure analysis of **14** (see below). Anal. Calcd for $C_{26}H_{24}Hf$ (514.97); C, 60.64; H, 4.70. Found: C, 60.65; H, 4.56. ^{1}H NMR (benzene-d_6): δ 6.6–7.1 (m, 10 H, Ph), 5.83 (s, 10 H, Cp), 3.03 (t, 2 H, β-CH_2), 1.21 (t, ^3J(HH) = 7 Hz, 2 H, α-CH_2). ^{13}C NMR (benzene-d_6): δ 191.9 (s, C2), 150.8 (s, C3), 146.3, 144.7 (s, each, Ph ipso C), 129.0, 127.3 (d each, 158, 156 Hz, Ph ortho), 128.1, 127.7 (d each, 159, 158 Hz, Ph meta), 125.7, 123.1 (d each, 160, 161 Hz, Ph para), 111.2 (d, 173 Hz, Cp), 44.9 (t, 122 Hz, C5), 31.7 (t, 125 Hz, C4). The pentane/benzene mother liquor of the above described preparation was evaporated to dryness in vacuo. The resulting yellow solid residue was recrystallized from 10 mL of refluxing benzene. At room temperature, large crystals of 1,1-bis(cyclopentadienyl)-2,3,4,5-tetraphenyl-1-hafnacyclopentadiene (**15**) appeared, which were isolated by filtration (300 mg). Anal. Calcd for $C_{38}H_{30}Hf$ (665.13); C, 68.62; H, 4.55. Found: C, 69.89; H, 4.60. MS: *m/e* 666 (M^+), 488 (M^+ − tolane), 310 (M^+ − 2 tolane). ^{1}H NMR (benzene-d_6): δ 6.65–7.10 (m, 20 H, Ph), 5.95 (s, 10 H, Cp).

Crystal Structure Determination. A yellow crystal of **14**, obtained by recrystallization from methylene chloride, was sealed under argon in a thin-walled capillary tube. Preliminary photographic studies revealed $\bar{1}$ Laue symmetry. Unit cell dimensions were obtained from the best fit of the angular settings of 50 reflections containing 25 Friedel-related pairs to verify diffractometer and crystal alignment. Crystal parameters along with details of the data collection and refinement are available in Table II. Corrections to the intensity data were applied for a linear 17% decay and for absorption (empirical Ψ-scan method, seven reflections, 36 scans each). The space group was initially assumed to be $P\bar{1}$, and later shown to be correct by the chemically reasonable solution and refinement of the structure.

The structure was solved by heavy-atom methods, and a difference map phased on the Hf atom location revealed the positions of the remaining nonhydrogen atoms. Following anisotropic refinement of these atoms, the four hydrogen atoms bonded to C(1) and C(2) were located and refined as isotropic contributions. The remaining Cp and phenyl ring hydrogen atoms were placed in idealized, updated locations, but not refined. In all 261 least-squares parameters were refined by using 3317 reflections, $F_o \geq 3\sigma(F_o)$.

Atomic coordinates are provided in Table III and selected bond distances and angles in Table IV. Additional crystallographic data are available as supplementary material (see paragraph at end of paper).

Acknowledgment. Financial aid from the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie is greatfully acknowledged.

Registry No. **4a**, 12116-66-4; **5a**, 83719-75-9; **5a**-d_4, 110682-56-9; **10**, 52089-63-1; **12**, 83731-62-8; **13**, 83731-64-0; **14**, 110682-58-1; **16**, 83780-94-3; Cp, 542-92-7; $CH_2{=}CH_2$, 74-85-1; PhC≡CPh, 501-65-5; 1,4-dilithiobutane, 2123-72-0; 1,4-dichlorobutane, 110-56-5; butadiene, 106-99-0; bis(cyclopentadienyl)hafnium dibromide, 37260-83-6; 1,4-dibromobutane, 110-52-1; *n*-butane, 106-97-8.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (4 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.