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THE ORGANOMETALLIC CHEMISTRY OF THE LANTHANIDE ELEMENTS IN LOW OXIDATION STATES

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I. INTRODUCTION

In the three decades following the discovery of ferrocene,¹ organometallic chemistry was investigated extensively and became a major field of chemical research. During this period, research efforts were focused primarily on the transition metals and the organometallic chemistry of the lanthanide elements received comparatively little attention. This situation is understandable when one considers

how the chemistry of the lanthanides was viewed during the time in which organometallic chemistry was being developed.

The early studies on organolanthanide complexes suggested that their chemistry was limited. For example, the first well-documented reports in this area, which concerned the simple cyclopentadienyl complexes $(C_5H_5)_3Ln$,² showed that these compounds were rather ionic and suggested that organolanthanide complexes would merely be trivalent versions of alkali and alkaline earth metal organometallic species.

In general, all of the lanthanide elements traditionally were thought to have a very similar chemistry, in contrast to the diverse chemistry observed for a row of transition elements. Furthermore, most lanthanide chemistry centered on a single oxidation state, the trivalent state. Of the few lanthanide elements which had readily accessible non-trivalent oxidation states, Ce^{4+} , Sm^{2+} , Eu^{2+} and Yb^{2+} , none had both the +4 and the +2 oxidation state readily available on the same metal. Hence, the diversity of oxidation states found with transition metals was not present in the lanthanide series and the two-electron processes common in transition-metal chemistry, such as oxidative addition and reductive climination, were not possible at a single lanthanide metal center. In addition, many reagents of interest to organometallic chemists, e.g. CO, unsaturated hydrocarbons, hydrogen, phosphines, isocyanides, nitrogen etc., were not thought to have a substantial chemistry with these ionic metal complexes. Finally, many reaction pathways important in organometallic synthesis and catalysis were not thought to be available to these elements. All of these factors suggested that lanthanide chemistry would not be as interesting as transition-metal chemistry.

In addition to the problem of an anticipated limited chemistry, the organolanthanide complexes were experimentally more difficult than many transition-metal systems. Almost all organolanthanides are extremely air- and moisture-sensitive and even the metal trihalide starting materials are hydrolytically unstable. Purification and isolation of organolanthanide compounds is difficult because the complexes decompose on chromatographic supports, generally cannot be sublimed in high yield, and frequently undergo ionic redistribution reactions giving mixtures during crystallization attempts. Moreover, the paramagnetism of many of the metals precluded characterization by NMR spectroscopy, the organometallic chemist's most common method of analysis.

Despite the limitations and difficulties described above, it was realized that the lanthanides had the potential for some unique chemistry distinct from anything possible with main-group or transition metals.³ The basis for this contention was that the lanthanide elements have a special combination of physical properties, including size, type of valence orbital, ionization potential, electron affinity etc., which is not duplicated anywhere else in the periodic table. Hence, a lanthanide element, if placed in the proper oxidation state and coordination environment, could display an unusual chemistry.

In the past few years, the status of organolanthanide chemistry has changed dramatically. The goal of demonstrating a unique organometallic chemistry with these metals has been realized in terms of unusual compounds, unprecedented structures, and spectacular reactivity.⁴⁻⁷ Increasing numbers of investigators are turning their attention to 4*f*-element chemistry and it is currently one of the most rapidly developing areas of organometallic chemistry.

The most extensively developed area of organolanthanide chemistry has involved trivalent complexes and a substantial body of experimental data is now available. Principles regarding structure and reactivity are emerging for trivalent species as outlined in a recent review⁵ and in Section II.

This Report focuses on the organometallic chemistry of the lanthanides in oxidation states less than +3. This area is at that exciting stage of development in which many unusual structures and reactions have been observed, but the general principles governing this chemistry have yet to be determined. The field is in that frontier stage of exploration in which each new piece of data has the potential of providing key insights into general principles.

Low oxidation state organolanthanide chemistry is described in parts of other reviews of organolanthanide chemistry,^{4,5,7-10} but only one of these concentrates solely on this topic.⁷ In that review, the emphasis was on applications of divalent ytterbium and samarium chemistry to organic synthesis. This review will concentrate on the synthesis and reactivity of divalent and zero-valent organometallic systems and will start with a background section describing basic principles of the chemistry of these elements and their trivalent complexes.

II. TRADITIONAL PRINCIPLES OF ORGANOLANTHANIDE CHEMISTRY

II.1. Properties of the elements

The main factor which distinguishes the lanthanide elements from other metallic elements is that their valence orbitals are the 4f orbitals. The main factor which differentiates the 4f orbitals from valence orbitals of other metallic elements is their relatively limited radial extension. Calculations on lanthanide ions, which have $[Xe]4f^n$ electron configurations, suggest that the 4f orbitals do not extend significantly beyond the filled $5s^25p^6$ orbitals of the xenon inert gas core.¹¹ Consequently, a trivalent lanthanide ion looks like a closed-shell inert-gas electron cloud with a tripositive charge, a situation which has a major effect on the chemical and physical properties of these metals and their complexes.

One effect of the small radial extension of the lanthanides' valence orbitals is that the metals' orbital interactions with ligands are smaller than those in transition-metal complexes. This is the traditional explanation of why the chemistry tends to be much more ionic.¹² Electrostatic factors appear to be more important in determining the stability, structure and chemistry of lanthanide complexes than orbital generalizations. Consistent with this, the physical properties arising from a given $4f^n$ configuration for a lanthanide ion, e.g. the optical spectrum and the magnetic moment, are relatively similar regardless of the nature of the attached ligand.¹²⁻¹³

Another consequence of the limited radial extension of the 4f orbitals is that the chemistry of the trivalent lanthanide ions can be similar in many systems regardless of the 4fⁿ configuration.¹² Hence, a single symbol, Ln, often has been used in the past to describe the chemistry of all the elements in the series. For example, one similarity in the chemistry of the lanthanide metals is that for each element the +3 oxidation state is the most stable. Another example is the similarity in structure and reactivity of the (C_5H_5)₃Ln(thf) complexes^{2,15,16} (except for the single radioactive system, Ln = Pm). This contrasts sharply with the large variation in structure and stability of transition-metal (C_5H_5)₂M complexes as M is varied across a row of the periodic table.¹⁷

Some differences in the chemistry of the individual lanthanides are observed due to the variations in the radial size of the metals. Radial size diminishes gradually from La^{3+} (1.061 Å) to Lu^{3+} (0.848 Å) as the series is crossed.¹⁸ The other basis for differences in chemistry between the metals arises with the four elements for which non-trivalent oxidation states are accessible under normal reaction conditions: Ce^{4+} (4f⁰), Eu^{2+} (4f⁷), Yb^{2+} (4f¹⁴), and Sm^{2+} (4f⁶). Differences in trivalent chemistry arise for these elements primarily under strongly oxidizing or reducing conditions. Differences in lower oxidation state chemistry will be discussed in Section III.

Two other important general features of the lanthanide metals are their size and electronegativity. Compared to transition metals the lanthanides are quite large. High coordination numbers of 8-12 are common in lanthanide complexes.¹² The lanthanides are also rather electropositive compared to transition metals¹⁹ and are quite oxophilic.

II.2. Stability principles for trivalent species

Given these physical properties, two generalizations on organolanthanide stability traditionally have been followed in order to obtain isolable organolanthanide complexes. First, electrostatic interactions must be optimized by using stable organic anions to balance the charge of the metal cation. Second, additional stability often can be gained by choosing large, bulky anions which can completely occupy the coordination sphere of the metal and sterically block decomposition pathways. The polyhapto anions $C_5H_5^-$ and $C_8H_8^{2-}$ meet both of these requirements and, not coincidentally, they are the most prevalent ligands in organolanthanide chemistry. The reason the smaller metals later in the lanthanide series, Lu, Yb and Er, have been investigated most extensively is that their small size makes steric saturation of the metal coordination sphere less difficult and hence provides more tractable complexes.

Since the electrostatic charge balance requirement for stability must always be met in organolanthanide complexes, the determining factor in stability/reactivity is often steric. Recent results in trivalent organolanthanide chemistry suggest emerging patterns of structure and reactivity which depend on the relative sizes of the ligands vs the metals.⁵ Quantitative assessment of this steric saturation is also under development.²⁰

Several basic generalizations appear to apply to trivalent organolanthanides based on the data currently available.⁵ High reactivity and limited stability are associated with free coordination sites, i.e. steric unsaturation, and with terminal, as opposed to bridging, ligands. High reactivity/limited stability can be caused by insufficient ligand bulk around the metal (steric unsaturation) or by excessive ligand bulk (steric oversaturation) when it leads to structures with open coordination positions and terminal ligands. Examples of these ideas follow. Since trivalent Y displays chemistry much like that of the late lanthanide ions of similar size [Ho(III) and Er(III)],²¹⁻²⁴ examples from Y chemistry will also be included.

The importance of terminal ligands and open coordination positions to organolanthanide reactivity can be readily seen from hydrogenolysis studies [reactions (1)-(4)]. For example, the bridged species $[(C_5H_5)_2Ln(\mu-CH_3)]_2$ (Ln = Y, Er, Yb or Lu) react slowly with H₂ in arene solvents in which they are fully bridged [reaction (1)]:^{23,25}

$$(C_{5}H_{5})_{2}Ln \xrightarrow{CH_{3}} Ln(C_{5}H_{5})_{2} + H_{2} \xrightarrow{toluene} very slow.$$
(1)

In contrast, the *tert*-butyl complexes, $(C_5H_5)_2Ln(CMe_3)$ (thf), which do not form bridged dimers, react rapidly with hydrogen in toluene to form the hydride dimers $[(C_5H_5)_2Ln(\mu-H)(thf)]_2$ [reaction (2)].²²

$$2(C_5H_5)_2Ln(CMe_3)(thf) + 2H_2 \xrightarrow[rapid]{toluene}_{rapid} [(C_5H_5)_2Ln(\mu-H)(thf)]_2 + 2HCMe_3.$$
(2)

This demonstrates the higher reactivity available to terminal ligands.²³

In thf however, the *tert*-butyl complexes $(C_5H_5)_2Ln(CMe_3)$ (thf) are unreactive to hydrogen [reaction (3)]:²⁶

$$(C_5H_5)_2Ln(CMe_3)(thf) + H_2 \xrightarrow{thf}$$
 no reaction. (3)

The difference in reactivity in toluene vs thf presumably arises because in toluene some dissociation of thf occurs to give a free coordination position, whereas in thf the metal center is constantly solvated. Hence, even with the small reagent hydrogen and the large lanthanide metals, an open coordination position is needed for high reactivity.

These steric effects are subtle, however.²⁶ For example, hydrogenolysis in thf is possible when the alkyl group is methyl rather than *tert*-butyl [reaction (4)]:

$$2(C_{5}H_{5})_{2}Ln(CH_{3})(thf) + 2H_{2} \xrightarrow{thf} [(C_{5}H_{5})_{2}Ln(\mu-H)(thf)]_{2} + 2CH_{4}.$$
 (4)

Hence, $(C_5H_5)_2Ln(CH_3)$ (thf) reacts readily with H_2 in thf when Ln = Y or Er. Based on crystal structures of $(C_5H_5)_2Lu(CMe_3)$ (thf)²⁷ and $(C_5H_5)_2Yb(CH_3)$ (thf),²⁶ one can estimate that the main difference between a methyl and a *tert*-butyl $(C_5H_5)_2LnR(thf)$ complex for a given Ln is that the *tert*-butyl complex has a Ln—C bond approximately 0.1 Å longer than the Ln—C bond in the methyl complex. The longer distance presumably occurs because the *tert*-butyl complex is sterically too crowded to form a shorter "normal" Ln—C bond.^{26,28} Since the *shorter* Ln—C methyl bond is the Ln—C unit which is more reactive to hydrogen, the difference in reactivity appears to be steric.

Although hydrogenolysis of $(C_5H_5)_2Ln(CH_3)$ (thf) is facile in the for Ln = Er and Y, for Ln = Yb and Lu the reactivity is very low.²⁶ This presumably occurs because of the increased steric crowding in the coordination environment around these smaller metals. Hence, a change in metallic radius of just 0.03 Å can significantly affect reactivity.

Steric factors can affect structure as well as reactivity, a fact which is well illustrated by the many examples of dicyclopentadienyl lanthanide halide complexes characterized by X-ray diffraction. These complexes exist as symmetrically bridged dimers, $[(C_5H_4R)_2Ln(\mu-Cl)]_2$, when Ln is one of the smaller metals Sm-Lu and Y, and when the cyclopentadienyl ligand is C_5H_5 or $CH_3C_5H_4$.²⁹⁻³¹ Such complexes are generally considered sterically saturated. For the larger

lanthanides earlier in the series, La, Ce, Pr and Nd, $[(C_5H_5)_2Ln(\mu-Cl)]_2$ complexes are reported to be unstable with respect to ligand redistribution to the sterically more saturated (C₅H₅)₃Ln species.^{9,30} These early lanthanide $[(C_5H_5)_2Ln(\mu-Cl)]_2$ complexes are sterically unsaturated and therefore less stable. To obtain an isolable bis(cyclopentadienyl) lanthanide halide complex of a large early lanthanide metal, the steric bulk of the ligand set must be increased. This can be done substituted cyclopentadienyl ligand, with а as demonstrated in the structure $\{[(Me_3Si)_2C_5H_3]_2Pr(\mu-Cl)\}_2$,³² or by adding an "extra" ligand to the coordination sphere, as found in $[(C_5H_5)_2Nd(thf)(\mu-Cl)]_2$.³³

When sterically bulky ligands such as C_5Me_5 are used with the small metals late in the series, complexes such as $[(C_5Me_5)_2Ln(\mu-Cl)]_2$ are too sterically crowded to form. These sterically oversaturated systems distort from a symmetrical structure to accommodate the ligand-metal size imbalance. For Ln = Y, a monobridged structure, $[(C_5Me_5)_2Y(\mu-Cl)YCl(C_5Me_5)_2]$, is observed.³⁴ For the methyl and hydride Lu derivatives $[(C_5Me_5)_2LuZ]_n$ (Z = H or CH₃; n = 1 or 2), an equilibrium is reported to exist between a monobridged structure, $(C_5Me_5)_2Lu(\mu-Z)LuZ(C_5Me_5)_2$ and the monomer $(C_5Me_5)_2LuZ.^{6.35}$

The three classes of organolanthanide complexes, i.e. sterically saturated, sterically unsaturated, and sterically oversaturated compounds, display different types of reactivity due to the differences in terminal vs bridging groups and the relative availability of open coordination positions. This point is illustrated well by the metalation reactivity of organolanthanide hydrides with ethers, hydrocarbons and pyridine. The sterically saturated hydrides $[(C_5H_4R)Ln(\mu-H)(thf)]_2$ (R = H or CH₃; Ln = Er, Y or Lu) are stable to ethers, metalate only rather acidic hydrocarbons such as terminal alkynes, and do 1,2-LnH addition rather than metalation when reacted with pyridine.²³ In contrast, the sterically oversaturated $[(C_5Me_5)_2LuH]_n$ complex decomposes ethers, metalates pyridine to form a $(C_5Me_5)_2Lu(\eta^2-NC_5H_4)$ complex, and is such a powerful metalation reagent that not only benzene and Me₄Si are metalated, but even CH₄.^{36,37} The sterically unsaturated $[(C_5Me_5)_2Sm(\mu-H)]_2^{38}$ has intermediate reactivity—it decomposes ether and metalates pyridine, but metalates arenes only slowly.³⁹

Given that all of this reactivity involves the same, nominally ionic, Ln—H bond, it is clear that steric factors influence trivalent organolanthanide chemistry to a great extent. Obviously, the thermodynamic differences in bond strengths and the differences in the charge: radius ratio from one metal to another will also affect the chemistry. However, in many cases these factors are likely to be sufficiently similar that it is the steric parameters which will govern the observed variations in reactivity.

III. DIVALENT ORGANOLANTHANIDE CHEMISTRY

Divalent organolanthanide complexes are the most fully characterized and investigated of the available low oxidation state lanthanide organometallics. Consequently, this is the first class of low-valent species which will be presented in detail. This section is organized into three parts: a brief description of divalent-metal properties, a discussion of synthesis and structure organized according to ligand, and a discussion of reactivity.

III.1. Background

Although divalent lanthanide ions for almost all of the elements in the series have been generated by irradiating trivalent ions doped into CaF_2 ,⁴⁰⁻⁴² only three elements have divalent states which are chemically accessible in organometallic systems under normal conditions: Eu, Yb and Sm. It is only for these elements that X-ray crystallographic structures of divalent organolanthanide complexes are available. A report of a Ce(II) complex formed by K reduction is in the literature,^{43,44} but this result remains to be structurally confirmed.

The aqueous reduction potentials for the $Ln^{3+}-Ln^{2+}$ couple are reported to be -0.35 V for Eu, -1.1 V for Yb and -1.5 V for Sm (vs NHE)^{45,46} indicating that Eu²⁺ should be the most stable and Sm²⁺ the most reactive in terms of reducing power. As described in Section II, complexes of the smaller Yb²⁺ ion could be the most stable in terms of steric saturation of the metal coordination sphere and Sm²⁺ could be the most reactive in this regard.

Sm(II) is most desirable not only in terms of high reactivity, but also when NMR characterization

is considered. Sm provides the only Ln(II)-Ln(III) system in which both oxidation states have complexes which are NMR-accessible.⁴⁷ Despite room-temperature magnetic moments of 3.4-3.8 μ_B for Sm(II) and 1.3-1.9 μ_B for Sm(III), ¹H NMR resonances are reasonably sharp and are found within ± 10 ppm of the normal 0-10-ppm region where diamagnetic resonances are located. This is not true for Eu(II), Eu(III) or Yb(III), which have room temperature magnetic moments in the ranges 7.4-8.0, 3.4-4.2 and 4.2-4.9 μ_B , respectively.^{48,49} Of course, diamagnetic Yb(II) provides NMR-observable complexes.

Divalent organolanthanide complexes differ in appearance from trivalent species in that their colors are more intense and these colors vary as the ligand set is changed. For trivalent species, the colors arise from Laporte-forbidden $4f \rightarrow 4f$ transitions.^{12,13} Due to the limited radial extension of the 4f orbitals, crystal field splitting is very small and hence the colors vary little as the ligand set is changed. Another consequence of the limited radial extension is that little vibronic coupling occurs to relax the Laporte-forbidden nature of the transitions. Hence, the colors of the complexes are pale. In contrast, the colors of the divalent lanthanide ions are attributed to Laporte-allowed $4f \rightarrow 5d$ transitions.^{14,40} The energies of these transitions change as the ligand set varies. The variation in color with ligand environment is greatest with Sm(II) and Yb(II). Organometallic Sm(II) compounds can be green or purple and Yb(II) species can be yellow, red, blue, green or purple. Eu(II) organometallics, on the other hand, are almost always yellow, orange or red.

III.2. Synthesis and structure

III.2(a) Cyclooctatetraenyl complexes. The first divalent organolanthanide complexes were prepared by taking advantage of the fact that Eu and Yb dissolve in liquid ammonia to form highly reducing solutions of $[Ln(NH_3)_x^{2^+}] [e^-(NH_3)_4]_2$.⁵⁰ The cyclooctatetraenyl species, EuC₈H₈ and YbC₈H₈, were obtained by adding 1,3,5,7-cyclooctatetraene to solutions of Eu and Yb in liquid ammonia [reaction (5)]:

$$Ln + 1,3,5,7-C_8H_8 \xrightarrow{NH_3(1)} LnC_8H_8.$$
 (5)

The compounds precipitate from the ammonia solution and are insoluble in hydrocarbons and ethers. Soluble adducts are formed in pyridine and dimethylformamide, but have never been fully characterized. C_8H_8Yb can also be prepared by metal vapor methods from zero-valent Yb and 1,3,5,7- C_8H_8 .⁵¹ Reduction of [K(glyme)] [Ce(C_8H_8)₂] in glyme with excess K is reported to form [K(glyme)]₂[Ce(C_8H_8)₂], the only organocerium(II) complex in the literature.⁴³ Neither structural characterization nor reaction chemistry have been reported for any of the divalent cyclooctatetraenyl species.

III.2(b) Complexes containing unsubstituted cyclopentadienyl ligands. Divalent cyclopentadienyl complexes were also originally obtained from liquid-ammonia reactions. For Eu, an NH_3 solvate is initially formed [reaction(6)]:

$$Eu + 3C_5H_6 \xrightarrow{NH_3(1)} (C_5H_5)_2Eu(NH_3) + C_5H_8$$
 (6)

which can be desolvated by heating to 120-200°C in vacuo.¹⁵ This complex is not soluble in hydrocarbons and common ethers, but dissolves in liquid ammonia and dimethylformamide.

For Yb, which has a less stable divalent oxidation state, the reaction analogous to 6 is more complex. The trivalent complex $(C_5H_5)_3$ Yb (NH_3) is obtained in the reaction despite the reducing conditions and sublimation gives trivalent products as well as $(C_5H_5)_2$ Yb.^{15,52,53} This exemplifies in part the general trend in divalent lanthanide chemistry that Eu(II) complexes are least difficult to obtain in pure form, Yb(II) chemistry is more complex, and Sm(II) chemistry is the most difficult.

A variety of ammonia-free synthetic routes to $(C_5H_5)_2$ Yb are known. One type of reaction involves reduction of $[(C_5H_5)_2$ YbCl]₂ with Na,⁵³ Yb⁵³ or *tert*-butyllithium^{26,27} [reactions (7)–(9) the $(C_5H_5)_2$ Yb product in these and the following reactions is generally isolated as an ether adduct]:

$$[(C_{5}H_{5})_{2}YbCl]_{2} + 2Na \rightarrow 2(C_{5}H_{5})_{2}Yb + 2NaCl,$$
(7)

The organometallic chemistry of the lanthanide elements

$$3[(C_{5}H_{5})_{2}YbCl]_{2} + 2Yb \rightarrow 6(C_{5}H_{5})_{2}Yb + 2YbCl_{3},$$
(8)

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$$[(C_{5}H_{5})_{2}YbCl]_{2} + 2LiCMe_{3} \rightarrow 2(C_{5}H_{5})_{2}Yb + HCMe_{3} + H_{2}C = CMe_{2} + 2LiCl.$$
(9)

Reduction of $(C_5H_5)_3$ Yb with Na⁵³ or Yb^{54,55} also gives $(C_5H_5)_2$ Yb [reactions (10) and (11)]:

$$(C_5H_5)_3Yb + Na \rightarrow (C_5H_5)_2Yb + NaC_5H_5,$$
 (10)

$$2(C_5H_5)_3Yb + Yb \rightarrow 3(C_5H_5)_2Yb.$$
 (11)

 $(C_5H_5)_2$ Yb(thf) can be obtained by decomposition of $[(C_5H_5)_2$ Yb(μ -H)(thf)]₂ and $\{[(C_5H_5)_2 Yb(\mu-H)]_3(\mu_3-H)\}$ atthough this is not a preparatively desirable synthesis.²⁶

Recently, syntheses have been reported which start from Yb metal, which is a more convenient starting material than the YbCl₃ reagent needed for reactions (7)–(11). For example, $(C_5H_5)_2$ Yb can be prepared from the reaction of C_5H_5 Tl with excess Yb metal,⁵⁴ a reaction which is reported to have $(C_5H_5)_3$ Yb as an intermediate [reaction (12)]:

$$6C_5H_5Tl + 3Yb \rightarrow 6Tl + 2(C_5H_5)_3Yb + Yb \rightarrow 3(C_5H_5)_2Yb + 6Tl.$$
 (12)

Yb metal, which has been activated with $HgCl_2$ to form an amalgam, is also reported to be successful [reaction (13)]:⁵⁵

$$(C_5H_5)_2Hg + Yb \rightarrow Hg + (C_5H_5)_2Yb.$$
⁽¹³⁾

 $YbI_2(thf)_x$ prepared from Yb metal and ICH_2CH_2I in thf also can be used as a precursor to $(C_5H_5)_2Yb$ [reaction (14)]:⁵⁶

$$YbI_2 + 2C_5H_5Na \rightarrow (C_5H_5)_2Yb + 2NaI.$$
(14)

The acid-base reaction of cyclopentadiene with $(C_6F_5)_2$ Yb and $(C_6F_5)_2$ Eu, both obtainable from the elemental metal [see Section III.2(g.)], have also been used to form $(C_5H_5)_2$ Yb (MeOCH₂CH₂OMe) and $(C_5H_5)_2$ Eu(thf).⁵⁷

 $(C_5H_5)_2$ Sm(thf) was first prepared from $(C_5H_5)_3$ Sm by reduction with KC₁₀H₈ [cf. reaction (10)].⁵⁸ A more recent synthesis employs the divalent precursor SmI₂(thf)_x, in a reaction analogous to reaction (14).⁵⁶ A reported synthesis⁵⁹ of $(C_5H_5)_2$ Sm(thf)₂ from Hg(C₅H₅)₂ and Sm according to reaction (13) has been subsequently shown to give only $(C_5H_5)_3$ Sm(thf).⁶⁰ Unfortunately, since $(C_5H_5)_2$ Sm(thf) is insoluble in common solvents, the chemistry of this organometallic complex of the most reactive divalent lanthanide metal was not explored. A subsequent study of the $(C_5H_5)_3$ Sm-K system in the presence of benzophenone indicates that extraction of the insoluble product with dimethoxyethane (dme) gives a soluble material characterized by elemental analysis as divalent KSm(C₅H₅)₃.⁶⁰

Recently, a bis(cyclopentadienyl) Yb complex was characterized by X-ray diffraction as a dme adduct, $(C_5H_5)_2$ Yb(MeOCH₂CH₂OMe).⁶¹ The structure (Fig. 1) is typical of a bent metallocene with two additional ligands. A summary of structural data on all of the crystallographically characterized divalent organolanthanide complexes discussed in this review is presented in Table 1.

III.2(c) Complexes containing monosubstituted cyclopentadienyl ligands. Although the first divalent organolanthanide complexes were prepared in 1965,¹⁵ no structural data on any low-valent organolanthanides were reported until 1980. The first X-ray structure determination of a divalent organolanthanide complex involved the methyl-substituted derivative $(CH_3C_5H_4)_2Yb(thf)$.²⁵ This complex can be synthesized by alkali metal reduction of $[(CH_3C_5H_4)_2YbCl]_2$ [cf. reaction (7)], by transmetalation with $TlC_5H_4CH_3^{54}$ [cf. reaction (12)], by reaction of $CH_3C_5H_5$ with $Yb(C \equiv CC_6H_5)_2^{57}$ and by thermolysis, photolysis or hydrogenolysis of $[(CH_3C_5H_4)_2YbCH_3]_2$ [(15)–(17)]:²⁵

	Table 1. Sti	uctural data on di	valent organolanthanid	le complexes, (C ₅ R ₅),	LnL [,] "		
		Average	Range of		Ring centroid-Ln-		
	Formal	$Ln-C(C_sR_s)$	$Ln-C(C_{s}R_{s})$	Ln-L	ring centroid	L-Ln-L	
	coordination	distance	distances	distance (Å)	angle ^b	angle ^b	
Complex	number	(¥)	(y)	donor atom of L	(_)	٥)	References
(C ₅ H ₅) ₂ Yb(dme)	×	2.72	2.60(3)-2.91(5)	2.45(3), O 2.50(3), O	129	67.2(9)	61
[(MeC ₅ H ₄)(thf)Yb(µ-MeC ₅ H ₄)],	10	2.76 2.87 2.91	2.75(3)-2.77(3) 2.79(3)-2.94(3) 2.88(3)-2.94(3)	2.53(2), O	1	ŀ	25
[(Me ₃ Si)C ₅ H ₄] ₂ Yb(thf) ₂	œ	2.75	2.64(4)-2.84(4)	2.42(2), O 2.39(3), O	133	85	63
(C ₅ Me ₅) ₂ Yb(thf) · 0.5CH ₃ C ₆ H ₅ ⁴	7	2.66(2)	2.643(7)-2.694(8)	2.412(5), O	143.5(3)		69
(C,Me,)2Yb(NC,H,)2	œ	2.74(4)	2.692(7)-2.770(8)	2.586(7), N 2.544(6), N	136.3(3)	82.5(2)	72
(C ₅ Me ₅) ₂ Yb(thf)(NH ₃)	œ	2.77(4)	2.70(4)-2.83(4)	2.46(3), O 2.55(3), N	139.31	87.5(9)	73
(C ₅ Me ₅) ₂ Sm(thf) ₂	œ	2.86(3)	2.81(1)-2.91(1)	2.61(2), O 2.65(2), O	136.7	82.6(4)	47, 75, 79
(C ₅ Me ₅) ₂ Sm	6	2.79(1)	2.775(6)-2.815(6)	I	140.1	I	78, 79
(C ₅ Me ₅) ₂ Eu(OEt ₂)	7	2.795(7)	5	2.594(4), O	٩	e,	ſ
(C _s Me _s) ₂ Eu	6	2.79(1)	2.765(10)-2.822(9)	I	140.3	ł	79
[(C,Me,)(thf)2Eu(µ-C≡CPh)]2	7	2.82(2)	9	2.62(1), O	ļ	I	92
[(C ₅ Me ₅)(thf) ₂ Sm(µ-1)] ₂	7	2.81(2)	2.77(2)-2.84(3)	2.62(2), O 2.66(2), O			75
"[(C ₅ Me ₅) ₂ Yb(μ-C≡CPh) ₂] ₂ Yb ^b For (C ₅ R ₅) ₂ LnL ₂ complexes. These distances are for the brid	, in which the u	nique ytterbium is irands which are o	divalent [coordination	number 4, Yb—C =	2.52(1)Å] ⁹² is not	included in th	iis table.
The toluene is not coordinated	to the metal.						
^f Unpublished results cited in R	ef. 92.						

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Fig. 1. Structure of (C₅H₅)₂Yb(CH₃OCH₂CH₂OCH₃). White circles are carbon atoms.

$$[(CH_3C_5H_4)_2YbCH_3]_2 \xrightarrow[80^{\circ}C]{\text{pentane}-Et_2^O} 2(CH_3C_5H_4)_2Yb, \qquad (15)$$

$$[(CH_3C_5H_4)_2YbCH_3]_2 \xrightarrow{h\nu}_{\text{toluene, 5}^{\circ}C} 2(CH_3C_5H_4)_2Yb, \qquad (16)$$

$$[(CH_{3}C_{5}H_{4})_{2}YbCH_{3}]_{2} + 2H_{2} \xrightarrow{\text{toluene}}{30^{\circ}C} 2[(CH_{3}C_{5}H_{4})_{2}YbH] \rightarrow 2(CH_{3}C_{5}H_{4})_{2}Yb.$$
(17)

These latter three reactions are significant in divalent organolanthanide chemistry in that they demonstrate that access to the reactive Yb(II) oxidation state is possible without using strongly reducing conditions (e.g. alkali metal present). These reactions may provide the basis for interesting catalytic cycles involving the Yb(III)-Yb(II) couple.

The actual crystals used in the X-ray study of $(CH_3C_5H_4)_2$ Yb(thf)²⁵ were prepared in an attempt to derivatize an Yb-3-hexyne cocondensation product⁶² [reaction (18) (see Section IV)]:

$$YbC_6H_{10} + 2CH_3C_5H_5 \xrightarrow{thr} (CH_3C_5H_4)_2Yb(thf).$$
 (18)

As shown in Fig. 2, $(CH_3C_5H_4)_2Yb(thf)$ is polymeric in the solid state forming a chain structure in which the monomeric (μ -CH₃C₅H₄) (CH₃C₅H₄)Yb(thf) units are linked by bridging methylcyclopentadienyl groups.²⁵ Apparently, a monomeric (CH₃C₅H₄)₂Yb(thf) unit is sterically unsaturated and polymerizes to increase steric saturation in the solid state. Isopiestic molecular-weight studies indicate that in thf, (CH₃C₅H₄)₂Yb(thf) also increases its coordination number and exists as a disolvate in solution.

The trimethylsilyl-substituted cyclopentadienyl complex $(Me_3SiC_5H_4)_2Yb(thf)_2$ was prepared from $[(Me_3SiC_5H_4)_2YbCl]_2$ according to reaction (7) using Na(Hg) as the reductant in thf.⁶³ The thf of solvation can be displaced by $Me_2NCH_2CH_2NMe_2$ (tmeda) to form $(Me_3SiC_5H_4)_2Yb$ (tmeda) and the solvent-free $(Me_3SiC_5H_4)_2Yb$ can be obtained by sublimation at 308°C. In contrast to the polymeric nature of $(CH_3C_5H_4)_2Yb(thf)$, $(Me_3SiC_5H_4)_2Yb(thf)_2$ crystallizes as a monomer with a bent metallocene structure analogous to that of $(C_5H_5)_2Yb(dme)$ in Fig. 1.

The divalent methylcyclopentadienyl Sm complex $(CH_3C_5H_4)_2$ Sm can be made from $[(CH_3C_5H_4)_2$ SmCl]₂ by reduction, but, like the unsubstituted analog, it is insoluble in common solvents.⁶⁴

The indenyl complexes $(C_9H_7)_2$ Yb(thf)₂ and $(C_9H_7)_2$ Eu(thf) have been prepared from indene and Yb(C₆F₅)₂ and Eu(C₆F₅)₂ [Section III.2(g.)], respectively.⁵⁷

III.2(d) Solvated pentamethylcyclopentadienyl complexes. The pentamethylcyclopentadienyl ligand, C_5Me_5 , has proven to be of great importance in organometallic chemistry. As demonstrated by Bercaw and co-workers with Ti and Zr complexes^{65,66} and as subsequently shown by Marks *et al.* for actinide complexes,^{67,68} the C_5Me_5 ligand provides solubility and crystallinity to systems difficult to fully characterize using simple unsubstituted C_5H_5 ligands. Utilization of this ligand in divalent organolanthanide chemistry has had similarly spectacular results.

Bis(pentamethylcyclopentadienyl) complexes of all three readily accessible divalent lanthanides are known. $(C_5Me_5)_2Eu(thf)$ was prepared from trivalent EuCl₃ and three equivalents of NaC₅Me₅



Fig. 2. Structure of $[(CH_3C_5H_4)(thf)Yb(\mu-CH_3C_5H_4)]_n$. Three units of the continuous chain are shown. White circles are carbon atoms.

in a reaction in which NaC₅Me₅ functions as a reducing agent [reaction (19)]:⁶⁹

$$EuCl_3 + 3NaC_5Me \xrightarrow[reflux]{thf} (C_5Me_5)_2Eu(thf).$$
(19)

This is not an efficient use of the NaC₅Me₅ reagent, but the simple reaction of two equivalents of NaC₅Me₅ with EuCl₂ fails to generate the desired product. Reaction (19) is quite sensitive to specific conditions: using LiC₅Me₅ instead of NaC₅Me₅ or toluene instead of thf fails to give $(C_5Me_5)_2Eu(thf)$. Depending on crystallization conditions, the europium complex can be isolated as the mono-thf solvate or as $(C_5Me_5)_2Eu(thf)(OEt_2)$.

 $(C_5Me_5)_2Yb(thf)$ can be prepared from YbI₂ by the route of reaction (14), but the success of the reaction depends on the specific reagents used. YbBr₂(thf)₂-KC₅Me₅-ethers⁷⁰ and YbCl₂(thf)_x-NaC₅Me₅-thf⁶⁹ are productive combinations whereas YbCl₂-NaC₅Me₅-Et₂O and YbCl₂-LiC₅Me₅-thf are not.⁶⁹ In addition to the mono-thf solvate, $(C_5Me_5)_2Yb(OEt_2)$,⁶⁹ $(C_5Me_5)_2Yb(thf) \cdot \frac{1}{2}CH_3C_6H_5$,⁶⁹ $(C_5Me_5)_2Yb(thf)_2$,⁷⁰ and $(C_5Me_5)_2Yb(CH_3OCH_2CH_2OCH_3)$ ⁷⁰ have been isolated by varying the conditions of crystallization. In a variation of reaction (7), bis(pentamethylcyclopentadienyl) complexes of Yb can also be prepared by reduction of the trivalent KCl adducts $(C_5Me_5)_2YbCl_2K(solvent)_x$ in CH₃CN or CH₃OCH₂CH₂OCH₃ [reaction (20)]:⁷¹

$$(C_5Me_5)_2YbCl_2K(solvent)_x + Na(Hg) \rightarrow (C_5Me_5)_2Yb(solvent)_y.$$
(20)

This reaction was found to be solvent-dependent with thf being a less desirable solvent than dme. Reaction (20) is an inferior synthesis in general for $(C_5Me_5)_2$ Yb(solvent) complexes when compared to reaction (14). $(C_5Me_5)_2$ Yb(dme) can also be prepared by reduction of trivalent $(C_5Me_5)_2$ Yb(dme) (PF₆) with KH or LiCH₂CMe₃ [cf. reactions (17) and (9), respectively].⁷⁰ $(C_5Me_5)_2$ Yb(NC₅H₅)₂ has been obtained by displacing Et₂O from $(C_5Me_5)_2$ Yb(OEt₂) with pyridine.⁷² The mono-thf and bis-pyridine adducts have both been structurally characterized as typical bent metallocene structures (cf. Fig. 1).



Fig. 3. Side view of the structure of $(C_5Me_5)_2Sm(thf)_2$. The two thf molecules overlap such that only one oxygen atom can be seen from this perspective.

 C_5Me_5H reacts with liquid-ammonia solutions of Eu and Yb at low temperature over a 24–36-h period to form bis(pentamethylcyclopentadienyl) products.⁷³ Crystallization of these products from thf gives $(C_5Me_5)_2Eu(thf)$ and $(C_5Me_5)_2Yb(thf)(NH_3)$. The latter complex has been characterized by X-ray crystallography.⁷³

Mono (pentamethylcyclopentadienyl) Yb complexes such as $(C_5Me_5)YbI$ and $[(C_5Me_5)YbI_2]^-$ are thought to be intermediates in the $YbI_2-C_5Me_5^-$ and $YbI_2-(C_5Me_5)_2Yb$ reaction mixtures, but no details on these species were reported.^{70,71} Interestingly, YbI_2 has not been mentioned in the literature as a precursor to $(C_5Me_5)_2Yb(solvent)_x$.

The greatest impact of the C_5Me_5 ligand on divalent organolanthanide chemistry has been with Sm. The initially synthesized Sm(II) organometallics, $[(C_5H_5)_2Sm(thf)]_n$ and $[(CH_3C_5H_4)_2Sm(thf)]_n$, are insoluble in common solvents, possibly because with the larger radial size of the metal, more extensive oligomerization/polymerization occurs in the solid state than in the analogous Yb case (cf. Fig. 2). A consequence of this insolubility was that the organometallic chemistry of Sm(II), the most reactive of the divalent lanthanides, could not be investigated with the $(C_5H_4R)_2Sm(thf)$ systems. With the C_5Me_5 ligand, Sm(II) complexes are soluble and a rich and varied chemistry has developed as a consequence.

The initial synthesis of $(C_5Me_5)_2Sm(thf)_2$ was achieved via metal vapor methods [reaction (21) (cf. Section IV)]:^{47,74}

$$2Sm + 2C_5Me_5H \rightarrow \stackrel{\text{thf}}{\rightarrow} 2[(C_5Me_5)SmH(thf)_2] \rightarrow (C_5Me_5)_2Sm(thf)_2.$$
(21)

The bracketed intermediate Sm(II) hydride was not isolated in a pure form. The metal vapor method was also used to synthesize $(C_5Me_4Et)_2Sm(thf)_2$.⁷⁴ This species is similar to $(C_5Me_5)_2Sm(thf)_2$ in most respects except that $(C_5Me_4Et)_2Sm(thf)_2$ is more soluble. Like other bis(cyclopentadienyl) bis(ligand) divalent lanthanide complexes (e.g. Fig. 1), the structure of $(C_5Me_5)_2Sm(thf)_2$ has canted cyclopentadienyl rings and the oxygen atoms of the solvating thf molecules lie in a plane which bisects the (ring centroid)-metal-(ring centroid) angle (Fig. 3).

 $(C_5Me_5)_2Sm(THF)_2$ subsequently was prepared by solution methods according to reaction (14) using SmI₂(thf)_x and two equivalents of KC₅Me₅.⁷⁵ This is a much more convenient synthesis and readily allows the preparation of multigram quantities of this interesting complex. The SmI₂-KC₅Me₅ system contains several species including a mono(pentamethylcyclopentadienyl) complex, [(C₅Me₅) (thf)₂Sm(μ -I)]₂, which can be best isolated by reacting SmI₂(thf)_x with one equivalent of KC₅Me₅ [reaction 2)]:⁷⁵

$$2\mathrm{SmI}_{2}(\mathrm{thf})_{x} + 2\mathrm{KC}_{5}\mathrm{Me}_{5} \rightarrow [(\mathrm{C}_{5}\mathrm{Me}_{5})(\mathrm{thf})_{2}\mathrm{Sm}(\mu-\mathrm{I})]_{2}.$$
(22)



Fig. 4. Structure of $[(C_5Me_5)(thf)_2Sm(\mu-I)]_2$.

Crystallographic characterization of this complex reveals an iodide-bridged structure as shown in Fig. 4.

III.3(e) Unsolvated pentamethylcyclopentadienyl complexes. Almost all lanthanide complexes containing two cyclopentadienyl rings have one to three additional ligands in the coordination sphere of the metal. This is consistent with the large size of these metals and their tendency toward steric saturation in stable complexes. For many years, no structurally characterized simple bis(cyclopentadienyl) system analogous to ferrocene was known. Instead, stable bis(ring) *f*-element sandwich complexes were known only when the larger cyclooctatetraenyl rings were present as in $U(C_8H_8)_2^{76}$ and $[Ln(C_8H_8)_2]^{-.77}$ Although compounds of formula $(C_5H_5)_2Eu^{15}$ $(C_5H_5)_2Yb^{15,52,53}$ and $(Me_3SiC_5H_4)_2Yb^{63}$ could be obtained by high-temperature sublimation, no structural data were available on these systems. Based on the low ether solubility of $(C_5H_5)_2Eu^{15}$ and the polymeric 10-coordinate structure found for $[(CH_3C_5H_4)_2Yb(thf)]_n$ (Fig. 2),²⁵ it seemed likely that these unsolvated complexes might be oligomeric in the solid state.

The potential for isolating a monomeric unsolvated divalent bis(cyclopentadienyl) lanthanide complex seemed greater with C_5Me_5 ligands. The first such complex was made by metal vapor methods as a byproduct in the synthesis of $(C_5Me_5)_2Sm(thf)_2$ [reaction (23)]:^{47,74}

$$Sm + excess C_5 Me_5 H \rightarrow (C_5 Me_5)_2 Sm.$$
 (23)

This product was recovered in low yield from the alkane soluble fraction of the metal vapor reaction mixture. Unsolvated $(C_5Me_4Et)_2Sm$ was obtained in a similar manner.⁷⁴

Following the development of a high-yield solution synthesis of $(C_5Me_5)_2Sm(thf)_2$,⁷⁵ this species was examined as a precursor to $(C_5Me_5)_2Sm$. Direct desolvation was the obvious synthetic route, but data in the literature did not suggest this would be successful. For example, $[(C_5H_5)_2Sm(thf)]_n$ was reported to decompose on heating⁵⁸ and attempts to desolvate $(C_5Me_5)_2Yb(thf)_2$ at 90°C gave only $(C_5Me_5)_2Yb(thf)$.⁷⁰ Surprisingly, desolvation of $(C_5Me_5)_2Sm(thf)_2$ is rather facile and occurs at 75°C [reaction (24)]:⁷⁸

$$(C_5Me_5)_2Sm(thf)_2 \xrightarrow[vacuum]{75^{\circ}C}_{vacuum} (C_5Me_5)_2Sm + 2thf.$$
(24)

The desolvated product is soluble in arenes and can be sublimed to give X-ray quality crystals.

The surprising structure of $(C_5Me_5)_2Sm$ is shown in Fig. 5.^{78,79} The molecule crystallizes as a monomer with a (ring centroid)-metal-(ring centroid) angle of 140.1°, rather than the 180° angle anticipated for a parallel-ring structure analogous to that found for ferrocene⁸⁰ and decamethylferrocene, $(C_5Me_5)_2Fe.^{81}$ The (ring centroid)-metal-(ring centroid) angle in $(C_5Me_5)_2Sm$ is only slightly larger than the 136.7° angle found in $(C_5Me_5)_2Sm(thf)_2$ (Fig. 3). It is as though



Fig. 5. Structure of $(C_5Me_5)_2Sm$.

removal of the two thf ligands had no effect on this structural feature.

For a predominantly ionic complex governed by electrostatic factors, a parallel-ring structure would be optimal for $(C_5Me_5)_2Sm$ since the anionic ligands would be as far apart as possible. Based on steric considerations a parallel-ring ferrocene-like structure would also be favored over the bent metallocene arrangement. A molecular orbital analysis also suggests that the parallel-ring structure is most stable, although it predicted that distortions would not be energetically costly.⁸²

The possibility that the bent structure was due to intermolecular interaction was carefully examined.⁷⁸ One methyl group of each $(C_5Me_5)_2Sm$ unit points toward a Sm atom of another unit, but the distances are too long for a substantial interaction (Sm—C, 3.22 Å; Sm—H, 2.75 Å). Moreover, this interaction comes from the side of the bent metallocene unit, not through the sterically most accessible, open, "front" part of the $(C_5Me_5)_2Sm$ unit. Attempts to obtain the gas-phase electron diffraction structure of $(C_5Me_5)_2Sm$ were unsuccessful due to the limited thermal stability of this complex.⁸³

To determine if the $4f^6$ -electron configuration of Sm²⁺ affected the structure, the structure of the $4f^7$ -system (C₅Me₅)₂Eu was also determined.⁷⁹ (C₅Me₅)₂Eu is isostructural with (C₅Me₅)₂Sm although the desolvation of (C₅Me₅)₂Eu(thf) was found to be significantly more difficult (multiple desolvation/sublimation reactions were necessary to get the solvate-free species).

The facile synthesis and unusual structure of $(C_5Me_5)_2Sm$ suggest that the principles of divalent organolanthanide chemistry may differ substantially from those of the trivalent species discussed in Section II. A reaction such as reaction (24), in which an oxygen donor adduct is removed to form an isolable sterically much less saturated species (eight-coordinate \rightarrow six-coordinate), does not follow the expected reactivity patterns for ionic, electropositive oxophilic trivalent lanthanides. The observed structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ follow neither the traditional electrostatic nor steric principles.

The best current explanation for the bent structures is the polarization argument used to explain why some heavy alkaline earth metal dihalides, MX_2 , are bent rather than linear in the gas phase.^{18,84,85} In a parallel-ring $(C_5Me_5)_2Ln$ structure analogous to a linear MX_2 structure, polarization of the cation by one C_5Me_5 anion could diminish the electrostatic interaction between the cation and the second C_5Me_5 anion directly opposite. A bent structure may optimize the polarization of a large cation by two anions and may give better total electrostatic bonding for the two rings. This argument provides an electrostatic rationale for the bent structures of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Eu$ without involving 4f-orbital participation and without invoking high-energy 5d and 6s orbitals (via a stereochemically active lone pair argument).⁸⁶ If these polarization effects are generally valid for divalent organolanthanides, this may be an important differentiating factor between divalent and trivalent lanthanide chemistry.

III.2(f) Alkynide complexes. Several divalent organolanthanide complexes involving alkynyl ligands, $-C \equiv CR$, have been reported in the literature. Transmetalation with Hg reagents has been

used to obtain $Yb(C \equiv CC_6H_5)_2$ and $Eu(C \equiv CC_6H_5)_2(thf)_{0.25}$ [reaction (25)]:⁸⁷

$$Yb + Hg(C \equiv CC_6H_5)_2 \rightarrow Yb(C \equiv CC_6H_5)_2 + Hg.$$
⁽²⁵⁾

 $Yb(C \equiv CCMe_3)_2$ has been prepared in solution by the same method but was not isolated. Divalent Yb alkynides can also be obtained from $Yb(C_6F_5)_2(thf)_4$ (see next section) by an acid-base reaction.⁸⁷

$$Yb(C_6F_5)_2(thf)_4 + 2HC \equiv CC_6H_5 \rightarrow Yb(C \equiv CC_6H_5)_2 + 2C_6F_5H.$$
(26)

Attempts to repeat reaction (26) with HC \equiv CCMe₃ gave an explosive product.⁸⁷ The reaction of methylcyclopentadiene with Yb(C₆F₅)₂(thf)₄ similarly gives an explosive material.⁵⁷ On the basis of ebulliometric measurements, Yb(C \equiv CC₆H₅)₂ is associated into a trimer or tetramer in boiling thf.⁸⁷

Eu in liquid ammonia is reported to react with propyne to form a divalent complex [reaction (27)]:

$$Eu + excess HC \equiv CCH_3 \xrightarrow{NH_3^{(1)}} Eu(C \equiv CCH_3)_2, \qquad (27)$$

but the analogous Yb reaction does not give a pure product presumably due to contamination by $Yb(NH_2)_2$.⁸⁸ Structural information has not yet been obtainable on these alkynide products.

Divalent alkynides can also be made from terminal alkynes by metal vapor methods. Hence, reaction of Yb metal with 1-hexyne forms complexes of general formula $[HYb_2(C \equiv CC_4H_9)_3]_n$.⁸⁹ Isopiestic molecular-weight studies indicated that this species is highly associated in solution and no X-ray quality single crystals of this oligomer were obtainable. Based on the structures of $[(C_5H_5)_2Er(\mu-C \equiv CCMe_3)]_2^{90}$ and $[(CH_3C_5H_4)_2Sm(\mu-C \equiv CCMe_3)]_2^{91}$ oligomerization via alkynide bridges is quite possible. A possible route to the observed product is given in reactions (28)–(30) (R = C_4H_9):

$$Yb + HC \equiv CR \rightarrow HYbC \equiv CR, \tag{28}$$

$$HYbC \equiv CR + HC \equiv CR \rightarrow Yb(C \equiv CR)_2 + H_2, \tag{29}$$



Reaction (28) is a basic oxidative addition of a C-H bond. Reaction (29), a hydride-based

metalation, is well precedented in organolanthanide and organoyttrium hydride chemistry.^{23,87} The oligomerization shown in reaction (30) is expected based on the steric unsaturation of the mono- and bimetallic precursors (cf. Fig. 2).

Using the C₅Me₅ ligand, structures of the type shown above have been confirmed crystallographically. The complexes (C₅Me₅)₂Ln(OEt₂) (Ln = Yb or Eu) react with HC=CC₆H₅ to give mixed-valent and divalent alkynide-bridged species [reactions (31) and (32), $R = C_6H_5$]:⁹²

+
$$(C_5Me_5)_2Yb(OEt_2)$$
 + $4HC \equiv CR \rightarrow 2C_5Me_5H + H_2$

$$+ (C_{5}Me_{5})2Yb Yb Yb (C_{5}Me_{5})_{2}$$

$$+ (C_{5}Me_{5})2Yb Yb (C_{5}Me_{5})_{2}$$

$$(31)$$

$$(31)$$

$$C C$$

$$R R$$

$$2(C_5Me_5)_2Eu(OEt_2) + 2HC \equiv CR \xrightarrow{\text{thf}} 2C_5Me_5H + [(C_5Me_5)(\text{thf})_2Eu(\mu-C \equiv CR)]_2.$$
(32)

In both reactions the terminal alkyne gives up a proton to C_5Me_5 , ⁹³ but with the more strongly reducing Yb system some oxidation of the metal occurs. Magnetic studies show no exchange in the mixed-valent trimetallic Yb system. The Eu dimer has a structure analogous to that of $[(C_5Me_5)$ (thf)₂Sm(μ -I)]₂⁷⁵ shown in Fig. 4.

III.2(g) Alkyl and aryl complexes. Reactions of alkyl and aryl iodides with Eu, Yb and Sm metal have been reported to form divalent alkyl and aryl lanthanide halide complexes.⁹⁴ These are complex systems, however, and a variety of both trivalent and divalent products may be present including RLnI, LnI_2 ,⁷¹ RLnI₂ etc. The reaction mixtures behave like Grignard reagents. No structural data has been obtainable on these systems.

Subsequent studies of the RX-Ln system using Yb and C_5Me_5I in the presence of LiI led to the identification of the trivalent complexes $(C_5Me_5)YbI_3Li(Et_2O)_2$ and $(C_5Me_5)_2YbI_2Li(Et_2O)_2$ as well as YbI₂.^{70,71} The complexity of RX-Ln systems in general is demonstrated well by this case. For example, $(C_5Me_5)YbI_3Li(Et_2O)_2$ is obtained in 30% yield in 15 h but subsequently is converted to $(C_5Me_5)_2YbI_2Li(Et_2O)_2$, which is obtained in 30% yield in 24-48 h. In addition, no organometallic products are isolated in the absence of LiI. The LiI-free reaction of ytterbium metal and C_5Me_5I gives only $C_{10}Me_{10}$, YbI₃ and YbI₂.⁷¹

Divalent lanthanide aryl complexes can be obtained using fluorinated aryl mercury reagents [reaction (33)]:^{95,96}

$$(C_6F_5)_2Hg + Yb \xrightarrow{\text{thf}} (C_6F_5)_2Yb(\text{thf})_4 + Hg.$$
(33)

 $(C_6F_5)_2$ Yb(thf)₄ is not very stable thermally and $(2,3,5,6-F_4C_6H)_2$ Yb, prepared in the same way, is less stable. $(2,3,4,5-C_6F_4H)_2$ Hg reacts with Yb but gives a product too unstable to isolate. Neither $(C_6H_5)_2$ Hg nor $(C_6Cl_5)_2$ Hg are reported to react with Yb. Recently, however, NMR and hydrolytic data have been cited to suggest that $(C_6H_5)_2$ Hg–Yb does form Yb $(C_6H_5)_2$ (thf)_n.⁹⁷ Sm reactions with $(C_6F_5)_2$ Hg and $(C_6F_4H)_2$ Hg are more complex and a mixture of products is formed. The course of reactions such as reaction (33) have been followed by quenching with acid and identifying the products.⁹⁸

Transmetalation as shown in reaction (33) also reportedly can be used to make divalent derivatives of ferrocene,⁹⁹ $C_5H_5Mn(CO)_3$,⁹⁹ and carboranes.¹⁰⁰ Hence, $(C_5H_5FeC_5H_4)_2Yb$, $[(CO)_3MnC_5H_4]_2Yb$ and $(\eta^1-C_2B_{10}R)_2Yb$ (R = CH₃ or C₆H₅) are obtained from the reaction of Yb with Hg(C₅H₄FeC₅H₅)₂, Hg[C₅H₄Mn(CO)₃]₂ and Hg(C₂B₁₀R)₂, respectively. $(C_5H_4I)Fe(C_5H_5)$ and $(C_5H_4I)Mn(CO)_3$ are reported to react with Yb metal to form $C_5H_5FeC_5H_4YbI$ and $(CO)_3MnC_5H_4YbI$, respectively.⁹⁹ Reaction of LiC₂B₁₀C₆H₅ with LnI₂ (Ln = Eu, Yb or Sm) is said to form $[\eta^1-C_2B_{10}(C_6H_5)]LnI$. Metalation of $C_2B_{10}C_6H_5$ with

"CH₃YbI" forms similar products.¹⁰¹ Transmetalation of Eu, Sm and Yb with Hg[C₆H₅Cr(CO)₃]₂ is reported to form divalent complexes, [(CO)₃CrC₆H₅]₂Ln(thf)_n.⁹⁷ Lowered v_{CO} absorptions in the IR spectra suggest Ln—O—C coordination. The only ¹H NMR resonance cited for the phenyl protons was δ 5.645, $J(^{171}Yb-^{1}H) = 80$ Hz. This is unusual since coupling to ^{171}Yb , which has a natural abundance of only 14.3%, has not been observed previously for divalent Yb organometallic species.

The formation of a divalent methyl complex $(C_5Me_5)Yb(CH_3)_2Li$ by displacement of $C_5Me_5^-$ in $(C_5Me_5)_2Yb$ by CH_3^- has been mentioned in the literature but no details of this reaction were revealed [reaction (34)]:⁷⁰

$$(C_5Me_5)_2Yb + 2CH_3Li \rightarrow (C_5Me_5)Yb(CH_3)_2Li + LiC_5Me_5.$$
(34)

An additional class of divalent lanthanide complexes which have some metal hydrocarbon interactions involves the bis(trimethylsilyl) amido ligand, $-N[Si(CH_3)_3]_2$. Although these complexes do not possess formal metal carbon σ -bonds, the conformations of the $(Me_3Si)_2N$ groups are such that long-distance metal-CH interactions are observed. Reaction of EuI₂ or YbI₂ with NaN(SiMe₃)₂ gives either Ln[N(SiMe₃)₂]₂(R₂O)_x or NaLn[N(SiMe₃)₂]₃, depending on the ether solvent used and the manner of recrystallization.¹⁰² Crystal structures of NaLn[N(SiMe₃)₂]₃ (Ln = Eu or Yb) and Yb[N(SiMe₃)₂]₂(Me₂PCH₂CH₂PMe₂) (obtained by displacing the R₂O of solvation with the diphosphine) show that some of the methyl groups are oriented to bring the carbon atoms within 2.86-3.04 Å of Yb and 2.97-3.14 Å of Eu. Similarly, Yb[N(SiMe₃)₂(AlMe₃)]₂ has six methyl groups within 2.756(2)-3.202(3) Å of Yb(II).¹⁰³

III.3 Reactivity

Although the reactivity of divalent organolanthanide complexes is only beginning to be explored, some general types of reactivity are discernible. An attempt to organize these reactions into general classes is made in the following subsections. The first three subsections deal with reactions which might be expected for complexes which are one-electron reducing agents and which contain electropositive lanthanide metal centers. In each of these cases, the metal gets oxidized and forms a sterically saturated complex containing a new bond or bonds to the most electronegative ligands available in the system. Subsequent sections deal with less traditional lanthanide reactivity patterns and ultimately to unprecedented types of reactivity. Applications of divalent lanthanide chemistry to organic chemistry will not be discussed here since they recently have been comprehensively reviewed elsewhere.⁷

III.3(a) Oxidation reactions involving halide, pseudohalide and aryl ligands. Bis(cyclopentadienyl) Yb and Sm complexes react with a variety of alkyl halides to form dicyclopentadienyl halide complexes. Many systems have been observed to have this reactivity including: (a) $(CH_3C_5H_4)_2Yb(thf)$ and $(CH_3C_5H_4)_2Sm(thf)$ with CH_3I , Me_3CCl and $H_2C=CHCH_2Br$,¹⁰⁴ (b) $(C_5Me_5)_2Yb(dme)$ with CH_2Cl_2 ,^{70,105} (c) $(C_5Me_5)_2Sm(thf)_2$ with Me_3CCl and ICH_2CH_2I ,¹⁰⁶ and (d) $(C_5Me_5)_2Yb(OEt_2)$ with $n-C_4H_9Cl$ and $C_6H_5CH_2Cl$.¹⁰⁷ The trivalent halide complexes $(C_5R_5)_2LnX(solvent)$ are generally the main products of these reactions. $(C_5Me_5)_2SmCl(thf)$ and $(C_5Me_5)_2SmI(thf)$ have been made preparatively by route (c) above and have been crystallographically characterized.¹⁰⁶ The $(C_5Me_5)_2Yb(OEt_2)-C_6H_5CH_2Cl$ system has been studied in detail and found to give a variety of products in the presence of a slight excess of RX [reaction (35)]:¹⁰⁷

$$(C_{5}Me_{5})_{2}Yb(OEt_{2}) + 1.52C_{6}H_{5}CH_{2}Cl \rightarrow 0.48(C_{5}Me_{5})_{2}YCl + 0.52(C_{5}Me_{5})YbCl_{2} + Et_{2}O + 0.52C_{5}(CH_{3})_{5}(CH_{2}C_{6}H_{5}) + 0.5(C_{6}H_{5}CH_{2})_{2}, \quad (35)$$

The reactivity of $(C_5H_5)_2$ Yb in thf or dme with metal halides and pseudohalides has also been studied. Reactions of the divalent ytterbium species with HgX₂, TlX, AgX₂ and CuX salts where

 $X = O_2CMe, O_2CC_6F_5, O_2CC_5H_4N, Cl, Br, I, C_6F_5, C \equiv CPh, CH(OCMe)_2 \text{ or } CH(OCPh)_2 \text{ have been examined [reactions (36) and (37)]:}^{108}$

$$(C_{5}H_{5})_{2}Yb(solvent) + MX \rightarrow (C_{5}H_{5})_{2}YbX(solvent) + M(M = Tl or Cu),$$
(36)

$$2(C_5H_5)_2 Yb(solvent) + MX_2 \rightarrow 2(C_5H_5)_2 YbX(solvent) + M(M = Hg \text{ or } Ag).$$
(37)

The crystal structure of the $O_2CC_6F_5$ reaction product has been determined to be the dimer $(C_5H_5)_2Yb(O-C(C_6F_5)-O)_2Yb(C_5H_5)_2$. Similarly, $(CH_3C_5H_4)_2Sm(thf)$ can be oxidized with HgI₂ or I₂ to give $(CH_3C_5H_4)_2SmI(thf)$.¹⁰⁴ A toluene suspension of YbCl₃ can be used as an oxidant to transform $(C_5Me_5)_2Yb(thf)$ into $(C_5Me_5)_2YbCl(thf)$.¹⁰⁵ $(C_5Me_5)_2Yb(dme)$ can be oxidized by the ferricinium ion [reaction (38)]:⁷⁰

$$(C_5Me_5)_2Yb(dme) + [(C_5H_5)_2Fe] [PF_6] \rightarrow (C_5Me_5)_2Yb(dme)(PF_6) + (C_5H_5)_2Fe.$$
 (38)

 $(C_5Me_5)_2Sm(thf)_2$ reacts with $Hg(C_6H_5)_2$ to provide a halide-free synthesis of a trivalent phenyl complex [reaction(39)]:⁷⁴

$$2(C_5Me_5)_2Sm(thf)_2 + Hg(C_6H_5)_2 \rightarrow 2(C_5Me_5)_2Sm(C_6H_5)(thf) + Hg.$$
(39)

Oxidation of the mono(pentamethylcyclopentadienyl) anion $[C_5Me_5YbI_2]^-$ by C_5Me_5I is also reported to occur [reaction (40)]:⁷⁰

$$(C_5Me_5)YbI_2Li + C_5Me_5I \rightarrow (C_5Me_5)YbI_3Li + C_5Me_5.$$
(40)

The aryl complexes⁹⁵ (C₆F₅)₂Yb(thf)₄ and (p-HC₆F₄)Yb(thf)₄ generated *in situ* in thf, react with the transition-metal halides Rh(CO)Cl(PPh₃)₂, NiCl₂(bipy) (bipy = 2,2'-bipyridine), NiCl₂(PPh₃)₂ and PtCl₂(bipy) to form complexes in which the halide ligands have been replaced by fluorinated aryl groups, i.e. RRh(CO)(PPh₃)₂, R₂Ni(bipy) (R = C₆F₅ or p-HC₆F₄), (C₆F₅)₂Ni(PPh₃)₂ and (C₆F₅)₂Pt(bipy).⁹⁶ YbCl₂ is the presumed byproduct. The (C₆F₅)₂Yb(thf)₄ complex also transfers C₆F₅ to Ph₃SnCl to form Ph₃SnC₆F₅. At low temperature I₂ reacts with (C₆F₅)₂Yb(thf)₄ to form C₆F₅I. With HgCl₂, some oxidation of (C₆F₅)₂Yb(thf)₄ occurs giving Hg metal as well as (C₆F₅)₂Hg. (C₆F₅)₂YbCl or YbCl₃ were possible byproducts.⁹⁶ The decomposition of the divalent Yb fluoro-aryl complexes with CO₂⁹⁶ and the decomposition of the divalent Yb alkynides with H₂O have also been studied.⁸⁷

III.3(b) Oxygen abstraction reactions. $(C_5Me_5)_2Sm(thf)_2$ reacts with a variety of oxygen-containing substrates including CH₃CH₂CHCH₂O, NO, N₂O and C₅H₅NO to form the trivalent oxide complex [(C₅Me₅)₂Sm]₂(μ —O) (Fig. 6).¹⁰⁹ The epoxide system [reaction (41)]:

$$(C_{5}Me_{5})_{2}Sm(thf)_{2} + CH_{3}CH_{2}CHCH_{2} \rightarrow (C_{5}Me_{5})_{2}Sm - O - Sm(C_{5}Me_{5})_{2}$$
$$+ CH_{3}CH_{2}CH = CH_{2} \qquad (41)$$

and the pyridine N-oxide reaction give the oxide product in approximately 50% yield. The other reactions are much more complicated and give mixtures of many products of which the oxide is just one component. The oxide complex is structurally interesting in that the Sm-O-Sm unit is crystallographically linear.

III.3(c) Reduction of transition-metal carbonyl complexes. Divalent Yb and Sm organometallics are strong enough reducing agents to react with many transition-metal carbonyl complexes to form anions.¹¹⁰ Although the simple unsubstituted cyclopentadienyl complexes like $(C_5H_5)_2$ Yb will react with transition-metal carbonyls,¹¹¹ reactions with C_5Me_5 derivatives give products which are easier to characterize. The reactivity of $(C_5Me_5)_2$ Yb(OEt₂) has been extensively studied in this regard.¹¹²⁻¹¹⁵



Fig. 6. Structure of $[(C_5Me_5)_2Sm]_2(\mu-O)$.

Reaction (42):

$$2(C_5Me_5)_2Yb(OEt_2) + Co_2(CO)_8 \xrightarrow{\text{thf}} (C_5Me_5)_2(thf)Yb(\mu - OC)Co(CO)_3$$
(42)

shows a simple reduction sequence in which the metal-metal bond in $\text{Co}_2(\text{CO})_8$ is cleaved to generate the anion $[\text{Co}(\text{CO})_4]^{-.112}$ The product exists as a tight ion pair in which an isocarbonyl linkage, Yb-O-C-Co, is present. This reactivity is typical in that the divalent lanthanide gets oxidized and gets an additional electronegative ligand. The $\text{Mn}_2(\text{CO})_{10}$ system is similar in that trivalent Yb and $\text{Mn}(\text{CO})_5^-$ anions are formed. However, the structure of the product is complex and contains dimers, $[(C_5\text{Me}_5)_2\text{Yb}] [(\mu-\text{OC})\text{Mn}(\text{CO})_3(\mu-\text{CO})]_2 [\text{Yb}(\text{C}_5\text{Me}^5)_2]$, as well as a polymeric chain, $\{[(C_5\text{Me}_5)_2\text{Yb}] [(\mu-\text{OC})_3\text{Mn}(\text{CO})_2]\}_n^{.113}$

 $Fe(CO)_5$ reacts with $(C_5Me_5)_2Yb(OEt_2)$ to form an analog of $Na_2Fe(CO)_4$ [reaction (43)]:¹¹⁴

$$2(C_{5}Me_{5})_{2}Yb(OEt_{2}) + Fe(CO)_{5} \rightarrow (CO)_{3}Fe[(\mu-CO)Yb(C_{5}Me_{5})_{2}(thf)]_{2}.$$
 (43)

However, when the trinuclear transition-metal carbonyl $Fe_3(CO)_{12}$ was reacted with $(C_5Me_5)_2$ Yb(OEt₂), an iron-iron bond was broken, a carbonyl ligand was lost, and an $Fe_3(CO)_{11}^{2-}$ unit was formed which was attached to two $[(C_5Me_5)_2Yb]^+$ moieties via four isocarbonyl linkages [reaction (44)]:¹¹⁴

$$2(C_5Me_5)_2$$
Yb(OEt₂) + Fe₃(CO)₁₂ \rightarrow

 $(C_{5}Me_{5})_{2}Yb \qquad Fe-CO Yb(C_{5}Me_{5})_{2} + CO.$ $(C_{5}Me_{5})_{2}Yb \qquad Fe-CO Yb(C_{5}Me_{5})_{2} + CO.$ (44) $Fe(CO)_{3}$

Reductive formation of tight ion pairs containing isocarbonyl connections has also been reported for $(C_5Me_5)_2Yb(OEt_2)$ with $(C_5H_5)_2Fe_2(CO)_4$, $(C_5H_5)_2Mo_2(CO)_6$ and $(C_5H_5)Co(CO)_2$.¹¹⁵

 $(C_5Me_5)_2Sm(thf)_2$ reduces $Co_2(CO)_8$ to form a $(C_5Me_5)_2SmCo(CO)_4$ complex, but the structure of the compound is unknown because a refinable solution to the X-ray data was not readily obtainable. Interestingly, when $SmI_2(thf)_x$ reduces $Co_2(CO)_8$, a $Co(CO)_4^-$ product is obtained which *does not* have isocarbonyl connections. The product of this reaction, $[SmI_2(thf)_5] [Co(CO)_4]$, has discrete $[SmI_2(thf)_5]^+$ and $Co(CO)_4^-$ units.¹¹⁶

III.3(d) Substitution reactions. As described in Section III.2(d), the solvating ether ligands in $(C_5Me_5)_2YbL_x$ and $(C_5Me_5)_2EuL_x$ (x = 1 or 2) can be readily substituted with other ethers.⁶⁹

Hence, depending on crystallization conditions, complexes with $L_x = thf$, $(thf)_2$, Et_2O , (thf) (Et_2O) or dme can readily be obtained. These complexes have not been formed by deliberate substitution reactions, but rather by specific crystallization procedures.⁶⁹ Therefore, a definitive pattern of substitution reactivity has yet to be reported. The direct substitution of Et_2O from $(C_5Me_5)_2Yb(OEt_2)$ by pyridine in toluene has been studied however [reaction (45)]:⁷²

$$(C_5Me_5)_2Yb(OEt_2) + 4C_5H_5N \rightarrow (C_5Me_5)_2Yb(NC_5H_5)_2 + 2NC_5H_5 + Et_2O.$$
 (45)

Given the lability of the solvating ligands in solution, this type of substitution reactivity is expected.

Displacement of C_5Me_5 ligands from $(C_5Me_5)_2LnL_x$ complexes has also been reported. SmI₂ reacts with $(C_5Me_5)_2Sm(thf)_2$ in a ligand redistribution reaction to form a structurally characterized dimer [reaction (46) (Fig. 4)]:⁷⁵

$$(C_5Me_5)_2Sm(thf)_2 + SmI_2 \rightarrow [(C_5Me_5)(thf)_2Sm(\mu-I)]_2.$$
 (46)

Displacement of C_5Me_5 from an unspecified solvate of $(C_5Me_5)_2$ Yb by LiI [reaction (47)]:

$$(C_5Me_5)_2Yb + 2LiI \rightarrow (C_5Me_5)YbI_2Li + LiC_5Me_5$$
(47)

and MeLi [reaction (34)] has been reported to give $(C_5Me_5)YbI_2Li$ and $(C_5Me_5)YbMe_2Li$, respectively.⁷⁰ If the Yb in these products is not solvated and is therefore formally five-coordinate, this would be an unusual reaction. When Li and I are replaced by K and Br in reaction (47), the reverse reaction is preferred.⁷⁰

III.3(e) CO reduction. The reduction of CO by $(C_5Me_5)_2Sm(thf)_2^{47,117}$ provides an excellent example of the unique reactivity available through this divalent lanthanide oxidation state. $(C_5Me_5)_2Sm(thf)_2$ reacts under a variety of conditions with CO to give complex mixtures of products. Under 90 psi of CO in THF, a crystalline product separates which was crystallographically characterizable [reaction (48)]:

The remarkable dimeric product contains four Sm(III) centers and the equivalent of six CO molecules. Hence, in reaction (48) six CO units have been reduced by four electrons and the reductive homologation has formed two ketenecarboxylate units.

The most interesting feature in the formation of the ketenecarboxylate complex is that complete cleavage of one CO triple bond must have occurred to give the central, oxygen-free carbon of the C=C-C skeleton. Although CO cleavage is thought to occur in heterogeneous Fischer-Tropsch systems,¹¹⁸ this rarely occurs in homogeneous systems. Complete CO cleavage is not observed in the extensive studies of CO reduction by molecular early transition-metal,^{65,119} actinide¹²⁰ and lanthanide¹²¹ hydride systems.

Although metal hydride reduction of CO has been heavily investigated, hydrogen-free reduction of CO using one-electron reducing agents as in reaction (48) has received much less attention. The closest related system is the two-electron reduction of two CO molecules by alkali metals which is reported to form an insoluble alkyne diolate [reaction 49)]:¹²²

$$2K + 2CO \rightarrow 2[KOC \equiv COK]. \tag{49}$$

The relationship between reactions (48) and (49) can be seen by comparing KOCCOK with the

atom connectivity on the right hand (or left hand) side of the ketenecarboxylate dimer, O

SmOCCCOSm. Both the K and Sm systems contain MOCCOM units involving two-electron reduction of two CO molecules. The samarium system, a two-electron-three-CO system, has an extra CO formally "inserted" between a C and O bond. The insolubility of the KOC \equiv COK product may be responsible for the lack of further homologation in this system compared to the Sm system. Hence, $(C_5Me_5)_2Sm(thf)_2$, although strongly reducing like the alkali metals, is differentiated from those reducing agents by its solubility. The C_5Me_5 ligands provide solubility to the reducing agent as well as to intermediate reduction products and allow $(C_5Me_5)_2Sm(thf)_2$ to accomplish chemistry different from that of the alkali metal.

The reactivity of $(C_5Me_5)_2Sm(thf)_2$ with CO can also be compared with that of $(C_5Me_5)_2Ti$. Both organometallic reagents are soluble, strongly reducing complexes of oxophilic metals. As shown in reaction (50):

$$(C_5Me_5)_2Ti + 2CO \rightarrow (C_5Me_5)_2Ti(CO)_2, \tag{50}$$

decamethyltitanocene forms a carbonyl¹²³ complex rather than reducing the CO. Since the 4f valence orbitals of Sm(II) are not as suitable for carbonyl complex formation as those of Ti(II), this is less likely for Sm and reduction occurs.

Considering the comparisons above and the fact that neither $(C_5Me_5)_2Yb^{70,92}$ nor $(C_5Me_5)_2Eu(thf)$ react with CO, $(C_5Me_5)_2Sm(thf)_2$ appears to be a unique reducing agent in the periodic table. The combination of strong reducing power, oxophilicity, solubility and lack of *d* valence orbitals is not duplicated by any other reducing agent presently available.

 $(C_5Me_5)_2Sm(thf)_2$ is not the only Sm(II) reagent which reacts with CO, however. Both $(C_5Me_5)_2Sm$ and $[(C_5Me_5)(thf)_2Sm(\mu-I)]_2$ reduce CO.^{117,124} Again, mixtures of complex products are obtained. The reaction of $(C_5Me_5)_2Sm$ with CO provides X-ray quality crystals but the molecule is so complex that a solution to the X-ray data has not been found.

III.3(f) Reduction of internal alkynes and azobenzene. $(C_5Me_5)_2Sm(thf)_2$ reacts with $C_6H_5C\equiv CC_6H_5$ instantaneously to form a black product characterized by elemental analysis as $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$.³⁸ A possible formation pathway and structure are shown in reaction (51):

$$(C_{5}Me_{5})_{2}Sm(thf)_{2} + C_{6}H_{5}C \equiv CC_{6}H_{5} \rightarrow [(C_{5}Me_{5})_{2}Sm](C_{6}H_{5})C = \dot{C}(C_{6}H_{5}) + 2 thf$$

$$(C_{5}Me_{5})_{2}Sm(thf)_{2} \rightarrow (C_{5}Me_{5})_{2}Sm(C_{5}Me_{5})_{2} + 4thf.$$
(51)

This reaction has some precedent in reactions of alkali metals with arylalkynes, except that in the heterogeneous alkali metal systems, polymerization or dimerization of the radical generally occurs.¹²⁵ The more soluble $(C_5Me_5)_2Sm(thf)_2$ may more readily trap the radical to give the bimetallic product. Once again the solubility of $(C_5Me_5)_2Sm(thf)_2$ may be responsible for chemistry different from that of the alkali metals.

 $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ is unusual in several respects.³⁸ Room-temperature magnetic-susceptibility measurements indicate that it contains Sm(III) centers. Given this oxidation state, the black color of this complex is abnormal since virtually all Sm(III) complexes are pale orange, yellow or red. Also unexpected is the fact that the complex reacts with excess th to regenerate $(C_5Me_5)_2Sm(thf)_2$ and $C_6H_5C\equiv CC_6H_5$. Given the strongly reducing nature of Sm(II), this Sm(III) to Sm(II) conversion under mild conditions was unanticipated. The structure shown in reaction (51) is unproven but is consistent with spectroscopic data, hydrolysis to *trans*-stilbene, and the structure of the azobenzene complex described below. $(C_5Me_5)_2Sm(thf)_2$ reacts with $C_6H_5N=NC_6H_5$ to form an intensely colored product which also has unusual properties [reaction (52)]:¹²⁶

$$2(C_{5}Me_{5})_{2}Sm(thf)_{2} + C_{6}H_{5}N = NC_{6}H_{5} \rightarrow N = N - C_{6}H_{5} + 4thf.$$
(52)
$$C_{6}H_{5} = Sm(C_{5}Me_{5})_{2}Sm(C_{5}Me_{5})_{2}$$

The complex has an overall structure like that proposed for $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ and, given the N for C change, could be viewed as an azobenzene base adduct of $(C_5Me_5)_2Sm(II)$. However, room-temperature magnetic-susceptibility measurements indicate that the metal is in the trivalent oxidation state and the Sm—N distances, 2.40(1) and 2.41(1) Å, are consistent with single σ -bonds. This suggests the presence of a $[(C_6H_5)NN(C_6H_5)]^{2-}$ dianion. However, the 1.25(1) Å NN distance is the same as the N=N double-bond distances in a variety of azobenzene structures. As shown in Fig. 7, the molecule is distorted in that the N—C (phenyl) distances are stretched from a normal 1.42 Å to 1.56–1.61 Å. In addition, the Sm atoms are displaced asymmetrically such that both come within 2.29–2.34 Å of the *ortho* hydrogens of a single phenyl ring in a bonafide agostic¹²⁷ Sm–H interaction. The ability of Sm(II) to structurally distort azobenzene in this way is remarkable.

Attempts to get $(C_5Me_5)_2$ Yb(OEt₂) to react with $C_6H_5C\equiv CC_6H_5$ in analogy to reaction (51) were unsuccessful.⁹²

In the presence of hydrogen, $(C_5Me_5)_2Sm(thf)_2$ reacts with alkynes such as $C_6H_5C\equiv CC_6H_5$ and $CH_3CH_2C\equiv CCH_2CH_3$ to form systems which are active hydrogenation catalysts.³⁸ Formation of an enediyl-like structure [cf. reaction (51)] followed by hydrogenolysis of the Sm—C bond, a well-established reaction^{22,23} may give the SmH unit which could be the active catalyst [reactions (53)–(55), $(Cp^5=C_5Me_5)$]:

$$2Cp_{2}^{5}Sm(thf)_{2} + RC \equiv CR \rightarrow \begin{array}{c} Cp_{2}^{5}Sm \\ R \end{array} \xrightarrow{C=C} \begin{array}{c} R \\ SmCp_{2}^{5} \end{array} \xrightarrow{H_{2}} 2[Cp_{2}^{5}SmH], \end{array} (53)$$

$$[Cp_{2}^{5}SmH] + RC \equiv CR \rightarrow \begin{array}{c} Cp_{2}^{5}Sm \\ R \end{array} \xrightarrow{C} = C \xrightarrow{H_{2}} [Cp_{2}^{5}SmH] + H \xrightarrow{H} C = C \xrightarrow{R} (54)$$

$$[Cp_{2}^{5}SmH] + RHC = CHR \rightarrow Cp_{2}^{5}SmCHRCH_{2}R \xrightarrow{H_{2}} [Cp_{2}^{5}SmH] + RCH_{2}CH_{2}R.$$
(55)

This scheme is supported by the isolation of the structurally characterized dimer $[(C_5Me_5)_2]$



Fig. 7. Structure of $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$. Sm2 is 2.36 Å from the hydrogen atom on phenyl carbon atom a. Sm1 is 2.32 Å from the hydrogen atom on phenyl carbon atom b.

 $Sm(\mu-H)]_2$ from a stoichiometric reaction like reaction (53).³⁸ In addition, the *cis* addition and hydrogenolysis sequence [reactions (54) and (55)] has been demonstrated for other lanthanide and yttrium hydrides.²³ A subsequent mechanistic study of lanthanide-based hydrogenation catalysis reconfirms the above result.¹²⁸

III.3(g) Productive CH and CO activation via Sm(II). The reaction of the $(C_5Me_5)_2$ Sm(thf)₂-C₆H₅C=CC₆H₅ reaction product with CO has led to a remarkably facile stereospecific synthesis of a tetracyclic hydrocarbon [reaction (56)]:¹²⁹

$$2(C_{5}Me_{5})_{2}Sm(thf)_{2} + C_{6}H_{5}C \equiv CC_{6}H_{5} -4 thf$$

$$((C_{5}Me_{5})_{2}Sm)_{2}C_{2}(C_{6}H_{5})_{2} = 2CO$$

$$(C_{5}Me_{5})_{2}SmO$$

$$(C_{5}Me_{5})_{2}SmO$$

$$(S6)$$

$$(56)$$

Based on the proposed structure of the product of the $(C_5Me_5)_2Sm(thf)_2-C_6H_5C\equiv CC_6H_5$ reaction [see reaction (51)] and earlier studies of CO insertion into lanthanide-carbon σ -bonds,¹³⁰ the scheme shown below was proposed to explain this synthesis $[(C_5Me_5)_2Sm$ is shown as Sm in a box].



Activation of CO by insertion into the Sm—C bonds could give two dihaptoacyl units with considerable Sm–O interaction and carbene character on the acyl carbon atoms. Insertion of these carbene-like centers into ortho C—H bonds would give the two five-membered rings. The proximity of the ortho C—H bonds to the samarium-containing moiety in the agostic hydrogen structure of $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ [reaction (52)] gives support for this possible mode of CH activation. If this synthesis is generally applicable, it would be a valuable way to make polycyclic hydrocarbons in a stereospecific manner from simple starting materials, namely alkynes and CO.

III.3(h) Reactions with alkenes and dienes. Attempts to make ethene or butadiene complexes of $(C_5Me_5)_2Yb(thf)$ failed,⁷⁰ a result which was not surprising in view of the traditional picture of lanthanides as oxophilic hard acids which have little affinity for unsaturated hydrocarbons. However, $(C_5Me_5)_2Sm(thf)_2$ was found to polymerize ethene.^{47,131} Further studies of the catalytic

activity of $(C_5Me_5)_2$ Yb(OEt₂) and $(C_5Me_5)_2$ Eu(OEt₂) in ethene polymerization reactions have shown that these complexes do have low activity.¹³¹

 $(C_5Me_5)_2Sm(thf)_2$ also interacts with other alkenes. It readily isomerizes *cis*-stilbene to the *trans* isomer.¹³² It reacts with cyclohexene in a complex reaction which gives a product which on the basis of preliminary X-ray data contains a short 3.03-Å Sm—Sm distance.¹³³ It reacts readily with cyclohexadienes and with cyclopentadiene. In the latter case, $(C_5Me_5)_2SmC_5H_5$ is formed.¹³³ In addition, $(C_5Me_5)_2Sm(thf)_2$ in the presence of hydrogen and alkenes leads to a catalytic hydrogenation system [see reactions (53)–(55)].¹³⁴

III.4. Principles of structure and reactivity for divalent organolanthanides

Since only 13 divalent organolanthanide complexes have been structurally characterized (Table 1), any firm structural conclusions may be premature at this point. However, 10 of the structures do follow traditional principles of organolanthanide chemistry. The $(C_5R_5)_2Ln(solvent)_x$ systems have typical "bent metallocene plus x ligand" structures in the cases in which the steric bulk of the ligand set is sufficient to confer steric saturation on the complex. When this is not the case, e.g. with $(CH_3C_5H_4)_2$ Yb(thf) (Fig. 2),²⁵ oligomerization occurs to increase the steric saturation around the metal. Similarly, the monocyclopentadienyl systems such as $[(C_5Me_5)Sm(thf)_2(\mu-I]_2 (Fig. 4)^{75}$ and $[(C_5Me_5)Eu(thf)_2(\mu-C=CC_6H_5)]_2^{92}$ form bridged structures to gain a higher coordination number.

Although the majority of divalent organolanthanide structures follow traditional principles, the remarkable $(C_5Me_5)_2Ln$ complexes ($(Ln = Sm \text{ or } Eu)^{78,79}$ do not. The bent, sterically unsaturated structures are unexpected on the basis of both electrostatic and steric arguments and this structure occurs regardless of the 4*f*-electron configuration or reduction potential of the metal [a differentiating factor in reactivity (see below)].

The unusual geometry of the $(C_5Me_5)_2Ln$ complexes may signal the existence of an entire series of unanticipated structural possibilities for divalent organolanthanides. These complexes strongly indicate that the traditional principles of trivalent organolanthanide chemistry will not carry over directly to divalent systems. One of the exciting questions currently being explored in this area is how generally available are such sterically unsaturated divalent species.

Like the structural features discussed above, the reactivity of divalent complexes follows traditional organolanthanide principles in many cases. For example, there are numerous examples in Sections III.3(a)–(c) in which the metal gets oxidized and forms a sterically saturated trivalent complex which contains a new ligand involving the most electronegative of the donor atoms available in the system. As expected, reactivity parallels reduction potential, with Sm(II) more reactive than Yb(II) which is more reactive than Eu(II). The substitution reactions in Section III.3(d) are also expected considering the lability of solvating species and the tendency toward ligand redistribution reactions found for trivalent species.

Most of the unusual chemical reactivity observed for divalent organolanthanides is found with Sm(II) species. In many cases, what distinguishes Sm(II) from Yb(II) and Eu(II) is its greater reducing power. This opens up avenues of reactivity to Sm(II) which are unavailable to the other divalent lanthanide systems. Prime examples are the reductions of CO and $C_6H_5C\equiv CC_6H_5$ which succeed for Sm(II) and fail for Yb(II). Sm(II) has proven to be a unique one-electron reductant due to its special combination of physical properties. Hence, the Sm(II)-based reductive homologation of CO to $O_2C--C\equiv C\equiv O$ is a non-traditional unprecedented CO reduction. However, the reaction follows traditional organolanthanide principles in that sterically saturated oxygen-bound products are formed. Likewise the unusual distortions rendered to $C_6H_5N=NC_6H_5$ in the reaction with $(C_5Me_5)_2Sm(thf)_2$ can be traditionally explained given the formation of a highly reduced organic species. An electropositive lanthanide with a strong tendency to achieve a high coordination number will coordinate to whatever electron rich species are available. Hence, in the azobenzene complex the short Sm-N distance and agostic Sm-H interactions occur. The productive CH and CO activations discussed in III.3(g) are seen to follow traditional principles of organolanthanide-CO chemistry given the unusual features of $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$.

There is, however, an observed Sm(II) chemistry which does not follow traditional organolanthanide principles. The facile desolvation of $(C_5Me_5)_2Sm(thf)_2$ to form the sterically unsaturated $(C_5Me_5)_2Sm$ was unexpected. The difference in the desolvation tendencies of $(C_5Me_5)_2Sm(thf)_2$ and $(C_5Me_5)_2Eu(thf)$ is also unusual given the adjacent position of Sm and Eu in the periodic table. The facile reversal of the $(C_5Me_5)_2Sm(thf)_2$ reduction of $C_6H_5C\equiv CC_6H_5$ by thf, i.e. the formation of Sm(II) from Sm(III) under very mild conditions, was unanticipated. The unusual reactivity of $(C_5Me_5)_2Sm$ with cyclohexene is another example of non-traditional chemistry. These results, like the unusual structure of the $(C_5Me_5)_2Ln$ complexes, suggest there may be a major part of divalent organolanthanide reactivity which will not follow the traditional principles of the trivalent metals.

IV. ZERO OXIDATION STATE CHEMISTRY: THE CHEMISTRY OF THE METALS

In the mid-1970s, when only a limited amount of trivalent organolanthanide chemistry was known and almost no divalent organolanthanide chemistry was explored, there was an impetus to do rather speculative, highly exploratory synthetic studies in oxidation states other than +3 or +2.¹³⁵ The goal was to demonstrate a broader chemistry for the lanthanides than had previously been observed. It was anticipated that by taking a non-traditional approach to lanthanide chemistry, new areas in the field would be opened up and a greater potential for these elements in all oxidation states would be demonstrated.

An intriguing non-trivalent lanthanide oxidation state suitable for non-traditional exploration and available to all of the metals was the formally zero oxidation state of the metals. Although some reactivity was accessible from the bulk metal (see Section IV.3), a much more reactive form of the metal was available in the vapor phase. The metal vapor technique, in which a metal is vaporized from a resistively-heated tungsten container under high vacuum and is cocondensed with a potential ligand at -125 to -196° C, had proven useful in the synthesis of a variety of unusual low-valent transition-metal complexes.¹³⁶⁻¹⁴⁰ This method provided the opportunity to study zerovalent lanthanide chemistry and also had the potential to generate zero-valent lanthanide complexes.

IV.1. Background

The stability of zero oxidation state complexes of transition metals depends in large part on the transfer of the excess electron density on the metal center back to the ligands via back bonding. Given the limited radial extension of the 4f orbitals, the possibility of stabilizing a zero-valent lanthanide complex by backbonding of the 4f electron density seemed remote. However, the atomic spectra of the lanthanides show that *in low oxidation states*, the 5d orbitals are close in energy to the 4f levels and that a variety of mixed 4f-5d-6s electron configurations are low in energy.^{13,141} Hence, it is possible that the valence electrons of a low-valent lanthanide metal would possess 5d as well as 4f character. This electronic situation would be unique among metals and might provide the basis not only for new lanthanide chemistry but also for new types of metal-centered chemistry in general. As an example, zero-valent Er in a neutral complex could have single-electron approximation configurations such as $4f^{13}5d^1$, $4f^{12}5d^2$ and $4f^{11}5d^26s^1$ as well as the $4f^{12}6s^2$ configuration of the elemental metal. The chemistry of an uncharged $5d^1$ or $5d^2$ metal would certainly be unusual.

IV.2. Lanthanide metal vapor reactivity

IV.2(a) Reactions with CO. One of the early studies of zero-valent lanthanide metal vapor chemistry involved the matrix isolation reaction of the metals with CO.¹⁴² Based on IR data, a variety of metal carbonyl complexes, $Ln(CO)_n$ (n = 1-6), were postulated. This was not a preparative-scale experiment, however, and the postulated complexes were not stable except at very low temperature. Hence, unambiguous confirmation of the formula and structure of these complexes could not be obtained.

IV.2(b) Reactions with substituted alkynes and alkenes. One major focus of the study of zero oxidation state lanthanide chemistry on a preparative scale involved reactions with unsaturated hydrocarbons.^{3,143,144} Although alkenes and alkynes were not known as ligands or reactants with the trivalent lanthanides at that time, it was important to explore the potential of the zero-valent lanthanide metals to interact with such substrates given the importance of unsaturated hydrocarbon reactions in organometallic chemistry.

These exploratory studies demonstrated that the lanthanide metals have an extensive chemistry with unsaturated hydrocarbons and generated some of the most unusual organolanthanide species currently known. The lanthanide metal vapor reactions (57)-(61):

$$Ln + H_2C = CH - CH = CH_2 \rightarrow Ln(C_4H_6)_3 \quad (Nd, Sm \text{ or } Er), \quad (57)^{135}$$

$$Ln + H_2C = C(CH_3) - C(CH_3) = CH_2 \rightarrow Ln(C_6H_{10})_2$$
 (La, Nd, Sm or Er), (58)¹³⁵

$$Ln + CH_3CH = CH_2 \rightarrow Ln(C_3H_6)_3 \quad (Er), \tag{59}^{145}$$

$$Ln + CH_3CH_2C \equiv CCH_2CH_3 \longrightarrow Ln_2(C_6H_{10})_3 \quad (Nd \text{ or } Er), \tag{60}^{62}$$

$$\rightarrow \text{Ln}(\text{C}_6\text{H}_{10}) \qquad (\text{Sm or Yb}) \qquad (61)^{62}$$

illustrate the main features of this chemistry. In each case, the metal was vaporized at temperatures ranging from 500-1600°C depending on the specific lanthanide involved and cocondensed with the unsaturated hydrocarbon at -196°C. The product was isolated on a preparative scale in an inertatmosphere glove box and the product formula was determined by complete elemental analysis. Yields varied depending on the specific metal-ligand combination, but as much as 2-3 g of isolated product were obtained in some of the systems.^{3,144}

The metal vapor reaction products differed from traditional organolanthanide complexes in many ways. First, the observed stoichiometries had low ligand: metal ratios. For example, the Yband Sm-3-hexyne products [reactions (60) and (61)] had formal ligand: metal ratios of 1:1, whereas most organolanthanides are commonly 9- or 10-coordinate. Second, the stoichiometries varied in an unusual manner depending on the ligand and metal. For example, 2,3-dimethyl substitution of the butadiene ligand changed the ligand: metal ratio from 3:1 [reaction (57)] to 2:1 [reaction 58)]. In the 3-hexyne system, changing from Nd and Er to Yb and Sm changed the ratio from 1.5:1 [reaction (60)] to 1:1 [reaction (61)]. Traditionally, the stoichiometries of organolanthanide complexes are invariant to minor substitutional changes on the ligand and are similar for each lanthanide in the series. Third, in contrast to traditional organolanthanides, which have pale colors (see Section III.1), the metal vapor products were intensely colored materials which displayed strong charge transfer absorptions in the near IR and visible regions. Fourth, the room-temperature magnetic moments for these complexes were often outside the range of "free-ion" values previously reported for organolanthanide compounds. Consistent with this, the NMR spectra of the La, Sm and Lu products were broad and uninformative whereas these metals, when trivalent, provide sharp interpretable spectra. The lanthanum butadiene product displayed an EPR absorption $(La^{3+} is 4f^{0})$. Finally, the solution behavior of these complexes was unusual. For example, the 3-hexyne product $[ErC_9H_{15}]_n$ was dimeric in arenes, i.e. n = 2 [e.g. $Er_2(C_6H_{10})_3$], but in concentrated solution or in thf it was highly associated with n > 10. This is just the opposite of the trend found for traditional organolanthanides which are more highly associated in arenes than in thf.^{21,30} Unfortunately, because these metal vaporization products oligomerized rather than crystallized in concentrated solution, these species were not structurally characterized by X-ray diffraction.

Analysis of possible zero-valent reaction pathways suggested three conceivable structural types for these products and initiated further experimental studies to verify them.¹⁴⁴ For the Er-3-hexyne product, $(ErC_9H_{15})_n$, one possibility was a π -complex as shown in A below:



This structure has an alternate cyclometallopropene form (A') which may be more reasonable for

these complexes considering the electropositive nature of the lanthanides. No π -complexes of lanthanides have yet been observed. However, η^2 -coordination of C=N double bonds to trivalent Er and Y centers has been structurally characterized in formimidoyl complexes^{145,146} and numerous examples of unsaturated hydrocarbons participating in lanthanide reactions are now known.^{5,6,23,128,133}

Alternatively, the lanthanide may not interact with the unsaturated bond at all, but instead could insert into C—H bonds by oxidative addition as in B:



This type of C—H activation reaction subsequently was demonstrated in lanthanide metal vapor reactions with terminal alkynes⁸⁹ and $C_5Me_5H_1^{47}$

A third possibility for the reaction of a lanthanide metal with an alkyne is radical formation (structure C) as has been postulated for the Al-HC \equiv CH system based on matrix EPR spectroscopy.¹⁴⁷ If the monovalent Er in the initially formed radical oxidatively inserts into a C—H



linkage and the resulting Er—H adds to excess 3-hexyne in the matrix, the radical-forming reaction can be rationalized to form a product with the exact formula determined experimentally (in contrast to structure **B** which is low in hydrogen). Subsequent studies of the reduction of $C_6H_5C \equiv CC_6H_5^{38}$ and $C_6H_5N = NC_6H_5^{126}$ by $(C_5Me_5)_2Sm(thf)_2$ [see reactions (51) and (52)] support this reaction pathway. Interestingly, the diphenylethyne and azobenzene products are intensely colored like the metal vapor reaction products. Structure **C** fits the available data best, but remains to be structurally established.

IV.2(c) Reactions with unsubstituted alkenes and cyclopropane. Since the reactions leading to structures **B** and **C** in the previous section required that substituents attached to the multiplybonded carbon contain hydrogen for C—H activation, it was of interest to investigate metal vapor reactions involving smaller unsaturated hydrocarbons which lacked these potentially reactive sites. Accordingly, the reactions of ethene and 1,2-propadiene were surveyed with Sm, Yb and Er. The reactivity of two other small hydrocarbons, propene and cyclopropane, was also studied for comparison. These studies indicated an even wider range of reactivity was possible for the lanthanides.¹⁴⁸ In contrast to the reactions discussed in the previous section, lanthanide metal vapor reactions with these smaller hydrocarbons did not provide soluble products (with the exception of the erbium product, $Er(C_3H_6)_3$ [reaction(59)]). Information on reaction pathways was obtained primarily by analyzing the products of hydrolysis of the metal vapor reaction product.

In ethene reactions, these data indicated that simple stable π -complexes (type A in the previous

section) were not predominant products and that σ -bonded linkages, such as CH_2 — CH_2 (type A' in the previous section) or LnCH₂CH₂Ln were more likely.¹⁴⁸ The data suggested that alkene insertion and polymerization were occurring as in organolithium chemistry.¹⁴⁹ Lanthanide-based alkene polymerization¹⁵⁰ has been heavily studied subsequently.^{151,152} Hydrolytic formation of CH₄ and homologated three-carbon products from the ethene reaction products suggested that the lanthanides had the capacity to break and reform C—C bonds. The presence of Ln—H moieties was also indicated and was consistent with activation of C—H bonds by oxidative addition.

The major reactivity patterns observed in ethene reactions were also found in reactions of lanthanide metal vapor with 1,2-propadiene, propene and cyclopropane, although the larger hydrocarbons gave less complex reaction products.¹⁴⁷ With 1,2-propadiene as the substrate,

Ln Lnoxidative addition of CH and the formation of CH_2 — $C=CH_2$ or $LnCH_2$ — $C=CH_2$ appeared to be the major routes of reaction. Propene reacted with lanthanide metal vapor primarily by CH oxidative addition to form insoluble allyl hydride complexes. With Er, however, $[Er(C_3H_6)_3]_n$, was obtained. Hydrolysis products also included propyne which indicated that extensive dehydrogenation of propene occurred in this system.

In the cyclopropane-Er system, oxidative addition of C—H to form cyclopropyl Er hydride groups as well as ring cleavage and dehydrogenation reactions were inferred from the hydrolytic data. The fact that the relatively inert C—H bonds in cyclopropane could be activated by a lanthanide metal testifies to the high reactivity found in these systems.¹⁴⁸

IV.2(d) Reactions with readily reducible or acidic hydrocarbons. The metal vapor reactions described in this section involve substrates which are readily convertible to stable organic anions. As described in Section III.2(a), YbC₈H₈ can be prepared by reacting Yb metal vapor with 1,3,5,7-C₈H₈.⁵¹ When this reaction is carried out with lanthanide metals which do not have a readily accessible divalent state, for example, La, Ce, Nd or Er, a different type of product is obtained. Extraction with thf gives trivalent species consisting of a tight ion pair of $[(C_8H_8)2n]^{-.51}$ Hence, complete oxidation of the metal can occur under these conditions with the proper reducible substrate.

When hydrocarbon substrates containing acidic hydrogen are used, oxidative addition of CH readily occurs. As described in Section III.2(f), ytterbium reacts with 1-hexyne to form alkynide hydride complexes $[HYb_2(C \equiv CC_4H_9)_3]_n$.⁸⁹ With Sm, trivalent alkynide hydride complexes are formed and may involve some dimetalated as well as monometalated alkynide ligands. The Er reaction also forms trivalent alkynide hydrides and is even more complex than the Sm system.⁸⁹ The complexity of these systems increases as the stability of the divalent oxidation state decreases.

The reactions of Sm metal vapor with C_5Me_5H and C_5Me_4EtH also give C—H oxidative addition products [see Sections III.2(d) and (e)].^{47,74} For C_5Me_5H , a thf workup gives an unstable divalent hydride, [(C_5Me_5)SmH(thf)₂], which transforms to (C_5Me_5)₂Sm(thf)₂.⁴⁷ Again, oxidative addition of C—H explains this result. When a thf-free workup of the Sm— C_5Me_5H reaction mixture was carried out, an interesting alkane-soluble product was isolated which contained nitrogen by elemental analysis. Addition of toluene to this product liberated N₂ gas and left (C_5Me_5)₂Sm. Unfortunately, definitive identification of the nitrogen complex was not possible.⁷⁴

In a similar reaction to those above, Yb metal vapor reacts with C_5H_6 to form $(C_5H_5)_2$ Yb.¹⁵³

IV.2(e) Catalytic activity of metal vapor products. In the course of characterizing the lanthanide metal vapor 3-hexyne products, it was discovered that these complexes had the capacity to initiate catalytic hydrogenation of alkynes to alkenes and alkanes.⁶² A variety of lanthanide metal vapor products have been found to generate catalytic hydrogenation systems. Not only the 3-hexyne

Ln

reaction products, but also the products of lanthanide metal cocondensations with 1-hexyne, 2,3dimethylbutadiene, $(CH_3)_3SiC\equiv CSi(CH_3)_3$ and $P(C_6H_5)_3$ are able to do this.¹⁵⁴ Using 3-hexyne as a substrate, these catalytic systems generally give high yields of *cis*-3-hexene, many with >95% stereospecificity.

Although catalytic hydrogenation of alkynes can be accomplished in many other ways, this catalytic system was significant because it was the first time an *f*-element complex had been observed to catalytically activate hydrogen in homogeneous solution.⁶² The result had additional importance because the metal hydride complexes presumably involved in the catalyses provided the first evidence for the existence of discrete molecular lanthanide hydrides. The existence of lanthanide hydride complexes subsequently was demonstrated crystallographically²² and fully characterized lanthanide hydrides were shown to have catalytic activity in hydrogenation reactions.³⁸ High levels of catalytic hydrogenation activity have subsequently been observed under optimized conditions.¹²⁸

IV.3. Bulk metal, metal amalgam, and activated metal reactions

Lanthanide metals in the form of powders, filings or ingots have been used in a variety of systems as reagents. In some cases, the metal is "activated" by addition of Hg or HgCl₂ to form an amalgam. When ytterbium is used, divalent products are often obtained and many of these reactions have been discussed in Section III.2. These include oxidation reactions using alkyl and cyclopentadienyl halide reagents, transmetalation reactions with cyclopentadienyl, aryl, alkynyl, carboranyl, transition-metal, mercury and thallium reagents, and reductions of $(C_5H_5)_2$ YbCl and $(C_5H_5)_3$ Yb with Yb. The latter two reductions and some of the transmetalations can give clean reactions, whereas the RX reactions are generally complex. Extension of these reactions to samarium tends to give more complex results due to the formation of Sm(III) products. As is observed in metal vapor reactions with terminal alkynes, the complexity of these oxidations often increases with decreasing stability of the divalent oxidation state.

Lanthanide elements which do not have a readily accessible divalent oxidation state also participate in oxidations of the type described above to give trivalent products. The reactions of Ce and La with alkyl and aryl iodides⁹⁴ and Pr, Nd, Gd and Ho with triphenylmethylchloride, benzyl chloride and phenyl bromide¹⁵⁵ have been studied. Mixtures of colored products corresponding to $R_a Ln X_{3-a}$ are thought to be present. In a related approach the reactions of La, Tm and Yb with C- and B-mercuriocarboranes have been investigated.¹⁰⁰ Tris(cyclopentadienyl) complexes of Ce, Nd, Gd and Er have been prepared from the metals and thallous cyclopentadienides.⁵⁴

A variety of lanthanide metals have been reacted with transition-metal reagents including $Hg[Co(CO)_4]_2$,¹⁵⁶ $Mn(CO)_5Br$,¹⁵⁷ $C_3H_5Fe(CO)_3I$,¹⁵⁷ $C_5H_5Cr(CO)_3HgCl^{157}$ and $[(C_5H_5)Mo(CO)_3]_2$.^{157,158} These are complex reactions and only recently has a product been crystallographically characterized. The reaction of "lanthanum amalgam" with $[(C_5H_5)Mo(CO)_3]_2$ forms (thf)₅La[(μ -OC)Mo(CO)_2(C_5H_5)]₃ · (thf).¹⁵⁸

Reduction of PrCl₃ with K in thf gives an activated reduced form of praseodymium which has an organometallic chemistry. Treatment of the reduced praseodymium with 1,5-cyclooctadiene at room temperature gives products from which 1,3,5,7-cyclooctatetraene can be isolated upon oxidation.¹⁵⁹ The exact oxidation state of the lanthanide was not determined. The C₈H₁₂ to C₈H₈²⁻ conversion which apparently occurs led to the development of a high-temperature K-based preparation of 1,3,5,7-C₈H₈ from 1,5-C₈H₁₂.¹⁶⁰

IV.4. General principles governing zero-valent lanthanide chemistry

Since little structural evidence is available on most of the products reported in Section IV, this area of low-valent lanthanide chemistry cannot be analyzed as precisely as was done for trivalent and divalent systems in Sections II.2 and III.4, respectively. The identity of many of the products discussed in Section IV remains unknown. Given what we now know about the reactivity/stability of sterically unsaturated trivalent organolanthanides (Section II.2), and strongly reducing divalent lanthanides (Section III.3) it is not surprising that the zero-valent lanthanide systems would be difficult to fully characterize. However, the goal of much of this chemistry, namely to broaden

organolanthanide chemistry in general, has been achieved.

These studies demonstrated several key aspects about the capacity of the lanthanides to participate in organometallic chemistry. The lanthanides were clearly shown to interact with the unsaturated hydrocarbons, a class of ligands previously uncommon in lanthanide chemistry. The lanthanides were shown to have the potential to effect a variety of interesting transformations on hydrocarbon substrates including C—H activation by oxidative addition, two-electron reduction of unsaturated C—C bonds, C—C cleavage, oligomerization, dehydrogenation, homologation and catalytic hydrogenation. The metal vapor reactions generated products which could catalytically activate hydrogen and which could probably generate molecular lanthanide hydride complexes.

The metal vapor syntheses in particular generated a variety of unusual organolanthanide complexes and "defined a set of conditions under which a variety of remarkable hydrocarbon activation reactions take place in the presence of the lanthanide metals".¹⁴⁸ These studies demonstrated the potential of the lanthanide metals and indicated areas where further development should take place in the field. As stated previously "the challenge in this area is to control this reactivity so that it can be used selectively"¹⁴⁸ and this is being done.

V. CONCLUSIONS

The organometallic chemistry of the lanthanide metals in low oxidation states has grown enormously since the isolated reports of the first complexes of this type appeared in the 1960s. The greatest development has occurred in the past few years and the rate of growth shows no signs of diminishing. The field is still too young to have a definable scope and potential at the present time, although recent results are starting to provide a basis for developing general principles.

The utility of the elemental metals in organolanthanide chemistry has been clearly shown in terms of demonstrating reactivity and the potential of lanthanides in general. The value of zero-valent lanthanide chemistry in forming isolable complexes has yet to be realized.

Although only three of the lanthanide elements have accessible divalent oxidation states, it is clear that divalent chemistry will be an important component of the organolanthanide field. The strong reducing capacity of Sm(II) will continue to distinguish it not only as a special lanthanide, but also as a special reducing reagent in chemistry in general. Clearly, low oxidation state lanthanide complexes have much to offer the field of organometallic chemistry.

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REFERENCES

- T. J. Kealy and P. L. Pauson, *Nature (London)* 1951, 168, 1039; S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.* 1952, 632-3; G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.* 1952, 74, 2125; E. O. Fischer and W. Pfab, *Z. Naturforsch.* 1952, 7B, 377.
- 2. J. M. Birmingham and G. Wilkinson, J. Am. Chem. Soc. 1956, 78, 42.
- 3. W. J. Evans, S. C. Engerer, P. A. Piliero and A. L. Wayda, In Fundamental Research in Homogeneous Catalysis (Edited by M. Tsutsui) Vol. 3, p. 941. Plenum Press, New York (1979).
- J. H. Forsberg and T. Moeller, In Gmelin Handbook of Inorganic Chemistry, 8th Edn, Sc, Y, La-Lu, Part D6 (Edited by T. Moeller, U. Kruerke and E. Schleitzer-Rust), p. 137 (and references therein). Springer, Berlin (1983).
- 5. W. J. Evans, Adv. Organomet. Chem. 1985, 24, 131 (and references therein).
- 6. P. L. Watson and G. W. Parshall, Acc. Chem. Res. 1985, 18, 51 (and references therein).
- 7. H. B. Kagan and J. L. Namy, In Handbook on the Physics and Chemistry of Rare Earths (Edited by K. A. Gschneidner, Jr and L. Eyring), Vol. 6, Chap. 50. Elsevier, Amsterdam (1984).
- 8. T. J. Marks and R. D. Ernst, In *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel), Chap. 21. Pergamon Press, Oxford (1982).
- 9. T. J. Marks, Prog. Inorg. Chem. 1978, 24, 51.

- 10. W. J. Evans, In *The Chemistry of the Metal-Carbon Bond* (Edited by F. R. Hartley and S. Patai), Chap. 12. Wiley, New York (1982).
- 11. A. J. Freeman and R. E. Watson, Phys. Rev. 1976, 9, 217; H. M. Crosswhite and A. P. Paszek, personal communication.
- 12. T. Moeller, In Comprehensive Inorganic Chemistry (Edited by J. C. Bailar, Jr), Vol. 4, Chap. 44. Pergamon Press, Oxford (1973).
- 13. G. H. Dieke, In Spectra and Energy Levels of Rare Earth Ions in Crystals (Edited by H. M. Crosswhite and H. Crosswhite). Wiley, New York (1968).
- 14. W. T. Carnall, In Handbook on the Physics and Chemistry of Rare Earths (Edited by K. A. Gschneidner, Jr and L. Eyring), Vol. 3, Chap. 24. Elsevier, Amsterdam (1979).
- 15. E. O. Fischer and H. Fischer, J. Organomet. Chem. 1965, 3, 181.
- 16. S. Manastyrskyj and M. Dubeck, Inorg. Chem. 1964, 3, 1647.
- 17. C. M. Lukehart, Fundamental Transition Metal Organometallic Chemistry. Brooks/Cole, Belmont, CA (1985).
- 18. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th Edn. Wiley. New York (1980).
- 19. J. E. Huheey, Inorganic Chemistry, 3rd Edn, p. 146 (and references therein). Harper & Row, New York (1983).
- 20. R. D. Fischer and L. Xing-Fu, J. Less Common Met. 1985, 112, 303.
- 21. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, J. Chem. Soc., Dalton Trans. 1979, 54.
- 22. W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1982, 104, 2008.
- 23. W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1984, 106, 1291.
- 24. W. J. Evans, J. H. Meadows and T. P. Hanusa, J. Am. Chem. Soc. 1984, 106, 4454.
- 25. H. A. Zinnen, J. J. Pluth and W. J. Evans, J. Chem. Soc. Chem. Commun. 1980, 810.
- 26. W. J. Evans, R. Dominguez and T. P. Hanusa, Organometallics 1986, 5, 263.
- 27. W. J. Evans, A. L. Wayda, W. E. Hunter and J. L. Atwood, J. Chem. Soc., Chem. Commun. 1981, 292.
- 28. H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, Organometallics 1982, 1, 1194.
- 29. E. C. Baker, L. D. Brown and K. N. Raymond, Inorg. Chem. 1975, 14, 1376.
- 30. R. E. Maginn, S. Manastryskyj and M. Dubeck, J. Am. Chem. Soc. 1963, 85, 672.
- 31. H. G. Brittain, J. H. Meadows and W. J. Evans, Organometallics 1985, 4, 1585.
- 32. M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, J. Chem. Soc., Chem. Commun. 1981, 1190.
- 33. Z. Jin, Y. Lui and W. Chen, personal communication.
- 34. W. J. Evans, T. T. Peterson, M. D. Rausch, W. E. Hunter, H. Zhang and J. L. Atwood, Organometallics 1985, 4, 554.
- 35. P. L. Watson and D. C. Roe, J. Am. Chem. Soc. 1982, 104, 6471.
- 36. P. L. Watson, J. Chem. Soc., Chem. Commun. 1983, 276.
- 37. P. L. Watson, J. Am. Chem. Soc. 1983, 105, 6491.
- 38. W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1983, 105, 1401.
- 39. W. J. Evans and J. W. Grate, unpublished results.
- 40. Chapter 12 in Ref. 13.
- 41. D. S. McClure and Z. Kiss, J. Chem. Phys. 1963, 39, 3251; Z. J. Kiss and P. N. Yocom, J. Chem. Phys. 1964, 41, 1511.
- 42. N. B. Mikheev, Inorg. Chim. Acta 1984, 94, 241.
- 43. A. Greco, S. Cesca and G. Bertolini, J. Organomet. Chem. 1976, 113, 321.
- 44. H. R. Bronstein, J. Phys. Chem. 1969, 73, 1320.
- 45. L. R. Morss, Chem. Rev. 1976, 76, 827 (and references therein); S. G. Bratsch and J. J. Lagowski, J. Phys. Chem. 1985, 89, 3317.
- 46. P. G. Varlashkin and J. R. Peterson, J. Less-Common Met. 1983, 94, 333.
- 47. W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1981, 103, 6507.
- 48. S. A. Cotton and F. A. Hart, The Heavy Transiton Elements. Wiley, New York (1975).
- 49. W. J. Evans and M. A. Hozbor, in preparation.
- 50. R. G. Hayes and J. L. Thomas, J. Am. Chem. Soc. 1969, 91, 6876.
- 51. C. W. DeKock, S. R. Ely, T. E. Hopkins and M. A. Brault, Inorg. Chem. 1978, 17, 625.
- 52. R. G. Hayes and J. L. Thomas, Inorg. Chem. 1969, 8, 2521.
- 53. F. Calderazzo, R. Pappalardo and S. Losi, J. Inorg. Nucl. Chem. 1966, 28, 987.
- 54. G. B. Deacon, A. J. Koplick and T. D. Tuong, Polyhedron 1982, 1, 423; G. B. Deacon, A. J. Koplick and T. D. Tuong, Aust. J. Chem. 1984, 37, 517.
- 55. G. Z. Suleimanov, L. F. Rybakova, Ya. A. Nuriev, T. Kh. Kurbanov and I. P. Beletskaya, J. Organomet. Chem. 1982, 235, C19.
- 56. J. L. Namy, P. Girard and H. B. Kagan, Nouv. J. Chim. 1981, 5, 479.

- 57. G. B. Deacon and R. H. Newnham, Aust. J. Chem. 1985, 38, 1757.
- 58. G. W. Watt and E. W. Gillow, J. Am. Chem. Soc. 1969, 91, 775.
- 59. G. Z. Suleimanov, T. Kh. Kurbanov, Ya. A. Nuriev, L. F. Rybakova and I. P. Beletskaya, Dokl. Chem. 1982, 265, 254.
- 60. G. B. Deacon, G. N. Pain and T. D. Tuong, Polyhedron 1985, 4, 1149.
- 61. G. B. Deacon, P. I. MacKinnon, T. W. Hambley and J. C. Taylor, J. Organomet. Chem. 1983, 259, 91.
- 62. W. J. Evans, S. C. Engerer, P. A. Piliero and A. L. Wayda, J. Chem. Soc., Chem. Commun. 1979, 1007.
- 63. M. F. Lappert, P. I. W. Yarrow, J. L. Atwood, R. Shakir and J. Holton, J. Chem. Soc., Chem. Commun. 1980, 987.
- 64. W. J. Evans and H. A. Zinnen, unpublished results.
- 65. P. T. Wolczanski and J. E. Bercaw, Acc. Chem. Res. 1980, 13, 121 (and references therein).
- 66. J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, J. Am. Chem. Soc. 1978, 100, 2716 (and references therein).
- 67. P. J. Fagan, J. M. Manriquez, E. A. Maata, A. M. Seyam and T. J. Marks, J. Am. Chem. Soc. 1981, 103, 6650.
- 68. T. J. Marks, Science 1982, 217, 989.
- 69. T. D. Tilley, R. A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D. H. Templeton, Inorg. Chem. 1980, 19, 2999.
- 70. P. L. Watson, J. Chem. Soc., Chem. Commun. 1980, 652.
- 71. P. L. Watson, J. F. Whitney and R. L. Harlow, Inorg. Chem. 1981, 20, 3271.
- 72. T. D. Tilley, R. A. Andersen, B. Spencer and A. Zalkin, Inorg. Chem. 1982, 21, 2647.
- 73. A. L. Wayda, J. L. Dye and R. D. Rogers, Organometallics 1984, 3, 1605.
- 74. W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, Organometallics 1985, 4, 112.
- 75. W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1985, 107, 941.
- A. Streitwieser, Jr, U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson and C. A. Harmon, J. Am. Chem. Soc. 1973, 95, 8644.
- 77. K. O. Hodgson, F. Mares, D. F. Starks and A. Streitwieser, Jr, J. Am. Chem. Soc. 1973, 95, 8650.
- 78. W. J. Evans, L. A. Hughes and T. P. Hanusa, P. J. Am. Chem. Soc. 1984, 106, 4270.
- 79. W. J. Evans, L. A. Hughes and T. P. Hanusa, Organometallics 1986, 5, 1285.
- 80. J. D. Dunitz, L. E. Orgel and A. Rich, Acta Cryst. 1956, 9, 393.
- 81. D. P. Freyberg, J. L. Robbins, K. N. Raymond and J. C. Smart, J. Am. Chem. Soc. 1979, 101, 892.
- 82. J. V. Ortiz and R. Hoffmann, Inorg. Chem. 1985, 24, 2095.
- 83. A. Haaland, personal communication.
- 84. A. Buchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 1964, 86, 4544.
- 85. M. Guido and G. Gigli, J. Chem. Phys. 1976, 65, 1397.
- P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y.-H. Tsay, Chem. Ber. 1980, 113, 757; J. L. Atwood,
 W. E. Hunter, A. H. Cowley, R. A. Jones and C. A. Stewart, J. Chem. Soc., Chem. Commun. 1981, 925.
- G. B. Deacon and A. J. Koplick, J. Organomet. Chem. 1976, 146, C43; G. B. Deacon, A. J. Koplick and T. D. Tuong, Aust. J. Chem. 1982, 35, 941.
- 88. E. Murphy and G. E. Toogood, Inorg. Nucl. Chem. Lett. 1971, 75, 755.
- 89. W. J. Evans, S. C. Engerer and K. M. Coleson, J. Am. Chem. Soc. 1981, 103, 6672.
- 90. J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, Inorg. Chem. 1981, 20, 4115.
- 91. W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, Organometallics 1983, 2, 709.
- 92. J. M. Boncella, T. D. Tilley and R. A. Andersen, J. Chem. Soc., Chem. Commun. 1984, 710.
- 93. R. D. Fischer and G. Bielang, J. Organomet. Chem. 1980, 191, 61.
- 94. D. F. Evans, G. V. Fazakerley and R. F. Phillips, J. Chem. Soc. A 1971, 1931.
- 95. G. B. Deacon and D. G. Vince, J. Organomet. Chem. 1976, 112, C1; G. B. Deacon, W. D. Raverty and D. G. Vince, J. Organomet. Chem. 1977, 135, 103.
- 96. G. B. Deacon, P. I. Mackinnon and T. D. Tuong, Aust. J. Chem. 1983, 36, 43.
- 97. G. Z. Suleimanov, V. N. Khandozhko, P. V. Petrovskii, R. Yu. Mekhdrev, E. K. Nadezda and I. P. Beletskaya, J. Chem. Soc., Chem. Commun. 1985, 596.
- 98. G. B. Deacon, A. H. Koplick, W. D. Raverty and D. G. Vince, J. Organomet. Chem. 1979, 182, 121 (and references therein).
- G. Z. Suleimanov, P. V. Petrovskii, Y. S. Bogachev, I. L. Zhuravleva, E. I. Fedin and I. P. Beletskaya, J. Organomet. Chem. 1984, 262, C35.
- G. Z. Suleimanov, V. I. Bregadze, N. A. Koval'chuk and I. P. Beletskaya, J. Organomet. Chem. 1982, 235, C17.
- G. Z. Suleimanov, V. I. Bregadze, N. A. Koval'chuk, Kh. S. Khalilov and I. P. Beletskaya, J. Organomet. Chem. 1983, 255, C5.
- 102. T. D. Tilley, R. A. Andersen and A. Zalkin, J. Am. Chem. Soc. 1982, 104, 3725.

- 103. T. D. Tilley, R. A. Andersen and A. Zalkin, Inorg. Chem. 1984, 23, 2271.
- 104. H. A. Zinnen and W. J. Evans, unpublished results; H. A. Zinnen, Ph.D. dissertation, University of Chicago (1982).
- 105. T. D. Tilley and R. A. Andersen, Inorg. Chem. 1981, 20, 3267.
- 106. W. J. Evans, J. W. Grate, K. R. Levan, I. Bloom, T. T. Peterson, R. J. Doedens, H. Zhang and J. L. Atwood, *Inorg. Chem.* 1986, 25, 3614.
- 107. R. G. Finke, S. R. Keenan, D. A. Schiraldi and P. L. Watson, Organometallics 1986, 5, 598.
- 108. G. B. Deacon, G. D. Fallon, P. I. MacKinnon, R. H. Newnham, G. N. Pain, T. D. Tuong and D. L. Wilkinson, J. Organomet. Chem. 1981, 277, C21.
- 109. W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter and J. L. Atwood, J. Am. Chem. Soc. 1985, 107, 405.
- 110. R. E. Dessy, R. B. King and M. Waldrop, J. Am. Chem. Soc. 1966, 88, 5112.
- 111. W. J. Evans and W. M. Cwirla, unpublished results.
- 112. T. D. Tilley and R. A. Andersen, J. Chem. Soc., Chem. Commun. 1981, 985.
- 113. J. M. Boncella and R. A. Andersen, Inorg. Chem. 1984, 23, 432.
- 114. T. D. Tilley and R. A. Andersen, J. Am. Chem. Soc. 1982, 104, 1772.
- 115. R. A. Andersen, INOR 10, 190th American Chemical Society National Meeting, Chicago, IL (1985).
- 116. W. J. Evans, I. Bloom, J. W. Grate, L. A. Hughes, W. E. Hunter and J. L. Atwood, *Inorg. Chem.* 1985, 24, 4620.
- 117. W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang and J. L. Atwood, J. Am. Chem. Soc. 1985, 107, 3728.
- H. H. Storch, N. Golumbic and R. B. Anderson, *The Fischer-Tropsch Reaction and Related Syntheses*. Wiley, New York (1951). V. Ponec, *Catal. Rev.—Sci. Eng.* 1978, 18, 1515; C. Masters, *Adv. Organomet. Chem.* 1979, 17, 61; H. H. Kung, *Catal. Rev.—Sci. Eng.* 1980, 22, 235; K. Klier, *Adv. Catal.* 1982, 31, 243; B. D. Dombek, *Adv. Catal.* 1983, 322, 325.
- 119. G. Erker, Acc. Chem. Res. 1984, 17, 103.
- 120. D. A. Katahira, K. G. Moloy and T. J. Marks, Organometallics 1982, 1, 1723 (and references therein).
- 121. W. J. Evans, J. W. Grate and R. J. Doedens, J. Am. Chem. Soc. 1985, 107, 1671.
- 122. W. Büchner, Chem. Ber. 1966, 99, 1485; W. Büchner, Helv. Chim. Acta 1963, 46, 2111.
- 123. J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, J. Am. Chem. Soc. 1972, 94, 1219; M. Bottrill, P. D. Gavens and J. McMeeking, In Comprehensive Organometallic Chemistry (Edited by G. W. Wilkinson, F. G. A. Stone and E. W. Abel), Chap. 22.2. Pergamon Press, Oxford (1982).
- 124. W. J. Evans, D. K. Drummond and T. A. Ulibarri, unpublished results.
- 125. H. O. House, Modern Synthetic Reactions, p. 205 (and references therein). W. A. Benjamin, Menlo Park, CA (1972).
- 126. W. J. Evans, D. K. Drummond, S. G. Bott and J. L. Atwood, Organometallics, in press.
- 127. M. Brookhart and M. L. H. Green, J. Organomet. Chem. 1983, 250, 395.
- 128. G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, J. Am. Chem. Soc. 1985, 107, 8111.
- 129. W. J. Evans, D. K. Drummond, L. A. Hughes, H. Zhang and J. L. Atwood, J. Am. Chem. Soc. 1986, 108, 1722.
- 130. W. J. Evans, A. L. Wayda, W. E. Hunter and J. L. Atwood, J. Chem. Soc., Chem. Commun. 1981, 706.
- 131. P. L. Watson and T. Herskovitz, ACS Symp. Ser. 1983, 212, 459.
- 132. W. J. Evans and T. P. Hanusa, unpublished results.
- 133. W. J. Evans, T. A. Ulibarri and T. P. Hanusa, unpublished results.
- 134. W. J. Evans and R. E. King, III, unpublished results.
- 135. W. J. Evans, S. C. Engerer and A. C. Neville, J. Am. Chem. Soc. 1978, 100, 331.
- 136. P. A. Skell and M. J. McGlinchey, Angew. Chem., Int. Ed. Engl. 1975, 14, 195.
- 137. P. L. Timms and T. W. Turney, Adv. Organomet. Chem. 1977, 15, 53.
- 138. K. J. Klabunde, Chemistry of Free Atoms and Particles. Academic Press, New York (1980).
- 139. J. R. Blackborow and D. Young, Metal Vapor Synthesis in Organometallic Chemistry. Springer, Berlin (1979).
- 140. M. Moskovits and G. A. Ozin (Eds), Cryochemistry. Wiley, New York (1976).
- 141. W. C. Martin, R. Zalubas and L. Hogan, Atomic Energy Levels. The Rare Earth Elements. National Standard Reference Data Series, No. 60, National Bureau of Standards (U.S.), Washington, DC (1978).
- 142. R. K. Sheline and J. L. Slater, Angew. Chem., Int. Ed. Engl. 1975, 14, 309 (and references therein).
- 143. M. J. McGlinchey and P. S. Skell, in Ref. 140; P. S. Skell, Proc. Int. Congr. Pure Appl. Chem. 1971, 23, 215.
- 144. W. J. Evans, In The Rare Earths in Modern Sciences and Technology (Edited by G. J. McCarthy, J. J. Rhyne and H. E. Silber), Vol. 3, p. 61. Plenum Press, New York (1982).
- 145. W. J. Evans, J. H. Meadows, W. E. Hunter and J. L. Atwood, Organometallics 1983, 2, 1252.
- 146. W. J. Evans, T. P. Hanusa, J. H. Meadows, W. E. Hunter and J. L. Atwood, Organometallics, in press.
- 147. P. H. Kasai, D. McLeod, Jr and T. Watanabe, J. Am. Chem. Soc. 1977, 99, 3521.
- 148. W. J. Evans, K. M. Coleson and S. C. Engerer, Inorg. Chem. 1981, 20, 4320.

- 149. V. Rautenstrauch, Angew. Chem., Int. Ed. Engl. 1975, 14, 259.
- 150. D. G. Ballard, A. Courtis, J. Holton, J. McMeeking and R. Pearce, J. Chem. Soc., Chem. Commun. 1978, 994.
- 151. P. L. Watson, J. Am. Chem. Soc. 1982, 104, 337.
- 152. P. L. Watson and D. C. Roe, J. Am. Chem. Soc. 1982, 104, 6471.
- 153. W. J. Evans and S. C. Engerer, unpublished results.
- 154. W. J. Evans, I. Bloom and S. C. Engerer, J. Catal. 1983, 84, 468.
- 155. B. A. Dolgoplosk, E. I. Tinyakova, I. N. Markevich, T. V. Soboleva, G. M. Chernenko, O. K. Sharaev and V. A. Yakovlev, J. Organomet. Chem. 1983, 255, 71.
- 156. R. S. Marianelli and M. T. Durney, J. Organomet. Chem. 1971, 32, C41.
- 157. A. E. Crease and P. Legzdins, J. Chem. Soc., Chem. Commun. 1973, 775.
- 158. A. A. Pasynskii, I. L. Eremenko, G. Z. Suleimanov, Yu. A. Niriev, I. P. Beletskaya, V. E. Shklover and Yu. T. Struchkov, J. Organomet. Chem. 1984, 266, 45.
- 159. W. J. Evans, A. L. Wayda, C. W. Chang and W. M. Cwirla, J. Am. Chem. Soc. 1978, 100, 333.
- 160. W. J. Evans, D. J. Wink, A. L. Wayda and D. A. Little, J. Org. Chem. 1981, 46, 3925.