

The rather elegant fit of all these complexes and considerations demonstrates the reality of these ring currents, their potential value as a structural tool, and the accuracy of the Evans method, when used as described, for evaluating small differences in magnetic susceptibilities.

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Organometallic Thermochemistry. Metal Hydrocarbyl, Hydride, Halide, Carbonyl, Amide, and Alkoxide Bond Enthalpy Relationships and Their Implications in Pentamethylcyclopentadienyl and Cyclopentadienyl Complexes of Zirconium and Hafnium

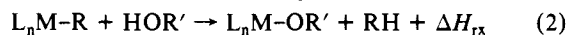
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Abstract: Metal-ligand bond disruption enthalpies (D) have been determined in the series Cp'_2MX_2 , Cp_2MX_2 , $Cp'MX_3$ ($M = Zr, Hf$; $Cp' = \eta^5-Me_5C_5$; $Cp = \eta^5-C_5H_5$; $M = Zr, Hf$; $X =$ hydrocarbyl, hydride, alkoxide, amide, halide) and in $Cp'_2Zr(CO)_2$ by anaerobic isoperibol batch-titration calorimetry. Heats of solution in toluene were measured followed by heats of reaction with HCl , I_2 , C_6F_5OH , C_6H_5OH , CF_3CH_2OH , or t -BuOH in toluene. Derived $D(M-X)$ values decrease in the order $OH \approx Cl >$ alkoxide $\approx NH_2 >$ phenoxide $> I \approx H >$ aryl $> Me >$ alkyl, metallacyclopentane $> \eta^1:\eta^5-CH_2C_5Me_4$ $M-C$ σ bond $> CO$. By using $D(Cl_3M-Cl)$ as a reference point, $D(M-X)$ values are found to be rather large (e.g., for $M = Zr(R)$: 78 (H), 73 (Ph), 67 (Me) kcal/mol) and not highly sensitive to ancillary η^5 -cyclopentadienyl ligation. $D(Hf-X) - D(Zr-X)$ is estimated to be ca. 4 kcal/mol. Ancillary alkoxide ligands enhance $D(Zr-H)$ in the $Cp'_2ZrH_2/Cp'_2Zr(OR)H$ series by ca. 5 kcal/mol. The metallacycle $Cp'_2ZrCH_2(ChEt)_2CH_2$ exhibits negligible ring strain while that in the zirconandane $Cp'_2ZrCH_2CH_2-o-C_6H_4$ is ca. -10 kcal/mol. A plot of $D(Zr-X)$ vs $D(H-X)$ is not linear but shows very substantial scatter. However, reasonably linear plots are observed within ligand subgroups such as hydrocarbyls, alkoxides, and halides. This behavior can be qualitatively explained on the basis of metal and ligand electronegativities. The quantities $D(M-H) - D(M-Me)$ and $D(M-I) - D(M-Me)$ vary considerably across the transition-metal series and are informative indices of metal-ligand bonding. The former is small for the present group 4 compounds and the latter large. The present data are used to semiquantitatively interpret a number of group 4 centered transformations. Among the conclusions drawn are that β -H elimination processes are usually endothermic; many C-H activating cyclometalation processes are endothermic, hence entropically driven (e.g., $Cp'_2ZrPh_2 \rightarrow Cp'_2Zr(Ph)(\eta^1:\eta^5-CH_2C_5Me_4) + PhH$); $Zr(II) \rightarrow Zr(IV)$ oxidative additions are highly exothermic; $D(Cp'_2Zr-benzene) \approx 120$ kcal/mol; early transition metal/lanthanide/actinide $M(\eta^1:\eta^5-CH_2C_5Me_4)$ species are energetically poised to serve as intermediates in a number of addition and elimination processes; and the large magnitude of $D(M-OR)$ is one major driving force for the formation of alkoxide-like end products in group 4 centered CO activation chemistry.

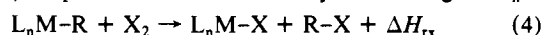
It is becoming increasingly apparent that metal-ligand bond enthalpy data can afford invaluable insights into important reaction patterns in organometallic chemistry and catalysis.^{1,2} Recent research in this laboratory has concentrated on measuring relative solution-phase homolytic bond disruption enthalpies³ (formally defined in the gas phase for the adiabatic process shown in eq 1) $D(L_nM-R) = \Delta H^\circ_f(L_nM) + \Delta H^\circ_f(R^\cdot) - \Delta H^\circ_f(L_nM-R)$ (1) $L_n =$ ancillary ligand array

in organoactinides by protonolytic (eq 2 and 3)⁴ or halogenolytic



$$\Delta H_{rx} = D(L_nM-R) + D(H-OR') - D(L_nM-OR') - D(R-H) \quad (3)$$

(eq 4 and 5)⁵ isoperibol titration calorimetry.⁶ Assuming the L_nM



$$\Delta H_{rx} = D(L_nM-R) + D(X_2) - D(L_nM-X) - D(R-X) \quad (5)$$

fragment remains structurally/energetically invariant (vide infra), relative $D(L_nM-R)$ parameters, "anchored" to estimated (usually from \bar{D} or D_1 data for homoleptic derivatives⁴) $D(L_nM-OR')$ or $D(L_nM-X)$ values, can be obtained with high precision. Such $D(L_nM-R)$ data, while only "semiabsolute" in that they are anchored to estimated $D(L_nM-OR)/D(L_nM-X)$ data, are invaluable for understanding transformations among L_nMR/L_nMR' species.⁴ In addition, it has recently been proven possible to determine absolute $D(L_nU-X)$ parameters via calorimetry of $L_nU/L_nUX/L_nUR$ ensembles.^{5a}

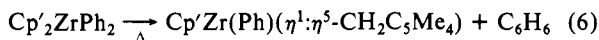
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(3) This quantity has been variously referred to as bond disruption enthalpy, bond dissociation enthalpy, bond enthalpy, bond energy, and bond strength. We prefer the terminology of Pilcher and Skinner.^{2a}

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In the present contribution, we focus in a comparative fashion upon bond enthalpy trends in a series of cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp') zirconium and hafnium complexes.^{7,8} Key issues concern trends in metal-hydrocarbyl/alkoxide/amide/halide/hydride/carbonyl bond enthalpies, ancillary ligand effects on these bond enthalpies, strain energies in metallocycles and other internally metalated derivatives, the reliability of various anchors, and deductions that follow concerning group 4 metal-centered stoichiometric and catalytic transformations. As one example, we analyze thermodynamic aspects of eq 6,⁹ in which intramolecular arene extrusion yields, via an ortho-phenylene intermediate, a metalated Cp' complex.



Experimental Section

General Methods. All procedures were performed with standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled Vacuum Atmospheres glovebox. Argon and nitrogen (Matheson, prepurified) and hydrogen (Linde) were purified by passage through sequential columns of MnO on vermiculite and Davison 4Å molecular sieves. Toluene, pentane, and diethyl ether (Mallinckrodt) were dried over sodium and molecular sieves, distilled from Na/K benzophenone under a nitrogen atmosphere, and transferred under argon flush into storage flasks containing a titanocene/Zn indicator. For calorimetric studies, toluene was distilled an additional time from Na/K on the high-vacuum (10⁻⁶ Torr) line into a flask directly connected to the calorimeter. Toluene-d₈ and C₆D₆ were vacuum distilled from Na/K. Iodine was freeze-pump-thawed and sublimed in vacuo. The titrants C₆F₅OH and CF₃CH₂OH were freeze-pump-thawed and sublimed in vacuo three times from 3Å molecular sieves; *t*-butyl alcohol was distilled in vacuo from 4Å molecular sieves and then distilled from calcium hydride. Hydrogen chloride (technical grade) was purchased from Matheson Gas Products and used without further purification.

¹H and ¹³C NMR spectra were recorded on a JEOL FX-270 (270 MHz ¹H; 67.80 MHz ¹³C) or a Varian XL-400 (400 MHz ¹H; 100 MHz ¹³C) spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to SiMe₄. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls sandwiched between KBr salt plates in an O-ring sealed, air-tight holder. GC/MS studies were performed on a Hewlett-Packard 5985 instrument and interfaced data system with 15-eV electron impact ionization. Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Müllheim, West Germany.

Syntheses. Cp'₂ZrCl₂,¹⁰ Cp'₂ZrMe₂,¹¹ Cp'₂Zr(OH)₂,¹² Cp'₂ZrPh₂,^{9,13} Cp'₂Zr(Ph)(η¹:η⁵-CH₂C₅Me₄),⁹ Cp'₂Zr(CO)₂,¹⁴ Cp'₂Zr(H)(NH₂),¹²

Cp'₂HfCl₂,¹⁵ Cp'₂HfH₂,^{15b} Cp'₂HfI₂,^{15b} Cp'₂ZrMe₃,¹⁶ Cp₂ZrMe₂,¹⁷ and Cp₂ZrI₂¹⁸ were prepared as described in the literature.

Cp'₂ZrH₂ was prepared from (Cp'₂ZrN₂)₂N₂ as described in the literature.¹¹ A more convenient, alternative procedure, however, was to heat a solution of Cp'₂ZrMe₂ (1.21 g, 3.08 mmol) in 30 mL of toluene at 70 °C under 1 atm of H₂ for 1 week. The toluene was then removed in vacuo and ca. 15 mL of pentane condensed in. The resulting yellow solution was filtered under H₂ and then slowly cooled to -78 °C to give 0.85 g of pale yellow crystalline Cp'₂ZrH₂ (76% yield), with spectroscopic properties identical with those reported for Cp'₂ZrH₂.¹¹

Cp'₂Zr(H)Ph. A dark red solution of 0.32 g (0.73 mmol) of Cp'₂Zr(Ph)(η¹:η⁵-CH₂C₅Me₄) in 20 mL of pentane was stirred under 1 atm of H₂ for 30 min to give a colorless solution. This solution was reduced in volume to ca. 5 mL, cooled to -78 °C, and filtered. The resulting colorless microcrystals were dried in vacuo to give 0.15 g of product (46% yield). The low yield is presumably due to the small amount of material being handled and high solubility of Cp'₂Zr(H)Ph. The reaction proceeds quantitatively by NMR analysis.

¹H NMR (C₆D₆): δ 7.31–7.26 (m, 1 *o*-H, 2 *m*-H), 7.11 (t, 1 *p*-H, *J*_{HH} = 5.93 Hz), 6.42 (d, 1 *o*-H, *J*_{HH} = 7.90 Hz), 6.34 (s, 1 H), 1.76 (s, 30 H, C₅Me₅). IR (Nujol mull, cm⁻¹): 3040 (sh), 2960 (sh), 2720 (m), 2030 (w), 1960 (w), 1855 (w), 1810 (w), 1762 (w), 1585 (s), 1565 (sh), 1520 (sh), 1484 (sh), 1427 (sh), 1412 (sh), 1305 (w), 1243 (m), 1165 (m), 1100 (w), 1057 (sh), 1042 (sh), 1023 (s), 991 (m), 955 (w), 900 (w), 825 (m), 805 (m), 770 (s), 719 (s), 703 (s), 641 (w). Anal. Calcd for C₂₆H₃₆Zr: C, 71.01; H, 8.25. Found: C, 70.08; H, 8.22.

Cp'₂Zr(OH)Ph. To a solution of 0.29 g (0.66 mmol) of Cp'₂Zr(Ph)(η¹:η⁵-CH₂C₅Me₄) in 15 mL of toluene was added several drops of H₂O. The mixture was stirred several minutes until the red solution became colorless. The resulting Cp'₂Zr(OH)Ph hydrolyzes only very slowly. The toluene and excess H₂O were next removed in vacuo, and 15 mL of pentane was condensed into the flask. The resulting solution was cooled slowly to -11 °C. Large colorless crystals grew in ca. 15 h. Filtration and removal of the solvent gave 0.18 g of product (61% yield).

¹H NMR (C₆D₆): δ 7.52 (d, 1 *o*-H, *J*_{HH} = 6.60 Hz), 7.27 (m, 2 *m*-H), 7.16 (t, 1 *p*-H, *J*_{HH} = 7.2 Hz), 7.05 (d, 1 *o*-H, *J*_{HH} = 7.26 Hz), 4.98 (s, 1 OH), 1.68 (s, 30 Cp' H). IR (Nujol mull, cm⁻¹): 3680 (m), 3642 (s), 3047 (sh), 2725 (w), 1560 (s), 1413 (m), 1265 (w), 1234 (w), 1168 (w), 1059 (m), 1050 (m), 1026 (s), 993 (w), 915 (w), 828 (m), 810 (w), 713 (s), 708 (s), 630 (sh). Anal. Calcd for C₂₆H₃₆OZr: C, 68.52; H, 7.96. Found: C, 68.60; H, 7.89.

Cp'₂ZrCH₂CH₂-*o*-C₆H₄. To a solution of 1.00 g (2.31 mmol) of Cp'₂ZrCl₂ in 35 mL of diethyl ether was added 2.9 mL (4.9 mmol) of PhLi (1.7 M in cyclohexane-ether) via syringe at -78 °C. The solution was allowed to warm to room temperature with stirring and was stirred for an additional 4 h. The diethyl ether was next removed in vacuo, 35 mL of pentane was condensed in, and the solution was filtered. The colorless solid on the frit was washed by condensing ca. 10 mL of pentane back onto the frit. The pentane was then removed from the filtrate in vacuo, leaving a pale yellow precipitate (Cp'₂ZrPh₂). Toluene (20 mL) was condensed onto the precipitate, the resulting solution was placed under 1 atm of ethylene, and the solution was stirred at 80 °C for 18 h. The toluene was then removed in vacuo, and 40 mL of pentane was condensed into the flask. The resulting yellow-orange solution was filtered and then reduced in volume to ca. 30 mL. The solution was slowly cooled to -78 °C and then filtered cold. The resulting crystals were then recrystallized from 30 mL of pentane under ethylene. It was necessary to warm the solution slightly to get the compound completely into solution, which was then cooled to -78 °C. Filtration of the cold solution gave 0.79 g of bright yellow crystals (73% yield from Cp'₂ZrCl₂). The zirconaindan, Cp'₂ZrCH₂CH₂-*o*-C₆H₄, can also be prepared by stirring a toluene solution of Cp'₂Zr(Ph)(η¹:η⁵-CH₂C₅Me₄) under 1 atm of ethylene at 90 °C for 4 h.

¹H NMR (C₆D₆): δ 7.06–7.03 (m, 2 H), 6.95 (d, 1 H, *J*_{HH} = 6.98 Hz), 6.54 (d, 1 H, *J*_{HH} = 6.46 Hz), 3.18 (t, 2 H, *J*_{HH} = 7.56 Hz), 1.70 (s, 30 H), 0.91 (t, 2 H, *J*_{HH} = 7.56 Hz). IR (Nujol mull, cm⁻¹): 3120 (sh), 3083 (sh), 3025 (sh), 2794 (sh), 2712 (m), 2040 (w), 1925 (w),

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1895 (w), 1830 (w), 1800 (w), 1660 (w), 1560 (w), 1480 (sh), 1420 (sh), 1302 (s), 1255 (w), 1240 (s), 1218 (w), 1160 (m), 1135 (w), 1100 (m), 1058 (m), 1017 (s), 963 (w), 934 (m), 865 (m), 844 (m), 800 (m), 772 (s), 730 (s), 600 (sh), 583 (sh). Anal. Calcd for $C_{28}H_{38}Zr$: C, 72.20; H, 8.22. Found: C, 72.12; H, 8.25.

$Cp'_2ZrCH_2(CH_2Et)_2CH_2$. To a solution of 1.48 g (3.43 mmol) of Cp'_2ZrCl_2 in 50 mL of diethyl ether at $-78^\circ C$ was added 5 mL (1.55 M in hexane, 7.75 mmol) of *n*-BuLi via syringe under an argon flush. The solution was allowed to warm to room temperature with stirring and was then stirred an additional 12 h. The diethyl ether was then removed in vacuo and 40 mL of pentane condensed into the flask. The solution was warmed to ca. $30^\circ C$ and filtered. The colorless precipitate on the frit was washed once with 10 mL of pentane. The orange filtrate was reduced in volume to ca. 8 mL, and a yellow precipitate formed. The solution was cooled to $-78^\circ C$ and filtered. The yellow precipitate was then dried in vacuo. Sublimation (10^{-5} Torr) at 105 – $115^\circ C$ gave 0.60 g of $Cp'_2ZrCH_2(CH_2Et)_2CH_2$ (35% yield). The product was characterized by MS, NMR, IR, and elemental analysis. Reaction with water gave $Cp'_2Zr(OH)_2$ and 3,4-dimethylhexane by NMR analysis. Product isolation after 30 min of reaction recovered substantial amounts of Cp'_2ZrCl_2 (ca. 50% yield). After 1 h of reaction, the yellow solution began to turn rust-colored. Product isolation after 4 h yielded what appeared to be (by NMR) a mixture of $Cp'_2Zr(n-Bu)_2$ (cf., $Cp'_2Hf(n-Bu)_2$, vide infra) and $Cp'_2ZrCH_2(CH_2Et)_2CH_2$. Reaction of 0.205 g (0.474 mmol) of Cp'_2ZrCl_2 with 2 equiv of *n*-BuLi under 1 atm of 1-butene in diethyl ether gave a golden-yellow solution. The diethyl ether was removed after 2 days of stirring. Workup in pentane (vide supra) yielded 0.20 g (89%) of $Cp'_2ZrCH_2(CH_2Et)_2CH_2$ as a yellow crystalline solid.

1H NMR (C_6D_6 , assignments were made by selective decoupling experiments): δ 1.80 (s, 30 H, C_3Me_3), 1.48 (m, 2 H, $C(\beta)H$), 1.05 (m, 10 H, CH_2CH_3), 0.76 (d-d, 2 $C(\alpha)H$, $^2J_{HH} = 11.9$ Hz, $^3J_{HH} \approx 11.9$ Hz), -0.14 (d-d, 2 $C(\alpha)H$, $^2J_{HH} = 11.9$ Hz, $^3J_{HH} = 4.59$ Hz). ^{13}C NMR (C_6D_6): δ 117.79 (s, C_3Me_3), 55.31 (t, $C(\alpha)H_2$, $J_{CH} = 116.7$ Hz), 47.75 (d, $C(\beta)H$, $J_{CH} = 184.0$ Hz), 31.70 (t, CH_2CH_3 , $J_{CH} = 124.0$ Hz), 11.54 (q, C_3Me_3 , $J_{CH} = 125.2$ Hz), 11.38 (q, CH_2CH_3 , $J_{CH} \approx 125.2$ Hz). IR (Nujol mull, cm^{-1}): 3630 (m), 2905 (sh), 2730 (w), 1490 (w), 1440 (sh), 1263 (m), 188 (w), 1020 (m), 960 (w), 801 (m), 520 (s), 385 (sh), 340 (s), 325 (sh). Anal. Calcd for $C_{28}H_{46}Zr$: C, 70.97; H, 9.78. Found: C, 70.85; H, 9.93.

$Cp'_2Zr(H)(O-t-Bu)$. Cp'_2ZrH_2 (0.29 g, 1.80 mmol) was placed in a frit reaction apparatus. Next, *t*-BuOH (0.20 mL, 2.1 mmol) was sublimed into the apparatus and then ca. 10 mL of pentane was distilled into the reaction vessel via vacuum transfer. Evolution of gas (H_2) occurred immediately. After the reaction mixture was stirred for 30 min, the volatiles were removed in vacuo. The resulting colorless solid was washed with ca. 2 mL of cold pentane and then dried in vacuo to give 0.31 g of fine colorless polycrystalline powder (89% yield).

1H NMR (C_6D_6): δ 5.72 (s, 1 H), 2.00 (s, 30 H), 1.29 (s, 9 H). IR (Nujol mull, cm^{-1}): 2710 (w), 2387 (w), 1760 (w), 1582 (m), 1428 (sh), 1350 (sh), 1250 (w), 1213 (sh), 1180 (s), 1060 (w), 1018 (sh), 981 (s), 820 (m), 800 (w), 775 (m), 620 (sh), 600 (sh), 590 (sh). Anal. Calcd for $C_{24}H_{40}OZr$: C, 66.15; H, 9.25. Found: C, 66.09; H, 9.29.

$Cp'_2Zr(Me)(OC_6H_5)$. A solution of 0.412 g (1.05 mmol) of Cp'_2ZrMe_2 and 0.099 g (1.05 mmol) of C_6H_5OH in 30 mL of toluene was stirred for 12 h. The volatiles were then removed in vacuo and ca. 10 mL of pentane was distilled into the reaction apparatus. The resulting colorless solution was slowly cooled to $-78^\circ C$. The colorless crystals which formed overnight were filtered off and dried in vacuo to give 0.41 g of colorless product (83% yield).

1H NMR (C_6D_6): δ 7.15 (d-d, 2 *m*-H), 6.74 (t, 1 *p*-H, $J_{HH} = 6.89$ Hz), 6.57 (d, 2 *o*-H, $J_{HH} = 7.25$ Hz), 1.77 (s, 30 H), 0.13 (s, 3 CH_3). IR (Nujol mull, cm^{-1}): 3065 (w), 2711 (w), 1762 (w), 1587 (s), 1557 (sh), 1487 (sh), 1288 (s), 1160 (m), 1065 (w), 1020 (w), 997 (w), 874 (s), 824 (m), 752 (s), 691 (m), 615 (sh). Anal. Calcd for $C_{27}H_{36}OZr$: C, 69.03; H, 8.15. Found: C, 69.06; H, 8.18.

Cp'_2ZrI_2 . A solution of 0.600 g (1.39 mmol) of Cp'_2ZrCl_2 and 0.400 g (1.02 mmol) of BI_3 in 20 mL of toluene was stirred for 3 h at room temperature. The volatiles were then removed in vacuo and the resulting precipitate washed with ca. 10 mL of pentane and dried in vacuo to give 0.74 g of bright yellow powder (87% yield).

1H NMR (C_6D_6): δ 1.955 (s). IR (Nujol mull, cm^{-1}): 2715 (w), 2390 (w), 1760 (m), 1470 (sh), 1384 (sh), 1016 (s), 950 (w), 823 (s), 805 (w), 720 (m). Anal. Calcd for $C_{20}H_{30}I_2Zr$: C, 39.03; H, 4.91. Found: C, 38.98; H, 4.92.

$Cp'_2Zr(OC_6F_5)_2$. A solution of 1.50 g (3.83 mmol) of Cp'_2ZrMe_2 and 1.60 g (8.69 mmol) of C_6F_5OH in 30 mL of pentane was stirred at room temperature for 6 h. The reaction mixture (containing a white precipitate)

was cooled to $-78^\circ C$ and filtered. The pentane was then evaporated and the colorless precipitate on the frit dried in vacuo to give 2.56 g of $Cp'_2Zr(OC_6F_5)_2$ (92% yield).

1H NMR (C_6D_6): δ 1.66 (s, 30 H). IR (Nujol mull, cm^{-1}): 1652 (m), 1537 (sh), 1515 (s), 1322 (m), 1315 (m), 1188 (sh), 1180 (s), 1040 (sh), 1028 (s), 1015 (sh), 992 (s), 843 (sh), 818 (s), 671 (m). Anal. Calcd for $C_{32}H_{30}O_2F_{10}Zr$: C, 52.81; H, 4.15. Found: C, 52.85; H, 4.21.

$Cp'_2Zr(OC_6H_5)_2$. A solution of 0.38 g (0.97 mmol) of Cp'_2ZrMe_2 and 0.20 g (2.1 mmol) of C_6H_5OH in 20 mL of toluene was stirred at room temperature for 30 h. The volatiles were then removed in vacuo, and the white precipitate was washed with ca. 1 mL of cold toluene and then dried in vacuo to give 0.32 g (60% yield).

1H NMR (C_6D_6): δ 7.26 (d-d, 4 *m*-H, $J_{HH} = 7.91$, 7.26 Hz), 6.96 (d, 4 *o*-H, $J_{HH} = 7.91$ Hz), 6.82 (t, 2 *p*-H, $J_{HH} = 7.26$ Hz), 1.84 (s, 30 H). IR (Nujol mull, cm^{-1}): 3065 (w), 2730 (w), 1585 (s), 1485 (s), 1470 (sh), 1297 (s), 1275 (s), 1235 (sh), 1162 (m), 1148 (sh), 1065 (w), 1020 (w), 998 (w), 869 (s), 750 (s), 694 (m), 615 (sh). Anal. Calcd for $C_{32}H_{40}O_2Zr$: C, 70.15; H, 7.36. Found: C, 70.03; H, 7.40.

$Cp'_2Zr(OCH_2CF_3)_2$. To a solution of 0.80 g (2.0 mmol) of Cp'_2ZrMe_2 in 20 mL of toluene was added 0.50 mL (6.9 mmol) of CF_3CH_2OH via syringe under an argon flush. The solution was stirred 1 h and then the volatiles were removed in vacuo. Toluene (ca. 1 mL) was next condensed into the flask and the resulting solution stirred briefly, and then the volatiles were again removed in vacuo to give 1.0 g of analytically pure $Cp'_2Zr(OCH_2CF_3)_2$ (90% yield) as a colorless powder.

1H NMR (C_6D_6): δ 4.32 (q, 4 H, $J_{FH} = 9.45$ Hz), 1.74 (s, 30 H). IR (Nujol mull, cm^{-1}): 2750 (w), 1485 (sh), 1273 (s), 1180 (sh), 1141 (s), 1060 (w), 1018 (m), 950 (s), 820 (m), 800 (w), 715 (w), 670 (s), 570 (sh). Anal. Calcd for $C_{24}H_{34}O_2F_6Zr$: C, 51.50; H, 6.12. Found: C, 51.56; H, 6.15.

Cp'_2HfMe_2 . To a solution of 3.00 g (5.77 mmol) of Cp'_2HfCl_2 in 40 mL of diethyl ether was added 8.0 mL (12.8 mmol) of MeLi (1.6 M in diethyl ether) via syringe. This solution was stirred for 3 days at room temperature and then worked up as described for Cp'_2ZrMe_2 ¹¹ to give 1.92 g of colorless microcrystalline product (73%).

1H NMR (C_6D_6): δ 1.80 (s, 30 H), -0.70 (s, 6 H). IR (Nujol mull, cm^{-1}): 2719 (w), 2390 (w), 2000 (w), 1760 (m), 1427 (sh), 1385 (sh), 1257 (w), 1134 (m), 1023 (m), 822 (s), 800 (m), 720 (w), 700 (w), 630 (w), 600 (w), 525 (w), 460 (m), 430 (w). Anal. Calcd for $C_{22}H_{36}Hf$: C, 55.16; H, 7.57. Found: C, 55.09; H, 7.53.

$Cp'_2Hf(n-Bu)_2$. Into a solution of 1.00 g (1.94 mmol) of Cp'_2HfCl_2 in 30 mL of diethyl ether was syringed 3.0 mL (1.6 M in hexane, 4.8 mmol) of *n*-BuLi under an argon flush. The solution was then stirred at room temperature for 3 days to give a gold-colored solution. The diethyl ether was removed in vacuo and 50 mL of pentane condensed into the flask. The resulting solution was filtered and the precipitate on the frit was washed by condensing ca. 10 mL of pentane back onto the frit. The filtrate was reduced in volume to ca. 15 mL and cooled to $-78^\circ C$. The cold solution was next filtered and the crystals dried in vacuo to give 0.70 g of colorless product (81% yield).

1H NMR (C_6D_6): δ 1.84 (s, 30 H, C_3Me_3), 1.44 (t-t, 4 H, βCH_2), 1.23 (m, 4 H, γCH_2), 1.05 (t, 6 H, CH_3 , $J_{HH} = 7.25$ Hz), -0.14 (t, 4 H, αCH_2 , $J_{HH} = 8.64$ Hz). IR (Nujol mull, cm^{-1}): 2937 (sh), 2724 (w), 1495 (w), 1338 (m), 1278 (m), 1030 (s), 1000 (m), 987 (s), 950 (m), 874 (w), 845 (w), 810 (w). Anal. Calcd for $C_{28}H_{48}Hf$: C, 59.72; H, 8.59. Found: C, 59.90; H, 8.68.

$Cp'_2Hf(OC_6F_5)_2$ was prepared in a manner analogous to that for $Cp'_2Zr(OC_6F_5)_2$ (vide supra).

1H NMR (C_6D_6): δ 1.715 (s). IR (Nujol mull, cm^{-1}): 1650 (w), 1507 (s), 1495 (sh), 1317 (w), 1195 (sh), 1185 (m), 1026 (s), 995 (m), 987 (sh), 800 (w). Anal. Calcd for $C_{32}H_{30}O_2F_{10}Hf$: C, 47.16; H, 3.71. Found: C, 47.32; H, 3.84.

$Cp'HfMe_3$. To a solution of 2.04 g (4.86 mmol) of $(Cp'HfCl_2)_2$ ^{15b} in 50 mL of diethyl ether was added 5.2 mL (15.1 mmol) of MeMgBr (2.9 M in diethyl ether) via syringe at $-78^\circ C$. The solution was allowed to warm to room temperature with stirring and was stirred for an additional 15 h. The diethyl ether was then removed in vacuo, and 40 mL of pentane was condensed into the flask. The resulting solution was stirred ca. 1 h and then filtered. The precipitate was washed twice by condensing ca. 10 mL of pentane in the top of the frit apparatus. The solvent was then evaporated from the filtrate, leaving 1.5 g of analytically pure, off-white $Cp'HfMe_3$ (86% yield).

1H NMR (C_6D_6): δ 1.80 (s, 15 H), 0.07 (s, 9 H). IR (Nujol mull, cm^{-1}): 2740 (w), 1450 (s), 1430 (sh), 1256 (w), 1130 (s), 1020 (m), 995 (s), 776 (sh). Anal. Calcd for $C_{13}H_{24}Hf$: C, 43.52; H, 6.74. Found: C, 43.43; H, 6.81.

$Cp'Hf(OC_6F_5)_3$. $Cp'HfMe_3$ (0.40 g, 1.1 mmol) was placed in a frit reaction apparatus and ca. 0.60 g (3.26 mmol) of C_6F_5OH was sublimed into the apparatus on the vacuum line. Pentane (20 mL) was then condensed into the flask and the solution stirred 15 min. The solution

was next cooled to $-78\text{ }^{\circ}\text{C}$ and filtered. The volatiles were removed in vacuo and the colorless precipitate on the frit dried in vacuo to give 0.60 g of $\text{Cp}'\text{Zr}(\text{OC}_6\text{F}_5)_3$ (62% yield).

^1H NMR (toluene- d_6): δ 1.78 (s). IR (Nujol mull, cm^{-1}): 2780 (w), 2500 (w), 1651 (m), 1510 (s), 1485 (sh), 1355 (w), 1330 (sh), 1315 (s), 1195 (w), 1193 (sh), 1178 (s), 1138 (w), 1030 (s), 1010 (sh), 985 (s), 805 (w), 720 (w), 601 (m). Anal. Calcd for $\text{C}_{28}\text{H}_{15}\text{O}_3\text{F}_5\text{Zr}$: C, 38.97; H, 1.75. Found: C, 39.01; H, 1.84.

NMR Titrations. Prior to a calorimetric experiment, a solution of the compound of interest in C_6D_6 or toluene- d_6 was placed in a Wilmad screw-capped NMR tube fitted with a septum. The solution was titrated with a solution of the calorimetry titrant in C_6D_6 or toluene- d_6 by incrementally injecting it through the septum with a syringe, followed by vigorous shaking. The reaction was monitored by ^1H NMR to determine if it was quantitative and sufficiently fast for calorimetry and whether it was sequential (replaced one ligand at a time). For the reaction of a compound with HCl, C_6D_6 saturated with HCl gas was added to the compound of interest in an NMR tube and the NMR spectrum recorded.

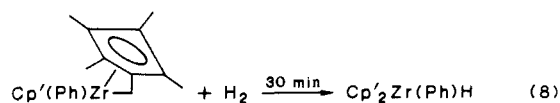
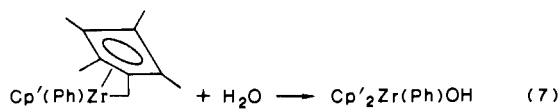
Titration Calorimetry. The calorimeter employed in these studies was an extensively modified version of a TRONAC Inc. Model 458 isoperibol calorimeter and constant temperature bath. The design of the calorimeter and the procedure used are discussed elsewhere.^{5a,19}

The chemistry used in the calorimetry studies must be such that the titration reaction is clean, quantitative, and fast. As noted above, NMR studies of the titration process provide information on these questions. Furthermore, analysis of the heat evolved versus equivalents of titrant added during the calorimetry experiment provides an additional internal check on the stoichiometry of the titration process. In present work, sharp, well-defined endpoints were observed when the stoichiometrically appropriate amount of titrant had been added. The titrants used were alcohols, phenols, and iodine. For the reaction of a compound with HCl, a solution of the compound in toluene was titrated into a solution of HCl in toluene.

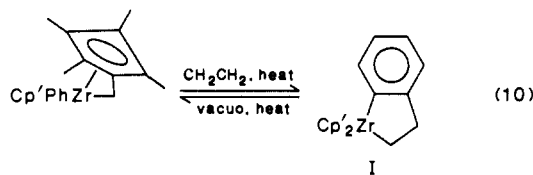
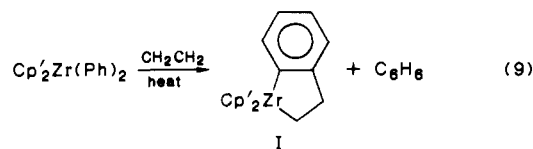
Kinetic Measurements. The rate of reaction of $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)$ (10 mg, 0.023 mmol) with ethylene (≤ 0.06 to < 0.006 M) in C_6D_6 was measured by monitoring the increase in integrated ^1H NMR peak intensity, A , of a CH_2 group (2 H) in the product, $\text{Cp}'_2\text{ZrCH}_2\text{CH}_2\text{-}o\text{-C}_6\text{H}_4$, and the decrease in integrated ^1H NMR peak intensity, B , of a CH_2 group (1 H) in the reactant. The proportion of unreacted starting material is then equal to $B/(1/2A + B)$. The reactions were carried out in a constant-temperature bath at temperatures ranging from 51 through $90\text{ }^{\circ}\text{C}$. To record a spectrum, the sample NMR tube was removed from the bath and immediately cooled in dry ice-acetone to stop the reaction. The spectrum was then quickly recorded at room temperature and the sample tube returned to the bath. Kinetic, Arrhenius, and Eyring plots were fit by linear least-squares techniques. Confidence limits are expressed at the 95% confidence level.²⁰

Results

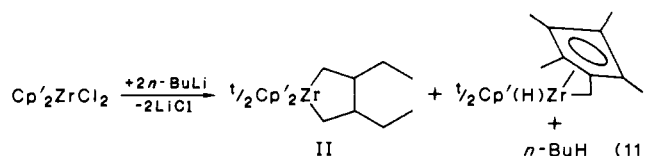
Syntheses. In most cases, known complexes employed in this study were prepared and purified by the literature procedures. For $\text{Cp}'_2\text{ZrH}_2$, stirring $\text{Cp}'_2\text{ZrMe}_2$ under 1 atm of H_2 for 1 week at $70\text{ }^{\circ}\text{C}$ proved to be more convenient than the published methodology. The bridging methylene bond in $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)$ rapidly undergoes cleavage by H_2O to give $\text{Cp}'_2\text{Zr}(\text{OH})\text{Ph}$ (eq 7) and with H_2 to give $\text{Cp}'_2\text{Zr}(\text{H})\text{Ph}$ (eq 8) within ca. 30 min. The thermolysis of $\text{Cp}'_2\text{ZrPh}_2$ to form



$\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)$ ⁹ is diverted by ethylene to form zirconaindan, $\text{Cp}'_2\text{ZrCH}_2\text{CH}_2\text{-}o\text{-C}_6\text{H}_4$ (I), as shown in eq 9. Complex $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)$ also undergoes reaction with ethylene to give $\text{Cp}'_2\text{ZrCH}_2\text{CH}_2\text{-}o\text{-C}_6\text{H}_4$ (eq 10). This process can be reversed by heating the solid zirconaindan in vacuo.

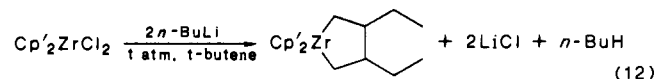


The attempted synthesis of $\text{Cp}'_2\text{Zr}(n\text{-Bu})_2$ from $\text{Cp}'_2\text{ZrCl}_2$ and $n\text{-BuLi}$ yields zirconacyclopentane²¹ II (in $< 50\%$ yield) plus an orange-red residue (eq 11). The color and ^1H NMR spectrum

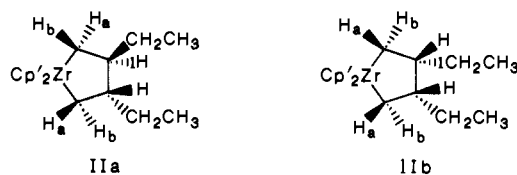


of the residue are reminiscent of orange-red $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)$ (see Experimental Section for details). Workup after shorter reaction times yields mixtures of $\text{Cp}'_2\text{ZrCl}_2$, $\text{Cp}'_2\text{ZrCH}_2(\text{CHEt})_2\text{CH}_2$, and what is presumed to be $\text{Cp}'_2\text{Zr}(n\text{-Bu})_2$ by NMR analysis. Mechanistic details and the thermodynamics of this reaction are discussed later in this contribution. Reaction of $\text{Cp}'_2\text{ZrCl}_2$ with 2 equiv of $n\text{-BuLi}$ in diethyl ether under 1 atm of 1-butene gives exclusively (89% after workup in pentane)

$\text{Cp}'_2\text{ZrCH}_2(\text{CHEt})_2\text{CH}_2$ with no orange-red residue (eq 12). The basic connectivity of this metallacyclopentane follows from ^1H



and ^{13}C NMR spectra (see Experimental Section for details). Furthermore, the magnetic equivalence of the Cp' ligands favors C_2 structure IIa over C_s structure IIb. In the case of hafnium,



the reaction analogous to eq 11 cleanly yields $\text{Cp}'_2\text{Hf}(n\text{-Bu})_2$. Qualitatively, this complex appears to be considerably more thermally stable, either in solution or as a solid, than the zirconium analogue.

The compounds $\text{Cp}'_2\text{M}(\text{OR})_2$ ($\text{OR} = \text{OC}_6\text{F}_5$, OC_6H_5 , $\text{OC}_2\text{H}_4\text{CF}_3$; $\text{M} = \text{Zr}$ and $\text{OR} = \text{OC}_6\text{F}_5$; $\text{M} = \text{Hf}$) were prepared by simple protonolysis reactions of $\text{Cp}'_2\text{MMe}_2$ compounds with the appropriate alcohol or phenol to form $\text{Cp}'_2\text{M}(\text{OR})_2$ and CH_4 .

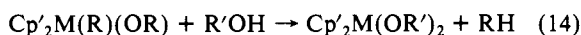
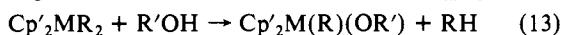
The complex $\text{Cp}'_2\text{HfMe}_2$ was prepared by a method analogous to that reported for $\text{Cp}'_2\text{ZrMe}_2$,¹¹ i.e., by the reaction of $\text{Cp}'_2\text{HfCl}_2$ ¹⁵ with MeLi . However, a significantly longer reaction time is required for Hf than for Zr. The trialkyl compound, $\text{Cp}'\text{HfMe}_3$, was prepared from $(\text{Cp}'\text{HfCl}_3)_x$ ^{15b} and MeMgBr in a manner similar to that reported for $\text{Cp}'\text{ZrMe}_3$ ¹⁶ except that again a longer reaction time is needed. However, unlike $\text{Cp}'\text{ZrMe}_3$ which is thermally unstable at room temperature, $\text{Cp}'\text{HfMe}_3$ shows no decomposition at room temperature over a period of several days in solution.

(21) (a) Sanner, R. D. Ph.D. Thesis, California Institute of Technology, 1977. $\text{Cp}'_2\text{ZrCH}_2(\text{CHEt})_2\text{CH}_2$ was synthesized by reaction of $(\text{Cp}'_2\text{ZrN}_2)_2\text{N}_2$ with 1-butene.^{21b} (b) Referenced in: McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281-315.

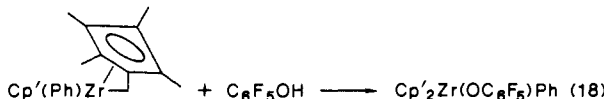
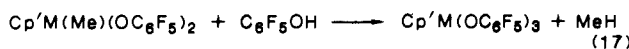
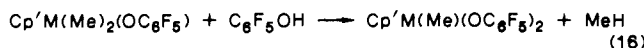
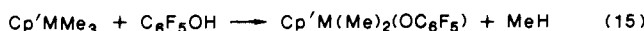
(19) Schock, L. E.; Marks, T. J., manuscript in preparation.

(20) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. In *Experiments in Physical Chemistry*, 3rd ed.; McGraw-Hill: New York, 1974; pp 27-58.

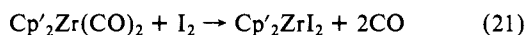
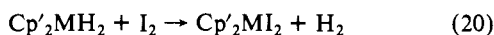
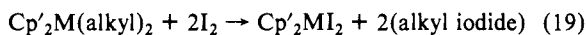
Reactions for Calorimetry. NMR Titrations. Unlike the $\text{Cp}'_2\text{ThR}_2$ compounds ($\text{R} = \text{hydrocarbyl, hydride, etc.}$),^{4a,b} $\text{Cp}'_2\text{MR}_2$ ($\text{M} = \text{Zr, Hf}$) compounds do not readily undergo protonolysis with *tert*-butyl alcohol. The hydride $\text{Cp}'_2\text{ZrH}_2$ reacts most rapidly, with the first hydride ligand being replaced by *tert*-butoxide within seconds. The second hydride ligand is not replaced even after stirring for 2 h at room temperature. $\text{Cp}'_2\text{Zr}(\text{NH}_2)\text{H}$ undergoes rapid reaction with *tert*-butyl alcohol to give $\text{Cp}'_2\text{Zr}(\text{O}-t\text{-Bu})\text{H}$ with the subsequent hydride replacement being extremely slow. In contrast, $\text{Cp}'_2\text{ZrMe}_2$ does not react with *tert*-butyl alcohol within 12 h at 25 °C as judged by NMR analysis. The reactions of more acidic alcohols or phenols with most of the difunctional compounds of interest are more rapid and are sequential (eq 13 and 14); however, the majority are not rapid enough to allow reliable measurement of ΔH_{rx} by calori-



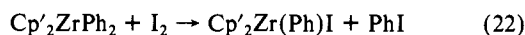
metry. $D(\text{Zr}-\text{H})$ can be measured in $\text{Cp}'_2\text{ZrH}_2$ and in $\text{Cp}'_2\text{Zr}(\text{H})(\text{OR}')$ by titration with $\text{C}_6\text{F}_5\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$, or $\text{CF}_3\text{CH}_2\text{OH}$. $D(\text{Zr}-\text{H})$ can also be measured for $\text{Cp}'_2\text{Zr}(\text{Ph})\text{H}$ by titration with $\text{C}_6\text{F}_5\text{OH}$. However, $D(\text{Hf}-\text{H})$ in $\text{Cp}'_2\text{HfH}_2$ can only be measured by $\text{C}_6\text{F}_5\text{OH}$ titration, and for $\text{Cp}'_2\text{Hf}(\text{H})(\text{OC}_6\text{F}_5)$, $\text{Hf}-\text{H}$ bond protonolysis by $\text{C}_6\text{F}_5\text{OH}$ is too slow to allow measurement of ΔH_{rx} . Interestingly, $\text{C}_6\text{F}_5\text{OH}$ does not react with $\text{Cp}'_2\text{ZrPh}_2$ over the course of several days, yet it sequentially replaces both hydroxide ligands in $\text{Cp}'_2\text{Zr}(\text{OH})_2$ in less than 10 min. As has been observed before,¹⁵ $\text{Cp}'_2\text{HfR}_2$ compounds generally react less rapidly than the analogous $\text{Cp}'_2\text{ZrR}_2$ compounds. $D(\text{Zr}-\text{Me})$ can be measured in the single-ring $\text{Cp}'\text{M}(\text{Me})_n(\text{OC}_6\text{F}_5)_{3-n}$ complexes ($\text{M} = \text{Zr, Hf}$) by titration with $\text{C}_6\text{F}_5\text{OH}$ (eq 15–17). The complex $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ undergoes rapid reaction with 1 equiv of $\text{C}_6\text{F}_5\text{OH}$ (eq 18), but the $\text{Zr}-\text{Ph}$ bond is unreactive toward $\text{C}_6\text{F}_5\text{OH}$ over a period of days.



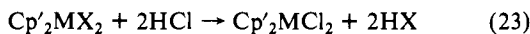
It was found that I_2 undergoes rapid and quantitative reaction with all of the $\text{Cp}'_2\text{MR}_2$ compounds studied where $\text{R} = \text{H}$ or alkyl. Rapid reaction is also observed with $\text{Cp}'_2\text{Zr}(\text{CO})_2$. However, in all cases, the ligand cleavage is not stepwise under titration conditions (eq 19, 20, 21). In contrast, only the first $\text{R} = \text{aryl}$



is cleaved rapidly enough by I_2 to accurately measure ΔH_{rx} (eq 22).



To measure $D(\text{M}-\text{X})$ where $\text{X} = \text{alkoxide, phenoxide, iodide}$ (or other ligands as an internal, self-consistency check), the compound of interest was treated with anhydrous HCl in toluene (eq 23) to yield $\text{Cp}'_2\text{MCl}_2$ rapidly and quantitatively by NMR



analysis. The complexes $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ and $\text{Cp}'_2\text{Zr}(\text{OH})\text{Ph}$ undergo reaction with HCl to form $\text{Cp}'_2\text{Zr}(\text{Cl})\text{Ph}$ which then undergoes further reaction with HCl to form $\text{Cp}'_2\text{ZrCl}_2$, but at a very much lower rate. The enthalpy of the interaction of the alcohol or phenol product with the HCl -toluene solution was measured independently and accounted for in the data analysis.

Derivation of Bond Disruption Enthalpies. Enthalpies of solution of the complexes of interest, followed by enthalpies of reaction with alcohols/phenols, anhydrous HCl , or I_2 , were measured in an isoperibol titration calorimeter specially designed to handle exceedingly air-sensitive compounds.¹⁹ The resulting ΔH_{rx} values can then be related to changes in bond disruption enthalpies for protonolytic or halogenolytic processes via eq 3 ($\text{R}'\text{O} = \text{Cl}$ for HCl titrations) or eq 5 ($\text{X} = \text{I}$), respectively. Equation 24 is applicable to the case of $\text{Cp}'_2\text{Zr}(\text{CO})_2$ (eq 21),

$$\Delta H_{\text{rx}} = 2D(\text{Zr}-\text{CO}) + D(\text{I}_2) - 2D(\text{Zr}-\text{I}) \quad (24)$$

and eq 25 to $\text{Cp}'_2\text{MH}_2$ compounds (eq 20). Relevant $D(\text{H}-\text{OR}')$,

$$\Delta H_{\text{rx}} = 2D(\text{Zr}-\text{H}) + D(\text{I}_2) - 2D(\text{Zr}-\text{I}) - D(\text{H}_2) \quad (25)$$

$D(\text{R}-\text{H})$, $D(\text{HCl})$, $D(\text{I}_2)$, and $D(\text{R}-\text{I})$ data are available in the literature²² or can be reasonably estimated.

The central focus of the present effort is to provide bond disruption enthalpy information useful for understanding transformations among chemically interrelated species such as $\text{Cp}'_2\text{MR}_2/\text{Cp}'_2\text{MR}'_2$. As such, *relative* bond enthalpies are the first priority, although placing these data on an absolute scale (*vide infra*) and discerning the influence of ancillary ligation (*i.e.*, transferability) are also of interest. Even within the present treatment, it is assumed that differential R/R' -based enthalpy-consuming or -releasing reorganizations of the Cp_2M , $\text{Cp}'_2\text{M}$, or $\text{Cp}'\text{M}$ fragments are energetically insignificant in eq 2 and 4 (or eq 1). This contention is supported by a substantial body of metrical data for tetravalent organozirconium and -hafnium complexes.²³ Situations of the type $\text{Cp}_2\text{MX}_2/\text{Cp}_2\text{M}(\text{CO})_2$ appear to be a possible exception; however, structural relaxation effects are manifested in $\text{M}-\text{C}(\text{Cp})$ distance changes of only ca. 0.03 Å.^{9,24} Importantly, any deviations introduced in $D(\text{L}_n\text{M}-\text{R})$ values by these effects are intrinsic to the actual ligation environment and will (must) therefore be implicitly included in any subsequent estimations of $\text{L}_n\text{M}-\text{R} \rightarrow \text{L}_n\text{M}-\text{R}'$ reaction enthalpies.

As noted above, placing derived $D(\text{M}-\text{R})$ data on an absolute or semiabsolute scale would be desirable. In the present case of HCl and I_2 titrants, this requires the corresponding $D(\text{L}_n\text{M}-\text{X})$ values in $\text{Cp}'_2\text{ZrX}_2$, $\text{Cp}'_2\text{ZrX}_2$, and $\text{Cp}'_2\text{HfX}_2$. Since these data are not available, we make the reasonable approximation of eq 26, where first MX_4 bond dissociation enthalpy data ($\text{MX}_4 \rightarrow \text{MX}_3 + \text{X}^*$) are available in the literature.²⁵ Recent organo-

$$D(\text{L}_n\text{M}-\text{X}) \approx D_1(\text{MX}_4) \quad (26)$$

uranium thermochemistry^{5a} supports this approximation in that $D(\text{Cp}'_3\text{U}-\text{I}) = 62.4$ (0.4) kcal/mol ($\text{Cp}' = \text{Me}_3\text{SiC}_5\text{H}_4$) while $D_1(\text{U}\text{I}_4) = 66$ (8) kcal/mol. While D_1 most accurately describes the majority of dissociation processes of interest here ($\text{M}(\text{IV}) \rightarrow \text{M}(\text{III})$), D_1 and \bar{D} are within 1.5 kcal/mol for ZrCl_4 ²⁵ so that choosing between these anchor points becomes unnecessary. Further support for the constancy of eq 26 for $\text{X} = \text{halogen}$ derives from measurement of the average $D(\text{Zr}-\text{I})$ for $\text{Cp}'_2\text{ZrI}_2$ via eq 23, 27, and 28. The value obtained (*vide infra*), 80.4 (0.5) kcal/mol, compares favorably to $\bar{D}(\text{ZrI}_4) = 82.6$ kcal/mol.²⁵ Thus,

$$\frac{1}{2}\Delta H_{\text{rx}} = D(\text{L}_n\text{M}-\text{X}) + D(\text{H}-\text{Cl}) - D(\text{L}_n\text{M}-\text{Cl}) - D(\text{X}-\text{H}) \quad (27)$$

$$D(\text{L}_n\text{M}-\text{X}) = \frac{1}{2}\Delta H_{\text{rx}} - D(\text{H}-\text{Cl}) + D(\text{L}_n\text{M}-\text{Cl}) + D(\text{X}-\text{H}) \quad (28)$$

$$\text{M} = \text{Zr, Hf}; \text{X} = \text{OR, I}$$

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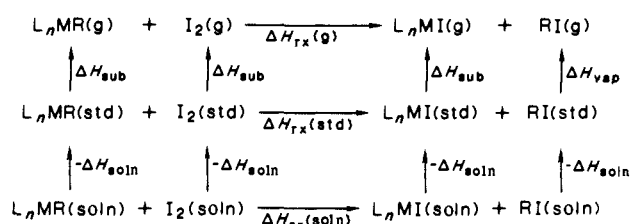
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Table I. Enthalpies of Solution in Toluene, Enthalpies of Reaction with HCl in Toluene (Per Mole of Compound), and the Derived Bond Disruption Enthalpies of Cp'₂MR₂/Cp'₂MX₂ Complexes (kcal/mol)^a

compound	ΔH_{soln}	ΔH_{rx}	bond	$D(\text{M-R})/$ $D(\text{M-X})$
HCl	4.800 ^c			
Cp' ₂ ZrCl ₂	3.48 (0.41)		est	115.7
Cp' ₂ Zr(OH) ₂ ^b	3.40 (0.29)	-36.5 (0.5)	ave	115.4 (1.8)
Cp' ₂ Zr(OH)Ph ^b		-17.1 (0.4)	OH	115.3 (1.5)
Cp' ₂ Zr(OCH ₂ CF ₃) ₂ ^b	3.77 (0.35)	-30.8 (0.2)	ave	103.2 (2.5)
Cp' ₂ Zr(OC ₆ H ₅) ₂ ^b		-17.8 (0.2)	ave	90.9 (2.3)
Cp' ₂ Zr(OC ₆ F ₅) ₂ ^b	3.30 (0.24)	-16.7 (0.8)	ave	90.9 (2.9)
Cp' ₂ ZrI ₂	4.73 (0.23)	-6.8 (0.3)	ave	80.4 (0.5)
Cp' ₂ ZrH ₂	2.68 (0.16)	-74.6 (0.8)	ave	80.3 (0.9)
Cp' ₂ Zr(OPh)Me		-56.7 (0.4)	OPh	(90.9)
			Me	70.6 (1.0)
Cp'Zr(Ph)(η^1 : η^5 -CH ₂ C ₅ Me ₄)	3.42 (0.26)	-57.4 (0.6)	CH ₂	44.0 (1.7)
Cp' ₂ HfCl ₂	3.71 (0.23)		est	117.0
Cp' ₂ HfI ₂		-6 (3)	ave	82.1 (3)
Cp' ₂ Hf(OC ₆ F ₅) ₂ ^b	3.26 (0.46)	-15.6 (0.2)	ave	98 (3)
Cp' ₂ HfMe ₂	3.68 (0.16)	-90.0 (1.0)	ave	74.8 (1.3)

^aQuantities in parentheses are estimated uncertainties. For ΔH_{soln} and ΔH_{rx} , they are the 95% confidence limits (see text and ref 20), while for $D(\text{M-R})/D(\text{M-X})$ they also include reported uncertainties in all contributing parameters except $D(\text{M-Cl})$ (the anchor point—see text). Bond designates whether $D(\text{M-R})/D(\text{M-X})$ is for the first or second R ligand to be replaced by the titrant (1st or 2nd), for the average of the first and second ligands replaced (ave), or is estimated from literature values as described in the text (est). ^bThe reaction of the ROH products with HCl/toluene solution is exothermic by ca. 1 kcal/mol. The enthalpies for these reactions were measured separately and accounted for in the calculations. ^cFrom ref 26.

Scheme I. Cycle Relating Solution Phase to Gas Phase Bond Disruption Enthalpies

substituting two Cp' ligands for two X ligands in ZrX₄ has a similar effect on Zr-X bond enthalpies for X = I as for X = Cl, i.e., the relative $D(\text{M-X})$ values are, in this instance, securely transferable. For titrations with alcohols or phenols, the present treatment also requires $D(\text{L}_n\text{M-OR})$ data that are not in general available (vide infra). These were also measured via eq 23, 27, and 28, assuming $D(\text{H-OC}_6\text{F}_5) = D(\text{H-OC}_6\text{H}_5)$ and $D(\text{H-OC}_6\text{H}_5) = D(\text{H-OCH}_2\text{CH}_3)$.

Formally, eq 1 pertains to the gas phase,² and indeed existing $D(\text{H-OR})$, $D(\text{H-Cl})$, $D(\text{I-I})$, $D(\text{R-H})$, $D(\text{R-I})$, and $\bar{D}(\text{MX}_4)$ data are also gas-phase values.^{22,25} Scheme I illustrates how solution-phase calorimetry data, using iodinolysis as an example, can be referenced to the gas phase. While such conversions are straightforward,⁴ they probably introduce greater uncertainty in $D(\text{L}_n\text{M-R})$ values than their use warrants. Thus, while ΔH_{soln} , ΔH_{vap} , or ΔH_{sub} data are available or can be securely estimated for most organic reagents and products of interest (as well as for HCl and I₂),²⁶ ΔH_{sub} values for most organometallic reactants and products are unknown and are usually assumed to cancel on either side of the equation.⁴ Although there is literature support for this approximation,^{2d,27} it seems tenuous for greatly differing R and X ligands. Closely related is a problem that is encountered in ΔH_{rx} when titrants of greatly differing ΔH_{sub} or ΔH_{vap} are employed. An example is the titration of Cp'₂Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄) with HCl, I₂, and C₆F₅OH (vide infra). Although solution-phase $D(\text{Zr-CH}_2)$ values agree within experimental error, derived gas-phase values for HCl, I₂, and C₆F₅OH differ from the solution-phase results by -5.8, -11.7, and -11.9 kcal/mol,

Table II. Enthalpies of Solution in Toluene, Enthalpies of Reaction with I₂ in Toluene (Per Mole of I₂), and the Derived Bond Disruption Enthalpies (kcal/mol) for Zr and Hf Complexes^a

compd	ΔH_{soln}	ΔH_{rx}	bond	$D(\text{M-R})/$ $D(\text{M-X})$ $D(\text{M-L})$
I ₂	3.85 (0.05)			
Cp' ₂ ZrI ₂ ^b	4.73 (0.29)		ave	80.4 (0.5)
Cp' ₂ ZrH ₂	2.68 (0.16)	-73.9 (0.8)	ave	77.6 (1.3)
Cp' ₂ ZrPh ₂	1.75 (0.10)	-37.1 (1.0)	1st	73.1 (3.5)
Cp' ₂ ZrMe ₂	3.52 (0.08)	-35.0 (0.3)	ave	67.0 (1.0)
Cp' ₂ ZrCH ₂ (CHEt) ₂ CH ₂	2.74 (0.25)	-40.3 (1.4)	ave	53.5 (2.9)
Cp' ₂ ZrCH ₂ CH ₂ -o-C ₆ H ₄	3.97 (0.41)	-35.1 (0.2)	CH ₂	63.1 (1.7)
Cp'Zr(Ph)(η^1 : η^5 -CH ₂ C ₅ Me ₄)	3.42 (0.26)	-45.7 (0.9)	CH ₂	47.3 (2.9)
Cp' ₂ Zr(CO) ₂	3.41 (0.31)	-45.8 (0.4)	ave	39.7 (0.9)
Cp ₂ ZrMe ₂	3.37 (0.12)	-34.8 (0.3)	ave	67.2 (1.0)
Cp' ₂ HfI ₂	3.11 (0.09)	-70.9 (0.7)	ave	81.0 (3.7)
Cp' ₂ HfMe ₂	3.68 (0.16)	-31.7 (0.4)	ave	72.0 (3.7)
Cp' ₂ Hf(<i>n</i> -Bu) ₂	5.03 (0.47)	-39.0 (0.4)	ave	56.5 (4.4)

^aUncertainties and bond designations are explained in footnote a of Table I. ^bFrom Table I.

respectively, due mainly to the large differences in ΔH_{sub} values for the titrants. It seems likely that such disparities are largely an artifact of assuming ΔH_{sub} is identical for all organometallic reagents and reaction products. For these reasons combined with the fact that ΔH_{soln} values for all reagents of interest are small for nonpolar solvents such as toluene^{4,26} and because we wish to understand chemical transformations in solution, we restrict our discussion here to solution-phase $D(\text{L}_n\text{M-R})$ data.

Thermochemical Data. The results of the thermochemical experiments are set out in Tables I-IV. The enthalpies of solution of the various complexes in toluene are quite small and are very similar. For reactions that do not sequentially remove the ligands, R, the average ΔH_{rx} and $D(\text{M-R})$ are reported. Otherwise, the ligand involved in the bond cleavage reaction is designated (i.e., if there are several identical ligands, R, then whether the first, second, or third of these ligands is involved in the cleavage reaction is indicated). The values for $D(\text{M-R})$ given in parentheses were obtained from another thermochemical measurement. The uncertainties reported for ΔH_{soln} and ΔH_{rx} are 95% confidence limits,²⁰ and the errors in $D(\text{M-R})$ include the 95% confidence limit of ΔH_{rxn} plus the reported errors in other BDEs used in the calculation of $D(\text{M-R})$, except for the error reported in $D(\text{M-Cl})$, which will affect all members of a given L_nMR series equally and is not included. $D_1(\text{MCl}_4)$ is used as the anchor, since the absolute value of $D(\text{L}_n\text{M-Cl})$ in each series is, of course, not exactly known. Tables I, II, and III present the data obtained from titrations with HCl, I₂, and C₆F₅OH, respectively. Excellent internal consistency is demonstrated by the reaction of the same compound with

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Table III. Enthalpies of Solution in Toluene, Enthalpies of Reaction with C₆F₅OH in Toluene (Per Mole of C₆F₅OH), and the Derived Bond Disruption Enthalpies (kcal/mol) for Zr and Hf Complexes^a

compound	ΔH_{soln}	ΔH_{rx}	bond	$D(\text{M-R})/D(\text{M-X})$
C ₆ F ₅ OH	3.30 (0.36)			
Cp' ₂ Zr(OC ₆ F ₅) ₂	3.30 (0.24)			
Cp' ₂ Zr(OH) ₂	3.40 (0.29)	-8.0 (0.3)	1st	115.4 (2.5)
		-4.6 (0.4)	2nd	118.8 (2.6)
Cp' ₂ Zr(OC ₆ F ₅)(O- <i>t</i> -Bu)		-4.9 (0.8)	O- <i>t</i> -Bu	104.6 (3.0)
Cp' ₂ Zr(NH ₂)H	2.37 (0.13)	-6.2 (0.5) ^b	NH ₂	100.7 (3.6)
Cp' ₂ Zr(O- <i>t</i> -Bu)H		-23.4 (1.9)	H	83.2 (3.1)
Cp' ₂ ZrH ₂	2.68 (0.16)	-34.2 (0.3)	1st	74.4 (1.5)
		-24.7 (0.6)	2nd	83.9 (1.8)
Cp' ₂ Zr(Ph)H	2.65 (0.17)	-29.9 (0.5)	H	78.7 (1.7)
Cp'Zr(Ph)(η^1 : η^5 -CH ₂ C ₅ Me ₄)	3.42 (0.26)	-48.3 (0.8)	CH ₂	44.1 (3.0)
Cp'ZrMe ₃	2.83 (0.12)	-44.9 (0.5)	1st	64.6 (1.9)
		-41.8 (0.7)	2nd	67.7 (2.1)
		-36.7 (1.0)	3rd	72.8 (2.4)
Cp' ₂ HfH ₂	3.11 (0.09)	-34.3 (0.5)	1st	76.8 (0.8)
Cp'Hf(OC ₆ F ₅) ₃	6.65 (0.05)			
Cp'HfMe ₃	2.42 (0.10)	-42.6 (0.3)	1st	69.4 (0.8)
		-41.1 (0.4)	2nd	70.9 (0.9)
		-39.1 (0.9)	3rd	72.9 (1.4)

^aUncertainties and bond designations are explained in footnote *a* of Table I. ^b ΔH_{rxn} is for the reaction of this compound with *t*-BuOH.

Table IV. Enthalpies of Reaction in Toluene (Per Mole of Reactant) and Derived Zirconium-Hydride Bond Disruption Enthalpies (kcal/mol) Obtained with Various Titrants^a

compound	reactant	ΔH_{rx}	bond	$D(\text{M-H})$
Cp' ₂ ZrH ₂	C ₆ F ₅ OH	-34.2 (0.3)	1st	74.4 (1.5)
		-24.7 (0.6)	2nd	83.9 (1.8)
	C ₆ H ₅ OH	-31.7 (0.4)	1st	75.1 (0.7)
		-20.7 (0.7)	2nd	84.7 (1.0)
	CF ₃ CH ₂ OH	-27.0 (0.5)	1st	75.4 (0.9)
		-20.1 (0.2)	2nd	82.3 (0.6)
	HCl	-74.6 (0.4) ^b	ave	80.3 (0.5)
	I ₂	-73.9 (0.6)	ave	77.6 (1.1)
Cp' ₂ Zr(H)(O- <i>t</i> -Bu)	C ₆ F ₅ OH	-23.4 (1.9)	H	83.2 (3.1)
Cp' ₂ Zr(H)Ph	C ₆ F ₅ OH	-29.9 (0.5)	H	78.7 (1.7)

^aUncertainties and bond designations are explained in footnote *a* of Table I. ^bA solution of Cp'₂ZrH₂ was titrated into an HCl/toluene solution, therefore, ΔH_{rx} is per mol of Cp'₂ZrH₂.

different titrants to give $D(\text{Zr-R})$ values that are identical within experimental error, e.g., Cp'Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄), Cp'₂HfMe₂(average), Cp'₂ZrH₂(average). Cases of stepwise scission reveal disparities between first and second $D(\text{M-R})$ values that can be attributed to effects of the ancillary σ -bonded ligand (vide infra).

Kinetic Data for Reaction of Cp'Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄) with Ethylene. For a complete thermochemical analysis of eq 6, it was also necessary to establish the molecularity and activation energetics of eq 10. The reaction of Cp'Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄) with ethylene obeys first-order kinetics in the disappearance of Cp'Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄) for greater than 3 half-lives. The derived rate constants are independent of ethylene concentration over a concentration range of ca. 0.06 to 0.006 M. Arrhenius (Figure 1) and Eyring plots yield the parameters $E_{\text{act}} = 21.3$ (5), $\Delta H^\ddagger = 20.6$ (5) kcal/mol, $\Delta S^\ddagger = -15.4$ (5) eu, $\log A = 9.4$ (3).

Discussion

In this section, we focus first upon trends in metal-ligand bond enthalpies, then upon ancillary sigma-bonded ligand effects, and finally upon implications for organo-zirconium and -hafnium chemistry.

Overall Trends in Bond Enthalpies. It can be seen from Tables I-IV that zirconium-ligand and hafnium-ligand bond disruption enthalpies, for a wide range of metal-ligand bonds, are rather similar. Significant differences in zirconium and hafnium organometallic chemistry observed here and elsewhere^{12,15b} are thus more likely kinetic in origin rather than arising from large differences in bond enthalpies. The present bond enthalpies are roughly comparable to those we reported earlier for Cp'₂ThR₂^{4a} and Cp₃ThR^{4b} complexes (anchored to a more approximate $\bar{D}(\text{Th}(\text{OR})_4)$)⁴ and somewhat greater than for the similar series of

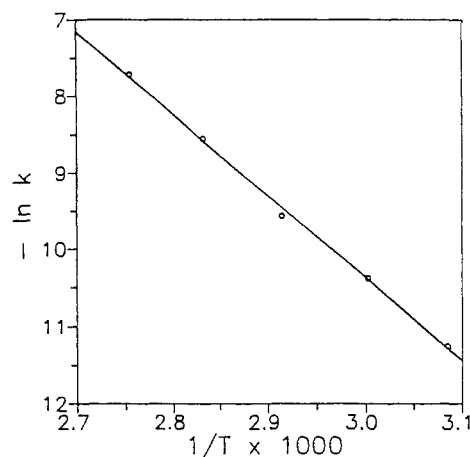


Figure 1. Arrhenius plot for the reaction of Cp'Zr(Ph)(η^1 : η^5 -CH₂C₅Me₄) with ethylene to yield Cp'₂ZrCH₂CH₂-*o*-C₆H₄. The units of *k* are s⁻¹.

organouranium complexes.^{4c,5a} As we suggested earlier for the actinides,⁴ simple Pauling-type bond ionicity/bond energy relationships²⁸ provide a qualitative overall explanation for the relatively large metal-ligand bond enthalpies exhibited by electro-positive transition elements such as zirconium and hafnium. Such effects will of course be modulated by the metal oxidation state as well as the particular electronic and steric characteristics of the ligation sphere. Complementary explanations have focused upon metal-ligand orbital overlap and repulsion as well as promotion energies.^{29,30}

In the present group 4 complexes, the overall ordering of metal-ligand bond enthalpies is Cl \approx OH > alkoxide \approx NH₂ > phenoxide > I \approx H > aryl > alkyl > CO. Where comparable data exist (halides, alkoxides, amides, alkyls), this trend parallels that of the homoleptic MR₄/MX₄ analogues (Figure 2)^{2b,31} with one interesting exception: $D(\text{M-OR}) - D(\text{M-Cl})$ (Figure 2). In the Cp'₂MX₂ series, $D(\text{M-OR}) - D(\text{M-Cl})$ is ca. -12 kcal/mol while in the MX₄ series (based upon *D* values) the corresponding

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(29) (a) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, 109, 1351-1358. (b) Ziegler, T.; Tschinke, V.; Versluis, L.; Baerends, E. J. in ref 1. We thank these authors for allowing us to quote their work.

(30) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1987**, 109, 5573-5580 and references therein.

(31) Zr-NH₂ \rightarrow Zr-NMe₂ corrections have been made using $D(\text{H-NH}_2) - D(\text{H-NMe}_2) = -16$ kcal/mol.²²

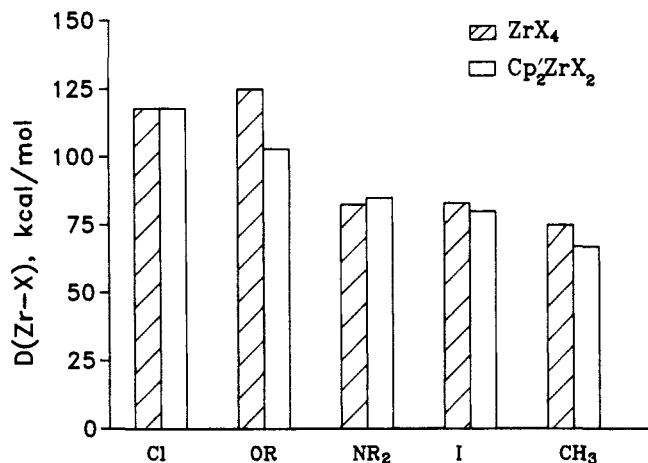


Figure 2. Comparison of average $D(\text{Zr-X})$ data obtained in the present study of $\text{Cp}'_2\text{ZrX}_2$ compounds with those obtained in homoleptic systems (from ref 2b). The ZrMe_4 datum is an estimate (see ref 2b), while a $\text{ZrNH}_2 \rightarrow \text{ZrNMe}_2$ correction for $\text{Cp}'_2\text{ZrX}_2$ has been applied with use of $D(\text{H-NH}_2) - D(\text{H-NMe}_2)$ (see ref 31).

quantity is ca. +7 kcal/mol. The diminished bond enthalpies in the $\text{Cp}'_2\text{M}(\text{OR})_2$ system can be rationalized on the basis of two factors: (i) changes in ligand \rightarrow metal π donation; (ii) increased interligand nonbonded repulsions.

There is now considerable structural, spectroscopic, reactivity, and theoretical evidence for ligand \rightarrow metal donation (e.g., III)



in complexes with lone pair bearing ligands and electron-deficient metal centers (e.g., actinides, d^0 transition elements).^{32,33} In the present systems, it is reasonable that the large electron donor capacity of ligands such as Cp' would somewhat reduce the π acidity of the metal center, thus weakening ligand \rightarrow metal π -bonding.³⁴ There is also structural evidence for considerable steric congestion in $\text{Cp}'_2\text{MX}_2/\text{Cp}_2\text{MX}_2$ complexes. Although there are few data available for simple $\text{Cp}'_2\text{ZrR}_2$ compounds, congestion evident in $\text{Cp}'_2\text{ThR}_2$ complexes³⁵ argues that it will be even greater in the case of the smaller group 4 ion. Calculation of intramolecular nonbonded contacts from the published coordinates of $\text{Cp}'_2\text{ZrO}(2)\text{CH}=\text{C}[\text{Zr}(\text{I})\text{Cp}'_2]\text{O}(1)$ ³⁶ reveals a number of contacts less than the sum of Me (2.0 Å) and O (1.5 Å) van der Waals radii,³⁷ viz., 9 O(1)-C(Cp') contacts in the range 2.92–3.49 Å; 7 O(2)-C(Cp') contacts in the range 2.93–3.47 Å; and 9 C-(enediolate)-C(Cp', Cp) contacts in the range 2.92–3.35 Å. As further examples, the crystal structure of $(\text{Cp}'\text{ZrCl})_2\text{O}$ ³⁸ exhibits two O-C(Cp) contacts less than 3.0 Å, while the structure of $(\text{Cp}'_2\text{ZrMe})_2\text{O}$ ³⁹ exhibits O-C(Cp) contacts of 2.78 Å (two) and

(32) For evidence in actinide complexes, see: (a) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985. (b) Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragalà, I.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257–1261. (c) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 2907–2912. (d) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *95*, 207–209. (e) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *85*, L31–32.

(33) For evidence in group 4 complexes, see: (a) Chamberlain, L. R., et al. *J. Am. Chem. Soc.* **1987**, *109*, 290–302 and references therein. (b) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014. (c) Gell, K. I.; Rosin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846–1855. (d) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855–1859.

(34) Alternatively, coulombic Zr-OR attractive effects are enhanced as the number of electronegative alkoxide ligands on zirconium increases.

(35) (a) Marks, T. J. *In The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J.; Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Chapter 23. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56. (c) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I., Eds.; Reidel: Dordrecht, 1985; Chapter 4.

(36) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178–5186.

(37) (a) Reference 28a, p 152. (b) Reference 28b, pp 256–260.

(38) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr.* **1974**, *B30*, 2267–2269.

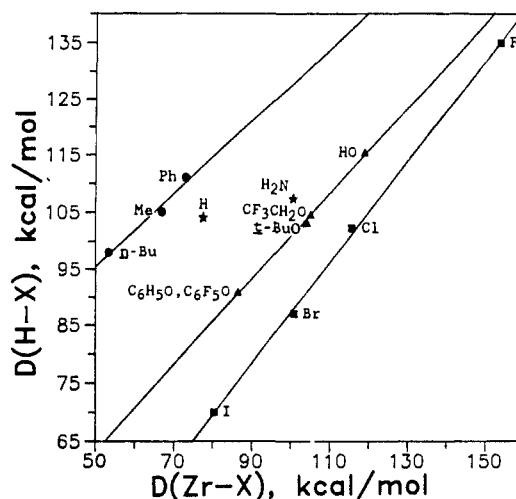


Figure 3. Correlations between $D(\text{H-X})$ values and the corresponding average $D(\text{Zr-X})$ values obtained for $\text{Cp}'_2\text{ZrX}_2$ complexes in this study. Ligands of the same type are indicated by separate symbols, and the lines represent least-squares fits to these data points. $D(\text{Zr-F})$ and $D(\text{Zr-Br})$ data are estimated (see text).

3.29 Å (two), Me-C(Cp) contacts of 2.58, 2.99, and 3.00 Å, and two O-Me contacts of 3.47 Å. Restricted rotation of hydrocarbyl groups is observed in the NMR spectroscopy of various $\text{Cp}'_2\text{Zr}(\text{R})\text{R}'$ complexes⁴⁰ as well as in $\text{Cp}'\text{Zr}(\text{Ph})(\eta^1\text{-}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ and $\text{Cp}'_2\text{ZrPh}_2$.⁹

Roughly linear correlations between $D(\text{H-X})$ and relative $D(\text{L}_n\text{M-X})$ values have recently been noted for $\text{L}_n\text{M} = \text{Cp}'\text{Ru}(\text{PMe}_3)_2$, $(\text{dppe})\text{Pt}(\text{Me})$ and $\text{X} =$ a variety of ligands including several hydrocarbyls.²¹ In general, such a relationship could have useful predictive value and its applicability clearly warrants further scrutiny. While full justification for the $D(\text{H-X})/D(\text{M-X})$ correlation has not been offered, its applicability clearly implies a bonding regime where large steric or π -bonding effects are either inoperative or fortuitously cancel. Also implicit is the absence of energetically significant multihapto (e.g., η^2 -benzyl⁴¹) or "agostic" bonding interactions. A portion of our published organothorium results has been quoted to suggest the possibility of deviations (unspecified) in cases of π -donor ligands (e.g., OR or NR_2) and electron-deficient metal centers.²¹ The present group 4 results afford the first opportunity to test the generality of the $D(\text{H-X})/D(\text{M-X})$ correlation at an archetypical early transition metal center.

The present $D(\text{M-X})$ data are plotted in Figure 3 versus literature $D(\text{H-X})$ values.²² The self-consistency of $\text{ZrX}_4/\text{Cp}'_2\text{MX}_2$ results for $\text{X} = \text{Cl}$ and I noted earlier suggests that it is reasonable to also include ZrX_4 -derived data for $\text{X} = \text{F}$ and Br. It can be seen in Figure 3 that the linear $D(\text{H-X})/D(\text{M-X})$ correlation has little validity in this early transition metal system. Interestingly, however, the data in Figure 3 do fall into "families" of similar ligands that exhibit roughly linear plots having differing slopes.

The pattern of the data in Figure 3 no doubt reflects a complex combination of steric and electronic factors. It is, however, instructive to inquire about the gross features of this and more linear $D(\text{H-X})$ vs $D(\text{L}_n\text{M-X})$ plots by using a modified version of the bond enthalpy equation of Matcha (eq 29).⁴² This formalism interrelates diatomic single bond homolytic bond enthalpies and

$$D(\text{A-B}) = \frac{1}{2}[D(\text{A}_2) + D(\text{B}_2)] + 105(1 - e^{-0.219(x_A - x_B)^2}) \quad (29)$$

(39) Hunter, W. E.; Hrcncir, D. C.; Bynum, R. U.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750–755.

(40) Jeffery, J.; Lappert, M. F.; Luong-Thu, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 1081–1083.

(41) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692–4696 and references therein.

(42) (a) Matcha, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4859–4862. We employ the formulation using an arithmetic mean expression for $D(\text{A-B})$ since this leads more straightforwardly to useful relationships such as eq 29. Both arithmetic and geometric mean approaches have been employed in the Pauling formulation,^{28a,42b} with the latter preferred in cases of sign ambiguities. (b) Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1983; Chapter 24.

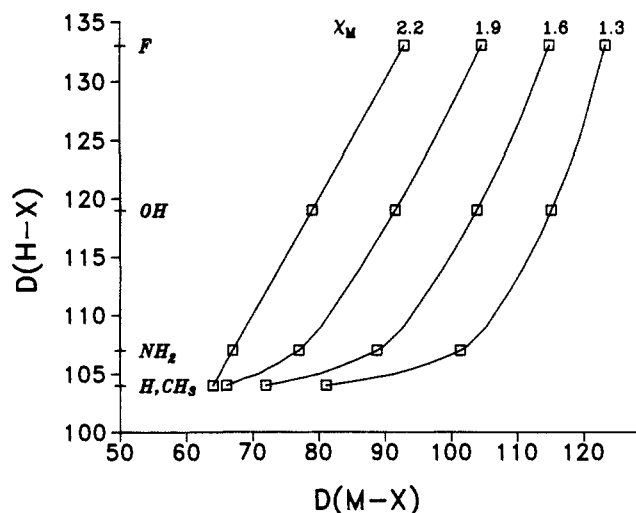


Figure 4. Families of $D(H-X)$ versus $D(M-X)$ curves generated from eq 30 for the metal Pauling electronegativities and X ligands indicated.

Pauling electronegativities and gives far better agreement with experiment than the original Pauling formulation.²⁸ After rearrangement, it is possible, via the corresponding expressions for $D(M-X)$ and $D(H-X)$, to arrive at eq 30. Assuming that Pauling electronegativities are approximately valid,^{28b,c} it can be seen that

$$D(M-X) = D(H-X) + \frac{1}{2}[D(M_2) - D(H_2)] + \frac{1}{2}(e^{-0.219(\chi_H - \chi_X)^2} - e^{-0.219(\chi_M - \chi_X)^2}) \quad (30)$$

for M constant, the X dependence of $D(M-X)$ arises from $D(H-X)$ and the exponential terms. In cases of relatively electronegative middle and late transition elements (second and third row Ru and Pt are good examples) χ_M approaches χ_H (2.20)^{28b,c} so that $(\chi_H - \chi_X) \approx (\chi_M - \chi_X)$ and the exponential term becomes small. Hence, in this regime $D(M-X) \approx D(H-X) + (\text{constant})$, in accord with linear $D(M-X)$ versus $D(H-X)$ plots having slopes near unity. In contrast, for situations where M is a more electropositive metal such that $\chi_M < \chi_H$, and where $\chi_X \geq \chi_H$ (valid for most ligands of interest^{28b,c}), the first exponential term in eq 30 will dominate the second and $D(M-X)$ will be greater than otherwise anticipated (i.e., displaced to the right in the $D(H-X)$ vs $D(M-X)$ plot). Numerical experiments indicate that as χ_X increases from 2.2 to 3.5, the positive adjustment to $D(M-X)$ increases and then levels off beyond $\chi \approx 3.0$. The effect of incrementally decreasing χ_M from 2.2 to 1.3 (that for Zr(II)^{28b,c}) is to incrementally displace the family of curves to higher $D(M-X)$ values. These results are plotted for several first row ligands in Figure 4.⁴³ In summary, this approximate treatment indicates that less electropositive metal centers ($\chi_M \approx \chi_H$) and ligands with electronegativities near χ_H (e.g., hydrocarbyls)^{28b,c} will exhibit the least departure from "normal" $D(H-X)$ versus $D(M-X)$ plots²¹ whereas more electropositive M and more electronegative X should skew the plot to the right. Although steric and other electronic effects are also no doubt operative in Figure 3, it is noteworthy that data for X = alkoxide, amide, Cl, and F appear to follow this qualitative trend. Data for M = thorium (Figure 5) and uranium^{5a} exhibit similar characteristics.

The quantities $D(M-H) - D(M-Me)$ ⁴ and $D(M-I) - D(M-Me)$ ^{5a} are informative, M-dependent gauges of differences in bonding and are also of considerable chemical significance. We noted earlier that $D(M-H) - D(M-Me)$ ⁴ is rather small for actinide systems and associated this with, among other factors,

(43) (a) We assume that $D(M_2)$ in eq 30 remains approximately constant. Typical estimates²⁸ support this: $D(Zr_2) \approx 25$, $D(Mo_2) \approx 31$, $D(Ru_2) \approx 26$, $D(Pt_2) \approx 23$ kcal/mol. (b) Second-row ligands such as Cl are displaced even further to the right, suggesting that other effects (e.g., charge-dependent electronegativity effects^{28b}), not included in this approximate treatment, are also operative.

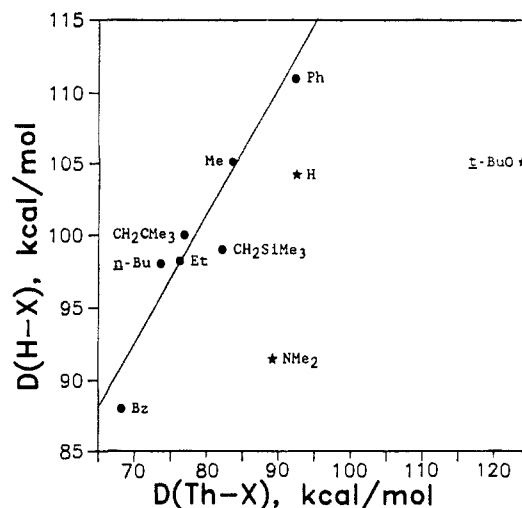


Figure 5. Correlations between $D(H-X)$ and $D(Th-X)$ values (from ref 4a) for the X ligands indicated in organothorium complexes $Cp_2^*Th(Cl)X$ and $Cp_2^*Th(OR)X$. Ligands of the same type are indicated by separate symbols, and the line represents a least-squares fit to the X = hydrocarbyl data points.

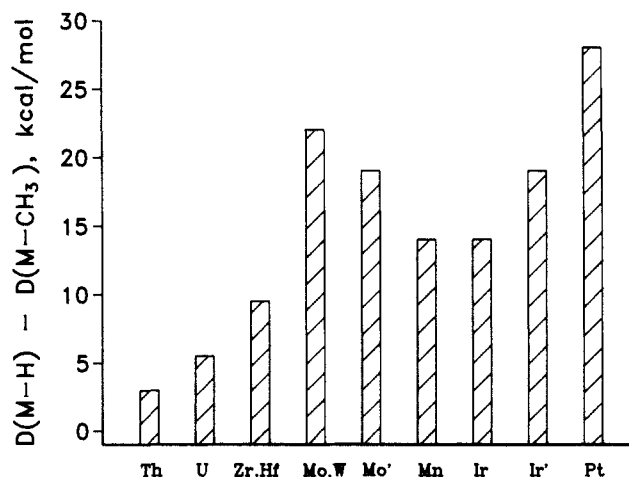


Figure 6. Comparison of $D(M-H) - D(M-CH_3)$ for various transition-metal complexes. Key: Th = $Cp_2^*Th(OR)X$ (ref 4a,c); U = $Cp_2^*U(OR)X$ (ref 4c); Zr, Hf = average $Cp_2^*MX_2$ (this work); Mo, W = average $Cp_2^*MX_2$ (ref 2k); Mo' = $CpMo(CO)_3X$ (ref 44b); Mn = $Mn(CO)_5X$ (ref 27a); Ir = $Ir(PMe_3)_2(Cl)(I)(CO)X$ (ref 2d); Ir' = $Cp^*Ir(PMe_3)_3X_2$ (ref 44c); Pt = $Pt(PEt_3)_2X_2$ (ref 44d, adjusted assuming $D(Pt-Me) - D(Pt-Et) \approx 5$ kcal/mol).

the electropositive character of the metals and accompanying bond polarity/ligand polarizability effects.^{4,44a} It can be seen in Figure 6 that the present zirconium and hafnium systems conform to this general trend. As the transition-metal series is traversed to the right, there is a general increase in $D(M-H) - D(M-Me)$,^{44b-d} which is qualitatively in accord with the aforementioned electronegativity/polarizability arguments as well as with repulsive/attractive interactions between filled/empty metal d orbitals and filled methyl σ and " π " MOs.²⁹ Attempts to analyze these trends via eq 29 are complicated by the fact that the proposed electronegativities^{28b,c} of H (2.20) and Me ("best" = 2.30^{28b}) are so similar. However, calculated (vide infra) trends are in qualitative accord with Figure 6. With respect to $D(M-I) - D(M-Me)$, it can be seen in Figure 7 that there is a general diminution

(44) (a) Bruno, J. W.; Duttera, M. R.; Fendrick, C. M.; Smith, G. M.; Marks, T. J. *Inorg. Chim. Acta* **1984**, *94*, 271-277. (b) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D., ref 1. We thank these authors for permission to quote their data. (c) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D., ref 1. We thank these authors for permission to quote their data. (d) Brainard, R. L.; Whitesides, G. M., *Organometallics* **1985**, *4*, 1550-1557.

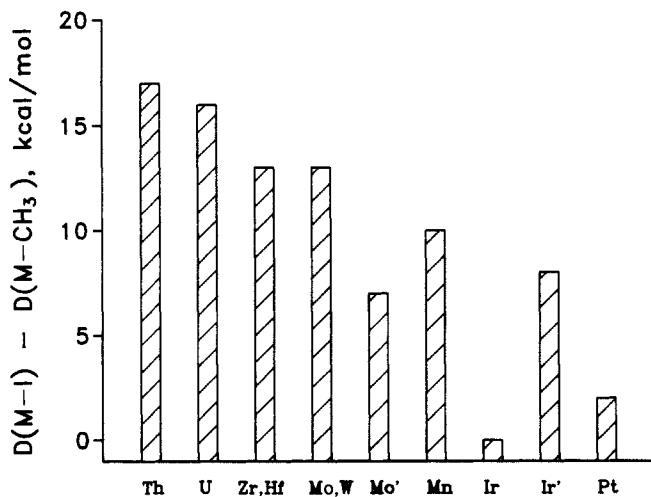


Figure 7. Comparison of $D(M-I) - D(M-CH_3)$ for various transition-metal complexes. Key: Th = average Cp'_2ThX_2 (ref 4a) assuming $D(Th-I) = D(ThI_4)$; U = Cp''_3UX (ref 5a); Zr, Hf = average Cp'_2MX_2 (this work); Mo, W = average Cp_2MX_2 (ref 2k); Mo' = $CpMo(CO)_3X$ (ref 44b); Mn = $Mn(CO)_5X$ (ref 27a); Ir = $Ir(PMe_3)(Cl)(I)(CO)X$ (ref 2d); Ir' = $Cp'Ir(PMe_3)_2X$ (ref 44c); Pt = $Pt(PPh_3)_2(I)X$ (ref 2d).

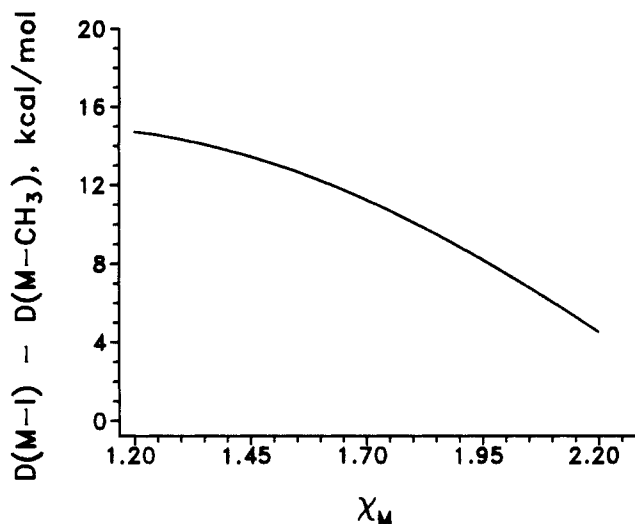


Figure 8. Correlation between $D(M-I) - D(M-CH_3)$ calculated via eq 31 (with the nonexponential term set equal to zero—see footnote 45) and metal Pauling electronegativity.

as the transition-metal series is traversed to the right.^{5a} Reference to eq 31 with $\chi_I = 2.66$ and $\chi_{Me} = 2.30$ ^{28bc} indicates that $D(M-I) - D(M-Me) =$

$$\frac{1}{2}[D(I_2) - D(Me_2)] + 105(e^{-0.219(\chi_M - \chi_{Me})^2} - e^{-0.219(\chi_M - \chi_I)^2}) \quad (31)$$

$- D(M-Me)$ decreases as χ_M increases (see Figure 8).⁴⁵ A description based on attractive/repulsive interactions between filled ligand orbitals and empty/filled metal orbitals^{5a,29,41} is also appealing and not necessarily exclusive of the former explanation.

Trends in Hydrocarbyl and Related Bond Enthalpies. The present $D(Zr-R)$ and $D(Hf-R)$ data follow closely parallel trends, with the latter being perhaps slightly greater in magnitude (ca. 4 kcal/mol) than the former. After this small adjustment, it can be seen that the combined data adhere to the trend $H \geq Ph > Me > n-Bu$, which has been observed in a number of other f- and d-block organometallic systems.^{2a,d,f,i-k,4,46} The only anomaly in

the present and much of the literature data may be that $D(M-H) \geq D(M-Ph)$ ⁴⁷ despite the fact that $D(H-Ph) - D(H-H) = 7$ kcal/mol. The disparate steric demands of H and Ph suggest that nonbonded effects play a significant role in these orderings. Indeed, restricted phenyl group rotation is observed in Cp'_2ZrPh_2 .⁹

The present data also provide information on strain energies in early transition metal metallacycles. If this quantity is defined as the diminution in metal-ligand bond enthalpy from that expected in an acyclic analogue,^{4a} it can be seen that the strain in zirconacyclopentane $Cp'_2ZrCH_2(CHEt)_2CH_2$ (II) must be rather small. Thus, correcting for $Cp'_2Hf(n-Bu)_2 \rightarrow Cp'_2Zr(n-Bu)_2$ (Table II, ca. -4 kcal/mol) yields a predicted unstrained (average⁴⁸) Zr-C bond enthalpy indistinguishable from that in II (52.5 (4.4) vs 53.5 (2.9) kcal/mol). This result can be compared to approximate strain energies in thoracyclobutanes $Cp'_2ThCH_2C(Me)_2CH_2$ and $Cp'_2ThCH_2Si(Me)_2CH_2$ of 15 and 8 kcal/mol, respectively,^{4a} as well as strain energies of 9–13 kcal/mol for platinacyclobutanes⁴⁹ and 8 kcal/mol for cyclobutane⁵⁰ (vs 25 kcal/mol for cyclobutane⁵⁰). Interestingly, zirconaindan complex $Cp'_2ZrCH_2CH_2-o-C_6H_4$ (I) exhibits a “negative” ring strain (ca. 10 kcal/mol) in that the $ZrCH_2CH_2$ bond enthalpy is greater than would be predicted from $Cp'_2Zr(Et)_2$ (estimated from Figure 3) or $Cp'_2Zr(n-Bu)_2$. The explanation appears to reside in the tightly constrained character of the chelate ring and diminished nonbonded repulsions vis-à-vis $Cp'_2Zr(n-Bu)_2$. Ring-metalated complex $Cp'Zr(Ph)(\eta^1:\eta^5-CH_2C_5Me_4)$ provides another example of a potentially strained ring system. Indeed, the average measured $D(Zr-CH_2)$ of 45 kcal/mol (Tables I–III) is rather small. The most realistic model for an unstrained $Zr-CH_2C_5Me_4$ bond would appear to be Zr-benzyl, for which no data exist. However, extrapolation from existing thorium and uranium data⁴ suggests that $D(Zr-CH_2Ph) \approx 50$ kcal/mol. Thus, the strain energy in $Cp'Zr(Ph)(\eta^1:\eta^5-CH_2C_5Me_4)$ is small but nonzero.

The average $D(Zr-CO)$ value of 39.7 (0.9) kcal/mol determined for $Cp'_2Zr(CO)_2$ (eq 21 and 24) in the present study is rather strong and compares favorably with recent D_1 values of 36.8, 40.5, and 41.5 kcal/mol reported for $Cr(CO)_6$, $Mo(CO)_6$, and $Fe(CO)_5$, respectively.⁵¹ It also compares favorably with an average $D(Ti-CO)$ value of 41.1 (1.9) kcal/mol recently reported for $Cp_2Ti(CO)_2$.⁵² All of these data are substantially higher than the corresponding value for the only known uranium carbonyl (Cp'_3UCO), 10.3(0.2) kcal/mol.^{5a}

Ancillary Ligand Effects. The degree to which the supporting ligands may modify $D(M-R)$, i.e., the transferability of $D(M-R)$ between environments, is also of interest. Assuming the $MX_4 \rightarrow Cp'_2MX_2$ transferability of Cl and I (vide infra) is generalizable to other ancillary ligand arrays, and then it can be seen (Table II) that $Cp'_2ZrMe_2 \rightarrow Cp_2ZrMe_2$ has negligible effect on $D(Zr-Me)$. Thus, differential steric effects appear to be minor or are cancelled by other factors here. If it is assumed that $D(M-OC_6F_5)$ is the same in Cp'_2M and $Cp'M$ -environments, then the $Cp'MMe_3$ data of Table III imply that $D(Zr-Me)$ and $D(Hf-Me)$ are not highly sensitive to ancillary ligation (see also Figure 2)—there is a ca. 3 kcal/mol “weakening” of the first M-Me bond versus Cp'_2MMe_2 . However, the aforementioned (Figure 2) $Cp'ZrX_2/ZrX_4$ effects on $D(Zr-OR)$ suggest that an invariant $D(M-OC_6F_5)$ is not an entirely satisfactory approximation and that $D(Cp'Zr(X)_2-OR)$ is probably slightly greater than $D(Cp'_2Zr(X)-OR)$. The result will be an apparent, slight

(47) In several instances, this inequality is not statistically significant.

(48) The strain energy will only be operative in the cleavage (ring-opening) of the first M-C bond. Ancillary ligand effects (vide infra) tend to slightly enhance the apparent second bond enthalpy (from $M(X)R \rightarrow MX_2$ calorimetry). This small effect must be taken into account in viewing $D(M-R)$ average data.

(49) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194.

(50) Reference 22b, pp 60–63, 273.

(51) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905–3912.

(52) Calhorda, M. J.; Dias, A. R.; Minas da Piedade, M. E.; Salema, M. S.; Martinho Simoes, J. A. *Organometallics* **1987**, *6*, 734–738 and references therein.

(45) Because $D(I_2) - D(Me_2)$ is negative (a common artifact when the arithmetic mean is used in eq 29),⁴² we arbitrarily set it equal to zero in eq 31. This in no way affects the χ_M dependence of the function.

(46) (a) Baird, M. C. *J. Organomet. Chem.* **1974**, *64*, 289–300. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219.

"weakening" of $D(\text{M}-\text{Me})$ in the monopentamethylcyclopentadienyl environment. It seems unlikely that the effect will be larger than ca. 5 kcal/mol, and it may well decrease with increasing aryl oxide substitution (π donation).

Closely connected with the above discussion is the observation in the $\text{Cp}'\text{MMe}_3$ and metal hydride data of Tables III and IV that alkoxide substitution increases the apparent bond enthalpies of remaining $\text{M}-\text{Me}$ and $\text{M}-\text{H}$ functionalities. The effect is greater for hydrides, with the $\text{Cp}'\text{M}(\text{OR})_n\text{Me}_{3-n}$ data exhibiting small 1–4 kcal/mol variations on the order of those previously noted for the $\text{Cp}'_2\text{Th}(\text{OR})_n\text{R}_{2-n}$ series.^{4a} The thorium^{4a} and $\text{Cp}'_2\text{Zr}(\text{H})\text{Ph}$ data (Table IV) suggest that alkoxide ancillary ligand effects are greater than those of Cl and Ph. The magnitude of the present group 4 hydride/alkoxide effects requires a more detailed analysis than was previously warranted. Assuming that $D(\text{M}-\text{H})$ is not independent of ancillary σ ligation, a two-step titration for the present bis(pentamethylcyclopentadienyl) complexes ($\text{MH}_2 \rightarrow \text{M}(\text{OR})\text{H} \rightarrow \text{M}(\text{OR})_2$) evolving two heats of reaction, ΔH^1_{rx} and ΔH^2_{rx} , can be expressed (see eq 2 and 3) as in eq 32–35. If the simplifying

$$\Delta H^1_{\text{rx}} = 2D(\text{M}(\text{H})-\text{H}) + D(\text{RO}-\text{H}) - D(\text{M}(\text{H})-\text{OR}) - D(\text{M}(\text{OR})-\text{H}) - D(\text{H}_2) \quad (32)$$

$$D(\text{M}(\text{H})-\text{H}) = \frac{1}{2}[D(\text{M}(\text{H})-\text{OR}) + D(\text{M}(\text{OR})-\text{H}) + D(\text{H}_2) + \Delta H^1_{\text{rx}} - D(\text{RO}-\text{H})] \quad (33)$$

$$\Delta H^2_{\text{rx}} = D(\text{M}(\text{H})-\text{OR}) + D(\text{M}(\text{OR})-\text{H}) + D(\text{RO}-\text{H}) - 2D(\text{M}(\text{OR})-\text{OR}) - D(\text{H}_2) \quad (34)$$

$$D(\text{M}(\text{OR})-\text{H}) = 2D(\text{M}(\text{OR})-\text{OR}) + D(\text{H}_2) + \Delta H^2_{\text{rx}} - D(\text{M}(\text{H})-\text{OR}) - D(\text{RO}-\text{H}) \quad (35)$$

approximation is made that $D(\text{M}-\text{OR})$ is relatively insensitive to ancillary σ ligand effects (less sensitive than $D(\text{M}-\text{H})$), then $D(\text{M}(\text{OR})-\text{OR}) \approx D(\text{M}(\text{H})-\text{OR}) = D(\text{M}-\text{OR})$, and eq 35 reduces to eq 36. Substituting for $D(\text{M}(\text{OR})-\text{H})$ in eq 33 then yields eq 37. This treatment indicates that while $D(\text{M}(\text{OR})-\text{H})$ is

$$D(\text{M}(\text{OR})-\text{H}) = D(\text{M}-\text{OR}) + D(\text{H}_2) + \Delta H^2_{\text{rx}} - D(\text{RO}-\text{H}) \quad (36)$$

$$D(\text{M}(\text{H})-\text{H}) = D(\text{M}-\text{OR}) + D(\text{H}_2) - D(\text{RO}-\text{H}) + \frac{\Delta H^1_{\text{rx}} + \Delta H^2_{\text{rx}}}{2} \quad (37)$$

accurately determined by measurement of ΔH^2_{rx} , apparent $D(\text{M}(\text{H})-\text{H})$ values obtained from ΔH^1_{rx} must be corrected by a factor of ca. $+1/2(\Delta H^2_{\text{rx}} - \Delta H^1_{\text{rx}})$. The average correction to the first bond $D(\text{M}-\text{H})$ data in Table IV is +4.6 kcal/mol.⁵³ Thus, the data still evidence an enhancement in $D(\text{M}-\text{H})$ effected by the ancillary alkoxide ligation. An explanation proposed earlier^{4a,c} involves the tendency of hard alkoxide ligands to stabilize high metal oxidation states, rendering the reduction implicit in homolytic bond dissociation (eq 1) more energetically demanding. It is also conceivable that the greater electronegativity of oxygen vis-à-vis most other ancillary ligands may increase the overall positive charge on the metal and enhance attractive metal–ligand coulombic forces.

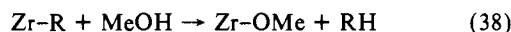
Thermochemistry of Various Group 4 Centered Transformations

The present bond disruption enthalpy data afford an opportunity to scrutinize the driving forces for a number of early transition metal reaction patterns and to compare and contrast them with those characteristic of middle/late and f-block transition metals. We begin with the driving forces for simple cleavage and insertion/elimination processes, proceed to reductive elimination/oxidative addition/reductive coupling processes, discuss $\text{M}(\eta^1-\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)$ reaction patterns together with an analysis of eq 6, and conclude with some remarks on CO activation. Relevant bond

(53) Regarding the assumption $D(\text{M}(\text{OR})-\text{OR}) \approx D(\text{M}(\text{H})-\text{OR})$, overestimation of the former term, which might be lower due to steric congestion or π saturation, would have the effect of increasing both the calculated $D(\text{M}(\text{H})-\text{H})$ and $D(\text{M}(\text{OR})-\text{H})$ (the latter to a greater degree).

enthalpy data for organic fragments are taken from standard sources,²² and it is assumed that the effects of metal substituents largely attenuate within two σ bonds. General reactions are illustrated for zirconium. It is also assumed that the $T\Delta S$ (translational, rotational) contribution to ΔG from creating an additional particle near or slightly above room temperature is ca. –6 to –12 kcal/mol per reaction (we employ the average, –9 kcal/mol).^{4,54}

Protonolysis of zirconium–alkyl and –hydride bonds in the present compounds is found to be highly exothermic (eq 38 and 39). In comparison to later transition metals,^{1,2} the driving force

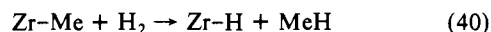


$$\Delta H_{\text{calcd}} \approx -36 \text{ kcal/mol (R = Me); } -27 \text{ kcal/mol (R = H)}$$



$$\Delta H_{\text{calcd}} \approx -30 \text{ kcal/mol (R = Me); } -21 \text{ kcal/mol (R = H)}$$

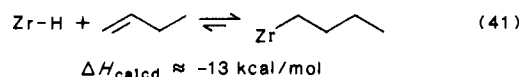
is the great strength of the metal–heteroelement bonds vis-à-vis $D(\text{Zr}-\text{R})$. For late transition elements, eq 38 and 39 are estimated to be near thermoneutrality or possibly endothermic for the metal hydrides.²¹ Hydrogenolysis of group 4 hydrocarbyls (eq 40) is



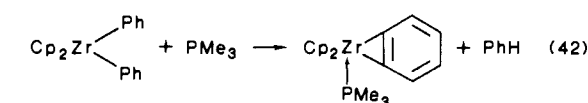
$$\Delta H_{\text{calcd}} \approx -9 \text{ kcal/mol}$$

also predicted to be exothermic; however, because $D(\text{Zr}-\text{H}) - D(\text{Zr}-\text{Me})$ is relatively small, such processes will not be as exothermic as for most later transition metals.

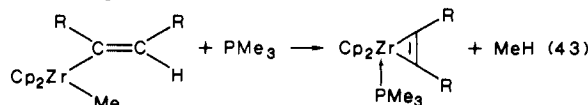
Also as a consequence of the relatively small $D(\text{Zr}-\text{H}) - D(\text{Zr}-\text{alkyl})$ values found, β -hydride elimination can be estimated to be endothermic in most group 4 systems (eq 41).⁵⁵ Such chemistry and the ability to manipulate the thermodynamics thereof is important to hydrozirconation^{8h} and Ziegler–Natta



catalysis.^{4,56} As regards the former, ΔG will not be so negative (ca. –4 kcal/mol assuming $T\Delta S \approx +9$ kcal/mol) as to prohibit facile double bond migration processes.^{8h} For many later transition metals, ΔH (eq 41) is estimated to be nearer to thermoneutral (see Figure 6), while it is somewhat more exothermic for f-elements.⁴ Hydrocarbon elimination processes as in eq 42 and 43 serve as pathways to novel, useful, and isolable alkyne complexes.⁵⁷



$$\Delta H_{\text{calcd}} \lesssim 33 - D(\text{Zr}-\text{benzyne}) \text{ kcal/mol}$$



$$\Delta H_{\text{calcd}} \lesssim 35 - D(\text{Zr}-\text{alkyne}) \text{ kcal/mol}$$

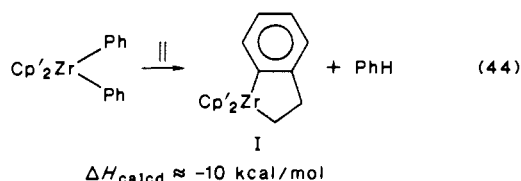
(54) (a) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6807. (b) Page, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: New York, 1984; pp 1–54. (c) Page, M. I.; Jencks, W. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683.

(55) $D(\text{Hf}-\text{Me}) - D(\text{Hf}-n\text{-Bu})$ appears to be somewhat larger in $\text{Cp}'_2\text{HfR}_2$ than in $\text{Cp}'_2\text{ThR}_2$ ^{4a} complexes (ca. 16 vs 10 kcal/mol). If this trend is steric in origin, it will presumably be smaller for Cp_2HfR_2 . Hence, eq 41 is likely more exothermic for $\text{Cp}_2\text{Zr}(\text{X})\text{R}^{\text{8h}}$ systems.

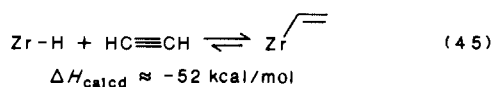
(56) (a) Quirk, R. P.; Hsieh, H. L.; Klingensmith, G. C.; Tait, P. J., Eds. *Transition Metal Catalyzed Polymerization. Alkenes and Dienes*; Harwood Publishers for MMI Press: New York, 1983. (b) Cavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982. (c) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.

(57) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411–7413. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544–2546.

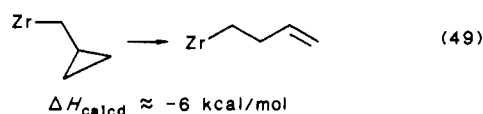
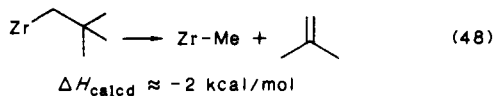
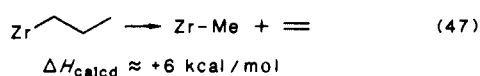
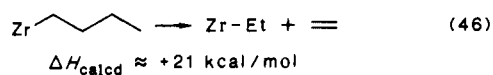
Making the reasonable assumption⁵⁸ that $D(\text{Zr-PMe}_3) \approx D(\text{Zr-CO})$, then for eq 42 and 43 to be exothermic, we find $D(\text{Zr-benzyne}) \geq 33$ and $D(\text{Zr-alkyne}) \geq 35$ kcal/mol, respectively. Further remarks will be made about these quantities in the following discussion. Closely related to eq 42 is the process by which zirconaindan I is formed (eq 44). This is estimated to be exo-



thermic. Not unexpectedly, the insertion of alkynes into group 4-hydride bonds (eq 45)^{8h,59} is estimated to be more exothermic than for olefin insertion.



Also related to eq 41 are β -alkyl elimination processes. Although none have, to our knowledge, been reported for group 4, chemical similarities to Lu⁶⁰ and Sc⁶¹ prompt a thermodynamic analysis of similar, hypothetical group 4 processes (eq 46-49).⁶² Making the pragmatic assumption that all $D(\text{Zr-alkyl})$ in eq



46-49 $\approx D(\text{Zr-}n\text{-Bu})$ except for alkyl = Me,⁶³ it can be seen that ΔH decreases in the order eq 46 > 47 > 48 > 49. Equation 46 is in essence the reverse of the propagation step in ethylene coordinative polymerization and is expected to be highly exothermic.^{4a,c,56} The difference in estimated exothermicity vis-à-vis eq 47 lies in the greater magnitude of $D(\text{Zr-Me})$. This same factor is operative in eq 48 as well as lower $D(\text{C-C})$ values when tertiary centers^{22,64} are involved. Relief of cyclopropyl ring strain is doubtless important in driving eq 49.⁶⁵

(58) Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529-2537.

(59) (a) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281-315. (b) We assume $D(\text{Zr-vinyl}) \approx D(\text{Zr-Ph})$.

(60) Watson, P. J.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-56.

(61) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21-39.

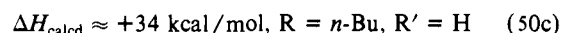
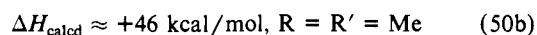
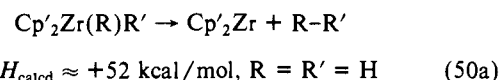
(62) For examples in organoaluminum chemistry, see: (a) Pfohl, W. *Ann.* **1960**, *629*, 207-209. (b) Ziegler, K.; Nagel, K.; Pfohl, W. *Ann.* **1960**, *629*, 210-221. (c) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 2165-2166.

(63) Comparisons to $\text{Cp}'_2\text{ThR}_2$ $D(\text{Th-R}) - D(\text{Th-R}')$ data⁴ suggest that interligand nonbonded repulsions are larger in $\text{Cp}'_2\text{ZrR}_2/\text{Cp}'_2\text{HfR}_2$ compounds. The effect is suggested by $D(\text{M-Me}) - D(\text{M-}n\text{-Bu})$ ⁵⁵ and may be even greater for R = neopentyl and cyclopropylmethyl.

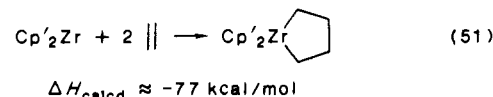
(64) (a) Steric factors are also no doubt important in such reactions. Enthalpy changes calculated from tabulated^{64b} ΔH° data for neopentane \rightarrow isobutylene + methane and *n*-butane \rightarrow propylene + methane are rather similar (+18.2 and +17.3 kcal/mol, respectively). (b) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data on Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986; Appendix Table 1.2.

(65) ΔH for eq 49 was estimated from the average of enthalpies^{64b} for methylcyclopropane \rightarrow 1-butene and cyclopropane \rightarrow propylene.

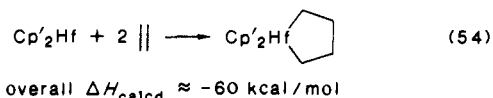
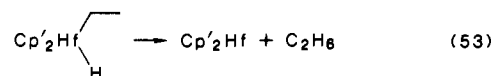
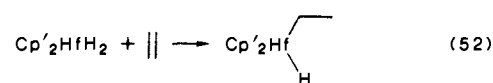
Reductive elimination processes, when not coupled to other bond-forming reactions, are estimated to be highly endothermic in the present group 4 compounds (eq 50). This is in contrast to many later transition metals^{2h,66} and reflects the greater



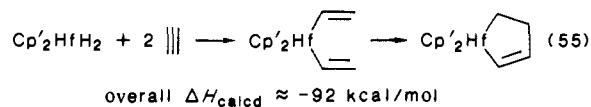
magnitudes of Zr,Hf-ligand bond enthalpies. For the same reason, reductive coupling reactions should be highly exothermic (eq 51)



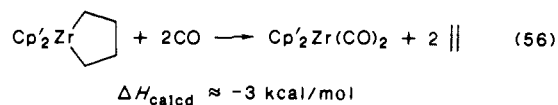
and in combination with reductive elimination processes (eq 50) plausibly explain sequences such as eq 52-54,^{15b} as well as formation of II (eq 12) via $\text{Cp}'_2\text{Zr}(\text{H})(n\text{-Bu})$ and analogous acet-



ylene chemistry (eq 55).^{59a,67} The major driving force in such



sequences is Hf-C/C-C bond formation and olefin or acetylene hydrogenation (ca. -34 or -66 kcal/mol). It is also conceivable that the endothermicity of eq 53 and similar processes (cf. eq 50c) is moderated in the presence of excess ethylene by formation of an ethylene complex.⁶⁸ Assuming $D(\text{M-ethylene})/D(\text{M-CO}) \approx 0.8$,^{2b} then $D(\text{Hf-ethylene}) \approx 32$ kcal/mol, thus rendering eq 53 significantly closer to thermoneutrality (cf. eq 50c). Although neutral ligands such as CO can, in principle, alter the thermodynamics of reductive coupling (e.g., eq 56), in practice alternative transformations are usually (but not always⁶⁹) observed, such as



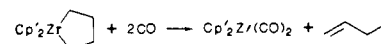
migratory CO insertion and associated followup chemistry driven

(66) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245 and references therein.

(67) This estimate assumes $D(\text{M-vinyl}) \approx D(\text{M-Ph})$ and negligible ring strain in the metallacyclopentene. Cyclopentane and cyclopentene have small, nearly identical ring strains.⁵⁰

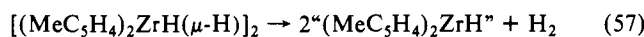
(68) For somewhat different titanium chemistry, see: (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006-1014. (b) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136-1143.

(69) Processes such as



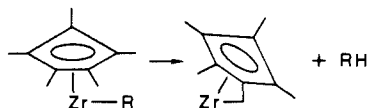
are calculated to be exothermic by ca. -30 kcal/mol. Analogous transformations have been observed in organotitanium systems.⁶⁸

by the very large $D(\text{M}-\text{O})$ (vide infra).^{2a,f,g} The present data indicate that homolytic eliminations as in eq 57⁷⁰ will also be rather endothermic.



$$\Delta H_{\text{calcd}} \approx +35 \text{ kcal/mol of Zr}$$

The results of this study afford an opportunity to assess the thermodynamics of reactions involving $\text{M}(\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ species, which are ubiquitous in group 4 and organo-f-element chemistry. Interestingly, the product $\text{M}-\text{CH}_2$ bond is found to be rather weak, and a number of abstraction processes apparently require entropic assistance to be exergonic (eq 58).⁷¹ Indeed, eq 58b and 58c suggest the viability of hydrocarbon activation



$$\Delta H_{\text{calcd}} \approx -3 \text{ kcal/mol, R} = n\text{-Bu} \quad (58a)$$

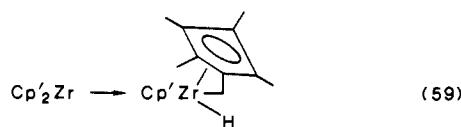
$$\approx +6 \text{ kcal/mol, R} = \text{Me} \quad (58b)$$

$$\approx +5 \text{ kcal/mol, R} = \text{Ph} \quad (58c)$$

$$\approx +13 \text{ kcal/mol, R} = \text{H} \quad (58d)$$

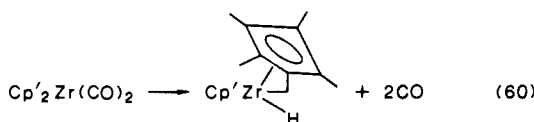
by the reverse reaction (demonstrated for $(\text{Cp}'_2\text{LuMe})_2 + \text{CH}_4$ ⁷²). Equation 58d indicates that the pathway for methyl H/D exchange in many Cp' hydride systems by reversible H_2 elimination requires an endothermic first step. Conversely, hydrogenolysis of the $\text{M}-\text{CH}_2$ linkage should be (and is vide supra) favorable. In later transition-metal systems having larger $D(\text{M}-\text{H}) - D(\text{M}-\text{alkyl})$, processes as in eq 58d are expected to be more endothermic, and to our knowledge, facile H/D exchange is not common.

Viewed as intramolecular oxidative addition products, $\text{M}(\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ complexes are also plausible endpoints of prior reductive elimination processes (eq 59). Coupling this transformation to eq 50c renders the butane reductive elimination process



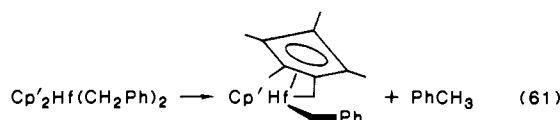
$$\Delta H_{\text{calcd}} \approx -35 \text{ kcal/mol}$$

essentially thermoneutral. The presence of such a product in the $\text{Cp}'_2\text{ZrCl}_2 + 2n\text{-BuLi}$ reaction when excess 1-butene is not present (vide supra) is thus understandable (eq 11 via $\text{Cp}'_2\text{Zr}(\text{H})(n\text{-Bu})$). While oxidative addition processes similar to eq 59 are not expected to be exothermic for $\text{Cp}'_2\text{Zr}(\text{CO})_2$ (eq 60), it is noteworthy that N_2 elimination from $(\text{Cp}'_2\text{ZrN}_2)_2$ affords just such a product.⁷³

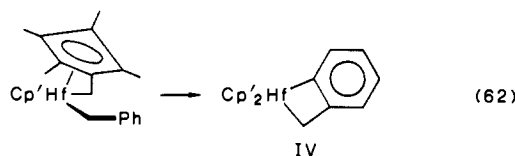


$$\Delta H_{\text{calcd}} \approx +46 \text{ kcal/mol}$$

Other group 4 centered multistep C-H activation processes are also amenable to thermochemical analysis. The formation of metallacycle IV⁷⁴ proceeds via α -elimination to yield an alkylidene which then rearranges to an $\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$ complex (eq 61). Estimating $D(\text{Hf}-\text{CH}_2\text{Ph})$ from thorium or uranium data ($D(\text{M}-\text{CH}_2\text{Ph}) \approx D(\text{M}-n\text{-Bu}) - 3 \text{ kcal/mol}$),^{4a,5a} it can be seen that eq 61 is anticipated to be slightly endothermic and likely requires entropic assistance. Thermodynamic estimates for eq 62 are



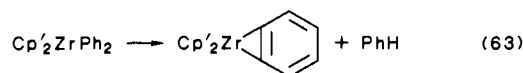
$$\Delta H_{\text{calcd}} \approx +4 \text{ kcal/mol}$$



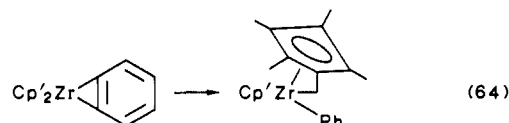
$$\Delta H_{\text{calcd}} \approx \geq -5 \text{ kcal/mol}$$

complicated by lack of information on strain energy in metallacycle IV. If it is assumed that this term is negligible, i.e., $D(\text{Hf}-\text{CH}_2) \approx D(\text{Hf}-\text{CH}_2\text{Ph})$ (cf. zirconaindan I where it is "negative"), then eq 62 is projected to be slightly exothermic, with the driving force arising principally from $\text{Cp}'-\text{CH}_3$ and $\text{Hf}-\text{Ph}$ bond formation. Strain in the metallacyclic ring will shift ΔH in the endothermic direction. In summary, estimates for the sequence eq 61 and 62 indicate that the overall process is approximately thermoneutral or slightly endothermic and that entropic factors are important in shifting the equilibrium toward products.

The intramolecular C-H activation process of eq 6 was shown on the basis of kinetic, isotopic labeling, crossover, and trapping experiments to proceed via the sequence shown in eq 63 and 64,⁹ where a benzyne (*o*-phenylene) complex is a kinetically demon-



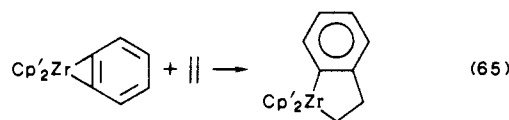
$$\Delta H_{\text{calcd}} \approx 146 - D(\text{Zr-benzyne}) \text{ kcal/mol}$$



$$\Delta H_{\text{calcd}} \approx -141 + D(\text{Zr-benzyne}) \text{ kcal/mol}$$

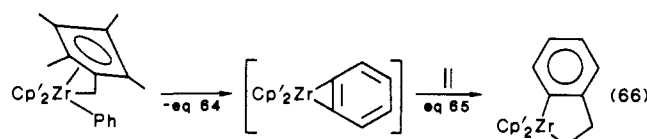
$$\Delta H_{\text{calcd}}(\text{eq 63 and 64}) \approx +5 \text{ kcal/mol}$$

strated intermediate that can be efficiently intercepted with ethylene to yield zirconaindan I (eq 9 and eq 10). Kinetic studies indicate that ΔH^\ddagger for eq 63 = 22.5 (3) kcal/mol.⁹ In the present investigation, it was found that heating the $\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$ complex in the presence of ethylene also yields the zirconaindan



$$\Delta H_{\text{calcd}} \approx -159 + D(\text{Zr-benzyne}) \text{ kcal/mol}$$

in a process that is kinetically independent of ethylene concentration over a tenfold range ($\Delta H^\ddagger = 20.6$ (5) kcal/mol; $\Delta S^\ddagger = -15.4$ (5) eu). This observation implies that an intermediate, presumably the same *o*-phenylene, is being trapped (eq 66).



$$\text{overall } \Delta H_{\text{calcd}} \approx -18 \text{ kcal/mol}$$

The above observations have interesting general implications for group 4 centered intramolecular C-H activation processes, for bond enthalpies in early transition metal-*o*-phenylene and alkyne complexes, and for $\text{M}(\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)$ chemistry. First, (eq 63 + eq 64) is estimated to be slightly endothermic. This case represents a further example where an intramolecular C-H activating cyclometalation process is found to be entropically driven.^{4a}

(70) (a) Bajgur, C. S.; Jones, B. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 1929-1936. (b) This calculation assumes $D(\text{M}-\text{H}_{\text{bridge}}) - D(\text{M}-\text{H}_{\text{terminal}}) \approx 10 \text{ kcal/mol}$.^{4c,70c} (c) Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491-493.

(71) Assuming $D(\text{Me}_4\text{C}_3\text{H}_2-\text{H}) \approx D(\text{PhCH}_2-\text{H})$.

(72) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493.

(73) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *167*, 136-148.

(74) Bulls, A. R.; Schaefer, W. R.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219-1226.

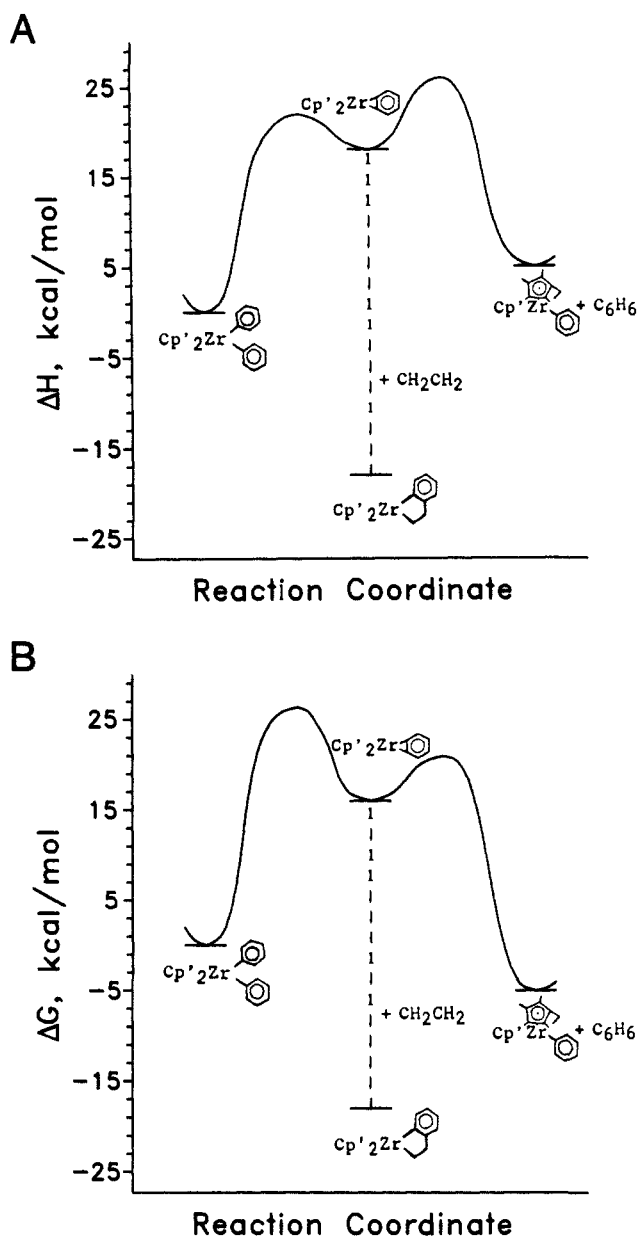


Figure 9. (A) Enthalpy profile for the thermolytic transformations of $\text{Cp}'_2\text{ZrPh}_2$ based upon experimental bond enthalpy and kinetic data. (B) Free energy profile for the thermolytic transformations of $\text{Cp}'_2\text{ZrPh}_2$ at 350 K based upon experimental bond enthalpy and kinetic data. The $T\Delta S$ contribution to ΔG for all processes creating (consuming) a particle is estimated to be -9 kcal/mol ($+9$ kcal/mol). In both profiles, the position of the orthophenylene (benzyne) intermediate is approximate.

Second, to be compatible with the kinetic data⁹ (eq 63; ΔH^* , Figure 9, left) $D(\text{Zr}-\text{benzyne})$ must be very large—greater than ca. 123 kcal/mol. Interestingly, such a large bond enthalpy is qualitatively in accord with a Zr(IV)/ σ^2 electronic structural formulation (two metal-carbon σ bonds) and not incompatible with the observed reaction patterns (eq 43, 64, 65). Indeed, despite the relatively large magnitude of $D(\text{Zr}-\text{benzyne})$, the extensive reactivity of such complexes can be readily understood in that two M-R,X σ bonds and a strong Ph-R,H bond are formed in most transformations.^{8a,57,75,76} Comparison to later transition-metal $D(\text{M}-\text{alkyne})$ values is hampered by a paucity of data; however,

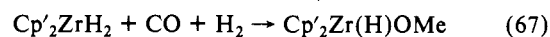
(75) (a) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246–1247. (b) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45–60. (c) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659–3660. (d) Boekel, C. P.; Teuben, J. H.; deLiefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 161–165.

(76) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

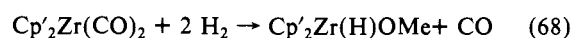
existing information suggests this quantity can vary from ca. 20 to 90 kcal/mol^{2b,d,77} depending on the coordination environment. The thermochemical data also suggest that the ubiquity of M($\eta^1-\eta^5-\text{CH}_2\text{C}_5\text{Me}_4$) species in group 4, lanthanide, and actinide chemistry reflects the weakness of the Cp' C–H bond and the entropic advantage inherent in the elimination processes by which they are most commonly formed, balanced by the relatively weak M–CH₂ bond and reduced steric crowding⁹ vis-à-vis potential L_nMR_2 products. Hence, M($\eta^1-\eta^5-\text{CH}_2\text{C}_5\text{Me}_4$) complexes are ideally poised energetically to be intermediates.

Figure 9 presents approximate enthalpy and free energy profiles for the $\text{Cp}'_2\text{ZrPh}_2$ thermolytic chemistry. The free energy profile is estimated for 350 K and assumes that the $T\Delta S$ contribution to ΔG for expelling the product particle per reaction stoichiometry is ca. -9 kcal/mol. It explains the absence of significant exogenous arene (e.g., toluene, benzene-*d*₆) exchange into the starting material (“arene metathesis”⁷⁶) on the time scale of the thermolytic synthesis or kinetic runs⁹ as well as the absence of detectable quantities ($<0.5\%$ by ¹H NMR) of $\text{Cp}'_2\text{ZrPh}_2$ present in the equilibrium with $\text{Cp}'_2\text{Zr}(\text{Ph})(\eta^1-\eta^5-\text{CH}_2\text{C}_5\text{Me}_4)$. This situation stands in contrast to $\text{Cp}'_2\text{AnPh}_2$ compounds (An = Th,U) where arene metathesis occurs and M($\eta^1-\eta^5-\text{CH}_2\text{C}_5\text{Me}_4$) species are not detected in appreciable quantities.⁷⁶ The reason $\Delta G > 0$ for the actinide systems may reflect slightly greater relative $D(\text{M}-\text{Ph})$ values due to diminished interligand crowding around the larger metal ion, a less negative $-T\Delta S$ term for the same reason, or a smaller relative $D(\text{M}-\text{CH}_2)$ in the product.

Early transition metals,^{8f,g} lanthanides,⁷⁸ and actinides^{4,35a,c,79} exhibit a rich CO activation chemistry. One pervasive feature is the prevalence of alkoxide-like end products. The reason has qualitatively been argued as the great magnitudes of $D(\text{M}-\text{OR})$.^{79f} This can be seen more quantitatively in processes such as eq 67 and 68,¹¹ where $D(\text{Zr}-\text{OMe}) \approx 103$ kcal/mol is a major part of

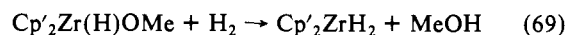


$$\Delta H_{\text{calcd}} \approx -45 \text{ kcal/mol}$$

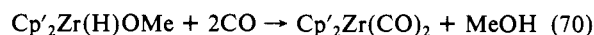


$$\Delta H_{\text{calcd}} \approx -15 \text{ kcal/mol}$$

the driving force.⁸⁰ Subsequent steps to close a methanol-forming catalytic cycle must then be highly endothermic (eq 69) or at least thermoneutral and endergonic (eq 70) and compete with undesirable termination processes as in eq 71, as well as other competing

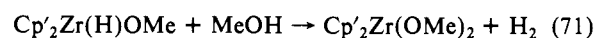


$$\Delta H_{\text{calcd}} \approx +31 \text{ kcal/mol}$$



$$\Delta H_{\text{calcd}} \approx +1 \text{ kcal/mol}$$

intermolecular chemistry.^{8g,79}



$$\Delta H_{\text{calcd}} \approx -21 \text{ kcal/mol}$$

(77) (a) Evans, A.; Mortimer, C. T.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *96*, C58–C60. (b) McNaughton, J. L.; Mortimer, C. T.; Burgess, J.; Hacker, M. J.; Kennett, R. D. W. *J. Organomet. Chem.* **1974**, *71*, 287–290.

(78) (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177. (b) Schumann, H. in ref 35c, Chapter 1. (c) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474–495. (d) Evans, W. J. *Polyhedron* **1987**, *5*, 603–835.

(79) (a) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064. (b) Moloy, K. G.; Fagan, T. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56–67. (c) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467–4476. (d) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576–3578. (e) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723–1726. (f) Fagan, P. J.; Maatta, E. A.; Marks, T. J. *A.C.S. Symp. Ser.* **1981**, *152*, 53–78.

(80) These estimates assume $D(\text{CO})$ is unaltered by coordination to a metal and that $D(\text{Zr}-\text{OMe})$ is invariant with ancillary σ ligand. The approximate character is illustrated by comparing the sums of eq 67 + eq 69 or eq 68 + eq 70 with the calculated ΔH for formation of gaseous methanol from $\text{CO} + 3\text{H}_2$, -21.8 kcal/mol.^{22b,64b}

Conclusions

These results further illustrate the utility of thermochemically derived bond enthalpy data in understanding organotransition-metal bonding and reactivity patterns. In the present, archetypical early transition metal systems, it can be seen that many distinctive characteristics can be understood on the basis of the electropositive nature and redox properties of the metal centers vis-à-vis those of later transition elements.

Acknowledgment. We are grateful to the NSF for support of this research under grant CHE8306255. L.E.S. thanks Dow Chemical Co. for a fellowship. We thank Dr. G. E. Kellogg for assistance with some of the graphics.

Registry No. Cp₂ZrCl₂, 54039-38-2; Cp₂ZrMe₂, 67108-80-9; Cp₂Zr(OH)₂, 91294-93-8; Cp₂ZrPh₂, 79847-76-0; Cp⁺Zr(Ph)(η¹:η⁵-

CH₂C₅Me₄), 105501-02-8; Cp₂Zr(CO)₂, 61396-31-4; Cp₂Zr(H)(NH₂), 91295-10-2; Cp₂HfCl₂, 85959-83-7; Cp₂HfH₂, 81956-87-8; Cp₂HfI₂, 92786-75-9; Cp⁺ZrMe₃, 81476-64-4; Cp₂ZrMe₂, 12636-72-5; Cp₂ZrI₂, 1298-41-5; Cp₂ZrH₂, 61396-34-7; Cp₂Zr(H)Ph, 112532-20-4; Cp₂Zr(OH)Ph, 116436-94-3; Cp₂ZrCH₂CH₂-o-C₆H₄, 116436-95-4; Cp₂ZrCH₂(CH₂)₂CH₂, 116558-25-9; Cp₂Zr(H)(O-*t*-Bu), 116436-96-5; Cp₂Zr(Me)(OC₆H₅), 116436-97-6; Cp₂ZrI₂, 68209-12-1; Cp₂Zr(OC₆F₅)₂, 116436-98-7; Cp₂Zr(OC₆H₅)₂, 116436-99-8; Cp₂Zr(OCH₂CF₃), 116437-00-4; Cp₂HfMe₂, 116437-01-5; Cp₂Hf(*n*-Bu)₂, 116437-02-6; Cp₂Hf(OC₆F₅)₂, 116437-03-7; Cp⁺HfMe₃, 113161-86-7; Cp⁺Hf(OC₆F₅)₃, 116437-04-8; Cp⁺HfCl₃, 75181-08-7.

Supplementary Material Available: A table giving bond disruption enthalpy data used in deriving the present *D*(M-R) and *D*(M-L) results (1 page). Ordering information is given on any current masthead page.

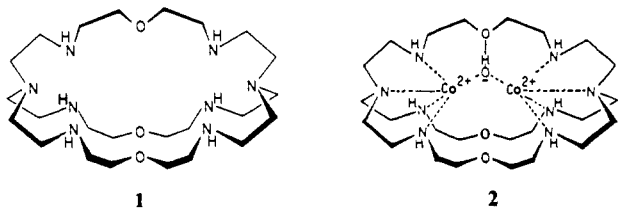
Dicobalt-O-BISTREN Cryptate as a Reversible Dioxygen Carrier for Oxygen Separation and Transport

Ramunas J. Motekaitis and Arthur E. Martell*

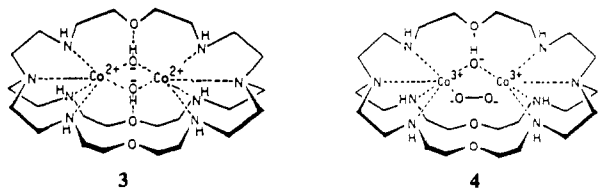
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255. Received March 31, 1988

Abstract: Spectrophotometric studies of the dioxygen complex of the dicobalt-O-BISTREN cryptate have been carried out over the temperature range 25–95 °C. The dioxygen complex is nearly completely formed at low temperature and nearly completely dissociated at 95 °C. No degradation of the dioxygen complex to inert complexes was observed below 65 °C. At the highest temperature studied (95.0 °C), slow metal-centered degradation of the dioxygen complex to the inert binuclear cobalt(III) cryptate was observed. The facile formation and dissociation of the dioxygen complex from 35 to 75 °C indicates that the dicobalt(II) complex of O-BISTREN would be an effective and efficient oxygen carrier for oxygen separation and transport.

The binuclear cobalt(II) complex of the cryptand ligand O-BISTREN (**1**) was first prepared by Lehn et al.,¹ and its intensely colored brown dioxygen complex was mentioned in a review by Lehn.² The dioxygen complex was first prepared in aqueous



solution, and the corresponding dioxygen formation constants were reported by Motekaitis et al.³ Potentiometric equilibrium studies, which resulted in the equilibrium constants listed in Table I, showed that the simple binuclear complex Co₂(O-BISTREN)⁴⁺ is never more than a minor species in aqueous solution but is further stabilized by hydroxide ion bridging, resulting in conversion to the major hydrolyzed species Co₂(OH)(O-BISTREN)³⁺ (**2**) and Co₂(OH)₂(O-BISTREN)²⁺ (**3**) at neutral and high pH. The



(1) Lehn, J. M.; Pine, S. H.; Watanabe, E.; Willard, A. K. *J. Am. Chem. Soc.* **1977**, *99*, 6766.

(2) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441.

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Table I. Equilibrium Constants^a for the O-BISTREN-Cobalt(II)-Dioxygen System

equilibrium quotient ^b	log K	equilibrium quotient ^b	log K
[HL ⁺]/[L][H ⁺]	9.89	[CoL ²⁺]/[Co ²⁺][L]	11.20
[H ₂ L ²⁺]/[HL ⁺][H ⁺]	9.23	[Co ₂ L ⁴⁺]/[Co ²⁺] ² [L]	16.80
[H ₃ L ³⁺]/[H ₂ L ²⁺][H ⁺]	8.29	[CoLOH ⁺][H ⁺]/[CoL ²⁺]	-9.13
[H ₄ L ⁴⁺]/[H ₃ L ³⁺][H ⁺]	7.65	[Co ₂ LOH ³⁺][H ⁺]/[Co ₂ L ⁴⁺]	-7.20
[H ₅ L ⁵⁺]/[H ₄ L ⁴⁺][H ⁺]	6.64	[Co ₂ L(OH)O ₂ ³⁺]/[Co ₂ L(OH) ²⁺][H ⁺]	1.20
[H ₆ L ⁶⁺]/[H ₅ L ⁵⁺][H ⁺]	6.01	[Co ₂ LOH ³⁺] ₂ Po ₂ /[Co ₂ L(OH) ²⁺] ² [H ⁺]	-8.80

^a *t* = 25.00 °C; *μ* = 0.100 M (KCl). ^b L = O-BISTREN.

dioxygen complex formed from **2** and **3** is the dibridged *μ*-hydroxo-*μ*-peroxy type, Co₂(OH)(O₂)(O-BISTREN)³⁺ (**4**), having an unexpectedly low oxygenation constant (*K*_{O₂} = [**4**]/[**2**]*P*_{O₂} = 10^{1.2} atm⁻¹), compared to those of cobalt complexes of comparable polyamines such as the tetramine TREN itself.⁴ The distribution curves in Figure 1 show that dioxygen complex **4** is nearly completely formed in aqueous solution, with a maximum concentration of approximately 90% at p[H] 8. At higher p[H] it dissociates and is completely replaced by the dihydroxo-bridged binuclear complex, **3**. The exceptionally low stability of **4** was rationalized as the result of steric crowding of the dioxygen in the cryptate cavity.

During the past several years there has been much interest in dioxygen carriers for the chemical separation of oxygen from air and other gaseous mixtures, and several metal chelate systems have been developed for that purpose.⁵ It has been noted⁶ that

(4) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155.