Acknowledgment. We thank Jan van Mechelen (K.S.L.A.) for the crystal structure determination of compound 1. We also wish to thank a reviewer for their useful comments.

Supplementary Material Available: Experimental, analytical, spectroscopic, and crystal data, tables of positional parameters and anisotropic thermal parameters, and full listings of bond distances and angles (22 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

Synthesis of New Monomeric Zirconium and Hafnium Hydride Butadiene Complexes. The X-ray Structure of (η^5-Cyclopentadienyl)(η^4-butadiene)[1,2-bis(dimethylphosphino)ethane]hydridozirconium

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Summary: Room-temperature reaction of CpM(dmpe)(η^4-butadiene)Cl (**1**) [M = Zr, Hf; dmpe = 1,2-bis(dimethylphosphino)ethane] with $NaH_2Al(OCH_2CH_2OCH_3)_2$ [Red-Al] led to the new zirconium and hafnium hydrides CpM(dmpe)(η^4-butadiene)H [M = Zr (**2a**), 60%; M = Hf (**2b**), 57%] as pale yellow crystals. **2a** is monoclinic, space group $P2_1/n$, with a = 8.175 (2) Å, b = 15.706 (3) Å, c = 15.516 (2) Å, β = 99.41 (1)°, V = 1965.4 (7) Å^3, and Z = 4. Fast insertion reactions of CH_2CHR (R = H, Me, Et; 26 °C, 1 atm) into the Zr–H bond led to the formation of the corresponding alkyl derivatives CpM(dmpe)(η^4-butadiene)R [R = Et (**3**); R = n-Pr (**4**); R = n-Bu (**5**)] in good yield and crystalline form.

The chemistry of the M–H bond is continually receiving a great deal of attention in view of its involvement in many fascinating chemical processes.[1] In the chemistry of group IVB (group 4) metals, the synthesis and the reactivity of this functionality are well established for the bis(cyclopentadienyl)titanium and -zirconium derivatives,[2] while the analogous hafnium congeners remain much less characterized.[3] However, apart from these systems, this literature is surprisingly poor and limited to only two reports.[4] We now report the synthesis and characterization of the novel zirconium and hafnium hydrides CpM(dmpe)(η^4-butadiene)H [M = Zr (**2a**); M = Hf (**2b**)] together with a preliminary study on their reactivity with α-olefins.

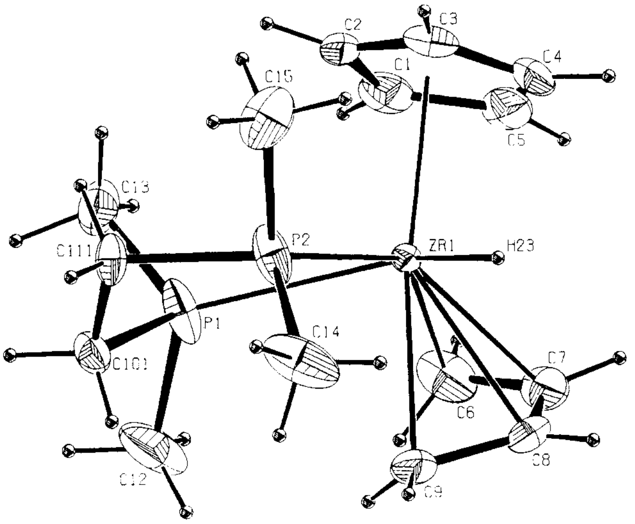

Figure 1. ORTEP drawing of CpZr(dmpe)(η^4-butadiene)H, independent molecule 1, showing the labeling scheme. Selected bond distances (Å) and angles (deg): Zr(1)–H(23) = 1.80 (5); Zr(1)–C(6) = 2.418 (3); Zr(1)–C(7) = 2.421 (3), Zr(1)–C(8) = 2.440 (3); Zr(1)–C(9) = 2.443 (3); Zr(1)–P(1) = 2.725 (1); Zr(1)–P(2) = 2.704(1); C(8)–C(9) = 1.430 (5); C(7)–C(8) = 1.382 (5); C(6)–C(7) = 1.425 (6); P(1)–Zr(1)–P(2) = 71.55 (3); C(6)–C(7)–C(8) = 119.1 (3); C(7)–C(8)–C(9) = 118.8 (3).

The compounds CpM(dmpe)(η^4-butadiene)Cl (M = Zr, Hf) (1)[5,6] react with $NaH_2Al(OCH_2CH_2OCH_3)_2$ (Red-Al) in toluene to give light brown solutions which, when cooled, produce pale yellow-crystals of **2** (Zr, 60%; Hf, 57%).

$$\underset{\textbf{1}}{\text{CpM(dmpe)}(\eta^4\text{-butadiene})\text{Cl}} \xrightarrow[\text{toluene}]{NaH_2Al(OCH_2CH_2OCH_3)_2} \underset{\textbf{2a}:\ M = Zr \quad \textbf{2b}:\ M = Hf}{\text{CpM(dmpe)}(\eta^4\text{-butadiene})\text{H}} \qquad (1)$$

An X-ray analysis carried out on a single crystal of **2a** reveals the unit cell composed of discrete monomeric units.[7] The geometry around zirconium is distorted octahedral (Figure 1) with the Cp ring centroid on the apical vertex and the dmpe ligand on two equatorial positions. The *s-cis*-butadiene ligand is symmetrically η^4-bonded to the metal with the two terminal carbon atoms C(6) and C(9) occupying respectively one equatorial and the second apical position [Cp(centroid)–Zr–C(6) = 104.9 (1)°; Cp(centroid)–Zr–C(9) = 167.6 (9)°]. No significant differences have been found between the Zr–C(diene) distances [ranging from 2.418 (3) to 2.440 (3) Å], suggesting an almost perfect η^4-mode of coordination for this fragment. This bonding mode, which is common for the late transition metals,[8] has never been observed for the group IVB metals, the distortion around the coordinated butadiene being explained in terms of high contribution of σ complex character.[9] The hydride, which occupies the fourth

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(7) **2a** is monoclinic in the space group $P2_1/n$. Cell data: a = 8.175 (2) Å, b = 15.706 (3) Å, c = 15.516 (2) Å, β = 99.41 (1)°, V = 1965.4 (7) Å^3, Z = 4, R = 0.034, R_w = 0.036, and GOF = 1.430 for a fit of 407 variables to 4156 observations. Structure was solved by standard Patterson methods; hydrogen atom positions were located and refined isotropically. Supplementary material contains full details on structure determination.

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equatorial position, was located by difference Fourier methods and satisfactorily refined [Zr–H = 1.80 (5) Å; Cp(centroid)–Zr–H = 97.4 (3)°].

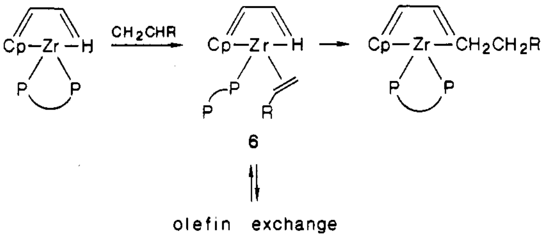
In the ^{1}H NMR spectrum[10] the characteristic terminal hydride resonance appears as a low-field triplet [δ = 7.20 ppm ($J_{\mathrm{P-H}}$ = 5.2 Hz) (**2a**); δ = 7.27 ppm ($J_{\mathrm{P-H}}$ = 5.2 Hz) (**2b**)]. A broad and intense band in the IR spectrum is tentatively assigned to the M–H stretching mode [1420 cm^{-1} (**2a**); 1460 cm^{-1} (**2b**)].

Compound **2a** rapidly reacts with α-olefins (1 atm, room temperature) to give terminally bonded alkyl derivatives CpM(dmpe)(η^4-butadiene)R in crystalline form and good yield[10] (eq 2). Internal olefins such as *cis*-2-butene and terminally disubstituted olefins like isobutene fail to react with these hydride complexes.

$$\underset{\mathbf{2a}}{\mathrm{CpM(dmpe)(\eta^4\text{-butadiene})H}} + \mathrm{CH_2CHR} \xrightarrow{\text{toluene}} \mathrm{CpM(dmpe)(\eta^4\text{-butadiene})CH_2CH_2R} \qquad (2)$$

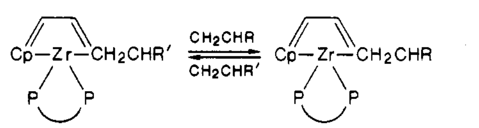
$$\begin{array}{l}\mathbf{3}\text{: R = H}\\ \mathbf{4}\text{: R = Me}\\ \mathbf{5}\text{: R = Et}\end{array}$$

A puzzling question arises from the possible insertion pathway into the Zr–H bond because no empty orbitals are available on **2a** for the necessary olefin precoordination.[11] However, dissociation of one of the two phosphorus atoms of the chelating phosphine might possibly provide the empty coordination site (eq 3).[12] In a subsequent step, hydride transfer to the coordinated olefin transforms intermediate **6** into the final insertion product. Preliminary evidence for the formation of **6** is provided by the ability of the alkyl derivatives **3**, **4**, and **5** to reversibly transform into each other by reaction with an excess of the corresponding α-olefin (1 atm, room temperature) (eq 4). The equilibrium shown in eq 4 can be approached from both sides of eq 4 and is easily shifted by adding or removing an olefin.



(3)

The present results suggest that the hydrozirconation reaction might in fact be an equilibrium. The situation should be similar to the insertion of olefins into the Nb–H bond of permethylniobocene(III) olefin hydride complexes,[11b] where the presence of β-hydrogens in the alkyl chain is a prerequisite for exchange. In agreement with that, CpZr(η^4-butadiene)(dmpe)CH$_3$ does not react with olefins (ethylene, propylene), even after long reaction times and using severe reaction conditions (5 atm, 80 °C).



(4)

Further study of the chemistry of these hydrides is in progress.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, and bond lengths and angles and spectroscopic and analytical data (14 pages); a listing of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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[10] The structure of all the complexes has been assigned on the basis of their spectroscopic and analytical details (available as supplementary material) and direct synthesis from **1** and the corresponding alkyllithium or Grignard reagents. The presence of terminally bonded alkyl chains has been demonstrated by NMR techniques [attached proton test (APT-NMR)].

[11] See, for example: (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

[12] Whereas the possibility of slippage of the Cp ring cannot be ruled out, a η^4-butadiene $\rightleftharpoons$ η^2-butadiene rearrangement process seems quite improbable on the basis of the simple consideration that η^2-butadiene should react not dissimilarly from a normal η^2-bonded α-olefin. The insertion or exchange products expected in this case have never been observed.

Regio- and Stereospecific Conversion of Chromium Dienes into Olefins via Anionic Allyl Complexes

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Summary: Pseudooctahedral chromium diene complexes react with trialkylborohydride reagents to give allylic anions resulting from addition of H$^-$ at the least crowded position and then rearrangement to the syn isomer. The product allylic anions can be isolated as tetraethylammonium salts and they react in CD$_3$CN solution with electrophiles to give free olefins.

There are relatively few examples of isolable diene complexes that can be conveniently made in large quantities and manipulated to give functionalized products.[3] We have begun research on the easily prepared chromium diene complexes of the stoichiometry Cr(CO)$_3$(P(OMe)$_3$)(η^4-diene) and find that it is possible to convert the dienes into *trans*-olefins stereospecifically.

The required starting materials are made photolytically with a reaction developed by Kreiter.[4] The diene complexes react with trialkylborohydrides MBHR$_3$ (M = Li, K; R = ethyl, *sec*-butyl)[5] in THF at reduced temperature. The use of potassium as a counterion permits the isolation of good yields of pure, crystalline derivatives after counterion exchange with tetraethylammonium bromide in THF at −20 °C (eq 1).[6,7]

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