Synthesis, Structure, and Reactions of Hydride, Borohydride, and Aluminohydride Compounds of the f-Elements

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I. Introduction

The huge interest of the hydride complexes of the d-transition metals is expressed by the thousands of articles, reviews, and books devoted to their synthesis, structure, and reactivity.[1] In comparison, the domain of the lanthanide and actinide hydrides seems to be excessively limited. As an illustration, only a few molecular dihydrides of the f-elements have been reported, opposed to the hundreds of transition metal polyhydrides; the sole example of a dihydrogen compound, $Cp*_2Eu(H_2)$, could be detected by NMR,[2] whereas the number of such "nonclassical" transition metal hydrides is increasing rapidly since a decade. However, the hydride complexes are far from not having played any role in the spectacular growth of f-element chemistry, during the last 20 years, showing that their underdeveloped situation was not only the result of a chemical necessity but also reflected a disfavored historical background. Today, lanthanide and actinide hydrides are more attractive with their unique structural features and their catalytic activity which is often very much higher than that of d-transition metal catalysts.

The objective of this review is to draw up a first assessment of the syntheses, structures and reactions of molecular f-element hydrides; the hydride complexes of scandium, yttrium, and lanthanum will be included because of their close similarity. This review will also present the properties of the borohydride, aluminohydride, and alane compounds of these metals; being generally more stable than their analogues in the d-transition series, these complexes are interesting for studying the coordination modes and the chemical behavior of the BH_4, AlH_4, and AlH_3 ligands. The complexes with agostic C−H bonds will not be treated here, nor the poly(pyrazolyl) borate compounds which were the subject of a recent review.[3] The hydride, borohydride, and aluminohydride complexes of the f-elements have been considered in some more general reviews or monographs covering the chemistry of lanthanides and actinides; the most recent are those of Edelmann,[4] Schumann,[5] Soloveichik,[6] Schaverien,[7] Bochkarev,[8] and Ephritikhine.[9]

II. Synthetic Routes to Homonuclear Lanthanide Hydrides

While reaction of lanthanide elements with hydrogen afforded the metal-like solids of general formula LnH_x which can be regarded as interstitial compounds,[10] no molecular lanthanide hydride was prepared by oxidative addition of H_2 to the metal center. Coordination of H_2 to $Cp*_2Eu$ in C_6D_{12} was detected spectroscopically;[2] in that case, oxidation of Eu(II) is unlikely. The lanthanide hydrides LnH_x have not been used for the preparation of molecular complexes.

Michel Ephritikhine was born in Algiers, Algeria, in 1947. He obtained his Ph.D. in organic chemistry in 1974 at the University of Paris under the supervision of J. Levisalles. His postdoctoral work with M. L. H. Green in Oxford confirmed his interest in organometallic and inorganic chemistry. From 1976 to 1984, he was in the group of H. Felkin in Gif sur Yvette where he studied the chemistry of rhenium polyhydrides and the C−H bond activation of alkanes. In 1984, he joined the Commissariat à l'Energie Atomique in Saclay to work on uranium chemistry. He presently holds the position of Research Director in the CNRS.

A. Insertion of Zerovalent Metals into Carbon−Hydrogen Bonds

Reactions of zerovalent samarium and erbium with neutral unsaturated hydrocarbons provided the first evidence for the existence of organolanthanide hydrides. The various products, which were quite unstable, could not be properly characterized, and the presence of hydride ligands was revealed only by decomposition reactions with CCl_4 or H_2O. Thus, cocondensation of samarium metal vapor with pentamethylcyclopentadiene afforded, after extraction in THF, a solid which analyzed for $Cp*SmH(THF)_2$, the product expected from simple oxidative addition of C_5Me_5H to samarium; the latter was readily transformed in THF into $Cp*_2Sm(thf)_2$.[11] Samarium and erbium also reacted with 1-hexyne to form trivalent alkynide hydrides, the formula of which might be better represented as $[Ln(C_6H_9)_{2-x}(C_6H_8)_xH_{1-x}]_n$ ($0 < x < 0.5$) to account for the increased amount of dimetalation with these metals; similar reaction of ytterbium gave the divalent hydride $[Yb(C_6H_9)_{1.5}H_{0.5}]_n$ as the primary product.[12] Reactions of the above metals with ethylene, propene, or 1,2-propadiene are even more complicated; the presence of hydride moieties indicates that metal insertion into C−H bonds is an important reaction, but cleavage of carbon−carbon multiple bonds, homologation, oligomerization, and dehydrogenation are also observed.[13] This approach to organolanthanide hydrides, envisaged about 1980, has not been developed.

B. Reactions of Halide Complexes with $MAlH_4$ (M = Li or Na) or NaH

Reactions of transition metal halide compounds with MBH_4 (M = alkali metal) constitute a classical route to hydride derivatives. This way was not used for the synthesis of f-element hydrides because the first formed borohydrides are generally quite stable, being resistant to BH_3 elimination. Aluminohydrides dissociate AlH_3 more easily and a few organolanthanide hydrides have been synthesized by treating chloride precursors with $LiAlH_4$ or $NaAlH_4$ (eqs 1−4).

With the exception of $[(1,3-^tBu_2-C_5H_3)_2LuH]_2$ which was readily obtained by decomposition of $(1,3-^tBu_2-$

$$2(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2LuCl \xrightarrow[\text{in Et}_2O-\text{pentane}]{\text{LiAlH}_4} $$
$$[(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2LuH]_2 \quad (1)$$

$$2(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2LnCl \xrightarrow[\text{in THF}]{\text{NaAlH}_4,\ \text{NEt}_3} $$
$$[(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2LnH]_2 \quad (2)$$

$$Ln = Ce,\ Sm$$

$$[(C_5H_4CH_2CH_2OMe)_2YCl]_2 \xrightarrow[\substack{\text{in toluene}-\text{pentane}}]{\substack{(1)\ \text{LiAlH}_4 \\ (2)\ \text{NEt}_3,\ 50\ ^\circ\text{C}}} $$
$$[(C_5H_4CH_2CH_2OMe)_2YH]_2 \quad (3)$$

$$3Cp_2LuCl \xrightarrow[\text{in C}_6H_6-\text{Et}_2O]{\text{LiAlH}_4,\ \text{NEt}_3} (Cp_2LuH)_3 \quad (4)$$
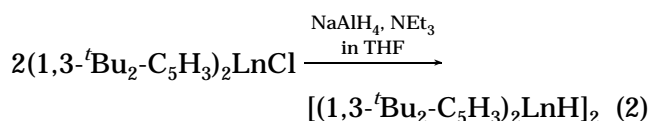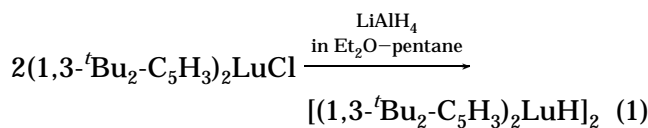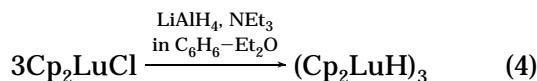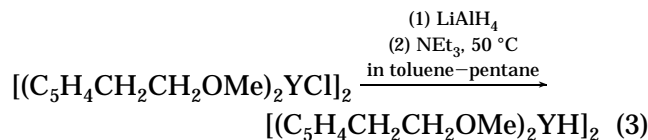
$C_5H_3)_2LuAlH_4$ (eq 1),[14] the other hydrides synthesized according to eqs 2−4 could be isolated only by using an excess of triethylamine.[15,16] Treatment of the chlorides $[(C_5H_4CH_2CH_2OMe)_2YCl]_2$[15] and $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2LnCl$ (Ln = Ce, Sm)[16] with $LiBH_4$ gave the corresponding borohydrides which were not transformed into the hydrides in the presence of NEt_3. Formation of the trimer $(Cp_2LuH)_3$ in benzene−diethyl ether was not reproducible and was accompanied with that of $[Cp_2LuH \cdot NEt_3]_2$.[17]

The THF adduct $[Cp_2LuH \cdot THF]_2$ was obtained by treating $Cp_2LuCl(THF)$ with NaH in tetrahydrofuran (eq 5).[18,19] The hydrides $[\{(C_5H_4CH_2CH_2)_2O\}LnH]_2$ (Ln = Y, Gd, Er, Yb, Lu)[20] and $[(C_5H_4CH_2CH_2OMe)_2LnH]_2$ (Ln = Y, La, Pr, Ho)[21] were similarly synthesized from their chloride precursors (eqs 6 and 7). It is interesting to note that $[Me_2Si(C_5H_4)_2YbCl]_2$ was transformed into the hydrido-chloride complex $[\{Me_2Si(C_5H_4)_2Yb(THF)\}_2(\mu\text{-H})(\mu\text{-Cl})]$ which was inert towards an excess of NaH (eq 8).[22]

$$2Cp_2LuCl(THF) \xrightarrow{\text{NaH, THF}} [Cp_2LuH \cdot THF]_2 \quad (5)$$

$$[\{(C_5H_4CH_2CH_2)_2O\}LnCl]_2 \xrightarrow{\text{NaH, THF}} $$
$$[\{(C_5H_4CH_2CH_2)_2O\}LnH]_2 \quad (6)$$

$$Ln = Y,\ Gd,\ Er,\ Yb,\ Lu$$

$$[(C_5H_4CH_2CH_2OMe)_2LnCl]_2 \xrightarrow{\text{NaH, THF}} $$
$$[(C_5H_4CH_2CH_2OMe)_2LnH]_2 \quad (7)$$

$$Ln = Y,\ La,\ Pr\ \text{and}\ Ho$$

$$[Me_2Si(C_5H_4)_2YbCl]_2 \xrightarrow{\text{NaH, THF}} $$
$$[\{Me_2Si(C_5H_4)_2Yb(THF)\}_2(\mu\text{-H})(\mu\text{-Cl})] \quad (8)$$

C. Other Syntheses of Organolanthanide Hydrides by Using NaH, Na, or AlH$_3$

The following are three examples of preparations (depicted by eqs 9−11) each one appears to be unique in its type:
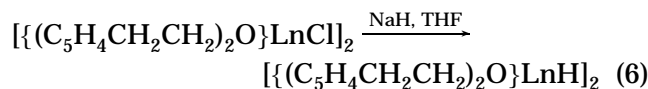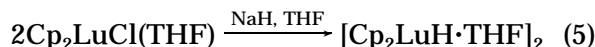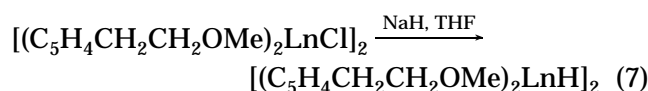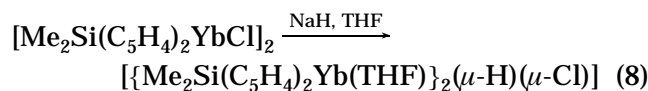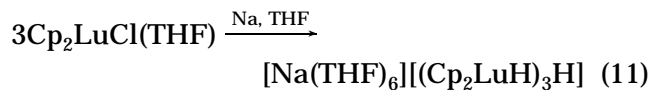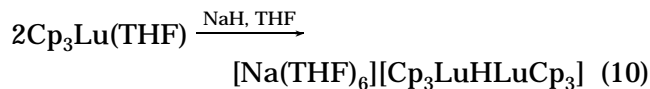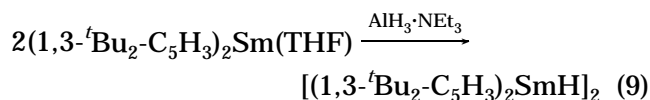
$$2(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2Sm(THF) \xrightarrow{\text{AlH}_3 \cdot \text{NEt}_3} $$
$$[(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2SmH]_2 \quad (9)$$

$$2Cp_3Lu(THF) \xrightarrow{\text{NaH, THF}} $$
$$[Na(THF)_6][Cp_3LuHLuCp_3] \quad (10)$$

$$3Cp_2LuCl(THF) \xrightarrow{\text{Na, THF}} $$
$$[Na(THF)_6][(Cp_2LuH)_3H] \quad (11)$$

The oxidation reaction (eq 9) has been shown to involve samarium(III) aluminohydride intermediates.[16] Formation of the anion $[Cp_3LuHLuCp_3]^-$ by addition of NaH to $Cp_3Lu(THF)$ was straightforward[23] and it is surprising that such an approach to lanthanide hydrides has not been further developped, in view of the easy formation of anionic "ate" complexes in f-element chemistry. The synthesis of the neodymium analogue $[Cp_3NdHNdCp_3]^-$, by treatment of Cp_2NdCl_2Li with sodium methylnaphtalide has been briefly reported;[24] the mechanism of this reaction, and also that of eq 11 leading to the trinuclear anion $[(Cp_2LuH)_3H]^-$ [23] have not been clarified.

D. β-Hydrogen Elimination Reactions of Alkyl Compounds

The β-hydride elimination is a transformation of great importance in organometallic chemistry, being an essential step in many catalytic cycles and a practical route to a number of transition metal hydrides. However, this reaction appeared much less facile with alkyl compounds of the f-elements. Thermochemical studies indicated that for lanthanides and actinides, β-hydride elimination would be significantly more endothermic than for middle or late transition metals.[25] While *tert*-butyl compounds of the transition metals are rare because of their instability towards β-H elimination, such complexes of the lanthanides could be more easily isolated.

Thermal decomposition of the lutetium complex $Cp_2Lu(^{t}Bu)(THF)$ required 75 °C in toluene, whereas the erbium and yttrium analogues decomposed at 20 °C overnight (eq 12); this different behavior can be correlated with the metallic radius and hence coordinative saturation.[26] These transformations were not clean, the yields of the hydrides being about half those of the hydrogenolysis reactions (*vide infra*); in particular, it was shown that $[Cp_2LuH]_2$ reacted with its *tert*-butyl precursor to give Cp_3Lu and tertiobutane.[18]

$$2Cp_2Ln(^{t}Bu)(THF) \rightarrow $$
$$[Cp_2LnH]_2 + 2CH_2{=}CMe_2 \quad (12)$$

$$Ln = Y,\ Er,\ Lu$$

The solvent plays an important role in these reactions. Thus, treatment of Cp_2LuCl with $^{t}BuLi$ in diethyl ether instead of THF readily afforded the trinuclear anion $[(Cp_2LuH)_3H]^-$, isolated in 12% yield (eq 13);[26] the diethyl ether molecule in $Cp_2Ln(^{t}Bu)(Et_2O)$ is more labile than THF and its dissociation provides a free coordination site for β-H elimination. The yttrium complex $[Li(THF)_4][(Cp_2YH)_3H]$ was

Scheme 1. Transition State for the β-Hydrogen Elimination Reaction
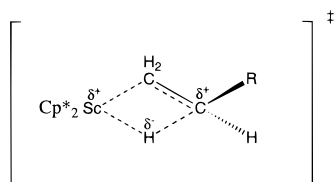
subsequently synthesized in 75% yield by treating [Cp$_2$YH(THF)]$_2$ with ^{t}BuLi, with Cp$_2$Y(^{t}Bu)(THF) and Cp$_3$Y(THF) as byproducts.[27] However, reaction of [Cp$_2$YD(THF)]$_2$ with ^{t}BuLi gave the perdeuterio product [Li(THF)$_4$][(Cp$_2$YD)$_3$D], indicating that the *tert*-butyl group did not provide an H$^-$ ion for the trimer. Formation of the trimetallic hydride could be explained by the reaction of [Cp$_2$YH(THF)]$_2$ with the anionic dihydride intermediate [Cp$_2$YH$_2$]$^-$.

$$3Cp_2LuCl \xrightarrow[\text{(2) THF}]{\text{(1) }^t\text{BuLi in Et}_2\text{O}}$$

$$[Li(THF)_4][(Cp_2LuH)_3H] \quad (13)$$
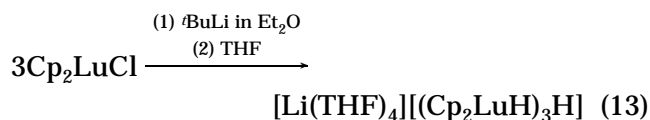
The course of the β-hydrogen elimination reaction can also be modified by the presence of small amount of LiCl, which is the byproduct of the synthesis of the alkyl complex. The trinuclear anion [(Cp$_2$-ErH)$_3$Cl]$^-$ was formed by heating Cp$_2$Er(^{t}Bu)(THF) in toluene in the presence of LiCl (eq 14).[26]

$$3Cp_2Er(^tBu)(THF) \xrightarrow{\text{LiCl}}$$

$$[Li(THF)_4][(Cp_2ErH)_3Cl] \quad (14)$$

The isobutyl derivatives Cp$_2$Ln(^{i}Bu)(THF) also decomposed into the corresponding hydrides;[28] in the case of Cp*$_2$Lu(^{i}Bu),[29,30] the rate constant of β-H elimination (5×10^{-5} s^{-1}) is much less than that of β-alkyl elimination (1.5×10^{-4} s^{-1}).

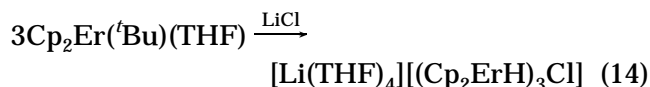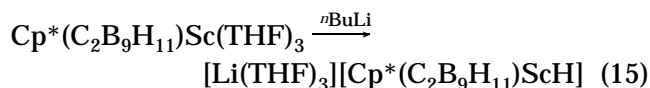The anionic scandium hydride [Li(THF)$_3$][Cp*-(C$_2$B$_9$H$_{11}$)ScH] was isolated in 30% yield from the reaction of Cp*(C$_2$B$_9$H$_{11}$)Sc(THF)$_3$ with *n*-butyllithium (eq 15); here again, the hydrogenolysis route is more interesting, giving the product in quantitative yield.[31]

$$Cp*(C_2B_9H_{11})Sc(THF)_3 \xrightarrow{^n\text{BuLi}}$$

$$[Li(THF)_3][Cp*(C_2B_9H_{11})ScH] \quad (15)$$

It should be noted here that scandium alkyl complexes of general formula Cp*$_2$ScCH$_2$CH$_2$R reacted with 2-butyne to give the alkenyl product Cp*$_2$-ScCMe=CMeH, resulting from addition of the hydride Cp*$_2$ScH to the alkyne. These reactions allowed measurement of the β-hydrogen elimination rates and determination of the activation parameters. The data are on agreement with a four-centered transition state (Scheme 1), with partial positive charge at the β carbon; the hydrogen would be transferred to the metal as H$^-$ and its transfer would precede Sc–C bond cleavage.[32]

E. Synthesis of Hydrocarbyl–Hydride and Alkoxy–Hydride Complexes from Their Hydride Precursors

A series of complexes with both bridging Et$_2$Si(C$_5$-Me$_4$)(C$_5$H$_4$), alkyl, and hydride ligands, Ln$_2$[μ-Et$_2$Si-(C$_5$Me$_4$)(C$_5$H$_4$)]$_2$(μ-H)(μ-R) (Ln = Lu and R = Et, ^{n}Pr or ^{n}Hex; Ln = Y and R = Et or ^{n}Pr) were synthesized by reacting the corresponding dimeric hydrides with α-olefins.[33]

The yttrium hydride [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)YH]$_2$ was similarly transformed into a series of μ-alkyl derivatives [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)Y]$_2$(μ-H)(μ-CH$_2$CH$_2$R) (R = H, Me, Et, ^{n}Bu) and the μ-acetylide [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)Y]$_2$(μ-H)(μ-C≡CSiMe$_3$).[34,35]

Hydride complexes can undergo σ-bond metathesis with C–H bonds to give either H/H exchange or metalation (*vide infra*). Thus were synthesized the internally metalated compounds Cp*$_2$Ln(μ-H)(μ-CH$_2$C$_5$Me$_4$)LnCp*, by thermolysis of the bispentam-ethylcyclopentadienyl lanthanide hydrides [Cp*$_2$-LnH]$_2$ (Ln = Y, Sm).[36–38]

The three μ_2 hydrides of the yttrium complex [Li(THF)$_4$][(Cp$_2$YH)$_3$H] were successively substituted with methanol, with eventual formation of [Li(THF)$_3$]$_2$-[(Cp$_2$YOMe)$_3$H]$_2$.[39]

These syntheses will be presented again in the paragraphs concerning the reactions of the hydrides.

F. Hydrogenolysis of Alkyl Complexes

Hydrogenolysis of alkyl compounds is by far the most common route to lanthanide hydrides and all those which will be presented from here have been synthesized by this method. The hydrogenolysis reaction, a particular case of σ-bond metathesis reaction, has been the subject of many experimental and theoretical studies;[40] it is generally recognized that this process is concerted and involves a four-center heterolytic transition state (eq 16).
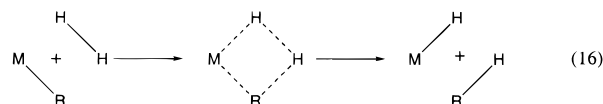
The first isolated molecular lanthanide hydrides [(C$_5$H$_4$R)$_2$LnH(THF)]$_2$ (Ln = Y, Er, Lu; R = H or Me) were synthesized according to eq 17.[41]

$$2(C_5H_4R)_2Ln(^tBu)(THF) + H_2 \rightarrow$$

$$[(C_5H_4R)_2LnH(THF)]_2 + 2^tBuH \quad (17)$$

$$Ln = Y, Er, Lu$$
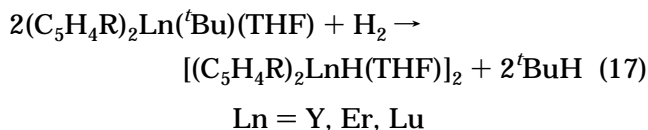
The reaction is very dependent on small changes in the size of the metal, the size of the ligands, in particular that of the alkyl group, and the coordinating ability of the solvent.[41,42] These effects can be explained by the more or less difficult access to a monomeric, unsolvated, and coordinatively unsaturated species. For example, Cp$_2$Y(^{t}Bu)(THF) did not react with H$_2$ in THF but was transformed into the corresponding hydride in toluene; in this solvent, dissociation of THF occurred more easily, to give the active species Cp$_2$Y(^{t}Bu). In contrast, the bridged dimer [Cp$_2$YMe]$_2$ was inert toward hydrogen in toluene, whereas Cp$_2$Y(Me)(THF) was hydrogeno-lyzed in THF and even more rapidly in mixed 1:10 THF/alkane or 1:10 THF/arene solvents; in this case, the presence of a small amount of THF would effect a bridge cleavage leading to Cp$_2$Y(Me)(THF) and Cp$_2$Y(Me) which is the more active species. Replace-ment of the Me ligand by CH$_2$SiMe$_3$, which is not as

bulky as ^tBu, did not stop the hydrogenolysis reaction. The reactivity of $Cp_2Ln(Me)(THF)$ also differs markedly with Ln since the complexes of Y and Er are hydrogenolyzed in THF but not those of Lu and Yb.[42]

The presence of alkali salts has also an influence on the hydrogenolysis reaction; thus, $(Cp_2YMe)_2$ reacted with H_2 in the presence of LiCl to give the trinuclear compound $[Li(THF)_4][(Cp_2YbH)_3H]$.[42]

After these first observations, most of the lanthanide hydrides have been synthesized by hydrogenolysis of $[Ln]$-CH_2TMS or $[Ln]$-$CH(TMS)_2$ complexes in alkane or arene solvents. These sterically bulky and highly lipophilic alkyl groups prevent the undesirable coordination of ether molecules or halide ligands during the preparation of the alkyl complexes; they also impede some possible decomposition reactions via β-H or β-alkyl elimination.

III. Classification and Structure of the Homonuclear Lanthanide Hydrides

With the exception of $[YbH_2(THF)]_n$[43] and $[\{p\text{-}X\text{-}C_6H_4C(NSiMe_3)_2\}_2YH]_2$ (X = H, OMe)[44,45] the molecular lanthanide hydrides are cyclopentadienyl complexes. These have been characterized by the classical spectroscopic methods (IR, RMN, RX). Infrared bands in the region 1350 and >1400 cm^{-1} were assigned to Ln$-\mu$H$-$Ln and terminal Ln$-$H vibrations respectively, by evaluating the isotope shift of deuterated analogues. The nuclear spin momentum of yttrium ($I = 1/2$, monoisotopic) is a very important tool in the interpretation of the NMR spectra since first and second order couplings with the nuclei bonded to the metal are observed. The ^{89}Y NMR spectra of $[(C_5H_4Me)_2YH(THF)]_2$ and $[Li(THF)_4][(Cp_2$-YH)$_3$H] exhibited signals at -92 and -67 ppm relative to YCl_3 in H_2O.[46] The complexes have been widely studied by crystallography, despite the principal difficulty to locate hydrogen atoms by this method.

The homonuclear lanthanide hydrides and their characterization are listed in Table 1.

A. Lanthanide Hydrides without Cyclopentadienyl Ligands

The exact structure of $[YbH_2(THF)]_n$ is not known; a few broad bands at ca 1250 cm^{-1} were attributed to stretching of Yb$-$H$-$Yb bridges.[43]

The only well-characterized molecular lanthanide hydrides without cyclopentadienyl ligand are the bis-(trimethylsilyl)benzamidinate yttrium compounds $[\{p\text{-}X\text{-}C_6H_4C(NSiMe_3)_2\}_2YH]_2$ (X = H, OMe);[44,45] the dimeric crystal structure (X = H)[45] (Figure 1) is retained in solution, as shown by the triplet hydride resonance in the ^{1}H NMR spectra.

B. Monocyclopentadienyl Hydrides

Only a few monocyclopentadienyl lanthanide hydrides have been described.

The crystal structure of the scandium complex $[Me_2Si(C_5Me_4)(\eta^1\text{-}N^tBu)Sc(PMe_3)H]_2$ has been briefly reported.[47,48] This dimer is partially dissociated in solution, as shown by the ^{31}P NMR spectrum.

The dinuclear structures of $[Cp^*(O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3)YH]_2$ and of its derivatives $[Cp^*(O\text{-}2,6\text{-}^tBu_2$-
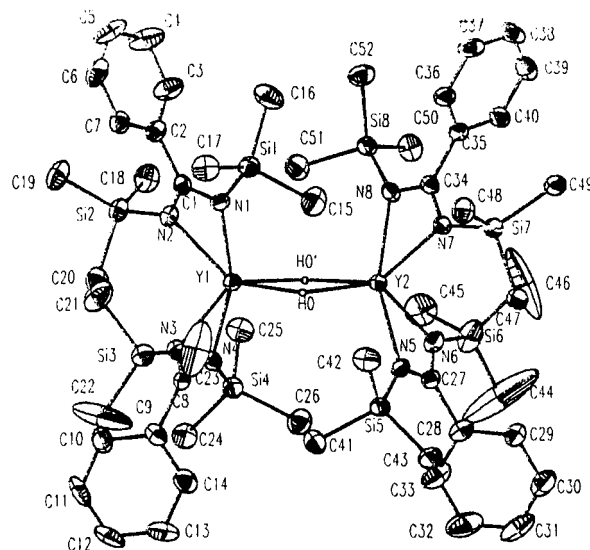
Figure 1. Crystal structure of $[\{PhC(NSiMe_3)_2\}_2YH]_2$. (Reprinted from ref 45. Copyright 1996 American Chemical Society.)

$C_6H_3)Y]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)$ (R = H, Me, Et, ^nBu) and the μ-acetylide $[Cp^*(O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3)Y]_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)$ were, here again, indicated by the diagnostic triplet ^{1}H NMR signal of the hydride ligand.[34,35]

The scandium hydride $[Li(THF)]_2[Cp^*(C_2B_9H_{11})\text{-}ScH]_2$ was characterized by its crystal structure which indicates that the two anionic $[Cp^*\text{-}(C_2B_9H_{11})ScH]^-$ fragments held together by reciprocal β-H dative bonding from the dicarbollide ligand to the electron deficient scandium.[31]

C. Biscyclopentadienyl Hydrides

1. Mononuclear Compounds

While the complexes $Cp^*_2LnH(THF)$ can be simply prepared by dissolving the dimers $[Cp^*_2LnH]_2$ in THF, only the scandium[49−51] and yttrium[52] derivatives have been reported; none was characterized by crystallography. The scandium complex is more convenient to use than $[Cp^*_2ScH]_n$ which is unstable in solution in the absence of an atmosphere of H_2 (*vide infra*). In the ^{1}H NMR spectrum of Cp^*_2YH-(THF), the hydride signal appears as a doublet with $J_{YH} = 81.74$ Hz. The two scandium hydrides (C_5-$Me_5)(C_5H_2Me_3)Sc(PMe_3)H$ and $Me_2Si(C_5Me_4)_2Sc$-(PMe$_3$)H have been reported in a review.[51]

2. Dimeric Complexes

The dimeric complexes in which each metal is surrounded by two bridging hydrides and two cyclopentadienyl ligands are the most common in the series of lanthanide hydrides. The compounds $[Cp^*_2$-LnH]$_2$ are known for Ln = Y,[37,52,53] La,[54] Ce,[55,56] Nd,[54,57] Sm,[54,58,59] and Lu.[54] The exact molecularity of the unstable scandium derivative $[Cp^*_2ScH]_n$ is unknown; this compound is however a valuable synthetic reagent when prepared *in situ*.[49,50] The IR spectra of the complexes $[Cp^*_2LnH]_2$ exhibit Ln$-$H$-$Ln vibrations between 1120 and 1270 cm^{-1}, typically 1140 cm^{-1}. Only the samarium derivative was crystallographically characterized, but the hydride ligands were not located (Figure 2); one Cp^*_2Sm unit is rotated with respect to the other such that the molecule possesses a pseudo S_4 axis coincident with

Table 1. Homonuclear Lanthanide Hydrides and Their Characterization

complexes	analyses[a]	infrared data[b]	¹H NMR data[c]	X-ray diffraction data[d]	ref(s)
		Complexes without Cyclopentadienyl Ligands			
[YbH$_2$(THF)]$_n$	C,H,Yb	1250 (890)			43
[{PhC(NSiMe$_3$)$_2$}$_2$YH]$_2$	C,H,Y	1300, 1257, 1246	benzene-d_6: 8.26 (t, 27.6)	Y−H 2.19(3), 2.17(3)	45
[{p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$}$_2$YH]$_2$			benzene-d_6: 8.31 (t, 27.8)		
		Monocyclopentadienyl Complexes			
[Me$_2$Si(C$_5$Me$_4$)(η^1-N^{t}Bu)Sc(PMe$_3$)H]$_2$	C,H,N	1152 (~815)	toluene-d_8: 4.45 (br)	H···H′ 2.13(4)	47,48
[Cp*(O-2,6-^{t}Bu$_2$C$_6$H$_3$)YH]$_2$	C,H,Y		benzene-d_6: 5.64 (t, 35.2)		
[Cp*(O-2,6-^{t}Bu$_2$C$_6$H$_3$)Y]$_2$(μ-H) (μ-CH$_2$CH$_2$R)					34
R = H	C,H		benzene-d_6: 5.35 (t, 41.2)		34
R = Me	C,H		5.30 (t, 39.5)		34
R = Et			5.27 (t, 40)		34
R = ^{n}Bu	C,H		5.33 (t, 40.2)		34
R = C≡CSiMe$_3$	C,H		5.09 (t, 37)		34
[Li(THF)]$_2$[Cp*(C$_2$B$_9$H$_{11}$)ScH]$_2$	C,H		benzene-d_6: 5.23 (br)	Sc−H(B) 2.19, 2.17	31
		Biscyclopentadienyl Complexes			
Cp*$_2$ScH(THF)	C,H	1390 (990)	toluene-d_8 (−95 °C): 73 (calculated)		49
Cp*$_2$YH(THF)	C,H	1295 (920)	benzene-d_6: 6.17 (d, 81.74)		52
[Cp*$_2$ScH]$_n$	unstable				49
[Cp*$_2$YH]$_2$	C,H	1272 (920), 655 (465)	toluene-d_8: 5.45 (t, 37.5)		37,52
[Cp*$_2$LaH]$_2$	C,H,La	1120 (800), 940 (660), 750 (510)	benzene-d_6: 10.21		54
[Cp*$_2$CeH]$_2$	C,H,Ce	1120 (795), 940 (660), 770 (540)	cyclohexane-d_{12}: 168 (br)		55
[Cp*$_2$NdH]$_2$	C,H,Nd	1135 (810)	not located		54
[Cp*$_2$SmH]$_2$	Sm	1140 (820)	benzene-d_6: 15.61 (br)	Sm···Sm 3.905 (3)	54,58
[Cp*$_2$LuH]$_2$	cryoscopy	1345 (970), 1100 (860), 650 (420)	cyclohexane-d_{12}: 9.11		54
[(1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$CeH]$_2$	Ce	1130		Ce−H 2.52, 2.64	16
[(1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$SmH]$_2$	Sm	1150		Sm−H 1.80, 2.75	16
[(1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$LuH]$_2$	Lu	1280 (930), 1090 (785), 820 (590)		Lu−H 2.27, 2.32	14,16
[Me$_2$Si(C$_5$Me$_4$)$_2$NdH]$_2$	C,H,Si,Nd	1122 (830)	not located		61
[Me$_2$Si(C$_5$Me$_4$)$_2$SmH]$_2$	C,H,Si,Sm	1125 n	toluene-d_8: 5.34 (br)		61
[Me$_2$Si(C$_5$Me$_4$)$_2$LuH]$_2$	C,H	1120 (820)	toluene-d_8: 9.25		61
[Me$_2$Si(C$_5$H$_3$-3-^{t}Bu)$_2$ScH]$_2$	C,H		not located		62
[Me$_2$Si(C$_5$Me$_4$)$_2$Y]$_2$(μ-H)$_2$	unstable		benzene-d_6: 5.29 (t, 33.3)		63
Y$_2$[μ-(C$_5$Me$_4$)SiMe$_2$(C$_5$Me$_4$)]$_2$[μ-H]$_2$	C,H		benzene-d_6: 3.87 (t, 34.4)		63
[Me$_2$Si(C$_5$H$_2$-2-TMS-4-^{t}Bu)$_2$YH]$_2$			4.87 (t, 31)		64
[Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)YH]$_2$, R* = (+)-neomenthyl			benzene-d_6: 4.28 (t, 32)		65
[(R,S)-(BnBp)Y]$_2$(μ-H)$_2$ and enantiomer homochiral dimer	C,H		benzene-d_6: 4.98 (t, 31.4)		66
[(R,S)-(BnBp)Y](μ-H)$_2$[Y(S,R)-(BnBp)] and enantiomer homochiral dimer	C,H		benzene-d_6: 5.97 (t, 31.4)		66
Lu$_2$[μ-Et$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)][μ-H]$_2$	C,H	1230 (882), 926 (661), 650 (480)	toluene-d_8: 5.87	Lu−H 2.13(4), 2.16(4) Lu···Lu 3.390(1)	33
Lu$_2$[μ-Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)][μ-H]$_2$	C,H,Lu	superimposable	benzene-d_6: 5.92		33
Y$_2$[μ-Et$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)][μ-H]$_2$		superimposable	benzene-d_6: 3.03 (t, 35.3)		33
[Cp$_2$YH(THF)]$_2$	Y	1315 (945)	THF-d_8: 2.02 (t, 27)		41
[Cp$_2$ErH(THF)]$_2$	Er	1330 (960)			41
[Cp$_2$LuH(THF)]$_2$	Lu	1345 (970), 945 (677), 687 (485)	THF-d_8: 4.69	Lu−H 1.99(21), 2.10(21)	41,19,23
[Cp$_2$YbH(THF)]$_2$	Yb	1350 (920)	not located		42
[(C$_5$H$_4$Me)$_2$YH(THF)]$_2$		1240 (900)	THF-d_8: 2.31 (t, 27.2)	Y−H 2.17(8), 2.19(8)	41
[(C$_5$H$_4$Me)$_2$ErH(THF)]$_2$		1300			41
[(C$_5$H$_4$Me)$_2$LuH(THF)]$_2$	Lu	1340 (960)	THF-d_8: 4.99		41
[(1,3-Me$_2$C$_5$H$_3$)$_2$YH(THF)]$_2$	Y	1100−1300	THF-d_8: 2.82 (t, 28)	Y−H 2.03(7), 2.27(6)	68
[(CH$_2$)$_3$(C$_5$H$_4$)$_2$YH(THF)]$_2$	C,H,Y	1302	THF-d_8: 2.16 (t, 23.8)		69
[(CH$_2$)$_3$(C$_5$H$_4$)$_2$DyH(THF)]$_2$	C,H,Dy	not assigned			69
[(CH$_2$)$_3$(C$_5$H$_4$)$_2$ErH(THF)]$_2$	C,H,Er	not assigned			69
[(CH$_2$)$_3$(C$_5$H$_4$)$_2$LuH(THF)]$_2$	C,H,Lu	not assigned	THF-d_8: 4.02		69
[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$YH]$_2$	C,H,Y	not assigned	THF-d_8: 2.57		20
[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$GdH]$_2$	C,H,Gd	not assigned			20
[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$ErH]$_2$	C,H,Er	not assigned			20
[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$LuH]$_2$	C,H,Lu	not assigned	THF-d_8: 4.50		20
[(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$YH]$_2$	C,H,Y	not assigned	benzene-d_6: 1.85 (t, 28)	Y−H 2.02(6)−2.15(6)	21
[(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$LaH]$_2$	C,H,La	not assigned	benzene-d_6: 6.86		21
[(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$PrH]$_2$	C,H,Pr	not assigned			21
[(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$HoH]$_2$					21

Table 1. (Continued)

complexes	analyses[a]	infrared data[b]	¹H NMR data[c]	X-ray diffraction data[d]	ref(s)
[Me₂Si(C₅H₄)₂Yb(THF)]₂(μ-H)(μ-Cl)				Yb−H 1.903(4), 2.10(3)	22
Lu₂[μ-Et₂Si(C₅Me₄)(C₅H₄)]₂(μ-H)(μ-Et)	C,H	1273 (920)	toluene-d₈: 5.02	Lu···Lu 3.392(1)	33
Lu₂[μ-Et₂Si(C₅Me₄)(C₅H₄)]₂(μ-H)(μ-ⁿPr)					33
Lu₂[μ-Et₂Si(C₅Me₄)(C₅H₄)]₂(μ-H)(μ-ⁿHex)	C,H	1282	toluene-d₈: 5.19		33
Y₂[μ-Et₂Si(C₅Me₄)(C₅H₄)]₂(μ-H)(μ-Et)			toluene-d₈: 2.34 (t, 38.4)		33
Y₂[μ-Et₂Si(C₅Me₄)(C₅H₄)]₂(μ-H)(μ-ⁿPr)		1275	toluene-d₈: 2.40 (t, 38.2)		33
Cp*₂Y(μ-H)(μ-CH₂C₅Me₄)YCp*	C,H,Y	1260	cyclohexane-d₁₂: 3.66 (dd, 29 and 48)	Y−H 2.10(7), 2.14(7)	37
Cp*₂Sm(μ-H)(μ-CH₂C₅Me₄)SmCp*	C,H,Sm	1160	not located	Sm−H 2.05(11), 2.11(9)	36
[(1,3-Me₂C₅H₃)₂YH]₃	Y	1450 (1015)	benzene-d₆: 1.98 (overlap)	Y···Y 4.10(1)	68
[Cp₂LuH]₃				Lu−μ₂-H 1.56(5), 2.13(5) Lu−μ₃-H 1.86(5), 2.22(5)	17
[Li(THF)₄][(Cp₂YH)₃H]	C,H,Y,Li	1305 (930), 1170 (835), 850 (605), 667 (475)	THF-d₈: 0.75 (m, μ₂-H), −1.03 (m, μ₃-H)		27
[Li(THF)₄][(Cp₂YbH)₃H]	C,H,Yb,Li	1210 (850)	not located		42
[Li(THF)₃][(Cp₂LuH)₃H]	C,H,Lu,Li	1205	THF-d₈ (500 MHz): 1.83 (q, 7.8, μ₂-H), 3.93 (d, 7.8, μ₃-H)		26
[Na(THF)₆][(Cp₂LuH)₃H]	C,H,Lu	1245	THF-d₈ (80 MHz): 3.95 (d, 7)		23
[Li(THF)₃]₂[(Cp₂YOMe)₃H]₂	Y	1335, 1170	THF-d₈: 0.30 (q, 18.4, μ₃-H)	Y···Y 3.75(1)−3.78(1)	39
M[Cp₂Y(μ-H)]₂[Cp₂Y(μ-OMe)][μ₃-H], M = Li(THF)₄	Y	1305, 1175	THF-d₈: −0.45 (m, μ₃-H), 0.99 (td, μ₂-H)		39
M[Cp₂Y(μ-H)][Cp₂Y(μ-OMe)]₂[μ₃-H], M = Li(THF)₄	Y	1320, 1160	THF-d₈: −0.46 (qd, μ₃-H), 1.13 (td, μ₂-H)		39
[Li(THF)₄][(Cp₂ErH)₃Cl]		1250, 1200		Er−μ₂-H 1.99−2.54 Er−μ₃-H 2.02−2.39	26
Triscyclopentadienyl Complexes					
[Na(THF)₆][Cp₃LuHLuCp₃]·2THF	not assigned	not located		Lu−H 2.09	23
[Li(DME)₃][Cp₃NdHNdCp₃]				Nd−H 2.190	24

[a] Elements which have been analyzed. [b] Ln−H (Ln−D) IR vibrations in cm⁻¹. [c] Chemical shifts δ (multiplicity, coupling constants in Hz, assignment) of the hydride signal. [d] Distances in Å.
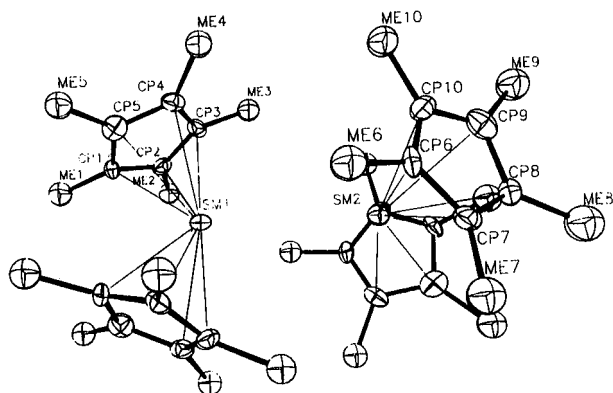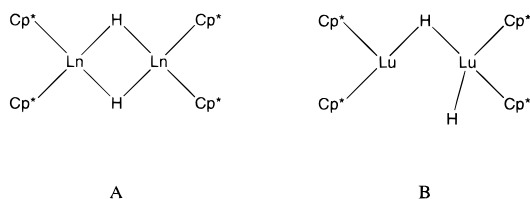

Figure 2. Crystal structure of [Cp*₂SmH]₂. (Reprinted from ref 58. Copyright 1983 American Chemical Society.)

the crystallographic C₂ axis.[58] These complexes are supposed to have a symmetric structure A in solution, as shown by the triplet NMR signal (J_{YH} = 37.5 Hz) corresponding to the hydride ligand in [Cp*₂YH]₂.[37] However, the IR spectrum (ν-Lu-H = 1345 cm⁻¹)[54] and the low temperature NMR spectra[30] revealed that the lutetium complex would adopt the asymmetric configuration B.

A   B

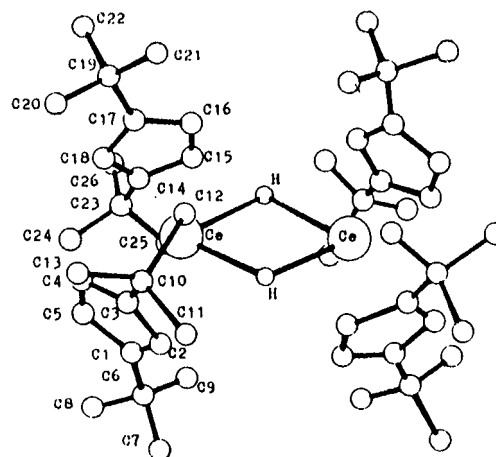The hydrides [(1,3-ᵗBu₂-C₅H₃)₂LnH]₂ (Ln = Ce, Sm, Lu) which, in contrast to their bis(pentamethylcy-

Figure 3. Crystal structure of [(C₅H₃ᵗBu₂)₂CeH]₂. (Reprinted from ref 16. Copyright 1992 Elsevier Science S.A.)

clopentadienyl) analogues, do not form adducts with Lewis bases such as THF, have been crystallographically characterized. The three centrosymmetrical dimers are isostructural. However, unlike the cerium[16] and lutetium[14] derivatives (Figure 3), the bridging hydride atoms in [(1,3-ᵗBu₂-C₅H₃)₂SmH]₂ protrude out of the bisector plane of the bent sandwich (1,3-ᵗBu₂-C₅H₃)₂Sm and the SmH₂Sm bridge is asymmetric;[16] the reasons for these differences are not clear.

Theoretical calculations using the extended Hückel method indicated that in the compounds [Cp*₂LnH]₂, symmetric hydride bridges are more stable than asymmetric ones. When the Cp₂Ln planes coincide, the Ln₂H₂ plane is perpendicular to the Cp₂Ln planes; when the Cp₂Ln planes are orthogonal, the Ln₂H₂ plane bisects them.[60]
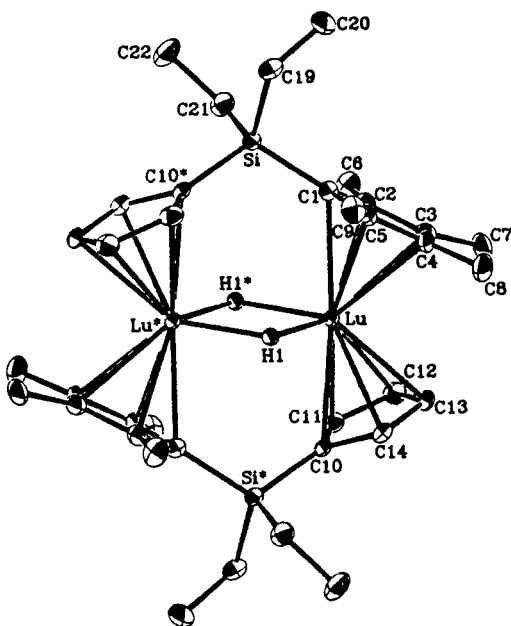
Figure 4. Crystal structure of $Lu_2[\mu\text{-}Et_2Si(C_5Me_4)(C_5H_4)]_2$-$[\mu\text{-}H]_2$. (Reprinted from ref 33. Copyright 1990 American Chemical Society.)

The hydride compounds of general formula $[Me_2Si(C_5H_{4-x}R_x)(C_5H_{4-x}R'_x)LnH]_2$ with chelating bis(cyclopentadienyl) ligands were expected to be more reactive than their $[Cp^*_2LnH]_2$ analogues, because of the opening of their coordination sphere. The dimeric structure of the complexes $[Me_2Si(C_5Me_4)_2LnH]_2$ (Ln = Nd, Sm, Lu)[61] was demonstrated by cryoscopy and mass spectrometry, and that of $[Me_2Si(C_5H_3\text{-}3\text{-}^tBu)_2ScH]_2$, by ebulliometry.[51,62] The yttrium hydride $[Me_2Si(C_5Me_4)_2Y]_2(\mu\text{-}H)_2$, initially formed by hydrogenolysis of $Me_2Si(C_5Me_4)_2YCH(SiMe_3)_2$, was unstable with respect to ligand redistribution and was slowly isomerized into $Y_2[\mu\text{-}(C_5Me_4)SiMe_2(C_5Me_4)]_2[\mu\text{-}H]_2$, in which both the hydride and $Me_2Si(C_5Me_4)_2$ ligands are in bridging position.[63] The yttrium complexes $[Me_2Si(C_5H_2\text{-}2\text{-}TMS\text{-}4\text{-}^tBu)_2YH]_2$[64] and $[Me_2Si(C_5Me_4)(C_5H_3R^*)YH]_2$ (R^* = (+)-neomenthyl)[65] are also dimers, as shown by the diagnostic triplet hydride signal (J_{YH} = $\sim$30 Hz) in the ^1H NMR spectra. The chiral hydrido species $[Me_2Si(C_5Me_4)(C_5H_3R^*)LnH]_2$ (Ln = Y, Nd, Sm, Lu) are, unlike the achiral compounds $[Cp^*_2LnH]_2$ and $[Me_2Si(C_5Me_4)_2LnH]_2$, thermally unstable in solution at ambient temperature; structure A has been assigned to these hydrides.[65] The new linked bis(cyclopentadienyl) ligand $(C_5H_3\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu)Si(OC_{10}H_6C_{10}H_6O)$ (BnBpH₂) was designed to coordinate to transition metals to afford a single enantiomeric C_2-symmetric ansametallocene.[66] Steric interactions between the 3 and 3' methyne positions of the 1,1'-binaphth-2,2'-diolate ring of the chiral linker with the α-SiMe₃ substituents on the cyclopentadienyl rings force enantioselective metalation of this ligand. Thus, the (S)-yttrocene (R,S)-(BnBp)YCl(THF) was obtained with the ligand prepared from (R)-(+)-1,1'-bi-2-naphthol. Hydrogenolysis of rac-(BnBp)YCH(SiMe₃)₂ gave a kinetic mixture of both heterochiral and homochiral dimers (R,S)-(BnBp)Y(μ-H)₂Y(S,R)-(BnBp) and (R,S)-(BnBp)Y(μ-H)₂Y(R,S)-(BnBp) which was converted after several hours into the pure homochiral dimers. The racemic dimer was characterized by its crystal structure.[66]
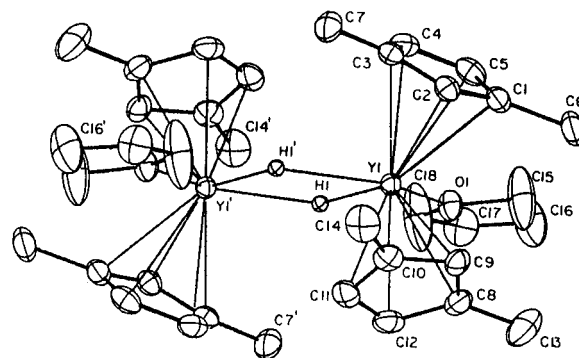

Figure 5. Crystal structure of $[(1,3\text{-}Me_2C_5H_3)_2YH(THF)]_2$. (Reprinted from ref 68. Copyright 1987 American Chemical Society.)

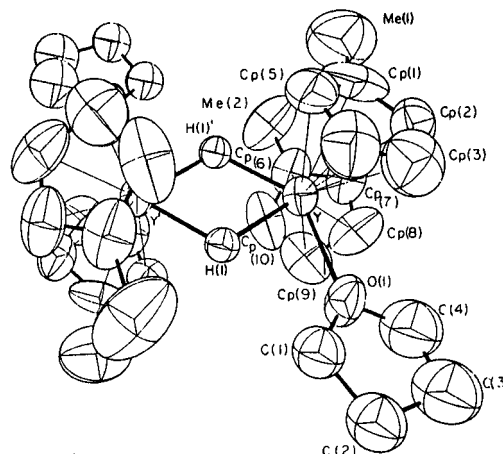**Figure 6.** Crystal structure of $[(C_5H_4Me)_2YH(THF)]_2$. (Reprinted from ref 41. Copyright 1982 American Chemical Society.)

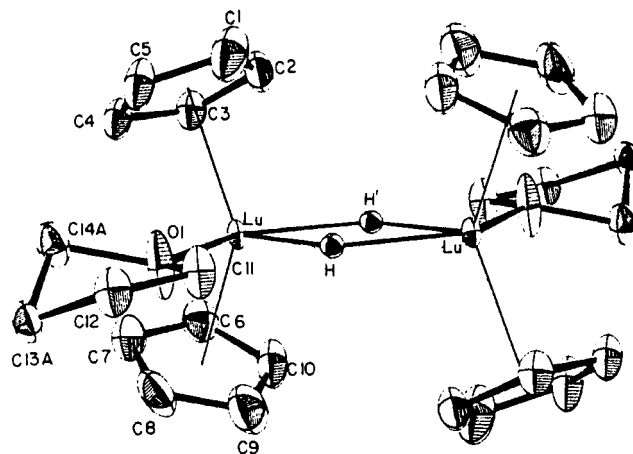**Figure 7.** Crystal structure of $[Cp_2LuH(THF)]_2$. (Reprinted with permission from ref 23. Copyright 1986 Elsevier Science S.A.)

In order to further open the metal coordination sphere, the properties of lanthanide complexes based upon $R_2Si(C_5Me_4)(C_5H_4)$ supporting coordination have been explored. Hydrogenolysis of the monomeric alkyls $R_2Si(C_5Me_4)(C_5H_4)LnCH(TMS)_2$ (Ln = Lu and R = Me or Et; Ln = Y and R = Et) afforded the corresponding hydrides.[33] The IR and NMR data supported a symmetric $Ln(\mu\text{-}H)_2Ln$ arrangement but the crystal structure of $Lu_2[\mu\text{-}Et_2Si(C_5Me_4)(C_5H_4)]_2$-$[\mu\text{-}H]_2$ revealed that redistribution of the cyclopentadienyl ligands has occurred to give the unusual spanning ligation pattern (Figure 4). The central core is of approximately rhombic geometry with each
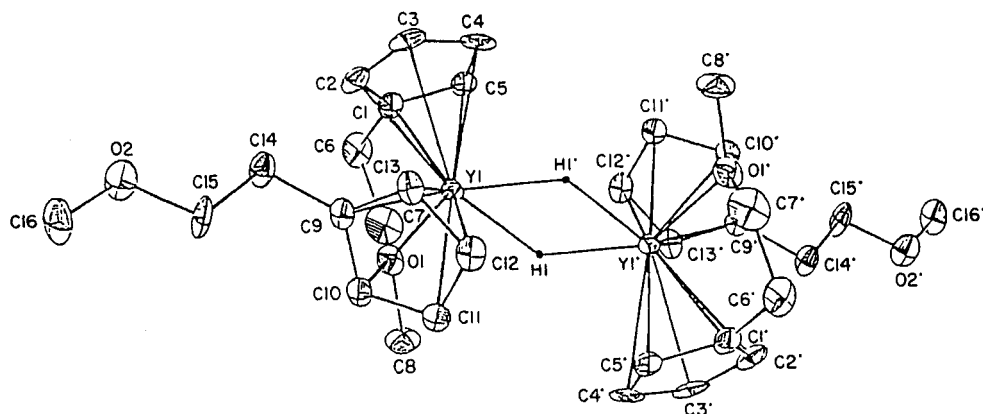
Figure 8. Crystal structure of $[(MeOCH_2CH_2C_5H_4)_2YH]_2$. (Reprinted with permission from ref 21. Copyright 1994 Elsevier Science S.A.)

hydride ligand bridging the two metal centers in a symmetrical fashion; the short Lu···Lu distance, 3.390(1) Å is likely a consequence of the bridging ligation environment.

The complexes $[(C_5H_xR_{5-x})_2LnH(THF)]_2$ constitute another important family of organolanthanide hydrides. Their IR spectra generally contain a strong, broad absorption centered at 1300–1350 cm^{-1}. The complexes $[Cp_2LnH(THF)]_2$ are known for Ln = Y,[41,67] Er,[41,42] Lu,[18,19,23,41] and Yb.[42] The ring-substituted derivatives $[(C_5H_4Me)_2LnH(THF)]_2$ (Ln = Y, Er, Lu)[41,67] and $[(1,3-Me_2C_5H_3)_2YH(THF)]_2$[68] have also been isolated. The latter compound was characterized by crystallography (Figure 5), as well as $[(C_5H_4-Me)_2YH(THF)]_2$[41] (Figure 6) and $[Cp_2LuH(THF)]_2$[19,23] (Figure 7). The structures, which are quite similar, indicate that the four cyclopentadienyl ring centroids do not adopt the tetrahedral geometry found in $[Cp^*_2-SmH]_2$ but are closer to the square-planar configuration. The Ln_2H_2 core, which is located in the bisector plane of the $(C_5H_4R)_2Ln$ sandwiches, is symmetrical with practically equal Ln–H bond distances in $[(C_5H_4Me)_2YH(THF)]_2$ (2.17 and 2.19 Å) but the Ln–H bridging bonds seem to be asymmetric in $[(1,3-Me_2C_5H_3)_2YH(THF)]_2$ (2.03 and 2.27 Å).

The compounds $[Me_2Si(C_5H_4)_2LnH(THF)]_2$ (Ln = Y, Yb), which are much less stable than $[Me_2Si(C_5Me_4)-(C_5H_4)LnH]$, could not be isolated; high-resolution mass spectrometry studies suggested that they are dimeric with the ligands $Me_2Si(C_5H_4)_2$ in a chelating mode.[22]

The complexes $[(CH_2)_3(C_5H_4)_2LnH(THF)]_2$ are known for Ln = Y, Dy, Er, and Lu.[69] Their dimeric structure is indicated by the triplet hydride signal in the ^1H NMR spectrum of the yttrium compound.

Lanthanide hydrides with cyclopentadienyl ligands bearing a donor-functionalized side chain have been considered because of the possible stabilization of π-complexes by intramolecular coordination of the functional group and participation of the side arm in catalytic processes. The complexes $[O(CH_2-CH_2C_5H_4)_2LnH]_2$ have been described for Ln = Y, Gd, Er and Lu.[20] The presence of an intramolecular bond between the metal and the oxygen atom of the 1,1′-(3-oxapentamethylene) bridge is inferred from the IR spectra. The complexes $[(MeOCH_2CH_2C_5H_4)_2LnH]_2$ are known for Ln = Y,[15,21] La, Pr, and Ho.[21] The centrosymmetric crystal structure of the yttrium derivative shows that only one pending ether function is coordinated to the metal center (Figure 8).[21]
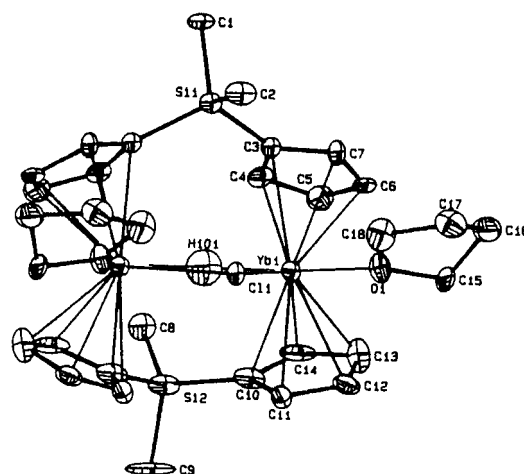

Figure 9. Crystal structure of $[Me_2Si(C_5H_4)_2Yb(THF)]_2$-$(\mu$-H$)(\mu$-Cl$)$. (Reprinted with permission from ref 22. Copyright 1993 Elsevier Science S.A.)

3. Dinuclear Chloro–Hydride and Alkyl–Hydride Compounds

The chloro–hydride derivative $[Me_2Si(C_5H_4)_2Yb-(THF)]_2(\mu$-H$)(\mu$-Cl$)$ decomposed above −20 °C; its crystal structure could, however, be determined (Figure 9) and revealed the bridging ligation mode of the cyclopentadienyl ligands.[22]

In the crystal structure of $Lu_2[\mu$-$Et_2Si(C_5Me_4)-(C_5H_4)]_2(\mu$-H$)(\mu$-Et$)$, the Lu···Lu distance (3.392(1) Å) is identical to that determined in the dimeric hydride and the μ-Et fragment is bound very unsymmetrically.[33] The complexes $Ln_2[\mu$-$Et_2Si(C_5Me_4)(C_5H_4)]_2(\mu$-H$)(\mu$-R$)$ (Ln = Y and R = Et or ^nPr; Ln = Lu and R = ^nPr or ^nHex) would have a similar structure from the NMR spectra.[33] The crystal structure of the complexes $Cp^*_2Ln(\mu$-H$)(\mu$-$CH_2C_5Me_4)LnCp^*$ (Ln = Y, Sm) (Figure 10) revealed that the hydride ligand is bridging symmetrically with Sm–H distances equal to 2.05(11) and 2.11(9) Å[36] and Y–H = 2.10(7) and 2.14(7) Å.[37]

4. The Trimeric Complexes

Two compounds of this class have been isolated and characterized by their crystal structure. The yttrium hydride $[(1,3-Me_2C_5H_3)_2YH]_3$ is seen as a trimer with three equivalent $(1,3-Me_2C_5H_3)_2Y$ units connected by μ_2-H bridges (Figure 11).[68] The hydride ligands in $[Cp_2LuH]_3$ could be located (Figure 12); one of those was found to occupy the central position of the

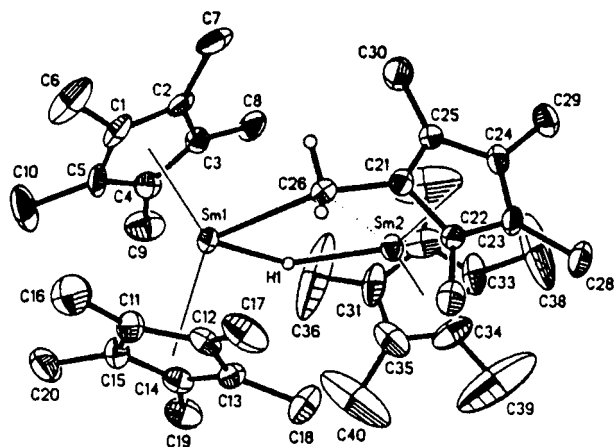**Figure 10.** Crystal structure of $Cp^*_2Sm(\mu\text{-H})(\mu\text{-CH}_2C_5\text{-}Me_4)SmCp^*$. (Reprinted from ref 36. Copyright 1991 American Chemical Society.)

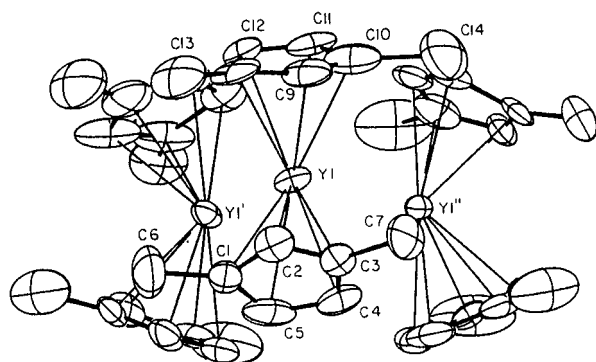**Figure 11.** Crystal structure of $[(1,3\text{-Me}_2C_5H_3)_2YH]_3$. (Reprinted from ref 68. Copyright 1987 American Chemical Society.)

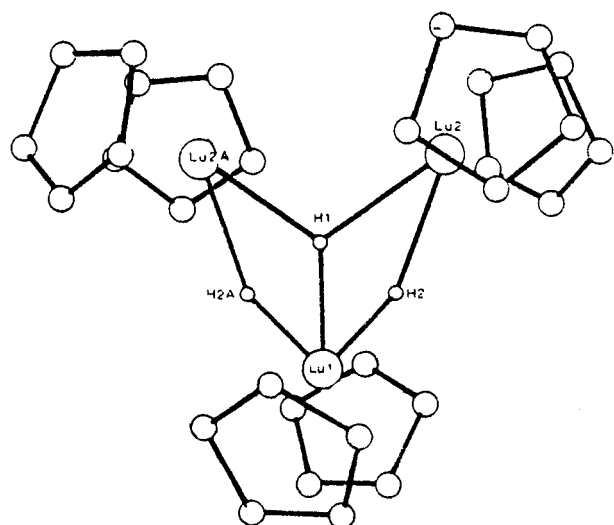**Figure 12.** Crystal structure of $[Cp_2LuH]_3$. (Reprinted with permission from ref 17. Copyright 1991 Elsevier Science S.A.)

triangular metal core with a μ_3 ligation mode and this situation would explain why the Lu···Lu distances are 0.4−0.5 Å shorter than the Y···Y distances in $[(1,3\text{-Me}_2C_5H_3)_2YH]_3$ while the difference between the metal covalent radii is only 0.06 Å.[17]

5. The Trinuclear Complexes M[{ (C₅HₓR₅₋ₓ)₂LnH}₃H] [M = Li(THF)₄ or Na(THF)₆] and Their Derivatives

The trinuclear anions $[(Cp_2LnH)_3H]^-$ (Ln = Lu,[23,26] Y,[27] and Yb[42]) and $[\{(1,3\text{-Me}_2C_5H_3)_2YH\}_3H]^-$ [68] have been characterized by their NMR spectra which

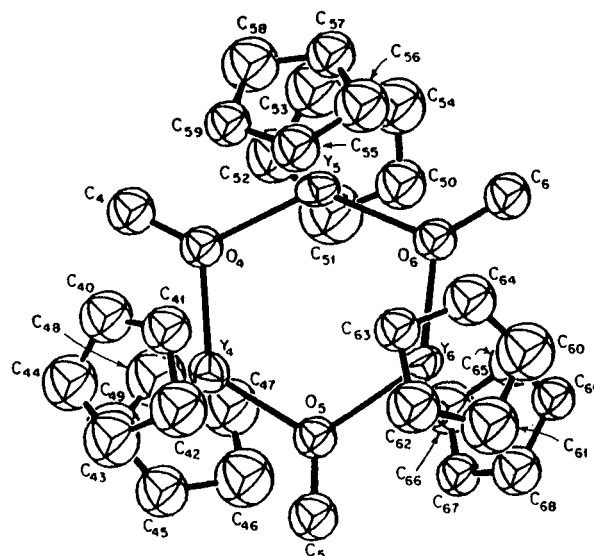**Figure 13.** Crystal structure of the anion of $[Li(THF)_3]_2\text{-}[(Cp_2YOMe)_3H]_2$. (Reprinted from ref 39. Copyright 1988 American Chemical Society.)
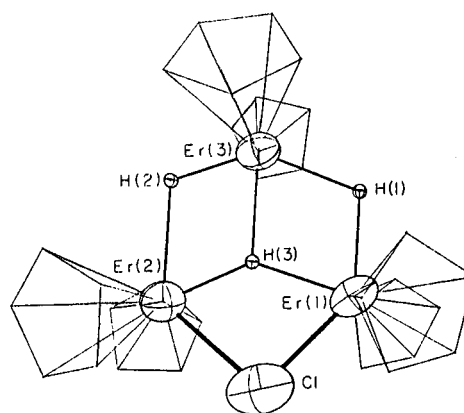
Figure 14. Crystal structure of the anion of $[Li(THF)_4]\text{-}[(Cp_2ErH)_3Cl]$. (Reprinted from ref 26. Copyright 1982 American Chemical Society.)

exhibit two signals corresponding to the inequivalent hydride ligands. In particular, the central μ_3-hydride in the yttrium complexes gives rise to a 10-line multiplet, resulting from coupling with the three equivalent μ_2-hydrides and the three equivalent Y nuclei.

The μ_3-hydride ligand was not located in the crystal structure of $[Li(THF)_3]_2[(Cp_2YOMe)_3H]_2$ (Figure 13) but it was characterized by its quartet ^1H NMR signal (J_{YH} = 18.4 Hz). The other alkoxy−hydride anions $[Cp_2Y(\mu\text{-H})]_x[Cp_2Y(\mu\text{-OMe})]_{3-x}[\mu_3\text{-H}]^-$ (x = 1, 2) were also characterized by NMR spectroscopy.[39]

The crystal structure of the complex $[Li(THF)_4][(Cp_2ErH)_3Cl]$ was determined; the μ_3-hydride is located at 0.06 Å out of the plane of the metal atoms whereas the μ_2-hydrides were found to be 0.49 and 0.14 Å out of this plane (Figure 14).[26]

D. Triscyclopentadienyl Hydrides

Only two complexes of this type have been reported: $[Na(THF)_6][Cp_3LuHLuCp_3]\cdot2THF$[23] and $[Li(DME)_3][Cp_3NdHNdCp_3]$.[24] Their crystal structure was determined (Figure 15). The Ln−H−Ln bridge is linear, the Lu−H and Nd−H bond distances being respectively equal to 2.09 and 2.190 Å. The lutetium hydride ligand was not detected by NMR.

Figure 15. Crystal structure of the anion of [Na(THF)$_6$]-[Cp$_3$LuHLuCp$_3$]·2THF. (Reprinted with permission from ref 23. Copyright 1986 Elsevier Science S.A.)
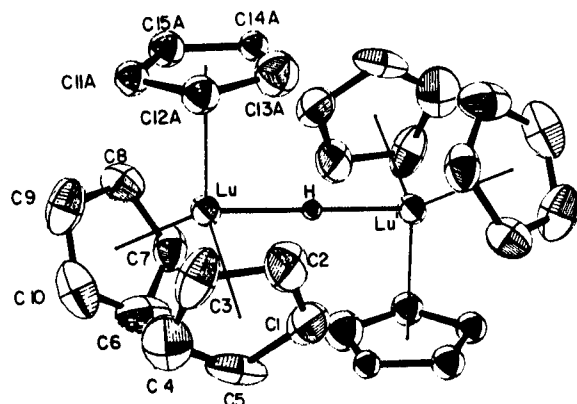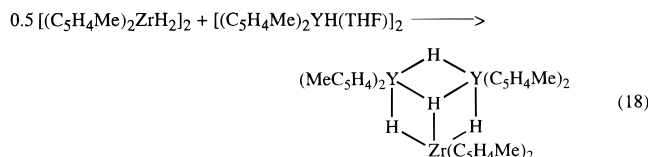
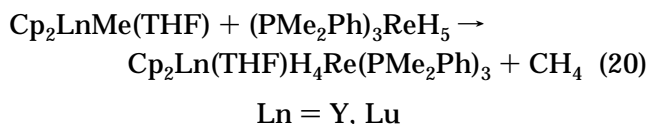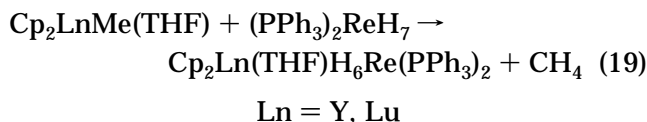## IV. Synthesis and Structure of Heteronuclear Lanthanide Hydrides

Mixed-metal polyhydride compounds associating 4f-elements and d-transition metals are not common; these are listed in Table 2.

The mechanism of formation of the trinuclear anion [(Cp$_2$YH)$_3$H]$^-$ (*vide supra*) suggested that a variety of reagents similar to [Cp$_2$YH$_2$]$^-$ would react with [Cp$_2$-YH(THF)]$_2$ to give mixed-metal compounds. Indeed, reaction of [(C$_5$H$_4$Me)$_2$ZrH$_2$]$_2$ with [(C$_5$H$_4$Me)$_2$YH-(THF)]$_2$ afforded the neutral heterometallic tetrahydride [(C$_5$H$_4$Me)$_2$YH]$_2$[(C$_5$H$_4$Me)$_2$ZrH]H (eq 18).[27] As observed in the case of [(Cp$_2$YH)$_3$H]$^-$, the μ_3-H NMR resonance is a 10-line multiplet.

A series of heterometallic polyhydride complexes of rhenium with yttrium or lutetium have been synthesized by using the bimetallic alkane elimination reaction M—Me + M′—H → CH$_4$ + M—M′. Thus,

$$0.5 [(C_5H_4Me)_2ZrH_2]_2 + [(C_5H_4Me)_2YH(THF)]_2 \longrightarrow$$

$$(MeC_5H_4)_2Y \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle Zr(C_5H_4Me)_2}{|}}{\underset{H}{\overset{H}{|}}}} Y(C_5H_4Me)_2 \quad (18)$$

Cp$_2$LnMe(THF) (Ln = Y, Lu) reacted with (PPh$_3$)$_2$-ReH$_7$ or (PMe$_2$Ph)$_3$ReH$_5$ according to eqs 19 and 20.[70]

$$Cp_2LnMe(THF) + (PPh_3)_2ReH_7 \rightarrow$$
$$Cp_2Ln(THF)H_6Re(PPh_3)_2 + CH_4 \quad (19)$$
$$Ln = Y, Lu$$

$$Cp_2LnMe(THF) + (PMe_2Ph)_3ReH_5 \rightarrow$$
$$Cp_2Ln(THF)H_4Re(PMe_2Ph)_3 + CH_4 \quad (20)$$
$$Ln = Y, Lu$$

The crystal structure of Cp$_2$Y(THF)H$_6$Re(PPh$_3$)$_2$ (Figure 16) revealed the presence of two Re—H—Y bridges and four hydrides terminally bound to rhenium. The hydride ligands could not be located in the crystal structure of Cp$_2$Y(THF)H$_4$Re(PMe$_2$Ph)$_3$ but the coupling constant of their doublet {^{31}P}^{1}H NMR resonance (J_{YH} = 14.7 Hz) suggested that two are in bridging positions.

The complexes Cp$_2$LnMe(THF) (Ln = Y, Lu) also reacted with Re$_2$H$_8$(PMe$_2$Ph)$_4$ to give trinuclear hydrides (eqs 21 and 22).[70,71a]

$$Cp_2YMe(THF) + Re_2H_8(PMe_2Ph)_4 \rightarrow$$
$$Cp_2Y(THF)Re_2H_7(PMe_2Ph)_4 + CH_4 \quad (21)$$

$$Cp_2LuMe(THF) + Re_2H_8(PMe_2Ph)_4 \rightarrow$$
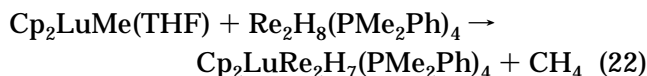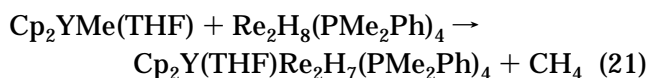$$Cp_2LuRe_2H_7(PMe_2Ph)_4 + CH_4 \quad (22)$$

Table 2. Heteronuclear Lanthanide and Actinide Hydrides and Their Characterization

complexes	analyses[a]	infrared data[b]	^{1}H NMR data[c]	X-ray diffraction data[d]	ref(s)
[(C$_5$H$_4$Me)$_2$YH]$_2$[(C$_5$H$_4$Me)$_2$ZrH]H	C,H,Y,Zr	1299	benzene-d_6: -1.57 (m, μ_2-H), -2.99 (m, μ_3-H)		27
Cp$_2$Y(THF)H$_6$Re(PPh$_3$)$_2$	Y	not assigned	benzene-d_6: -5.65 (td, 13.4 and 8.3)	Re—H 1.50(8)−1.57(8) Re−μ-H 1.48(8), 1.59(8) Y−μ-H 2.28(9), 2.44(6)	70
Cp$_2$Lu(THF)H$_6$Re(PPh$_3$)$_2$	Lu	not assigned	benzene-d_6: -5.30 (t, 13.8)		70
Cp$_2$Y(THF)H$_4$Re(PMe$_2$Ph)$_3$	Y	not assigned	benzene-d_6: -7.90 (m)	Re···Y 3.108(5)	70
Cp$_2$Lu(THF)H$_4$Re(PMe$_2$Ph)$_3$	Lu	not assigned	benzene-d_6: -7.36 (q, 16)		70
Cp$_2$Y(THF)Re$_2$H$_7$(PMe$_2$Ph)$_4$	Y	not assigned	benzene-d_6: -8.87 (br)	Re···Y 3.090(2), Re···Re 2.576(1)	71
Cp$_2$LuRe$_2$H$_7$(PMe$_2$Ph)$_4$	Lu	not assigned	benzene-d_6: -8.62 (br)	Re···Lu 3.068(1), Re···Lu 3.025(1), Re···Re 2.561(1)	71
Cp*$_2$Y(μ-η^1,η^5-C$_5$H$_4$)(μ-H)$_2$WCp	*		benzene-d_6: -14.25 (d, 6.3)		72
Cp*$_2$Sm(μ-η^1,η^5-C$_5$H$_4$)(μ-H)$_2$WCp	*		not visible	Sm···W 3.402(1)	72
[(PMe$_3$)$_3$WH$_5$]$_2$Yb(diglyme)			THF-d_8 (-20 °C): -3.63 (q, μ-H), -4.75 (q, W—H)	W···Yb 3.2253(5), 3.2595(5)	73
[Cp$_2$NbH$_2$]$_2$Yb(diglyme)			THF-d_8: -9.3 (br)	Nb-μH 1.77(7), 1.71(7) Yb-μH 2.32(8), 2.33(7)	73
[Ph$_3$GeH]$_2$Yb(THF)$_4$	C,H	2030, 1300		Ge−H 1.48, 1.5 Yb−H 1.64, 1.67	43
Cp$_3$UH$_6$Re(PPh$_3$)$_2$	C,H,P	1860, 1810	THF-d_8: -30.89 (t, 13)		142
Cp$_3$UH$_6$Re(P[C$_6$H$_4$F]$_3$)$_2$	C,H,P	1860, 1810	benzene-d_6: -36.72 (t, 13.5)		142
(C$_5$H$_4$^{t}Bu)$_3$UH$_6$Re(PPh$_3$)$_2$	C,H,P		THF-d_8: -25.65 (t, 12)		143
(C$_5$H$_4$SiMe$_3$)$_3$UH$_6$Re(PPh$_3$)$_2$	C,H,P		THF-d_8: -24.40 (t, 14)		143
[K(18-crown-6-)][Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$]	C,H,P		THF-d_8 (-80 °C): -36.5 and 23.0	Re···U 3.255(8)	144
Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$	C,H,P,Cl		THF-d_8 (-70 °C): -61.0 and -114.7		143
K[Cp*$_2$(BH$_4$)UH$_6$Re(PPh$_3$)$_2$]	C,H,P		THF-d_8: 13.3 (br, 180)		143
Cp*Cp$_2$UH$_6$Re(PPh$_3$)$_2$	C,H,P		THF-d_8: -35.6 (t, 14)		143

^{a} Elements which have been analyzed, except when not precised (∗). ^{b} IR vibrations in cm^{-1}. ^{c} Chemical shifts δ (multiplicity, coupling constants in Hz, assignment) of the hydride signal. ^{d} Distances in Å.
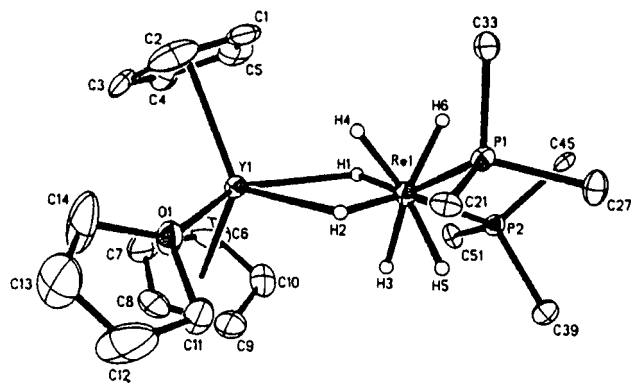
Figure 16. Crystal structure of $Cp_2Y(THF)H_6Re(PPh_3)_2$. (Reprinted from ref 70. Copyright 1992 American Chemical Society.)
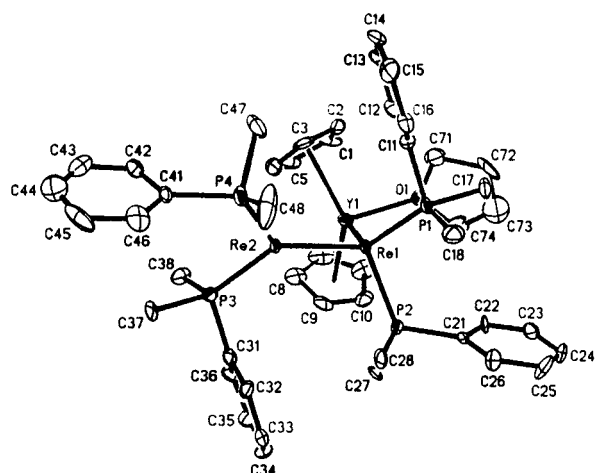
Figure 17. Crystal structure of $Cp_2Y(THF)Re_2H_7(PMe_2Ph)_4$. (Reprinted from ref 71. Copyright 1990 American Chemical Society.)
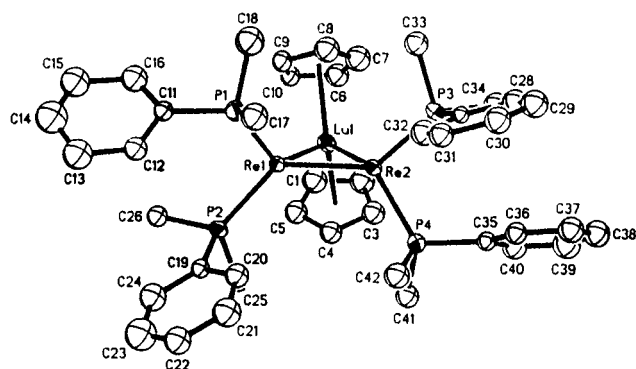
Figure 18. Crystal structure of $Cp_2LuRe_2H_7(PMe_2Ph)_4$. (Reprinted from ref 71. Copyright 1990 American Chemical Society.)

Figure 19. Crystal structure of $[(PMe_3)_3WH_5]_2Yb(diglyme)$. (Reprinted with permission from ref 73. Copyright 1993 The Royal Society of Chemistry.)
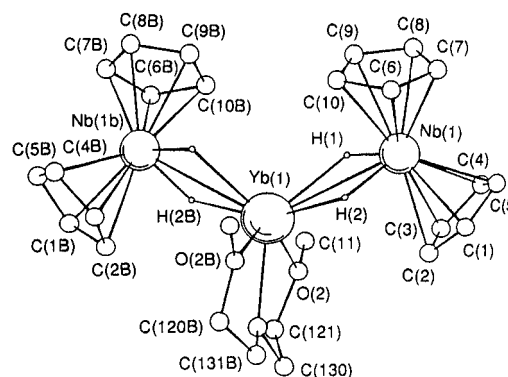
Figure 20. Crystal structure of $[Cp_2NbH_2]_2Yb(diglyme)$. (Reprinted with permission from ref 73. Copyright 1993 The Royal Society of Chemistry.)
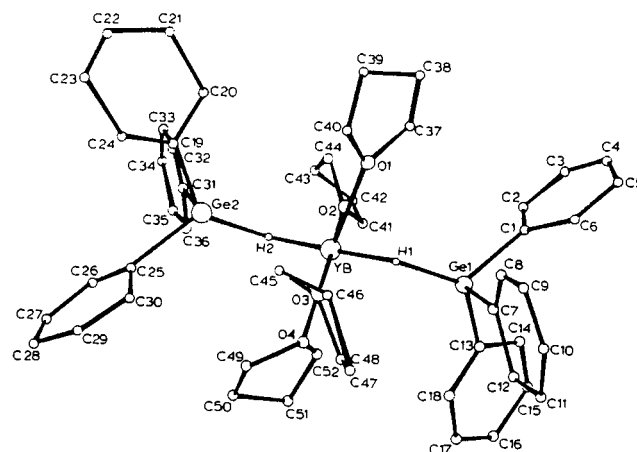
Figure 21. Crystal structure of $(Ph_3GeH)_2Yb(THF)_4$. (Reprinted with permission from ref 43. Copyright 1989 Elsevier Science S.A.)

The two complexes have been crystallographically characterized. The yttrium–rhenium compound is a fluxional molecule which contains an open L-shaped YRe_2 unit (Figure 17). Reversible dissociation of THF from this complex gave the yttrium analogue of $Cp_2LuRe_2H_7(PMe_2Ph)_4$ which contains a closed triangular $LuRe_2$ core (Figure 18).

The complexes $[Cp^*_2LnH]_2$ (Ln = Y, Sm) reacted with Cp_2WH_2 to give Ln–W heterobimetallic compounds, by dehydrocoupling between the Ln–H bond and the C–H, but not the weaker W–H bond, of the tungsten compound (eq 23).[72]

Reaction of YbI_2 with $K[(PMe_3)_3WH_5]$ in the presence of diglyme gave the trinuclear compound

$$0.5\ [Cp^*_2LnH]_2 + Cp_2WH_2 \rightarrow$$
$$Cp^*_2Ln(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-H})_2WCp + H_2\ \ (23)$$

$[(PMe_3)_3WH_5]_2Yb(diglyme)$ (eq 24) which was characterized by crystallography (Figure 19).[73] The NMR spectra are in agreement with the presence of three hydrogens bridging from each tungsten to the ytterbium. Similar reaction of YbI_2 with $K[Cp_2NbH_2]$ afforded $[Cp_2NbH_2]_2Yb(diglyme)$ (eq 25), the crystal structure of which showed the two $Yb(\mu\text{-H})_2Nb$ bridges (Figure 20); the average Nb–H and Yb–H distances are 1.74 and 2.32 Å respectively.

$$2K[(PMe_3)_3WH_5] + YbI_2 \xrightarrow{DME-diglyme}$$
$$[(PMe_3)_3WH_5]_2Yb(diglyme) + 2KI \quad (24)$$

$$2K[Cp_2NbH_2] + YbI_2 \xrightarrow{DME-diglyme}$$
$$[Cp_2NbH_2]_2Yb(diglyme) + 2KI \quad (25)$$
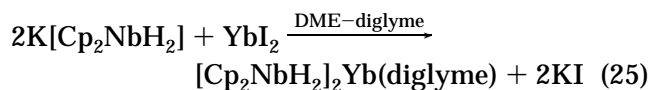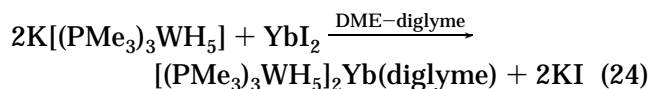
The Yb$-$Ge complex $(Ph_3GeH)_2Yb(THF)_4$ has been prepared from naphthalene$-$ytterbium, according to eq 26; the crystal structure indicates that the hydride ligands form μ_2-bridges between Yb and Ge atoms (Figure 21).[43]

$$(C_{10}H_8)Yb(THF)_3 + 2Ph_3GeH \xrightarrow{THF}$$
$$[Ph_3GeH]_2Yb(THF)_4 + C_{10}H_8 \quad (26)$$
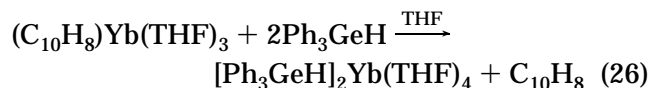
V. Synthesis and Structure of Borohydride, Aluminohydride, and Alane Compounds of the Lanthanides

A. Borohydride Compounds

The BH_4^- ion forms a variety of covalent complexes with transition metals and f-elements. The general aspects of the synthesis, characterization and properties of these compounds have been described[74] and only some essential features will be presented here for the understanding of this review.

Coordination of BH_4^- occurs through bridging hydrogen atoms. The mononuclear complexes invariably adopt a tridentate (C) or bidentate (D) structure; the BH_4 moiety can also link two metal centers in a dimeric or polymeric compound (E). When accurate X-ray analysis is not possible, infrared spectroscopy is the straightforward method of recognizing these distinct ligation modes; bidentate complexes are characterized by a strong broad band centered at around 2415 cm^{-1} and a sharp singlet at $\sim$2125 cm^{-1}, whereas tridentate complexes exhibit a sharp band at 2420 cm^{-1} and a strong broad band centered at $\sim$2230 cm^{-1}. ^{1}H NMR spectroscopy is very useful for detecting the borohydride ligand which exhibits a broad quartet ($J = 80-90$ Hz) due to the nuclear spin quantum number of $^3/_2$ of ^{11}B. However, this method does not allow the bidentate and tridentate coordination modes to be distinguished, because of the rapid interchange of the bridging and terminal hydrogens.
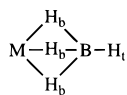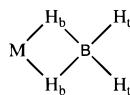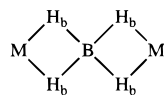
$$C \qquad\qquad D \qquad\qquad E$$

1. The Trivalent Complexes Ln(BH$_4$)$_3$ and Their Derivatives

These complexes have been reported in previous reviews[74] and will be briefly described here.

The series of complexes $Ln(BH_4)_3(THF)_n$ (Ln = La to Nd[75] and Y to Lu[76]) were first synthesized by treating the corresponding alkoxides $Ln(OMe)_3$ with diborane in THF (eq 27).

$$Ln(OMe)_3 + 2B_2H_6 \xrightarrow{THF}$$
$$Ln(BH_4)_3(THF)_n + B(OMe)_3 \quad (27)$$
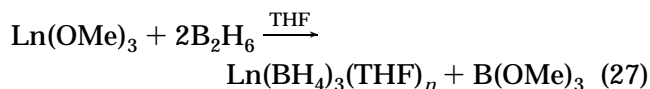
However, the most usual route to these lanthanide borohydrides is the metathesis reaction of $LnCl_3$ with $LiBH_4$ or $NaBH_4$ (eq 28).[77-79] Similar reaction in pyridine afforded the adducts $Ln(BH_4)_3(py)_2$ (M = La, Ce, Nd).[78] The ammoniac complexes $Ln(BH_4)\cdot6NH_3$ (Ln = Sc, Y, La) and $La(BH_4)_3\cdot4NH_3$ were obtained by condensation of NH_3 on $Ln(BH_4)_3(THF)_n$.[80]

$$LnCl_3 + 3LiBH_4 \xrightarrow{THF}$$
$$Ln(BH_4)_3(THF)_n + 3LiCl \quad (28)$$
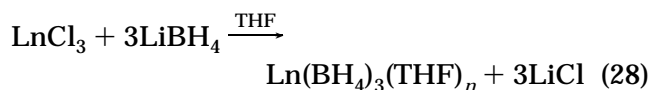
The complexes $Y(BH_4)_3(THF)_3$[81] and $Sc(BH_4)_3$-$(THF)_2$[79] have been characterized by their crystal structure. In both compounds, one BH_4 ligand is bidentate and two are tridentate; this structure was found to be the most stable from *ab initio* calculations on the model compound $Sc(BH_4)_3(PH_3)_2$.[82] The M$\cdots$B distance is significantly shorter for tridentate coordination than for bidentate coordination (Y$\cdots$B = 2.58(1) and 2.68(2) Å). The three M$-$H bond distances for the tridentate BH_4 groups are different (Y$-$H$_b$ = 2.20(11), 2.41(12), and 2.48(12) Å) whereas the M$-$B$-$H$_t$ angle is not linear (Y$-$B$-$H$_t$ = 161-(10)°); this coordination geometry supports the mechanism proposed for the exchange between bridged and terminal hydrogens in solution.[83] The structure of $Y(BH_4)_3(THF)_2$ is built up from $[Y(BH_4)_2(THF)_4]^+$ cations and $[Y(BH_4)_4]^-$ anions; all the BH_4 groups are tridentate from the Y$\cdots$B distances (2.52 Å in the cation and 2.41 Å in the anion).[84]

The methylborohydride compounds $Ln(BH_3Me)_3$-(OEt_2) (M = Lu, Yb, Ho) have been prepared by reaction of $LnCl_3$ with $LiBH_3Me$ in diethyl ether and were transformed into $Ln(BH_3Me)_3(THF)$ or $Ln(BH_3$-$Me)_3(L)_2$ (L = THF and Ln = Ho or Yb; L = py and Ln = Ho).[85] The tridentate coordination of the BH_3-Me ligands was established by IR spectroscopy and confirmed by the crystal structures of $Yb(BH_3Me)_3$-(OEt_2) and $Ho(BH_3Me)_3(py)_2$; the Ln$-$B$-$C angles are close to 180° with the average Yb$\cdots$B and Ho$\cdots$B distances equal to 2.45 ± 0.04 and 2.50 ± 0.02 Å, respectively.

Treatment of the anhydrous trichlorides $LnCl_3$ with 2 equiv of $LiBH_4$ afforded the chloro bisborohydrides of Y,[86] Sm, Gd, Tb, Dy, Er and Yb;[87] the europium complex $EuBr(BH_4)_2\cdot2.4THF$ was prepared in a similar way.[88]

It is noteworthy that the above complexes did not serve to prepare a series of derivatives. The bisbenzamidinate compound $[PhC(NSiMe_3)_2]_2Y(BH_4)(THF)$ was obtained by treatment of the corresponding chloride with $LiBH_4$.[45]

2. The Divalent Complexes Ln(BH$_4$)$_2$ and Their Derivatives

The sole lanthanide(II) borohydrides so far reported are the europium and ytterbium compounds $(MeCN)_4Ln(BH_4)_2$ (Ln = Eu, Yb), $(C_5H_5N)_4Yb(BH_4)_2\cdot2$ C_5H_5N and $(C_5H_5N)_{1.8}Eu(BH_4)_2$ which have been prepared by treating the corresponding dichlorides with $NaBH_4$ in acetonitrine or pyridine. The pseudooctahedral crystal structures of the two ytterbium compounds revealed the tridentate coordination of the BH_4 ligands which are relatively *cis* in the acetonitrile adduct and *trans* in the pyridine adduct (Figures 22 and 23).[89]
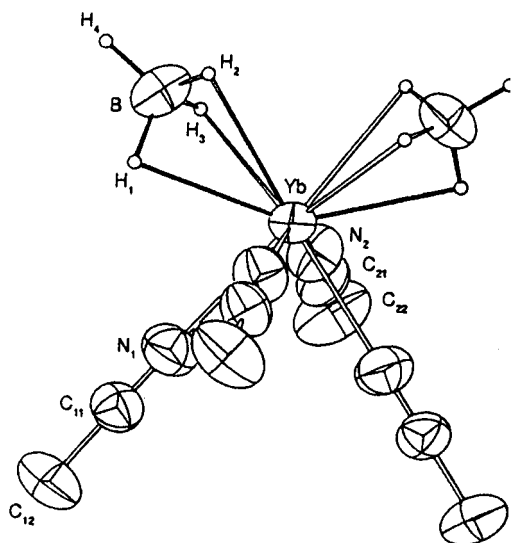
Figure 22. Crystal structure of $(MeCN)_4Yb(BH_4)_2$. (Reprinted from ref 89. Copyright 1991 American Chemical Society.)
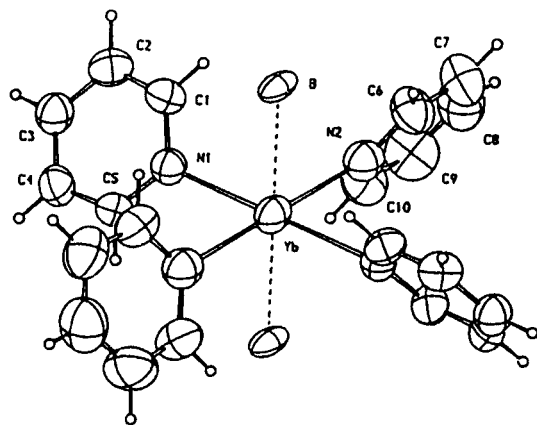

Figure 23. Crystal structure of $(C_5H_5N)_4Yb(BH_4)_2 \cdot 2C_5H_5N$. (Reprinted from ref 89. Copyright 1991 American Chemical Society.)

3. Organolanthanide Borohydrides

The organolanthanide borohydrides have been synthesized by reaction of a halide precursor with $LiBH_4$ or $NaBH_4$; as in the case of the hydrides, most of them are biscyclopentadienyl compounds (Table 3).

The only triscyclopentadienyl lanthanide borohydride is the cerium complex $Cp_3Ce(BH_4)$; another Ce(IV) borohydride, $(indenyl)_2Ce(BH_4)_2$, has also been reported.[90] The IR spectra indicated that in both compounds, the BH_4 groups are bidentate.

The BH_4 group was found to be tridentate in Cp_2-$Sc(BH_4)$,[91] as shown by IR and multinuclear magnetic resonance spectroscopy studies, whereas it is bidentate in the ring substituted compound $(C_5H_3TMS_2)_2$-$Sc(BH_4)$, characterized by its crystal structure (Sc$-$H $= 2.03(4)$ Å and Sc$\cdots$B $= 2.52(2)$ Å) (Figure 24).[92] The crystal structure of $[(1,3\text{-}^tBu_2\text{-}C_5H_3)_2Ce(BH_4)]_2$ revealed the novel ligation mode of the BH_4 ligand (F) which is tetradentate, with cerium and boron bonded through triple hydrogen bridges (Figure 25);[93] the samarium analogue is isostructural.[16] By comparison of their broad and intense IR absorption bands at 2250$-$2280 cm^{-1}, it was suggested that all the unsolvated biscyclopentadienyl lanthanide borohydrides have the same dimeric structure with the $\mu\text{-}\eta^3$: η^3 BH_4 groups; the molecular nature of these com-
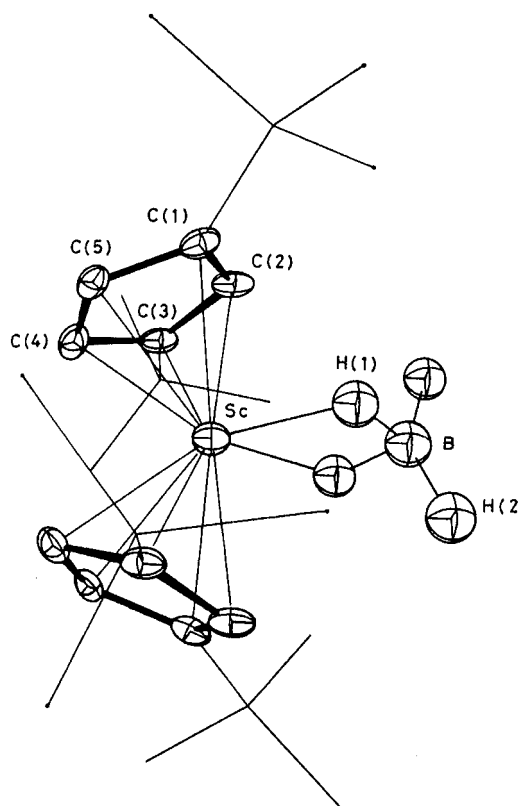
Figure 24. Crystal structure of $(C_5H_3TMS_2)_2Sc(BH_4)$. (Reprinted with permission from ref 92. Copyright 1983 The Royal Society of Chemistry.)
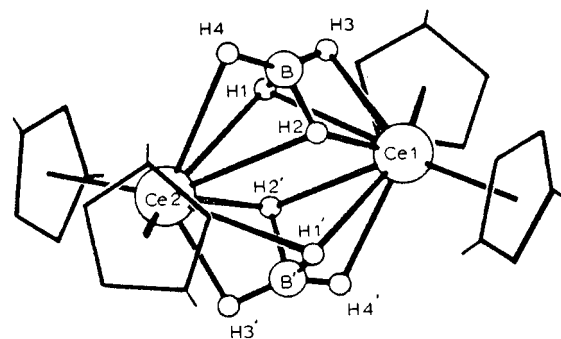
Figure 25. Crystal structure of $[(C_5H_3{}^tBu_2)_2Ce(BH_4)]_2$. (Reprinted with permission from ref 93. Copyright 1991 Elsevier Science S.A.)

Figure 26. Crystal structure of $(C_5H_4CH_2CH_2OMe)_2Y$-(BH_4). (Reprinted with permission from ref 15. Copyright 1993 Elsevier Science S.A.)

plexes would be in agreement with their solubility in hydrocarbons.

Table 3. Organolanthanide Borohydride Complexes and Their Characterization

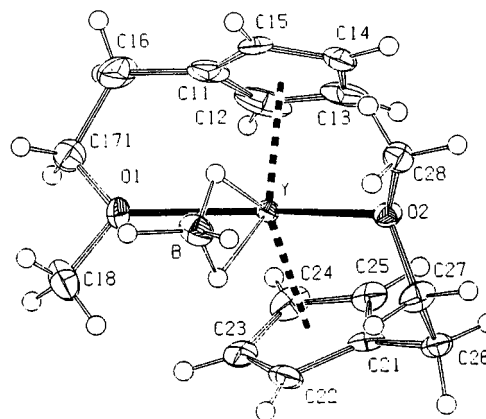| complexes	analyses[a]	infrared data[b]	^{1}H NMR data[c]	X-ray diffraction data[d]	ref(s)
Cp$_3$Ce(BH$_4$)	C,H,Ce	2505, 2380			90
(indenyl)$_2$Ce(BH$_4$)$_2$	C,H,Ce	2530, 2385			90
Cp$_2$Sc(BH$_4$)		2490, 2180, 2130	toluene-d_8 (100 °C): 0.65 (q, 86)		91
(C$_5$H$_3$TMS$_2$)$_2$Sc(BH$_4$)	*	~2415, ~2125		Sc—H 2.03(4) Sc···B 2.52(2)	92
[(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Ce(BH$_4$)]$_2$	C,H,Ce	2400, 2250, 2290, 2180		Ce—H 2.52–2.85 Ce···B 2.93(2)	93
[(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Sm(BH$_4$)]$_2$	Sm	2420, 2280		Sm···B 2.833(6), 2.882(6)	16
Cp$_2$Sm(BH$_4$)(THF)	Sm	2428 (1800), 2279 (1661), 2223 (1640)			95
Cp$_2$Er(BH$_4$)(THF)	Er	2380, 2290, 2230, 2175			95
Cp$_2$Yb(BH$_4$)(THF)	C,H	2393 (1797), 2353 (1735), 2238 (2171 (1589)			95
Cp$_2$Lu(BH$_4$)(THF)	C,H,Lu	2400, 2360, 2180, 2140	benzene-d_6: 1.07 (q, 84)		18,94
(C$_5$H$_3$TMS$_2$)$_2$Ln(BH$_4$)(THF) Ln = Y, Yb	*	~2415, ~2125			92
(C$_5$H$_3$TMS$_2$)$_2$Ln(BH$_4$)(THF) Ln = La, Pr, Nd, Sm	*	~2420, ~2140			92
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Y(BH$_4$)	C,H,Y	2419, 2367, 2294, 2226	benzene-d_6: 0.62 (q, 83)		15
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$La(BH$_4$)	C,H,La	2421, 2300, 2207	not visible		96
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Pr(BH$_4$)	C,H,Pr	2404, 2254, 2190		Pr···B 2.757(18)	96
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Nd(BH$_4$)	C,H,Nd	2404, 2260, 2184		Nd···B 2.664(25)	96
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Sm(BH$_4$)	C,H,Sm	2364, 2212, 2200			96
(C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Gd(BH$_4$)	C,H,Gd	2364, 2217, 2186, 2161			96

[a] Elements which have been analyzed except when not precised (*). [b] Ln—H (Ln—D) and B—H (B—D) IR vibrations in cm^{-1}. [c] Chemical shifts δ (multiplicity, coupling constants in Hz, assignment) of the BH$_4$ signal. [d] Distances in Å.
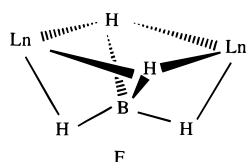
In the complexes Cp$_2$Ln(BH$_4$)(THF), the borohydride ligands are bidentate for Ln = Lu[18,94] or Yb,[95] and tridentate for Ln = Sm,[95] reflecting the contraction in ionic radius; the THF ligand can be removed for Ln = Lu, Yb, and Er to give the compounds [Cp$_2$-Ln(BH$_4$)]$_n$ which were supposed to be polymeric with Ln(μ_2-H)$_2$B(μ_2-H)$_2$Ln bridges. Other complexes of general formula (C$_5$H$_3$TMS$_2$)$_2$Ln(BH$_4$)(THF) have been isolated;[92] these are tridentate for Ln = La, Pr, Nd, and Sm, and bidentate for Ln = Y and Yb.

The complexes (C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Ln(BH$_4$) (Ln = Y, La, Pr, Nd, Sm, Gd) adopt a monomeric structure with the ether functions of both cyclopentadienyl ligands coordinated to the metal. The crystal structure of the yttrium derivative clearly shows the bidentate ligation of the BH$_4$ ligand (Figure 26).[15] From the IR spectra, the Sm and Gd analogues would also be bidentate while the La, Pr, and Nd derivatives would be tridentate, in agreement with the crystal structures (Pr···B = 2.757(18) Å, Nd···B = 2.664(25) Å) (Figure 27).[96]

In the bis(pentamethylcyclopentadienyl) series, it is surprising that the only compounds with Ln—μ-H—B bridges are Cp*$_2$Ln(H$_2$BMes$_2$) (Ln = Y, Sm) which were prepared by addition of (Mes$_2$BH)$_2$ to the corresponding hydride.[97]

B. Aluminohydride and Alane compounds

The AlH$_4$ and AlH$_3$ ligands may adopt a variety of coordination modes in mononuclear and polynuclear compounds; the structure of the complexes, most generally prepared by reaction of a lanthanide chlo-
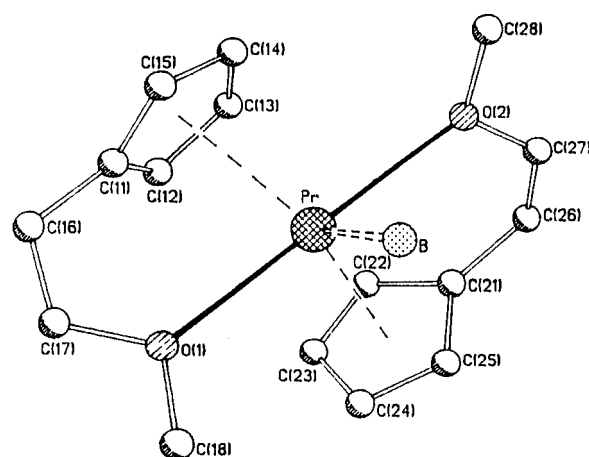
Figure 27. Crystal structure of (C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$Pr-(BH$_4$). (Reprinted with permission from ref 96. Copyright 1994 Elsevier Science S.A.)

ride with LiAlH$_4$ or AlH$_3$, depends markedly upon the experimental conditions.

Reaction of [Cp$_2$LnCl]$_2$ with LiAlH$_4$ in the presence of a Lewis base L gave the dimeric compounds [Cp$_2$-Ln(AlH$_4$·L)]$_2$ which adopt either the structure G or H represented below
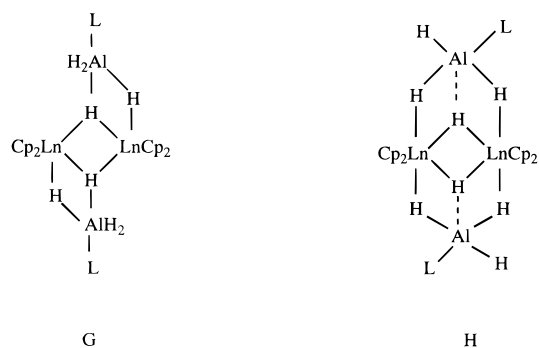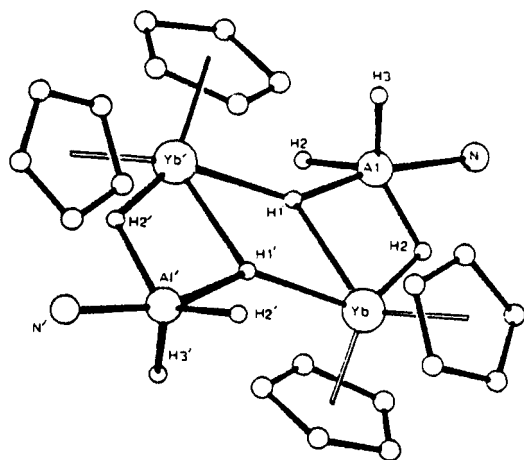
Figure 28. Crystal structure of [Cp$_2$Yb(AlH$_4$·NEt$_3$)]$_2$·C$_6$H$_6$. (Reprinted with permission from ref 17. Copyright 1991 Elsevier Science S.A.)

The bridging hydrogen atoms could be located in the type G crystal structures of [Cp$_2$Yb(AlH$_4$·NEt$_3$)]$_2$·C$_6$H$_6$[17] (Figure 28) and [Cp$_2$Y(AlH$_4$·THF)]$_2$;[98] the geometrical parameters are listed in Table 4. Similar structures would be adopted by [Cp$_2$Y-(AlH$_4$·NEt$_3$)]$_2$[99] and [Cp$_2$Lu(AlH$_4$·L)]$_2$ (L = THF, Et$_2$O or NEt$_3$).[100] The two etherate complexes [Cp$_2$Y-(AlH$_4$·OEt$_2$)]$_2$ and [Cp$_2$Y(AlH$_4$)]$_2$OEt$_2$ were isolated from the reaction of [Cp$_2$YCl]$_2$ with LiAlH$_4$ in benzene–diethyl ether;[99] their formation seems to be related to changes in crystallization conditions. The hemietherate was characterized by its crystal structure but the hydrogen atoms were not located; structure H was assigned to the monoetherate, on the basis of IR analysis. Accurate X-ray structure determination revealed that configuration H is adopted by the samarium complexes [Cp$_2$Sm(AlH$_4$·NEt$_3$)]$_2$[101] and [(C$_5$H$_4$^{t}Bu)$_2$Sm(AlH$_4$·THF)]$_2$ (Figure 29);[102] the latter was obtained by oxidation of Na-[(C$_5$H$_4$^{t}Bu)$_3$Sm] with AlH$_3$ in THF. In these com-
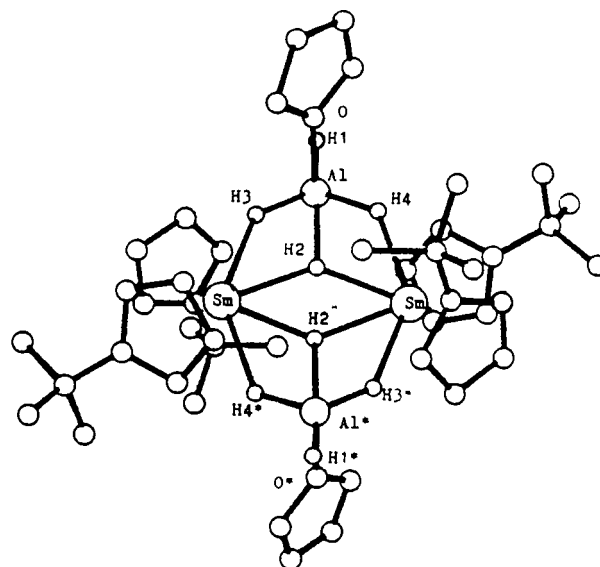
Figure 29. Crystal structure of [(C$_5$H$_4$^{t}Bu)$_2$Sm(AlH$_4$·THF)]$_2$. (Reprinted with permission from ref 102. Copyright 1990 Elsevier Science S.A.)

pounds, the Al−μ_3-H distance is rather long and this bond should be treated as secondary rather than covalent. It is noteworthy that the lutetium complex [Cp$_2$Lu(AlH$_4$·NEt$_3$)]$_2$ was obtained under the form H, as a benzene solvate, when its preparation from [Cp$_2$LuCl]$_2$ was performed with an excess of triethylamine.[17] This solvate was resistant to X-ray irradiation, in contrast to the benzene-free compound which, after exposition to hard X-rays, was dissociated into the monomer Cp$_2$Lu(μ_2-H)AlH$_3$·NEt$_3$, a unique example of aluminohydride with a monodentate AlH$_4$ group.[100]

The ring-substituted derivatives [(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$-Lu(AlH$_4$·L)]$_2$ (L = Et$_2$O, NEt$_3$) were unstable in diethyl ether and decomposed into the octanuclear compound [(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$LuH]$_4$[AlH$_4$·Et$_2$O]$_2$[AlH$_4$]$_2$;

Table 4. Lanthanide Aluminohydride Complexes and Their Characterization

complexes	analyses[a]	infrared data[b]	Ln···Ln	Ln···Al	Ln-μ_3-H	Ln-μ_2-H	Al-μ_3-H	Al-μ_2-H	ref(s)
					X-ray diffraction data[c]				
[Cp$_2$Y(AlH$_4$·THF)]$_2$	Al,Y	1813, 1650, 1288	3.75	3.24, 4.0	2.2	2.2	2.0	1.6	98,99
[Cp$_2$Y(AlH$_4$·NEt$_3$)]$_2$	Al,Y	1816 (1308), 1661 (1200), 1275 (910	3.70	3.3, 4.1					99
[Cp$_2$Y(AlH$_4$·OEt$_2$)]$_2$	Al,Y	1863 (1345), 1662 (1207), 1301 (945)							99
[Cp$_2$Y(AlH$_4$)]$_2$OEt$_2$	Al,Y	1835, 1780, 1660, 1580, 1365	4.38	3.21, 3.55					99
[Cp$_2$Sm(AlH$_4$·NEt$_3$)]$_2$			4.07, 4.10	3.3		1.7, 2.4		1.7−1.9	101
[(C$_5$H$_4$^{t}Bu)$_2$Sm(AlH$_4$·THF)]$_2$			4.23	3.28	2.4	2.3	1.8	1.6	102
[(C$_5$H$_4$^{t}Bu)$_2$Sm]$_2$(μ-H)(μ-AlH$_4$·TMEDA)	Al		3.71	3.04		2.1		1.7	101
(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Sm(μ_2-D)$_2$AlD(TMEDA)				2.29		1.6, 2.0		1.8, 2.0	104
[Cp$_2$Yb(AlH$_4$·NEt$_3$)]$_2$·C$_6$H$_6$	Al,Y		3.62	3.26, 3.73	2.1	2.2	2.3	1.6	17
[Cp$_2$Lu(AlH$_4$·THF)]$_2$	Al,Lu	1830, 1675, 1255	isostructural with the Y analogue						100
[Cp$_2$Lu(AlH$_4$·Et$_2$O)]$_2$	Al,Lu	1885, 1670, 1320							100
[Cp$_2$Lu(AlH$_4$·NEt$_3$)]$_2$	Al,Lu	1810 (1305), 1660 (1200), 1305 (930)	isostructural with the Y analogue						100
[Cp$_2$Lu(AlH$_4$·NEt$_3$)]$_2$·C$_6$H$_6$			3.61	3.26, 4.09	2.4, 1.7	2.6	2.7	1.7, 1.9	17
[Cp$_2$Lu(μ_2-H)AlH$_3$·NEt$_3$			3.64	3.23		1.8		1.8	100
[(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$LuH]$_4$[AlH$_4$·Et$_2$O]$_2$[AlH$_4$]$_2$	Al,Lu		3.35	2.9−3.2					14
(1,3-^{t}Bu$_2$-C$_5$H$_3$)$_5$Sm$_4$H$_3$(AlH$_4$)$_4$·2TMEDA	Al,Sm		3.75	2.9−3.2					103
[Cp$_2$YCl(AlH$_3$·NEt$_3$)]$_2$	Al,Y,Cl		4.38	3.62		2.1		1.8	105
[Cp$_2$Y]$_2$(μ-Cl)(μ-AlH$_4$·NEt$_3$]·C$_6$H$_6$	Al,Y,Cl	1700−1900	3.95	3.24	2.1	2.4	1.9	1.5−1.7	106
(Cp$_2$Y)$_2$(AlH$_4$Cl)·2THF	C,H,Cl,Y	1580, 1155							106
[Cp$_2$YCl(AlH$_3$·Et$_2$O)]$_n$			4.38	3.63		2.3		1.5	107

[a] Are given the elements which have been analyzed. [b] ν(Al−H) and ν(Ln−H) in cm^{-1} (the values in parentheses correspond to the deuterated analogues). [c] Distances in Å.
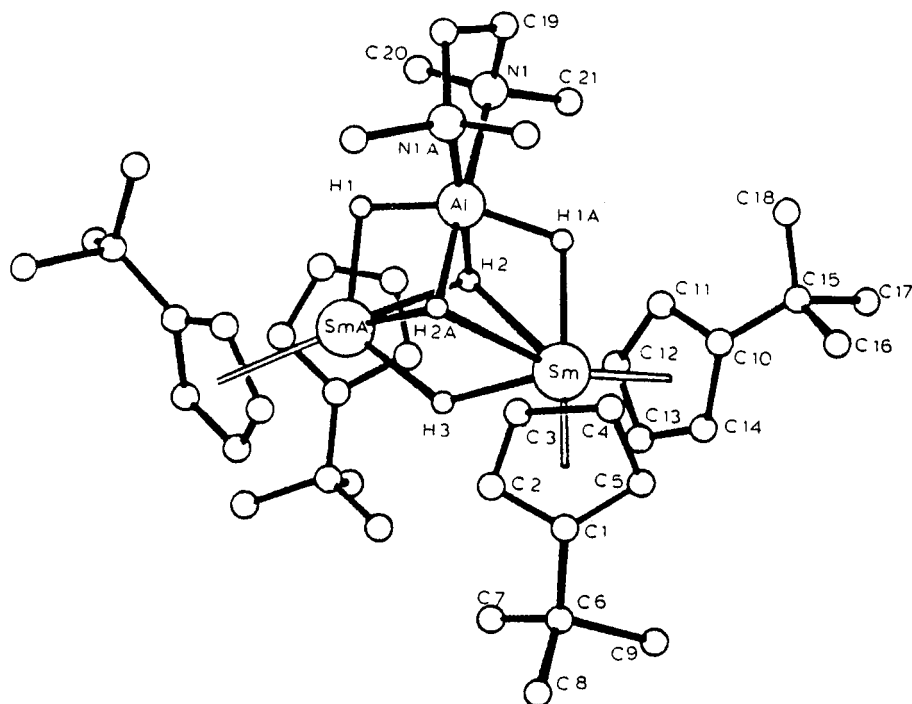
Figure 30. Crystal structure of [(C$_5$H$_4$^{t}Bu)$_2$Sm]$_2$(μ-H)(μ-AlH$_4$·TMEDA). (Reprinted with permission from ref 101. Copyright 1991 Elsevier Science S.A.)
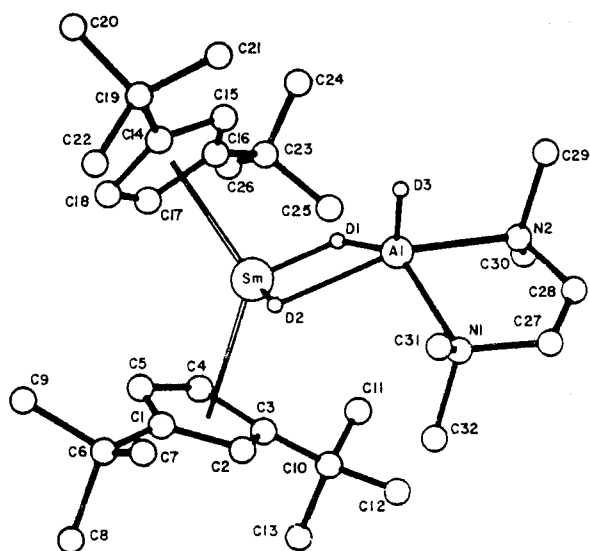
Figure 31. Crystal structure of (C$_5$H$_3$^{t}Bu$_2$)$_2$Sm(μ_2-D)$_2$AlD-(TMEDA). (Reprinted with permission from ref 104. Copyright 1992 Elsevier Science S.A.)
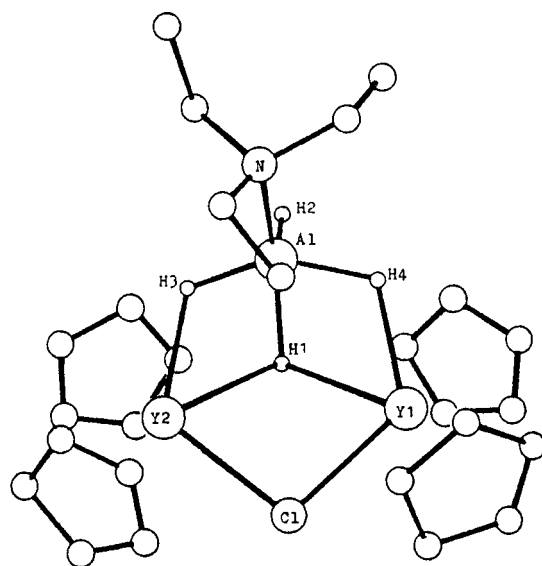
Figure 32. Crystal structure of [Cp$_2$Y]$_2$(μ-Cl)(μ-AlH$_4$·NEt$_3$]·C$_6$H$_6$. (Reprinted with permission from ref 106. Copyright 1987 Elsevier Science S.A.)

the mechanism of this reaction is not elucidated. The crystal structure indicated that the four Lu atoms, which form a tetrahedron, are bound by bridging hydrogens and tridentate AlH$_4$ and tetradentate (AlH$_4$·Et$_2$O) groups.[14]

Treatment of (C$_5$H$_4$^{t}Bu)$_2$SmCl with LiAlH$_4$ in the presence of TMEDA afforded the trinuclear complex [(C$_5$H$_4$^{t}Bu)$_2$Sm]$_2$(μ-H)(μ-AlH$_4$·TMEDA) in which the AlH$_4$ group adopts the μ-η^3:η^3 ligation mode (Figure 30).[101] It is likely that this reaction proceeds by the formation of the "normal" aluminohydride [(C$_5$H$_4$^{t}-Bu)$_2$Sm(AlH$_4$·TMEDA)]$_2$ which would decompose in the presence of the strong Lewis base. If the Lewis base is in large excess, further decomposition of the complexes (C$_5$H$_4$R)$_2$Ln(AlH$_4$·L) would occur to give, depending on Ln and C$_5$H$_4$R, the corresponding hydrides [(C$_5$H$_4$R)$_2$LnH]$_2$, as depicted by eqs 1−4. The

strength of bonding of AlH$_3$ in the compounds (C$_5$H$_4$R)$_2$Ln(AlH$_4$·L) could be related to the length of Ln−μ_2-H and Al−μ_3-H bonds which decrease in the order Y, Sm > Yb > Lu; as a result, the lutetium aluminohydrides were easily transformed into the hydrides with an excess of triethylamine.

The reactions of the two complexes (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$-Sm and Cp$_2$YCl with AlH$_3$ have been studied; the nature of the products is, here again, dependent on the experimental conditions. The octanuclear complex (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_5$Sm$_4$H$_3$(AlH$_4$)$_4$·2TMEDA was isolated from the reaction of (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Sm with AlH$_3$ in the presence of TMEDA; the exact number of hydrogen atoms could not be determined by the crystal structure and was fixed by assuming that all the Sm atoms were in the +3 oxidation state.[103] When AlH$_3$ was replaced by AlD$_3$, oxidation of sa-

Figure 33. Crystal structure of $[Cp_2YCl(AlH_3 \cdot NEt_3)]_2$. (Reprinted with permission from ref 105. Copyright 1983 Elsevier Science S.A.)

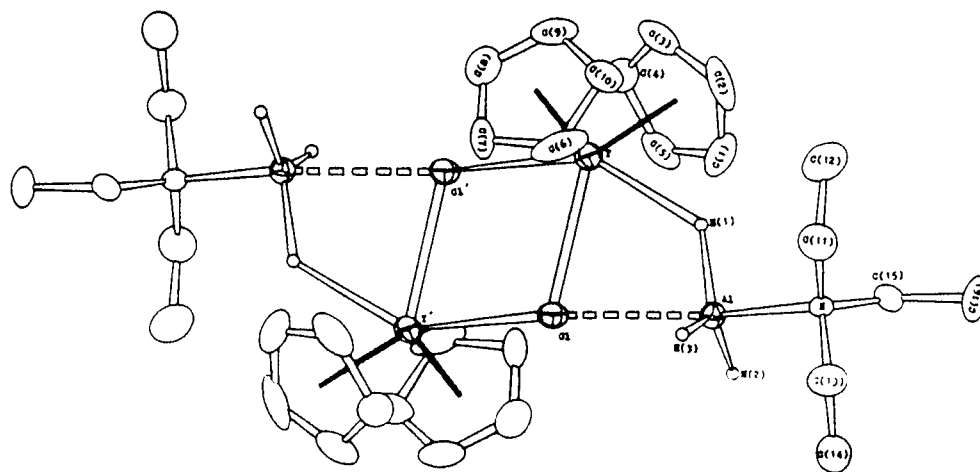marium did not occur and the product was the alane adduct $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2Sm(\mu_2\text{-}D)_2AlD(TMEDA)$ (Sm–D = 1.6(1) and 2.0(1) Å) (Figure 31).[104]

Reaction of Cp_2YCl with $AlH_3 \cdot NEt_3$ gave the dimeric adduct $[Cp_2YCl(AlH_3 \cdot NEt_3)]_2$ when the alane was added to the yttrium complex solution[105] whereas the chloro–aluminohydride complex $[Cp_2Y]_2(\mu\text{-}Cl)(\mu\text{-}AlH_4 \cdot NEt_3] \cdot C_6H_6$ was formed by reversing the order of addition;[106] this latter compound was alternatively prepared by treatment of Cp_2YCl with 0.5 equiv of $LiAlH_4$ in the presence of NEt_3. The crystal structures showed that in $[Cp_2Y]_2(\mu\text{-}Cl)(\mu\text{-}AlH_4 \cdot NEt_3] \cdot C_6H_6$ (Figure 32), the fragment $Cp_2YHClYCp_2$ is linked to the $AlH_3 \cdot NEt_3$ moiety via two μ_2 and one μ_3 hydrogen atoms, whereas in $[Cp_2YCl(AlH_3 \cdot NEt_3)]_2$ (Figure 33), the $AlH_3 \cdot NEt_3$ moiety is attached to the $(Cp_2YCl)_2$ fragment by one Y–H–Al bridge and a weak secondary Al–Cl bond. In the etherate analogue $[Cp_2YCl(AlH_3 \cdot Et_2O)]_n$, another Al–H–Y bridge ensures the polymeric structure.[107] The structure of the THF adduct $(Cp_2Y)_2(AlH_4Cl) \cdot 2THF$ would be different from that of $[Cp_2Y]_2(\mu\text{-}Cl)(\mu\text{-}AlH_4 \cdot NEt_3] \cdot C_6H_6$, according to the IR data.[106]

VI. Synthesis of the Homonuclear Uranium and Thorium Hydrides

The binary hydrides ThH_2 and UH_3, obtained by reaction of H_2 with the metals,[108] are not practical reagents for synthetic purposes, in particular because of the low solubility of these polymeric compounds. The uranium hydride was used for the reduction of PhX (X = Cl, Br, I) and oxygenated organic molecules.[109]

A. β-Hydrogen Elimination Reactions of Alkyl Compounds

In contrast to the lanthanide hydrides, no hydride of a 5f-element could be isolated from a β-H elimination reaction of an alkyl precursor.

Thermal decomposition of the unstable and not characterized alkyl compounds formed in the reaction of UCl_4 with RLi gave comparable amounts of alkane and alkene. These results were explained by the reaction of a U(IV) or U(III) hydride, resulting from β-H elimination, with an alkyl species according to eq 29a,b.[110–112]

$$[U]\text{-}CH_2CH_2R \rightarrow [U]\text{-}H + CH_2{=}CHR \quad (29a)$$

$$[U]\text{-}H + [U]\text{-}CH_2CH_2R \rightarrow 2[U] + RCH_2CH_3 \quad (29b)$$
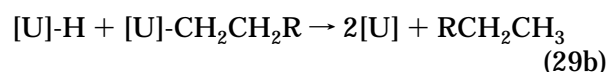
Photolysis of the thorium alkyls Cp_3ThR would occur by the same mechanism.[113] It is noteworthy that the complexes Cp_3AnR are thermally very stable, indicating that β-H elimination is not a favored process in organo f-element chemistry.[114]

B. Substitution Reactions of Halide Complexes

The bis(trimethylsilyl) amide complexes $[N(TMS)_2]_3AnH$ have been prepared by reaction of the corresponding chlorides with $LiBEt_3H$.[115] These hydrides were also obtained by treating $AnCl_4$ with 4 equiv of $NaN(TMS)_2$; in this case, THF is the source of the hydrogen atom.[116]

The complexes $(C_5H_4R)_3UH$ (R = ^tBu or TMS),[117,118] $(C_4Me_4P)_3UH$,[119] $(C_5H_4PPh_2)_3UH$,[120] $(C_5H_4TMS)_3ThH$, and $(C_9H_6TMS)_3ThH$[121] were synthesized from their chloride precursor, by treatment with $LiBEt_3H$ or $NaBEt_3H$. It is noteworthy that these reagents were not used for the preparation of lanthanide hydrides.

C. Formation of Anionic Hydrides by Addition of NaH

Addition of NaH to the triscyclopentadienyl U(III) complexes $(C_5H_4R)_3U$ afforded the hydrido-bridged anions $[(C_5H_4R)_3UHU(C_5H_4R)_3]^-$ (R = H or Me) or the monomeric anions $[(C_5H_4R)_3UH]^-$ (R = ^tBu or TMS); these latter were alternatively prepared by sodium amalgam reduction of $(C_5H_4R)_3UH$.[122,123]

D. Synthesis of $Cp^*_2Th(X)H$ Complexes from $[Cp^*_2ThH_2]_2$

The compounds $Cp^*_2Th(OCH^tBu_2)H$ and $Cp^*_2Th(O\text{-}2,6\text{-}^tBu_2C_6H_3)H$ have been prepared by reaction of $[Cp^*_2ThH_2]_2$ with $^tBu_2CO$ and $2,6\text{-}^tBu_2C_6H_3OH$ respectively,[124] whereas $[Cp^*_2Th(Cl)H]_2$ was obtained by comproportionation of $[Cp^*_2ThH_2]_2$ and $[Cp^*_2ThCl_2]_2$[125] (*vide infra* the reactions of $[Cp^*_2ThH_2]_2$). The chloro–hydride complex was alternatively synthesized by hydrogenolysis of $Cp^*_2Th(CH_2TMS)(Cl)$.

E. Hydrogenolysis of Alkyl Complexes

As for the lanthanide hydrides, hydrogenolysis of alkyl precursors is the most straightforward route to

actinide hydrides and with the exceptions presented above, all have been synthesized by this way. Also in this case, the alkyl ligands are generally CH_2TMS and $CH(TMS)_2$, and the hydrogenolysis was performed in noncoordinating solvents. Thus were synthesized the hydrides $[Cp*_2AnH_2]_2$ which were very important for reactivity studies; in contrast, An–C bond hydrogenolysis has never been observed for alkyl Cp_3AnR compounds, presumably for steric reasons.

Kinetic studies showed that hydrogenolysis of the complexes $Cp*_2An(X)(R)$ exhibits a first-order rate law at constant H_2 pressure. The rate constants depend markedly on the nature of the R ligand, the metal, and ancillary ligands; they correlate qualitatively with the An–R bond disruption energies. It is noteworthy that π-donating alkoxide ligands effect a marked decrease ($\sim 10^6$) in the rate of hydrogenolysis. The small enthalpies of activation and the large negative entropies of activation are in agreement with a concerted mechanism involving a polar "het-erolytic" four-center transition state with significant H–H bond cleavage.[126]

VII. Classification and Structure of the Homonuclear Actinide Hydrides

Most of these complexes, which are listed in Table 5, are cyclopentadienyl derivatives; with the exception of the anions $[(C_5H_4R)_3UH]^-$ and $[(C_5H_4R)_3-UHU(C_5H_4R)_3]^-$ and of the neutral compounds $[Cp*_2-UH]_n$ and $Cp*_2UH(DMPE)$, they are found in the +4 oxidation state.

A. Metalloorganic Hydrides

The bis(trimethylsilyl) amide compounds $[(TMS)_2-N]_3AnH$ are monomeric in the solid state.[115,116] The dimeric compound $[(DME)U(BH_4)_3H]_2$ is the sole actinide hydride to have been prepared from the corresponding borohydride; the distance between the uranium atoms (4.12 Å) is similar to that found between the thorium atoms in $[Cp*_2ThH_2]_2$.[127] In the trimeric hydrido aryloxide complex $[Th(O-2,6-^tBu_2-$

Table 5. Actinide Hydrides and Their Characterization

complexes	analyses[a]	infrared data[b]	^1H NMR data[c]	X-ray diffraction data[d]	ref(s)
		Metalloorganic Complexes			
$[(TMS)_2N]_3ThH$	C,H,N	1480 (1060)	benzene-d_6: 0.63		115,116
$[(TMS)_2N]_3UH$	C,H,N	1430 (1020)	not visible		115,116
$[(DME)U(BH_4)_3H]_2$	C,H,B	2140, 1195, 1170	not visible	U···U 4.12	127
				U···B 2.53(6), 2.64(4)	
$[Th(O-2,6-^tBu_2-C_6H_3)_2H_2]_3$	C,H	1336 (954), 975 (705), 795 (560)	benzene-d_6: 20.54	Th–H 2.0–2.6	128
		Monocyclopentadienyl Complexes			
$[Cp*Th(O-2,6-^tBu_2-C_6H_3)H_2]_3$	C,H		benzene-d_6: 18.54		129
$[(Cp*)(COT)ThH]_x$		1147 (843)	not visible		130
		Biscyclopentadienyl Complexes			
$[Cp*_2ThH_2]_2$	C,H	1404 (1002), 1370 (979), 1215 (873), 1114 (803), 844 (609), 650 (465)	benzene-d_6: 19.2	Th–H 2.03(1), 2.29(3)	125,132
				Th···Th 4.007(8)	
$[Cp*_2UH_2]_2$		1335, 1180	benzene-d_6: 316.8		125
$[Me_2Si(C_5Me_4)_2ThH_2]_2$		1285 (918), 1155, 654 (462), 481	benzene-d_6: 18.36	Th···Th 3.632(2)	134
$Cp*_2UH(dmpe)$	C,H,P	1219 (870)	not visible	H not located	136
$Cp*_2Th(O^tBu)H$	C,H	1359 (981)	benzene-d_6: 17.4		125
$Cp*_2Th(OCH^tBu_2)H$	C,H	1355 (971)	toluene-d_8: 17.1		124
$Cp*_2Th(O-2,6-^tBu_2C_6H_3)H$	C,H	1365	benzene-d_6: 19.1		124
$Cp*_2Th(OSiMe_2^tBu)H$			benzene-d_6: 18.0		126
$Cp*_2Th\{(1S)-endo-bornoxide\}H$	C,H	1348	benzene-d_6: 17.7		137
$Cp*_2U(O^tBu)H$	C,H	1363	benzene-d_6: 267.1		137
$Cp*_2U(OCH^tBu_2)H$			benzene-d_6: 276.7		126
$Cp*_2U(OSiMe_2^tBu)H$	C,H,Si	1395 (988)	not visible		138
$Cp*_2U\{(R)-2-butoxide\}H$		1339	benzene-d_6: 265.9		137
$Cp*_2U\{(1R,2S,5R)-menthoxide\}H$	C,H	1420, 1292	benzene-d_6: 267.9		137
$Cp*_2U\{(1S)-endo-bornoxide\}H$	C,H	1363	benzene-d_6: 269.6		137
$Cp*_2U\{(1S,2S,5R)-neomenthoxide\}H$	C,H	1370	benzene-d_6: 269.2		137
$[Cp*_2Th(Cl)H]_2$		1229, 1152, 829, 672	benzene-d_6: 19.0		125
$[Cp*_2ThH][Co(B_9C_2H_{11})_2]$	C,H		benzene-d_6: 19.04		139
		Triscyclopentadienyl Complexes			
$(C_5H_4^tBu)_3UH$	C,H		toluene-d_8: 276.1	H not located	117,118
$(C_5H_4SiMe_3)_3UH$	C,H,U	1395 (1015)	toluene-d_8: 290.5		117,118
$(C_5H_4SiMe_3)_3ThH$	C,H,Si,Th	1460	benzene-d_6: 12.94		121
$(C_5H_4PPh_2)_3UH$			benzene-d_6: 305		120
$(C_9H_6SiMe_3)_3ThH$	C,H,Th	1485 (1055)	toluene-d_8: 14.73		121
$(C_4Me_4P)_3UH$	C,H,P		toluene-d_8: 333.4	H not located	119
$[Na(18-crown-6)][(C_5H_4^tBu)_3UH]$	C,H,Na		THF-d_8: 521.3		123
$[Na(18-crown-6)][(C_5H_4SiMe_3)_3UH]$	C,H,Na	1405 (1020)	THF-d_8: 547.1		123
$[Na(THF)_2][(Cp_3U)_2(\mu-H)]$	C,H,Na,U		THF-d_8: 293	U–H 2, 2.4	122,123
$[Na(THF)_2][\{(C_5H_4Me)_3U\}_2(\mu-H)]$	C,H,Na		THF-d_8: 302.2		123
$[Na(18-crown-6)][\{(C_5H_4SiMe_3)_3U\}_2(\mu-H]$			THF-d_8: 319.2	U···U 4.4638(4)	123

[a] Elements which have been analyzed. [b] An–H (An–D) IR vibrations in cm^{-1}. [c] Chemical shifts δ of the hydride singlet signals. [d] Distances in Å.
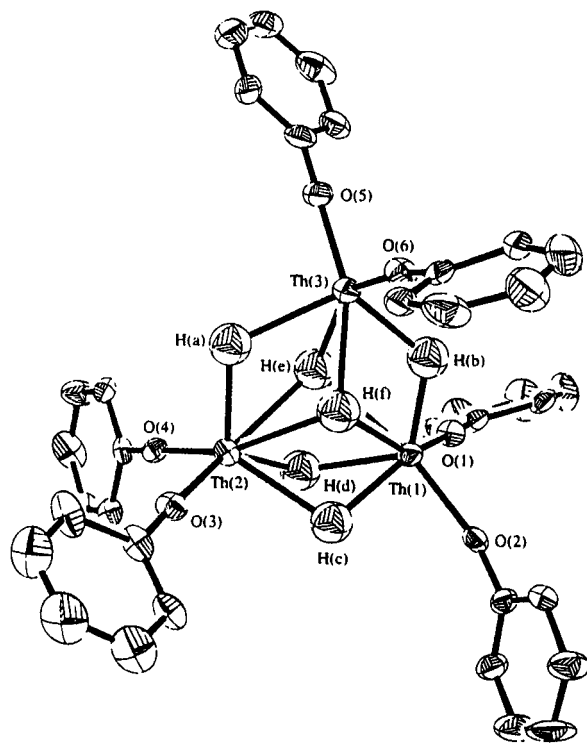
Figure 34. Crystal structure of [Th(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)$_2$H$_2$]$_3$. (Reprinted from ref 128. Copyright 1995 American Chemical Society.)

C$_6$H$_3$)$_2$H$_2$]$_3$, each face of the trimetallic core is capped by a μ_3-H ligand, two sides are each bridged by a μ_2-H ligand while the third side is bridged by two μ_2-H ligands (Figure 34);[128] this central M$_3$(μ_3-H)$_2$(μ_2-H)$_4$ core appears to be structurally unprecedented among metal hydride complexes.

B. Monocyclopentadienyl Complexes

Only two compounds of this class have been reported. The mono(pentamethylcyclopentadienyl)-thorium complex [Cp*Th(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)H$_2$]$_3$, which is a trimer from molecular weight determination, would have a structure similar to that of [Th(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)$_2$H$_2$]$_3$.[129] The mixed-ring complex [(Cp*)-(COT)ThH]$_x$, supposed to be oligomeric, was characterized by its broad IR band at 1147 cm^{-1} which was shifted to 843 cm^{-1} upon deuteration.[130]

C. Biscyclopentadienyl Hydrides

The bis(pentamethylcyclopentadienyl) complexes [Cp*$_2$AnH$_2$]$_2$ were the first organoactinide hydrides to have been isolated.[124,125,131] The dimeric crystal structure of [Cp*$_2$ThH$_2$]$_2$ was determined by neutron diffraction (Figure 35);[132] the two Cp*$_2$ThH fragments are linked by two hydrogen bridges and the Th$_2$(μ-H)$_2$ core is nearly planar. In the ring-bridged compound [Me$_2$Si(C$_5$Me$_4$)$_2$ThH$_2$]$_2$, the Me$_2$Si ligation significantly opens the thorium coordination sphere and the short Th$\cdots$Th distance (3.632(2) Å), in combination with infrared spectra, suggests a Th(μ-H)$_4$Th structure (Figure 36).[133,134] The uranium compound [Cp*$_2$UH$_2$]$_2$ was stable under H$_2$ pressure, being otherwise transformed into the U(III) hydride [Cp*$_2$-UH]$_n$;[125,135] the diphosphine adduct Cp*$_2$UH(DMPE) was characterized by X-ray analysis (Figure 37).[136]

A large series of monomeric compounds of general formula Cp*$_2$An(OR)H have been reported. The OR
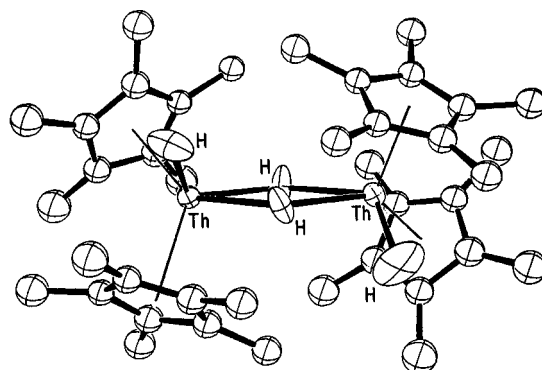
Figure 35. Crystal structure of [Cp*$_2$ThH$_2$]$_2$. (Reprinted with permission from ref 132. Copyright 1979 American Association for the Advancement of Science.)
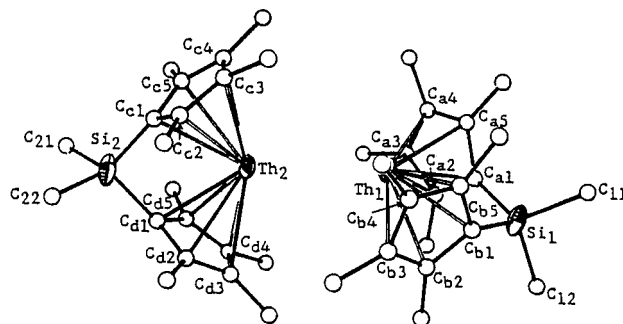
Figure 36. Crystal structure of [Me$_2$Si(C$_5$Me$_4$)$_2$ThH$_2$]$_2$. (Reprinted from ref 134. Copyright 1988 American Chemical Society.)
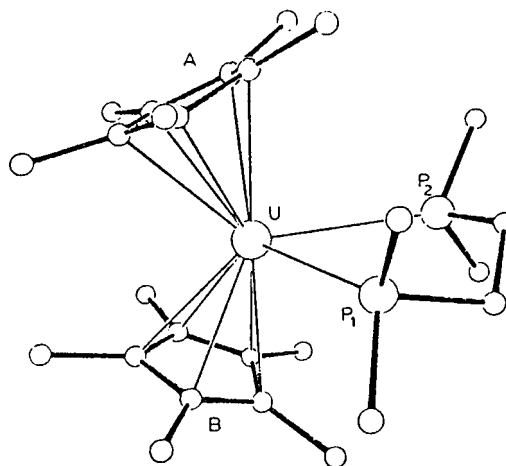
Figure 37. Crystal structure of Cp*$_2$UH(DMPE). (Reprinted from ref 136. Copyright 1982 American Chemical Society.)

groups are O^{t}Bu,[125] OCH^{t}Bu$_2$,[124] O-2,6-^{t}Bu$_2$C$_6$H$_3$,[124] OSiMe$_2$^{t}Bu,[126] and (1S)-endo-bornoxide[137] for the thorium complexes and O^{t}Bu,[137] OCH^{t}Bu$_2$,[126] OSiMe$_2$^{t}-Bu,[138] (1R,2S,5R)-menthoxide, (R)-2-butoxide, (1S)-endo-bornoxide, and (1S,2S,5R)-neomenthoxide for the uranium complexes.[137] All these complexes exhibit a band at ~1360 cm^{-1} in their infrared spectra; the hydride ^{1}H NMR resonances are visible near 17 and 270 ppm for the thorium and uranium compounds, respectively. From the IR spectrum, it is likely that the chloro−hydride complex [Cp*$_2$Th-(Cl)H]$_2$ adopts a dimeric structure analogous to that of [Cp*$_2$ThH$_2$]$_2$ with terminal Cl ligands in place of the terminal hydride ligands.[125]

The thorium compound [Cp*$_2$ThH][Co(B$_9$C$_2$H$_{11}$)$_2$] is a unique example of a cationic actinide hydride; it

was characterized by the ^{1}H NMR signal at 19.04 ppm but its exact structure awaits further elucidation.[139]

D. Triscyclopentadienyl Hydrides

The three neutral compounds $(C_5H_4R)_3UH$ (R = ^{t}Bu, TMS)[117,118] and $(C_5H_4TMS)_3ThH$[121] have been isolated. Substitution of the cyclopentadienyl ligand is essential for the stability of these complexes, since Cp$_3$UH could neither be prepared or even detected; it seems likely that the steric bulk of the cyclopentadienyl ring prevents the bimolecular H$_2$ elimination process which, from thermochemical data, would be closed to thermoneutrality to be entropically driven.[140] The uranium hydrides give rise to very shifted paramagnetic ^{1}H NMR signals at ~280 ppm, and the compound $(C_5H_4PPh_2)_3UH$ could be detected in solution by its resonance at 305 ppm.[120] The crystal structure of $(C_5H_4{}^tBu)_3UH$ was determined; the geometrical parameters are quite similar to those of the trigonal planar compound $(C_5H_4TMS)_3U$. The tris-(indenyl) complex $(C_9H_6TMS)_3ThH$[121] and $(C_4Me_4P)_3$-UH, the first tris(phospholyl)−metal compound,[119] are also very stable; the latter is isostructural to $(C_4Me_4P)_3UCl$.

The anionic uranium(III) hydrides [Na(18-crown-6)][$(C_5H_4R)_3UH$] could be isolated for R = ^{t}Bu and TMS; the hydride NMR signals are visible at 521 and 547 ppm.[123] For R = H or Me, these complexes are not stable and the hydrido-bridged derivatives [Na-(THF)$_2$][$(C_5H_4R)_3UHU(C_5H_4R)_3$] were obtained.[122,123] This difference is due to both steric and electronic effects; if the anion [$(C_5H_4{}^tBu)_3UHU(C_5H_4{}^tBu)_3$]$^-$ could not be detected, [Na(18-crown-6)][C_5H_4-TMS)$_3$UHU(C$_5$H$_4$TMS)$_3$], which is partially dissociated in solution, was isolated and crystallographically characterized (Figure 38).[123] The structure is composed of discrete cation−anion pairs (U···U = 4.4638-(4) Å), in contrast to that of [Na(THF)$_2$][Cp$_3$UHUCp$_3$] which consists of infinite puckered chains of Cp$_3$-UHUCp$_3$ and Na(THF)$_2$ fragments linked by Na−Cp bonds (Figure 39); the bent U−H−U bridge is similar to that invariably found in the series of the bridged monohydride transition metal complexes, which was explained by back-bonding from M(dp) to the M−H σ*-orbital.[141]
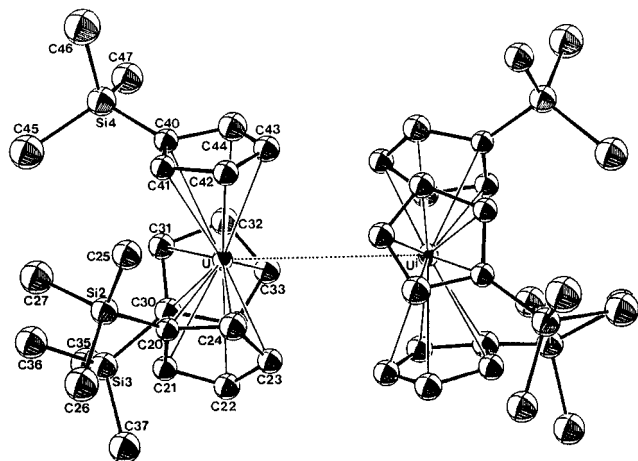
Figure 38. Crystal structure of the anion of [Na(18-crown-6)][$(C_5H_4TMS)_3UHU(C_5H_4TMS)_3$]. (Reprinted with permission from ref 123. Copyright 1992 Elsevier Science S.A.)
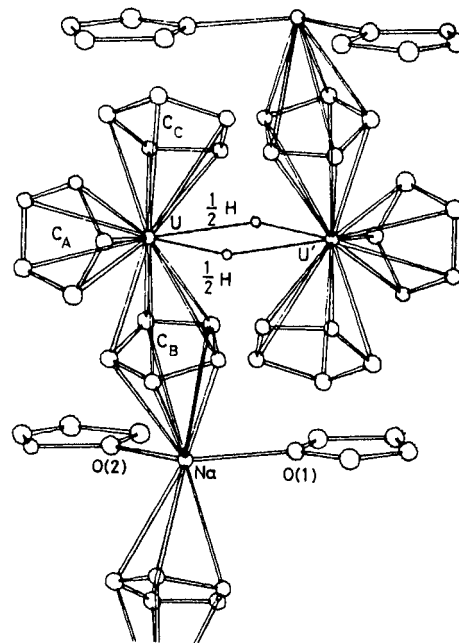
Figure 39. Crystal structure of [Na(THF)$_2$][Cp$_3$UHUCp$_3$]. (Reprinted with permission from ref 122. Copyright 1989 The Royal Society of Chemistry.)

VIII. Synthesis and Structure of the Heteronuclear Actinide Hydrides

The complexes are listed in Table 2.

The bimetallic uranium−rhenium hexahydrides Cp$_3$UH$_6$Re(PPh$_3$)$_2$ and Cp$_3$UH$_6$Re(P[C$_6$H$_4$F]$_3$)$_2$ were prepared by the metathesis reaction 30.[142]

$$Cp_3UCl + [K(THF)_2][ReH_6(PAr_3)_2] \rightarrow$$
$$Cp_3UH_6Re(PAr_3)_2 + KCl \quad (30)$$

$$Ar = Ph, C_6H_4F$$
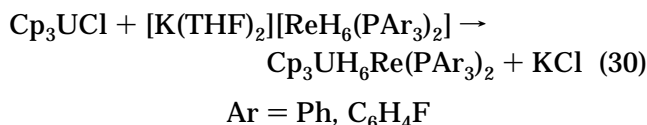
However, the ring-substituted derivatives $(C_5H_4R)_3$-UH$_6$Re(PPh$_3$)$_2$ could not be isolated from $(C_5H_4R)_3$-UCl and [K(THF)$_2$][ReH$_6$(PPh$_3$)$_2$] because of their reverse cleavage by KCl which led to an equilibrium mixture.[143] These complexes were cleanly synthesized by using the cationic precursor [$(C_5H_4R)_3U$]-[BPh$_4$] (eq 31).

$$[(C_5H_4R)_3U][BPh_4] + [K(THF)_2][ReH_6(PPh_3)_2] \rightarrow$$
$$(C_5H_4R)_3UH_6Re(PPh_3)_2 + KBPh_4 \quad (31)$$

$$R = {}^tBu, TMS$$
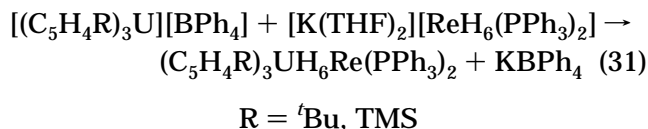
At 30 °C, the six hydride ligands were apparently equivalent in the NMR spectrum and a slow limiting spectrum could not be obtained; in view of the tridentate configuration of the borohydride ligand in Cp$_3$U(BH$_4$) (*vide infra*) and the structure of several rhenium−transition metal polyhydrides, it is assumed that at least three hydrogens are bridging in these compounds.

Reaction of Cp*$_2$UCl(THF) and [K(THF)$_2$][ReH$_6$-(PPh$_3$)$_2$] did not afford the metathesis product with elimination of KCl but gave the addition compound [K(THF)$_2$][Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$] (eq 32);[143,144] the

$$Cp*_2UCl(THF) + [K(THF)_2][ReH_6(PPh_3)_2] \rightarrow$$
$$[K(THF)_2][Cp*_2(Cl)UH_6Re(PPh_3)_2] \quad (32)$$
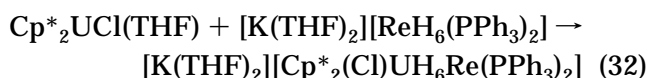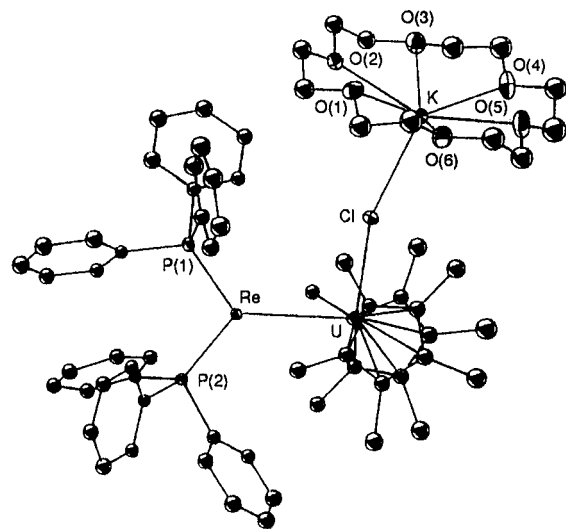
Figure 40. Crystal structure of [K(18-crown-6)]-[Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$]. (Reprinted with permission from ref 144. Copyright 1994 The Royal Society of Chemistry.)

borohydride was similarly prepared. These complexes are unique examples of anionic heterobimetallic polyhydrides and are also the first compounds in which a transition metal and a trivalent actinide are maintained in close proximity. The hydrogen atoms could not be located in the crystal structure of [K(18-crown-6)][Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$] (Figure 40) but the NMR spectra indicated the presence of three bridging hydrogens in a U(μ-H)$_3$Re fragment and three terminal rhenium hydrogens. The neutral complex Cp*$_2$(Cl)UH$_6$Re(PPh$_3$)$_2$ was prepared by oxidation of the corresponding anion and its treatment with KCp afforded the triscyclopentadienyl derivative Cp*Cp$_2$UH$_6$Re(PPh$_3$)$_2$.[143]

IX. Synthesis and Structure of the Actinide Borohydrides and Aluminohydrides

The tetraborohydride complexes An(BH$_3$R)$_4$ (R = H, alkyl), generally prepared from AnCl$_4$, served as precursors to a number of organoactinide derivatives, by substitution of their BH$_3$R ligands; their reduction led to the formation of stable uranium(III) borohydrides. As in the case of the lanthanide borohydrides, the ligation mode of the BH$_4$ groups was determined by IR spectroscopy and X-ray diffraction analysis; the An···B distances are respectively equal to *ca.* 2.5 and 2.9 Å for tridentate and bidentate ligands.

A. The Tetravalent Complexes An(BH$_3$R)$_4$ (R = H, Me) and Their Derivatives

The actinide tetraborohydrides, in particular those of uranium, were extensively studied during the period of the Manhattan project. These volatile compounds were synthesized by treating AnF$_4$ or AnCl$_4$ with Al(BH$_4$)$_3$ or LiBH$_4$. Thus, U(BH$_4$)$_4$[145] and Th(BH$_4$)$_4$[146] were first prepared according to the solvent-free reaction depicted by eq 33. The Pa, Np and Pu analogues were also obtained by this way.[147]

$$AnF_4 + 2Al(BH_4)_3 \rightarrow An(BH_4)_4 + 2Al(BH_4)F_2 \quad (33)$$
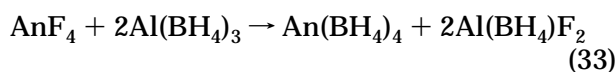
The synthesis of U(BH$_4$)$_4$ by reaction of finely powdered UCl$_4$ and LiBH$_4$ (eq 34) must be performed

in a vacuum vibration ball mill[148] but the thorium analogue can be prepared in diethyl ether since in that case, the solvent can be completely removed by vacuum distillation.[149]

$$AnCl_4 + 4LiBH_4 \rightarrow An(BH_4)_4 + 4LiCl \quad (34)$$
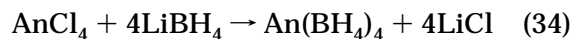
The crystal structure of U(BH$_4$)$_4$ was determined by neutron diffraction. Each uranium atom is surrounded by six BH$_4$ groups in a pseudooctahedral configuration; two are tridentate in a *cis* position, whereas the four others are attached to the metal by two hydrogen atoms and use their remaining two hydrogen atoms to bridge neighboring uranium atoms in a helical polymeric structure.[150] The thorium and protactinium borohydrides are isomorphous with U(BH$_4$)$_4$ but Np(BH$_4$)$_4$ and Pu(BH$_4$)$_4$ have a monomeric tetrahedral structure with tridentate BH$_4$ ligands.[146,151] A second crystalline form of U(BH$_4$)$_4$ has been obtained by condensation of the vapors at low temperature.[152,153] In that case, the tridentate BH$_4$ ligands are in *trans* position and the equatorial bridging BH$_4$ groups ensure the two dimensional polymeric structure. The infrared and Raman spectra showed that the molecular tetrahedral structure of the gaseous molecules is maintained in aromatic solvents; the electronic spectrum can also be assigned in T_d symmetry.[154,155]

Treatment of U(BH$_4$)$_4$ with excess BMe$_3$ gave the methyl derivative U(BH$_3$Me)$_4$.[156] However, the complexes An(BH$_3$Me)$_4$ (An = Th, U, Np,[157] and Pa[158]) were best synthesized by reacting AnCl$_4$ or PaCl$_5$ with LiBH$_3$Me (eq 35).

$$AnCl_4 + 4LiBH_3Me \rightarrow An(BH_3Me)_4 + 4LiCl \quad (35)$$

X-ray diffraction analysis revealed that these monomeric compounds adopt a tetrahedral configuration with tridentate BH$_3$Me ligands. Other U(BH$_3$R)$_4$ compounds (R = thexyl, isopinocampheyl) were synthesized by reaction of U(BH$_4$)$_4$ with substituted alkenes (eq 36);[159] it is noteworthy that only tetra- and trisubstituted alkenes could be thus hydroborated, less substituted olefins being unreactive.

$$U(BH_4)_4 + 4Me_2C=CMe_2 \rightarrow$$
$$U(H_3BCMe_2CMe_2H)_4 \quad (36)$$
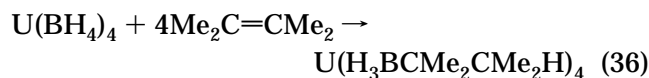
The complexes An(BH$_3$R)$_4$ (R = H, Me) give adducts with Lewis bases; most of these have been characterized by their X-ray crystal structure (Table 6). The monoetherates [U(BH$_4$)$_4$(OMe$_2$)]$_n$ and [U(BH$_4$)$_4$(OEt$_2$)]$_n$ (Figure 41) form infinite linear chains in which the U and B atoms are attached by double-hydrogen-bridge bonds and the other BH$_4$ groups are tridentate; the Me$_2$O and Et$_2$O ligands are relatively in *trans* and *cis* positions along the chain.[160] The *n*-propyl ether adduct [U(BH$_4$)$_4$(O^{n}Pr$_2$)]$_2$ forms an unsymmetrical dimer bridged with one bridging BH$_4$ group, the terminal borohydride ligands being tridentate; the two ether molecules are coordinated to the same uranium atom (Figure 42).[161] The two complexes U(BH$_4$)$_4$(OPPh$_3$)$_2$[162] and U(BH$_4$)$_4$(OPPh$_3$)$_2$·2C$_6$H$_6$[163] are monomeric with *trans* triphenylphosphine oxide ligands; in the solvated compound, two BH$_4$ are bidentate and the two others are tridentate, whereas in the nonsolvated product (Figure 43), three

Table 6. X-ray Diffraction Data of the Lewis Base Adducts of the Actinide Borohydrides An(BH₃R)₄ and An(BH₃R)₃ (R = H, Me)

complexes	X-ray diffraction data^a	ref(s)
[U(BH₄)₄(OMe₂)]$_n$	U···B$_b$ (bridging) 2.87(2), 2.90(2) U···B$_t$ 2.49(4), 2.53(2)	160
[U(BH₄)₄(OEt₂)]$_n$	U···B$_b$ (bridging) 2.89(1) U···B$_t$ 2.52(1), 2.55(1) U−H(B$_b$) 2.26(6)−2.55(5) U−H(B$_t$) 2.19(6)−2.48(6)	160
[U(BH₄)₄(O^{n}Pr₂)]₂	U−B$_b$ (bridging) 2.84(5), 2.90(4) U···B$_t$ 2.49(6), 2.55(5)	161
U(BH₄)₄(THF)₂	U···B$_t$ 2.52(2), 2.60(2) U−H(B$_t$) 2.16, 2.39, 2.70	164,165
U(BH₄)₄(OPPh₃)₂	U···B$_b$ 2.84(5) U···B$_t$ 2.51(5), 2.58(5), 2.65(6) U−H(B$_b$) 2.1 U−H(B$_t$) 2.0, 2.5, 2.8	162
U(BH₄)₄(OPPh₃)₂·2C₆H₆	U···B$_b$ 2.75(3) U···B$_t$ 2.55(3)	163
[Th(BH₃Me)₄]₂(OEt₂)	av Th···B$_t$ (bridging) 2.96 av Th···B$_t$ 2.57 av Th−H (bridged) 2.5	167
[Th(BH₃Me)₄(THF)]₂	av Th···B$_t$ (bridging) 3.08 av Th···B$_t$ 2.62 av Th−H (bridged) 2.5	167
U(BH₃Me)₄(THF)₂	U···B$_t$ 2.554(15), 2.583(17)	168
[U(BH₃Me)₄(THT)]₂	U···B$_t$ 2.47−2.59	168
U(BH₃Me)₄(Me₂PCH₂CH₂PMe₂)	U···B$_t$ 2.56(1), 2.58(1)	169
U(BH₃Me)₄(MeOCH₂CH₂OMe)	U···B$_t$ 2.52(2)−2.58(2)	170
U(BH₃Me)₄(Me₂NCH₂CH₂NMe₂)	U···B$_t$ 2.51(2)−2.56(2) U···B$_b$ 2.72(2)	170
U(BH₃Me)₄(MeSCH₂CH₂SMe)	U···B$_t$ 2.54(1), 2.57(1)	170
U(BH₄)₃(THF)₃	U···B$_t$ 2.63(2), 2.64(2), 2.69(1)	179
U(BH₄)₃(Me₂PCH₂CH₂PMe₂)₂	U···B$_t$ 2.68(4) U···B$_b$ 2.84(3)	177
U(BH₄)₃(Ph₂Ppy)₂	U···B$_t$ 2.61(2), 2.656(8)	178
U(BH₃Me)₃(Me₂PCH₂CH₂PMe₂)₂	U···B$_t$ 2.62(1), 2.66(1)	169

^{a} Distances in Å; B$_t$ and B$_b$ are the boron atoms of tridentate and bidentate BH₄ ligands.
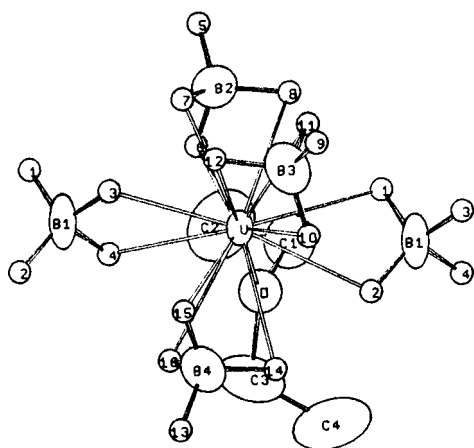
Figure 41. Crystal structure of [U(BH₄)₄(OEt₂)]$_n$. (Reprinted from ref 160. Copyright 1978 American Chemical Society.)

Figure 42. Crystal structure of [U(BH₄)₄(O^{n}Pr₂)]₂. (Reprinted from ref 161. Copyright 1978 American Chemical Society.)

tridentate and one bidentate BH₄ groups are present. The tetrahydrofuran adduct U(BH₄)₄(THF)₂ is also monomeric with *trans* THF ligands (Figure 44); all the BH₄ groups are tridentate.[164,165] It is interesting to note that in these complexes, the tridentate BH₄ ligands are not symmetrically oriented, one of the bridging hydrogen atoms being closer to the uranium center (2.0−2.1 Å) than the other two (2.4−2.8 Å) and the value of the angle U−B−H$_t$ is around 160°; these geometrical parameters suggested that some uranium borohydrides can be regarded as uranium hydrides coordinating to a BH₃ molecule.[166] The solid-state structure of U(BH₄)₄(THF)₂ is retained in

solution but in dichloromethane, the *trans* octahedral complex U(BH₄)₄(OPPh₃)₂ is in rapid equilibrium with its most abundant *cis* isomer.[166]

In contrast to the BH₄ group, the methylborohydride ligand cannot form bidentate hydrogen bridges between two metal centers. In the compounds [Th(BH₃Me)₄]₂(OEt₂) and [Th(BH₃Me)₄(THF)]₂, the thorium atoms are linked by two Th−H−BH(Me)−H−Th bridges, in which the unique H atom bridges the two Th atoms; the other BH₃Me ligands are tridentate.[167] The THF adduct is centrosymmetric (Figure
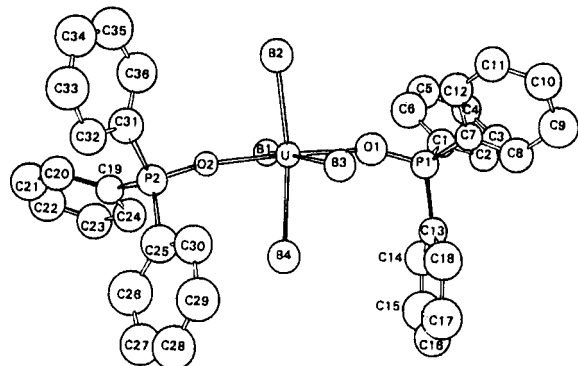
Figure 43. Crystal structure of U(BH$_4$)$_4$(OPPh$_3$)$_2$. (Reprinted with permission from ref 162. Copyright 1987 International Union of Crystallography.)

Figure 44. Crystal structure of U(BH$_4$)$_4$(THF)$_2$. (Reprinted from ref 164. Copyright 1978 American Chemical Society.)

Figure 45. Crystal structure of [Th(BH$_3$Me)$_4$(THF)]$_2$. (Reprinted from ref 167. Copyright 1985 American Chemical Society.)

Figure 46. Crystal structure of [Th(BH$_3$Me)$_4$]$_2$(OEt$_2$). (Reprinted from ref 167. Copyright 1985 American Chemical Society.)

Figure 47. Crystal structure of [U(BH$_3$Me)$_4$(THT)]$_2$. (Reprinted with permission from ref 168. Copyright 1987 Elsevier Science S.A.)
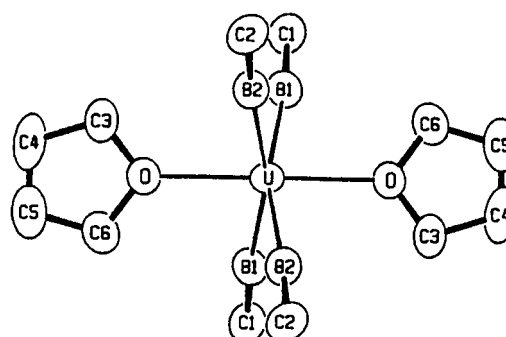
Figure 48. Crystal structure of [U(BH$_3$Me)$_4$(THF)]$_2$. (Reprinted with permission from ref 168. Copyright 1987 Elsevier Science S.A.)

45) while only one Et$_2$O molecule is coordinated to one Th atom (Figure 46); this difference was explained by steric factors. The structure of the tetrahydrothiophene adduct of U(BH$_3$Me)$_4$, [U(BH$_3$Me)$_4$-(THT)]$_2$ (Figure 47), is different from that of the THF adduct, U(BH$_3$Me)$_4$(THF)$_2$ (Figure 48);[168] the two U atoms are bridged by the sulfur atoms of the tetrahydrothiophene ligands, whereas the crystal structure of U(BH$_3$Me)$_4$(THF)$_2$ is very similar to that of U(BH$_4$)$_4$(THF)$_2$. Addition of the chelating ligands

Me$_2$PCH$_2$CH$_2$PMe$_2$, MeOCH$_2$CH$_2$OMe, Me$_2$NCH$_2$CH$_2$-NMe$_2$, and MeSCH$_2$CH$_2$SMe to U(BH$_3$Me)$_4$ gave the corresponding monomeric octathedral adducts;[169,170] all the BH$_3$Me ligands are tridentate, except in the Me$_2$NCH$_2$CH$_2$NMe$_2$ complex where one B atom is coordinated to the metal center through a bidentate hydrogen bridge (Figure 49).

The anionic complexes LiTh(BH$_4$)$_5$ and Li$_2$Th(BH$_4$)$_6$ were prepared by addition of LiBH$_4$ to Th(BH$_4$)$_4$; the IR spectra indicate that the BH$_4$ ligands are tridentate.[149]

A series of complexes U(BH$_4$)$_3$(OR)(THF)$_2$ and U(BH$_4$)$_2$(OR)$_2$(THF)$_2$ (R = ^{i}Pr, Cy, CHPh$_2$) were

Figure 49. Crystal structure of U(BH₃Me)₄(Me₂NCH₂CH₂-NMe₂). (Reprinted from ref 170. Copyright 1987 American Chemical Society.)
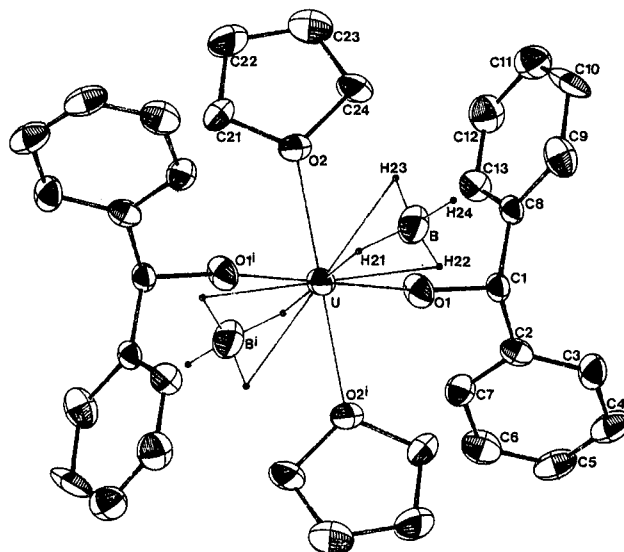
Figure 51. Crystal structure of U(BH₄)₂(OCHPh₂)₂(THF)₂. (Reprinted with permission from ref 171. Copyright 1993 Editions Gauthier-Villars.)
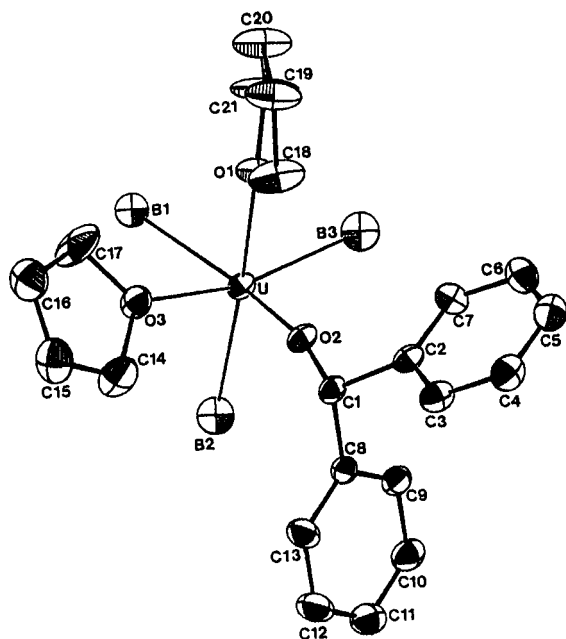
Figure 50. Crystal structure of U(BH₄)₃(OCHPh₂)(THF)₂. (Reprinted with permission from ref 171. Copyright 1993 Editions Gauthier-Villars.)

isolated from the reactions of U(BH₄)₄ with acetone, cyclohexanone, and benzophenone. The crystal structures showed that in U(BH₄)₃(OCHPh₂)(THF)₂, the two equatorial THF ligands (and the two equatorial BH₄ groups) are in relative *cis* positions (Figure 50), whereas they are *trans* in U(BH₄)₂(OCHPh₂)₂(THF)₂ (Figure 51); all the BH₄ ligands are tridentate.[171] These alkoxyborohydrides could also be formed by treating U(BH₄)₄ with the corresponding alcohol. Thus was prepared (ᵗBu₃CO)U(BH₄)₃(THF) which adopts a pentagonal bipyramidal configuration in the solid state, with the tridentate BH₄ ligands lying in the equatorial plane (Figure 52).[172] However, (ᵗBu₃-CO)₂U(BH₄)₂ was synthesized by reaction of (ᵗBu₃-CO)₂UCl₂(THF)₂ with TlBH₄ and its further treatment with ᵗBu₃COLi afforded the trisalkoxide complex (ᵗBu₃CO)₃U(BH₄).[172] The trisamide compound [(TMS)₂N]₃Th(BH₄) was synthesized from the chloride precursor (Figure 53).[173] In both compounds, the distances U···B (2.58(2) Å) and Th···B (2.61(3) Å) are characteristic of tridentate BH₄ ligands.

The complex LU(BH₄)₃ (L = CpCo[P(O)(OEt)₂]₃) was prepared by treating U(BH₄)₄ with NaL.[174]
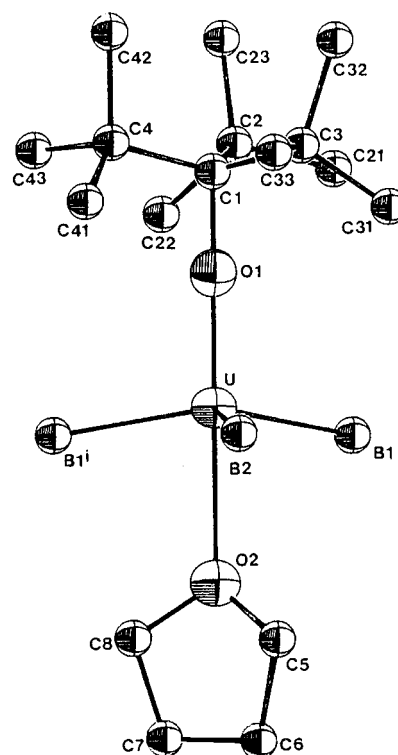
Figure 52. Crystal structure of (ᵗBu₃CO)U(BH₄)₃(THF). (Reprinted with permission from ref 172. Copyright 1991 Elsevier Science S.A.)

B. The Trivalent Complexes An(BH₃R)₃ (R = H, Me) and Their Derivatives

The first Lewis base adducts of U(BH₄)₃, U(BH₄)₃-(THF)ₓ,[175] and U(BH₄)₃(18-crown-6),[176] which were made by treating UCl₃(THF)ₓ or UCl₃(18-crown-6) with LiBH₄, could not be well characterized. Treatment of U(BH₄)₃(THF)ₓ with DMPE gave the phosphine adduct U(BH₄)₃(DMPE)₂ which adopts a pentagonal-bipyramidal crystal structure with two tridentate and one bidentate BH₄ ligands.[177] Similar reaction of U(BH₄)₃(THF)ₓ with 2-(diphenylphosphino)pyridine (Ph₂Ppy) afforded U(BH₄)₃(Ph₂Ppy)₂ in which all the borohydrides are tridentate (Figure 54).[178]
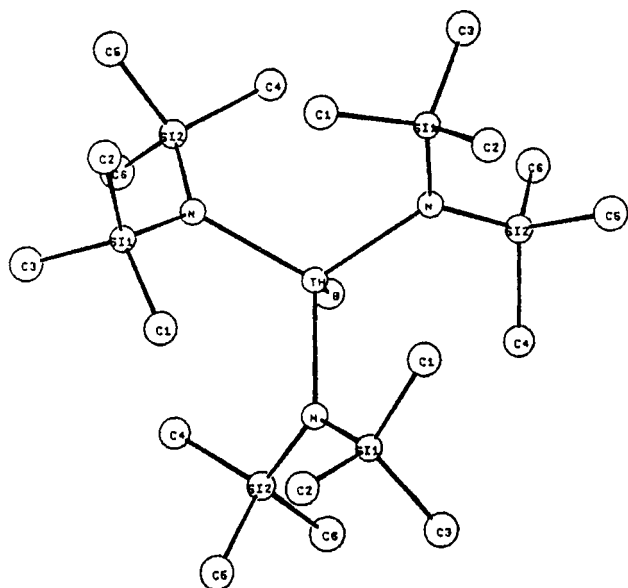
Figure 53. Crystal structure of $[(TMS)_2N]_3Th(BH_4)$. (Reprinted from ref 173. Copyright 1979 American Chemical Society.)
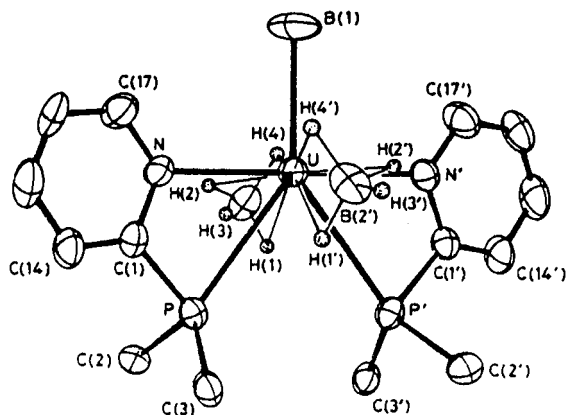
Figure 54. Crystal structure of $U(BH_4)_3(Ph_2Ppy)_2$. (Reprinted with permission from ref 178. Copyright 1984 The Royal Society of Chemistry.)
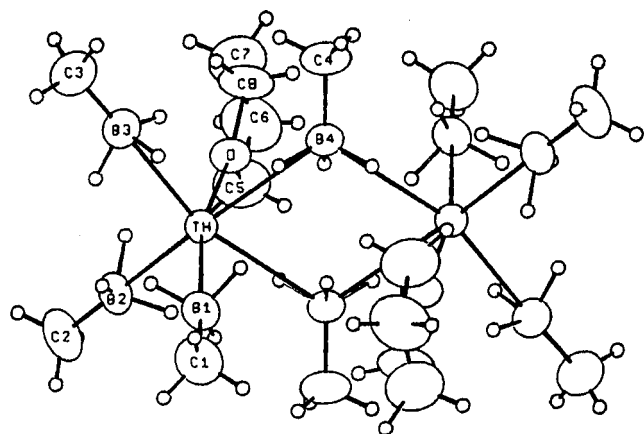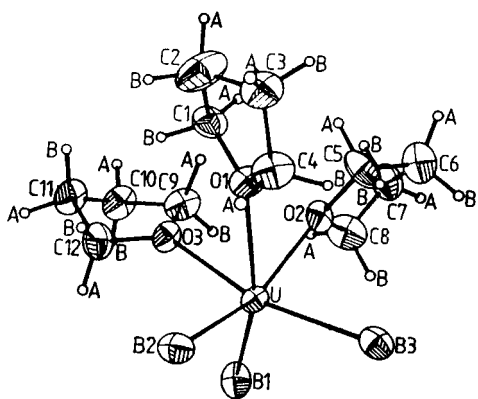

Figure 55. Crystal structure of $U(BH_4)_3(THF)_3$. (Reprinted with permission from ref 179. Copyright 1986 Hüthig GmbH.)

Reaction of UH_3 and BH_3 in THF gave the complex $U(BH_4)_3(THF)_3$; the facial octahedral crystal structure (Figure 55) revealed the tridentate coordination of the borohydride ligands. Reaction 37 represents a unique transformation of UH_3 into a molecular compound.[179]
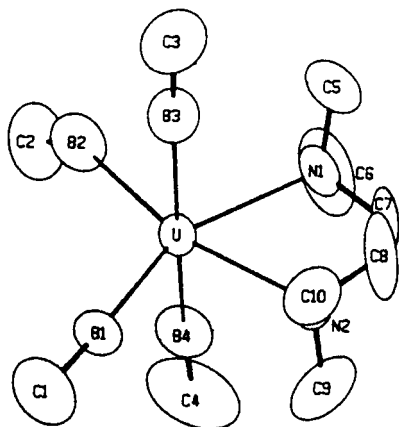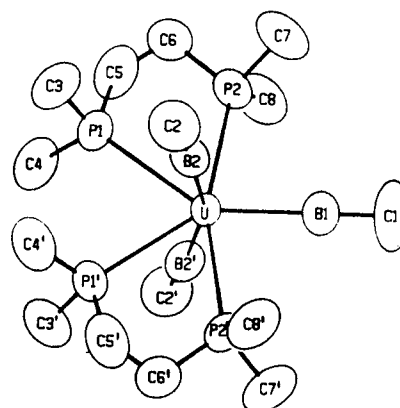

Figure 56. Crystal structure of $U(BH_3Me)_3(DMPE)_2$. (Reprinted from ref 169. Copyright 1984 American Chemical Society.)
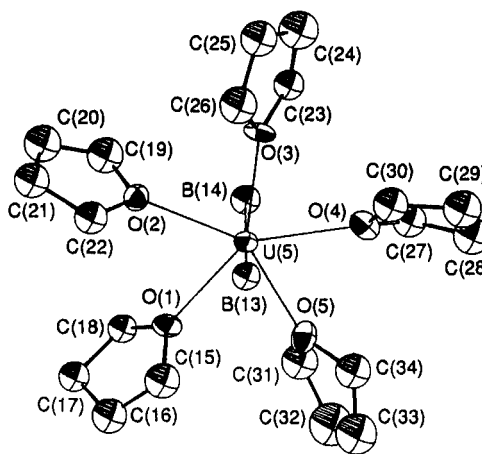
Figure 57. Crystal structure of the cation of $[U(BH_4)_2-(THF)_5][BPh_4]$. (Reprinted with permission from ref 186. Copyright 1994 The Royal Society of Chemistry.)

$$UH_3 + BH_3 \xrightarrow{\text{THF}} U(BH_4)_3(THF)_3 \qquad (37)$$
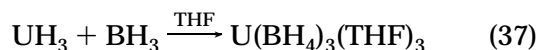
Thermal or photochemical decomposition of $U(BH_4)_4$ led to the formation of $U(BH_4)_3$, according to eq 38.[145,180−182]

$$2U(BH_4)_4 \rightarrow 2U(BH_4)_3 + B_2H_6 + H_2 \qquad (38)$$
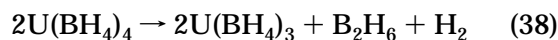
The complexes $U(BH_4)_3(PEt_3)_2$ and $U(BH_4)_3(PEt_2-Ph)_2$ were synthesized by reducing $U(BH_4)_4$ in the presence of the phosphine; their structure was not determined with precision.[183] The diphosphine compound $U(BH_3Me)_4(DMPE)$ was heated in toluene in the presence of DMPE to give the U(III) derivative $U(BH_3Me)_3(DMPE)_2$; the pentagonal-bipyramidal crystal structure showed that the three BH_3Me ligands are tridentate (Figure 56).[169] Reduction of $U(BH_4)_4$ in the presence of 18-crown-6 or dicyclohexyl-(18-crown-6) (dcc) gave the complexes $U_3(BH_4)_9(18$-crown-$6)_2$ and $U_3(BH_4)_9(dcc)_2$, the ^1H NMR spectra of which indicated that the uranium was inserted into the macrocycle.[184] Partial oxidation of $U_3(BH_4)_9(dcc)_2$ in CH_2Cl_2 gave crystals of $[U(BH_4)_2(dcc)][UCl_5(BH_4)]$.[185] Protonation of $U(BH_4)_3(THF)_3$ by means of NEt_3-$HBPh_4$ afforded the cationic complex $[U(BH_4)_2(THF)_5]$-$[BPh_4]$ (eq 39) which adopts a pentagonal-bipyramidal structure with the tridentate borohydride ligands in apical positions (Figure 57).[186]

$$U(BH_4)_3(THF)_3 + NEt_3HBPh_4 \rightarrow$$
$$[U(BH_4)_2(THF)_5][BPh_4] + BH_3 + NEt_3 + H_2 \quad (39)$$
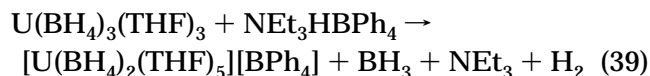
Addition of $LiBH_4$ to $U(BH_4)_3(THF)_3$ in the presence of 18-crown-6 ether gave the anionic compound $[Na(18\text{-crown-}6)][U(BH_4)_4]$.[187]

C. Organoactinide Borohydrides

Tetravalent organoactinide borohydrides were generally prepared by the two classical metathetical reactions represented by eqs 40 and 41. The other routes (eqs 42 and 43), i.e. insertion of BH_3 into a An-X bond or treatment of a borohydride ligand with a proton acidic molecule, are less usual.

$$[An](BH_4)_{n+1} + R^- \rightarrow [An](BH_4)_n(R) + BH_4^- \quad (40)$$

$$[An](Cl)_n(R) + nBH_4^- \rightarrow [An](BH_4)_n(R) + nCl^- \quad (41)$$

$$[An](BH_4)_{n+1} + RH \rightarrow$$
$$[An](BH_4)_n(R) + BH_3 + H_2 \quad (42)$$

$$[An](X)(R) + 2BH_3 \rightarrow [An](BH_4)(R) + BH_2X \quad (43)$$
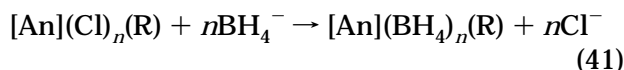
Reactions 40 and 41 were also useful for the preparation of trivalent compounds, which were alternatively synthesized by reduction of their U(IV) precursors. A number of these compounds were synthesized from the arene complex (mesitylene)U-$(BH_4)_3$. The organoactinide borohydride compounds are listed in Table 7.

1. Arene Complexes

Thermal decomposition of $U(BH_4)_4$ in mesitylene afforded red crystals of (mesitylene)U$(BH_4)_3$;[188,189] the NMR spectra in toluene revealed the reversible dissociation of the arene ligand, in competition with the aromatic solvent. Displacement of the mesitylene molecule by hexamethylbenzene gave $(C_6Me_6)U$-
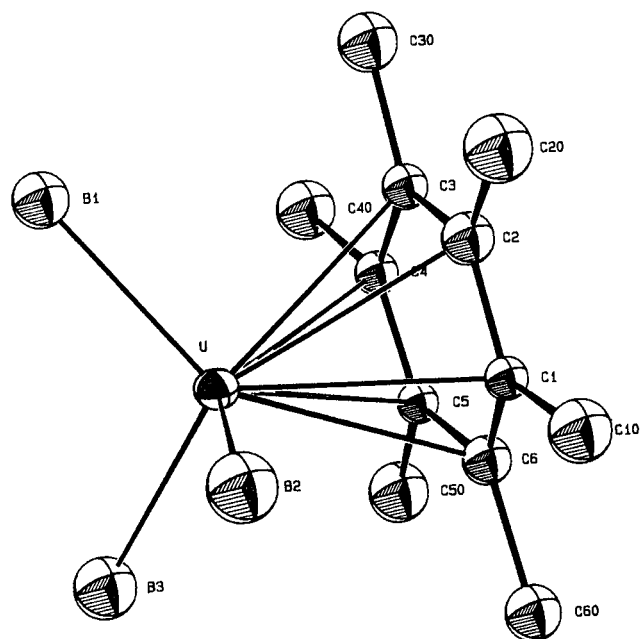
$(BH_4)_3$ which did not undergo arene exchange with benzene. This monomeric complex adopts a tetrahedral crystal structure, with tridentate BH_4 ligands (Figure 58).[189]

2. Cyclopentadienyl Complexes

The monocyclopentadienyl complex $CpU(BH_4)_3$ was isolated from the reaction of $U(BH_4)_4$ or (mesitylene)U$(BH_4)_3$ with TlCp or cyclopentadiene in toluene or pentane;[166,187,189,190] it was also obtained in diethyl ether from UCl_4, by successive treatment with $NaBH_4$ and TlCp.[191] Whatever its mode of preparation, this complex was purified by sublimation; its remarkable volatility and solubility in nonpolar solvents can be accounted for by the covalent and monomeric crystal structure (Figure 59) in which the BH_4 ligands are terminal and tridentate.[190] The pentamethylcyclopentadienyl derivative $Cp^*U(BH_4)_3$ was prepared by treatment of $U(BH_4)_4$ with KCp^*.[192] The phosphidocyclopentadienyl complexes $(C_5R_4PPh_2)U(BH_4)_3$ (R = H, Me) could not be isolated from their solution, being easily transformed into the borane adducts $(C_5R_4PPh_2 \cdot BH_3)U(BH_4)_3$.[193]

In the presence of the Lewis base L (L = THF, DME, HMPA), the sterically unsaturated compound $CpU(BH_4)_3$ was readily converted into an equimolar mixture of $Cp_2U(BH_4)_2$ and $U(BH_4)_4L_2$ (eq 44); the

$$2CpU(BH_4)_3 + 2L \rightarrow Cp_2U(BH_4)_2 + U(BH_4)_4L_2 \quad (44)$$
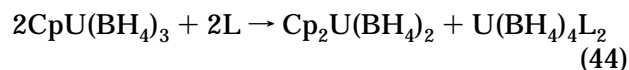
intermediates $CpU(BH_4)_3L_2$ could be detected by low-temperature ^1H NMR spectroscopy.[194] The peculiar behavior of these adducts is in striking contrast to that of the chloride analogues $CpUCl_3L_2$ which are quite stable in solution. The distinct stability of $CpU(BH_4)_3L_2$ and $CpUCl_3L_2$ cannot be explained by steric factors since the Cl and BH_4 ligands are isosteric. This difference can be accounted for by the higher electron donating ability of the borohydride ligands; the adducts $CpU(BH_4)_3L_2$ should be destabilized because of the too much important electron density on the metal.[172,195] In contrast to $CpU(BH_4)_3$, Cp^*U-$(BH_4)_3$ was perfectly stable in tetrahydrofuran;[192] the NMR spectra revealed that this complex does not coordinate the free Lewis base molecule, certainly a


Figure 58. Crystal structure of $(C_6Me_6)U(BH_4)_3$. (Reprinted with permission from ref 189. Copyright 1989 Elsevier Science S.A.)

Figure 59. Crystal structure of $CpU(BH_4)_3$. (Reprinted with permission from ref 190. Copyright 1985 The Royal Society of Chemistry.)

Table 7. Organoactinide Borohydrides and Their Characterization
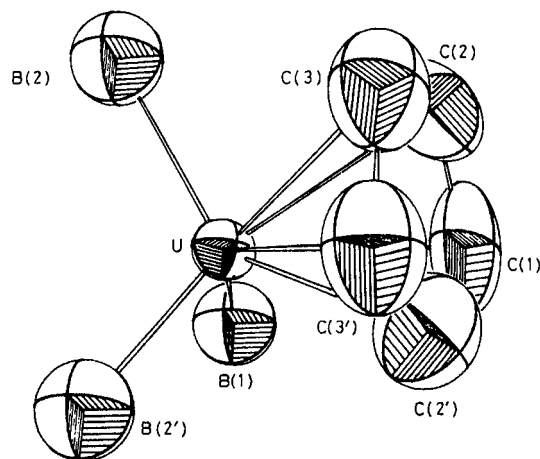
complexes	analyses[a]	^{1}H NMR data[b]	X-ray diffraction data[c]	ref
		Arene Complexes		
$(C_6H_3Me_3)U(BH_4)_3$	C,H,B	toluene-d_8: 150 (br, 480)		189
$(C_6Me_6)U(BH_4)_3$	C,H,B	benzene-d_6: 150 (br, 530)	U···B$_t$ 2.49(4), 2.54(3), 2.69(3)	189
		Cyclopentadienyl Complexes		
$CpU(BH_4)_3$	C,H,B	toluene-d_8: 53.2 (q, 78)	U···B$_t$ 2.45(5), 2.56(5)	166,187
$Cp^*U(BH_4)_3$	C,H,B	toluene-d_8: 42.5 (q, 82)		192
$Na[Cp^*U(BH_4)_3]$	C,H,B	THF-d_8: 96.6 (br, 415)		192
$[Na(THF)_6][Cp^*U(BH_4)_3]_2$			U···B$_t$ 2.57(2)−2.68(2)	196
$(C_5H_4PPh_2)U(BH_4)_3$		benzene-d_6: 61		193
$(C_5Me_4PPh_2)U(BH_4)_3$		benzene-d_6: 50.9		193
$(C_5H_4PPh_2·BH_3)U(BH_4)_3$		benzene-d_6: 73		193
$(C_5Me_4PPh_2·BH_3)U(BH_4)_3$	C,H	benzene-d_6: 67.6		193
$(Cp)(COT)U(BH_4)(OPPh_3)$	C,H,B,P	toluene-d_8: −13.71 (q, 75)		197
$(Cp^*)(tmp)U(BH_4)_2$	C,H,P	toluene-d_8: −48.14 (q, 80)		192
$[Na(THF)_2][(Cp^*)(tmp)U(BH_4)_2]$	C,H,B,Na,P	THF-d_8: 49 (br, 320)		192
$[(Cp^*)(tmp)(U(BH_4)]_2$		toluene-d_8: 138 (br, 270), 109 (br, 360) (minor isomer)		198
$(C_5H_5)_2Th(BH_4)_2$	C,H			191
$(C_5H_5)_2U(BH_4)_2$	C,H	benzene-d_6: −19.3 (q)	U···B$_t$ 2.58−2.63	199
$[Na(18\text{-crown-}6)][Cp_2U(BH_4)_2]$	C,H,B,Na	THF-d_8: 61.1 (q, 78)		187
$(C_5H_4Me)_2U(BH_4)_2$	U	benzene-d_6: −21.15 (q)		191
$(C_5H_4SiMe_3)_2U(BH_4)_2$	U	benzene-d_6: −18.07 (q)		191
$(C_5H_4PPh_2)_2U(BH_4)_2$		benzene-d_6: −12.0 (br, 260)		193
$(C_5Me_4PPh_2)_2U(BH_4)_2$		benzene-d_6: −53		193
$(C_5H_4PPh_2·BH_3)_2U(BH_4)_2$	C,H,B,P	benzene-d_6: −20.2 (br, 270)		193
$(C_5Me_4PPh_2·BH_3)_2U(BH_4)_2$		not visible		193
$Cp^*_2U(BH_4)_2$	C,H,B	toluene-d_8: −62.58 (q, 80)	U···B$_t$ 2.58(3)	192
$[Na(THF)_x][Cp^*_2U(BH_4)_2]$		THF-d_8: 33.5 (br, 240)		192
$Cp_3Th(BH_4)$	C,H	toluene-d_8: 6.70 (q, 86)		203
$Cp_3U(BH_4)$	mass spectrum	benzene-d_6: −60.0 (q)	U···B$_t$ 2.48	191,204,205
$[Na(18\text{-crown-}6)][Cp_3U(BH_4)]$	C,H,B,Na	THF-d_8 (−80 °C): 12.4 (br, 350)		210
$(C_5H_4SiMe_3)_3U(BH_4)$	C,H,Si,B	toluene-d_8: −56.42 (q, 88)		206
$Cp_3U(BH_3Et)$	C,H	benzene-d_6: −66.4 (q)		205
$Cp_3U(BH_3Ph)$	C,H	benzene-d_6: −76.8 (q)		205
$Cp_3U(HBBN)$	C,H,B	benzene-d_6: −55 (br, 300)	U···B$_t$ 2.78(3)	209
		Indenyl, Pentadienyl, Cyclohexadienyl, and Phospholyl Complexes		
$(C_9H_7)_3Th(BH_4)$	Th			211
$(dmpd)U(BH_4)_3$	C,H,B	toluene-d_8: 110.4 (q, 85)	U···B$_t$ 2.50(3), 2.52(3), 2.54(3)	187
$(dmch)U(BH_4)_3$	C,H,B	toluene-d_8: 76.9 (q, 85)		213
$(tmp)U(BH_4)_3$	C,H,B,P	toluene-d_8: 58.7 (q, 81)		215
$[Na(15\text{-crown-}5)][(tmp)U(BH_4)_3]$	C,H,B,P	THF-d_8: −109 (br, 540)		215
$(dmpd)_2U(BH_4)_2$	C,H,B	toluene-d_8: 0.53 (q, 85)		187
$[K(18\text{-crown-}6)][(dmpd)_2U(BH_4)_2]$	C,H,B,K	THF-d_8: 72.5 (br, 320)		187
$(dmch)_2U(BH_4)_2$	C,H,B	toluene-d_8: 69.9 (q, 85)		213
$[K(18\text{-crown-}6)][(dmch)_2U(BH_4)_2]$	C,H,B,K	THF-d_8: 72.7 (q, 82)		213
$[(dmch)_2U(BH_4)]_x$	C,H,B	toluene-d_8: 30 (br, >1000)		213
$(dmch)_2U(BH_4)(THF)$	C,H,B	toluene-d_8: 90 (br, 900)		213
$(dmch)_2U(BH_4)(OPPh_3)$	C,H,B,P	toluene-d_8: 122.5 (br, 380)		213
$(tmp)_2U(BH_4)_2$	C,H,B,P	toluene-d_8: −36.7 (q, 86)	U···B$_t$ 2.55; U−H 2.29	214,215
$[Na(15\text{-crown-}5)][(tmp)_2U(BH_4)_2]$	C,H,B,P,Na	THF-d_8: 68.8 (br, 320)		215
$[(tmp)_2U(BH_4)]_2$	C,H,B	toluene-d_8: 165 (br, 300)	U···B$_t$ 2.59(1)	198,215
		Cyclooctatetraene and Cycloheptatrienyl Complexes		
$(C_8H_8)Th(BH_4)_2$		benzene-d_6: 3.11 (q, 85)		216
$(COT)U(BH_4)_2(PPh_3)$		toluene-d_8: 140 (br, 800)		197
$(COT)U(BH_4)_2(THF)$	C,H,B	toluene-d_8: 126.2 (q, 83)		197
$(COT)U(BH_4)_2(OPPh_3)$	C,H,B,P	THF-d_8: 71.6 (q, 83)	U···B$_t$ 2.57(1), 2.66(1)	197
$[K(18\text{-crown-}6)][(COT)U(BH_4)_3]$	C,H,B	THF-d_8: 56.7 (q, 80)		217
$[(COT)U(BH_4)(OEt)]_2$	C,H,B	THF-d_8: −84.8 (br, 280)	U···B$_t$ 2.594(8)	217
$[(COT)U(BH_4)(O^iPr)]_2$	C,H,B	THF-d_8: −88.3 (q, 85)		217
$[(COT)U(BH_4)(O^tBu)]_2$		THF-d_8: −88.8 (q, 85)		217
$[C_8H_6\text{-}1,4\text{-}(SiMe_3)_2]U(BH_4)_2$	*	benzene-d_6: 122.5 (br)		218
$M[(BH_4)_3U(C_7H_7)U(BH_4)_3]$ (M = $[U(BH_4)_2(THF)_5]$)		THF-d_8 (M = K): 63.4 (q, 85)	av U···B$_t$ 2.58	186

^{a} Elements analyzed, except when not specified (*). ^{b} δ of the BH$_4$ signals (multiplicity, coupling constant or half height width in Hz). ^{c} Distances in Å.

result of its more important electron richness, Cp* being more electron donating than Cp.

Sodium amalgam reduction of Cp*U(BH$_4$)$_3$ gave the anionic U(III) complex Na[Cp*U(BH$_4$)$_3$].[192] The mixed-valent charge-transfer compound [Na(THF)$_6$][Cp*U-(BH$_4$)$_3$]$_2$ was unexpectedly isolated from the reaction of U(BH$_4$)$_3$(THF)$_x$ with Cp*$_2$Th(PPh$_2$)$_2$. In the crystal structure, the geometrical parameters are not significantly different in the independent Cp*U(BH$_4$)$_3$ moieties; the BH$_4$ ligands are tridentate.[196]

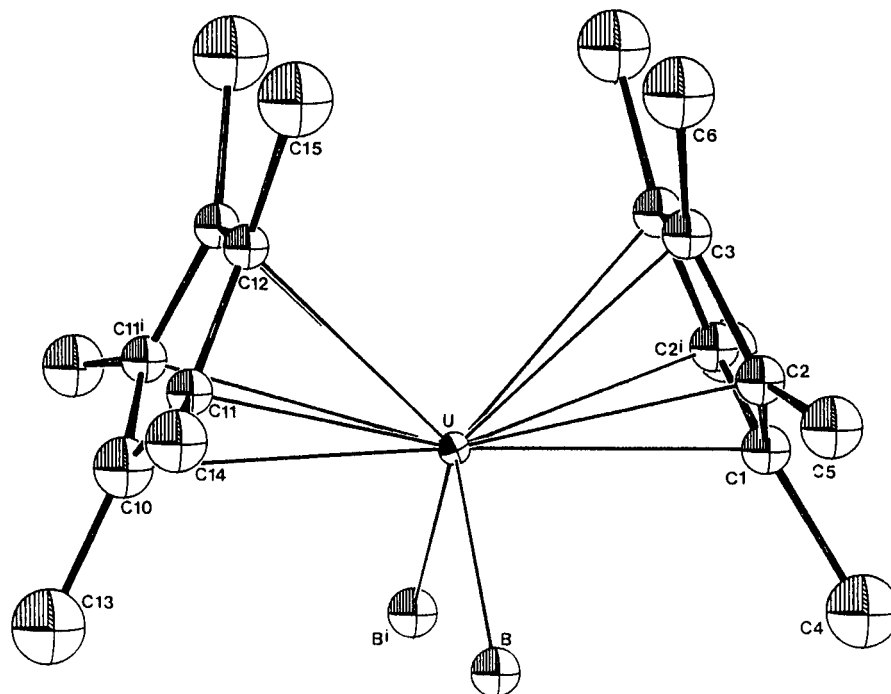The mixed-ring complex (Cp)(COT)U(BH$_4$)(THF) was made by reaction of (COT)U(BH$_4$)$_2$(THF) with

Figure 60. Crystal structure of Cp*$_2$U(BH$_4$)$_2$. (Reprinted with permission from ref 192. Copyright 1994 Elsevier Science S.A.)

TlCp and was transformed into (Cp)(COT)U(BH$_4$)-(OPPh$_3$).[197] Reaction of Cp*U(BH$_4$)$_3$ with Ktmp (tmp = tetramethylpholyl) gave (Cp*)(tmp)U(BH$_4$)$_2$ which was reduced into the corresponding U(III) anion[192] or the neutral dimeric compound [(Cp*)-(tmp)U(BH$_4$)]$_2$[198] by means of sodium amalgam in diethyl ether or toluene, respectively.

The biscyclopentadienyl complexes (C$_5$H$_4$R)$_2$An-(BH$_4$)$_2$ (An = Th and R = H;[191] An = U and R = H,[199] Me, TMS,[191] PPh$_2$[193]) were synthesized by treating AnCl$_4$ successively with LiBH$_4$ or NaBH$_4$ and the thallium salt of the cyclopentadienyl anion. Cp$_2$U-(BH$_4$)$_2$ was more conveniently prepared by treatment of Cp$_2$U(NEt$_2$)$_2$ with BH$_3$·Me$_2$S.[200] The phosphidocyclopentadienyl derivatives were alternatively obtained by reaction of U(BH$_4$)$_4$ or U(BH$_4$)$_3$(THF)$_3$ with TlC$_5$H$_4$PPh$_2$; (C$_5$Me$_4$PPh$_2$)$_2$U(BH$_4$)$_2$ was similarly prepared from U(BH$_4$)$_4$ and KC$_5$Me$_4$PPh$_2$.[193] These complexes, which were characterized in solution, were easily converted into the borane adducts (C$_5$R$_4$-PPh$_2$·BH$_3$)$_2$U(BH$_4$)$_2$ (R = H, Me). The two compounds (C$_5$H$_3${TMS}$_2$)$_2$U(BH$_4$)$_2$[201] and Cp*$_2$U(BH$_4$)$_2$[192] were prepared from the corresponding chlorides; the latter was characterized by its crystal structure (Figure 60) which indicates the tridentate coordination of the BH$_4$ group, with a U···B distance (2.58(3) Å) similar to those found in Cp$_2$U(BH$_4$)$_2$.[199]

The anionic U(III) complexes [Na(18-crown-6)]-[Cp$_2$U(BH$_4$)$_2$][187,202] and [Na(THF)$_x$][Cp*$_2$U(BH$_4$)$_2$][192] were synthesized by sodium amalgam reduction of their neutral tetravalent precursors. The neutral compound (C$_5$H$_3${TMS}$_2$)$_2$U(BH$_4$)(THF) was obtained from the corresponding chloride,[201] whereas Cp*$_2$U-(BH$_4$)(THF) was prepared by hydrogenolysis of an equimolar mixture of Cp$_2$U(BH$_4$)$_2$ and Cp*$_2$UMe$_2$.[192]

The triscyclopentadienyl compounds Cp$_3$An(BH$_4$) (An = Th,[203] U[204]) and (C$_5$H$_4$PPh$_2$)$_3$U(BH$_4$)[120] have been prepared from the corresponding chlorides. The crystal structure of Cp$_3$U(BH$_4$) revealed the tridentate coordination of the BH$_4$ ligand,[191] in agreement

with the IR spectra.[203] The ^{11}B-decoupled NMR spectrum, which exhibits collapse of the BH$_4$ resonance at low temperature, revealed for the first time in a metal borohydride, slowing of the dynamic intramolecular rearrangement process.[205]

The ring-substituted complex (C$_5$H$_4$TMS)$_3$U(BH$_4$) was isolated from the insertion reaction of BH$_3$ into the U−H bond of the corresponding hydride.[206] Insertion of borane into the U−X bond of the complexes Cp$_3$UX (X = Me, Et, Ph, NEt$_2$, OMe, F, CONEt$_2$, COBu) led to the formation of Cp$_3$U(BH$_4$) according to eq 45; in some cases (X = Me, Et, Ph), the intermediate Cp$_3$U(BH$_3$X) was detected.[207,208]

$$Cp_3UX \xrightarrow{BH_3} Cp_3U(BH_3X) \xrightarrow{BH_3}$$
$$Cp_3U(BH_4) + BH_2X \quad (45)$$
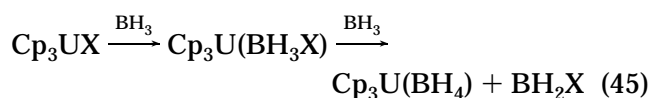
Reaction of Cp$_3$U(BH$_4$) with BR$_3$ (R = Et, Ph) afforded the substituted derivatives Cp$_3$U(BH$_3$R) in which the BH$_3$R groups are tridentate.[205]

Treatment of Cp$_3$UCl with Na(HBBN) (BBN = 9-borabicyclo(3.3.1)nonane) gave Cp$_3$U(HBBN), the first metal complex with a HBBN ligand; the IR spectrum and crystal structure indicate that the boron hydride ligand is coordinated to the metal center through two hydrogen bridges.[209]

The uranium(III) compound [Na(18-crown-6)][Cp$_3$U-(BH$_4$)] was synthesized by reduction of Cp$_3$U(BH$_4$) with sodium amalgam in the presence of 18-crown-6 ether.[202,210]

3. Indenyl, Pentadienyl, Cyclohexadienyl, and Phospholyl Complexes

The tris(indenyl) compound (C$_9$H$_7$)$_3$Th(BH$_4$) was prepared from the corresponding chloride; the BH$_4$ ligand is tridentate from the IR spectrum.[211]

A series of uranium borohydride complexes with 2,4-dimethylpentadienyl (dmpd),[187,188,212] 6,6-dimeth-
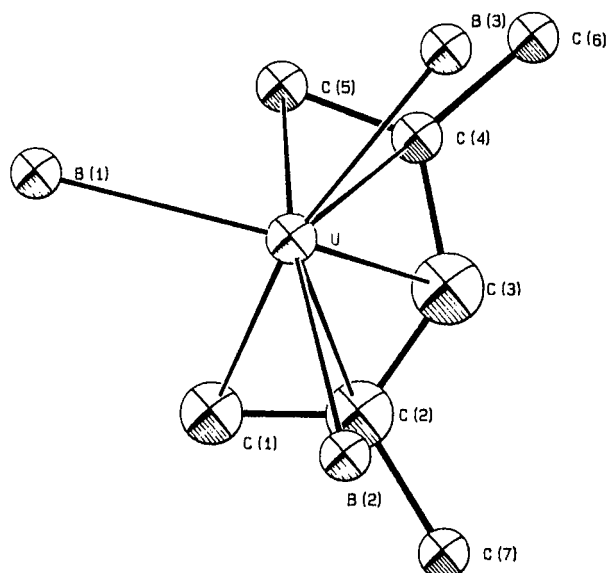
Figure 61. Crystal structure of (dmpd)U(BH$_4$)$_3$. (Reprinted with permission from ref 187. Copyright 1989 Elsevier Science S.A.)
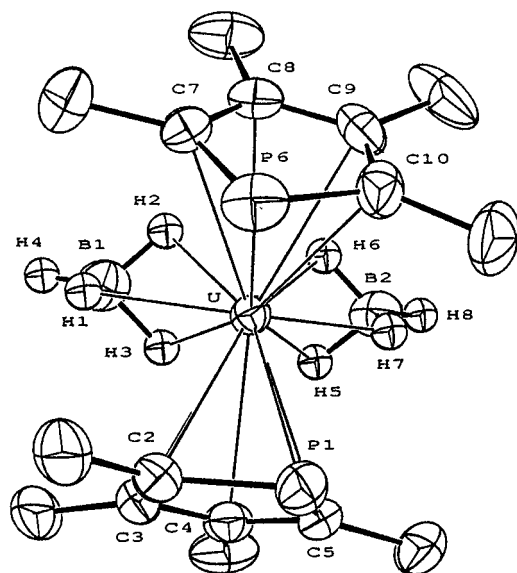

Figure 62. Crystal structure of (tmp)$_2$U(BH$_4$)$_2$. (Reprinted with permission from ref 214. Copyright 1990 VCH.)

ylcyclohexadienyl (dmch),[188,212,213] or tetramethylphospholyl (tmp) ligands[198,214,215] have been prepared from U(BH$_4$)$_4$ and (mesitylene)U(BH$_4$)$_3$. The volatile uranium(IV) derivatives LU(BH$_4$)$_3$ (L = dmpd, dmch, tmp) are, like CpU(BH$_4$)$_3$, unstable in coordinating solvents; the crystal structure of (dmpd)U(BH$_4$)$_3$ has been determined (Figure 61).[187] In contrast to Cp$_2$U-(BH$_4$)$_2$ and (tmp)$_2$U(BH$_4$)$_2$, the pentadienyl and cyclohexadienyl analogues were not stable in THF, being reduced into U(III) borohydrides.[187,213] The crystal structure of (tmp)$_2$U(BH$_4$)$_2$[214] (Figure 62) is very similar to that of Cp*$_2$U(BH$_4$)$_2$, confirming that the tetramethylphospholyl group is a steric mimic of the ubiquitous pentamethylcyclopentadienyl ligand. With the exception of [Na(15-crown-5)][(tmp)U-(BH$_4$)$_3$],[215] the anionic U(III) complexes [Na(crown-ether)][LU(BH$_4$)$_3$] (L = Cp, dmpd, dmch) could not be isolated because of their ready disproportionation (eq 46).

$$2[LU(BH_4)_3]^- \rightarrow [L_2U(BH_4)_2]^- + [U(BH_4)_4]^- \quad (46)$$

The complexes [M(crown-ether)][L$_2$U(BH$_4$)$_2$] (M = Na or K; L = dmpd, dmch, tmp) are stable and extraction of the dmch and tmp derivatives with pentane or toluene gave the neutral compounds [(dmch)$_2$U(BH$_4$)]$_x$[213] and [(tmp)$_2$U(BH$_4$)]$_2$.[198,215] The latter, which is fluxional in solution, was characterized by its crystal structure (Figure 63); the two uranium metals are bridged by two μ-η^5,η^1-phospholyl ligands and the tridentate BH$_4$ ligands are *cis* to the (UP)$_2$ ring.[198]

4. Cyclooctatetraene and Cycloheptatrienyl Complexes

The monocyclooctatetraene thorium complexes (C$_8$H$_7$R)Th(BH$_4$)$_2$ (R = H, ^{n}Bu) were prepared by treating Th(BH$_4$)$_4$(THF)$_2$ with (C$_8$H$_7$R)$_2$Th or K$_2$COT in THF.[216] Reaction of U(BH$_4$)$_4$ with (COT)$_2$U or cyclooctatetraene in toluene afforded the polymeric compound [(COT)U(BH$_4$)$_2$]$_n$ which was converted into the anionic complex [K(18-crown-6)][(COT)U(BH$_4$)$_3$][217] or the Lewis base adducts (COT)U(BH$_4$)$_2$(L) (L = PPh$_3$, THF, OPPh$_3$).[197] The crystal structure of (COT)U(BH$_4$)$_2$(OPPh$_3$) shows it to have a three-legged piano stool configuration with tridentate BH$_4$ ligands (Figure 64). The alkoxoborohydrides [(COT)U-(BH$_4$)(OR)]$_2$ (R = Et, ^{i}Pr, ^{t}Bu) were synthesized by reaction of [(COT)U(BH$_4$)$_2$]$_n$ with the corresponding alcohol;[217] in the crystal structure of [(COT)U(BH$_4$)-(OEt)]$_2$, the two uranium atoms are linked by two OEt bridges (Figure 65). The complex [C$_8$H$_6$-1,4-(SiMe$_3$)$_2$]U(BH$_4$)$_2$ was prepared by treating UCl$_4$ with LiBH$_4$ and the lithium salt of the cyclooctatetraene dianion.[218]

The first cycloheptatrienyl complex of an f-element, [U(BH$_4$)$_2$(THF)$_5$][(BH$_4$)$_3$U(C$_7$H$_7$)U(BH$_4$)$_3$] was isolated from the reaction of U(BH$_4$)$_4$ and KC$_7$H$_9$;[186] the crystal structure shows that the two U(BH$_4$)$_3$ fragments are bridged by a μ-η^7,η^7-C$_7$H$_7$ ligand (Figure 66). Such inverse sandwich compounds containing an M(μ-η^n,η^n-C$_n$H$_n$)M' unit were known for n = 5, 6, and 8, and the above complex is the first example with n = 7. Treatment of U(BH$_4$)$_4$ with 4 equiv of KC$_7$H$_9$ afforded the first cycloheptatrienyl sandwich compound K[U(η-C$_7$H$_7$)$_2$].[219]

D. Actinide Aluminohydrides

By comparison with the lanthanide series, a very few actinide aluminohydrides have been reported. Reaction of UCl$_3$ with 3 equiv of LiAlH$_4$ gave a gray powder, formulated as U(AlH$_4$)$_3$, which decomposed above −20 °C.[220] The cyclopentadienyl compounds Cp$_3$U(AlH$_4$)[221,222] and Cp$_2$U(AlH$_4$)$_2$[200] were obtained by treatment of the corresponding borohydrides with LiAlH$_4$ in diethyl ether. These complexes are presumably polymeric; the IR spectra exhibit broad bands at 1750 and 705 cm^{-1}, characteristic of bridging and terminal AlH$_4$ groups. Treatment of Cp$_2$U-(NEt$_2$)$_2$ with LiAlH$_4$ led to the formation of the ate complex LiCp$_2$U(AlH$_4$)$_2$(NEt$_2$).[200]
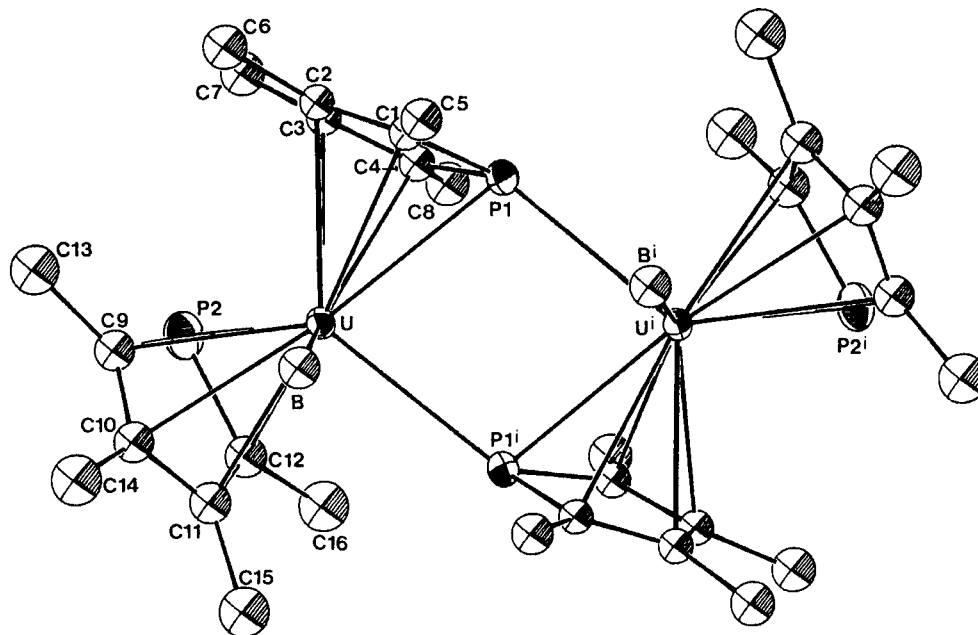
Figure 63. Crystal structure of [(tmp)$_2$U(BH$_4$)]$_2$. (Reprinted with permission from ref 198. Copyright 1994 Elsevier Science S.A.)
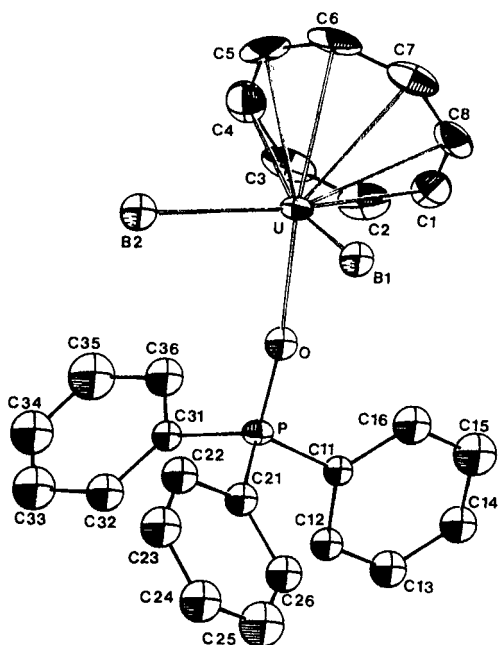
Figure 64. Crystal structure of (COT)U(BH$_4$)$_2$(OPPh$_3$). (Reprinted with permission from ref 197. Copyright 1990 Elsevier Science S.A.)

X. Reactions of the Lanthanide Hydrides

A. Stoichiometric Reactions

The classical addition reactions to unsaturated molecules will be examined first, followed by the σ-bond metathesis reactions, which are more typical of d^0 and d^{0}f^n complexes.

1. Addition Reactions

Addition of lanthanide hydrides to alkene C=C bonds, a most important elementary step in the
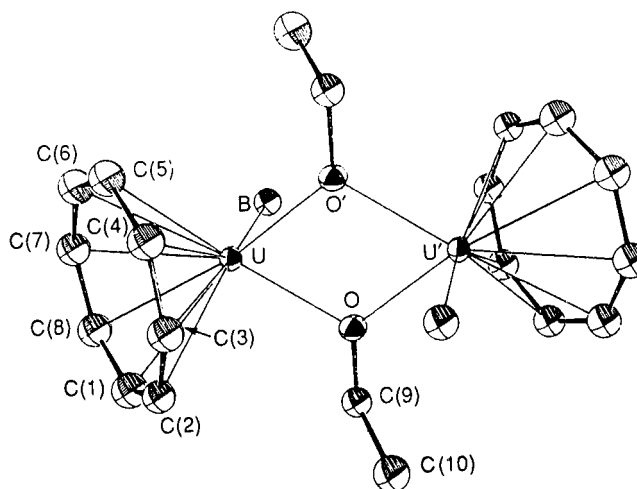
Figure 65. Crystal structure of [(COT)U(BH$_4$)(OEt)]$_2$. (Reprinted with permission from ref 217. Copyright 1992 The Royal Society of Chemistry.)
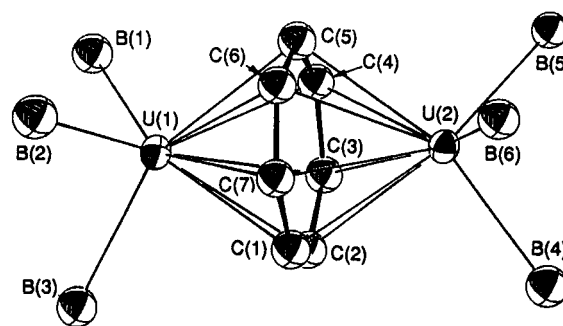
Figure 66. Crystal structure of the anion of [U(BH$_4$)$_2$-(THF)$_5$][(BH$_4$)$_3$U(C$_7$H$_7$)U(BH$_4$)$_3$]. (Reprinted with permission from ref 186. Copyright 1994 The Royal Society of Chemistry.)

catalytic hydrogenation or polymerization of olefins, has been extensively studied. The scandium hydride [Cp*$_2$ScH]$_n$ reacted with ethylene, propene[49] and a series of substituted styrenes CH$_2$=CHC$_6$H$_4$-p-X (X

Scheme 2. Reactions of [(Cp*SiNR)(PMe$_3$)ScH]$_2$ with Alkenes

(Cp*SiNR)(PMe$_3$)ScCH$_2$CH(Me)R'   (Cp*SiNR)(PMe$_3$)ScCH(Ph)CH$_2$CH$_2$Ph

CH$_2$=C(Me)R'   CH$_2$=CHPh

[(Cp*SiNR)(PMe$_3$)ScH]$_2$

CH$_2$=CH$_2$ CH$_2$=CHMe

[(Cp*SiNR)(PMe$_3$)Sc]$_2$ [μ_2,η^2, η^2-C$_2$H$_4$]   [(Cp*SiNR)Sc]$_2$[μ-^{n}Pr]$_2$
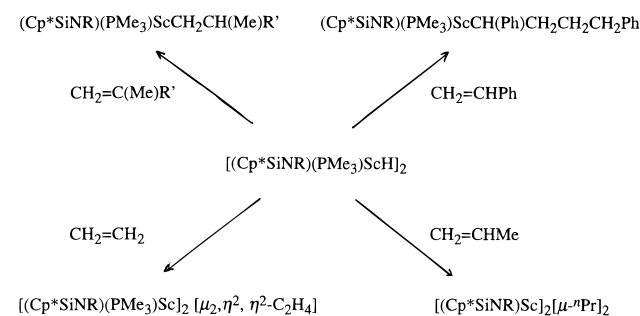
= H, Me, NMe$_2$, CF$_3$)[32,223] to give the corresponding alkyls (eq 47).

$$1/n[\text{Cp*}_2\text{ScH}]_n + \text{CH}_2=\text{CHR} \rightarrow$$
$$\text{Cp*}_2\text{ScCH}_2\text{CH}_2\text{R} \quad (47)$$

$$\text{R} = \text{H, Me, C}_6\text{H}_4\text{-}p\text{-X}$$
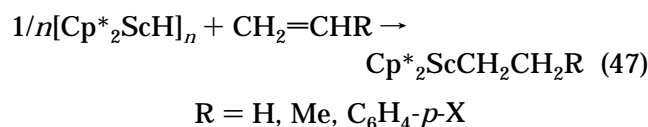
The dimeric yttrium hydride [(C$_5$H$_4$R)$_2$YH(THF)]$_2$ (R = H, Me) was similarly transformed into (C$_5$H$_4$R)$_2$Y(CH$_2$CH$_2$R')(THF) (R' = H, Me).[67] The isobutyl complex Me$_2$Si(C$_5$Me$_4$)$_2$Sc(PMe$_3$)(^{i}Bu) was prepared by addition of the parent hydride to CH$_2$=CMe$_2$; it slowly decomposed into the methyl derivative Me$_2$Si(C$_5$Me$_4$)$_2$Sc(PMe$_3$)(Me), implicating β-Me elimination of propene.[224] Monomeric alkyl complexes were obtained by treating [(Cp*SiNR)-(PMe$_3$)ScH]$_2$ ((Cp*SiNR) = (η^5-C$_5$Me$_4$)Me$_2$Si(η^1-N^{t}Bu)) with 2-methyl-1-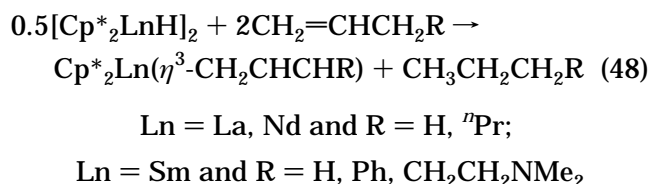pentene or isobutene (Scheme 2); reaction with styrene gave a unique double insertion product resulting from sequential 1,2- and 2,1-styrene insertion.[48] Treatment of [(Cp*SiNR)(PMe$_3$)-ScH]$_2$ with 2 equiv of CH$_2$=CH$_2$ produced an unusual ethylene bridged dimer and 1 equiv of ethane, whereas the same reaction with propene afforded a phosphine-free, alkyl-bridged scandium dimer.[48]
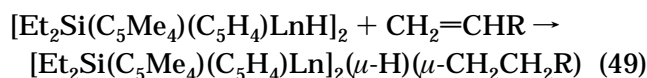
The bis(pentamethylcyclopentadienyl)lanthanide hydrides [Cp*$_2$LnH]$_2$ (Ln = La, Nd,[54] and Sm[225-227] reacted with 2 equiv of terminal alkenes to give η^3-allyl complexes, according to eq 48.

$$0.5[\text{Cp*}_2\text{LnH}]_2 + 2\text{CH}_2=\text{CHCH}_2\text{R} \rightarrow$$
$$\text{Cp*}_2\text{Ln}(\eta^3\text{-CH}_2\text{CHCHR}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{R} \quad (48)$$

$$\text{Ln} = \text{La, Nd and R} = \text{H, }^n\text{Pr};$$
$$\text{Ln} = \text{Sm and R} = \text{H, Ph, CH}_2\text{CH}_2\text{NMe}_2$$

The samarium hydride was similarly transformed into the crotyl derivative by treatment with *cis*- or *trans*-2-butene.[226] These reactions certainly proceed by initial addition of the hydride to the C=C bond, followed by metalation of the alkene.
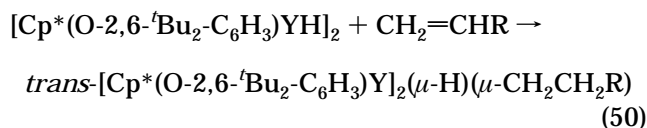
In contrast to [Cp*$_2$LnH]$_2$ and [Me$_2$Si(C$_5$Me$_4$)$_2$-LnH]$_2$ which readily reacted with α-olefins to give allyl compounds or polymerization products (*vide infra*), the ring-bridged dinuclear lanthanide hydrides [Et$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)LnH]$_2$ (Ln = Y, Lu) were slowly transformed into μ-hydridoalkyl derivatives (eq 49).[33]

Terminal alkenes also reacted with [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)YH]$_2$ to give the corresponding μ-alkyl species (eq 50).[34,228] Reaction of the corresponding

$$[\text{Et}_2\text{Si(C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{LnH}]_2 + \text{CH}_2=\text{CHR} \rightarrow$$
$$[\text{Et}_2\text{Si(C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{Ln}]_2(\mu\text{-H})(\mu\text{-CH}_2\text{CH}_2\text{R}) \quad (49)$$

$$\text{Ln} = \text{Y and R} = \text{H, Me; Ln} = \text{Lu}$$
$$\text{and R} = \text{H, Me, }^n\text{Bu}$$

$$[\text{Cp*}(\text{O-2,6-}^t\text{Bu}_2\text{-C}_6\text{H}_3)\text{YH}]_2 + \text{CH}_2=\text{CHR} \rightarrow$$
$$\textit{trans-}[\text{Cp*}(\text{O-2,6-}^t\text{Bu}_2\text{-C}_6\text{H}_3)\text{Y}]_2(\mu\text{-H})(\mu\text{-CH}_2\text{CH}_2\text{R}) \quad (50)$$

$$\text{R} = \text{H, Me, }^n\text{Bu}$$
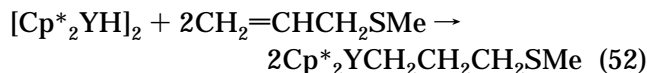
deuteride with propene afforded selectively *trans* [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)Y]$_2$(μ-D)(μ-CH$_2$CHDMe), confirming the non reversibility of olefin insertion.

Here should be noted the reactions of 1-hexene with [Cp$_2$LuH(THF)]$_2$,[19] [(CH$_2$)$_3$(C$_5$H$_4$)$_2$LnH(THF)]$_2$ (Ln = Y, Dy, Er, Lu),[69] and [O(CH$_2$CH$_2$C$_5$H$_4$)$_2$LnH]$_2$ (Ln = Y, Gd, Er, Yb and Lu)[20] which afforded *n*-hexane after hydrolysis. Moreover, 1-hexene and 1-octene were also reduced into the corresponding alkanes by using NaH in the presence of great variety of lanthanide complexes, in particular Cp$_3$Ln (Ln = Y, La, Pr, Nd, Sm, Tb, Er, Yb, Lu),[229,230] (C$_5$H$_4$R)$_2$-YCl (R = H, Me), O(CH$_2$CH$_2$C$_5$H$_4$)$_2$YCl, (CH$_2$)$_n$(C$_5$H$_4$)$_2$-YCl (n = 3, 5),[230,231] MeN(CH$_2$CH$_2$C$_5$H$_4$)$_2$LnCl (Ln = Y, Sm, Nd).[231] The reactivity of the hydrides generated *in situ* is determined largely by the "cone angle of reaction" formed by the two cyclopentadienyl rings in the bent metallocenes and can be adjusted by varying the ligands on the metal; metal tuning of reactivity can also be achieved by taking advantage of the well-known lanthanide contraction, early lanthanide hydrides being more reactive than the later ones.

The reactions depicted by eqs 51 and 52 are the sole examples of lanthanide hydride additions to olefins with ether[51] and thioether[232] functions.

$$\text{Me}_2\text{Si(C}_5\text{Me}_4)_2\text{Sc(PMe}_3)\text{H} + (\text{CH}_2=\text{CHCH}_2)_2\text{O} \rightarrow$$
$$\text{Me}_2\text{Si(C}_5\text{Me}_4)_2\text{Sc(CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2) \quad (51)$$

$$[\text{Cp*}_2\text{YH}]_2 + 2\text{CH}_2=\text{CHCH}_2\text{SMe} \rightarrow$$
$$2\text{Cp*}_2\text{YCH}_2\text{CH}_2\text{CH}_2\text{SMe} \quad (52)$$
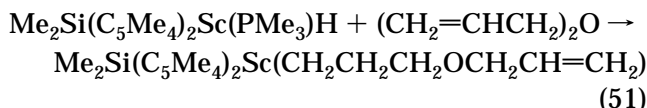
The samarium hydride [Cp*$_2$SmH]$_2$ reacted with 4 equiv of methyl methacrylate to give a keto enolate compound (eq 53).[233] The reaction is likely to proceed by initial 1,4-addition of the hydride to the conjugated ester, yielding the intermediate Cp*$_2$SmOC-(OMe)=CMe$_2$ which would add a second molecule of methacrylate to afford the eight-membered ring product.

[Cp*$_2$SmH]$_2$ + 4 CH$_2$=CMeCO$_2$Me ⟶

(53)
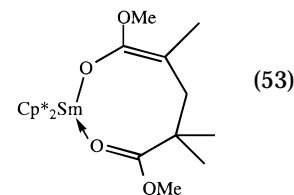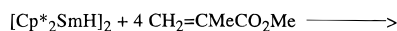
Stoichiometric reactions of lanthanide hydrides with dienes are also rare. The η^3-allyl compounds

Scheme 3. Reactions of *meso*-[Me₂Si(C₅H₃-3-ᵗBu)₂ScH]₂ with Dienes[a]
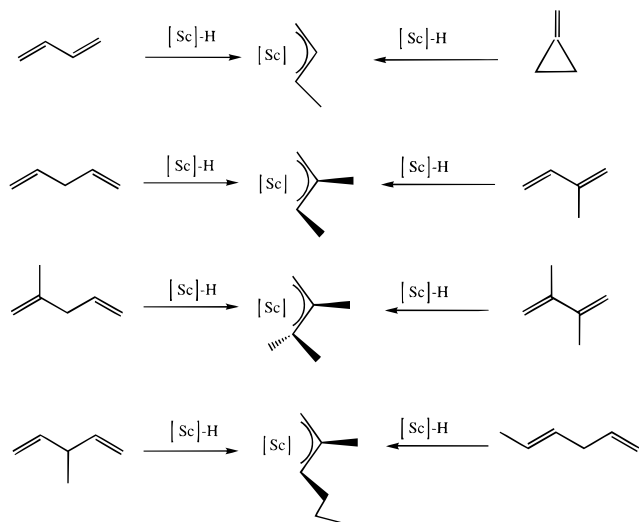
[a] All reactions at 80 °C in C_6D_6.

$Cp^*_2Sc(\eta^3-C_3H_5)$[49,50,51,223] and $(C_5H_4R)_2Y(\eta^3-C_3H_5)$-(THF) (R = H, Me)[67] were synthesized by reaction of the parent hydrides with 1,2-propadiene (eq 54). Treatment of $[Cp^*_2SmH]_2$ with 1,3-butadiene afforded the crotyl derivative.[226]

$$1/n[Cp^*_2ScH]_n + H_2C=C=CH_2 \rightarrow$$
$$Cp^*_2Sc(\eta^3-C_3H_5) \quad (54)$$

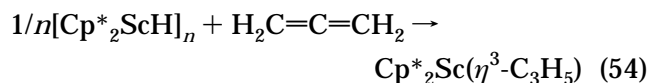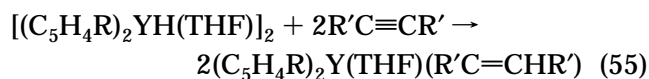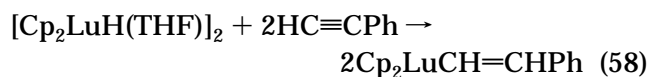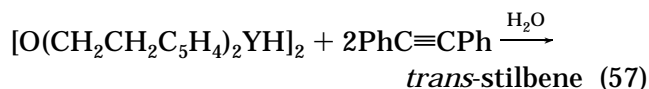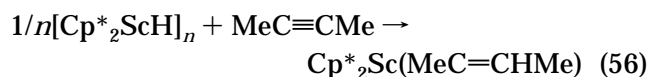The scandium hydride *meso*-[Me₂Si(C₅H₃-3-ᵗBu)₂ScH]₂ reacted with 1,4-butadiene, 1,4-pentadiene, 2-methyl-1,4-pentadiene, and 3-methyl-1,4-pentadiene to give the allyl derivatives (Scheme 3) which were alternatively obtained by treatment of the hydride with methylenecyclopropane, isoprene, 2,3-dimethylbutadiene, and 1,4-hexadiene; ^{13}C-labeling experiments showed that these skeletal rearrangements would proceed by a mechanism involving β-alkyl elimination.[62]

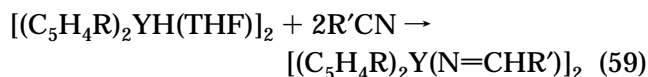Some addition reactions of lanthanide hydrides with alkynes have been reported (eqs 55–58).

$$[(C_5H_4R)_2YH(THF)]_2 + 2R'C\equiv CR' \rightarrow$$
$$2(C_5H_4R)_2Y(THF)(R'C=CHR') \quad (55)$$

$$R = H, Me; R' = Et, Ph$$

$$1/n[Cp^*_2ScH]_n + MeC\equiv CMe \rightarrow$$
$$Cp^*_2Sc(MeC=CHMe) \quad (56)$$

$$[O(CH_2CH_2C_5H_4)_2YH]_2 + 2PhC\equiv CPh \xrightarrow{H_2O}$$
$$trans\text{-stilbene} \quad (57)$$

$$[Cp_2LuH(THF)]_2 + 2HC\equiv CPh \rightarrow$$
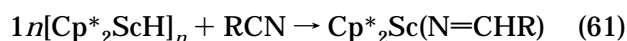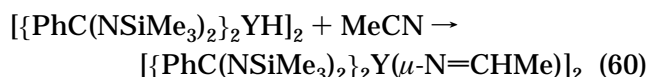$$2Cp_2LuCH=CHPh \quad (58)$$

cis-Olefins were formed by hydrolysis or hydrogenolysis of the alkenyl complexes isolated from reactions 55[67] and 56[32,51] and it is surprising that *trans*-stilbene was obtained by reaction 57 between diphenylacetylene and $[O(CH_2CH_2C_5H_4)_2YH]_2$ (made *in situ* from its chloride precursor).[20] In contrast to

$[Cp_2YH(THF)]_2$ which reacted with terminal alkynes to give alkynide derivatives (*vide infra*), $[Cp_2LuH(THF)]_2$ was transformed into the alkenyl complex by treatment with phenylacetylene (eq 58).[19]
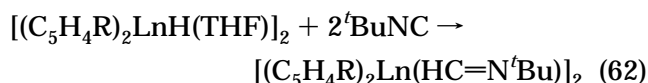
Addition of lanthanide hydrides to the $C\equiv N$ bond of nitriles and isonitriles gave alkylideneamido and N-alkylformimido complexes, as shown with reactions 59,[67] 60,[234] 61,[235] and 62.[236,237]

$$[(C_5H_4R)_2YH(THF)]_2 + 2R'CN \rightarrow$$
$$[(C_5H_4R)_2Y(N=CHR')]_2 \quad (59)$$

$$R = H, Me; R' = Me, {}^tBu$$

$$[\{PhC(NSiMe_3)_2\}_2YH]_2 + MeCN \rightarrow$$
$$[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}N=CHMe)]_2 \quad (60)$$

$$1n[Cp^*_2ScH]_n + RCN \rightarrow Cp^*_2Sc(N=CHR) \quad (61)$$

$$R = {}^tBu, p\text{-}C_6H_4OMe, p\text{-}C_6H_4Me$$

$$[(C_5H_4R)_2LnH(THF)]_2 + 2{}^tBuNC \rightarrow$$
$$[(C_5H_4R)_2Ln(HC=N^tBu)]_2 \quad (62)$$

$$Ln = Y \text{ and } R = H, Me; Ln = Er \text{ and } R = H$$

The yttrium hydride $[(C_5H_4R)_2YH(THF)]_2$ also reacted with pyridine in polar solvents to give the 1,2-addition product which rearranged into the 1,4-isomer (eq 63);[67] the 1,2-inserted product of reaction 64 did not suffer subsequent isomerization.[233]

$$0.5 [(C_5H_4R)_2YH(THF)]_2 + NC_5H_5 \longrightarrow$$

$$0.5 [\{PhC(NSiMe_3)_2\}_2YH]_2 + NC_5H_5 \longrightarrow$$
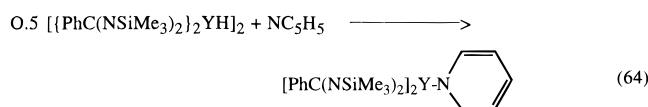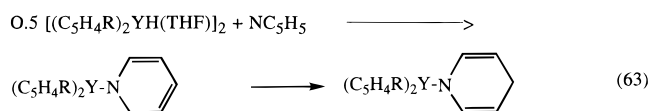
Reactions of lanthanide hydrides with ketones and aldehydes received little attention. Addition of $[Cp^*_2LaH]_2$ to di-*tert*-butyl ketone (eq 65)[238] and addition of $[Cp_2LuH(THF)]_2$ to benzaldehyde (eq 66)[239] afforded the corresponding alkoxide derivatives.

$$[Cp^*_2LaH]_2 + 4{}^tBu_2CO \rightarrow$$
$$2Cp^*_2La(OCH^tBu_2)(OC^tBu_2) \quad (65)$$

$$[Cp_2LuH(THF)]_2 + 2PhCHO \rightarrow$$
$$2Cp_2Lu(OCH_2Ph)(THF) \quad (66)$$
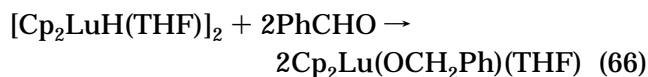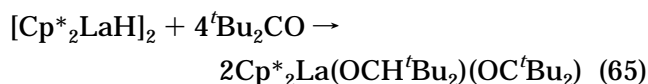
Some reactions of lanthanide hydrides with carbon monoxide were reported (eqs 67–69). Treatment of $[Cp^*_2SmH]_2$ with CO led to the formation of a *cis* enediolate complex, isolated as its $OPPh_3$ adduct, which isomerized to the *trans* isomer; both isomers have been crystallographically characterized.[240] Addition of the scandium hydride $Cp^*_2ScH(THF)$ to the carbonyl ligand of $Cp_2M(CO)$ (M = Mo, W) or $CpCo(CO)_2$ afforded scandoxycarbene compounds.[241]

$$[Cp*_2SmH]_2 + 2CO \rightarrow$$
$$[Cp*_2Sm(THF)]_2(\mu\text{-OCH}=\text{CHO}) \quad (67)$$

$$Cp*_2ScH(THF) + CpCo(CO)_2 \rightarrow$$
$$Cp*_2ScOCH=Co(CO)Cp \quad (68)$$

$$Cp*_2ScH(THF) + Cp_2M(CO) \rightarrow$$
$$Cp*_2ScOCH=MCp_2 \quad (69)$$
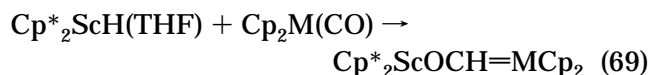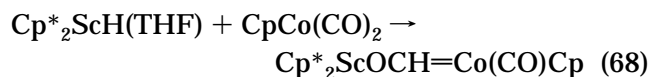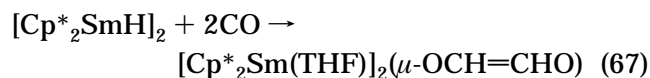
$$M = Mo, W$$

2. Deoxygenation of Organoheteroatom Oxides and a Reaction of $^nBu_3P=Te$

The system Cp_3Sm/NaH or LiAlH_4 was able to deoxygenate triphenylarsine oxide, diphenyl sulfoxide, azoxybenzene, pyridine *N*-oxide, and triphenylphosphine oxide;[242] no lanthanide complexes were isolated from these reactions. Treatment of [Me_2Si-(C_5H_3^tBu)_2ScH]_2 with $^nBu_3P=Te$ gave a μ-telluride complex (eq 70).[243] The mechanism of these reactions has not been studied.

$$[Me_2Si(C_5H_3{}^tBu)_2ScH]_2 + {}^nBu_3P=Te \rightarrow$$
$$[Me_2Si(C_5H_3{}^tBu)_2Sc]_2(\mu\text{-Te}) + H_2 + P{}^nBu_3 \quad (70)$$
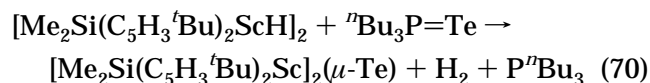
3. σ-Bond Metathesis Reactions

The lanthanide hydrides [Ln]−H are extremely reactive toward a great variety of A−B σ-bonds and are transformed into the derivatives [Ln]−A (or [Ln]−B), with liberation of B−H (or A−H). The mechanism of these σ-bond metathesis reactions was studied by several experimental and theoretical approaches;[40] it is generally accepted that this formal 2s + 2s process occurs via a four-center transition state.

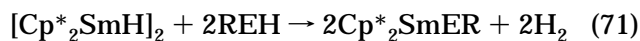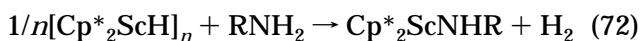It is likely that activation of H−X and C−X bonds (X = O, N, S, halogen) is favored by initial coordination of the heteroatom ligand to the metal complex, thus leading to the formation of the [Ln]−X bond. Activation of C−H bonds can produce either H/H exchange or metalation reactions; extended Hückel calculations showed, in agreement with the reactions observed between the complexes Cp*_2LnH (Ln = Sc, Y, Lu) and hydrocarbons RH, that H/H exchange is easier for R = aryl than for R = alkyl because an sp² carbon can better stabilize the [H-R-H]⁻ moiety in the transition state.[244]

Reactions of lanthanide hydrides with water or alcohols have not been studied much, although they are convenient routes to hydroxides and alkoxides. The holmium hydroxide [(MeOCH_2CH_2C_5H_4)_2Ho-(OH)]_2 was obtained by partial hydrolysis of the parent hydride and was crystallographically characterized.[21] Treatment of the trinuclear anionic hydride [(Cp_2YH)_3H]⁻ with methanol, giving the alkoxy−hydride anions [[Cp_2Y(μ-H)]_x[Cp_2Y(μ-OMe)]_{3-x}(μ_3-H)]⁻ has already been mentioned.[39] The samarium hydride [Cp*_2SmH]_2 reacted with alcohols and also with ^{n}PrSH, Et_2PH, and Me_2NH, according to eq 71; these reactions were useful for the determination of absolute metal−ligand bond disruption enthalpies.[225] A series of amide compounds were synthesized by reaction of [Cp*_2ScH]_n with primary amines (eq 72).[234]
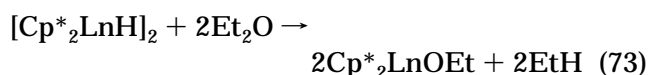
$$[Cp*_2SmH]_2 + 2REH \rightarrow 2Cp*_2SmER + 2H_2 \quad (71)$$
$$REH =$$
$$^tBuOH, {}^tBu_2CHOH, {}^nPrSH, Et_2PH, and Me_2NH$$

$$1/n[Cp*_2ScH]_n + RNH_2 \rightarrow Cp*_2ScNHR + H_2 \quad (72)$$

$$R = H, Me, Ph, {}^tBu, p\text{-}C_6H_4OMe$$

Lanthanide hydrides [Ln]−H were invariably transformed into the corresponding halides [Ln]−X by reaction with the organic halides RX. Iodinolysis of (Cp*_2LnH)_2 allowed the determination of the absolute bond disruption enthalpies D(Ln−H) which are equal to 66.6 (La), 56.5 (Nd), 52.4 (Sm), and 66.7 (Lu) Kcal/mol.[245] These values, which showed no apparent trend, may be compared to those of ∼60 Kcal/mol for the Ln⁺-H bond dissociation energies determined by mass spectroscopy.[246] The hydrides [Cp*_2LnH]_2 (Ln = Sc,[50] Sm,[225] Ce[55]) reacted with MeI to give the corresponding iodides; formation of Cp*_2LnMe was not detected while both alkyl exchange and alkyl coupling were observed in the reactions of Cp*_2ScR with organic halides.[225] For these reactions, radical pathways are likely alternatives to the σ-bond metathesis mechanism. Reactions of [Cp*_2SmH]_2 with *n*-amyl chloride and *n*-butyl bromide permitted the disruption enthalpies of the Sm−Cl and Sm−Br bonds to be calculated.[225] Reductive dehalogenation of organic halides was performed with the systems Cp_3Ln/NaH (Ln = Y, La, Sm, Gd, Lu)[247] and [O(CH_2-CH_2C_5H_4)_2YH]_2/NaH.[20]

The C−O bonds of ethers could be activated by the complexes [Cp*_2LnH]_2. The ethoxide compounds Cp*_2LnOEt (Ln = Lu,[248] Sm,[36] Y, La, Ce[233]) were thus obtained by cleavage of diethyl ether (eq 73); they further reacted with [Cp*_2LnH]_2 to give the μ-oxo complexes [Cp*_2Ln]_2(μ-O) (Ln = Y, La, Ce) according to eq 74.[232] Asymmetric substituted dialkyl ethers ROR′ were cleaved by [Cp*_2LnH]_2 (Ln = Y, La, Ce)[232] to give a mixture of Cp*_2LnOR and Cp*_2LnOR′ (eq 75) in proportions which were strongly dependent on the alkyl substituents but were relatively insensitive to the nature of the metal; similarities with both S_N1 and S_N2 type substitution reactions were observed. The order of reactivity Et_2O, ^{n}BuOEt > ^{t}BuOMe > ^{t}BuOEt reflected the increasing steric bulk of the ethers and suggested that the first step of the reaction was formation of the adduct Cp*_2LnH-(ROR′).

$$[Cp*_2LnH]_2 + 2Et_2O \rightarrow$$
$$2Cp*_2LnOEt + 2EtH \quad (73)$$
$$Ln = Y, La, Ce, Sm, Lu$$

$$[Cp*_2LnH]_2 + 2Cp*_2LnOEt \rightarrow$$
$$2[Cp*_2Ln]_2(\mu\text{-O}) + 2EtH \quad (74)$$
$$Ln = Y, La, Ce$$
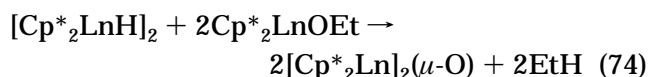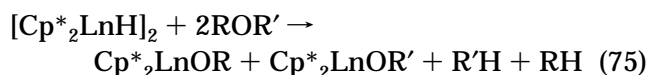
$$[Cp*_2LnH]_2 + 2ROR' \rightarrow$$
$$Cp*_2LnOR + Cp*_2LnOR' + R'H + RH \quad (75)$$
$$Ln = Y, La, Ce; R = {}^tBu \text{ and}$$
$$R' = Me, Et; R = {}^nBu, R' = OEt$$

Reaction of [Cp*_2YH]_2 with vinyl ethyl ether and allyl ethyl ether afforded the yttrium ethoxide Cp*_2-

YOEt, with elimination of ethylene and propene, respectively.[232]

Ring opening of tetrahydrofuran by $[Cp*_2LnH]_2$ (Ln = Sm[36] and Y[232]) led to the formation of the butoxide derivative (eq 76). Similar reactions of 1,4-dioxane with $[Cp*_2YH]_2$[232,50] or hexamethylcyclotrisiloxane with $[Cp*_2SmH]_2$[36] gave bimetallic compounds in which the $Cp*_2Ln(THF)$ moieties are bridged by a OCH_2CH_2O or $OSiMe_2OSiMe_2O$ fragment (eqs 77 and 78).

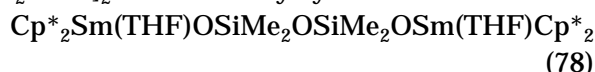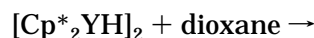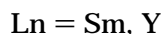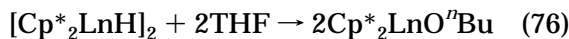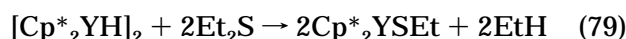$$[Cp*_2LnH]_2 + 2THF \rightarrow 2Cp*_2LnO^nBu \quad (76)$$

$$Ln = Sm, Y$$

$$[Cp*_2YH]_2 + dioxane \rightarrow$$
$$Cp*_2Y(THF)OCH_2CH_2OY(THF)Cp*_2 \quad (77)$$

$$[Cp*_2SmH]_2 + hexamethylcyclotrisiloxane \rightarrow$$
$$Cp*_2Sm(THF)OSiMe_2OSiMe_2OSm(THF)Cp*_2 \quad (78)$$
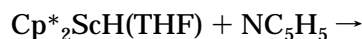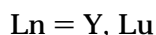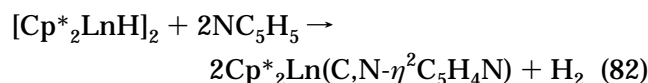
Diethyl sulfide reacted with $[Cp*_2YH]_2$ in a manner similar to that of Et_2O, giving the thiolate derivative (eq 79).

$$[Cp*_2YH]_2 + 2Et_2S \rightarrow 2Cp*_2YSEt + 2EtH \quad (79)$$

However, other organic sulfides were activated predominantly by CH activation to form the corresponding metalation products (eq 80); thiophene and furan are metalated at the α-position (eq 81).[232]

$$[Cp*_2YH]_2 + 2RCH_2SMe \rightarrow$$
$$2Cp*_2YCHRSMe + H_2 \quad (80)$$

$$R = H, Ph$$

$$E = O, S$$
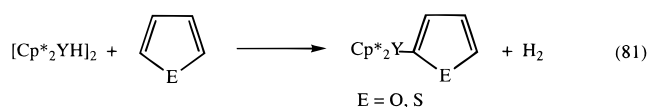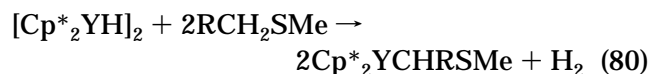
The complexes $[Cp*_2LnH]_2$ (Ln = Y,[249] Lu[248]) and $Cp*_2ScH(THF)$[49,50] reacted with pyridine to give the orthometalated compound (eqs 82 and 83); reaction of the scandium hydride was reversible. The metalation reaction 82 seems different from the addition reaction 63, but $Cp*_2Ln(C,N-\eta^2C_5H_4N)$ reacted with H_2 (1 bar) to give the 1,4 hydride addition product $Cp*_2Y(NC_5H_6)$, presumably via the intermediate $Cp*_2Y(NC_5H_5)H$.

$$[Cp*_2LnH]_2 + 2NC_5H_5 \rightarrow$$
$$2Cp*_2Ln(C,N-\eta^2C_5H_4N) + H_2 \quad (82)$$

$$Ln = Y, Lu$$

$$Cp*_2ScH(THF) + NC_5H_5 \rightarrow$$
$$Cp*_2Sc(C,N-\eta^2C_5H_4N) + H_2 + THF \quad (83)$$

Treatment of $[Cp*_2SmH]_2$ with 2-phenyl-1-pyrroline afforded the orthometalation product (eq 84); such C–H bond activation reactions were also observed with acyclic aromatic ketimines and aldimines.[250]
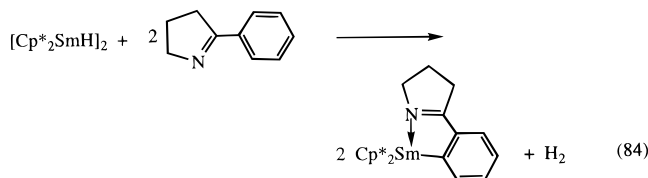
The yttrium hydride $[\{PhC(NSiMe_3)_2\}_2YH]_2$ reacted with α-picoline to form the α-picolyl derivative (eq 85).[234]
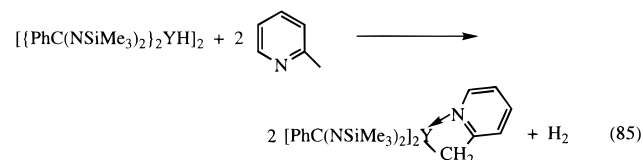
H/D exchange between lanthanide hydrides and deuterium ($[Ln]-H + D_2 \rightarrow [Ln]-D + HD$) is an easy process, whereas arene CH bonds are also readily activated to give H/H exchange or metalation. The facile H/D exchange of $[Ln]-H$ with D_2 or C_6D_6 was used for the catalytic deuteration of a variety of organic molecules (*vide infra*). In benzene solution, $[Cp*_2ScH]_n$ is in equilibrium with $Cp*_2ScPh$ and H_2 (eq 86); the Sc–H bond dissociation energy (BDE) is 1.5(4) kcal mol^{-1} higher than the BDE of the Sc–Ph bond.[49] In deuterated benzene or toluene, $[Cp*_2YH]_2$ was immediately transformed at 20 °C into the corresponding deuteride, whereas its thermolysis afforded the binuclear complex $Cp*_2Y(\mu-H)(\mu-\eta^1,\eta^5-CH_2C_5Me_4)YCp*$. In addition to the fast nonproductive H/H exchange and the slow intramolecular CH activation of the Me group of a Cp* ligand, metalation of solvent molecules was observed when the H_2 gas generated was removed quickly (eq 87).[37] In contrast to toluene, the derivatives PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $PPh_2=CH_2$) were metalated preferentially at the ortho position. The yttrium hydride was also efficient for the metalation of 2-butyne (eq 88).[251]

$$1/n[Cp*_2ScH]_n + PhH \rightarrow Cp*_2Sc-Ph + H_2 \quad (86)$$

$$[Cp*_2YH]_2 + 2RH \rightarrow 2Cp*_2YR + 2H_2 \quad (87)$$

$$R = Ph, CH_2Ph$$

$$[Cp*_2YH]_2 + 2MeC\equiv CMe \rightarrow$$
$$2Cp*_2YCH_2C\equiv CMe + H_2 \quad (88)$$
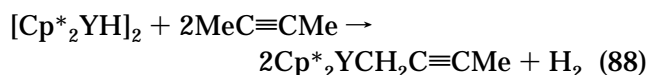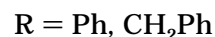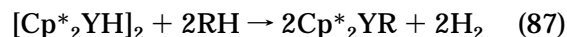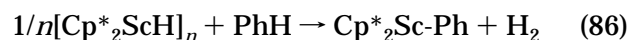
The lutetium hydride $[Cp*_2LuH]_2$ reacted with benzene, the ylide CH_2PPh_3, and tetramethylsilane to give stable metalation products (Scheme 4).[248,252]

The samarium hydride $[Cp*_2SmH]_2$ was transformed in toluene into a mixture of the self-metalation product and the benzyl complex $Cp*_2SmCH_2Ph$; in contrast to the other $[Cp*_2LnH]_2$ compounds, $[Cp*_2SmH]_2$ showed no appreciable reactivity with benzene.[36]

Metalation of terminal alkynes is also a facile reaction. Alkynide complexes were synthesized from $[(C_5H_4R)_2YH(THF)]_2$,[67] $Cp*_2ScH$,[49] $[Cp*Y(O-2,6-^tBu_2-$

Scheme 4. C−H Bond Activation Reactions of [Cp*₂LuH]₂

Cp^*_2LuPh Cp^*_2Lu—⟨ ⟩—$LuCp^*_2$

C_6H_6 Cp^*_2LuPh

$[Cp^*_2LuH]_2$

Me_4Si CH_2PPh_3

$Cp^*_2LuCH_2SiMe_3$ Cp^*_2Lu⟨PPh₂⟩
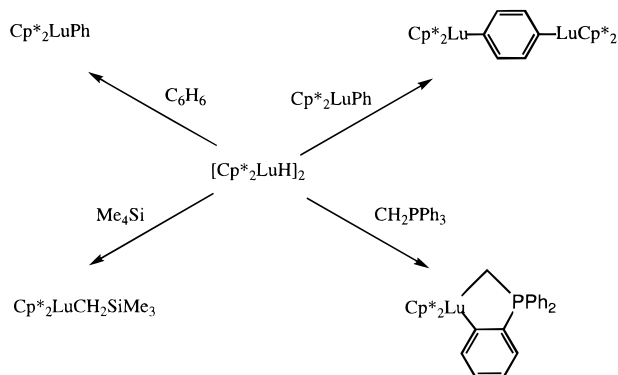
$C_6H_3)H]_2$,[34,228] $[O(CH_2CH_2C_5H_4)_2YH]_2$,[20] and $[\{PhC-(NSiMe_3)_2\}_2YH]_2$[234] according to eqs 89−93.

$$[(C_5H_4R)_2YH(THF)]_2 + 2HC{\equiv}C^tBu \rightarrow$$
$$[(C_5H_4R)_2Y\text{-}C{\equiv}C^tBu]_2 + 2H_2 \quad (89)$$

$$R = H, Me$$

$$Cp^*_2ScH + HC{\equiv}CMe \rightarrow Cp^*_2Sc\text{-}C{\equiv}CMe + H_2 \quad (90)$$

$$[Cp^*Y(OAr)H]_2 \xrightarrow[-H_2]{HC{\equiv}CSiMe_3}$$
$$[Cp^*Y(OAr)]_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3) \xrightarrow[-H_2]{HC{\equiv}CSiMe_3}$$
$$2Cp^*Y(OAr)(C{\equiv}CSiMe_3)(THF)_2 \quad (91)$$

$$Ar = C_6H_3{}^tBu_2$$

$$[O(CH_2CH_2C_5H_4)_2YH]_2 + 2HC{\equiv}CPh \rightarrow$$
$$O(CH_2CH_2C_5H_4)_2Y(C{\equiv}CPh) + 2H_2 \quad (92)$$

$$[\{PhC(NSiMe_3)_2\}_2YH]_2 + 2HC{\equiv}CR \rightarrow$$
$$[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}C{\equiv}CR)]_2 + 2H_2 \quad (93)$$
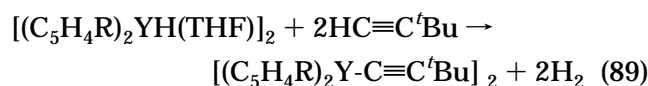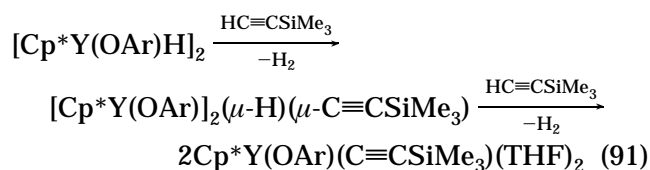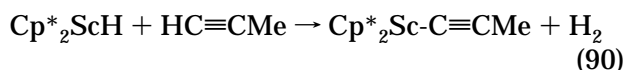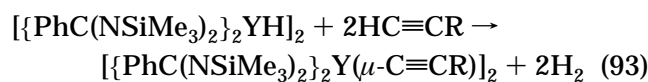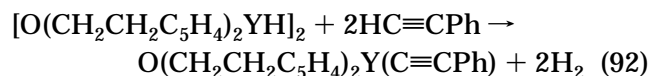
$$R = H, Me, {}^nPr, {}^tBu, SiMe_3, Ph$$

Reaction of phenylacetylene with $[Cp^*_2SmH]_2$ did not give the alkynide compound $[Cp^*_2SmC{\equiv}CPh]_2$, as previously reported[225] but afforded the coupling diyne product (eq 94).[253] Other alkynes reacted differently and with $HC{\equiv}C^tBu$ (eq 95), two products were isolated and identified by their crystal structure: the uncoupled alkynide complex and the butadienyl compound, the formation of which is not well understood.[254]

$$[Cp^*_2SmH]_2 + 2HC{\equiv}CPh \rightarrow$$
$$(Cp^*_2Sm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph) \quad (94)$$

$$[Cp^*_2SmH]_2 + 2HC{\equiv}C^tBu \rightarrow$$
$$[Cp^*_2Sm\text{-}C{\equiv}C^tBu]_2 +$$
$$Cp^*_2Sm[{}^tBuCH{=}CC({}^tBu){=}CH_2] \quad (95)$$
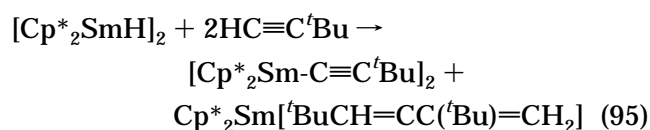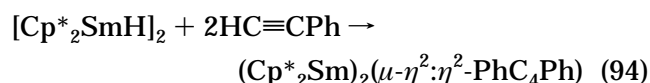
B. Catalytic Reactions

1. H/D Exchange Reactions

Exchange of hydrogen for deuterium between D_2 or C_6D_6 and the Cp* ring is common for the [Cp*₂-

LnH]₂ hydrides and was reported for Ln = La, Nd,[54] Sm,[54,58] and Lu.[54,248,252] The hydride ligands of [Cp*₂-YH]₂ were very rapidly exchanged for deuterium at room temperature in C_6D_6 and in the presence of $CH_2(SiMe_3)_2$, catalytic H/D exchange was observed between the Me groups of the SiMe₃ fragments and C_6D_6, the methylene group being not affected. The methyl group of toluene was also deuteriated by [Cp*₂YH]₂ in C_6D_6 but the phenyl ring was affected at a much lower rate, showing the preference for sp³ CH bonds. Deuteration of the Cp* ligands occurred at higher temperatures and was complete within 4 h at 100 °C.[52] The scandium hydrides $[Cp^*_2ScH]_n$ and $Cp^*_2ScH(THF)$ catalyzed the intermolecular H/D exchange between C_6D_6 and a variety of organic molecules. The order of reactivity of CH bonds: aryl CH > Cp*, α-THF, PMe₃ > CH₄, SiMe₄, cyclopropane, $PhCH_3$ > $CH_3CH_2CH_3$ ≫ β-THF, cyclopentane, cyclohexane, cyclooctane, $CH_3CH_2CH_3$ indicated that steric factors and s character of the CH bond correlate more closely with reactivity than does the CH bond dissociation energy.[49,50] $[Cp^*_2ScH]_n$ was an efficient catalyst for the large-scale synthesis of $C_5(CD_3)_5H$ ($[^2H_{30}]Cp^*H$); 10 turnovers per day were observed at 145 °C under 1 atm of D_2 with 0.1 equiv of the scandium hydride and the typical isotopic purity was 95% after 4−5 week reaction times.[255]

2. Isomerization Reactions

Terminal alkenes were isomerized into *cis*- and *trans*-2-alkenes by using the systems Cp_3Ln/NaH, when the ratio $Cp_3Ln/1$-alkene was less than 0.25 (Ln = Y, La, Pr, Nd, Sm, Tb, Er, Yb, Lu). The catalytic activities could be related to the ionic radii of the Ln metals; Cp_3Y and Cp_3Lu were the best catalysts for the isomerization of 1-hexene.[230,256] Other organoyttrium complexes were efficient for the isomerization of 1-octene, in the order: Cp_2YCl, Cp_3Y > $MeN(CH_2CH_2C_5H_4)_2YCl$, $(MeOCH_2CH_2C_5H_4)_2YCl$ > YCl_3.[256]

Stoichiometric reactions of the scandium hydride $[Me_2Si(C_5H_3{}^tBu)_2ScH]_2$ with 1,4-pentadienes gave η^3-allyl complexes but when used in excess, these dienes were catalytically isomerized via C−C σ-bond activation (eqs 96 and 97).[62] The scandium hydride catalyzed the cyclization of α,ω-diolefins (eq 98), a particular example of α-olefin dimerization (*vide infra*).[51]

$$R = H, Me \quad (96)$$

$$(97)$$
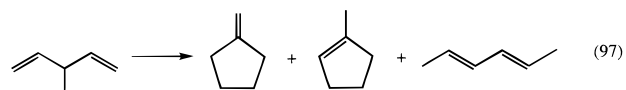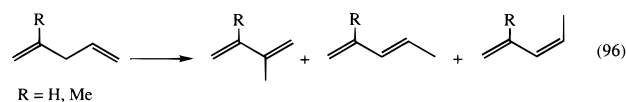
Methylenecycloalkanes were also formed in excellent yields and under milder conditions with $Me_2Si(C_5Me_4)_2Sc(PMe_3)H$; methylenecyclohexane was thus obtained in 97% yield at 25 °C by using this catalyst which was also quite efficient for the cyclization of diallyl silanes, sulfides and amines (eq 99).[51] Neither 1,3-butadiene nor 1,4-pentadiene could be cyclized, due to the endothermicity of this transformation; inversely, methylenecyclopropane and methylene cyclobutane were catalytically opened by the scandium hydrides (eqs 100 and 101).[51,223]

(98)

n = 1-5

(99)

E = Me$_2$Si, S, NMe

(100)

(101)
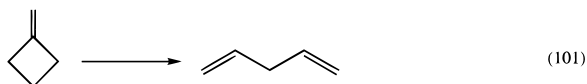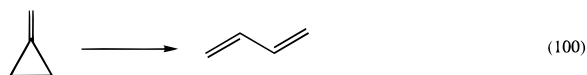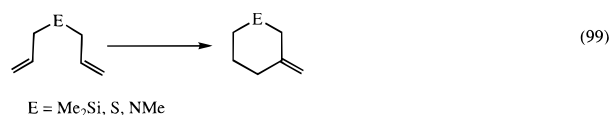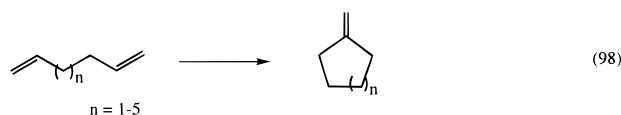
3. Hydrogenation Reactions

a. Hydrogenation of Alkenes and Alkynes. The first homogeneous catalytic hydrogenation of unsaturated hydrocarbons was performed by using the alkynide hydride complexes formed by cocondensation of lanthanide metals with internal alkynes. Thus, 3-hexyne was transformed into 3-hexene (>96% *cis*); the rates of these reactions were low, typically 3×10^{-3} turnovers/min.[12,257] Initial experiments revealed the catalytic activity of [Cp*$_2$SmH]$_2$[58] and (C$_5$H$_4$R)$_2$YH(THF)[67] in the hydrogenation of diphenylacetylene and 3-hexyne; slow rates were again observed. The biscyclopentadienyl lanthanide hydrides were subsequently found to be in fact very efficient catalysts for the hydrogenation of C≡C and C=C bonds. Hydrogenation of 1-hexene catalyzed by [Cp*$_2$LnH]$_2$ or [Me$_2$Si(C$_5$Me$_4$)$_2$LnH]$_2$ (Ln = La, Nd, Sm, Lu) in cyclohexane or toluene solutions was first order in catalyst and first order in H$_2$ pressure, $v_{(1-hexene)} = k_3[Ln][H_2]$, in agreement with the catalytic cycle (Scheme 5) and the sequence shown in eqs 102−104 where k_2 and K_2 are very large and Ln−C bond hydrogenolysis (k_3) is rate-limiting.[258]

The activity was inversely proportional to the metal ionic radius (Lu > Sm > Nd > La), suggesting that higher charge/radius ratios accelerate the heterolytic activation of H$_2$ in the σ-bond metathesis process (eq 104); for constant Ln, the [Cp*$_2$LnH]$_2$ hydrides are more reactive than [Me$_2$Si(C$_5$Me$_4$)$_2$LnH]$_2$. With [Cp*$_2$-LuH]$_2$, 120 000 turnovers/h were measured ($k_3 = 7$ 700 M^{-1} s^{-1}); these performances should be compared with those of RuHCl(PPh$_3$)$_3$ (3000 turnovers/h) or [(COD)Ir(PCy$_3$)(NC$_5$H$_5$)][PF$_6$] (6400 turnovers/h).

$$\{[Ln]\text{-}H\}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[Ln]\text{-}H \qquad K_1 \qquad (102)$$

$$[Ln]\text{-}H + R(\text{-}H) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ln]\text{-}R \qquad K_2 \qquad (103)$$

$$[Ln]\text{-}R + H_2 \overset{k_3}{\longrightarrow} [Ln]\text{-}H + RH \qquad (104)$$
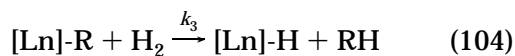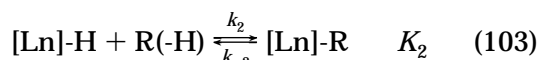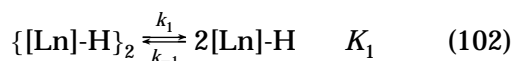
For all catalysts except [Cp*$_2$LuH]$_2$, the rate law for hydrogenation of cyclohexene was $v_{(cyclohexane)} = k_{obs}[Ln]^{1/2}[olefin]$, indicating that addition of the lanthanide hydride to the sterically shielded C=C bond (k_2) is now rate-limiting. In this case, the reaction was much slower, the sensitivity of the rate to ionic radius was reversed and the more "open" Me$_2$-Si(C$_5$Me$_4$)$_2$Ln moieties were more reactive. For [Cp*$_2$-

Scheme 5. Catalytic Cycle for the Hydrogenation of Olefins
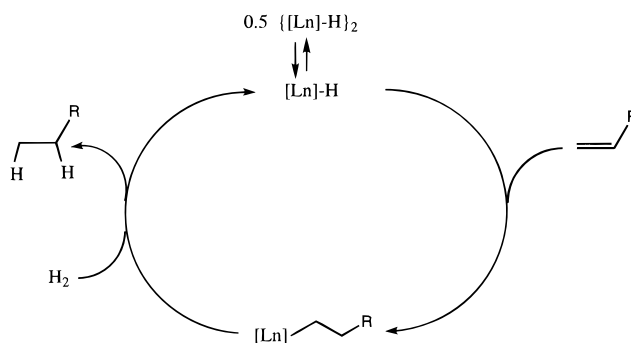
Scheme 6. The Chiral Catalyst Precursors Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)LnE(SiMe$_3$)$_2$ [Ln = Y, La, Nd, Sm, Lu; E = CH, N; R* = (+)-Neomenthyl, (−)-Menthyl, (−)-Phenylmenthyl]
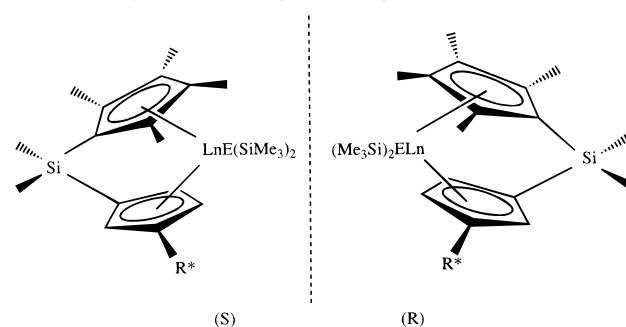
LuH]$_2$, the rate law was first order in olefin and first order in catalyst, suggesting that the dimer is largely dissociated or reacts directly with the olefin. Reaction of 1-hexene and cyclohexene with D$_2$ afforded, in a non-mass-transport-limited regime, hexane-1,2-d_2 and cyclohexane-1,2-d_2 respectively; these hydrogenations were much less rapid in the presence of THF. Hydrogenation of 3-hexyne occurred in two stages; the rate laws corresponding to the first stage (3-hexyne → *cis*-3-hexene) were reminiscent of the 1-hexene system, whereas for the second stage (3-hexene → hexane), they parallel those for cyclohexene.

The complexes Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Sm, Yb) are efficient precatalysts for the diastereoselective hydrogenation of chiral exo-methylene-substituted cyclopentanes and cyclohexanes; the *cis* diastereoisomer is the major product.[259]

The lutetium hydride [Et$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)Lu]$_2$(μ-H)$_2$ catalyzed the hydrogenation of 1-hexene with initial turnover frequencies of ∼21 h^{-1}, but its activity slowed down dramatically as it was transformed into the inert isomer Lu$_2$[μ-(C$_5$Me$_4$)SiEt$_2$(C$_5$H$_4$)]$_2$(μ-H)$_2$.[33]

The chiral hydrides [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)LnH]$_2$, formed *in situ* by hydrogenolysis of the amide or alkyl precursors (Scheme 6), are very efficient for the catalytic asymmetric deuteration or hydrogenation of styrene and 2-phenyl-1-butene;[260,261] they are more reactive than the parent [Cp*$_2$LnH]$_2$ complexes, presumably reflecting lessened steric constraints.

Hydrogenation of 2-phenyl-1-butene with (S)-, (R)-, and (S,R)-[Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)LnCH(SiMe$_3$)$_2$ (R* = (+)-neomenthyl) obeys the rate law $v = k[Ln]^{1/2}[H_2]$, indicating that the olefin insertion, the step in which stereochemistry is fixed, is rapid and irreversible while hydrogenolysis of the Sm alkyl intermediate

Scheme 7. The Pseudo *meso*-Me$_2$Si(C$_5$H$_3$R)(C$_5$H$_3$R*) Ancillary Ligation [Ln = Y, Lu; R* = (−)-Menthyl]
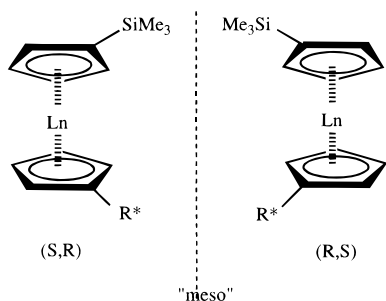
is rate limiting, with $kH_2/kD_2 = 1.5-2.3$ at 25 °C. The (*S*) catalyst induced the selective formation of the (*S*) product and the (*R*) catalyst selects for the (*R*) product; (*S*) and (*R*) phenylbutanes were formed at 25 °C under 1 atm of H$_2$ with enantiomeric excesses of 19 and 73% and with turnover frequencies of 4000 and 5700 h^{-1}, respectively; no major nonlinear effects were observed with (*S*) + (*R*) mixtures (eq 105). The
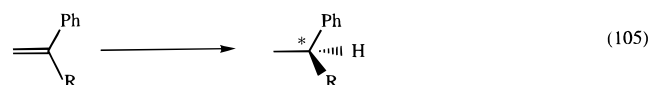
ee values are the highest yet reported for the hydrogenation of these alkenes; they vary with the size of the lanthanide (La > Nd > Sm > Y > Lu). Enantioselection in these reactions is best explained by the frontal approach of the olefin along the ring centroid−metal−ring centroid angle bisector.

In order to reduce the reactivity and to increase the selectivity of the catalyst, [Cp*$_2$YH]$_2$, which has a small "cone angle of reaction", has been chosen for the selective hydrogenation of substituted dienes. A series of α,ω-dienes were thus transformed into internal alkenes, disubstituted C=C bonds being not affected. For example, 4-vinylcyclohexene was hydrogenated into 4-ethylcyclohexene after 2 h at 20 °C, with 1% of the precatalyst Cp*$_2$YMe(THF) in benzene or toluene solution under 1 atm. H$_2$ pressure (eq 106).[262]
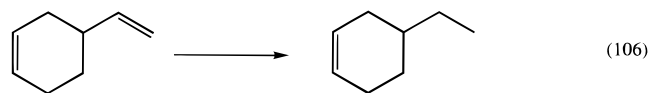
The yttrium and lutetium complexes having pseudo *meso*-Me$_2$Si(C$_5$H$_3$R)(C$_5$H$_3$R*) ancillary ligation (R = SiMe$_3$, R* = (−)-menthyl) (Scheme 7) were effective precatalysts for asymmetric hydrogenation or deuteration of styrenic and nonstyrenic olefins (eqs 107−110).[263] They were however less reactive than the Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)Ln-based systems, the apparent rate constant for 2-phenyl-1-butene hydrogenation being ~1 order of magnitude lower and reflecting lower Ln−C bond hydrogenolytic reactivity. The highest enantioselectivities were obtained with the Lu complex in hydrogenation of 2-phenyl-1-butene

Scheme 8. Catalytic Cycle for the Hydrogenation of 'BuCN
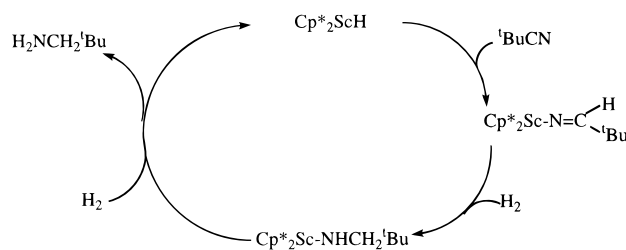
(45% ee) and deuteration of styrene (10% ee) and 1-pentene (30% ee).
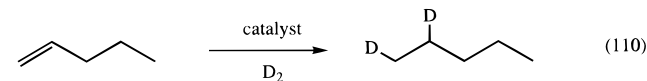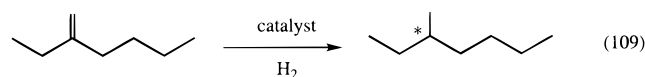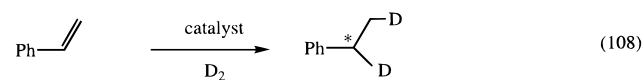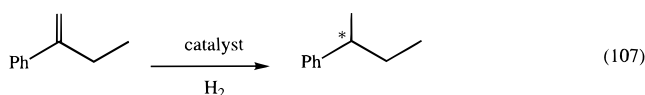
Other systems were found to have a low catalytic activity for 1-hexene hydrogenation: [(CH$_2$)$_3$(C$_5$H$_4$)$_2$-Ln(H(THF)]$_2$ (Ln = Y, Dy, Er, Lu),[69] Cp$_3$Sm/NaH,[231] and [O(CH$_2$CH$_2$C$_5$H$_4$)$_2$YCl/NaH.[230] Thus, 1-hexene was hydrogenated in 75% yield in the presence of 10% of this latter system at 45 °C under 4 atm H$_2$ pressure.

b. Hydrogenation of tert-Butyl Cyanide. Hydrogenation of C=X bonds catalyzed by lanthanide hydrides have not been reported, except that of 'BuCN in the presence of [Cp*$_2$ScH]$_n$; the catalytic cycle is represented in Scheme 8. The reaction was carried out at 80 °C under 4 atm. H$_2$ but the number of turnovers was limited because of irreversible insertion of the nitrile into the Sc−N bond of the amide intermediate.[51,235]

4. Polymerization Reactions

a. Alkenes. The generally accepted mechanism for lanthanide hydride-catalyzed alkene polymerization involves olefin insertion into the Ln−H bond, followed by sequential insertion of the olefin into the resulting Ln−C bond; termination and chain transfer would occur by β-hydrogen elimination, by β-alkyl elimination, by olefin metalation, and in some cases, by hydrogenolysis of the Ln−C bond. It is clear that alkyl complexes [Ln]−R would be also active for these reactions.[252]

The hydrides [Cp*$_2$LnH]$_2$ (Ln = La, Nd, Lu) were found to be highly active catalysts for the polymerization of ethylene.[54,57] The reaction was extremely rapid, producing voluminous quantities of polyethylene within seconds of contacting the two reagents;

the catalysts were active for at least 2 weeks. These activities are comparable to or in excess of those reported for the most active homogeneous ethylene polymerization catalysts so far described and approach those of heterogeneous "third generation" Ziegler−Natta catalysts. The turnover frequencies was higher than 1800 s^{-1} at 25 °C under 1 atm H$_2$ pressure for Ln = La (product M_n = 227000−676000); activities were in the order La > Nd ≫ Lu. The kinetics of the reaction and the molecular weight characteristics of the polymer, which are much affected by mass-transport effects, suggest that the "living polymer" regime is operative for these systems; the least active and less mass-transport influenced Lu catalyst exhibited polydispersities M_w/M_n consistently below 2.0. Chain transfer by β-hydride elimination was not important. The Cp*$_2$Ln coordination sphere is apparently too constricted to support the rapid polymerization of bulkier olefins; allylic C−H activation and η^3-allyl formation were found to compete with olefin insertion into the Ln−C bond. However, some formation of 2-methylundecane was observed by hydrogenation of 1-hexene with [Cp*$_2$-NdH]$_2$ at 20 °C under a deficiency of hydrogen.

The [Me$_2$Si(C$_5$Me$_4$)$_2$LnH]$_2$ hydrides were ∼10 times more active than the corresponding [Cp*$_2$LnH]$_2$ hydrides under the same conditions.[61] Oligomerization of propene with [Me$_2$Si(C$_5$Me$_4$)$_2$LuH]$_2$ at 66 °C gave a complex mixture with greater than 20 components having carbon contents at least as high as C21. Reaction of 1-hexene with [Me$_2$Si(C$_5$Me$_4$)$_2$LuH]$_2$ under 1 atm of ethylene afforded a rubbery copolymer in which the ratio ethylene/1-hexene was ∼3:1, indicating, not surprisingly, that ethylene was more easily inserted into the Ln−C bond than the bulkier 1-hexene.

The hydride generated *in situ* from (*R,S*)-(BnBp)-YCH(SiMe$_3$)$_2$ polymerized 1-pentene to highly isotactic poly-1-pentene (M_n = 119 000, M_w/M_n = 1.44).[66]

Ethylene was rapidly polymerized with [Cp*$_2$-ScH]$_n$,[50] but the alkyl complexes obtained from other α-olefins (eq 47) were further transformed into the *trans* alkenyl products with elimination of alkane.[49,50] The less sterically unencumbered scandium hydrides [SiMe$_2$(C$_5$Me$_4$)$_2$ScH]$_2$, [SiMe$_2$(C$_5$H$_3$-3-^{t}Bu)$_2$ScH]$_2$, (Cp)-(Cp*)ScH(PMe$_3$), and (Cp*)(C$_5$H$_2$Me$_3$)Sc(PMe$_3$)H rapidly and selectively (> 98%) catalyze the dimerization of α-olefins to the "head-to-tail" dimers (eq 111).[51,223]

$$2CH_2=CHR \rightarrow CH_2=C(R)CH_2CH_2R \quad (111)$$

$$R = Me, Et, \,^nPr, \, p\text{-}C_6H_4Me$$
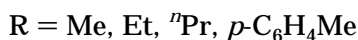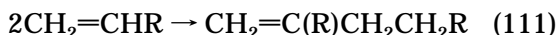
In the presence of [{(C$_5$Me$_4$)Me$_2$Si(η^1-N^{t}Bu)}(PMe$_3$)-ScH]$_2$, propene, 1-butene, and 1-pentene were slowly polymerized into linear, atactic products of low molecular weight (M_n = 3000−7000) with polydispersity index M_w/M_n of 1.7−2.1; all Sc centers were active during the polymerization. Selectivity for "head-to-tail" insertion was > 99%; chain transfer was relatively slow and appeared to occur by β-H elimination.[47,48] Similar results were obtained by using the yttrium hydride [Me$_2$Si(C$_5$H$_2$-2-TMS-4-^{t}Bu)$_2$YH]$_2$ as the catalyst.[64]

The benzamidinate yttrium hydride [{PhC-(NSiMe$_3$)$_2$}$_2$YH]$_2$, which did not react with propene and 1-hexene, was modestly active in ethylene po-

lymerization (65 °C, 4 atm H$_2$); the polyethylene obtained (M_n = 46 300) had a broad molecular weight distribution (M_w/M_n = 5.2).[48,234] The alkoxy hydride [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)YH]$_2$ exhibited similar performances for polymerization of ethylene, was also inactive toward propene and 1-butene, but surprisingly, its dissolution in neat 1-hexene, giving the μ-hydride-μ-hexyl derivative (eq 50), induced slow formation of poly(1-hexene) with M_n = 9400 and M_w/M_n = 1.67.[34] The low reactivity of these yttium complexes, in a comparison with their biscyclopentadienyl analogues, was explained by their higher electropositive character which would not favor the initial interaction with the olefin.

b. Alkynes. While reaction of the benzamidinate yttrium hydride [{PhC(NSiMe$_3$)$_2$}$_2$YH]$_2$ with small 1-alkynes HC≡CR (R = H, Me, ^{n}Pr) was stopped with the formation of the dimeric acetylides (eq 93), catalytic dimerization of the bulkier acetylenes (R = ^{t}Bu, SiMe$_3$, Ph) was observed at room temperature.[44,234] The "head-to tail" dimers were selectively obtained from HC≡C^{t}Bu and HC≡CPh (eq 112) but the regioselectivity was reversed for HC≡CSiMe$_3$, yielding exclusively the "head-to-head" coupled product (eq 113); the origin of this change was proposed to be of an electronic nature. The same results were

$$2HC\equiv CR \rightarrow RC\equiv C-CR=CH_2 \quad (112)$$

$$R = \,^tBu, Ph$$

$$2HC\equiv CSiMe_3 \rightarrow$$
$$\textit{trans } Me_3SiC\equiv C-CH=CHSiMe_3 \quad (113)$$
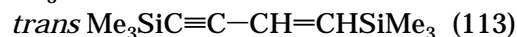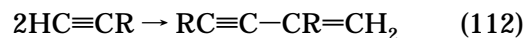
obtained with the alkyl compounds {PhC(NSiMe$_3$)$_2$}$_2$-YR, in contrast to the Cp*$_2$LnR-catalyzed coupling of HC≡CSiMe$_3$ and HC≡CPh which gave either mixtures of "head-to tail" and "head-to-head" isomers (Ln = Y) or formation of higher oligomers (Ln = La, Ce).[264]

c. 1,5-Hexadiene and Methylenecyclopropane. The yttrium hydride [Cp*(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)YH]$_2$ catalyzed the cyclopolymerization of 1,5-hexadiene to poly-(methylene-1,3-cyclopentanediyl) (eq 114),[34] in contrast to *meso*-[Me$_2$Si(C$_5$H$_3$-3-^{t}Bu)$_2$ScH]$_2$ or Me$_2$Si(C$_5$-Me$_4$)$_2$Sc(PMe$_3$)H which induced the cyclization of α,ω-dienes into methylenecycloalkanes (eq 98). In the cyclopolymerization process, the insertion of 1,5-diene into an Y−CH$_2$−cyclopentane intermediate, which is favored over β-H elimination and formation of the cyclized product, would be characterized by a large negative ΔS value.

(114)
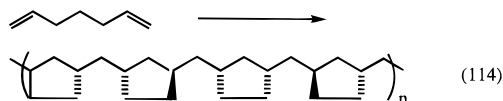
The lutetium hydride [Cp*$_2$LuH]$_2$ catalyzed the homopolymerization of methylenecyclopropane into [CH$_2$CH$_2$C(CH$_2$)]$_n$ at room temperature (eq 115).[265]

(115)
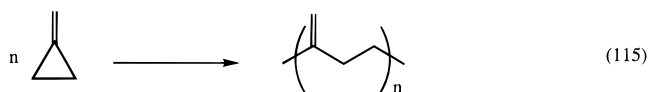
The catalyst was rapidly deactivated due to formation of a Lu−allyl species but could be regenerated

Scheme 9. Mechanism of the Polymerization of Methylenecyclopropane Catalyzed by [Cp*₂LuH]₂

Scheme 10. Catalytic Cycle for the Dehydrogenation of Silanes
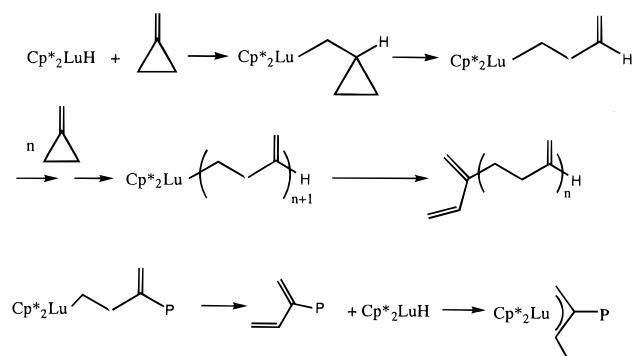
by brief exposure of the reaction mixture to hydrogen. The mechanism of this polymerization would involve a β-alkyl shift-based ring-opening reaction (Scheme 9); the diene species obtained from β-H elimination would undergo 1,4-reinsertion into the Ln–H bond to give the deactivation allyl product.

The samarium and lanthanum compounds [Cp*₂-LnH]₂ reacted quite differently with methylenecyclopropane, yielding the dimer 1,2-dimethylene-3-methylcyclopentane (eq 116).[265] This catalytic transformation was explained by initial dimerization of methylenecyclopropane into the triene 3-methylene-1,6-heptadiene ($n = 1$ in Scheme 9) which would be further cyclized by the lanthanide hydride into the final product.

(116)
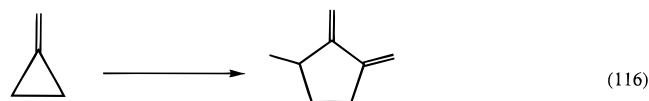
The lanthanide hydrides [Cp*₂LnH]₂ (Ln = La, Sm, Lu) were also able to catalyze the copolymerization of methylenecyclopropane and ethylene into high molecular weight ($M_n = 7000–42000$) [CH₂CH₂]$_x$[CH₂-CH₂C(CH₂)]$_y$ having an exclusively ring-opened microstructure; with [Cp*₂LaH]₂, more than 50% of the methylenecyclopropane was located at the chain ends in a dienyl structure. The activity of the catalysts in incorporating methylenecyclopropane into the polymer followed the orded Lu > Sm > La.

d. Methyl Methacrylate. The samarium hydride [Cp*₂SmH]₂ was very efficient for the homogeneous polymerization of methyl methacrylate. Complete conversion was observed in 1 h at 0 °C with 200 equiv of the substrate; the keto enolate complex of eq 53 is an intermediate in this reaction. Ideal living polymerization prevailed throughout the catalytic process, as shown by the very narrow polydispersity ($M_w/M_n = 1.02–1.04$) for high molecular weight polymer ($M_n > 50\,000$) and the high syndiotacticity (>95% at −95 °C).[233] Stereoregular polymerization of methyl methacrylate could be achieved by using the chiral C_1 symmetric hydride Me₂Si(C₅Me₄)(C₅H₃R*)YH (R* = (+)-neomenthyl).[266]

The complexes [Cp*₂LnH]₂ (Ln = Sm, Yb, Lu) also catalyzed the block polymerization of ethylene with alkyl methacrylates or lactones (eqs 117 and 118); a two-step procedure was occurring: rapid homopolymerization of ethylene with 3% catalyst followed
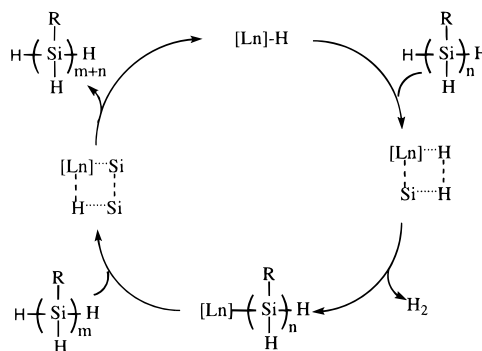
by slower copolymerization with methacrylate or lactone. The AB-type copolymers were obtained in high yields; the relative molar ratio of polyethylene to polymethacrylate or polylactone could be controlled in the range 100:1 to ~100:100 when M_n of the initial polyethylene was ~10 300.[267]

$$\text{Cp*}_2\text{Sm(CH}_2\text{CH}_2)_n\text{R} \xrightarrow{m\text{CH}_2=\text{CMeCO}_2\text{Me}}$$
$$\text{Cp*}_2\text{SmOC(OMe)}=\text{C(Me)CH}_2([\text{C(Me)}-$$
$$(\text{CO}_2\text{Me})\text{CH}_2])_{m-1}(\text{CH}_2\text{CH}_2)_n\text{R} \quad (117)$$

$$\text{R} = \text{H, Me}$$

$$\text{Cp*}_2\text{Sm(CH}_2\text{CH}_2)_n\text{R} \xrightarrow{m[\text{O(CH}_2)_x\text{CO}]}$$
$$\text{Cp*}_2\text{Sm-[OCH}_2(\text{CH}_2)_x\text{CO}]_m(\text{CH}_2\text{CH}_2)_n\text{R} \quad (118)$$

$$\text{R} = \text{H, Me; } x = 3, 4$$
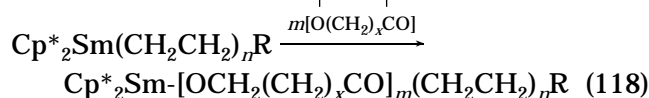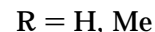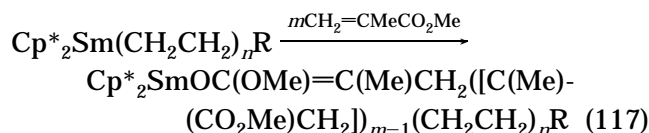
5. Dehydrogenative Oligomerization of PhSiH₃

The complexes [Cp*₂LnH]₂ catalyzed the rapid dehydrogenative oligomerization of PhSiH₃ (eq 119).[268] Typical substrate/catalyst ratios were >100:1 and at 25 °C, the relative order of reactivity (N_t, h^{-1}): Lu (5200) > Y (3310) > Sm > (2140) > Nd (1010) > La (80). The kinetic data reveal no parallels with lanthanide III/II redox characteristics and support the catalytic cycle shown in Scheme 10, which involves four center bond-scission/bond-forming sequences.

$$n\text{PhSiH}_3 \rightarrow \text{H[Si(Ph)(H)]}_n\text{H} + (n-1)\text{H}_2 \quad (119)$$

This M–Si/M–H transposition process is supported by the characterization of several group 4-centered stoichiometric model reactions[269] and thermochemical results[270] which indicate that the steps in Scheme 10 possess no major thermodynamic impediments.

6. Hydrocyclization of Dienes

The catalytic cycle for the hydrocyclization of α,ω-dienes is represented in Scheme 11.

The yttrium hydride [Cp*₂YH]₂, made *in situ* from Cp*₂YMe(THF) was active for the hydrocyclization of 1,5-hexadienes and 1,6-heptadienes (eqs 120–122);[271] thus, 1,5-hexadiene was totally converted into

Scheme 11. Catalytic Cycle for the Hydrocyclization of α,ω-Dienes
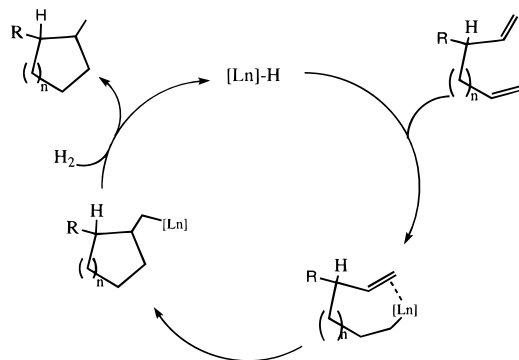
methylcyclopentane within 45 mn at 25 °C with 5 mol % of the catalyst under 1−2 atm of H_2.

$$R = H; OCPh_3, Ph \tag{120}$$

$$70\% \qquad 25\% \tag{121}$$

$$85\% \qquad 5\% \tag{122}$$
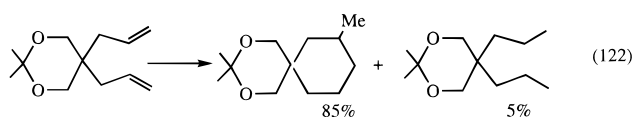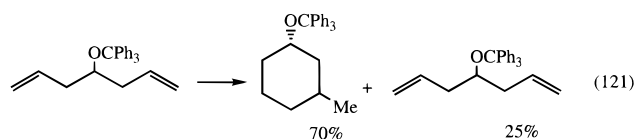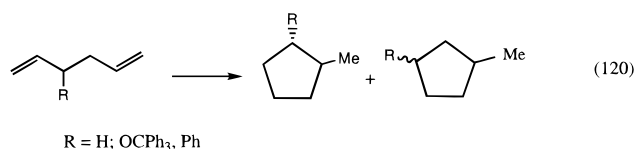
The remarkable regioselectivity can be explained by initial addition of the yttrium hydride to the least sterically hindered and most electron-rich C=C bond with subsequent cyclization leading to 1,2-disubstituted cyclopentanes. In spite of its Lewis acidity, the catalyst was also active with olefins having functional groups such as ethers, acetals, and dithioacetals. Cyclization of 1,6-dienes was also efficient but complicated by reduction of the olefins to form acyclic alkanes.

Reductive cyclization of 1,5-hexadienes was also performed at 22 °C under 1 atm of H_2 with 0.5% of $Me_2Si(C_5H_3SiMe_3)(C_5H_3R^*)LnH$ (R* = (−)-menthyl) (eq 123);[263] the catalyst was however deactivated in the presence of any Lewis base.

$$R = H, Me \tag{123}$$
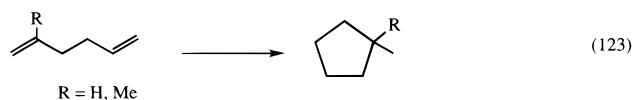
The scandium hydride $Me_2Si(C_5Me_4)_2Sc(PMe_3)H$ cleanly catalyzed (25 °C, 4 atm H_2) the hydrocyclization of *trans,trans*-1,6-dideuterio-1,5-hexadiene into a mixture of *cis*- and *trans*-dideuterio-methylcyclopentane (eq 124).[272] The excess of *trans* product probed for an α-C−H interaction in the transition state for olefin insertion and provided a good evidence for the modified Green−Rooney pathway for chain propagation in Ziegler−Natta polymerization of olefins.[273] A 60:40 mixture of methylcyclohexane and

Scheme 12. Catalytic Cycles for the Hydrosilylation of Alkenes
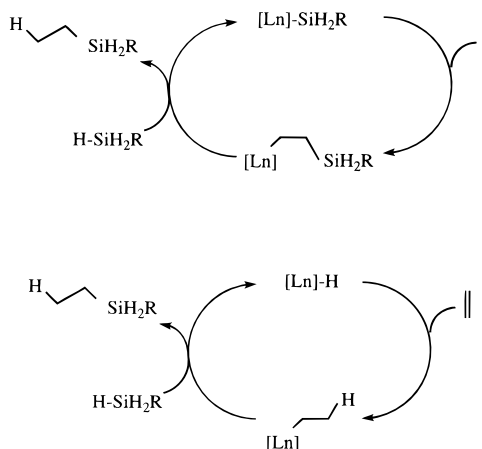
n-heptane was obtained from 1,5-heptadiene, whereas 1,7-octadiene was totally converted into *n*-octane.

$$\tag{124}$$
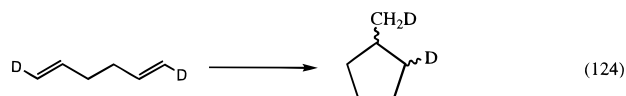
7. Hydrosilylation of Alkenes

The two catalytic cycles represented in Scheme 12 are feasible from thermochemical data.[270]

Hydrosilylation of styrene was performed in benzene at 80 °C in the presence of 4% $[Cp^*_2NdH]_2$ (eq 125).[274] The regioselectivity was very sensitive to the nature of the silane; in the case of $PhSiH_3$, the branched compound was formed with unusual selectivity (69%), whereas the linear isomers were the major products with $PhMeSiH_2$ or n-$C_6H_{13}SiH_3$ (91 and 77% regioselectivity, respectively). Linear isomers were obtained with 100% regioselectivity in the reactions of 1-decene and 2-heptene, whatever the nature of silanes.

$$RCH=CH_2 + R'PhSiH_2 \rightarrow$$
$$RCH_2CH_2SiR'PhH + RCH(SiR'PhH)CH_3 \tag{125}$$
$$R = Ph, n\text{-}C_6H_{13}; R' = H, Me$$
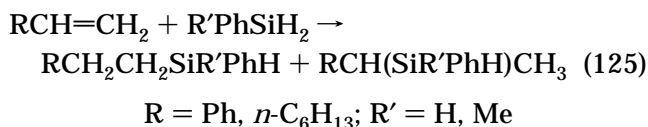
The yttrium hydride $[Cp^*_2YH]_2$ was also active in the hydrosilylation of alkenes; 1,1- and 1,2-disubstituted olefins were much less reactive than monosubstituted alkenes (eqs 126 and 127), and as a consequence, excellent chemoselectivities could be achieved with dienes containing a terminal olefin and any internal olefin (eq 128).[275] This system was tolerant of various functional groups, such as halides, ethers, and acetals.

$$+ PhSiH_3 \longrightarrow \qquad SiH_2Ph \tag{126}$$

$$+ PhSiH_3 \longrightarrow \qquad SiH_2Ph \tag{127}$$

$$+ PhSiH_3 \longrightarrow \qquad SiH_2Ph \tag{128}$$
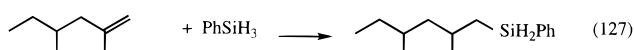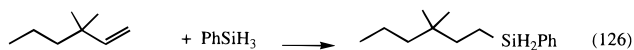
Hydrosilylation of chiral *exo*-methylene-substituted cyclopentanes and cyclohexanes was performed with $PhSiH_3$ in the presence of $Cp^*_2LnCH(SiMe_3)_2$ (Ln =

Scheme 13. Catalytic Cycle for the Cyclization of Aminoolefins
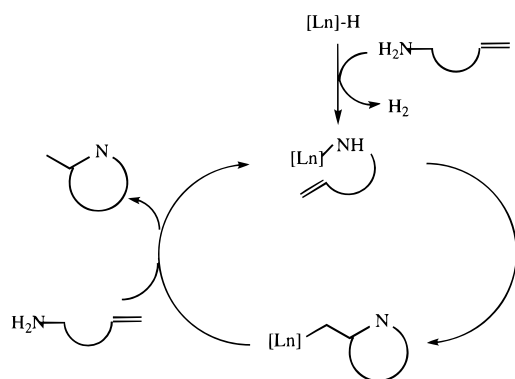
Sm, Yb) as precatalysts; the reaction was diastereoselective, giving the *cis* product preferentially, and regiospecific, the silane being placed exclusively at the terminal position of the double bond.[259]

8. Cyclization of Aminoolefins

The biscyclopentadienyl lanthanide hydrides [Cp*$_2$-LnH]$_2$ (Ln = Y, La, Nd, Sm, Lu) are efficient catalysts for the regiospecific cyclization of various aminoolefins (Scheme 13).[227,276,277]

The reactions were carried out in hydrocarbon solvents, the rates being significantly slower in donor solvents such as THF; the products were isolated in >85% yield and were >95% pure. Representative examples are depicted by eqs 129−132.

$$R^1 = R^2 = H; \ R^1 = R^2 = Me; \ R^1 = H \ and \ R^2 = Me \quad (129)$$

$$(130)$$

$$(131)$$

$$(132)$$
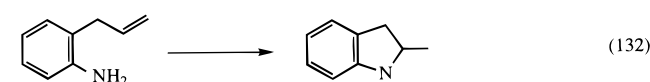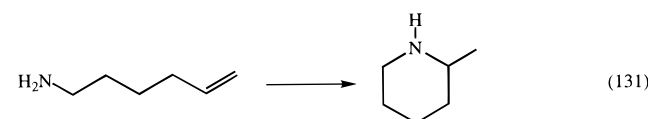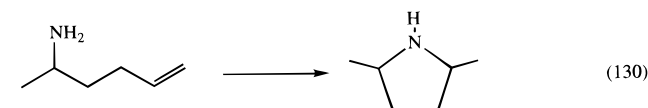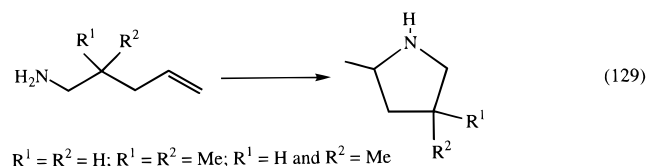
The complexes Cp*$_2$LaR (R = H, CH(TMS)$_2$, N(TMS)$_2$, η^3-C$_3$H$_5$) exhibited similar activities in the cyclization of H$_2$N(CH$_2$)$_2$CH=CH$_2$, suggesting the presence of the common amido intermediate Cp*$_2$-LnNH(CH$_2$)$_3$CH=CH$_2$ in the catalytic cycle (Scheme 13). In fact, mechanistic observations (kinetic isotope effects, diastereoselection in the formation of 2,5-dimethylpyrrolidine) revealed that amine ligands were coordinated to the catalytic species and that these had a marked influence on the stereoselectivity of the ring-closure process.

Kinetic studies indicated that the turnover-limiting step is olefin insertion/cyclization; reactions were zero order in substrate whereas $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values suggest a highly organized transition state. In accord with this picture are the product selectivities, the wide variation of cyclization rates with substrate architecture, in particular the Thorpe−Ingold effect of *gem*-dimethyl groups on cyclization of H$_2$N-(CH$_2$)$_3$C=CH$_2$, and the ordering of precatalyst activities: Cp*$_2$LaR > Cp*$_2$SmR > Cp*$_2$LuR > and Et$_2$Si(C$_5$H$_4$)(C$_5$Me$_4$)LuR > Me$_2$Si(C$_5$Me$_4$)$_2$LuR > Cp*$_2$-LuR (R = CH(TMS)$_2$) which parallels the olefin insertion reactivities. The secondary amine MeNH-CH$_2$CH$_2$CH=CH$_2$ could be cyclized with Me$_2$Si(C$_5$-Me$_4$)$_2$NdCH(TMS)$_2$ (25 °C, N_t = 11 h^{-1}) (eq 133) but remained intact in the presence of Cp*$_2$LaCH(TMS)$_2$.

$$(133)$$
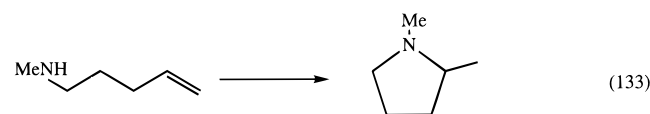
The chiral complexes Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)LnR (Ln = La, Sm; R* = (−)-menthyl, (+)-neomenthyl; R = N(TMS)$_2$, CH(TMS)$_2$) were used for the enantioselective cyclization of aminoolefins (eq 134).[278] Turn-

$$(134)$$

R = H or Me and n = 1; R = Me and n = 2
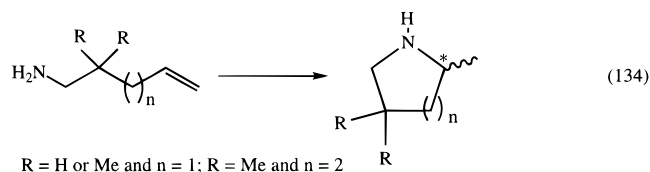
over frequencies were ~10× those of Cp*$_2$Ln catalysts; the % ee (~50−70%) increased with decreasing temperature and decreasing metal ionic radius; (*S*) and (*R*) precatalysts led to the formation of products of net opposite configuration. These chiral complexes should also mediate the diastereoselective cyclization of aminoolefins; thus, (*R*)-Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R*)SmR (R* = (+)-neomenthyl) effected the cyclization of 2-aminohex-5-ene to yield *trans*-2,5-dimethylpyrrolidine with >95% diastereoselectivity (eq 135).

$$(135)$$
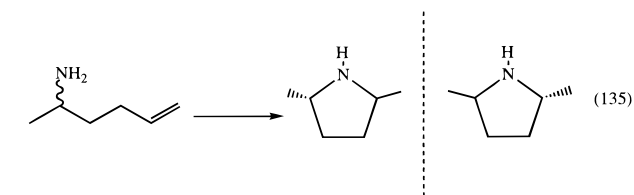
9. Dehalogenation of Organic Halides

Organic halides were dehalogenated by sodium hydride in the presence of 5−10% of Cp$_3$Ln (Ln = Y, La)[279] and various bis(cyclopentadienyl)lanthanide chlorides.[20,231] Aryl bromides and benzyl chloride were reduced easily but so was 1-bromohexadecane; *m*-bromochlorobenzene and *p*-chloroiodobenzene were transformed into chlorobenzene. The likely catalytic cycle for these transformations is represented in Scheme 14.

10. Hydroboration of Olefins

The complexes [Cp*$_2$LnH]$_2$ (Ln = La, Sm) catalyzed the anti-Markovnikov addition of catecholborane to a variety of olefins, in the order terminal > terminal disubstituted > internal disubstituted > trisubsti-

Scheme 14. Catalytic Cycle for the Dehalogenation of Organic Halides
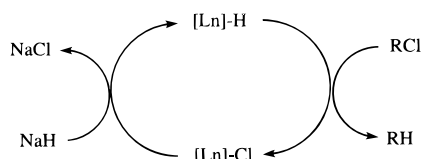
Scheme 15. Catalytic Cycle for the Hydroboration of Alkenes
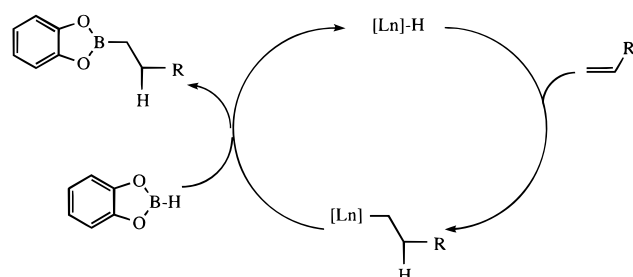
tuted and La > Sm; this trend parallels the steric demands at the metal center. With 5% [Cp$_2$LaH]$_2$, 1-hexene, cyclohexene, and 1-methylcyclohexene were hydroborated at room temperature with turnover frequencies of 200, 50, and 10 h^{-1} respectively; no reaction was observed for tetrasubstituted 2,3-dimethyl-2-butene.[280] A catalytic cycle for this transformation is represented in Scheme 15; the alkyl complexes Cp$^*_2$LnR, which react with catecholborane to give the hydride, may be used as precatalysts.

The benzamidinate compound [{PhC(NSiMe$_3$)$_2$}$_2$-YH]$_2$ exhibited a modest activity in hydroboration of 1-hexene with catecholborane.[281]

XI. Reactions of the Actinide Hydrides and Borohydrides

A. Stoichiometric Reactions of Actinide Hydrides

1. Addition Reactions

Stoichiometric addition reactions of actinide hydrides to C=C and C≡C bonds are relatively scarce. The thorium hydride [Cp$^*_2$ThH(μ-H)]$_2$ reacted with ethylene to give the corresponding diethyl complex (eq 136);[125] no reaction was observed with (C$_5$H$_4$-SiMe$_3$)UH.[206]

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 4CH_2{=}CH_2 \rightarrow 2Cp^*_2ThEt_2 \quad (136)$$
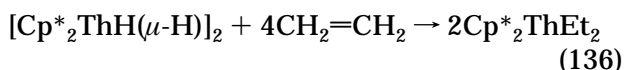
Olefin insertion into the An–H bond of Cp$^*_2$An-(OR)H complexes has been studied in details, providing additional insight into ancillary ligand effects on the kinetics of organo f-element-catalyzed olefin hydrogenation.[137] The rate law for the reaction of Cp$^*_2$Th(O^{t}Bu)H with cyclohexene was $v = k$[olefin]-[Th-H] with $k_{THF}/k_{toluene} = 0.59$, $k_{Th-H}/k_{Th-D} = 1.4$ and $k_U/k_{Th} = 1.5$; the parameters $\Delta H = 9.0(5)$ kcal/mol and $\Delta S = -47.2(1)$ eu suggest a highly ordered transition state. The rate was very sensitive to the nature of the alkoxide ligand and was decreased by a factor ~10^3 when O^{t}Bu was replaced with OCH^t-Bu$_2$. Olefins reacted in the order: ethylene > 1-hexene > 4-methoxy-styrene > styrene ≫ cyclohexene; reaction of *cis*-2-butene gave the *sec*-butyl derivative which slowly rearranged into the *n*-butyl isomer.

Reactions of complexes having chiral OR* ligands with prochiral olefins or ketones showed that diastereoselectivity roughly parallels increasing steric demands of the OR* groups and substrates. From molecular mechanisms/graphics analysis, it appears that the olefin would approach toward the metal center between the U–H and U–O bond rather than from the side.

Reactions of [Cp$^*_2$ThH(μ-H)]$_2$[124,125,282] and (C$_5$H$_4$-TMS)$_3$UH[206] with ketones giving alkoxide derivatives are depicted by eqs 137–139.

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 4Me_2CO \rightarrow \\ 2Cp^*_2Th(OCHMe_2)_2 \quad (137)$$

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 2{}^tBu_2CO \rightarrow \\ 2Cp^*_2Th(OCH^tBu_2)H \quad (138)$$

$$(C_5H_4TMS)_3UH + Me_2CO \rightarrow \\ (C_5H_4TMS)_3U(OCHMe_2) \quad (139)$$
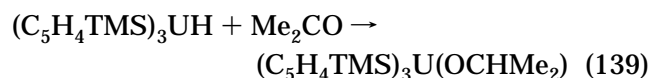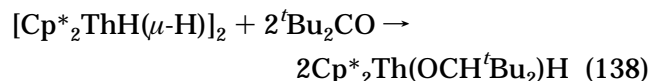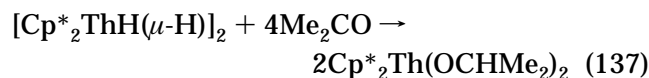
The thorium hydrides Cp$^*_2$Th(OR)H reacted with carbon monoxide to give the binuclear *cis* enediolate compounds (eq 140).[124,281,283] At 25 °C, the reaction required a few minutes for R = ^{t}Bu and several hours for R = CH^{t}Bu$_2$ but did not occur with R = 2,6-^{t}Bu$_2$-C$_6$H$_3$. Kinetic studies revealed that the initially

$$2Cp^*_2Th(OR)H + 2CO \rightarrow \\ [Cp^*_2Th(OR)]_2(\mu\text{-}OCH{=}CHO) \quad (140)$$
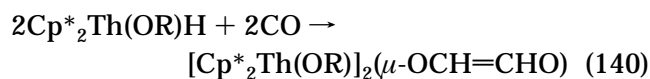
formed η^2-formyl complex Cp$^*_2$Th(η^2-CHO)(OR) would attack, in a rate-limiting step, the hydride to produce a [Th]OCH$_2$[Th] species; the latter would undergo subsequent carbonylation and rearrangement to yield the diolate compound. When reaction 140 was carried in the presence of hydrogen, the major product was Cp$^*_2$Th(OMe)(OR), resulting from hydrogenolysis of the intermediate [Th]OCH$_2$[Th]. The formyl complexes could be characterized by IR and NMR spectroscopy at low temperature; it was found that CO insertion was reversible.

The hydride [Cp$^*_2$ThH(μ-H)]$_2$ reacted with CO$_2$ to give unidentified products but Cp$^*_2$Th(OCH^{t}Bu$_2$)H was transformed into the formate compound Cp$^*_2$-Th(O$_2$CH)(OCH^{t}Bu$_2$).[284] Treatment of (C$_5$H$_4$TMS)$_3$UH with carbon dioxide afforded the monodentate formate derivative (eq 141) which further reacted with the uranium hydride to give a dioxymethylene complex (eq 142); this transformation 2 [M]–H + CO$_2$ → [M]–O–CH$_2$–O–[M] had been proposed as an important step in the catalytic reduction of CO$_2$.[206]

$$(C_5H_4TMS)_3UH + CO_2 \rightarrow (C_5H_4TMS)_3U(OCHO) \quad (141)$$

$$(C_5H_4TMS)_3UH + (C_5H_4TMS)_3U(OCHO) \rightarrow \\ (C_5H_4TMS)_3UOCH_2OU(C_5H_4TMS)_3 \quad (142)$$
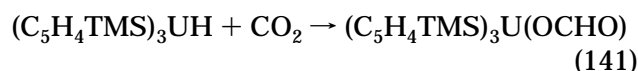
The uranium hydride (C$_5$H$_4$TMS)$_3$UH also reacted with MeCN and BH$_3$ to give the insertion products (eq 143 and 144).[206]

$$(C_5H_4TMS)_3UH + MeCN \rightarrow$$
$$(C_5H_4TMS)_3U(N=CHMe) \quad (143)$$

$$(C_5H_4TMS)_3UH + BH_3 \rightarrow$$
$$(C_5H_4TMS)_3U(BH_4) \quad (144)$$
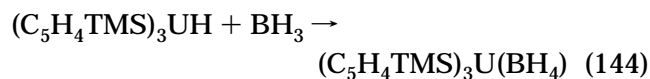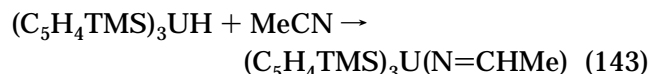
2. σ-Bond Metathesis Reactions

Classical alcoholysis of metal hydride bonds were observed with the complexes $[Cp^*_2ThH(\mu\text{-}H)]_2$,[25,124,125,281] $Cp^*_2An(OR)H$,[138] and $(C_5H_4TMS)_3UH$ (eqs 145−148);[118,206] the latter were converted into the thiolate derivatives by treatment with thiols.[285]

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 4\,^tBuOH \rightarrow$$
$$2Cp^*_2Th(O^tBu)_2 + 4H_2 \quad (145)$$

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 2ArOH \rightarrow$$
$$2Cp^*_2Th(OAr)H + 2H_2 \quad (146)$$

$$Ar = 2,6\text{-}^tBu_2C_6H_3$$

$$Cp^*_2An(OR)H + MeOH \rightarrow$$
$$Cp^*_2Th(OMe)(OR) + H_2 \quad (147)$$

$$An = Th \text{ and } R = 2,6\text{-}^tBu_2C_6H_3 \text{ or } CH^tBu_2;$$
$$An = U \text{ and } R = SiMe_2\,^tBu$$

$$(C_5H_4TMS)_3UH + REH \rightarrow$$
$$(C_5H_4TMS)_3UER + H_2 \quad (148)$$

$$ER = OEt, O^iPr, S^nBu, S^iPr$$
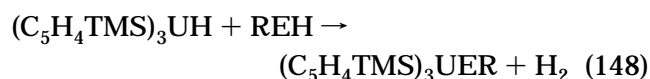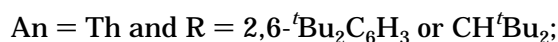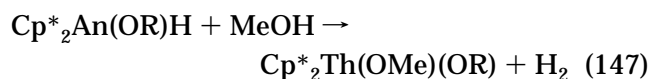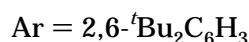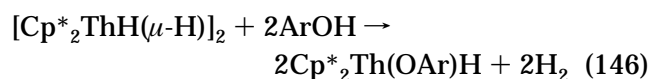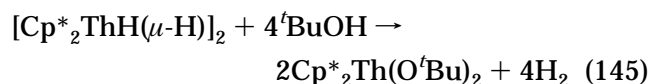
Reactions 145 and 147 served for the calculation of the relative Th−H and U−H bond disruption enthalpies, equal respectively to ∼93 and 82 kcal/mol, by using $D(Th-O) = 124$ kcal/mol and $D(U-O) = 115$ kcal/mol.[25,138]

The first hydroxide complexes of a 5f-element were prepared by hydrolysis of the corresponding hydrides (eq 149). Reaction of $(C_5H_4R)UOH$ with $(C_5H_4R)_3UH$ gave the μ-oxo derivative $[(C_5H_4R)U]_2(\mu\text{-}O)$ (eq 150).[286]

$$(C_5H_4R)_3UH + H_2O \rightarrow (C_5H_4R)_3UOH + H_2 \quad (149)$$

$$R = {}^tBu, SiMe_3$$

$$(C_5H_4R)_3UOH + (C_5H_4R)_3UH \rightarrow$$
$$[(C_5H_4R)_3U]_2(\mu\text{-}O) + H_2 \quad (150)$$

$$R = SiMe_3$$
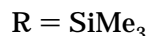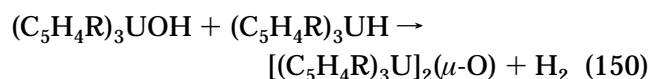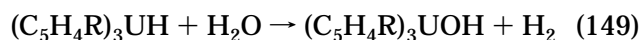
The hydrides $[Cp^*_2AnH(\mu\text{-}H)]_2$ reacted with chloroform to give the corresponding dichlorides,[125,131] whereas the chloro−hydride $[Cp^*_2ThCl(\mu\text{-}H)]_2$ was obtained by the metathesis reaction depicted by eq 151; similar reaction with the uranium analogues led to the formation of the U(III) chloride $[Cp^*_2UCl]_3$.

$$[Cp^*_2ThH(\mu\text{-}H)]_2 + 2Cp^*_2ThCl_2 \rightarrow$$
$$2[Cp^*_2ThCl(\mu\text{-}H)]_2 \quad (151)$$
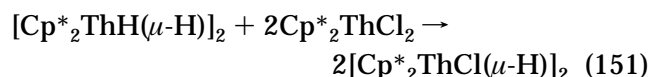
The monohydrides $[(Me_3Si)_2N]_3AnH$,[115] $(C_5H_4R)_3\text{-}UH$ (R = ^tBu, SiMe_3),[117,118] and $[Na(18\text{-}crown\text{-}6)][(C_5H_4TMS)_3UH]$[123] were transformed into the correspond-

ing chlorides by reaction with CCl_4, $CHCl_3$ and ^nBuCl, respectively.

The iodonolysis reactions of eqs 152 and 153 were used for the determination of the absolute bond disruption enthalpies $D(U-H) = 60$ kcal/mol[287] and $D(Th-H) = 64$ kcal/mol;[121] these values are less than those determined by alcoholytic titration and are similar to the small number of available $D(M-H)$ data for transition metal complexes.[288]

$$2(C_5H_4R)_3AnH + I_2 \rightarrow 2(C_5H_4R)_3AnI + H_2 \quad (152)$$

$$An = U \text{ and } R = TMS, {}^tBu; An = Th \text{ and } R = TMS$$

$$2(C_9H_6TMS)_3ThH + I_2 \rightarrow 2(C_9H_6TMS)_3ThI + H_2 \quad (153)$$
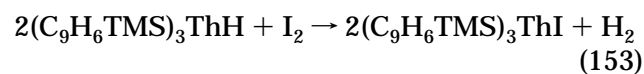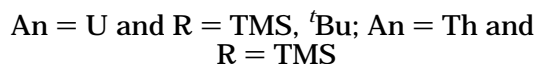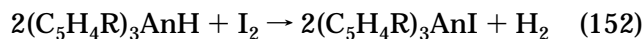
The hydride ligands of $[Cp^*_2ThH(\mu\text{-}H)]_2$, $Cp^*_2Th\text{-}(O^tBu)H$,[125] and $(C_5H_4R)_3UH$[206] were exchanged with D_2. Complete exchange of all 55 hydrogen atoms of $[(Me_3Si)_2N]_3AnH$[289] was observed at room temperature under 1 atm D_2 (40 equiv, five cycles); the metallocycle compound which is formed by thermolysis of the hydride is a likely intermediate in this process (eq 154).

$$[(Me_3Si)_2N]_3AnH \rightarrow$$
$$[(Me_3Si)_2N]_2\overline{AnN(SiMe_3)(SiMe_2CH_2)} + H_2 \quad (154)$$
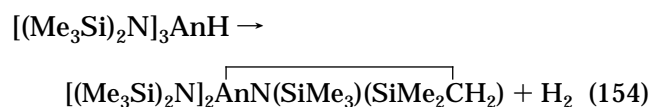
Only one reaction of an actinide hydride with an alkyne has been reported (eq 155).[206]

$$(C_5H_4TMS)_3UH + HC{\equiv}CPh \rightarrow$$
$$(C_5H_4TMS)_3U(C{\equiv}CPh) + H_2 \quad (155)$$
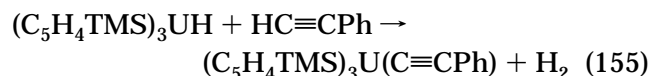
3. Other Reactions of Actinide Hydrides, Including Protonation and Deprotonation

The reactions reported here have not been described with lanthanide hydrides.

Protonation of $(C_5H_4R)_3UH$ with NEt_3HBPh_4 afforded the triscyclopentadienyl U(IV) cations (eq 156),[117,118] whereas the neutral complexes $(C_5H_4R)_3U\text{-}(THF)$ (R = H, TMS) were obtained by similar treatment of the anionic U(III) hydrides (eq 157).[123]

$$(C_5H_4R)_3UH + NEt_3HBPh_4 \rightarrow$$
$$[(C_5H_4R)_3U][BPh_4] + H_2 + NEt_3 \quad (156)$$

$$R = {}^tBu, TMS$$

$$[Na(THF)_2][Cp_3UHUCp_3] + NEt_3HBPh_4 \rightarrow$$
$$2Cp_3U(THF) + H_2 + NEt_3 + NaBPh_4 \quad (157)$$
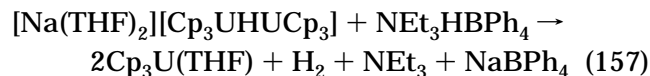
The hydrides $[(Me_3Si)_2N]_3AnH$ possess some protonic character, as shown by their treatment with butyllithium followed by addition of methyl bromide (eq 158).[115]

$$[(Me_3Si)_2N]_3AnH \xrightarrow[\text{(2) MeBr}]{\text{(1) }^nBuLi} [(Me_3Si)_2N]_3AnMe$$
$$(158)$$
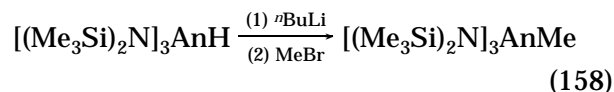
Treatment of the hydrides $[Cp^*_2AnH_2]_2$ with trimethyl phosphite gave the corresponding methoxide compounds and phosphinidene-bridged products (eq

159); reaction is much more rapid for An = U than for An = Th.[290]

$$5[Cp^*_2AnH_2]_2 + 4P(OMe)_3 \rightarrow 2Cp^*_2An(OMe)_2 + 4[Cp^*_2An(OMe)]_2PH + 8H_2 \quad (159)$$
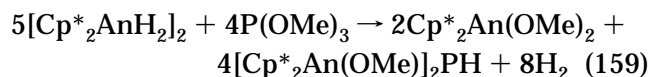
Photochemistry of lanthanide and actinide hydrides has not been considered. Only the UV irradiation of $(C_5H_4R)_3UH$, yielding to quantitative formation of $(C_5H_4R)_3U$ (eq 160),[118] was reported.

$$2(C_5H_4R)_3UH \rightarrow 2(C_5H_4R)_3U + H_2 \quad (160)$$

$$R = {}^tBu, TMS$$
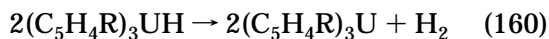
B. Stoichiometric Reactions of Actinide Borohydrides and Aluminohydrides

The synthesis of uranium borohydrides from $U(BH_4)_n$ (n = 3, 4) and their derivatives have been described in IX.C. Subsequent substitution of BH_4 ligands by reaction with alkali metal salts of anionic reagents was useful for the preparation of various organouranium compounds. Selected examples are depicted by eqs 161−163.[192,291]

$$(tmp)U(BH_4)_3 + 3LiCH_2Ph \rightarrow (tmp)U(CH_2Ph)_3 + 3LiBH_4 \quad (161)$$

$$(tmp)_2U(BH_4)_2 + 2LiR \rightarrow (tmp)_2UR_2 + 2LiBH_4 \quad (162)$$

$$R = Me, CH_2TMS$$

$$(COT)U(BH_4)_2 + 2NaSR \rightarrow (COT)U(SR)_2 + 2NaBH_4 \quad (163)$$

$$R = {}^nBu, {}^iPr$$
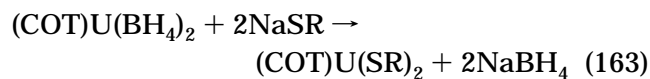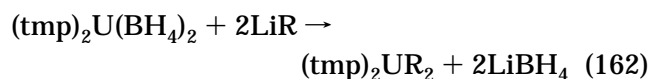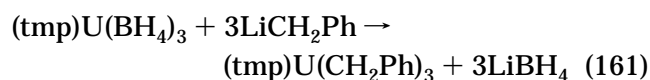
Alcoholysis or thiolysis reactions of borohydride precursors were interesting for the preparation of the complexes $(COT)U(OR)_2$[217,292] and $U(SPh)_4$[293] (eqs 164 and 165) since treatment of $(COT)UX_2$ or UX_4 (X = Cl or BH_4) with NaOR or NaSPh gave the "ate" compounds $Na[(COT)U(BH_4)_2(OR)]$[217] and $[Na(THF)_3]_2$-$[U(SPh)_6]$.[294]

$$(COT)U(BH_4)_2 + [2(1+n)]ROH \rightarrow$$
$$(COT)U(OR)_2 + 2B(OR)_nH_{3-n} + [2(1+n)]H_2 \quad (164)$$

$$R = Et, {}^iPr, {}^tBu$$

$$U(BH_4)_4 + [4(1+n)]PhSH \rightarrow$$
$$U(SPh)_4 + 4B(SPh)_nH_{3-n} + [4(1+n)]H_2 \quad (165)$$
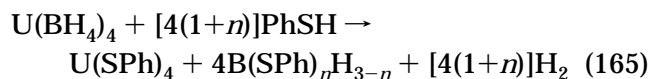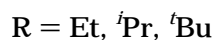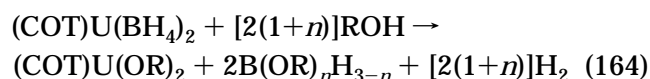
The uranium aluminohydrides $Cp_3U(AlH_4)$[221,222] and $Cp_2U(AlH_4)_2 \cdot nEt_2O$[199] behaved as if they were the hypothetical corresponding hydrides in their addition reactions with Me_2CO, Me_2CHO, MeCN, ${}^tBuNC$, ${}^tBuNCO$, BH_3, pyridine, and their metathesis reactions with alcohols or methyl iodide. Treatment of $Cp_2U(AlH_4)_2 \cdot nEt_2O$ with acetic acid afforded the cluster $[Cp(CH_2CO_2)_5U_2O]_2$. These aluminohydrides were more reactive than the borohydride analogues; for example, $Cp_3U(BH_4)$ did not react with MeCN, ${}^tBuNC$ or pyridine.

Scheme 16. Catalytic Cycle for the Hydrogenation of Alkenes with Cationic Thorium Hydrides
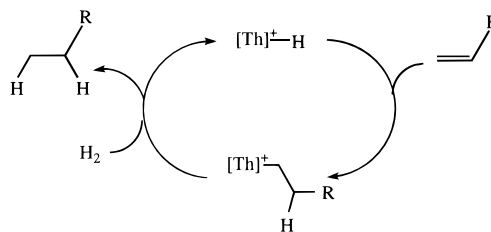
C. Catalytic Reactions of Actinide Hydrides, Borohydrides, and Aluminohydrides

1. Hydrogenation Reactions

The actinide hydrides $[Cp^*_2AnH_2]_2$ catalyzed the hydrogenation of 1-hexene in toluene solution at 24 °C under 0.9 atm H_2 with turnover frequencies N_t of 0.5 (Th) and 7.0 h^{-1} (U); diphenylacetylene was hydrogenated under the same conditions into 1,2-diphenylethane.[125,295] The activity of $[Cp^*Th(O-2,6-{}^tBu_2-C_6H_3)H_2]_3$ was comparable in the hydrogenation of 1-hexene with N_t = 10 h^{-1}.[129] The thorium hydride with the chelating bis(tetramethylcyclopentadienyl) ligand $[Me_2Si(C_5Me_4)_2ThH_2]_2$ was much active; it catalyzed the hydrogenation of 1-hexene at a rate 10^3 faster than $[Cp^*_2ThH_2]_2$.[296] As in the case of the $(Cp^*_2LnH)_2$ catalysts, the rate was zero order in olefin and first order in catalyst, hydrogenolysis rather than olefin insertion being rate limiting.

The complexes $Cp^*_2AnMe_2$ were supported on dehydroxylated alumina and activated by hydrogen and the resulting surface species exhibited very high catalytic activity for the hydrogenation of propene; the turnover frequencies were as high as 0.5 s^{-1} at −63 °C, 10 times greater than those observed with typical Pt/SiO_2 catalysts under the same conditions.[295,297] High-resolution solid-state ^{13}C NMR studies revealed that methyl transfer occurred from Th to Al on the surface of the support.[298] A two-step mechanism was then proposed for the hydrogenation of olefins on supported $Cp^*_2ThMe_2$ catalyst, which is analogous to that established for Cp^*_2LnR catalysts (Scheme 16).[297]

Kinetic data were in agreement with this scheme. Hydrogenations were essentially zero order in olefin; for isobutylene, the activation enthalpies for olefin insertion and alkyl hydrogenolysis were comparable. With supported $Cp^*_2ThMe_2$, the olefins reacted in the order: *cis*-2-butene > *trans*-2-butene > propylene > isobutylene. Other organoactinides were supported on alumina and their relative activities for propylene hydrogenation followed the order: $Cp^*_2ThMe_2$ > Me_2-$Si(C_5Me_4)_2ThBu_2$ > $[Me_2Si(C_5Me_4)_2ThH_2]_2$ > Cp^*_2-$ThMe(O_3SCF_3)$ > $[Me_2Si(C_5Me_4)_2UH_2]_2$ ≫ $(C_8H_7$-${}^nBu)_2U$. These results, which are different from those obtained in homogeneous solution, showed the role of the surface in modulating catalytic activity. The activity of $Cp^*_2ThMe(O_3SCF_3)$ confirmed that Cp^*_2-$ThMe^+$ sites would be formed on the alumina support.[296]

The complexes $Cp^*Th(CH_2Ph)_3$, $Th(1,3,5-CH_2C_6H_3$-$Me_2)_4$, and $Th(\eta^3$-allyl)$_4$, when supported on alumina, were found to be very active catalysts for olefin and arene hydrogenation.[299] With the allyl complex, benzene was hydrogenated (90 °C, 180 psi H_2) with

$N_t = \sim 25\,000$ h^{-1}, by following the rate law $N_t = k[\text{benzene}]^0[\text{PH}_2]$ with $N_t(\text{H}_2)/N_t(\text{D}_2) = 3.5 \pm 0.3$. These performances are better than those of the known homogeneous catalysts and rivil or exceed those of the most active heterogeneous catalysts. The different arenes reacted in the order: benzene > toluene > p-xylene > naphthalene. Here again, it is likely that cation [Th-H]$^+$ and [Th-R]$^+$ species are the active sites; their characterization using D$_2$O poisoning, hydrogenolysis, and CHCl$_3$ dosing indicated that a maximum of $8 \pm 1\%$ of the Th surface sites are of catalytic significance.

A series of cationic complexes of the type Cp*$_2$-ThMe$^+$X$^-$ (X = BPh$_4$,[300] B(C$_6$F$_5$)$_4$,[301] and [B(C$_6$F$_5$)$_2$]$_2$-(CHCH$_2^t$Bu)(H)[302]) were considered as models for the active surface species. For 1-hexene hydrogenation, the reactivity of [Cp*$_2$ThMe][B(C$_6$F$_5$)$_4$] was approaching the reactivity of supported Cp*$_2$ThMe$_2$/Al$_2$O$_3$ catalyst.[303]

The thorium hydride [Cp*$_2$ThH$_2$]$_2$ was a catalyst for the hydrogenation of η^2-acyl compounds into alkoxide derivatives (eq 166).[304]

$$\text{Cp*}_2\text{An}(\eta^2\text{-COR})(\text{Cl}) + \text{H}_2 \rightarrow$$
$$\text{Cp*}_2\text{An}(\text{OCH}_2\text{R})(\text{Cl}) \quad (166)$$
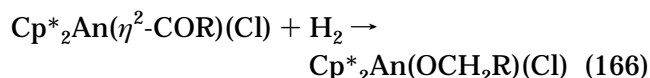
An = Th and R = CH$_2^t$Bu; An = U and R = Ph

In the absence of hydrogen, the thorium acyl complex was transformed into the *trans*-enolate isomer (eq 167).

$$\text{Cp*}_2\text{Th}(\text{COCH}_2^t\text{Bu})(\text{Cl}) \rightarrow$$
$$\text{Cp*}_2\text{Th}(\text{O-CH=CH}^t\text{Bu})(\text{Cl}) \quad (167)$$
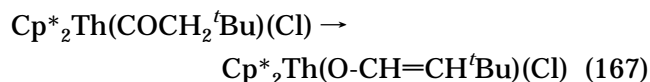
Reactions 166 and 167 can be explained by formation of the common intermediate Cp*$_2$(Cl)[OCH(CH$_2$-^{t}Bu)]ThHCp*$_2$ resulting from insertion of the carbene-like acyl complex into the Th−H bond, followed by hydrogenolysis or β-H elimination.

2. Polymerization Reactions

The hydrides [Cp*$_2$AnH$_2$]$_2$ were marginally active (An = U) or inactive (An = Th) for the catalysis of ethylene polymerization in solution. When supported on alumina, [Cp*$_2$ThH$_2$]$_2$ exhibited some catalytic activity but was much less efficient than Cp*$_2$AnMe$_2$. With the hydride, conversion in the first pulse of ethylene was 49% and conversion fell to zero by the 14th pulse, whereas with Cp*$_2$ThMe$_2$, initial adsorption of ethylene was $\sim$100% and at the 45th pulse, adsorption was 30%.[297]

3. Hydroalumination and Hydroboration of Olefins

Terminal alkenes reacted with LiAlH$_4$ in THF at 20 °C in the presence of 1% UCl$_3$ (or U(AlH$_4$)$_3$) to give, after hydrolysis, the corresponding n-alkane in almost quantitative yield (eq 168).[220] The olefin hydroalumination is regiospecific and involves anti-Markovnikov addition.

Alkenes were hydroborated with LiBH$_4$ in the presence of 1% UCl$_4$ and were transformed, after oxidation of the reaction mixture with alkaline hydrogen peroxide, into the anti-Markovnikov alcohols (eq 169).[159] Most striking was the order of
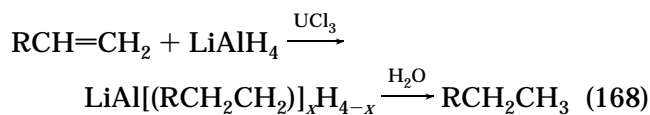
$$\text{RCH=CH}_2 + \text{LiAlH}_4 \xrightarrow{\text{UCl}_3}$$
$$\text{LiAl}[(\text{RCH}_2\text{CH}_2)]_x\text{H}_{4-x} \xrightarrow{\text{H}_2\text{O}} \text{RCH}_2\text{CH}_3 \quad (168)$$
$$\text{R} = \text{H, C}_n\text{H}_{2n+1} \text{ with } n = 1-6$$

reactivity of the alkenes: tetramethylethylene > 1-methylcyclohexene, 2-methyl-2-pentene $\gg$ 2-methylpropene or 1-hexene (no reaction); this sequence is opposite to that invariably observed so far in hydroboration reactions. This reaction is likely to proceed by addition of uranium borohydride species to the C=C bond.

$$\text{Me}_2\text{C=CMe}_2 + \text{LiBH}_4 \xrightarrow{\text{UCl}_4}$$
$$\text{LiBH}_3(\text{CMe}_2\text{CMe}_2\text{H}) \xrightarrow{\text{H}_2\text{O}_2/\text{OH}^-}$$
$$\text{Me}_2\text{C(OH)CHMe}_2 \quad (169)$$
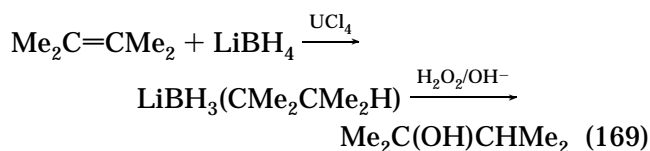
XII. Conclusion

The chemistry of the hydride, borohydride, and aluminohydride compounds of the f-elements did not enjoy a harmonious development and exhibits today both backward steps and significant advances. This state is particularly evident by regarding the borohydride and aluminohydride complexes. If the An-(BH$_3$R)$_4$ derivatives were considered in the 1950's, during the period of the Manhattan project, for their possible utility in isotope separation processes, it is only 30 years after that their interest in organometallic chemistry was assessed, with the synthesis of a series of uranium compounds which proved to be often more stable and more easily handled than their chloride analogues. A number of cyclopentadienyl derivatives have been isolated, as well as their pentadienyl, cyclohexadienyl, and phospholyl counterparts, in the oxidation states +3 and +4. By comparison, the chemistry of the organolanthanide borohydrides has been neglected and it is surprising that the potential of the Ln(BH$_4$)$_3$ compounds, which also have been known since the 1950's, has not been exploited. The chemistry of the aluminohydride complexes seems actually to follow an opposite course, due to the activity of only one research group on the synthesis of biscyclopentadienyl lanthanide derivatives. As it is often the case in the growth of emerging areas of chemistry, these first studies were mainly concerned with the preparation and structure of new compounds; they revealed in particular the flexibility and the novel ligation modes of the BH$_4$ and AlH$_4$ groups. The bridging ability of these ligands favor the building of stable polynuclear compounds, when the experimental conditions are well controlled. It is likely that subsequent efforts will be devoted to the reactivity of these complexes and their use in catalysis, in particular in hydroboration and hydroalumination reactions.

It has been less than 20 years since the first organo-f-element hydrides were isolated and since this date, their chemistry did not cease undergoing spectacular development, encouraged by the discovery of remarkable structural and chemical features. Although neutral hydrides are generally and efficiently prepared by hydrogenolysis of alkyl precursors, other routes using alkali metal hydrides should

be considered for the synthesis of anionic compounds. Like the other lanthanide and actinide complexes which have been so far synthesized, most of these hydrides contain the ubiquitous bis(cyclopentadienyl) ligand set. A rich and versatile body of structures and reactions could be built up by tuning the lanthanide metal center and/or modifying the cyclopentadienyl ring substituents. It is likely that other types of hydrides will be prepared in the future, with ligands such as cyclooctatetraene or allyl; a special attention would be paid to sterically unsaturated and/ or cationic hydrides which are expected to be more reactive. Lanthanide and actinide hydrides are useful starting materials for the preparation of a number of compounds, obtained by addition or σ-bond metathesis reactions. Such hydrides are particularly efficient in the activation of CH bonds of various organic molecules, including alkanes. The exceptional performances of the catalysts, especially those of hydrogenation and polymerization of unsaturated organic substrates, clearly promoted the outstanding qualities of the f-element complexes which, being not duplicated by compounds of the d-transition series, become more and more attractive. One of the most important and promising advances in catalysis was the design of chiral complexes which were efficient in the asymmetric hydrogenation of alkenes or enantioselective cyclization of aminoolefins. If the work on actinide complexes suffered from the difficulties in using radioactive products, their immobilization on the surface of metal oxides has offered many advantages, with a unique and enhanced catalytic activity and a better characterization of the adsorbed species.

The chemistry of the hydride complexes of the f-elements is a young discipline which has reached a first determining stage in its maturity. The peculiar properties of these hydrides, which should not be missed any longer beside those of the d-transition metals, contribute significantly to the knowledge of the metal−hydrogen bond.

XIII. List of Abbreviations

An	actinide metal (thorium or uranium)
Ln	lanthanide metal
R	organic group
Me	methyl, CH_3
Et	ethyl, C_2H_5
Pr	propyl, C_3H_7
Bu	butyl, C_4H_9
Hex	hexyl, C_6H_{13}
TMS	trimethylsilyl, $SiMe_3$
Ph	phenyl, C_6H_5
Mes	mesitylenyl, C_6H_2-2,4,6-Me_3
Ar	aryl
Cp	cyclopentadienyl, C_5H_5 (usually η^5)
Cp*	pentamethylcyclopentadienyl, C_5Me_5, (usually η^5)
dmpd	2,4-dimethylpentadienyl, C_7H_{11}
dmch	6,6-dimethylcyclohexadienyl, C_8H_{11}
tmp	tetramethylphospholyl, C_4Me_4P
COT	cyclooctatetraene, C_8H_8 (usually η^8)
n, i, t	normal, iso, tertiary
o, m, p	ortho, meta, para
η^n	hapticity (n = number of atoms participating in a bond)
μ_n	bridging (n = number of atoms participating in a bond; $\mu = \mu_2$)

THF	tetrahydrofuran, C_4H_8O
THT	tetrahydrothiophene, C_4H_8S
py	pyridine, C_5H_5N
DMPE	(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
TMEDA	tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$
HMPA	hexamethylphosphoramide, $(Me_2N)_3PO$
NMR	nuclear magnetic resonance
UV	ultraviolet
IR	infrared

XIV. References

(1) (a) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1. (b) Crabtree, R. H. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, J. A., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, p 689. (c) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (d) Kubas, G. T. *Acc. Chem. Res.* **1988**, *21*, 120. (e) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.
(2) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538.
(3) Santos, I.; Marques, N. *New J. Chem.* **1995**, *19*, 551.
(4) Edelmann, F. T. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1995; Vol. 4, p 11.
(5) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(6) Soloveichik, G. L. *New J. Chem.* **1995**, *19*, 597.
(7) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.
(8) Bochkarev, M. N.; Zakharov, L. N.; Kalinina, G. S. *Organoderivatives of Rare Earth Elements*, Kluwer Academic Publishers, London, 1995.
(9) Ephritikhine, M. *New J. Chem.* **1992**, *16*, 451.
(10) (a) Mueller, W. M.; Blackledge, J. P.; Libowitz, G. G. *Metal Hydrides*; Academic Press: New York, 1968. (b) Korst, W. L.; Warf, J. C. *Inorg. Chem.* **1966**, *5*, 1719. (c). Warf, J. C.; Korst, W. L.; Hardcastle, K. I. *Inorg. Chem.* **1966**, *5*, 1726. (d) Hardcastle, K. I.; Warf, J. C. *Inorg. Chem.* **1966**, *5*, 1728. (e) Warf, J. C.; Hardcastle, K. I. *Inorg. Chem.* **1966**, *5*, 1736.
(11) (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112.
(12) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672.
(13) Evans, W. J.; Coleson, K. M.; Engerer, S. C. *Inorg. Chem.* **1981**, *20*, 4320.
(14) Knjazhanski, S. Y.; Lobkovsky, E. B.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *419*, 311.
(15) Laske, D. A.; Duchateau, R.; Teuben, J. H.; Spek, A. L. *J. Organomet. Chem.* **1993**, *462*, 149.
(16) Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289.
(17) Knjazhanskij, S. Y.; Bulychev, B. M.; Kireeva, O. K.; Belsky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *414*, 11.
(18) Schumann, H.; Genthe, W. *J. Organomet. Chem.* **1981**, *213*, C7.
(19) Qian, C.; Deng, D.; Ni, C.; Zhang, Z. *Inorg. Chim. Acta* **1988**, *146*, 129.
(20) Xie, Z.; Qian, C.; Huang, Y. *J. Organomet. Chem.* **1991**, *412*, 61.
(21) Deng, D.; Jiang, Y.; Qian, C.; Wu, G.; Zheng, P. *J. Organomet. Chem.* **1994**, *470*, 99.
(22) Qiao, K; Fischer, R. D.; Paolucci, G. *J. Organomet.Chem.* **1993**, *456*, 185.
(23) Schumann, H.; Genthe, W.; Hahn, E. Hossain, M. B.; Van der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67.
(24) Shen, Q.; Chen, W.; Jin, Y.; Shan, C. *Pure Appl. Chem.* **1988**, *60*, 1251.
(25) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.
(26) Evans, W. J.; Meadows, J. H.; Wayda, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015.
(27) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454.
(28) Schumann, H.; Jeske, G. *Z. Naturforsch.* **1985**, *40b*, 1490.
(29) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.
(30) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.
(31) Bazan, G. C.; Schaefer, W. P., Bercaw, J. E. *Organometallics* **1993**, *12*, 2126.
(32) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.
(33) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.
(34) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.
(35) Schaverien, C. J.; Frijns, J. H. G.; Heeres, H. J.; Van den Hende, J. R.; Teuben, J. H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 642.
(36) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.
(37) Booij, M.; Deelman, B. J.; Duchateau, R.; Postman, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.

(38) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682.
(39) Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439.
(40) (a) Steigerwald, M. L.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 308. (b) Rabaâ, H.; Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327. (c) Folga, E.; Ziegler, T.; Fan, L. *New. J. Chem.* **1991**, *15*, 741. (d) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636.
(41) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.
(42) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263.
(43) Bochkarev, M. N.; Penyagina, I. M.; Zakharov, L. N.; Rad'kov, Y. F.; Fedorova, E. A.; Khorshev, S. Y.; Struchkov, Y. T. *J. Organomet. Chem.* **1989**, *378*, 363.
(44) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.
(45) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.
(46) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324.
(47) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.
(48) (a) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Inorg. Chem.* **1988**, *7*, 1409. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.
(49) Thompson, M. E.; Baxter, S. M.; Bulls, A. R., Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
(50) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.
(51) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74.
(52) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.
(53) den Haan, K. H.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 333.
(54) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.
(55) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma A.; Teuben J. H. *Organometallics* **1988**, *7*, 2495.
(56) Renkema, J.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 241.
(57) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200.
(58) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
(59) Evans, W. J.; Chamberlain, L. R., Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.
(60) Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 2095.
(61) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.
(62) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
(63) Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *Inorg. Chim. Acta.* **1996**, *242*, 205.
(64) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606.
(65) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.
(66) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.
(67) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.
(68) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279.
(69) Ye, C.; Qian, C.; Yang, X. *J. Organomet. Chem.* **1991**, *407*, 329.
(70) Alvarez, D., Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5500.
(71) Alvarez, D.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5674.
(72) Radu, N. S.; Gantzel, P. K.; Don Tilley, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1175.
(73) Green, M. L. H.; Hughes, A. K.; Michaelidou, D. M.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1993**, 591.
(74) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (b) Marks, T. J.; Kolb, J. R. *Inorg. Chem.* **1981**, *20*, 297.
(75) Klejnot, O. Dissertation, University of Munich, 1955.
(76) Zange, E. *Chem. Ber.* **1960**, *93*, 652.
(77) (a) Morris, J. H.; Smith, W. E. *J. Chem. Soc., Chem. Commun.* **1970**, 245. (b) Mirsaidov, U.; Kurbonbekov, A.; Rotenberg, T. G.; Dzhuraev, K. *Inorg. Materials (USSR)* **1978**, *14*, 1340. (c) Mirsaidov, U.; Kurbonbekov, A. *Dokl. Akad. Nauk. Tadzh. SSR* **1979**, *22*, 313; *Chem. Abstr.* **1979**, *91*, 185190. (d) Mirsaidov, U.; Rakhimova, A.; Dymova, T. N. *Dokl. Akad. Nauk. SSSR* **1977**, *236*, 120. (e) Mirsaidov, U. *Russ. J. Inorg. Chem.* **1977**, *22*, 1555. (f) Semenenko, K. N.; Kravchenko, O. V.; Kravchenko, S. E.; Polyakova, V. B. *Inorg. Mater. (USSR)* **1977**, *13*, 1811. (g) Kravchenko, O. V.; Kravchenko, S. E.; Polyakova, V. B.; Semenenko, K. N. *Koord. Khim.* **1980**, *6*, 76. (h) Mirsaidov, U.;

Rakhimova, A.; Dymova, T. N. *Inorg. Mater. (USSR)* **1979**, *15*, 1248. (i) Mirsaidov, U.; Shaimuradov, I. B.; Khikmatov, M. *Russ. J. Inorg. Chem.* **1986**, *31*, 753.
(78) Mirsaidov, U.; Rotenberg, T. G.; Dymova, T. N. *Dokl. Akad. Nauk Tadzh. SSR* **1976**, *19*, 30; *Chem. Abstr.* **1976**, *85*, 136374.
(79) Lobkovskii, E. B.; Kravchenko, S. E.; Semenenko, K. N. *J. Struct. Chem. (USSR)* **1977**, *18*, 312.
(80) Kravchenko, O. V.; Kravchenko, S. E.; Polyakova, V. B.; Semenenko, K. N. *Koord. Khim.* **1980**, *6*, 1030.
(81) Segal, B. G.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 844.
(82) Lledos, A.; Duran, M.; Jean, Y.; Volatron, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 216.
(83) (a) Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1964**, *3*, 1978. (b) Marks, T. J.; Shimp, L. A. *J Am. Chem. Soc.* **1972**, *94*, 1542.
(84) Lobkovskii, E. B.; Kravchenko, S. E.; Kravchenko, O,. V. *J. Struct. Chem. (USSR)* **1982**, *23*, 582.
(85) Shinomoto, R.; Zalkin, A.; Edelstein, N. M. *Inorg. Chim. Acta.* **1987**, *139*, 97.
(86) (a) Bruki, A.; Rossmanith, K. *Monatsh. Chem.* **1959**, *90*, 481. (b) Rossmanith, K. *Monatsh. Chem.* **1961**, *92*, 768; **1964**, *95*, 1424.
(87) (a) Noth, H. *Angew. Chem.* **1961**, *73*, 371. (b) Rossmanith K.; Muckenhuber, E. *Monatsh. Chem.* **1961**, *92*, 600.
(88) Rossmanith, K. *Monatsh. Chem.* **1966**, *97*, 863.
(89) White, J. P.; Deng, H.; Shore, S. G. *Inorg. Chem.* **1991**, *30*, 2337.
(90) Kapur, S.; Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1689.
(91) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, M.; Sayer, B. G.; Thompson J. I. A.; McGlinchey, J. *Inorg. Chem.* **1984**, *23*, 1072.
(92) Lappert, M. F.; Singh, A.; Atwood, J. L; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1983**, 206.
(93) Lobkovsky, E. B.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L.; Antipin, M. Y. *J. Organomet. Chem.* **1991**, *406*, 343.
(94) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194.
(95) Marks, T. J.; Grynkewich, G. W. *Inorg. Chem.* **1976**, *15*, 1302.
(96) Deng, D.; Zheng, X.; Qian, C.; Sun, J.; Zhang, L. *J. Organomet. Chem.* **1994**, *466*, 95.
(97) Radu, N. S.; Tilley, T. D. *Phosphorous, Sulfur, Silicon* **1994**, *87*, 209.
(98) Bel'skii, V. K.; Bulychev, B. M.; Erofeev, A. B. Soloveichik, G. L. *J. Organomet. Chem.* **1984**, *268*, 107.
(99) Belsky, V. K.; Erofeev, A. B.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1984**, *265*, 123.
(100) Knjazhanski, S. Y.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1987**, *327*, 173.
(101) Belsky, V. K.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *419*, 299.
(102) Gun'ko, Y. K.; Bulychev, B. M.; Sizov, A. I.; Bel'sky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1990**, *390*, 153.
(103) Belsky, V. K.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *420*, 43.
(104) Gun'ko, Y. K.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1992**, *440*, 47.
(105) Lobkovsky, E. B.; Soloveichik, G. L.; Bulychev, B. M.; Erofeev, A. B.; Gusev, A. I.; Kirillova, N. I. *J. Organomet. Chem.* **1983**, *254*, 167.
(106) Erofeev, A. B.; Bulychev, B. M.; Bel'skii, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1987**, *335*, 189.
(107) Lobkovskii, E. B.; Soloveichik, G. L.; Erofeev, A. B.; Bulychev, B. M.; Bel'skii, V. K. *J. Organomet. Chem.* **1982**, *235*, 151.
(108) Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4172; **1947**, *69*, 1719.
(109) Deacon, G. B.; Tuong, T. D.; Franklin, G. R. *Inorg. Chim. Acta* **1986**, *111*, 193.
(110) Marks, T. J.; Seyam, A. M. *J. Organomet. Chem.* **1974**, *67*, 61.
(111) Evans, W. J.; Wink, D. J.; Stanley, D. R. *Inorg. Chem.* **1982**, *21*, 2565.
(112) Seyam, A. M. *Inorg. Chim. Acta* **1983**, *77*, L123.
(113) (a) Kalina, D. G.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 3877. (b) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1860.
(114) Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703.
(115) Turner, H. W.; Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 2782.
(116) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.
(117) Berthet, J. C.; Le Maréchal, J. F.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1991**, 360.
(118) Berthet, J. C.; Le Maréchal, J. F.; Lance, M.; Nierlich, M.; Vigner, J.;. Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1573.
(119) Gradoz, P.; Boisson, C.; Baudry, D.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1720.
(120) Baudry, D.; Dormond, A.; Hafid, A. *New J. Chem.* **1993**, *17*, 465.
(121) Jemine, X.; Goffart, J.; Ephritikhine, M.; Fuger, J. *J. Organomet. Chem.* **1993**, *448*, 95.
(122) Le Maréchal, J. F.; Villiers, C.; Charpin, P.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1989**, 308.

(123) Berthet, J. C.; Villiers, C.; Le Maréchal, J. F.; Delavaux-Nicot, B.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Organomet. Chem.* **1992**, *440*, 53.

(124) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051.

(125) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

(126) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.

(127) Baudry, D.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M. Vigner, J. *J. Chem. Soc., Chem. Commun.* **1987**, 739.

(128) Clark, D. L.; Grumbine, S. K.; Scott, B. L.; Watkin, J. G. *J. Am. Chem. Soc.* **1995**, *117*, 9089.

(129) Butcher, R. J.; Clark, D. L.; Grumbine, S. K.; Scott, B. L.; Watkin, J. G. *Organometallics* **1996**, *15*, 1488.

(130) Gilbert, T. M.; Ryan, R. R.; Sattelberger, A. P. *Organometallics* **1989**, *8*, 857.

(131) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939.

(132) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* **1979**, *203*, 172.

(133) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J. *Organometallics* **1984**, *3*, 819.

(134) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828.

(135) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. M.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170.

(136) Duttera, M. R.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 865.

(137) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515.

(138) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275.

(139) Yang, X.; King, W. A.; Sabat, M.; Marks, T. J. *Organometallics* **1993**, *12*, 4254.

(140) Marks, T. J.; Gagne, M. R.; Nolan, S. P.; Schock, L. E.; Seyam, A. M.; Stern, D. *Pure Appl. Chem.* **1989**, *61*, 1665.

(141) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(142) Baudry, D.; Ephritikhine, M. *J. Organomet. Chem.* **1986**, *311*, 189.

(143) Cendrowski-Guillaume, S. M.; Ephritikhine, M. *J. Chem. Soc., Dalton. Trans.* **1996**, 1487.

(144) Cendrowski-Guillaume, S. M.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1655.

(145) Schlesinger, H. I.; Brown, H. C. *J. Am. Chem. Soc.* **1953**, *75*, 219.

(146) Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488.

(147) Banks, R. H.; Edelstein, N. M.; Rietz, R. R.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1978**, *100*, 1957.

(148) (a) Volkov, V. V.; Myakishev, K. G. *Radiokhimiya* **1976**, *18*, 512. (b) Volkov, V. V.; Myakishev, K. G. *Radiokhimiya* **1980**, *22*, 745.

(149) Ehemann, M.; Nöth, H. *Z. Anorg. Allg. Chem.* **1971**, *386*, 87.

(150) (a) Bernstein, E. R.; Keiderling, T. A.; Lippard, S. J.; Mayerle, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 2552 (b) Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; La Placa, S. J.; Lippard, S. J., Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009.

(151) Banks, R. H.; Edelstein, N. M.; Spencer, B.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1980**, *102*, 620.

(152) Charpin, P.; Marquet-Ellis, H.; Folcher, G. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1143.

(153) Charpin, P.; Nierlich, M.; Vigner, D.; Lance, M.; Baudry, D. *Acta Crystallogr.* **1987**, *C43*, 1465.

(154) Folcher, G.; Lambard, J.; Marquet-Ellis, H. *Nouv. J. Chim.* **1980**, *4*, 737.

(155) (a) Bernstein, E. R.; Keiderling, T. A. *J. Chem. Phys.* **1973**, *59*, 2105. (b) Banks, R. H.; Edelstein, N. *J. Chem. Phys.* **1980**, *73*, 3589.

(156) Schlesinger, H. I.; Brown, H. C.; Horvitz, L.; Bond, A. C.; Tuck, L. D.; Walker, A. O. *J. Am. Chem. Soc.* **1953**, *75*, 222.

(157) (a) Shinomoto, R.; Gamp, E.; Edelstein, N. M.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 2351. (b) Gamp, E.; Shinomoto, R.; Edelstein, N. M.; McGarvey, B. R. *Inorg. Chem.* **1987**, *26*, 2177.

(158) Kot, W. K.; Edelstein, N. M. *New J. Chem.* **1995**, *19*, 641.

(159) Villiers, C.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1995**, 979.

(160) Rietz, R. R.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. Templeton L. K. *Inorg. Chem.* **1978**, *17*, 653.

(161) Zalkin, A.; Rietz, R. R.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1978**, *17*, 661.

(162) Charpin, P.; Nierlich, M.; Chevrier, G.; Vigner, D.; Lance, M; Baudry, D. *Acta Crystallogr.* **1987**, *C43*, 1255.

(163) Charpin, P.; Lance, M.; Soulié, E.; Vigner, D.; Marquet-Ellis, H. *Acta Crystallogr.* **1985**, *C41*, 1723.

(164) Rietz, R. R.; Edelstein, N. M.; Ruben, H. W.; Templeton, D. H. Zalkin, A. *Inorg. Chem.* **1978**, *17*, 658.

(165) Charpin, P.; Nierlich, M.; Vigner, D.; Lance, M.; Baudry, D. *Acta Crystallogr.* **1987**, *C43*, 1630.

(166) Baudry, D.; Ephritikhine, M. *J. Organomet. Chem.* **1988**, *349*, 123.

(167) Shinomoto, R.; Brennan, J. G.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1985**, *24*, 2896.

(168) Shinomoto, R.; Zalkin, A.; Edelstein, N. M. *Inorg. Chim. Acta* **1987**, *139*, 91.

(169) Brennan, J.; Shinomoto, R.; Zalkin, A.; Edelstein, N. *Inorg. Chem.* **1984**, *23*, 4143.

(170) Shinomoto, R.; Zalkin, A.; Edelstein, N. M.; Zhang, D. *Inorg. Chem.* **1987**, *26*, 2868.

(171) Adam, R.; Villiers, C.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *New. J. Chem.* **1993**, *17*, 455.

(172) Baudin, C.; Baudry, D.; Ephritikhine, M.; Lance, M.; Navaza, A.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1991**, *415*, 59.

(173) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221.

(174) Baudry, D.; Ephritikhine, M.; Kläui, W.; Lance, M.; Nierlich, M.; Vigner, J. *Inorg. Chem.* **1991**, *30*, 2333.

(175) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533.

(176) Moody, D. C.; Penneman, R. A.; Salazar, K. V. *Inorg. Chem.* **1979**, *18*, 208.

(177) Wasserman, H. J.; Moody, D. C.; Ryan, R. R. *J. Chem. Soc., Chem. Commun.* **1984**, 532.

(178) Wasserman, H. J.; Moody, D. C.; Paine, R. T.; Ryan, R. R.; Salazar, K. V. *J. Chem. Soc., Chem. Commun.* **1984**, 533.

(179) Männ, D.; Nöth, H. *Z. Anorg. Allg. Chem.* **1986**, *543*, 66.

(180) Ghiassee, N.; Clay, P. G.; Walton, G. N. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2909.

(181) Paine, R. T.; Schonberg, P. R.; Light, R. W.; Danen, W. C.; Freund, S. M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1577.

(182) (a) Ghiassee, N.; Clay, P. G.; Walton, G. N. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 117. (b) Ghiassee, N.; Clay, P. G.; Walton, G. N. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 149.

(183) Ban, B.; Folcher, G.; Marquet-Ellis, H.; Rigny, P. *Nouv. J. Chim.* **1985**, *9*, 51.

(184) Dejean-Meyer, A.; Folcher, G.; Marquet-Ellis, H. *J. Chim. Phys.* **1983**, *80*, 579.

(185) Dejean, A.; Charpin, P.; Folcher, G.; Rigny, P.; Navaza, A.; Tsoucaris, G. *Polyhedron* **1987**, *6*, 189.

(186) Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1994**, 847.

(187) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 163.

(188) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1369.

(189) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 155.

(190) Baudry, D.; Charpin, P.; Ephritikhine, M.; Folcher, G.; Lambard, J.; Lance, M.; Nierlich, M.; Vigner, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1553.

(191) Zanella, P.; Brianese, N.; Casellato, U.; Ossola, F.; Porchia, M.; Rossetto, G.; Graziani, R. *Inorg. Chim. Acta.* **1988**, *144*, 129.

(192) Gradoz, P.; Baudry, D.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1994**, *466*, 107.

(193) (a) Hafid, A.; Dormond, A.; Baudry, D. *New J. Chem.* **1994**, *18*, 557. (b) Baudry, D.; Dormond, A.; Hafid, A; Raillard, C. *J. Organomet. Chem.* **1996**, *511*, 37.

(194) Baudry, D.; Dorion, P.; Ephritikhine, M. *J. Organomet. Chem.* **1988**, *356*, 165.

(195) Baudin, C.; Ephritikhine, M. *J. Organomet. Chem.* **1989**, *364*, C1.

(196) Ryan, R. R.; Salazar, K. V.; Sauer, N. N.; Ritchey, J. M. *Inorg. Chim. Acta.* **1989**, *162*, 221.

(197) Baudry, D.; Bulot, E.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *J. Organomet. Chem.* **1990**, *388*, 279.

(198) Gradoz, P.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1994**, *481*, 69.

(199) Zanella, P.; De Paoli, G.; Bombieri, G.; Zanotti, G.; Rossi, R. *J. Organomet. Chem.* **1977**, *142*, C21.

(200) Brianese, N.; Casellato, U.; Ossola, F.; Porchia, M.; Rossetto, G.; Zanella, P.; Graziani, R. *J. Organomet. Chem.* **1989**, *365*, 223.

(201) Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Zhang H. *Inorg. Chim. Acta* **1987**, *139*, 13.

(202) Le Maréchal, J. F.; Bulot, E.; Baudry, D.; Ephritikhine, M.; Hauchard, D.; Goffart, R. *J. Organomet. Chem.* **1988**, *354*, C17.

(203) Marks, T. J.; Kennelly, W. J.; Kolb, J. R.; Shimp, L. *Inorg. Chem.* **1972**, *11*, 2540.

(204) Anderson, M. L.; Crisler, L. R. *J. Organomet. Chem.* **1969**, 17, 345.

(205) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 27.

(206) Berthet, J. C.; Ephritikhine, M. *New. J. Chem.* **1992**, *16*, 767.

(207) Rossetto, G.; Porchia, M.; Ossola, F.; Zanella, P.; Fischer, R. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1460.

(208) Porchia, M.; Brianese, N.; Ossola, F.; Rossetto, G.; Zanella, P. *J. Chem. Soc., Dalton Trans.* **1987**, 691.

(209) Zanella, P.; Ossola, F.; Porchia, M.; Rossetto, G.; Chiesi Villa, A.; Guastini, C. *J. Organomet. Chem.* **1987**, *323*, 295.

(210) Le Maréchal, J. F.; Villiers, C.; Charpin, P.; Nierlich, M.; Lance, M.; Vigner, J.; Ephritikhine, M. *J. Organomet. Chem.* **1989**, *379*, 259.

(211) Goffart, J.; Michel, G.; Gilbert, B. P.; Duyckaerts, G. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 393.

(212) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1316.
(213) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Organomet. Chem.* **1990**, *397*, 169.
(214) Baudry, D.; Ephritikhine, M.; Nief, F.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1485.
(215) Gradoz, P.; Baudry, D.; Ephritikhine, M.; Nief, F.; Mathey, F. *J. Chem. Soc., Dalton Trans.* **1992**, 3047.
(216) Le Vanda, C.; Solar, J. P.; Streitwieser, A. *J. Am. Chem. Soc.* **1980**, *102*, 2128.
(217) Arliguie, T.; Baudry, D.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1019.
(218) Burton, N. C.; Cloke, F. G. N.; Hitchcock, P. B.; de Lemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1462.
(219) Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1995**, 183.
(220) Le Maréchal, J. F.; Ephritikhine, M.; Folcher, G. *J. Organomet. Chem.* **1986**, *309*, C1.
(221) Ossola, F.; Brianese, N.; Porchia, M.; Rossetto, G.; Zanella, P. *J. Organomet. Chem.* **1986**, *310*, C1.
(222) Ossola, F.; Brianese, N.; Porchia, M.; Rossetto, G.; Zanella, P. *J. Chem. Soc., Dalton Trans.* **1990**, 877.
(223) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.
(224) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.
(225) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.
(226) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.
(227) Gagné, M. R.; Nolan, S. P., Marks, T. J. *Organometallics* **1990**, *9*, 1716.
(228) Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 11.
(229) Qiand, C.; Deng, D.; Ye, C.; Xie, Z; Ge, Y.; Li, Y.; Gu, Y. *Inorg. Chim. Acta* **1987**, *140*, 21.
(230) Qian, C.; Ge, Y.; Deng, D.; Gu, Y.; Zhang, C. *J. Organomet. Chem.* **1988**, *344*, 175.
(231) Qian, C.; Zhu, D. *J. Chem. Soc., Dalton Trans.* **1994**, 1599.
(232) Deelman, B. J.; Booij, M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306.
(233) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.
(234) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291.
(235) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.
(236) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252.
(237) Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.
(238) Heeres, M. J.; Maters, M.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1992**, *11*, 350.
(239) Beletskaya, I. P.; Voskoboinikov, A. Z.; Magomedov, G. K. *Metalloorgan. Khim.* **1989**, *2*, 810 (cited in ref 8).
(240) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671.
(241) St. Clair, M. A.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1989**, *8*, 17.
(242) Qian, C.; Zhu, D. *Synlett* **1990**, 417.
(243) Piers, W. E.; Ferguson, G.; Gallagher, J. F. *Inorg. Chem.* **1994**, *33*, 3784.
(244) Deelman, B. J.; Teuben, J. H.; Macgregor, S. A.; Eisenstein, O. *New J. Chem.* **1995**, *19*, 691.
(245) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. *ACS Symp. Ser.* **1990**, *428*, 159.
(246) (a) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15. (b) Elkind, J. L.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 3151.
(247) Qian, C.; Zhu, D.; Gu, Y. *J. Organomet. Chem.* **1991**, *401*, 23.
(248) (a) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.
(249) Deelman, B. J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881.
(250) Radu, N. S.; Buchwald, S. L.; Scott, B.; Burns, C. J. *Organometallics* **1996**, *15*, 3913.
(251) Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508.
(252) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, 18, 51.
(253) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628.
(254) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.
(255) O'Hare, D.; Manriquez, J.; Miller, J. S. *J. Chem. Soc., Chem. Commun.* **1988**, 491.
(256) Qian, C.; Zhu, D.; Li, D. *J. Organomet. Chem.* **1992**, *430*, 175.

(257) Evans, W. J.; Bloom, I.; Engerer, S. C. *J. Catalysis* **1983**, *84*, 468.
(258) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.
(259) Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1996**, *524*, 275.
(260) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761.
(261) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.
(262) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266.
(263) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765.
(264) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980.
(265) Jia, L.; Yang, X.; Seyan, A. M.; Albert, I. D. L.; Fu, P. F.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 7900.
(266) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276.
(267) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115.
(268) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543.
(269) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043.
(270) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450.
(271) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123.
(272) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406.
(273) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.
(274) Sakakura, T.; Lautenschlager, H. J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40.
(275) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347.
(276) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108.
(277) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.
(278) Gagné, M. R.; Brard, L.; Conticello, V. P., Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003.
(279) Qian, C.; Zhu, D.; Gu, Y. *J. Mol. Catal.* **1990**, *63*, L1.
(280) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.
(281) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121.
(282) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.
(283) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723.
(284) Moloy, K. G.; Marks, T. J. *Inorg. Chim. Acta* **1985**, *110*, 127.
(285) Leverd, P. C.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1996**, *507*, 229.
(286) Berthet, J. C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *460*, 47.
(287) Jemine, X.; Goffart, J.; Berthet, J. C. Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2439.
(288) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.
(289) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728.
(290) (a) Bruno, J. W.; Duttera, M. R.; Fendrick, C. M.; Smith, G. M.; Marks, T. J. *Inorg. Chim. Acta* **1984**, *94*, 271. (b) Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907.
(291) Leverd, P. C.; Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 501.
(292) Arliguie, T.; Baudry, D.; Berthet, J. C.; Ephritikhine, M.; Le Maréchal, J. F. *New J. Chem.* **1991**, *15*, 569.
(293) Leverd, P. C.; Lance, M.; Vigner, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 237.
(294) Leverd, P. C.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2251.
(295) Bowman, R. G.; Nakamura, R.; Fagan, P. J.; Burwell, R. L.; Marks, T. J. *J. Chem. Soc., Chem. Commun.* **1981**, 257.
(296) Gillespie, R. D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1990**, *6*, 1465.
(297) He, M. Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641.
(298) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653.
(299) Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358.
(300) Lin, Z.; Le Maréchal, J. F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.
(301) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.
(302) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.
(303) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.
(304) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576.