

RECENT ADVANCES IN ORGANOLANTHANIDE CHEMISTRY

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Summary

Historically, the lanthanide elements have received less attention from organometallic chemists than the transition elements. The apparent reasons for this situation and recent developments leading to increased interest in organolanthanide chemistry are discussed.

The first well-characterized organometallic complexes of the lanthanide elements, the tris(cyclopentadienyl) species, $(C_5H_5)_3Ln$, were prepared in 1954 by Wilkinson and Birmingham [1] as part of a general investigation of cyclopentadienyl complexes [2]. The impetus for doing this research was not necessarily to develop the chemistry of the lanthanide metals, but rather to explore the limits of the cyclopentadienyl ligand system. Many subsequent research efforts in organolanthanide chemistry were similarly stimulated by interest in the ligands involved rather than in the metals. In 1969–1970, Hayes and Thomas [3] and Streitwieser and coworkers [4] prepared cyclooctatetraene lanthanide complexes to study the $C_8H_8^{2-}$ ligand and to compare the complexes with the previously synthesized uranocene [5]. Similarly, the studies of Lappert and coworkers involving neopentyl and trimethylsilylmethyl derivatives of the transition metals [6] eventually spread to the lanthanide series elements [7]. Other research groups involved in organolanthanide chemistry were frequently as interested or more interested in the actinide systems they were also studying [8]. In fact, it is only recently that research groups such as ours have concentrated on the lanthanide elements per se with the intention of developing the general organometallic chemistry of these elements specifically.

The major reason that relatively little emphasis had been placed on organolanthanide chemistry compared to organotransition metal chemistry is that the chemistry of the lanthanide metals appeared to be very ionic and consequently rather limited. Organolanthanide complexes were more often compared to alkali or alkaline earth organometallics than to transition metal complexes and the available chemistry was viewed to be correspondingly narrower. The classic experimental evidence for this ionic character was that the cyclopentadienyl complexes, $(C_5H_5)_3Ln$, react with $FeCl_2$ to form ferrocene [1]. Interactions of lanthanides with

small molecule substrates of interest to organometallic and catalytic chemists, e.g. CO, H₂ and neutral unsaturated hydrocarbons, had not been observed and perhaps were not expected based on the ionic nature of the chemistry.

The ionic character of the lanthanide complexes arises because the 4*f* valence orbitals have a rather limited radial extension. Calculations on lanthanide ions, which have [Xe]4*f*^{*n*} electron configurations, suggest that the 4*f* orbitals do not extend significantly beyond the filled 5*s*²5*p*⁶ orbitals of the xenon inert gas core [9]. Consequently, the lanthanide ion looks like a closed shell electron cloud with a +3 charge. In support of this picture, the trivalent lanthanide ions have similar chemical properties regardless of the 4*f*^{*n*} electron configuration and a single symbol, Ln, can often be used to describe the chemistry of the whole series. Furthermore, for a given lanthanide ion, the physical properties arising from the 4*f*^{*n*} configuration, such as the optical spectrum and the magnetic moment, are generally the same regardless of the nature of the attached ligand [10]. Metal orbital interactions with the ligands are less important than in transition metal complexes. With these physical properties, electrostatic considerations rather than orbital generalizations, like the transition metals' 18 electron rule, seemed to govern the structure and bonding of the complexes as well as their chemistry.

Despite the historical lack of interest in organolanthanide chemistry and despite the apparent limitation in the chemistry due to the ionic character, lanthanide chemistry seemed worth exploring in its own right. The 4*f* elements constitute a unique series of metals in the periodic table and have an unusual combination of physical properties. Distinctive chemical properties associated with this special collection of physical properties should be accessible if the lanthanides can be placed in the proper chemical environment. Since the lanthanides are relatively abundant in the earth's crust, the development of novel chemistry could have practical applicability. To pursue these goals properly, a concerted effort specifically centered on the lanthanides and involving both exploratory investigations and basic studies of, for example, the chemistry of the Ln–C bond, seemed appropriate. We initiated such a program in 1975 and, as described below, we now have examples of lanthanide metal interaction with a variety of catalytically interesting small molecules including CO, H₂ and unsaturated hydrocarbons. In addition, we have examples of unusual organometallic reactivity and structure, and even catalytic activity.

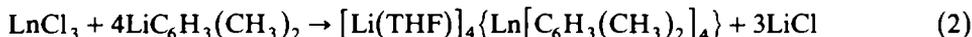
These recent advances suggest an even broader chemistry will be available to the lanthanide elements. In support of this contention, an increasing number of research groups are turning their attention to lanthanide chemistry. Key features in the recent development of organolanthanide chemistry are discussed below.

Chemistry of the Ln–C bond

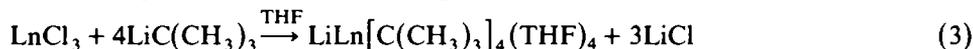
Traditionally, the two features most important in the synthesis of a stable lanthanide organometallic complex were (a) to optimize electrostatic interactions and (b) to fill the coordination sphere of the metal with bulky ligands to sterically inhibit decomposition pathways [11]. Since the cyclopentadienide ion could satisfy both requirements, early studies of Ln–C single bonds focused on cyclopentadienyl derivatives (eq. 1, R = CH₃, C₆H₅, C≡CC₆H₅, CH₂SiC(CH₃)₃) [12,13]. Up until 1978, the only fully-characterized non-cyclopentadienyl Ln–C bonded complexes



were two 2,6-dimethylphenyl complexes (eq. 2, Ln = Yb, Lu) [14].

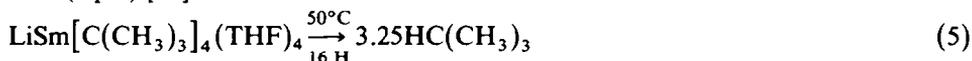


A key ligand in our basic investigation of Ln–C bond-making and bond-breaking processes has been the *t*-butyl ligand, $\text{C}(\text{CH}_3)_3$. Based on transition metal chemistry, a Ln– $\text{C}(\text{CH}_3)_3$ unit with nine β -hydrogen atoms might not be expected to be stable due to β -hydrogen elimination. However, one of the potentially important aspects of organolanthanide chemistry is that the rules for stability of these complexes may differ substantially from those of organotransition metal complexes. In fact, the lanthanide *t*-butyl unit is quite stable and homoleptic [15] as well as heteroleptic [16,17] complexes can be obtained (eqs. 3 and 4).



The importance of these two classes of organolanthanides and the advantages of not allowing ourselves to be constrained by the rules of traditional organotransition metal chemistry became evident when we investigated basic Ln–C bond-breaking processes with these complexes.

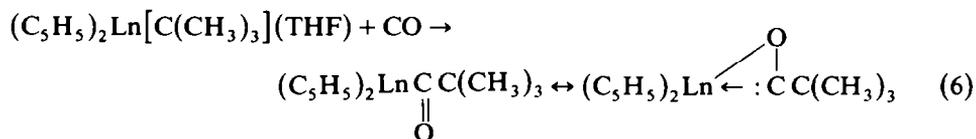
Investigation of the thermal decomposition of the tetrakis(*t*-butyl) complexes gave a remarkable result: although the complexes contain 36 β -hydrogen atoms, the β -hydrogen elimination product, 2-methylpropene, was not isolated from the reaction (eq. 5) [15].



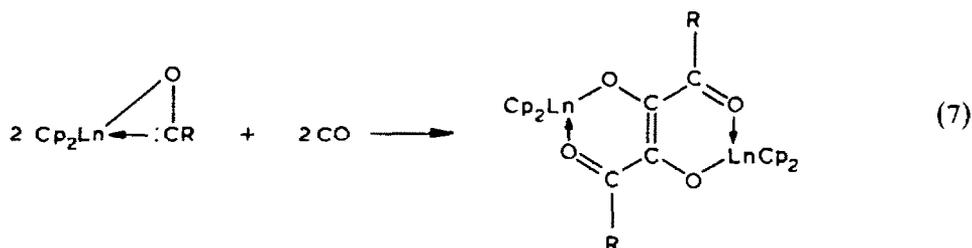
Only 2-methylpropane was obtained. The fact that β -hydrogen elimination is not the preferred mode of decomposition demonstrates the potential of organolanthanides to display unique organometallic reactivity.

The bis(cyclopentadienyl) *t*-butyl complexes proved to be very important for a different reason. Previously-characterized $(\text{C}_5\text{H}_5)_2\text{LnR}$ complexes had been found to exist either as electron deficient alkyl bridged dimers in arene solutions or as monomeric THF solvates in THF [13]. The *t*-butyl complexes differed in that they remained as monomeric THF solvates in the arene solution and even could be crystallized from arenes as the THF solvate, $(\text{C}_5\text{H}_5)_2\text{Ln}[\text{C}(\text{CH}_3)_3](\text{THF})$ [16]. The reactivity of these *t*-butyl complexes was significantly enhanced over other alkyl complexes presumably because a $(\text{C}_5\text{H}_5)_2\text{LnR}(\text{THF}) \rightleftharpoons (\text{C}_5\text{H}_5)_2\text{LnR} + \text{THF}$ equilibrium could provide a coordinatively unsaturated, unsolvated monomer unattainable with the bridging dimeric alkyls in arene solvents or the fully solvated monomeric alkyls in THF. In Ln–C bond-breaking reactions involving CO and H_2 , the $(\text{C}_5\text{H}_5)_2\text{Ln}[\text{C}(\text{CH}_3)_3](\text{THF})$ complexes proved to be important precursors which allowed us to observe reactivity unavailable to the methyl analogs under the same conditions.

Carbon monoxide (CO) reacts with lanthanide *t*-butyl complexes to break the Ln–C bond and form an acyl complex (eq. 6) [18].



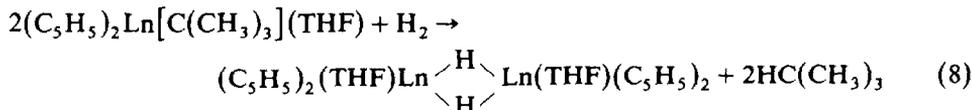
Like early transition metal and actinide acyls [19], a strong interaction exists between the oxygen and the oxophilic lanthanide metal and the ligand should be considered a dihapto acyl. Further reaction with CO forms a bimetallic enedione-diolate complex in which four CO molecules have been coupled and two C-C bonds and one C=C bond have been formed (eq. 7; Cp = C₅H₅, R = C(CH₃)₃).



This reaction provided the first example of CO activation by a lanthanide and the first instance of multiple coupling of CO without using pentamethyl-substituted cyclopentadienide as co-ligand [18,20]. Although CO reacts with analogous lanthanide methyl complexes, the chemistry is more complex and less tractable than in the *t*-butyl case.

Chemistry of the Ln-H bond

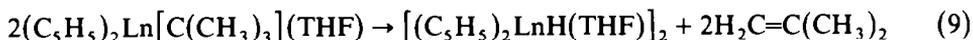
Another Ln-C bond-breaking reaction in which the (C₅H₅)₂Ln[C(CH₃)₃](THF) complexes proved crucial was hydrogenolysis to form the first crystallographically characterized complexes containing lanthanide metal hydrogen bonds (eq. 8) [21].



Our early attempts to make lanthanide hydrides by hydrogenolysis of [(C₅H₅)₂YbCH₃]₂ in toluene provided some hydride containing species [22], but the reaction required approximately two weeks and was complicated by conversion of the Yb³⁺-H⁻ to Yb²⁺ species. The reaction of (C₅H₅)₂Ln[C(CH₃)₃](THF) with H₂ in toluene, on the other hand, occurs very quickly. The desired hydride starts to precipitate from solution shortly after the H₂ is added and 70% yields can be achieved from an overnight reaction [21]. Interestingly, the reaction of the *t*-butyl complex with H₂ in THF does not form the hydride at ambient conditions, presumably because the constant state of solvation prevents hydrogen from attacking the Ln-C bond. These results stimulated us to try to modify the solution environment of (C₅H₅)₂LnCH₃ complexes such that the concentration of reactive monomeric unsolvated species would be increased. Using mixed ether/arene or alkane solvent systems, this can be achieved and the hydrides can now be obtained from methyl precursors also [23]. These results suggest that although the organo-lanthanides may not initially appear to participate in some desired reaction pathway, by understanding and manipulating a variety of subtle factors, the desired reactivity can be achieved.

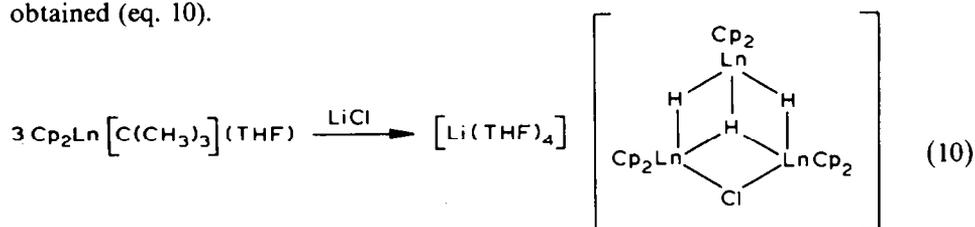
Another Ln-C bond-breaking process of interest with the (C₅H₅)₂Ln[C(CH₃)₃]-

(THF) complex was the β -hydrogen elimination reaction (eq. 9).

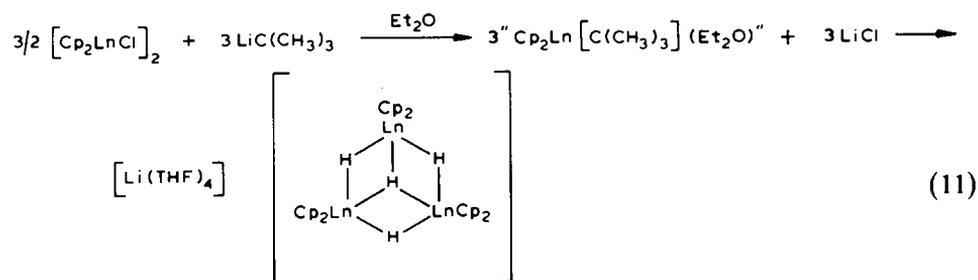


Although this was not a facile reaction with the homoleptic *t*-butyl complexes (*vide supra*), it does occur in the heteroleptic cyclopentadienyl ligand environment. The lutetium complex requires a temperature of 75°C, whereas complexes of the larger metals, erbium and yttrium, decompose at ambient temperature [24]. The latter result is not unexpected since the metal coordination sphere of the larger metal is less sterically saturated. However, it is interesting to note that the sterically more saturated methylcyclopentadienyl analogs, $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Ln}[\text{C}(\text{CH}_3)_3](\text{THF})$, are less stable with respect to β -hydrogen elimination. Again, subtle factors appear to govern reactivity/stability patterns in these organolanthanide systems.

In the course of studying reaction 9, we noticed that if there was any residual LiCl present during the β -hydrogen elimination reaction, a different hydride product was obtained (eq. 10).



The crystallographically characterized product had incorporated one LiCl per three lanthanide atoms forming a trimeric trihydride [24]. The coordination environment of each metal in the trimer was like that found in the dimeric hydrides with a hydride or chloride bridge replacing the THF of solvation in the dimers. The most remarkable feature of the trimer is the location of the central hydrogen coplanar with the metals. This is unique in metal hydride chemistry, since transition metal trimers generally do not have enough room to accommodate a hydrogen atom in the center of the triangle. If a slight change is made in the above β -hydrogen elimination reaction, i.e. if diethyl ether is substituted for THF, a trimeric tetrahydride is isolated which has incorporated one LiH per three lanthanide atoms (eq. 11).



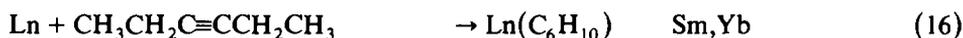
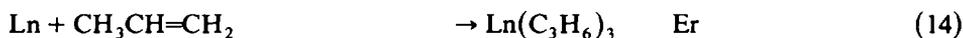
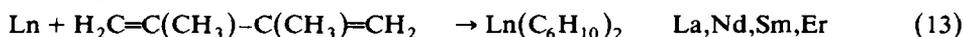
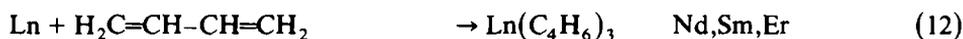
Given the variety of magnetic and spectral properties available in the lanthanide series, these complexes should be ideal candidates for the study of hydrogen surrounded by metals. Although the relevance of the internal hydrogen to hydrogen storage materials, such as interstitial hydrides, remains to be determined, it is clear that some interesting and unique structures are accessible via organolanthanide chemistry. The observed diversity of structures available by making small changes in

lanthanide hydride synthesis reactions suggests a variety of other unusual molecules will be accessible in this area. Furthermore, both the doubly-bridging hydride and chloride ligands should provide synthetic entry points to many other new classes of polymetallic lanthanide hydrides.

Since the above complexes were the first well-characterized examples of Ln-H bonds, we have initiated a study of the chemistry of this new metal hydrogen linkage. Although the study of Ln-H bond-breaking processes is just beginning, it is already apparent that a wide range of reactivity will be observed. The dimeric hydrides react with most classes of unsaturated hydrocarbons examined so far including alkenes, alkynes, nitriles, isonitriles, and CO. Preliminary structural data on some of these reaction products suggest that additional, unusual organometallic structures will be accessible via these hydrides [23].

Lanthanide unsaturated hydrocarbon interactions

In addition to the basic investigations of Ln-C and Ln-H bond-making and bond-breaking discussed above, we have pursued some exploratory synthetic projects designed to develop new areas of organolanthanide chemistry. One approach employed was to investigate the zero valent chemistry of the lanthanides using the metal vapor technique pioneered by Skell, Timms, Klabunde and others [25]. The method involves generation of zero valent lanthanide vapor by resistively heating an ingot at high temperature in a high vacuum reactor and cocondensing the vapor at -196°C with a potential ligand. We have used this technique to study how the lanthanides interact with neutral unsaturated hydrocarbons, a class of molecules previously thought to be unreactive with the lanthanides. As shown in reactions 12-16, this method allows the preparative scale synthesis of a variety of new classes of organolanthanides [26-30].

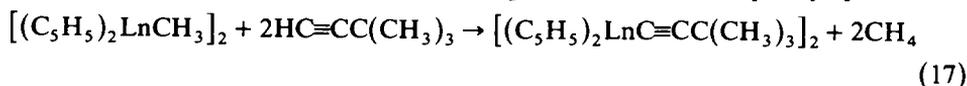


These complexes differ from traditional organolanthanides in several respects. First of all, the observed stoichiometries have low ligand-to-metal ratios. For example, the ytterbium and samarium 3-hexyne products have formal ligand-to-metal ratios of one, whereas most organolanthanides are commonly nine or ten coordinate. Second, the stoichiometries vary in an unusual manner depending on ligand and metal. For example, 2,3-dimethyl substitution of the butadiene changes the ligand-to-metal ratio from three (eq. 12) to two (eq. 13). In the 3-hexyne system, changing from neodymium and erbium to ytterbium and samarium changes the ratio from 1.5 (eq. 15) to one (eq. 16). Generally, organometallic stoichiometries are similar across the series and are invariant to methyl substitution. Third, the physical properties of these complexes differ from those of traditional trivalent organolanthanides. The optical spectra of these complexes contain strong charge transfer bands in the near-infrared-visible region instead of the usual sharp and weak $4f-4f$ transitions. Room temperature magnetic moments are often outside the range of values previ-

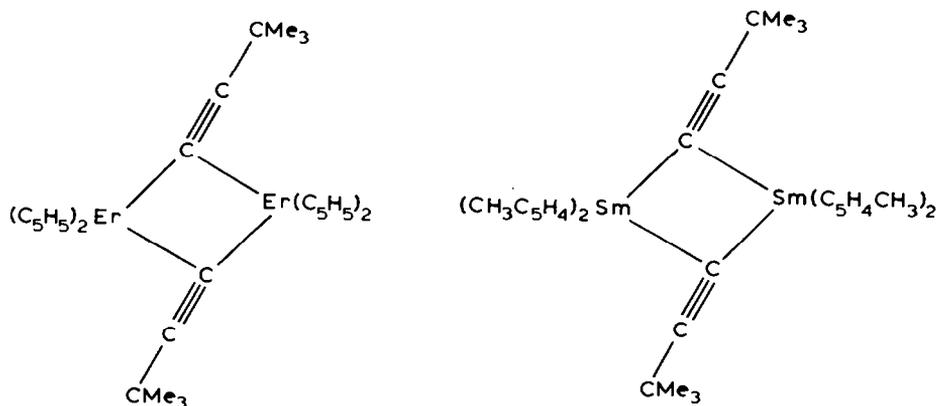
ously reported for organolanthanide compounds. Fourth, the solution behavior of these complexes is unusual. The complexes are highly associated in solution and display an unusual molecular weight dependence on solvent. For example, molecular weight measurements indicate that the 3-hexyne product $[\text{ErC}_9\text{H}_{15}]_n$, is dimeric in arenes, i.e. $n = 2$ ($\text{Er}_2(\text{C}_6\text{H}_{10})_3$), but in concentrated solution or in tetrahydrofuran, it is highly associated with $n > 10$. This is just opposite the trend found for traditional organolanthanides which are more highly associated in arenes than in THF. Since the metal vaporization products oligomerize rather than crystallize in concentrated solution, these species have not yet been structurally characterized by X-ray diffraction and their precise bonding modes remain to be determined.

The most important property of these metal vapor complexes which had not been previously observed for an *f* element complex was that they have the capacity to catalytically activate molecular hydrogen in homogeneous solution [27,28]. Catalytic hydrogenation of alkynes and alkenes is effected by these species at room temperature under one atm of hydrogen often with high stereospecificity (3 hexyne \rightarrow > 96% *cis*-3-hexene). Hence, these exploratory studies demonstrated not only that a wider variety of organic ligands can be used to generate organolanthanide complexes (i.e. one is not limited to common stable organic anions), but these studies also demonstrate that the lanthanides have the capacity to function in homogeneous catalytic reactions involving small molecule transfer. We have pursued the catalytic aspects of organolanthanide chemistry with the hydrides discussed above and have found that they also are catalytically active in homogeneous hydrogenation reactions.

The interaction of lanthanide metals with unsaturated hydrocarbons has been investigated in two other respects. As part of our general study of Ln-C bond forming, we synthesized some alkynide complexes as shown in eq. 17 [31].

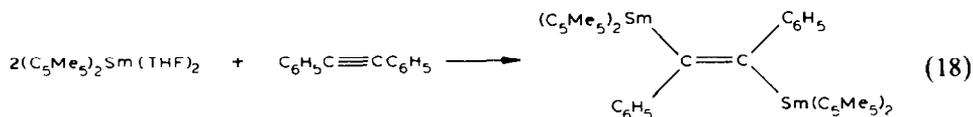


These complexes had the interesting property that they are dimeric even in THF. To investigate this apparently strong alkynide bridge, an X-ray crystallographic investigation was carried out [32]. In contrast to the symmetrically bridged $[(\text{C}_5\text{H}_5)_2\text{LnCH}_3]_2$ and $[(\text{C}_5\text{H}_5)_2\text{LnCl}]_2$ dimers [13,33], the alkynide bridge is tipped asymmetrically toward one of the two equivalent $(\text{C}_5\text{H}_5)_2\text{Er}$ units which it connects.

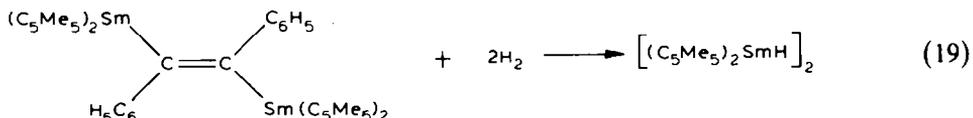


A second alkyne bridged dimer, $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{SmC}\equiv\text{CC}(\text{CH}_3)_3]_2$, was crystallographically studied to determine if this asymmetry was general. It too had unequal Sm-C \equiv C angles with an even greater disparity than in the erbium case [34]. For a purely electrostatically bonded system, a symmetric structure would be expected. Asymmetric alkyne bridges are known in aluminum, indium, and beryllium chemistry and are explained by covalent bonding schemes [35]. These results and preliminary X-ray data on complexes involving carbon nitrogen multiple bonds [23] suggest that organolanthanide chemistry is not necessarily limited to simple ionic structures as has been previously observed.

We have also studied the interaction of a divalent lanthanide center with unsaturated hydrocarbons. Using metal vapor techniques, we were able to synthesize the divalent samarium complex, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$, the first soluble organosamarium(II) complex [36]. Since the Sm^{III}/Sm^{II} reduction potential is -1.5 V, this complex is highly reactive. It reacts with diphenylacetylene to form an enediyl complex (eq. 18), a reaction which defines a new reductive type of lanthanide unsaturated hydrocarbon interaction [37].



The reactivity of this complex is remarkable in several respects. First, it can be reconverted into the Sm^{II} precursor with THF. This is significant because it is the first evidence that the reversibility necessary for catalysis involving the Ln^{III}/Ln^{II} couple may be available with the very reactive Sm^{II}. Second, the enediyl complex reacts with H₂ to form a new class of lanthanide hydrides, exemplified by the unsolvated dimer $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ (eq. 19).



This hydride is unusual in itself, since the relatively large samarium would be expected to be nine coordinate like the THF-solvated metals in the dimer hydrides discussed above. Third, the divalent samarium complex, the enediyl and the samarium hydride all function as precursors to catalytic hydrogenation systems. Interestingly, the rates of the catalytic activity they initiate on a given substrate are different, which implies that the catalyses proceed by different catalytic pathways. The enediyl generates the fastest catalytic system with rates 3000 times faster than those of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ with 3-hexyne as a substrate. This drastic rate increase caused only by the presence of 0.5 equivalent of $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ per metal suggests that low valent lanthanide complexes of alkenes and alkynes may play a unique role in the activation of molecular hydrogen via new mechanistic pathways.

Conclusion

The results discussed above indicate that lanthanide chemistry is not as limited as it once was thought to be. A field that started as a novel set of metals which formed

ionic complexes with traditional stable organic anions has evolved into a full-fledged area of organometallic chemistry complete with a wide range of reactions with small molecules of practical interest, with distinctive structural and reactivity patterns, and even with catalytic chemistry. The results of the past few years indicate that as a frontier area of organometallic chemistry, organolanthanide chemistry has a very bright future.

Acknowledgments

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