JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Perspective

A Rare-Earth Metal Retrospective to Stimulate All Fields

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Cite This: *J. Am. Chem. Soc.* 2021, 143, 18354−18367

ABSTRACT: Formulating insightful questions and experiments is crucial to the advancement of science. The purpose of this Perspective is to encourage scientists in all areas of chemistry to ask more "What if?" questions: What if we tried this experiment? What if we used these conditions? What if that idea is not correct? To stimulate this thinking, a retrospective analysis of a specific field, in this case rare-earth metal chemistry, is presented that describes the "What if?" questions that could have and should have been asked earlier based on our current knowledge. The goal is to provide scientists with a historical perspective of discovery that exemplifies how previous views in chemistry were often narrowed by predominant beliefs in principles that were incorrect. The same situation is likely to exist today, but we do not realize the limitations! Hopefully, this analysis can be used as a springboard for posing important "What if?" questions that should be asked right now *in every area of chemical research*.

■ INTRODUCTION

This Perspective was inspired in part by a passage from *Advice to a Young Investigator* by Santiago Ramón y Cajal:[1]

> *What a wonderful stimulant it would be for the beginner if his instructor, instead of amazing and dismaying him with the sublimity of great past achievements, would reveal instead the origin of each scientific discovery, the series of errors and missteps that preceded it.*

Ramón y Cajal is referring to the fact that young people can be intimidated by reading the current literature about one amazing discovery after another because it leads to the expectation that they, too, should be able to immediately make such discoveries. However, descriptions of recent breakthroughs do not tell the whole story. The discoveries are often the result of years of developments and missteps within that field.

Students will also read review articles on their new research area that typically cover the advances since the last review article. This is appropriate, but it also means that a multi-decade analysis of the development of a field is rarely available. As a result, younger scientists do not have the perspective to fully appreciate how many substantial opportunities may currently exist for them to make new discoveries.

Even for researchers with years of experience, it is worthwhile to reflect on the bigger picture. It is easy to get so immersed in the details of a project that the broader "What if?" questions do not get asked. It is hoped that this Perspective will stimulate both new and experienced researchers to ask more "What if?" questions across all disciplines.

Whitesides has pointed out that developing insightful questions is critical to making new discoveries.[2] Scientist do this routinely. However, it is necessary to have a historical perspective to realize that not only can small challenges to the status quo be made which will lead to incremental advances, but major paradigms may also be wrong and should be tested with the appropriate "What if?" questions.

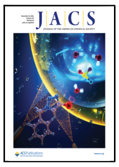
The decision to write this Perspective was prompted by the realization that the students in our research group had no idea how much progress has been made in rare-earth metal chemistry since the 1960s, when it was viewed as an uninteresting and extremely limited area. When W.J.E. (co-author of this paper) started working in the rare-earth metal area in the 1970s, both his doctoral and postdoctoral advisors thought he was crazy and had no future. He was even told by a funding agency to find a more productive part of the periodic table to explore! Reviews in the rare-earth metal area do not capture this perspective.

The students in our group also were unaware that many of the current advances could have been made *decades earlier* if the appropriate "What if?" questions had been asked. The goal of recounting this rare-earth metal history, of course, is to stimulate the application of the appropriate "What if?" questions to our current state of knowledge.

We hope that this Perspective will be useful to scientists in all areas of chemistry; it is not intended just for rare-earth metal chemists. The lessons that can be gleaned from analyzing this specific set of rare-earth metal anecdotes are general, and similar stories exist in other areas. The new "What if?" questions, both in rare-earth metal chemistry and in other areas, will not be the same as those in the past. However, researchers in all areas should consider that knowledge in their area currently may be as primitive as rare-earth metal chemistry was in 1960. Hence, this retrospective has the potential to stimulate big ideas in any area of chemistry.

Note that this is neither a review of rare-earth metal chemistry nor a chronology of its development. Rather, it is a collection of

Received: August 18, 2021
Published: October 22, 2021



retrospective vignettes describing specific instances when the appropriate "What if?" questions could have made a big difference in the development of the field. Also note that the symbol Ln will be used to represent the 17 rare-earth metals which are defined as scandium, yttrium, and the lanthanides.

Background on Early Rare-Earth Metal Chemistry: Boring. The classic quote on the limited nature of rare-earth metal chemistry comes from *Understanding Chemistry* by Pimentel and Spratley in 1971:[3]

> *Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, that statement tells the whole boring story about the other 14 elements.*

The initially reported coordination chemistry of the rare-earth metals reflected this view. The +3 oxidation state was predominant, and the 14 elements after La displayed chemistry similar to that of La.[4] This similarity arose because the 4f valence orbitals have a limited radial extension.[5] Unlike the other elements in the periodic table, the valence electrons of the lanthanides do not extend beyond the electron density of the inert gas core and cannot engage in significant covalent bonding, as shown in Figure 1.

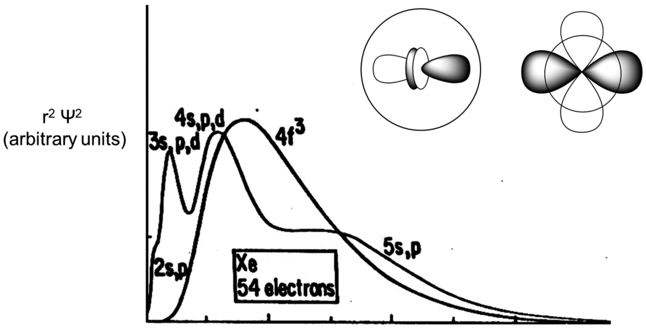


Figure 1. Plot of the radial extension of Nd(III) atomic orbitals,[5] along with a cartoon of a 4f and 5d orbital extension from the nucleus. The circles represent the radial extent of the core electron density.

Hence, the number of 4f valence electrons in the $4f^n$ electron configuration did not affect the reaction chemistry in the primarily ionic rare-earth metal complexes. This was very different from transition metal chemistry, in which there are big differences in chemistry when the electron count is changed by one. For example, moving from Fe to Co in the metallocene series changes the stable $(C_5H_5)_2Fe$ into the highly reducing $(C_5H_5)_2Co$.

The main difference in the chemistry of the rare-earth metals was caused by the decreasing ionic radius of these metals as the series is traversed from La to Lu, i.e., the lanthanide contraction, Figure 2.

The ionic radius of each metal is about 0.015 Å smaller than the previous one.[6] This change was so small that the properties of adjacent elements were very similar and therefore thought to be "boring".

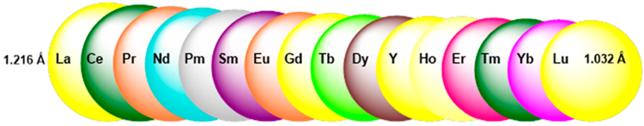


Figure 2. Plot of the six-coordinate ionic radius of the rare-earth metals. Each sphere is drawn to scale relative to each other.[6]

Further evidence of this view was found in the chemistry of $4d^0$ Y(III), which has an ionic radius similar to that of $4f^{10}$ Ho(III).[6] Y(III) displays chemistry like Ho(III) since a $4d^0$ electron configuration is equivalent to a $4f^{10}$ configuration buried in the inert gas core, Figure 1. Furthermore, the small ionic radius of $3d^0$ Sc(III) would place it 23rd in the series in Figure 2, assuming a 0.015 Å decrease in size per element. As a result, Sc(III) often forms complexes with lower coordination numbers than the other rare-earth metals, but the reaction chemistry is similar.

The "boring" nature of the rare-earth metals in the early days also arose because the diversity of known compounds was very limited. This resulted from the belief outlined in the first vignette below.

VIGNETTES ON THE LIMITATIONS OF RARE-EARTH METAL CHEMISTRY

1. The Belief That Stable Lanthanide Complexes Exist Only with Anionic Oxygen-Donor-Atom Ligands. The following quote sums up the situation for rare-earth metal complexes prior to 1963:[7]

> *The complex chemistry of the lanthanides has so far been limited, with rather few exceptions, to ligands containing anionic oxygen as a donor atom. There was an especial lack of information about complexes with ligands having nitrogen as the donor and because of this it has been often assumed that such compounds are relatively unstable.*

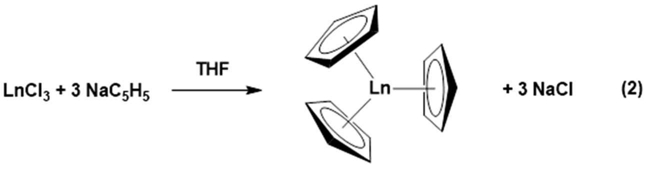
It seems unbelievable now, in 2021, that in the 1960s it was widely believed that lanthanide complexes would only form stable complexes with oxygen donor atom ligands.[7,8] Even nitrogen donor ligands were not expected to form stable complexes! However, as a calibration, it should be noted that in the 1950s, it was thought that transition metal carbon bonds were inherently unstable.[9]

The view that Ln−N bonds were weak was derived from studies in aqueous solution. In water as a solvent, weak nitrogen donor ligands did not displace solvated water and strong nitrogen donor ligands generated enough hydroxide in solution to precipitate insoluble lanthanide hydroxides.[10]

Simply changing the solvent to ethanol or acetonitrile made it possible to synthesize lanthanide complexes of nitrogen donor ligands, i.e., the Ln−N bond is not inherently weak, eq 1.[11]

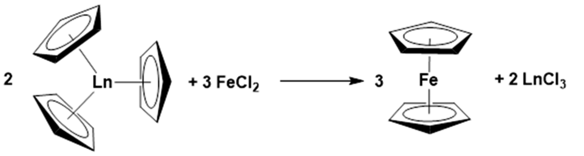
$$\mathrm{Ln(NO_3)_3 + 4\ H_2NCH_2CH_2NH_2 \xrightarrow{CH_3CN} [Ln(H_2NCH_2CH_2NH_2)_4][NO_3]_3} \qquad (1)$$

The narrow view of solvents in the 1960s is particularly striking when it is realized that Gilman was examining lanthanum reactions in Et_2O as early as 1945,[12] and Wilkinson used tetrahydrofuran (THF) in 1954 to make the first cyclopentadienyl rare-earth metal complexes, $(C_5H_5)_3Ln$, where Ln = Sc, Y, La, Ce, Pr, Nd, Sm, and Gd, eq 2.[13]



What if a change in your current research as simple as going from water to non-aqueous solvent would mimic the advance in 1963 that overturned the belief that only Ln−O bonds were stable?

2. The Belief That Rare-Earth Metals Are Just +3 Extensions of Alkali and Alkaline-Earth Metals. To examine the chemistry of the rare-earth metal cyclopentadienides in eq 2, Wilkinson reacted these with $FeCl_2$, eq 3. These reactions formed ferrocene and showed that the $(C_5H_5)_3Ln$ complexes had reaction chemistry like alkali and alkaline-earth metal complexes such as NaC_5H_5 and $Mg(C_5H_5)_2$.[13,14] Although this was a good comparative reaction, it led to the view that the rare-earth metals were just +3 versions of the ionic +1 alkali metals and the +2 alkaline-earth metals. This did not help improve the popularity of the rare-earth metals. This was a periodic extension that was reasonable at the time, but proved to be wrong.



(3)

What if a periodic trend in your current research could be misguiding the whole field?

3. The Belief That Ln–C Single Bonds Are Unstable. After his 1954 communication on the reaction in eq 2, Wilkinson published a full paper on $(C_5H_5)_3Ln$ complexes that added Dy, Er, and Yb to the list of examples.[14] The first sentence of that paper stated the following view on the instability of Ln–C alkyl and aryl bonds:

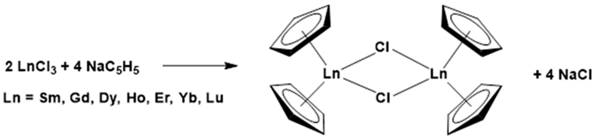
> *It seems fairly certain that alkyl and aryl derivatives of scandium, yttrium, lanthanum and the rare earth elements either do not exist or have an existence so transitory that they cannot be isolated.*

In retrospect, we know that an extensive selection of rare-earth metal alkyl and aryl complexes, both homoleptic, LnR_3,[15] and heteroleptic, $(C_5R_5)_2LnR$[16] (R = alkyl, aryl), can be synthesized and crystallographically characterized.[17] However, in the 1950s this was not thought possible. In support of this view, a 1955 review by F. A. Cotton discounted the few previous claims of organometallic rare-earth metal complexes.[18]

What if a generalization in your current research, such as you cannot synthesize a certain type of element–element bond, is not accurate and when this is overturned, it could lead to an entire new field of chemistry?

4. The Belief That Organometallic Rare-Earth Metal Chemistry Was Limited Primarily to the Smaller Metals, Sm–Lu. Most of the early contributions to organometallic rare-earth metal chemistry supported this belief even though Wilkinson had made $(C_5H_5)_3Ln$ complexes from La to Yb via eq 2.[13,14] Several examples are detailed here.

$[(C_5H_5)_2LnCl]_2$, Ln = Sm–Lu. Nine years after Wilkinson's report of the $(C_5H_5)_3Ln$ complexes in 1954, eq 2, compounds formulated as $[(C_5H_5)_2LnCl]_2$, eq 4, were published by a group at the Ethyl Corporation in Detroit in search of a better octane booster than tetraethyllead.[19] However, this paper reported results only for the later lanthanides, Ln = Sm, Gd, Dy, Ho, Er, Yb, and Lu.



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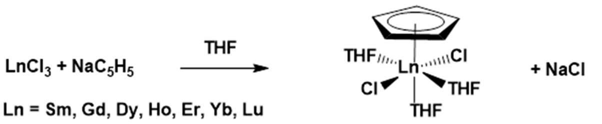
$(C_5H_5)LnCl_2(THF)_3$, Ln = Sm–Lu. A subsequent paper was published by the Ethyl Corporation group in the same year on compounds formulated as $(C_5H_5)LnCl_2(THF)_3$, again for the smaller lanthanides, Ln = Sm, Eu, Gd, Dy, Ho, Er, Yb, and Lu, eq 5.[20] In this paper the authors wrote:



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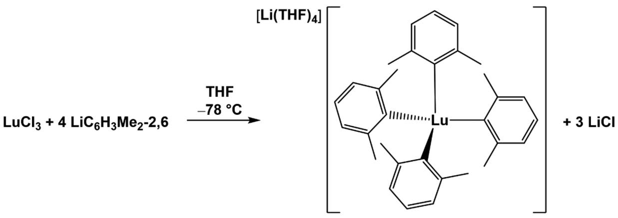
> *Although the cyclopentadienyl dichlorides of the lanthanides from samarium to lutetium are readily prepared, all attempts to isolate similar complexes with lanthanum, praseodymium, and neodymium have failed. This same behavior of the lanthanide series was encountered with the lower lanthanides during the preparation of the dicyclopentadienyllanthanide chlorides. As suggested then, the lanthanide contraction may be playing some subtle role in defining the stability of the mixed cyclopentadienyl chloride derivatives. Such a behavior is not present with the tricyclopentadienyllanthanides, as all members of the series readily yield this complex. As yet, a thorough explanation for these observations cannot be offered.*

These papers led to the belief that certain classes of organometallic complexes were not accessible for the larger early lanthanides.

$[Li(THF)_4][Ln(C_6H_3Me_2\text{-}2,6)_4]$, Ln = Lu Only. This focus on the smaller lanthanides persisted in 1972, when Hart and Hursthouse published the first X-ray crystal structure of a complex containing a Ln–C single bond in $[Li(THF)_4][Lu(C_6H_3Me_2\text{-}2,6)_4]$, eq 6.[21] Only the Lu complex was isolated, and the authors reported that:

> *Our attempts to prepare analogous compounds of lighter lanthanides have so far failed.*



(6)

$(C_5H_5)_2LnR$, Ln = Gd–Yb. The suggestion that organometallic complexes of the larger early lanthanides could not be prepared was reiterated in 1975 in a paper by Tsutsui on "$(C_5H_5)_2LnMe$" and "$(C_5H_5)_2LnPh$" complexes of Ln = Gd, Er, and Yb, and "$(C_5H_5)_2Ln(C{\equiv}CPh)$" complexes of Ln = Gd, Ho, Er, and Yb, eq 7.[22]

$$(C_5H_5)_2LnCl + LiR \longrightarrow (C_5H_5)_2LnR + LiCl \qquad (7)$$

R = Me, Ph
Ln = Gd, Er, Yb

R = C≡CPh
Ln = Gd, Ho, Er, Yb

The authors wrote:

> *It has been suggested that the size of the lanthanides influenced the success or failure of a particular reaction. Smaller (heavier) lanthanides seem to favor σ-bond formation as attempts to prepare 2,6-dimethylphenyl derivatives for lanthanides larger than Yb have been unsuccessful. It was also noted that cyclopentadienyl-lanthanides chlorides could not be prepared with elements larger than samarium. This was attributed to some subtle effect of the lanthanide contraction.*

As late as 1982, the large early metals, La−Nd, were not viewed as being favorable candidates for forming stable complexes.[23] Hence, throughout the 28 years after Wilkinson reported the $(C_5H_5)_3Ln$ complexes, eq 2, it was incorrectly believed that the larger lanthanides would not form other classes of complexes analogous to their smaller analogs! No one asked the appropriate questions about how early rare-earth metal complexes could be stabilized.

What if in your research area there are twice as many substances available for successful research, but the current view is that half aren't viable for some reason?

Recognizing the Importance of Steric Saturation. With the benefit of hindsight, the limitation of the organometallic chemistry in eqs 4−7 to the later smaller lanthanides, Sm−Lu, was an issue of steric saturation. We now know that complexes can be made for all the lanthanides regardless of the size of the metal if the steric bulk of the ligand set is large enough to sterically saturate the metal center.[24] The lanthanide contraction was involved, because it was easier to sterically saturate the smaller, later metals with the ligands that were being used at that time.

The importance of steric saturation was realized when the pentamethylcyclopentadienyl ligand was introduced to rare-earth metal chemistry. The C_5Me_5 ligand was initially used in organometallic chemistry by R. B. King in 1966,[25,26] but this ligand did not become popular, possibly because it had to be synthesized rather than purchased. In 1971, Brintzinger and Bercaw employed C_5Me_5 to overcome problems previously encountered with the C−H activation chemistry of "titanocene", i.e., "$(C_5H_5)_2Ti$".[27] The early transition metal chemistry of the C_5Me_5 ligand flourished in the Bercaw lab during the 1970s[28,29] with the discovery of molecules like $(C_5Me_5)_2(N_2)Zr{-}N{=}N{-}Zr(N_2)(C_5Me_5)_2$.[30] Later, the ligand was introduced to the actinides when the Bercaw Ph.D. student Juan Manriquez began postdoctoral study in the Marks group.[31] Several groups subsequently made the first C_5Me_5 complexes of the rare-earth metals in the early 1980s.[32−34]

The C_5Me_5 ligand allowed heteroleptic bis(cyclopentadienyl) complexes, $[(C_5Me_5)_2LnA]_n$ (A = anionic ligand), to be synthesized across the lanthanide series. This provided the data that led to an analysis of rare-earth metal chemistry based on steric saturation which continues to be used to this day.[24] For example, the $[(C_5H_5)_2Ln(\mu\text{-}Cl)]_2$ complexes in eq 4 were not isolated with the large metals like La because these formally eight-coordinate ionic complexes were unstable with respect to ligand redistribution. This combination of metals and ligands forms the more sterically saturated nine-coordinate $(C_5H_5)_3Ln$ and $LnCl_3$, which is nine-coordinate in the solid state, eq 8.[35]

$$6\,\mathrm{LnCl_3} + 12\,\mathrm{NaC_5H_5} \xrightarrow{-\,12\,\mathrm{NaCl}} \text{" }3\,[(\mathrm{C_5H_5})_2\mathrm{Ln}(\mu\text{-}\mathrm{Cl})]_2\text{ "} \longrightarrow 2\,\mathrm{LnCl_3} + 4\,(\mathrm{C_5H_5})_3\mathrm{Ln} \tag{8}$$

$[(C_5Me_5)_2LnA]_n$ complexes did not engage in this ligand redistribution because the analogous product, $(C_5Me_5)_3Ln$, is so sterically oversaturated that it does not form by ligand redistribution. In fact, it is difficult to synthesize $(C_5Me_5)_3Ln$ complexes in general.[36] The increased size of C_5Me_5 provided steric saturation to the early metals such that heteroleptic $[(C_5Me_5)_2LnA]_n$ complexes could be isolated for all the lanthanides, La through Lu. These compounds proved to be very useful for developing productive Ln−C and Ln−H reactivity through compounds like $[(C_5Me_5)_2LnR]_n$ (R = alkyl, aryl) and $[(C_5Me_5)_2LnH]_n$.[17,37]

Since the C_5Me_5 ligand was available as early as 1960[38] and both the Ethyl Corporation and Tsutsui groups recognized that the lanthanide contraction was important, asking the "What if?" question of using a larger cyclopentadienyl ligand with larger metals would have led to a breakthrough 20 years earlier. In fact, Tsutsui had investigated the indenyl ligand, a larger cyclopentadienyl ligand with a benzo substituent, in 1968 and synthesized the tris(cyclopentadienyl) species, $(C_9H_7)_3Ln$, of Ln = La, Sm, Gd, Tb, Dy, and Yb.[39] However, this larger cyclopentadienyl was not used to make bis(cyclopentadienyl) halides, alkyls, and hydrides.

What if the introduction of just one ligand could completely erase a long-held concept that was incorrect?

5. The Belief That Rare-Earth Metal Redox Chemistry Was Limited to One-Electron Reactions.

Although it became established by 1985 that all of the lanthanides were available for organometallic reaction chemistry,[37,39] rare-earth metal chemistry was still viewed as very limited. The following paragraph in a prominent organometallic textbook of the time showed the narrow view of rare-earth metal chemistry in 1987:[40]

> *The organometallic chemistry of the f-block elements (lanthanides and actinides) is not discussed. Although the high ionic character, oxophilic character, high coordination number, and coordinative unsaturation of these f-block metals has given rise to distinctive complexes and reactivity—especially in insertion reactions—these elements lack the variable oxidation states, backbonding ability, and orbital extension which are crucial to reactivity of d-block transition metals.*

The "lack of variable oxidation states" referred to the fact that the only rare-earth metal ions accessible in molecular complexes useful for reaction chemistry beyond the stable Ln(III) ions were Eu(II), Yb(II), Sm(II), and Ce(IV). This meant that there were only four redox couples in rare-earth metal chemistry and all were only one-electron couples. Since much of the power of transition metal-based catalysis comes from two-electron oxidative addition/reductive elimination combinations, the application of rare-earth metal complexes to catalysis looked very limited.

In addition, the two most accessible +2 rare-earth metal ions, Eu(II) and Yb(II), were not strong reductants, with generic Ln(III)/Ln(II) reduction potentials of −0.35 and −1.15 V vs SHE, respectively.[41,42] The more reducing Sm(II) (−1.55 V vs SHE) was considered a difficult element with which to do research prior to 1982, since it was the largest lanthanide that gave isolable organometallic complexes from eqs 4−7. Samarium complexes were believed to be on the borderline of being unstable species.

The advent of the C_5Me_5 ligand helped develop the reaction chemistry of +2 rare-earth metal ions. Efforts to synthesize complexes of lanthanides in oxidation state zero by metal vapor chemistry,[43−45] i.e., the reaction of elemental metal vapor, Ln, with neutral ligands, L, to form LnL_x complexes,[46,47] led to the reaction of Sm metal with C_5Me_5H, eq 9.

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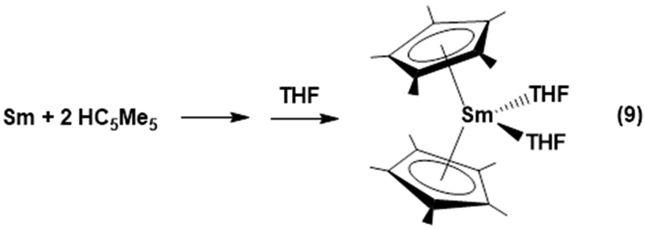
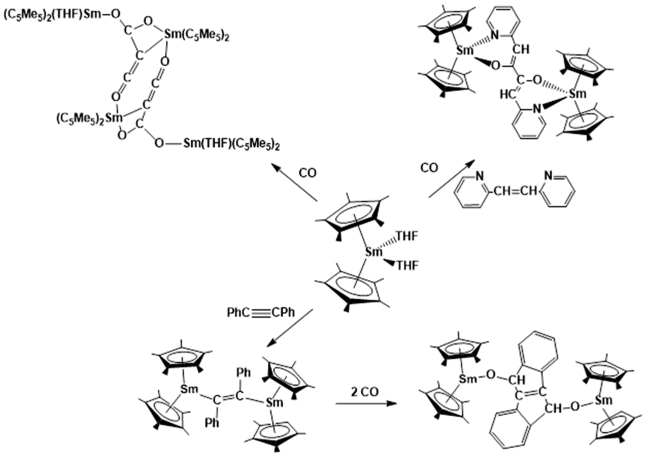
J. Am. Chem. Soc. 2021, 143, 18354−18367



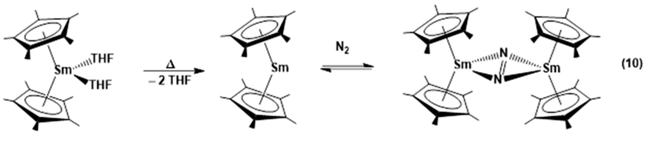
This provided the soluble Sm(II) organometallic species, $(C_5Me_5)_2Sm(THF)_2$,[48] that expanded rare-earth reduction chemistry considerably due to its combination of solubility and significant reducing power. This complex reacted with CO,[49] olefins,[50] and alkynes,[51] Scheme 1, all of which were previously thought to be too soft to react with the very ionic, hard, rare-earth metals.

Scheme 1. Reactions of $(C_5Me_5)_2Sm(THF)_2$ with CO and Unsaturated Hydrocarbons



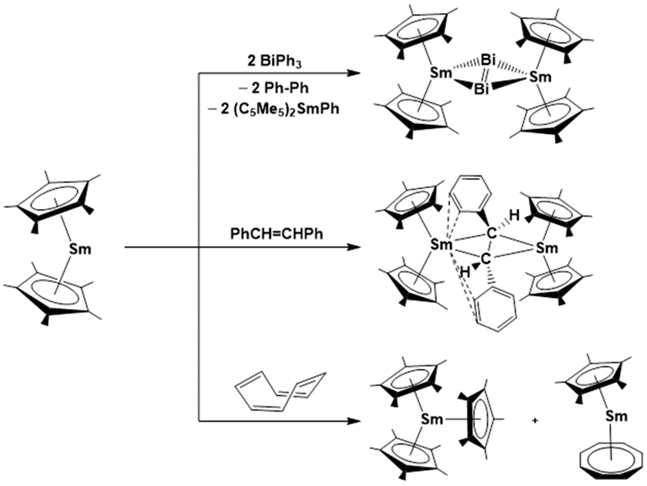
$(C_5Me_5)_2Sm(THF)_2$ was initially discovered by metal vapor methods rather than by ionic metathesis from KC_5Me_5 and SmI_2[52] because SmI_2 was not yet known as a common reagent in 1981. The metallocene was subsequently made from SmI_2,[53] and now SmI_2 is a common reagent in organic synthesis laboratories.[54]

It was subsequently found that $(C_5Me_5)_2Sm(THF)_2$ could be desolvated to form decamethylsamarocene $(C_5Me_5)_2Sm$,[55] eq 10. Surprisingly, this complex was bent, in contrast to the neutral +2 transition metallocenes like ferrocene that have parallel rings, eq 3. $(C_5Me_5)_2Sm$ was more reactive than $(C_5Me_5)_2Sm(THF)_2$ and showed that rare-earth metal complexes could even react with dinitrogen,[56] eq 10, another soft substrate that was thought to have no chemistry with these hard ionic metal ions.



Many unusual reactions subsequently were found with $(C_5Me_5)_2Sm$, Scheme 2.[57−59] The reactions of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ disproved the myths in the paragraph from the organometallic textbook[40] at the beginning of this section. These reactions demonstrated that the lanthanides could accomplish unusual activation of small molecules and could accomplish two-electron reduction chemistry even though only one-electron redox couples were available.

Scheme 2. Unusual Reactions with $(C_5Me_5)_2Sm$



As this chemistry expanded, it became clear that the appropriate stoichiometry for reactions of these one-electron reductants with substrates was 2:1. In retrospect, this type of chemistry makes sense, as the one-electron reduction of a substrate forms a radical. This radical species will try to spin pair by dimerizing or reacting with another source of one electron. Since the Sm(II) reagent is a source of an electron, this leads to bimetallic complexes with the substrate activated by a two-electron reduction.

What if simply changing the reaction stoichiometry from 1:1 to 2:1 could overcome generalizations believed to limit the development of your field?

6. The Belief That the Lack of Backbonding Prevents Reactivity with Unsaturated Small Molecules. The rare-earth metal-based activation of CO, N_2, and unsaturated hydrocarbons in Schemes 1 and 2 showed that the other limitation described in the 1987 organometallics textbook,[40] namely lack of "backbonding ability and orbital extension", was, in fact, not a limitation "crucial to reactivity" if reductive chemistry was involved. It was well established in transition metal chemistry that backbonding via the Chatt−Dewar−Duncanson model was important for binding substrates.[60] This backbonding was not expected to be possible with the ionic rare-earth metals due to the limited radial extension of the 4f orbitals, Figure 1.

However, the ionic rare-earth metals do function as Lewis acids that can interact with small molecules and can facilitate reduction by Ln(II) ions. Once the small molecules are activated by reduction, they are converted into dianions by another equivalent of the previously denigrated one-electron reductants. These reduced-substrate dianions are now in the presence of Ln(III) ions that can trap and stabilize them via strong electrostatic interactions. Many unusual activations and unusual structures were isolated by this route.[49,50,56−59]

The statement about the lack of "variable oxidation states, backbonding ability, and orbital extension"[40] was *not incorrect.* This is an accurate assessment. However, the assumption that these metals did not have interesting organometallic chemistry because they were not like transition metals was the wrong conclusion. In general, different is not bad. In this case, it just meant that small-molecule activation reactions would occur in a different way, i.e., through reduced substrate anionic intermediates.

What if simply changing the charge on one component of your reaction system, e.g., from a neutral ligand to an anion, could lead to new opportunities for reaction chemistry?

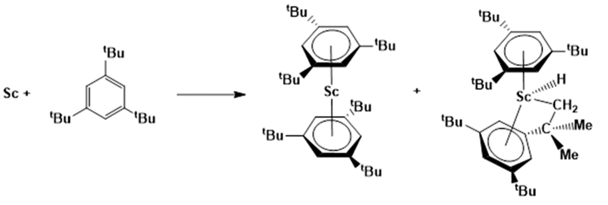
7. The Belief That Only Eu(II), Yb(II), and Sm(II) Would Form Molecular Complexes of Ln(II) Ions. Examples of Eu(II), Yb(II), and Sm(II) complexes were discovered as early as 1906.[61,62] They were all reductants since their Ln(III) ions were more stable. Their existence was rationalized based on the quantum mechanical stabilization of half-filled and filled 4f shells. Complexes of the $4f^7$ Eu(II) ion were more stable, i.e., less reducing, than those of $4f^{14}$ Yb(II), as shown by their generic −0.35 and −1.15 V vs SHE reduction potentials, respectively.[41,42] The $4f^6$ Sm(II) ion (−1.55 V vs SHE) was the most reactive since its configuration was only approaching a half-filled shell. The next most likely Ln(II) ion to exist, $4f^{13}$ Tm(II), had an estimated reduction potential of −2.3 V,[41,42] which was thought to be too reducing to exist in any solvent. All other lanthanides had estimated Ln(III)/Ln(II) reduction potentials more negative than −2.7 V and were assumed to be inaccessible in solution.[41,42,63]

However, through solid-state studies, Nd(II) was identified in 1959,[64] Tm(II) in 1960,[65] and Dy(II) in 1966.[66] These +2 ions were identified in metal dihalides, LnX_2 (X = halide), that were synthesized under solvent-free conditions, typically from the metal and iodine in sealed tantalum vessels at high temperature, eq 11. LnI_2 compounds could be made for the other lanthanides as well, such as La, Ce, Pr, and Gd, but in these cases the compounds were not the salt-like $Ln^{2+}(I^-)_2$ compounds of Tm, Dy, and Nd but instead black, metallic, or semiconducting Ln(III) compounds $(Ln^{3+})(I^-)_2(e^-)$, with an electron delocalized in the lattice.[67,68] It was assumed that the lattice electron was in a band formed by the 5d orbitals since the 4f orbitals had too little radial extension to form a delocalized band structure. Hence, even under the extreme reducing conditions of eq 11, Ln(II) ions would not form for the other metals. Although Tm(II), Dy(II), and Nd(II) were known in the solid state, their very negative calculated reduction potentials suggested that extension of their chemistry to soluble molecular species was not possible since these ions would react with solvents. Attempts to make these species in solution were consistent with this view, and only fleeting intense colors from transient species were observed.[69−73] Claims of Tm(II) being stable in THF were made as early as 1983,[73,74] but were not substantiated by X-ray crystallography.

$$(Ln^{2+})(I^-)_2 \longleftarrow Ln + I_2 \longrightarrow (Ln^{3+})(I^-)_2(e^-) \qquad (11)$$

Ln = Nd, Sm, Eu, Dy, Tm, Yb   Ln = La, Ce, Pr, Gd, Tb, Ho, Er, Lu

In 1991, Cloke reported a Sc(II) complex obtained by decomposition of a zero-valent Sc(0) complex made by metal vapor methods, eq 12.[75] In 1996–1998, Sc(I) and Sc(II) complexes were reported from metal vapor syntheses, eq 13,[76] X-ray crystal structures were reported for the Sc(0) and Sc(I) complexes, but not for the Sc(II) complex.[77]



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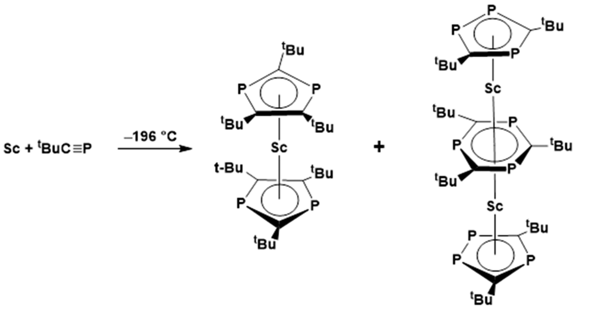
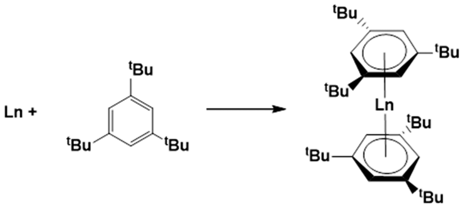


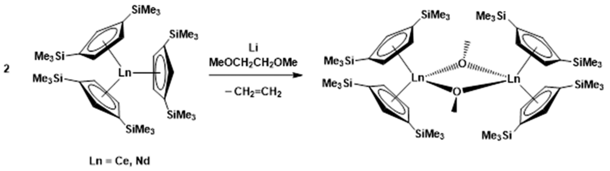
(13)

These results should have prompted rare-earth metal chemists to study more oxidation states. Indeed, the early results of Cloke on the formally Ln(0) complexes, $Ln(arene)_2$, eq 14,[78,79] made by metal vapor chemistry should have provided the stimulus. This did not happen, perhaps because these low oxidation state complexes were made by metal vapor methods and viewed as some exotic trapped species not accessible by solution synthetic methods. In this sense, these compounds were like the unusual species observed in gas-phase studies and cryogenic co-condensations in liquid helium and appeared to be accessible only with highly specialized vacuum equipment.



(14)

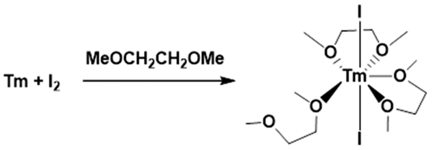
Earlier unsubstantiated reports of possible Ce(II)[80] and Nd(II)[81,82] complexes stimulated Lappert to try reductions of Cp''_3Ln with Ln = Ce and Nd in 1995 [$Cp'' = C_5H_3(SiMe_3)_2$]. These reactions formed methoxide complexes, eq 15, by C–O cleavage of the dimethoxyethane (DME) solvent.[83] He attributed this to a Ln(II) intermediate that could not be isolated. This was consistent with the earlier view that Ln(II) ions other than Eu, Yb, and Sm would decompose solvents.



(15)

In 1997–1998, Lappert reported EPR evidence for La(II)[84] and a $[K(18\text{-crown-}6)(C_6H_6)_2][(Cp^{tt}{}_2La)_2(C_6H_6)]$ ($Cp^{tt} = C_5{}^tBu_2H_3$) complex[85] that could be formulated as a La(II) $(C_6H_6)^-$ species. However, there was ambiguity in the oxidation state assignment because the complex could also be a La(III) complex of a benzene trianion.

At this same time, Bochkarev was also thinking about Ln(II) complexes beyond Eu, Yb, and Sm, but he was focused on the Tm, Dy, and Nd examples known in the solid state.[62,67,68] In 1997, Bochkarev synthesized TmI_2 from Tm and I_2 in dimethoxyethane, but he was not able to crystallize it. He asked our group to collaborate to get crystals. We agreed, although we were skeptical that Bochkarev had made the compounds because we believed it was not possible. Bochkarev sent us samples, but they did not diffract and we were not surprised. However, when we made a fresh batch and tried recrystallization, much to our amazement, single crystals of $TmI_2(DME)_3$ were isolated, eq 16.[86]



(16)

Bochkarev subsequently made DyI_2 and NdI_2 directly from the elements,[87] and crystallographic confirmation of molecular Ln(II) complexes of Dy(II) and Nd(II) was obtained on $DyI_2(DME)_3$[88] and $NdI_2(THF)_5$.[89] Even though these complexes decompose in minutes in THF at room temperature, which is consistent with earlier views on these Ln(II) ions, they were soluble, isolable, molecular species with solution chemistry that could be pursued at low temperature.

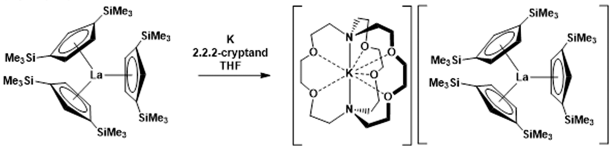
In retrospect, as early as 1959,[64] the existence of these Tm(II), Dy(II), and Nd(II) oxidation states in solid-state materials should have been pursued more vigorously by the molecular community. Clearly the solid-state systems had lessons for the molecular chemists that were not heeded. The fact that these oxidation states existed in a crystal field of halides in the solid state should have been taken as a lead to find other crystal fields that would stabilize them in molecular species.

What if that there are twice as many oxidation states available as you currently use in your chemistry? Imagine that the exotic species formed in the gas phase, in the solid state, in biological matrices, in nanoparticles, under high pressure, or in some extreme environments could also be accessible in solution with the right "What if?" experiment.

8. The Belief That Only Eu(II), Yb(II), Sm(II), Tm(II), Dy(II), and Nd(II) Would Form Molecular Complexes of Ln(II) Ions. By 2001, following the Bochkarev breakthroughs, it was established by X-ray crystallography that six members of the rare-earth metal series could form soluble molecular complexes containing Ln(II) ions.[70,90,91] At this point the molecular chemistry was fully consistent with the solid-state chemistry in this regard. LnI_2 compounds of Eu, Yb, Sm, Tm, Dy, and Nd were salt-like $(Ln^{2+})(I^-)_2$ compounds, whereas the LnI_2 compounds of the other metals existed as trivalent species, $(Ln^{3+})(I^-)_2(e^-)$ species with the (e^-) in a delocalized band originating from 5d orbitals, eq 11.

A convergence of several studies overcame the belief that there were only six Ln(II) ions available in solution as detailed in the following sections.

A La(II) Complex. In 2008, 13 years after his first attempt to make Ce(II) and Nd(II) compounds, Lappert published the X-ray crystal structure of a complex that was clearly an isolable La(II) species, eq 17.[92] However, the structure of the La(II) complex was unusual in that the bond distances were very similar to those of the La(III) precursor, Cp''_3La. All previous data on Ln(II) complexes showed bond distances for Ln(II) complexes that were 0.1−0.2 Å larger than their Ln(III) analogs,[93] a situation that followed their ionic radii.[6]



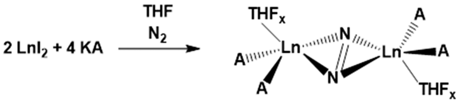
(17)

Lappert explained this discrepancy by that fact that La was at the beginning of the lanthanide series, where the 5d and 4f orbitals were similar in energy, such that La(II) was $5d^1$ not $4f^1$.[92] He also reported a Ce(II) analog, but this co-crystallized with a Cp''_3Ce complex that had similar bond distances.

The 2008 Lappert report was a major breakthrough, but extensions to the rest of the series were not immediately reported. Perhaps this was because it was thought that this was possible only with the metals at the beginning of the series. It is also possible that other metals were investigated, but did not crystallize,[94] or that other research groups, in deference to Professor Lappert, did not want to duplicate research already in progress in his laboratory.

What if an odd result in your area of chemistry that does not quite fit with the norm is the harbinger of a major new development in the field?

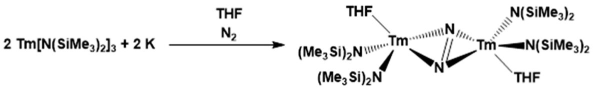
Reduced Dinitrogen Chemistry. Information on Ln(II) oxidation states beyond Eu, Yb, Sm, Tm, Dy, and Nd was also collected from reactivity studies involving the reduction of dinitrogen. Although the recently discovered TmI_2,[86] DyI_2,[88] and NdI_2[89] did not reduce N_2, addition of certain anionic ligands, A, to the diiodide complexes under N_2 led to $[A_2(THF)_xLn]_2N_2$ complexes containing $(N{=}N)^{2-}$ ions, eq 18.[95,96]



(18)

Ln = Nd, Dy, Tm
A = $C_5H_3(SiMe_3)_2$, $N(SiMe_3)_2$, $OC_6H_3{}^tBu_2$-2,6; x = 0, 1

Subsequently, it was found that these reduced dinitrogen $Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ complexes could be made by reduction of LnA_3 complexes without the difficult requirement of isolating LnI_2 starting materials, as shown for Tm in eq 19.[97]



(19)

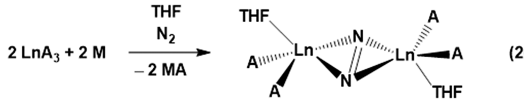
These results suggested that not only Tm(II), Dy(II), and Nd(II) chemistry, but also lanthanide-based dinitrogen activation discovered in 1988 with Sm (II), eq 10,[56] could have been accessed *decades earlier* in 1973 if the makers of the $Ln[N(SiMe_3)_2]_3$ complexes[98] had just tried to generate Tm(II), Dy(II), or Nd(II) complexes by reducing their trivalent compounds under N_2.

However, the belief that these ions were not accessible in solution was perhaps too strong such that these "What if?" reactions were never done. It is also possible that reductions were done, but because the intense colors of Ln(II) did not persist, it was assumed that decomposition had occurred, and the reactions were not pursued further. Indeed, if someone had investigated these reactions, they probably made the first rare-earth metal complexes of the $(N{=}N)^{2-}$ ligand, and these could have been isolated in 1973!

What if new classes of complexes or new reaction types could be discovered in your area of chemistry if you just investigated why a reaction did not go as planned based on a fading color?

https://doi.org/10.1021/jacs.1c08288

LnA$_3$/M Reactions. Although the Tm[N(SiMe$_3$)$_2$]$_3$/K reaction in eq 19 gave a reduced dinitrogen (N═N)$^{2-}$ product, the intense color of Tm(II) expected to be the active species was not observed. To probe the intermediacy of Ln(II), reactions with other rare-earth metals that had no known +2 oxidation states, i.e., Y, Gd, Tb, Ho, Er, and Lu, were tried and found to form similar Ln$_2$(μ-η^2:η^2-N$_2$) complexes with a variety of anionic ligands, A, eq 20.[97,99–105]



(20)

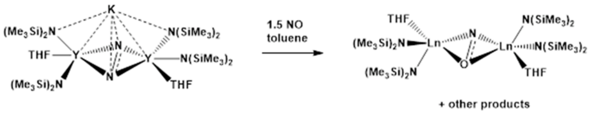
Ln = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu
A = C$_5$Me$_5$, C$_5$Me$_4$H, N(SiMe$_3$)$_2$, OC$_6$H$_3{}^t$Bu$_2$-2,6, C$_5$H$_3{}^t$Bu$_2$

The 2004 paper on these reactions stated that if Ln(II) intermediates were involved, this was the first evidence of Y(II), Gd(II), Tb(II), Ho(II), Er(II), and Lu(II).[99] However, it was not believed that they could exist in solution due to their very negative Ln(III)/Ln(II) reduction potentials.[41,42] Hence, the mechanism of N$_2$ reduction was unknown, and reactions by combinations like Gd[N(SiMe$_3$)$_2$]$_3$/K were a mystery, since the Gd(III)/Gd(II) 4f^7 to 4f^8 reduction potential was calculated to be −3.9 V vs SHE[41,42] and K had a generic redox potential of only −2.9 V vs SHE.[106,107]

Investigations of the LnA$_3$/K/N$_2$ chemistry continued and led to the first examples of complexes of the radical trianion, (N$_2$)$^{3-}$, eq 21.[104,108] Investigation of the reactivity of the (N$_2$)$^{3-}$ ligand led to the first isolation of the (NO)$^{2-}$ radical dianion, eq 22.[109]

(21)

Ln = Y, La, Gd, Tb, Dy, Lu

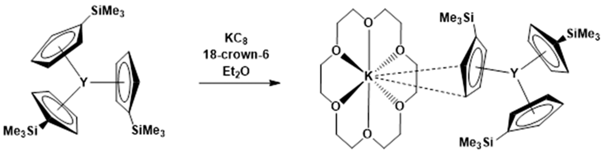


(22)

Despite decades of research on reduction of dinitrogen and nitric oxides in bioinorganic, catalytic, and industrial chemistry, these ions were never observed in isolated complexes. The identification of these simple diatomic radical anions was probably possible because of the ionic nature of the rare-earth metal complexes: this did not allow the trapped radical to communicate with the external environment and spin pair. Hence, this ionic nature of the rare-earth metal ions, originally viewed as a limitation, proved to offer new opportunities in small-molecule activation.

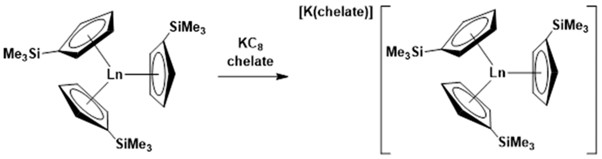
What if one of the main limitations in the chemistry you presently study is actually the basis for a major breakthrough in another area?

Evidence for Ln(II) intermediates in the N$_2$ reduction in eq 20 was not obtained until 2011, when the first EPR spectrum of Y(II) was obtained from a Y[N(SiMe$_3$)$_2$]$_3$/K reduction under argon.[110] In that same year, the first molecular complex of Y(II), [K(18-crown-6)][(C$_5$H$_4$SiMe$_3$)$_3$Y], was crystallographically characterized, eq 23.[111]



(23)

This synthesis was published as a stand-alone result because the authors did not anticipate that there would be analogous chemistry with other lanthanides. When analogous chemistry was found for Er(II) and Ho(II) in 2012,[112] this too was published on its own, because again it was not anticipated that this reaction chemistry would apply to the whole lanthanide series. However, in 2013, it was found that these (C$_5$H$_4$SiMe$_3$)$_3$Ln/K reactions would make molecular Ln(II) complexes for all the rest of the lanthanides, eq 24.[113]



(24)

Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
chelate = 18-crown-6, 2.2.2-cryptand

The isolation of Ln(II) complexes across the lanthanide series via potassium reduction was surprising because the estimated Ln(III)/Ln(II) redox potentials for 4f^n to 4f^{n+1} reactions[41,42,114,115] were more negative than the generic value of −2.9 V (vs SHE) for potassium. The new reductions were possible because the redox reaction involved a 4f^n to 4f^{n}5d^1 reduction based on structural, spectroscopic, magnetic, and theoretical analyses. Recently, the Ln(III)/Ln(II) reduction potentials for the entire series of (C$_5$H$_4$SiMe$_3$)$_3$Ln complexes have been determined experimentally via electrochemistry[121] and are between −2.55 and −2.74 V (vs SHE) for the 4f^{n}5d^1 Ln(II) complexes, which is well within the range for potassium reduction (−2.9 V vs SHE). Hence, the very reasonably calculated Ln(III)/Ln(II) redox potentials that had been used as a guide to Ln(II) chemistry with Eu, Yb, Sm, Tm, Dy, and Nd were calculated for the "wrong" redox reaction for the other lanthanide metals.[41,42,114,115]

The possibility of a 4f^n to 4f^{n}5d^1 reduction was actually foreshadowed by the solid-state LnI$_2$ chemistry.[61,62] As described above, LnI$_2$ complexes were known for the entire series, but only Eu, Yb, Sm, Tm, Dy, and Nd had 4f^{n+1} Ln(II) configurations. The rest were 4f^n Ln(III) complexes with a delocalized electron in a band formed by the 5d orbitals; i.e., they were 4f^{n}5d^1 compounds. The presence of a 5d electron in a Ln compound in the solid state was not controversial as early as the 1960s, probably because many electronic configurations are possible in the solid state.

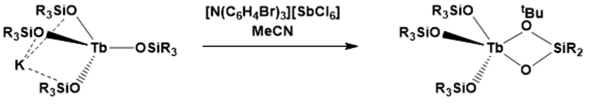
In retrospect, one can connect the dots and see the relationship between the solid-state results and the new 4f^{n}5d^1 Ln(II) ions, but it would have taken a big leap of imagination to suggest molecular 4f^{n}5d^1 species on the basis of the solid-state results. The discovery by Lappert[92] that La(II) was 5d^1 could have been linked to the solid-state results. Likewise, if someone had examined the f to d promotion energies for Ln(II) ions, known for decades in gas phase literature,[122] this would have suggested that reduction of 4f^7 Gd(III) species should be tried since this could form half-filled shell 4f^{7}5fd^1 Gd(II) ions. We now find that Gd is one of the best rare-earth metals for forming a wide variety of isolable 4f^{n}5d^1 Ln(II) complexes.[113,123–125] A hint of the 4f^{n}5d^1 series was also in the 3d^1 Sc(II) species reported in 1991,[76] but this species was not isolable in pure form for crystallographic characterization, and the chemistry was thought to be more transition-metal like.

What if other types of electron configurations could be accessed in the chemistry you do? What if there were other features in your chemistry as fundamental as new oxidation states and valence electron configurations that were accessible if only the proper experiment was done?

When this Perspective was initially conceived, the plan was to end at this point. However, recent developments have added another section!

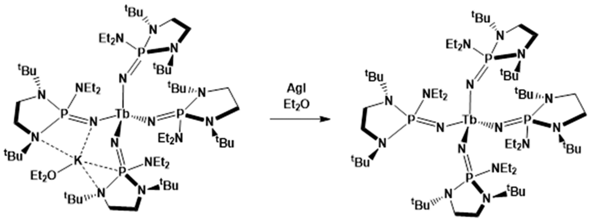
9. The Belief That Only Ce(IV) Would Form Molecular Complexes of Ln(IV). During the decade during which new +2 oxidation states were being found for the rare-earth metals and the actinides,[126−130] the idea arose that a similar breakthrough should be possible on the higher oxidation state side.[63] However, it was not clear how to achieve that. Extensive efforts by many groups explored exotic oxidants to expand Ce(IV) chemistry,[131] but extension to other metals was not published. The single molecular example of Tb(IV), the half-filled shell equivalent of Ce(IV), was from Hobart and Petersen in 1980 in 5.5 M carbonate solution.[132]

Then in 2017, *two groups* reported the first crystal structures of Tb(IV) complexes! In one case the special nature of alkoxysiloxide ligands used by Mazzanti seemed to be the reason for this breakthrough, along with a particular oxidant, magic blue, eq 25.[133] In the other case, a ligand carefully designed by La Pierre with just the right electronic and steric profile to stabilize Tb(IV) was developed, eq 26,[134] and the simple oxidant, Ag$^+$, was sufficient.



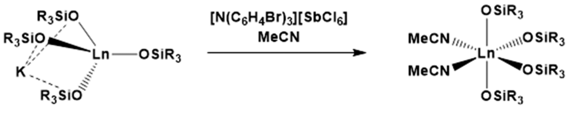
(25)

R = O^{t}Bu



(26)

Subsequently it was found that the triphenylsiloxide ligand, OSiPh$_3$, could stabilize Tb(IV) in a simple octahedral complex, eq 27.[135] Ln(OSiPh$_3$)$_3$ complexes were known in 1991,[136] so the potential to make Tb(IV) was present 20 years earlier if the appropriate "What if?" questions had been asked. The chemistry of the siloxides has since been extended to Pr(IV) with OSiPh$_3$, eq 27.[137]



(27)

Ln = Tb, Pr; R = Ph

It should be noted that, long before the molecular species were isolated, the existence of both Tb(IV) and Pr(IV) was known in over 30 solid-state examples, including commercially available mixed-valent Pr$_6$O$_{11}$ and Tb$_4$O$_7$.[138] Hence, this parallels the discovery of molecular complexes of Tm(II), Dy(II), and Nd(II), which had solid-state species known decades before.

What if results or compounds seemingly available only under special conditions, as simple as using strongly basic conditions, could be accessed using the methods of your current chemistry?

■ SUMMARY

It is worth repeating that many things become clear in a retrospective analysis that are difficult to realize in real time. The purpose of this Perspective is not to fault any of the previous researchers in the field. Those scientists, including our group, were doing the cutting-edge research they thought to be most important. In many cases, the "What if?" experiments described here that would have led to breakthroughs were outside the primary areas of interest.

For example, Wilkinson and co-workers could have identified the first Y(II) complex when they made (C$_5$H$_5$)$_3$Y in 1954,[13] simply by adding a reducing agent to a solution of this compound and observing the intense dark color that forms.[111] However, they were interested in developing the chemistry of the cyclopentadienyl ligand across the periodic table and were much more interested in expanding transition metal chemistry than finding new oxidation states in rare-earth metal chemistry. Similarly, Dubeck and co-workers were interested in octane boosters for gasoline and not organometallic rare-earth metal chemistry.[19,20] Tsutsui was most interested in transition metals and catalysis and just dabbled in rare-earth metal chemistry.[39]

In fact, the general belief that the rare-earth metals had limited chemistry meant that few groups were focused specifically on these elements until the 1980s. The experimental difficulty of studying these air-sensitive complexes also contributed to the dearth of activity in the area. Professor Schumann, who published a prodigious amount of organometallic rare-earth metal chemistry,[16] once told W.J.E. that he had tried to do rare-earth metal chemistry many years before his first rare-earth metal publications,[139] but he gave up the effort because the chemistry was too difficult experimentally for his group at that time.

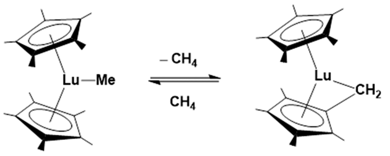
However, if someone had been interested in expanding organometallic rare-earth metal chemistry in 1966, when the first organometallic complexes of C$_5$Me$_5$ were published,[25,26] they could have discovered most of modern rare-earth metal chemistry in the 1960s with the 1950s methods used by Wilkinson!

What if currently there is an underdeveloped area that could be opened up just by combining decades-old technology with something as simple as a highly substituted ligand?

So perhaps one lesson from this retrospective is to look for underdeveloped areas that have potential and consider the "What if?" questions needed to develop them. Whitesides suggests "to start by identifying areas where change would matter, and then ask if imaginable science might cause this change."[2]

It should also be realized that some breakthroughs in science have no obvious prior results that could have allowed them to have been discovered earlier. In the rare-earth metal area, the metalation of methane by Watson at DuPont, eq 28,[140] is one example.

This reaction, which provided the first homogeneous activation of methane, was unexpected by the entire organometallic community and was only found by careful kinetic analysis. The results came out of a project to compare Lu and Hf, not a plan to study methane reactivity.[141] Another example is the zero-valent complexes described by Cloke, eq 14.[79] These metal



(28)

vapor reactions were extensions of transition metal chemistry,[142] but there was no precedent for the compounds isolated. Another unexpected synthetic discovery involved the sterically crowded $(C_5Me_5)_3Ln$ complexes, Scheme 2.[36,143] There was no basis to expect that an entire series of complexes could be synthesized that had metal−ligand bond distances 0.1 Å longer than previously observed. The isolation of the first examples of $(N_2)^{3-}$,[104] eq 21, and $(NO)^{2-}$,[109] eq 22, with rare-earth metals, was also unexpected. The fact that there were no clear forerunners for some of these advances in rare-earth metal chemistry suggests that much is still to be learned in this area.

OUTLOOK

Going forward in the rare-earth metal area, there seem to be several new targets involving oxidation states. Ln(0) chemistry is still limited to metal vapor chemistry, and Ln(I) complexes have only been realized with Sc, although Sm(I) was identified by Fong in 1966[144] by radiolytic methods in solid-state KCl matrices.[145] The discovery of methods to make Tb(IV) and Pr(IV) complexes suggests that it is only a matter of time until more Ln(IV) states are isolated. Even Pr(V) has been postulated in the literature.[146] Multiple bonding remains to be developed, and it seems likely that complexes containing ligands like CO should be accessible with the "right" ligand environment.[147,148] Although the rare-earth metals are effective in catalytic olefin, diene, and ring-opening polymerization and in the "hydroelementation" reactions[149] such as hydrogenation, hydrosilylation, and hydroamination, it seems that developing catalysis more broadly with these elements should be possible with the proper systems. For example, the oxophilicity of the f elements is often suggested as a barrier to catalysis with oxygen-containing substrates, since strong M−O bonds will form that will end the catalytic cycle. Eisen and co-workers have shown this is not true for uranium,[150,151] and rare-earth metal analogs probably exist. Conducting reactions under more unusual conditions also seems like a promising area. For example, new realms of rare-earth metal chemistry could be accessed by stopped-flow spectroscopy in microfluidic reactors or by conducting reactions in mini-reactors made of graphene or metal−organic frameworks. Roald Hoffmann has made a strong case to look at chemistry under extreme conditions such as high pressure to guide us to new chemistry.[152] Recent results in single-molecule magnet chemistry[153−155] and the use of organometallic rare-earth metal compounds as quantum bits, i.e., qubits,[156] suggest that these are also promising areas for the utilization of the special properties of the rare-earth metal ions.

However, the most important breakthroughs that will occur in rare-earth metal chemistry and in chemistry in general in the next decade are probably not definable right now. Although we may not be able to envision these breakthroughs at present, they are there, waiting to be discovered. The dots are there in front of us, if we can figure out how to connect them. We just need to formulate the proper "What if?" questions.

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the U.S. National Science Foundation (CHE-1855328 to W.J.E.) for support.

REFERENCES

(1) Ramón y Cajal, S. In *Advice to a Young Investigator*; Swanson, N., Swanson, L. W., Eds.; The MIT Press: Cambridge, MA, 1999; pp 10−11.

(2) Whitesides, G. M. Assumptions: Taking Chemistry in New Directions. *Angew. Chem., Int. Ed.* **2004**, *43*, 3632.

(3) Pimentel, G. C.; Spratley, R. D. *Understanding Chemistry*; Holden-Day: San Fransisco, CA, 1971; p 862.

(4) Moeller, T. The Chemistry of the Lanthanides. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; pp 1−101.

(5) Crosswhite, H. M.; Crosswhite, H.; Carnall, W. T.; Paszek, A. P. Spectrum Analysis of U^{3+}:$LaCl_3$. *J. Chem. Phys.* **1980**, 72, 5103−5117.

(6) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751−767.

(7) Hart, F. A.; Laming, F. P. Some O-Phenanthroline Complexes of Yttrium and the Lanthanides. *Proc. Chem. Soc. London* **1963**, 107.

(8) Thompson, L. C. Complexes. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Jr., Eds.; North-Holland Publishing Company: Amsterdam, 1979; pp 209−297. DOI: 10.1016/S0168-1273(79)03008-7

(9) Jaffé, H. H.; Doak, G. O. On the Stability of Metallo-Organic Compounds. *J. Chem. Phys.* **1953**, *21*, 196−200.

(10) Forsberg, J. H. Complexes of Lanthanide (III) Ions with Nitrogen Donor Ligands. *Coord. Chem. Rev.* **1973**, *10*, 195−226.

(11) Forsberg, J. H.; Moeller, T. Tris- and Tetrakisethylenediamine Chelates of Tripositive Lanthanide Ions. *J. Am. Chem. Soc.* **1968**, *90*, 1932.

(12) Gilman, H.; Jones, R. G. Organometallics Compounds of Titanium, Zirconium, and Lanthanum. *J. Org. Chem.* **1945**, *10*, 505−515.

(13) Wilkinson, G.; Birmingham, J. M. Cyclopentadienyl Compounds of Sc, Y, La, Ce and Some Lanthanide Elements. *J. Am. Chem. Soc.* **1954**, *76*, 6210.

(14) Birmingham, J. M.; Wilkinson, G. The Cyclopentadienides of Scandium, Yttrium and Some Rare Earth Elements. *J. Am. Chem. Soc.* **1956**, *78*, 42−44.

(15) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. Synthesis and Structural Characterisation of the First Neutral Homoleptic Lanthanide Metal(III) Alkyls: $[LnR_3]$ [Ln = La or Sm, R = $CH(SiMe_3)_2$]. *J. Chem. Soc., Chem. Commun.* **1988**, 3, 1007.

(16) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. Synthesis, Structure, and Reactivity of Organometallic. π-Complexes of the Rare Earths in the Oxidation State Ln^{3+} with Aromatic Ligands. *Chem. Rev.* **1995**, *95*, 865−986.

(17) Edelmann, F. T. Scandium, Yttrium, and the Lanthanide and Actinide Elements, Excluding Zero Oxidation State Complexes. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier B.V.: Amsterdam, 1995; pp 11−212.

(18) Cotton, F. A. Alkyls and aryls of transition metals. *Chem. Rev.* **1955**, *55*, 551−594.

(19) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. The Dicyclopentadienyllanthanide Chlorides. *J. Am. Chem. Soc.* **1963**, *85*, 672−676.

(20) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. The Preparation of Cyclopentadienyllanthanide Dichlorides. *Inorg. Chem.* **1963**, *2*, 904−905.

(21) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. Preparation and Molecular Structure of a σ-Bonded Lanthanide Phenyl. *J. Chem. Soc., Chem. Commun.* **1972**, 1225−1226.

(22) Ely, N. M.; Tsutsui, M. Organolanthanides and Organoactinides. XV. Synthesis and Properties of New σ-Bonded Organolanthanide Complexes. *Inorg. Chem.* **1975**, *14*, 2680−2687.

(23) Evans, W. J. Synthesis of Organolanthanide and Organoactinide Complexes. In *The Chemistry of the Metal Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley, 1982; pp 489−537.

(24) Evans, W. J. Organometallic Lanthanide Chemistry. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press, 1985; pp 131−177. DOI: 10.1016/S0065-3055(08)60415-3

(25) King, R. B.; Fronzaglia, A. Organometallic Chemistry of the Transition Metals. XV. New Olefinic and Acetylenic Derivatives of Tungsten. *Inorg. Chem.* **1966**, *5*, 1837−1846.

(26) King, R. B.; Bisnette, M. B. Organometallic Chemistry of the Transition Metals XXI. Some π-Pentamethylcyclopentadienyl Derivatives of Various Transition Metals. *J. Organomet. Chem.* **1967**, *8*, 287−297.

(27) Brintzinger, H. H.; Bercaw, J. E. Bis(Pentamethylcyclopentadienyl)Titanium(II). Isolation and Reactions with Hydrogen, Nitrogen, and Carbon Monoxide. *J. Am. Chem. Soc.* **1971**, *93*, 2045−2046.

(28) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. Reduction of Carbon Monoxide Promoted by Alkyl and Hydride Derivatives of Permethylzirconocene. *J. Am. Chem. Soc.* **1978**, *100*, 2716−2724.

(29) Manriquez, J. M.; Bercaw, J. E. Preparation of a Dinitrogen Complex of Bis(Pentamethylcyclopentadienyl)Zirconium(II). Isolation and Protonation Leading to Stoichiometric Reduction of Dinitrogen to Hydrazine. *J. Am. Chem. Soc.* **1974**, *96*, 6229−6230.

(30) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. Structure of μ-Dinitrogen-Bis(Bis(Pentamethylcyclopentadienyl)-Dinitrogenzirconium(II)), $\{(\eta^5\text{-}C_5(CH_3)_5)_2ZrN_2\}_2N_2$. *J. Am. Chem. Soc.* **1976**, *98*, 8351−8357.

(31) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. Bis(Pentamethylcyclopentadienyl)Actinide Chemistry: Properties of Stable Thorium and Uranium Dialkyls and Hydrides. *J. Am. Chem. Soc.* **1978**, *100*, 3939−3941.

(32) Wayda, A. L.; Evans, W. J. Synthesis of a Bis(Pentamethylcyclopentadienyl) Derivative of Neodymium. *Inorg. Chem.* **1980**, *19*, 2190−2191.

(33) Tilley, T. D.; Andersen, R. A. Pentamethylcyclopentadienyl Derivatives of the Trivalent Lanthanide Elements Neodymium, Samarium, and Ytterbium. *Inorg. Chem.* **1981**, *20*, 3267−3270.

(34) Watson, P. L.; Whitney, J. F.; Harlow, R. L. (Pentamethylcyclopentadienyl)Ytterbium and -Lutetium Complexes by Metal Oxidation and Metathesis. *Inorg. Chem.* **1981**, *20*, 3271−3278.

(35) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford Press, 1984.

(36) Evans, W. J.; Davis, B. L. Chemistry of Tris(Pentamethylcyclopentadienyl) f-Element Complexes, $(C_5Me_5)_3M$. *Chem. Rev.* **2002**, *102*, 2119−2136.

(37) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. Highly Reactive Organolanthanides. Systematic Routes to and Olefin Chemistry of Early and Late Bis(Pentamethylcyclopentadienyl) 4f Hydrocarbyl and Hydride Complexes. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103.

(38) DeVries, L. Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene, 1,2,3,4,5,5-Hexamethylcyclopentadiene, and 1,2,3,4,5-Pentamethylcyclopentadienylcarbinol. *J. Org. Chem.* **1960**, *25*, 1838.

(39) Tsutsui, M.; Gysling, J. A New Series of Organolanthanides: $Ln(Indenyl)_3$. *J. Am. Chem. Soc.* **1969**, *91*, 3175−3178.

(40) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 6−7.

(41) Morss, L. R. Comparative Thermochemical and Oxidation-Reduction Properties of Lanthanides and Actinides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: Amsterdam, 1994; pp 239−291.

(42) Morss, L. R. Thermochemical Properties of Yttrium, Lanthanum, and the Lanthanide Elements and Ions. *Chem. Rev.* **1976**, *76*, 827−841.

(43) Evans, W. J.; Engerer, S. C.; Neville, A. C. Nonaqueous Reductive Lanthanide Chemistry. 1. Reaction of Lanthanide Atoms with 1,3-Butadienes. *J. Am. Chem. Soc.* **1978**, *100*, 331−333.

(44) Evans, W. J.; Engerer, S. C.; Coleson, K. M. Reactivity of Lanthanide Metals with Unsaturated Hydrocarbons: Terminal Alkyne Reactions. *J. Am. Chem. Soc.* **1981**, *103*, 6672−6677.

(45) Evans, W. J.; Coleson, K. M.; Engerer, S. C. Reactivity of Lanthanide Metal Vapor with Unsaturated Hydrocarbons. Reactions with Ethene, Propene, and 1,2-Propadiene. *Inorg. Chem.* **1981**, *20*, 4320−4325.

(46) Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer, 1979.

(47) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academis Press: New York, 1980.

(48) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. Syntheis and X-Ray Crystal Structure of a Soluble Divalent Organosamarium Complex. *J. Am. Chem. Soc.* **1981**, *103*, 6507−6508.

(49) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. Reductive Homologation of Carbon Monoxide to a Ketenecarboxylate by a Low-Valent Organolanthanide Complex: Synthesis and X-Ray Crystal Structure of $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$. *J. Am. Chem. Soc.* **1985**, *107*, 3728−3730.

(50) Evans, W. J.; Drummond, D. K. Insertion of Two CO Moieties into an Alkene Double Bond to Form a $RCH{=}C(O)C(O){=}CHR^{2-}$ Unit via Organosamarium Activation. *J. Am. Chem. Soc.* **1988**, *110*, 2772−2774.

(51) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. Facile Stereospecific Synthesis of a Dihydroxyindenoindene Unit from an Alkyne and Carbon Monoxide via Samarium-Mediated Carbon Monoxide and CH Activation. *J. Am. Chem. Soc.* **1986**, *108*, 1722−1723.

(52) Girard, P.; Namy, J. L.; Kagan, B. Divalent Lanthanide Derivatives in Organic Synthesis. 1. Mild Preparation of SmI_2 and YbI_2 and Their Use as Reducing or Coupling Agents. *J. Am. Chem. Soc.* **1980**, *102*, 2693−2698.

(53) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. Solution Synthesis and Crystallographic Characterization of the Divalent Organosamarium Complexes $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$. *J. Am. Chem. Soc.* **1985**, *107*, 941−946.

(54) Procter, D. J.; Flowers, R. A.; Skrydstrup, T. *Organic Synthesis Using Samarium Diiodide*; Royal Society of Chemistry: Cambridge, 2009.

(55) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. Synthesis and Crystallographic Characterization of an Unsolvated, Monomeric Bis(Pentamethylcyclopentadienyl) Organolanthanide Complex, $(C_5Me_5)_2Sm$. *J. Am. Chem. Soc.* **1984**, *106*, 4270−4272.

(56) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Isolation and X-Ray Crystal Structure of the First Dinitrogen Complex of an f-Element Metal, $[(C_5Me_5)_2Sm]_2N_2$. *J. Am. Chem. Soc.* **1988**, *110*, 6877−6879.

(57) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. Organosamarium-Mediated Synthesis of Bismuth Bismuth Bonds: X-Ray Crystal Structure of the First Dibismuth Complex Containing a Planar $M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ Unit. *J. Am. Chem. Soc.* **1991**, *113*, 9880−9882.

(58) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Reactivity of $(C_5Me_5)_2Sm$ with Aryl-Substituted Alkenes: Synthesis and Structure of a Bimetallic Styrene Complex That Contains an η^2-Arene Lanthanide Interaction. *J. Am. Chem. Soc.* **1990**, *112*, 219−223.

(59) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. The Reactivity of $(C_5Me_5)_2Sm(THF)_2$ with Bis(2-Pyridyl)Ethene Including the Synthesis of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PyCHCHpy)]$ from $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}1,2,3,4\text{-}(Py)_4C_4H_4]$ by Reductive C-C Bond Cleavage. *Organometallics* **1993**, *12*, 4664−4667.

(60) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2014; pp 134−162.

(61) Meyer, G. Reduced Halides of the Rare-Earth Elements. *Chem. Rev.* **1988**, *88*, 93−107.

(62) Meyer, G. The Divalent State in Solid Rare-Earth Metal Haldes. In *The Rare Earth Elements: Fundamentals and Applications*; Atwood, D. A., Ed.; Wiley: New York, 2012; pp 241−300.

(63) Woen, D. H.; Evans, W. J. Expanding the +2 Oxidation State of the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes. In *Handbook on the Physics and Chemistry of Rare Earths*; Bünzli, J.-C., Pecharsky, V. K., Eds.; Elsevier B.V., 2016; pp 1−57.

(64) Druding, L. F.; Corbett, J. D. Rare Earth Metal-Metal Halide Systems. the Preparation of Neodymium(II) Halides. *J. Am. Chem. Soc.* **1959**, *81*, 5512−5512.

(65) Asprey, L. B.; Kruse, F. H. Divalent Thulium. Thulium Di-Iodide. *J. Inorg. Nucl. Chem.* **1960**, *13*, 32−35.

(66) Corbett, J. D.; McCollum, B. C. Rare Earth Metal-Metal Halide Systems. IX. The Dysprosium-Dysprosium(III) Chloride System and the Preparation of Dysprosium(II) Chloride. *Inorg. Chem.* **1966**, *5*, 938−940.

(67) Meyer, G.; Meyer, H. J. Unusual Valences in Rare-Earth Halides. *Chem. Mater.* **1992**, *4*, 1157−1168.

(68) Meyer, G.; Wickleder, M. S. Simple and Complex Halides. *Handbook on the Physics and Chemistry of Rare Earths*; Elsevier Science: Amsterdam, 2000; pp 53−129.

(69) Nief, F. Molecular Chemistry of the Rare-Earth Elements in Uncommon Low-Valent States. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Bunzil, J.-C. G., Pecharsky, V. K., Eds.; Elsevier Science: Amsterdam, 2010; pp 241−300.

(70) Bochkarev, M. N. Molecular Compounds of "New" Divalent Lanthanides. *Coord. Chem. Rev.* **2004**, *248*, 835−851.

(71) Kamenskaya, A. N.; Mikheev, N. B.; Konovalova, N. A. Reduction of Thulium, Samarium, and Ytterbium Halides to the Bivalent State in Hexamethylphosphoramide Solutions. *Russ. J. Inorg. Chem.* **1977**, *22*, 1152−1155.

(72) Kamenskaya, A. N.; Bukietynska, K.; Mikheev, N. B.; Spitsyn, V. I.; Jezowska-Trzebiatowska, B. Properties of Non-Aqueous Solutions of Lanthanide Dihalides. *Russ. J. Inorg. Chem.* **1979**, *24*, 633−637.

(73) Kamenskaya, A. N.; Mikheev, N. B.; Kholmogorova, N. Solutions of Lanthanide Di-Iodides in Tetrahydrofuran. *Russ. J. Inorg. Chem.* **1983**, *28*, 1420−1423.

(74) Kamenskaya, A. N.; Mikheev, N. B.; Spytsin, V. I. Complex Compounds of Bivalent Samarium and Thulium with Crown Ethers. *Dokl. Akad. Nauk SSSR* **1984**, *275*, 913−916.

(75) Cloke, F. G. N.; Khan, K.; Perutz, R. N. η-Arene Complexes of Scandium(0) and Scandium(II). *J. Chem. Soc., Chem. Commun.* **1991**, No. 19, 1372−1373.

(76) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F. The First Example of a Formal Scandium(I) Complex: Synthesis and Molecular Structure of a 22-Electron Scandium Triple Decker Incorporating the Novel 1,3,5-Triphosphabenzene Ring. *J. Am. Chem. Soc.* **1996**, *118*, 7630−7631.

(77) Arnold, P. L.; Cloke, F. G. N.; Nixon, J. F. The First Stable Scandocene: Synthesis and Characterisation of Bis(η-2,4,5-Tri-Tert-Butyl-1,3-Diphosphacyclopentadienyl)Scandium(II). *Chem. Commun.* **1998**, *1*, 797−798.

(78) Brennan, J. G.; Cloke, F. G. N.; Sameh, A. A.; Zalkin, A. Synthesis of Bis(η-1,3,5-Tri-t-Butylbenzene) Sandwich Complexes of Yttrium(0) and Gadolinium(0); the X-Ray Crystal Structure of the First Authentic Lanthanide(0) Complex, $[Gd(\eta\text{-}Bu^t{}_3C_6H_3)_2]$. *J. Chem. Soc., Chem. Commun.* **1987**, No. 21, 1668−1669.

(79) Cloke, F. G. N. Zero Oxidation State Compounds of Scandium, Yttrium, and the Lanthanides. *Chem. Soc. Rev.* **1993**, *22*, 17−24.

(80) Greco, A.; Cesca, S.; Bertolini, G. New π-Cyclooctatetraenyl and π-Cyclopentadienyl Complexes of Cerium. *J. Organomet. Chem.* **1976**, *113*, 321−330.

(81) Wedler, M.; Recknagel, A.; Edelmann, F. T. Nichtklassische Und Reaktivitit Organolanthanoid(II)Komplexe: Darstelung Der Ersten Organoneodym(II)Verbindung. *J. Organomet. Chem.* **1990**, *395*, C26−C29.

(82) Kirillov, E. N.; Trifonov, A. A.; Nefedov, S. E.; Eremenko, I. L.; Edelmann, F. T.; Bochkarev, M. N. Attempted Synthesis of Divalent Neodymium Derivatives. Crystal Structure of the Nd(III) Complex $[\{NdCl_2(2,4,6\text{-t-}Bu_3C_6H_2O)(\mu\text{-}Cl)(THF)\}Li(THF)_2]_2$. *Z. Naturforsch., B: J. Chem. Sci.* **1999**, *54b*, 1379−1384.

(83) Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. Activation of a CO Bond by Reaction of a Tris(Cyclopentadienyl)Lanthanide Complex with an Alkali Metal in Dimethoxyethane (DME); Crystal Structures of $[Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}OMe)_2Li(DME)]$ and $[\{Ce(\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3)_2(\mu\text{-}OMe)\}_2]$. *J. Organomet. Chem.* **1995**, *499*, 213−219.

(84) Cassani, M. C.; Lappert, M. F.; Laschi, F. First Identification by EPR Spectra of Lanthanum(II) Organometallic Intermediates (and $E_{1/2}$ for La^{3+}-La^{2+}) in the C-O Bond Activation of Dimethoxyethane. *Chem. Commun.* **1997**, *2*, 1563−1564.

(85) Cassani, M. C.; Duncalf, D. J.; Lappert, M. F. The First Example of a Crystalline Subvalent Organolanthanum Complex: $[K([18]\text{-}Crown\text{-}6)\text{-}(\eta^2\text{-}C_6H_6)_2][(LaCp^{tt}{}_2)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]\cdot 2C_6H_6$ ($Cp^{tt} = \eta^5\text{-}C_5H_3Bu^t{}_2\text{-}1,3$). *J. Am. Chem. Soc.* **1998**, *120*, 12958−12959.

(86) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. Synthesis and Structure of the First Molecular Thulium(II) Complex: $[TmI_2(MeOCH_2CH_2OMe)_2]$. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 133−135.

(87) Bochkarev, M. N.; Fagin, A. A. A New Route to Neodymium(II) and Dysprosium(II) Iodides. *Chem. - Eur. J.* **1999**, *5*, 2990−2992.

(88) Evans, W. J.; Allen, N. T.; Ziller, J. W. The Availability of Dysprosium Diiodide as a Powerful Reducing Agent in Organic Synthesis: Reactivity Studies and Structural Analysis of $DyI_2(DME)_3$ and Its Naphthalene Reduction Product. *J. Am. Chem. Soc.* **2000**, *122*, 11749−11750.

(89) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. $[NdI_2(THF)_5]$, the First Crystallographically Authenticated Neodymium(II) Complex. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176−3178.

(90) Evans, W. J. The Expansion of Divalent Organolanthanide Reduction Chemistry via New Molecular Divalent Complexes and Sterically Induced Reduction Reactivity of Trivalent Complexes. *J. Organomet. Chem.* **2002**, *647*, 2−11.

(91) Evans, W. J. Recent Advances in f Element Reduction Chemistry. *J. Organomet. Chem.* **2002**, *652*, 61−68.

(92) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. Lanthanum Does Form Stable Molecular Compounds in the + 2 Oxidation State. *Angew. Chem., Int. Ed.* **2008**, *47*, 1488−1491.

(93) Evans, W. J.; Foster, S. E. Structural Trends in Bis-(Pentamethylcyclopentadienyl)Lanthanide and Yttrium Complexes. *J. Organomet. Chem.* **1992**, *433*, 79−94.

(94) Coles, M. P.; Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. Syntheses and Structures of the Crystalline, Hightly Crowded 1,3-Bis(Trimethylsilyl)Cyclopentadienyls $[MCp''_3]$ (M = Y, Er, Yb), $[PbCp''_2]$, $[\{YCp''_2(\mu\text{-}OH)\}_2]$, $[(ScCp''_2)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2H_4)]$, $[YbCp''_2Cl(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)]$, and $[\{KCp''\}_\infty]$. *Organometallics* **2012**, *31*, 2682−2690.

(95) Evans, W. J.; Allen, N. T.; Ziller, J. W. Expanding Divalent Organolanthanide Chemistry: The First Organothulium(II) Complex and the in Situ Organodysprosium(II) Reduction of Dinitrogen. *Angew. Chem., Int. Ed.* **2002**, *41*, 359−361.

(96) Evans, W. J.; Zucchi, G.; Ziller, J. W. Dinitrogen Reduction by Tm(II), Dy(II), and Nd(II) with Simple Amide and Aryloxide Ligands. *J. Am. Chem. Soc.* **2003**, *125*, 10−11.

(97) Evans, W. J.; Lee, D. S.; Ziller, J. W. Reduction of Dinitrogen to Planar Bimetallic $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes of Y, Ho, Tm, and Lu Using the $K/Ln[N(SiMe_3)_2]_3$ Reduction System. *J. Am. Chem. Soc.* **2004**, *126*, 454−455.

(98) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low Co-Ordination Numbers in Lanthanide and Actinide Compounds. Part I. The Preparation and Characterization of Tris{bis(Trimethylsilyl)-Amido}-lanthanides. *J. Chem. Soc., Dalton Trans.* **1973**, No. 10, 1021.

(99) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. Expanding the LnZ_3/Alkali-Metal Reduction System to Organometallic and Heteroleptic Precursors: Formation of Dinitrogen Derivatives of Lanthanum. *Angew. Chem., Int. Ed.* **2004**, *43*, 5517−5519.

(100) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. Expanding Dinitrogen Reduction Chemistry to Trivalent Lanthanides via the LnZ_3/Alkali Metal Reduction System: Evaluation of the Generality of Forming $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes via LnZ_3/K. *J. Am. Chem. Soc.* **2004**, *126*, 14574−14582.

(101) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. The Elusive$(C_5Me_4H)_3Lu$: Its Synthesis and $LnZ_3/K/N_2$ Reactivity. *Organometallics* **2005**, *24*, 6393−6397.

(102) Evans, W. J.; Lee, D. S.; Ziller, J. W.; Kaltsoyannis, N. Trivalent $[(C_5Me_5)_2(THF)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Complexes as Reducing Agents Including the Reductive Homologation of CO to a Ketene Carboxylate, $(\mu\text{-}\eta^4\text{-}O_2C\text{-}C{=}C{=}O)^{2-}$. *J. Am. Chem. Soc.* **2006**, *128*, 14176−14184.

(103) Evans, W. J.; Lorenz, S. E.; Ziller, J. W. Investigating Metal Size Effects in the $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ Reduction System: Reductive Reactivity with Complexes of the Largest and Smallest Trivalent Lanthanide Ions, La^{3+} and Lu^{3+}. *Inorg. Chem.* **2009**, *48*, 2001−2009.

(104) Evans, W. J.; Fang, M.; Zucchi, G. L. G.; Furche, F.; Ziller, J. W.; Hoekstra, R. M.; Zink, J. I. Isolation of Dysprosium and Yttrium Complexes of a Three-Electron Reduction Product in the Activation of Dinitrogen, the $(N_2)^{3-}$ Radical. *J. Am. Chem. Soc.* **2009**, *131*, 11195−11202.

(105) Demir, S.; Lorenz, S. E.; Fang, M.; Furche, F.; Meyer, G.; Ziller, J. W.; Evans, W. J. Synthesis, Structure, and Density Functional Theory Analysis of a Scandium Dinitrogen Complex, $[(C_5Me_4H)_2Sc]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$. *J. Am. Chem. Soc.* **2010**, *132*, 11151−11158.

(106) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877−910.

(107) CRC Handbook of Chemistry and Physics. In *CRC Handbook of Chemistry and Physics*; Haynes, W. M., Lide, D. R., Bruno, T. J., Eds.; CRC Press, 2016; pp 943−950.

(108) Fang, M.; Bates, J. E.; Lorenz, S. E.; Lee, D. S.; Rego, D. B.; Ziller, J. W.; Furche, F.; Evans, W. J. $(N_2)^{3-}$ Radical Chemistry via Trivalent Lanthanide Salt/Alkali Metal Reduction of Dinitrogen: New Syntheses and Examples of $(N_2)^{2-}$ and $(N_2)^{3-}$ Complexes and Density Functional Theory Comparisons of Closed Shell Sc^{3+}, Y^{3+}, and Lu^{3+} versus $4f^9$ Dy^{3+}. *Inorg. Chem.* **2011**, *50*, 1459−1469.

(109) Evans, W. J.; Fang, M.; Bates, J. E.; Furche, F.; Ziller, J. W.; Kiesz, M. D.; Zink, J. I. Isolation of a Radical Dianion of Nitrogen Oxide $(NO)^{2-}$. *Nat. Chem.* **2010**, *2*, 644−647.

(110) Fang, M.; Lee, D. S.; Ziller, J. W.; Doedens, R. J.; Bates, J. E.; Furche, F.; Evans, W. J. Synthesis of the $(N_2)^{3-}$ Radical from Y^{2+} and Its Protonolysis Reactivity To Form $(N_2H_2)^{2-}$ via the $Y[N(SiMe_3)_2]_3/KC_8$ Reduction System. *J. Am. Chem. Soc.* **2011**, *133*, 3784−3787.

(111) MacDonald, M. R.; Ziller, J. W.; Evans, W. J. Synthesis of a Crystalline Molecular Complex of Y^{2+}, [(18-Crown-6)K]-$[(C_5H_4SiMe_3)_3Y]$. *J. Am. Chem. Soc.* **2011**, *133*, 15914−15917.

(112) MacDonald, M. R.; Bates, J. E.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Expanding Rare-Earth Oxidation State Chemistry to Molecular Complexes of Holmium(II) and Erbium(II). *J. Am. Chem. Soc.* **2012**, *134*, 8420−8423.

(113) MacDonald, M. R.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Completing the Series of + 2 Ions for the Lanthanide Elements: Synthesis of Molecular Complexes of Pr^{2+}, Gd^{2+}, Tb^{2+}, and Lu^{2+}. *J. Am. Chem. Soc.* **2013**, *135*, 9857−9868.

(114) Mikheev, N. B.; Auerman, L. N.; Rumer, I. A.; Kamenskaya, A. N.; Kazakevich, M. Z. The Anomalous Stabilisation of the Oxidation State 2+ of Lanthanides and Actinides. *Russ. Chem. Rev.* **1992**, *61*, 990−998.

(115) David, F. H. About Low Oxidation States, Hydration and Covalence Properties of *f*-Elements. *Radiochim. Acta* **2008**, *96*, 135−144.

(116) Fieser, M. E.; MacDonald, M. R.; Krull, B. T.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Structural, Spectroscopic, and Theoretical Comparison of Traditional vs Recently Discovered Ln^{2+} Ions in the $[K(2.2.2\text{-Cryptand})][(C_5H_4SiMe_3)_3Ln]$ Complexes: The Variable Nature of Dy^{2+} and Nd^{2+}. *J. Am. Chem. Soc.* **2015**, *137*, 369−382.

(117) Meihaus, K. R.; Fieser, M. E.; Corbey, J. F.; Evans, W. J.; Long, J. R. Record High Single-Ion Magnetic Moments Through $4f^n5d^1$ Electron Configurations in the Divalent Lanthanide Complexes $[(C_5H_4SiMe_3)_3Ln]^-$. *J. Am. Chem. Soc.* **2015**, *137*, 9855−9860.

(118) Lauher, J. W.; Hoffmann, R. Structure and Chemistry of Bis(Cyclopentadienyl)-ML_n Complexes. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

(119) Strittmatter, R. J.; Bursten, B. E. Bonding in Tris(η^5-Cyclopentadienyl) Actinide Complexes. 5. A Comparison of the Bonding in Np, Pu, and Transplutonium Compounds with That in Lanthanide Compounds and a Transition-Metal Analogue. *J. Am. Chem. Soc.* **1991**, *113*, 552−559.

(120) Denning, R. G.; Harmer, J.; Green, J. C.; Irwin, M. Covalency in the 4f Shell of Tris-Cyclopentadienyl Ytterbium ($YbCp_3$)-A Spectroscopic Evaluation. *J. Am. Chem. Soc.* **2011**, *133*, 20644−20660.

(121) Trinh, M. T.; Wedal, J. C.; Evans, W. J. Evaluating Electrochemical Accessibility of $4f^n5d^1$ and $4f^{n+1}$ Ln(II) Ions in $(C_5H_4SiMe_3)_3Ln$ and $(C_5Me_4H)_3Ln$ Complexes. *Dalton Trans.* **2021**, *50*, 14384−14389.

(122) Dorenbos, P. f - d Transition Energies of Divalent Lanthanides in Inorganic Compounds. *J. Phys.: Condens. Matter* **2003**, *15*, 575−594.

(123) Ryan, A. J.; Darago, L. E.; Balasubramani, S. G.; Chen, G. P.; Ziller, J. W.; Furche, F.; Long, J. R.; Evans, W. J. Synthesis, Structure, and Magnetism of Tris(Amide) $[Ln\{N(SiMe_3)_2\}_3]^{1-}$ Complexes of the Non-Traditional + 2 Lanthanide Ions. *Chem. - Eur. J.* **2018**, *24*, 7702−7709.

(124) Jenkins, T. F.; Woen, D. H.; Mohanam, L. N.; Ziller, J. W.; Furche, F.; Evans, W. J. Tetramethylcyclopentadienyl Ligands Allow Isolation of Ln(II) Ions across the Lanthanide Series in $[K(2.2.2\text{-Cryptand})][(C_5Me_4H)_3Ln]$ Complexes. *Organometallics* **2018**, *37*, 3863−3873.

(125) Angadol, M. A.; Woen, D. H.; Windorff, C. J.; Ziller, J. W.; Evans, W. J. Tert-Butyl(Cyclopentadienyl) Ligands Will Stabilize Nontraditional + 2 Rare-Earth Metal Ions. *Organometallics* **2019**, *38*, 1151−1158.

(126) MacDonald, M. R.; Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Identification of the + 2 Oxidation State for Uranium in a Crystalline Molecular Complex, [K(2.2.2-Cryptand)]-$[(C_5H_4SiMe_3)_3U]$. *J. Am. Chem. Soc.* **2013**, *135*, 13310−13313.

(127) La Pierre, H. S.; Scheurer, A.; Heinemann, F. W.; Hieringer, W.; Meyer, K. Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding. *Angew. Chem., Int. Ed.* **2014**, *53*, 7158−7162.

(128) Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Synthesis, Structure, and Reactivity of Crystalline Molecular Complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ Anion Containing Thorium in the Formal + 2 Oxidation State. *Chem. Sci.* **2015**, *6*, 517−521.

(129) Su, J.; Windorff, C. J.; Batista, E. R.; Evans, W. J.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L.; Woen, D. H.; Yang, P. Identification of the Formal + 2 Oxidation State of Neptunium:

Synthesis and Structural Characterization of $\{Np^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$. *J. Am. Chem. Soc.* **2018**, *140*, 7425−7428.

(130) Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. Identification of the Formal + 2 Oxidation State of Plutonium: Synthesis and Characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^{-}$. *J. Am. Chem. Soc.* **2017**, *139*, 3970−3973.

(131) Anwander, R.; Dolg, M.; Edelmann, F. T. The Difficult Search for Organocerium(IV) Compounds. *Chem. Soc. Rev.* **2017**, *46*, 6697−6709.

(132) Hobart, D. E.; Samhoun, K.; Young, J. P.; Norvell, V. E.; Mamantov, G.; Peterson, J. R. Stabilization of Praseodymium(IV) and Terbium(IV) in Aqueous Carbonate Solution. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 321−328.

(133) Palumbo, C. T.; Zivkovic, I.; Scopelliti, R.; Mazzanti, M. Molecular Complex of Tb in the + 4 Oxidation State. *J. Am. Chem. Soc.* **2019**, *141*, 9827−9831.

(134) Rice, N. T.; Popov, I. A.; Russo, D. R.; Bacsa, J.; Batista, E. R.; Yang, P.; Telser, J.; La Pierre, H. S. Design, Isolation, and Spectroscopic Analysis of a Tetravalent Terbium Complex. *J. Am. Chem. Soc.* **2019**, *141*, 13222−13233.

(135) Willauer, A. R.; Palumbo, C. T.; Scopelliti, R.; Zivkovic, I.; Douair, I.; Maron, L.; Mazzanti, M. Stabilization of the Oxidation State +IV in Siloxide-Supported Terbium Compounds. *Angew. Chem., Int. Ed.* **2020**, *59*, 3549−3553.

(136) Evans, W. J.; Golden, R. E.; Ziller, J. W. A Comparative Synthetic and Structural Study of Triphenylmethoxide and Triphenylsiloxide Complexes of the Early Lanthanides, Including X-Ray Crystal Structures of $La_2(OCPh_3)_6$ and $Ce_2(OSiPh_3)_6$. *Inorg. Chem.* **1991**, *30*, 4963−4968.

(137) Willauer, A. R.; Palumbo, C. T.; Fadaei-Tirani, F.; Zivkovic, I.; Douair, I.; Maron, L.; Mazzanti, M. Accessing the +IV Oxidation State in Molecular Complexes of Praseodymium. *J. Am. Chem. Soc.* **2020**, *142*, 5538−5542.

(138) Gompa, T. P.; Ramanathan, A.; Rice, N. T.; La Pierre, H. S. The Chemical and Physical Properties of Tetravalent Lanthanides: Pr, Nd, Tb, and Dy. *Dalton Trans.* **2020**, *49*, 15945−15987.

(139) Schumann, H.; Müller, J. Metallorganische Verbindungen Der Lanthaniden. *J. Organomet. Chem.* **1978**, *146*, C5−C7.

(140) Watson, P. L. Methane Exchange Reactions of Lanthanide and Early-Transition-Metal Methyl Complexes. *J. Am. Chem. Soc.* **1983**, *105*, 6491−6493.

(141) Watson, P. L.; Parshall, G. W. Organolanthanides in Catalysis. *Acc. Chem. Res.* **1985**, *18*, 51−56.

(142) Cloke, F. G. N.; Green, M. L. H. Synthesis of Zerovalent Bis(η-Arene) Compounds of Zirconium, Hafnium, Niobium, Tantalum, and Tungsten Using the Metal Vapours. *J. Chem. Soc., Dalton Trans.* **1981**, No. 9, 1938−1943.

(143) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. Synthesis and X-Ray Crystal Structure of the First Tris(Pentamethylcyclopentadienyl)Metal Complex: $(\eta^5\text{-}C_5Me_5)_3Sm$. *J. Am. Chem. Soc.* **1991**, *113*, 7423−7424.

(144) Fong, F. K.; Cape, J. A.; Wong, E. Y. Monovalent Samarium in Potassium Chloride. *Phys. Rev.* **1966**, *151*, 299−303.

(145) Fong, F. K.; Fenn, J. B.; Mccaldin, J. O. Reactions in Crystalline Lattices: Chemistry of Lower Valence States of Lanthanides. *J. Chem. Phys.* **1970**, *53*, 1559−1565.

(146) Zhang, Q.; Hu, S. X.; Qu, H.; Su, J.; Wang, G.; Lu, J. B.; Chen, M.; Zhou, M.; Li, J. Pentavalent Lanthanide Compounds: Formation and Characterization of Praseodymium(V) Oxides. *Angew. Chem., Int. Ed.* **2016**, *55*, 6896−6900.

(147) Maron, L.; Eisenstein, O.; Andersen, R. A. The Bond between CO and Cp'$_3$U in Cp'$_3$U(CO) Involves Back-Bonding from the Cp'$_3$U Ligand-Based Orbitals of π-Symmetry, Where Cp' Represents a Substituted Cyclopentadienyl Ligand. *Organometallics* **2009**, *28*, 3629−3635.

(148) Evans, W. J.; Kozimor, S. A.; Nyce, G. W.; Ziller, J. W. Comparative Reactivity of Sterically Crowded nf^3 $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3U$ Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex. *J. Am. Chem. Soc.* **2003**, *125*, 13831−13835.

(149) Weiss, C. J.; Marks, T. J. Organo-f-Element Catalysts for Efficient and Highly Selective Hydroalkoxylation and Hydrothiolation. *Dalton Trans.* **2010**, *39*, 6576−6588.

(150) Liu, H.; Ghatak, T.; Eisen, M. S. Organoactinides in Catalytic Transformations: Scope, Mechanisms and Quo Vadis. *Chem. Commun.* **2017**, *53*, 11278−11297.

(151) Batrice, R. J.; Kefalidis, C. E.; Maron, L.; Eisen, M. S. Actinide-Catalyzed Intermolecular Addition of Alcohols to Carbodiimides. *J. Am. Chem. Soc.* **2016**, *138*, 2114−2117.

(152) Rahm, M.; Cammi, R.; Ashcroft, N. W.; Hoffmann, R. Squeezing All Elements in the Periodic Table: Electron Configuration and Electronegativity of the Atoms under Compression. *J. Am. Chem. Soc.* **2019**, *141*, 10253.

(153) Goodwin, C. A. P.; Ortu, F.; Reta, D.; Chilton, N. F.; Mills, D. P. Molecular Magnetic Hysteresis at 60 K in Dysprosocenium. *Nature* **2017**, *548*, 439−442.

(154) Guo, F.; Day, B. M.; Chen, Y.; Tong, M.; Mansikkamäki, A.; Layfield, R. A. Magnetic Hysteresis up to 80 K in a Dysprosium Metallocene Single-Molecule Magnet. *Science* **2018**, *362*, 1400−1403.

(155) Gould, C. A.; McClain, K. R.; Yu, J. M.; Groshens, T. J.; Furche, F.; Harvey, B. G.; Long, J. R. Synthesis and Magnetism of Neutral, Linear Metallocene Complexes of Terbium(II) and Dysprosium(II). *J. Am. Chem. Soc.* **2019**, *141*, 12967−12973.

(156) Ariciu, A. M.; Woen, D. H.; Huh, D. N.; Nodaraki, L. E.; Kostopoulos, A. K.; Goodwin, C. A. P.; Chilton, N. F.; McInnes, E. J. L.; Winpenny, R. E. P.; Evans, W. J.; Tuna, F. Engineering Electronic Structure to Prolong Relaxation Times in Molecular Qubits by Minimising Orbital Angular Momentum. *Nat. Commun.* **2019**, *10*, 1−8.