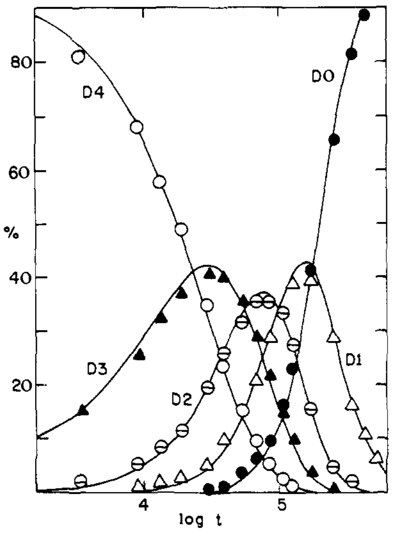

Figure 1. Kinetic plot (time in sec) for the dedeuteration of aqueous 0.206 *M* cyclopentanone-2,2,5,5-d_4 containing 0.0986 *M* total 3-dimethylaminopropionitrile at pH 7.627 and 35°. The curves are based on Scheme I with $k = 9.00 \times 10^{-6}$ sec^{-1}.

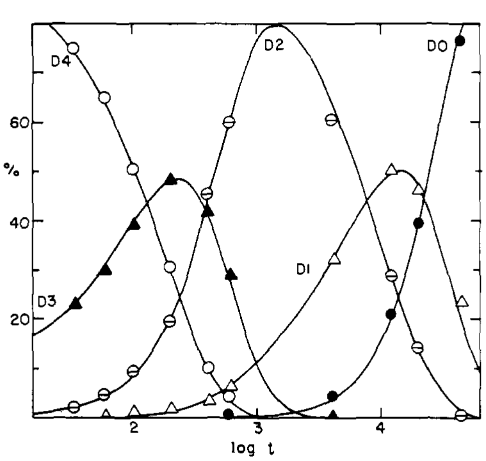

Figure 2. Kinetic plot (time in sec) for the dedeuteration of 0.206 *M* cyclopentanone-2,2,5,5-d_4 containing 0.00509 *M* aqueous **1** at pH 8.03 and 35°. The curves are based on Scheme II with $k_d = 4.77 \times 10^{-5}$ sec^{-1} and $k_i = 266 \times 10^{-5}$ sec^{-1}.

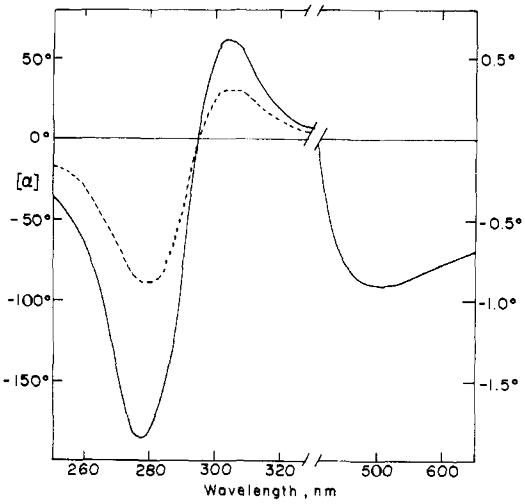

Figure 3. ORD curve for cyclopentanone extracted from aqueous 1.0 *M* cyclopentanone-2,2,5,5-d_4 containing 0.00236 *M* total **1** at pH 6.5 and 35° after 15 hr; right, neat; left, solid line, aqueous 0.092 *M* solution; dashed line, similar solution also containing 0.322 *M* free and 0.080 *M* protonated 3-dimethylaminopropionitrile after 4765 sec at 35°.

than deuterium[7]) would suggest an *R* configuration for the CO-CHD-CH_2 grouping in the principal products of partial dedeuteration. However, molecular models of transition states for bifunctionally catalyzed dedeuteration *strongly* indicate an *S* configuration.

Supplementary Material Available. Additional details are in the Appendix, which will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3550.

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(1) This investigation was supported in part by Grant GM 18593 from the National Institute of General Medical Sciences. Part XVIII in the series "Catalysis of α-Hydrogen Exchange:". For part XVII see J. Hine and S. S. Ulrey, *J. Org. Chem.*, **39**, 3231 (1974).

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(3) The reaction in water at 35° was quenched with acid; then the ketone was extracted and its deuterium content determined by mass spectral measurements. Further kinetic details are given in the Appendix.

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An Unusual Type of Organolanthanide Complex Containing the Allyl Moiety: $(\eta^5\text{-}C_5H_5)_2LnC_3H_5$

Sir:

In our work on organometallic complexes of the lanthanides, we have previously reported the preparation of σ-alkynyl derivatives from dicyclopentadienyllanthanide chlorides.[1] These contained the first metal-carbon σ bonds known for most of these elements. We subsequently prepared alkyl and aryl derivatives of these elements[2] and wished to extend the work to derivatives containing the allyl (C_3H_5) moiety. Allyl complexes of the d-block transition metals are well known,[3] and numerous non-transition metal-allyl complexes have been synthesized.[4] However, actinide-allyl complexes are rare,[3b,5,6] and lanthanide-allyl complexes have been heretofore unknown. We now report the first organolanthanide complexes to contain the allyl ligand: $Cp_2LnC_3H_5$ (Cp = η^5-C_5H_5; Ln = Sm, Er, Ho).

The complexes are prepared by the reaction of the appropriate Cp_2LnCl[7] with allylmagnesium bromide in THF-ether solution at −78° as shown in eq 1. The mixture is

$$Cp_2LnCl + C_3H_5MgBr \xrightarrow[-78°]{\text{THF-ether}} Cp_2LnC_3H_8 + MgBrCl \tag{1}$$

warmed to room temperature, and dioxane is added to precipitate the magnesium halides.[8-10]

Table I. Visible Spectra of the $Cp_2LnC_3H_5$ Compounds[a,b]

Cp_2SmCl		Cp_2Sm allyl		Cp_2HoCl		Cp_2Ho allyl		Cp_2ErCl		Cp_2Er allyl	
λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ
425 sh	88	425 br	85	458 sh	89.8	464 sh	112	528 sh	46.4	529 sh	57.8
430 sh	87.2	430 br	84			425 sh	29.4	381.5 sh	83.4	384 sh	124.4
		513 vb	97.3					369 sh	15.2	373 sh	132.4

[a] Recorded as 10^{-2} *M* solutions in THF on a Beckman Model 25 spectrophotometer. [b] Key: sh = sharp, br = broadened somewhat, vb = very broad.

The complexes are very sensitive to air and moisture, decomposing within seconds upon exposure. However, they are quite thermally stable. On heating in sealed, argon filled capillaries, all three complexes darkened above 200° but did not melt below 300°.

The ir spectra of the complexes in Nujol mulls show bands at about 3100, 1440, 1010, and 790 cm^{-1}, characteristic of a η^5-cyclopentadienyl ligand.[11] The presence of the allyl moiety is indicated by ir bands at 3090 (C-H stretch), 1200 (C-H bend), and 735 cm^{-1} (skeletal twist).[12] Comparison of the lanthanide complexes and the analogous uranium derivative $Cp_3UC_3H_5$[6] indicates that the allyl group is bonded trihapto to the lanthanide and monohapto to the uranium. The lanthanide complexes show a strong band at 1533 cm^{-1} attributed to the delocalized C-C stretch characteristic of π or η^3-allyl moieties.[13] In contrast, $Cp_3UC_3H_5$ shows a weak band at 1630 cm^{-1} arising from the C=C stretch characteristic of σ or η^1-allyl moieties.[13]

The formation of a η^3-allyl-lanthanide bond in preference to a monohapto bond is very interesting. The σ-bonded Cp_2LnR complexes we have previously prepared[1,2,9] are coordinatively unsaturated and have a coordination number (CN) of 7 while the $Cp_2LnC_3H_5$ complexes can be considered to have a CN of 8. Thus, given the opportunity, the Cp_2LnR complexes have expanded their CN from 7 to 8 where R = allyl. For many d-block transition metal complexes which loosely obey the 18-electron rule, the behavior of the allyl moiety as a one-electron (σ) ligand or a three-electron (π) ligand depends largely on the electronic requirements of the metal. However, for the lanthanides, whose complexes have no such rule and where the bonding is essentially ionic, this type of behavior will be largely a function of steric requirements.

The fact that the lanthanide-allyl bond is trihapto and the uranium-allyl bond is monohapto indicates that the coordination site around the metal is quite constrained for the R group in Cp_3UR complexes. This is in agreement with the conclusions of Marks based on NMR studies of the R = isopropyl complex.[6]

The ir spectrum of the Sm-allyl complex in THF (a strong Lewis base) shows the C-C stretch to be essentially unshifted, indicating that there is little tendency for the allyl group to undergo a π-σ rearrangement in the presence of a strongly coordinating solvent. THF is known to coordinate to the metal in numerous organolanthanide complexes,[14] including the lanthanide-allyl complexes (vide infra). The absence of an allyl π-σ rearrangement in the presence of THF suggests that the steric requirements are not so great as to produce coordinative saturation in the complex. For the lanthanides and actinides, coordinative unsaturation must therefore be dominated by a combination of electrostatic vs. steric requirements. This is not true for the transition metals, where electrostatic considerations predominate.

The solid complexes are all brightly colored and change color when dissolved in THF. Samarium gives the most drastic change, as the yellow solid gives a burgundy solution.[15] Bright yellow THF solutions arise from the pale yellow-orange Ho-allyl complex, and light orange solutions are obtained from the pink Er-allyl complex.[16] The colors obtained in solution are the same as the original reaction mixtures, which, upon work-up yield the different colored solids. These color changes are attributed to the formation of stable THF adducts in solution consistent with the formulation of these complexes as coordinatively unsaturated Lewis acids.

Table I presents the main features of the visible spectra of the allyl complexes and the parent chloro complexes. The spectra of the allyl products resemble those of the parent Cp_2LnCl_2 in regard to peak position with one major difference; the Ho and Sm complexes show a totally new band, and the Er complex has a band which is dramatically increased in intensity.[17]

The new bands may be due to some interaction between THF and the delocalized π system of the allyl moiety or may arise from cyclopentadienyl-metal bonds which are shifted as a result of changes in coordination around the metal. It should be noted that the visible spectrum of the samarium allyl complex in benzene (a noncoordinating solvent) does not show the broad absorption seen in THF. Therefore, the new bonds most probably arise from THF-lanthanide interactions which may be considered to be low intensity ligand to metal charge-transfer bands.

Clearly, these lanthanide-allyl complexes constitute an important new variety of organolanthanide compounds. Further investigations into the physical properties and spectra of these novel compounds are continuing.

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(8) Without the addition of dioxane (about 5 ml per 60 ml of THF), the allyl-lanthanide complex could not be freed of magnesium halides.

(9) The detailed procedure for isolation and purification of these complexes has been described elsewhere. N. Ely and M. Tsutsui, submitted for publication.

(10) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Anal. Calcd for $C_{13}H_{15}Sm$: Sm, 46.75. Found: Sm, 45.45. Calcd for $C_{13}H_{15}Ho$: Ho, 49.06. Found: Ho, 48.61. Calcd for $C_{13}H_{15}Er$: Er, 49.41. Found: Er, 48.17.

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(15) Attempts to isolate a burgundy samarium complex have been unsuccessful. Precipitation with hexane or removal of THF causes the resulting solid to revert to a yellow color.

(16) Color changes in THF solutions have also been observed for some other Cp_2LnR complexes, but no general trends with regard to ligands can be discerned.

(17) It is, of course, possible that this band in the Er spectrum is a new band, and coincidentally absorbs at the same place as the weak band already present.

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

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Hydridotrichlorostannatocarbonylbis(triphenylphosphine)platinum(II), $PtH(SnCl_3)(CO)(PPh_3)_2$, as a Selective Hydroformylation Catalyst

Sir:

There are relatively few literature references to the use of platinum complexes as hydroformylation catalysts, and these few appear only in the patent literature[1-3] and none of them are hydrido complexes. We have prepared the new complex, $PtH(SnCl_3)(CO)(PPh_3)_2$ (**1**) and have found that it is an active catalyst for the hydroformylation of 1-pentene at 100° and 3000 psi of synthesis gas ($CO-H_2 = 1:1$). Analysis of the aldehydes in the product showed more than 95% of the straight chain compound, hexanal. The crystalline catalyst can be recovered unchanged from the reaction mixture and may be reused without any loss of activity.

Other platinum(II) hydrides that are converted to the carbonyl complex under the reaction conditions may be used as catalysts. Thus *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (**2**) or *trans*-$[PtHCl(PPh_3)_2]$ (**3**), to which excess $SnCl_2 \cdot 2H_2O$ (mole ratio 1:5) is added, also function as effective catalysts, and **1** can be recovered from the reaction mixtures.

The reported method[4] for the preparation of **2** was modified. To a stirred solution of *trans*-$[PtHCl(PPh_3)_2]$[5] (0.76 g), benzene (25 ml), and ether (75 ml) was added 1.2 g $SnCl_2 \cdot 2H_2O$. After stirring the mixture for 30 min, the orange-yellow precipitate of **2** was filtered and washed with ether, yield 0.76 g.

A suspension of 5 g of **2** in 250 ml of benzene was placed in a 300-ml autoclave. After the autoclave was flushed three times with N_2 (1000 psi) and once with CO (1000 psi), the autoclave was charged with CO (1500 psi) and with H_2 (1500 psi), and the mixture was heated at 100°. After 6 hr, the autoclave was cooled and depressured, whereupon greenish yellow crystals separated from the solution. These crystals were filtered and washed with benzene and then with pentane: yield 4.1 g; mp 93-95° dec; ir $\nu_{(Pt-H)}$ 2165 cm^{-1}, $\nu_{(C\equiv O)}$ 2050 cm^{-1}, $\nu_{(Sn-Cl)}$ 335, 314, 292 cm^{-1} (Nujol mull). Anal. Calcd: C, 45.6; H, 3.2; Cl, 10.9. Found: C, 45.4; H, 3.2; Cl, 10.5.

At the present time, we are unsure of the exact structure of the relatively unstable complex, **1**. It may be a four-coordinate ionic salt, $[Pt(H)(CO)(PPh_3)_2]^+SnCl_3^-$, analogous to the corresponding known[6] BPh_4^- salt, or it may be a five-coordinate compound, in which case it would be quite unusual. On drying under vacuum, or on exposure to air for several days, it loses CO and gives *trans*-$[PtH(SnCl_3)(PPh_3)_2]$. Attempts to recrystallize the carbonyl complex resulted in the formation of *trans*-$[PtHCl(PPh_3)_2]$ with extrusion of CO and $SnCl_2$.

A typical hydroformylation reaction was performed as follows. $PtH(SnCl_3)(CO)(PPh_3)_2$ (2.4 g, 2.5 mmol) and 150 ml of benzene were charged into a 300-ml autoclave which was equipped with an equalizing pressure addition vessel containing 1-pentene (17.5 g, 250 mmol). After the autoclave was sealed and flushed with N_2 and CO, H_2 (1500 psi) and CO (1500 psi) were charged, and the solution was heated to 100° with stirring. 1-Pentene was then added to the autoclave and the reaction mixture stirred with heating for 2.5 hr. The product was analyzed by GLC; essentially all the olefin had disappeared and the aldehyde product consisted of 95% hexanal and 5% 2-methylpentanal.

Essentially similar results were obtained when complexes **2** or **3** (to which was added $SnCl_2 \cdot 2H_2O$) were employed as catalysts.

The rate of the reaction catalyzed by **1** is about five times that of a $Co_2(CO)_8$-catalyzed reaction carried out under the same conditions. Although a $Co_2(CO)_6(PR_3)$ catalyst[7] also leads to relatively high selectivity to straight-chain product, the rate of hydroformylation with this catalyst is negligible at 100°. $Rh(Cl)(CO)(PPh_3)_2$ or other modified Rh catalysts operate effectively at 100°, but the ratio of straight- to branched-chain aldehydes[8] is usually about 3 compared to a ratio of about 20 with the Pt catalyst, **1**.

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Characterization of Oligomers of Tetrakis(phenyl isocyanide)rhodium(I) in Acetonitrile Solution

Sir:

There has been considerable recent interest in the optical spectra and electrical conductivities of platinum compounds in which direct metal-metal interactions are present.[1-6] Perhaps the best known examples are the double salts, such as $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt or MGS).[1] Low solubility of the double salts has generally restricted study to solid samples, although it should be noted that Isci and Mason have obtained electronic spectra for certain $[Pt(CNR)_4][Pt(CN)_4]$ complexes in ethanol solution.[6]

Many simple platinum salts also possess unusual properties.[2,3] The planar ions in these compounds, as in MGS, stack face-to-face in infinite columns. However, with the exception of one or two mixed-valence aggregates, notably $[Pt(C_2O_4)_2]_n^{1.6n-}$, complete dissociation to monomeric fragments occurs in solution. Even the copper-colored, mixed-valence Krogmann's salt, $K_2Pt(CN)_4Cl_{0.3} \cdots 3H_2O$,