SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY
OF COMPLEXES OF LANTHANIDE AND ACTINIDE
METALS IN UNUSUAL OXIDATION STATES
AND COORDINATION ENVIRONMENTS

MASTER

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The objective of this investigation was to synthesize new classes of lanthanide and actinide complexes in order to demonstrate experimentally that these metals have a broader chemistry than is presently assumed and to provide a basis for seeking unusual catalytic transformations which involve these metals. In our original proposal we described our plans to focus on nonaqueous reductive chemistry and to vary the type of lanthanide metal, ligand, and synthesis method until a combination was discovered which produced the desired result: interesting classes of new f orbital metal complexes. The metal alternatives included typical light and heavy lanthanides, metals with half-filled or nearly half-filled f shells, and metals with either filled or empty f shells. Phosphines, arsines, phosphites, cyanide, isonitriles, silyls and stannyls were among the ligands considered. Synthetic approaches included chemical and electrochemical reduction of higher valent salts in a variety of solvents, and direct metal-ligand reactions using matrix isolation—metal vaporization techniques or using "activated" metals made by reductive methods.

We did not have to try many variations before we found successful combinations. Both metal atomization and chemical reduction to form activated metals proved to be suitable synthetic techniques to attain our goals. The reactions appear to be general to nearly all the lanthanide metals. The ligands investigated to date are not the π -bonding ligands we initially considered but instead, π -bonding diene species such as butadiene, dimethylbutadiene, cyclooctadiene and norbornadiene. The results obtained in the past six months developed in the following way.

The metal vaporization technique was investigated first since it is a good survey method for synthesis of complexes of potentially low stability. Since

the reaction products are generated at low temperature, species of limited stability are more easily detected. Since the only reagents present are the metal and the ligand, interpretation of results is usually less complicated. We built a metal atom reactor of the Timms' design¹ and, for practice, attempted the synthesis of some known lanthanide cyclopentadienyl compounds:

(Ln = lanthanide metal)

Analogous reactions were known for transition metals. Initially we were unsuccessful in isolating $\text{Ln}(\text{C}_5\text{H}_5)_3$ species but we did notice that definite reactions were occurring at low temperature involving several colored intermediates. It seemed to us that these colored species could involve cyclopentadiene coordinating as a diene ligand and hence we investigated some other diene systems.

As described in a previously submitted preprint,² co-condensation of lanthanide metals with 1,3-butadiene ($1,3\text{-C}_4\text{H}_6$) or 2,3-dimethyl-1,3-butadiene ($2,3\text{-(CH}_3)_2\text{-1,3-C}_4\text{H}_6$) produces three types of organolanthanide complexes differentiated by their solubility in pentane, toluene and tetrahydrofuran (THF). Much of this past six months has been spent characterizing these species. The THF soluble species are formed in highest yield and have been most completely characterized. Elemental analysis shows that when butadiene is the ligand, complexes of empirical formula $\text{Ln}(\text{C}_4\text{H}_6)_3$ (Ln = Nd, Sm, Er) are obtained. When dimethylbutadiene is used, $\text{Ln}[(\text{CH}_3)_2\text{C}_4\text{H}_6]_2$ is obtained (Ln = La, Nd, Sm, Er).

These compounds differ from all other organolanthanide complexes in several respects. First, it is unusual to be able to obtain such good analytical data. Generally, for organolanthanides, incomplete carbon and hydrogen combustion is observed. Second, the stoichiometries are difficult to reconcile with known

lanthanide chemistry. If the dienes coordinate as π -ligands, the metals are formally zero-valent. If the dienes coordinate as dialkyl-2-butene moieties, the metals must be in the +6 oxidation state in the butadiene series and the +4 oxidation state in the dimethylbutadiene series. Other structural possibilities for these compounds involving dimeric or trimeric species would be equally novel to organolanthanide chemistry.

The physical properties of these new complexes are also unusual. The sharp, line-like, 4f-4f optical transitions normally observed for lanthanide complexes are not observed in the visible and near infrared regions. Instead a single broad band dominates the spectrum. The room temperature magnetic moments are similarly not consistent with known Ln^{3+} species. Most unusual in this respect is the lanthanum complex, which is the first paramagnetic organolanthanum complex ever observed. Nmr spectroscopy has not been useful in structural elucidation, in contrast to the usual case for La, Nd and Sm organometallic compounds.

Regardless of the actual structure of these complexes, or the oxidation state of the lanthanide, the fact that butadienes are good reagents for organolanthanide synthesis is remarkable. In this sense alone, we feel we have broadened the field.

The reaction of dienes with the lanthanide metals was further investigated by examining chemical reduction syntheses:

Following Rieke's method for the preparation of activated metals,³ we attempted the preparation of activated lanthanide metals and investigated subsequent reaction with 1,5-cyclooctadiene, 1,5- C_8H_{12} . Reduction of CeCl_3 and PrCl_3 with potassium resembles typical Rieke reactions although we find that added KI is de-

trimental to our lanthanide reactions. The results of this study, described below, are more fully detailed in a previously submitted preprint.⁴

Reduction of lanthanide trihalides forms black slurries which react with 1,5- C_8H_{12} to form red-brown products of limited stability. Since the rapid decomposition of these products severely complicates characterization, oxidative decomposition was attempted to minimally identify organic species present. The surprising result was that upon dry air oxidation of the red-brown praseodymium reaction product, 1,3,5,7-cyclooctatetraene (1,3,5,7- C_8H_8) was obtained. Somehow, the starting diene, 1,5- C_8H_{12} , loses hydrogen to form a C_8H_8 moiety! A likely formula for the red-brown product is $K^+[Pr^{3+}(C_8H_8^{2-})(C_8H_{10}^{2-})]$, which could have the following structure.

Oxidation of the $C_8H_8^{2-}$ present would form the observed 1,3,5,7- C_8H_8 .

To determine if the 1,5- C_8H_{12} to 1,3,5,7- C_8H_8 conversion really involved the praseodymium, several control experiments were studied. The room temperature reaction of potassium or Na-K alloy with 1,5- C_8H_{12} leaves the diene unchanged. The reaction of potassium with 1,5- C_8H_{12} at reflux does form $C_8H_8^{2-}$, however, providing a convenient laboratory synthesis of this dianion. The praseodymium is necessary for the room temperature reaction to occur. The role of this metal in the conversion and the development of a truly catalytic

scheme are under further investigation. Other metals, e.g. magnesium, do not promote this $1,5\text{-C}_8\text{H}_{12}$ to $\text{C}_8\text{H}_8^{2-}$ conversion and it is possible the room temperature transformation has specific size requirements which are met by praseodymium. In our original proposal we anticipated the possibility that the radial properties of the lanthanide metals might be exploited in just this way to develop unique transformations of organic substrates.

In summary, it would appear that the field of nonaqueous reductive lanthanide chemistry is quite fertile. Further investigation should broaden considerably the scope of lanthanide chemistry and lead to the discovery of more unusual reactions. My personal feeling is that we have only scratched the surface.

As Principal Investigator, on this project I have spent 50% of my time on this research from February to June 1977 when I was teaching and full time during July, August and September. I expect to spend 50% of my time on this project during October, November and December and full time in the Winter of 1977-1978.

References

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