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Digest paper

Recent progress in the chemistry of lanthanide-ligand multiple bonds

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ABSTRACT

Metal-ligand multiple bonds have received significant attention in the past few decades. A series of novel species with lanthanide-ligand multiple bonds have recently been isolated. This short review summarizes the synthesis and reactivity of these novel complexes.

Contents

Introduction

Chemical bonding is the cornerstone of chemistry. In the past few decades, transition metal complexes containing metal-ligand multiple bonds have received increasing attention due to their extensive applications in synthetic chemistry and small-molecule activation.[1–3] Significant progress has been made in the chemistry of transition metal-ligand multiple bonds, especially for transition metal carbene complexes, which have revolutionized organic synthesis, culminating in the 2005 Nobel Prize in chemistry.[4]

In addition, a large number of metal-ligand multiple bonds involving the actinide elements,[5] as well as scandium and yttrium,[6] have been investigated. However, in comparison, examples of well-defined lanthanide-ligand multiple bonds lag far behind.

In principle, the 4f electrons in lanthanoid metals lie deep inside the electron shell, and as a result rarely participate in multiple bonding. Moreover, the bonding of lanthanides is principally ionic and highly polarized in nature. Therefore, the synthesis and stabilization of molecules containing lanthanide–ligand multiple bonds is a challenge.

In the past few years, organometallic chemists have made great developments in lanthanide chemistry,[7] especially in the chemistry of lanthanide-ligand multiple bonds. Some elegant examples of lanthanide-ligand multiple bonds in carbene ($M{=}C$), imido ($M{=}N$), and oxo ($M{=}O$) complexes have been reported. In this review, we will focus on the synthesis and reactivity of these novel complexes. However, NHC-type lanthanide carbene adducts are not included in this short review.[8]

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Lanthanide-carbon multiple bonds

Transition metal carbene complexes, which contain a metal-carbon double bond, are well-known as key intermediates in alkene metathesis. Back-donation from the metal to the carbon is important in the formation of metal-carbon double bonds. The back-donation effect is more common in the d-block transition metals compared with the f-block lanthanide metals. Therefore, metal-carbene complexes with d-block transition metals have been widely investigated. In contrast, for lanthanide metals, there are very limited examples of carbene complexes.

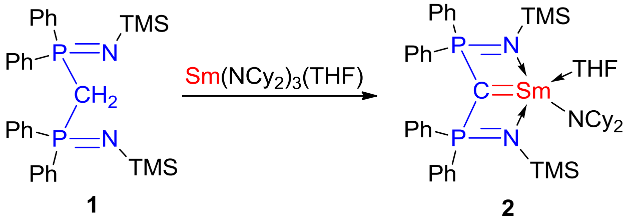
In 2000, Cavell and co-workers reported the synthesis of a samarium carbene complex by the double deprotonation of the bis(iminophosphorano)methane ligand.[9] As shown in Scheme 1, after treatment of the NCN-pincer type ligand **1** with samarium tris(dicyclohexylamide), the Sm-carbene complex **2** was isolated as a yellow solid. This was the first example of a lanthanide metal–carbon double bond with a dianionic carbene ligand. The bis(iminophosphorano)methane ligand is an useful precursor for the synthesis of lanthanide-carbene complexes, probably due to the bulky TMS group on the nitrogen atom and electron-rich nature of this ligand.

X-ray study showed that the Sm–carbon bond distance was shorter than the analogous distances in other neutral carbene ligand complexes of samarium. Based on this fact, as well as the P–N bond distances in the fused four-membered rings, the authors suggested that complex **2** has a delocalized structure.

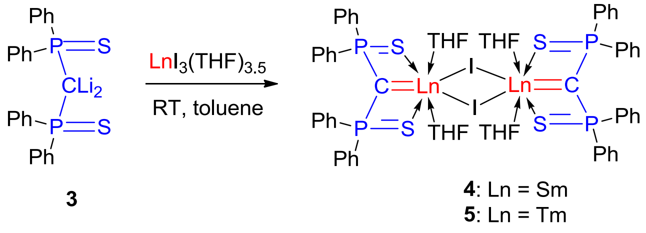
Floch, Nief, Mézailles, and co-workers used the SCS-pincer type dianionic ligand **3** to synthesize samarium and thulium carbene complexes.[10] By the reaction of $SmI_3(THF)_{3.5}$ or $TmI_3(THF)_{3.5}$ with one equivalent of dianionic ligand **3**, the lanthanide-carbene complexes **4** and **5** were generated, respectively (Scheme 2). Complex **5** represents the first late-lanthanide alkylidene complex.

The Ln=C double bond in these species showed nucleophilic character similar to the Schrock-type transition metal carbene complexes. After treatment of complex **4** or **5** with benzophenone, the Wittig-like reaction product **8** was formed (Scheme 3). This result shows that the electronic characters of early- and late-lanthanide carbenes are similar.

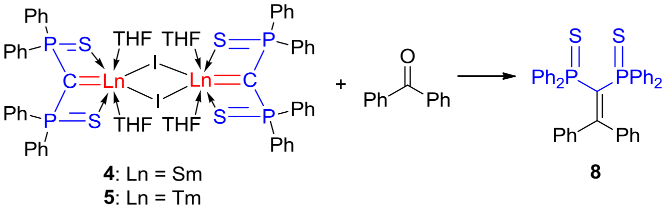
Interestingly, treatment of $SmI_3(THF)_{3.5}$ or $TmI_3(THF)_{3.5}$ with two equivalents of dianionic ligand **3** led to the formation of the first homoleptic samarium and thulium carbene complexes **6** and **7**, which contain two Ln=C bonds (Scheme 4).



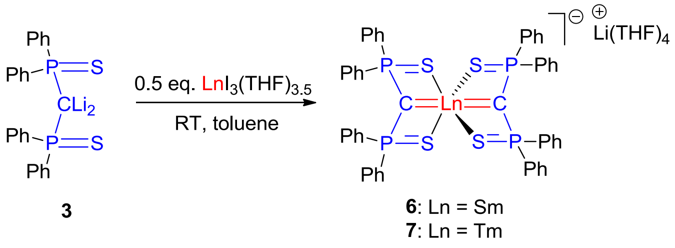
Scheme 1.



Scheme 2.



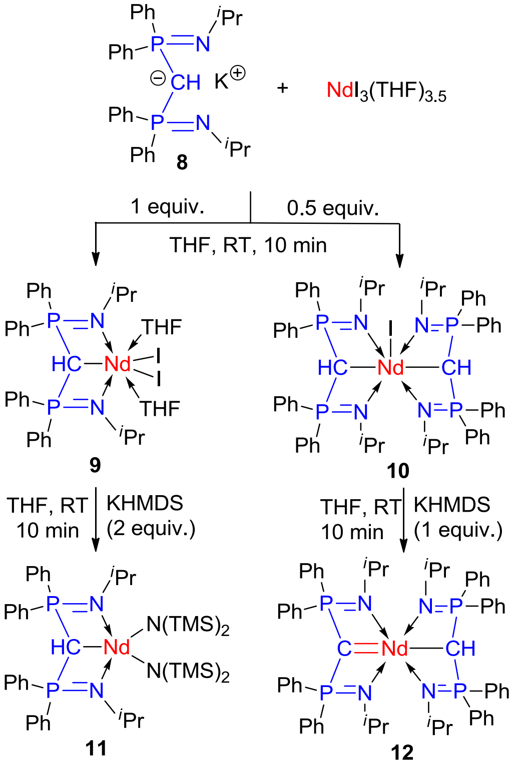
Scheme 3.



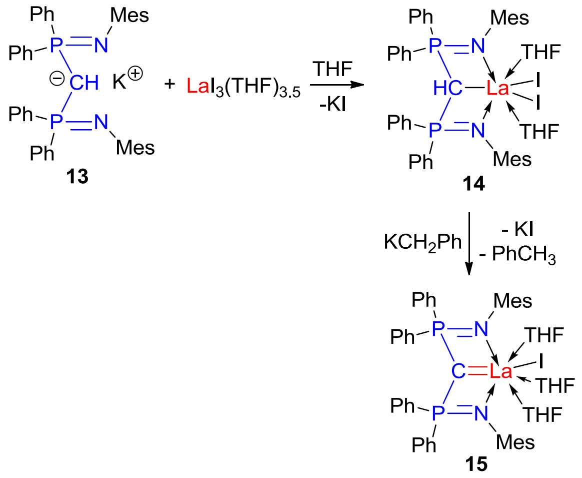
Scheme 4.

Therefore, the use of different ratios of the ligand and the metal will lead to the formation of different products. Floch and co-workers found that treatment of monoanionic ligand **8** with $[NdI_3(THF)_{3.5}]$ in a 1:1 ratio enabled the synthesis of the neodymium iodide complex **9** (Scheme 5), whereas a 2:1 ligand: metal ratio yielded bisalkyl neodymium complex **10**.[11] The first lanthanide alkyl-carbene mixed complex **12** was formed by treating one equivalent of KHMDS with **10** in THF, whereas the reaction of two equivalents of KHMDS with complex **9** afforded the new alkyl neodymium complex **11**.

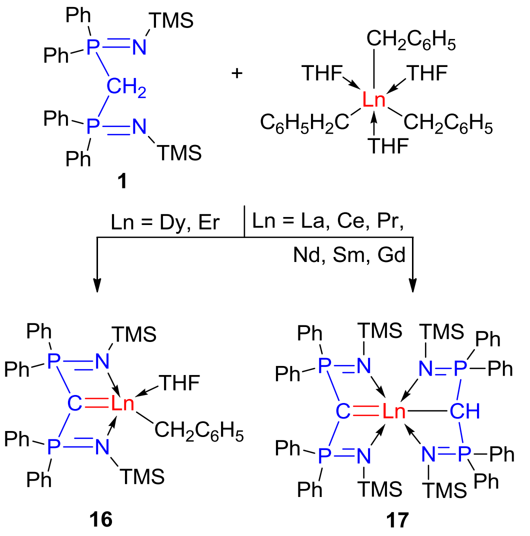
The monoanionic NCN-type pincer ligand **13** was also found to react with $LaI_3(THF)_4$ to yield the alkyl lanthanum complex **14**



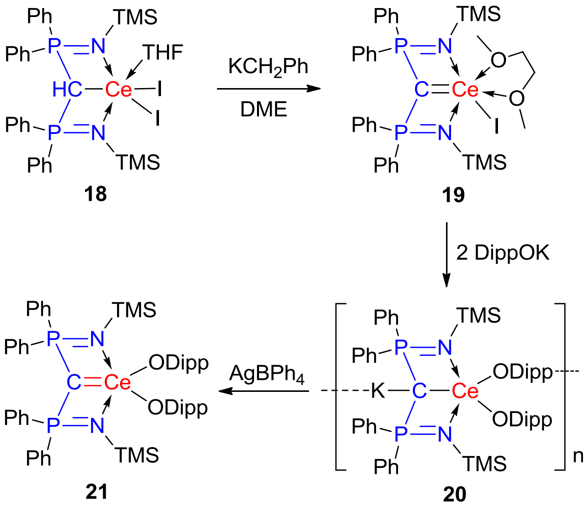
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

(Scheme 6),[12] which could be deprotonated in the presence of KCH_2Ph, leading to the formation of complex **15,** which contained a La═C double bond. DFT study revealed that the La═C bond is highly ionic and its orbital contribution originates mainly from the carbon.

Homoleptic lanthanide alkyls are effective starting materials for the synthesis of carbene complexes. Liddle and co-workers reported the synthesis of a series of lanthanide carbene derivatives by the reaction of NCN-type pincer ligand **1** with a lanthanide tribenzyl precursor (Scheme 7).[13] Complexes **17** were probably formed via the reaction of ligand **1** with lanthanide carbene intermediates with structures similar to complexes **16**.

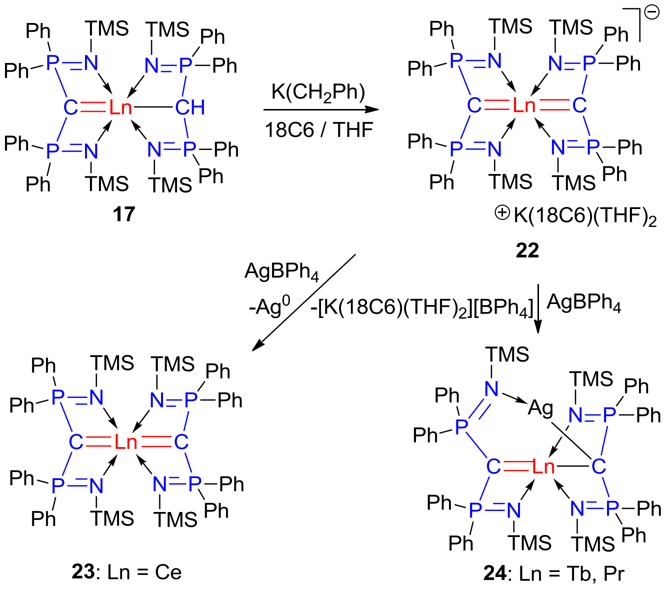
In 2013, Liddle and co-workers reported the first cerium(IV) carbene complex employing an NCN-type pincer ligand.[14] As shown in Scheme 8, by treatment of complex **18** with one equivalent of benzyl potassium in DME, cerium(III) carbene **19** was formed. The larger aryloxide ligand $DippO^-$ could replace the DME and iodine ligands on the cerium, leading to the formation of bis(aryloxide) cerium(III) complex **20**. In the presence of $AgBPh_4$, the one-electron oxidation product, cerium(IV) carbene **21**, was isolated as dark purple crystals.

The Ce═C double bond in complex **21** shows Wittig-like reactivity, and could react with 9-anthracene carboxaldehyde or benzaldehyde to yield the corresponding alkene products. DFT study suggested that the cerium(IV) carbene is polarized and the bond is of predominantly electrostatic character.

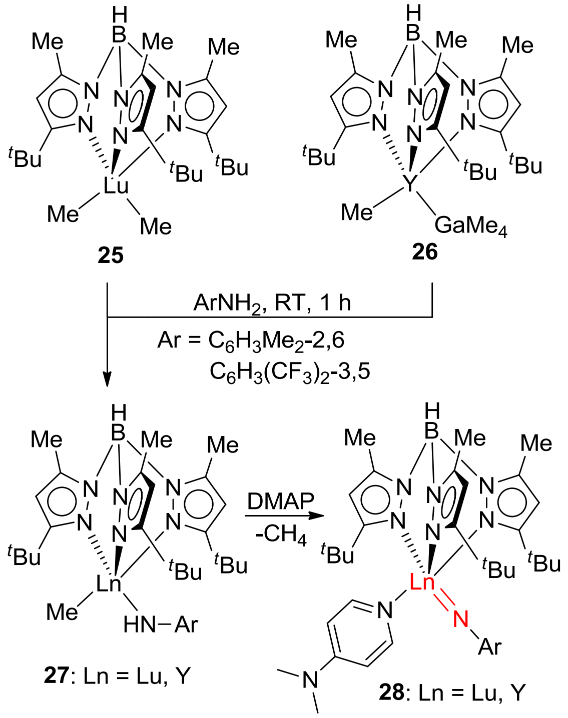
Very recently, Liddle and co-workers reported a tetravalent cerium, bis(carbene) complex **23** with trans C═Ce═C unit by the oxidation of complex **22** with $AgBPh_4$ (Scheme 9).[15] The Ce═C distance (2.385 Å) in **23** was the shortest example observed for Ce-C double bond thus far. Both experimental and theoretical data confirm the presence of an *inverse-trans-influence* in complex **23**. Attempts to oxidize complexes **22-Pr** and **22-Tb** with $AgBPh_4$ to synthesize the analogous bis(carbene) Tb(IV) and Pr(IV) were failed, instead isolation of complexes **24**.

Lanthanide-nitrogen multiple bonds

The chemistry of metal–nitrogen multiple bonds has received enormous attention in recent years because complexes containing such bonds are thought to be key intermediates in nitrogen fixa-



Scheme 9.



Scheme 10.

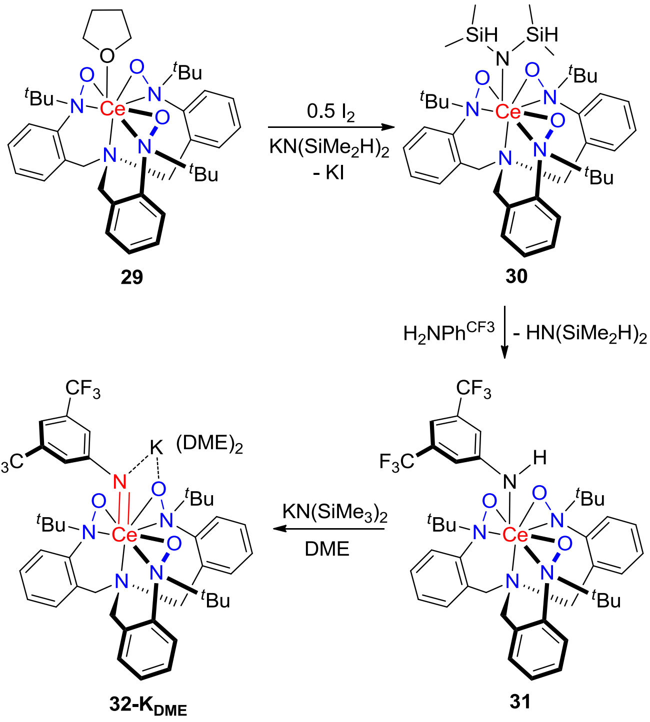
tion. Numerous imido-containing complexes with d-block transition metals have been reported. However, examples of imido complexes with lanthanide elements are largely unexplored. Dehnicke and co-workers reported a series of lanthanide complexes with phosphine imine ligands.[16] In addition, polynuclear lanthanide imido species in which –NR groups act as bridging ligands have also been synthesized.[17] These examples were discussed in an excellent review by Gordon and Giesbrecht in 2004,[18] and thus will not be discussed here.

The first terminal lanthanide-imido complex was synthesized by Anwander and co-workers in 2015.[19] They employed the super bulky monoanionic ligand, $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ {hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate}, as a framework for the synthesis of a Ln═N multiple bond. As shown in Scheme 10, treatment of $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{LuMe_2}]$ or $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Y(GaMe_4)(Me)}]$ with anilines at room temperature for 1 h led to the formation of the anilido-functionalized products **27**, which could be used to generate the corresponding terminal imide complexes **28** after the elimination of methane in the presence of the Lewis base DMAP. The Ln═N double bond character in these complexes was confirmed by the almost linear Ln—N—C(aryl) bond angles and very short Ln—N distances.

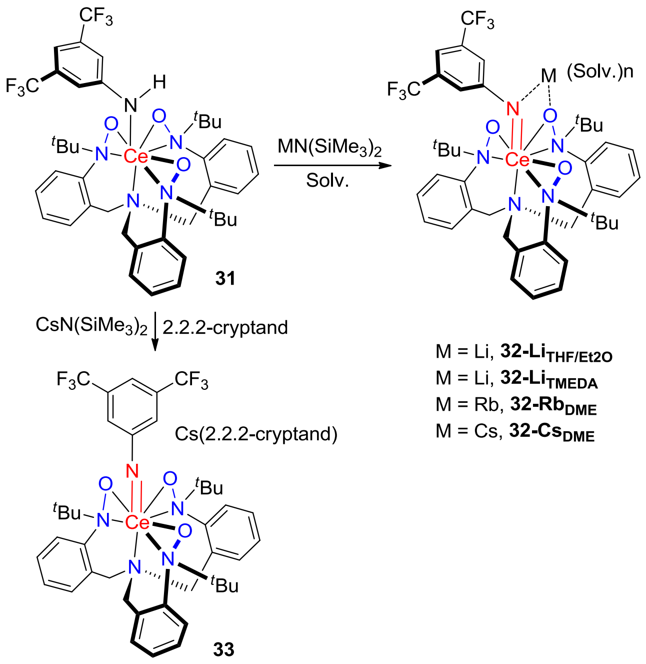
Therefore, the ancillary ligand, the lanthanide metal center, and the aniline are crucial factors for the synthesis of a Ln═N double bond. One possible route to increase the bonding between the lanthanide metal and nitrogen is to increase the oxidation state of the metal. Most lanthanide metals prefer the trivalent oxidation state. However, the +4 oxidation state is possible for cerium. Gordon and co-workers investigated the orbital interaction between the lanthanide metal and main group elements using DFT calculations, and found that the synthesis of a Ce═N double bond using the +4 oxidation state of cerium was a promising target.[20]

Recently, Schelter and co-workers achieved this target.[21] They employed a unique tris(hydroxylaminato) ligand framework, TriNO_x^{3-}, to synthesize the first crystallographically characterized Ce(IV)═N double bond complex. As shown in Scheme 11, treating complex **29** with 0.5 equivalent of I_2 and $\mathrm{KN(SiHMe_2)_2}$ led to salt metathesis reactions which gave complex **30**, which could further react with 3,5-bis(trifluoromethyl) aniline to produce complex **31**. This complex went on to form air- and moisture-sensitive Ce(IV)-imido complex **32** when upon addition of one equivalent of $\mathrm{KN(SiMe_3)_2}$. The Ce—N bond distance (2.119 Å) observed in complex **32** was much shorter than that found in complex **31** (2.379 Å), which further confirmed the double bond character of the Ce═N bond in **32**.

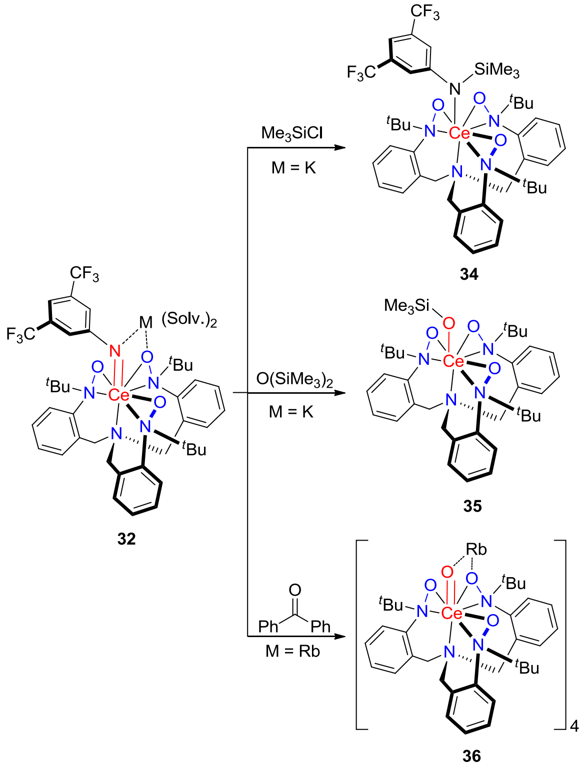
It is worth mentioning that the coordinated alkali metal cation is also an important factor in the stabilization of the Ce═N double bond. Therefore, Schelter and co-workers also investigated the



Scheme 11.



Scheme 12.



Scheme 13.

impact of different alkali metal cations on the Ce=N bond.[22] As shown in Scheme 12, a series of Ce(IV)–N imido complexes with different counterions were synthesized by the reaction of complex **31** with one equivalent of the alkali metal amide. Interestingly, the first complex with an unsupported Ce(IV)=N double bond unit was also isolated by the reaction of complex **31** with $CsN(SiMe_3)_2$ in the presence of 2.2.2-cryptand (Scheme 12). The Ce=N bond distance in complex **33** was only 2.077 Å, which is the shortest recorded Ce–N bond length.

The polarized Ce(IV)=N double bond in complex **32** was confirmed by its nucleophilic character. Schelter and co-workers found that **32-K$_{DME}$** could react with Me_3SiCl or unreactive $(SiMe_3)_2O$ to give Ce-N complex **34** or Ce—O complex **35** (Scheme 13). More interestingly, treatment of complex **32-Rb$_{DME}$** with benzophenone gives the unusual Ce(IV)=O complex **36**. This represented the first transformation of a Ce=N double bond to a Ce=O double bond (Scheme 13).

Lanthanide-oxygen multiple bonds

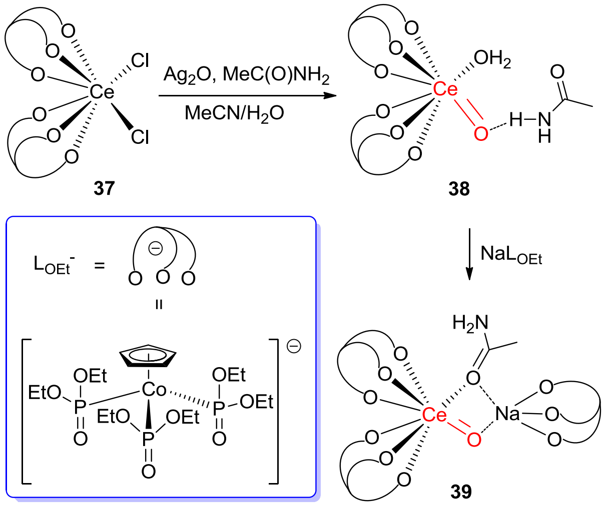
Terminal metal-oxo complexes have been proposed to be important intermediates in metal-catalyzed oxidation processes. Both transition metal and actinide element complexes with terminal oxo ligands are well documented. However, the analogous 4f lanthanide metal–oxo complexes are less developed. Lappert and co-workers reported the synthesis of a Ce(IV)-oxo complex, $[M]_2[Ce(\mu\text{-}O)(N(SiMe_3)_2)_3]_2$ (M = Na, K), by the reaction of $Ce(N(SiMe_3)_2)_3$ with dioxygen in the presence of $MN(SiMe_3)_2$.[23] The Ce—O bonds in these species are quite short, and can be represented by the resonance structures Ce=O—M and Ce^+—O^-—M.

Leung and co-workers reported the first example of a Ce(IV)=O double bond employing super bulky ligands.[24] As shown in Scheme 14, treatment of complex **37** with one equivalent of Ag_2O in the presence of acetamide and water gave complex **38** as a yellow solid, which featured a short Ce=O bond (1.857 Å). DFT investigation showed that the hydrogen bond between acetamide and the oxygen atom plays an important role in stabilizing the Ce=O double bond. Complex **38** represents the first terminal oxo species with a lanthanide element.

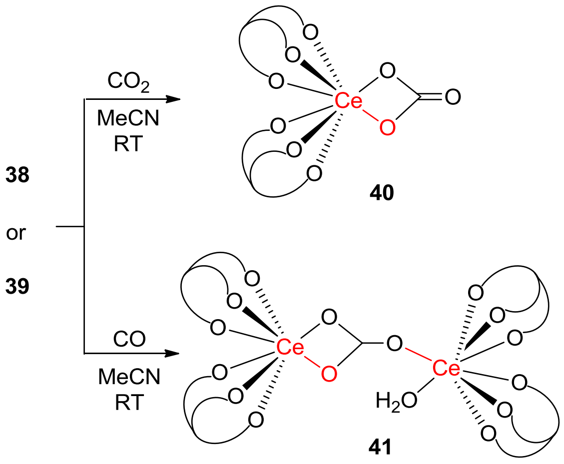
An oxo-bridged bimetallic cerium–sodium oxo complex, **39**, was isolated by the reaction of **38** with one equivalent of NaL_{OEt}. The Ce=O bonds in both **38** and **39** can react with carbon dioxide in air or can be reduced by carbon monoxide to form the cerium (IV) carbonate complex **40** or the dinuclear cerium(III) carbonate complex **41** (Scheme 15). These results indicate that the coordinated NaL_{OEt} has a small influence on the properties of Ce(IV)=O double bond.

The Ce=O double bond in complex **38** exhibits obvious nucleophilic character. Therefore, Leung and co-workers further studied its reactivity towards electrophiles.[25] As shown in Scheme 16, treatment of complex **38** with acetic anhydride gave the diacetate complex **42**. Similarly, ditriflate complex **43** was formed after recrystallization from the reaction of **38** and methyl triflate in MeCN. In addition, complex **38** could also react with two equivalents of $B(C_6F_5)_3$ to form the dicationic complex **44**.

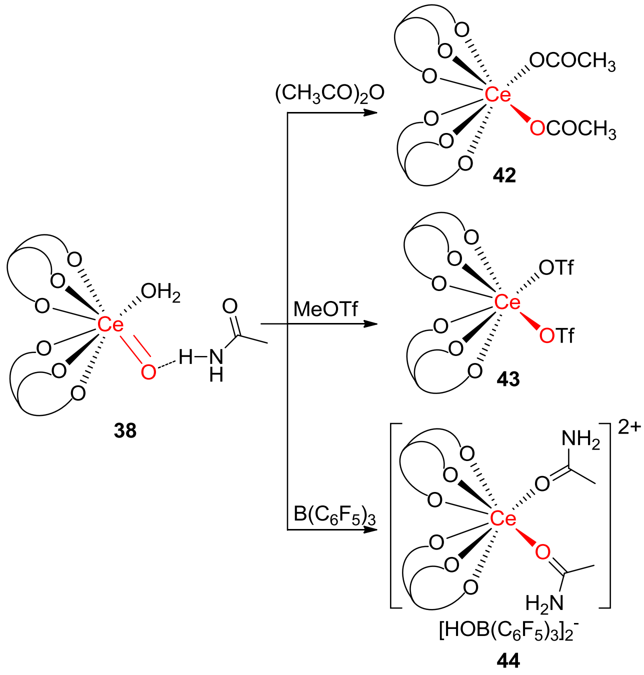
The oxo ligand in complex **38** can be further reacted with Brønsted acids (Scheme 17). Protonation of **38** with HCl or HNO_3 gave the corresponding chloride or nitrate complexes **45**, respectively. Weaker acids, such as phenol, could also protonate the Ce=O bond, leading to the formation of complex **46**. In addition,



Scheme 14.



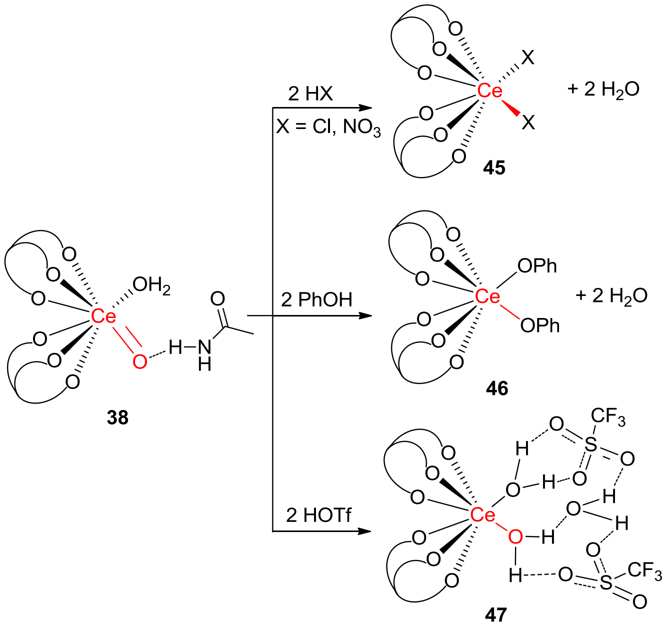
Scheme 15.



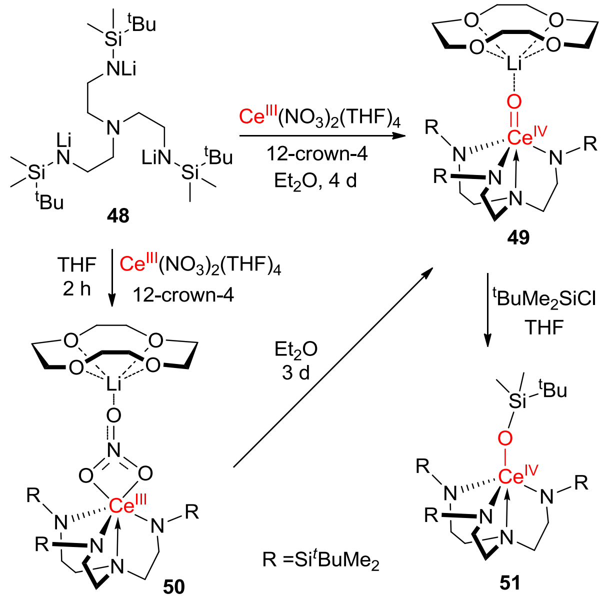
Scheme 16.

the dicationic cerium aqua complex **47**, for which an X-ray structure was obtained, was also recrystallized from the reaction of **38** with two equivalents of triflic acid. In summary, the Ce=O double bond in complex **38** was polarized, and showed nucleophilic, oxidizing, and Brønsted basic properties.

Recently, Hayton and co-workers reported the synthesis of the heterobimetallic Ce(IV)=O complex **49** by the reaction of ligand **48** with $[Ce(NO_3)_3(THF)_4]$ in the presence of 12-crown-4 (Scheme 18).[26] The formation of complex **49** from the inner-sphere reduction of the Ce(III) nitrate complex **50** was also proposed. The Ce(IV)=O bond in **49** was also nucleophilic and could react with t-$BuMe_2SiCl$ to give complex **51**. This result demonstrated that nitrate reduction could be an effective route for the synthesis of f-element oxo complexes.

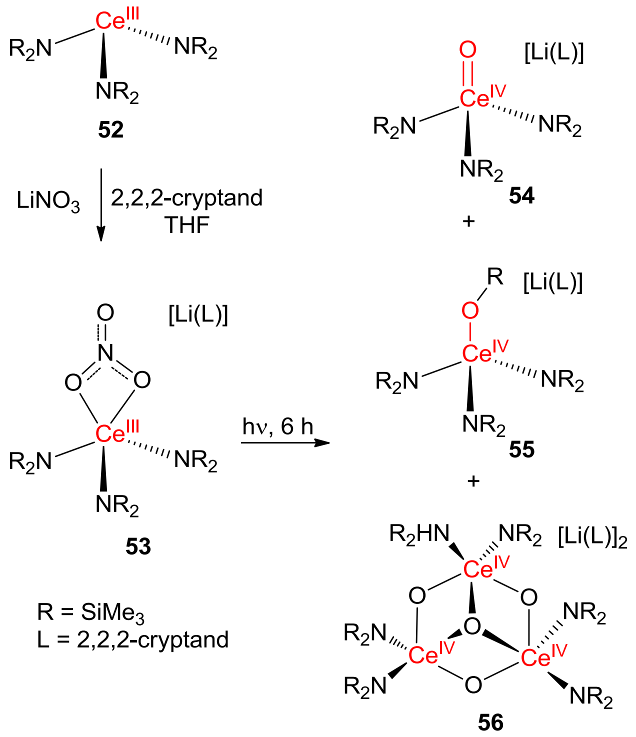


Scheme 17.



Scheme 18.

Hayton and co-workers further developed this method for the synthesis of Ce(IV)=O complexes. Very recently, they reported the first example of an unsupported Ce(IV) oxo complex (**54**) by the photochemical cleavage of nitrate in complex **53** (Scheme 19),[27] which was generated from the reaction of $LiNO_3$ with **52** in the presence of 2.2.2-cryptand. During the photolysis of complex **53**, the Ce(III) silyloxide complex **55** and the Ce(IV) oxo cluster **56** were also isolated.



Scheme 19.

Conclusions and perspectives

Overall, lanthanide complexes with multiply bonded ligands have been achieved using terminal carbene, imido, and oxo groups. The lanthanide elements, ancillary ligands, and steric bulk groups are crucial factors in the stabilization of these highly reactive species. Further studies of the lanthanide–ligand multiple bonds could focus on the following aspects: i) the catalytic properties of these unique species; ii) synthesis of Schrock-type lanthanide carbene complexes, in which the carbene carbon is not attached to heteroatoms; iii) generation of lanthanide multiple bonds with atoms other than the second period elements; and iv) whether it is possible to achieve aromaticity (which has been the domain of s-, p-, and d-element-containing cycles) in f-block metallacycles. The study of novel lanthanide–ligand multiple bonds and their properties will continue to flourish in the future.

Acknowledgements

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