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# Electronic Structure, Molecular Geometry, and Bonding Energetics in Zerovalent Yttrium and Gadolinium Bis(arene) Sandwich Complexes. A Theoretical ab Initio Study†

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The first ab initio study of bonding and bonding energetics in zerovalent rare earth bis(arene) sandwich complexes is presented. The $d^3$ ground state and $d^2s^1$ first excited state [$(e_{2g})^3$ and $(e_{2g})^2(a_{1g}{}^1)$ configurations, respectively] electronic structures and geometries of the $M(\eta^6\text{-}C_6H_6)_2$ complexes, where M = Y and Gd, have been investigated by using relativistic effective core potentials with MP2, MP4, and coupled-cluster ab initio wave functions. The two electronic states lie close in energy but exhibit significant differences in bonding interactions and geometries. The greater stabilities found in the ground states of both complexes are associated with greater metal → ligand back-bonding interactions and, hence, shorter M−C bond lengths. Computed ground state electronic configurations agree well with experimental EPR and magnetic susceptibility data, while metrical parameters are in very good agreement with diffraction data. The metal−arene interactions, both ligand-to-metal donation and metal-to-ligand back-donation, are similar in both complexes. The role of electron correlation appears crucial to correctly predicting the metal−arene dissociation energies. The Hartree−Fock energy is actually repulsive compared to that of the ground state fragments, while the inclusion of correlation effects through perturbative and coupled-cluster procedures predicts bound molecules, even though the binding energies remain underestimated.

## Introduction

Metal atom vapor syntheses using sterically encumbered arene ligands such as 1,3,5-tri-*tert*-butylbenzene (TBB) have recently afforded stable 16- and 15-electron bis(arene) sandwich complexes of both early d and f transition metals. In particular, unusual complexes of large atomic radius elements of both group 4 (Zr, Hf) and the rare earths have been reported,[1,2] and great interest has been associated with their structures, bonding, reactivities, and stabilities.[1,2] For the rare earth complexes, stability trends within the series have been rationalized in terms of a "promotion energy" model.[2b] Within this simple model, a $d^1s^2$ atomic configuration, either in the ground state or in an easily accessible excited state, is required to obtain stable metal−ligand bonding. In contrast, synthetic efforts with rare earth elements having $f^ns^2$ ground states and high $f^ns^2 \rightarrow f^{n-1}d^1s^2$ atomic excitation energies (Sm, Eu, Tm, and Yb) proved unsuccessful. Note that this simple bonding model is also in agreement with thermochemically determined rare earth−arene bond energy trends within this series.[3,4] Moreover, Yin *et al.*[5] recently reported gas phase FT/ICR mass spectrometric studies of the interaction between singly charged rare earth ions and 1,3,5-tri-*tert*-butylbenzene. They found that ions having the largest $f^ns^1 \rightarrow f^{n-1}d^1s^1$ excitation energies ($Sm^+$, $Eu^+$, $Tm^+$, and $Yb^+$) form $Ln(TBB)_2{}^+$ sandwich complexes, while $Ln(TBB)_2{}^+$ species are not formed for other rare earth ions and, instead, mediate C−H and C−C bond activation.[5]

In spite of the aforementioned experimental results, a theoretical understanding of electronic structure and those factors affecting the stability of rare earth−arene bonding in these unusual complexes is still lacking.[6] In this context, a systematic theoretical investigation using high-level ab initio computational methods can provide insight into bond stability and electronic interactions, as well as into the geometrical structures of these complexes. In a recent contribution, we reported an ab

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(6) (a) Only a molecular mechanics study, addressed to the steric interactions, on $M(TBB)_2$ (M = Y, Gd, and Yb) and $Gd(C_6H_6)_2$ has been reported.[6b] (b) Ren, J.; Amberger, H.-D. *J. Mol. Struct.* (*Theochem*) **1991**, *236*, 231.

**Table 1. Calculated Bond Lengths (Å), Bond Angles (deg), Relative Energies (kcal/mol), Dissociation Energies $\bar{D}$ (kcal/mol), and Bond Orders ($\sigma$) for $Y(C_6H_6)_2$ and $Gd(C_6H_6)_2$[a]**

| | state | $R_{M-C}$ | $R_{C-C}$ | $R_{C-H}$ | $\theta$[b] | $\Delta E_{SCF}$ | $\Delta E_{MP2}$ | $\bar{D}_{SCF}$ | $\bar{D}_{MP2}$ | $\sigma_{M-C}$ | $\sigma_{C-C}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Y(C_6H_6)_2$ | $^2E_{2g}$ | 2.664 | 1.420 | 1.070 | 2.9 | 7.1 | 0.0 | −3.8 | 29.8 | 0.23 | 1.20 |
| | $^4A_{2g}$ | 2.814 | 1.410 | 1.069 | 1.6 | 0.0 | 14.6 | | | 0.17 | 1.27 |
| exp[c] | $^2E_{2g}$ | | | | | | | | 72 | | |
| $Gd(C_6H_6)_2$[d] | $^9E_{2g}$ | 2.702 | 1.419 | 1.071 | 3.1 | 17.4 | 0.0 | −4.1 | 31.5 | 0.22 | 1.21 |
| | | (2.608) | (1.448) | (1.093) | (3.3) | | | | (35.0) | | |
| | $^{11}A_{2g}$ | 2.815 | 1.409 | 1.069 | 1.3 | 0.0 | 4.2 | | | 0.15 | 1.27 |
| exp[c] | $^9E_{2g}$ | 2.630 (4) | 1.414 (5) | | | | | | 68 | | |
| $C_6H_6$ | $^1A_{1g}$ | | 1.396 | 1.071 | | | | | | | 1.37 |
| | | | (1.426) | (1.094) | | | | | | | |
| exp | | | 1.397 | 1.084 | | | | | | | |

[a] Experimental values are reported for comparison. [b] $\theta$: Angle between the $C_6$ ring and the C−H bond vector. [c] Experimental values are taken from refs 2d, 3, and 4. [d] Values in parentheses refer to the MP2-optimized structure.

initio study of metal−ligand bonding and dissociation energies of zerovalent group 4 and group 6 metal−bis(arene) complexes.[4] Good agreement with experimental metal−arene dissociation enthalpies was obtained, and it was found that the metal-to-ligand back-donation increases upon descending a period and that this trend parallels the metal−arene dissociation energies.[4]

This contribution extends the ab initio analysis to the electronic states, molecular structures, and dissociation energies (DE) of the open shell rare earth organometallics $M(\eta^6\text{-}C_6H_6)_2$ (M = Y and Gd). Within the $M(TBB)_2$ rare earth series, the M = Y and Gd members exhibit the strongest metal−ligand bonding.[3,4]

## Theoretical Methods

Because of the structural complexity of the present $M(TBB)_2$ complexes, calculations were necessarily performed on simpler $M(\eta^6\text{-}C_6H_6)_2$ model molecules. The use of these models does not significantly affect the quantitative description of the principal bonding features, since there is evidence that alkyl ring substitution in metal bis(benzene) sandwich complexes has little effect on the metal−ligand bonding energetics (a few kilocalories/mole in terms of bond enthalpies).[4,7]

The RECP (relativistic effective core potentials) of Stevens *et al.*,[8] which explicitly treat the $(n-1)s^2$,$(n-1)p^6$ semicore electrons ($4s^2$ and $4p^6$ for Y, $5s^2$ and $5p^6$ for Gd) and basis set, contracted as [4211/4211/311] and [4211/4211/21/61], were used for the yttrium and gadolinium atoms, respectively. The standard all-electron Dunning basis set (DZV) was used for the C and H atoms.[9]

The geometries of all states analyzed in the two complexes were fully optimized by using gradient techniques at the Hartree−Fock level and imposing $D_{6h}$ symmetry. More accurate values of both the relative stability of various electronic states and, in turn, of the bond dissociation energies were evaluated by using single-point MP2 energy calculations on the optimized HF geometries. In addition, the effects of a truncated basis set and of high-order correlation effects on $Y(C_6H_6)_2$ were investigated by using single-point MP2 calculations, including a polarization *d* function (DZP) on the C atoms ($\alpha = 0.75$), single-point MP3, MP4-SDQ, and coupled-cluster double-excitation (CCD) calculations, using the DZV basis set. In the MP and CC procedures, all of the electrons (except the 1s core electrons of the C atoms) were correlated. The Mulliken scheme[10] has been used to compute atomic orbital and bond populations. All of the calculations were performed by using the HONDO8[11] and G92[12] programs on IBM ES/9000 and Cray C90 computers.

## Results and Discussion

**Electronic States and Metrical Parameters.** Several electronic states were investigated for the $Y(C_6H_6)_2$ complex. In particular, two states, $^4A_{2g}$ $[(e_{2g})^2(a_{1g})^1]$ (associated with the $d^2s^1$ metal electronic configuration) and $^2E_{2g}$ $[(e_{2g})^3]$ ($d^3$ metal configuration), are found to be the most stable. Moreover, calculations at the HF level of theory indicate that the $^4A_{2g}$ state is 7.1 kcal/mol more stable than the $^2E_{2g}$ state. However, the inclusion of correlation effects through the MP2 procedure yields an inverted energetic ordering and indicates that the $^2E_{2g}$ state represents the ground state (Table 1). This result agrees well with EPR and magnetic susceptibility measurements,[2b,d] which both indicate a doublet ground state. Similarly, HF calculations on the $Gd(C_6H_6)_2$ complex indicate that the $^9E_{2g}$ $[(a_{2u})^1(b_{1u})^1(b_{2u})^1(e_{1u})^2(e_{2u})^2(e_{2g})^3]$ state ($f^7d^3$ metal configuration) is less stable than the $^{11}A_{2g}$ $[(a_{2u})^1(b_{1u})^1(b_{2u})^1(e_{1u})^2(e_{2u})^2(e_{2g})^2(a_{1g})^1]$ state ($f^7d^2s^1$ metal configuration). Correlation effects reverse the energetic stability of these two states. Thus, the $^9E_{2g}$ state is found to be the most stable ($\Delta E_{MP2} = 4.2$ kcal/mol) and represents the ground state of $Gd(C_6H_6)_2$, again in agreement with magnetic susceptibility measurements.[2b]

HF-optimized geometrical parameters for the $^9E_{2g}$ state of $Gd(C_6H_6)_2$ are in good agreement with those determined by X-ray diffraction[2d] (Table 1). The calculated Gd−C bond length (2.702 Å) is only slightly longer (0.07 Å) than the experimental average value in $Gd(TBB)_2$ (2.630 Å).[2d] Previous calculations on $Cr(C_6H_6)_2$[4,13] and $Ti(C_6H_6)_2$[4] at similar levels of theory yielded a

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**Table 2. Eigenvalues (eV) and Atomic Metal Population (in Parentheses) for the Ground ($d^3$) and Lower Lying Excited ($d^2s^1$) States of $Y(C_6H_6)_2$ and $Gd(C_6H_6)_2$**

| | Y | | Gd | | |
|---|---|---|---|---|---|
| MO | $^2E_{2g}$ ($d^3$) | $^4A_{2g}$ ($d^2s^1$) | $^9E_{2g}$ ($f^7d^3$) | $^{11}A_{2g}$ ($f^7d^2s^1$) | character |
| $4e_{2u}$ | | | 20.03 (100) | 19.18 (100) | $f_{x^2z} + f_{y^2z} + f_{xyz}$ |
| $6e_{1u}$ | | | 20.04 (100) | 19.21 (100) | $f_{z^2x} + f_{z^2y}$ |
| $3b_{2u}$ | | | 20.10 (100) | 19.27 (100) | $f_{y^2x} + f_{x^3}$ |
| $2b_{1u}$ | | | 20.10 (100) | 19.29 (100) | $f_{x^2y} + f_{y^3}$ |
| $6a_{2u}$ | | | 20.12 (100) | 19.26 (100) | $f_{z^3} + f_{x^2z} + f_{y^2z}$ |
| $6a_{1g}$ | | 4.16 (100) | | 4.21 (100) | $s + d_{z^2}$ |
| $4e_{2g}$ | 3.90 (47) | 3.87 (56) | 3.87 (49) | 3.84 (50) | $d_{xy} + d_{x^2-y^2}$ |
| $5e_{1u}$ | 10.00 (2) | 10.01 (2) | 9.77 (2) | 9.72 (1) | $\pi_2 + p_x + p_y$ |
| $4e_{1g}$ | 10.41 (11) | 10.27 (7) | 10.26 (10) | 10.06 (6) | $\pi_2 + d_{xz} + d_{yz}$ |
| $5a_{2u}$ | 13.68 (9) | 14.06 (6) | 13.40 (6) | 13.66 (5) | $\pi_1 + p_z$ |
| $3e_{2u}$ | 13.58 (0) | 13.77 (0) | 13.43 (0) | 13.57 (0) | $\sigma_{C-C}$ |
| $3e_{2g}$ | 13.60 (0) | 13.78 (0) | 13.47 (0) | 13.58 (0) | $\sigma_{C-C}$ |
| $5a_{1g}$ | 14.56 (14) | 14.68 (11) | 14.36 (10) | 14.39 (8) | $\pi_1 + d_{z^2} + s$ |
| overall back-bonding interaction[a] | 1.59 | 0.88 | 1.53 | 1.00 | |
| overall ligand-to-metal interaction[a] | 0.98 | 0.70 | 0.80 | 0.54 | |

[a] See ref 16.

similar, slight overestimation of the M−C bond lengths. This represents a well-established feature of ab initio HF calculations on zerovalent metal complexes caused by underestimation of the back-bonding interactions. Thus, ground state geometry optimization at the MP2 level gives a Gd−C bond length (2.608 Å) in more favorable agreement with experiment. Unfortunately, no experimental structural data have been reported for $Y(TBB)_2$.[14] Nevertheless, considering the aforementioned limits of the HF method on $Gd(C_6H_6)_2$, an estimated 2.60 Å Y−C bond distance is certainly reasonable for the $Y(TBB)_2$ complex. The comparable Gd−C and Y−C interatomic distances are in good agreement with the similar atomic radii of Gd and Y metals.[15] The calculated C−C bond lengths in the two arene complexes are almost identical for the ground states (Table 1) and are close to the experimental value found in $Gd(TBB)_2$.[2d] Note that both calculated distances are longer (0.023 Å) than that in the calculated benzene free ligand as a consequence of the M → L back-donation (vide infra), which weakens the benzene C−C $\pi$ bonds.

The M−C bond lengths in the $^4A_{2g}$ (Y) and $^{11}A_{2g}$ (Gd) lower lying excited states of these complexes are longer (Y = 0.15 Å, Gd = 0.11 Å) than those of ground states and, hence, result in lower M−C bond orders (Table 1). This observation, together with the shorter C−C calculated bond lengths, suggests weaker M−C bonding in the $^1A_{2g}$ and $^{11}A_{2g}$ excited states.

**Electronic Structure.** The metal−arene bonding in $M(C_6H_6)_2$ can be qualitatively described in terms of synergistic ligand-to-metal donation (L → M) involving the filled $\pi_1$ and $\pi_2$ orbitals of the $(C_6H_6)_2$ ligand cluster and the empty metal orbitals of appropriate symmetry, as well as M → L back-donation from the filled metal orbitals to the virtual $\pi_3$ and $\pi_4$ $(C_6H_6)_2$ ($\pi^*$) cluster orbitals (Figure 1). Note that the ligand $\pi_1$ and $\pi_2$ orbitals all have symmetry counterparts in the metal valence AOs, while among the empty $\pi_3/\pi_4$ ligand combinations, only the $e_{2g}$ orbital can be involved in back-bonding since the remaining $(C_6H_6)_2$ cluster $\pi^*$ orbitals do not have appropriate metal orbital counterparts (Figure 1).

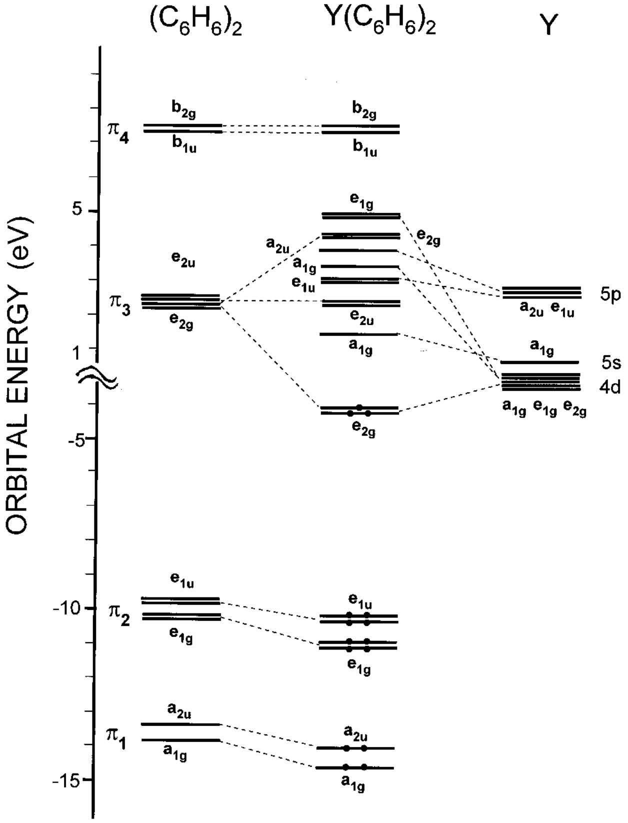

**Figure 1.** Orbital interaction diagram for the $^2E_{2g}$ state of $Y(C_6H_6)_2$.

Eigenvalues and atomic population analysis of the highest energy filled MOs associated with the $^2E_{2g}$ and $^4A_{2g}$ states of $Y(C_6H_6)_2$ are reported in Table 2. As far as the $^2E_{2g}$ ground state is concerned, the $4e_{2g}$ MO contains almost equal contributions from the $e_{2g}$ in-phase $\pi_3$ ligand and metal $4d_{xy}$, $4d_{x^2-y^2}$ orbitals. This indicates a strong M → L back-donation similar to that found for the group 4 and group 6 congeners.[4] The MOs involved in the L → M donation ($5a_{1g}$, $5a_{2u}$, $4e_{1g}$, $5e_{1u}$) are largely ligand-centered with appreciable metal participation. Similarly, in the $^4A_{2g}(d^2s^1)$ excited state (Table 2), there is evidence for M → L back-bonding ($4e_{2g}$ MO) as well as L → M donation ($5e_{1u}$, $4e_{1g}$, $5a_{2u}$, and $5a_{1g}$). In contrast, the $6a_{1g}$ orbital remains almost pure metal 5s in character because of symmetry constraints

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(14) Preliminary X-ray diffraction data reported in ref 2d indicate that $Y(TBB)_2$ is isostructural with $Gd(TBB)_2$.

(15) Emsely, J. *The Elements*, 2nd ed.; Clarendon: Oxford, 1991.

(no $\pi^*$ virtual orbitals possess $a_{1g}$ symmetry). An obvious consequence is that the metal−ligand bonding in the $^4A_{2g}(d^2s^1)$ state has a smaller back-bonding contribution (0.88 eu) than in the $^2E_{2g}(d^3)$ state (1.59 eu) (Table 2).[16] Similarly, smaller L → M donation effects are observed upon passing from the $Y(C_6H_6)_2$ $^2E_{2g}$ (0.98 eu) to the $^4A_{2g}$ (0.70 eu) state. The net result is a reduced overall metal−ligand interaction. These data are in good agreement with the longer Y−C and shorter C−C bond lengths found in the $^4A_{2g}$ state with respect to those in the $^2E_{2g}$ state (Table 1).

The population analysis for the $^9E_{2g}$ and $^{11}A_{2g}$ states of $Gd(C_6H_6)_2$ is reported in Table 2. The MO compositions are similar to those found for the $^2E_{2g}$ and $^4A_{2g}$ states of $Y(C_6H_6)_2$ in terms of both donative and back-donative interactions. Note, however, that the $4e_{2u}$−$6a_{2u}$ MOs represent the seven partially filled 4f subshells. The atomic characters indicate that they are *completely localized* on the metal atom and therefore do not take part in metal−ligand bond formation.

The present findings are in complete agreement with the earlier qualitative bonding model proposed by Cloke *et al.*[1,2b] Therefore, similar to that generally found for $Ln^{3+}$ complexes,[17] the metal−ligand bonding in zerovalent rare earth bis(arene) sandwich complexes is dominated by metal d subshells, while the 4f electrons only act as spectators. In addition, the close similarities among molecular structures found for the ground states of the present Y and Gd benzene complexes and, in particular, the comparable back-donative interactions (Tables 2) suggest that analogous metal−ligand interactions are likely operating in all of the rare earth bis(arene) complexes because of the similar radial extensions of the 5d orbitals. Therefore, in accordance with earlier arguments, the stability of these complexes[1,2b] and the differences in metal−ligand bond dissociation energies[3,4] are governed largely by atomic excitation energies.[2b,3,4]

In this context, it is interesting to compare the present results on $Y(C_6H_6)_2$ with those of the homologous zirconium complex.[4] Thus, the calculated Y−C bond length of 2.664 Å is longer than the Zr−C bond length (2.487 Å),[4] and the difference (0.177 Å) is close to the difference in atomic radii of the two atoms (0.18 Å).[15] In addition, the back-donation in $Y(C_6H_6)_2$, which is smaller than that in the zirconium homologue[4] (1.59 vs 1.92 eu), is also evident in the shorter calculated C−C bond length in $Y(C_6H_6)_2$ vs that in $Zr(C_6H_6)_2$ (1.420 vs 1.426 Å).

**Dissociation Energies.** At the HF level, the values of the metal−arene bond dissociation energies [$\bar{D}$(M−arene)][18] of both $Y(C_6H_6)_2$ and $Gd(C_6H_6)_2$ (Table 1) are indicative of unbound (relative to the ground states of $C_6H_6$ and metal starting fragments) systems. The inclusion of correlation effects, through the MP2 procedure, results in bonded states. Nevertheless, agreement with the experimental values[3,4] remains poor because only ∼42% of the experimental dissociation energy is estimated. The calculated dissociation energy for $Gd(C_6H_6)_2$ using the optimized MP2 geometry is only slightly improved (3.5 kcal/mol). Therefore, the HF geometry adopted for post-HF calculations should not significantly affect calculated dissociation energy values. The results obtained on dissociation energy of the present complexes stand in contrast to those obtained for the homologous group 4 and group 6 element zerovalent bis(arene) complexes, where the MP2 approach gave rather accurate values of dissociation energies.[4] The effects associated with the basis set and high-order correlation energies were, therefore, tested for $Y(C_6H_6)_2$ (Table 3). The inclusion of polarization functions on the carbon atoms still yielded an unbound (−0.8 kcal/mol) system. The calculated DZP/MP2 dissociation energy (38.2 kcal/mol) compares more favorably with the experimental data, even though the theoretical value is still far from the experimental value (72 kcal/mol).[4] This suggests that the discrepancies between the calculated and experimental M−arene dissociation energies are not caused by truncation of the basis set. Rather, a consistent amount of binding energy is expected to arise from high-order correlation effects. Nevertheless, the calculated MP3 (20.2 kcal/mol) and MP4-SDQ (18.4 kcal/mol) dissociation energies decrease with respect to the MP2 value and, as consequence, do not improve the agreement with the experimental data. Finally, the dissociation energy was also evaluated by using more sophisticated CCD procedures[19] within a single reference configuration approach, which, in principle, can partially resolve the degeneracy problem[19] associated with the $^2E_{2g}$ state. Nevertheless, the calculated dissociation energy (17.6 kcal/mol) is still below the experimental value.

**Table 3. Calculated Metal−Arene Dissociation Energies (kcal/mol) at Various Levels of Theory for $Y(C_6H_6)_2$**

| | SCF | MP2 | MP3 | MP4-SDQ | CCD |
|---|---|---|---|---|---|
| DZV | −3.8 | 29.8 | 20.2 | 18.4 | 17.6 |
| DZP | −0.8 | 38.2 | | | |
| exp | | 72 | | | |

It therefore appears that the discrepancies between the theoretical and experimental M−arene bond energies are partially due to the limited basis set and depend upon configuration state functions neglected when a single HF determinant is used as a reference in applying the correlated MP and CC methods to the $Y(C_6H_6)_2$ degenerate $^2E_{2g}$ ground state. In this perspective, we believe that only an *explicit treatment* of such correlation effects using multireference configuration interaction procedures, through (at least) two reference configurations, can provide more accurate results. Currently, the limitations of presently available computational resources preclude such an investigation.

## Conclusions

The present results represent the first RECP ab initio analysis of bonding and bonding energetics in zero-

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(16) An estimation of the degree of L → M and M → L interactions can be obtained by multiplying, respectively, the metal and ligand atomic contributions in the MOs involved by the electron occupation number.

(17) (a) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (b) Di Bella, S.; Gulino, A.; Lanza, G.; Fragalà, I.; Stern, D.; Marks, T. J. *Organometallics* **1994**, *13*, 3810. (c) Schumann, H. In *Fundamental and Technological Aspects of Organo f-Element Chemistry*; Marks, T. J., Fragalà I., Eds; D. Reidel: Dordrecht, The Netherlands, 1985; Chapter 1. (d) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (e) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, pp 173.

(18) $\bar{D}$(M−arene) bond dissociation energy refers to the process: $M(arene)_2$ (g) → M (g) + 2arene (g), 2*D*.

(19) See, for example: Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

valent rare earth bis(arene) complexes. They provide an appealing picture of the metal−ligand bonding for two representative M(arene)$_2$ complexes. It has been demonstrated that the bonding in both the Y and Gd complexes is very similar and is dominated by metal-to-ligand back-donation. The 4f gadolinium orbitals remain atomic in nature and do not provide significant bonding interactions with the ligands. In agreement with EPR and magnetic susceptibility measurements, the most stable electronic state of both complexes is a d$^3$ (e$_{2g}$$^3$) metal configuration. Moreover, the calculated Gd−C bond length is in good agreement with experimental diffraction data on Gd(TBB)$_2$. The low-lying excited states of both complexes are associated with a d$^2$s$^1$ [(e$_{2g}$)$^2$(a$_{1g}$)$^1$] metal configuration, which has weaker M−C$_6$H$_6$ bonding, as a consequence of reduced back-bonding interactions. The close analogies between the bonding details in Y(C$_6$H$_6$)$_2$ and Gd(C$_6$H$_6$)$_2$ suggest that comparable bonding interactions can be expected across the rare earth series. The relative stabilities of the M(TBB)$_2$ complexes are, moreover, expected to be largely governed by atomic promotion energies, in agreement with the earlier bonding model proposed by Cloke *et al.*[1,2]

In regard to quantitative analysis of bonding energetics, the calculated metal−arene bond dissociation energies remain underestimated with respect to the experimental data, despite the efforts (in terms of available computer resources) performed using CCD procedures. It is likely that the neglect of configuration state functions due the single reference configuration presently adopted in the description of the degenerate $^2E_{2g}$ and $^9E_{2g}$ states precludes more quantitative agreement. This aspect of the electronic structure remains for future investigations.

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