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Metal−Ligand Bonding and Bonding Energetics in Zerovalent Lanthanide, Group 3, Group 4, and Group 6 Bis(arene) Sandwich Complexes. A Combined Solution Thermochemical and ab Initio Quantum Chemical Investigation

Wayne A. King,[†] **Santo Di Bella,**[‡] **Giuseppe Lanza,**[‡] **Karl Khan,**[§] **David J. Duncalf,**[§] **F. Geoffrey N. Cloke,**[§] **Ignazio L. Fragala,***[,‡] **and Tobin J. Marks***[,†]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, Dipartimento di Scienze Chimiche, Universitá di Catania, 95125 Catania, Italy, and School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

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Abstract: In this paper we report a comparative experimental thermochemical and ab initio quantum chemical study of metal−ligand bonding and bonding energetics in the group 3, lanthanide, group 4, and group 5 zerovalent bis(arene) sandwich complexes Sc(TTB)$_2$ (**1**) Y(TTB)$_2$ (**2**), Gd(TTB)$_2$ (**3**), Dy(TTB)$_2$ (**4**), Ho(TTB)$_2$ (**5**), Er(TTB)$_2$ (**6**), Lu(TTB)$_2$ (**7**), Ti(TTB)$_2$ (**8**), Zr(TTB)$_2$ (**9**), Hf(TTB)$_2$ (**10**), Ti(toluene)$_2$ (**11**), and Nb(mesitylene)$_2$ (**12**) (TTB = η^6-(1,3,5-^{t}Bu)$_3$C$_6$H$_3$). Derived $\bar{D}$(M−arene) values by iodinolytic batch titration calorimetry in toluene for the process M(arene)$_{2(\text{solution})}$ → M° + 2arene$_{(\text{solution})}$ are rather large (kcal/mol): 45(3) (**1**), 72(2) (**2**), 68(2) (**3**), 47(2) (**4**), 56(2) (**5**), 57(2) (**6**), 62(2) (**7**), 49(1) (**8**), 55(2) (**11**), 64(3) (**9**), 67(4) (**10**), and 73(3) (**12**). Ab initio relativistic core potential calculations on M(C$_6$H$_6$)$_2$, M = Ti, Zr, Hf, Cr, Mo, W, reveal that the metal−ligand bonding is dominated by strong (greater in group 4 than in the group 6 congeners) δ back-bonding from filled metal d$_{xy}$ and d$_{x^2-y^2}$ orbitals to unoccupied arene π orbitals, which decreases in the order Hf > Zr > Ti > W > Mo > Cr. Calculated geometries and $\bar{D}$(M−C$_6$H$_6$) values (at the MP2 level) yield parameters in favorable agreement with experiment. The latter analyses evidence a great sensitivity to electron correlation effects. Marked, group-centered dependences of the measured $\bar{D}$(M−arene) values on the sublimation enthalpies of the corresponding bulk metals, on the metal atomic volumes, and, for the lanthanides and Y, on the corresponding free atom f → d promotion energies are also evident.

The recent advent of several classes of thermally stable (sublimable) *zerovalent* lanthanide, group 3, and group 4 bis(arene) sandwich complexes portends a rich, intricate, and, at the same time, paradoxical organometallic chemistry.[1] In particular, these complexes appear to violate the traditional description of lanthanide/group 3 metal−ligand bonding,[2,3] and to a large extent group 4 metal−ligand bonding,[4] as being substantially if not predominantly electrostatic in nature, with the metals in high formal oxidation states and the ligands bearing formal negative charges. Indeed, other lanthanide and group 3 complexes of neutral olefins, alkynes, and arenes are generally quite labile, and the bonding, although largely unquantified, appears to be weak.[5] In contrast, the classical description of metal−arene bonding in middle and late transition metal complexes is one of weak arene → metal σ and π donation and *strong* metal → ligand π/δ back-donation.[6] The latter interaction is, of course, largely without precedent in organo-f-element and group 3 organometallic chemistry.[7]

The above considerations raise intriguing questions about the bonding energetics and bonding in these new classes of zerovalent bis(arene) complexes. Should they be viewed as metastable and containing "matrix-isolated" metal atoms trapped in sterically-shielded organic cavities, or is there strong covalent

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[†] Northwestern University.

[‡] Universitá di Catania.

[§] University of Sussex.

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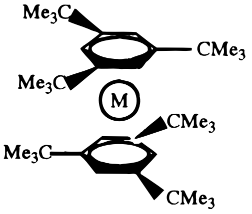
metal−ligand bonding? The current availability of a large series of compounds of varying metal size and electronic configuration renders a combined experimental and theoretical study very attractive and of greatest potential information yield in addressing the above issues. In the present paper, we report a quantitative solution reaction thermochemical study of metal−ligand bond enthalpies[8] in a large series of lanthanide (Gd, Dy, Ho, Er, Lu),[9] group 3 (Sc, Y), and group 4 (Ti, Zr, Hf) bis(arene) complexes, principally containing the η^6-(1,3,5-^{t}Bu)$_3$C$_6$H$_3$ (TTB) ligand (**A**). For comparative purposes, bonding energetics in a titanium bis(toluene) complex and in a niobium bis(mesitylene) complex (Nb(Mes)$_2$) are also examined. We additionally report a relativistic effective core potential (RECP)[10] ab initio electronic structure study and analysis of bonding and bonding energetics, at various levels of correlated wave functions, for the closed shell Ti, Zr, and Hf members of the above series, and present a comparative analysis of the Cr, Mo, and W congeners. Surprisingly few calculations are available for metal bis(arene) sandwich complexes, and those that have been reported (nonempirical local density functional,[11] qualitative ab initio[12]) focus on qualitative descriptions of the bonding only in classical Cr(C$_6$H$_6$)$_2$, without consideration of other metals or of bonding energetics.



A

Experimental Section

Materials and Methods. All manipulations of organometallic complexes were carried out under an atmosphere of purified argon using standard high-vacuum techniques, or in a Vacuum Atmospheres glovebox under purified nitrogen (1−2 ppm O$_2$). Solvents used were predried from appropriate drying agents. The toluene used in the calorimetric measurements was additionally stored over Na/K alloy and vacuum transferred immediately prior to use. Iodine was sublimed prior to use. ^{1}H NMR spectra were recorded on a Varian XL-400 (400 MHz) or a Varian Gemini (300 MHz) spectrometer. X-ray powder diffraction was performed using a Norelco Philips Electronic Instruments 57.3 mm Debye−Scherrer camera using Ni-filtered Cu Kα radiation.

The M(TTB)$_2$ complexes, M = Sc (**1**), Y (**2**), Gd (**3**), Dy (**4**), Ho (**5**), Er (**6**), Lu (**7**), Ti (**8**), Zr (**9**), and Hf (**10**), were prepared and purified at Sussex using published procedures.[1] Ti(toluene)$_2$ (**11**) was generously supplied by Dr. S. D. Ittel of DuPont CRD and was vacuum sublimed prior to use. Nb(mesitylene)$_2$ (**12**) was prepared and purified according to the literature procedure.[13]

Representative arene complexes were selected for analysis by ^{1}H NMR titrations in order to verify that calorimetric reactions were sufficiently quantitative and rapid for accurate thermochemistry. NMR titrations were performed in Wilmad screw-capped NMR tubes fitted with septa. Known amounts of complex were dissolved in C$_6$D$_6$ and reacted with a stock solution of I$_2$ which was incrementally injected using a Hamilton gas-tight syringe. Each injection was followed by vigorous shaking, and an ^{1}H NMR spectrum was then recorded as quickly as possible. An adamantane internal proton standard was used to quantify the free arene produced in titrations of the paramagnetic complexes. For diamagnetic group 4 complexes, the residual proton impurity in the C$_6$D$_6$, when standardized using the original concentration of M(arene)$_2$ and corrected for the added C$_6$D$_6$, provided a convenient method of quantifying the amount of free arene produced by the end of the titration. The following arene complexes were selected from each group: complex **2**, selected for the diamagnetic reaction product YI$_3$; complex **8**, selected for the solubility of TiI$_4$ in benzene; complex **10**, to ensure that no differences exist in the reactivity of the first, second, and third row group 4 arene complexes; and complex **12**.

Powder X−ray Diffraction Measurements. Selected metal iodide products from the bis(arene) iodinolysis reactions were analyzed by X-ray powder diffraction to verify correct reaction product and stoichiometry for each group. Representative metal arene complexes were selected from group 3 (complex **2**), group 4 (complex **10**, selected for the low solubility of HfI$_4$ in toluene), and group 5 (complex **12**). Reactions were performed by injecting a known amount of stock I$_2$ solution in toluene into a stirring solution containing a known amount of metal arene complex dissolved in toluene. Halides were isolated by removal of the supernatant by syringe after the solids were allowed to settle. Any excess I$_2$ was removed by washing the resulting metal halide with toluene, and the product was then dried under high vacuum. The YI$_3$ (isolated as a white solid), HfI$_4$ (isolated as a white solid), and NbI$_5$ (isolated as a black solid) were handled under an inert atmosphere. Samples were then loaded into X-ray capillaries and flame-sealed. X-ray powder diffraction was performed using standard Debye−Scherrer techniques.

Titration Calorimetry. Solution reaction calorimetry was performed in a Tronac Model 450 isoperibol calorimeter extensively modified for the study of extremely air- and moisture-sensitive compounds.[14] A typical experiment was performed as follows. A metal bis(arene) solution of known concentration in toluene was prepared on the day of the experiment. An ampule of metal bis(arene) complex (ca. 15−20 mg) dissolved in ∼5 mL of toluene and a toluene solution containing stoichiometrically excess I$_2$ were also prepared on the day of the experiment. The I$_2$ solution flask, ampule, and metal bis(arene) solution flask were fitted to the calorimeter. The calorimeter was then evacuated and back-filled several times with Ar. The metal bis(arene) solution was next introduced into the titration buret. As an integrity check of the atmosphere of the calorimeter, the bis(arene) ampule was then discharged into the reaction dewar. If the arene color was observed to bleach, no measurements were attempted. The reaction dewar was next placed under a slight vacuum and filled with the I$_2$ solution. The system was then placed under an Ar atmosphere, stirring was initiated, and the reaction dewar was lowered into the constant temperature bath of the apparatus (25.000 ± 0.001 °C) for thermal equilibration. A series

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of electrical calibration runs was then performed. Next, a series of bis(arene) solution injections was carried out using the calibrated motor-driven buret (ca. 12-24 individual injections per run). At the end of the series of titrations, a further set of electrical calibrations was performed. An experimental heat capacity was then derived from the electrical calibration runs. Given the molarity of the titrant and the buret delivery rate, the enthalpy of reaction was calculated.

The heats of solution of TTB and $Y(TTB)_2$ were measured by successively breaking 3−4 sealed ampules containing weighed quantities of the compounds of interest in the temperature-equilibrated, toluene-filled calorimeter. The result from breaking the first ampule (generally somewhat less endothermic, presumably due to exothermic reaction with trace contaminants) was always discarded.

Solubility of HfI_4 and NbI_5 in Toluene. Saturated toluene solutions of HfI_4 (Cerac) and NbI_5 (Cerac) were prepared at room temperature under an Ar atmosphere by stirring a suspension of 0.683 g of HfI_4 or 2.186 g of NbI_5 in 50 mL of dry toluene for 6 h at 25 °C. Stirring was then halted, and the suspended solid was allowed to settle to the bottom of the flask. Next, a volume of toluene solution, 40.0 mL, was carefully withdrawn by syringe and transferred to a second flask where the solvent was removed *in vacuo*. The colors of the resulting solids were appropriate (HfI_4, white solid; NbI_5, black solid) for the authentic metal halides. These samples were weighed to yield the following approximate solubilities in toluene: HfI_4, 6.5×10^{-5} g/mL; NbI_5, 6.48×10^{-4} g/mL.

Theoretical Methods. Because of the molecular and electronic structural complexity of the present $M(TTB)_2$ complexes, calculations were necessarily performed on the simpler, closed shell $M(\eta^6\text{-}C_6H_6)_2$ (M = Ti, Zr, Hf, Cr, Mo, and W) molecules. The use of this structurally abbreviated model is not expected to significantly affect the quantitative description of the principal bonding features, and there is evidence that ring alkyl substitution in $Ti(C_6H_5Me)_2$ (vide infra), as well as methyl substitution in $Cr(C_6H_6)_2$,[8e] induces metal−arene bond enthalpy changes of less than 8 kcal/mol.

The RECP (relativistic effective core potentials) of Stevens *et al.*, which explicitly treat the $(n-1)s^2$, $(n-1)p^6$ semicore electrons and a basis set contracted as [4121/4121/311] were used for the transition metals.[15] The standard all-electron DZV bases were used for C and H atoms.[16] The geometries of all the molecules were optimized for the $^1A_{1g}$ state, using gradient techniques at the restricted Hartree−Fock (RHF) level, imposing D_{6h} symmetry. In order to estimate the dissociation energy, single-point energy calculations, including a polarization "d" function (DZP) on the C atoms ($\alpha = 0.75$) or using correlated wave functions, were performed on optimized geometries. In the second-order Møller−Plesset (MP2) perturbative procedure[17] all the electrons (except the ls core electrons of the C atoms) were correlated. Correlation effects were also considered in the group 4 complexes through the generalized valence bond (GVB) method in the perfect pairing approximation.[18] In this model, each bond of the molecule is described by two electronic configurations, one involving two electrons in the bonding orbital, the other one involving a double excitation of the electrons into the antibonding orbital. In the present calculations, the GVB procedure was limited to the correlation of the two δ bonding orbitals $(e_{2g})^4$ in the two δ^* antibonding orbitals. The dynamic correlation effects were also considered using the configuration interaction procedure including all single and double excitations (CISD) from the single Hartree−Fock reference. In order to reduce the number of configurations in the CISD calculations, all the corelike (ls of C atoms and $(n-1)$s and $(n-1)$p of the metals) orbitals and their virtual orbital counterparts were omitted. The highest 23 virtual orbitals were also omitted. The resulting active orbitals generate ~400 000 configurations. The correction formula proposed by Langholl and Davidson was used to avoid the largest part of the size consistency errors inherent in the CISD approach (CISD+Q).[19]

All the calculations were performed using the HONDO8[20] code on IBM ES/9000 and CRAY C-90 computers.

Results

This section begins with a discussion of the reaction chemistry used to measure heats of reaction and to derive metal−arene bond enthalpies, followed by a presentation of the experimental data. Next, theoretical results are presented, focusing on derived molecular structures, electronic structure, and bonding patterns, followed by calculation of metal−arene bond enthalpies.

Calorimetric Reaction Chemistry. Three iodinolytic reaction types were employed in solution reaction calorimetric studies of metal−arene bonding energetics (eqs 1−3).

$$\mathrm{M(TTB)_{2(s)}} + {}^{3}/_{2}\mathrm{I_{2(s)}} \rightarrow \mathrm{MI_{3(c)}} + \mathrm{2TTB_{(s)}} \tag{1}$$

M = Sc (**1**), Y (**2**), Gd (**7**), Dy (**4**), Ho (**5**), Er (**6**), Lu (**7**)

$$\mathrm{M(arene)_{2(s)}} + \mathrm{2I_{2(s)}} \rightarrow \mathrm{MI_{4(c\ or\ s)}} + \mathrm{2arene_{(s)}} \tag{2}$$

M, arene = Ti, TTB (**8**), Zr, TTB (**9**), Hf, TTB (**10**),
Ti, toluene (**11**)

$$\underset{\mathbf{12}}{\mathrm{Nb(mesitylene)_{2(s)}}} + {}^{5}/_{2}\mathrm{I_{2(s)}} \rightarrow \mathrm{NbI_{5(s)}} + \mathrm{2mesitylene_{(s)}} \tag{3}$$

Here s refers to the solution phase and c to the crystalline phase. In eq 2, TiI_4 is soluble in toluene, whereas the solubility of HfI_4 (and, by inference, ZrI_4) in toluene at 25 °C was determined to be calorimetrically insignificant (~6.5×10^{-5} g/mL; vide infra). The solubility of NbI_5 in toluene at 25 °C was determined to be calorimetrically significant (~6.48×10^{-4} g/mL; vide infra). Using ^1H NMR as an in situ monitor, the $M(arene)_2$ complexes were titrated with I_2 to verify the stoichiometries depicted in eqs 1−3 and to ensure the kinetics were rapid enough for accurate calorimetry. Thus, complex **2** was titrated with I_2 using the procedure detailed in the Experimental Section. The purple color of **2** disappeared at I_2:Y = 1.5, verifying the stoichiometry of eq 1. Precipitation of YI_3 was complete, and only free TTB signals (correct integration versus an adamantane internal standard) were visible in the ^1H NMR. The X-ray powder diffraction pattern of the recovered YI_3 was found to be identical to that of an authentic YI_3 sample (Cerac). Similarly, the stoichiometry and kinetics were examined for complexes **8** and **10** to verify the necessary characteristics of eq 2 for the group 4 $M(arene)_2$ complexes. Complex **8** was titrated using the above procedure. The purple color of **8** disappeared at I_2:Ti = 2.0, yielding a clear red solution of TiI_4 and free arene. In the course of the titration, the signals of **8** disappeared and free ligand signals appeared and increased in intensity. During the titration, a red solid precipitated and paramagnetic broadening was evident in the spectrum. However, by the titration end point, the red solid had completely dissolved, and the spectrum exhibited no paramagnetic broadening. No starting material was evident in the spectrum. Furthermore, reaction with an I_2 solution in stoichiometric excess proved to be rapid, yielding only the diamagnetic NMR spectrum of the free arene. The residual proton impurity in the C_6D_6, when standardized using the original concentration

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of **8** and corrected for the added C_6D_6, yielded a 1.0:1.0 ratio of bound TTB in the starting material to free TTB at the completion of the titration. Compound **10** was also reacted with excess I_2 using the same experimental and NMR analytical procedures as for **8**. The reaction was rapid and quantitative. No starting material was observed after complete addition of the I_2 solution, and the TTB formed in the titration was in a 1.0:1.0 ratio with that in starting **10**. The X-ray powder pattern of the recovered HfI_4 was identical to one generated using literature *d* spacings.[21] Compound **12** was titrated using procedures analogous to those for **1**. Free mesitylene ^1H NMR resonances ceased growing in after the addition of $^5/_2$ equiv of I_2. Furthermore, the mesitylene resonances gave appropriate integration with respect to the internal proton standard for the stochiometry of eq 3. Precipitation of metal halide ceased and the intense red-purple color of the solution disappeared after the addition of 2.5 equiv of I_2. Four minor ^1H resonances grew in during the titration. Thus, two sharp resonances appeared at δ 1.79 and 1.19 ppm, and two broad resonances appeared at δ 2.08 and 1.16 ppm. The sharp resonances exhibited a 3.0:1.0 intensity ratio, while the broad resonances also exhibited a 3.0:1.0 intensity ratio. These observations suggest that two intermediates are observed by NMR. However, by completion of the titration, no products other than free mesitylene were observed.

Metal Halide Solubility Studies. $LaCl_3$ and $CeCl_3$ solubilities in benzene are reported to be $\sim 3 \times 10^{-6}$ g of $LnCl_3$/100 g of benzene.[22] This indicates that the lanthanide halides are essentially insoluble in benzene and, it is reasonable to assume the LnI_3 compounds produced in calorimetric titrations (eq 1) to be virtually insoluble in toluene. There is some indication in the literature that $ZrCl_4$ and ZrI_4 are slightly soluble in benzene.[23] Thus, the solubility of HfI_4 in toluene was estimated and assumed to be comparable to that of ZrI_4. Under the experimental thermochemical conditions used to investigate **10** (eq 2), the small quantity of bis(arene) introduced into the calorimeter to check the integrity of the calorimeter atmosphere is estimated to completely saturate the toluene solution with HfI_4 on addition of the I_2 solution. Under these conditions, the HfI_4 produced during subsequent titration is reasonably assumed to be insoluble in toluene. Furthermore, it is reasonable to take the solubility of ZrI_4 in toluene to be the same as that of HfI_4, such that, under the experimental conditions used to measure **9** (eq 2), the quantity of bis(arene) introduced into the calorimeter to check the calorimeter atmosphere integrity is also calculated to saturate the solution with ZrI_4 on introduction of the I_2 solution. Furthermore, ZrI_4 produced during the subsequent titration is taken to be insoluble in toluene under these conditions. $NbCl_5$ is reported to be quite soluble in bezene, 0.810 g/100 g of solvent.[24] This prompted the measurement of the solubility of NbI_5 in toluene. Under the experimental calorimetric conditions used to measure **12** (eq 3), the bulk of the NbI_5 produced during the thermochemical titration is estimated to remain in solution.

Derivation of Metal−Arene Bond Enthalpies. The above information is combined with measured heats of iodinolysis (eqs 1−3), tabulated standard heats of formation of the corresponding MI_3,[25] MI_4 ($\Delta H_f°$ for $TiI_{4(s)}$ in toluene is taken as the $\Delta H_f°$ of $TiI_{4(s)}$ in benzene),[26] ScI_3,[27] and NbI_5[28] products, the heats of sublimation of the bulk metals,[29] and the heat of solution of I_2 in toluene[30] to yield average metal−arene bond dissociation enthalpies as shown in eqs 4−19 (s = solution phase, c = crystalline phase, g = gas phase). Here $\bar{D}$ describes the metal−arene bond disruption enthalpy process *in solution* where $Ln^0_{(g)}$ is taken to be "unsolvated". Thus, $\bar{D}$ measures the enthalpy required to strip both arene ligands from the metal to produce free, solvated arene ligands (the measured heat of solution of TTB in toluene is essentially negligible, 2.4(2) kcal/mol) and the bare, electronically relaxed metal atom.

Lanthanides, Group 3

$$\begin{array}{rlll}
M(TTB)_{2(s)} + {}^3/_2I_{2(s)} & \rightarrow MI_{3(c)} + 2TTB_{(s)} & \Delta H_{rxn} & (4) \\
{}^3/_2I_{2(c)} & \rightarrow {}^3/_2I_{2(s)} & {}^3/_2\Delta H_{soln} & (5) \\
MI_{3(c)} & \rightarrow M^0_{(c)} + {}^3/_2I_{2(c)} & -\Delta H_f° & (6) \\
M^0_{(c)} & \rightarrow M^0_{(g)} & \Delta H°_{sub} & (7) \\
\hline
M(TTB)_{2(s)} & \rightarrow M^0_{(g)} + 2TTB_{(s)} & 2\bar{D}(M-TTB) & (8)
\end{array}$$

Group 4

$$\begin{array}{rlll}
M(arene)_{2(s)} + 2I_{2(s)} & \rightarrow MI_{4(c)} + 2arene_{(s)} & \Delta H_{rxn} & (9) \\
[M(arene)_{2(s)} + 2I_{2(s)} & \rightarrow MI_{4(s)} + 2arene_{(s)} & \Delta H_{rxn} & (9a)] \\
2I_{2(c)} & \rightarrow 2I_{2(s)} & 2\Delta H_{soln} & (10) \\
MI_{4(c)} & \rightarrow M^0_{(c)} + 2I_{2(c)} & -\Delta H_f° & (11) \\
[MI_{4(s)} & \rightarrow M^0_{(c)} + 2I_{2(c)} & -\Delta H_f° & (11a)] \\
M^0_{(c)} & \rightarrow M^0_{(g)} & \Delta H°_{sub} & (12) \\
\hline
M(arene)_{2(s)} & \rightarrow M^0_{(g)} + 2arene_{(s)} & 2\bar{D}(M-arene) & (13)
\end{array}$$

Group 5

$$\begin{array}{rlll}
Nb(Mes)_{2(s)}\ (\mathbf{12}) + {}^5/_2I_{2(s)} & \rightarrow NbI_{5(s)} + 2Mes_{(s)} & \Delta H_{rxn} & (14) \\
{}^5/_2I_{2(c)} & \rightarrow {}^5/_2I_{2(s)} & {}^5/_2\Delta H_{soln} & (15) \\
NbI_{5(c)} & \rightarrow Nb^0_{(c)} + {}^5/_2I_{2(c)} & -\Delta H_f° & (16) \\
NbI_{5(s)} & \rightarrow NbI_{5(c)} & -\Delta H_{soln} & (17) \\
Nb^0_{(c)} & \rightarrow Nb^0_{(g)} & \Delta H°_{sub} & (18) \\
\hline
Nb(Mes)_{2(s)}\ (\mathbf{12}) & \rightarrow Nb^0_{(g)} + 2Mes_{(s)} & 2\bar{D}(Nb-Mes) & (19)
\end{array}$$

Several comments are in order regarding the metal halide input data. The ΔH_{soln} for $TiI_{4(c)}$ in toluene is taken to be that in benzene, 7 kcal/mol,[26a] since the rate of $TiI_{4(c)}$ dissolution was found to be too slow for accurate ΔH_{soln} measurements in the present apparatus. The same situation was found for $NbI_{5(c)}$

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[25] (a) $\Delta H_f°(YI_{3(c)})$: Xiang-Yu, W.; Zhu, J. T.; Goudiakas, J.; Fuger, J. *J. Chem. Thermodyn.* **1988**, *20*, 1995−1202. (b) $\Delta H_f°(DyI_{3(c)})$: Morss, L. R.; Spence, T. G. *Z. Anorg. Allg. Chem.* **1992**, *116*, 162−168. (c) $\Delta H_f°$ data for the other LnI_3's were calculated from the corresponding ΔH_{sol} values of the metals (Gd,[25d] Ho,[25e] Er,[25f] Lu,[25g]). $\Delta H_f°(HI_{(s)})$[26a] and ΔH_{sol} values of the corresponding LnI_3's[25] were calculated using methods described elsewhere.[25a,b] (d) Spedding, F. H.; Flynn, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 1474−1477. (e) Bettonville, S.; Goudiakas, J.; Fuger, J. *J. Chem. Thermodyn.* **1987**, *19*, 595−604. (f) Fuger, J.; Morss, L. R.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1980**, *1076*−1078. (g) Morss, L. R. *Chem. Rev.* **1976**, *76* (6), 827−841. (h) Bommer, H.; Hohmann, E. Z. *Z. Anorg. Allg. Chem.* **1941**, *248*, 383−396.

[26] (a) $\Delta H_f°(TiI_{4(benzene)})$: Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Harlow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. (Errors are reported as ±2−20 units for data reported in kilocalories. Errors are taken as the maximum value for the given range.) (b) $\Delta H_f°(ZrI_{4(c)})$: Chase, M. W.; Davies, C. A.; Downey, J. R., Jr.; Feurir, D. J.; McDonald, R. A.; Syverund, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*. (c) $\Delta H_f°(HfI_{4(c)})$: Barin, I.; Savert, F.; Schultze-Rhonhelt, E.; Shu Sheng, W. *Thermodynamical Data of Pure Substances*; VCH Publishers: New York, 1989. (No errors are reported for HfI_{4c}. Errors are taken to be comparable to values reported for the other $MI_{4(c)}$'s, M = Ti, Zr.)

[27] $\Delta H_f°(ScI_{3(c)})$: Best, E.; Kischstein, G. In *Gmelin Handbuch der Anorganischen Chemie Sc, Y, La-Lu*; Bergmann, H., Hinz, I., Krasther, W., Merlet, P., Vetter, U., Eds.; Springer-Verlag: Berlin, 1978; Part C6, pp 179−179.

Table 1. Enthalpies of Reaction, Auxiliary Data, and Derived Metal−Arene Bond Enthalpies Obtained from Reaction of Zerovalent Metal Bis(arene) Complexes with I_2 in Toluene

complex	ΔH_{rxn}(eq) (kcal/mol) (eq = 1, 2, 3)	$\Delta H_f°$ ($MI_3/MI_4/MI_5$) (kcal/mol)	$\Delta H°_{sub}$(M) (kcal/mol)	$\bar{D}$(M−arene) (kcal/mol)
$Sc(TTB)_2$ (**1**)	−130(2)	−125(3)	90(1)	45(3)
$Y(TTB)_2$ (**2**)	−116(3)	−153.2(6)	101.5(5)	72(2)
$Gd(TTB)_2$ (**3**)	−108(3)	−143.2(9)	95.0(5)	68(2)
$Dy(TTB)_2$ (**4**)	−128(2)	−147(2)	69.4(1)	47(2)
$Ho(TTB)_2$ (**5**)	−111(2)	−146(1)	71.9(2)	56(2)
$Er(TTB)_2$ (**6**)	−115(3)	−148(1)	75.8(1)	57(2)
$Lu(TTB)_2$ (**7**)	−125(3)	−141(1)	102.2(4)	62(2)
$Ti(TTB)_2$ (**8**)	−105(1)	−82.5(2)	112.3(5)	49(1)
$Ti(PhMe)_2$ (**11**)	−92(2)	−82.5(2)	112.3(5)	55(2)
$Zr(TTB)_2$ (**9**)	−143(3)	−117(2)	146(1)	64(3)
$Hf(TTB)_2$ (**10**)	−140(4)	−118(2)	148(1)	67(4)
$Nb(Mes)_2$ (**12**)	−109(2)	−64(1)[a]	172(1)	73(3)
$Cr(C_6H_6)_2$			95(3)	39.4(1)[b]
$Cr(PhEt)_2$			95(3)	37.5(1)[b]
$Cr(Mes)_2$			95(3)	36.0(1)[b]
$Mo(C_6H_6)_2$			157(5)	59.0(1)[b]
$W(PhMe)_2$			203(10)	72.6(1)[b]

[a] There is some question in the literature about the accuracy of this value. See ref 28. [b] Literature data from ref 8e.

dissolution, so ΔH_{soln} was estimated from eq 20 using tabulated

$$\frac{\Delta H_{soln}(NbI_5)}{\Delta H_{soln}(TiI_4)} \approx \frac{\Delta H°_{sub}(NbI_5)}{\Delta H°_{sub}(TiI_4)} \tag{20}$$

heats of sublimation[31] and the aforementioned heat of solution for TiI_4 in benzene. Finally, because of the high solubility of TiI_4 in toluene, eq 9 is replaced with eq 9a and eq 11 with eq 11a.

Enthalpies of iodinolysis of M(arene)$_2$ complexes, auxiliary data, and derived average metal−arene bond enthalpies are presented in Table 1. All uncertainties for ΔH_{rxn} are reported to 95% confidence limits. Reported uncertainties in auxiliary data are included in calculating the metal−arene bond enthalpies. The estimated enthalpy of solution for $NbI_{5(c)}$ is included in the calculation of $\bar{D}$(Nb−Mes) with an estimated error of ±2 kcal/mol. The enthalpies of solution for the M(arene)$_2$ complexes in toluene are expected to be small and constant and to approximately cancel that of the free arenes in toluene solution (for example, $\Delta H_{soln}(Y(TTB)_2) = 3.5(8)$ kcal/mol versus $\Delta H(TTB)_{soln} = 2.4(2)$ kcal/mol). The obvious exception here is when the arene ligand is toluene which will possess no enthalpy of solution in toluene.

Examination of the present experimental $\bar{D}$(M−arene) results and literature data[8e] for chromium, molybdenum, and tungsten arene complexes (Table 1) reveals several interesting trends. First and most striking is the general observation that the metal−ligand bonding in the zerovalent lanthanide, group 3, and group 4 complexes is in no way unusually weak. *Indeed, the metal−arene bonding is quite strong*. Thus, $\bar{D}$(M−arene) values are 9−36 kcal/mol greater than that for analogously ligated Cr(mesitylene)$_2$ and are in the range found for second and third row group 6 bis(arene) complexes. In both the group 3 and group 4 series (as for group 6), $\bar{D}$(M−arene) values increase as the periodic table is descended. Although both the data base and statistical differences are limited, arene alkyl substitution appears to destabilize group 4 metal−arene bonding as found in group 6.[8e] Finally, monotonic $\bar{D}$(M−arene) variations across the periodic table (e.g., across the lanthanides; Sc → Ti; Y → Zr → Nb → Mo; Hf → W) are not evident, and the reasons underlying this behavior will be a subject in the Discussion.

Theoretical Results. Molecular Structure. Calculated structural parameters for the group 4 and group 6 $M(C_6H_6)_2$ molecules are listed in Table 2. The M−C bond lengths follow the order Zr > Hf > Ti and Mo > W > Cr, as qualitatively expected on the basis of atomic radii.[32] In particular, the shorter (relative to Zr−C and Mo−C) Hf−C and W−C bond lengths are principally due to the lanthanide contraction which reduces the spatial extension of 5d orbitals. A similar trend in metal−carbon bond lengths is observed for group 6 zerovalent metal carbonyl complexes both experimentally[33] and theoretically.[34] The present calculated Ti−C (2.305 Å) and Cr−C (2.233 Å) bond lengths are in reasonable agreement with the experimental average values reported for $Ti(C_6H_5Me)_2$ (2.25 Å)[35] and for $Cr(C_6H_6)_2$ (2.150 Å).[36] Previous calculations on $Cr(C_6H_6)_2$, at a similar theoretical level, yielded an identical overestimation of the Cr−C bond length.[37] This represents a well-documented artifact in ab initio SCF calculations on zerovalent metal complexes, caused by underestimation of back-bonding interactions.[34]

The calculated C−C bond lengths in all of the present complexes appear to be slightly longer than those in the benzene free ligand (1.396 Å) because of π back-donation effects involving the uppermost filled metal orbitals and the π_3 antibonding, ligand-based virtual orbitals (vide infra). The C−C bond lengthening versus that in benzene decreases in the order Hf > Zr > Ti and W > Mo > Cr, thus indicating greatest back-donation for the heavy atoms. Similar C−C bond lengths (1.415 Å) have been reported in the X-ray structures of $Ti(C_6H_5Me)_2$,[35] $Cr(C_6H_6)_2$,[36] and other metal(0) bis(arene) complexes.[1] The present benzene H atoms are calculated to be bent (∼3°) out of the benzene C_6 (away from the metal atom) plane to minimize repulsive interactions, as found in the experimental X-ray structures of $Cr(C_6H_6)_2$[36] and $Ti(C_6H_5Me)_2$[35] complexes.

Electronic Structure and Bonding. Magnetic susceptibility measurements have shown that zerovalent group 4 bis(arene) complexes are all diamagnetic, having a formally d^4 metal atomic configuration.[1d,38] Eigenvalues and atomic population

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[28] (a) $\Delta H_f°(NbI_{5(c)})$: Bergmann, H.; Feicht, H.; Hinz, I.; Junker, A.; Koch, E.; Koeber, K.; Koschel, D.; MOsch, W.; Neibuhr, J.; Stess, P.; Waschk, S.; Zeeck, E. In *Gmelins Handbuch der Anorganischen Chemie*; Banse, H., Bitterer, H., Holzapfel, K., Koch, E., Kreuzbichler, I., Lehl, H., Rieger, H., Swars, K., Eds.; Springer-Verlag: Berlin, 1970; Teil B1, pp 252−253. (b) It has been suggested from empirical thermochemical relationships for the MX_n halide series that the literature value for $\Delta H_f°(NbI_{5(c)})$ (−64(1) kcal/mol) may be in error. Benson has suggested an estimated value of −51.5 kcal/mol for $\Delta H_f°NbI_{5(c)}$. An error of 3 kcal/mol was assumed for this estimated value. We estimate *D*(Nb−Mes) from this approximated value of $NbI_{5(c)}$ to be 67(4) kcal/mol (Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1987**, *91*, 3631−3637). We prefer to accept the current experimental value of $\Delta H_f°(NbI_{5(c)})$ in absence of further measurements on $NbI_{5(c)}$.

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[38] Cloke, F. G. N.; Dix, A. N.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150−1159.

Table 2. Calculated Bond Lengths (Å) and Average Metal−Arene Bond Enthalpies ($\bar{D}$, kcal/mol) for $M(C_6H_6)_2$ Complexes (M = Ti, Zr, Hf, Cr, Mo, W)

	$R_{M-C}{}^a$	$R_{C-C}{}^a$	R_{C-H}	$\bar{D}_{SCF}{}^b$	$\bar{D}_{GVB}$	$\bar{D}_{CISD(Q)}$	$\bar{D}_{MP2}$	$\bar{D}_{exp}{}^c$
$Ti(C_6H_6)_2$	2.305 (2.25)	1.424 (1.415)	1.068	−26.3 (−20.2)	−11.4	11.8	58.1	55
$Zr(C_6H_6)_2$	2.487	1.426	1.068	1.3 (7.5)	7.4	25.0	53.9	64
$Hf(C_6H_6)_2$	2.432	1.430	1.068	1.5 (7.7)	5.6	25.3	56.9	67
$Cr(C_6H_6)_2$	2.233 (2.150)	1.417 (1.423)	1.070	−68.8			41.3	39.4
$Mo(C_6H_6)_2$	2.367	1.420	1.069	−34.3			42.1	59.0
$W(C_6H_6)_2$	2.350	1.423	1.068	5.8			72.2	72.6

[a] The value in parentheses refers to the experimental structural data for $Ti(C_6H_5Me)_2$[35] and $Cr(C_6H_6)_2$.[36] [b] Values in parentheses refer to the calculation using the DZP basis set. [c] Values refer to experimental data for $M(arene)_2$ complexes in Table 1.

Table 3. Ab Initio Eigenvalues and Mulliken Population Analyses for $M(C_6H_6)_2$ Complexes (M = Ti, Zr, Hf, Cr, Mo, and W)

A. M = Ti, Zr, and Hf

	$-\epsilon$ (eV)			metal population			
MO	Ti	Zr	Hf	Ti	Zr	Hf	character
$4e_{2g}$	5.32	4.84	4.89	54	52	47	$d_{xy} + d_{x^2-y^2} + \pi_3$
$4e_{1g}$	10.30	10.71	10.77	14	14	18	$\pi_2 + d_{xz} + d_{yz}$
$5e_{1u}$	10.47	10.16	10.32	5	3	4	$\pi_2 + p_x + p_y$
$5a_{2u}$	13.47	13.54	13.54	13	10	15	$\pi_1 + p_z$
$3e_{2u}$	13.50	13.59	13.59	0	0	0	σ_{c-c}
$3e_{2g}$	13.58	13.63	13.64	0	0	0	σ_{c-c}
$5a_{1g}$	14.87	14.72	15.02	13	11	18	$\pi_1 + d_{z^2} + s$
$4e_{1u}$	16.41	16.42	16.45	0	0	0	σ_{c-c}

B. M = Cr, Mo, and W

	$-\epsilon$ (eV)			metal population			
MO	Cr	Mo	W	Cr	Mo	W	character
$4e_{2g}$	6.17	6.00	5.88	68	64	56	$d_{xy} + d_{x^2-y^2} + \pi_3$
$6a_{1g}$	9.89	7.14	6.50	92	86	88	$d_{z^2} + \sigma^*_{c-c}$
$4e_{1g}$	9.80	10.52	10.70	15	17	19	$\pi_2 + d_{xz} + d_{yz}$
$5e_{1u}$	10.45	10.12	10.28	6	3	5	$\pi_2 + p_x + p_y$
$5a_{2u}$	13.31	13.40	13.46	13	12	14	$\pi_1 + p_z$
$3e_{2u}$	13.39	13.54	13.56	0	0	0	σ_{c-c}
$3e_{2g}$	13.51	13.61	13.64	1	1	1	σ_{c-c}
$5a_{1g}$	14.89	14.74	15.13	7	9	21	$\pi_1 + d_{z^2} + s$
$4e_{1u}$	16.30	16.39	16.43	0	0	0	σ_{c-c}

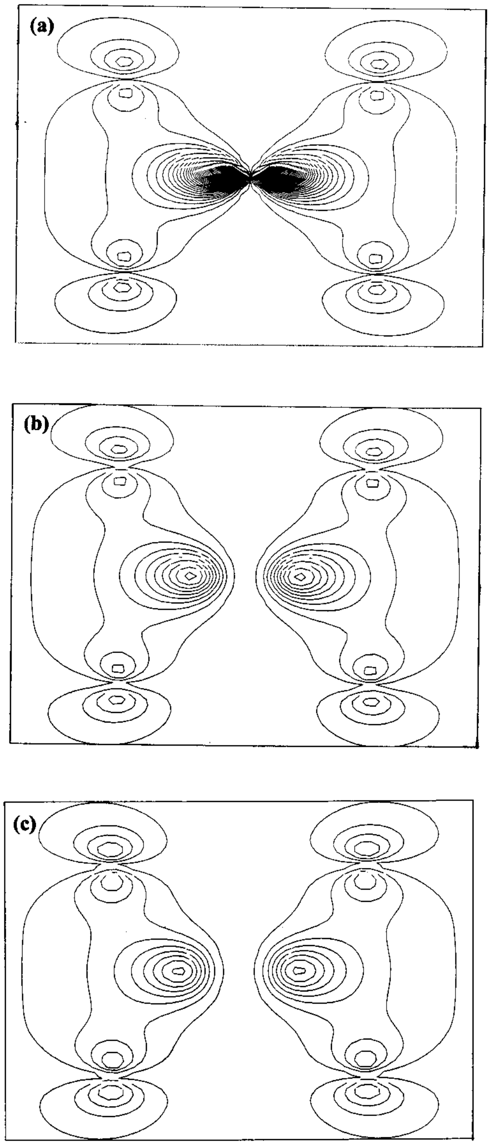

Figure 1. Electron density contour plots of the $4e_{2g}$ orbital (*xz* plane) of (a) $Ti(C_6H_6)_2$, (b) $Zr(C_6H_6)_2$, and (c) $Hf(C_6H_6)_2$. The contour value is 0.004 e = $a_0{}^3$.

analyses for the $^1A_{1g}$ ground states of the group 4 $M(C_6H_6)_2$ complexes are reported in Table 3A and those for the group 6 analogues in Table 3B. Classically, the bonding in $M(C_6H_6)_2$ compounds can be described[6,11,12] in terms of relatively *weak* L → M donation involving the filled π_1 and π_2 benzene orbitals and the empty metal d_{z^2}, p_z, and $d_{xz} + d_{yz}$ orbitals ($5a_{1g}$, $5a_{2u}$, and $5e_{1u}$ MOs in Table 3) and a *strong* M → L δ "back-donation" from the filled $d_{xy} + d_{x^2-y^2}$ metal (d^4) orbitals to the unoccupied π_3 (benzene) orbitals ($4e_{2g}$ MO). The back-donation represents the greatest source of stabilization in the present complexes (vide infra).

The Mulliken population analysis of the uppermost MOs of the present groups 4 and 6 $M(C_6H_6)_2$ complexes argues, as in the case of earlier analyses of $Cr(C_6H_6)_2$,[11,12] that δ back-donation is the principal bonding interaction. An estimation of its magnitude can be obtained from the ligand atomic contribution to the $4e_{2g}$ MOs (Table 3). In particular, the M → L back-donation increases along the series Ti < Zr < Hf (1.84, 1.92, and 2.12 eu, respectively). This is also evident from the density contour plot of the $4e_{2g}$ MO which indicates an increasing charge delocalization and M−C overlap along the series (Figure 1). This trend is a clear indication of a tendency for stronger M → L electron charge transfer for the heavier metals. This observation accounts well for both the increased C−C bond lengths and the increasing dissociation energies along the series (vide infra). Interestingly, the ab initio calculations on the group 6 $M(C_6H_6)_2$ congeners ($(6a_{1g})^2(4e_{2g})^4$, d^6 metal configuration) indicate *substantially less* M → arene δ back-donation than in the group 4 series, with Cr < Mo < W (1.28, 1.44, 1.76 eu, respectively). Note that the back-donation again increases with increasing atomic number.

Dissociation Energies. The calculated metal−arene bond dissociation energies for the present $M(C_6H_6)_2$ complexes are reported in Table 2. At the HF level of theory, $TiC(_6H_6)_2$ is found to be unbound (relative to the ground state of Ti and C_6H_6) by 26.3 kcal/mol, while the Zr and Hf complexes are slightly bound. The same situation is found for $Cr(C_6H_6)_2$ and $Mo(C_6H_6)_2$. The inclusion of the polarization functions on the C atoms (DZP bases) does not significantly change the results.

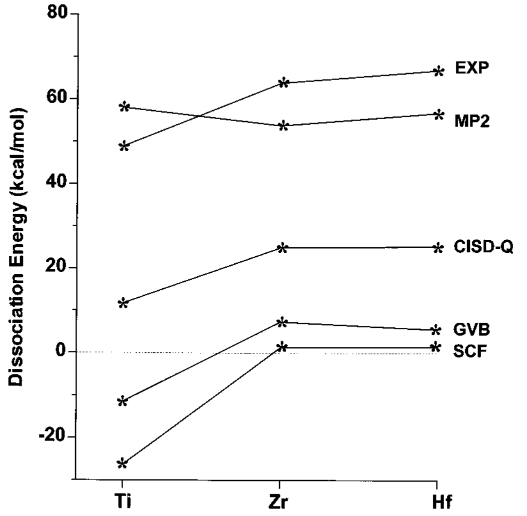

Figure 2. Experimental and calculated metal−arene bond enthalpies for $M(TBB)_2$ and $M(C_6H_6)_2$ complexes (M = Ti, Zr, and Hf) using the formalisms described in the text.

In fact, only a uniform improvement of ~6 kcal/mol is obtained. Due to the good quality of the present basis set, no significant further improvements are expected for calculations using a complete basis set. This observation suggests that changes of correlation energy associated with molecule formation represent the major stabilizing factor in the present complexes. It is interesting, however, to note that the trend in the calculated $M-C_6H_6$ bond energies predicted at the HF level (Ti < Zr < Hf) is similar to that of the experimental $\bar{D}$(M−arene) values (Table 1), even though the dissociation energy of the Ti complex is considerably underestimated (Figure 2).

The inclusion of correlation effects, through the MP2 procedure (DZV bases), brings the calculated absolute values of the group 4 and group 6 dissociation energies into more favorable agreement with the experimental values (Table 2 and Figure 2). However, the dissociation energies of the Zr, Hf, and Mo complexes are slightly underestimated, probably due to the limited basis set (see above), while the relative trend is correctly predicted. In contrast, the calculated dissociation energies of $Ti(C_6H_6)_2$ and $Cr(C_6H_6)_2$ are slightly overestimated relative to the experimental values. Similar observations have also been made for various metal(0) carbonyl complexes of the first transition series[34b,c] and arise from well-recognized shortcomings of the MP2 method.[39]

In order to explicitly take into account intrapair (left−right) correlation effects in the back-bonding portion of the metal−arene interaction, the GVB 4/4 ($\delta-\delta^*$) approach[18] was also employed. In this case, the calculated metal−arene dissociation energies increase ~5 kcal/mol relative to the HF for the Zr and Hf complexes, and a considerable improvement (15 kcal/mol) is observed for $Ti(C_6H_6)_2$. This indicates that the back-bonding effects are better described by the simpler SCF wave functions for the Zr and Hf complexes than for the $Ti(C_6H_6)_2$ complex, as also suggested by the contribution of the HF configuration (95.2%, 98.0%, and 98.7% for Ti, Zr, and Hf complexes, respectively) to the GVB wave function.

The inclusion of correlation energy within the CISD(Q) approach, although accounting for ~40% of the total dissociation energy (Table 2) due to the truncated Cl expansion, leads to a dissociation energy trend along the series in good agreement with experiment (Figure 2). This improvement over the MP2 dissociation energy trend is due to the greater flexibility of the CISD wave function to describe left−right correlation effects. Clearly, more quantitative binding energies are expected when the complete CISD expansion is employed.

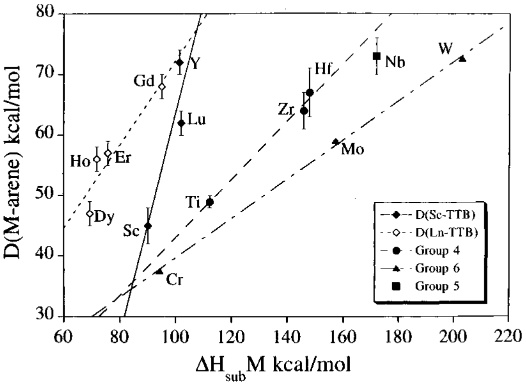

Figure 3. Sublimation enthalpies of the bulk metals (from ref 29) versus calorimetrically determined $\bar{D}$(M−arene) values. Lines are least-squares fits to the data.

Discussion

Bonding and Bonding Energetics. The present thermochemical results indicate that metal−arene bonding in group 3, lanthanide, and group 4 $M(TTB)_2$ complexes is very strong. These complexes are clearly not analogous to cryogenic matrix-isolated species. The ab initio RECP quantum chemical analysis of the groups 4 and 6 complexes evidences qualitatively similar bonding, i.e., highly covalent and dominated by strong metal → ligand δ back-donation which increases as the group is descended. However, the back-donation is substantially greater for group 4 than for group 6. The general trend for first and second row metals of decreasing metal−arene bond enthalpies in $M(arene)_2$ complexes as the periodic table is traversed to the right can be attributed to a combination of decreased orbital overlap/decreased M → L back-donation and increased interligand nonbonded repulsions with declining metallic radius. The trend of decreasing $\bar{D}$(M−arene) with increasing arene alkyl substitution observed here (Table 1) is in accord with this picture. In regard to the quantitative aspects of metal−ligand bonding energetics, the present calculations on the group 4 and group 6 complexes are in reasonably good agreement with experiment. Complementary theoretical studies of the open shell group 3 and lanthanide $M(arene)_2$ congeners are presently in progress,[40] are enormously more computation-intensive, and will be reported at a later date when complete.

Additional qualitative chemical insight into metal−ligand bond energy trends among and between families of organometallic molecules can be obtained by examining how $\bar{D}$(M−L) values depend upon the heats of sublimation of the corresponding bulk metals.[8e] The latter quantities measure the enthalpy changes from another "ligated" zerovalent metal valence state to the bare, electronically relaxed, zerovalent metal atoms. As can be seen in Figure 3, the group 3, lanthanide, group 4, and group 6 $\bar{D}$(M−arene) data segregate into approximately linear but separate plots, arguing for strong similarities in bonding determinants both within and between series. The only exception is the M = Lu data point which falls substantially away from the lanthanide line but on the group 3 line, perhaps

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(39) (a) It is well known that the single-reference MP2 approach does not correctly describe the dissociation energy of first row transition metal zerovalent complexes,[34b,c] since intrapair correlation effects, which are critical for the first row transition elements, are not explicitly included in a single-reference MP2 treatment.[39b,c] (b) Kozlowski, P. M.; Davidson, E. R. *Chem. Phys. Lett.* **1994**, *222*, 615−620. (c) Siegbahn, P. E.; Svensson, M. *Chem. Phys. Lett.* **1993**, *216*, 147−154.

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Table 4. Calculated Metal−Arene Bond Enthalpies Derived from Metallic Enthalpies of Sublimation

M(arene)$_2$	ΔH_{sub}(M)^a (kcal/mol)	estimated $\bar{D}$(M−arene) (kcal/mol)	measured $\bar{D}$(M−arene) (kcal/mol)
		Group 3	
Sc (**1**)	90.3	46	45
Y (**2**)	101.5	66	72
La	103.0	69	
Lu (**7**)	102.2	67	62
		Lanthanides	
Ce	101	72	
Pr	85.0	61	
Nd	78.3	57	
Sm	49.4	37	
Eu	41.9	32	
Gd(**3**)	95.0	69	68
Tb	92.9	67	
Dy (**4**)	69.4	51	47
Ho (**5**)	71.9	53	56
Er (**6**)	75.8	55	57
Tm	55.5	41	
Yb	36.4	28	
		Group 4	
Ti (**8**)	112.3	49	49
Zr (**9**)	146	65	64
Hf (**10**)	148	66	67
		Group 5	
V	122.9	52	
Nb (**2**)	172	73	73
Ta	186.8	79	
		Actinides	
Th	137.5	61	
U	125	88	

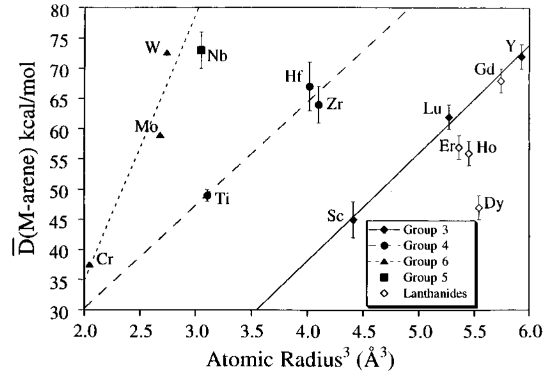

Figure 4. Experimental $\bar{D}$(M−arene) values versus the corresponding metal radii cubed.

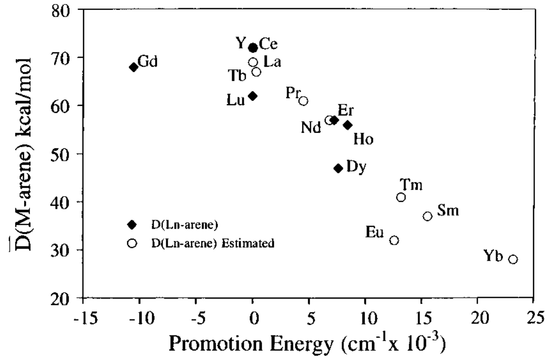

Figure 5. Experimental and estimated (from Figure 3) $\bar{D}$(M−TTB) values versus free atom f^{n}s^2 → f^{n-1}d^{1}s^2 promotion energies (from ref 41). The promotion energy is taken to be zero for Y° (4d^{1}5s^2 ground state).

reflecting that Lu is the only closed f shell (4f^{14}) member of the lanthanide bis(arene) series examined. Beyond the above bonding considerations, the relationships in Figure 3 are useful in estimating $\bar{D}$(M−arene) values for other, presently unknown, members of the lanthanide bis(arene) series. These estimated data are included in Table 4. It can be seen that predicted D(Ln−TTB) values are lowest for lanthanides having the most stable divalent states (Sm, Eu, Yb) and are, in general, slightly higher for the earlier lanthanides. However, these thermochemical parameters do not completely correlate with observed Ln(TTB)$_2$ thermal stabilities; e.g., La(TTB)$_2$ is unstable above 0 °C, Pr(TTB)$_2$ unstable above 40 °C, Sm(TTB)$_2$ unstable above −30 °C, and Ce(TTB)$_2$ inisolable.[1] These observatins argue that Ln(TTB)$_2$ thermal decomposition channels are unlikely to involve simple Ln−arene dissociation (the reverse of the metal atom vapor synthetic process) as the predominant driving force (as opposed to ring metalation[1a] and other processes).

Other thermochemical considerations support this contention (vide infra). Figure 4 examines the relationship between $\bar{D}$(M−arene) and the cube of the metal atomic radius (essentially the atomic volume),[32] which should, to some extent, account for orbital overlap and ligand−ligand repulsive effects. It can be seen that, for the groups 4 and 6 complexes, there are significant, group-centered correlations with experimental metal−arene bond enthalpies. The correlation is less convincing for the lanthanides where promotion energy effects appear to play a major role (vide infra), and only two data points are available for group 3.

Previous discussions of bonding in the Ln(TTB)$_2$ complexes have indirectly implicated the role of the lanthanide 5d orbitals in the metal−ligand bonding and have qualitatively correlated observed Ln(TTB)$_2$ thermal stabilities with the energetic demands of populating the 5d orbitals (free atom f^{n}s^2 → f^{n-1}d^{1}s^2 promotion energies for lanthanides).[1c] The present $\bar{D}$(Ln−TTB) data base offers the first thermochemical perspective on this correlation. Qualitatively, it would be expected that, if f^{n}s^2 → f^{n-1}d^{1}s^2 promotion energies were important in metal−ligand bond strengths, metals such as Gd°, which has a 4f^{7}5d^{1}6s^2 ground state,[41] and Y°, which has a 4d^{1}5s^2 ground state,[41] would have the strongest metal−ligand bonding, all other factors such as orbital overlap and nonbonded repulsions being approximately constant (which is likely unrealistic in the case of Sc). Reference of Table 1 confirms this notion, while Figure 5 shows an approximately linear relationship between tabulated[41] free atom f^{n}s^2 → f^{n-1}d^{1}s^2 promotion energies and experimental or estimated (from the aforementioned ΔH_{sub} correlations; Table 4) $\bar{D}$(Ln−TTB) data.

Chemical Implications. With reference to Ln(TTB)$_2$ thermal stability, it is of interest to calculate enthalpies for the hypothetical decomposition process of eq 21. It can be seen in Figure 6 that this process is actually *endothermic* for the lanthanide arene complexes, reflecting the relatively low cohesive energies of the bulk lanthanide metals.[29] In contrast, this decomposition

$$\mathrm{M(arene)}_{2(s)} \rightarrow \mathrm{M}_{(c)} + 2\mathrm{arene}_{(s)} \qquad (21)$$

mode is estimated to be *exothermic* for the groups 4−6 arene complexes, reflecting the greater metallic lattice enthalpies.[29] These results convey two interesting suggestions. First, the reverse of eq 21 is predicted to be *exothermic* for lanthanides and Y, and thus might, in principle, be a useful synthetic route. Small scale attempts to observe a reaction between TTB (in solution or as a neat melt) with Y powder (neat or activated with HgCl$_2$) were unsuccessful. The intense purple color of Y(TTB)$_2$ was not detected over the course of 14 days at

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(41) Brewer, L. In *Systematics and the Properties of the Lanthanides*; Sinha, S. P., Ed.; D. Reidel Publishing Co.: Boston, 1983; pp 17−69.

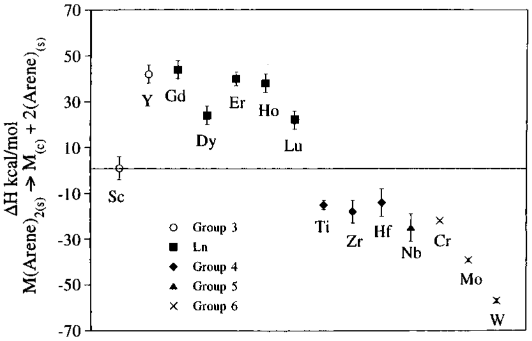

Figure 6. Calculated enthalpies for the decomposition process of eq 21 for various zerovalent bis(arene) complexes.

temperatures as high as 100 °C. This result may indicate that the activation energy for the reverse of eq 21 is very high (formation of an initial single-ring species should be endothermic) and/or that $Y(TTB)_2$ is not stable under the reaction conditions. The second suggestion from the data in Figure 6 is that the transition metal bis(arene) complexes are in fact metastable, *kinetic products* of the metal atom vapor synthesis, rather than thermodynamic sinks.

The present thermochemical data also provide a perspective on the anticipated nature of metal−arene bonding energetics involving other f-elements—specifically actinides. Since Th has a $6d^27s^2$ ground state[42] reminiscent of group 4 metals, it seems reasonable to estimate $\bar{D}$(Th−TTB) from the group 4 correlation line in Figure 3 (Table 4). The derived disruption enthalpy, ~61 kcal/mol, is comparable to those of the heavier group 4 congeners. U has a $5f^36d^17s^2$ ground state[42] and seems more reasonably classified among the lanthanides, yielding from Figure 3 $\bar{D}$(U−TTB) ≈ 89 kcal/mol (~52 kcal/mol if placed on the group 4 line). These estimates suggest that zerovalent actinide arene complexes are likely to be thermodynamically stable with respect to eq 21 and are plausible synthetic targets, although initial synthetic studies are inconclusive.[43] Interestingly, $U(TTB)_2^+$ has been detected mass spectrometrically in the gas phase reaction of U^+ with TTB.[44]

The present thermochemical data also provide information on alternate synthetic routes to metal arene complexes. Metathetical reactions such as eq 22 should be exothermic when M^1 = a group 4, 5, or 6 metal and M^2 = a lanthanide or Y, with

$$M^1(\text{arene})_{2(s)} + M^2_{(c)} \rightarrow M^2(\text{arene})_{2(s)} + M^1_{(c)} \quad (22)$$

the driving forces being the greater lattice cohesive energy of M^1 versus that of M^2 and the strong M^2−arene bonding. Some representative examples are given in eqs 23−26.

$$\text{Zr(TTB)}_{2(s)} + \text{Y}_{(c)} \rightarrow \text{Y(TTB)}_{2(s)} + \text{Zr}_{(c)} \quad (23)$$
$$\Delta H_{\text{calcd}} \approx -61 \text{ kcal/mol}$$

$$\text{Hf(TTB)}_{2(s)} + \text{Ho}_{(s)} \rightarrow \text{Ho(TTB)}_{2(s)} + \text{Hf}_{(c)} \quad (24)$$
$$\Delta H_{\text{calcd}} \approx -51 \text{ kcal/mol}$$

$$\text{Mo}(\text{C}_6\text{H}_6)_{2(s)} + \text{Er}_{(c)} \rightarrow \text{Er}(\text{C}_6\text{H}_6)_{2(s)} + \text{Mo}_{(c)} \quad (25)$$
$$\Delta H_{\text{calcd}} \approx -76 \text{ kcal/mol}$$

$$\text{W(PhMe)}_{2(s)} + \text{Ti}_{(c)} \rightarrow \text{Ti(PhMe)}_{2(s)} + \text{W}_{(c)} \quad (26)$$
$$\Delta H_{\text{calcd}} \approx -55 \text{ kcal/mol}$$

Likewise, it should in principle be possible to couple exothermic[45] alkyne trimerization reactions with arene complexation to yield arene complexes (e.g., eqs 27−31). A number of transition metal complexes are, of course, active alkyne trimerization catalysts.[46]

$$\text{Y}_{(c)} + 6\text{HC}{\equiv}\text{CH}_{(s)} \rightarrow \text{Y}(\text{C}_6\text{H}_6)_{2(s)} \quad (27)$$
$$\Delta H_{\text{calcd}} \approx -330 \text{ kcal/mol (Y)}$$

$$\text{Y}_{(c)} + 6\text{MeC}{\equiv}\text{CMe}_{(s)} \rightarrow \text{Y}(\text{Me}_6\text{C}_6)_{2(s)} \quad (28)$$
$$\Delta H_{\text{calcd}} \approx -292 \text{ kcal/mol (Y)}$$

$$\text{Ti}_{(c)} + 6\text{HC}{\equiv}\text{CH}_{(s)} \rightarrow \text{Ti}(\text{C}_6\text{H}_6)_{2(s)} \quad (29)$$
$$\Delta H_{\text{calcd}} \approx -274 \text{ kcal/mol(Ti)}$$

$$\text{Hf}_{(c)} + 6\text{HC}{\equiv}\text{CH}_{(s)} \rightarrow \text{Hf}(\text{C}_6\text{H}_6)_{2(s)} \quad (30)$$
$$\Delta H_{\text{calcd}} \approx -274 \text{ kcal/mol (Hf)}$$

$$\text{W}_{(c)} + 6\text{HC}{\equiv}\text{CH}_{(s)} \rightarrow \text{W}(\text{C}_6\text{H}_6)_{2(s)} \quad (31)$$
$$\Delta H_{\text{calcd}} \approx -230 \text{ kcal/mol (W)}$$

A calculation for eqs 27−31 in which the metal reagent is gaseous yields estimated exothermicities which are greater by the corresponding ΔH_{sub} parameters. Interestingly, while free arenes are reported to be formed in such metal atom vapor reactions, bis(arene) complexes have not, to our knowledge, been formed in high yield.[47]

Acknowledgment. This research was supported by the U.S. National Science Foundation (T.J.M., W.A.K.; Grant CHE9104112), the Ministero dell Universitá e della Ricerca Scientifica e Tecnologica (S.D.B., G.L., I.L.F.; MURST, Rome), the Consiglio Nazionale delle Ricerche (S.D.B., G.L., I.L.F.; CNR, Rome), and ICI (D.J.D., K.K., F.G.N.C.). The CINECA computer center (Casalecchio di Reno, BO, Italy) is also gratefully acknowledged for providing a grant of computer time.

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