Modeling C_5H_5 with Atoms or Effective Group Potential in Lanthanide Complexes: Isolobality Not the Determining Factor

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DFT(B3PW91) calculations have been used to propose models for C_5H_5 (Cp) in lanthanides at a low computational cost. The H exchange reaction, $Cp_2LnH^* + H_2 \rightarrow Cp_2LnH + HH^*$, previously studied with C_5H_5 has been used as a benchmark. The Cp ligand has been replaced by H, by Cl, and also by an effective group potential (EGP). The three models give results close to that with C_5H_5 for the entire lanthanide series (La to Lu). As expected, the EGP gives the best agreement. Surprisingly, H gives better results than Cl. The electron donating ability (Cp closer to H than to Cl) is more important than isolobality (Cp and Cl).

Introduction

Lanthanide systems have attracted increasing attention in the recent years. Although experimental studies are numerous, theoretical studies on systems of chemical interest other than LnX_3[1−11] are still relatively few. Such calculations present two challenges: the metal and the ligands. Partial occupation of f orbitals has been a major difficulty for theoretical studies. Calculations have been preferentially carried out on f^0 (La) and f^{14} (Lu) although few calculations on Sm, Eu, Gd, and Yb have been published.[12−29] Limitation of the calculations to selected lanthanides has not been considered as an issue because it is currently believed that the properties of members of a lanthanide family are closely related. Indeed, 4f electrons were shown not to participate explicitly in the lanthanide−ligand bond.[30] Reactivity is supposed to be similar within a family. However, experimental proof for the entire Ln series is lacking and our recent theoretical study on hydrogen exchange (eq 1) shows that reactivity varies in a nonmonotonic way with the lanthanide within the series.[31]

$$(C_5H_5)_2Ln\text{-}H^* + H{-}H \rightarrow (C_5H_5)_2Ln\text{-}H + H^*\text{-}H \qquad (1)$$

The energy barrier varies from 0.67 to 8 kcal mol^{-1} with the smallest value around Pm and Sm. This is an important variation for an energy barrier. Similar differences in activation energies for other reactions could make a reaction feasible only for selected members of the series. No complete study can therefore be limited to only La and Lu without risking missing an important aspect of the chemistry of lanthanides. Another challenge for the calculation of lanthanide complexes is associated with the large size of the molecular systems associated with the large Ln ionic radii favoring high coordination number and bulky ligands. Under such circumstances, computational time becomes an important factor. Establishing the validity of efficient models for representative ligands becomes a key issue.

Any substituted cyclopentadienyl ligand is successfully represented by C_5H_5, but C_5H_5 is still computationally demanding. We have therefore studied various models of C_5H_5 in the reaction of eq 1, previously studied with C_5H_5, as reference. Models of C_5H_5 have been often used for transition metal complexes, and C_5H_5 is often replaced by a single atom. Schaeffer used H for C_5H_5 in Cp_2TiH_2,[32] but the most widely used model is Cl,[33−36] because C_5H_5 and Cl are isolobal: the occupied valence orbitals are a set of *a* and *e* orbitals. Quantitative differences could still be important: the difference in the energy of the Cp and Cl occupied orbitals and the difference in the overlap of these orbitals with Ln, both indicative of different electron donating power and a total lack of back-bonding in the case of Cl. Failures in the replacement of Cp by Cl have been noted. In $Cp_2M(H_3)$ (M = Nb, Ta), the replacement of Cp by Cl lead to a hydrido/dihydrogen structure being preferred over the experimentally observed trihydride complex as expected from the lower electron donating ability of Cp complex.[37,38] Recent work by Rappé and co-workers on the reaction of $CpReO_3$ to olefins has shown that the replacement of Cp by Cl lead to wrong thermodynamic values.[39] Successful modeling of Cp by Cl is also limited to d^0 complexes, and failure has been found for d^2 complexes.[40] This also suggests that Cl will not be an appropriate model for Cp for any reaction with change in the metal oxidation state. Despite failures, successes have been obtained, and trends are usually properly represented with Cl. This suggests that modeling Cp can be of some use in the case of lanthanide complexes where the d^0 configuration is dominant and where reactions occur without change in oxidation state.

The effective group potential (EGP) has been recently suggested as an alternative way to model ligands,[41−43] and EGPs for CH_3, SiH_3, NH_3, PH_3, and η^5-C_5H_5 have been established. The EGP has been used in a number of systems.[44] In an EGP, a group of atoms is replaced by fictitious atoms associated with energy levels and orbitals necessary for representing the metal−ligand bond. Thus, CH_3 is represented by a fictitious atom with

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TABLE 1: Geometrical Parameters for H_2LnH Complexes

lanthanide center	r(Ln−L)/ Å	r(Ln−H)/ Å	α(L−Ln−L)/ degrees	Σ/ degrees
La	2.12	2.12	111	333.1
Ce	1.94	1.94	112	335.1
Pr	2.08	2.08	111	333.1
Nd	2.07	2.07	111	333.0
Pm	2.06	2.06	111	334.1
Sm	2.04	2.04	111	334.5
Eu	2.33	2.33	120	360.0
Gd	2.02	2.02	112	336.6
Tb	2.01	2.01	111	333.9
Dy	2.00	2.00	113	340.8
Ho	1.99	1.99	114	343.2
Er	1.98	1.98	115	345.6
Tm	1.97	1.97	116	348.9
Yb	2.24	2.24	120	360.0
Lu	1.96	1.96	118	354.9

a single electron in an sp orbital and an operator in the Hamiltonian which describes properly the metal−Me bonding. In this work, we compare the explicit C_5H_5 ligand to three models: H, Cl, and EGP to represent the essential features of the reaction in eq 1, previously studied with C_5H_5. Reaction 1 is an especially challenging benchmark for models because of the flatness of the potential energy surface.

Computational Details

In previous studies, we have shown that lanthanide elements could be represented with the Stuttgart large core pseudopotential (ECPs).[45−47] This large core includes the f electrons, and the valence orbitals are represented by the optimized basis set associated with the ECP augmented by a set of polarization f functions. For Cl, the 10 inner electrons have been represented by an ECP[48] and the valence electrons by the basis set associated with the ECP augmented by a set of d polarization functions.[49] The carbon and H have been represented by 6-31 G** basis sets.[50] The effect of C_5H_5 has been mimicked by five electrons allowed to occupy the space spanned by p atomic orbitals ($\alpha = 0.312\,463\,2$) centered at the edges of a pentagonal ring. The previously published multicenter EGP has been recently improved.[44] The main improvement is based on the fact that the EGP has now been extracted from an isolated cylopentadienyl anion to force the electrons to occupy three π orbitals analogous to the π orbitals of $C_5H_5^-$. Test calculations have been carried out on $(C_5H_5)MH_4$ (M = V, Ta, and Nb). In the case of the EGP, constraints (Ln−EGP distance and EGP−Ln−EGP angles equal to experimental values) have been introduced during the geometry optimization process. All calculations have been carried out with the Gaussian 98 set of programs[51] modified to incorporate the EGP. The DFT method was used with the B3PW91 hybrid functional.[52,53] The nature of the extrema (minima and transition states) was assigned using analytical frequency calculations.

Results and Discussions

a. Reagents: X_2LnH (L = H, Cl) vs Cp_2LnH. The geometrical parameters for the comparison between X_2LnH (X = H, Cl) and Cp_2LnH concern the Ln−H bond length and the X−Ln−H and X−Ln−H angles. The data are shown in Tables 1−3. In the case of C_5H_5, the centroid of the ring is used for defining measurements. This comparison separates artificially one H in the case of $H_2Ln{-}H$ as in the study of TiH_4 as a model of Cp_2TiH_2.[32] The three systems, X_2LnH (X = H, Cl) and Cp_2LnH,[31] have similar structures. The Ln center is in a trigonal pyramidal coordination or in a trigonal planar geometry depending on the lanthanide, but the bond angles vary with X. The X−Ln−X angle increases with the steric bulk of X: H < Cl < Cp. Trends within the lanthanide series are similar for the three systems. There is a tendency for the X−Ln−X angle to be slightly larger for late lanthanides. The singularity for Ce(IV) for which the bond angles are the smallest is presented for the two models (H, Cl). The degree of pyramidalization of Ln, given by the sum $\sum$ of the angles (X−Ln−X + 2 X−Ln−H) follows similar variations for the three systems. Thus, the presence of an empty coordination site at the lanthanide, key to the chemical properties of Cp_2LnH, is present in the two models.

TABLE 2: Geometrical Parameters for Cl_2LnH Complexes

lanthanide center	r(Ln−L)/ Å	r(Ln−H)/ Å	α(L−Ln−L)/ degrees	Σ/ degrees
La	2.61	2.10	118	337.5
Ce	2.43	1.94	103	296.4
Pr	2.57	2.07	119	338.9
Nd	2.55	2.05	117	337.7
Pm	2.54	2.04	119	339.7
Sm	2.53	2.02	120	340.3
Eu	2.77	2.27	123	360.0
Gd	2.50	2.00	121	344.3
Tb	2.49	1.99	122	346.1
Dy	2.48	1.98	122	347.9
Ho	2.47	1.97	123	349.7
Er	2.45	1.96	124	352.0
Tm	2.45	1.96	126	359.3
Yb	2.68	2.18	123	360.0
Lu	2.43	1.94	125	359.2

TABLE 3: Geometrical Parameters for Cp_2LnH Complexes

lanthanide center	r(Ln−X)/ Å	r(Ln−H)/ Å	α(X_1−Ln−X_2)/ degrees	Σ/ degrees
La	2.50	2.14	134	336.8
Ce	2.32	1.96	130	317.8
Pr	2.46	2.11	137	343.3
Nd	2.44	2.10	138	346.1
Pm	2.43	2.09	139	349.9
Sm	2.42	2.08	140	353.0
Eu	2.66	2.33	130	360.0
Gd	2.39	2.06	141	359.9
Tb	2.38	2.04	141	360.0
Dy	2.37	2.03	141	360.0
Ho	2.36	2.02	141	360.0
Er	2.34	2.00	140	360.0
Tm	2.34	1.99	140	360.0
Yb	2.59	2.22	131	360.0
Lu	2.32_5	1.97	140	360.0

A qualitative but useful parameter to compare the two models to $Cp_2Ln{-}H$ is the Mulliken charge on the X ligands; it averages −0.27 for X = H, −0.56 for X = Cl, and −0.26 for X = Cp which follows the electronegativity of X. Cp and H are equivalent electron donors to the lanthanide, whereas Cl is notably lesser so. The lanthanide is thus more charged with Cl which accounts for slight lengthening of the Ln-H bond in the order Cl < H < Cp. The difference in Ln−H bond length in $X_2Ln{-}H$ with respect to the reference $Cp_2Ln{-}H$ system remains small because it is less than 0.03% (X= H) and 0.06% (X = Cl). The geometry of the reagents are thus close for the three systems.

b. Transition States X_2LnH_3 (X = H, Cl) vs Cp_2LnH_3. Selected parameters are shown in Tables 4−6 where the mean square deviation Δ to the C_5H_5 model[5] gives an estimate of the adequacy of the replacement of C_5H_5 by a model. As shown previously, the transition state for the H exchange in eq 1 is best viewed as an almost linear H_3^- ligand in interaction with a cationic X_2Ln^+ fragment (Figure 1). Remarkably, the transition

TABLE 4: Selected Distances for the Hydrogen Exchange Transition State, $H_2Ln(H_3)$

Ln	r_e(Ln−H$_A$)	r_e(Ln−H$_B$)	r_e(Ln−H$_C$)	r_e(H$_A$−H$_B$)	r_e(H$_B$−H$_C$)
La	2.264	2.251	2.264	1.027	1.027
Ce	2.141	2.140	2.089	0.902	1.221
Pr	2.229	2.213	2.229	1.027	1.027
Nd	2.214	2.196	2.214	1.027	1.027
Pm	2.201	2.181	2.200	1.028	1.029
Sm	2.187	2.166	2.187	1.029	1.029
Eu	2.433	2.340	2.434	1.047	1.047
Gd	2.163	2.139	2.163	1.030	1.030
Tb	2.151	2.125	2.151	1.031	1.032
Dy	2.140	2.113	2.140	1.032	1.032
Ho	2.128	2.100	2.129	1.033	1.033
Er	2.118	2.088	2.118	1.034	1.034
Tm	2.108	2.077	2.109	1.035	1.035
Yb	2.367	2.261	2.366	1.051	1.052
Lu	2.090	2.056	2.090	1.036	1.036
δ(%)	−0.10	+0.28	−0.23	+0.21	−0.08

TABLE 5: Selected Distances for the Hydrogen Exchange Transition State, $Cl_2Ln(H_3)$

Ln	r_e(Ln−H$_A$)	r_e(Ln−H$_B$)	r_e(Ln−H$_C$)	r_e(H$_A$−H$_B$)	r_e(H$_B$−H$_C$)
La	2.247	2.243	2.247	1.027	1.027
Ce	2.429	2.391	1.975	0.775	1.863
Pr	2.210	2.202	2.211	1.027	1.028
Nd	2.194	2.184	2.195	1.027	1.029
Pm	2.179	2.168	2.180	1.028	1.030
Sm	2.165	2.151	2.166	1.029	1.030
Eu	2.379	2.295	2.380	1.046	1.046
Gd	2.138	2.121	2.140	1.031	1.031
Tb	2.125	2.106	2.127	1.032	1.033
Dy	2.113	2.092	2.114	1.033	1.033
Ho	2.101	2.078	2.102	1.034	1.034
Er	2.089	2.064	2.090	1.035	1.035
Tm	2.079	2.051	2.080	1.037	1.036
Yb	2.308	2.209	2.307	1.051	1.052
Lu	2.059	2.029	2.060	1.039	1.038
δ(%)	−0.43	+0.10	−1.77	−0.67	+3.51

TABLE 6: Selected Distances for the Hydrogen Exchange Transition State, $Cp_2Ln(H_3)$

Ln	r_e(Ln−H$_A$)	r_e(Ln−H$_B$)	r_e(Ln−H$_C$)	r_e(H$_A$−H$_B$)	r_e(H$_B$−H$_C$)
La	2.276	2.262	2.294	1.015	1.043
Ce	2.149	2.148	2.099	0.897	1.214
Pr	2.239	2.220	2.254	1.023	1.035
Nd	2.229	2.202	2.230	1.028	1.030
Pm	2.212	2.183	2.213	1.029	1.031
Sm	2.196	2.166	2.197	1.029	1.031
Eu	2.427	2.327	2.427	1.047	1.047
Gd	2.169	2.134	2.170	1.030	1.031
Tb	2.153	2.117	2.154	1.031	1.031
Dy	2.140	2.102	2.141	1.031	1.032
Ho	2.127	2.087	2.128	1.031	1.032
Er	2.114	2.073	2.115	1.032	1.032
Tm	2.103	2.060	2.104	1.032	1.032
Yb	2.350	2.237	2.350	1.049	1.050
Lu	2.083	2.037	2.084	1.033	1.033

state does not have C_{2v} symmetry for early lanthanide as central H_B is not equidistant to external H_A and H_C.

For the two models, the Ln−H_A(H_C) are found to be shorter (negative δ), whereas the Ln−H_B is found to be longer (positive δ) than with Cp. As expected from the higher positive charge on lanthanide for X = Cl, and the almost identical charge for X = H and Cp, δ is larger for X = Cl than H but remains small (<2%). Because of the flat potential energy surface (see below), the H_A−H_B and H_B−H_C distances are challenging to reproduce. The two models reproduce well the strong asymmetric transition state for Ce(IV) which is best described as hydride/dihydrogen complex. None of the models reproduce the very small asymmetry for La and Pr (probably not even significant with Cp). It thus appears that the geometries are well reproduced with the two models because $\delta < 1\%$ for the Ln−H bonds and $\delta < 4\%$ for the $H_B\cdots H_A$ or $H_B\cdots H_C$ bonds. This is satisfying because the energy barrier is small and therefore the potential energy surface is flat.

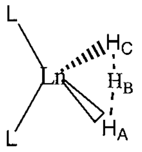

Figure 1. Structure of the transition state.

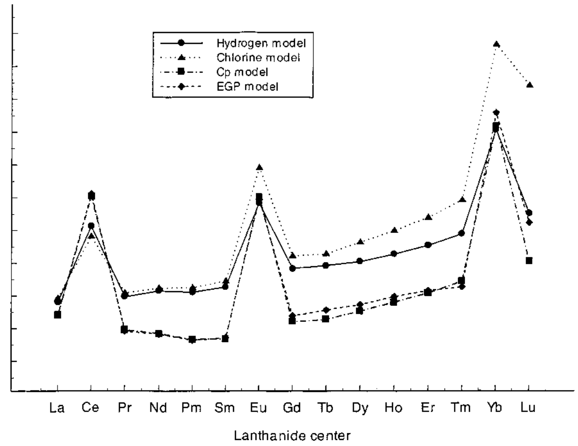

Figure 2. Variation of the energy barrier (kcal mol^{-1}) in the entire lanthanide series for the three different models.

TABLE 7: Hydrogen Exchange Energy Barrier for the Three Different L Ligand in kcal mol^{-1}

lanthanide center	$\Delta E^{\#}$(H_2)	$\Delta E^{\#}$(Cl_2)	$\Delta E^{\#}$(Cp_2)
La	1.81	1.93	1.41
Ce	4.12	3.81	5.05
Pr	1.97	2.09	0.96
Nd	2.15	2.24	0.85
Pm	2.11	2.25	0.67
Sm	2.28	2.46	0.69
Eu	4.84	5.92	5.03
Gd	2.84	3.22	1.21
Tb	2.93	3.29	1.28
Dy	3.05	3.64	1.54
Ho	3.28	4.00	1.81
Er	3.55	4.40	2.09
Tm	3.90	4.94	2.45
Yb	7.09	9.68	7.20
Lu	4.54	8.43	3.06

c. Activation Energies for the H Exchange Reaction. The energy barrier is the difference in energy ΔE (Table 7) between the separated reagents (X_2LnH and H_2) and the transition state because no H_2 adducts were located as minimum in the case of Cp. The small activation energies obtained for the whole lanthanide series with Cp is also qualitatively reproduced with the two models. Energy barriers are higher by as much as 3 kcal mol^{-1} with respect to the reference Cp system (Figure 2). The variation of activation energies with the lanthanide is qualitatively well reproduced. The smallest activation energies are obtained for Pm for Cp and Pr (next to Pm) for Cl and H. The energy barrier is the highest for X = Cl and is lower for H and then for Cp. This closely follows again the electronegativity of X. More electron donating X (Cl < H < Cp) increases the hydridic character in the reactant as noted earlier.[31] A notable exception to the order in the activation barriers is obtained for Ce(IV) for which the energy barrier increases in the order Cl

TABLE 8: Geometrical Parameters for Cp_2LnH Complexes (EGP case)

lanthanide center	*r*(Ln−X)/ Å	*r*(Ln−H)/ Å	α(X_1−Ln−X_2)/ degrees	Σ/ degrees
La	2.50	2.25	134	348.3
Ce	2.32	1.99	130	327.4
Pr	2.46	2.21	137	353.3
Nd	2.44	2.20	138	355.5
Pm	2.43	2.18	139	357.4
Sm	2.42	2.14	140	359.3
Eu	2.66	2.40	130	360.0
Gd	2.39	2.14	141	360.0
Tb	2.38	2.12	141	360.0
Dy	2.37	2.11	141	360.0
Ho	2.36	2.10	141	360.0
Er	2.34	2.09	140	360.0
Tm	2.34	2.07	140	360.0
Yb	2.59	2.29	131	360.0
Lu	2.32_5	2.05	140	360.0

TABLE 9: Selected Distances for the Hydrogen Exchange Transition State, $Cp_2Ln(H_3)$, Calculated with the Effective Group Potential

Ln	$r_e(Ln-H_A)$	$r_e(Ln-H_B)$	$r_e(Ln-H_C)$	$r_e(H_A-H_B)$	$r_e(H_B-H_C)$
La	2.284	2.257	2.299	1.015	1.043
Ce	2.127	2.156	1.128	1.027	1.028
Pr	2.286	2.250	2.286	1.041	1.042
Nd	2.265	2.229	2.265	1.041	1.042
Pm	2.246	2.209	2.246	1.042	1.042
Sm	2.229	2.192	2.229	1.042	1.042
Eu	2.516	2.392	2.516	1.061	1.061
Gd	2.199	2.158	2.199	1.042	1.042
Tb	2.182	2.141	2.183	1.042	1.042
Dy	2.168	2.125	2.168	1.043	1.043
Ho	2.148	2.103	2.148	1.043	1.043
Er	2.139	2.095	2.141	1.043	1.044
Tm	2.128	2.081	2.129	1.044	1.044
Yb	2.434	2.301	2.434	1.064	1.064
Lu	2.106	2.057	2.107	1.044	1.045
δ(%)	+1.45	+1.20	+1.55	+2.04	−0.06

< H < Cp. The electron donating group stabilizes more the cationic highly unsaturated $X_2Ce(H)^+$ reagent. The main conclusion is that despite some small differences within the lanthanide family the most important reactivity aspects (geometry of reagents and transition states, geometry of transition state) are properly represented by the two models. The lowest barriers are obtained for Cp, with the exception of the Ce(IV) case. Interestingly, despite the isolobality between Cl and Cp, the hydride gives results closer to that of Cp in this reaction. We associate this with the similar electron donating ability of Cp and H to a lanthanide ion. The electron donating ability of X appears as an important factor for modeling the spectator Cp ligand. This leads us to investigate the replacement of Cp by an effective group potential which reproduces with high accuracy the group electron donating ability.

d. EGP vs Cp. The calculations were carried out for the whole lanthanide series. The geometrical optimization leads to Ln−H only 0.10 Å longer than with real Cp (Table 8). The degree of pyramidalization Σ is found to be in excellent agreement with the real Cp value, where the planar shape is preferred from Gd to Lu. The agreement for the geometry of the transition states is also excellent for all variables. Even the difficult distances to reproduce, H_A-H_B and H_B-H_C, are obtained with an accuracy of 2% (Table 9). The activation barriers (Table 10) deviate from the values calculated with Cp by only 0.4 $kcal.mol^{-1}$ (average value vs the 2−3 $kcal\ mol^{-1}$ deviation with X = H, Cl). In particular, the EGP and Cp calculations lead to the same behavior for the activation barrier (Figure 2). The minimum activation barrier is found for the same atom, Pm. The significant improvement in reproducing the effect of Cp (in comparison to H or Cl) is clearly because the EGP is constructed to reproduce precisely the electronic properties of Cp. Bond lengths obtained with the EGP are slightly longer than those with the other model, but the activation barriers are found to be better with the EGP than with the other models. This means that the electronic effects are keys to calculations of proper activation barrier. Because the use of EGP is also computationally efficient (computational time ratio EGP/Cp = 5), it is a promising technique to investigate further.

TABLE 10: Hydrogen Exchange Energy Barrier with Explicit Cp Ligand and EGP in kcal mol^{-1}

lanthanide center	$\Delta E^{\#}(Cp_2)$	$\Delta E^{\#}(Cp^{\#}_2)$
La	1.41	1.43
Ce	5.05	5.12
Pr	0.96	0.92
Nd	0.85	0.83
Pm	0.67	0.64
Sm	0.69	0.72
Eu	5.03	4.95
Gd	1.21	1.39
Tb	1.28	1.57
Dy	1.54	1.73
Ho	1.81	1.98
Er	2.09	2.16
Tm	2.45	2.28
Yb	7.20	7.60
Lu	3.06	4.24

Conclusions

The present studies show that replacements of Cp by H or Cl reproduce the essential geometrical and energetic aspects of the simple metathesis reaction $Cp_2Ln-H^* + H_2 \rightarrow Cp_2Ln-H + H-H^*$. This is a challenging system to reproduce because the energy barrier is low and the potential energy surface is flat for the whole reaction path. Deviations from the Cp case are small, and trends are fairly well reproduced. Both models show that the lowest energy barrier is obtained not far from the middle of the lanthanide series, but they do not agree fully on which lanthanide gives the lowest barrier (Pm for Cp and Pr for H and Cl). In contrast to what could have been anticipated, the best replacement for Cp is not the isolobal Cl atom but is H. A factor more important than isolobality appears to be the electron donating ability of X. Cp and H have similar electron donating properties with respect to lanthanide, whereas Cl is too much of an electron acceptor. Some test calculations with EGP for representing Cp gives very promising results with competitive computational times. This is an interesting line for further research especially if EGPs for a variety of time demanding substituted cyclopentadienyl are established.

References and Notes

(1) Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Angew. Chem., Int. Ed*. **1999**, *38*, 1086.

(2) Cundari, T. R.; Sommerer, S. O.; Strohecker, L. A.; Tipett, L. *J. Chem. Phys*. **1995**, *103*, 7058.

(3) Gutowski, M.; Boldyrev, A. I.; Simons, J.; Rak, J.; Blazejowski, J. *J. Am. Chem. Soc*. **1996**, *118*, 1173.

(4) Adamo, C.; Maldivi, P. *Chem. Phys. Lett*. **1997**, *268*, 61.

(5) Adamo, C.; Maldivi, P. *J. Phys. Chem. A* **1998**, *102*, 6812.

(6) Hargittai, M. *J. Phys. Chem. A* **1999**, *103*, 7552.

(7) Adamo, C.; Maldivi, P. *J. Phys. Chem. A* **1999**, *103*, 7554.

(8) Hartwig, R.; Koch, W. *Chem. Eur. J*. **1999**, *5*, 312.

(9) Adamo, C.; Barone, V. *J. Comput. Chem*. **2000**, *21*, 1153.

(10) Groen, C. P.; Oskam, A.; Kovacs, A. *Inorg. Chem*. **2000**, *39*, 6001.

(11) Hong, G.; Dolg, M.; Li, L. *Chem. Phys. Lett*. **2001**, *334*, 396.

(12) Kaupp, M.; Schleyer P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc*. **1992**, *114*, 8202.

(13) Kaupp, M.; Schleyer P. v. R. *Organometallics* **1992**, *11*, 2765.

(14) Strout, D. L.; Hall, M. B. *J. Phys. Chem*. **1996**, *100*, 18007.

(15) Cosentino, U.; Demetrio, P.; Calabi, L.; Maiocchi, A. *THEOCHEM* **1997**, *392*, 75.

(16) Wu, Z. J.; Meng, Q. B.; Zhang, S. Y. *Chem. Phys. Lett*. **1997**, *267*, 271.

(17) Roszak, S.; Balasubramanian, K. *Chem. Phys. Lett.* **1997**, *264*, 80.

(18) Dehnen, S.; Burgstein, M.; Roesky, P. W. *J. Chem. Soc., Dalton Trans*. **1998**, 2425.

(19) Broclawik, E.; Eilmes, A. *J. Chem. Phys*. **1998**, *108*, 3498.

(20) Boehme, C.; Wipff, G. *Inorg. Chem*. **1999**, *38*, 5734.

(21) Boehme, C.; Wipff, G. *J. Phys. Chem*. **1999**, *103*, 6023.

(22) Schurhammer, R.; Erhart, V.; Troxler, L.; Wipff, G. *J. Chem. Soc., Perkin Trans 2* **1999**, 2423.

(23) Gang, H. G.; Li, L. M. *Theor. Chem. Acc* **1999**, *102*, 121.

(24) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, P. H. M. *J. Am. Chem. Soc*. **1999**, *121*, 1381.

(25) Hong, G.; Dolg, M.; Li, L. *Int. J. Quantum Chem*. **2000**, *80*, 201.

(26) Akasaka, T.; Wakahara, T.; Nagase, S.; Kobayashi, K.; Waelchi, M.; Yamamoto, K.; Kondo, M.; Shirakura, S.; Okubo, S.; Maeda, Y.; Kato, T.; Kako, M.; Nakadaira, Y.; Nagahata, R.; Gao, X.; Van Caemelbecke, E.; Kadish, K. M. *J. Am. Chem. Soc*. **2000**, *122*, 9316.

(27) Hieringer, W.; Eppinger, J.; Anwander, R.; Herrmann, W. A. *J. Am. Chem. Soc*. **2000**, *122*, 11983.

(28) Tobish, S.; Nowak, T.; Bogel, H. *J. Organomet. Chem*. **2001**, *619*, 24.

(29) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans*. **1997**, 1.

(30) Maron, L.; Eisenstein, O. *J. Phys. Chem. A* **2000**, *104*, 7140.

(31) Maron, L.; Eisenstein, O. *J. Am. Chem. Soc.* **2001**, *123*, 1036.

(32) Thomas, J. R.; Quelch, G. E.; Seidi, E. T.; Schaeffer, H. F., III. *J. Chem. Phys.* **1992**, *96*, 6857.

(33) Ziegler, T.; Folga, E. *J. Am. Chem. Soc.* **1993**, *115*, 636.

(34) Steigerwald, M. L.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 308.

(35) Folga, E.; Ziegler, T. *Can. J. Chem.* **1992**, *70*, 333.

(36) Hyla-Krispin, I.; Silveiro, S. J.; Niu, S.; Gleiter, R. *J. Mol. Catal. A* **1997**, *115*, 183.

(37) Barthelat, J. C.; Daudey, J. P.; De Loth, J. P.; Poilblanc, R. *J. Am. Chem. Soc.* **1991**, *113*, 9896.

(38) Camanyes, S.; Maseras, F.; Moreno, M.; Lledos, A.; Lluch, J. M.; Bertran, J. *J. Am. Chem. Soc.* **1996**, *118*, 4617.

(39) Pietsch, M. A.; Russo, T. V.; Murphy, R. B.; Martin, R. L.; Rappé, A. K. *Organomettalics* **1998**, *17*, 2716.

(40) Sini, G.; Macgregor, S. A.; Eisenstein, O.; Teuben, J. H. *Organometallics* **1994**, *13*, 1049.

(41) Alary, F.; Poteau, R.; Heully, J. L.; Barthelat, J. C.; Daudey, J. P. *Theor. Chem. Acc.* **2000**, *104*, 174.

(42) Poteau, R.; Ortega, I.; Alary, F.; Ramirez Solis, A.; Barthelat, J. C.; Daudey, J. P. *J. Phys. Chem. A* **2001**, *105*, 198.

(43) Poteau, R.; Alary, F.; Abou El Makarim, H.; Heully, J. L.; Barthelat, J. C.; Daudey, J. P. *J. Phys. Chem. A* **2001**, *105*, 206.

(44) Alary, F.; Poteau, R.; Heully, J. L.; Maron, L.; Daudey, J. P.; Trinquier, G. To be submitted.

(45) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173.

(46) Dolg, M.; Fulde, O.; Küchle, W.; Neumann, C.-S.; Stoll, H. *Chem. Phys.* **1991**, *94*, 3011.

(47) Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1993**, *85*, 441.

(48) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(49) Maron, L.; Teichteil, C. *Chem. Phys.* **1998**, *237*, 105.

(50) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(52) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(53) See, for example: Burke, K.; Perdew, J. P.; Yang, W. In *Electronic Density Functional Theory: Recent Progress and New Directions*; Ed. Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: New York, 1998.