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Luminescence Spectra of a Series of Cerium(III) Halides and Organometallics. Probes of Bonding Properties Using 4f–5d Excited States

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Room-temperature luminescence spectra have been recorded under a range of conditions for series of 11 cerium(III) compounds containing halide, alkyl, aryl, ether, nitrile, and cyclic aromatic hydrocarbon ligands (Cp, C_5Me_5, and COT). The compounds exhibit emission bands arising from the Laporte allowed decay of the lowest ^2D state ($4f^05d^1$) to one or both of the spin–orbit components (5/2, 7/2) of the ^2F ground state ($4f^15d^0$). The energies of the emission maxima are highly dependent on the nature of the ligand sphere, indicating a sizable nephelauxetic effect arising from covalent character in the metal–ligand bonding. The magnitude of these effects appears to increase in the general order halide < alkyl, aryl < Cp < COT, C_5Me_5. The accessibility of the cerium(III) 5d-derived excited state makes this metal a sensitive probe of the effects of 5d orbitals on covalent bonding and may allow its use as a luminescent probe into the nature of a variety of environments.

Introduction

The ability of organolanthanides to adopt high coordination numbers and induce a variety of interesting organic reactions[1] has prompted questions regarding their bonding properties. Specific among these are questions regarding the degree of metal–ligand covalency and the degree of participation of the lanthanide 4f orbital in such bonding. It is now generally agreed that the 4f orbitals are largely shielded from external interactions by the outer 5s and 5p orbitals,[2] and this leads to less involvement of f orbitals in lanthanide bonding than is generally assumed to operate in the actinides. Thus, the 4f electron configuration has little or no effect on the (nearly identical) structures of the $(C_5Me_5)_2Ln$ derivatives of Sm and Eu, both of which are found to exhibit pronounced bending and small centroid–metal–centroid angles (140.1° vs. 140.3°).[3] Further, a model that assumes weak metal–ligand interactions and more significant ligand–ligand steric interactions has proven successful in predicting structural features of organolanthanides with a number of different ligand sets and geometries.[4] Thus, several authors have been prompted to describe the bonding of organolanthanide(II) and organolanthanide(III) compounds as wholly ionic.[5] This stands in contrast to the case of the cerium(IV) compound $(COT)_2Ce$ (COT = cyclooctatetraenyl dianion), for which substantial covalency and f orbital participation are indicated;[6] this presumably reflects the polarizing power of the tervalent cerium center.

It is perhaps worth noting that if there exists a significant degree of covalency in organolanthanide compounds, it will primarily involve lathanide 5d orbitals. Previous attempts to investigate such effects have included studies of the luminescence spectra of Cp_3Tb,[7] Cp_2TbX,[8] and $TbCl_3$[9] complexes as well as Cp_3Yb,[10] $(C_5Me_5)_2Eu$,[11] and $(C_5Me_5)_2Yb$[12] complexes. Several of these compounds have been observed to luminesce at energies lower than would be expected for true ionic compounds, and this has been taken as evidence of some covalent character.[7-9] Except for the divalent $(C_5Me_5)_2Yb$ compound, however, all of the systems described above luminesce as a result of transitions that are confined wholly within the 4f manifold. Recently, one of us reported that the cerium(III) compound $[Li][(C_5Me_5)_2CeCl_2]$ exhibited strong luminescence in the solid state at room temperature.[13] Cerium(III) has long been known to have a lowest excited state which is $4f^05d^1$ in nature.[14] As such, compounds of this metal should represent a better test of covalent character in tervalent organolanthanides since the luminescent transition originates in a state derived from population of the 5d orbital. We have previously reported studies resulting in the preparation of organocerium(III) compounds with unusually open coordination spheres.[15] In this work we have chosen to study the luminescence behavior of a number of cerium(III) compounds, and this represents the most complete series yet reported for a given metal. These efforts were

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motivated in part by a desire to use this metal as a sensitive probe to derive a semiquantitative ranking of the interaction strengths for various important organolanthanide ligand sets. Further, the report that the aquo ion $[Ce(H_2O)_9]^{3+}$ undergoes efficient photodissociation[16] indicates the synthetic potential of photochemical methods and suggests the importance of understanding the properties of and deactivation pathways available to the $4f^05d^1$ excited state. Lastly, the recent reports of luminescence from polymer-doped cerium(III) ion[17] and the dependence of luminescence energy on ligand sphere (described herein) indicates the potential utility of this ion in probing metal ion binding sites in complex media.

Experimental Section

General Considerations. All of the organocerium compounds used in this work are air- and moisture-sensitive, and they were prepared and manipulated under a dry nitrogen or argon atmosphere. Compounds were prepared by using standard Schlenk techniques and glassware with Solv-Seal joints. Solid transfers were carried out in a Vacuum Atmospheres Corp. glovebox. Toluene, tetrahydrofuran, and ether were distilled from sodium benzophenone ketyl under nitrogen. Anhydrous cerium(III) chloride was purchased from Aldrich and heated under vacuum before use. This was dissolved in tetrahydrofuran to give the complex $CeCl_3(THF)_x$ (x = 3 or 4). The following compounds were prepared according to literature methods: $[Li(OEt_2)_2][(C_5Me_5)_2CeCl_2]$,[13,15] $CeI_3(THF)_x$ (x = 3, 4),[15] $(C_5Me_5)CeI_2(THF)_3$,[15] $[Li(tmed)]_3[CeMe_6]$,[18a] $[Li(tmed)][(C_5Me_5)_2Ce(CH_3)_2]$[18b] (tmed = *N,N,N′,N′*-tetramethylethylenediamine), $[K(diglyme)][(COT)_2Ce]$,[5b] $[Li(THF)_4][CePh_4]$,[19] $Cp_3Ce(THF)$,[20] and $Cp_3Ce(NCMe)_2$.[4b]

NMR spectra were obtained on a Varian XL-400 spectrometer and ultraviolet–visible spectra on a Hewlett-Packard 8451A diode array spectrophotometer.

Luminescence Samples. The compound of interest was dissolved in the appropriate solvent (usually tetrahydrofuran, see text) in the glovebox; unless otherwise noted, concentrations were 1×10^{-4} M. The solutions were added to a 4-mm i.d. pyrex tube, and the tube was attached to the Schlenk line. The solutions were frozen in liquid nitrogen and the tubes sealed with a torch. Solid samples were sealed in a similar fashion.

Luminescence Spectra. All excitation and luminescence data were obtained using a Spex Fluorolog II instrument. The emission was collected at right angles to the excitation beam, and all data were recorded at room temperature. Correction of the spectra data was effected by the Spex DM1B laboratory computer.

Results and Discussion

The gaseous cerium(III) ion is known to have a lowest excited state ($4f^05d^1$) which is 49 737 cm^{-1} above the ground state.[21] When CeF_3 is doped into the tetragonal sites of a CaF_2 crystal lattice, this gap decreases by almost 18 000 to 31 928 cm^{-1}, and the resulting material exhibits an absorption at 313 nm.[22] The decrease is thought to reflect a lowering of the energy of the first excited state brought on by the ionic crystal field splitting of the 5d orbital set.

Table I. Excitation and Emission Data (nm)[a]

compound	excitation wavelength	emission[b] $^2F_{5/2}$	$^2F_{7/2}$	dβ[c]
$[Li][(C_5Me_5)_2CeMe_2]$	375	544	d	43.7
$[Li][(C_5Me_5)_2CeCl_2]$	315	538	615	42.4
$[K(diglyme)][(COT)_2Ce]$	350	495	d	36.7
$(C_5Me_5)CeI_2(THF)_3$	332	467	506	32.7
$Cp_3Ce(THF)$	340	458	482	27.6
$Cp_3Ce(NCMe)_2$	340	421	460	27.0
$[Li(THF)_4][CePh_4]$	350	413	d	24.2
Cp_3Ce[e]	340	408	d	23.2
$[Li(tmed)]_3[CeMe_6]$[f]	340	380	403	17.6
$CeI_3(THF)_x$	300	377	405	17.2
$CeCl_3(THF)_x$	320	360	385	12.9

[a] Spectra were obtained from solutions that were 10^{-3}–10^{-4} M in tetrahydrofuran at 25 °C, unless otherwise noted. [b] Emission lines are attributed to transitions from excited ^2D state to state indicated. [c] In percentages from Jorgenson (eq 1); see text. [d] Low-energy band not resolved (see text). [e] Saturated toluene solution. [f] Ether solution.

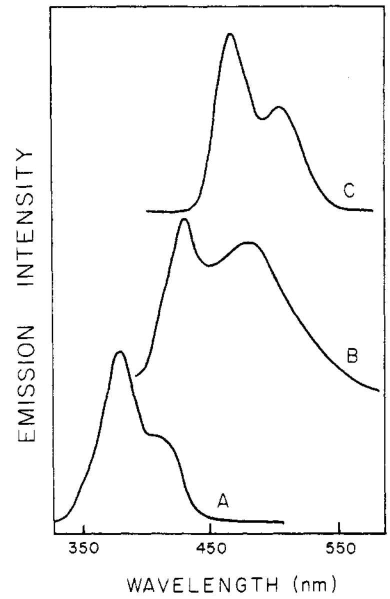

Figure 1. Luminescence spectra of (A) $CeI_3(THF)_x$, (B) $[(C_5Me_5)CeI_2(THF)_x]_y$, and (C) $(C_5Me_5CeI_2(THF)_3$. The spectra are shown in arbitrary units and have been normalized to equivalent intensities.

Blasse and Bril have supported cerium(III) in various metal oxide host lattices and observed luminescence spectra (over the range 29 500 to 43 500 cm^{-1}, depending on the particular metal oxide support) containing two bands; these are normally separated by ca. 2000 cm^{-1}.[23] The presence of two bands results from spin–orbit splitting of the ground state into $^2F_{5/2}$ and $^2F_{7/2}$ components, of which the former is the lower in energy. The relative constancy of this separation is consistent with the notion that the 4f states are not greatly perturbed by the nature of the ligand sphere. The emission bands are presumed to result from transitions out of the lowest component of the first excited state (^2D), and the presence of 5 bands in the *absorption* spectrum of $[Ce(H_2O)_9]^{3+}$ indicates that the ^2D state is split by some combination of spin–orbit coupling and ligand field interactions.[16] In at least one case, it has been estimated that ligand field effects are an order of magnitude more important than spin–orbit effects for the ^2D first excited state.[23a]

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General Considerations. Table I contains a listing of the compounds studied here, with their luminescence wavelengths listed in order of increasing energy from top to bottom. As is indicated, the compounds exhibit spectra with emission bands in the range from 360 to 650 nm. In most of the cases, the spectra contain the expected two bands corresponding to $^2F_{5/2} \leftarrow {}^2D$ and $^2F_{7/2} \leftarrow {}^2D$ emissive transitions; these are usually well-isolated with separations of ca. 1100–2300 cm^{-1}, but the low-energy $^2F_{7/2}$ derived band is sometimes seen as a shoulder on the more intense $^2F_{5/2}$ band (representative spectra are shown in Figure 1). Also given in Table 1 are the excitation wavelengths. Excitation spectra were obtained while monitoring the $^2F_{5/2} \leftarrow {}^2D$ emission band, but similar spectra can be obtained by monitoring the $^2F_{7/2} \leftarrow {}^2D$ emission; the values given are the maxima of the broad excitation bands. Although some of these excitation bands exhibit structure derived from ligand field splitting of the excited ^2D state, the general broadness precludes a close analysis of this structure. Most of the compounds exhibit absorptions in the range 215–300 nm, with the low-energy bands tailing out past 300 nm. The excitation bands reside on the red edge of these lower energy absorption bands, indicating that there may be a weaker band obscured by the tail.

There are a few compounds for which only one emission band is observed, most notable of which is the compound $[K(diglyme)][(COT)_2Ce]$; this compound exhibits only one luminescence band at 495 nm (10^{-4} M in tetrahydrofuran solution), and it is much broader than that observed for other compounds in the series. We have attempted to obtain low-temperature (77 K) spectra for this and a few other compounds in the series, but these were not appreciably sharpened relative to the corresponding spectra at ambient temperature. Hence we have chosen to focus our attention on the ambient-temperature spectra. In their work with metal oxide-supported materials, Blasse and Bril noted that the low-energy luminescence band can be lost at high effective cerium(III) concentrations due to self-absorption effects.[23b] As such, we chose to study the luminescence of the $[K(diglyme)][(COT)_2Ce]$ salt as a function of concentration in THF solvent. Nonetheless, we were unable to observe any evidence of the low-energy band, even down to 10^{-6} M. In their report of the synthesis of this compound, Streitwieser and co-workers considered the possibility that both charge-transfer and intraligand states contributed to its absorption spectrum.[5b] Indeed, whereas most of the cerium(III) compounds studied here are light yellow in color, this particular salt is dark green. The ready accessibility of these other excited states is thus thought to be the cause of the inordinate broadening exhibited in the luminescence spectrum of the compound, and these transitions may serve to obscure the low-energy component of the f–d transitions.

The ordering of luminescent energies in Table I is thought to reflect an increase in covalent character from bottom to top. The criterion used here to determine covalency (decreasing emission energy) is similar to one applied previously to absorption spectra by Jorgenson.[24] He suggested that the absorption energy for a given compound (ν) be compared to that for the aquo ion of the same metal (ν_{aquo}); the degree to which the absorptions of the compound in question are lowered relative to those of the aguo ion is then attributed to a nephelauxetic effect arising from partial covalent overlap. This relationship is expressed in eq 1, in which $d\beta$ is the fractional difference in β for the

$$\nu - \nu_{aquo} = d\sigma - (d\beta)\nu_{aquo} \qquad (1)$$

compound of interest relative to that of the aquo ion (β = the nephelauxetic ratio) and $d\sigma$ is a temperature-dependent correction term that adjusts for ground-state-energy differences between the two compounds (the latter is usually small, amounting to only 200–300 cm^{-1}). Equation 1 was used to determine $d\beta$ values for the compounds studied here, and these are included in Table I. The utility of $d\beta$ for a compound is that it is considered to be slightly more than twice the percentage of covalent character in the compounds metal–ligand bonds.[24]

Cerium Halides. The Jorgensen criterion (eq 1) was previously applied to the compounds $TbCl_3$ and $TbCl_3 \cdot 3.5(THF)$ and indicated an increase in covalency arising from THF complexation in the latter.[9] The aquo ion $[Ce(H_2O)_9]^{3+}$ exhibits luminescence bands at 313 and 333 nm (either in aqueous solution or when doped into crystals of $[La(H_2O)_9][EtOSO_3]_3$).[16] When these are compared to the 360- and 385-nm bands of $CeCl_3(THF)_x$ (Table I), the Jorgenson criterion again indicates that there exists some degree of covalency in the latter. Further, it is also possible to discern a slight difference between this chloride (ca. 6% covalency) and the analogous $CeI_3(THF)_x$ (ca. 8% covalency), with the latter emitting at lower energies. Increased covalent character in the iodide is also indicated by the reported melting points of the anhydrous halides (CeF_3, 1437 °C; $CeCl_3$, 802 °C; $CeBr_3$, 722 °C; CeI_3, 761 °C).[25] It is interesting to note that the bromide does not fit into the general trend of decreasing melting point with increasing halide size. We are interested in determining if the luminescence bands of $CeBr_3(THF)_x$ appear at longer wavelengths than those of the iodide, but we have yet to prepare a suitably pure sample of anhydrous $CeBr_3$. We also note the agreement between these results and those obtained from a combination of photoelectron spectroscopy and theory by Russic et al.[26] These authors detect covalencies on the order of 8–14% for $CeCl_3$, the majority of which is derived from the cerium 5d orbitals. They also note a small but steady increase in covalent character upon going from chloride to iodide.

Cerium Alkyls and Aryls. The σ-bonded organometallic salts $[Li(tmed)]_3[CeMe_6]$ and $[Li(THF)_4][CePh_4]$ exhibit high-energy emission bands at 380 and 413 nm, respectively. The low-energy band of the latter compound is not resolved. It would appear from these wavelengths that these cerate salts exhibit little more covalency than do the cerium halides. This result argues against the prediction of Tsutsui and co-workers,[27] who suggested that alkyls and aryls might prove more covalent in nature than compounds containing π-ligands; theory has also predicted the latter for U(VI).[28] It may be that the higher valent metal ions are better able to polarize the localized electron density on a σ-bound carbon. Effects similar to those described above were observed for $Cp_3Tb(THF)$ and $Cp_2TbMe(THF)$, with the indication that replacement of a Cp in the former by a methyl in the latter resulted in blue-shifted luminescence.[8] We note that it is possible that an intrinsically greater alkyl covalency could be partially

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masked by the differences in the coordination spheres. In comparison the compounds $[Li(ether)_2][(C_5Me_5)_2CeCl_2]$ and $[Li(tmed)][(C_5Me_5)_2CeMe_2]$ one observes only a small red shift (ca. 10 nm) in the emission of the latter. In their PES study of the $(C_5Me_5)_2UX_2$ (X = Cl, Me), Ciliberto et al.[29] obtained evidence for diminished Cp*–U bonding in the chloro compound due to X–U π bonding. Hence it is also possible that the greater covalency expected in the aforementioned cerium methyl linkage (vs. the cerium chloride linkage) is masked by an offsetting effect of the Cp*–Ce linkages. Lastly, we note that direct comparisons with the permethyl compound $[Li(tmed)]_3[CeMe_6]$ compound are somewhat tenuous because of concentration and ion pairing effects to be discussed later.

Cyclopentadienyl and Cyclooctatetraenyl Systems. Turning our attention next to the π-ligand organometallics, we note that the data in Table I support a rough general trend in which the emission energies decrease in the order $C_5H_5 > COT \geq C_5Me_5$. In their report of the syntheses of several of the tris(cyclopentadienyl)lanthanides, Birmingham and Wilkinson noted that all of the compounds exhibited magnetic and spectroscopic properties similar to those of the aqueous ions. Moreover, all of the compounds were found to be air-sensitive, with Cp_3Ce standing out as the analogue most susceptible to air oxidation.[20] Also, the solid-state structures of the Cp_3Ln series are known to vary with lanthanide ion size and preferred coordination number.[1a] While the structure of Cp_3Ce has not been determined, that of Cp_3La is known to consist of complex polymeric arrays best formulated as $[(\eta^5\text{-}Cp)_2La(\mu\text{-}\eta^2\text{:}\eta^5\text{-}Cp)]_x$.[30] Lastly, Nugent et al. have used the solid-state UV–visible spectra of some Cp_3Ln and Cp_3Ac analogues (Ln = Pr, Nd, Er; Ac = Am, Cm) to study their bonding properties.[5a] They note that the f–f absorption spectra for these compounds exhibit red shifts relative to the aquo ions of 1040 cm^{-1} or less. By calculating the various nephelauxetic ratios ($d\beta$) and applying the Jorgenson criterion,[24] they were able to conclude that the bonding in the lanthanide compounds consisted of ca. 3% (or less) covalent character. Our data on the Cp_3Ce series stand in contrast to these reports. We have studied three compounds, Cp_3Ce, $Cp_3Ce(THF)$, and $Cp_3Ce(NCMe)_2$. The uncomplexed (sublimed) Cp_3C_3 was dissolved to the saturation point in toluene (estimated to be between 10^{-5} and 10^{-4} M), a solvent chosen because it is not anticipated to exhibit appreciable Lewis basicity; this solution showed but one luminescence band. The other adducts were prepared and dissolved in the respective Lewis base solvents so as to ensure complete complexation. The luminescence data for all three compounds indicate a substantial lowering of the excited-state energies, with emission maxima ranging from 408 to 465 nm. These correspond to red shifts from the aquo ion emissions of at least 8500 cm^{-1}; when compared to the red shifts observed by Nugent et al. ($\leq$1040 cm^{-1}), it would appear that the cerium compounds involve much greater covalencies than the 1–3% calculated for the other Cp_3Ln by these authors from f–f spectra. Moreover, the data in Table I also indicate that complexation of Lewis base leads to an increase in the nephelauxetic effect relative to that for the uncomplexed species and that this is slightly dependent on the number and/or type of Lewis bases in the complex (note that the assignment of two CH_3CN molecules in the nitrile complex has been verified crystallographically[4b]). It is also of interest that in their studies of Cp_3Yb complexes of the Lewis bases pyrrolidine, PEt_3, tetrahydrothiophene, and THF, Schlesener and Ellis found that the adducts luminesce (from f–f states) at slightly *higher* energies than does the free Lewis acid.[10] While we are not sure why this trend is opposite that seen here for Cp_3Ce, we suspect it reflects the very different character of the excited states for the two series of compounds.

The pentamethylcyclopentadienyl ligand has been utilized frequently in transition-metal and f-element organometallics and has exhibited the ability to saturate the coordination sphere as well as donate a great deal of electron density to formally high-valent metal centers.[1,31] This ability is illustrated for the C_5Me_5 compounds studied here; these fall at the low-energy end of the luminescence series. Although it is difficult to assess the effects of coligands, it would appear that the effects of C_5Me_5 groups are additive since the emission of the $(Li(ether)_2]$-$[(C_5Me_5)_2CeX_2]$ derivatives (X = Cl or Me) are at significantly lower energy than that of the mono(pentamethylcyclopentadienyl) compound $(C_5Me_5)CeI_2(THF)_3$. This is true in spite of the fact that the iodide ligands in the latter should contribute more covalent character than the chloride ligands in the former. However, the fact that the bis(pentamethylcyclopentadienyl) derivative is formally anionic should not be overlooked as a possible contributing factor (vide infra). Similar caution applies to comparisons between C_5H_5 and C_5Me_5 ligands. Although the compounds containing either one *or* two of the latter ligands emit at lower energies than the compounds containing three of the former, the differences in ligand geometries make direct comparisons tenuous. Unfortunately, there are as yet no isostructural analogues of the two ligands known for cerium, for which $(C_5H_5)MX_2$ or $(C_5H_5)_2MX$ derivatives are unavailable.

We noted earlier the difficulty in determining the exact f–d emission energy for the $[K(diglyme)][(COT)_2Ce]$ salt. Nonetheless, if we take the observed emission maximum as a reasonable approximation of the ${}^2F_{5/2} \leftarrow {}^2D$ energy, it becomes clear that the effects of the COT ligands are comparable to those of the C_5Me_5 ligands. This suggests an interesting experimental comparison of this salt with $[Li(ether)_2][(C_5Me_5)_2CeCl_2]$. Streitwieser and co-workers have reported the fact that treatment of $[K(diglyme)][(COT)_2Ce]$ with an oxidant such as AgI results in ready conversion to the cerium(IV) compound $(COT)_2Ce$ (eq 2),[6]

$$[K][(COT)_2Ce] + AgI \xrightarrow[THF]{} (COT)_2Ce + Ag + KI \quad (2)$$

one of only two authentic cerium(IV) organometallics (the other being $Cp_3Ce(OCHMe_2)$[32]). In a similar fashion, we have attempted to oxidize the C_5Me_5 compound, using either electrochemical methods or $AgBF_4$. In the former case, the result was irreversible oxidation at highly positive potential (ca. +2.1 V vs. Ag/Ag^+ in THF). Similarly, the chemical oxidation yielded only C_5Me_5 oxidation products in a reaction reminiscent of an ionic cyclopentadienide. As such, we are presently unable to discern a threshold luminescence energy below which chemical oxidation to cerium(IV) organometallics may be expected. However, the presence of the $(COT)_2Ce^-$ anion near the low-energy end of our series is at least consistent with the observed oxidation chemistry.

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Table II. Medium Effects on the Luminescence Spectra of Selected Compounds[a]

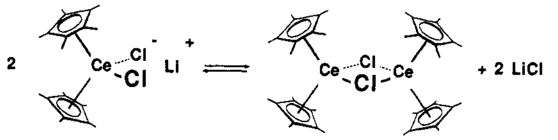
compound	medium	emission $^2F_{5/2}$	emission $^2F_{7/2}$
$[(C_5Me_5)CeI_2(THF)_x]_y$	THF	467	506
	toluene	430	480
	solid	382	415[b]
$[Li][(C_5Me_5)_2CeCl_2]$	THF	538	615
	toluene	458	485
	solid	558[c]	628[c]
$[Li(tmed)]_3[CeMe_6]$	ether	380	403
	solid	528	*d*

[a] Solution spectra were recorded in the indicated solvent at ca. 10^{-4} M. Solid $(C_5Me_5)CeI_2(THF)_x$ was largely desolvated in vacuo (see text). [b] There is an additional weak line observed at 505 nm. This is not believed to result from a $^2F_{7/2} \leftarrow {}^2D$ transition because it occurs at a separation of 4300 cm^{-1} from the higher energy peak. [c] Data from ref 13. [d] Low-energy band not resolved.

The data described herein indicate that compounds with Cp and COT ligands exhibit more metal–ligand covalency than do metal alkyls. This is at odds with a theoretical comparison of the hypothetical $[(C_5H_5)U]^{5+}$ and $[(C_5H_5)Fe]^+$ ions with the corresponding methyl compounds.[28] Unlike the iron cases, the U(VI) ion showed much less covalent interaction (almost none) with the Cp ligand than with the methyl ligand. This may be due to a significant orbital contraction in the high valent ion and leads to the prediction that π-ligand compounds are held together by an ionic–electrostatic interaction between the metal ion and the *anionic* π-ligand. However, we do not believe that this description holds for lower valent Ln(III) systems. Recently, Cotton and co-workers have prepared several hexamethylbenzene complexes of U(IV), U(III), and Sm(III) that appear to involve a significant degree of covalent bonding.[33,34] It appears that the M–arene bonding is somewhat stronger in the M(III) systems than it is in the M(IV) systems, a trend which is not consistent with wholly ionic bonding.

Environmental Effects. In previous studies, luminescence spectra were studied as a function of environment by recording spectra in ether solvents, aromatic hydrocarbon solvents, and the solid state.[7,8] The rationale for this was that very often the nuclearity of organolanthanides changes from monomeric in donating solvents to dimeric or oligomeric in the absence of donor solvents.[1] Since many of the organolanthanides are paramagnetic, NMR methods are often unsuitable for studies of this behavior and luminescence may provide an alternative mode of inquiry into the nature of these compounds. We have performed similar studies on a few of the compounds in the cerium(III) series, specifically $(C_5Me_5)CeI_2(THF)_3$, $[Li(tmed)]_3[CeMe_6]$, and $[Li(ether)_2][(C_5Me_5)_2CeCl_2]$. The results are presented in Table II. In some cases the compounds exhibit only one of the expected two emission bands; in these cases we have assumed that this band is due to the $^2F_{5/2} \leftarrow {}^2D$ transition, but an incorrect assignment would not change the qualitative nature of the conclusions.

In the report of the synthesis of $(C_5Me_5)CeI_2(THF)_3$ we noted that either prolonged evacuation in the solid state or prolonged stirring in aromatic solvents leads to conversion of this monomeric compound to a less soluble derivative which analyzed for $[(C_5Me_5)CeI_2(THF)_x]_y$ with $x \leq 1$; we were unable to determine y because of the insolubility of the oligomeric compound in aromatic solvents.[15] We surmise that, since oligomerization is accompanied by loss of THF ligands, the oligomer employs bridging iodide ligands to saturate the cerium(III) coordination sphere. This behavior is accompanied by a steady increase in luminescence energy (more ionic character) on moving from THF solvent, to toluene solvent, to the solid state (Table II). Moreover, when the luminescence spectrum of this compound in THF solution is monitored over time, it indicates that substantial oligomerization occurs over a period of a few days and is largely complete within a week. Compounds of general formula Cp_2TbX are also thought to dimerize through bridging X groups in the absence of donor solvents.[8] Interestingly, both $[Li(tmed)]_3[CeMe_6]$ and $[Li(ether)_2][(C_5Me_5)_2CeCl_2]$ show somewhat different trends. The former emits at fairly high energy in ether solution (10^{-4} M), but the emission energy is significantly lower in the solid state. The latter compound shows an increase in luminescence energy on going from THF to toluene solution, but then it also shows a dramatic drop in emission energy on going to the solid state. These drops in energy in the solid state are most unusual, but it should be noted that both of these salts contain anionic cerium species for which oligomerization via Ce–X–Ce bridges is not liable to occur. Instead, the solid state is liable to be dominated by ion pairing effects,[13,18] which apparently function so as to lead to decreased emission energy. The increase in the luminescence energy of $[Li(ether)_2][(C_kMe_5)_2CeCl_2]$ in toluene may reflect a tendency toward redistribution, so that Ce–Ce bridging *does* occur between neutral species (e.g., eq 3).



(3)

This suggestion is in line with the fact that sublimation of the ionic compound is known to result in loss of LiCl and a sublimate with empirical formula $(C_5Me_5)_2CeCl$.[13] Moreover, the forward component of an analogous equilibrium has been observed to hinder the synthesis of $[Li(OEt_2)_2][(C_5Me_5)_2LaCl_2]$ unless the workup is carried out under low temperature conditions.[35] The different behaviors indicated by the luminescence data for toluene solution and the solid state would be consistent with the greater mobility of the toluene solute vs. that of the crystalline material, with the toluene solution mobility permitting the redistribution process as shown in eq 3.

Summary. We have presented luminescence data for a wide range of cerium(III) halides and organometallics. The emissions of interest arise from f–d transitions; in this respect the cerium systems differ from those of other lanthanides, which are known to emit from f–f states. This leads to several unique features in the cerium systems. Since the f–d transitions are Laporte allowed, the emission is much more intense than that normally observed for the lanthanide systems with Laporte forbidden f–f transitions. Also, the emissive lifetimes are expected to be much shorter than those measured for terbium compounds (ca. 200–300 μs);[7,8] although we have not yet measured lifetimes, other cerium(III) systems have been found to exhibit luminescence lifetimes of ca. 10^{-7} s.[22] Most important,

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since the cerium excited states involve 5d character, the luminescence data are a sensitive test of covalent bonding character and the involvement of 5d orbitals in this bonding.[2] The results are consistent with the expectation that these figure more prominently than do 4f orbitals in covalent bonding, since the shifts in emission maxima (relative to the aquo ion) are much greater for organocerium compounds than for any other series of organolanthanide compounds studied thus far. Therefore, while the chemical properties of these compounds do indicate predominant ionic character, our data are indicative of a significant degree of covalency (up to ca. 20–25%) that increases in the rough order halides < alkyls, aryls < cyclopentadienyls < COT, C_5Me_5. It is clear that the luminescent cerium(III) center represents a sensitive probe of environmental effects, and we intend to build a wider luminescence data base for making predictions and assignments.

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Hydrozirconation of Aromatic Olefins

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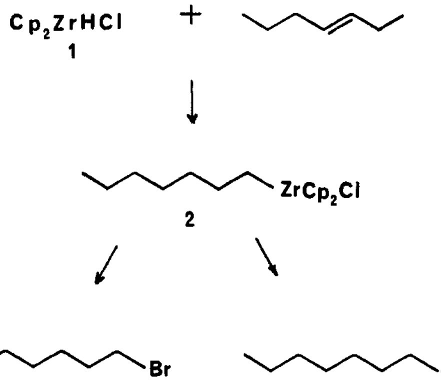
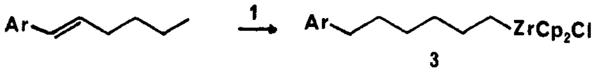
The hydrozirconation of aromatic olefins was found to give mixtures of benzylic and terminally substituted alkyl zirconiums. In contrast to the behavior of simple acyclic olefins, movement of the zirconium to the end of the chain is sluggish and incomplete. At moderate temperatures, the benzylic product predominates almost exlusively, and this was exploited to determine the stereochemistry of oxidation of secondary alkyl zirconiums by *tert*-butyl hydroperoxide and oxygen.

Introduction

The hydrozirconation reaction was discovered by Wailes, Weigold, and Bell[1] and later developed by Schwartz.[2] The zirconium hydride 1, known as Schwartz's reagent, reacts with an isolated olefinic bond to generate an alkyl zirconium species. Reversal of the addition occurs at moderate temperatures and can lead to the original olefin or to a new olefin in which the double bond has moved to an adjacent position.[3] In simple linear alkenes, the zirconium rapidly migrates to the most stable position at the end of the chain, to give 2, and thus a method is provided for the synthesis of simple terminally substituted alkyl compounds, by reaction of 2 with various electrophiles. We have previously applied the process to the synthesis of long-chain compounds, in which symmetrical disubstituted olefins are converted to the terminal alcohols or halides.[3]





Hydrozirconation has not been used extensively in synthesis because the reagent reduces a wide range of functional groups, including carbonyl and halogen. The oxazoline group is stable to the reagent and has been used to protect the carboxylic acid group during hydrozirconation.[4] However, mixtures of products are formed resulting from interaction of the oxazolyl group with the zirconium. Oleyl oxazoline, for example, has been reported to give products of substitution in the 3- and 18-positions.[4] In this paper, we report an investigation into the use of an aromatic ring as a source of latent functionality at one chain terminus, with the idea that hydrozirconation would generate terminally substituted intermediate 3, which with proper manipulation would provide access to a variety of α,ω-disubstituted compounds. During the course of this work, we have found that a mixture of benzylic and terminal zirconium compounds is formed and that it is not possible to drive the zirconium entirely to the terminal position. This reduces the utility of the process in the originally intended sense; however, the formation of the benzylic zirconiums does provide access to secondary alkyl

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