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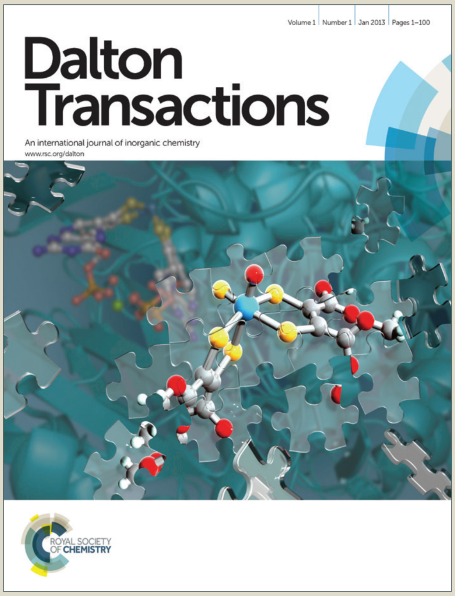

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Rare-Earth Metal π-Complexes of Reduced Arenes, Alkenes, and Alkynes: Bonding, Electronic Structure, and Comparison with Actinides and Other Electropositive Metals

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Rare-earth metal complexes of reduced π ligands are reviewed with an emphasis on their electronic structure and bonding interactions. This perspective discusses reduced carbocyclic and acyclic π ligands; in certain categories, when no example of a rare-earth metal complex is available, a closely related actinide analogue is discussed. In general, rare-earth metals have a lower tendency to form covalent interactions with π ligands compared to actinides, mainly uranium. Despite predominant ionic interactions in rare-earth chemistry, covalent bonds can be formed with reduced carbocyclic ligands, especially multiply reduced arenes.

Introduction

The development of the organometallic chemistry of f elements has paralleled that of transition metal organometallic chemistry with early milestones including the isolation of mono-, bis-, or tris-cyclopentadienyl metal complexes[1-3] and the famous uranocene molecule.[4, 5] In the last decade, a renaissance featuring compounds containing metal-element multiple bonds, metal arene complexes, molecular complexes with the metal in a low oxidation state, and the display of an unprecedented reactivity for small molecule activation has been observed. In addition to a showcase of beautiful synthetic methods, theoretical studies have contributed to the understanding of the electronic structure of these new molecules. New concepts, such as inverse trans influence[6] and sterically induced reduction[7] have been introduced. Recently, following a long debate against the preponderance of ionic interactions, covalent bonding has been accepted in actinide chemistry,[8-10] especially for uranium, featuring the contribution of both 5f and 6d orbitals. Several excellent reviews and articles have covered some of the latest advancements in the field.[11-17] Herein, we present a critical review of rare-earth metal complexes supported by reduced carbocyclic and acyclic π ligands, including cyclopropenyl, cyclobutadienyl, arenes, cycloheptatrienyl, cyclooctatetraenyl, fused arenes, alkenes, dienes, and alkynes. Besides briefly summarizing examples from the literature, the main purpose of this perspective is to highlight the bonding and electronic structure of these rare-earth metal π complexes; in addition, we will discuss the similarities and differences in bonding and electronic structure between rare-earth metal complexes and those of closely related actinides and, in some cases, other electropositive metals, such as alkali, alkali earth, or early transition metals.

The present perspective includes not only reduced six-membered rings but also three-, four-, seven-, and eight-membered carbon rings, alkenes, and alkynes (Chart 1a). For reduced carbocyclic rings, negatively charged arenes, except for the cyclopentadienyl anion (Cp^-) or its fused analogues such as indenyl, are surveyed. Neutral π ligands are also omitted. Albeit the assignment of the negative charge on π ligands is somewhat arbitrary, we will use the following qualitative criterion: the formal charge of the π ligands in a complex is calculated taken into account that rare-earth metals have a +3 oxidation state, except for ytterbium and europium, which are usually more stable in the +2 oxidation state in their organometallic chemistry. For instance, $(Cp^*{}_2Sm)_2(\mu-\eta^2:\eta^2\text{-}(E)\text{-stilbene})$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[18] qualifies to be included in our discussion, while $Sm(AlCl_4)_3(C_6Me_6)$[19] does not. Another important criterion is that the metal ion should coordinate to the π face of the π ligand, i.e., metallocycles of butadiene will not be included. Typical coordination modes include side-on, inverse sandwich, and sandwich (Chart 1b). This perspective focuses on rare-earth metal (scandium, yttrium, and lanthanides) complexes; however, when such complexes are absent and structurally similar complexes of actinides are available and relevant, they will be included in the corresponding section. In order to discuss electronic structures comparatively, we only selected compounds that have been characterized by X-ray crystallography. However, the purpose of this perspective is not to summarize all existing literature examples, but rather to extract useful information from isolated examples in order to discuss the bonding and electronic structure of rare-earth metal complexes.

The review is organized as follows: first, carbocyclic π ligands except arenes will be discussed in the order of their ring size from the smallest, three-membered ring, to the

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largest, eight-membered ring; then, arenes and aryl substituted arene complexes of rare-earth metals will be surveyed; after that, fused arenes, alkenes, and alkynes will be included.

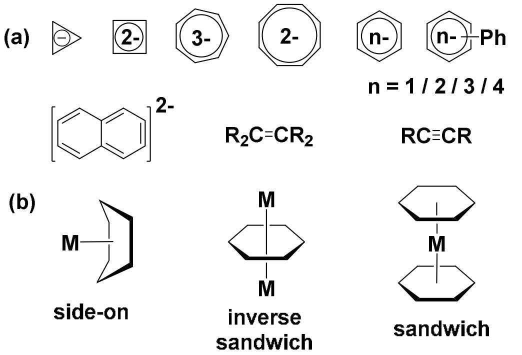


Chart 1. (a) π Ligands discussed in this perspective; (b) Typical coordination modes for metals and π ligands: side-on, inverse sandwich, and sandwich.

Part 1. Survey of Rare-Earth Metal π Complexes

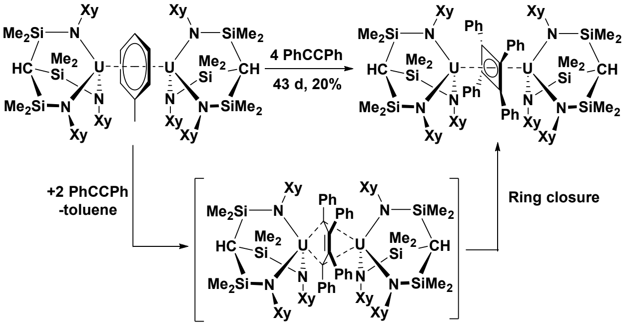
1. Carbocylic π ligands with a ring size of three, four, seven, and eight

1.1 C_3 rings

The simplest example of a reduced three-membered ring is the cyclopropenyl anion, $C_3H_3^-$, which is considered to be either antiaromatic[20] or nonaromatic.[21] The substituted cyclopropenyl, such as triphenylcyclopropenyl and tributylcyclopropenyl, forms complexes with late transition metals by reacting $C_3R_3^+X^-$ (X = halogen) and metal carbonyls. However, in those complexes, the cyclopropenyl is best described as an aromatic cation and not as an anion. No cyclopropenyl lanthanide complexes have been reported, likely due to two reasons: first, Ln(III) ions are highly Lewis acidic and lack the necessary π basicity to stabilize an interaction with the cyclopropenyl cation; second, although Ln(III) ions could stabilize the negative charge of the cyclopropenyl anion by an electrostatic interaction, its antiaromaticity or nonaromaticity makes its isolation elusive. To date, there is no example of a cyclopropenyl anion metal complex reported.

1.2 C_4 rings

Cyclobutadiene has been long sought after by synthetic chemists. Despite the fact that free cyclobutadiene C_4H_4 has not been isolated, the cyclobutadienyl dianion can be stabilized by metal complexes and it fulfills the Hückel rule for aromaticity. Although lanthanide dianionic cyclobutadienyl complexes are still unknown, a uranium analogue has recently been synthesized by reacting the inverse sandwich uranium toluene complex $[U(Ts^{Xy})]_2(\mu\text{–}\eta^6\text{:}\eta^6\text{-}C_7H_8)$ (Ts^{Xy} = $HC(SiMe_2NAr)_3$; Ar = 3,5-$Me_2C_6H_3$) with excess diphenylacetylene for a prolonged period of time to form an inverse sandwich uranium dianionic cyclobutadienyl complex, $[U(Ts^{Xy})]_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_4Ph_4)$.[22] The formation of the cyclobutadiene dianion is proposed to occur through a formal [2+2] cycloaddition: first, two equivalents of diphenylacetylene are reductively coupled to form a metallocycle of 1,3-butadieneyl, which then undergoes ring closure to form the cyclobutadienyl dianion (Scheme 1). The ability of uranium to induce this ring closure echoes that of transition metals. Indeed, some transition metals, such as cobalt, can readily promote this transformation under microwave conditions to generate various C_4R_4 rings in high yield.[23]



Scheme 1. Formation of an inverse sandwich cyclobutadienyl dianion complex of uranium, $[U(Ts^{Xy})]_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_4Ph_4)$, and proposed reaction intermediate.

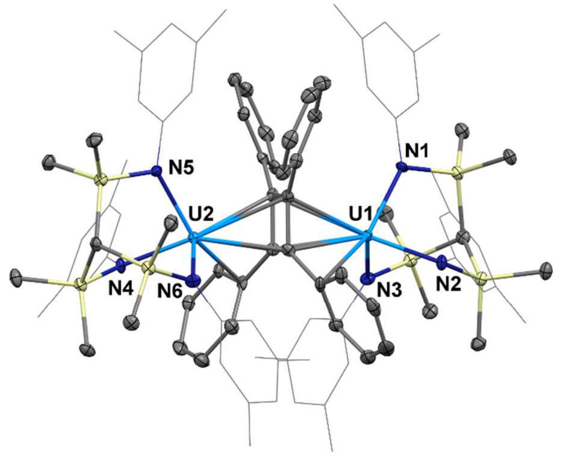


Figure 1. Solid state molecular structure of $[U(Ts^{Xy})]_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_4Ph_4)$ with hydrogen atoms omitted for clarity. Adapted by permission from Macmillan Publishers Ltd: Nature Communications, copyright (2013).[22]

The solid state molecular structure of $[U(Ts^{Xy})]_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_4Ph_4)$ (Figure 1) showed an asymmetric coordination pattern with a relatively wide range of U-C_{ring} distances of 2.655(5)-2.871(5) Å and a U-C_{ipso} distance of 2.864(5) Å. The electronic structure of $[U(Ts^{Xy})]_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_4Ph_4)$ has been studied by density functional theory (DFT) calculations. The calculated charges on uranium (+3.08) and on the C_4 ring (-2.36) are consistent with the formulation of two uranium(IV) ions and a dianion of C_4Ph_4. It was found that the orbital mixing between uranium 5f and 6d orbitals and the π orbitals of cyclobutadienyl was important: both donation from filled π orbitals to empty uranium orbitals and back-donation from uranium orbitals to empty π^* orbitals were found. It is interesting to note that the interaction between filled π orbitals of C_4Ph_4 and empty uranium orbitals has π character while the back-donation from filled uranium orbitals to empty π^* orbitals of the C_4Ph_4 ring has δ character. Another feature of the electronic structure is the dominance of 5f over 6d orbital participation in both π and δ interactions. This was explained to be the result of the relatively small size of the C_4 ring compared to that of C_6 or C_8 arenes. The highly angular requirement of the interaction may account for the dominance of 5f orbital participation, while in uranocene, the much larger COT ring size allows a δ interaction and more participation of 6d orbitals.[11, 22] The dominance of 5f orbital participation may also explain why a lanthanide analogue of this dianionic cyclobutadienyl uranium complex has still not been isolated since the 4f orbitals of lanthanides are core-like and, therefore, almost non-bonding, while their 5d orbitals are not well suited for bonding.

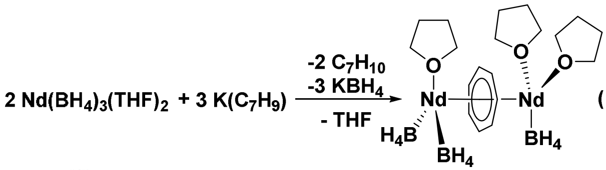
1.3 C_5 rings

Cyclopentadienyl is one of the most common ligands in organometallic chemistry. Because of its strong aromaticity, it is an exceptionally stable anion and usually serves as an ancillary ligand for metal ions. Given its ubiquitous presence in the organometallic chemistry of f elements, we are not going to discuss any cyclopentadienyl lanthanide complexes in this perspective.

1.4 C_7 rings

Despite the absence of compounds with reduced C_3 and C_4 rings, lanthanides do form stable complexes with cycloheptatrienyl. There are two ways for cycloheptatrienyl (C_7H_7) to achieve aromaticity: by losing an electron to form the 6π-electron tropylium cation, $C_7H_7^+$, or by accepting three electrons to form the 10π-electron trianion, $C_7H_7^{3-}$. While the tropylium cation is more common in organic chemistry, metal complexes show ambiguous assignments of the cycloheptatrienyl ligand charge. In the case of late transition metal complexes, it is usually considered to be +1 and the interaction to be covalent.[24] For early transition metals, the situation becomes more complicated since the metal is highly electropositive and the line between complete electron transfer from metal to ligand and partial electron transfer, i.e., back-donation, becomes blurry. For example, the oxidation state of titanium in CpTi(η^7-C_7H_7) is either 0 if $C_7H_7^+$ or +4 if $C_7H_7^{3-}$. In both cases, the seven-membered ring satisfies Hückel's rule. Initially, the first assignment was suggested but it was later found that the latter formulation, Ti(IV) and $C_7H_7^{3-}$, was more appropriate.[24] It is important to note that there is a significant orbital overlap between the 3d orbitals of titanium and the π orbitals of the cycloheptatrienyl ring indicating covalent bonding.[24]

Despite a good number of examples of trianionic cycloheptatrienyl complexes of early transition metals and actinides,[25-29] only one example of a cycloheptatrienyl trianion complex of a lanthanide is known,[29] an inverse sandwich complex of neodymium with the formula $[(THF)(BH_4)_2Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(THF)_3]$ (THF = tetrahydrofuran, Figure 2). Assigning a +3 oxidation state for neodymium, the cycloheptatrienyl ligand carries a 3- charge and fulfills Hückel's rule. The cycloheptatrienyl ring was found to be planar; however, due to a high degree of disorder, the C-C distance within the ring could not be determined accurately. Nonetheless, the interactions between the two Nd(III) ions and the cycloheptatrienyl ligand are almost identical despite the fact that the two Nd(III) ions differ in their coordination sphere by the number of borate and tetrahydrofuran ligands. This neodymium complex was synthesized by reacting two equivalents of $Nd(BH_4)_3(THF)_2$ and three equivalents of potassium cycloheptadienyl, $K(C_7H_9)$ (Equation 1). Disproportionation of $K(C_7H_9)$ led to the in situ formation of $K_3(C_7H_7)$, which then underwent a salt metathesis reaction to form the inverse sandwich complex with the concomitant formation of KBH_4 as a by-product. Despite this facile synthesis, the neodymium complex remains the sole structurally characterized cycloheptatrienyl complex of a lanthanide.



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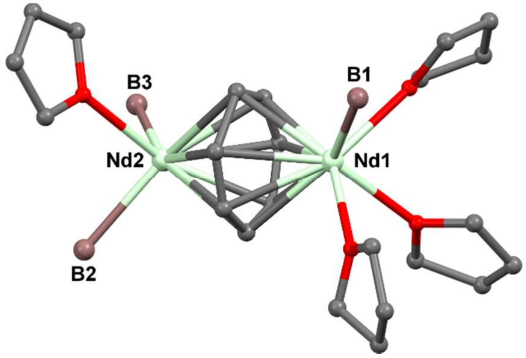


Figure 2. Solid state molecular structure of $[(THF)(BH_4)_2Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(THF)_3]$ with hydrogen atoms omitted for clarity. Adapted with permission from The Royal Society of Chemistry.[29]

1.5 C_8 rings

The cyclooctatetraenyl dianion (COT) is an intriguing ligand in organometallic chemistry. Neutral 1,3,5,7-cyclooctatetraene is a non-aromatic, non-planar molecule with alternating C-C distances typical of C-C double and single bonds; upon a two-electron reduction, it becomes planar with uniform C-C distances. Similarly to the cyclopentadienyl anion, COT forms a strong interaction with lanthanides and actinides that is mainly ionic. However, it carries a higher negative charge density and has a larger size than cyclopentadienyl. Therefore, there is more orbital overlap between the metal and the cyclooctatetraenyl ligand, i.e., a stronger covalent interaction is found between COT and the metal ion. The most famous COT complex is probably uranocene, $U(COT)_2$, which is a sandwich complex.[4, 5] Lanthanides also form sandwich complexes with COT, but because of their predominant trivalent oxidation state, anionic Ln(COT)$_2^-$ species are usually formed,[30] except for Eu and Yb, which prefer to form the neutral complexes Eu(COT) and Yb(COT),[31, 32] and Ce, which can form the neutral Ce(COT)$_2$ complex.[33, 34] The bonding interaction between U(IV) and COT in U(COT)$_2$ is a textbook example of a δ covalent interaction between uranium 5f and 6d orbitals and the frontier molecular orbitals of the COT ligand.[35] Lanthanide COT sandwich complexes were found to exhibit a similar covalent interaction but to a lesser extent.[36] It is interesting to note that some lanthanide sandwich COT complexes or mixed cyclopentadienyl and cyclooctatetraenediyl complexes, such as [K(18-crown-6)][Er(COT)$_2$][37, 38] and (η^5-C$_5$Me$_5$)Er(COT),[39] are among the best examples of single-molecule magnets reported.

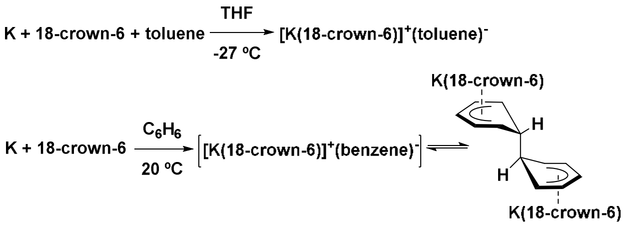
2. Anionic six-membered ring arene complexes

Six-membered ring arenes, classic aromatic molecules, with one or more phenyl rings either linked or sharing one side (fused), are common ligands in organometallic chemistry. Arenes can serve as both neutral and anionic ligands in complexes with highly electropositive metals. The first lanthanide arene complex, Sm(η^6-C$_6$Me$_6$)(η^2-AlCl$_4$)$_3$, was reported in 1986 by Cotton and Schwotzer.[19] Between 1987 and 1993, Cloke et al. reported a series of sandwich rare-earth metal arene complexes with a formal oxidation state of zero for the metal.[40-42] They resemble sandwich benzene complexes of transition metals, such as Cr(C$_6$H$_6$)$_2$; however, the metal-arene bond was found to be even stronger than that of Cr(C$_6$H$_6$)$_2$.[43] Lappert and co-workers isolated and structurally characterized several lanthanide benzene complexes with various degrees of benzene reduction.[44-46] Fryzuk et al. reported the synthesis of inverse sandwich dianionic biphenyl complexes of lanthanides.[47] Recently, we synthesized the first rare-earth metal arene complexes in which the phenyl ring sandwiched by two metal ions is quadruply reduced.[48, 49] For fused arenes, other examples of rare-earth fused-arene complexes are known and have been summarized in a comprehensive review.[50] In most cases, the fused arenes are doubly reduced and the negative charge is delocalized over the whole π-electron system.

2.1 Anionic benzene or alkyl substituted benzene complexes

2.1.1 Radical anionic C$_6$ complexes

The benzene radical anion has been proposed as an intermediate in Birch reductions.[51] However, its isolation and characterization is difficult due to its radical character as well as the extremely negative reduction potential of benzene.[52] Although no rare-earth metal complex of the benzene radical anion is known, Lappert and co-workers succeeded in isolating and structurally characterizing the potassium crown ether salt of the toluene radical anion and the benzene radical anion dimer by treating potassium metal with the corresponding arenes in the presence of crown ethers, which encapsulate the potassium ion (Scheme 2).[53] The crystal structure of the toluene radical anion showed various C-C distances within the ring and that the coordination of potassium to the ring carbon atoms also differs significantly (K-C distances range from 3.04 to 3.31 Å). The unsymmetrical nature of the toluene radical anion could rise from the methyl substitution or its high polarizability.



Scheme 2. Reduction of toluene and benzene by potassium metal in the presence of 18-crown-6.

2.1.2 Dianionic C$_6$ complexes

The benzene dianion forms stable complexes with various rare-earth metals as the 1,4-cyclohexa-2,5-dienyl ligand (benzene 1,4-dianion, Equation 2).[44, 46] In all cases, the benzene dianion is sandwiched by a rare-earth metal ion and a potassium ion, which is solvated by a crown ether. The benzene 1,4-dianion in [K(18-crown-6)][LaCp′′$_2$(η^2-C$_6$H$_6$)] (Cp′′ = η^5-1,3-(SiMe$_3$)$_2$-C$_5$H$_3$, Figure 3) adopts a boat-type configuration with the two out of plane carbon atoms showing the closest contact to the lanthanide ions. The negative charges are localized on these carbon atoms, and the C-C distances also reflect this trend of localization (C2-C3 is 1.35 Å, close to a C-C double bond; C1-C2 is 1.47 Å, close to a C-C single bond). Therefore, the benzene 1,4-dianion is best described as an interrupted π-electron system, with strong σ bond character between C1 / C4 and the lanthanide ions.

$$\mathrm{LnCp''_3} \xrightarrow[\mathrm{C_6H_6}]{\substack{\mathrm{2K,\ 2(18\text{-}crown\text{-}6)} \\ \mathrm{-K(18\text{-}crown\text{-}6)Cp''}}} \mathrm{[K(18\text{-}crown\text{-}6)][LnCp''_2(\eta^2\text{-}C_6H_6)]} \quad (2)$$

Ln = La, Ce, Pr, Nd; Cp'' = η^5-1,3-(SiMe$_3$)$_2$-C$_5$H$_3$

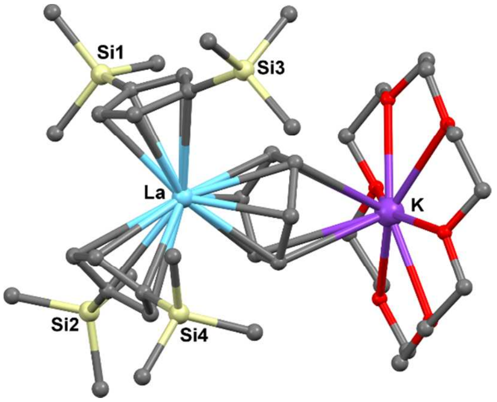


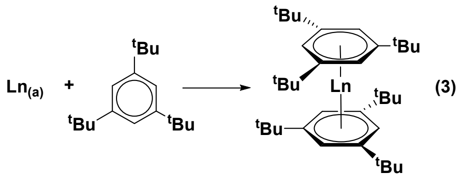
Figure 3. Solid state molecular structure of [K(18-crown-6)][LaCp′′$_2$(η^2-C$_6$H$_6$)] (Cp′′ = η^5-1,3-(SiMe$_3$)$_2$-C$_5$H$_3$) with hydrogen atoms omitted for clarity. Adapted with permission from The Royal Society of Chemistry.[46]

2.1.3 Trianionic C_6 complexes

The benzene trianion has not been identified in any transition metal complexes. Nonetheless, we found one structurally characterized compound that likely contains a trianionic benzene ligand in our opinion. Lappert et al. reported the synthesis and characterization of [K([18]crown-6)(η^2-C_6H_6)$_2$][(LaCp$^{tt}_2$)$_2$(μ-η^6:η^6-C_6H_6)] and proposed two possible formulations: two La(II) ions with a benzene monoanion or two La(III) ions with a trianionic benzene ligand.[45] The authors preferred the former because, at that time, a triply reduced benzene seemed implausible. However, an examination of its geometrical parameters and other anionic radical or dianionic benzene compounds reveals that the formulation of two La(III) ions coordinated to a trianionic benzene ligand is more appropriate. For example, the average C-C distance in reduced benzene complexes is usually used to determine the extent of reduction of the benzene ligand since the extra electrons are added to the anti-bonding π orbitals of benzene and, therefore, the weakened π bond results in lengthened C-C distances. In the case of [K([18]crown-6)(η^2-C_6H_6)$_2$][(LaCp$^{tt}_2$)$_2$(μ-η^6:η^6-C_6H_6)], the average C-C distance is longer than the average C-C distance of the benzene dianion.[46] The almost planar benzene ring and rather short La-C distances suggest a strong interaction between lanthanum and the reduced benzene ligand. In view of the recent advances in the organometallic chemistry of f elements, especially the isolation and characterization of tetraanionic biphenyl complexes (see below),[48, 49, 54] the formulation of a benzene trianion in [K([18]crown-6)(η^2-C_6H_6)$_2$][(LaCp$^{tt}_2$)$_2$(μ-η^6:η^6-C_6H_6)] seems appropriate.

2.1.4 Miscellaneous

Between the late 1980s and early 1990s, Cloke and co-workers published a series of papers on sandwich benzene complexes of rare-earth metals.[40-43] Typically, sterically demanding benzene derivatives, such as 1,3,5-tri-*tert*-butylbenzene, were required to obtain stable products characterized as Ln(1,3,5-C_6H_3-Bu^t_3)$_2$. The sandwich complexes were synthesized by co-condensation of arene vapors and lanthanide atoms (Equation 3).



(3)

Stable for Ln = Sc, Y, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu
dec > 40ºC Pr, dec > 0ºC La, dec > -30ºC Sm
Unstable for Ln = Ce, Eu, Tm, Yb

It was found that the bonding interaction between the rare-earth metal ion and arene is exceptionally strong, even stronger than the interaction between chromium and benzene in Cr(C_6H_6)$_2$.[43] In their reports, the authors formulated the sandwich complexes as two neutral arenes sandwiching a zero valent metal ion. However, when taking into account the strong metal-arene bonding interaction and the electronic structure of the inverse sandwich lanthanide arene complexes reported afterwards, in the opinion of the authors, it seems appropriate to formulate this class of complexes as containing an M(III) ion sandwiched by two reduced arenes. The observed magnetic moment and EPR signal could be explained by the presence of unpaired electrons in partially filled anti-bonding π orbitals, while a strong interaction with metal based orbitals could induce coupling with the metal nucleus. In some respect, the sandwich lanthanide benzene complexes could be viewed as molecular analogues of the graphite intercalation compounds such as C_6Yb, which was found to show superconductivity.[55]

2.2 Anionic aryl-substituted benzene complexes

Biphenyl, *p*-terphenyl, and 1,3,5-triphenylbenzene are typical aryl substituted benzenes. Unlike the case of fused arenes, the phenyl rings linked by a C_{ipso}-C_{ipso} single bond are only weakly conjugated and considered separate π-electron systems. Therefore, their anions can behave similarly to those of benzene. However, in some cases, the shortening of the C_{ipso}-C_{ipso} bond could result in strong conjugation of the neighboring phenyl rings, delocalization of the π-electron system, and sharing of the negative charge. These two opposite effects lead to two different coordination modes of biphenyl: coordination of rare-earth metal ions to the same phenyl ring, i.e., localization of negative charges, and coordination of rare-earth metal ions to two different phenyl rings, i.e., delocalization of negative charges.

2.2.1 Dianionic aryl substituted benzene complexes

Fryzuk et al. reported the synthesis and characterization of dianionic 4,4′-dimethylbiphenyl complexes of yttrium and lutetium.[47] Albeit an unusual synthetic route from a proposed metal phenyl intermediate was used, the biphenyl dianion was a typical π ligand (Scheme 3a). Two coordination modes were observed in the solid state molecular structures: two yttrium ions coordinated to different phenyl rings in [(P_2N_2)Y]$_2$[$\mu-\eta^6$:$\eta^{6'}$-(C_6H_5)$_2$] (Figure 4) and two yttrium ions coordinated to the same phenyl ring in [(P_2N_2)Y]$_2$[$\mu-\eta^6$:η^6-C_6H_4Me-4(C_6H_4Me-4′)$_2$] ((P_2N_2) = [PhP($CH_2SiMe_2NSiMe_2CH_2$)$_2$PPh]). Despite the difference in their solid state structures, both compounds showed fluxional behavior in solution and, in both cases, the phenyl rings were indistinguishable on the ^{1}H NMR time scale in solution at room temperature. This suggests that the negative charges are equally distributed between the phenyl rings and the interaction between yttrium and the dianionic biphenyl ligand is mainly electrostatic in nature. Recently, Evans et al. obtained a monometallic lanthanide complex of the biphenyl dianion, [K(2.2.2-cryptand)][(η^5-$C_5H_4SiMe_3$)$_2$Y(η^6-C_6H_5-Ph)] (Figure 5), utilizing a divalent lanthanide starting material, [K(2.2.2-cryptand)][(η^5-$C_5H_4SiMe_3$)$_3$Y] (Scheme 3b).[56] This reaction demonstrated the reducing power of a molecular yttrium(II) species. The crystal structure of the anion [(η^5-$C_5H_4SiMe_3$)$_2$Y(η^6-C_6H_5-Ph)]$^-$ showed coordination of the (η^5-$C_5H_4SiMe_3$)$_2$Y moiety to one of the phenyl rings. The structural data argued for the localization of the two negative charges on the coordinating phenyl ring, which is structurally similar to the benzene 1,4-dianion described by Lappert and co-workers in [K(18-crown-6)][η^5-1,3-$C_5H_3(SiMe_3)_2]_2La(\eta^2$-$C_6H_6$)][46] (see section 2.1.2). However, definite ^1H and ^{13}C NMR spectroscopic assignments were not possible due to the inability to obtain pure samples of [K(2.2.2-cryptand)][(η^5-$C_5H_4SiMe_3)_2Y(\eta^6$-C_6H_5-Ph)].

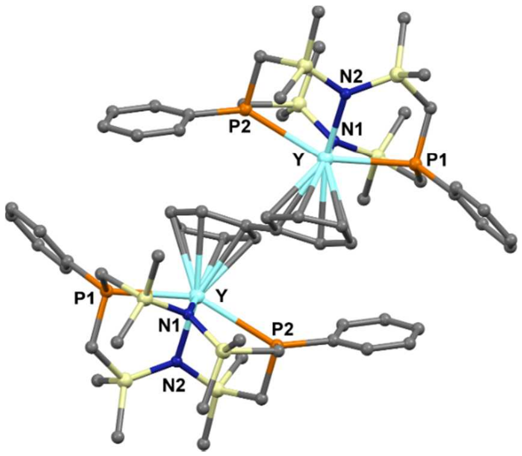


Figure 4. Solid state molecular structure of [$(P_2N_2)Y]_2[\eta^6:\eta^{6'}$-$(C_6H_5)_2$] with hydrogen atoms omitted for clarity. Adapted with permission from *J. Am. Chem. Soc.*, 1997, **119**, 9071. Copyright (1997) American Chemical Society.

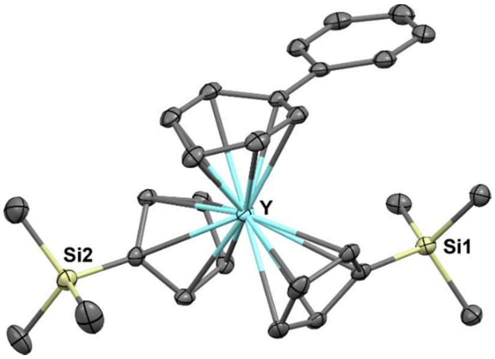
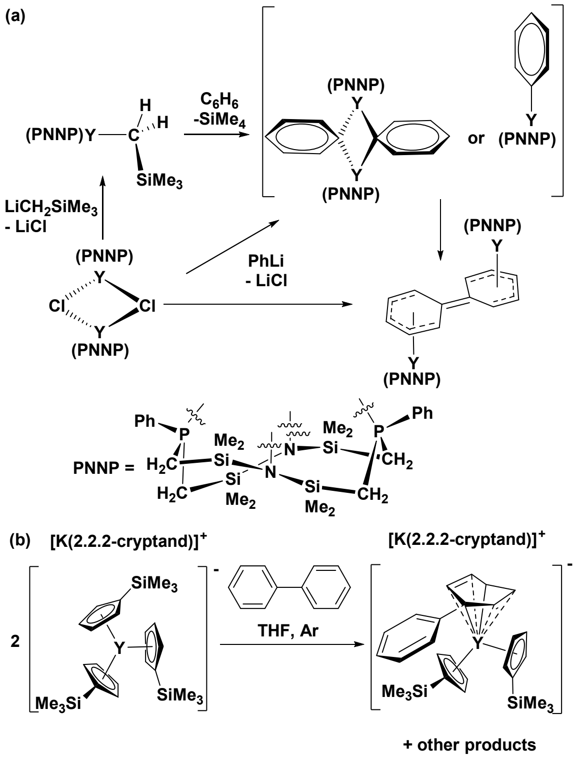


Figure 5. Solid state molecular structure of the anion of [K[(η^5-$C_5H_4SiMe_3)Y(\eta^6$-C_6H_5-Ph)] with hydrogen atoms omitted for clarity. Adapted with permission from *Organometallics*, 2015, **34**, 2287. Copyright (2015) American Chemical Society.

2.2.2 Tetraanionic aryl substituted benzene complexes

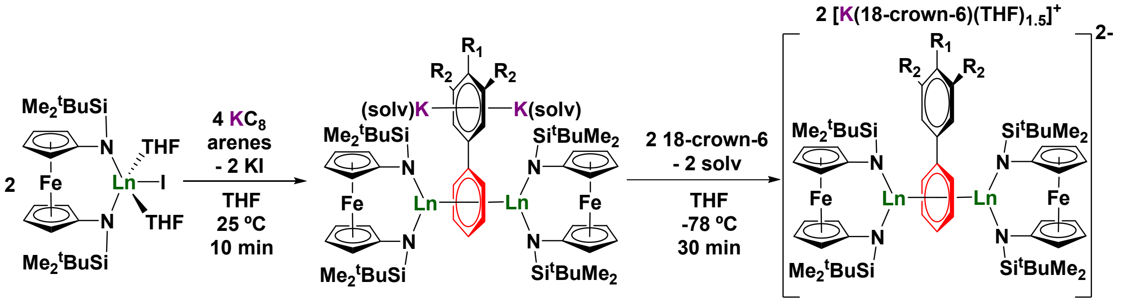
In 2013, our group reported the synthesis and characterization of inverse sandwich rare-earth metal complexes of biphenyl, *p*-terphenyl, and 1,3,5-triphenylbenzene with a general formula [$(NN^{TBS})Ln]_2(\mu-\eta^6:\eta^6$-arene)[K(solvent)]$_2$ (Scheme 4),[48] in which the metal is supported by a ferrocene diamide ligand, NN^{TBS} = fc(NSi^{t}BuMe$_2$)$_2$, fc = 1,1'-ferrocenediyl.[57-61] Despite the difference in arenes, all bimetallic complexes share the same coordination mode as evidenced by their respective solid state structures: two (NN^{TBS})Ln (Ln = Sc, Y, La, and Lu) moieties bind to opposite sides of one of the phenyl rings (the end ring for *p*-terphenyl and 1,3,5-triphenylbenzene).

A variable temperature ^1H NMR spectroscopic study confirmed that this asymmetric structure is maintained in solution and no fluxional behavior was observed as was previously reported for rare-earth metal complexes of dianionic biphenyl or naphthalene.[47, 62-64]



Scheme 3. (a) Synthesis of [$(P_2N_2)Y]_2[\eta^6:\eta^{6'}$-$(C_6H_5)_2$] by two different methods; (b) Reaction of [K(2.2.2-cryptand)][(η^5-$C_5H_4SiMe_3)_3Y$] and biphenyl to form [K[(η^5-$C_5H_4SiMe_3)Y(\eta^6$-C_6H_5-Ph)] as one of the products.

This unusual structural rigidity pointed to the possibility of an unprecedented benzene tetraanion stabilized by coordination to rare-earth metal ions and by a weak conjugation with the other phenyl substituent(s). Compounds Y_2K_2-biph, [$(NN^{TBS})Y]_2[K(toluene)]_2(\mu-\eta^6:\eta^6$-$C_6H_5C_6H_5$) (Figure 6), and Y_2K_2-biph-crown$_2$, [$(NN^{TBS})Ln]_2(\mu-\eta^6:\eta^6$-$C_6H_5Ar$)[K(18-crown-6)(THF)$_{1.5}$]$_2$ (Figure 7), were singled out for a detailed study. X-ray crystallographic data of Y_2K_2-biph showed that the two phenyl rings of the biphenyl ligand are distinct from each other: the phenyl ring sandwiched by two (NN^{TBS})Y moieties has a longer average C-C distance, of 1.46 Å, than the average C-C distance of 1.41 Å of the adjacent phenyl ring and also longer than that found for the aforementioned benzene dianions.[45, 46] This phenomenon is more prominent upon removal of the potassium ions by a crown ether in Y_2K_2-biph-crown$_2$. The longer the C-C distance, the more reduced the phenyl ring is. Other evidence supporting the formulation of a benzene tetraanion included: ^{89}Y NMR chemical shifts reflecting shielding effects from the aromatic ring current of the 6C, 10π benzene tetraanion, and DFT calculations favoring the localization of the four negative charges on one phenyl ring. The successful isolation of a series of rare-earth metal complexes containing the aryl substituted benzene tetraanion demonstrates the predicting power of Hückel's rule.



Ln: Sc, Y, La, Lu, Gd, Dy, Er
arenes: R$_1$ = R$_2$ = H, biphenyl; R$_1$ = Ph, R$_2$ = H, *p*-terphenyl; R$_1$ = H, R$_2$ = Ph, 1,3,5-triphenylbenzene
solv: Et$_2$O or toluene

Scheme 4. Synthesis of $[(NN^{TBS})Ln]_2(\mu-\eta^6:\eta^6\text{-}C_6H_5Ar)[K(solv)]_2$ and $[(NN^{TBS})Ln]_2(\mu-\eta^6:\eta^6\text{-}C_6H_5Ar)[K(18\text{-crown-}6)(THF)_{1.5}]_2$ (Ar = C_6H_5 for biphenyl, 4-PhC_6H_4 for *p*-terphenyl, and 3,5-$Ph_2C_6H_3$ for 1,3,5-triphenylbenzene).

Another important information obtained from DFT calculations is that the covalent interaction between the arene ligand and the rare-earth metal ions also plays an important role in stabilizing the highly negatively charged benzene ring. The HOMO and HOMO-1 of Y$_2$K$_2$-biph showed significant δ overlap of the benzene π^* orbitals and metal based orbitals. Rare-earth metal complexes are usually considered to engage in ionic interactions due to the high electropositive character of rare-earth metals. However, in Y$_2$K$_2$-biph, the energy level of the benzene π^* orbitals is close enough to the energy level of the empty 4d orbitals of the yttrium(III) ion to induce a covalent bonding interaction and stabilize the high electron density of the benzene tetraanion. Later on, the dysprosium and erbium analogues of these inverse sandwich biphenyl complexes were found to show single-molecule magnet properties.[49]

Inverse sandwich arene complexes of uranium[12, 13, 26, 29, 65-75] are structurally similar to the rare earth stabilized benzene tetraanion, however, most uranium complexes were found to contain a bridging benzene dianion instead of a tetraanion. The strong interaction between uranium ions and benzene usually involves four electrons and δ overlap between uranium 5f or 6d orbitals and π^* orbitals of benzene.[12, 13, 65, 66] It is interesting to note that, for uranium, this binding mode (two uranium moieties coordinated to the same phenyl ring) is preferred over other possibilities: a series of $\mu-\eta^6:\eta^6$-arene-bridged diuranium hexakisketimide complexes of a variety of arenes, including naphthalene, biphenyl, (*E*)-stilbene, and *p*-terphenyl all showed the same coordination motif through the entire series.[12]

Besides f elements, Westerhausen et al.[54] reported an enthralling inverse sandwich calcium complex of 1,3,5-triphenylbenzene, $[(THF)_3Ca]_2(\mu-\eta^6:\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)$ (Equation 4). The complex was formulated as two calcium(I) ions and a 1,3,5-triphenylbenzene dianion. However, in the opinion of the authors, structural data support the formulation of two calcium(II) ions and a 1,3,5-triphenylbenzene tetraanion: the average C-C distance in the central benzene ring was 1.46 Å, same as for Y$_2$K$_2$-biph, although DFT calculations reported in the original paper provided different results. Nonetheless, it is clear that all four electrons from two calcium atoms are involved in a bonding interaction in the product.

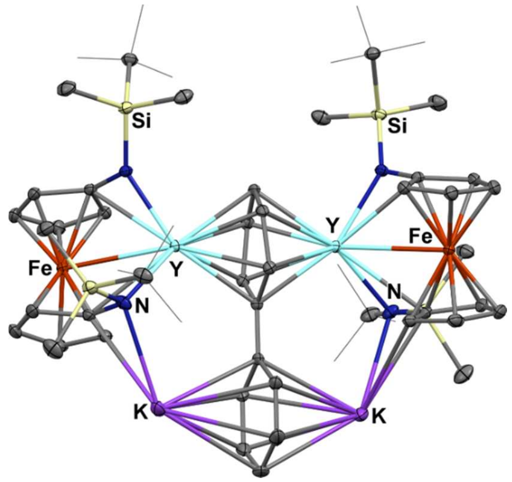
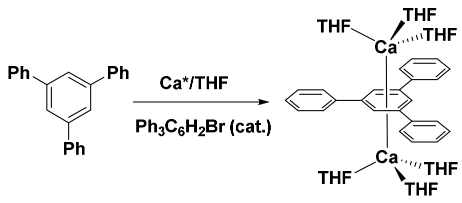


Figure 6. Solid state molecular structure of $[(NN^{TBS})Y]_2[K(toluene)]_2(\mu-\eta^6:\eta^6\text{-}C_6H_5C_6H_5)$ with hydrogen atoms omitted for clarity.



(4)

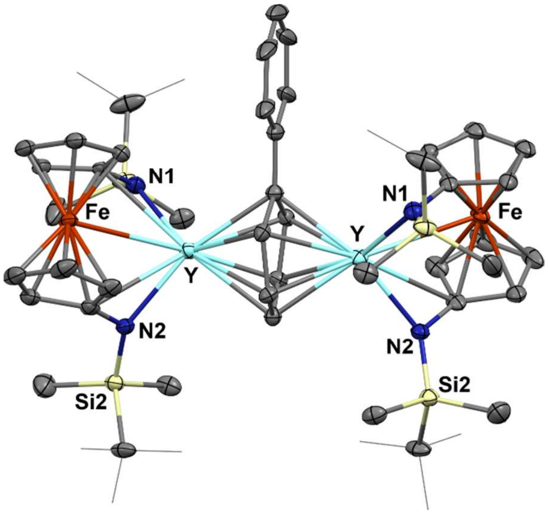


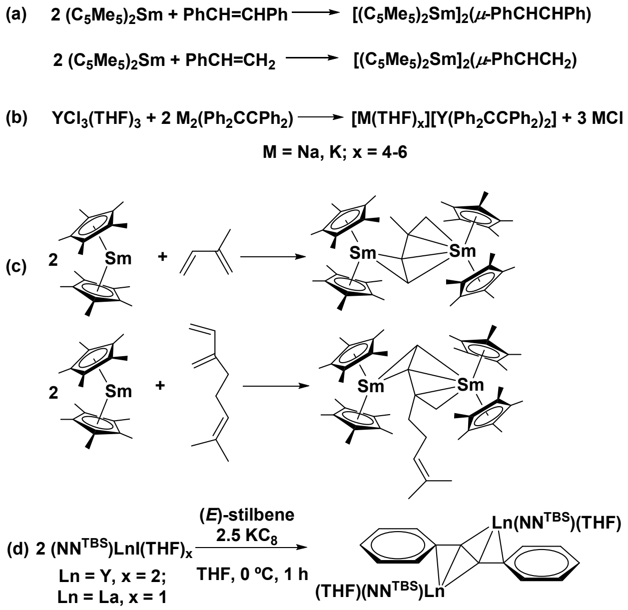
Figure 7. Solid state molecular structure of the anion of $[(NN^{TBS})Ln]_2(\mu{-}\eta^6{:}\eta^6\text{-}C_6H_5Ar)[K(18\text{-crown-}6)(THF)_{1.5}]_2$ with hydrogen atoms omitted for clarity.

3. Anionic fused arene complexes

Fused arenes, such as naphthalene and anthracene, are more prone to reduction than benzene because the larger the π-electron system is, the better the negative charge is stabilized. As a result, more rare-earth metal complexes of reduced fused arene are known than of reduced benzene. Bochkarev has written a comprehensive review on rare-earth metal arene complexes and a large portion of the review was focused on fused arene complexes.[50] Therefore, we are not going to discuss individual examples but rather summarize their general features. First, most fused arene complexes of rare-earth metals contain a doubly reduced arene ligand. Second, in the case of bimetallic compounds, the two metal ions (two rare-earth metal ions or one rare-earth metal ion and one alkali metal ion) coordinate to opposite faces of different phenyl rings. Third, alternating C-C distances were observed, indicating a localization of π bonds and negative charges, i.e., interruption of the π-electron system. Indeed, the geometric parameters are almost identical for dianionic naphthalene complexes of lithium[76] and dianionic naphthalene complexes of rare-earth metals.[63, 64] Therefore, all three features point to an ionic interaction in these complexes.

4. Anionic alkene or diene complexes

Lanthanide alkene complexes are much less abundant compared to transition metal alkene complexes. The lack of ability for back-donation of Ln(III) ions prevents the formation of stable lanthanide neutral alkene complexes. However, fully reduced alkenes or partially reduced dienes can form stable complexes with rare-earth metals. Evans et al. had reported several examples of samarium complexes of doubly reduced alkenes, including (*E*)-stilbene and styrene, by reacting the solvent free $(C_5Me_5)_2Sm$ and alkenes (Scheme 5a),[18] a bimetallic yttrium / alkali metal complex of the tetraphenylethylene dianion, $[M(THF)_x][Y(Ph_2C{=}CPh_2)]$, by reacting $YCl_3(THF)_3$ and $M_2(Ph_2C{=}CPh_2)$ (M = Na, K; x = 4-6) (Scheme 5b),[77] and samarium complexes of doubly reduced dienes, such as isoprene and myrcene, by reacting $(C_5Me_5)_2Sm$ and the corresponding substituted butadienes (Scheme 5c).[78] Unlike yttrium tetraphenylethylene complexes, the formation of samarium alkenes or dienes complexes was reversible: addition of THF regenerated $(C_5Me_5)_2Sm(THF)_2$ and free alkenes or dienes.[78] Mashima and co-workers reported the crystal structure of a diene-bridged dilanthanum complex, $[LaI_2(THF)_3(\mu{-}\eta^4{:}\eta^4\text{-PhCH=CHCH=CHPh})LaI_2(THF)_3]$.[79] Recently, our group reported the synthesis of yttrium and lanthanide complexes of the (*E*)-stilbene dianion. Treating $(NN^{TBS})LnI(THF)_2$ (NN^{TBS} = 1,1'-fc$(NSi^tBuMe_2)_2$, Ln = Y and La) with KC_8 in the presence of (*E*)-stilbene in THF resulted in the formation of $[(NN^{TBS})Ln(THF)]_2[\mu{-}\eta^2{:}\eta^2\text{-}(E)\text{-stilbene}]$ (Scheme 5d). Adding additional KC_8 did not lead to further reduction but instead to the scrambling of one $(NN^{TBS})Ln(THF)$ moiety by a potassium ion, i.e., formation of $[(NN^{TBS})Ln(THF)][\mu{-}\eta^2{:}\eta^{6'}\text{-}(E)\text{-stilbene}][K(THF)]$.[80] All aforementioned rare-earth metal complexes of alkenes and dienes adopt an inverse sandwich structure with the metal ion coordinated to the π electrons of the alkene or diene ligand.



Scheme 5. (a) Synthesis of samarium alkene complexes; (b) Synthesis of sandwich yttrium tetraphenylethylene anion; (c) Synthesis of samarium diene complexes; (d) Synthesis of yttrium and lanthanum complexes of (*E*)-stilbene dianion supported by a ferrocene diamide ligand.

5. Anionic alkyne or benzyne complexes

Albeit examples of lanthanide reduced alkene complexes exist, rare-earth metal complexes of reduced alkynes remain elusive to synthetic chemists. The stronger π bond in alkynes is probably responsible for this absence. Indeed, alkyne complexes of f elements are essentially unknown, although examples of dianionic species derived from the dimerization of terminal alkynes were reported by several groups. [81-85]

Dalton Transactions

PERSPECTIVE

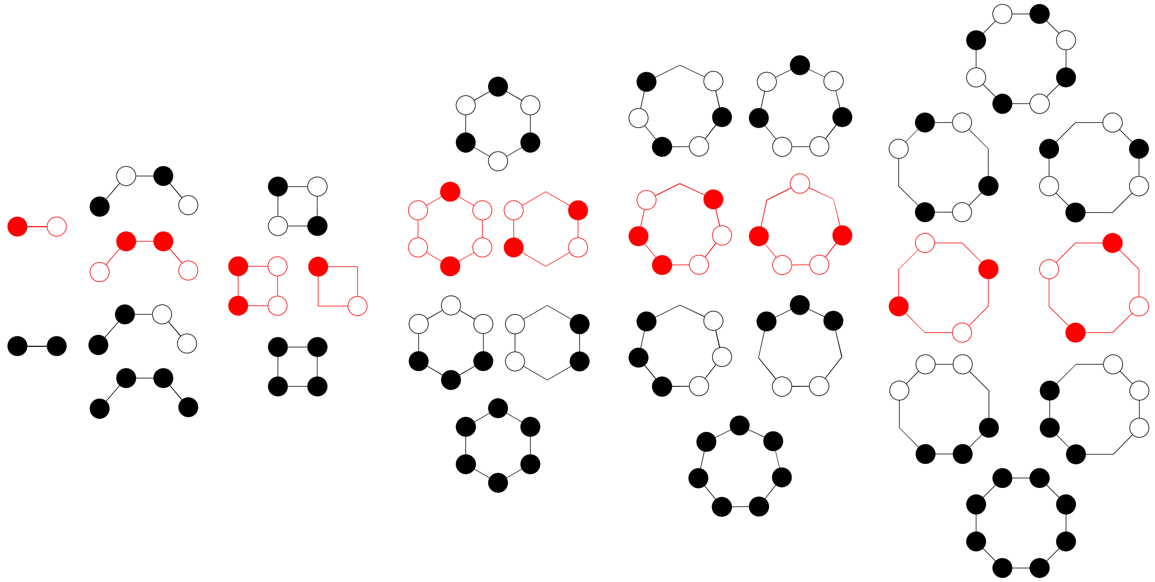
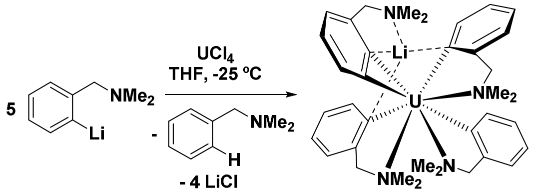


Chart 2. Frontier molecular orbitals for four, six, seven, and eight-membered carbocyclic rings. The orbitals highlighted in red are the HOMOs of the corresponding reduced π ligands that can participate in π or δ interactions with metal-based d orbitals.

In these cases, C–C homocoupling reactions were achieved using lanthanocene(III) complexes with terminal alkynes as substrates. For example, phenylacetylene reacted with different mono- (in the +2 or +3 oxidation state) or bimetallic (in the +3 oxidation state) samarocene complexes to afford a new class of trienediyl complexes of samarium(III), $\{(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-Ph–C=C=C=C–Ph})$.[82, 83]



(5)

Recently, Hayton et al. reported the only example of an isolated and structurally characterized uranium benzyne complex, $[Li][U(2,3\text{-}C_6H_3CH_2NMe_2)(2\text{-}C_6H_4CH_2NMe_2)_3]$ (Equation 5).[86] The tilted π orbitals of benzyne match well the 6d and 5f orbitals of uranium. If uranium is assigned its normal +4 oxidation state, then the benzyne ligand is doubly reduced.

Part 2: Discussion on bonding and electronic structure

Historically, rare-earth metals have been considered to be highly electrophilic, and, therefore, they are assumed to form ionic bonds via electrostatic interactions. This is essentially true for the aqueous chemistry of rare-earth elements since their electronegativity is small (from 1.36 for scandium to 1.1 for lanthanum, Pauling scale)[87, 88] and the hydration energy of rare-earth ions is large.[89] However, in organometallic chemistry, this assumption may not hold. Recently, several systematic studies on the covalency of lanthanide and actinide complexes were reported.[8, 90] The participation of both 5f and 6d orbitals of actinides in bonding has now been well established.[9, 91, 92] Unlike actinides, however, the 4f orbitals of lanthanides are core-like and rarely participate in bonding interactions with ligands. Therefore, that leaves the 5d orbitals for lanthanides (and 3d for scandium or 4d for yttrium) that can participate in bonding interactions. The empty d orbitals of trivalent rare-earth ions are usually high in energy as shown by the extremely negative redox potential for the couple $Ln^{II/III}$.[89] In order to match the energy level of empty d orbitals of Ln(III), the corresponding ligand based orbitals have to be high in energy and diffused in space. Typical π donors like cyclopentadienyl do not meet these criteria because of their low-lying HOMOs. In contrast, the π^* orbitals of some carbocyclic or acyclic ligands have the right symmetry, i.e., π or δ, are high enough in energy, and are delocalized over a large space. For example, the reduction potential of benzene, biphenyl, and naphthalene has been measured to be -3.42,[52] -2.69, and -2.50 eV (vs. SCE),[93] respectively. These values are comparable to the reduction potential of most $Ln^{II/III}$ couples; therefore, the HOMOs of these reduced arenes is able to match the LUMOs of Ln(III) fragments in energy.

From Chart 2, it is clear that the HOMOs of some reduced π ligands, such as acyclic alkenes, dienes, and cyclobutadienyl, have π character, while the HOMOs of the reduced carbocyclic rings with a ring size equal or larger than six have δ character. This leads to two different types of bonding interactions, π and δ. In some cases, both π and δ interactions are possible: for example, rare-earth metal (*E*)-stilbene complexes can have a π interaction between metal ions and the double bond of (*E*)-stilbene;[18, 80] however, in the case of uranium (*E*)-stilbene complexes, both uranium ions coordinate to the same phenyl ring and, therefore, form δ interactions.[12] Another interesting comparison is between two yttrium biphenyl complexes: in $[(NN^{TBS})Y]_2[K(toluene)]_2[\mu-\eta^6:\eta^6\text{-}C_6H_5C_6H_5]$ (Y_2K_2-biph, see section 2.2.2), the yttrium ions coordinate to the same phenyl ring and DFT calculations indicated the presence of strong δ interactions,[48] while in $[(P_2N_2)Y]_2[\mu-\eta^6:\eta^{6'}\text{-}(C_6H_5)_2]$, the yttrium ions coordinate to different phenyl rings and exhibit fluxional behavior in solution.[47] A fluxional behavior has also been observed in most rare-earth fused arene complexes and is attributed to the loose ionic interaction between the metal ion and the reduced arene anion.[50] Based on these observations, it is evident that δ interactions are stronger than π interactions and have a predominant covalent character. The fact that uranium prefers δ interactions with reduced arenes while lanthanides prefer to form π interactions when both δ and π interactions are accessible, as in the case of the reduced (*E*)-stilbene complex discussed above,[80] indicates that uranium is more prone to form covalent interactions than lanthanides. This can be explained by the following: first, lanthanides are more electropositive than actinides (electronegativity: La 1.1, Lu 1.27; Th 1.3, U 1.38, Pauling scale);[87, 88] second, while the 4f orbitals of lanthanides are core-like and do not participate in bonding interactions, the 5f orbitals of actinides are more diffused and capable to form bonding interactions with ligands.

Despite the fact that lanthanides are less likely than actinides to form covalent interactions with π ligands, covalent interactions between lanthanides and π ligands can be possible in some complexes. For instance, in Y_2K_2-biph, since both yttrium ions coordinate to the same phenyl ring, the negative charges are mainly localized on that phenyl ring. The quadruple reduction results in the filling of both π_4 and π_5 orbitals of benzene (see the orbitals in red in Chart 2) that have δ symmetry. The right symmetry and the high energy of π_4 and π_5 orbitals of benzene match well the empty 4d orbitals of yttrium ions, leading to a strong bonding interaction. The significant orbital overlap suggested by density functional theory calculations is indicative of a covalent interaction. The lack of fluxional behavior in solution also supports this view since covalent interactions are localized and rigid. A recent theoretical study on arene anions supported by metal ions agreed with the interpretation of this electronic structure.[48, 94]

Conclusions

Compared to actinides like uranium, rare-earth metals are less involved in covalent bonding. This is partially because they are more electropositive, however, probably more important, because of orbital mismatch. For actinides, both 6d and 5f orbitals can participate in bonding interactions, and, benefiting from a more acute angle, 5f orbitals are dominant in covalent interactions. In the case of lanthanides, 4f orbitals are core-like and do not participate in bonding, which leaves only the 5d orbitals for bonding. Besides their high energy level, d orbitals are less efficient in covalent bonding interactions than f orbitals. However, despite the lower tendency to form covalent interactions, lanthanides and group 3 metals can still form δ interactions with highly reduced π ligands such as the quadruply reduced benzene. For the future, if we take into account the recent advancements in low valent rare-earth metal chemistry such as the isolation of molecular divalent lanthanide complexes,[95-98] lanthanide reduced arene complexes,[48] and the unprecedented reactivity of lanthanide complexes under reducing conditions,[57] we are certain that the organometallic chemistry of rare-earth metals will witness another era of blossoming with an emphasis on ligand field effects[95] and covalent bonding interactions.[90]

Acknowledgements

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References

1. H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.
2. S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953.
3. B. E. Bursten and R. J. Strittmatter, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1069.
4. A. Streitwieser and U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, 1968, **90**, 7364.
5. A. Zalkin and K. N. Raymond, *J. Am. Chem. Soc.*, 1969, **91**, 5667.
6. R. G. Denning, *J. Chem. Phys. A*, 2007, **111**, 4125.
7. W. J. Evans, *J. Organomet. Chem.*, 2002, **647**, 2.
8. R. G. Denning, J. C. Green, T. E. Hutchings, C. Dallera, A. Tagliaferri, K. Giarda, N. B. Brookes and L. Braicovich, *J. Chem. Phys.*, 2002, **117**, 8008.
9. L. A. Seaman, G. Wu, N. Edelstein, W. W. Lukens, N. Magnani and T. W. Hayton, *J. Am. Chem. Soc.*, 2012, **134**, 4931.
10. M. L. Neidig, D. L. Clark and R. L. Martin, *Coord. Chem. Rev.*, 2013, **257**, 394.
11. S. T. Liddle, *Coord. Chem. Rev.*, 2015, **293–294**, 211.
12. P. L. Diaconescu and C. C. Cummins, *Inorg. Chem.*, 2012, **51**, 2902.
13. B. Vlaisavljevich, P. L. Diaconescu, W. W. Lukens, L. Gagliardi and C. C. Cummins, *Organometallics*, 2013, **32**, 1341.

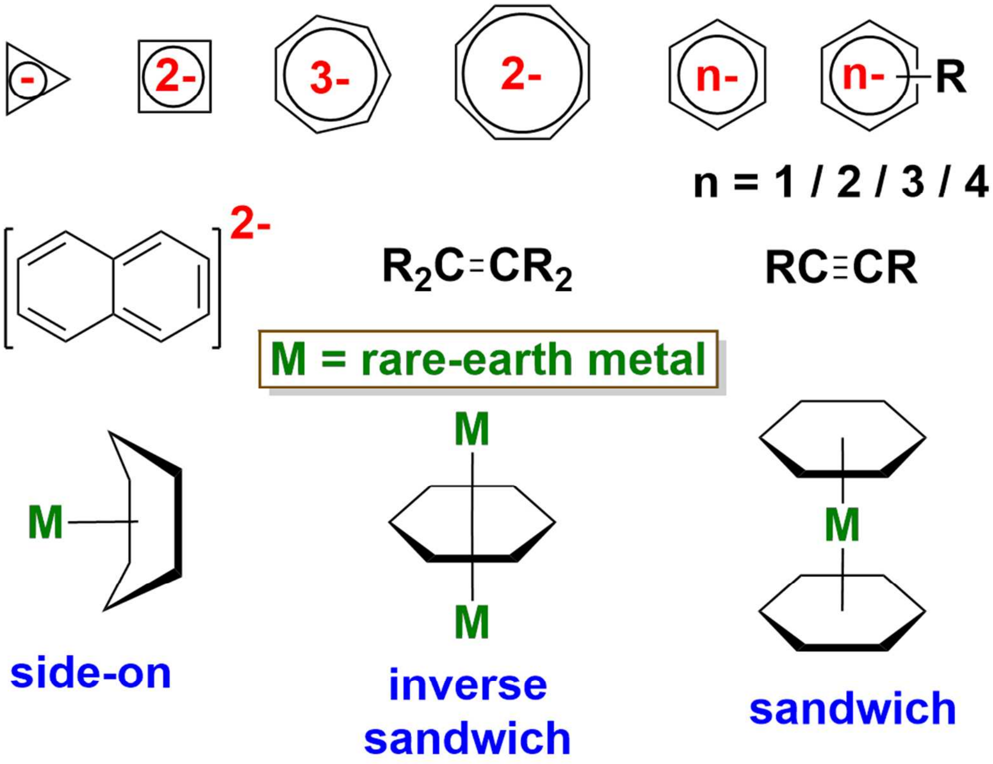
14. S. Fortier and T. W. Hayton, *Coord. Chem. Rev.*, 2010, **254**, 197.
15. A. R. Fox, S. C. Bart, K. Meyer and C. C. Cummins, *Nature*, 2008, **455**, 341.
16. D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, **266–267**, 2.
17. H. S. La Pierre and K. Meyer, in *Prog. Inorg. Chem.*, ed. K. D. Karlin, John Wiley & Sons, Inc., 2014, vol. 58, pp. 303.
18. W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1990, **112**, 219.
19. F. A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, 1986, **108**, 4657.
20. R. Breslow, J. Brown and J. J. Gajewski, *J. Am. Chem. Soc.*, 1967, **89**, 4383.
21. S. R. Kass, *J. Org. Chem.*, 2013, **78**, 7370.
22. D. Patel, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Commun.*, 2013, **4**, 2323.
23. G. Bertrand, L. Tortech, D. Fichou, M. Malacria, C. Aubert and V. Gandon, *Organometallics*, 2011, **31**, 126.
24. M. L. H. Green and D. K. P. Ng, *Chem. Rev.*, 1995, **95**, 439.
25. J. T. Miller and C. W. Dekock, *J. Organomet. Chem.*, 1981, **216**, 39.
26. T. Arliguie, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1994, 847.
27. T. Arliguie, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1995, 183.
28. J. Li and B. E. Bursten, *J. Am. Chem. Soc.*, 1997, **119**, 9021.
29. T. Arliguie, M. Lance, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1997, **14**, 2501.
30. F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851.
31. C. J. Schaverien, in *Advances in Organometallic Chemistry*, eds. F. G. A. Stone and W. Robert, Academic Press, 1994, vol. Volume 36, pp. 283.
32. F. T. Edelmann, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2466.
33. N. M. Edelstein, P. G. Allen, J. J. Bucher, D. K. Shuh, C. D. Sofield, N. Kaltsoyannis, G. H. Maunder, M. R. Russo and A. Sella, *J. Am. Chem. Soc.*, 1996, **118**, 13115.
34. M. D. Walter, C. H. Booth, W. W. Lukens and R. A. Andersen, *Organometallics*, 2009, **28**, 698.
35. A. H. H. Chang and R. M. Pitzer, *J. Am. Chem. Soc.*, 1989, **111**, 2500.
36. N. Hosoya, K. Yada, T. Masuda, E. Nakajo, S. Yabushita and A. Nakajima, *J. Phys. Chem. A* 2014, **118**, 3051.
37. K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2013, **135**, 17952.
38. L. Ungur, J. J. Le Roy, I. Korobkov, M. Murugesu and L. F. Chibotaru, *Angew. Chem. Int. Ed.*, 2014, **53**, 4413.
39. S.-D. Jiang, B.-W. Wang, H.-L. Sun, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2011, **133**, 4730.
40. J. G. Brennan, F. G. N. Cloke, A. A. Sameh and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, 1987, 1668.
41. D. M. Anderson, F. G. N. Cloke, P. A. Cox, N. Edelstein, J. C. Green, T. Pang, A. A. Sameh and G. Shalimoff, *J. Chem. Soc., Chem. Commun.*, 1989, 53.
42. F. G. N. Cloke, *Chem. Soc. Rev.*, 1993, **22**, 17.
43. W. A. King, T. J. Marks, D. M. Anderson, D. J. Duncalf and F. G. N. Cloke, *J. Am. Chem. Soc.*, 1992, **114**, 9221.
44. M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock, M. F. Lappert and F. Laschi, *Organometallics*, 1999, **18**, 5539.
45. M. C. Cassani, D. J. Duncalf and M. F. Lappert, *J. Am. Chem. Soc.*, 1998, **120**, 12958.
46. M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1996, 1987.
47. M. D. Fryzuk, J. B. Love and S. J. Rettig, *J. Am. Chem. Soc.*, 1997, **119**, 9071.
48. W. Huang, F. Dulong, T. Wu, S. I. Khan, J. T. Miller, T. Cantat and P. L. Diaconescu, *Nat. Commun.*, 2013, **4**, 1448.
49. W. Huang, J. J. Le Roy, S. I. Khan, L. Ungur, M. Murugesu and P. L. Diaconescu, *Inorg. Chem.*, 2015, **54**, 2374.
50. M. N. Bochkarev, *Chem. Rev.*, 2002, **102**, 2089.
51. H. E. Zimmerman, *Acc. Chem. Res.*, 2012, **45**, 164.
52. J. Mortensen and J. Heinze, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 84.
53. P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *J. Am. Chem. Soc.*, 2001, **123**, 189.
54. S. Krieck, H. Görls, L. Yu, M. Reiher and M. Westerhausen, *J. Am. Chem. Soc.*, 2009, **131**, 2977.
55. T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith and N. T. Skipper, *Nat. Phys.*, 2005, **1**, 39.
56. C. M. Kotyk, M. R. MacDonald, J. W. Ziller and W. J. Evans, *Organometallics*, 2015, **34**, 2287.
57. W. Huang, F. Dulong, S. I. Khan, T. Cantat and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2014, **136**, 17410.
58. W. Huang and P. L. Diaconescu, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. J.-C. Bünzli and V. Pecharsky, Elsevier, Amsterdam, The Netherlands, 2014, vol. 45, pp. 261.
59. P. L. Diaconescu, *Comments Inorg. Chem.*, 2010, **31**, 196.
60. P. L. Diaconescu, *Acc. Chem. Res.*, 2010, **43**, 1352.
61. C. T. Carver, M. J. Monreal and P. L. Diaconescu, *Organometallics*, 2008, **27**, 363.
62. W. Huang and P. L. Diaconescu, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4090.
63. W. Huang, S. I. Khan and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2011, **133**, 10410.
64. M. D. Fryzuk, L. Jafarpour, F. M. Kerton, J. B. Love and S. J. Rettig, *Angew. Chem. Int. Ed.*, 2000, **39**, 767.
65. P. L. Diaconescu and C. C. Cummins, *J. Am. Chem. Soc.*, 2002, **124**, 7660.
66. P. L. Diaconescu, P. L. Arnold, T. A. Baker, D. J. Mindiola and C. C. Cummins, *J. Am. Chem. Soc.*, 2000, **122**, 6108.
67. M. J. Monreal, S. I. Khan, J. L. Kiplinger and P. L. Diaconescu, *Chem. Commun.*, 2011, **47**, 9119.
68. W. J. Evans, S. A. Kozimor, J. W. Ziller and N. Kaltsoyannis, *J. Am. Chem. Soc.*, 2004, **126**, 14533.
69. W. J. Evans, C. A. Traina and J. W. Ziller, *J. Am. Chem. Soc.*, 2009, **131**, 17473.
70. W. J. Evans and S. A. Kozimor, *Coord. Chem. Rev.*, 2006, **250**, 911.
71. D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, *Nature Chem.*, 2011, **3**, 454.
72. D. Patel, F. Moro, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2011, **50**, 10388.
73. P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nature Chem.*, 2012, **4**, 668.
74. V. Mougel, C. Camp, J. Pécaut, C. Copéret, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem. Int. Ed.*, 2012, **124**, 12446.

75. C. Camp, V. Mougel, J. Pécaut, L. Maron and M. Mazzanti, *Chem. Eur. J.*, 2013, **19**, 17528.
76. C. Melero, A. Guijarro and M. Yus, *Dalton Trans.*, 2009, 1286.
77. D. M. Roitershtein, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 1998, **120**, 11342.
78. W. J. Evans, D. G. Giarikos, C. B. Robledo, V. S. Leong and J. W. Ziller, *Organometallics*, 2001, **20**, 5648.
79. K. Mashima, H. Sugiyama and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1994, 1581.
80. W. Huang, P. M. Abukhalil, S. I. Khan and P. L. Diaconescu, *Chem. Commun.*, 2014, **50**, 5221
81. C. E. Kefalidis, L. Perrin and L. Maron, *Dalton Trans.*, 2014, **43**, 4520.
82. W. J. Evans, R. A. Keyer and J. W. Ziller, *Organometallics*, 1990, **9**, 2628.
83. W. J. Evans, R. A. Keyer and J. W. Ziller, *Organometallics*, 1993, **12**, 2618.
84. H. J. Heeres, J. Nijhoff, J. H. Teuben and R. D. Rogers, *Organometallics*, 1993, **12**, 2609.
85. C. M. Forsyth, S. P. Nolan, C. L. Stern, T. J. Marks and A. L. Rheingold, *Organometallics*, 1993, **12**, 3618.
86. L. A. Seaman, E. A. Pedrick, T. Tsuchiya, G. Wu, E. Jakubikova and T. W. Hayton, *Angew. Chem. Int. Ed.*, 2013, **52**, 10589.
87. L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 3570.
88. A. L. Allred, *J. Inorg. Nucl. Chem.*, 1961, **17**, 215.
89. L. R. Morss, *Chem. Rev.*, 1976, **76**, 827.
90. M. W. Löble, J. M. Keith, A. B. Altman, S. C. E. Stieber, E. R. Batista, K. S. Boland, S. D. Conradson, D. L. Clark, J. Lezama Pacheco, S. A. Kozimor, R. L. Martin, S. G. Minasian, A. C. Olson, B. L. Scott, D. K. Shuh, T. Tyliszczak, M. P. Wilkerson and R. A. Zehnder, *J. Am. Chem. Soc.*, 2015, **137**, 2506.
91. K. Street and G. T. Seaborg, *J. Am. Chem. Soc.*, 1950, **72**, 2790.
92. R. M. Diamond, K. Street and G. T. Seaborg, *J. Am. Chem. Soc.*, 1954, **76**, 1461.
93. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
94. A. Falceto, D. Casanova, P. Alemany and S. Alvarez, *Chem. Eur. J.*, 2014, **20**, 14674.
95. M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2015, **137**, 369.
96. M. R. MacDonald, J. E. Bates, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2012, **134**, 8420.
97. M. R. MacDonald, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 15914.
98. P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem. Int. Ed.*, 2008, **47**, 1488.

Biographies

Paula Diaconescu is Professor of Chemistry in the UCLA Chemistry & Biochemistry department, which she joined in 2005. She obtained her Ph.D. degree from Massachusetts Institute of Technology and was a postdoctoral fellow at the California Institute of Technology. Her earlier education was completed in Romania, where she obtained her B.S. from the University of Bucharest and conducted research at the University Politehnica of Bucharest. The Diaconescu group is interested in the design and synthesis of molecules such as metal complexes with specific geometric and electronic properties, especially of f elements, and those that can function as redox switchable catalysts.

Wenliang Huang obtained his Ph.D. degree from University of California, Los Angeles in 2013. He studied organometallic chemistry of rare-earth metals and actinides with a focus on redox transformations under the supervision of Professor Paula L. Diaconescu. Before that, he graduated from Peking University with a B.S. degree in 2008. Currently, he is a postdoctoral researcher in the Department of Chemistry at Massachusetts Institute of Technology working with Professor Stephen L. Buchwald.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2-
3-
2-
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R
n = 1 / 2 / 3 / 4
2-
$R_2C=CR_2$
$RC\equiv CR$
M = rare-earth metal
M
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side-on
inverse sandwich
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