Photoelectron Spectroscopy of f-Element Organometallic Complexes. 12.[†] A Comparative Investigation of the Electronic Structure of Lanthanide Bis(polymethylcyclopentadienyl)hydrocarbyl Complexes by Relativistic ab Initio and DV-Xα Calculations and Gas-Phase UV Photoelectron Spectroscopy

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The electronic structure of the bis(polymethylcyclopentadienyl)lanthanide hydrocarbyl complexes $Cp'_2LnCH(SiMe_3)_2$ and $Me_2SiCp''_2LnCH(SiMe_3)_2$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$; $Cp'' = \eta^5\text{-}(CH_3)_4C_5$; Ln = La, Ce, Nd, Sm, Lu) is investigated by means of relativistic effective core potential ab initio and discrete variational Xα calculations and by experimental gas-phase He I/He II photoelectron spectroscopic measurements. The lanthanide–ligand bonding is dominated by interactions involving the metal 5d subshells, while metal 4f orbitals are only marginally involved in the bonding. Good agreement between experimental and calculated ionization energies is found in the case of the lanthanum complex. Metal f^{-1} ionizations, observed in the He II spectra of the Ln = Ce, Nd, Sm, and Lu complexes, are interpreted on the basis of the ion states generated upon ionization of the corresponding f^n ground states and are consistent with a gradual energetic stabilization of 4f orbitals across the lanthanide series. Analysis of the photoelectron data indicates pronounced similarity in the lanthanide–ligand bonding on traversing the lanthanide series.

Introduction

The past decade has witnessed intense and growing activity in lanthanide element chemistry which parallels a sharpening awareness of the unique features of 4f-element ions.[1] The lanthanide 4f subshells have traditionally been considered to be extensively shielded by 5s and 5p electrons,[1,2] greatly contracted, largely atomic in nature, and acting purely *as spectators* in the chemical bonding.[1] Lanthanide ions have therefore generally been considered to be hard acceptors forming predominantly ionic bonds.[1] Nevertheless, growing evidence suggests non-negligible metal 4f covalency as well as a major role played by 5d subshells in the metal–ligand bonding.[3–5] For example, Hartree–Fock–Slater SCF first-principles discrete variational (DV-Xα) relativistic calculations combined with photoelectron (PE) spectra of lanthanide trihalides provide evidence that the metal–ligand bonding is dominated by overlap between metal 5d and halogen np atomic orbitals (AOs),[4] while DV-Xα calculations combined with PE spectra of Ce(IV) organometallic complexes have suggested a remarkable covalency involving *both* 4f and 5d metal AOs.[3a,c] Similar investigations on bis(cyclopentadienyl)Ln(II) (Ln = Sm, Eu, Yb) complexes have, in contrast, indicated that the bonding is predominantly ionic.[6]

In recent years, a considerable trivalent organolanthanide synthetic chemistry has been developed, using ancillary cyclopentadienyl ligands, to form a wide variety of highly reactive $Cp'_2Ln{-}X$ and $Me_2SiCp''_2{-}Ln{-}X$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$; $Cp'' = \eta^5\text{-}(CH_3)_4C_5$; X = σ-bonded ligand) complexes.[1,7–9] These complexes form the basis for a large body of novel stoichiometric and homogeneous catalytic organolanthanide chemistry.[7–9] Nevertheless, no theoretical and/or experimental investigations of the electronic structure of this important

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[†] For part 11 see ref 20a.

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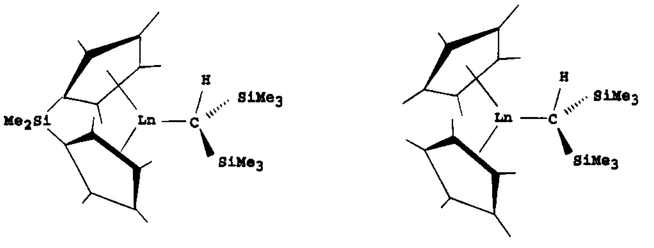
Chart 1



Ln = La, 1
Ln = Nd, 2
Ln = Sm, 3
Ln = Lu, 4

Ln = Ce, 5
Ln = Sm, 6

class of compounds has been undertaken to date. In this intriguing context, we were prompted to initiate a comprehensive study of bis(polymethylcyclopentadienyl)lanthanide hydrocarbyl complexes[7] (Chart 1; Ln = La, Ce, Nd, Sm, Lu) which combines relativistic effective core potential (RECP) ab initio and DV-Xα calculations with experimental He I/He II PE measurements. We report the results of this study herein.

Experimental Section

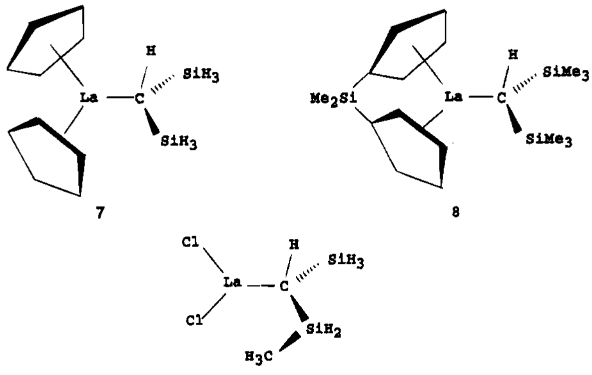
The following series of closely related lanthanide cyclopentadienyl complexes (Chart 1) $Me_2SiCp''_2LnCH(TMS)_2$ (Ln = La (**1**), Nd (**2**), Sm (**3**), and Lu (**4**); TMS = $SiMe_3$) and (Cp'_2-$LnCH(TMS)_2$ (Ln = Ce (**5**), and Sm (**6**)) were synthesized according to the published procedures.[7] They were purified by recrystallization and/or sublimation in vacuo and were always handled under a prepurified argon or nitrogen atmosphere. They gave satisfactory elemental, NMR, and MS analyses.[7]

High-resolution UV PE spectra were acquired as described elsewhere.[10] Resolution measured on the He 1 s^{-1} line was always around 25 meV. The spectra were recorded in the 155–185 °C temperature range depending upon the particular complex. The spectral profiles remained constant within ±15 °C, thus ruling out gas-phase decomposition processes. No quantitative estimations of the PE band intensities were made because of the rather overlapped nature of the spectral features.

Computational Details

In ab initio ECP calculations, atomic core electrons for the La atom were replaced by the relativistic ECPs of Hay *et al.*[11] They account explicitly for the outermost core orbitals (5s, 5p). Valence Gaussian bases were contracted in a double-ζ quality for 6s and 5d functions. The 6p and 4f orbitals were described by a single Gaussian function with 0.04 and 0.25 exponents, respectively. These exponents were optimized on the $LaCl_3$ molecule.[12] The standard 6-31G basis sets of Pople *et al.*[13] were adopted for the Cl, Si, C, and H atoms. Calculations were performed using the HONDO-8 code.[14]

Chart 2



7
8
9

DV-Xα calculations[15] were carried out at a nonrelativistic level within the self consistent charge procedure (SCC) as described elsewhere.[15] Numerical AOs (through 6p on La, 3d on Si, 2p on C, and 1s on H) were used as basis functions.[15] The frozen core approximation was used throughout the calculation.[15] The ionization energies (IEs) were evaluated using both the ab initio ΔSCF procedure and the Slater transition-state (TS) formalism[16] to account for reorganization effects upon ionization.

Because of the structural complexity of the present molecules, calculations were made only for an archetypical La complex adopting simpler models (Chart 2). In particular, the model $Cp_2LaCH(SiH_3)_2$ (**7**, Cp = η^5-C_5H_5), which adopts simpler Cp_2 and SiH_3 groups instead of the Cp'_2, $Me_2SiCp''_2$, and TMS fragments, was used for ground state calculations. Calculations on **7** were made using both nonrelativistic DV-Xα as well as RECP ab initio methods. The model $Me_2SiCp_2LaCH(TMS)_2$ (**8**), where only the $Me_2SiCp''_2$ moiety was replaced by the simpler Me_2SiCp_2 group, was used for IE calculations within the Xα TSIE formalism.

The geometrical parameters of the Me_2SiCp_2La— and Cp_2-La— fragments were adopted from X-ray diffraction data on the homologous Nd(III) complex[7] (**2**) after correction for differences in the ionic radii.[17] The geometries of the >LaCH-$(SiH_3)_2$ and >$LaCH(TMS)_2$ moieties were adapted from the optimized structure of the related $Cl_2LaCH(SiH_3)SiH_2Me$ (**9**) model (Chart 2) which, in turn, was fully optimized using the ab initio gradient technique.[18] In all of the presently adopted models, C_s symmetry was assumed.[19]

Results and Discussion

Electronic Structure of $Me_2SiCp''_2LaCH(TMS)_2$. Ground state (GS) RECP ab initio and DV-Xα results on **7** are compared in Table 1. It is evident that results are very similar. The HOMO 37a′ (22a′ in Xα calculation) formally represents the La—C σ bond and has comparable 3% (4%) metal 5d contributions in both

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Table 1. Ab Initio and DV-Xα Eigenvalues and Population Analysis for the Topmost Filled MOs in $Cp_2LaCH(SiH_3)_2$

	eV		La							
MO[a]	$-\epsilon$	ΔSCF	s[b]	p[c]	5d	4f	CH	2Cp	$2SiH_3$	character
					Ab Initio					
37a′	7.56	6.16	1	6	3	0	51	27	12	σ La—C
36a′	8.42	7.51	0	1	6	2	3	88	0	$\pi_2 + d_{xz}$
24a″	8.81	7.90	0	4	4	2	2	88	0	$\pi_2 + d_{xy} + p_y$
23a″	9.39		0	0	14	1	1	84	0	$\pi_2 + d_{yz}$
35a′	9.62		0	0	14	0	16	63	7	$\pi_2 + d_{z^2} + d_{x^2-y^2}$
22a″	10.65		0	0	1	0	48	1	50	CH—Si
34a′	11.76		0	0	1	0	40	1	58	CH—Si

overall charge
$La = 4f^{0.21}\ 5d^{1.21}\ s^{2.12},\ p^{6.25} = +1.21$
$[CH(SiH_3)_2] = -0.52,\ 2Cp = -0.69$

	(eV)		La							
MO[d]	$-\epsilon$	TSIE	6s	6p	5d	4f	CH	2Cp	$2SiH_3$	character
					DV-Xα					
22a′	4.89	6.97	0	1	4	6	60	15	20	σ La—C
21a′	5.890	7.98	0	0	7	4	1	88	0	$\pi_2 + d_{xz} + f_{z^3}$
14a″	5.893	8.05	0	0	3	2	1	94	0	$\pi_2 + d_{xy}$
13a″	6.29	8.27	0	0	14	1	0	85	0	$\pi_2 + d_{yz}$
20a′	6.55		0	0	11	0	6	81	3	$\pi_2 + d_{z^2} + d_{x^2-y^2}$
12a″	7.20		0	0	1	1	44	0	54	CH—Si
19a′	7.94		0	0	0	0	40	1	59	CH—Si

overall charge
$La = 4f^{0.30},\ 5d^{0.84},\ 6s^{0.03},\ 6p^{0.05} = +1.78$
$[CH(SiH_3)_2] = -0.58,\ 2\ Cp = -1.20$

[a] 37a′ = HOMO. [b] Values refer to 5s and 6s orbital population. [c] Values refer to 5p and 6p orbital population. [d] 22a′ = HOMO.

cases. In the Xα calculations, the HOMO possesses a 6% 4f contribution which is lacking in the ab initio data. This represents an expected trend mostly due to neglect of relativistic effects.[20] Moreover, the La—C σ bond is expected to be strongly polarized in view of the calculated high negative charge (−1.31 eu) associated with the carbon atom.

The 36a′–35a′ (21a′–20a′) MOs represent the La—Cp bonding interactions. Their sequence and atomic composition are almost identical with both calculations. The La—Cp bonding is clearly dominated by interactions involving the metal 5d AOs, as found in a number of 5f cyclopentadienyls.[5,10,20] The major metal—ligand contribution is found in the more internal 35a′ and 23a″ (20a′ and 13a″) MOs. These MOs thus provide the major contribution to the stabilization of the Cp_2 cluster. Contributions due to 4f orbitals are of minor relevance and comparable at both levels of calculation. Close similarities are also found as far as the 22a″ and 34a′ (12a″, 19a′) MOs are concerned. They formally represent C—Si σ bonds and are almost totally ligand-centered, thus having only minor metal contributions. Moreover, the effects of electronic reorganization upon ionization have been evaluated for the topmost filled. MOs using RECP ab initio as well as nonrelativistic DV-Xα methods within the ΔSCF procedure and the transition state formalism, respectively. In both cases, these effects are not large enough to upset the ground state MO energy sequence (Table 1).

Taken together, these results are tuned well with our earlier contentions:[20b,c] (i) more computationally efficient nonrelativistic DV-Xα calculations can be used with confidence to describe the bonding in lanthanide organometallics, and (ii) the IE sequence in PE spectra of the same complexes can be efficiently reproduced even using a nonrelativistic DV-Xα treatment.

DV-Xα GS calculations on the more realistic structural model **8** evidence no significant differences from the above results (Table 2). In particular, a similar energy dispersion and energy sequence of MOs representing the La—C (35a′) and Cp—La (34a′–33a′) interactions are observed. Of course, a larger variety of MOs follows the aforementioned group of orbitals. Some of these (25a″–23a″ and 31a′) are localized on the TMS moieties and are counterparts of those representing the Si—C σ bonds in $SiMe_4$.[21] Similarly, the 22a″ MO represents Si—C σ bonds in the >$SiMe_2$ bridging fragment while 30a′ and 29a′ are associated with perturbations of the same fragment on the π systems of the Cp rings. Finally, MOs 28a′ and 27a′ represent σ orbitals delocalized over on the entire ligand framework.

A +1.21 eu overall charge on the La atom is found in the ab initio calculation on model **7** (Table 1, top). Somewhat larger values, identical for models **7** and **8** (+1.78 eu), are evident in the Xα calculations (Tables 1, bottom, and 2). The calculated charges on the lanthanum atom are considerably different than the formal +3, thus suggesting a ligand-to-metal donation. Moreover, the distribution of electrons accumulated in the lanthanum atomic orbitals indicates, in all cases, the primary role of the metal 5d orbitals in the bonding. Comparison of Xα and ab initio data indicates that the aforementioned differences are due to the expected[20] underestimation of 5d, 6s, and 6p metal—ligand admixture in the nonrelativistic Xα approach.[22]

Photoelectron Spectra. The PE spectra of all of the present complexes are similar (Figures 1–3). Minor differences are, however, observed upon substitution of the Cp ring ligands, as well as upon changing the nature of the central metal atom. Moreover, highly reproducible additional features are observed in the He II spectra of the Ln = Ce, Nd, Sm, and Lu complexes. They have either the form of low intensity onset features (x) when Ln = Ce, Nd, and Sm or of intense structures in the 16–17 eV range in the spectrum of the Lu complex. All of these additional features are invariably absent in spectra of the La complex. Relevant PE data are set out in Table 3. IE data for La complex **1** are also

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(18) (a) The ab initio gradient optimization[18b] of model **9** gives the following geometrical parameters: La—Cl = 2.70 Å; La—C = 2.53 Å; C—Si = 1.90 Å; Si—Me = 1.94 Å; Cl—La—Cl = 130.3°; La—C—Si = 113.6°; C—Si—Me = 112.3°. (b) Lanza, G.; Di Bella, S.; Fragalà, I. To be published.

(19) (a) X-ray data on **2** show unsymmetrical, not uncommon[8c9f,19b] coordination of the $-CH(SiMe_3)_2$ fragment to the $Me_2SiCp''_2Nd$ group with possible secondary Nd--Me interactions.[7b] No evidence of a major interaction is found in solution since ^1H NMR spectra indicate magnetically equivalent $SiMe_3$ units down to low temperatures and, hence, a small interconversion energy barrier to interchange of the Si—Me groups.[7b] Because PE spectra were run in the gas-phase at high temperatures, a symmetric coordination of the $-CH(TMS)_2$ fragment is a reasonable approximation. (b) For further examples see: Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637.

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(22) Note that the comparison between literature RECP ab initio[12] and relativistic DV-Xα[4] data on the simpler LaX_3 (X = F and Cl) molecules indicates very similar values as far as the total atomic lanthanum population is concerned. Clearly, the inclusion of relativistic effects is expected to lead to comparable results with both relativistic (ab initio and DV-Xα) methods.

Table 2. DV-Xα Eigenvalues and Population Analysis for the Topmost Filled MOs of $Me_2SiCp_2LaCH(TMS)_2$, as Well as Experimental IEs

	−eV		eV	La								
MO[a]	GS	TSIE	IE[b]	6s	6p	5d	4f	CH	$SiMe_2$	2Cp	2TMS	character
36a′	3.36			0	0	6	83	1	0	10	0	$f_{x(x^2-3y^2)}$
35a′	5.11	7.19	7.1 (a′)	0	0	3	5	55	1	16	20	σ La−C
34a′	5.75	7.89		0	0	7	5	1	0	87	0	$\pi_2 + d_{xz} + f_{z^3}$
27a″	6.07	8.16	7.4 (a)	0	0	4	2	1	0	93	0	$\pi_2 + d_{xy}$
26a″	6.38	8.36		0	0	13	1	0	0	86	0	$\pi_2 + d_{yz}$
33a′	6.40	8.38	8.0 (a″)	0	0	11	0	6	6	72	5	$\pi_2 + d_{z^2} + d_{x^2-y^2}$
25a″	6.95	8.93	9.0 (b)	0	0	1	0	23	0	0	76	TMS
24a″	7.17	9.13		0	0	0	0	10	0	0	90	TMS
32a′	7.23	9.24		0	0	0	0	14	0	0	86	TMS
23a″	7.71	9.68	9.9 (c)	0	0	0	0	5	0	0	95	TMS
22a″	7.94	10.00		0	0	0	0	0	91	9	0	Si−Me
31a′	7.98	10.05		0	0	0	0	8	0	0	92	TMS
30a′	8.24	10.08		0	0	1	0	0	49	50	0	Si−Me + π_2
29a′	8.43	10.29	10.3 (c′)	0	0	0	0	0	35	65	0	π_1 + Si−Me
28a′	8.56	10.35		0	0	0	0	23	1	44	32	CH(TMS) + π_2
27a′	8.68	10.72	11.6 (d)	0	0	2	0	17	1	55	25	CH(TMS) + π_2

overall charge
La = $4f^{0.30}$, $5d^{0.84}$, $6s^{0.03}$, $6p^{0.05}$ = +1.78
$-CH(TMS)_2 = -0.57$, $Me_2SiCp_2 = -1.21$

[a] 36a′ = LUMO; 35a′ = HOMO. [b] Experimental PES-derived IEs. See Figure 1.

Table 3. Relevant PE Spectroscopic Data for $Me_2SiCp''_2LnCH(SiMe_3)_2$ and $Cp'_2LnCH(SiMe_3)_2$ Complexes

band label	La (1)	Ce (5)	Nd (2)	Sm (3)	Sm (6)	Lu (4)	assignment
x		6.2	6.3[a]	6.5[a]	6.4[a]	16.2	4f Ln
a′	7.1	6.9	7.0	7.0	6.9	6.9	σ Ln−C
a	7.4	7.2	7.2	7.5	7.2	7.2	π Ln−Cp
a″	8.0	7.8	8.0	8.1	7.7	7.9	π Ln−Cp
b	9.0	9.1	9.0	9.3	9.1	8.9	σ Si−Me
c	9.9	9.8	9.8	10.0	10.0	9.7	σ Si−Me
c′	10.3	10.3	10.3	10.4	10.5	10.3	σ Si−Me
d	11.6	10.8	11.1	11.2	11.0	11.0	σ Si−Me

[a] See text.

compared with the computed TSIEs values for model structure **8** in Table 2. It is evident that the theoretical values provide a good fit of the experimental data.

In the 7−8.5 eV region, the spectra of **1** show a band envelope labeled a−a″ in Figure 1. The lower IE shoulder a′, in accordance with the calculations (Table 2) as well as with earlier data on several closely related f-element polycyclopentadienyl hydrocarbyl complexes,[10,20a,23,24] can be safely assigned to the ionization of the 35a′ MO representing the La−C σ bond. The principal features a and a″ doubtless represent ionization of the Cp π_2-related MOs. The associated IE values are similar to IE data for the corresponding MOs in bis(cyclopentadienyl) complexes of a variety of metals.[20c,23,24] They also agree well with TSIEs values once the expected downward shift, due to the omission of the ring methyl groups in metal **8**, is taken into account.[25]

Bands a−a″ have a 3:1 relative intensity ratio in the spectra of compounds **1**−**4**, where two identical η^5-$(CH_3)_4C_5$ rings are bridged by a >$SiMe_2$ group. In contrast, they exhibit a simpler doublet structure in the spectra of unbridged Ce (**5**) and Sm (**6**) complexes (Figure 2 and 3), likely a consequence of the wider Cp−M−Cp angles[26] in the latter complexes. Finally, a shift (~0.27 eV) to lower IE values is associated with bands a′−a″ on passing from the bridged to unbridged Sm(III) complexes (Table 3), consistent with expected alkyl silyl substituent effects.[27] Bands b, c, c′, and d, present in all of the spectra, can be assigned to ionizations of MOs associated with the Si−C σ bonds. This assignment agrees both with calculations (Table 2) as well as with earlier results on several silyl derivatives.[23,28]

The aforementioned onset features in the spectra of some of the present complexes (Ln = Ce, Nd and Sm) (Figures 2 and 3) are likely associated with f^{-1} ionizations. They are barely detectable in the He I spectra, but their relative intensities increase in the He II spectra. This is an expected behavior which parallels the well-known relative increase of 4f cross-sections under the more energetic He II radiation.[3c,4,6,29] The close similarity (in terms of IEs associated with bands a−d) of the present PE spectra indicates a minor involvement (hence, minor perturbation upon ligation) of $4f^n$ electrons in the metal−ligand bonding. This suggests that 4f subshells largely maintain an atomic character in the present complexes and, in addition, that $4f^{-1}$ ionizations can, therefore, be interpreted on an atomic basis. The Ln = La, Ce, Nd, Sm, and Lu complexes have f^n (n = 0, 1, 3, 5, and 14, respectively) ground state configurations. The Ce(III) complex has a ^2F ground state while ^4I and ^6H ground states can be anticipated for the Ln = Nd, and Sm complexes,

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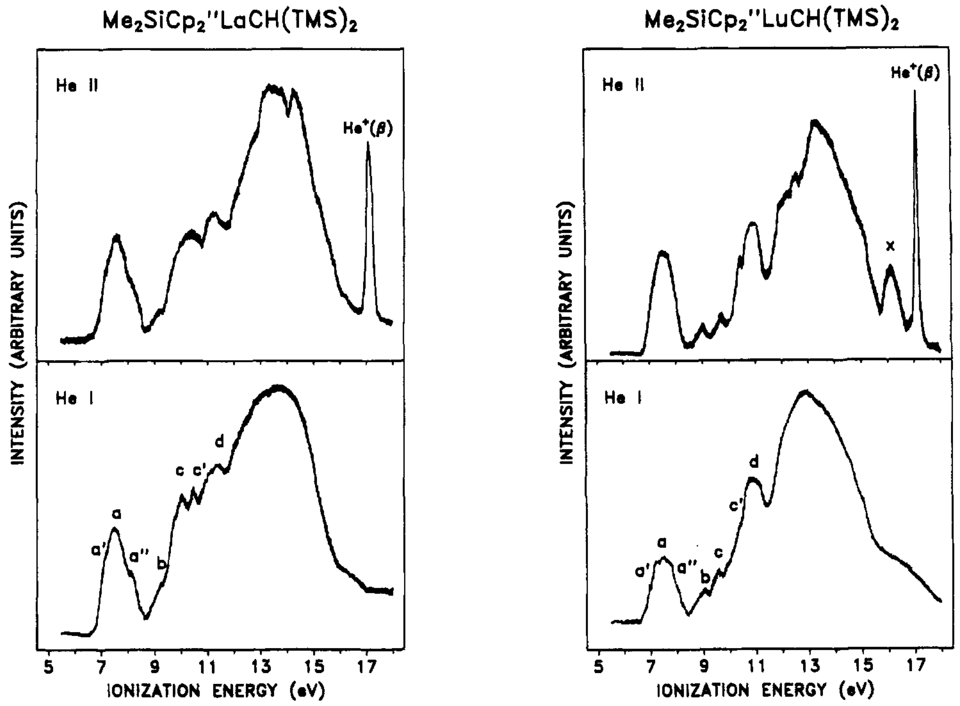

Figure 1. Gas phase He I and He II PE spectra (5.5−18 eV) of $Me_2SiCp''_2LnCH(TMS)_2$; Ln = La, Lu.

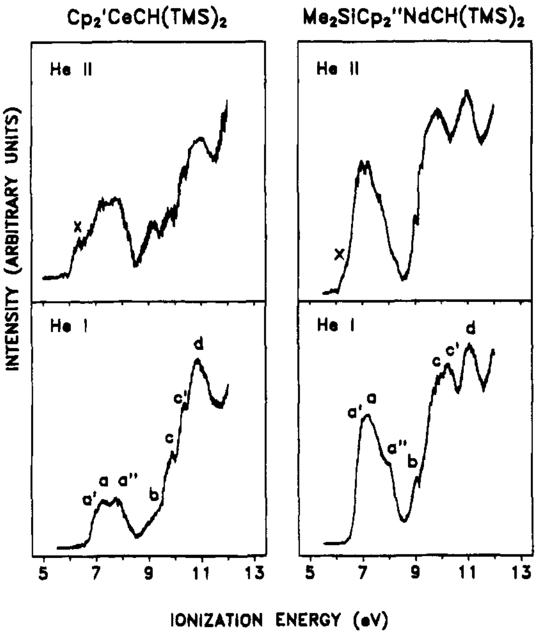

Figure 2. Gas phase He I and He II PE spectra (5.5−12 eV) of $Cp'_2CeCH(TMS)_2$ and $Me_2SiCp''_2NdCH(TMS)_2$.

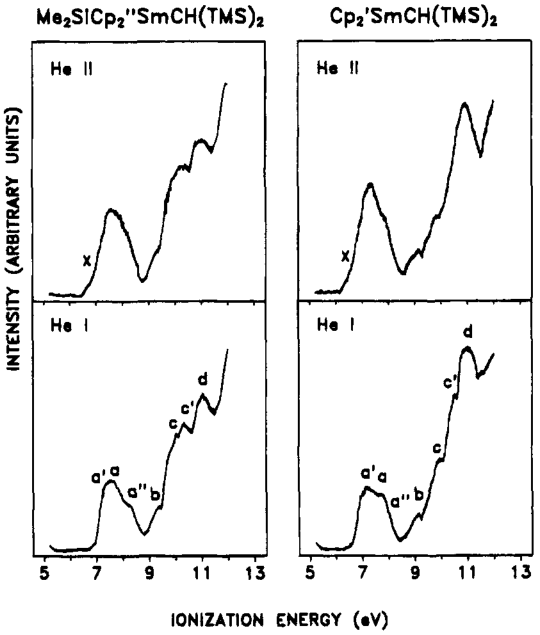

Figure 3. Gas phase He I and He II PE spectra (5.5−12 eV) of $Me_2SiCp''_2SmCH(TMS)_2$ and $Cp'_2SmCH(TMS)_2$.

respectively (Table 4).[30] There is a surprising paucity of information on gas phase PE spectra of Ln-containing complexes.[3a,c,4,6,29] Nevertheless, reference to PE data on $Ce[N(SiMe_3)_2]_3$[29a] suggests that the onset band x in the present Ce(III) complex can be safely assigned to production of the ^1S ion state upon ionization from the ^2F ground state. Assignment of the spectra of the Ln = Nd, Sm complexes is not unambiguous. In fact, upon ionization from the ^4I state of the f^3 ground configuration of the Nd complex, two states, ^3H and ^3F, are produced (Table 4).[31,32] Nevertheless, only a low intensity onset shoulder (x) is detectable in the He II spectrum (Figure 2). Therefore, in analogy to the assignment of the PE spectrum of $Nd[N(SiMe_3)_2]_3$,[29a] we suggest that these ionizations are hidden under the more intense a envelope or, tentatively, that shoulder x is associated with the production of the ^3H ground ion state.

In the present Sm complexes, ionization from the ^6H ground state results in the production of several ion

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[30] Cox, P. A. *Struct. Bonding (Berlin)* **1975**, *24*, 59.

[31] (a) The energy separation of final state terms upon ionization from any f^n configuration can be estimated, within a crystal field approach,[6,31b,c] from optical data[31d] of the preceding f^{n-1} Ln^{3+} ion. (b) Campagna, M.; Wertheim, G. K.; Baer, Y. In *Topics in Applied Physics*; Ley, L., Cadorna, M., Eds.; Springer-Verlag: Berlin 1979; Vol. 27, Chapter 4, p 217. (c) Cox, P. A.; Baer, Y.; Jørgensen, C. K. *Chem. Phys. Lett.* **1973**, *22*, 433. (d) Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4412, 4424.

[32] In particular, the energy separation between the two states can be estimated from data of the Pr^{3+} ion[31d] and is around 0.6 eV.

Table 4. States Arising on Ionization of f^n Free-Ion Configurations with First-Order Spin-Orbit Coupling[a]

initial state		final state		multiplet components	
		LS	intensity	*J*	intensity[b]
f^1	$^2F_{5/2}$	^1S	1.000		
f^3	$^4I_{9/2}$	^3H	2.333	4	1.890
				5	0.424
		^3F	0.667	2	0.563
f^5	$^6H_{5/2}$	^5I	2.758	4	1.755
				5	0.919
		^5G	1.266	2	0.513
				3	0.575
				4	0.165
		^5F	0.500	1	0.168
				2	0.234
		^5D	0.476	0	0.149
				1	0.224
f^{14}	$^1S_0$	^2F	14.000	7/2	8.000
				5/2	6.000

[a] From ref 30. [b] Only multiplet components with normalized intensity greater than 0.1 are listed.

states (Table 4). Analogously to the Nd complex, a more pronounced onset shoulder, x, is detectable in the He II spectra (Figure 3). No PE data have been reported to date for any Sm(III) complexes. Nevertheless, the lowest energy f^{-1} ionization has been observed in the 5–6 eV region in the PE spectrum of Cp'_2Sm.[6] Therefore, the shoulder x around 6.4–6.5 eV (Figure 3) can be tentatively associated with production of the ^5I ion state. The lower intensity features due to the remaining states are not detectable because of the more intense proximate structures.[31,33] The unresolved nature of the 4f bands in both of the present Nd and Sm complexes precludes the observation of any band splitting due to spin-orbit coupling of the ion states generated upon ionization. Note that the present organometallic PE data are consistent with a gradual energetic stabilization of 4f-orbitals across the lanthanide series, as observed in earlier PE studies of lanthanide trihalides.[4]

Turning now to the spectra of $Me_2SiCp''_2LuCH(TMS)_2$ (Figure 1), we comment on the band at 16.19 eV. We have already noted that the band becomes detectable only in the He II spectrum and is definitively absent in the spectra of all other complexes in the present study. Therefore, the band can be safely associated with the production of the $^2F_{7/2}$ ion state arising from the ionization from the core-like $4f^{14}$ orbitals ($^1S_0$ ground state).[4] Unfortunately, the presence of the $He^+(\beta)$ ionization at 17.02 eV precludes the observation of the other expected band component ($^2F_{5/2}$) arising from spin-orbit coupling in the ^2F ion state, as previously observed in nonorganometallic Lu(III) complexes.[4] Furthermore, the IE value (16.19 eV) associated with the $^2F_{7/2}$ state is similar to that reported for LuI_3 (16.15 eV),[4] but expectedly lower than that reported for $LuCl_3$ (17.39 eV),[4] in accordance with the anticipated corelike nature of $4f^{14}$ orbitals, which should be mostly sensitive to electrostatic perturbations and, in turn, to the electron density on the metal center.

Conclusions

This contribution presents a comprehensive study of the electronic structure of a sizable series of polycyclopentadienyl lanthanide hydrocarbyl complexes. It has been demonstrated that the more computationally efficient, nonrelativistic DV-Xα approach satisfactorily reproduces the results obtained using the relativistic ECP ab initio method. Moreover, the good agreement between the experimental PE and the calculated TS IEs for lanthanum complex **1** further supports the applicability of the present approach.

The lanthanide–ligand bonding interactions are dominated by the metal 5d orbitals, while the metal 4f orbitals are only marginally involved in the bonding as also argued by the close similarity of the IE values associated with Ln-ligand ionizations on traversing the lanthanide series. The ionization from the Ln—C bonding orbital represents the lowest-energy, nearly constant PE feature followed by Ln—Cp ionizations, in all of the present He I spectra. Metal f^{-1} ionizations, observed in the He II spectra of the Ce, Nd, Sm, and Lu complexes, are interpreted on the basis of the states generated upon ionization of the f^n ground states. They have either the form of low intensity onset features when Ln = Ce, Nd, and Sm, or of intense structures in the 16–17 eV range in the spectrum of the Lu complex. Moreover, trends in the $4f^{-1}$ ionizations are consistent with a gradual energetic stabilization of 4f orbitals across the lanthanide series. Metal 4f orbitals appear corelike in character in the f^{14} Lu complex. The similarity of the lanthanide–ligand bonding in the present lanthanide series is consistent with the largely comparable chemical reactivity of these complexes.

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(33) Optical data of the Pm^{3+} ion[31d] indicate an energy separation between the ^5I and the remaining final state terms of the ion greater than 1.5 eV.