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Monocyclopentadienylzirconium and -hafnium Alkyls: Synthesis, Hydrogen-Transfer Reactions, and Catalytic Features in the Reactivity with α-Olefins. X-ray Structure of CpZr(η^4-butadiene)(dmpe)Cl [dmpe = 1,2-Bis(dimethylphosphino)ethane]

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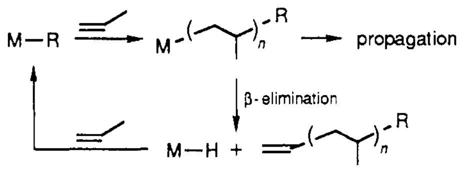
The dissociation of one of the two equatorial dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] of CpM(dmpe)$_2$X [X = Cl (**1**), Me (**2**); M = Zr (**a**), Hf (**b**)], allows the preparation of the new class of butadiene derivatives CpM(η^4-butadiene)(dmpe)X [X = Cl (**4a,b**), Me (**5a**)], via mild-condition ligand-replacement reaction. The structure of **4** was demonstrated by X-ray diffraction analysis. Crystal data are as follows: monoclinic, $P2_1/n$, $a = 8.230$ (1), $b = 15.896$ (1), $c = 16.571$ (1), $\beta = 95.43$ (1), $Z = 4$, $R = 0.043$, $R_w = 0.044$ for 2634 observed reflections. The symmetrical η^4 bonding mode of the butadiene moiety suggests that the low-valent character of zirconium is preserved on these compounds. Complex **4** is the starting material for the preparation of a series of linear alkyl and hydride derivatives CpM(η^4-butadiene)(dmpe)X [X = H (**6a,b**), Et (**7**), *n*-Pr (**10**), *n*-Bu (**11**)] via a simple substitution reaction. The same alkyl complexes can be also conveniently synthesized via insertion of an α-olefin into the Zr–H bond of **6**. Complex **7** is also formed in a one-step reaction of **2** with 3 equiv of ethylene. The alkyl derivatives **7**, **10**, and **11** are in equilibrium with the corresponding hydride **6** as demonstrated by the ability of **7** or **10** or **11** to transform into any other of these three compounds, upon reaction with the corresponding α-olefin. The presence of β-hydrogen is the prerequisite for the occurrence of these equilibria. This dynamic feature is responsible for the catalytic performance of **7** observed in the selective dimerization of ethylene to 1-butene. Deuterium-exchange experiments suggested that the catalytic cycle is initiated by H transfer from the β positions of the alkyl chain to the butadiene moiety.

Introduction

Since the initial discovery that mixtures of TiCl$_3$ and aluminum alkyls act as catalysts for the stereoselective olefin polymerization,[1] interest in the synthesis and reactivity of the M–C bond has experienced a steady growth of attention, especially for the group 4 transition metals.[2]

Key steps in the development of this chemistry were (a) the discovery of the general ability of the M–C bond to perform insertion reactions with the most diverse substrates[3] and (b) the ability of several alkyls to give reversible β-elimination reaction (related to the insertion of olefin into the M–H bond).[4]

These steps are the prerequisites for the initiation and closure of catalytic cycles, respectively:



The quite scarce ability of group 4 transition metal alkyl derivatives to give β-elimination reactions is the key to understanding the catalytic performances of these organometallic species.[5] Significant progress in improving catalytic abilities has been accomplished with the synthesis and characterization of d^0 cationic "naked alkyls", also

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known as the latest generation of Ziegler–Natta catalysts.[6] In contrast, only stoichiometric C–C bond formation is observed with several unsaturated substrates, when the number of d electrons is increased by reducing the formal oxidation state of the metal.[7] This seems to be especially true in the chemistry of group 4 transition metals, whose low-valent congeners, however, remain quite ill defined.[8] In an attempt to combine the ability of the zirconium alkyls to give insertion reactions with the strong reducing power of low-valent zirconium, we were especially interested in the reactivity of the low-valent Zr–C functionality.

Experimental Section

All operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen filled drybox (Braun, MB200). $CpZrCl_3(THF)_2$ and $CpHfCl_3(THF)_2$ were prepared according to published methods.[9,10] $CpM(dmpe)_2Cl$ (M = Zr, Hf) were synthesized as previously described.[11,12] Solvents were dried and distilled following standard procedures. Dmpe was synthesized as published (*Caution*: danger of major explosions).[13] Ethylene, propylene, 1-butene, butadiene, and CD_2CD_2 (Matheson) were used without further purification. Solvents used for magnetic resonance (benzene-d_6, THF-d_8) were vacuum transferred from Na/K alloy. ^1H and ^{13}C NMR spectra were recorded on Varian VXR 300 and Bruker WH 90 spectrometers. Chemical shifts are reported in units of δ, referenced to tetramethylsilane, and calculated from the position of the solvent absorption. Infrared (IR) spectra were recorded on the Unicam SP3-300 instrument: Nujol mulls were prepared in the drybox. Elemental analyses were carried out at the chemistry department of the University of Groningen. Gas-volumetric measurements were carried out using a high-vacuum line connected with a Töpler pump.

$CpZr(dmpe)_2Me$ (2). $CpZr(dmpe)_2Cl$ (4 g, 8.1 mmol) in 80 mL of THF was reacted with 2 equiv of a MeLi solution in ether. After 3 days the solution was evaporated to dryness and extracted with pentane. After cooling to −80 °C deep-red crystals of **2** were obtained from the resulting deep-red solutions (1.15 g, 3.65 mmol, 32%); ^1H NMR (90 MHz, C_6D_6, 27 °C) δ 4.44 (qt, J_{P-H} = 2.0 Hz, 5 H, Cp), 1.52–1.38 (m, 8 H, CH_2 dmpe), 1.26 (s, 12 H, CH_3 dmpe), 1.03 (s, 12 H, CH_3 dmpe), −1.86 (qt, J_{P-H} = 9.0 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, C_6D_6 25 °C) δ 82.76 (d, J_{C-H} = 166.1 Hz, Cp), 31.27 (t, J_{C-H} = 122.0 Hz, CH_2 dmpe), 20.09 (q, 132.0 Hz, CH_3 dmpe), 18.08 (q, J_{C-H} = 131.5 Hz, CH_3 dmpe).

Anal. Found (calcd) for $C_{18}H_{40}ZrP_4$: C, 45.63 (45.84); H, 8.30 (8.55); Zr, 19.45 (19.34).

$CpZr(dmpe)_2H$ (3). A solution of $CpZr(dmpe)_2Cl$ (0.55 g, 1.1 mmol) in ether (30 mL) was reacted at room temperature with an excess (4 equiv) of $LiHBEt_3$ in THF. After 15 days the solution was filtered, evaporated to dryness, and extracted with pentane. Deep-red crystals separated upon cooling to −80 °C (0.080 g, 0.17 mmol, 16%); ^1H NMR (90 MHz, C_6D_6, 27 °C) δ 4.57 (br s, 5 H, Cp), 1.39 (m, 4 H, CH_2 dmpe), 1.31 (br s, 12 H, CH_3 dmpe), 1.08 (br s, 12 H, CH_3 dmpe), 1.03 (m, 4 H, CH_2 dmpe); ^{13}C NMR (75 MHz, C_6D_6 25 °C) 82.83 (d, J_{C-H} = 170.3 Hz, Cp), 32.44 (br t, J_{C-H} = 124.4 Hz, CH_2 dmpe), 24.56 (br q, J_{C-H} = 128.9 Hz, CH_3 dmpe), 17.57 (q, J_{C-H} = 128.9 Hz, CH_3 dmpe).

Anal. Found (calcd) for $C_{17}H_{38}P_4Zr$: C, 45.10 (44.60); H, 8.53 (8.37); Zr, 19.67 (19.93).

$CpM(\eta^4$-butadiene)(dmpe)Cl (4) [M = Zr (a), Hf (b)]. Method A. In a standard experiment an ether solution (80 mL) of $CpM(dmpe)_2Cl$ (4.16 mmol) was saturated with 1,3-butadiene. The color of the solution turned yellow, and a bright-yellow crystalline solid precipitated. The solid was filtered and dried in vacuo (yield 3.43 mmol, 82%).

Method B. In a standard experiment $CpMCl_3(THF)_2$ (33.43 mmol) was dissolved in 250 mL of THF containing 1 equiv of dmpe. The solution was saturated with butadiene, and 2 equiv of Na/Hg (0.6%) was added. The solution rapidly turned red. After 1 day of stirring, the solution was filtered and evaporated to dryness. On addition of Et_2O (100 mL) analytically pure product precipitated, yield 62%. Crystals of **4a** suitable for X-ray analysis were grown from toluene solutions. $CpZr(\eta^4$-butadiene)(dmpe)Cl: ^1H NMR (90 MHz, C_6D_6, 80 °C) δ 6.04 (m, 2 H, butadiene), 5.53 (s, 5 H, Cp), 1.68 (m, 2 H, butadiene), 1.10 (pseudo-t, 4 H, CH_2 dmpe), 0.89 (t, 12 H, CH_3 dmpe), 0.66 (m, 2 H, butadiene); ^{13}C NMR (75 MHz, THF-d_8, −70 °C) δ 131.2 (d, J_{C-H} = 167.0 Hz, butadiene), 104.8 (d, J_{C-H} = 171.2 Hz, Cp), 96.9 (d, J_{C-H} = 156.7, butadiene), 55.3 (t, J_{C-H} = 149.3 Hz, butadiene), 40.0 (t, J_{C-H} = 140.3 Hz, butadiene), 28.3 (t, J_{C-H} = 132.9 Hz, CH_2 dmpe), 24.6, 14.5, 13.3, 9.5 (four m, dmpe).

Anal. Calcd (found) for $C_{15}H_{27}P_2ClZr$: C, 45.51 (45.53); H, 6.83 (6.95); Cl, 8.97 (8.93); Zr, 23.04 (23.16).

$CpHf(\eta^4$-butadiene)(dmpe)Cl: ^1H NMR (300 MHz, d_8-THF, −70 °C) δ 5.60 (m, 2 H, butadiene), 5.53 (m, 2 H, butadiene), 5.49 (s, 5 H, Cp), 1.89 (m, 4 H, CH_2 dmpe), 1.49, 1.41, 1.34, 1.29 (d, J_{P-H} = 6.6 Hz, 3 H, CH_3 dmpe), 2.10, 0.98 (two br m, 1 H, butadiene); ^{13}C NMR (75 MHz, THF-d_8, −70 °C) δ 131.6 (d, J_{C-H} = 163.5 Hz, butadiene), 103.4 (d, J_{C-H} = 170.4 Hz, Cp), 98.1 (d, J_{C-H} = 159.0 Hz, butadiene), 51.7 (t, J_{C-H} = 142.7 Hz, butadiene), 39.4 (t, J_{C-H} = 142.7 Hz, butadiene), 28.5 (t, J_{C-H} = 138.1 Hz, CH_2 dmpe), 16.0–9.40 (four m, dmpe).

Anal. Calcd (found) for $C_{15}H_{27}P_2ClHf$: C, 37.26 (37.15); H, 5.59 (5.50); Cl, 7.34 (7.30); Hf, 36.95 (36.97).

$CpM(\eta^4$-butadiene)(dmpe)H (6) [M = Zr (a), Hf (b)]. $NaH_2Al(OCH_2CH_2OCH_3)_2$ (1.4 mL, 3.4 M toluene) was added to a slurry of $CpM(\eta^4$-butadiene)(dmpe)Cl (4.70 mmol) in 50 mL of toluene. The yellow crystalline solid dissolved rapidly, and the suspension turned reddish-brown. The jellylike brown residue was filtered off, and the resulting solution was cooled to −80 °C, yielding CpM(butadiene)(dmpe)H·$^1/_2$toluene (2.94 mmol, 63%) as light yellow–brown crystals.

CpZr(dmpe)(η^4-butadiene)H: ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 7.23 (t, J_{P-H} = 5.2 Hz, 1 H hydride), 5.30 (s, 5 H, Cp), 4.99 (m, 2 H, butadiene), 1.57 (m, 2 H, butadiene), 1.12 (pseudo-d, 2 H, CH_2 dmpe), 0.90 (pseudo-d, 12 H, CH_3 dmpe), 0.80 (m, 2 H, CH_2 dmpe) 0.26 (m, 2 H butadiene); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 100.5 (d, J_{C-H} = 162.4 Hz, butadiene), 97.0 (d, J_{C-H} = 170.3 Hz, Cp), 92.9 (d, J_{C-H} = 166.7 Hz, butadiene), 45.5 (pseudo-q, J_{C-H} = 167.2 Hz, butadiene), 37.7 (t, J_{C-H} = 144.8 Hz, butadiene), 29.0 (pseudo-t, J_{C-H} = 132.0 Hz, CH_2 dmpe), 27.1 (pseudo-t, J_{C-H} = 132.0 Hz, CH_2 dmpe), 20.6, 17.3, 14.9, 11.9 (four m, CH_3 dmpe).

Anal. Calcd (found) for $C_{15}H_{28}ZrP_2\cdot{}^1/_2$toluene: C, 54.51 (54.76); H, 7.91 (7.88); Zr, 22.38 (22.46).

CpHf(dmpe)(η^4-butadiene)H: ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 7.27 (t, J_{P-H} = 5.2 Hz, 1 H hydride), 5.30 (s, 5 H, Cp), 5.00 (m, 2 H, butadiene), 1.51 (m, 2 H butadiene), 1.27 (pseudo-d, 2 H, CH_2 dmpe), 1.01 (br s, 12 H, CH_3 dmpe), 0.89 (m, 2 H, CH_2 dmpe), 0.13 (m, 2 H, butadiene); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 100.9 (d, J_{C-H} = 155.3 Hz, butadiene), 96.1 (d, J_{C-H} = 170.5 Hz, Cp), 91.6 (d, J_{C-H} = 164.7 Hz, butadiene), 42.4 (t, J_{C-H} = 145.0 Hz, butadiene), 36.5 (t, J_{C-H} = 144.8 Hz, butadiene), 29.7 (t, J_{C-H} = 122.0 Hz, CH_2 dmpe), 27.5 (t, J_{C-H} = 122.0 Hz, CH_2 dmpe), 21.2, 17.3, 14.8, 11.7 (four m, CH_3 dmpe).

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Anal. Calcd (found) for $C_{15}H_{28}P_2Hf$: C, 44.84 (44.92); H, 6.56 (6.49); Hf, 36.06 (36.36).

CpZr(η^4-butadiene)(dmpe)Me (5). Method A. A solution of MeLi (2.5 mL, 1.3 N) in Et_2O was added dropwise to a solution of $CpZr(dmpe)_2Cl$ (1.68 g, 3.43 mmol) in the same solvent (50 mL). The resulting red solution was saturated with 1,3-butadiene. After 1.5 h the solution was filtered and concentrated to a small volume. After cooling to −80 °C, yellow crystals separated (0.71 g, 1.89 mmol, 55%). Another crop of crystals was obtained after further concentration (0.34 g); total yield 1.05 g (82%).

Method B. A NMR tube containing a solution of $CpZr(dmpe)_2Me$ in C_6D_6 was pressurized with 1,3-butadiene. The solution turned light yellow within a few minutes, and CpZr(η^4-butadiene)(dmpe)Me was quantitatively formed together with 1 equiv of free dmpe; ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 5.84 (pseudo-q, 1 H, butadiene) 5.60 (pseudo-q, 1 H, butadiene), 5.23 (s, 5 H, Cp), 1.42 (m, 1 H, butadiene), 1.22 (m, 1 H, butadiene), 1.11 (m, 2 H, CH_2 of dmpe), 0.84 (s, 12 H, CH_3 of dmpe), 0.71 (pseudo-t, 2 H, CH_2 dmpe), 0.29 (pseudo-q, 1 H, butadiene), 0.05 (m, 1 H, butadiene), −0.28 (t, J_{P-H} = 7.27 Hz, 3 H, CH_3 dmpe); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 123.6 (d, J_{C-H} = 164.2 Hz, butadiene), 101.7 (d, J_{C-H} = 169.4 Hz, Cp), 97.0 (d, J_{C-H} = 160.8 Hz, butadiene), 50.5 (t, J_{C-H} = 143.7 Hz, butadiene), 36.7 (t, J_{C-H} = 152.9 Hz, butadiene), 27.5 (br t, CH_2 dmpe), 13.7 (q, J_{C-H} = 130.7 Hz, CH_3 dmpe), 7.20 (q, J_{C-H} = 127.6 Hz, CH_3).

Anal. Calcd (found) for $C_{16}H_{30}P_2Zr$: C, 51.17 (51.34); H, 8.05 (7.87); Zr, 24.29 (24.62).

CpZr(η^4-butadiene)(dmpe)Et (7). Method A. A solution of $CpZr(dmpe)_2Me$ (1.0 g, 2.1 mmol) in ether (50 mL) was saturated with ethylene. After 10 h the volatiles were removed in vacuo, and the resulting solid was extracted with pentane. On concentration and cooling to −30 °C CpZr(η^4-butadiene)(dmpe)Et was obtained as a light-yellow crystalline solid (0.21 g, 25%). Identification of CH_4: In a high-vacuum line connected with a Toepler pump, $CpZr(dmpe)_2Me$ (0.11 g, 0.24 mmol) was dissolved in 10 mL of toluene and reacted with 3 equiv of ethylene. After 10 h the gas mixture was pumped off and pure CH_4 (0.95 equiv) identified by GC.

Method B. A NMR tube containing a solution of CpZr(η^4-butadiene)(dmpe)H in C_6D_6 was saturated with ethylene. Quantitative formation of CpZr(η^4-butadiene)(dmpe)Et was observed within a few minutes.

Method C. A solution of EtLi (2.03 mmol) in benzene was added to a solution of CpZr(η^4-butadiene)(dmpe)Cl (2.03 mmol) in 50 mL of the same solvent. After evaporation to dryness and extraction of the residual solid with pentane, CpZr(η^4-butadiene)(dmpe)Et was obtained as light-yellow crystals upon cooling to −30 °C (yield 0.81 mmol, 40%). ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 5.88 (pseudo-t, 1 H, butadiene), 5.33 (pseudo-q, 1 H, butadiene), 5.29 (s, 5 H, Cp), 1.78 (t, 3 H, CH_3 of Et), 1.45 (m, 1 H, butadiene), 1.18 (pseudo-d, 1 H, butadiene), 1.01 (m, 5 H, butadiene and CH_2 of dmpe), 0.83 (pseudo-d, 12 H, CH_3 of dmpe), 0.40–0.14 (m, 3 H, butadiene and CH_2 of Et). Irradiation at 0.2 ppm transforms the triplet at 1.78 ppm into a singlet, while the irradiation at 1.78 ppm modifies the shape of the multiplet at 0.2 ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 124.9 (d, J_{C-H} = 168.6 Hz, butadiene), 101.2 (d, J_{C-H} = 176.4 Hz, Cp), 95.1 (d, J_{C-H} = 164.7 Hz, butadiene), 51.4 (t, J_{C-H} = 153.0 Hz, butadiene), 37.1 (t, J_{C-H} = 147.2 Hz, butadiene), 27.3 (t, J_{C-H} = 131.1 Hz, CH_2 of dmpe), 19.3 (pseudo-q, CH_3 of dmpe), 17.8 (pseudo-q, CH_3 of dmpe), 14.8, 13.8 (two broad-m. Et group).

Anal. Calcd (found) for $C_{17}H_{32}P_2Zr$: C, 52.44 (52.67); H, 8.22 (8.24); Zr, 23.39 (23.56); P, 15.93 (15.82).

CpZr(η^4-butadiene)(dmpe)(*n*-Pr) (10). CpZr(η^4-butadiene)(dmpe)H (0.8 g, 2.54 mmol) was dissolved in 30 mL of ether and saturated with an excess of propylene. After 1 day the resulting dark solution was concentrated and cooled to −30 °C, yielding 0.36 g of light-brown crystals (0.34 mmol, 35%): ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 5.86 (pseudo-q, 1 H, butadiene), 5.52 (pseudo-q, 1 H, butadiene), 5.27 (s, 5 H, Cp), 1.90 (m, 1 H, butadiene), 1.67 (m, 1 H, butadiene), 1.42 (pseudo-t, 3 H, CH_3 propyl), 1.14 (m, 2 H, CH_2 propyl), 1.05 (m, 5 H, CH_2 dmpe and butadiene), 0.81 (br s, 12 H, Me dmpe), 0.32 (m, 3 H, butadiene and CH_2 propyl); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 124.7 (d, J_{C-H} = 160.0 Hz, butadiene), 101.0 (d, J_{C-H} = 169.9 Hz, Cp), 95.3 (d, J_{C-H} = 155.4 Hz, butadiene), 51.3 (t, J_{C-H} = 145.8 Hz, butadiene), 37.0 (t, J_{C-H} = 144.1 Hz, butadiene), 31.2 (t, J_{C-H} = 139.3 Hz, CH_2 propyl), 29.4 (t, J_{C-H} = 138.4 Hz, CH_2 propyl), 27.3 (t, J_{C-H} = 134.7 Hz, CH_2 dmpe), 24.2 (q, J_{C-H} = 123.1 Hz, CH_3 dmpe), 14.88 (q, J_{C-H} = 135.8 Hz, CH_3 propyl).

Anal. Calcd (found) for $C_{18}H_{34}P_2Zr$: C, 53.61 (53.43); H, 8.43 (8.57); Zr, 22.58 (23.10).

CpZr(η^4-butadiene)(dmpe)(*n*-Bu) (11). CpZr(η^4-butadiene)(dmpe)H (0.7 g, 1.94 mmol) was dissolved in 35 mL of ether and saturated with 1-butene. After 1 day the solution was concentrated and cooled to −80 °C. CpZr(η^4-butadiene)(dmpe)(*n*-Bu) was obtained as light-brown crystals (yield 0.24 g, 5.7 mmol, 30%): ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 5.84 (pseudo-q, 1 H, butadiene), 5.51 (pseudo-q, 1 H, butadiene), 5.28 (s, 5 H, Cp), 1.91 (m, 1 H, butadiene), 1.70 (m, 2 H, CH_2 butyl), 1.48 (m, 1 H, butadiene), 1.23 (pseudo-t, 5 H, CH_2 and CH_3 butyl), 1.12 (pseudo-d, 4 H, CH_2 dmpe), 0.83 (pseudo-d, 12 H, CH_3 dmpe), 0.30 (m, 3 H, butadiene and CH_2 butyl), 0.15 (m, 1 H, butadiene); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 124.8 (d, J_{C-H} = 165.0 Hz, butadiene), 101.1 (d, J_{C-H} = 163.9 Hz, Cp), 95.3 (d, J_{C-H} = 155.4 Hz, butadiene), 51.3 (t, J_{C-H} = 145.0 Hz, butadiene), 38.9 (t, J_{C-H} = 138.3 Hz, CH_2 butyl), 37.1 (t, J_{C-H} = 143.1 Hz, butadiene), 32.4 (t, J_{C-H} = 128.3 Hz, CH_2 butyl), 27.3 (t, J_{C-H} = 120.0 Hz, CH_2 dmpe), 27.1 (t, J_{C-H} = 120.0 Hz, CH_2 butyl), 14.49 (q, J_{C-H} = 121.7 Hz, CH_3 dmpe), 13.8 (br q, J_{C-H} = 128.1 Hz, CH_3 butyl).

Anal. Calcd (found) for $C_{19}H_{36}P_2Zr$: C, 54.67 (54.65); H, 8.63 (8.70); P, 14.87 (14.55); Zr, 21.82 (21.81).

X-ray Diffraction. X-ray data were collected on an Enraf-Nonius CAD 4F diffractometer (graphite monochromated Mo Kα) for a yellowish transparent crystal obtained by recrystallization from toluene. Unit-cell parameters were calculated from the SET4 setting angles[14a] for 25 reflections in the range $12 < \theta < 15°$. The space group was derived from the observed systematic absences. The intensity data were corrected for *Lp* but not for absorption. The structure was solved with standard Patterson and Fourier methods (SHELXS-86)[14b] and refined on *F* by full-matrix least-squares analysis (SHELX-76).[14c] The structure was found to contain toluene molecules of crystallization, disordered over crystallographic inversion centers. The toluene molecule was refined as a rigid group with individual anisotropic thermal parameters. Refinement with anisotropic thermal parameters for the non-hydrogen atoms revealed relatively high thermal motion for the disordered toluene molecule. Hydrogen atoms on C6 and C9 were located from a difference map, and their positions refined with one common isotropic thermal parameter. All other hydrogen atoms were introduced at calculated positions [C–H = 0.98 Å] and refined with five common isotropic thermal parameters. Scattering factors were obtained from ref 15a and corrected for anomalous dispersion.[15b] The highest residual feature (0.66 e Å^{-3}) in a final Fourier map is interpretable as an alternative position of C(10). It was considered not worthwhile to include this minor disorder in the model in view of the overall relatively high thermal motion of all carbon atoms. The calculations of the geometrical data and the preparation of the thermal motion ellipsoid plot were performed with the program PLATON of the EUCLID package.[14d] Crystal data and numerical details on the structure determination are given in Table I; positional parameters for the non-hydrogen atoms are listed in Table II. Data collection was carried out from Utrecht, using the national SURF network, on the CAD4 serial no. 1 diffractometer located in Groningen. All calculations were carried out on a MicroVax cluster.

Results and Discussion

Reaction of $CpZr(dmpe)_2Cl$ (1) in THF with MeLi affords the replacement of chlorine with the methyl group during a slow reaction (3 days). Strangely, the utilization of 2 equiv of MeLi is necessary to cause the disappearance of the resonances of the starting material in the ^1H NMR

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Table I. Crystal Data and Details of the Structure Determination of 4

Crystal Data	
formula	$C_{15}H_{27}P_2ClZr\cdot{}^1/_2(C_7H_8)$
formula wt, g mol^{-1}	442.07
cryst syst	monoclinic
space group	$P2_1/n$
Z, no. of formulas per unit cell	4
$F(000)$/electron	916
cell parameters	
a, Å	8.230 (1)
b, Å	15.896 (1)
c, Å	16.571 (1)
β, deg	95.43 (1)
V, Å^3	2158.2 (3)
d_{calcd}, g cm^{-3}	1.360
μ_{calcd}, cm^{-1}	7.7
cryst size	0.4 × 0.3 × 0.3
Data Collection (293 K)	
diffractometer type	CAD4F
radiation Mo Kα (graphite mon), Å	0.71073
θ_{max}, deg	25
scan type $\omega/2\theta$	$\Delta\omega = 0.90 + 0.35 \tan\theta$
data set h,k,l	-9:9;0:18;0:19
no. of rflctns measd	4087
no. of unique rflctns	3791
no. of rflctns used in analysis [$I > 2.5\sigma(I)$]	2634
Refinement	
R, R_w, S	0.043, 0.044, 1.53
weighting scheme w^{-1}	$\sigma^2(F) + 0.0002F^2$
N_{par}, N_{ref}	253, 2634
Min, Max resd dens, e Å^{-3}	−0.44, 0.66

Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for $ZrClP_2C_{15}H_{27}\bullet{}^1/_2C_7H_8$

atom	x	y	z	U(eq),[a] Å^2
Zr	0.03607 (5)	0.14820 (3)	0.19076 (3)	0.0387 (2)
Cl	0.0835 (2)	0.1755 (1)	0.34865 (9)	0.0784 (6)
P(1)	−0.1495 (2)	0.20207 (9)	0.05351 (8)	0.0513 (5)
P(2)	−0.1375 (2)	0.29027 (9)	0.22552 (9)	0.0515 (5)
C(1)	0.2509 (9)	0.1539 (7)	0.0914 (6)	0.116 (4)
C(2)	0.2333 (8)	0.2398 (6)	0.1228 (6)	0.097 (4)
C(3)	0.2876 (8)	0.2410 (6)	0.2015 (6)	0.098 (4)
C(4)	0.3408 (7)	0.1604 (6)	0.2209 (6)	0.103 (4)
C(5)	0.3183 (9)	0.1069 (6)	0.1557 (6)	0.098 (4)
C(6)	−0.019 (1)	0.0217 (5)	0.1127 (5)	0.097 (4)
C(7)	0.0162 (9)	−0.0035 (4)	0.1974 (5)	0.081 (3)
C(8)	−0.078 (1)	0.0255 (4)	0.2550 (5)	0.082 (3)
C(9)	−0.2113 (9)	0.0793 (5)	0.2277 (5)	0.081 (3)
C(10)	−0.223 (1)	0.3097 (5)	0.0653 (4)	0.102 (3)
C(11)	−0.2814 (8)	0.3260 (4)	0.1421 (4)	0.085 (3)
C(12)	−0.3351 (8)	0.1477 (5)	0.0191 (5)	0.104 (3)
C(13)	−0.0609 (9)	0.2098 (5)	−0.0417 (4)	0.092 (3)
C(14)	−0.2685 (8)	0.2881 (5)	0.3078 (4)	0.082 (3)
C(15)	−0.0138 (8)	0.3828 (4)	0.2513 (4)	0.082 (3)

[a] U(eq) = one-third of the trace of the orthogonalized **U** matrix.

Table III. Selected Bond Distances (angstroms) and Angles (degrees)[a]

Distances			
Zr-Cl	2.645 (2)	Zr-C9	2.440 (8)
Zr-P1	2.753 (2)	Zr-cp	2.235 (4)
Zr-P2	2.762 (2)	C6-C7	1.462 (12)
Zr-C6	2.410 (8)	C7-C8	1.365 (11)
Zr-C7	2.420 (6)	C8-C9	1.431 (11)
Zr-C8	2.451 (7)		
Angles			
Cl-Zr-cp	98.4 (1)	P1-Zr-P2	70.16 (5)
Cl-Zr-P1	141.68 (5)	cp-Zr-P1	100.5 (1)
Cl-Zr-P2	71.95 (5)	C6-Zr-cp	101.1 (2)
cp-Zr-P2	111.7 (1)	C9-Zr-cp	166.4 (2)

[a] cp = cyclopentadienyl ring centroid.

spectrum and to obtain a chlorine-free compound. After workup, complex **2** (eq 1) can be recovered in moderate

$$\underset{\mathbf{1}}{\mathrm{CpZr(dmpe)_2Cl}} + 2\mathrm{MeLi} \rightarrow \underset{\mathbf{2}}{\mathrm{CpZr(dmpe)_2Me}} + \text{“intractable”} \tag{1}$$

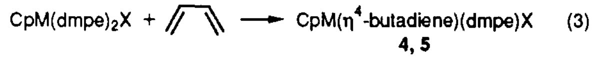
yield (32%) and analytically pure form, while a significant amount of intractable material containing zirconium can be isolated from the crude mixture. The structural similarities between **1** and **2** have been recently reported.[11,16] Attempts to use different alkyls have failed so far, probably due to unfavorable steric factors.

Substitution of chlorine in complex **1** can be achieved also with hydride, by slowly reacting (15 days, room temperature) THF solutions with an excess of $LiHBEt_3$ (eq 2).

$$\mathrm{CpZr(dmpe)_2Cl} \xrightarrow[\mathrm{THF}]{\mathrm{LiHBEt_3}} \underset{\mathbf{3}}{\mathrm{CpZr(dmpe)_2H}} \tag{2}$$

Attempts to prepare **3** using different hydrides [$LiAlH_4$, $NaH_2Al(OCH_2CH_2OCH_3)_2$] or via hydrogenolysis of **2** gave complicated mixtures only. Both **2** and **3** are thermally robust and can be heated for several hours at 90 °C without observing any appreciable decomposition. The resonance of the methyl group is observed in **2** as a quintet (−1.86 ppm, $J_{P-H} = 9.0$ Hz), while strangely, the hydride resonance cannot be located in the ^1H NMR spectrum of **3**. No signal attributable to the Me group has been located in the ^{13}C NMR spectrum of **2** in the range 250 to −50 ppm.

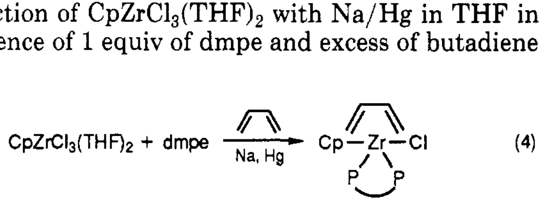
The common feature of **1** and **2** is the ability to dissociate in solution one chelating phosphine, allowing the mild-conditions preparation of several new compounds by simple ligand-substitution reaction.[12] For example, treatment of ether solutions of **1** with butadiene (room temperature, 1 atm) affords the preparation of the corresponding butadiene derivatives in good yield and crystalline form (eq 3).



4, 5

X = Cl (**4**), Me (**5**); M = Zr (**a**), Hf (**b**)

The chloro derivative CpZr(η^4-butadiene)(dmpe)Cl (**4a**) is a promising starting material for further synthetic work and can be more conveniently synthesized on a large scale by reduction of $CpZrCl_3(THF)_2$ with Na/Hg in THF in the presence of 1 equiv of dmpe and excess of butadiene (eq 4).



4

The utilization of different reducing agents such as butadiene–Mg leads to the formation of complicated mixtures. The replacement of chloride in **4** with hydride has been obtained by simple room-temperature reaction with $NaH_2Al(OCH_2CH_2OCH_3)_2$ (Red-Al). The corresponding CpM(η^4-butadiene)(dmpe)H (**6**) was obtained in good yield and crystalline form (eq 5). Reaction 3 cannot

$$\mathrm{CpM(\eta^4\text{-}butadiene)(dmpe)Cl} \xrightarrow{\text{Red-Al}} \mathrm{CpM(\eta^4\text{-}butadiene)(dmpe)H} \tag{5}$$
$$\mathrm{M = Zr\ (\mathbf{6a}),\ Hf\ (\mathbf{6b})}$$

be used for the synthesis of **6** due to the great tendency of these hydrides to insert butadiene into the M–H bond. The nearly perfect matching of the IR spectra of **4**–**6**

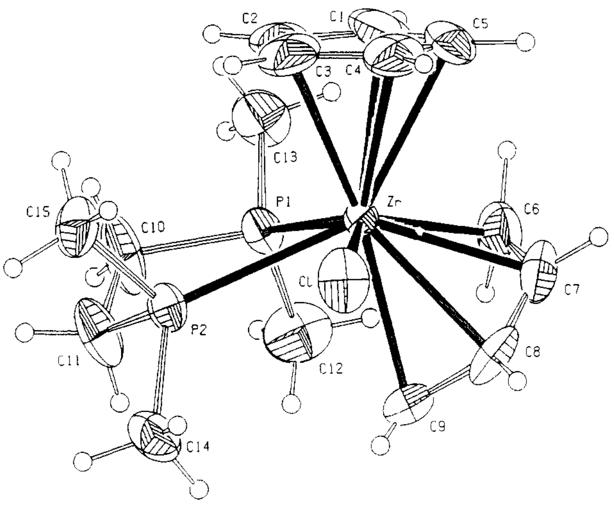
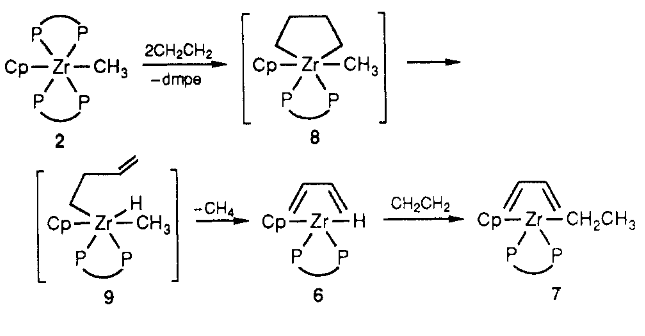


Figure 1. Thermal motion ellipsoid plot (30% probability level) with numbering scheme for complex 4. Partial conformational disorder has been found for the atoms C(10) and C(11).

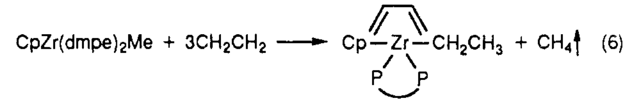
suggests that these compounds are isostructural, the only significant difference being the presence of an intense and broad resonance at 1420 and 1460 cm^{-1} for **6a** and **6b**, respectively. These absorptions are tentatively assigned to the M–H stretching mode. The ^{1}H and ^{13}C NMR spectra of the butadiene fragments for all the complexes showed the same patterns, consistent with six nonequivalent hydrogen and four nonequivalent carbon atoms. In the case of **6a** and **6b**, the two resonances attributed to the β-hydrogen of the butadiene ligand are considerably shifted to higher field in respect to all the other isostructural butadiene complexes reported in the present work. Complex **4** is highly fluxional at room temperature, and well-resolved NMR spectra could be recorded at low temperature (^{13}C) or high temperature (^{1}H). The reason for this fluxionality is not well understood at the moment, but a rapid exchange between possible conformations of the coordinated butadiene seems the most likely.

Complex **4** is isostructural with the previously reported CpZr(η^4-butadiene)(dmpe)H (ref 17) and consists of discrete monomeric units having a distorted octahedral geometry around the metal center. The severe conformational disorder found in both the interstitial molecule of toluene and the ethylene bridge of dmpe affects significantly the accuracy of the values of the bond distances and angles. However the overall geometry depicted in Figure 1 remains demonstrated. The Cp ring centroid occupies the apical vertex and the two P atoms together with Cl occupy three equatorial positions. The Zr–Cl distance [2.645 (2) Å] is quite long with respect to the corresponding distances found in the bis(cyclopentadienyl)Zr(IV) systems but compares well with that observed in complex **1**.[11] The *cis*-η^4-butadiene ligand occupies the axial position trans to the Cp ring and one equatorial vertex trans to one phosphorus atom using the two α-carbon atoms [C(6) and C(9)]. The arrangement of the butadiene ligand with respect to the metal center is highly symmetric, and the small differences found between the Zr–C(diene) distances [ranging between 2.410 (8) and 2.451 (7) Å] suggest a pronounced η^4 geometry for this fragment. It is quite surprising that such a bonding mode, which is a common feature for the late-transition-metal complexes,[18] is not observed for the group 4 transition metals, where the usual distortion around the coordinated butadiene is explained in terms of high contribution of σ-bond character.[19] We believe that the η^4 geometry in complexes **4** and **6** is a result of a significant extent of low-valent character of the transition metal stabilized by the chelating dmpe.

Scheme I



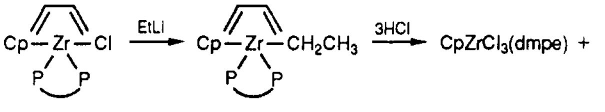
A deep orange–red solution of **2** in ether reacts with 3 equiv of ethylene within 24 h at room temperature. Evolution of 1 equiv of methane is observed along with the formation of the butadiene–alkyl species **7** (eq 6).



$$\mathrm{CpZr(dmpe)_2Me + 3CH_2CH_2 \longrightarrow Cp{-}Zr(\eta^4\text{-}C_4H_6)(dmpe){-}CH_2CH_3 + CH_4\uparrow} \qquad (6)$$

7

The striking similarity of the spectroscopic data suggests that this complex is isostructural with **4**–**6**. The structure of **7** was further confirmed by the product distribution obtained from chemical degradation with anhydrous HCl and direct synthesis from **4** and EtLi (eq 7).



$$\mathrm{Cp{-}Zr(\eta^4\text{-}C_4H_6)(dmpe){-}Cl \xrightarrow{EtLi} Cp{-}Zr(\eta^4\text{-}C_4H_6)(dmpe){-}CH_2CH_3 \xrightarrow{3HCl} CpZrCl_3(dmpe) +}$$

$\mathrm{CH_3CH_3}$ (33%) + $\mathrm{CH_2CH_2}$ (11%) + 1-butene (50%) + *trans*-2-butene (6%) (7)

Intriguing questions arise about the possible pathway for the formation of **7** in reaction 6. The quantitative evolution of CH_4 during the reaction together with the absence of any organic fragment that could be attributed to the insertion of olefin into the Zr–Me bond suggests the inability of these low-valent Zr species to undergo olefin insertion reaction. Furthermore this indicates that both the butadiene moiety and the alkyl chain are generated by the olefin exclusively, the first (butadiene) through reductive coupling and the second (alkyl) via insertion into a Zr–H bond of some reactive intermediate. The ability of **1** and **2** to dissociate in solution one chelating phosphine has been widely documented.[12,16] In analogy to what is commonly observed for the bis(cyclopentadienyl) systems, the resulting electronically and coordinatively unsaturated 14-electron d^2 species might promote the reductive coupling of olefin, forming the metallacycle (Scheme I).

In spite of their quite elusive behavior, these metallacycles are well-known to exist in equilibrium with coor-

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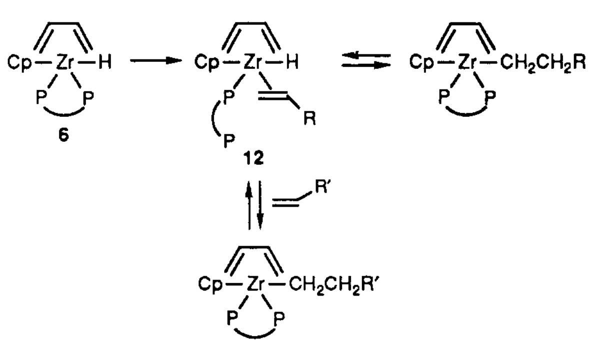
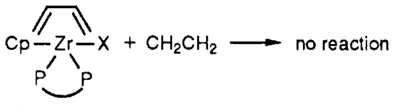
Scheme II



R, R′ = H (**7**), CH_3 (**10**), CH_2CH_3 (**11**)

dinated ethylene as well as being able to form hydride-butenyl derivatives by transferring hydride from the β-carbon atoms of the metallacycle to the metal center.[20] If we assume the presence of this type of dynamism, the intermediate **8** rearranges itself into the new intermediate hydride-methyl-butenyl **9**. Reductive elimination of methane followed by further hydrogen transfer from the butenyl chain to the metal center forms a butadiene-hydride species. The stability of this zirconium butadiene hydride species, its structure, and its ability to undergo fast olefin insertion into the Zr-H bond have been the subject of a previous paper.[17] Dissociation of one of the two phosphorus atoms of the chelating phosphine in complex **6** is believed to provide the free coordination site necessary for the olefin precoordination before the final insertion takes place (Scheme II).

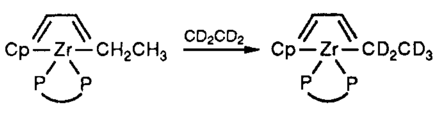
The alkyl derivatives **7**, **10**, and **11** react with the corresponding α-olefins, allowing the reversible transformation into any other of these three compounds. The equilibrium can be reached from both sides and pushed in the most preferred direction by just acting on the concentration of the α-olefin. To explain the presence of this equilibrium, it is necessary to assume that the intermediate **12** (Scheme II) is also formed by the alkyl species via reversible β-hydrogen elimination. In support of this idea, no reactivity with olefins was observed for **4** and **5** even under drastic conditions (eq 8). This result points out the surprising



(8)

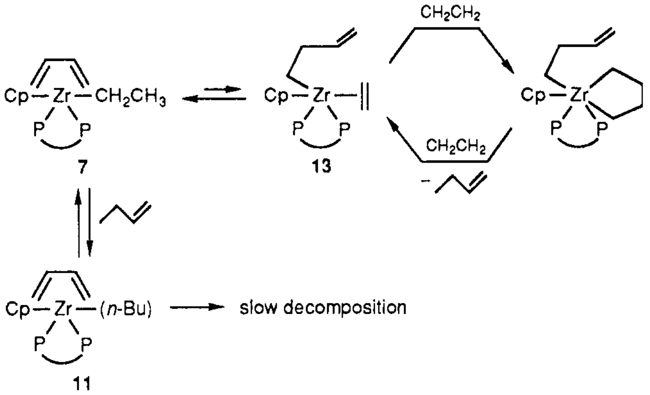
X = Cl, Me

reluctance of both the η^4-butadiene and Zr-C bond, in the present system, to undergo insertion reactions, sharply in contrast with what is commonly observed for the bis(cyclopentadienyl) system.[21] We believe that the low oxidation character of zirconium in the present system is responsible for this striking discrepancy. In accordance with Scheme II, fast incorporation of deuterium into the alkyl chain was observed within 1 h when a solution of **7** was exposed to an excess of C_2D_4 (room temperature, 1 atm; eq 9).



(9)

Scheme III



Conversely no incorporation of deuterium into the η^4-butadiene and the Cp ring was observed during this process, indicating that these ligands are not involved in the mechanism of the olefin exchange. However, some incorporation of deuterium into the butadiene ligand takes place over 12 h, resulting in the almost complete flattening of the spectrum with only the exception of the Cp and dmpe resonances. In comparable reaction times, complex **7** acts as a homogeneous catalyst for the slow and selective mild-conditions dimerization of ethylene to 1-butene (ca. 3 turnovers/day at room temperature and 1 atm; Scheme III). The absence of C_6 and C_8 products, previously observed in the Zr-promoted oligomerization of ethylene,[7a,b,22] indicates that the mechanism in the present system is highly stereoselective. As suggested by the deuterium-exchange experiments, the initial step in the catalytic cycle is probably hydrogen transfer from the ethyl group to the coordinated butadiene forming the butenyl derivative **13**, probably the real catalyst (Scheme III).

Further reaction with ethylene, hydrogen transfer from the metallacycle to the butenyl, elimination of 1-butene, and reaction with 2 more equiv of ethylene form the catalytic cycle.

In spite of these promising features, the present system is not suitable for applicative purposes. The 1-butene that is catalytically produced, slowly reacts with **7**, forming the thermally less stable butyl complex **11**, which is probably responsible for the full decomposition of the starting material observed after a few days.

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Registry No. **1a**, 114238-07-2; **1b**, 116148-79-9; **2a**, 115227-32-2; **3a**, 124992-94-5; **4a**, 115227-38-8; **4a**·$^1/_2C_7H_8$, 125074-95-5; **4b**, 118418-66-9; **5a**, 115227-35-5; **6a**, 115227-34-4; **6b**, 118418-64-7; **7a**, 115227-33-3; **10a**, 115227-36-6; **11a**, 118418-65-8; $CpZrCl_3(THF)_2$, 114238-08-3; butadiene, 106-99-0; ethylene, 74-85-1; propylene, 115-07-1; 1-butene, 106-98-9.

Supplementary Material Available: A unit-cell packing diagram, tables of thermal parameters, and extensive lists of bond distances, angles, and torsion angles (5 pages); lists of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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