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Thermochemistry of Zirconium and Niobium Organometallic Compounds

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Abstract: Reaction–solution calorimetry results for a number of bis(cyclopentadienyl)zirconium(IV) and -niobium(IV) complexes were used to discuss the energetics of Zr–H, Zr–C, Zr–O, Zr–I, Nb–C, Nb–I, and Nb–S bonds. From the enthalpies of reaction of Schwartz's reagent, $[Zr(Cp)_2(Cl)H]_n$, with HCl, I_2, and alcohols it was concluded that the zirconium–hydrogen bond does not seem to be significantly influenced by the polymeric nature of the substance. The reactions of the same complex with 1-hexene and cyclohexene, on the other hand, gave information on the thermochemistry of alkene insertion into the Zr–H bond and showed that in contrast to the expected order of reactivities (cyclic olefins being less reactive than linear 1-alkenes), the insertion of cyclohexene into the Zr–H bond of Schwartz's reagent is more exothermic than in the case of 1-hexene, although the $Zr–C_6H_{13}$ and $Zr–C_6H_{11}$ bond dissociation enthalpies are comparable. These results were also used to discuss the energetics of non-terminal olefins into the Zr–H bond of Schwartz's reagent. The enthalpies of formation of several complexes of the type $Zr(Cp)_2(Cl)OR$ (R = Me, Et, Pr, i-Pr, Bu, t-Bu, Oc, and Ph) were derived from the enthalpies of reaction of Schwartz's reagent with the corresponding alcohols, and the plot of $\Delta H_f^\circ[Zr(Cp)_2(Cl)OR,c]$ against the enthalpies of formation of liquid ROH yielded an excellent unit-slope linear correlation. The derived Zr–OR bond dissociation enthalpies are rather constant for R = alkyl and are close to the average Zr–O bond dissociation enthalpy in the dimer $[Zr(Cp)_2Cl]_2O$. The reaction with HCl in two different solvents (toluene and isopropyl ether) was used to obtain the enthalpy of formation of this complex and also to demonstrate that identification of gas phase and solution bond enthalpy data or even the identification of solution bond enthalpy data in different solvents should be made with great caution, particularly when the solvation of one of the reactants is highly exothermic. The thermochemical study of the complexes $Zr(Cp)_2Me_2$ and $Zr(Cp)_2C_4Ph_4$, through their reactions with HCl in toluene, allowed the comparison between the energetics of $Zr–C(sp^3)$ and $Zr–C(sp^2)$ bonds. This comparison indicated a strain-free metallacycle in the tetraphenylbutadiene complex. The bond enthalpy data for $M(Cp)_2Me_2$ and $M(Cp)_2Cl_2$ (M = Zr, Nb) obtained in this work support the conclusion based on Pauling's electronegativity equation that the difference $\bar{D}(M–Cl) - \bar{D}(M–Me)$ decreases with the increasing electronegativity of M. For M = Nb the enthalpies of reaction of the dimethyl complex with HCl and I_2 were both measured, yielding the Nb–I mean bond dissociation enthalpy. Finally, the calorimetric study of the reactions of $Nb(Cp)_2(SPh)_2$ and $Nb(Cp)_2(SC_6H_4Cl\text{-}p)_2$ with HCl in isopropyl ether afforded the enthalpies of formation of these complexes and their Nb–S bond dissociation enthalpies. These latter values are similar, indicating that the exo or endo conformations of the thiolate ligands and the possible existence of S–S bonding in $Nb(Cp)_2(SPh)_2$ are not reflected in the energetics of Nb–S bonds.

Introduction

Most of the available thermochemical information on zirconium organometallic compounds is contained in a recent publication by Schock and Marks.[2] These authors have studied the energetics of a variety of zirconium–ligand bonds in bis(pentamethylcyclopentadienyl) systems, $Zr(Cp^*)_2LL'$, and have also derived the zirconium–methyl mean bond dissociation enthalpy in the bis(cyclopentadienyl) complex $Zr(Cp)_2Me_2$. Some of these results as well as earlier data for zirconium complexes have been reviewed elsewhere.[3]

Despite this newly acquired knowledge on zirconium–ligand bonding energetics, no thermochemical information on Schwartz's reagent, $Zr(Cp)_2(Cl)H$, is available. This important hydrozirconation agent has a polymeric structure, $[Zr(Cp)_2(Cl)H]_n$,[4] thus lending some ambiguity to the interpretation of experimental enthalpy of reaction data in terms of zirconium–ligand bond dissociation enthalpies. In other words, it is relevant to know whether the monomer–monomer interactions have a significant contribution to the hydrozirconation energetics. While this question is difficult to quantify accurately at the present stage, a satisfactory answer can be obtained by comparing the thermochemistry of Schwartz's reagent with the results obtained by Schock and Marks for the bis(pentamethylcyclopentadienyl) systems, which are known to be monomeric.[4] This is one of the goals of the present paper, which also contains thermochemical data for several other bis(cyclopentadienyl)zirconium molecules, including the metallacycle $Zr(Cp)_2C_4Ph_4$, the dimer $[Zr(Cp)_2Cl]_2O$, the insertion products of 1-hexene and cyclohexene into the Zr–H bond of Schwartz's reagent, and a series of alkoxides $Zr(Cp)_2(OR)Cl$.

Another set of results described in this paper concerns the thermochemistry of several bis(cyclopentadienyl)niobium complexes. Thermochemical data for group 5 organometallic compounds are very scarce.[3,5] No information on the energetics of the niobium–carbon σ-bond in a coordinatively saturated complex has been reported,[6] and this fact alone motivated the thermochemical study of $Nb(Cp)_2Me_2$ through its reactions with hydrochloric acid and with iodine. The remaining niobium complexes addressed in the present studies are $Nb(Cp)_2(SPh)_2$ and $Nb(Cp)_2(SC_6H_4Cl\text{-}p)_2$. The main interest in this case was to assess if the exo conformation of the former complex and the

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endo conformation of the latter[7] would have a significant effect on the energetics of Nb–S bonds.

Experimental Section

All operations were carried out under vacuum or in an inert atmosphere, argon U or nitrogen U, with use of standard Schlenk techniques.[8] All glassware used to handle the complexes was thoroughly dried.

Materials. Most of the solvents were predried, dried, and distilled before use and kept in an inert atmosphere as recommended by Perrin et al.[9] Ethyl and isopropyl ethers were predried over sodium/benzophenone, treated with $LiAlH_4$ to remove peroxides, and distilled. Hexane was predried over CaH_2, dried by refluxing over sodium wire, distilled under nitrogen, and kept over 4-Å activated molecular sieves. Pentane and toluene were dried over sodium wire and distilled from sodium/potassium alloy. Tetrahydrofuran was predried over sodium wire and dried by refluxing over sodium and benzophenone. Acetonitrile was predried and distilled over P_2O_5. Toluene-d_8 and benzene-d_6 were predried over sodium, dried over sodium/potassium, distilled under argon into Schlenk tubes, and kept in a glovebox. $CDCl_3$ and CD_2Cl_2 were predried over 4-Å molecular sieves and distilled under argon into storage flasks. Dicyclopentadiene (Riedel-de Haën, 95%) was cracked to obtain the monomer. Lithium metal (Merck, 99%) was washed several times with diethyl ether to remove paraffin oil. Zirconium tetrachloride (Merck, 98%) was used as received. Aniline (Merck, >99%) was predried over CaH_2 and Na_2SO_4 and distilled at reduced pressure. Methyl iodide (Merck) was distilled at atmospheric pressure. Diphenylacetylene (Aldrich, 99%) was dried at reduced pressure (0.1 Torr) for 2 h, at 303 K. Thiophenol and 4-chlorothiophenol were purchased from Aldrich and used without further purification. Methanol (Merck, >99.8%), ethanol (Merck, >99.8%), propanol (Merck, >99.5%), 2-propanol (Pronalab, >99.7%), butanol (Panreac, >99%), *tert*-butyl alcohol (Panreac, >99%), and octanol (Merck) were predried over small slices of sodium and distilled. Phenol (Riedel-de Haën, 99.5%) was sublimed before use. Cyclohexene (Merck, >99.5%) and 1-hexene (Janssen, 99%) were dried over sodium/benzophenone and distilled under argon into storage Schlenks. Methyllithium (Merck, 1.4 M solution in diethyl ether) was titrated before use by Gilman and Cartledge's method.[10] Magnesium turnings (BDH), mercury dichloride (Merck, 99.5%), 1,2-dibromoethane (Merck), niobium pentachloride (Merck), and aluminum powder (BDH) were used without further purification. Zirconocene chloride hydride (Aldrich) was used as received and kept under argon in the dark.

Physical Measurements. C, H, N elemental analyses were made with Perkin-Elmer Elemental Analyzers Models 240 B and 240 C or Carlo Erba Model 1106. Infrared spectra were obtained with either a Perkin-Elmer 457 or Perkin-Elmer 683, calibrated with polystyrene film. Band intensity are referred to as following: vs, very strong; s, strong; m, medium; w, weak. Nuclear magnetic resonance spectra were obtained with a J.E.O.L.-JNM-100, a Bruker-CPX-300, or a Bruker-SY80-FT spectrometer and reported downfield in parts per million versus tetramethylsilane ($SiMe_4$) at 0.0 ppm or reported in parts per million versus deuterated solvents. Paramagnetic electron resonance spectra of niobium(IV) complexes were recorded on a Bruker ER 200-tt spectrometer equipped with a helium flux criostat ESR-9 (Oxford Instruments) and connected to a Nicolet 1180 computer. Gas–liquid chromatography was performed in a Perkin-Elmer Sigma-3B apparatus, equipped with a flame ionization detector and a 2 m length, 3 mm diameter column packed with 10% SE 30 from Altech Associates, supported on Gaz Chrom Q (80–100 mesh), and connected to a Shimadzu C-R1B integrator/recorder. Melting points of organic compounds were measured on a Reichert apparatus.

Syntheses. $Zr(Cp)_2Cl_2$ was prepared as described in the literature, with minor modifications,[11–13] and purified by sublimation. IR (KBr, cm^{-1}) 3100 m, 1865 w, 1760 w, 1660–1640 w, 1435 s, 1360 m, 1115 m, 1065 w, 1020–1015 vs, 935–920 w, 860–840 vs, 815 vs. Anal. Calcd for $ZrC_{10}H_{10}Cl_2$: C, 41.1; H, 3.4. Found: C, 41.0; H, 3.5.

$Zr(Cp)_2Me_2$ was prepared as reported elsewhere.[14,15] IR (KBr, cm^{-1}) 3060–3040 m, 2890 m, 2840 m, 2760 w, 1790 w, 1690 w, 1620–1600 w, 1425 s, 1405 m, 1350 w, 1255 w, 1120 m, 1060 m, 1010 vs, 905 w, 850 m, 815–800 vs, 770–730 vs, 620–610 m. Anal. Calcd for $ZrC_{12}H_{16}$: C, 57.3; H, 6.4. Found: C, 57.2; H, 6.5.

$Zr(Cp)_2C_4Ph_4$ was synthesized as described by Thanedar and Farona.[16] IR (KBr, cm^{-1}) 3070–3020 m, 1590 m, 1485–1475 m, 1440 m, 1360 m, 1260–1240 w, 1155 w, 1075 m, 1015 vs, 950 m, 910 m, 840–850 vs, 820 m, 695 m. Anal. Calcd for $ZrC_{38}H_{30}$: C, 79.0; H, 5.2. Found: C, 78.7; H, 5.3. The proton NMR spectrum in benzene-d_6 shows signals at δ = 6.01 (Cp, 10H) and δ = 6.65–7.04 (C_6H_5, 20H), ratio observed 2.1:1.0.

The complex $[Zr(Cp)_2Cl]_2O$ was first prepared by Samuel and Setton in 1962, but its empirical formula was established as $C_{10}H_9ZrCl$.[17] The correct structural formula was found one year later by Brainina et al.[18] and a preliminary X-ray structure was reported by Reid et al.[19] The sample used in the present studies was prepared by the method of Samuel and Setton. IR (KBr, cm^{-1}) 3100 m, 1815 w, 1730 w, 1640 w, 1440 s, 1360 m, 1260 w, 1065 w, 1020–1015 vs, 950 w, 850–840–810 vs, 795 m, 770–740 vs. Anal. Calcd for $Zr_2C_{20}H_{20}Cl_2O$: C, 45.3; H, 3.8. Found: C, 45.1; H, 3.9.

$Zr(Cp)_2(Cl)I$ was prepared by adding bis(cyclopentadienyl)zirconium chlorohydride (1.3 g; 5.0 mmol) to a stoichiometric quantity of iodine dissolved in toluene. The reaction was carried out in the dark, at room temperature, for 20 min. The solution was taken to dryness and the unreacted iodine removed by washing the residue several times with cold ethyl ether and hexane until a microcrystalline free powder of $Zr(Cp)_2(Cl)I$ was obtained. IR (KBr, cm^{-1}) 3090 m, 1730 w, 1630 w, 1435 m, 1360 w, 1435 m, 1360 w, 1070 w, 1015 s, 910 m, 820–800 vs, 720 vs, 605 m, 595 m. Anal. Calcd for $ZrC_{10}H_{10}ClI$: C, 31.3; H, 2.6. Found: C, 31.5; H, 2.7.

The complexes $Zr(Cp)_2(Cl)OR$ (R = Me, Et, Pr, and *i*-Pr) were synthesized by addition of an excess of the corresponding alcohol to a stirred suspension of $Zr(Cp)_2(Cl)H$ in toluene. The time of stirring varied from 20 min for methanol to 40 min in the case of 2-propanol and the excess varied between 1.5 and 4.0, respectively. A disappearance of the initial suspension of $Zr(Cp)_2(Cl)H$ was observed in each case and the reaction mixture was stirred for ca. 5 min after it became clear. The off-white products were obtained by removal of the solvent and the solids were washed several times with pentane. The complexes were sublimed under vacuum (10^{-3} Torr) at 40 °C, yielding pure white solids. Anal. Calcd for $ZrC_{11}H_{13}OCl$: C, 45.9; H, 4.5. Found: C, 45.6; H, 4.4. Anal. Calcd for $ZrC_{12}H_{15}OCl$: C, 47.7; H, 5.0. Found: C, 47.6; H, 5.1. Anal. Calcd for $ZrC_{13}H_{17}OCl$: C, 49.4; H, 5.4. Found: C, 49.1; H, 5.3. Anal. Calcd for $ZrC_{13}H_{17}OCl$ (iso): C, 49.4; H, 5.4. Found: C, 48.6; H, 5.1.

$Nb(Cp)_2Cl_2$ was prepared as described by Manzer.[20] Sublimation in vacuum (10^{-4} Torr/175 °C) gave $Nb(Cp)_2Cl_2$ as a brown crystalline solid. The IR spectrum (KBr, cm^{-1}) is similar to the one published by Siegert and Liefde Meijer:[21] 3100 m, 1435 m, 1360 w, 1260 w, 1120 w, 1070 w, 1020 s, 870 m, 820 vs. Anal. Calcd for $NbC_{10}H_{10}Cl_2$: C, 40.9; H, 3.4. Found: C, 40.6; H, 3.7.

The synthesis of $Nb(Cp)_2Me_2$ was also made according to the one reported by Manzer.[20] The product was purified by sublimation under vacuum (10^{-4} Torr) at 75 °C. Anal. Calcd for $NbC_{12}H_{16}$: C, 56.9; H, 6.4. Found: C, 56.6; H, 6.2.

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$Nb(Cp)_2(SPh)_2$ was prepared by the method of Douglas and Green.[22] IR (KBr, cm^{-1}) 3400 m, 3040 m, 2960 m, 1570 m, 1470 m, 1430 m, 1260 m, 1080 w, 820 s, 740 s, 690 s. Anal. Calcd for $NbC_{22}H_{20}S_2$: C, 59.9; H, 4.6. Found: C, 60.3; H, 4.8.

The complex $Nb(Cp)_2(SC_6H_4Cl\text{-}p)_2$ was synthesized by the method of Giddings for $Ti(Cp)_2(SPh)_2$.[23] IR (KBr, cm^{-1}) 3090 m, 1565 m, 1460 s, 1430 m, 1380 m, 1170 w, 1080 s, 1060 w, 1010 s, 920 w, 810 s, 530 m, 480 m. Anal. Calcd for $NbC_{22}H_{18}Cl_2S_2$: C, 51.8; H, 3.6. Found: C, 52.0; H, 3.6.

$Nb(Cp)_2I_2$ was prepared by addition of a toluene solution of I_2 to a suspension of $Nb(Cp)_2Me_2$, also in toluene. The mixture was stirred for 45 min and the solvent removed to dryness, at room temperature. The pasty solid was extracted with dichloromethane (3 × 10 mL) and the solvent volume was reduced until some of the red-brown microcrystalline product had precipitated upon cooling. The solid was further dried under vacuum for 2 h at 35 °C. Anal. Calcd for $NbC_{10}H_{10}I_2$: C, 25.2; H, 2.1. Found: C, 25.0; H, 2.1. The IR spectrum is similar to the one reported by Treichel and Werber with Nujol mulls.[24] The absence of a strong absorption band Nb–O–Nb at ≈680 cm^{-1} in the spectrum indicated no oxidation of $Nb(Cp)_2I_2$ to $[Nb(Cp)_2I]_2O$.[25] The EPR spectrum at 77 K showed a signal ($\langle g\rangle = 2.03$) indicating the presence of an unpaired electron.

The *cis,cis*-1,2,3,4-tetraphenylbuta-1,3-diene, $C_4H_2Ph_4$, was synthesized as described by Smith and Hoehn.[26] The melting point (184–185 °C) compared with published values.[27,28] Anal. Calcd for $C_{28}H_{22}$: C, 93.8; H, 6.2. Found: C, 93.1; H, 6.4.

Finally, the compound aniline hydrochloride, $PhNH_3Cl$, was prepared by following the method described in the literature.[29]

Calorimetry. The reaction–solution calorimeter previously described[12,30] was used to measure the reaction and solution enthalpies. When HCl–isopropyl ether and HCl–toluene solutions were used they were transferred, under inert atmosphere, from a Schlenk type burette to the argon-flushed calorimetric vessel. The glass bulbs containing the solid samples were sealed under argon.[31] The preparation of the hydrochloric acid solutions and the method used to determine the amounts of MeI and CH_4 in the gas phase and/or in solution for the reactions $Nb(Cp)_2Me_2$ with I_2 and $M(Cp)_2Me_2$ (M = Zr and Nb) with HCl were previously described.[32]

Results

Calorimetric measurements on reactions 1–13 were used to derive the standard enthalpies of formation of the complexes.

$$\mathrm{Zr(Cp)_2(Cl)H(c) + (HCl{:}19.18C_7H_8)(soln) \rightarrow Zr(Cp)_2Cl_2(soln) + H_2(g)} \tag{1}$$

$$\mathrm{Zr(Cp)_2(Cl)H(c) + I_2(soln) \rightarrow Zr(Cp)_2(Cl)I(soln) + HI(soln)} \tag{2}$$

$$\mathrm{Zr(Cp)_2(Cl)H(c) + 1\text{-}C_6H_{12}(soln) \rightarrow Zr(Cp)_2(Cl)C_6H_{13}(soln)} \tag{3}$$

$$\mathrm{Zr(Cp)_2(Cl)H(c) + c\text{-}C_6H_{10}(soln) \rightarrow Zr(Cp)_2(Cl)C_6H_{11}(soln)} \tag{4}$$

$$\mathrm{Zr(Cp)_2(Cl)H(c) + ROH(soln) \rightarrow Zr(Cp)_2(Cl)OR(soln) + H_2(g)} \tag{5a–h}$$

R = Me, Et, Pr, *i*-Pr, Bu, *t*-Bu, Oc, and Ph

$$\mathrm{Zr(Cp)_2Me_2(c) + 2(HCl{:}19.18C_7H_8)(soln) \rightarrow Zr(Cp)_2Cl_2(soln) + 0.4CH_4(soln) + 1.6CH_4(g)} \tag{6}$$

$$\mathrm{Zr(Cp)_2C_4Ph_4(c) + 2(HCl{:}19.18C_7H_8)(soln) \rightarrow Zr(Cp)_2Cl_2(soln) + C_4H_2Ph_4(soln)} \tag{7}$$

$$\mathrm{[Zr(Cp)_2Cl]_2O(c) + 2(HCl{:}19.18C_7H_8)(soln) \rightarrow 2Zr(Cp)_2Cl_2(soln) + H_2O(soln)} \tag{8}$$

$$\mathrm{[Zr(Cp)_2Cl]_2O(c) + 2(HCl{:}5.11C_6H_{14}O)(soln) \rightarrow 2Zr(Cp)_2Cl_2(soln) + H_2O(soln)} \tag{9}$$

$$\mathrm{Nb(Cp)_2Me_2(c) + 2(HCl{:}2.15C_6H_{14}O)(soln) \rightarrow Nb(Cp)_2Cl_2(soln) + 0.8CH_4(soln) + 1.2CH_4(g)} \tag{10}$$

$$\mathrm{Nb(Cp)_2Me_2(c) + 2I_2(soln) \rightarrow Nb(Cp)_2I_2(soln) + 2MeI(soln)} \tag{11}$$

$$\mathrm{Nb(Cp)_2(SPh)_2(c) + 2(HCl{:}2.15C_6H_{14}O)(soln) \rightarrow Nb(Cp)_2Cl_2(soln) + 2PhSH(soln)} \tag{12}$$

$$\mathrm{Nb(Cp)_2(SC_6H_4Cl\text{-}\mathit{p})_2(c) + 2(HCl{:}2.15C_6H_{14}O)(soln) \rightarrow Nb(Cp)_2Cl_2(soln) + 2\,\mathit{p}\text{-}ClC_6H_4SH(soln)} \tag{13}$$

The products of these reactions were confirmed by elemental analyses, IR spectroscopy, or EPR spectroscopy. The amounts of MeI and CH_4 present in the gas or liquid phases were evaluated by GC analysis. These experiments indicated that 95.1–98.6% of the methyl iodide formed in reaction 11 (analysis made for two runs) remained in the liquid phase and that the amounts of methane remaining in the HCl–toluene and HCl–isopropyl ether mixtures at the end of reactions 6 and 10 were 20 and 40%, respectively. The iodine–complex molar ratios varied from ca. 1.2 to 3.9 and from 9.0 to 10.2 respectively for reactions 2 and 11. The enthalpy of formation of the 0.48 M HCl–toluene solution, $\Delta H_f^\circ(HCl{:}19.18C_7H_8) = -120.9 \pm 1.7$ kJ mol^{-1}, was determined by measuring the enthalpy of reaction of this mixture with phenylamine (eq 14) and the associated enthalpy of dilution of HCl in toluene. The enthalpy of formation of the 3.02 M HCl–isopropyl ether solution, $\Delta H_f^\circ(HCl{:}2.15C_6H_{14}O) = -143.8 \pm 0.6$ kJ/mol, was determined by the reaction of this mixture with sodium hydroxide, as described elsewhere.[32]

$$\mathrm{(HCl{:}19.18C_7H_8)(soln) + PhNH_2(l) \rightarrow PhNH_3Cl(c) + 19.18C_7H_8(soln)} \tag{14}$$

Auxiliary values used in evaluating the thermochemical results were quoted from the literature and are collected in Table I.[32-39]

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The enthalpies of reactions 1–13 (ΔH_r) are shown in Table II, together with the results of several auxiliary experiments. All measurements were made at 298 K, and the results are averages of at least five runs. The errors presented are twice the standard deviation of the mean in each case. ΔH_{d1} and ΔH_{d2} refer to enthalpies of solution of the products formed in each reaction: ΔH_{d1} represents the enthalpy of solution of the organometallic complex (e.g. $Zr(Cp)_2Cl_2$, $Zr(Cp)_2(Cl)I$, etc.) and ΔH_{d2} represents the enthalpy of solution of the inorganic or organic product (e.g. HI, H_2O, CH_4). When appropriate, ΔH_{d3} stands for the enthalpy of dilution of HCl in the calorimetric solvent and was determined by breaking ampules containing pure solvent in the corresponding mixture. Finally, also when appropriate, ΔH_{d4} represents the enthalpy of solution of the non-organometallic reactant (I_2, 1-C_6H_{12}, c-C_6H_{10}, or alcohol) in the calorimetric solvent.

The standard enthalpies of formation of the crystalline complexes were calculated from equations given below and from data in Tables I and II, and collected in Table III. These values were then used to estimate metal–ligand bond dissociation enthalpies or mean bond dissociation enthalpies. In most cases these bond enthalpy data were derived from enthalpies of reactions similar to reactions 15 or 17 under the assumption that the enthalpies of sublimation of the complexes are similar. This assumption will be analyzed in the discussion section.

$$M(Cp)_2L_2(c) + 2X(g) \rightarrow M(Cp)_2X_2(c) + 2L(g) \quad (15)$$

$$\Delta H_r(15) = 2\bar{D}(M\text{–}L) - 2\bar{D}(M\text{–}X) \quad (16)$$

$$M(Cp)_2(Cl)L(c) + X(g) \rightarrow M(Cp)_2(Cl)X(c) + L(g) \quad (17)$$

$$\Delta H_r(17) = D(M\text{–}L) - D(M\text{–}X) \quad (18)$$

$Zr(Cp)_2(Cl)H$. The enthalpy of formation of Schwartz's reagent, −314.3 ± 3.6 kJ/mol, was calculated by 19, where ΔH_{d1}

$$\Delta H_f^\circ[Zr(Cp)_2(Cl)H,c] = -\Delta H_r(1) + \Delta H_{d1} + 19.18\Delta H_{d3} + \Delta H_f^\circ[Zr(Cp)_2Cl_2,c] - \Delta H_f^\circ(HCl{:}19.18C_7H_8) \quad (19)$$

and ΔH_{d3} have the meaning indicated above and $\Delta H_r(1)$ is the enthalpy of reaction 1. The calculated enthalpy of formation reflects, of course, the intermonomeric interactions of the compound $[Zr(Cp)_2(Cl)H]_n$, but it will be considered, as a working hypothesis, that the energetics of these interactions are negligible. It is possible, on this basis, to estimate the difference between Zr–Cl bond dissociation enthalpy in $Zr(Cp)_2Cl_2$ and Zr–H bond dissociation enthalpy in $Zr(Cp)_2(Cl)H$ by using eq 18 (L = H, X = Cl): $D(Zr\text{–}H) - D(Zr\text{–}Cl) = -127$ kJ/mol. Given the above assumptions, the uncertainty interval is probably no less than 20 kJ/mol. An "absolute" value of $D(Zr\text{–}H) = 364$ kJ/mol can be derived by considering that $D(Zr\text{–}Cl)$ in $Zr(Cp)_2Cl_2$ is similar to the mean bond dissociation enthalpy $\bar{D}(Zr\text{–}Cl) = 491$ kJ/mol in $ZrCl_4$.[40]

$Zr(Cp)_2(Cl)I$. The measured enthalpy of reaction 2, $\Delta H_r(2)$, and the remaining data for this system in Table II were used together with eq 20 to calculate $\Delta H_f^\circ[Zr(Cp)_2(Cl)I,c] = -418.9 \pm 4.3$ kJ/mol. This value yields the difference $D(Zr\text{–}I) - D(Zr\text{–}Cl) = -134$ kJ/mol (eq 18, L = I, X = Cl). Finally, the anchor used above, $\bar{D}(Zr\text{–}Cl) = 491$ kJ/mol, leads to $D(Zr\text{–}I) = 357$ kJ/mol.

$$\Delta H_f^\circ[Zr(Cp)_2(Cl)I,c] = \Delta H_r(2) - \Delta H_{d1} - \Delta H_{d2} + \Delta H_{d4} + \Delta H_f^\circ[Zr(Cp)_2(Cl)H,c] - \Delta H_f^\circ(HI,g) \quad (20)$$

$Zr(Cp)_2(Cl)C_6H_{13}$. The energetics of insertion of 1-hexene into the Zr–H bond in $Zr(Cp)_2(Cl)H$ is assessed by the enthalpy of reaction 3, $\Delta H_r(3)$. We did not isolate the complex $Zr(Cp)_2(Cl)C_6H_{13}$ so that its enthalpy of solution in toluene could be measured. It is expected, however, that this value is comparable to other enthalpies of solution shown in Table II. An estimate of ΔH_{d1} of 13 ± 4 kJ/mol, together with the enthalpy of solution of 1-hexene (ΔH_{d4}, Table II) and data in Tables I and III, leads to $\Delta H_f^\circ[Zr(Cp)_2(Cl)C_6H_{13},c] = -452.5 \pm 5.7$ kJ/mol, according to eq 21. This value was used to calculate $D(Zr\text{–}C_6H_{13}) = 317$ kJ/mol (eq 18, L = C_6H_{13}, X = Cl), by taking $D(Zr\text{–}Cl) = 491$ kJ/mol.

$$\Delta H_f^\circ[Zr(Cp)_2(Cl)C_6H_{13},c] = \Delta H_r(3) - \Delta H_{d1} + \Delta H_{d4} + \Delta H_f^\circ[Zr(Cp)_2(Cl)H,c] + \Delta H_f^\circ(C_6H_{12},l) \quad (21)$$

$Zr(Cp)_2(Cl)C_6H_{11}$. The calculation of the enthalpy of formation of the cyclohexyl complex (reaction 4), $\Delta H_f^\circ[Zr(Cp)_2(Cl)C_6H_{11},c] = -428.9 \pm 5.5$ kJ/mol, and the bond dissociation enthalpy, $D(Zr\text{–}C_6H_{11}) = 319$ kJ/mol, were as described for $Zr(Cp)_2(Cl)C_6H_{13}$.

$Zr(Cp)_2(Cl)OR$. The enthalpies of formation of the alkoxide complexes shown in Table III were calculated from eq 22 and data from Tables I and II. Equation 18 (L = OR, X = Cl) leads to the following $D(Zr\text{–}OR)$ values (kJ/mol): 484 (Me), 483 (Et), 484 (Pr), 489 (*i*-Pr), 486 (Bu), 481 (*t*-Bu), 505 (Oc), and 440 (Ph). The anchor was, as usual, $D(Zr\text{–}Cl) = 491$ kJ/mol.

$$\Delta H_f^\circ[Zr(Cp)_2(Cl)OR,c] = \Delta H_r(5) - \Delta H_{d1} + \Delta H_{d4} + \Delta H_f^\circ[Zr(Cp)_2(Cl)H,c] + \Delta H_f^\circ(ROH,c/1) \quad (22)$$

$Zr(Cp)_2Me_2$. The enthalpy of formation of the dimethyl complex (reaction 6), $\Delta H_f^\circ[Zr(Cp)_2Me_2,c] = -62.8 \pm 4.7$ kJ/mol, was derived from eq 23 and data from Tables I and II. As mentioned above, only ca. 20% of the methane remained in solution, so that a factor of 2 × 0.2 affects the respective solution enthalpy, ΔH_{d2}. The mean bond dissociation enthalpy $\bar{D}(Zr\text{–}Me)$ was derived as 279 kJ/mol from eq 16 by assuming that $\bar{D}(Zr\text{–}Cl) = 491$ kJ/mol.

$$\Delta H_f^\circ[Zr(Cp)_2Me_2,c] = -\Delta H_r(6) + \Delta H_{d1} + 0.4\Delta H_{d2} + 38.36\Delta H_{d3} + \Delta H_f^\circ[Zr(Cp)_2Cl_2,c] + 2\Delta H_f^\circ(CH_4,g) - 2\Delta H_f^\circ(HCl{:}19.18C_7H_8) \quad (23)$$

$Zr(Cp)_2C_4Ph_4$. Equation 24 and data from Tables I and II were used to calculate the enthalpy of formation of this complex, $\Delta H_f^\circ[Zr(Cp)_2C_4Ph_4,c] = 411.6 \pm 6.1$ kJ/mol. It is worth pointing out that the enthalpy of solution of $C_4Ph_4H_2$ (ΔH_{d2} for reaction 7, Table II) was measured in the calorimetric mixture containing stoichiometric amounts of $Zr(Cp)_2Cl_2$ and not in the pure solvent as in the previous systems.

$$\Delta H_f^\circ[Zr(Cp)_2C_4Ph_4,c] = -\Delta H_r(7) + \Delta H_{d1} + \Delta H_{d2} + 38.36\Delta H_{d3} + \Delta H_f^\circ[Zr(Cp)_2Cl_2,c] + \Delta H_f^\circ(C_4Ph_4H_2,c) - 2\Delta H_f^\circ(HCl{:}19.18C_7H_8) \quad (24)$$

The enthalpy of formation of tetraphenylbutadiene quoted from the literature[33] was originally claimed to refer to the *trans,trans* isomer.[41] However, the melting point reported in this early work, 183.6 °C, is substantially different from the true melting point

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of that isomer (148–149 °C)[42] and close to the value observed for the *cis,cis* isomer, 185–186 °C.[42] In the case of reaction 7, the tetraphenylbutadiene moiety retains the same configuration as in the zirconium complex, i.e. the *cis,cis* isomer is formed.[16,43]

The calculation of the mean Zr–C bond dissociation enthalpy in the metallacycle under the usual assumptions requires the estimate of the enthalpy of formation of the biradical $^{\bullet}CPh(CPh)_2PhC^{\bullet}$ in the gas phase. The value obtained, 1004 kJ/mol,[44] together with data from Tables I and III, leads to the enthalpy of reaction 25 and to $\bar{D}(Zr–C)$ = 397 kJ/mol.

$$Zr(Cp)_2C_4Ph_4(c) + 2Cl(g) \rightarrow Zr(Cp)_2Cl_2(c) + {}^{\bullet}CPh(CPh)_2PhC^{\bullet}(g) \quad (25)$$

$[Zr(Cp)_2Cl]_2O$. Two independent reactions (8 and 9) were used to derive the enthalpy of formation of this dimer. The calculations were made through eq 26 (where n = 19.18 and A = C_7H_8 refer to reaction 8, and n = 5.11 and A = $C_6H_{14}O$ to reaction 9) and data from Tables I and II. The enthalpies of solution of water (ΔH_{d2} for reactions 8 and 9, Table II) were measured in the calorimetric mixture containing stoichiometric amounts of $Zr(Cp)_2Cl_2$.

$$\Delta H_f^\circ\{[Zr(Cp)_2Cl]_2O,c\} = -\Delta H_r + 2\Delta H_{d1} + \Delta H_{d2} + 2n\Delta H_{d3} + 2\Delta H_f^\circ[Zr(Cp)_2Cl_2,c] + \Delta H_f^\circ(H_2O,l) - 2\Delta H_f^\circ(HCl{:}nA) \quad (26)$$

It is observed from the results in Table III that the two values obtained for the enthalpy of formation are in very good agreement. This also indicates that the values derived for the enthalpies of formation of the HCl:toluene and HCl:ether solutions (Table I) are reliable.

The Zr–O mean bond dissociation enthalpy can be calculated as 523 kJ/mol from the enthalpy of reaction 27 by identifying the enthalpies of sublimation of the dimer and $Zr(Cp)_2Cl_2$ and taking D(Zr–Cl) = 491 kJ/mol. This is analyzed in the Discussion section, but it is likely that this assumption leads to an upper limit of $\bar{D}$(Zr–O).

$$[Zr(Cp)_2Cl]_2O(c) + 2Cl(g) \rightarrow 2Zr(Cp)_2Cl_2(c) + O(g) \quad (27)$$

$Nb(Cp)_2Me_2$. As the enthalpy of formation of $Nb(Cp)_2Cl_2$ is not available, only the difference $\Delta H_f^\circ[Nb(Cp)_2Me_2,c] - \Delta H_f^\circ[Nb(Cp)_2Cl_2,c]$ = 361.8 ± 2.6 kJ/mol was derived from eq 28 and data from Tables I and II. About 40% of the methane remained in solution, so that a factor of 2 × 0.4 affects the respective solution enthalpy, ΔH_{d2}.

$$\Delta H_f^\circ[Nb(Cp)_2Me_2,c] - \Delta H_f^\circ[Nb(Cp)_2Cl_2,c] = -\Delta H_r(10) + \Delta H_{d1} + 0.8\Delta H_{d2} + 4.30\Delta H_{d3} + 2\Delta H_f^\circ(CH_4,g) - 2\Delta H_f^\circ(HCl{:}2.15C_6H_{14}O) \quad (28)$$

By considering similar enthalpies of sublimation of $Nb(Cp)_2Me_2$ and $Nb(Cp)_2Cl_2$, $\bar{D}$(Nb–Me) − $\bar{D}$(Nb–Cl) = −155.7 ± 1.4 kJ/mol is obtained from eq 16 (L = Me, X = Cl). In order to derive an absolute value of $\bar{D}$(Nb–Me) an estimate for $\bar{D}$(Nb–Cl) is required. Somewhat arbitrarily we have identified this value with $\bar{D}$(Nb–Cl) in $NbCl_5$, 407.5 kJ/mol,[45] which implies $\bar{D}$(Nb–Me) = 252 kJ/mol.

$Nb(Cp)_2I_2$. The enthalpy of formation of $Nb(Cp)_2Me_2$ relative to $Nb(Cp)_2Cl_2$ was used to calculate $\Delta H_f^\circ[Nb(Cp)_2I_2,c]$ = 144.1 ± 4.6 kJ/mol from eq 29 and data in Tables I and II. The enthalpy of solution of methyl iodide (ΔH_{d2}, reaction 11, Table II) was measured in toluene containing stoichiometric amounts of $Nb(Cp)_2I_2$.

$$\Delta H_f^\circ[Nb(Cp)_2I_2,c] - \Delta H_f^\circ[Nb(Cp)_2Me_2,c] = \Delta H_r(11) - \Delta H_{d1} - 2\Delta H_{d2} + 2\Delta H_{d4} - 2\Delta H_f^\circ(MeI,l) \quad (29)$$

$\bar{D}$(Nb–I) was evaluated as 321 kJ/mol from the enthalpy of reaction 16 (L = I, X = Cl) by taking the above result for $\bar{D}$(Nb–Cl).

$Nb(Cp)_2(SPh)_2$. The enthalpy of reaction 12 and the auxiliary data in Tables I and II allow the calculation of $\Delta H_f^\circ[Nb(Cp)_2(SPh)_2,c]$ = 450.2 ± 2.2 kJ/mol, relative to the unknown enthalpy of formation of the dichloride complex (eq 30). The enthalpy of solution of PhSH (ΔH_{d2}, reaction 12, Table II) was measured in the calorimetric solution containing stoichiometric amounts of $Nb(Cp)_2Cl_2$.

$$\Delta H_f^\circ[Nb(Cp)_2(SPh)_2,c] - \Delta H_f^\circ[Nb(Cp)_2Cl_2,c] = -\Delta H_r(12) + \Delta H_{d1} + 2\Delta H_{d2} + 4.30\Delta H_{d3} + 2\Delta H_f^\circ(PhSH,l) - 2\Delta H_f^\circ(HCl{:}2.15C_6H_{14}O) \quad (30)$$

$\bar{D}$(Nb–SPh) = 294 kJ/mol was finally obtained from eq 16 (L = SPh, X = Cl) and relies on $\bar{D}$(Nb–Cl) = 407.5 kJ/mol.

$Nb(Cp)_2(SC_6H_4Cl\text{-}p)_2$. The method used to calculate $\Delta H_f^\circ[Nb(Cp)_2(SC_6H_4Cl\text{-}p)_2,c] - \Delta H_f^\circ[Nb(Cp)_2Cl_2,c]$ = 369.3 ± 20.1 kJ/mol and $\bar{D}$(Nb–S) = 301 kJ/mol was as described for $Nb(Cp)_2(SPh)_2$. The enthalpy of solution of $p\text{-}ClC_6H_4SH$ (ΔH_{d2}, reaction 13, Table II) was measured in the calorimetric solution containing stoichiometric amounts of $Nb(Cp)_2Cl_2$. The high uncertainty interval that affects the value for the enthalpy of formation results from the conservative error assigned to the estimate of $\Delta H_f^\circ(p\text{-}ClC_6H_4SH,c)$. The enthalpy of formation of the radical $p\text{-}ClC_6H_4S$ (Table I) was calculated by identifying D(S–H) in that thiol with D(PhS–H) = 338 ± 8 kJ/mol.[39]

Discussion

Henry A. Skinner, considered by many the founder of organometallic thermochemistry, once said that thermochemical data are enthalpies of reaction and enthalpies of formation, the rest being speculation. With "the rest" he meant, of course, bond enthalpy data. While this comment does not apply to most gas-phase thermochemical studies involving organometallic fragments, it is still quite true for many studies dealing with coordinatively saturated complexes, where the calculation of bond dissociation enthalpies or mean bond dissociation enthalpies relies on assumptions regarding the enthalpies of sublimation of the complexes and/or estimates of other bond dissociation enthalpies, the so-called anchors.[3] Despite these problems, thermochemists pursue the somewhat speculative approach because, if used with caution, it provides useful insights into the energetics of metal–ligand bonds and also because it affords a simple method to estimate the thermochemistry of reactions that were not subject to experimental study.

The previous remarks apply to the data in the second column of Table IV, which, as referred in the Results section, rely on two

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[44] The estimate requires the value of $\Delta H_f^\circ(C_4Ph_4H_2,g)$. This quantity can be predicted by at least two methods. One involves the estimate of the sublimation enthalpy of the compound as 159 kJ/mol (Chickos, J. S.; Hesse, D. G.; Liebman, J. F. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer: Dordrecht, 1992) which, together with the experimental value for the solid (Table I), leads to $\Delta H_f^\circ(C_4Ph_4H_2,g)$ = 518 kJ/mol. The second method, yielding 490 kJ/mol, consists simply in taking the enthalpy of formation of 1,3-*cis*-butadiene[33] and adding a constant increment due to the replacement of four hydrogen atoms by phenyl groups (4 × 95 kJ/mol: Stein, S. E.; Rukkers, J. M.; Brown, R. L. *NIST Standard Reference Database 25*, Version 1.1, 1991). The former result, 518 kJ/mol, is probably more accurate than the latter and allows the calculation of $\Delta H_f^\circ({}^{\bullet}CPh(CPh)_2PhC^{\bullet},g)$ = 1004 kJ/mol by identifying the first and the second C–H bond dissociation enthalpies in tetraphenylcyclobutadiene with D(C–H) in ethylene, 461 ± 8 kJ/mol[3] (see also: Wu, C. J.; Carter, E. A. *J. Phys. Chem.* **1991**, *95*, 8352). We thank Professor Joel Liebman for comments on these estimates.

[45] Calculated from $\Delta H_f^\circ(NbCl_5,g)$ = −703.3 ± 8.4 kJ/mol.[46]

Table I. Auxiliary Thermochemical Data (kJ/mol)[a]

molecule	$\Delta H_f°$(c/l)	$\Delta H_f°$(g)
$Zr(Cp)_2Cl_2$(c)	−538.1 ± 2.9[b]	−433.1 ± 3.6[b]
CH_4(g)		−74.4 ± 0.4[c]
c-C_6H_{10}(l)	−38.5 ± 0.6[c]	−5.0 ± 0.7[c]
1-C_6H_{12}(l)	−74.2 ± 1.6[c]	−43.5 ± 1.6[c]
cis,cis-$C_4H_2Ph_4$(c)	358.9 ± 3.1[c,d]	
HCl:19.18C_7H_8(soln)	−120.9 ± 1.7[e]	
HCl:2.15$C_6H_{14}O$(soln)	−143.8 ± 0.6[e]	
HCl:5.11$C_6H_{14}O$(soln)	−144.1 ± 0.7[f]	
HCl(g)		−92.307[g]
HI(g)		26.48 ± 0.10[g]
MeI(l)	−12.3 ± 1.5[c]	14.7 ± 1.3[c]
H_2O(l)	−285.830[g]	−241.818[g]
MeOH(l)	−239.1 ± 0.3[c]	−201.5 ± 0.3[c]
EtOH(l)	−277.5 ± 0.4[c]	−235.2 ± 0.4[c]
PrOH(l)	−302.6 ± 0.5[c]	−255.1 ± 0.5[c]
i-PrOH(l)	−318.1 ± 0.5[c]	−272.8 ± 0.5[c]
BuOH(l)	−327.3 ± 0.4[c]	−275.0 ± 0.4[c]
t-BuOH(l)	−359.2 ± 0.8[c]	−312.5 ± 0.8[c]
OcOH(l)	−426.5 ± 0.7[c]	−355.5 ± 0.8[c]
PhOH(c)	−165.1 ± 0.8[c]	−96.4 ± 0.9[c]
PhSH(l)	63.7 ± 0.8[c]	112.4 ± 0.9[c]
p-ClC_6H_4SH(c)	(13 ± 10)	(80 ± 10)
$PhNH_2$(l)	31.3 ± 1.0[c]	87.1 ± 1.0[c]
$PhNH_3Cl$(c)	−178.2 ± 1.6[c]	
H(g)		217.965[g]
O(g)		249.170[g]
Cl(g)		121.679[g]
I(g)		106.838[g]
Me(g)		146.9 ± 0.6[h]
c-C_6H_{11}(g)		58 ± 4[h]
C_6H_{13}(g)		(33 ± 8)[i]
MeO(g)		18 ± 4[h]
EtO(g)		−17 ± 4[h]
PrO(g)		−41 ± 4[h]
i-PrO(g)		−52 ± 4[h]
BuO(g)		−63 ± 4[h]
t-BuO(g)		−91 ± 5[h]
OcO(g)		(−144 ± 4)
PhO(g)		51 ± 8[j]
PhS(g)		233 ± 8[k]
p-ClC_6H_4S(g)		(200 ± 13)

[a] Values in parentheses are estimates. [b] Reference 36. [c] Reference 33. [d] See text. [e] This work. [f] Reference 32. [g] Reference 34. [h] Reference 35. [i] Relies on D(C–H) = 418 kJ/mol. [j] Average value from refs 37 and 38. [k] Reference 39.

assumptions: (1) identical sublimation enthalpies of the complexes involved in reactions 15, 17, 25, and 27; and (2) similar Zr–Cl and Nb–Cl bond dissociation enthalpies to $\bar{D}$(Zr–Cl) in $ZrCl_4$ and $\bar{D}$(Nb–Cl) in $NbCl_5$, respectively. The first assumption may lead to relatively large errors (see below), but we believe that in most of the systems studied the values given in Table IV are valid for the gas phase within ca. 20 kJ/mol. The arbitrariness of the anchors chosen, on the other hand, hinders reliable quantitative comparisons of M–L bond dissociation enthalpies for two different metals.

An alternative procedure to derive bond enthalpy data, avoiding the inconvenience of assumption 1, is to consider the enthalpies of reactions 1–13 with all reactants and products in solution.[2,3] The bond dissociation enthalpies in the third column of Table IV were directly derived from the experimental enthalpies of reaction given in Table II, after subtracting the enthalpies of solution of the reactant complexes. These enthalpies of solution are usually in the range of 10–15 kJ/mol, so that it is fair to accept 15 ± 5 kJ/mol as the value for $Zr(Cp)_2$(Cl)H.

There are several values of Zr–H bond dissociation enthalpies reported by Schock and Marks that can be compared with our solution result in Table IV, 390 ± 5 kJ/mol. For example, D_s(Zr–H) = 372 ± 9 kJ/mol in $Zr(Cp^*)_2$(OPh)H, 357 ± 10 kJ/mol in $Zr(Cp^*)_2(OC_6F_5)$H, and 347 ± 8 kJ/mol in $Zr(Cp^*)_2(OCH_2CF_3)$H.[2,3] (The subscript "s" indicates a solution value.) The fact that these results, which are also anchored in $\bar{D}$(Zr–Cl) = 491.4 kJ/mol, are at least about 20 kJ/mol lower than the value in Table IV could suggest that the intramolecular interactions in $Zr(Cp)_2$(Cl)H are not negligible.[46] This simple comparison may, however, be misleading. The value D_s(Zr–H) = 372 ± 9 kJ/mol in $Zr(Cp^*)_2$(OPh)H, for instance, relies on the enthalpy of reaction 31a in toluene, measured as −86.6 ± 2.9 kJ/mol by Schock and Marks, and on the *mean* zirconium–

$$Zr(Cp^*)_2(OPh)H(soln) + PhOH(soln) \rightarrow Zr(Cp^*)_2(OPh)_2(soln) + H_2(g) \quad (31a)$$

phenoxide bond dissociation enthalpy in $Zr(Cp^*)_2(OPh)_2$, obtained from the enthalpy of reaction between this complex and HCl, yielding $Zr(Cp^*)_2Cl_2$.[2] Early studies from our group indicate that the enthalpy required to cleave the first M–L bond in a system of the type $M(Cp)_2L_2$ is lower than the enthalpy required to break the second bond (generating the $M(Cp)_2$ fragment).[47] In other words, if one uses D(Zr–Cl) = 491.4 kJ/mol to evaluate D(Zr–H) in Schwartz's reagent, a higher value should be used for $\bar{D}$(Zr–Cl) in $Zr(Cp^*)_2Cl_2$, implying upward adjustments of $\bar{D}$(Zr–OPh) in $Zr(Cp^*)_2(OPh)_2$ and D(Zr–H) in $Zr(Cp^*)_2$(OPh)H. We have no way of deciding if the value 491.4 kJ/mol is more appropriate for D(Zr–Cl) than $\bar{D}$(Zr–Cl), but the point here was simply to show that the above conclusion regarding the weight of the intramolecular interactions in the reaction energetics of Schwartz's reagent may be incorrect. This is indeed supported by the direct comparison of the enthalpies of reactions 31b (−72 ± 3 kJ/mol)[2] and 5 h, −80.6 ± 1.2 kJ/mol, which are similar, as could be expected if those intramolecular interactions were small.

$$Zr(Cp^*)_2(OPh)H(c) + PhOH(soln) \rightarrow Zr(Cp^*)_2(OPh)_2(soln) + H_2(g) \quad (31b)$$

The comparison between ΔH_r(31b) and ΔH_r(5h) indicates, therefore, that there is nothing unusual about the energetics of the Zr–H bond in *crystalline* $Zr(Cp)_2$(Cl)H, despite the polymeric structure of this molecule. Another confirmation is provided by the second solution value shown in Table IV, D_s(Zr–I) = 378 ± 5 kJ/mol. The difference D_s(Zr–H) − D_s(Zr–I) = 12.0 ± 5.0 kJ/mol, compares with $\bar{D}$(Zr–H) − $\bar{D}$(Zr–I) = 4.2 ± 1.8 kJ/mol, obtained by Schock and Marks for the complexes $Zr(Cp^*)_2L_2$ (L = H, I).[2,3]

The gas-phase value for D(Zr–I) in Table IV is fairly close to $\bar{D}$(Zr–I) = 348.2 ± 2.1 kJ/mol in ZrI_4. This agreement seems consistent with the choice of $\bar{D}$(Zr–Cl) in $ZrCl_4$ as the anchor. Finally, it also noted that reaction 32 is thermoneutral

$$Zr(Cp)_2Cl_2(c) + Zr(Cp)_2I_2(c) \rightarrow 2Zr(Cp)_2(Cl)I(c) \quad (32)$$

(ΔH_r = 1.8 ± 11.0 kJ/mol), or, in other words, the enthalpy of formation of the chloro–iodide complex is the average of the enthalpies of formation of $Zr(Cp)_2Cl_2$ and $Zr(Cp)_2I_2$. This is not unprecedented: equilibrium studies in THF of reaction 33, by Druce et al., afford $\Delta H_r(33) \cong -4$ kJ/mol.[48]

$$Zr(Cp)_2Cl_2(soln) + Zr(Cp)_2Br_2(soln) \rightarrow 2Zr(Cp)_2(Cl)Br(soln) \quad (33)$$

The general mechanism of insertion of an alkene into a metal–hydrogen bond, reaction 34 (R = H or alkyl), is well established.[49]

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(46) The replacement of Cp by Cp* ligands in these systems has a very small effect on the energetics of metal–ligand bonds. See, for example, refs 2 and 3.

(47) Calhorda, M. J.; Dias, A. R.; Galvão, A. M.; Martinho Simões, J. A. *J. Organomet. Chem.* **1986**, *307*, 167.

(48) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(49) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 52.

Table II. Thermochemical Results (kJ/mol)[a]

reaction[b] no.	$-\Delta H_r$	ΔH_{d1}	ΔH_{d2}	ΔH_{d3}	ΔH_{d4}
1	90.7 ± 1.2	13.55 ± 0.26		−0.070 ± 0.005	
2	120.1 ± 0.5	3.54 ± 0.24	−29.6 ± 2.3[c]		15.92 ± 0.16[c]
3	51.7 ± 1.0	(13 ± 4)			0.74 ± 0.06
4	63.5 ± 0.8	(13 ± 4)			0.41 ± 0.08
5a	66.6 ± 1.0	17.7 ± 1.0			3.13 ± 0.12
5b	71.9 ± 1.1	11.3 ± 0.5			6.95 ± 0.42
5c	70.2 ± 1.2	11.1 ± 1.2			4.33 ± 0.26
5d	69.5 ± 0.8	11.2 ± 0.8			3.67 ± 0.29
5e	68.3 ± 1.0	(11 ± 2)			3.40 ± 0.28
5f	60.5 ± 1.2	(11 ± 2)			4.6 ± 0.9
5g	71.0 ± 0.6	(11 ± 2)			5.40 ± 0.24
5h	80.6 ± 1.2	(13 ± 4)			15.91 ± 0.40
6	373.5 ± 1.0	13.55 ± 0.26	−5.1 ± 1.0[d]	−0.070 ± 0.005	
7	300.5 ± 2.5	13.55 ± 0.26	37.6 ± 1.3	−0.070 ± 0.005	
8	82.4 ± 0.5	13.55 ± 0.26	−14.3 ± 0.3	−0.070 ± 0.005	
9	37.5 ± 0.4	11.2 ± 0.4	−15.0 ± 0.4	−0.13 ± 0.04[e]	
10	216.4 ± 1.2	12.2 ± 0.6	−4 ± 2[e]	−0.55 ± 0.13	
11	289.9 ± 2.2	−14.0 ± 0.7	−0.9 ± 0.2		15.92 ± 0.16[c]
12	26.0 ± 0.6	12.2 ± 0.6	−0.33 ± 0.07	−0.55 ± 0.13	
13	25.1 ± 0.7	12.2 ± 0.6	10.4 ± 0.7	−0.55 ± 0.13	

[a] Values in parentheses are estimates. [b] See text. Reactions 5a–h refer to R = Me, Et, Pr, *i*-Pr, Bu, *t*-Bu, Oc, and Ph, respectively. [c] Reference 30. [d] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. [e] Reference 32.

Table III. Enthalpies of Formation of the Crystalline Complexes

molecule	source[a]	$\Delta H_f°$(c)/(kJ/mol)
$Zr(Cp)_2(Cl)H$	1	−314.3 ± 3.6
$Zr(Cp)_2(Cl)I$	2	−418.9 ± 4.3
$Zr(Cp)_2(Cl)C_6H_{13}$	3	−452.5 ± 5.7
$Zr(Cp)_2(Cl)C_6H_{11}$	4	−428.9 ± 5.5
$Zr(Cp)_2(Cl)OMe$	5a	−634.6 ± 3.9
$Zr(Cp)_2(Cl)OEt$	5b	−668.1 ± 3.8
$Zr(Cp)_2(Cl)OPr$	5c	−693.9 ± 4.0
$Zr(Cp)_2(Cl)OPr$-*i*	5d	−709.4 ± 3.8
$Zr(Cp)_2(Cl)OBu$	5e	−717.5 ± 4.3
$Zr(Cp)_2(Cl)OBu$-*t*	5f	−740.4 ± 4.5
$Zr(Cp)_2(Cl)OOc$	5g	−817.4 ± 4.2
$Zr(Cp)_2(Cl)OPh$	5h	−557.1 ± 5.6
$Zr(Cp)_2Me_2$	6	−62.8 ± 4.7
$Zr(Cp)_2C_4Ph_4$	7	411.6 ± 6.1
$Zr(Cp)_2I_2$		−301.5 ± 6.3[b]
$[Zr(Cp)_2Cl]_2O$	8	−1027.7 ± 6.8
$[Zr(Cp)_2Cl]_2O$	9	−1030.3 ± 6.1
$Nb(Cp)_2Me_2$	10	361.8 ± 2.6[c]
$Nb(Cp)_2I_2$	11	144.1 ± 4.6[c]
$Nb(Cp)_2(SPh)_2$	12	450.2 ± 2.2[c]
$Nb(Cp)_2(SC_6H_4Cl$-*p*$)_2$	13	369.3 ± 20.1[c]

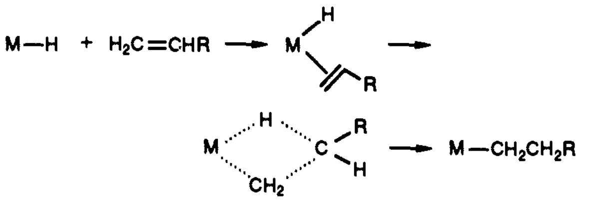
[a] Indicates the reaction which was used to derive the enthalpy of formation. [b] Calculated from data in ref 2 and ΔH_{d2} for reaction 11 (Table II). See text. [c] Value relative to $\Delta H_f°[Nb(Cp)_2Cl_2,c]$.

Table IV. Metal–Ligand Bond Dissociation Enthalpies (kJ/mol)

molecule	D(M–L)[a]	D_s(M–L)[b]
$Zr(Cp)_2(Cl)H$	364 ± 5	390 ± 5
$Zr(Cp)_2(Cl)I$	357 ± 5	378 ± 5
$Zr(Cp)_2(Cl)C_6H_{13}$	317 ± 10	315 ± 11
$Zr(Cp)_2(Cl)C_6H_{11}$	319 ± 7	314 ± 8
$Zr(Cp)_2(Cl)OMe$	484 ± 6	474 ± 8
$Zr(Cp)_2(Cl)OEt$	483 ± 6	477 ± 8
$Zr(Cp)_2(Cl)OPr$	484 ± 6	471 ± 8
$Zr(Cp)_2(Cl)OPr$-*i*	489 ± 6	477 ± 8
$Zr(Cp)_2(Cl)OBu$	486 ± 7	467 ± 8
$Zr(Cp)_2(Cl)OBu$-*t*	481 ± 7	470 ± 8
$Zr(Cp)_2(Cl)OOc$	505 ± 6	470 ± 8
$Zr(Cp)_2(Cl)OPh$	440 ± 10	415 ± 11
$Zr(Cp)_2Me_2$	279 ± 3[c]	290 ± 10[c,d]
$Zr(Cp)_2I_2$	358 ± 4[c]	349 ± 10[c]
$Zr(Cp)_2C_4Ph_4$	397 ± 3[c]	363 ± 3[c,e]
$[Zr(Cp)_2Cl]_2O$	523 ± 4[c]	474 ± 3[c]
$Nb(Cp)_2Me_2$	252 ± 2[c]	297 ± 3[c]
$Nb(Cp)_2I_2$	321 ± 2[c]	363 ± 4[c]
$Nb(Cp)_2(SPh)_2$	294 ± 8[c]	293 ± 5[c]
$Nb(Cp)_2(SC_6H_4Cl$-*p*$)_2$	301 ± 16[c]	293 ± 5[c]

[a] Bond dissociation enthalpies, unless indicated otherwise. Zr–L and Nb–L data are relative to $\bar{D}$(Zr–Cl) = 491.4 kJ/mol and $\bar{D}$(Nb–Cl) = 407.5 kJ/mol, respectively. The assigned uncertainties do not include the errors caused by the assumption of identical sublimation enthalpies (see text). [b] These solution values were directly derived from the experimental reaction enthalpies (eqs 1–13) by assuming that the enthalpies of solution of the reactant complexes are 15 ± 5 kJ/mol (see text). [c] Mean bond dissociation enthalpy. [d] This is the recommended value, but the solution result derived from the enthalpy of reaction 6 is 300 ± 3 kJ/mol. [e] The uncertainty does not include the error in the enthalpy of formation of the C_4Ph_4 radical.

It consists of a coordination of the olefin to the metal, followed by the hydride migration to the olefin, yielding an alkyl complex.



(34)

The process, which involves a coplanar four-centered transition state, requires that the metal center is coordinatively unsaturated.

The net enthalpy balance of reaction 34 for R = H, i.e. ethylene insertion into a metal–hydrogen bond, is obtained as $\Delta H_r(34)$ = D(M–H) − D(M–Et) − D(C_2H_4–H) = D(M–H) − D(M–Et) − 151 kJ/mol.[50] Since $T\Delta S_r(34) \approx -40$ kJ/mol,[51] the reaction will be thermodynamically favorable if D(M–H) − D(M–Et) < 111 kJ/mol. Although the experimental data for D(M–Et) are not abundant, these quantities can be estimated on the basis of available values for D(M–Me), assuming that D(M–Me) − D(M–Et) = D(Me–H) − D(Et–H).[3]

The condition D(M–H) − D(M–Et) < 111 kJ/mol is observed for most complexes, particularly in the case of f-elements and early transition metals, which yield the smallest differences D(M–H) − D(M–Et). This is evidenced by a selection of enthalpy data for reaction 34 given in Table V: $\Delta H_r(34)$ is usually less exothermic for late transition metal complexes. A noteworthy exception is seen in the case of the compounds Rh(tmp)R, for which the difference D(Rh–H) − D(Rh–C) is very low.[52] It is stressed that a comparison of the values in Table V is possible, despite the fact

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(50) Auxiliary data from refs 3 and 33.

(51) The entropy changes of organometallic reactions can be easily estimated by using suitable models involving organic molecules (Martinho Simões, J. A., to be published).

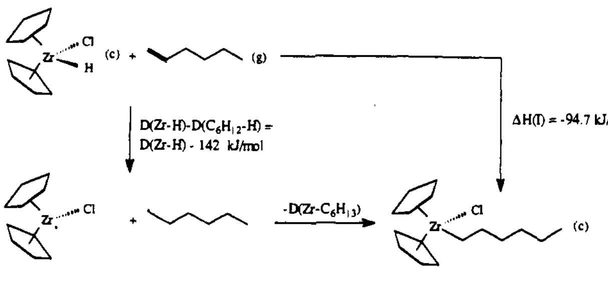
(52) Wayland, B. B. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer: Dordrecht, 1992.

Table V. Enthalpies of Ethylene Insertion into Metal–Hydrogen Bonds: $M-H + C_2H_4 \rightarrow M-C_2H_5$[a]

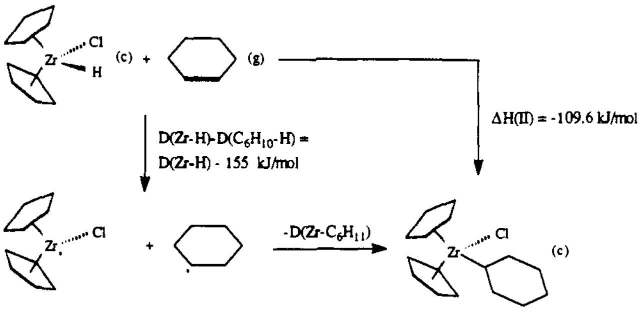
MH	$-\Delta H_r$ (kJ/mol)
$U(Cp^*)_2[OSi(t\text{-}Bu)Me_2]H$	108
$Zr(Cp^*)_2H_2$	78
$Zr(Cp^*)_2(OPh)H$	60
$Hf(Cp)_2H_2$	93
$Mo(Cp)_2H_2$	50
$Mo(Cp)(CO)_3H$	54
$W(Cp)_2H_2$	43
$Mn(CO)_5H$	75
Rh(tmp)H	124[b]
$Ir(Cl)(CO)(PMe_3)_2(I)H$	38
trans-$Pt(PEt_3)_2(Cl)H$	50

[a] Unless indicated otherwise, values were calculated from $D(M-H) - D(M-Et) = -151$ kJ/mol (see text) and bond enthalpies were taken from ref 3. [b] $D(Rh-H)$ and $D(Rh-Me)$ quoted from ref 52. tmp = tetrakis(2,4,6-trimethylphenyl)porphyrin dianion.

Scheme I



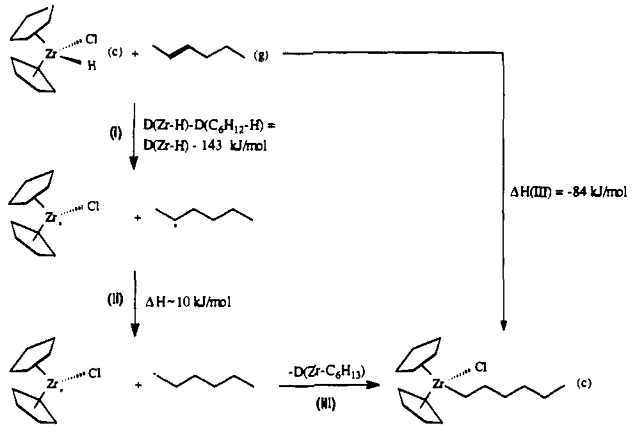
Scheme II



that some of them have been calculated from bond dissociation enthalpies that rely on a given anchor, since the value of the anchor cancels out when the difference $D(M-H) - D(M-Et)$ is derived. We estimate that the average reliability of data in Table V is ca. ±10 kJ/mol. Our results for the enthalpies of reactions 3 and 4 (or the bond dissociation enthalpies $D(Zr-C_6H_{11})$ and $D(Zr-C_6H_{13})$) are in the expected range, in keeping with the conclusion that the energetics of the intermolecular interactions in $Zr(Cp)_2(Cl)H$ are included in the experimental uncertainties of our measurements.

It is noted in Table II that the insertion of the cyclic olefin is more exothermic than in the case of the linear alkene, although the bond dissociation enthalpies $D(Zr-C_6H_{13})$ and $D(Zr-C_6H_{11})$ are comparable (Table IV). The similarity between the bond dissociation enthalpies is somewhat unexpected since one could have anticipated that the difference $D(C_6H_{13}-H) - D(C_6H_{11}-H) = 18 \pm 9$ kJ/mol would approximately hold for $D(Zr-C_6H_{13}) - D(Zr-C_6H_{11})$.[3] Although the bond enthalpy data in Table IV are affected by the sublimation enthalpy assumption, so that uncertainties of ca. 20 kJ/mol for each value are possible, we are now comparing two rather similar systems, $Zr(Cp)_2(Cl)C_6H_{13}$ and $Zr(Cp)_2(Cl)C_6H_{11}$, which must have very close enthalpies of sublimation. A likely cause for the higher exothermicity of reaction 4 is evidenced in Schemes I and II, where $\Delta H(I) = -94.7$ kJ/mol and $\Delta H(II) = -109.6$ kJ/mol are experimental values obtained from data in Tables I and II (or calculated from the enthalpies of formation in Tables I and III) and $D(Zr-H)$ is the bond dissociation enthalpy in $Zr(Cp)_2(Cl)H$. The *second* carbon–hydrogen bond dissociation enthalpy in cyclohexane (or the carbon–hydrogen bond dissociation enthalpy in cyclohexyl radical), Scheme II, can be evaluated as 155 kJ/mol from the enthalpies of formation of gaseous cyclohexane, cyclohexyl, and cyclohexene.[3,33] A similar exercise can be made in the case of Scheme I, yielding 142 kJ/mol for the carbon–hydrogen bond dissociation enthalpy in 1-hexyl. The formation of the carbon–hydrogen bond in Scheme I is therefore some 13 kJ/mol less exothermic than that in Scheme II, in keeping with the overall exothermicities of reactions 3 and 4. It is also interesting to note that the hydrogenation of 1-hexene is more exothermic than the hydrogenation of cyclohexene by 5 kJ/mol.[33] Although, as mentioned above, the C–H bond dissociation enthalpy is lower in hexyl than in cyclohexyl radical, this is more than compensated by the fact that the C–H bond dissociation enthalpy in hexane is larger than in cyclohexane (by 18 kJ/mol).

Scheme III



The energetics of insertion of some nonterminal alkenes into the Zr–H bond can be easily estimated from our data. For example, the enthalpy of the overall reaction in Scheme III[4a] is calculated as $\Delta H(III) = -84$ kJ/mol from the appropriate enthalpies of formation in Table III and $\Delta H_f°[(E)\text{-2-hexene,g}] = -53.9 \pm 1.6$ kJ/mol.[33] The lower exothermicity of insertions of nonterminal olefins is of course due to the migration of the double bond to the terminal position and to the fact that secondary and tertiary alkyl radicals are more stable than their primary isomers. In Scheme III $D(C_6H_{13}-H)$ is as derived above for Scheme I and the rearrangement in step ii is 10 kJ/mol endothermic.

Interestingly, the higher exothermicity of the insertion of cyclohexene relative to 1-hexene into the Zr–H bond is not in keeping with the observed order of reactivities (1-alkenes > cyclic alkenes).[4a] This is probably determined by the energetics of the olefin coordination step (reaction 34), which must be favored in the case of 1-alkenes on steric grounds.

The zirconium–oxygen bond dissociation enthalpies in the alkoxide complexes (Table IV) are rather similar, the average value being 487 kJ/mol. This constancy is not surprising, since the O–H bond dissociation enthalpies in the alcohols vary in a narrow range (430–437 kJ/mol).[35] However, it is also apparent from the data in Table IV that $D(Zr-O)$ show a slight increase with the size of the *n*-alkyl chain. This kind of trend had been noted before for other families of complexes and ligands,[53] but it has to be regarded with some caution after the assumption of identical sublimation enthalpies of the complexes $Zr(Cp)_2(Cl)$-OR. This is probably fairly accurate (ca. ±5–10 kJ/mol) for R = lower alkyl but it may correspond to an underestimate, for example, of the enthalpy of sublimation of the octyl compound,

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(53) Dias, A. R.; Martinho Simões, J. A. *Polyhedron* **1988**, *7*, 1531.

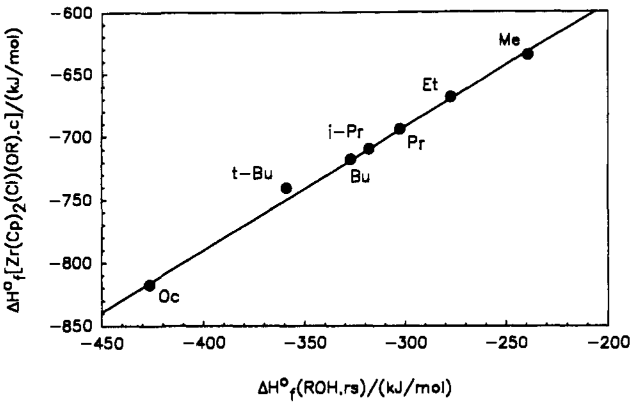

Figure 1. Standard enthalpies of formation of the crystalline zirconium alkoxide complexes plotted against the standard enthalpies of formation of the corresponding liquid alcohols.

implying that the value quoted in Table IV is an upper limit. The same can also happen in the case of $Zr(Cp)_2(Cl)OPh$, for which D(Zr–OPh) in Table IV is only 47 kJ/mol lower than $\langle D$(Zr–OR)$\rangle$, R = alkyl, although D(PhO–H) is 70 kJ/mol lower than $\langle D$(RO–H)$\rangle$.

Schock and Marks have reported the solution values of several Zr–O *mean* bond dissociation enthalpies in $Zr(Cp^*)_2L_2$ complexes, for example $\bar{D}_s(Zr–OCH_2CF_3) = 427 \pm 8$ kJ/mol, $\bar{D}_s(Zr–OC_6F_5) = 387 \pm 10$ kJ/mol, and $\bar{D}_s$(Zr–OPh) = 384 ± 8 kJ/mol.[54] Our solution values for D_s(Zr–OEt) and D_s(Zr–OPh) in Table IV are significantly higher, but this was justified above. The agreement between both experimental sets of data was evidenced by the comparison of the enthalpies of reactions 5h and 31 and can also be verified by the enthalpies of reaction 5b (corrected for the solution of $Zr(Cp)_2(Cl)H$), -86.9 ± 5.1 kJ/mol, and reaction 35, -84.1 ± 0.8 kJ/mol.[54]

$$Zr(Cp^*)_2(OCH_2CF_3)H(soln) + CF_3CH_2OH(soln) \rightarrow Zr(Cp^*)_2(OCH_2CF_3)_2(soln) + H_2(g) \quad (35)$$

The internal consistency of the enthalpies of formation of the crystalline zirconium *n*-alkoxides displayed in Table III can be appreciated in Figure 1, where these data are plotted against the enthalpies of formation of the alcohols in their standard reference states (i.e. their stable physical states at 298 K and 1 bar). The observed linear correlation (eq 36), with a slope close to 1, enables

$$\Delta H_f^\circ[Zr(Cp)_2(Cl)OR,c] = (0.982 \pm 0.014)\Delta H_f^\circ(ROH,rs) - (397.2 \pm 4.7) \quad (36)$$

accurate predictions of enthalpies of formation of other alkoxide compounds. The meaning of this type of trends has been discussed in detail in previous papers, involving many examples of different families of compounds.[55] Here it is only stressed that the linear plot is in keeping with the fact that the Zr–OR and RO–H bond dissociation enthalpies follow parallel trends.[56] Note, however, that the correlation deals with data for crystalline and liquid molecules, so that it also suggests that the enthalpies of sublimation of the complexes and the enthalpies of vaporization of the alcohols have parallel trends. The fact that the value for the *t*-BuO complex lies above the line indicates that this molecule is destabilized relative to *tert*-butyl alcohol. Steric effects have been invoked to explain a similar (but more notorious) observation in the case of *t*-BuONa,[55b] but recent experimental evidence obtained for lithium alkoxides indicates that electronic effects are probably the main cause of the relative destabilizations of the *tert*-butoxide molecules.[55c]

As pointed out in the Results section, the enthalpies of reactions 8 and 9 lead to similar values for the enthalpy of formation of crystalline $[Zr(Cp)_2Cl]_2O$. Although those results are thus thermochemically consistent, when they are used to derive the Zr–O bond dissociation enthalpy in solution, a large discrepancy (45 kJ/mol) is observed (it is assumed that the enthalpies of solution of the complex in the two calorimetric mixtures are similar within 10 kJ/mol). This stems, of course, from the different solvation enthalpies of HCl in the two solvents, which is not accounted for when the solution value of $\bar{D}_s$(Zr–O) is derived, because, as described above, this calculation relies on the gas-phase value of D(H–Cl). Reactions 8 and 9 emphasize, therefore, that not only the identification of gas-phase and solution bond enthalpy data but also the identification of solution data in two different solvents should be made with great caution, particularly when the solvation of one of the reactants or products is highly exothermic, as in the case of HCl. The solution value of $\bar{D}_s$(Zr–O) = 474 kJ/mol quoted in Table IV is based on the enthalpy of reaction 8, for which the enthalpy of formation of HCl is closer to the gas-phase value than in the case of reaction 9.

Despite the previous considerations, it is seen that $\bar{D}_s$(Zr–O) = 474 kJ/mol in the dimer is close to $\langle D_s$(Zr–OR)$\rangle$ = 472 kJ/mol for the zirconium alkoxides, which is perhaps not surprising, given the molecular structure of $[Zr(Cp)_2Cl]_2O$, where the bridging oxygen lies 194 pm from each of the two zirconium atoms.[4a] To our knowledge there are no structural data for the complexes $Zr(Cp)_2(Cl)OR$, but the Zr–O bond length is probably similar to the one in the dimer (in the analogous titanium dimer, and in $Ti(Cp)_2(Cl)OEt$ the Ti–O bond lengths are 183.7 and 185.5 pm, respectively).[57] Regarding the gas-phase value $\bar{D}$(Zr–O) = 523 kJ/mol in Table IV, it was stressed in the Results section that this is most likely an upper limit since it relies on identical sublimation enthalpies of $[Zr(Cp)_2Cl]_2O$ and $Zr(Cp)_2Cl_2$, and it is expected that $\Delta H_s^\circ[Zr(Cp)_2Cl]_2O$ exceeds $\Delta H_s^\circ[Zr(Cp)_2Cl_2]$. In the absence of experimental data, we have preferred to derive the value in Table IV on the basis of the above assumption.

The gas-phase zirconium–methyl mean bond dissociation enthalpy quoted in Table IV is a low limit, since it relies on similar sublimation enthalpies of $Zr(Cp)_2Me_2$ and $Zr(Cp)_2Cl_2$. In this case, however, the true gas-phase value of $\bar{D}$(Zr–Me) = 291 ± 3 kJ/mol can actually be derived since the sublimation enthalpies are available: 81.2 ± 2.1 and 105.1 ± 2.1 kJ/mol, respectively.[36] The solution value, $\bar{D}_s$(Zr–Me) = 300 ± 3 kJ/mol, is about 15 kJ/mol higher than the result reported by Schock and Marks, 285 ± 2 kJ/mol, which relies on the same anchor.[2,3] According to the discussion above on the cancellation of solution and solvation enthalpies, this small disagreement can be due to the fact that our solution value was derived from the enthalpy of reaction 6 (the enthalpy of solution of $Zr(Cp)_2Me_2$ in the calorimetric mixture was estimated as 15 ± 5 kJ/mol), which involves HCl, whereas Schock and Marks' value was calculated from the enthalpy of reaction 37 in toluene, $\Delta H_r(37) = -291.2 \pm 2.5$ kJ/mol.[2] We have used our own sample of the dimethyl

$$Zr(Cp)_2Me_2(soln) + 2I_2(soln) \rightarrow Zr(Cp)_2I_2(soln) + 2MeI(soln) \quad (37)$$

complex to make a single measurement of the enthalpy of the reaction of crystalline $Zr(Cp)_2Me_2$ with a toluene solution of iodine and obtained -291.4 kJ/mol, but in order to be comparable with Schock and Marks' result our value has to be corrected for

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[54] Results from ref 2. Some values have been slightly changed due to the use of different auxiliary data.

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the enthalpy of solution of $Zr(Cp)_2Me_2$ (14.1 kJ/mol),[2] yielding $\Delta H_r(37) = -305.5$ kJ/mol, or $\bar{D}_s(Zr{-}Me) = 278$ kJ/mol.

In summary, by taking all the data referred above, we recommend $\bar{D}_s(Zr{-}Me) = 290 \pm 10$ kJ/mol as the solution mean bond dissociation enthalpy in toluene.

An early static-bomb combustion value for the enthalpy of formation of $Zr(Cp)_2Me_2$, -44.4 ± 2.1 kJ/mol,[36] is not far from the value in Table III, although static-bomb calorimetry is probably not the best option to study the thermochemistry of group 4 organometallic compounds.[58] Table III also includes the enthalpy of formation of $Zr(Cp)_2I_2$, calculated from Schock and Marks' value of $\Delta H_r(37)$ and our result for $\Delta H_f^\circ[Zr(Cp)_2Me_2,c]$.

The solution and gas-phase zirconium–carbon bond dissociation enthalpies for the complex $Zr(Cp)_2C_4Ph_4$ shown in Table IV are at first sight surprisingly high, when compared to the values obtained for the dimethyl compound. We would expect to observe values in the same range for the difference between $\bar{D}$(C–H) in $C_4Ph_4H_2$ and D(Me–H), 22 kJ/mol, and for $\bar{D}_s[Zr{-}C(sp^2)] - \bar{D}_s(Zr{-}Me)$. The fact that we do not (e.g. the latter difference is 73 kJ/mol in solution) may be related to the assumptions regarding solvation enthalpies. A solution value of $D_s(Ir{-}C_2H_3) - \bar{D}_s(Ir{-}Me) = 83$ kJ/mol in the molecules $Ir(Cp^*)(PMe_3)(Br)C_2H_3$ and $Ir(Cp^*)(PMe_3)Me_2$, obtained by Stoutland et al. (by reaction with HCl), is also higher than anticipated.[3,59] Literature values for $D[M{-}C(sp^3)] - D[M{-}C(sp^2)]$ vary in a relatively wide range (ca. 20–80 kJ/mol).[3]

Although we cannot estimate an accurate gas-phase value of the Zr–C(sp^2) mean bond dissociation enthalpy in $Zr(Cp)_2C_4Ph_4$,[44] it is useful to compare the enthalpies of reactions 38–41, where all products and reactants are in their standard states, and which

$$Th(Cp^*)_2Me_2(c) + 2\text{-}C_4H_8(l) \rightarrow Th(Cp^*)_2C_4H_6(c) + 2CH_4(g) \quad (38)$$

$$\Delta H_r(38) = -43.7 \pm 15.3 \text{ kJ/mol}$$

$$Th(Cp^*)_2Me_2(c) + C_2Me_4(l) \rightarrow Th(Cp^*)_2CH_2(CMe)_2CH_2(c) + 2CH_4(g) \quad (39)$$

$$\Delta H_r(39) = -42.4 \pm 16.4 \text{ kJ/mol}$$

$$Zr(Cp^*)_2Me_2(c) + CH_2I(CHEt)_2CH_2I(l) \rightarrow Zr(Cp^*)_2CH_2(CHEt)_2CH_2(c) + 2MeI(l) \quad (40)$$

$$\Delta H_r(40) = -47.7 \pm 12.1 \text{ kJ/mol}$$

$$Zr(Cp)_2Me_2(c) + cis,cis\text{-}C_4Ph_4H_2(c) \rightarrow Zr(Cp)_2C_4Ph_4(c) + 2CH_4(g) \quad (41)$$

$$\Delta H_r(41) = -33.3 \pm 8.3 \text{ kJ/mol}$$

were calculated either from experimental enthalpies of formation or from experimental enthalpies of reaction and solution.[2,60-62] The striking feature of this set of results is their relatively narrow range, indicating that one can use an average value to predict enthalpies of formation of other (possibly strain-free) metallacycle complexes. The feature is even more interesting because reactions 38–41 include both metal–C(sp^3) and metal–C(sp^2) bonds. Finally, it is also noted that the enthalpies of analogous reactions involving metal–ethylene and metal–acetylene complexes (reactions 42 and 43) are not drastically different.[32] The smaller exothermicity of reaction 42, as compared to reactions 38–41, can be attributed to the formation of a strained three-membered metallacycle.

$$Mo(Cp)_2Me_2(c) + C_2H_6(g) \rightarrow Mo(Cp)_2C_2H_4(c) + 2CH_4(g) \quad (42)$$

$$\Delta H_r(42) = -18.3 \pm 9.9 \text{ kJ/mol}$$

$$Mo(Cp)_2Me_2(c) + cis\text{-}C_2Ph_2H_2(l) \rightarrow Mo(Cp)_2C_2Ph_2(c) + 2CH_4(g) \quad (43)$$

$$\Delta H_r(43) = -59.0 \pm 9.8 \text{ kJ/mol}$$

Unfortunately, a detailed interpretation of the relative constancy of the enthalpies of the above reactions in terms of bond dissociation enthalpies would be highly speculative as it would require estimates of the enthalpies of sublimation of the complexes.

The reaction between $Nb(Cp)_2Me_2$ and HCl (reaction 10) is considerably less exothermic (by 157.1 kJ/mol) than the equivalent reaction for the zirconium analogue. This results in part from the enthalpies of formation of the HCl solutions used, but the conclusion holds even after making the approximate correction. In this case a difference of about 111 kJ/mol is obtained. Independently of the anchors chosen in the Results section to derive the gas-phase mean bond dissociation enthalpies shown in Table IV, the difference between the enthalpies of reactions 6 and 10 thus accounts for the fact that $\bar{D}(Zr{-}Cl) - \bar{D}(Zr{-}Me) = 212$ kJ/mol is considerably higher than $\bar{D}(Nb{-}Cl) - \bar{D}(Nb{-}Me) = 156$ kJ/mol. There are a few other bis(cyclopentadienyl) systems that allow further comparison: $\bar{D}(Mo{-}Cl) - \bar{D}(Mo{-}Me) = 147$ kJ/mol, $\bar{D}(W{-}Cl) - \bar{D}(W{-}Me) = 141$ kJ/mol, $\bar{D}(Ti{-}Cl) - \bar{D}(Ti{-}Me) = 152$ kJ/mol.[32,53,63] As pointed out by several authors,[2,55a,64] it is possible to make crude predictions of the above and other metal–ligand bond dissociation enthalpy differences by using, for example, Pauling's electronegativity equation. It has been shown that $\bar{D}(M{-}Cl) - \bar{D}(M{-}Me)$ decreases with the electronegativity of M, i.e. is higher for more electropositive, early transition metals. The values observed for Zr, Nb, and Mo are in qualitative agreement with this trend. On the same basis, however, the difference for titanium looks too small. This issue has been discussed in detail elsewhere[3] and justifies the need of a confirmation of our early studies involving the titanium systems.

With regard to the niobium-methyl mean bond dissociation enthalpy in solution shown in Table IV, it is stressed that this value was directly calculated from the enthalpy of reaction 10, which involves an isopropyl ether-HCl solution (recall the discussion above on the thermochemistry of the complex $[Zr(Cp)_2Cl]_2O$). Therefore, $\bar{D}_s(Nb{-}Me) = 297 \pm 3$ kJ/mol is very likely an upper limit of the gas-phase value. As, on the other hand, $\bar{D}(Nb{-}Me) = 252 \pm 2$ kJ/mol is a lower limit, since the enthalpy of sublimation of $Nb(Cp)_2Me_2$ will be smaller than the enthalpy of sublimation of $Nb(Cp)_2Cl_2$, the two values in Table IV bracket the true gas-phase value anchored on $\bar{D}(Nb{-}Cl) = 407.5$ kJ/mol.

The enthalpy of reaction 11 together with an estimate for the enthalpy of solution of $Nb(Cp)_2Me_2$ in toluene (15 ± 5 kJ/mol)

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(62) The enthalpy of reaction 40 relies on the assumption that the enthalpies of solution of $CH_2I(CHEt)_2CH_2I(l)$ and 2MeI(l) in toluene are similar.

(63) The bond enthalpy differences were recalculated on the same simplifying assumption as that used in the present paper, i.e. identical sublimation enthalpies of the dimethyl and the dichloride complexes.

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leads to $\bar{D}_s$(Nb–I) – $\bar{D}_s$(Nb–Me) = 65.8 ± 2.8 kJ/mol (the value for $\bar{D}_s$(Nb–I) displayed in Table IV relies on $\bar{D}_s$(Nb–Me) derived above). This difference can be compared with $\bar{D}_s$(Zr–I) – $\bar{D}_s$(Zr–Me) = 58.9 ± 1.3 kJ/mol calculated from the enthalpy of reaction 37. Although the differences are close, according to the trend mentioned above, where $\bar{D}$(M–X) – $\bar{D}$(M–Me) decrease with the electronegativity of M, a higher value for the zirconium systems could be expected. We note, however, that the decrease of $\bar{D}$(M–X) – $\bar{D}$(M–Me) with the electronegativity is rather less pronounced for X = I than for X = Cl.[55a] Furthermore, even small differential solvation effects can reverse the observed trend: the enthalpies of formation in Table III lead to $\bar{D}$(Nb–I) – $\bar{D}$(Nb–Me) = 68.8 ± 2.7 kJ/mol and to $\bar{D}$(Zr–I) – $\bar{D}$(Zr–Me) = 79.3 ± 3.9 kJ/mol.

With the last two systems addressed in the present study we aimed to probe the energetics of the niobium–sulfur bond and, in particular, to find if different conformations of the thiolate ligands have any significant effect on Nb–S bond dissociation enthalpies. The PhS groups in the complex $Nb(Cp)_2(SPh)_2$ have an *exo* conformation, the angle S–Nb–S being rather small, 75.4°, whereas an *endo* conformation of the ligands is adopted in the complex $Nb(Cp)_2(SC_6H_4Cl$-*p*$)_2$, the angle S–Nb–S being 98.7°.[7] Moreover, the short S–S length in the case of $Nb(Cp)_2(SPh)_2$ led Darensbourg and co-workers to suggest some bonding character between the two sulfur atoms.[7b] In the chloro–thiolate complex the S–S is much longer, 380.7 pm. Despite these variations, one observes in Table II that the enthalpies of reactions 12 and 13 are almost identical, meaning that the above structural differences are not significantly reflected by the overall energetics of the two complexes. Indeed, the enthalpies of formation in Table III lead to about the same differences $\bar{D}$(Nb–Cl) – $\bar{D}$(Nb–S) for $Nb(Cp)_2(SPh)_2$ and $Nb(Cp)_2(SC_6H_4Cl$-*p*$)_2$, respectively 113.8 ± 8.1 and 106.4 ± 16.4 kJ/mol. This similarity is in keeping with the Nb–S bond lengths reported for the complexes, 251.6 and 250.9 pm, respectively.[7]

Conclusions

The thermochemical studies described in this paper led to the following main conclusions: (1) The energetics of the zirconium–hydrogen bond in crystalline Schwartz's reagent does not seem to be significantly influenced by the polymeric nature of the complex. (2) In contrast to the expected order of reactivities (cyclic olefins being less reactive than linear 1-alkenes), the insertion of cyclohexene into the Zr–H bond of Schwartz's reagent is more exothermic than 1-hexene, although the Zr–C_6H_{13} and Zr–C_6H_{11} bond dissociation enthalpies are comparable. (3) Insertions of nonterminal olefins into the Zr–H bond of Schwartz's reagent are less exothermic than insertions of terminal olefins due to the migration of the double bond to the terminal position and to the fact that secondary and tertiary alkyl radicals are more stable than their primary isomers. (4) A correlation between the enthalpies of formation of the complexes $Zr(Cp)_2(Cl)OR$ and the enthalpies of formation of the corresponding alcohols is observed. This type of correlation has been observed for many other families of molecules and allows the estimation of new data. (5) The reaction enthalpies of the dimer $[Zr(Cp)_2Cl]_2O$ with solutions of HCl in toluene and isopropyl ether demonstrate that identification of gas-phase and solution bond enthalpy data or even the identification of solution bond enthalpy data in different solvents should be made with great caution, particularly when the solvation of one the reactants (HCl in the present cases) is higher exothermic. (6) The enthalpies of reactions 38–41 are rather constant, enabling one to predict the energetics of other similar reactions, involving strain-free metallacycles. (7) The solution value of the Zr–C(sp^2) bond dissociation enthalpy in the metallacycle $Zr(Cp)_2C_4Ph_4$ is some 73 kJ/mol higher than the Zr–C(sp^3) bond dissociation enthalpy in $Zr(Cp)_2Me_2$, indicating a strain-free metallacycle. (8) The bond enthalpy data for niobium and zirconium complexes reported in this work support the conclusion based on Pauling's electronegativity equation that the difference $\bar{D}$(M–Cl) – $\bar{D}$(M–Me) decreases with the increasing electronegativity of M. (9) The Nb–S bond dissociation enthalpies in $Nb(Cp)_2(SPh)_2$ and $Nb(Cp)_2(SC_6H_4Cl$-*p*$)_2$ are similar, thus indicating that the different conformations of the thiolate ligands (*exo* and *endo*, respectively) and the possible existence of S–S bonding in the former complex are not reflected in the energetics of those bonds.

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