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# Reactions of Ketones with Low-Valent Lanthanides: Isolation and Reactivity of Lanthanide Ketyl and Ketone Dianion Complexes

Zhaomin Hou\* and Yasuo Wakatsuki

The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako,  
Saitama 351-0198, Japan Yasuo Wakatsuki

\*E-mail: houz@postman.riken.go.jp

Recent progress in the chemistry of structurally well-defined lanthanide ketyl and ketone dianion complexes is reviewed, with particular emphasis on the ligand effects on the reactivity of these complexes. It has been demonstrated that the stability and reactivity of the ketyl radical and ketone dianion species strongly depend on the steric and electronic properties of the ancillary ligands, the structure of their parent ketones, as well as the nature of the metals to which they are bound. Fine-tuning these factors can control the reactivity of these species. Generation and reactions of dianionic thioketone and imine species are also briefly described.

**Keywords:** Ketyl radicals, Ketone dianions, Lanthanides, pinacol coupling, Ligand effects

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## 1

## Introduction

Reactions of ketones with low-valent lanthanides such as  $\text{SmI}_2$  and the  $\text{Ln}$  ( $\text{Ln} = \text{Sm}, \text{Yb}$ ) metals constitute one of the most useful reactions in lanthanide-mediated organic synthesis, and occupy an important position in modern organic chemistry [1, 2]. It is well known that one-electron reduction of ketones by low-valent lanthanides easily produces the corresponding radical anion species, or ketyls. In the case of diaryl ketones, further one-electron transfer is also achievable to afford the corresponding ketone dianions. These highly reactive species play a very important role, as key intermediates, in a variety of useful reactions involving ketones, such as reductions, ketyl-olefin couplings, pinacol couplings, intermolecular cross couplings, and the Barbier-type reactions. Although other reducing metals such as alkali, alkaline earth, and low-valent titanium metals can also produce similar ketyls or ketone dianions upon reaction with ketones [3], the lanthanide species usually behave differently from those metal analogs and in many cases show higher reactivity and chemo-, regio- and stereo-selectivity.

Despite the extensive applications and importance of the lanthanide ketyl and ketone dianion species in organic synthesis, very little was known about their structures. Our understanding about the reactivity of this important class of species had relied solely on the analysis of the organic products obtained by hydrolysis work-up of the final reaction mixtures. Attempts to isolate these species were greatly hampered by their extremely high reactivity and air and moisture sensitivity [4].

It was not until very recently that significant progress has been made in this field. By using sterically demanding ancillary ligands under an extremely dry and oxygen-free inert atmosphere, several different types of lanthanide ketyl and ketone dianion complexes have been successfully isolated and many of them structurally characterized. Detailed studies on the reactivity of these well-defined complexes have offered unprecedented insights into the mechanistic aspects of the reactions of ketones with low-valent lanthanides, and also shed new lights on similar reactions with other reducing agents. This article is intended to highlight the recent progress in this area, with particular emphasis on the structure-reactivity relation of lanthanide ketyl and ketone dianion complexes.

## 2

## One-Electron Reduction of Ketones

The most difficult problem in isolating a ketyl species generated in one-electron reduction of ketones is due to its rapid hydrogen abstraction and/or coupling reactions. To suppress these decomposition reactions, it is essential to use sterically demanding reducing agents and highly conjugated ketones [5]. It has been found that several types of lanthanide reducing agents are able to afford isolable and structurally characterizable ketyl complexes in the reactions with benzo-

phenone and fluorenone. The structures and reactivity (stability) of the lanthanide ketyl complexes are strongly dependent on the ancillary ligands, solvents, and the structure of their parent ketones.

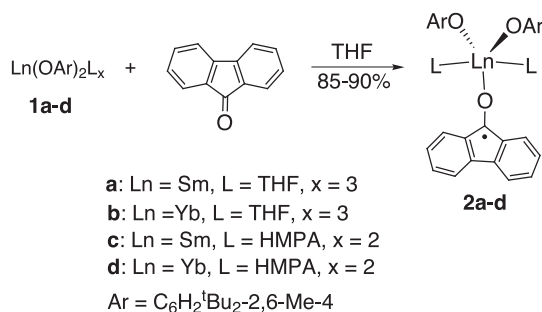
X-ray analyses have shown that the C-O bond distance of a ketyl unit is generally around 1.30 Å, which is longer than that of a free ketone (ca. 1.20 Å) and shorter than that of an alkoxide (ca. 1.40 Å). The radical carbon atom of a ketyl is still in a  $sp^2$ -hybrid state.

## 2.1

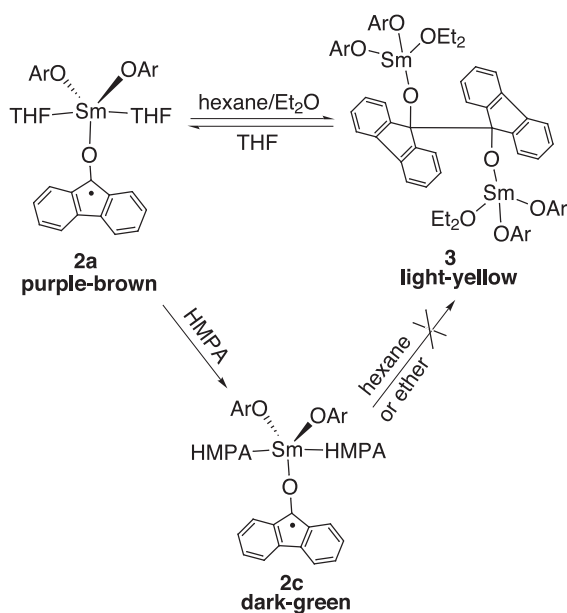
### Fluorenone Ketyl Complexes with an Aryloxy (ArO) Ligand

Reactions of the divalent lanthanide aryloxy complexes  $\text{Ln}(\text{OAr})_2(\text{L})_x$  (Ar =  $\text{C}_6\text{H}_2$ -*t*Bu<sub>2</sub>-2,6-Me-4; **1a**: Ln=Sm, L=THF, x=3; **1b**: Ln=Yb, L=THF, x=3; **1c**: Ln=Sm, L=HMPA, x=2; **1d**: Ln=Yb, L=HMPA, x=2) with 1 equivalent of fluorenone in THF at room temperature give the corresponding ketyl complexes **2a-d** as deeply-colored crystals in high yields (Scheme 1) [6, 7]. Complexes **2a-d** all have a similar structure in which one fluorenone ketyl and two ArO ligands are placed at the equatorial and two L (L=THF or HMPA) ligands are located at the apical positions of a distorted trigonal bipyramid.

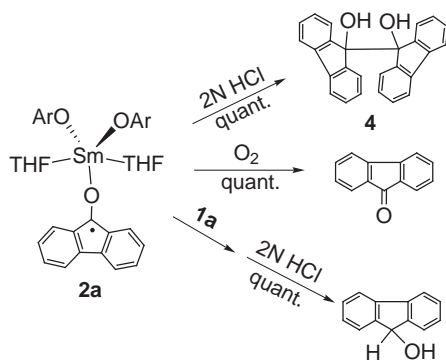
When the THF-coordinated complex **2a** is dissolved in hexane/ether, the two THF ligands are substituted by one molecule of  $\text{OEt}_2$ , and the ketyl radical dimerizes into a pinacolate (**3**) (Scheme 2) [6, 7]. More remarkably, the newly formed C-C bond in **3** (1.613(9) Å) can be easily broken to quantitatively regenerate the ketyl **2a** when **3** is dissolved in THF (Scheme 2), which unequivocally demonstrates that the pinacol coupling process of the ketyl radical is completely reversible. Addition of 2 equivalents of HMPA (per Sm) to a THF solution of **2a** or **3** gives almost quantitatively the corresponding HMPA-coordinated ketyl complex **2c** (Scheme 2). Since the coordination ability of HMPA is much stronger than that of THF [8], complex **2c** is much more stable than **2a**, and no change was observed when **2c** was treated similarly with hexane/ether. These results clearly demonstrate that the stability and reactivity of a ketyl species are strong-



Scheme 1



Scheme 2



Scheme 3

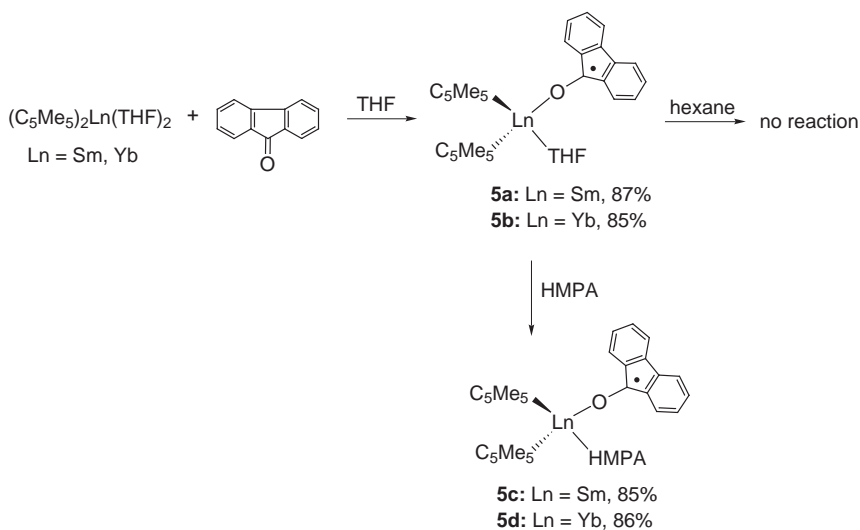
ly influenced by the ancillary ligands bound to the central metal, and HMPA is a better ligand than THF for the stabilization of a ketyl species [5, 7, 9].

Reflecting the typical reactivity of a ketyl species, hydrolysis of **2a** gives the corresponding pinacol-coupling product **4**, while air oxidation of **2a** yields fluorenone almost quantitatively (Scheme 3). Reaction of **2a** with one equivalent of **1a** produced a THF-insoluble purple precipitate which upon hydrolysis afforded fluorenol quantitatively, suggesting that a fluorenone dianion intermediate was formed [7, 9].

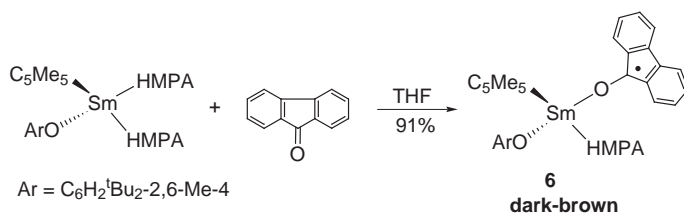
## 2.2

Fluorenone Ketyl Complexes with a  $C_5Me_5$  Ligand

The similar reactions of  $(C_5Me_5)_2Ln(THF)_2$  ( $Ln=Sm, Yb$ ) with 1 equivalent of fluorenone in THF give the corresponding ketyl complexes **5a,b** in 85–87% isolated yields (Scheme 4) [7]. Reactions of **5a,b** with 1 equivalent of HMPA afford the HMPA-coordinated ketyl complexes **5c,d**. In contrast with the ArO-ligated ketyl complexes **2a–d** which require two THF or HMPA ligands as an additional stabilizing moiety, the  $C_5Me_5$ -ligated complexes **5a–d** need only one THF or HMPA ligand for the stabilization of the ketyl species. This difference apparently results from the larger size of  $C_5Me_5$  as compared to that of the ArO ligand. Addition of hexane/ether to the THF-coordinated ketyl complexes **5a,b** did not cause any further reaction (Scheme 4), showing that the  $C_5Me_5$ -supported **5a,b** are more stable and less reactive than the ArO-supported **2a,b** (see also Sect. 2.1).



Scheme 4



Scheme 5

Reaction of  $(C_5Me_5)Sm(OAr)(HMPA)_2$  with 1 equivalent of fluorenone in THF also gives the corresponding ketyl complex **6** (Scheme 5) [7], demonstrating that the heteroleptic  $C_5Me_5/OAr$  ligand set [10] is also able to stabilize a ketyl species. It is also noteworthy that although the homoleptic analogs **2c** and **5c** are isolable, ligand redistribution of **6** to give either of these complexes was not observed. Complex **6** represents a rare example of a lanthanide complex which bears all different ligands.

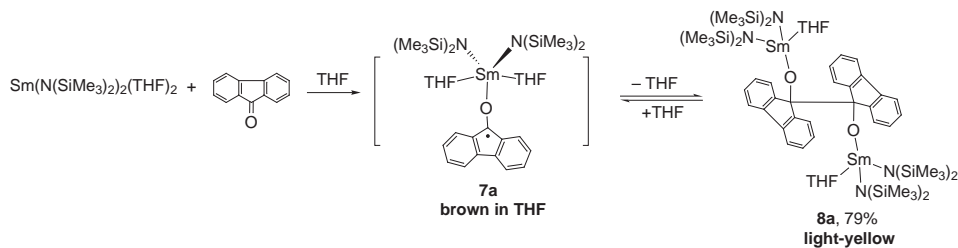
### 2.3

#### Fluorenone Ketyl Complexes with an $N(SiMe_3)_2$ Ligand

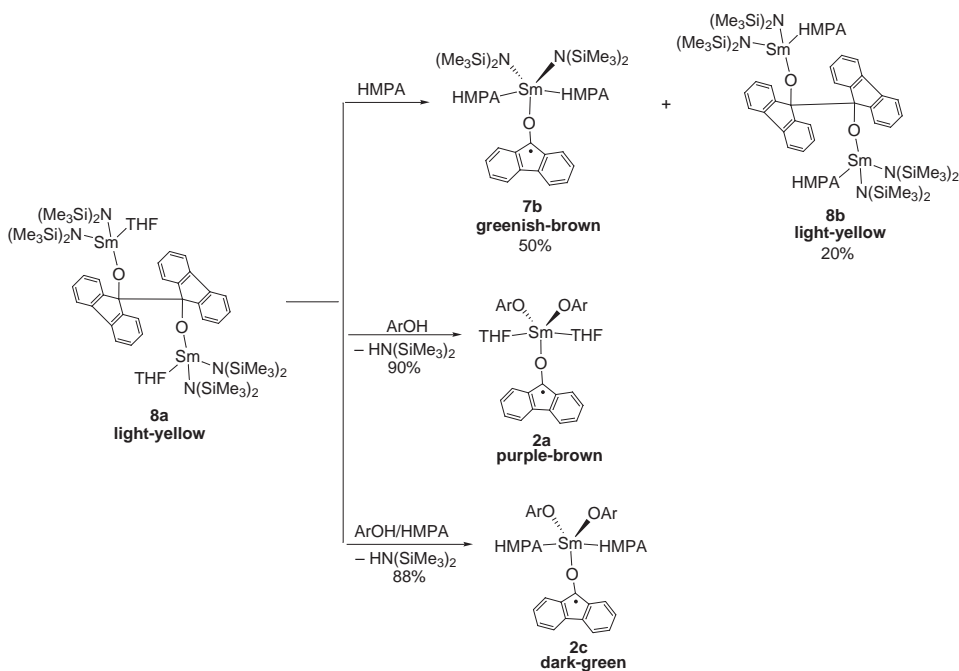
The ketyl species stabilized by  $N(SiMe_3)_2$  behaves a little differently from those by  $C_5Me_5$  and the  $ArO$  ligand. Reaction of  $Sm(N(SiMe_3)_2)_2(THF)_2$  with 1 equivalent of fluorenone in THF gave a brown solution whose UV-Vis spectrum was almost identical to that of the  $ArO$ -ligated ketyl complex **2a**, suggesting that the corresponding ketyl species **7a** was formed [7]. However, attempts to isolate the ketyl species **7a** from THF were unsuccessful and always resulted in the formation of the light yellow pinacolate **8a** (Scheme 6).

The central C-C bond in **8a** could also be cleaved by addition of a strongly coordinative solvent. Dissolving the light yellow **8a** in THF gave immediately a brown solution whose UV-Vis spectrum was the same as that of the solution originally obtained by the reaction of  $Sm(N(SiMe_3)_2)_2(THF)_2$  with fluorenone in THF (Scheme 6). Addition of 4 equivalents of HMPA to this THF solution afforded the bis(HMPA)-coordinated ketyl complex **7b** together with the mono(HMPA)-coordinated pinacolate complex **8b** (Scheme 7) [7].

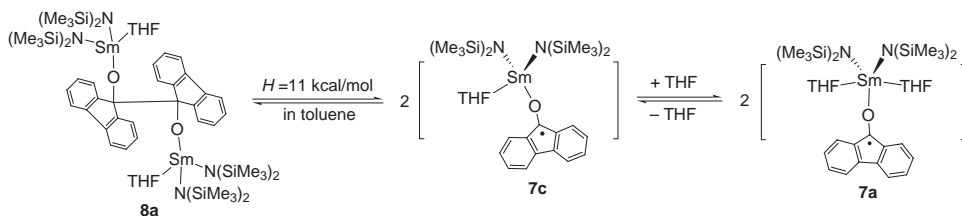
The isolation of the pinacolate **8a** rather than the ketyl **7a** from THF (Scheme 6) and the isolation of the mono(HMPA)-coordinated pinacolate **8b** together with the bis(HMPA)-coordinated ketyl **7b** in the reaction of **8a** or **7a** with HMPA (Scheme 7) contrast sharply with the similar reactions of the  $ArO$ -ligated complex **2a** or **3**, in which only the bis(THF or HMPA)-coordinated ketyl complexes were isolated (see also Sect. 2.1). These differences probably result from the difference in electron-donating ability between  $N(SiMe_3)_2$  and the  $ArO$  ligand. Since  $N(SiMe_3)_2$  is more electron-donating than the  $ArO$  ligand, dissociation of a neutral L (L=THF or HMPA) ligand from the central Sm atom in the



Scheme 6



Scheme 7



Scheme 8

(Me<sub>3</sub>Si)<sub>2</sub>N-ligated complexes **7a,b** would be easier than that in the ArO-ligated complexes **2a,c**, which thus causes pinacol-coupling of the ketyl radical in **7a,b** to occur more easily. In accord with this consideration, when 4 equivalents of ArOH were added to a THF solution of **8a**, the corresponding ArO-ligated ketyl complex **2a** was isolated in 90% yield with the release of HN(SiMe<sub>3</sub>)<sub>2</sub> (Scheme 7). The similar reaction of **8a** with ArOH in THF/HMPA yielded selectively the corresponding bis(HMPA)-coordinated ketyl complex **2c** (Scheme 7) [7].

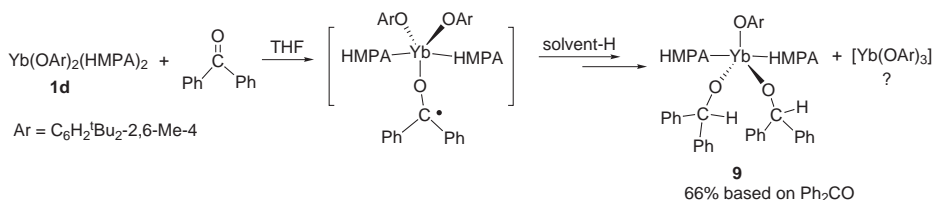
To gain more information concerning the C-C bond cleavage of the pinacolate **8a**, a variable-temperature UV-Vis spectroscopic study in toluene was carried out. The derived dissociation enthalpy  $\Delta H_{\text{diss}}$  for **8a** to give **7c** is 11 kcal/mol (Scheme 8) [7]. This value is much smaller than that reported for silicon benzo-

pinacolate,  $\text{Me}_3\text{SiOC}(\text{Ph})_2\text{C}(\text{Ph})_2\text{OSiMe}_3$  (31 kcal/mol) [11], but comparable with that reported for the  $\text{C}_\alpha\text{-C}_{\text{para}}$  bonds in the trityl dimer  $[\text{Ph}_3\text{C}]_2$  (11–12 kcal/mol) [12] and that for the dimeric titanium(IV) alkoxide/enolate complex  $[(^t\text{Bu}_3\text{SiO})_3\text{Ti}(\text{OCPh}_2)]_2$  (18 kcal/mol) [13]. Obviously the dissociation enthalpy for **8a** to give the bis(THF)-coordinated ketyl complex **7a** should be much smaller than this value, since this process is accompanied by the formation of two new Sm(III)-THF bonds (Scheme 8). Since the bond energy of a Sm(II)-THF bond in  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_n$  ( $n=1$  or  $2$ ) is about 5–7 kcal/mol [14], and a Sm(III)-THF bond is generally stronger than a Sm(II)-THF bond, the formation of two Sm(III)-THF bonds in the course of the transformation of **8a** to **7a** would release more than 10 kcal/mol, which could well compensate the enthalpy (11 kcal/mol) for the cleavage of the central C-C bond in **8a**. It is thus not difficult to understand that when a large excess of THF is present (e.g., in THF solution), the equilibria in Scheme 8 will be greatly shifted to the right, and complete dissociation of **8a** to **7a** will be easily achieved.

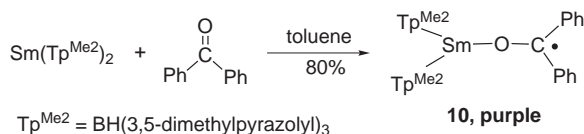
## 2.4

### Benzophenone Ketyl Complexes

Compared to the planar fluorenone ketyl, benzophenone ketyl is less conjugated and thus more reactive [15]. Reactions of benzophenone with the lanthanide reducing agents which were successfully used for the isolation of fluorenone ketyl complexes did not give a structurally characterizable benzophenone ketyl species, and in many cases yielded the corresponding hydrogen abstraction products. For example, reaction of **1d** with 1 equivalent of benzophenone in THF gave after a few weeks the colorless ytterbium(III) aryloxide/diphenylmethoxide complex  $\text{Yb}(\text{OCHPh}_2)_2(\text{OAr})(\text{HMPA})_2$  (**9**) via hydrogen radical abstraction from solvent by the initially generated ketyl radical species (Scheme 9) [7].



Scheme 9



Scheme 10



Recently, Takats and coworkers have successfully isolated a structurally characterizable lanthanide benzophenone ketyl complex (**10**) by using a further sterically demanding reducing agent,  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$  ( $\text{Tp}^{\text{Me}_2}=\text{BH}(3,5\text{-dimethylpyrazolyl})_3$ ) (Scheme 10) [16a]. Izod and coworkers have isolated and structurally characterized the corresponding benzophenone ketyl complex by using  $\text{Sm}(\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{OMe}))_2(\text{THF})$  as a reducing agent [16b]. These results again demonstrate that the behavior of a ketyl species is greatly influenced by the ancillary ligands.

## 2.5

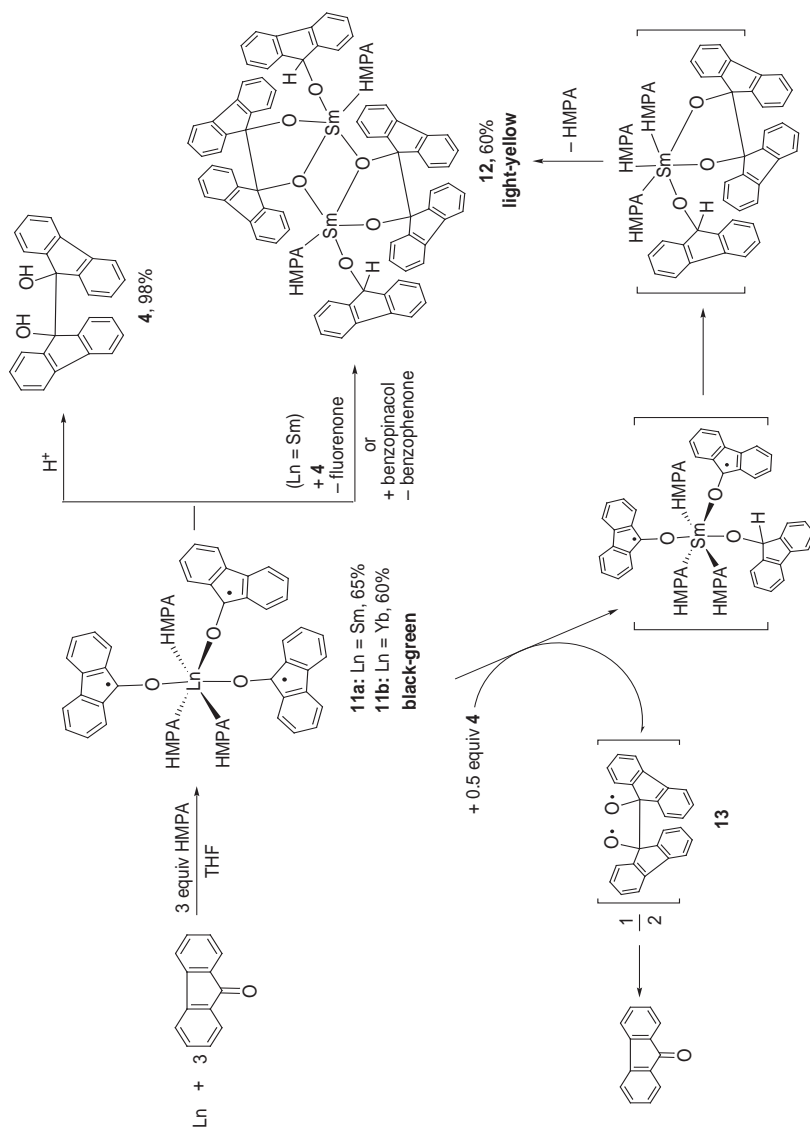
### Complexes Bearing Three Independent Ketyl Ligands

In contrast with the divalent lanthanide complexes, which are one-electron transfer agents and afford complexes consisting of one ketyl per metal ion upon reaction with ketones, the zero valent lanthanide metals are three-electron transfer agents, and their reactions with ketones, if straightforward, should yield complexes bearing three independent ketyl ligands. However, compared to mono(ketyl) complexes, the isolation of a multi(ketyl) metal species is generally more difficult and challenging, since intramolecular pinacol-coupling of ketyl radicals is also possible besides the common intermolecular reactions.

It has been found that the use of HMPA as a coordinating ligand can sufficiently suppress coupling reactions of the ketyl radicals in multi(ketyl) metal complexes to allow their isolation [5, 7, 15, 17]. Thus, reaction of Sm metal powder with 3 equivalents of fluorenone and 3 equivalents of HMPA in THF afforded the corresponding Sm(III) tris(fluorenone ketyl) complex **11a** as black-green blocks (Scheme 11) [7, 17]. An X-ray analysis has shown that this complex possesses an octahedral structure, in which the central Sm atom is coordinated in *mer*-type fashion by three ketyls and three HMPA ligands. The similar reaction of Yb metal with 3 equivalents of fluorenone gives the Yb(III) tris(ketyl) complex **11b** (Scheme 11), which is isostructural and isomorphous with **11a** [7].

Hydrolysis of **11a,b** gives almost quantitatively the corresponding pinacol **4** (Scheme 11). Interestingly, the reaction of **11a** with 0.5 equivalents of **4** yields the dimeric samarium(III) fluorenoxide/pinacolate complex **12** and fluorenone (Scheme 11) [7]. Further studies have confirmed that the formation of **12** is via hydrogen atom abstraction from the pinacol by one ketyl, followed by pinacol-coupling of the other two ketyls together with simultaneous release of two HMPA ligands in **11a** (Scheme 11). Homolytic C-C bond cleavage of the biradical species **13**, which is formed by dehydrogenation ( $-\text{H}^\cdot$ ) of pinacol **4**, affords fluorenone. It is noteworthy that the small steric change, which is caused by the transformation of one of the three fluorenone ketyls to a fluorenoxy unit, has imposed crucial influence on the stability and reactivity of the other two ketyls.

In contrast with the case of fluorenone, similar reactions of Ln/HMPA (Ln=Sm, Yb) with benzophenone did not give an isolable ketyl species and yielded finally decomposition products, demonstrating again that benzophenone ketyl is more reactive than fluorenone ketyl [7]. These reactions are also in sharp con-



Scheme 11

trast with those of Na/HMPA [5] or Ca/HMPA [5, 15] with benzophenone, in which the corresponding benzophenone ketyl species have been successfully isolated and structurally characterized. These results show that the nature of the reducing metals also strongly influences on the reactivity and stability of a ketyl species and the lanthanide ketyl species are more reactive than those of alkali and alkaline earth metals.

## 2.6

### Structure-Reactivity Relation of Lanthanide Ketyl Complexes

The results described above have demonstrated that the stability and reactivity of a ketyl species are extremely susceptible to the environment around the central metal ion. Both anionic and neutral (solvent) ligands play an important role in determining the behavior of a ketyl species. The sterically demanding bis(pentamethylcyclopentadienyl) ligand set  $(C_5Me_5)_2$  together with a neutral L (L=THF or HMPA) ligand offers a good stabilizing environment for a lanthanide fluorenone ketyl species, while the less bulky  $(ArO)_2$  or  $((Me_3Si)_2N)_2$  ligand set requires two L (L=THF or HMPA) ligands for the stabilization of the same ketyl species. In the latter case, dissociation of one of the two L ligands from the central metal ion easily occurs to cause pinacol-coupling of the ketyl, and this takes place more easily for the  $(Me_3Si)_2N$ -ligated complexes than for the  $ArO$ -ligated ones, due to the stronger electron-donating ability of  $N(SiMe_3)_2$ . Re-coordination of an L ligand to the metal atom of the resulting pinacolate easily cleaves the central C-C bond and regenerates the ketyl, which thus makes the pinacol-coupling process reversible. The relatively small dissociation enthalpy for the pinacolate complexes (e.g.,  $\Delta H_{diss}=11$  kcal/mol for **8a**) could well account for this reversibility. HMPA, as a neutral and strongly coordinating ligand, offers an excellent stabilizing moiety for both mono- and multi-ketyl complexes. The transformation of the tris(ketyl) complex **11a** to the fluorenoxide/pinacolate complex **12** provides unprecedented insights into the elementary steps of the hydrogenation and pinacol-coupling reactions of a ketyl species. Ketone-dependence of the stability of ketyls is also observed. In contrast to fluorenone ketyl complexes, the isolation of a structurally characterizable benzophenone ketyl complex is more difficult due to its less conjugated structure which makes it more reactive and less stable. However, by choosing an appropriate ligand set such as bis(hydrotris(3,5-dimethylpyrazolyl)borate), a structurally characterizable lanthanide benzophenone ketyl species can indeed be isolated. It is obvious from these results that the stability and reactivity of a ketyl radical species can be controlled through tuning the ancillary ligands bound to the central metal ion.

## 3

### Two-Electron Reduction of Ketones

Among all low-valent lanthanides, the zero valent Sm and Yb metals are the most often used reducing agents for the study of two-electron reduction of ketones.

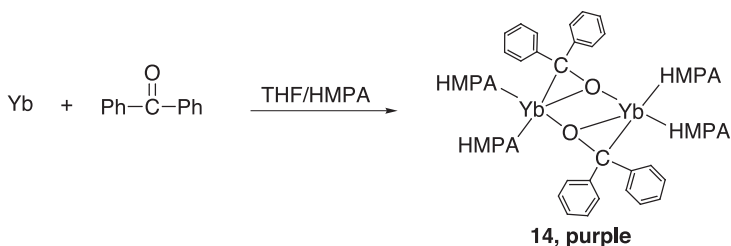
Although earlier studies showed that the formation of a samarium ketone dianion species was not as efficient as that of ytterbium [18–20], it was later found that samarium ketone dianion species could be generated similarly if the metal surface was sufficiently activated, e.g., by  $\text{ICH}_2\text{CH}_2\text{I}$  [21, 22]. Since the negatively charged carbon and oxygen atoms in a ketone dianion species are adjacent, the use of a sterically demanding lanthanide(II) reducing agent does not necessarily give a good result for the isolation of such species because of the steric repulsion between the resultant two closely located bulky metal moieties. Therefore, the control of the reactivity or stability of a ketone dianion species through tuning the ancillary ligands may not be as effective as in the case of ketyls. Moreover, compared to the mono-anionic ketyls, ketone dianions are more difficult to generate. They are more sensitive to air and moisture, and thus more difficult to handle. Probably due to these reasons, structurally characterized examples of ketone dianion species remain very scarce [23–25], and only one lanthanide ketone dianion complex,  $[\text{Yb}(\mu\text{-}\eta^1, \eta^2\text{-OCPh}_2)(\text{HMPA})_2]_2$ , has been isolated and structurally characterized to date (see below) [24]. The known ketone dianions are limited solely to those bearing two aromatic groups on the carbonyl carbon atom.

Despite these limitations, it has been found that the lanthanide ketone dianions are an interesting class of species which show unique reactivities. As described below, in lanthanide ketone dianion species the carbonyl carbon atom is completely changed from electrophilic to nucleophilic, and shows strong nucleophilicity towards a variety of organic substrates. Due to the delocalization of the negative charges in the aromatic groups, some reactions can also take place at the aromatic ring.

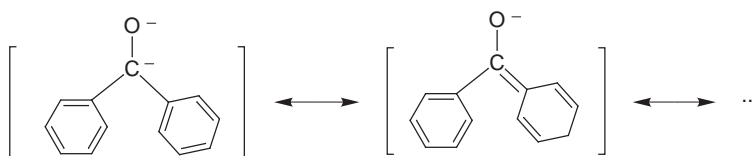
### 3.1

#### Isolation of an Ytterbium(II) Benzophenone Dianion Complex

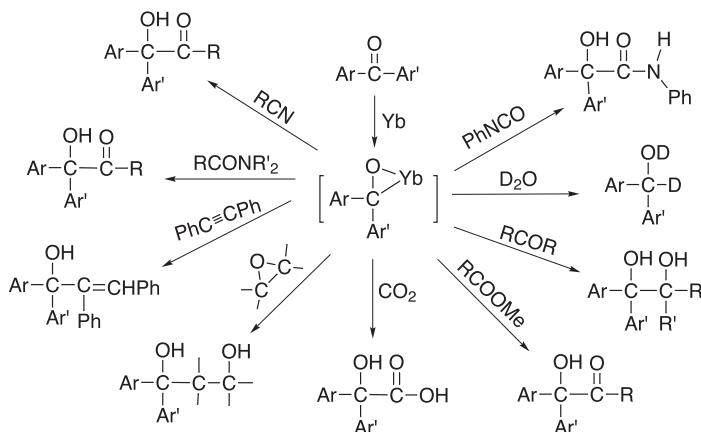
Reaction of Yb metal powder with 1 equivalent of benzophenone in THF/HMPA gives the Yb(II) benzophenone dianion complex  $[\text{Yb}(\mu\text{-}\eta^1, \eta^2\text{-OCPh}_2)(\text{HMPA})_2]_2$  (**14**) as purple crystals (Scheme 12) [21, 24]. X-ray analysis has revealed that complex **14** possesses a dimeric structure, in which the two Yb atoms are bridged by two benzophenone dianions. The bridge is built in such a manner



Scheme 12



Scheme 13



Scheme 14

that a benzophenone dianion uses its O atom to make a Yb-O bond with one Yb(II) ion and its C atom to make a Yb-C bond with the other Yb(II) ion to which the lone electron pair of the oxygen atom is also donated (Scheme 12). The C-O bond of the benzophenone dianion (1.39(6) Å) is longer than that of benzophenone ketyl (1.31(2) Å) [15, 16] and that of free benzophenone (1.23(1) Å) [26]. Similar to benzophenone ketyl, the carbonyl carbon atom in benzophenone dianion is still in an  $sp^2$ -hybrid state, which can thus allow good conjugation of the negative charges with the phenyl rings.

Consistent with the above structural observations, the  $^1\text{H}$  NMR signals for the phenyl groups in **14** in  $\text{THF-d}_8$  are greatly upfield shifted to as high as  $\delta$  5.63–7.04, demonstrating that the negative charges of the ketone dianion are indeed highly delocalized into the phenyl rings, especially to the para-positions ( $\delta$  5.63) (Scheme 13) [21,22]. As described in Sect. 3.3, this delocalization of electrons can have great influence on the reactivity of benzophenone dianion species.

### 3.2

#### Reactions of Ketone Dianions with Organic Electrophiles

It has been found that lanthanide ketone dianion species are excellent nucleophiles, which react smoothly with a variety of organic substrates such as ke-

tones, nitriles, epoxides, CO<sub>2</sub>, etc. to give after hydrolysis the corresponding unsymmetrical pinacols,  $\alpha$ -hydroxy ketones, 1,3-diols,  $\alpha$ -hydroxy carboxylic acids, etc., in good yields, respectively (Scheme 14) [18–20]. Compared to alkali metal ketone dianions, they are less basic and more nucleophilic, and selectively undergo addition reactions even with substrates bearing active  $\alpha$ -protons, such as aliphatic ketones and nitriles.

### 3.3

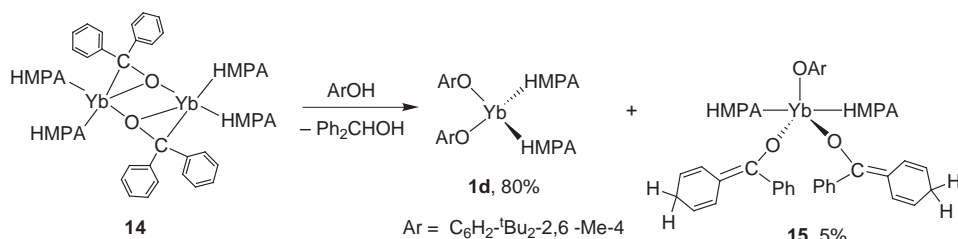
#### Reactions of Ketone Dianions with 2,6-Di-*tert*-Butylphenols

Most of the reactions of ketone dianion species, including those of main group and titanium metals, are known to occur at the carbonyl unit, as demonstrated in Sect. 3.2. However, it was found that the protonation reactions of lanthanide benzophenone dianion species with 2,6-di-*tert*-butylphenols can take place not only at the carbonyl group but also at the phenyl ring, due to the delocalization of the negative charges onto the aromatic groups. The selectivity between reactions at the carbonyl group and those at the aromatic ring in lanthanide diaryl ketone dianion species depends greatly on the nature of both metals and ketones.

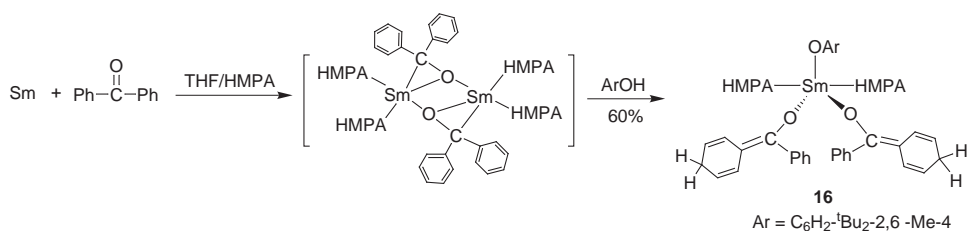
#### 3.3.1

##### *Benzophenone Dianion Species*

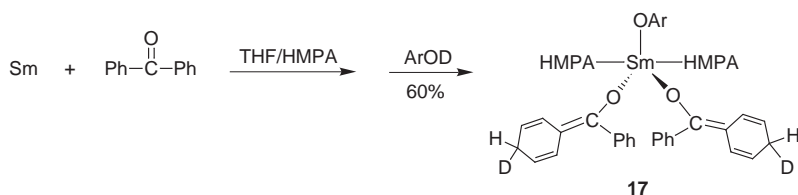
Reaction of the Yb(II)-benzophenone dianion complex **14** with ArOH (Ar = C<sub>6</sub>H<sub>2</sub>-*t*Bu<sub>2</sub>-2,6-R-4, R=H, Me) gave the corresponding ytterbium(II) bis(aryloxide) complex Yb(OAr)<sub>2</sub>(HMPA)<sub>2</sub> (**1d**) as a major product, which was formed by the protonation of both the carbon and oxygen atoms of the carbonyl unit with ArOH (Scheme 15) [22, 24]. Besides **1d**, an ytterbium(III) enolate complex (**15**) was also obtained as a minor product. In contrast, when the analogous Sm(II) benzophenone dianion species was allowed to react with ArOH, the samarium(III) enolate complex **16**, which is analogous to **15**, was formed as a major product, while the samarium(II) bis(aryloxide) complex Sm(OAr)<sub>2</sub>(HMPA)<sub>2</sub>, an analog of **1d**, was not observed (Scheme 16) [22, 27]. The similar reaction of the Sm(II) benzophenone dianion species with ArOD yielded the corresponding



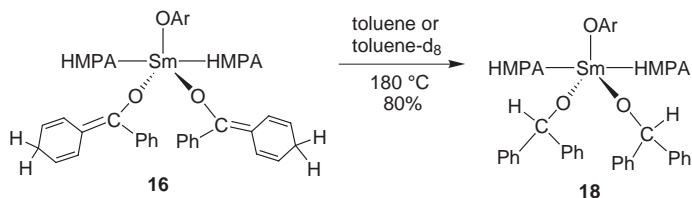
Scheme 15



Scheme 16



Scheme 17

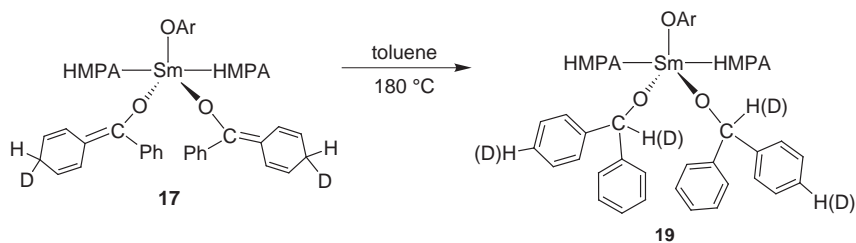


Scheme 18

deuterated enolate **17** (Scheme 17), suggesting that the formation of **15** and **16** is via the direct protonation of the para carbon atom of a phenyl group in the benzophenone dianion unit.

The formation of the enolate complexes **15** and **16** is apparently due to the delocalization of the negative charges in the phenyl groups of the benzophenone dianion species (see Scheme 13). The difference in reactivities observed between Sm(II) and Yb(II) benzophenone dianion species may result from differences in the two divalent metal ions. Since Sm(II) is more electron-donating [28] and bigger in size than Yb(II) [29], the negative charges in the Sm(II) benzophenone dianion species must be more delocalized into its phenyl rings, which are thus more easily protonated on the phenyl part and give a Sm(III) enolate species.

It is also interesting to note that the formation of the enolates **15** and **16** in the above reactions resembles well the Birch reduction of aromatic compounds bearing electron-withdrawing groups [30], in which metal enolate intermediates are believed to be formed via monoprotection of dianionic species. However, such species have never been well characterized. Complexes **15** and **16** are



Scheme 19

rare examples of structurally characterized metal enolate compounds which model the enolate intermediates formed in the Birch reductions.

When the enolate complex **16** was heated in toluene or toluene- $d_8$  at 180 °C overnight, intramolecular hydrogen transfer reaction occurred to give the corresponding aryloxide/diphenylmethoxide complex  $\text{Sm}(\text{OC}(\text{H})\text{Ph}_2)_2(\text{OAr})(\text{HMPA})_2$  (**18**) (Scheme 18) [22, 24]. The similar reaction of the deuterated enolate **17** yielded **19** selectively (Scheme 19); scrambling of deuterium at the phenyl ring was not observed. These results suggest that the formation of **18** from **16** is a one-step 1,5-hydrogen shift process. It is also noteworthy that even at high temperatures (up to 180 °C) ligand redistribution in these heteroleptic lanthanide complexes was not observed.

### 3.3.2

#### *Fluorenone Dianion Species*

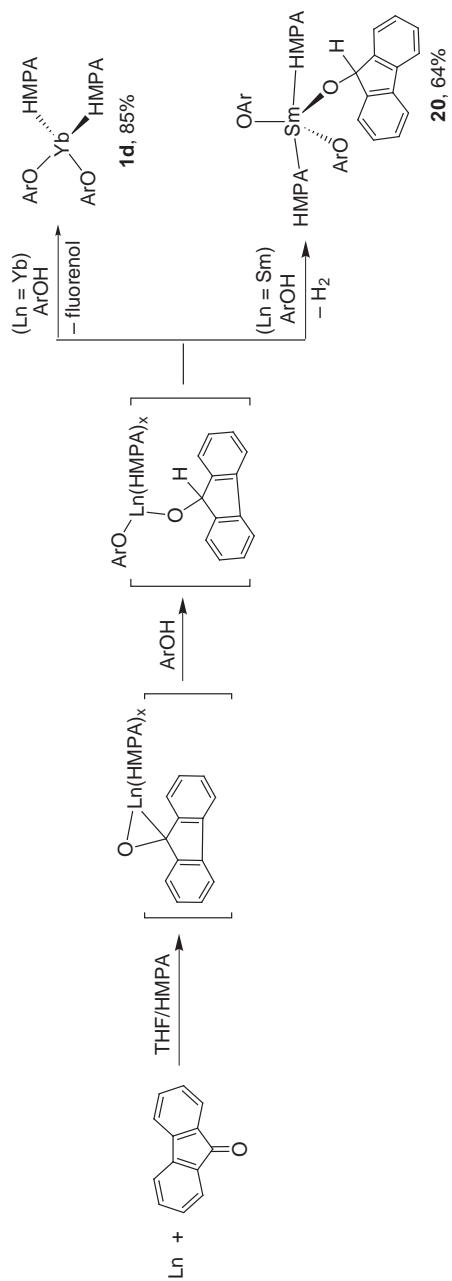
The protonation reaction of the Yb(II) fluorenone dianion species with ArOH is similar to the major reaction of the Yb(II) benzophenone dianion **14** with ArOH, occurring at both the C and O atoms of the carbonyl unit to afford **1d** and fluorenone (Scheme 20). However, the protonation reaction of the Sm(II) fluorenone dianion species with ArOH takes place only at the C atom and is accompanied by the oxidation of the Sm(II) ion to give the corresponding samarium(III) aryloxide/fluorenoxide complex **20** (Scheme 20), which again demonstrates the metal dependence of the reactivity of lanthanide ketone dianion species [22].

## 4

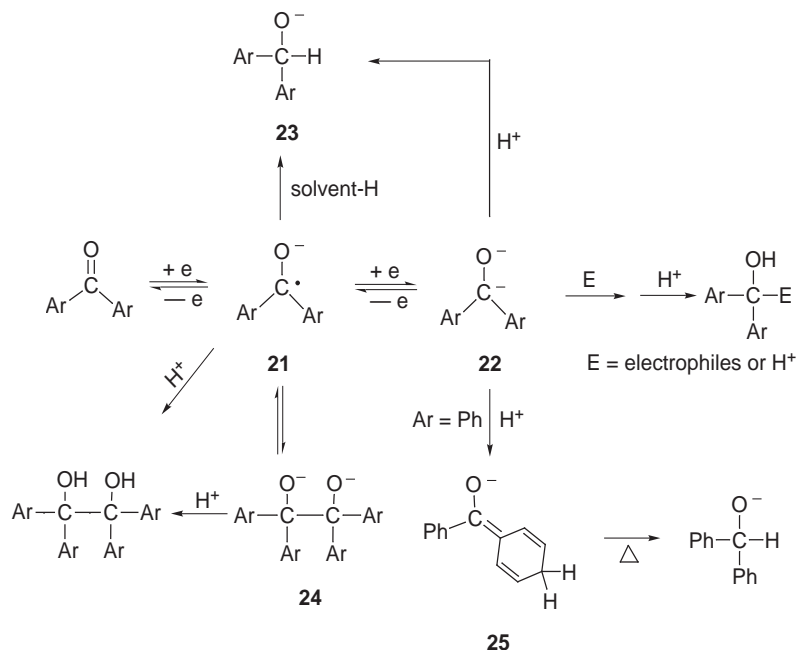
### **Ketone-Reduction Paths Based on Isolated Intermediates**

As described above, with the combination of appropriate lanthanide reducing agents, solvents, and substrates, almost all types of the key intermediates involved in the reduction of ketones have been isolated and structurally characterized (Scheme 21), such as the one-electron reduction product (ketyl radical **21**), its reversible coupling product (pinacolate **24**), hydrogen abstraction product (alkoxide **23**) and further one-electron reduction product (ketone dianion **22**), and the selective protonation products of the ketone anion (alkoxide **23** and eno-





Scheme 20



Scheme 21. Structurally characterized intermediates and their reactions

late 25). Structural and reactivity studies of these isolated intermediates have given rise to an ever clearer picture of the reaction paths in the reaction of ketones with low-valent lanthanides (Scheme 21), and thus offered unprecedented insights into the mechanistic aspects of these and related reactions.

## 5

### Dianionic Thioketone and Imine Species

Similar to diaryl ketones, aromatic thioketones and imines can also be reduced to the corresponding dianionic species. Fujiwara and coworkers have reported that the ytterbium diaryl thioketone dianion species, generated by reaction of Yb metal with the thioketones in THF/HMPA at low temperature, show good nucleophilicity towards organic substrates such as acetone and alkyl halides (Scheme 22) [31]. The thioketone dianion species seemed to be less stable than those of ketones. At room or higher temperatures, C-S bond cleavage reaction took place.

Reaction of *N*-(diphenylmethylidene)aniline with 1 equivalent of Yb metal in THF/HMPA gives the corresponding dianionic complex Yb( $\eta^2$ -Ph<sub>2</sub>CNPh)(HMPA)<sub>3</sub> (26) whose structure has been crystallographically determined (Scheme 23) [32]. The imine dianion complex 26 is more basic and less nucleophilic than ketone- and thioketone-dianion species. It reacts with CO<sub>2</sub> to give after hydrolysis the corresponding Yb(III) amino acid derivative [33], but with acetone to release



tially improved and our capability to access a variety of new target compounds will be dramatically enhanced. These topics remain to be challenged.

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## 7

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