rangement of $(CO)_3HFe(\mu\text{-}PR_2)PtL_2$ to the isomer containing the bridging hydride. For both systems the isomerization process involves rotational movement of a terminal hydride and two CO ligands about an axis defined by a metal–CO bond to place the hydride in a bridging position; the Os_3 cluster differs primarily in the presence of a second hydride ligand that remains bridging the metal–metal vector in both the reactant state and the proposed transition state. For both systems the energetics of the dynamic process are influenced by the identities of the phosphine ligands. Thus, $\Delta G°$ for the equilibrium in Figure 4 and $\Delta G^{\ddagger}$ for hydride exchange on $H(\mu\text{-}H)Os_3(CO)_{10}L$ both decrease as L = $P(OPh)_3$ > PPh_3 > PEt_3. This trend is most likely due to the stabilization of the bridging hydride, relative to the energy of terminal coordination, by the presence of more basic phosphines on the bridged metal atoms. If the transition state for hydride exchange in $H(\mu\text{-}H)Os_3(CO)_{10}L$ were to involve two terminal hydrides, then the $\Delta G^{\ddagger}$ value for exchange would be expected to increase as the basicity of L increases.

Conclusions. We have shown here that activation volumes for hydride fluxionality on metal clusters, while small in magnitude, can be measured and that the activation volume may allow a distinction to be made between possible mechanisms for intramolecular processes. The two values measured in this work support the proposal that migration of a bridging hydride to a terminal coordination site is associated with a positive change in volume.

Acknowledgment. J.B.K. acknowledges support by the National Science Foundation through Grant CHE8900921. A.E.M. acknowledges support by the Swiss National Science Foundation. We thank Dr. Lothar Helm and Professor J. Powell for helpful discussions.

Syntheses of [Ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium and -hafnium Hydride Complexes. Improved Syntheses of the Corresponding Dichlorides

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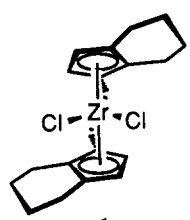
Received September 11, 1990

Treatment of $(EBTHI)MCl_2$ [M = Zr, 1; M = Hf, 2; EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)] with 2 equiv of $NaEt_3BH$ in C_6H_6 produces the hydride dimers $[(EBTHI)MH(\mu\text{-}H)]_2$ (M = Zr, 3; M = Hf, 4). The dimethylhafnium complex $(EBTHI)HfMe_2$ (5) is formed when 2 is treated with MeLi in C_6H_6. Complexes 3 and 4 can be protonated with the weak acid $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ to give monomeric cationic hydrides $[(EBTHI)M(H)(NPhMe_2)][Co(C_2B_9H_{11})_2]$ (M = Zr, 6; M = Hf, 7), in which the *N,N*-dimethylaniline ligand is very weakly coordinated to the metal. Improved syntheses of the dichloride complexes 1 and 2 are also described.

The synthesis of chiral, enantiomerically pure group 4 metallocene complexes has been an active area of research in the last few years, partly because these complexes show promise in effecting asymmetric synthesis.[1-3] The chiral zirconocene complex, $(EBTHI)ZrCl_2$ (1, EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)) was first reported by Brintzinger,[4] and a modified synthesis of 1 was later published by Collins.[5] The analogous hafnium complex, $(EBTHI)HfCl_2$ (2), has also been prepared, although in low yield.[6] As part of an ongoing project in which the utility of such compounds in asymmetric synthesis is being examined, we have prepared several derivatives of 1 and 2. Herein we report the syntheses of the bridged hydride dimers $[(EBTHI)MH(\mu\text{-}H)]_2$ (M = Zr, 3; M = Hf, 4) and the dimethylhafnium compound $(EBTHI)HfMe_2$ (5). Protonation of 3 or 4 with the weak acid, $[PhMe_2NH][Co(C_2B_9H_{11})_2]$, gives the corresponding cationic monomeric hydride species $[(EBTHI)M(H)(PhNMe_2)][Co(C_2B_9H_{11})_2]$ (M = Zr, 6; M = Hf, 7); the former, when enantiomerically enriched, catalyzes the asymmetric hydrogenation of α-ethylstyrene. In addition, improved syntheses for the dichloride complexes 1 and 2 are also described.



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Experimental Section

General Procedures. All manipulations were performed by using either a Vacuum Atmospheres drybox under N_2 or a Schlenk line under Ar, unless stated otherwise. Solvents were purified

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by distillation from Na/benzophenone, unless specified otherwise. Nuclear magnetic resonance spectra were recorded on a Bruker AC250, Varian XL300, or Varian Gemini 300-MHz spectrometer. Chemical shifts are reported vs Me_4Si. Infrared (IR) spectra were recorded on a Mattson Cygnus Starlab 100 Fourier transform spectrometer. Elemental microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

The compounds $MCl_4(THF)_2$ (M = Zr, Hf)[7] and $[PhMe_2NH][Co(C_2B_9H_{11})_2]$[8] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

1,2-Bis(3-indenyl)ethane.[9] One 800-mL bottle of *n*-BuLi (Aldrich, 1.6 M, 1.3 mol) was added via cannula to a solution of indene (150 mL, 1.3 mol) in THF (1.5 L, freshly opened bottle) at −78 °C under a nitrogen atmosphere. The solution turned orange, and a precipitate formed. Neat 1,2-dibromoethane (50 mL, 0.58 mol) was then added dropwise at the same temperature. The solution was allowed to warm to room temperature; the precipitate disappeared, and the solution turned red. After several hours at room temperature, saturated aqueous NH_4Cl (500 mL) was added to the solution. The solution was diluted with petroleum ether (1 L), and the organic layer was washed with brine (2 × 800 mL) and dried over $MgSO_4$. Evaporation of the solvent and filtration through a fritted funnel gave a brown residue, which was washed with hexanes to give 81 g (54%) of 1,2-bis(3-indenyl)ethane as a light tan solid.

***rac*-(EBTHI)ZrCl$_2$ (1).** This procedure differs from that reported by Collins[5] in that the dipotassium salt of the ligand is used, rather than the dilithium salt. A solution of 1,2-bis(3-indenyl)ethane (12.9 g, 50 mmol) in THF (50 mL) was added to a suspension of KH (4.4 g, 110 mmol) in THF (250 mL). When hydrogen generation had subsided, the excess KH was allowed to settle to the bottom of the flask. This solution and a solution of $ZrCl_4(THF)_2$ (18.9 g, 50 mmol) in THF (300 mL) were both added dropwise (~80–90 drops/min) via cannula to a flask containing rapidly stirring THF (300 mL) over 6–7 h.[10] A cloudy orange solution formed. After the addition was complete, the solution was purged with gaseous HCl for 10 min, rendering it bright yellow. Removal of the solvent gave a yellow solid. This was washed on a glass frit with 4 N HCl (200 mL), H_2O (200 mL), EtOH (100 mL), and Et_2O (100 mL). The product, a mixture of *rac*- and the previously unobserved *meso*-[ethylene-1,2-bis(η^5-1-indenyl)]$ZrCl_2$,[11] was an air-stable bright yellow powder (15.2 g). This powder was transferred to an autoclave containing CH_2Cl_2 (200 mL, freshly opened bottle), PtO_2 (0.50 g, 2.2 mmol), and a stirring bar. The autoclave was pressurized with H_2 (1500 psi) and allowed to stir at room temperature for 16 h. The contents of the autoclave were then diluted with CH_2Cl_2 (500 mL) and filtered through Celite. The Celite was washed with additional CH_2Cl_2 (300 mL). Removal of the solvent gave a gray residue. This contained a mixture of *rac*- and *meso*-(EBTHI)$ZrCl_2$ (~2:1 by ^1H NMR analysis). The *rac* isomer was obtained pure by stirring this mixture with hot toluene (150 mL) and then cooling to −20 °C for ~2 h. Colorless crystals of *rac*-(EBTHI)$ZrCl_2$ were isolated (8.7 g). Chunky, light green crystals of the *meso* isomer[12] could also be obtained by concentrating the mother liquor and cooling to −20 °C for several days, but the mother liquor was usually discarded. In general, overall yields of *rac*-1 of 40–50% from $ZrCl_4(THF)_2$ were obtained. This compound was identified by comparing its ^1H NMR spectrum with that reported in the literature.[5]

***rac*-(EBTHI)HfCl$_2$ (2).** In a procedure analogous to that used to synthesize 1, a solution of $HfCl_4(THF)_2$ (14.3 g, 31 mmol) in THF (350 mL) and a solution derived from 1,2-bis(3-indenyl)-ethane (8.0 g, 31 mmol) and KH (2.7 g, 67 mmol) in THF (350 mL) were added dropwise to a flask containing THF (350 mL), giving 5.84 g of the bright yellow product *rac*-[ethylene-1,2-bis-(η^5-1-indenyl)]$HfCl_2$ after workup. No meso compound was observed, although a small amount of *rac*-1 (<5%) was usually present. Hydrogenation of this material in CH_2Cl_2 (175 mL) for 16 h using H_2 (1500 psi) and PtO_2 (0.50 g, 2.2 mmol) at room temperature yielded colorless crystals of *rac*-(EBTHI)$HfCl_2$ (4.64 g, overall yield from $HfCl_4(THF)_2$, 30%). This compound was identified by comparing its ^1H NMR spectrum with that reported in the literature.[6]

[(EBTHI)ZrH(μ-H)]$_2$ (3). To a suspension of 1 (2.02 g, 4.74 mmol) in C_6H_6 (40 mL) at room temperature was added a THF solution of $NaEt_3BH$ (1.0 M, 9.95 mL, 9.95 mmol). The mixture was stirred for 2 h, during which time the solution became yellow and a fine white precipitate formed. After filtering via cannula, the solution was concentrated to 10 mL, and hexanes (30 mL) were added. This solution was then evaporated to dryness. The residue was washed with hexanes (2 × 30 mL) to give **3** as an air-sensitive pale yellow powder (1.10 g, 65%). ^1H NMR (300 MHz, C_6D_6): δ 6.56 (d, J = 2.5 Hz, 2 H, EBTHI), 6.36 (d, J = 3.1 Hz, 2 H, EBTHI), 5.24 (d, J = 2.9 Hz, 2 H, EBTHI), 5.16 (t, J = 7.5 Hz, 2 H, terminal Zr–H), 5.06 (d, J = 2.8 Hz, 2 H, EBTHI), 1.5–3.7 (m, 40 H, EBTHI), −1.29 (t, J = 7.5 Hz, 2 H, bridging Zr–H). $^{13}C\{H\}$ NMR (75 MHz, C_6D_6): δ 129.27, 124.00, 122.15, 121.57, 120.89, 114.52, 102.96, 101.98, 99.91, 99.14, 28.98, 27.77, 26.87, 26.19, 25.24, 25.04, 24.06, 23.98, 23.91. IR (KBr): 2931, 2897, 2850, 1555, 1551, 1548, 1449, 1442, 1434, 1377, 1324, 1275, 786 cm^{-1}. Anal. Calcd for **3**: C, 67.17; H, 7.33. Found: C, 67.14; H, 7.32.

[(EBTHI)HfH(μ-H)]$_2$ (4). In a procedure similar to the one used to prepare **3**, (EBTHI)$HfCl_2$ (0.680 g, 1.33 mmol) in C_6H_6 (20 mL) was treated with a THF solution of $NaBEt_3H$ (1.0 M, 2.65 mL, 2.65 mmol) to give **4** as an air-sensitive pale yellow powder (0.374 g, 70%). ^1H NMR (300 MHz, C_6D_6): δ 11.07 (t, J = 7.3 Hz, 2 H, terminal Hf–H), 6.44 (d, J = 1.5 Hz, 2 H, EBTHI), 6.26 (d, J = 3.1 Hz, 2 H, EBTHI), 5.12 (d, J = 2.9 Hz, 2 H, EBTHI), 4.99 (d, J = 3.1 Hz, 2 H, EBTHI), 3.63 (m, 2 H, EBTHI), 3.32 (t, J = 7.5 Hz, 2 H, bridging Hf–H), 3.14 (m, 2 H, EBTHI), 1.7–2.4 (m, 36 H, EBTHI). $^{13}C\{H\}$ NMR (75 MHz, C_6D_6): δ 128.61, 121.81, 120.24, 119.94, 119.65, 113.25, 102.36, 100.49, 99.27, 98.14, 28.45, 27.16, 26.70, 25.99, 25.17, 24.97, 24.04, 24.00, 23.84, 23.80. IR (KBr): 2931, 2851, 1617, 1610, 1443, 1435, 1381, 1364, 1348, 1005, 789, 749 cm^{-1}. Anal. Calcd for **4**: C, 53.99; H, 5.89. Found: C, 54.07; H, 5.67.

(EBTHI)HfMe$_2$ (5). To a suspension of **2** (1.00 g, 1.98 mmol) in THF (50 mL) at −10 °C was added a solution of MeLi (1.44 M, 2.90 mL, 4.18 mmol). The mixture was stirred for 15 min and then allowed to warm to room temperature. Stirring was continued for 1 h. The solvent was then removed in vacuo, and the residue was extracted with hot hexanes (80 mL). After filtering via cannula, the yellow solution was concentrated to 35 mL and cooled to −80 °C overnight. Air-sensitive pale yellow crystals of **5** were isolated (0.589 g, 64%). ^1H NMR (300 MHz, C_6H_6): δ 6.05 (d, J = 2.4 Hz, 2 H, EBTHI), 4.99 (d, J = 2.4 Hz, 2 H, EBTHI), 2.80 (m, 4 H, EBTHI), 2.43 (m, 4 H, ethylene bridge), 2.26 (m, 2 H, EBTHI), 1.96 (m, 2 H, EBTHI), 1.3–1.8 (m, 8 H, EBTHI), −0.30 (s, 6 H, HfMe). $^{13}C\{H\}$ NMR (75 MHz, C_6D_6): δ 124.26, 122.06, 119.81, 111.72, 104.98, 38.91, 27.09, 24.39, 23.59, 23.30, 23.08. Anal. Calcd for **5**: C, 55.87; H, 6.39. Found: C, 56.00; H, 6.35.

[(EBTHI)Zr(H)(PhNMe$_2$)][Co(C$_2$B$_9$H$_{11}$)$_2$] (6). The cationic zirconium hydride complex **6** (0.14 mmol) was generated by adding C_6H_6 (10 mL)[13] to a mixture of **3** (0.050 g, 0.14 mmol) and $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ (0.062 g, 0.14 mmol). The reaction mixture was allowed to stir at room temperature until a homo-

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(9) This is a slightly modified literature procedure.[6]

(10) It is important that the two solutions add at the same rate and that the addition be allowed to proceed over at least 5 or 6 h; otherwise the yield drops dramatically.

(11) The characteristic Cp–H signals appear at δ 6.71 (d, J = 3.0 Hz) and 6.56 (d, J = 3.0 Hz) for the *meso* compound in $CDCl_3$, in contrast to δ 6.60 (d, J = 3.0 Hz) and 6.22 (d, J = 3.0 Hz) for the previously reported *rac* compound.[5]

(12) *meso*-1: ^1H NMR (300 MHz, $CDCl_3$) δ 6.30 (d, J = 3.0 Hz, 1 H), 6.06 (d, J = 3.0 Hz, 1 H), 2.9–3.2 (m, 3 H), 2.3–2.65 (m, 3 H), 1.9–2.1 (m, 2 H), 1.5–1.65 (m, 2 H); $^{13}C\{H\}$ NMR (63 MHz, $CDCl_3$) δ 132.2, 130.3, 125.4, 121.1, 107.7, 28.3, 23.9, 23.0, 22.1, 21.9. IR (KBr) 3068, 2946, 2935, 2923, 2905, 2872, 2859, 2832, 1468, 1456, 1447, 1441, 1432, 818, 806 cm^{-1}. Anal. Calcd. for *meso*-1: C, 56.32; H, 5.67. Found: C, 56.53; H, 5.57. In contrast, in the ^1H NMR spectrum of *rac*-1, the characteristic Cp–H signals appear at δ 6.36 (d, J = 3.0 Hz) and 5.64 (d, J = 3.0 Hz).[5]

(13) Purified by initial distillation from Na/benzophenone, followed by vacuum transfer from the same.

geneous orange solution formed (~1.5 h). The conversion to **6** was quantitative, as observed by ^{1}H NMR spectroscopy; however, isolation of a clean solid proved difficult. Thus, **6** was generated and used in situ. ^{1}H NMR (300 MHz, C_6D_6): δ 6.6–7.3 (m, 5 H, NPh), 6.42 (d, J = 3.0 Hz, 1 H, EBTHI), 6.30 (s, 1 H, EBTHI), 6.10 (s, 1 H, Zr–H), 5.38 (d, J = 2.5 Hz, 1 H, EBTHI), 4.99 (d, J = 2.8 Hz, 1 H, EBTHI), 1.5–3.5 (broad m, EBTHI, NMe_2, $C_2B_9H_{11}$).

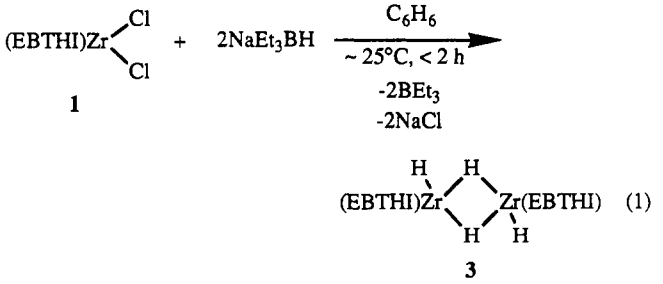
[(EBTHI)Hf(H)(PhNMe$_2$)][Co(C$_2$B$_9$H$_{11}$)$_2$] (7). In a procedure analogous to the one used to prepare **6**, the hafnium hydride cation **7** was generated in situ from **4** (0.062 g, 0.14 mmol) and $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ (0.062 g, 0.14 mmol) in C_6H_6 (10 mL).[13] ^{1}H NMR (300 MHz, C_6D_6): δ 10.86 (s, 1 H, Hf–H), 6.6–7.3 (m, 5 H, NPh), 6.34 (d, J = 3.1 Hz, 1 H, EBTHI), 6.21 (d, J = 2.6 Hz, 1 H, EBTHI), 5.41 (t, J = 3.0 Hz, 1 H, EBTHI), 4.87 (d, J = 3.2 Hz, 1 H, EBTHI), 1.5–3.5 (broad m, EBTHI, NMe_2, $C_2B_9H_{11}$).

(*S*)-(+)-2-Phenylbutane. Benzene (10 mL)[13] was added to a mixture of (*S*,*S*)-(EBTHI)$ZrMe_2$ (0.054 g, 0.14 mmol, 93% ee)[14] and $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ (0.062 g, 0.14 mmol). When the solution became homogeneous (1.5 h), 2-phenyl-1-butene (2.1 mL, 14 mmol, 100 equiv) was added. The solution was transferred to an autoclave, and a hydrogen atmosphere (1500 psi) was added. The solution was stirred at room temperature for 24 h. The pressure was released, and the solution was flushed through a short column of alumina, chasing with hexanes. The solvent was evaporated to give 1.71 g (13 mmol, 91% yield) of (*S*)-(+)-2-phenylbutane, $[\alpha]^{21}_D$ = +6.5° (c = 0.8, EtOH) (lit. +28.4°),[15] 23% ee. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (m, 2 H), 7.18 (m, 3 H), 2.59 (sextet, J = 6.7 Hz, 1 H), 1.59 (pentet, J = 7.5 Hz, 2 H), 1.23 (d, J = 6.7 Hz, 3 H), 0.82 (t, J = 7.2 Hz, 3 H).

Results and Discussion

The synthesis of *rac*-(EBTHI)$ZrCl_2$ (**1**) is similar to that reported by Collins,[5] in which an overall yield from $ZrCl_4(THF)_2$ of 32% was obtained. Collins has since reported[3] that his procedure can be rather capricious, giving overall yields anywhere from 20–60%. We obtained yields of only 20–30% using butyllithium as the deprotonating agent. Consistently better yields (40–50% of pure *rac*-**1** from $ZrCl_4(THF)_2$) are obtained by deprotonating the ligand, 1,2-bis(3-indenyl)ethane, with KH, and by allowing longer addition times (5–7 h vs 2 h) for the double-dilution reaction. It is interesting that significant amounts of the hitherto unobserved *meso* isomer are also produced. A ratio of 2:1 *rac*:*meso* is typically observed by ^{1}H NMR spectroscopy. The analogous preparation of the Hf complex **2** is also found to give a much better yield (30% vs 8%) than that reported by Ewen.[6]

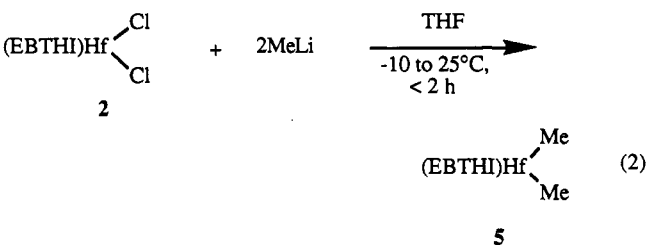
The dihydride dimer [(EBTHI)ZrH(μ-H)]$_2$ (**3**) is readily synthesized by treating the dichloride complex **1** with 2 equiv of $NaEt_3BH$ in C_6H_6 at room temperature for <2 h, to give **3** in 65% yield (eq 1). The hafnium dihydride **4**



(1)

is prepared similarly in 70% yield. The ^{1}H NMR spectrum of **3** exhibits two distinct hydride resonances [δ 5.16 (t), −1.29 (t)] at room temperature, which is indicative of a dimeric structure. Similar chemical shifts are observed for the bridging and terminal hydride ligands in the dimers [(C_5H_4Me)ZrH(μ-H)]$_2$ (δ 3.75, −2.98)[16] and [(C_9H_{11})$_2$ZrH(μ-H)]$_2$ (δ 4.59, −1.56).[17] The ^{1}H NMR spectrum of **4**, like **3**, also indicates a dimeric structure in solution. The extremely low field resonance observed at δ 11.07 (t), assigned to the terminal hydride ligands, is between the chemical shift reported by Bercaw[18] for $Cp^*_2HfH_2$ (δ 15.57) and the resonance observed for the terminal zirconium hydrides in **3** (δ 5.16). The resonance occurring at δ 3.32 (t), assigned to the bridging hydride ligands, is further downfield than the resonances observed for the terminal hydrides in **3**, [(C_5H_4Me)ZrH)]$_2$, and [(C_9H_{11})$_2$ZrH(μ-H)]$_2$ (δ −1.29, −2.98, −1.56, respectively), but it is significantly upfield of the region where terminal hafnium hydrides are typically found. In general, the resonances for hafnium hydride ligands are found further downfield in the ^{1}H NMR spectrum than the resonances for their zirconium analogues.[19]

The dimethylhafnium complex **5** is readily synthesized from **2** and MeLi (eq 2). Complex **5** was characterized by its elemental analysis and ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum is very similar to that reported for the



(2)

zirconium analogue.[20] Both complexes exhibit a resonance upfield of Me_4Si for the methyl ligands [δ −0.30 for **5**, and −0.09 for (EBTHI)$ZrMe_2$].

Metal hydride cations are of interest as possible intermediates in the polymerization and hydrogenation of olefins.[8a,21-24] We and others[25] have been interested in using these and related species as catalysts for asymmetric organic synthesis. In particular, we wished to explore cationic systems which employed $[Co(C_2B_9H_{11})_2]^-$ as the counterion, as recently developed by Hlatky and Turner,[8a,22] to avoid the problems of insolubility and decomposition which have been observed in related systems.[23,24] Thus, when **3** was treated with 2 equiv of $[PhMe_2NH][Co(C_2B_9H_{11})_2]$, the soluble monomeric hydride cation **6** was formed quantitatively in <1 h (eq 3). Analogous benzyl cations (as the acetonitrile or tetrahydrofuran adducts), with tetraphenylborate counterions, were recently

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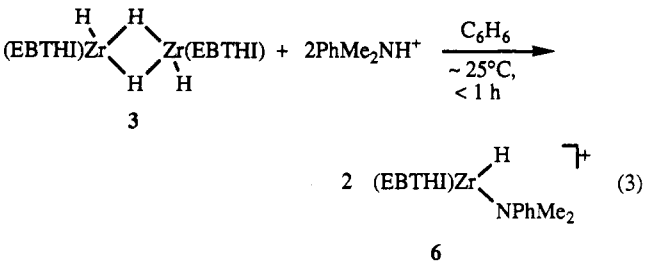
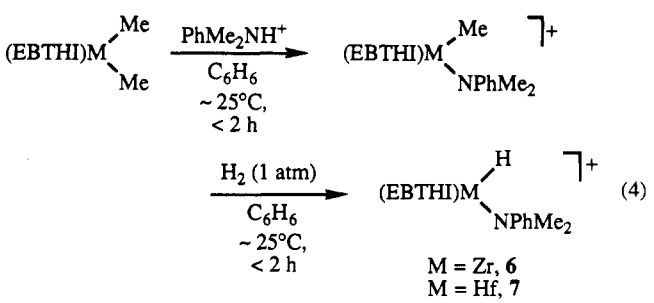


3

6 (3)

described by Jordan.[25b] The hafnium analogue **7** was synthesized in a similar manner and was somewhat less soluble in aromatic solvents. The use of base-free or weak base adducts of cationic metallocene complexes containing carborane or metallacarborane counterions has eliminated some of the problems noted above. Related protonation reactions of several dimethylzirconocene complexes with weak acids ($[n\text{-}Bu_3NH][BPh_4]$ or $C_2B_9H_{13}$) have been reported by Hlatky and Turner.[22] In complexes **6** and **7**, the conjugate base *N,N*-dimethylaniline is weakly coordinated to the metal and greatly increases the solubility of the complexes in aromatic solvents. Protonation of **3** with $[Ph_3NH][Co(C_2B_9H_{11})_2]$ in C_6H_6 gives an insoluble material, presumably due to the lack of coordination of the larger base. (Free NPh_3 is observed by ^1H NMR spectroscopy.)

The cationic hydride complexes **6** and **7** can also be prepared from the corresponding dimethyl complexes. Treatment of (EBTHI)MMe_2 (M = Zr, Hf) with 1 equiv of $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ gives the cationic methyl complexes $[(EBTHI)M(Me)(PhNMe_2)][Co(C_2B_9H_{11})_2]$. Subsequent hydrogenation with 1 atm of H_2 at room temperature for <1 h produces the corresponding hydride cation complexes in quantitive yield (eq 4). The pro-



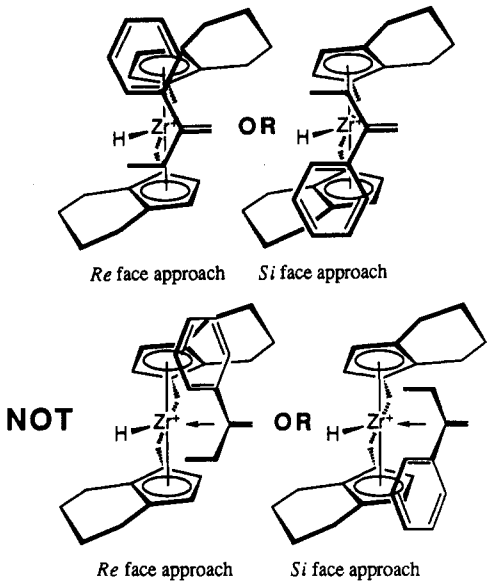
M = Zr, **6**
M = Hf, **7** (4)

duction of CH_4 was also observed by ^1H NMR spectroscopy (δ 0.18). A similar reaction of $Cp_2Zr(Me)(THF)^+$ with H_2 (1 atm, 23 °C, $t_{1/2}$ = 21 h) to give insoluble $[Cp_2Zr(H)(THF)][BPh_4]$ was reported by Jordan.[23] More recently, Jordan has shown that the benzyl complex $[(C_5H_4Me)_2Zr(CH_2Ph)(THF)][BPh_4]$ is also hydrogenated in THF (1 atm H_2, 23 °C, 72 h) to produce the soluble hydride species $[(C_5H_4Me)_2Zr(H)(THF)][BPh_4]$.[24] The ease of hydrogenation of the zirconium and hafnium complexes $[(EBTHI)M(Me)(PhNMe_2)][Co(C_2B_9H_{11})_2]$ gives evidence for the greater lability of $PhNMe_2$ as compared to THF.

The ^1H NMR spectrum of a C_6D_6 solution of **6** contains a broad singlet at δ 6.10 (1 H), which is absent from the spectrum of the corresponding deuteride complex $[(EBTHI)Zr(D)(PhNMe_2)][Co(C_2B_9H_{11})_2]$,[26] and this is assigned to the Zr–H ligand. Similarly, the ^1H NMR spectrum of the hafnium analogue **7** exhibits a broad singlet at δ 10.86 (1 H), assigned to the Hf–H ligand. These resonances are within the range normally observed for terminal hydrides

(26) This compound was prepared from $[(EBTHI)Zr(Me)(NPhMe_2)][Co(C_2B_9H_{11})_2]$ and D_2.

Scheme I



of group 4 metallocenes and are far downfield of the range observed for bridging hydrides.[27]

Attempts to isolate **6** or **7** gave impure orange solids with varying amounts of $PhNMe_2$ (0.5–1.0 equiv). These solids were considerably less soluble in C_6H_6 and decomposed over several weeks under inert atmosphere. Benzene solutions of **6** and **7** were extremely air- and moisture-sensitive, but showed no detectable decomposition after 3 days at room temperature. In addition, enantiomerically enriched **6**[14] was found to undergo only a minor amount of racemization after 3 days in C_6D_6 at room temperature (92% ee to 85% ee), as observed by ^1H NMR spectroscopy after treating with excess (*R*)-*O*-acetylmandelic acid.

As mentioned earlier, much of the interest in base-free group 4 metal cations derives from their possible intermediacy in Ziegler-Natta polymerizations and hydrogenations. We were therefore interested in the abilities of the enantiomerically pure cationic hydrides **6** and **7** to effect the asymmetric catalytic hydrogenation of olefins. Although (*S,S*)-**6** efficiently catalyzed the reduction of 2-phenyl-1-butene under 100 atm of hydrogen, the ee of the product was rather low (23% ee). A similar result (36% ee) was reported by Waymouth and Pino during the course of this investigation;[21] they used a homogeneous zirconium Ziegler-Natta-type catalyst. The low ee's indicate that, in this system, the energy difference between approaches of the different enantiofaces of the olefin to the catalyst is not large ($\Delta\Delta G^\ddagger \approx 0.4$ kcal/mol). Interestingly, in contrast to what we initally expected, the absolute configuration of the product derived from (*S,S*)-**6** was determined to be *S*. Our result, however, was consistent with the results obtained by Waymouth and Pino.[21] To explain their results, they supposed that the olefin might approach the metal more from the "front" of the complex than from the "side" (Scheme I).[21] This hypothesis explains both the low enantioselectivity and the reversal of the expected facial selectivity observed in both systems.

(27) Other representative chemical shifts for zirconium and hafnium hydrides: $(C_5H_4Me)_2Zr(H)(THF)^+$ δ 5.88;[24] $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ δ 3.75 (H), −2.98 (μ-H);[17] $Cp^*_2ZrH_2$ δ 7.46;[28] $[Cp_2Zr(R)(\mu\text{-}H)]_2$ ca. δ −2 (μ-H);[29] $Cp^*_2HfH_2$ δ 15.57.[19]

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In conclusion, we have prepared several interesting neutral and cationic derivatives of (EBTHI)$ZrCl_2$ and (EBTHI)$HfCl_2$. These compounds are potentially useful for the asymmetric synthesis of organic compounds.

Acknowledgment. This work was supported by the National Institutes of Health (Grant GM-34917) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. R.B.G. is the recipient of a National Science Foundation Graduate Fellowship (1987–90), for which he is grateful. R.A.D. was supported, in part, as a Postdoctoral Trainee NCI T32CA09112. S.L.B. acknowledges additional support as a Camille & Henry Dreyfus Teacher-Scholar (1989–94), a Fellow of the Alfred P. Sloan Foundation (1988–92), and a Union Carbide Innovation Recognition Awardee. We thank Dr. Howard W. Turner of Exxon Chemical for helpful discussions.

Group 4 *ansa*-Metallocenes in Oxidation State III: Synthesis, Characterization, and Chemical Behavior. Crystal Structure of $\{[\eta^5:\eta^5\text{-}(C_5H_4)_2Si(CH_3)_2]TiCl(PMe_2Ph)\}$

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Received August 6, 1990

Two new dimeric titanium(III) and zirconium(III) *ansa*-metallocenes $\{[(Me_2SiCp_2)MCl]_2\}$ (M = Ti (**2a**), Zr (**2b**)) were synthesized by reducing the dichlorometallocenes with Na/Hg. The same reduction of the titanium derivative in the presence of PMe_2Ph led to the monomeric titanium(III) complex $[(Me_2SiCp_2)TiCl(PMe_2Ph)]$ (**3**), which was also obtained by addition of PMe_2Ph to **2a**. Alkylation of **3** led to the titanium(III) alkyls $[(Me_2SiCp_2)TiR(PMe_2Ph)]$ (R = Me (**4**), CH_2SiMe_3 (**5**)). **4** was also obtained by reduction of $[(Me_2SiCp_2)TiClMe]$ (**6**) with Na/Hg in the presence of PMe_2Ph. All the titanium(III) complexes were paramagnetic, and their EPR behavior was studied, whereas the diamagnetic zirconium(III) derivative was characterized by NMR spectroscopy. All of them are easily oxidized by oxygen, and the intermediate dimeric $\{(\mu\text{-}O)[(Me_2SiCp_2)ZrCl]_2\}$ (**7**) was spectroscopically identified in solution. The structure of **3** has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$ with Z = 4 in a unit cell of dimensions a = 7.130 (3) Å, b = 15.201 (6) Å, c = 20.261 (6) Å, α = 105.42 (2)°, β = 96.20 (2)°, and γ = 92.46 (2)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 4449 observed reflections to R and R_w values of 0.0517 and 0.0696, respectively. The structure of **3** is very similar to that of comparable Ti(IV) compound $[(Me_2SiCp_2)TiCl_2]$, except for the much longer Ti–Cl bond (2.463 (2) against 2.356 (1) and 2.379 (2) Å), whereas no significant modifications are induced into the dimethylsilyl bridge.

Introduction

The synthesis and structural characterization of dichloro *ansa*-metallocenes of group 4 metals in oxidation state IV ($[X(C_5H_4)_2MCl_2]$, X = CH_2, C_2H_4, C_3H_6, R_2Si (R = Me, Et, *n*-Pr); M = Ti, Zr) have been extensively studied.[1]

A few alkyltitanium and -zirconium derivatives[2] with both cyclopentadienyl rings bridged by $-CH_2CH_2-$ or Me_2Si groups as well some hydrido complexes[3] have also been reported.

In contrast, the chemistry of the *ansa*-metallocenes of the group 4 metals in low oxidation states has been scarcely studied in spite of the expected stabilization of low-valent titanium and zirconium complexes produced by using two cyclopentadienyl rings bridged by an interannular group which hinders the participation of the cyclopentadienyl ligands in reactions involving rings C–H activation processes.

Some studies on electrochemical reduction have been published,[1f,p,3a,4] but to the best of our knowledge, only one

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