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Organolanthanides and Organoactinides. XV. Synthesis and Properties of New σ-Bonded Organolanthanide Complexes

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A series of new organolanthanide complexes containing σ bonds has been synthesized. The complexes are of the type (η^5-C_5H_5)$_2$LnR (R = methyl, phenyl, and phenylacetylide) and are synthesized by the reaction of the appropriate RLi compound with (η^5-C_5H_5)$_2$LnCl complexes. The new complexes have been characterized by vibrational and visible spectroscopy, as well as by magnetic susceptibility. The infrared data support the presence of ligands which are σ bonded to the metal. The magnetic data and, to a lesser extent, the visible data indicate that there is enhanced covalency in the lanthanide–carbon σ bond. The nature of this covalency and possible f-orbital involvement in the bonding are discussed.

Beginning with the preparation of uranocene in 1968 and the subsequent claim that the f orbitals were involved in the bonding,[3] there has been a dramatic resurgence of interest in the organometallic chemistry of the lanthanides and actinides. However, until the last three years, most of the work has been concerned with complexes which contained only π-bonded ligands.[4-10] Although σ-bonded organometallic compounds are well documented for the d-block transition metals,[11] they have been relatively unknown for the lanthanides and actinides. Consequently, much of the significant recent progress in the cheimstry of the f transition elements involves the synthesis and elucidation of properties of σ-bonded organoactinide complexes.[12-14] By contrast though, σ-bonded organolanthanide complexes have escaped the close scrutiny which their actinide analogs have undergone. Recently though, we communicated our preliminary results in synthesizing alkynyl,[15] alkyl, and aryl derivatives[16] for the lanthanides of the type (η^5-C_5H_5)$_2$LnR.[17] Generally, the complexes represent the first and only well characterized examples of compounds containing lanthanide–carbon σ bonds. These complexes also seemed to possess some degree of covalency (and possible 4f orbital involvement) in the σ bond. We now wish to present a detailed account of the synthesis and properties of these unique and unusual compounds.

Experimental Section

All operations of these organolanthanide complexes were performed in an atmosphere of prepurified argon using Schlenk techniques or in a drybox. Benzene and hexane were degassed, refluxed over finely divided LiAlH₄, and distilled under argon just prior to use. THF and toluene were distilled from blue sodium–benzophenone under argon immediately prior to use. Methyllithium was purchased from Alfa-Ventron, while anhydrous lanthanide trichlorides were obtained from Research Organic/Inorganic Chemical Corp. The Cp₂LnCl complexes (Cp = η^5-C_5H_5) were prepared by the method of Dubeck et al.[18] Melting points were determined in sealed argon-filled capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. We list below the syntheses for several of the new σ-bonded organolanthanide complexes, which are representative of all the complexes which were prepared. All the complexes not described below gave satisfactory elemental analyses.

Bis(η^5-cyclopentadienyl)gadolinium Phenylacetylide. Into a centrifuge Schlenk tube was placed 1.5 g (4.53 mmol) of Cp₂GdCl. Then, 60 ml of THF containing 4.65 mmol of freshly prepared lithium phenylacetylide[15] cooled to −78° was added to the Cp₂GdCl. With stirring, the solution was allowed to warm to room temperature over the course of several hours. By −50°, all of the solid material had dissolved, and by 0°, the solution (originally colorless) had begun to get darker until it had become dark red-orange. The reaction was allowed to stir overnight. At this time, the volume of THF was reduced in vacuo to about 5 ml. Then, 50 ml of toluene was added and an orange oil separated from the solution. The volume of the toluene–THF mixture was reduced in vacuo to 10 ml. During this time, the red-orange color disappeared, the solution becoming tan. Next, 50 ml of hexane was added. At this point, the mixture contained a tan solid and a tannish solution. The Schlenk tube was centrifuged and the solution was transferred away from the solid which was then dried. The crude material was purified by continuous extraction with benzene. The apparatus used was a Schlenk–Soxhlet extractor equipped with a coarse frit. About 60 ml of extractant (benzene in this case) was distilled into a centrifuge Schlenk tube and then used in the purification process. When the extraction began, the solution took on a yellow color, and after 1 hr, a yellow solid began to appear in the benzene. After the extraction was complete (as noted by the disappearance of the yellow color of the solid on the frit), the volume of benzene was reduced in vacuo to 10 ml, and 50 ml of hexane was added. After centrifugation of the Schlenk tube, the benzene–hexane was decanted from the pale yellow solid which was dried to give 0.7 g (40%) of Cp₂GdC≡CPh (Ph = phenyl), mp 279–282° dec. Anal. Calcd for $C_{18}H_{15}Gd$: Gd, 40.47. Found: Gd, 40.56. Ir data (cm⁻¹): 3103 (m), 3075 (m), 3039 (m), 2047 (vs), 1483 (s), 1440 (vs), 1331 (w), 1308 (w), 1256 (w), 1184 (w), 1155 (w), 1113 (w), 1093 (w), 1066 (w), 1008 (vs), 919 (w), 773 (vs), 758 (vs), 692 (s).

Bis(η^5-cyclopentadienyl)ytterbium Methyl. Into a centrifuge Schlenk tube was placed 1.5 g (4.42 mmol) of Cp₂YbCl. THF (60 ml) was added and the resulting orange-red solution was cooled to −78°. Then, 2.4 ml (4.5 mmol) of methyllithium in diethyl ether was syringed into the Schlenk tube. The solution instantly became wine red. The reaction was allowed to warm to room temperature with stirring during a 4-hr period and then to proceed overnight. The volume of THF was reduced to 10 ml in vacuo and 50 ml of toluene was added causing a white solid to precipitate from solution. The volume of the THF–toluene mixture was reduced (to 5 ml) during which time the color of the solution gradually changed from burgundy to orange. At this point, 50 ml of hexane was added which precipitated an orange solid. The crude material was extracted with benzene, this being completed in 1 hr. The volume of benzene was reduced and hexane was added to precipitate out the product. The orange solid was isolated,

washed with hexane, and finally dried to yield 0.6 g (42.6%) of Cp_2YbCH_3, mp 194–198° dec. Anal. Calcd for $C_{11}H_{13}Yb$: Yb, 54.37. Found: Yb, 53.82. Ir data (cm⁻¹): 3109 (m), 3082 (m), 2890 (w), 1436 (m), 1360 (w), 1328 (w), 1264 (w), 1193 (s), 1124 (w), 1103 (w), 1063 (w), 1012 (s), 901 (w), 886 (w), 845 (w), 783 (vs, br).

Bis(η⁵-cyclopentadienyl)erbium Phenyl. Into a centrifuge Schlenk tube was placed 1.2 g (3.63 mmol) of Cp_2ErCl and 0.30 g (3.63 mmol) of phenyllithium.[19] To this was added 60 ml of THF which had been cooled to –78°. The reaction was allowed to warm to room temperature during a 3-hr period and then stirred overnight. Initially, as the solids dissolved, the THF took on a pink color which did not darken or change during the course of the reaction. The volume of the THF was reduced in vacuo and 40 ml of toluene was added, causing a white solid to appear in solution. The volume of the solution was again reduced, and 40 ml of hexane was added causing a pink solid to precipitate. The impure material was extracted with benzene (1 hr) after it was isolated. When the extraction was completed, the volume of benzene was reduced to 5 ml, and 50 ml of cold hexane was added precipitating the complex from the solution. The light pink solid was isolated and dried in vacuo to yield 0.7 g (51.5%) of Cp_2ErPh, mp 128–130° dec. Ir data (cm⁻¹): 3103 (w), 3048 (m), 2994 (m), 2906 (w), 1483 (w), 1468 (w), 1441 (m), 1412 (m), 1347 (m), 1257 (w), 1225 (w), 1182 (m), 1051 (m), 1010 (s), 921 (w), 854 (s), 772 (s, br), 718 (m), 701 (s).

(η⁵-Cyclopentadienyl)holmium Bis(phenylacetylide). Into a centrifuge Schlenk tube was placed 0.9 g (1.74 mmol) of $CpHoCl_2\cdot$ $3THF$.[20] Then, 60 ml of a THF solution containing 3.6 mmol of lithium phenylacetylide was cooled to –78° and transferred into the reaction vessel. The reaction was allowed to stir and warm to room temperature over a 3-hr period. During this time, the solid material dissolved to give a beige solution which began to turn yellow at about 0°. After stirring overnight, the color had darkened until it was yellow-brown. The THF was reduced in volume to 5 ml, and 50 ml of toluene was added. The volume of the resulting mixture was also reduced in vacuo and 50 ml of hexane was added. A pale sand-colored solid was thus precipitated from the yellow toluene–hexane solution. This solution was subsequently evaporated to dryness and the resulting solid was washed with hexane and dried. The two solids were combined and purified by continuous extraction with benzene. After this was complete (1 hr), the benzene solution containing the purified material was concentrated in vacuo to 5 ml. At this point, 50 ml of hexane was added causing a voluminous sand-colored solid to precipitate from the solution. The solid was isolated, washed twice with 30-ml portions of hexane, and dried to yield 0.30 g (39.9%) of $CpHo(C\equiv CPh)_2$, dec pt 190–340°, darkening but no melting. Ir data (cm⁻¹): 3078 (m), 3055 (m), 2960 (m), 2881 (m), 2042 (m), 1592 (w), 1567 (w), 1482 (s), 1437 (s), 1343 (w), 1255 (m), 1191 (m), 1173 (m), 1097 (m), 1066 (m), 1038 (m), 1011 (s), 932 (m), 916 (m), 834 (w), 775 (s), 754 (s), 689 (s).

Spectroscopic Measurements. Infrared spectra were recorded on Beckman IR-8 and Perkin-Elmer 237 spectrometers as Nujol and Fluorolube mulls and examined between disk-shaped NaCl plates. The mulls were prepared in the drybox using Nujol and Fluorolube which had been deoxygenated and dried. The type of cell holder which was used was one in which the salt plates could be clamped together tightly to keep air from getting between them. In this manner, the samples to be examined could be handled in air for several hours with no noticeable sign of decomposition.

Visible spectra were recorded on a Beckman Model 25 spectrophotometer. The solutions were prepared in the following way. A 0.1-mmol sample of the compound to be studied was weighed in the drybox and placed in a small Schlenk tube. Then, outside the drybox, 10.0 ml of freshly distilled THF was syringed onto the solid, thus making 10^{-2} M solutions. Samples of these solutions were then syringed into special 1-cm glass cells which had been fused to a Schlenk adapter so that they could be maintained under an inert atmosphere. No sign of decomposition could be detected in the solutions after several hours. Due to the extreme difficulty encountered in very accurately weighing out milligram amounts of these compounds, values of the extinction coefficients obtained contain an estimated error of ±5%.

Glassware here, as well as at other times, was flame dried whenever possible. This was found to be especially necessary when working with very small amounts of these new organolanthanide complexes.

Magnetic Measurements. Magnetic susceptibilities were measured in the solid state by the Faraday method. The electronics of the system

were tied into a computer which gave continuous readouts of χ, χ_m, and μ_{eff} as the temperature was varied. The balance was calibrated with $HgCo(SCN)_4$. The results obtained in this manner are not corrected for the diamagnetism of the ligands, as this was determined to be quite small (generally 1–2% or less). We are grateful to Dr. Erik Pedersen and Mrs. Solveig Kallesoe for assistance in determining some of the magnetic data.

Results and Discussion

Synthesis and General Properties. New σ-bonded organolanthanide complexes of the type Cp_2LnR have been prepared as shown in eq 1. Methyl and phenyl derivatives were

$$Cp_2LnCl + RLi \xrightarrow{THF} Cp_2LnR + LiCl \qquad (1)$$
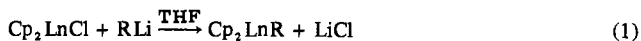
prepared for Gd, Er, and Yb, while phenylacetylide complexes were synthesized of Gd, Ho, Er, and Yb. Also synthesized was a bis(phenylacetylide) complex, $CpHo(C\equiv CPh)_2$, using $CpHoCl_2\cdot3THF$[20] as the precursor in eq 1 rather than the Cp_2LnCl complex. These particular metals were chosen because they span a representative range from the lighter to the heavier lanthanides for which Cp_2LnCl complexes are known.[18] These new complexes are the only ones known for these elements which contain metal–carbon σ bonds.

It has been suggested that the size of the lanthanides influenced the success or failure of a particular reaction. Smaller (heavier) lanthanides seem to favor σ-bond formation, as attempts to prepare 2,6-dimethylphenyl derivatives for lanthanides larger than Yb have been unsuccessful.[17a] It was also noted that cyclopentadienyllanthanide chlorides could not be prepared for elements larger than samarium. This was attributed to some subtle effect of the lanthanide contraction.[18,20] However, for the complexes which we synthesized, no general trends could be ascertained. For the phenylacetylide complexes, the reactions seemed to proceed more smoothly and in better yield on going from Yb to Gd, which is contrary to what might be expected. Conversely though, the phenyl and methyl compounds of Er and Yb seemed to form more readily than did those of Gd.

All of these new organolanthanide complexes are quite sensitive to oxygen and moisture, decomposing in the atmosphere in a matter of seconds or minutes. However, under an inert atmosphere, they seem indefinitely stable. Though the new σ-bonded complexes are air sensitive, their thermal stabilities are quite high. This is especially surprising in view of the previous unsuccessful attempts to prepare such complexes. With the exception of the erbium–phenyl complex (130°), all of them are stable to at least 150° in capillaries sealed under argon. The erbium–phenyl complex, though, showed no detectable sign of decomposition after 12 hr in refluxing THF.

Infrared Spectra. All the complexes have bands at ∼3100, 1440, 1010, and 780 cm⁻¹, indicative of η⁵-cyclopentadienyl ligands.[21] In addition, each type of derivative has characteristic bands which arise from and support the σ nature of the R groups.

All of the phenylacetylide complexes have a strong sharp band at ∼2050 cm⁻¹ arising from the $C\equiv C$ stretch.[22] The $C\equiv C$ stretch in the holmium–bis(phenylacetylide) compound at 2042 cm⁻¹ is weaker and broadened somewhat compared to the $Cp_2LnC\equiv CPh$ complexes but is similar to the absorptions observed for uranium–acetylide complexes.[13] Bands are also present which arise from the substituted phenyl moiety. These occur at 3075 (C–H stretch), 1483 (C–C stretch), and 758 and 692 cm⁻¹ (C–H out-of-plane bending). The appearance of these last two bands is characteristic of a monosubstituted phenyl ring (attached to the acetylene linkage here).

The methyl derivatives all have one band at ∼1190 cm⁻¹ which is quite characteristic. This strong absorption arises from the symmetric deformation of the methyl group and is
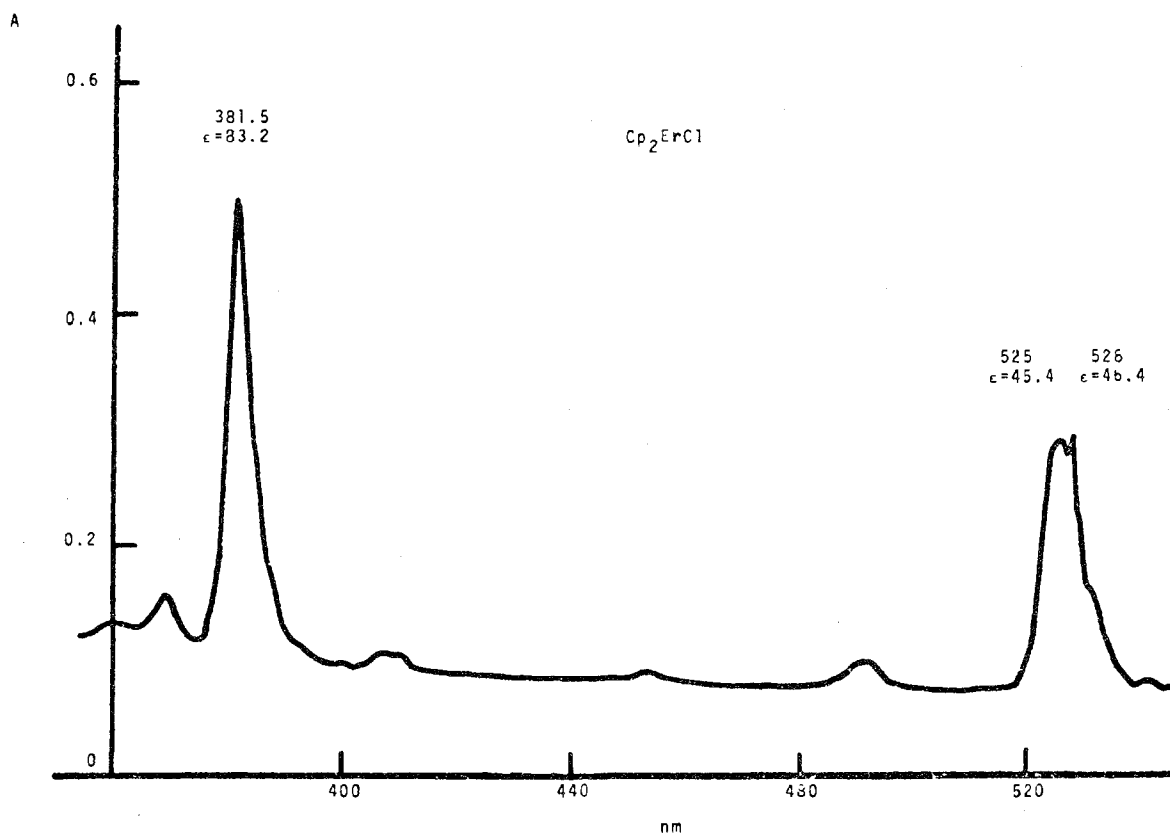
Figure 1. Visible spectrum of Cp$_2$ErCl.

characteristic of complexes containing a methyl ligand bound to a metal.[23] Also present in the spectra is a weak broad band centered at 2890 cm^{-1} (C–H stretching), as well as bands at 1360 and 1328 cm^{-1} (C–H bending).

The infrared spectra of the phenyl complexes are also distinctive. The characteristic C–H out-of-plane bending vibrations of the phenyl moiety occur at 718 and 701 cm^{-1}. These are shifted from where they come in the spectra of the phenylacetylide complexes. However, this is not unexpected since the phenyl moiety is bonded here to a metal (or from strictly an ionic viewpoint, it is a carbanion) while it is bonded to a carbon atom in the phenylacetylide complexes. Other bands present which arise from the phenyl ligand occur at 3048 cm^{-1} (C–H stretch) and 1412, 1468, and 1483 cm^{-1} (C–C stretch).

Visible Spectra. The visible spectra which have been obtained for these complexes reveal some unusual and informative properties. For clarity, a number of the spectra are shown in Figures 1–7. The spectra of all of the new σ-bonded organolanthanide complexes contain a charge-transfer (CT) band which originates in the uv and tails into the visible region. This indicates that there is at least some interaction, other than strictly ionic, between the ligand (R) and the lanthanide. The origin of the charge transfer is then assigned as ligand to metal. This is the assignment given to the CT bands present in the visible spectra of the cyclooctatetraenyllanthanide complexes by Streitwieser et al.[9] This is also consistent with the type of bonding found in σ-bonded organouranium complexes. For the uranium complexes, it is postulated that the R moiety transfers electron density into vacant metal orbitals.[12,13] It would thus appear that a similar mechanism is operative for these σ-bonded organolanthanide complexes.

Further evidence that the charge transfer is ligand to metal can be seen from the position of the CT band in the spectra. For the methyl, phenyl, and phenylacetylide derivatives of Gd and Er, the position of the CT band is shifted to higher energy

as the reducing strength of the ligand is decreased. This is evidenced also in the holmium–phenylacetylide complexes, as the CT band is shifted more into the visible region for the bis(phenylacetylide) derivative in relation to where it appears for Cp$_2$HoC≡CPh. Two R moieties should increase the amount of electron density transfered to the lanthanide, and the resultant CT band should be shifted to lower energy in the spectrum in relation to where it comes in the spectrum of Cp$_2$HoC≡CPh.[24] The observation of just this effect lends additional support for a lanthanide–carbon σ bond containing at least some degree of covalency.

One very interesting phenomenon was observed in the spectra of the phenylacetylide complexes of Er and Ho. The bands at 381 and 455 nm, respectively, have increased in intensity (more so for Er than for Ho) without shifting in position. Such bands are called hypersensitive. Only those transitions where $J = \pm 2$ are known to be hypersensitive in the lanthanides.[25] The origin of this hypersensitivity has been the subject of much debate. Early reports claimed that hypersensitivity arose from the inhomogeneous polarizability of the solvent.[26] Later work has shown that this effect could be accounted for simply by changing the point group symmetry of the lanthanide ion.[27] More recently, it has been shown that besides symmetry effects, hypersensitivity is also related to covalent interactions between the ligand and the lanthanide.[25]

The bands which change in intensities in the Er and Ho complexes areise from transitions which are known to be hypersensitive.[28] In THF solutions, the symmetries of the starting Cp$_2$LnCl complexes and the Cp$_2$LnC≡CPh complexes (Ln = Er, Ho) should be essentially identical. Therefore, the intensity changes should be attributable to enhanced covalency between the metal and the R moiety. This formulation is consistent with the assignment of the CT bands as previously mentioned and supports the magnetic susceptibility data which are discussed in the next section.

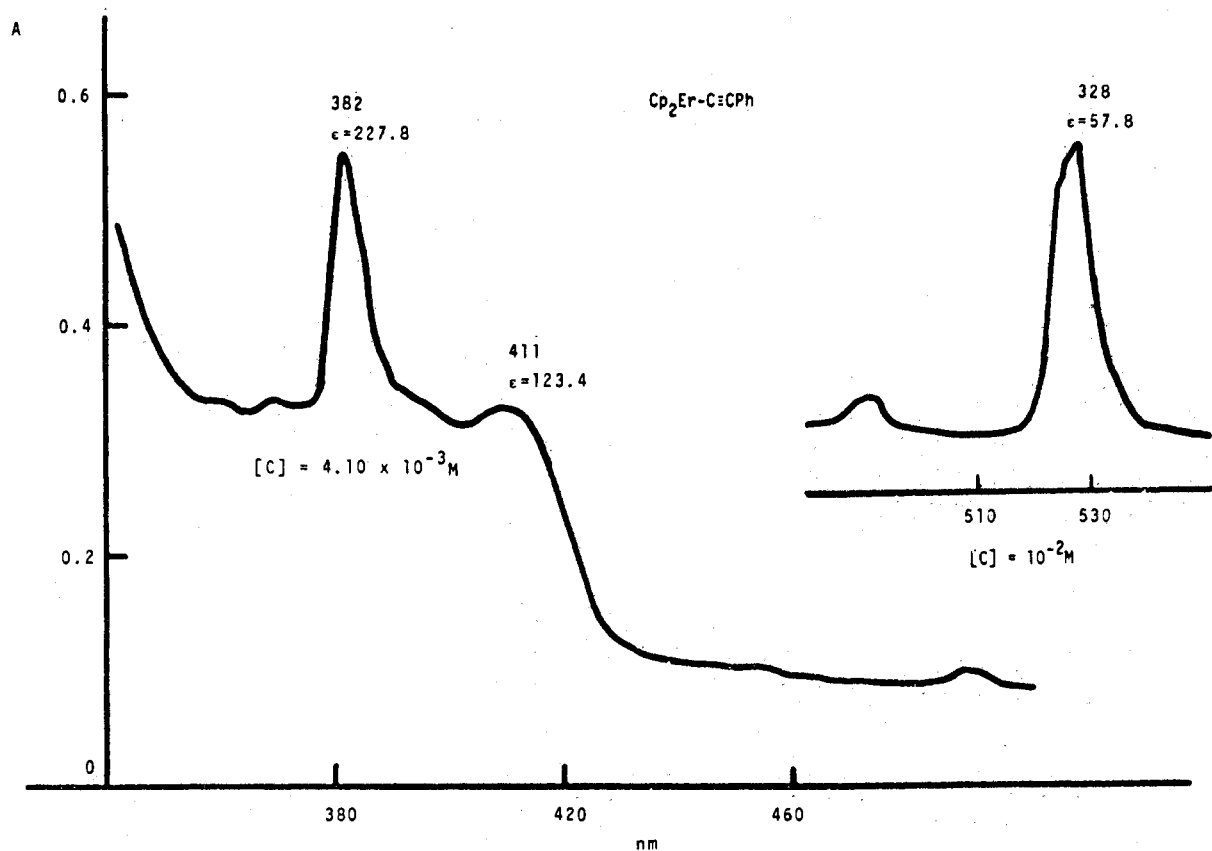However, for the phenyl and methyl complexes of Er, no

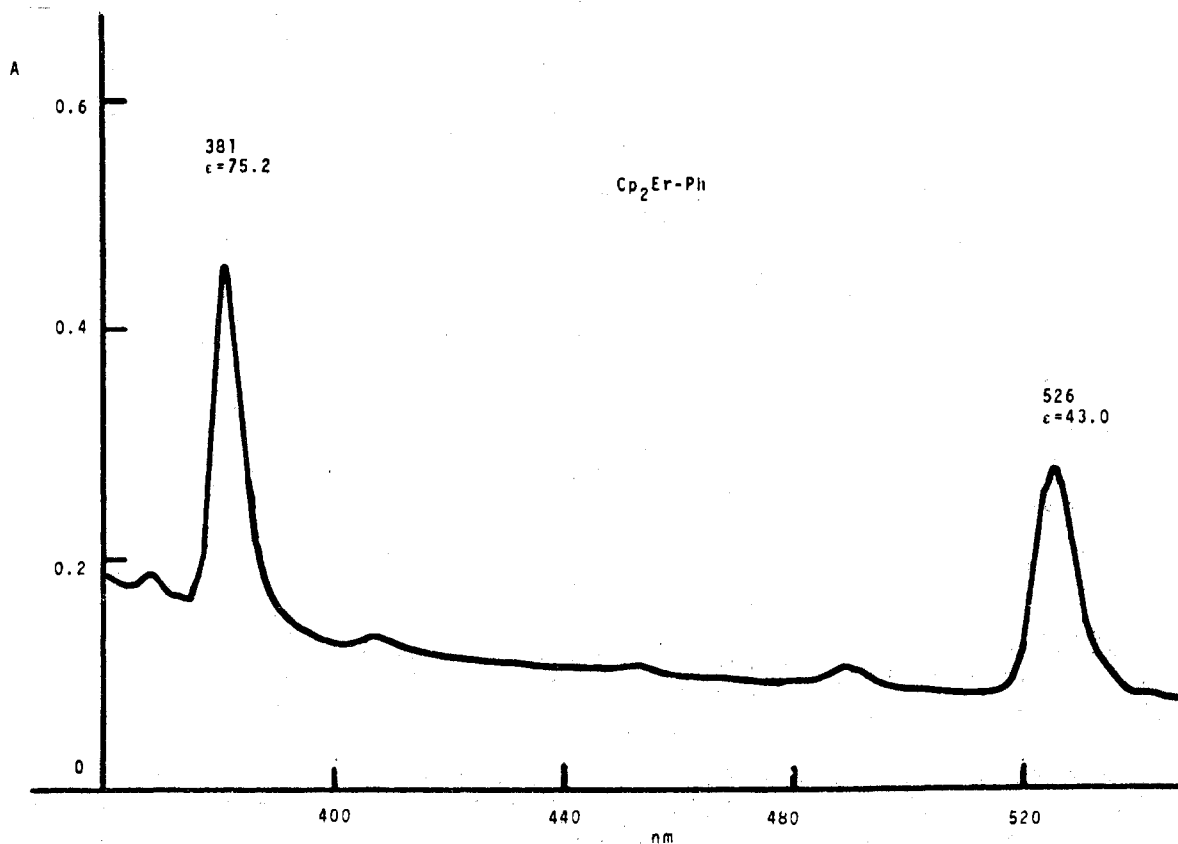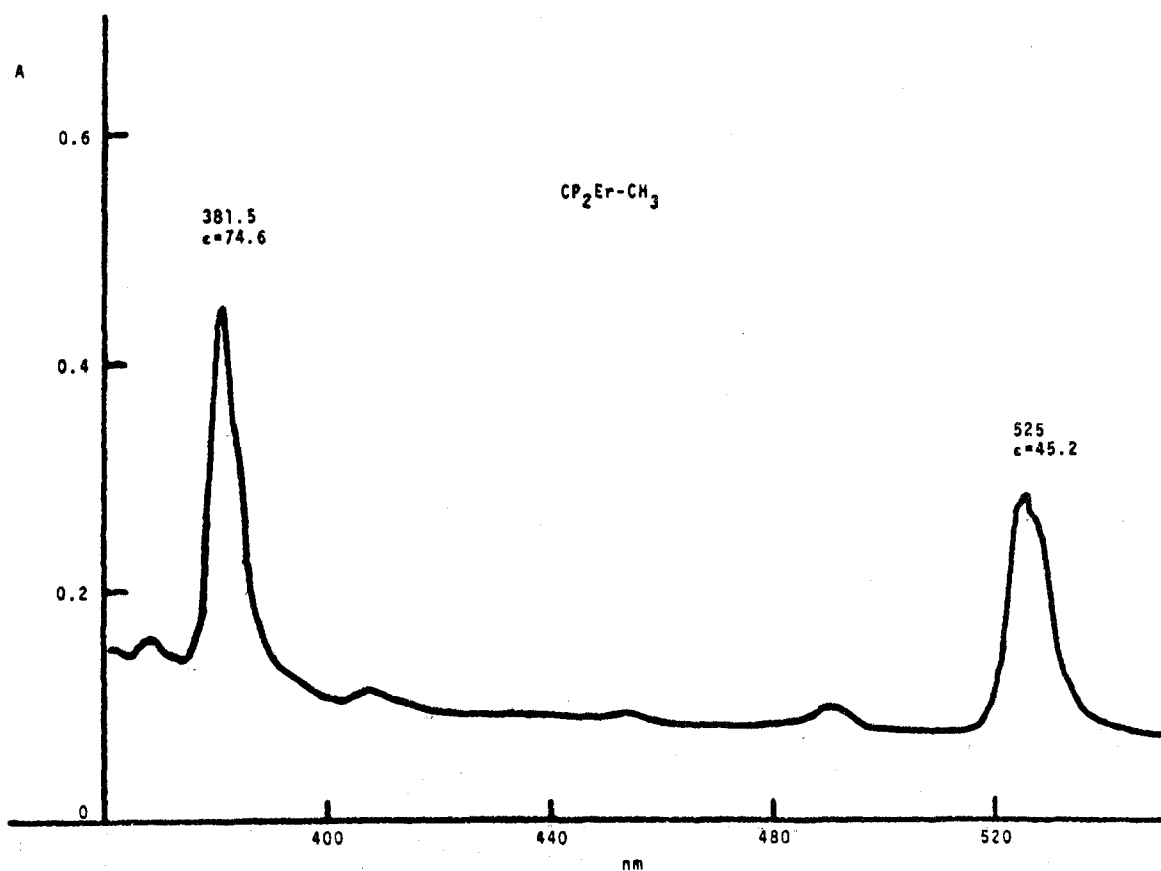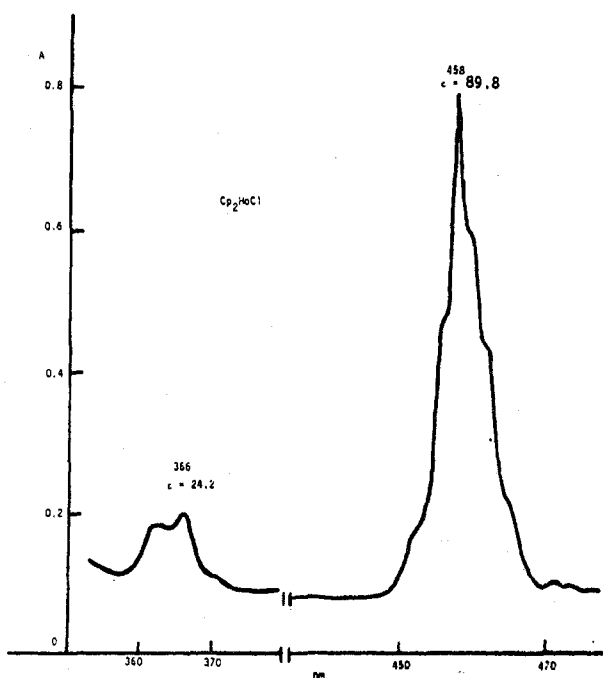**Figure 2.** Visible spectrum of $Cp_2ErC\equiv CPh$.

Figure 3. Visible spectrum of Cp_2ErPh.

evidence for hypersensitivity was observed. Thus, if hypersensitivity is a function of covalency only (which it probably is not), the implication is that covalent bonding is stronger in the phenylacetylide derivatives than in the methyl or phenyl complexes. This will have to remain as speculation until more detailed work is done using other R moieties whose reducing ability is intermediate between the phenylacetylide (most) and methyl (least) ligands.

Figure 4. Visible spectrum of Cp_2ErCH_3.

Figure 5. Visible spectrum of Cp_2HoCl.

Table I. Room-Temperature Magnetic Susceptibilities

Compd	Color	$10^6\chi_m$, cgsu	μ_{eff} (obsd), BM	μ_{eff} (theor[29]), BM
$Cp_2YbC{\equiv}CPh$	Orange	7,800	4.31	4.5
$Cp_2ErC{\equiv}CPh$	Pink	39,000	9.64	9.8
$Cp_2HoC{\equiv}CPh$	Sand	44,160	10.08	10.4
$CpHo(C{\equiv}CPh)_2$	Sand	47,750	10.48	10.4
$Cp_2GdC{\equiv}CPh$	Yellow	26,880	7.98	7.94
Cp_2YbPh	Orange	6,470	3.86	4.5
Cp_2GdPh	Lavender	24,408	7.69	7.94
Cp_2ErCH_3	Pink	38,500	9.41	9.8
Cp_2YbCH_3	Orange	7,442	4.14	4.5

Table II. Variable-Temperature Magnetic Susceptibilities

Compd	$\mu_{eff}(295$ K), BM	μ_{eff} (195°K), BM	$\mu_{eff}(77°K)$, BM
Cp_2ErCH_3	9.41	9.37	8.95
Cp_2YbCH_3	4.15	3.99	3.57
Cp_2YbPh	3.86	3.75	3.47
$Cp_2HoC{\equiv}CPh$	10.14	10.00	9.85
$CpHo(C{\equiv}CPh)_2$	10.48	10.45	10.11
Cp_3Er [30]	9.45	9.44	9.45
Cp_3Yb [30]	4.00	4.00	4.00
Cp_2HoCl [18]	10.30	10.30	
$CpErCl_2 \cdot 3THF$ [20]	9.68	9.68	

Magnetic Data. The magnetic susceptibilities for most of the new σ-bonded complexes have been determined. The values for μ_{eff} determined at room temperature (Table I) are in close agreement with the theoretically predicted values[29] and indicate that the complexes are all in the tripositive oxidation state. However, one unique and interesting phenomenon was observed. The overall magnetic moments (μ_{eff} in Bohr magnetons) are temperature dependent. Lower values of μ_{eff} were obtained as the temperature was steadily decreased. This is in marked contrast to all of the other cyclopentadienyllanthanide complexes which have been studied in this way. The Cp_3Ln,[30] Cp_2LnCl,[18] and $CpLnCl_2 \cdot 3THF$[20] complexes all have effective magnetic moments which are invariant with temperature. Table II lists the variable temperature magnetic moments.

It has been well established previously that the 4f electrons are very well shielded from the chemical environment by the
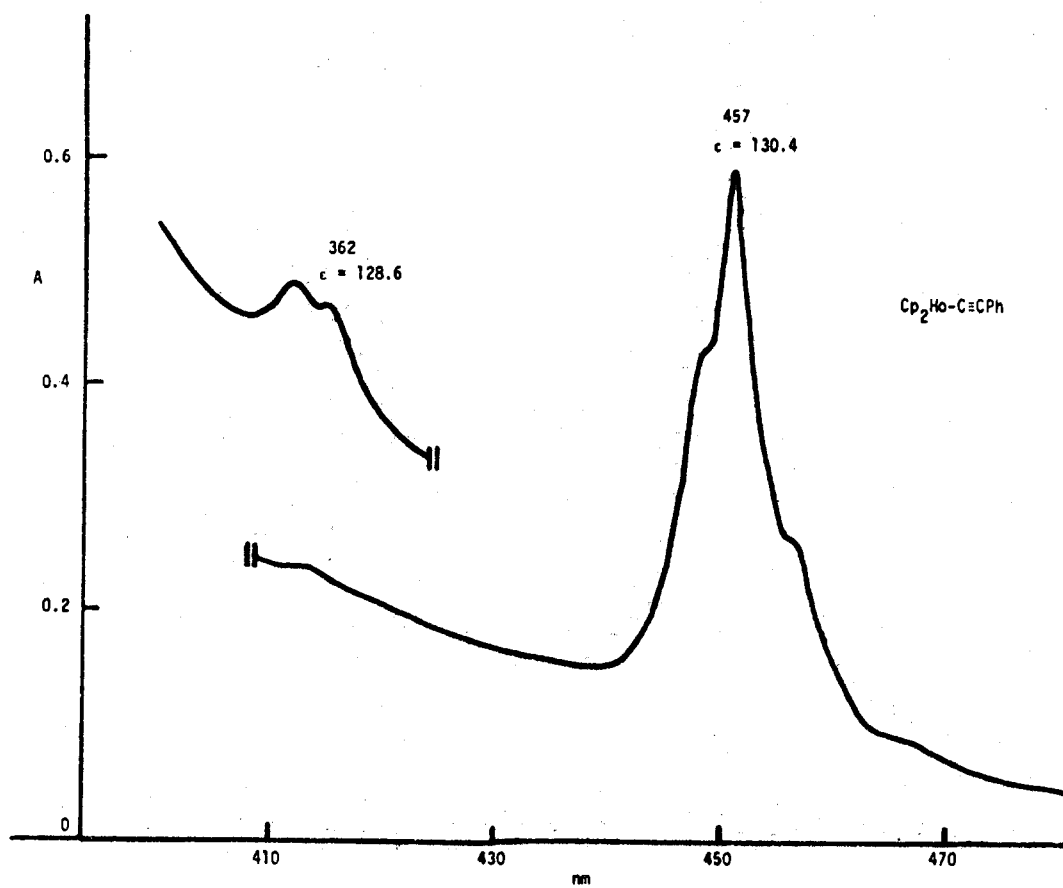
Figure 6. Visible spectrum of $Cp_2HoC\equiv CPh$.

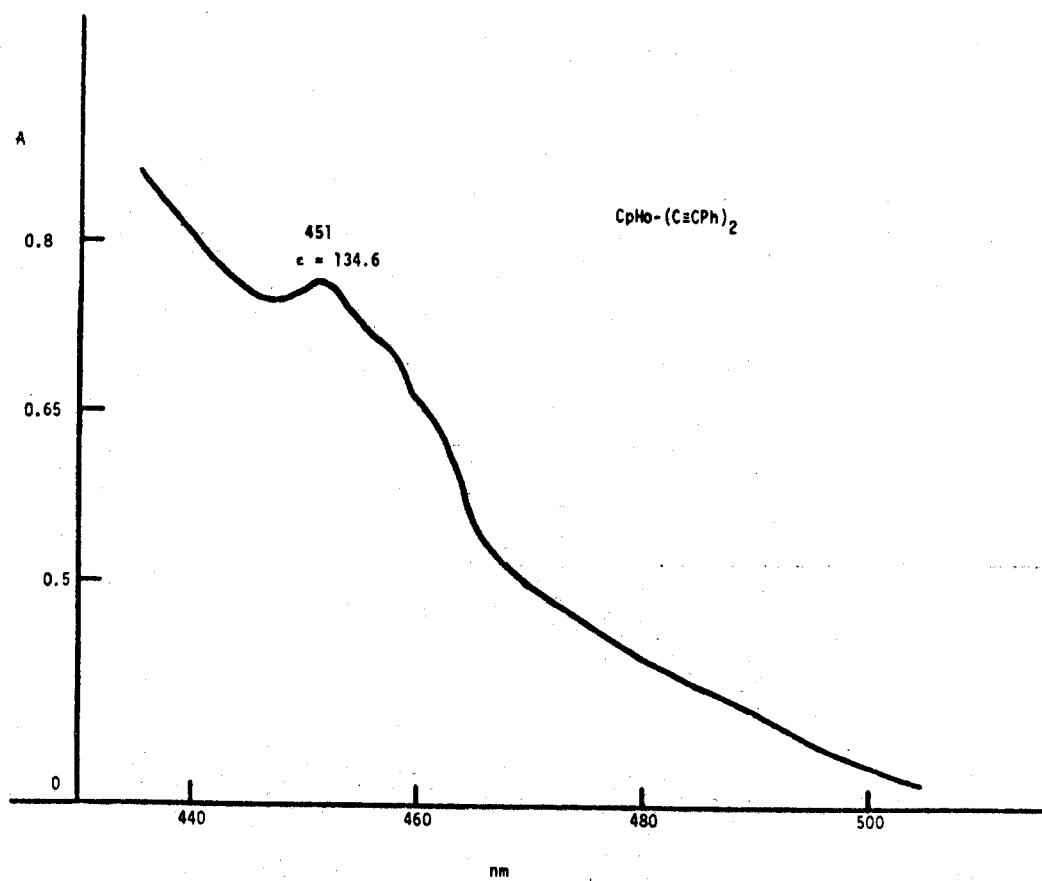**Figure 7.** Visible spectrum of $CpHo(C\equiv CPh)_2$.
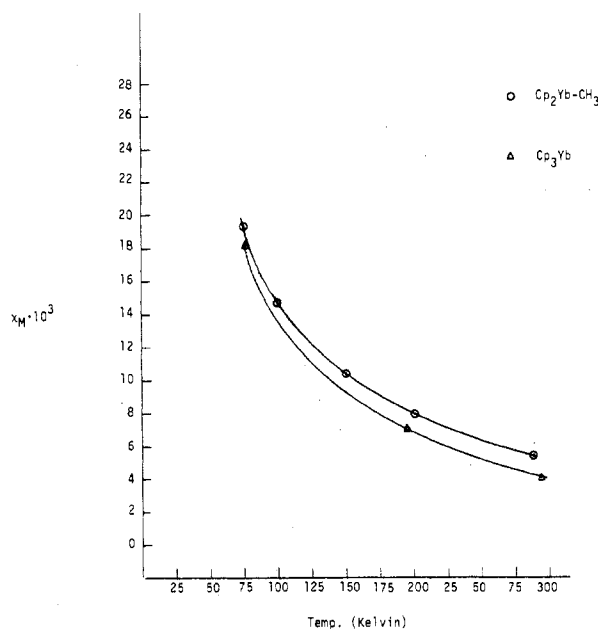
Figure 8. Magnetic susceptibility of Cp_2YbCH_3.

Figure 9. Cross section of the possible symmetry-allowed overlap of the ligand and metal orbitals.

$5s^2$ and $5p^6$ electrons.[31,32] They are thought to be shielded so much, in fact, that they do not take part to any appreciable extent in bonding. The experimental values for μ_{eff} which have been obtained by others are in excellent agreement with the values predicted by Van Vleck and seem to be independent of solvent, anion, or complexing ligand. The fact that the cyclopentadienyllanthanide complexes have an effective magnetic moment which is constant over a variable temperature range is consistent with this formulation. However, this is not true for σ-bonded Cp_2LnR complexes. The cause of this phenomenon is probably enhanced quenching of the orbital angular momentum and hence the orbital moment, which will result in lower values for μ_{eff}. A plot of χ_m vs. T for the ytterbium–methyl complex is shown in Figure 8. The results shown on the curve rule out a ferromagnetic effect, which could also cause a reduction in μ_{eff}, as the cause of the phenomenon observed.

Bonding. The question of f-orbital participation in the bonding of lanthanide (and actinide) complexes has been one of long-standing interest. Concerning the lanthanides, it was believed that, besides being well shielded, the 4f orbitals did not extend far enough spatially to enter into covalent bonding or to be split by ligand fields to any extent.[33] Recent work has shown that the bonding in a number of organolanthanide complexes is essentially ionic.[9,30,34] However, these complexes contain only π or polyhapto ligands, in which the negative charge (electron density) is "spread out" over several carbon atoms. By contrast, a monohapto carbanion such as $PhC{\equiv}C^-$ has its electron density concentrated on one carbon atom, where it could be more readily available for some type of localized interaction with the metal. This could possibly result in an enhancement of covalent bonding in lanthanide compounds.[35,36]

As one can readily infer from the magnetic data (and to a lesser extent, from the visible spectra), there does appear to be an increase in covalency in the bonding between metal and ligand in these σ-bonded complexes. Unfortunately, the relative degree of covalency and the orbitals involved in bonding are less readily delineated. Streitwieser et al. claimed that the stability of uranocene arises in part from the symmetry-allowed overlap of the e_{2u} orbitals on the rings with the f_{xyz}, $f_{z(x^2-y^2)}$ orbitals on uranium.[3b] A similar mechanism could be operative for the lanthanide–carbon σ bond. If one assumes that the symmetry of the metal in these Cp_2LnR
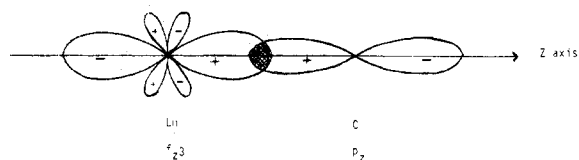
complexes is C_{2v}, the f_{z^3} orbital on the metal has the same symmetry as the p_z orbital on the carbon.[37] A cross section of the possible MO overlap is shown in Figure 9.[38] Of course, the d_{z^2} orbital will also have the same symmetry. Also, for the lanthanides, the 4f and 5d orbitals are of very similar energy. The question as to which is involved in the bonding is not readily answered. The magnitude of the data observed is not relatively large, and although there is definitely an enhancement of covalency in the bonding, it is probably not predominant; i.e., the σ bond still has more ionic character than covalent character. The data could be interpreted as being the result of f-orbital involvement in the bonding or as a perturbation of the 4f orbitals as a result of the ligand bonding with the 5d orbitals. The existence of 4f–5d hybrids is possible but considered unlikely. Clearly then, these σ-bonded complexes represent a rare example of lanthanide compounds where the bonding (at least in the σ bond) is not purely ionic. However, more work and more sophisticated studies are in order before the complete nature of the bonding in these novel complexes can be unraveled.

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(35) In compounds containing lanthanide–carbon σ bonds, the electron density (negative charge) of the ligand should be more available for localized interaction with the metal than for π-bonded systems. This could possibly lead to a greater enhancement of f-orbital participation in the bonding than in, for instance, the π-cyclopentadienyl ligand. When cyclopentadiene gains an electron to form the cyclopentadienyl anion, the stability of this anion arises from the ligand being able then to form a delocalized aromatic system. Because of the stability gained by the addition of the electron (and formation of the carbanion), the cyclopentadienyl ligand would be less likely to lose some of its electron density through covalent bonding than would a carbanion which is less stabilized (such as CH₃⁻) and has its negative charge more localized.³⁶ This is, of course, certainly not to say that ligands which are π bonded will not form strong covalent bonds by overlap of ligand orbitals with metal orbitals of the proper symmetry. However, this type of enhancement could be especially important in increasing the degree of covalency in compounds where the bonding is primarily ionic, such as the lanthanides.

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Competitive Pathways for the Aquation of the (Ethylenediamine)bis(oxalato)chromate(III) Ion in Acidic Media[1]

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Ion-exchange chromatography has been used to isolate and characterize intermediates in the aquation of the (ethylenediamine)bis(oxalato)chromate(III) ion. The complex Cr(C₂O₄)₂(NH₂CH₂CH₂NH₃)(H₂O) is the major intermediate at pH 1 and aquates in turn to *cis*-Cr(C₂O₄)₂(H₂O)₂⁻ with a first-order rate constant of $(1.9 \pm 0.1) \times 10^{-5}$ sec⁻¹ at 25.0°C. Two other intermediates, Cr(C₂O₄)(NH₂CH₂CH₂NH₂)(H₂O)₂⁺ and Cr(C₂O₄)(NH₂CH₂CH₂NH₃)(H₂O)₃²⁺, result from an oxalate aquation process which is operative at lower pH and leads to the product Cr(C₂O₄)(H₂O)₄⁺. The kinetics of the first step in the aquation of Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻ have been investigated spectrophotometrically at 570 nm, where first-step products are isosbestic with their ultimate reaction products. The rate of change of absorbance with time obeys simple first-order kinetics at hydrogen ion concentrations from 0.50 to 2.00 *M*. Observed rate constants for the process are described by $k_{obsd} = k_a + k_b[H^+] + k_c[H^+]^2$, where $k_a = 1.7 \times 10^{-5}$ sec⁻¹, $k_b = (7.69 \pm 0.11) \times 10^{-5}$ *M*⁻¹ sec⁻¹, and $k_c = (6.15 \pm 0.07) \times 10^{-5}$ *M*⁻² sec⁻¹ at 25.0°C and $\mu = 2.01$ *M* (KNO₃). Activation enthalpies, $\Delta H^{\ddagger}$, for k_a, k_b, and k_c, computed from data at 25.0, 35.0, and 45.0°C, are 20.6 ± 0.6, 17.6 ± 0.2, and 16.6 ± 0.6 kcal mol⁻¹, respectively, while activation entropies, $\Delta S^{\ddagger}$, are −11.4 ± 1.9, −18.3 ± 0.5, and −22.0 ± 1.8 cal mol⁻¹ deg⁻¹. Observed concentrations of mono(oxalato) and bis(oxalato) species at 1 and 10 half-lives are consistent with the aquation rate law if k_a is associated with primary, uncatalyzed ethylenediamine aquation, k_c describes second-order, hydrogen ion catalyzed oxalate aquation, and k_b describes acid-catalyzed aquation of both ethylenediamine (k_b') and oxalate (k_b''). At 25.0°C, $k_b' = (1.7 \pm 0.8) \times 10^{-5}$ *M*⁻¹ sec⁻¹ and $k_b'' = (6.0 \pm 0.9) \times 10^{-5}$ *M*⁻¹ sec⁻¹. A protonated, half-bonded oxalate ligand is proposed to account for hydrogen ion catalysis of the aquation process.

Introduction

Aquation processes of oxalatochromate(III) complexes have clearly been established as pH-dependent processes by past investigators. For example, aquation of Cr(ox)₃³⁻ to *cis*-Cr(ox)₂(H₂O)₂⁻ has as its rate law²,³ −d ln [Cr(ox)₃³⁻]/dt = $k'[H^+] + k''[H^+]^2$. The *cis*-Cr(ox)₂(H₂O)₂⁻ complex aquates in turn to Cr(ox)(H₂O)₄⁺ with a rate law given by⁴ −d ln [Cr(ox)₂(H₂O)₂⁻]/dt = $k[H^+]$. In both cases, only a single aquation step was noted for the loss of an oxalate ligand, and no evidence was found which would support the existence of large concentrations of monodentate oxalate species.

In contrast, ethylenediamine⁵ and polyamine complexes⁶⁻⁹ of chromium(III) aquate in distinct, stepwise fashion through monodentate or partially "unwrapped" species. These processes seem to be independent of pH in acid solution, or are, at worst, inversely dependent upon the hydrogen ion concentration. In the simplest case, Childers et al⁵ have found

that the Cr(en)(H₂O)₄³⁺ ion aquates in two pH-independent steps and have isolated the monodentate ethylenediamine complex intermediate Cr(enH)(H₂O)₅⁴⁺ using ion-exchange chromatography.

When both ethylenediamine and oxalate are coordinated to chromium(III), the question of relative ligand reactivity must ultimately arise and the kinetic interplay of the two, different bidentate ligands must be considered.

Schläfer¹⁰ has determined that the Cr(ox)₂(en)⁻ complex ion aquates to *cis*-Cr(ox)₂(H₂O)₂⁻ in two steps which are essentially pH independent. However, his investigations have been limited to pH values above 1.05 where hydrogen ion catalyzed aquation of the oxalate ligand should not be evident. The magnitude of Schläfer's first-order rate constants, when compared to the second- and third-order rate constants for oxalate aquation processes,¹⁻³ suggests that competitive aquation pathways should exist at lower pH values. Loss of