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New Lanthanide Alkyl and Aryl Derivatives of the Type $(\eta^5\text{-}C_5H_5)_2LnR$

Sir:

Recently, there has been a resurgence of interest in the organometallic chemistry of the actinides, with a great deal of the focus being on σ-bonded complexes.[1] However, σ-bonded organolanthanide compounds have avoided close scrutiny. The work done with organolanthanide complexes has been centered about the ionic π-bonded cyclopentadienyl[2] and cyclooctatetraenyl[3] ligands. The only well-characterized σ-bonded organolanthanide complexes are the lithium salts of the Lu and Yb tetrakis(2,6-dimethylphenyl) compounds[4] and a series of phenylacetylide complexes which we have synthesized: $(\eta^5\text{-}C_5H_5)_2LnC{\equiv}CPh$ (Ln = Gd, Er, Yb; Ph = phenyl).[5] We have now extended this series and would like to present our preliminary results in synthesizing alkyl and aryl derivatives of the type $(\eta^5\text{-}C_5H_5)_2LnR$ (Ln = Gd, Er, Yb; R = Ph, CH_3). The methyl derivatives are the only well characterized, stable lanthanide alkyls,[6,7] and the phenyl compounds are the first aryl derivatives known for Gd and Er. These are the only σ-bonded organolanthanide complexes known for these elements aside from the aforementioned Yb-aryl compound[4] and the phenylacetylide derivatives.[5]

The new complexes are prepared as shown in eq 1 by the reaction in THF of the appropriate $(\eta^5\text{-}C_5H_5)_2LnR$[8] with

$$(\eta^5\text{-}C_5H_5)_2LnCl + RLi \xrightarrow[-78^\circ]{THF} (\eta^5\text{-}C_5H_5)_2Ln\text{–}R + LiCl \qquad (1)$$

either methyl- or phenyllithium at −78°. The complexes are precipitated from the reaction solution by concentrating the solvent in vacuo and the addition first of toluene and then of hexane. The compounds are purified by continuous extraction with benzene.[9,10]

All of the compounds are very sensitive to oxygen and moisture, decomposing rapidly upon exposure. However, all of them are fairly thermally stable, as none either decompose or melt below 130° in argon filled capillaries. Indeed, it would seem that high thermal stabilities are the rule for $(\eta^5\text{-}C_5H_5)_2LnR$ compounds[5] as well as for $(\eta^5\text{-}C_5H_5)_3UR$ complexes.[1]

Infrared spectra of these compounds support the presence of methyl and phenyl moieties which are σ-bonded to the various lanthanides. For the phenyl complexes, the band at 3048 cm^{-1} is assigned as the C–H stretching vibration. The characteristic C–H out-of-plane bending vibrations appear at 718 and 701 cm^{-1} and are indicative of a monosubstituted phenyl ring. Bands at 1412, 1468, and 1483 cm^{-1} are assigned as C–C stretching vibrations while the series of absorptions between 1300 and 1000 cm^{-1} arises from the C–H in-plane bending modes.

For the methyl derivatives, the C–H stretching vibration is seen as a weak, broad absorption centered at 2890 cm^{-1}. All of the methyl complexes have a strong band at ~1190 cm^{-1}. Nakamoto ascribes this band to the symmetric deformation of the methyl group, and it is characteristic of complexes containing a methyl moiety bound to a metal.[11] Also present are bands at 1360 and 1328 cm^{-1} which are assigned as C–H bending vibrations of the methyl ligand.

In addition, all of the complexes have bands at ~3100, 1440, 1010, and 775 cm^{-1}, characteristic of η^5-cyclopentadienyl moieties.[12]

Visible spectra were obtained for both the methyl and phenyl derivatives of erbium. However, unlike the phenylacetylide complex,[5] there is no evidence of any hypersensitivity in the f–f transitions which were observed.[13-15] In this respect, the spectra resemble that of the starting chloride complex. These spectra did, however, show the presence of a charge transfer band which originates in the uv and extends into the visible region. Visible spectra of the gadolinium complexes were devoid of *f–f* transitions, but contained the tail end of a charge transfer band as in the erbium complexes. These are assigned as ligand to metal charge transfer bands,[3b,5,16] and indicate that there is at least some interaction, other than purely electrostatic, between the metal and the R group. The visible spectra of the ytterbium complexes are uninformative as they are dominated by a large charge transfer band which is present in the spectrum of the starting chloride complex.[17]

One of the reasons behind preparing these complexes was the desire to study f electron participation and covalency (if any) in the bonding. Studies of organolanthanide complexes which contain only π-bonded ligands have shown that the bonding is essentially ionic.[18] However, in compounds containing lanthanide-carbon σ bonds, the electron density of the σ-bonded 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 moiety. In this context, magnetic susceptibility studies of these alkyl and aryl complexes[19] have revealed some unusual results which may be attributed to this. The room temperature magnetic susceptibilities of these complexes (some of which are given in Table I) are all in agree-

Table I. Room Temperature Magnetic Susceptibilities of Some $(\eta^5\text{-}C_5H_5)_2LnR$ Complexes[a]

Compound	Color	$10^6\ \chi_m$, cgs	μ_{eff}(obsd)	Theor[20]
Cp_2ErPh[b]	Pink	37,790	9.53	9.6
Cp_2GdPh	Lavender	24,408	7.69	7.94
Cp_2YbCH_3	Orange	7,225	4.14	4.5
Cp_2ErCH_3	Pink	37,985	9.41	9.6

[a] Measured by the Faraday method. [b] $Cp = \eta^5\text{-}C_5H_5$.

Table II. Variable Temperature Magnetic Susceptibilities

Compound	μ_{eff} (295°K)	μ_{eff} (195°K)	μ_{eff} (77°K)
$CpErCl_2 \cdot 3THF$[21]	9.68	9.68	
Cp_2HoCl[8]	10.30	10.30	
Cp_3Yb[22]	4.00	4.00	4.00
Cp_3Er[22]	9.45	9.44	9.45
Cp_2ErCH_3	9.41	9.37	8.95
Cp_2YbPh	3.86	3.75	3.43

ment with the theoretical values.[20] However, as the temperature was decreased, values of μ_{eff} were also found to decrease. This is in sharp contrast to other lanthanide-cyclopentadienyl compounds, where values for μ_{eff} do not vary with the temperature. Representative values for the different types of compounds (including the alkyls and aryls) are listed in Table II. This unusual reduction of μ_{eff} is tentatively attributed to enhanced quenching of the orbital angular momentum of the f electrons by the electric and/or ligand field of the R moiety. This would cause a reduction in the orbital moment and hence in μ_{eff}. This might be viewed as evidence for at least some degree of covalency in the σ bond.[23]

Clearly, these σ-bonded organolanthanide derivatives constitute an important new type of organolanthanide complex and, indeed, of organometallic compounds in general. Additional work is currently in progress in order to further elucidate the properties of these unusual new compounds.

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(24) Work done in partial requirement for the Ph.D. degree at TAMU.

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Free Radical Cyclization of Unsaturated Hydroperoxides

Sir:

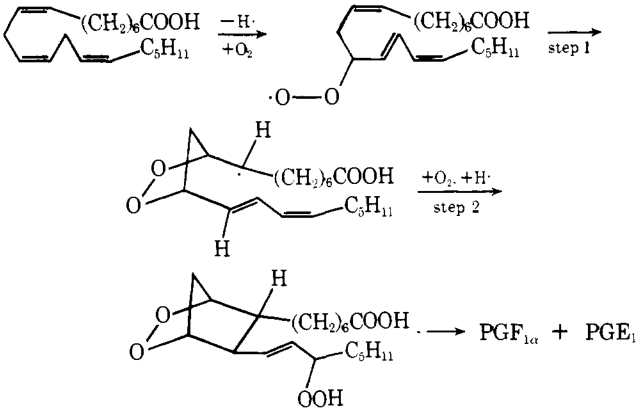
The biosynthesis of prostaglandins from polyunsaturated fatty acids has been studied by several investigators.[1] Although the precise details of the pathway of biosynthesis are unknown, the peroxy radical mechanism shown in Scheme I has been suggested.[2] In fact, an endo peroxide analogous to **1** has been isolated from the oxidation of arachidonic acid using the microsomal fraction of sheep vesicular gland as the enzyme source.[3]

Central to the proposed biosynthetic pathway are two consecutive radical cyclization reactions. In the first of these (step 1), the peroxide linkage is formed, while the second cyclization (step 2) completes the formation of the bicyclic peroxide structure.

In light of the potential importance of peroxy radical cyclizations in biological oxidation, it is remarkable that little information is available about this class of reaction. Peroxy radical cyclizations have been suggested[4] in the nonenzymic autoxidation of some unsaturated compounds, but the autoxidation format is not suitable for a systematic study of unsaturated peroxy radicals.

We report here a method for generating specific unsaturated peroxy radicals and also our preliminary observations regarding peroxy radical cyclizations. Of fundamental importance to this new method is the fact that hydroperoxide hydrogens (ROO*H*) are abstracted with relative ease by *tert*-butoxy radicals compared to the ease of abstraction of

Scheme I



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