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A Theoretical Study of Divalent Lanthanide (Sm and Yb) Complexes with a Triazacyclononane-Functionalized Tetramethylcyclopentadienyl Ligand

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A density functional theory (DFT) study of the divalent lanthanide complexes [$C_5Me_4SiMe_2(^iPr_2$-tacn)]LnI (Ln = Sm, Yb; tacn = 1,4-diisopropyl-1,4,7-triazacyclononane) is presented. A methodological study was done with various density functionals that employ large-core ECPs for the lanthanide atoms. The DFT results were compared with recent experimental X-ray structures for the compounds investigated here. The B3PW91 functional was found to give the best description of the complexes at an affordable level of computational effort. The geometry of the [$C_5Me_4SiMe_2(^iPr_2$-tacn)]LnI complexes was found to be a distorted trigonal bipyramidal and the essential structural features are correctly reproduced from the DFT calculations. Further model studies show that the computations can be simplified by replacing the methyl groups (which do not interact with the lanthanide center directly) with hydrogen atoms to still provide reasonable predictions for the structure of the complex.

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Introduction

The potential applications in organometallic chemistry of lanthanide complexes have stimulated a growing realization of the novel properties and chemical reactivity of lanthanide compounds. This has led to increasing attention being paid to the coordination chemistry of lanthanide compounds.[1−8] Considerable interest has been shown toward lanthanide alkyl and hydrides and most of these complexes can be stabilized by cyclopentadienyl groups, and these types of complexes have been the topic of most studies recently reported.[1−7,36,51−55] Besides the studies on the complexes of lanthanide with cyclopentadienyl and related ligands, some chelate complexes including some with a multiple bond between the lanthanide and the nonmetal atom (C and N, for example) have also been of interest.[9,10] Cavell and coworkers[9] explored the complex of samarium bound to the bis(iminophosphorano)methane group, which works as a dianionic carbene ligand system (Sm=C), and compared it to the complex in which samarium is bound to the dicyclohexylamino group. A compound containing a Sm_2N_2 core, which is connected to a discrete imido functionality, was reported recently.[11] The interactions between one Sm and the two bridging N were described as Sm=N_{br} (2.153 Å) and Sm−N_{br} (2.271 Å) bonds for the [(μ-ArN)Sm(μ-NHAr)(μ-Me)$AlMe_2$]$_2$ species. The chemical reactivity of several lanthanide complexes has also been explored by some research groups.[46,56,57]

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An improved understanding of the bonding between the lanthanide and substituents is important to better understand the structures, properties, and chemical reactivity of lanthanide compounds. Compared to the number of experimental studies, the number of theoretical studies for lanthanide complexes is limited, especially calculations for larger complexes. This sparse number of theoretical studies is probably due to the high computational effort for such calculations and the difficulty in dealing with the 4f electrons that can result in high spin configurations for lanthanide complexes. The treatment of the 4f orbital is still a subject of considerable challenge. Generally it is believed that 4f electrons contribute little in the bond formation and cleavage in many lanthanide complexes, so it is possible to deal with the 4f orbitals by employing effective core potentials (ECPs). To date there are not many theoretical studies on lanthanide (Sm or Yb) complexes and most of the studies concentrate on trivalent lanthanide species[11,15−17,49−51] and investigations for divalent lanthanide complexes are even rarer.[14]

Stoll and co-workers[14] carried out theoretical calculations for lanthanocenes ($Ln^{(II)}$) by employing the ECPs for lanthanide species developed by the Stuttgart−Dresden group[12,13] and found that the 4f shell of the lanthanide atom contributes little to the chemical bonding of these complexes. A preference for bent sandwich structures was determined for the $SmCp_2$ complex while linear structures were calculated for the Cp_2Yb species at the MP2 level of theory. Further systematic investigations for the $Ln^{(III)}[N(SiR_3)]_3$ (R = H, SiH_3) systems by Maron and Eisenstein[15] confirmed that there is little difference between the calculated structures when the 4f orbitals are treated as either core or valence shell orbitals. An admixture of 5d orbitals of Sm in the bonding was observed from Mulliken analysis for the $Sm^{(III)}[CH(SiH_2CH_3)(SiH_3)]_3$ complex.[17] The contribution of the 5d orbital was also found in the Sm−N bond[11] and this indicates that the donation of electrons to the 5d orbital of the lanthanide plays an important role in the bonding of some lanthanide complexes.

Recently Arnold and co-workers[19] reported new divalent lanthanide complexes for Sm and Yb containing a single Cp* (Cp* = $CpMe_4$) moiety and a second alkyl group of a neutral, tridentate triazacyclononane moiety. These species exhibited intriguing properties and suggest it is possible to considerably tune the reactivity of lanthanide complexes. Here we present a density functional theory (DFT) study on these two newly discovered divalent lanthanide complexes by employing different functionals that have been shown to be successful in describing the structures and reaction mechanisms for species in organic chemistry and employed in exploring the reactivity of transition metal species. A model exploration is also presented here for these divalent lanthanide complexes by replacing the methyl groups with hydrogen atoms to simplify the DFT computations.

Computational Details

The Gaussian98 suite[20] was used to studied the divalent lanthanide metal complexes with a triazacyclononane-functionalized tetramethylcyclopentadienyl ligand ($[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]LnI$, Ln = Sm, Yb; tacn = 1,4-diisopropyl-1,4,7-triazacyclononane) and the results from these calculations were compared to recent experimental X-ray crystal structures.[19] The large-core quasirelativistic effective core potentials (RECPs) optimized by the Stuttgart−Dresden group[12] were employed for lanthanide centers. That is, 4f electrons ($4f^6$ for Sm(II) and $4f^{14}$ for Yb(II), which are generally believed not to play important roles in bond formation or cleavage) are included in the core shell (fixed $[Kr]4d^{10}4f^6$-core for Sm(II) and $[Kr]4d^{10}4f^{14}$-core for Yb(II)) while 5s, 5p, and 6s electrons are explicitly considered in the valence shell. The corresponding 10-electron valence basis set was used for the divalent lanthanide atom and it was contracted as [7s6p5d]/(5s4p3d) with a supplement of an *f* function (with an exponent of 0.2776 for Sm and 0.306 for Yb).

Lanl2DZ RECPs[21] were employed for Si and I combined with their corresponding optimized valence basis sets and each was supplemented by a d function (with an exponent of 0.262 for Si and 0.266 for I, respectively) and so the basis set is contracted as [3s3p1d]/(2s2p1d). A 6-31G basis set[22] with one d polarization function on C and N was exclusively used on the C, N, and H atoms and the composite basis set, including C, N, H, Ln(large-core RECPs), and Si, I is denoted as BS1. This basis set is comprised of 517 basis functions contracted from 1005 primitive Gaussians for the full molecule. The effect of the d polarization function on C and N was also explored by comparison of the results from computations done with/without d polarization on the C and N atoms to the corresponding geometrical parameters from X-ray diffraction. The

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(43) $R_{\text{Yb−N}} = 2.331(13)$ Å[29] and $R_{\text{cov}}(\text{N}) = 0.75$ Å, so $R_{\text{cov}}(\text{Yb}) = 1.58$ Å. According to the relationship $R_{\text{vdW}} = R_{\text{cov}} + 0.80$,[40] $R_{\text{vdW}}(\text{Yb}) = 2.38$ Å.

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composite basis set with no d polarization functions imposed on the C and N atoms is denoted as BS2.

In addition, to estimate the contribution of the 4f orbitals in the bonding of the lanthanide complexes studied, computations were also performed that employed small-core RECPs combined with their corresponding optimized basis sets[13] for the Sm and Yb atoms. The small-core RECPs were also developed by the Stuttgart−Dresden group and the valence orbital of the lanthanide atom was expanded to $n = 4$, 5, 6 shells, that is, the 4f orbitals were explicitly included in the valence shell. One g function was added to the optimized basis set and so it was contracted as [32s19p9d8f1g]/[5s5p4d3f1g] for Sm and [32s17p8d8f1g]/[5s5p4d3f1g] for Yb. This basis set is comprised of 548 basis functions contracted from 1178 primitive Gaussians for the full molecule.

Geometry optimizations were performed without any symmetry constraint. A nonplanar structure for the Cp* ring (or Cp in the model compounds) was assumed. The ring was distorted by less than 1° so that the symmetry of the Cp* moiety was broken without much disturbance to the electronic structure. Ab initio (HF) and DFT (BLYP, B3LYP, BH&HLYP, and B3PW91) functionals were employed to perform the geometry optimization of the divalent lanthanide metal complexes. A direct comparison with experimental geometrical parameters was done to determine the deviation of the computational results at different levels of theory.

Results and Discussion

The rich reaction chemistry of divalent organolanthanide complexes coming from the accessibility of the Sm(II)/Sm(III) couple[23−25] has received much attention and many new complexes were produced, such as Cp_2Sm and $Cp_2Sm(THF)_2$,[26,27] $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$,[28] $[(Me_3Si)_2NSm(\mu\text{-}I)(DME)(THF)_2]_2$ (DME = dimethoxyethane),[29] etc. The successful incorporation of a single cyclopentadienyl (denoted as Cp) ligand that is linked to a neutral tridentate triazacyclononane moiety to the divalent Ln complexes[19] was recently reported. These complexes provide an interesting reference that encouraged us to theoretically explore the use of DFT methods to describe the structure and bonding in lanthanide chemistry.

This elegant work by Arnold and co-workers[19] obtained two X-ray diffraction structures of divalent lanthanide complexes that showed they had a distorted trigonal bipyramidal geometry about the lanthanide center. Density functional theory (DFT) works well for ionic, covalent, or metallic bonds and it was shown to be an effective method at a reasonable computational cost for some recent lanthanide calculations.[15] Here we carried out DFT level calculations for both the divalent Sm and Yb complexes reported by Arnold and co-workers[19] to estimate the effectiveness of different DFT functionals to calculate the structures of larger lanthanide divalent complexes. Several levels of theory including HF, BLYP, B3LYP, BH&HLYP, and B3PW91 were employed and the functionals used here are tabulated in Table 1. Selected bond lengths (in angstrom) and bond angles (in degree) are collected in Table 2 and two typical sketches (ORTEP view) of the divalent Sm and Yb complexes from B3PW91/BS1 calculation are shown in Figure 1. For comparison, the structural parameters and ORTEP view of the complexes from experiments[19] are also included in Table 2 and Figure 1. Comparison of calculations by using small-core and large-core RECPs for the lanthanide atom gives some information on the contribution of 4f orbitals and these results are tabulated in Table 3. The effect of polarization on the calculations was explored by using a d function on the C and N atoms and these results are listed in Table 4. Model studies were also done in which all of the methyl groups were replaced with hydrogen atoms. This may be typically done in theoretical studies to make the calculations computationally tractable. The model studies are compared to the corresponding calculations for the full molecules and these results are also given in Table 4.

Table 1. The Composition of the Different Levels of Theory Used in This Computational Study

level of comp	exchange func	local corr func	nonlocal corr func
HF	HF		
BLYP	Becke 88	LYP	LYP
B3LYP	Slater + HF + Becke 88	VWN + LYP	LYP
BH&HLYP	HF + LSDA + Becke 88	LYP	LYP
B3PW91	Slater + HF + Becke 88	VWN	PW91

Table 2. Comparison of the Structural Parameters from Different Levels of Computation[a]

	HF	BLYP	BH&HLYP	B3LYP	B3PW91	expt
			Sm			
Sm−I	3.2914	3.2600	3.237	3.2436	3.2332	3.2161(12)
Sm−N1	2.963	2.934	2.904	2.912	2.870	2.773
Sm−N2	2.868	2.850	2.808	2.829	2.804	2.663
Sm−N3	2.928	2.901	2.855	2.877	2.852	2.719
Sm−C1	2.848	2.840	2.809	2.816	2.799	2.767
Sm−C2	2.948	2.924	2.896	2.902	2.883	2.857
Sm−C3	3.038	3.022	2.983	2.994	2.971	2.949
Sm−C4	3.016	3.008	2.963	2.977	2.952	2.903
Sm−C5	2.908	2.899	2.860	2.871	2.849	2.794
Sm−Cp	2.683	2.665	2.632	2.639	2.617	2.583
Sm−Si	3.594	3.592		3.559	3.526	
C1−Si	1.850	1.855		1.846	1.846	
N1−Si	1.835	1.871		1.852	1.848	
I−Sm−N1	152.8	152.0	152.0	152.1	151.6	158.7
I−Sm−N2	92.2	89.7	90.4	90.1	89.4	91.7
I−Sm−N3	97.1	95.2	95.4	95.4	94.5	100.6
N1−Sm−N2	64.0	65.6	65.1	65.4	65.8	68.2
N1−Sm−N3	62.1	63.7	63.3	63.6	63.8	65.9
N2−Sm−N3	65.4	66.5	66.1	66.4	66.5	67.9
Cp−Sm−I	121.0	120.4	120.6	120.1	119.9	110.84
Cp−Sm−N1	86.2	87.5	87.3	87.7	88.4	90.1
Cp−Sm−N2	135.3	136.9	136.6	137.0	137.6	141.2
Cp−Sm−N3	130.0	131.8	131.4	131.8	132.6	132.1
			Yb			
Yb−I	3.1902	3.1629	3.1397	3.1484	3.1350	3.0613
Yb−N1	2.8337	2.823	2.783	2.793	2.759	2.600
Yb−N2	2.7999	2.781	2.729	2.753	2.726	2.584
Yb−N3	2.7552	2.735	2.693	2.715	2.692	2.573
Yb−C1	2.7613	2.750	2.720	2.727	2.710	2.657
Yb−C2	2.8245	2.802	2.773	2.780	2.762	2.714
Yb−C3	2.9305	2.907	2.865	2.879	2.857	2.782
Yb−C4	2.9487	2.925	2.880	2.895	2.872	2.768
Yb−C5	2.8578	2.836	2.800	2.811	2.791	2.695
Yb−Cp	2.5875	2.561	2.527	2.535	2.514	2.443
Yb−Si	3.4891	3.495	3.442	3.457	3.427	
C1−Si	1.8452	1.851	1.834	1.842	1.843	
N1−Si	1.8364	1.870	1.833	1.853	1.850	
I−Yb−N1	155.1	154.7	155.1	155.3	155.3	159.7
I−Yb−N2	96.5	95.2	95.6	95.8	95.6	96.0
I−Yb−N3	91.7	90.0	90.7	90.3	90.1	89.6
N1−Yb−N2	64.8	66.1	65.9	66.2	66.4	70.0
N1−Yb−N3	66.6	68.1	67.7	67.9	68.2	72.3
N2−Yb−N3	68.2	69.4	69.2	69.3	69.4	71.5
Cp−Yb−I	115.8	114.9	114.6	114.0	113.3	106.80
Cp−Yb−N1	89.1	90.3	90.2	90.6	91.3	93.37
Cp−Yb−N2	132.8	134.1	133.8	134.4	134.7	135.81
Cp−Yb−N3	138.0	138.9	139.0	139.2	139.9	143.5

[a] BS1 is used exclusively for the calculation results shown below. The experimental results are from ref 19.

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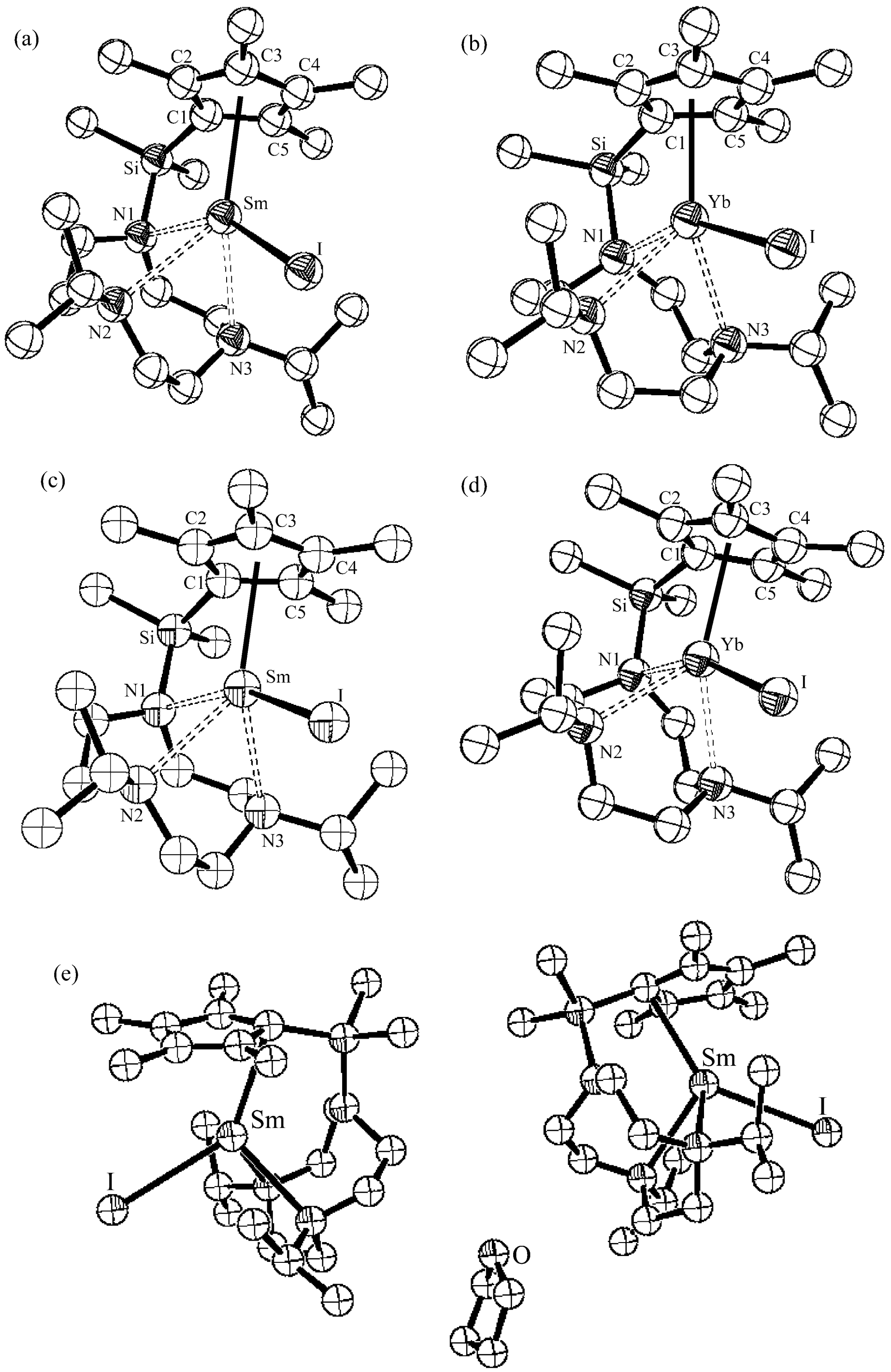

Figure 1. ORTEP view of the divalent lanthanide (Sm, Yb) complexes. (a) Optimized geometry for the Sm complex at the B3PW91/BS1 level of theory. (b) Optimized geometry for the Yb complex at the B3PW91/BS1 level of theory. (c) X-ray diffraction structure of the Sm complex based on data from ref 19. Only one of the molecules is shown here. (d) X-ray diffraction structure of the Yb complex based on data from ref 19. (e) X-ray diffraction structure of the Sm complex based on data from ref 19. Two molecules in the unit cell are shown here and one molecule of THF is included as well.

Comparison of the Levels of the DFT Calculations on the Full Molecule [$C_5Me_4SiMe_2(^iPr_2$-tacn)]-LnI (Ln = Sm, Yb) Systems. Here we used the combined the exchange functional of Becke's 1988 function[30] or Becke's 3-parameter functionals[31] with the correlation functional of LYP[32] or PW91.[33] These are commonly denoted as BLYP, B3LYP, and B3PW91, respectively. In addition the hybrid DFT method of BH&HLYP[34] was also employed. The results from the DFT calculations were compared to HF computations and to experimental results from the X-ray experiments. This was done to see how much the computational results were improved when the correlation effect is included in the DFT methods and which level of computation deals better with the bonding of divalent lanthanide complexes. The details of the functionals are tabulated in Table 1 and the selected structure parameters of the calculated structures were collected in Table 2 for comparison to experimental results.

Table 3. The Structural Parameters from the Calculations with the Treatment of Small-Core RECPs for the Ln (Sm, Yb) Atom[a]

		Sm			Yb	
M	full	model	expt[19]	full	model	expt[19]
M−I	3.1812	3.1467	3.2161(12)	3.1378	3.1088	3.0613
M−N1	2.8159	2.8490	2.773	2.6752	2.6750	2.600
M−N2	2.7700	2.7499	2.663	2.6318	2.5650	2.584
M−N3	2.7901	2.7800	2.719	2.6076	2.6130	2.573
M−C1	2.7341	2.7675	2.767	2.65746	2.6757	2.657
M−C2	2.8166	2.8131	2.857	2.7027	2.7092	2.714
M−C3	2.8887	2.8850	2.949	2.7958	2.7747	2.782
M−C4	2.8694	2.8736	2.903	2.8088	2.7636	2.768
M−C5	2.7765	2.7876	2.794	2.7299	2.6816	2.695
M-Cp	2.533	2.5592	2.583	2.4520	2.4481	2.443
M-Si	3.4657	3.4658		3.3667	3.3488	
C1−Si	1.8456	1.8254		1.8393	1.8200	
N1−Si	1.8467	1.8165		1.8550	1.8258	
I−M−N1	152.9	153.5	158.7	155.2	156.2	159.7
I−M−N2	89.3	92.7	91.7	93.7	92.0	96.0
I−M−N3	95.1	94.0	100.6	88.8	91.8	89.6
N1−M−N2	66.6	66.3	68.2	68.2	70.6	70.0
N1−M−N3	64.9	62.6	65.9	69.9	66.8	72.3
N2−M−N3	67.3	63.1	67.9	71.6	67.3	71.5
Cp−M−I	116.7	118.2	110.84	111.5	112.0	106.80
Cp−M−N1	90.2	88.3	90.1	93.2	91.8	93.37
Cp−M−N2	138.2	131.2	141.2	136.0	132.8	135.81
Cp−M−N3	134.9	140.4	132.1	140.7	145.4	143.5

[a] The basis sets for other atoms are the same as that in the BS1 basis set. Model calculation results are also included. The experimental results are from ref 19.

Table 4. Effect of Polarization on the Structural Parameters from the Calculations at the B3PW91/BS1 and B3PW91/BS2 Levels of Theory[a]

	full molecule		model		
B3PW91	BS2	BS1	BS2	BS1	expt[19]
Sm					
Sm−I	3.2496	3.2332	3.2221	3.204	3.2161(12)
Sm−N1	2.867	2.870	2.872	2.894	2.773
Sm−N2	2.764	2.804	2.762	2.808	2.663
Sm−N3	2.806	2.852	2.772	2.825	2.719
Sm−C1	2.808	2.799	2.840	2.834	2.767
Sm−C2	2.903	2.883	2.906	2.884	2.857
Sm−C3	3.002	2.971	3.004	2.964	2.949
Sm−C4	2.984	2.952	2.991	2.953	2.903
Sm−C5	2.868	2.849	2.880	2.862	2.794
Sm−Cp	2.638	2.617	2.664	2.641	2.583
Sm−Si	3.524	3.526	3.512	3.527	
C1−Si	1.842	1.846	1.821	1.824	
N1−Si	1.844	1.848	1.818	1.819	
I−Sm−N1	152.7	151.6	154.1	152.5	158.7
I−Sm−N2	89.4	89.4	92.1	91.9	91.7
I−Sm−N3	94.3	94.5	94.3	94.4	100.6
N1−Sm−N2	67.0	65.8	66.8	65.4	68.2
N1−Sm−N3	65.0	63.8	63.6	61.9	65.9
N2−Sm−N3	68.0	66.5	63.7	62.2	67.9
Cp-Sm−I	118.9	119.9	119.0	120.8	110.84
Cp-Sm−N1	88.3	88.4	86.9	86.7	90.1
Cp-Sm−N2	137.7	137.6	132.7	132.8	141.2
Cp-Sm−N3	132.7	132.6	138.1	136.6	132.1
Yb					
Yb−I	3.1573	3.1350	3.1266	3.1073	3.0613
Yb−N1	2.750	2.759	2.762	2.781	2.600
Yb−N2	2.683	2.726	2.638	2.682	2.584
Yb−N3	2.651	2.692	2.651	2.708	2.573
Yb−C1	2.727	2.710	2.749	2.741	2.657
Yb−C2	2.788	2.762	2.810	2.788	2.714
Yb−C3	2.892	2.857	2.906	2.863	2.782
Yb−C4	2.906	2.872	2.895	2.850	2.768
Yb−C5	2.816	2.791	2.788	2.763	2.695
Yb−Cp	2.541	2.514	2.561	2.533	2.443
Yb−Si	3.429	3.427	3.417	3.427	
C1−Si	1.838	1.843	1.817	1.822	
N1−Si	1.847	1.850	1.820	1.82	
I−Yb−N1	156.4	155.3	157.6	155.4	159.7
I−Yb−N2	95.1	95.6	92.6	92.5	96.0
I−Yb−N3	89.9	90.1	94.6	94.1	89.6
N1−Yb−N2	67.7	66.4	69.5	68.1	70.0
N1−Yb−N3	69.5	68.2	66.4	64.4	72.3
N2−Yb−N3	71.0	69.4	66.7	64.9	71.5
Cp−Yb−I	112.5	113.3	112.6	115.1	106.80
Cp−Yb−N1	91.0	91.3	89.8	89.5	93.37
Cp−Yb−N2	134.7	134.7	135.4	133.3	135.81
Cp−Yb−N3	139.9	139.9	140.6	141.2	143.5

[a] Model calculation results are also included. The experimental results are from ref 19.

Inspection of Table 2 indicates the HF calculations gave results with the largest deviation from the X-ray crystal structure parameters. All of the bond lengths considered were predicted to be longer than those from the X-ray experiments.[19] The angle of Cp−Ln−I is much larger than that in experiments (9.2% for Sm and 8.4% for Yb). Thus, the interaction between the N and lanthanide atom (Sm and Yb) was seriously underestimated (average deviation of 7.4% for the Sm complex and 8.1% for the Yb complex). The results were improved substantially when the DFT functionals were used. The bonding between Sm and Cp as well as Sm with I is reasonably good and deviations between the calculations and experiment range between 1.4−0.53% and 3.2−1.3%, respectively.

The geometry of divalent lanthanide complexes studied here was distorted trigonal bipyramidal from the DFT calculations and was in good agreement with the X-ray experimental results. Just like the reported X-ray diffraction results, the interaction between the Ln atom center and the Cp centroid is predicted to be in a η^5-manner. For the Sm(II) complex, the Sm−C bond lengths are calculated to be in the range of 2.799−2.971 Å and the distance between the Sm atom and the Cp centroid is calculated to be 2.617 Å at the B3PW91/BS1 level of theory, which is comparable to the experimental results with the Sm−C bond lengths in the 2.767−2.949 Å range corresponding to the experimental Sm−Cp-(centroid) distance of 2.583 Å. This is also reasonably consistent with the corresponding bond length of Sm−Cp of 2.534 Å in the $[(C_5Me_5)Sm(\mu\text{-I})(THF)_2]_2$ complex[28] and the average length of 2.79 Å for the Sm−C bonds in the Cp_2Sm complex.[35,36] The Yb case gives almost the same results with the distorted trigonal bipyramidal geometry well reproduced. The average Yb−C(η^5) distance is predicted to be 2.784 Å, which results in the Yb−Cp distance being 2.514 Å, and this is comparable to the experimental value of 2.443 Å. This value is also comparable to the average Yb−C experimental distances of 2.74 Å in the $(C_5Me_5)_2Yb(py)_2$ complex,[47] 2.66 Å in the $(C_5Me_5)_2Yb(THF)$ $(toluene)_{0.5}$ complex,[48] and 2.73 Å in the $[NaYb(C_5H_5)_3]$ complex.[7] In addition, the bond lengths between the Yb atom and the related ambient atoms are all predicted to be a little smaller than the corresponding bonds in the Sm complex (Ln−I as 3.135 vs 3.233 Å, Ln−Cp as 2.514 vs 2.617 Å, Ln−N as 2.692−2.2.759 vs 2.804−2.870 Å). This is consistent with the ionic radius of Yb being shorter than that of Sm at the same oxidation state, and the difference of Yb(II) and Sm(II) is generally cited as 0.18 Å.[37]

When DFT functionals are employed the interaction between Ln−N is described much better and the dative

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bonds are predicted to be 3.5%, 5.3%, 4.9% longer than the corresponding experimental values. A similar effect was also found for the full molecule Yb(II) complex. This indicates that the correlation between Ln and N is significant and should not be ignored. Inspection of the different levels of study in Table 2 indicates BLYP calculations gave an average deviation of 3.89% from the experimental values in the prediction of the Sm−I, Sm···N, and Sm−C(η^5) and Sm−Cp bonds. This changes to 3.03% for the B3LYP method, 2.62% for the BH&HLYP method, and 2.20% for the B3PW91 method. This comparison combined with results from a previous study[15] suggests that the B3PW91 method is probably the best one to use in modeling divalent lanthanide complexes insofar as the limited number complexes examined thus far are representative of divalent lanthanide compounds.

The Role of 4f Electrons for the Sm and Yb Divalent Lanthanide Complexes. The f electron density in lanthanide complexes is generally believed to be confined to the inner regions and so the 4f orbitals likely do not contribute very much in the formation and cleavage of bonds between the Ln atom and other nonmetal atoms. This is supported by the elegant work of Weinhold[38] and Eisenstein[15] and co-workers. For the bonding of Sm(III) and Yb(II) with a strong-field [NH_2] ligand, the population in the 4f orbitals was predicted to be 5.03 and 14.09, respectively, by NBO analysis and only a small perturbation in the 4f orbitals was observed.[15] In our present study, the divalent Ln is bonded to I and Cp ligands. In addition, the dative bond between Ln(II) and N is also noticeable. To explore the contribution to the bonding from the 4f orbitals coming from the divalent lanthanide, further calculations were performed by using small-core RECP optimized by the Stuttgart−Dresden group for the lanthanide atoms at the B3PW91 level of theory. As advised in ref 15, we use the ground state configuration with the highest spin number (which is 7 for the Sm(II) case) and so the electrons in the 4f shell are all unpaired and obey Hund's rule. Inspection of Table 4 indicates that the results from the small-core RECP become somewhat better than that from the calculations with large-core RECP for lanthanide relative to the experiment results. All of the bond lengths become slightly shorter when replacing the large-core RECPs with the small-core RECPs for Sm and give less deviation from the experimental values. For the Yb(II) case, the small-core RECPs calculation predicted a bond length of 2.452 Å for the Yb−Cp(centroid), which is almost the same as the experimental result. The prediction of the interaction of the Ln atom with N is also good with the average deviation calculated to be 2.73% for Sm and 2.03% for Yb relative to the experimental values. The f orbitals of Yb are fully occupied. According to basic chemical concepts, it does not seem possible for the 4f orbitals that are filled to mix with the valence orbital and thus contribute in bond formation. This is consistent with Eisenstein's analysis. Thus, the improvement in the geometry optimization may come from the small-core RECPs employed here dealing with the electron correlation in a better way than the large-core RECPs. Support for this comes from the Mulliken analysis for the open-shell Sm(II) complex. The spin density on Sm(II) is predicted to be 6.05 and no spin density was found on the other atoms. This indicates that there should be no donation or back-donation between the 4f orbitals of Sm and the ligands and the 4f orbitals do not contribute directly to the assembly of the complex. The calculation with large-core RECPs for Sm and Yb can give reasonable predictions on the bonding of lanthanide with ligands. Considering the computational cost, the calculations with large-core RECPs for the lanthanide atom are effective and affordable in predicting the structures of divalent lanthanide complexes.

Comparison of the DFT Results without and with Polarization Functions on the C and N Atoms. To study the effect of polarization functions on Cp and N atoms which are bound to a Ln center by a normal bond or dative bond, we optimized the geometry of the full molecular complex [$C_5Me_4SiMe_2(^iPr_2$-tacn)]-LnI (Ln = Sm, Yb) employing the basis set 6-31G on C and N with and without the d-polarization functions on these atoms at the B3PW91 level of theory. The results are summarized in Table 4. Examination of Table 4 indicates that at both levels of theory the distorted trigonal bipyramidal geometry of the divalent lanthanide complexes studied here is well described. The bond lengths of Ln−I, Ln−C, and Ln−N are influenced somewhat with the addition of the polarization function on N and C while the corresponding bond angles (among Ln, I, N, and Cp centroid) stay essentially unchanged. The bond lengths of Sm−I and Sm−Cp are better predicted and become slight shorter (−0.0164 Å and −0.021 Å) when adding the d polarization functions on C and N with the deviation between the computations and experiment being 0.53% and 1.32%, respectively.

For the bonding between Sm and the three N atoms, the X-ray diffraction results gave a value around 2.7 Å, and so they were assigned as a typical dative bond between samarium and bulky amine donors, but the difference among the three dative bonds is noticeable. The interaction between Sm and N^1, which is combined to Si, is much weaker relative to N^2 and N^3 (~0.110 Å and ~0.054 Å longer than the other two bonds determined by X-ray diffraction). This character is reproduced in our present computation and may result from the covalent bond of N^1−Si. Since the silicon center has a strong ability to stabilize an α anion, the delocalization of the lone pair on N^1 to Si results in a decrease of the Sm···N^1 interaction. This is consistent with the study of the Ln[$N(SiH_3)_2]_3$ complex by Eisenstein and co-workers.[16] Steric effects also act on the bonding of N^1 and Sm. The bond angle of N^1−Si−C^1 is about 106.1°. This is near the bond angle of a trigonal pyramidal geometry with a Si center. The constraint to maintain the geometry of the Si center resists closer contact of N^1 to the Si atom.

Comparison of the results from the calculations with and without polarization functions indicates both levels of calculation describe the geometry of the complexes essentially in the same way. But there are a few differences between the two calculations. The dative bond between Sm and N is better predicted with the average deviation of 3.47% relative to the experimental values when no polarization function is imposed on the C and N atoms. This average deviation becomes 4.57%

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when one d polarization function is added to the C and N atoms. This indicates that the polarization is not enough for the description of this dative bond. Imposing a d function on non-hydrogen atoms will provide a better description of the delocalization of the lone-pair electron among N, Si, and Cp, and the constrained geometry of the monoanionic ligand prevents interaction between N and Ln center. However, the bond between Ln and the Cp(centroid) as well as the I ligand is improved with the addition of d polarization on C and N: the deviation of the calculation relative to the experimental values being 1.32% and 0.53%, respectively, compared to deviations of 2.13% and 1.04%, respectively, with no d polarization.

Estimation of a Selected Model System. The exploration of divalent lanthanide complexes in the preceding sections indicated that DFT (B3PW91) calculations provided an effective method in modeling a class of similar lanthanide complexes. To simplify further lanthanide studies in the future, we performed some model studies where H atoms are used to replace the methyl groups in the full molecules (this has been widely used in theoretical studies to help make theoretical calculations computationally tractable for large systems). B3PW91 hybrid functionals were selected to perform the model simulations with the treatment of large-core RECPs for the lanthanide center (52 MWB on the Sm atom and 60 MWB on the Yb atom). Selected structural parameters from these model calculations are tabulated in Table 4. The I and N^1 atoms occupy the axial sites of the pyramidal structure and N^2, N^3, and Cp centroid occupy the equatorial positions. In the Sm(II) complex, the I−Sm−N^1 angle is predicted to be 152.5° at the B3PW91/BS1 level of theory and changes to 154.1° when the BS2 basis set is used. The angles of Cp−Sm−N^2, Cp−Sm−N^3, and N^2−Sm−N^3 moieties are predicted to be 132.8°, 136.6°, and 62.2°, respectively, at the B3PW91/BS1 level of theory. These results for the model compound are essentially the same as those from the full molecule computation. Similar results are also obtained for the model compound of the Yb(II) complex.

The most important parameters under our consideration, the Sm−I and Sm−Cp(centroid) bonds, are predicted to be 3.204 and 2.641 Å, respectively, in the model compound calculations. Comparison to the corresponding values in full molecule computation indicates that the Sm−I bond becomes shorter (−0.029 Å) while the Sm−Cp distance becomes longer (+0.024 Å). This shows that the methyl groups attached to Cp have a noticeable effect on the bonding of Sm with the Cp and I moieties and the increase of the Sm−Cp(centroid) distance should come from the missing methyl groups which work as good electron-donor groups. This results in the decrease of the electron density in the centroid of Cp. This is supported by the changes observed in the Si−C^1 and Si−N^1 bond length that systematically decrease by 0.022 and 0.029 Å, respectively, in the model compound. In the model molecule the Si atom is bound to two hydrogen atoms instead of two methyl groups in the full molecule. The delocalization of the p-electron between Si and C^1 with N^1 results in the strengthening of C^1−Si and N^1−Si bonds. Mulliken analysis shows the charge on the Sm atom is 0.53 for the full molecule and 0.62 for the model molecule. This suggests the Sm center becomes more electron deficient when replacing the $CpMe_4$ group with the Cp moiety. Similar observations were found for the Yb(II) case.

In recent theoretical studies[16,39] agostic interaction was recognized to exist between an electron-deficient transition metal and the relatively electron-rich Si−H bond. It is also understood that the agostic interaction between a transition metal and a C−H bond will be much weaker. In the present study, Mulliken population analysis indicates that there is no agostic interaction between Ln and H (Me) and no donation is found from the Ln center to H. This can also be extracted from analysis of the optimized geometry. Both the full molecule and model calculations for the Sm and Yb complexes show the distance between the Ln and H atoms is more than 2.8 Å. This is much longer than the typical agostic interaction of M···H, which is typically about 1.85 to 2.4 Å. X-ray diffraction experiments did not provide an accurate position of the H atoms and the H atoms were assigned to their idealized positions.[19] This gives the distance between the Ln center and H (Me) as more than 2.719 Å for Sm···H and 2.740 Å for Yb···H. Our calculated values appear comparable to the experiment results. But there exists stronger interaction between Ln and Si. The distance between Sm and Si is 3.527 and 3.526 Å, respectively, for the model compound and the full complex. This may imply that the interaction of Sm with Si is stronger than a van der Waals interaction (the van der Waals radii are 2.36 Å for Sm[39,40] and 2.10 Å for Si[41] to give a distance of 4.46 Å for Sm···Si). This appears to relate to the steric hindrance in the geometry of the tridentate triazacyclononane moiety. This is also true in the Yb case. The distance between Yb and Si is predicted to be 3.427 Å for the full molecule and is unchanged in the model molecule. This is much shorter than the van der Waals radius of Yb···Si (van der Waals radii of 2.38 Å for Yb[41−43] and 2.10 Å for Si lead to a Yb···Si distance of 4.48 Å).

In conclusion, the model system describes the Ln(II) complexes to a reasonable extent. The metal−ligand bond and the distorted trigonal bipyramidal geometry are well reproduced and in reasonable agreement with both the full molecule calculations and experimental geometry parameters. While representing a CH_3 group by a H atom is widely accepted and used to model large organometallic compounds, it does not work all the time. For example, in the case of $Ln[N(SiMe_3)_2]_3$, the representation of $N(SiH_3)_2$ for $N(SiMe_3)_2$ predicted an agostic Ln···Si−H interaction that does not exit in the full molecule[15] and special care may be needed in modeling large molecules. In the cases examined here, the features of the full molecules were well described in the model studies and no new interactions were observed.

Simple Analysis on the Electron Structure. Molecular orbital analysis provides useful information of the electron structure and may be helpful in understanding the stability of the compounds. For lanthanide complexes, Poli[39] and Gordon[44] and co-workers confirmed the participation of the 5d orbitals of Ln(III) in the bonding through molecular orbital analysis; Koga[45] concluded that qualitatively similar results could be obtained when the 4f orbitals of Sm were replaced by

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ECPs. This suggests that molecular orbital analysis can give reasonable results when employing large-core ECPs for the lanthanide atom. Here we present a simple natural orbital analysis (NBO) by employing large-core ECPs for Sm. Only the result obtained for the divalent samarium model complex is presented here. A neutral samarium atom theoretically has the electron configuration [Kr] $4d^{10}4f^{6}5s^{2}5p^{6}5d^{0}6s^{2}$ and a divalent samarium atom has the configuration [Kr] $4d^{10}4f^{6}5s^{2}5p^{6}5d^{0}6s^{0}$. NBO analysis gives the configuration for Sm(II) as follows: [core] $6s^{(0.07)}\ 5d^{(0.01)}6p^{(0.44)}6d^{(0.01)}$. This results in an atomic charge of 1.47 for the Sm atom. The atomic charge of I is predicted to be −0.78, which leads to the overall charge on the monoanionic ligand of −0.69. This indicates that Sm is a strong ionic divalent species in the complex studied. The charge on the Sm may be a little overestimated since the dative bonds between Sm and N are a little underestimated, which in turn may donate some electron density to the electron-deficient Sm center. In the NBO analysis, the divalent character of Sm is well illustrated and provides further support for the reliability of the results from our present study. We note that population analysis can be somewhat arbitrary with results varying with changes in the method and/or computational levels used. Previous studies predicted NBO charges of 1.14 for Yb(II) in $Yb(NH_2)_3$ (from B3PW91),[15] 1.90 on Sm(II) in Cp_2Sm (from HF),[14] and 1.70 for $ISmCH_2I$ (from B3LYP).[46] Considering the different chemical environments, the NBO charge on Sm(II) of 1.47 for our present study is reasonable.

Another important piece of information extracted from the NBO analysis is that the 5d orbitals of Sm do not contribute much in the present model study. This is consistent with our aforesaid analysis since the 5d orbitals prefer to participate in the covalent, dative bond, or other interactions. In our present study, the ionic bonds between Sm and I with Cp are the main interaction between Sm and the ambient atoms and this contribution comes mainly from the 6s orbitals of Sm. We note that some previous studies indicate that 5d orbitals of Sm(III) contribute significantly (with a population of 1.28−1.50[11,17]) to the bonding and this difference is related to the different electron configuration of the Ln atom and the different environment of the Ln in which the agostic interaction for these Ln(III) complexes was recognized to be important. This is a much different situation than the divalent lanthanide complexes studied here.

Conclusion

A theoretical investigation of the divalent lanthanide complexes (Ln = Sm and Yb) with different DFT functionals was presented. The effect of polarization and the participation of the 4f orbitals to the bonding in the complexes were also investigated. The geometry of the complexes was computed to be a distorted trigonal bipyramidal in agreement with experimental structures obtained from X-ray crystal data. B3PW91 functionals gave the best description of the complexes at an affordable computational effort. The divalent lanthanide atoms in the present study are predicted to have more ionic character and less 5d contribution in the bonding of the lanthanide center with the ambient atoms than was found for several trivalent lanthanide complexes investigated in previously reported studies. Addition of one d polarization on the C and N atom moderately improves the prediction of the ionic bond but does not provide a better description of the dative bond between the lanthanide center and N.

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Supporting Information Available: Selected output from the density functional theory calculations showing the Cartesian coordinates and total energies for the divalent lanthanide complexes investigated here. This material is available free of charge via the Internet at http://pubs.acs.org.

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