Organic Synthesis with Elemental Lanthanides – Going Beyond Samarium and Ytterbium

Guillaume Bousrez, Florian Jaroschik

To cite this version:

Guillaume Bousrez, Florian Jaroschik. Organic Synthesis with Elemental Lanthanides – Going Beyond Samarium and Ytterbium. European Journal of Organic Chemistry, 2022, 2022 (18), pp.e202200202. 10.1002/ejoc.202200202 . hal-03679902

EurJOC
European Journal of Organic Chemistry

Review
doi.org/10.1002/ejoc.202200202

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

Special Collection

Organic Synthesis with Elemental Lanthanides – Going Beyond Samarium and Ytterbium

Guillaume Bousrez[a] and Florian Jaroschik*[b]

Dedicated to our friend and colleague Prof. Peter Junk on the occasion of his 60th birthday

Lanthanide (Ln) metals are strong reducing agents ($E^0(Ln^{3+}/Ln^0) \approx -2.3$ V vs. NHE) which can be applied in various manners in organic synthesis. While samarium and ytterbium have been employed for more than 50 years, the last 20 years have seen the emergence of synthetic applications using other metals, such as lanthanum, cerium, praseodymium, neodymium or dysprosium. The large electron reservoir of lanthanide metals, the Lewis acidic character of the Ln^{3+} ions and their intermediate electronegativity compared to lithium or magnesium can provide unique reactivity patterns. This review provides an overview on the potential of these metals for synthetic organic chemistry in the following areas: 1) for Grignard type reactivity and radical generation, 2) in reduction chemistry involving carbonyl compounds and dehalogenation reactions and 3) in combination with transition metals.

1. Introduction

Elemental lanthanide metals were first employed in organic synthesis 50 years ago in the preparation of the first lanthanide Grignard type reagents by the Evans group.[1] Since then, many applications have been found for these metals in organic chemistry as reducing agents or for the generation of radical or organometallic intermediates. Despite the large number of elements in the lanthanide series going from lanthanum to lutetium (formally 15 metals, but promethium is a non-stable radioactive element), their use has long been limited to two elements, namely ytterbium and especially samarium.[2] This observation can be related to several factors:

1) The “magnesium-like” behavior of these two metals, which can both readily form relatively stable Ln^{2+} species, has been employed in Grignard-type chemistry and carbonyl and imine reductions. It should be noted that europium has similar “divalent” properties as Yb and Sm, but has very rarely been used in organic synthesis, which may be related to its lesser reactivity, lower abundance and higher cost.

2) The field of SmI_2 chemistry has seen a huge development since the 1980s.[3] Samarium metal is needed for the preparation of SmI_2 and can sometimes even replace SmI_2.

3) The other lanthanides form predominantly Ln^{3+} species ($E^0(Ln^{3+}/Ln^0) \approx -2.3$ V vs. NHE),[4] due to the instability of the corresponding Ln^{2+} oxidation state, leading to less controlled reaction outcomes and involving several mechanistic scenarios.

Over the last twenty years, “trivalent” lanthanide metals, e.g. lanthanum, cerium, praseodymium, neodymium, dysprosium, have been increasingly investigated. They show either similar reaction outcomes or completely different, often complementary, behavior compared to the “divalent” ytterbium and samarium. This mini-review aims to show the progress in this field, highlighting the differences and providing plausible explanations, whenever possible. Several examples will be presented where screening of a range of zero-valent lanthanide metals showed significant differences on the reaction results. One of the possible reasons could be the lanthanide contraction, which is well established for trivalent Ln^{3+} ions (La^{3+} 103 pm, Lu^{3+} 86 pm) but also present in zero-valent metals (La^0 188 pm, Lu^0 173 pm).[4] It is also important to emphasize that reactions with lanthanide metals are heterogeneous, hence, stirring, surface activation and solvents play an important role. Furthermore, controlling the atmosphere is essential as lanthanides react slowly with oxygen leading to the formation of a lanthanide oxide layer and metal passivation. Consequently, these metals need usually some activation, which can be chemical (I_2, Hg, iodomethane) or physical (filing, heat, ultrasound) or a combination of both. Banik and others have shown a large panel of activation methods for samarium, which can even include the use of highly polar or protic solvents.[2d,5] We have recently shown how to produce lanthanide filings in a glovebox under inert atmosphere to assure the same reaction conditions for all lanthanide metals.[6]

The manuscript has been divided into three main sections describing the use of lanthanide metals in Grignard-type and radical chemistry, followed by reduction chemistry and finally the combination of these metals with transition-metal chemistry. Nevertheless, some overlaps between different sections are possible.

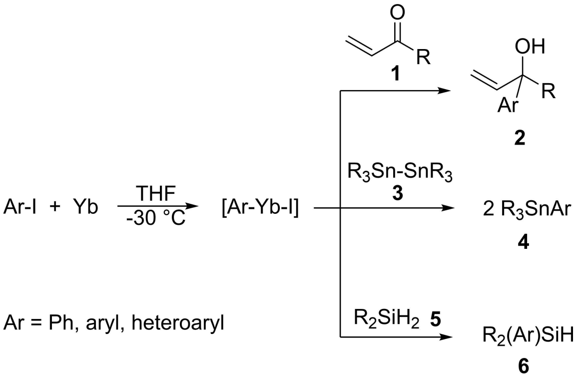
---

[a] *Dr. G. Bousrez*
Department of Materials and Environmental Chemistry
Stockholm University
Svante Arrhenius väg 16C, 10691 Stockholm, Sweden
[b] *Dr. F. Jaroschik*
ICGM, Univ. Montpellier, CNRS, ENSCM
34090 Montpellier, France
E-mail: florian.jaroschik@enscm.fr

Part of the “YourJOC Talents” Special Collection.

2. Lanthanide Grignards and Radical Processes

The "divalent" lanthanide metals Yb, Sm and Eu can react, in analogy to Mg, with organic halides R–X to form lanthanide Grignard type reagents "[R–Ln–X]". Even though, this area has been known for 50 years,[1] it remains a largely undeveloped playground with great potential for organic synthesis and some current developments will be shown in this section. The fundamental understanding of this chemistry is significantly hampered by the redox-activity of divalent lanthanides. Also, the application of "trivalent" lanthanides in this field is still in its early stages.



Scheme 1. Selected applications of [Ar–Yb–I] in organic synthesis.[7–9]

2.1. Aryl halides

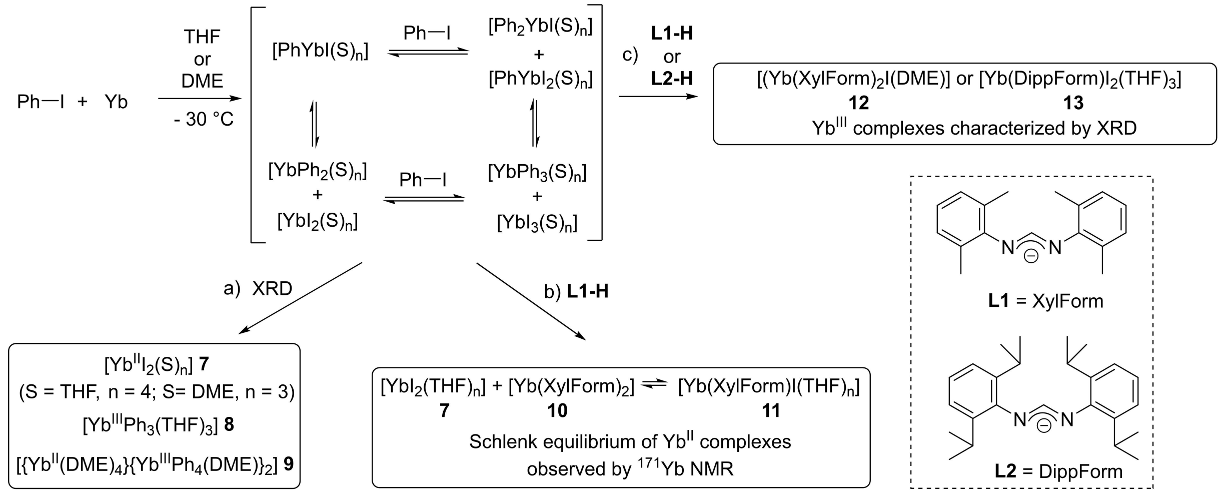
In organic synthesis, early works by the groups of Fujiwara and Petrov focused on the use of in-situ generated aryl and heteroaryl lanthanide halides "[(het)Ar–Ln–X]" employing mainly Yb metal (Scheme 1).[2a,e] These reagents were shown, for example, to undergo highly selective 1,2-addition onto α,β-unsaturated carbonyl compounds **1** and to cleave C–C, Sn–Si or Sn–Sn bonds, such as in **3** (Scheme 1).[7,8] Furthermore they were employed for the synthesis of hydrosilanes **6** from dihydrosilanes **5**,[9] and also in transition-metal catalysed cross-coupling reactions (see also section 4.2).[10] These results have mostly been reviewed.[2a,e]

From an organometallic point of view, the most widely studied reaction involves iodobenzene and Yb metal and recently new insights in this complex reaction have been obtained. (Scheme 2).[11] In ethereal solvents (THF, DME) at low temperatures, this mixture provides a dark red solution of "[PhYbI(S)$_n$]" containing divalent and trivalent species in equilibrium, as shown by magnetic measurement studies.[1] This was further corroborated by the isolation and structural characterization of several complexes: the divalent complexes [YbI_2(S)$_n$] **7** (S = THF, n = 4; S = DME, n = 3), the trivalent complex [$YbPh_3$(THF)$_3$] **8** and the mixed valent complex [{Yb^{II}-(DME)$_4$}[{Yb^{III}Ph$_4$(DME)}$_2$] **9** were isolated and analysed by X-ray diffraction studies (Scheme 2a).[11] The formation of the trivalent complexes may result from oxidation of the intermediate divalent "[PhYbI]" with PhI. Furthermore, a Schlenk equilibrium was evidenced by ^{171}Yb NMR spectroscopic studies when a protic ligand, such as Xylyl-substituted formamidine (**L1-H**), was added to the "[PhYbI(THF)$_x$]" mixture (Scheme 2b). Signals for the three divalent complexes [YbI_2(THF)$_n$] **7**, [Yb(XylForm)$_2$] **10** and [Yb(XylForm)I(THF)$_n$] **11** were detected. Trivalent Yb complexes could not be observed by ^{171}Yb NMR due to paramagnetism, however, trivalent complexes were isolated and structurally characterized, such as [Yb(XylForm)$_2$I(DME)] **12** and [Yb(DippForm)I_2(THF)$_3$] **13** (Scheme 2c), pointing towards the presence of trivalent species, such as [Ph_2YbI(S)$_n$] or [PhYbI_2(S)$_n$] in the reaction mixture.[11]

It should be noted that, in analogous reactions, europium metal provided mainly divalent "[REuI(S)$_n$]" (R = Me, Ph) species as shown by magnetic measurements and reactions with protic

Guillaume Bousrez was born in Charleville-Mézières (France). He completed his PhD at the Université de Reims (France) under the supervision of Prof. J. Szymoniak, Dr. J.-L. Vasse and Dr. F. Jaroschik. His doctoral thesis focused on group 4 metallocene reduction with elemental lanthanides for organic synthesis applications. After a one- year postdoctoral stay at the Centre de l'Energie Atomique (CEA, Saclay, France) where he worked on lignin depolymerisation, he moved to Townsville (Queensland, Australia) to work with Prof. P. C. Junk as a postdoctoral fellow on the synthesis of lanthanide-clusters. In 2017, he joined Prof. A.-V. Mudring's group in Stockholm (Sweden) as a postdoctoral fellow and since 2019 as a Researcher. His research interests focus on luminescent and magnetic ionic liquids.

Florian Jaroschik obtained his M.Sc. in chemistry from the Universität Regensburg, Germany, in 2004. For his Ph.D. studies, he moved to the Ecole Polytechnique in Palaiseau, France, where he worked under the supervision of Dr. F. Nief in the field of low-valent organolanthanide chemistry. After two one-year postdoctoral positions at Monash University, Australia, with Profs. G. Deacon and P. Junk in organolanthanide chemistry, and at the Université Pierre et Marie Curie, Paris VI, with Profs. L. Fensterbank and M. Malacria in gold catalysis, he joined the Institut de Chimie Moléculaire de Reims, France, as a CNRS Research Associate in November 2009. In 2017, he moved to the Institut Charles Gerhardt in Montpellier where he currently works on the synthesis and applications of new organolanthanide complexes and the development of new transformations in organic synthesis based on lanthanide metals, with a special focus on C-F bond activation.

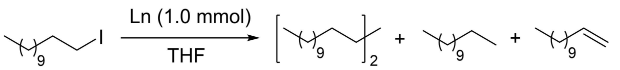


Scheme 2. Reaction of Yb with iodobenzene in the absence and presence of protic ligands showing the isolated divalent and trivalent Yb complexes.[11]

ligands.[1,11] In contrast, samarium formed the most unstable divalent complexes and the presence of divalent "[PhSmI(S)$_n$]" was evaluated to ca. 50% (c.f. 86% for Yb(II), 95% for Eu(II)). Reactions of PhI with "trivalent" metals, such as Ce or La indicated the formation of mainly trivalent species.[1]

2.2. Alkyl halides

In 2002, Sonoda and Nishiyama reported an important explorative study on the reaction of 1-iodododecane **14** with all fourteen lanthanide elements (except the radioactive promethium) in refluxing THF (Scheme 3).[12] It was found that from La to Gd good conversions were observed, whereas the heavier lanthanides provided poor results, except for Yb. Two main products were observed, the reductive dimerization (Wurtz-type coupling) product **15** and the simple dehalogenated reduction product **16**. Small amounts of elimination product **17** were also detected. Interestingly, different behavior was observed in the case of the divalent lanthanides: for Sm the main product was the reduction product **16**, whereas Eu and Yb furnished mainly the dimer **15**. Also, whereas La, Ce, Pr, Nd afforded the dimer **15** as major product, gadolinium led preferentially to the formation of **16**. These results were in relatively good agreement with a previous study by Petrov on the reaction of "divalent" lanthanides Eu, Sm and Yb and "trivalent" Ce with 1-iodo, 1-bromo and 1-chlorooctane in THF.[13]



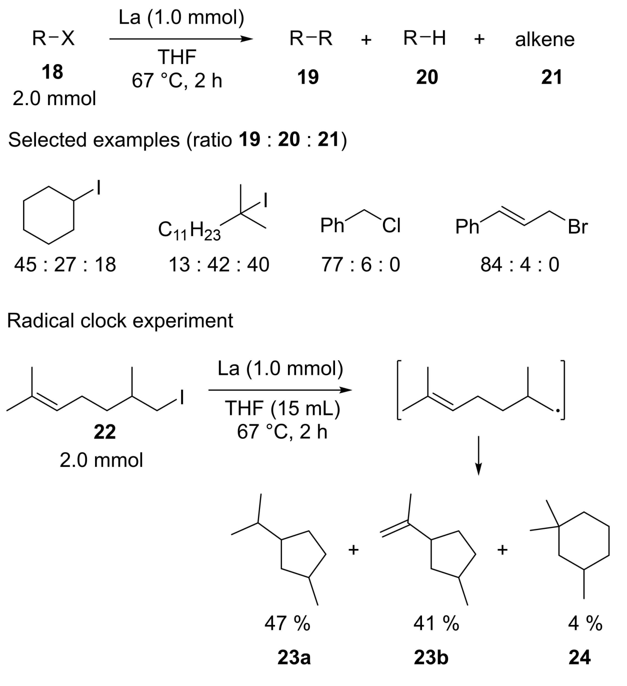
14
2.0 mmol

	15	**16**	**17**
La :	64 %	24 %	6 %
Ce :	45 %	33 %	5 %
Sm :	2 %	49 %	10 %
Eu :	59 %	27 %	4 %
Gd :	23 %	40 %	4 %
Yb :	39 %	27 %	3 %

Scheme 3. Ln-mediated dimerization of 1-iodododecane.[12]

Reactions of La with other primary, secondary and tertiary alkyl halides as well as benzyl and allyl halides **18** were then further investigated yielding in most cases the dimerized products **19** as major products (Scheme 4).[12]

An attempted Barbier-type reaction using cyclohexylmethyl ketone with 1-iodododecane provided only small amounts of the tertiary alcohol product, which would be the expected product for the intermediacy of an organolanthanum complex. Radical clock experiments using La metal with 7-iodo-2,6-



Scheme 4. La-mediated dimerization of primary, secondary and tertiary alkyl halides and mechanistic investigation.[12]

dimethyl-2-heptene **22** led mainly to 5-exo-cyclic ring-closure affording the methylcyclopentane products **23 a** and **23 b** shown in Scheme 4. Overall, these results point towards the possible involvement of radical processes when lanthanum is the reducing agent.[12]

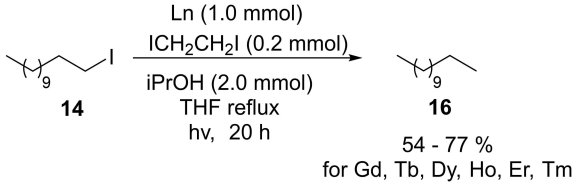
The synthetic utility of this La mediated dimerization process was subsequently shown in the synthesis of *dl*-Chamaejasmine **26** and derivatives (Scheme 5).[14] Even though the yields were only up to 20% for the dimerization reaction of starting compound **25**, this process was more efficient than, for example, with indium metal. It also shows the relatively good functional group tolerance of lanthanum metal.

The La/alkyl halide mediated process was then employed for the synthesis of a variety of unsymmetrical diorganyl selenides and tellurides **29** *via* Se–Se or Te–Te cleavage in substrates **28** (Scheme 6).[15] This reaction was suitable for a variety of alkyl and acyl halides **28**. In the case of Te, lower reaction temperatures provided often better results, especially upon addition of HMPA. Mechanistic control experiments indicated, that it is probably not an alkyl radical or lanthanum-Grignard type species which reacts with the diselenide but the La metal inserts first into the E–E bond to generate [La(EPh)$_n$] species, which then reacts via nucleophilic substitution with the organohalide.

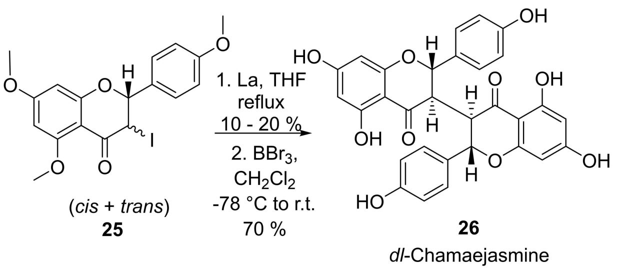
Lanthanide complexes are increasingly employed in photochemical reactions and photocatalytic processes.[16] Ogawa investigated whether the reactivity of lanthanide metals could be augmented under photoirradiation. As described above (Scheme 3), the heavier lanthanides did not react with iodododecane **14** under classical conditions.[17] It was shown that the combination of metal with diiodoethane in THF/isopropanol at 67 °C and exposure to light provided good conversions of the alkyl halide to the dehalogenated product **16** for all lanthanides (Scheme 7). For the lighter lanthanides an increase in yield was observed upon photoirradiation even at room temperature.

The generation of samarium(II) carbenoids from the reaction of diiodomethane with Sm metal has been exploited in Simmons-Smith type processes for the synthesis of cyclopropanes since Molander's seminal work in the 1980s.[18] This chemistry has been nicely reviewed previously.[19]

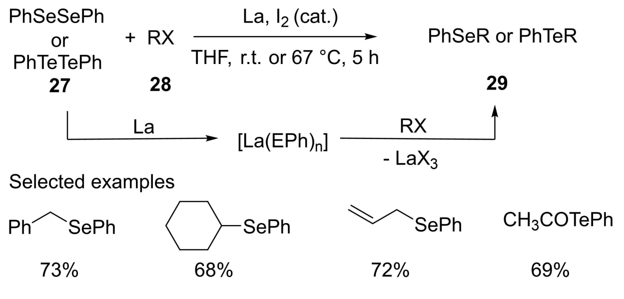
Very recently, the transformation of brominated oxime ethers was investigated using various lanthanide metals.[20] In the case of α-bromo oxime ethers **30**, the reaction yielded unexpectedly 2,4-diarylpyrroles **31** in a highly regioselective manner (Scheme 8).[20a] Ytterbium metal gave the best yields, even though Sm, Nd and Dy also provided the products. Different aryl substituents could be employed. A mechanism based on the initial metal insertion into the C–Br bond was suggested, however, without further evidence. Subsequently, the reaction of lanthanide metals with oxime ethers bearing a bromine group further along the alkyl chain was studied.[20b] In the case of γ-brominated substrates **32** only Yb and Sm gave



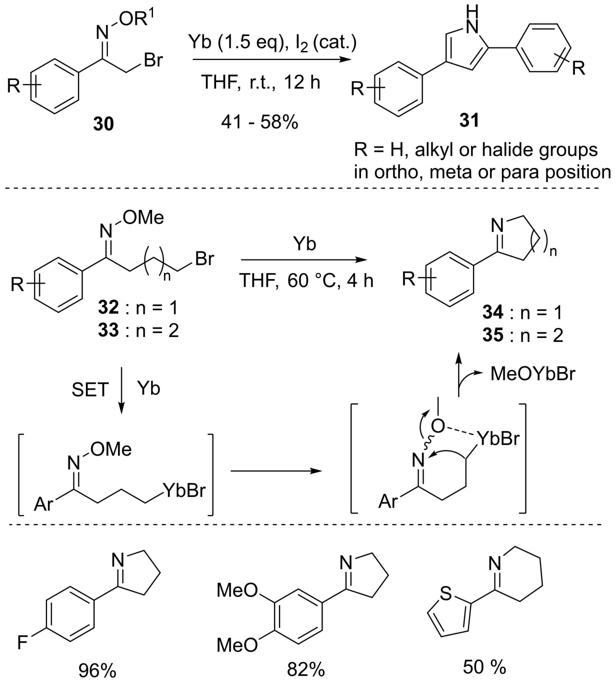
Scheme 7. Ln-mediated dehalogenation of iododecane under photoirradiation.[17]



Scheme 5. La-mediated synthesis of *dl*-Chamaejasmine.[14]



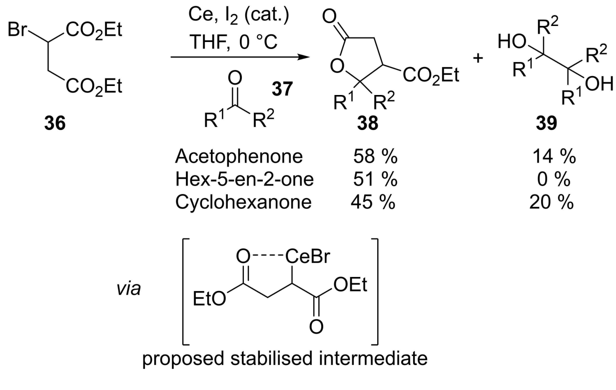
Scheme 6. Synthesis of unsymmetrical diorganyl selenides and tellurides using La metal and alkyl or acyl halides.[15]



Scheme 8. Yb-mediated transformations of brominated oxime ethers.[20]

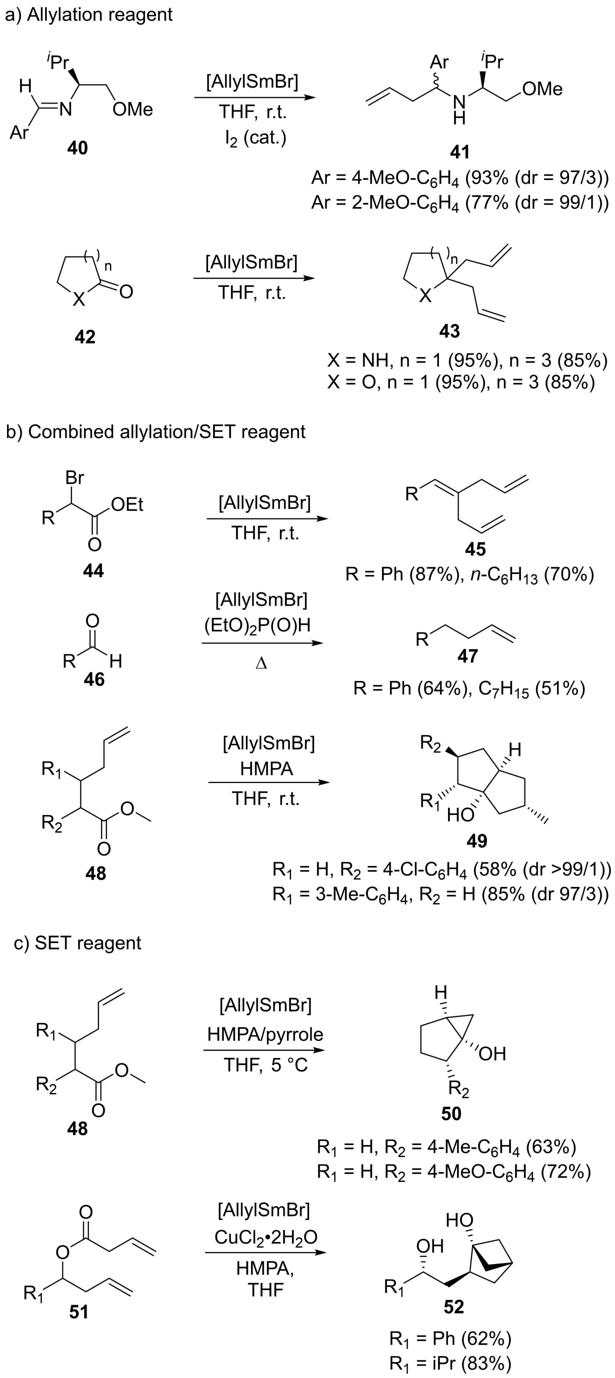
cyclized 5-membered imine products **34**, whereas other metals were not applicable. The highest yields were obtained with Yb metal at 60 °C and this methodology could be extended to a range of compounds with different substituents on the aryl ring. 6-membered products **35** could also be synthesized from precursors **33**, however larger ring sizes (8 or 10) were not formed. It was proposed that the initially formed organoytterbium species would attack the oxime nitrogen to form the imine while releasing an ytterbium-coordinated methoxy group (Scheme 8).[20b]

The chemistry of Ln-enolates and homoenolates has been studied since the 1990s.[21] In 2012, Rodrigue exploited the cerium mediated Reformatsky type reaction of ethyl bromosuccinate **36** with different ketones **37** to access paraconic acid analogues **38** in moderate yields (Scheme 9).[22] The proposed organocerium intermediate, obtained from cerium insertion into the C–Br bond, would be doubly stabilized as enolate and by the β-carbonyl ester group.



Scheme 9. Ce-mediated synthesis of paraconic acid derivatives.[22]

2.3. Allyl halides

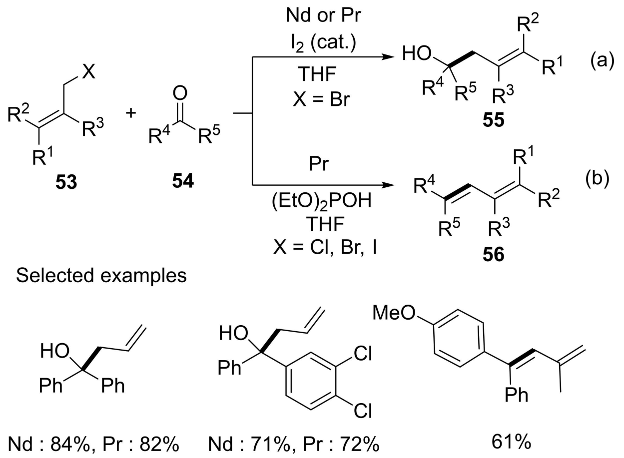


Scheme 10. Applications of [AllylSmBr] as a) an allylation reagent, b) a combined allylation/SET reagent and c) a SET reagent.[24,25]

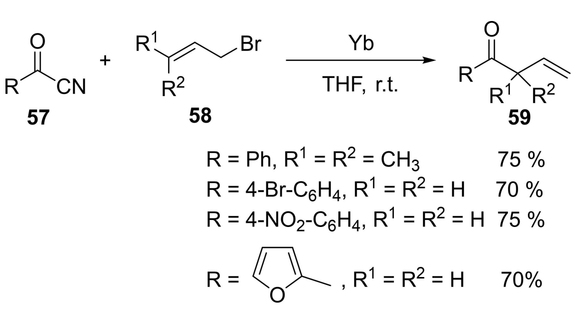
Allylsamarium bromide [AllylSmBr], readily obtained from samarium metal and allyl bromide in THF, was initially reported by Zhang in 1996 for the allylation of imines.[23] A stereoselective version of this reaction was reported in 1999 by Yanada and Ibuka, starting from the non-racemic imines **40** (Scheme 7).[24] Even though not much structural information on this divalent samarium reagent is available, it has attracted widespread interest as an allyl Grignard reagent, and more recently as a combined Grignard/SET reagent (SET = single electron transfer) or only as a highly potent SET reagent, in analogy to SmI_2.[25] Notably, the addition of proton sources and HMPA reduces its nucleophilic character and gives rise to an excellent SET reagent. Some applications are summarized in Scheme 10. The creation of quaternary diallyl carbon centers in compounds **43** was described starting from lactones or cyclic amides **42**.[25a] In 2010, Zhang showed the first use as a combined allyl Grignard/SET reagent in the one-pot synthesis of dienes and trienes, such as **45**, starting from α-halo-ketones and esters, such as **44**.[25c] Subsequently, the same group reported on the synthesis of terminal alkenes **47** from various aldehydes **46** by combining [AllylSmBr] with diethyl phosphate.[25d] More recently, Wang has explored the synthetic potential of this compound as a SET reagent. For example, the ester-alkene substrate **48** can react with [AllylSmBr] in THF/HMPA at room temperature to form the bicyclic skeletons **49** via an allylation/SET process.[25i] In contrast, addition of pyrrole to the reaction mixture and cooling to 5 °C led to the cyclopropanols **50** via a SET induced cyclization. Similarly, addition of $CuCl_2$ to the reaction of diallyl compound **51** with [AllylSmBr] in THF/HMPA provided only SET reactivity and a cascade cyclization to bicyclo[2.1.1]hexanols **52**.[25f]

Interestingly, this allyl chemistry is not limited to Sm (or Yb),[26] but it was shown that Nd and Pr could also form allyl lanthanide reagents for the selective allylation of ketones (Scheme 11a).[27] These Barbier type reactions were performed with catalytic amounts of iodine and provided exclusively the linear addition products **55** starting from a range of allyl halides **53** and diarylketones **54**. The intermediate formation of a divalent Ln-allyl species was proposed; however, this could not be confirmed so far, probably due to the very short-lived character of such highly reactive complexes. Furthermore, in the presence of diethylphosphate, the reaction with Pr furnished dienes **56** in a one-pot approach, in analogy to Sm (Scheme 11b).[28]

In contrast to this highly selective linear addition, it was shown that ytterbium provided the possibility to access β,γ-unsaturated ketones **59** in the reaction of allylbromides **58** with α-oxonitriles **57**.[29] The corresponding branched products were obtained in high yields and the reaction showed good functional group tolerance (Scheme 12).



Scheme 11. Nd and Pr mediated allylation of ketones and formation of dienes.[27,28]



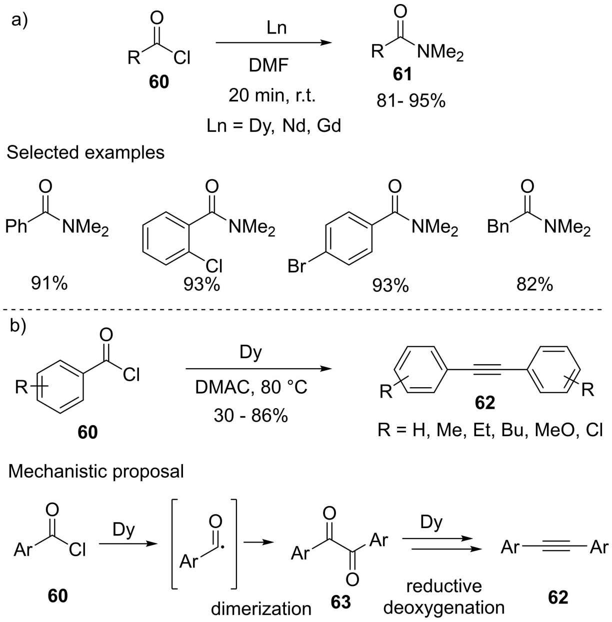
Scheme 12. Yb-mediated coupling of α-oxonitriles with allylbromides.[29]

2.4. Acyl chlorides

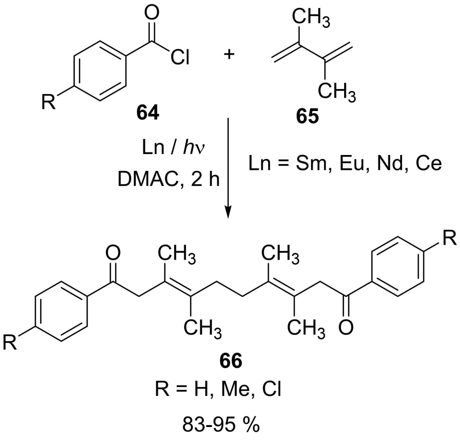
Early work by Petrov showed that the reaction of acyl chlorides with "divalent" Ln metals in THF afforded a mixture of diketones/benzoin and benzylphenyl ketone.[30] Furthermore, acylphosphonates and acylsilanes were studied by Fukuzawa, revealing insertion of the lanthanide metal into the C–P or C–Si bond and further reaction with electrophiles.[31]

More recently, the reaction of acyl chlorides **60** with various lanthanides in N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMAC) was investigated (Scheme 13).[32] It turned out that the major products in DMF at room temperature were dimethylbenzamide derivatives **61** (with Dy, Nd, Gd) (Scheme 13a). In contrast, in DMAC only Dy was reactive and furnished diphenylacetylenes **62** at 80 °C in high yields (Scheme 13b). In both cases, the initial formation of an acyl radical was proposed for the mechanism. This radical might react with DMF to provide dimethylbenzamides via cleavage of the DMF molecule. In DMAC, the radical would dimerize to the corresponding 1,2-dione **63**, which was isolated in the case of p-Cl-benzoyl chloride. Compound **63** would be further reduced by dysprosium metal to provide the acetylene **62**.[32]

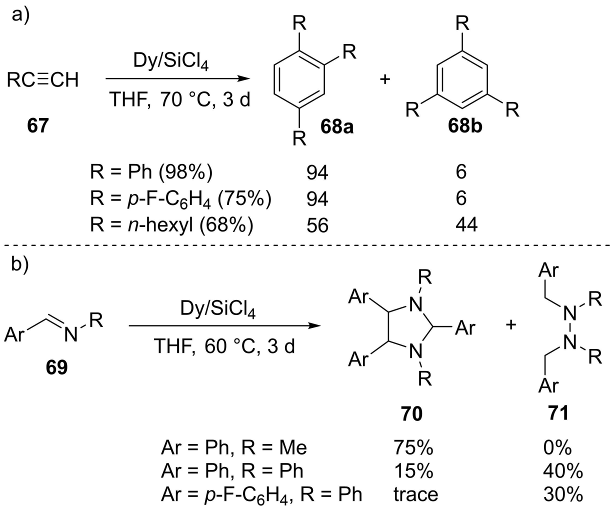
Additionally, the reductive coupling of different benzoyl chlorides **64** with 1,3 dienes **65** or styrenes was demonstrated using a Ln/DMAC/hv system (Xe lamp, Ln = Ce, Nd, Eu, Sm) (Scheme 14).[33] Exposure to light decreased the reaction time from 6 to 2 hours and increased the yield of **66** considerably by up to 60% compared to the reactions in the dark, depending on the lanthanide metal.



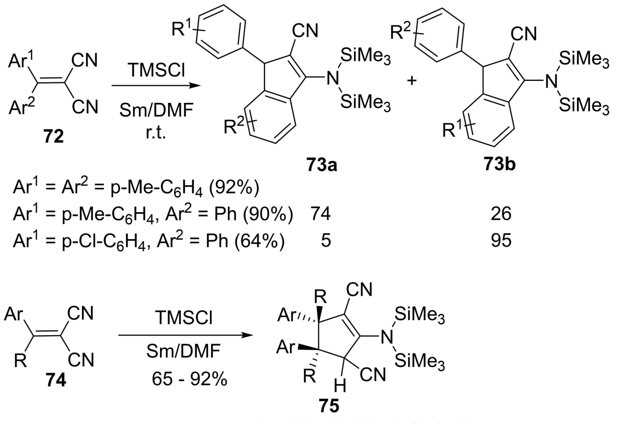
Scheme 13. Reaction of acyl chlorides with Ln in DMF and DMAC.[32]



Scheme 14. Reductive coupling of benzoyl chlorides with 1,3 dienes using Ln/DMAC/hv system.[33]



Scheme 15. (a) Alkyne cyclotrimerization and (b) reductive imine dimerisation with Dy/$SiCl_4$.[34]



Scheme 16. Transformation of gem-dicyanoethenes by Sm in DMF.[35]

2.5. Miscellaneous (radical) reactions

Radical cyclotrimerization of terminal alkynes **67** was induced by a mixture of dysprosium metal and tetrachlorosilane in refluxing THF (Scheme 15a).[34] The reaction showed high regioselectivity for aryl substituted alkynes, whereas alkyl substituents provided a near 1:1 ratio of **68a**:**68b**. Other lanthanides were less efficient and SmI_2 or sodium metal gave no product at all. The Dy/$SiCl_4$ system was also employed for the reductive dimerization of imines leading unexpectedly to imidazolines **70** and tetrasubstituted hydrazines **71** depending on the substituents on the imine (Scheme 15b).[34]

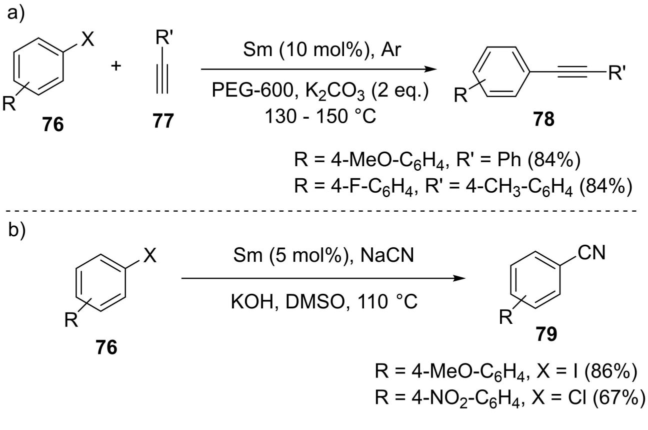
Two different reaction outcomes were observed in the reaction of Sm metal with gem-dicyanoethenes in DMF in the presence of trimethylsilyl chloride (Scheme 16).[35] For diaryl substituted substrates **72**, the formation of indene derivatives **73** was obtained. In the course of this reaction one cyano group was reduced and disilylated at the nitrogen atom. The substituent on the aryl group played an important role for the regioisomer formation, e.g. p-Me vs p-Cl led to an inversion of the ratio **73a**:**73b**.

On the other hand, aryl alkyl substituted gem-dicyanoethenes **74** led to dicyano substituted cyclopentenes **75** bearing again a disilylated amino group (Scheme 16).[35]

The use of lanthanides in catalytic amounts has been rarely described. In 2009, it was shown that Sm metal catalyzed the Sonogashira coupling of aryl iodides **76** and alkynes **77** (Scheme 17a).[36] Very recently, the cyanation of aryl halides under samarium catalysis was reported (Scheme 17b).[37] Good substrate scope was observed for aryl iodides and bromides **76**. A possible radical mechanism was proposed for the formation of **79**. The Sm metal could be recovered and reused at least 3 times in both processes.

3. Reduction Chemistry

Lanthanide metals often show intermediate reactivity between alkali and alkaline earth metals with respect to reduction



Scheme 17. Sm metal catalyzed (a) Sonogashira coupling and (b) cyanation of arylhalides.[36,37]

reactions. Due to their lower reactivity towards oxygen, they can be considered as a safer alternative to alkali metals. Various reduction systems have been reported, such as the Ln/LnI_2 system (Ln = Sm, Yb) for deoxygenative amide reduction,[38] SmI_2/Mischmetal for catalytic SmI_2 transformations[39] and Birch-type reductions of aromatics and alkenes using Yb in liquid ammonia.[40] Furthermore, the reduction of nitro groups to amines and the reduction and homocoupling reactions of imines and carbonyls using Sm-based conditions have been well investigated and reviewed by Banik.[2d,41] More recently, the Meerwein-Ponndorf-Verley reduction of carbonyls with Sm/iPrOH system was reported.[5c]

3.1. Carbonyl compounds

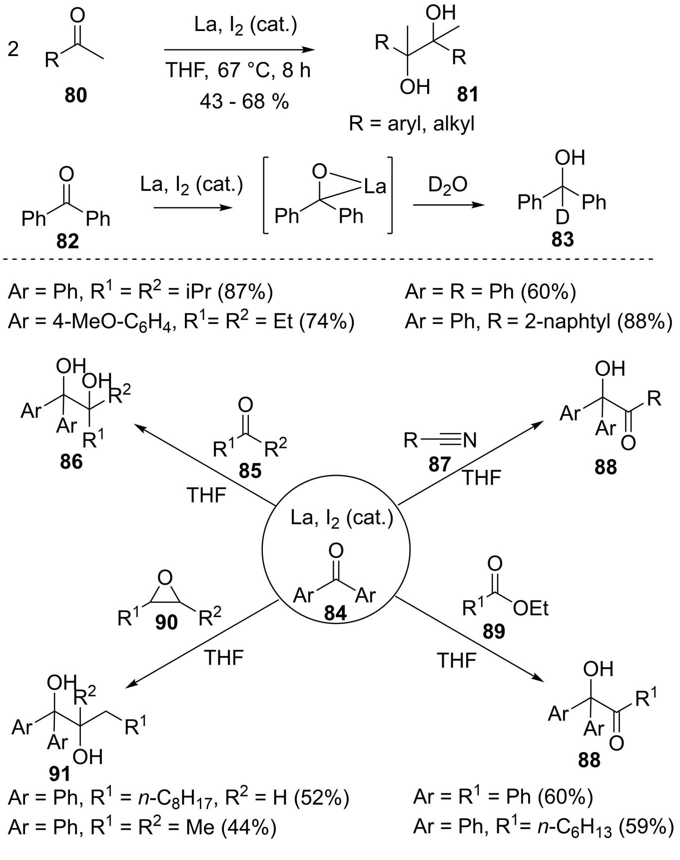
The Umpolung reaction of diarylketones, arylaldimines and diarylthioketones with Yb metal has been intensely studied.[42] The corresponding dianionic Yb-ketyl, iminyl or thioketyl products were structurally characterized, such as [Yb(Ph_2CO)$(HMPA)_2$] and [Yb(Ph_2CNPh)$(HMPA)_3$], and their reactivity investigated. Addition of other electrophiles, for example, CO_2 or esters to the Yb-ketyl complex provided the synthesis of cross-coupling products. These results have already been reviewed.[2a,42f]

From 2000 on, Nishiyama and Sonoda showed that the "trivalent" lanthanum could provide similar reaction outcomes with carbonyls and imines after activation with catalytic amounts of iodine.[43] A range of ketones **80** could be converted to the reductive dimerization products **81** (Scheme 18). No structural information on the reaction intermediates has been reported so far. Nevertheless, a radical process seems less plausible based on deuteration studies and the isolation of deuterated compound **83**, which are in favor of an organometallic lanthanum-ketyl type species (Scheme 18).[43] A range of cross-coupling reactions between the in situ generated lanthanum-ketyl complex and several electrophiles was carried out (Scheme 18).[44] Reaction with ketones **85** led to vicinal diols **86**, whereas addition of nitriles **87** or esters **89** afforded α-hydroxy ketones **88** under mild conditions. From the reaction with epoxides **90** the 1,2-diols **91** were obtained after initial Meinwald rearrangement.[44]

3.2. Dehalogenation reactions

The reduction potential of lanthanide metals and the formation of strong Ln-halogen bonds constitute powerful driving forces for the dehalogenation reactions of different dihalogenated organic substrates. An early example is the double debromination of 1,2-dibromocycloalkanes using samarium metal leading to cyclic alkenes.[45]

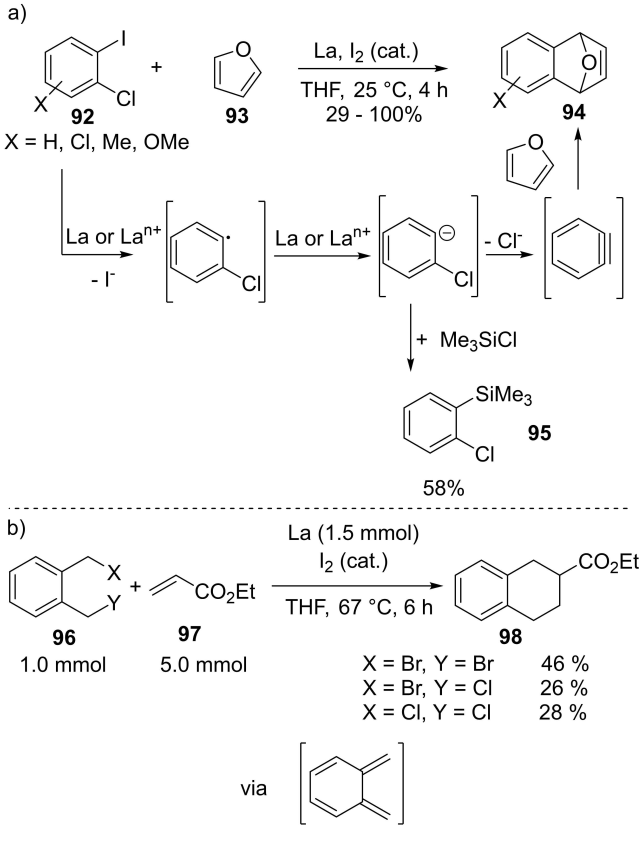
In 2001, Nishiyama reported the aryne formation from 1,2-dihalogenated arenes **92** using lanthanide metals in THF at room temperature (Scheme 19a).[46] The unstable aryne intermediate was trapped by furan **93** or other dienes. Interestingly, only the early lanthanides (La, Ce, Pr, Nd) and Yb could be employed providing moderate to excellent yields of the adduct **94**. Addition of catalytic amounts of iodine was necessary to obtain good reaction outcomes. It was suggested that two consecutive one-electron reductions occurred providing a phenyl anion and iodine abstraction. This intermediate could then either form the aryne or be quenched by an electrophile such as trimethylsilylchloride to yield **95**.



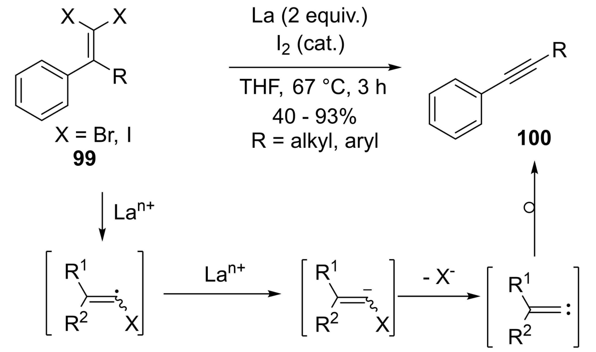
Scheme 18. Reduction of diarylketones by lanthanum metal and cross-coupling reactions.[43,44]

Subsequently, it was shown that dihalogen substituted o-xylenes **96** reacted with lanthanum metal to afford a reactive non-aromatic diene intermediate, which was trapped by electron-poor alkenes **97** to afford the corresponding Diels-Alder products **98** in moderate yields (Scheme 19b).[47]

Furthermore, the synthesis of alkynes **100** from gem-dihaloalkenes **99** via a Fritsch-Buttenberg-Wiechall (FBW) rearrangement was reported using iodine activated lanthanum metal in refluxing THF (Scheme 20).[48] This procedure provided access to a range of 1,2-diaryl and 1-aryl-2-alkylalkynes. Mechanistically, two consecutive one-electron reductions by the lanthanum metal and halide abstraction should lead to the generally proposed carbene intermediate of the FBW reaction which then rearranges to the alkyne product via a 1,2 aryl shift.



Scheme 19. La-mediated formation of (a) arynes and (b) non-aromatic dienes for Diels-Alder reactions.[46,47]



Scheme 20. La-mediated FBW rearrangement of gem-dihaloalkenes.[48]

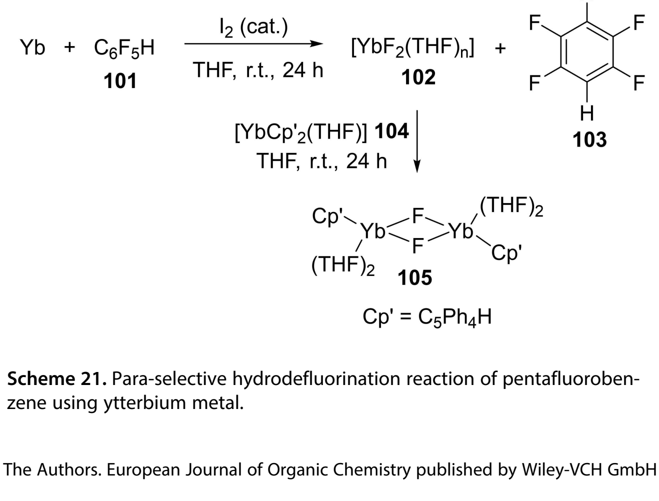
3.3. C–F bond activation

The C–F bond is one of the strongest C-heteroelement bonds requiring often harsh conditions for cleavage. Rare earth complexes have been applied for the selective C–F bond activation in aromatic compounds as this process is favored by the formation of very strong Ln–F bonds.[49] In 2014, the first example of zero-valent lanthanide metal mediated C–F bond activation was reported. The reaction of iodine-activated ytterbium metal with pentafluorobenzene **101** afforded regioselectively 1,2,4,5-tetrafluorobenzene **103** and [$YbF_2(THF)_n$] **102** (Scheme 21).[50a] A mechanism based on the formation of aryl radicals after reductive C–F bond cleavage was proposed. The formation of [$YbF_2(THF)_n$] under such mild conditions was confirmed by further reaction with an Yb sandwich complex [$Yb(C_5Ph_4H)_2(THF)$] **104** to yield the first divalent organoytterbium fluoride complex [$Yb(C_5Ph_4H)(\mu\text{-}F)(THF)_2]_2$ **105**. Very recently, this selective transformation was also achieved with europium metal.[50b]

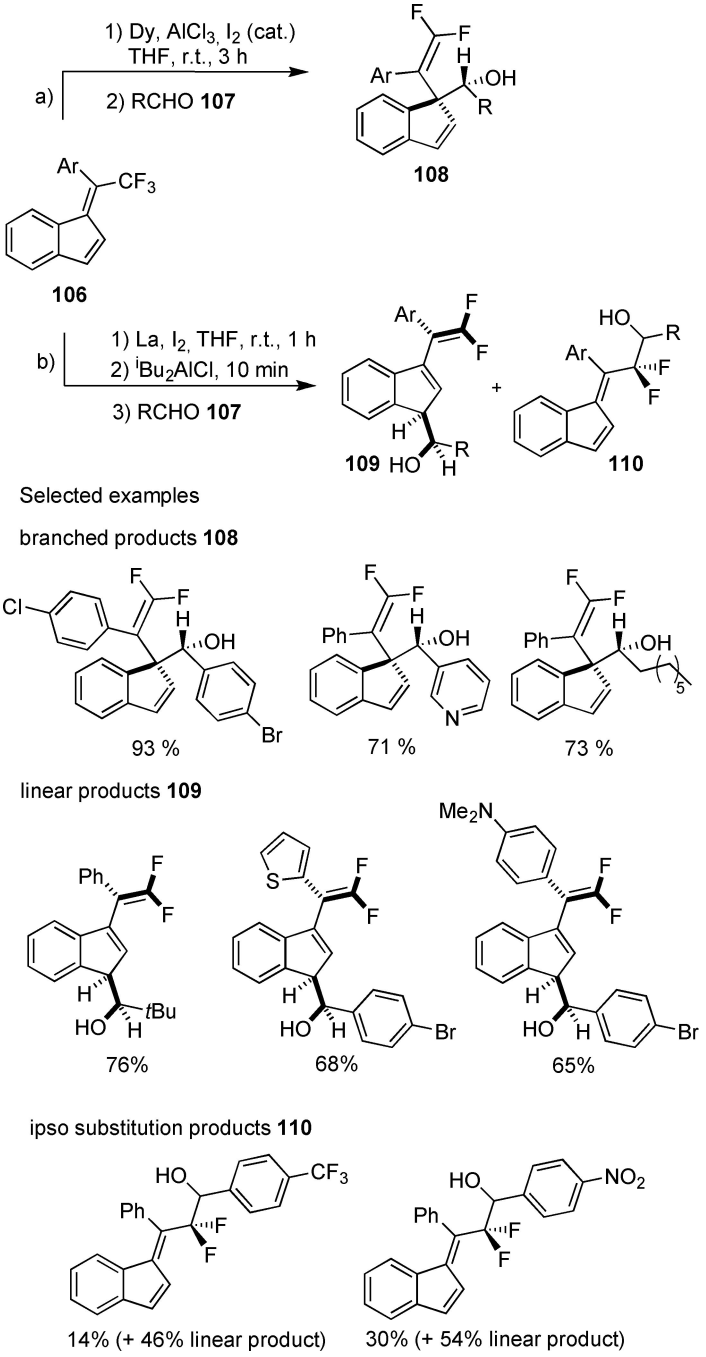
The combination of lanthanide metals with Lewis acids allowed selective single C–F bond activation in trifluoromethylated benzofulvenes **106** (Scheme 22).[51] Initially, it was found that iodine activated dysprosium metal reacted with **106** in the presence of three equivalents of $AlCl_3$ and a variety of aldehydes **107** to give the branched products **108** in excellent regio and diastereoselectivity and high yield (Scheme 22a).[51a] Other lanthanide metals were less efficient or provided a mixture of regioisomers. Different aryl groups on the benzofulvene **106** were tolerated. Subsequently, the reaction outcome was steered towards the selective formation of the linear product **109** by switching to lanthanum metal and in-situ generated LaI_3 as Lewis acid (Scheme 22b).[51b] In this case, most aliphatic and aromatic aldehydes **108** provided the linear product **110** again in high yield and diastereoselectivity. However, in the case of electron-poor aldehydes, e.g. the p-CF_3 or p-NO_2 substituted benzaldehydes, the unprecedented ipso-substitution occurred to some extent affording a mixture of **110** and **111**. A preliminary study has shown that nitroalkenes are also suitable electrophiles for this transformation leading selectively to the formation of linear products.[6]

In follow-up reactions, the branched product **108** could be converted to the spirocyclic product **112** via selective hydrogenation followed by S_NV cyclization (Scheme 23).[51a] Furthermore, the new benzofulvenes **113** were obtained from the reaction of linear product **109** with mesylchloride and triethylamine.[51b] Interestingly, when the electron-rich p-NMe_2-benzaldehyde was employed in the Dy or La mediated process shown in Scheme 22, benzofulvene **113** was obtained directly after spontaneous dehydration.[51]

Mechanistic insights on this new transformation of trifluoromethylated benzofulvenes were obtained from ^{19}F NMR spectroscopy, ESI-MS and DFT calculations.[51] These studies



Scheme 21. Para-selective hydrodefluorination reaction of pentafluorobenzene using ytterbium metal.



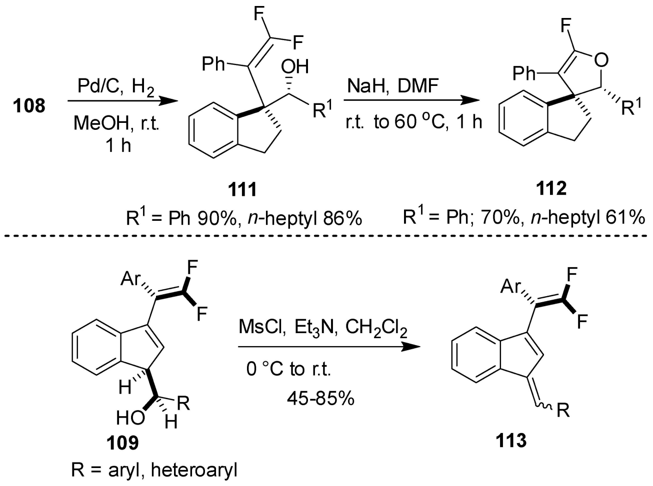
Scheme 22. Selective C–F activation in trifluoromethylated benzofulvenes leading to regio- and diastereoselective transformations.[51]

indicated the formation of a metal pentadienyl species **114** after the initial lanthanide-mediated C–F activation process in **106** (Scheme 24). This complex **114** is in equilibrium with the aluminum compound **115** via transmetallation. The aluminum species would lead selectively to the branched product, whereas the lanthanide species would form the linear product and to a certain extent the ipso-product.

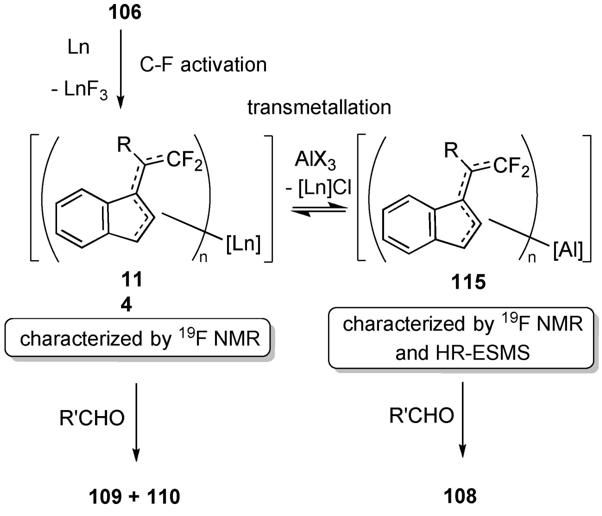
4. Combination with Transition Metals

4.1. Early TM

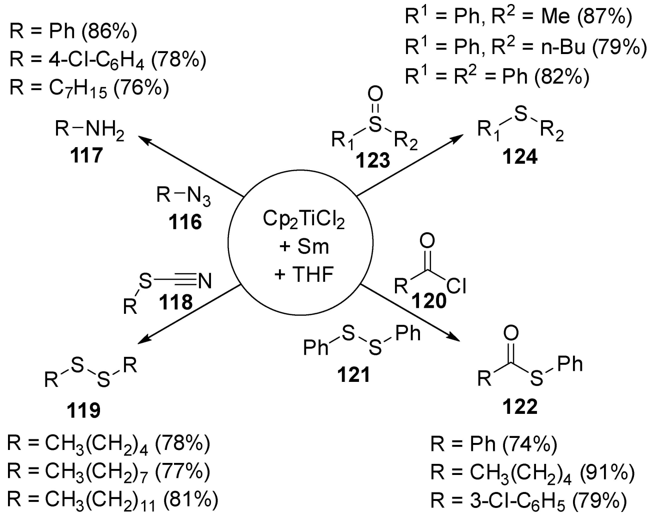
Starting from 1995 on, Zhang and coworkers studied the reduction of Cp_2TiCl_2 with samarium metal and explored the reactivity of this bimetallic system.[52] In most cases, similar reactivity was observed as with SmI_2 alone, leading to the proposition that an active $[Cp_2TiCl–SmCl_2]$ complex might form.[52a] Among the investigated reactions were the reduction



Scheme 23. Transformations of gem-difluoroalkenes **108** and **109** to spirocyclic product **112** and new benzofulvenes **113**.[51]



Scheme 24. Proposed mechanism of C–F activation in trifluoromethylated benzofulvene.[51]



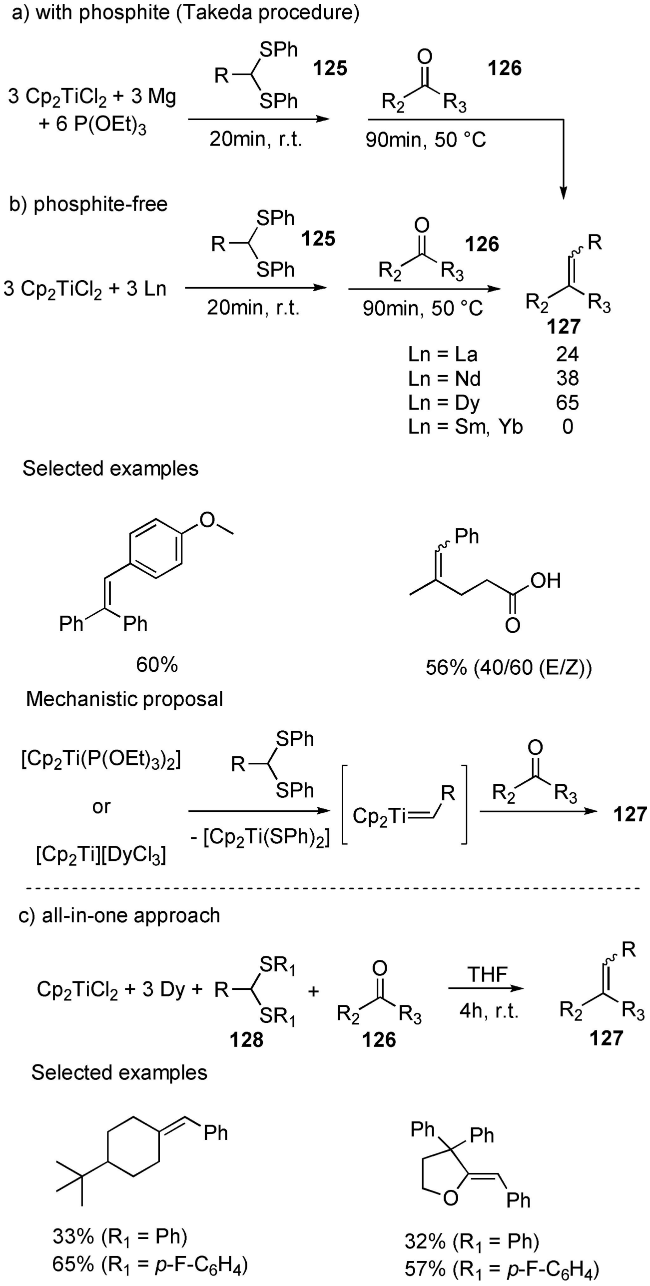
Scheme 25. Early applications of bimetallic Cp_2TiCl_2/Sm system.

of azides **116** to amines **117**, the synthesis of dialkyl disulfides **119** from alkylthiocyanates **118** via reductive cleavage of the C–S bond, the coupling of diaryldisulfides **121** with acylchlorides **120** to the thioesters **123**, as well as the reduction of sulfoxides **123** (Scheme 25).[52]

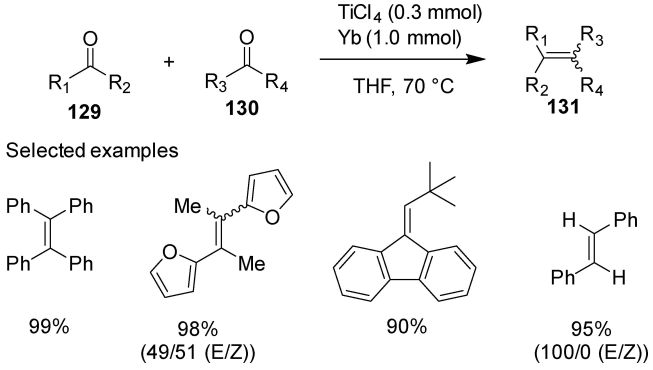
More recently, we investigated the use of a bimetallic titanocene/lanthanide system for the olefination of carbonyl groups using the Takeda approach.[53] This pathway requires a stabilized divalent titanocene species $[Cp_2Ti(P(OEt)_3)_2]$, usually obtained by the reduction of Cp_2TiCl_2 with Mg and $P(OEt)_3$, for the reaction with dithioacetals **125**, followed by addition of the carbonyl group **126** (Scheme 26a).[54] Our aim was to suppress the use of phosphite and to simplify the approach via an all-in-one procedure. It was found that among several tested lanthanides, dysprosium provided the best results in the absence of phosphite giving access to a range of alkenes **127** in a stepwise process, starting from aldehydes, ketones, esters and lactones **126** (Scheme 26b).[53] Upon introduction of a fluorine atom in the para position of the phenyl groups on the dithioacetal **128** it was also possible to obtain several products **127** in an all-in-one procedure, even at room temperature, whereas the sequential approach required heating to 50 °C (Scheme 26c). It should be noted that ytterbium and samarium could not be applied in this reaction in agreement with their formation of Ti(III) complexes (see above and below).

At the same time, Lin developed a highly efficient McMurry carbonyl olefination process using a catalytic $TiCl_4$/Yb system (Scheme 27).[55] A large range of aldehydes and ketones **129** and **130** could be reductively homo or cross-coupled to the corresponding alkenes **131**. Dy or Sm metal were also suitable reagents. A detailed mechanistic study was conducted, showing that the lanthanide metal had two roles in this procedure. The first was the generation of the active Ti(III) species by reduction of $TiCl_4$. Second, the metal served further as easily removable final oxygen trap by reacting with Ti–O species formed during the reductive coupling of the carbonyls.

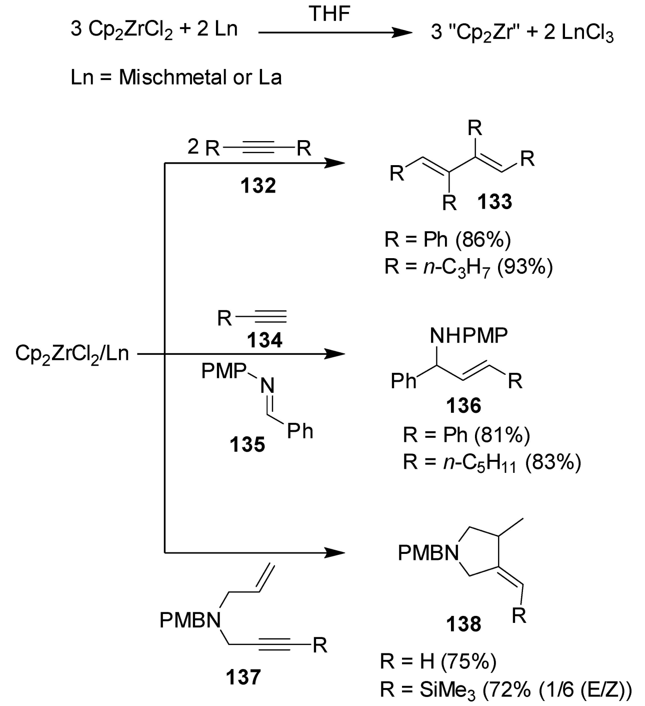
Low-valent zirconocene complexes are important intermediates for the reductive coupling of unsaturated organic compounds such as alkenes, alkynes or imines.[56] Starting from 2006 on, the groups of Szymoniak and Lamy have shown that the combination of zirconocene dichloride with lanthanides could open up new reaction behaviors and potentially lead to catalytic procedures. Initially, the reduction of Cp_2ZrCl_2 with Mischmetal was investigated providing a reactive zirconocene(II) intermediate $[Cp_2Zr]$ which could be employed in reductive coupling processes of internal alkynes **132** (Scheme 28).[57] Importantly, this reagent was also suitable for terminal alkynes **134**, allowing reductive homocoupling but also cross-coupling with imine **135** to afford allylamines **136**. Using the enyne precursor **137** the cyclized product **138** was obtained in an intramolecular fashion in good yields.



Scheme 26. Comparison of classical Takeda olefination with phosphite-free version using Cp_2TiCl_2/Dy system.[53,54]



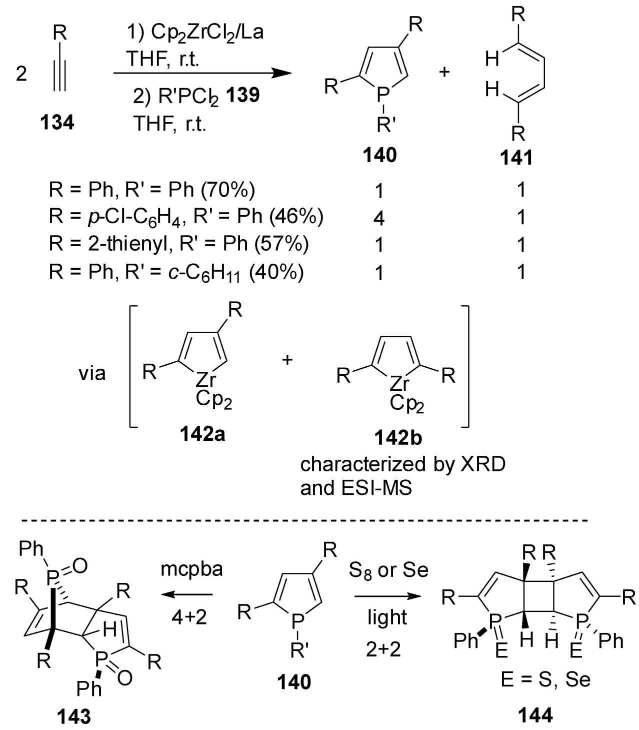
Scheme 27. McMurry carbonyl olefination using catalytic $TiCl_4$/Yb system.[55]



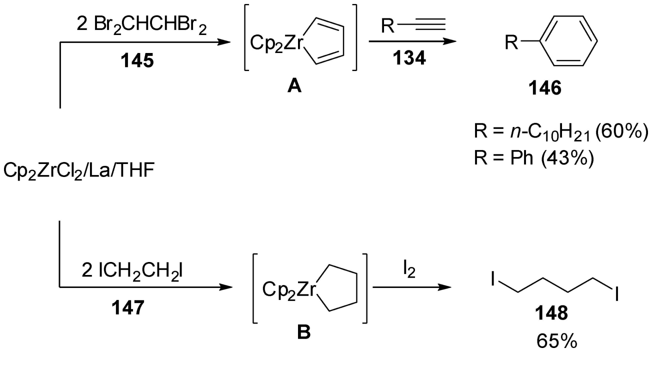
Scheme 28. Initial applications of Cp_2ZrCl_2/Ln system.[57]

The possibility of reductive dimerization of terminal alkynes provided a convenient entry point to accessing new phosphorus heterocycles bearing substituents selectively in the 1,2,4 positions (Scheme 29).[58] The reaction of Cp_2ZrCl_2 with La in the presence of various terminal alkynes **134** led to mixtures of zirconacyclopentadienes **142a** and **142b**. Only the less hindered complex **142a** reacted with $R'PCl_2$ to yield the desired phospholes **140**, whereas **142b** furnished the 1,4-disubsituted butadienes **141**. The reaction was selective with a range of terminal alkynes as well as differently substituted phosphine dichlorides. According to DFT studies and XRD studies on the 2,5-diphenyl substituted intermediate, the steric bulk around the metal center may be the reason for this selective reaction outcome.[58] Oxidation of these new phospholes **140** with oxygen led to classical [4+2] homodimerization products **143**, whereas with sulfur or selenium unexpected photoinduced [2+2] reactions occurred to afford products **144** in a highly regio and stereoselective manner (Scheme 29).[59]

The above described dehalogenation reactions with La metal (Scheme 19 and 20) further inspired this work to access the unsubstituted zirconacyclopentadiene complex **A** and zirconacyclopentane complex **B** (Scheme 30).[60] The reaction of La metal with tetrabromoethane **145** led to the in-situ generation of acetylene which reacted with $[Cp_2Zr]$ to form complex **A**. A [2+2+2] cyclotrimerization process was observed upon further reaction of **A** with terminal alkynes **134** leading to benzenes **146**. (Scheme 30). Similarly, reaction of La



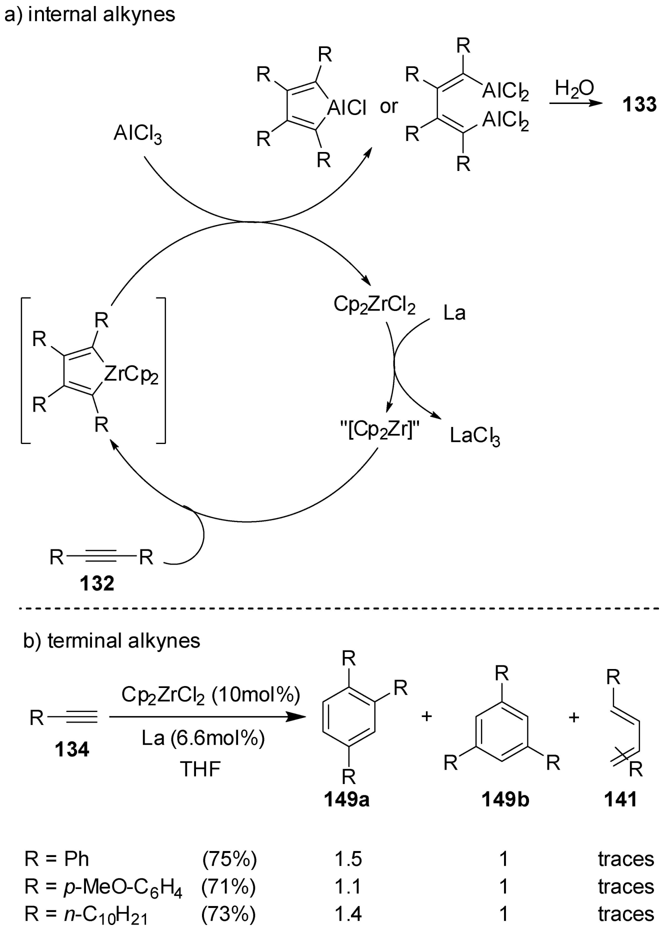
Scheme 29. Selective access to 1,2,4-trisubstituted phospholes and their reactivity.[58,59]



Scheme 30. Concomitant reduction and dehalogenation with the Cp_2ZrCl_2/Ln system.[60]

metal with 1,2-diiodoethane **147** provided ethylene and consequently complex **B**, which gave 1,4-diiodobutane **148** after reaction with iodine.[60]

Importantly, the reductive dimerization of internal alkynes **132** was rendered catalytic in Zr by addition of an excess of $AlCl_3$ (Scheme 31a).[61] Mechanistically, it was proposed that a transmetallation from Zr to Al would be involved regenerating starting Cp_2ZrCl_2. However, this process was only valid for internal alkynes, whereas for terminal alkynes **134** a [2+2+2] cyclotrimerization occurred to give an unselective mixture of benzenes **149**, even in the absence of $AlCl_3$ and with catalytic amounts of Zr and La (Scheme 31b). The mechanism behind this transformation has not been elucidated so far.[61]

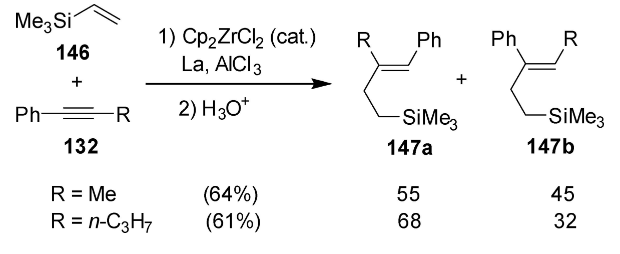


Scheme 31. Catalytic reductive dimerization and trimerization using the Cp_2ZrCl_2/Ln/$AlCl_3$ system.[61]

Finally, the combination of Cp_2ZrCl_2 with La also yielded highly selective reductive dimerization of imines[62] and the coupling of vinylsilane **146** with alkynes **147**, the latter also in the catalytic version with $AlCl_3$ (Scheme 32).[63]

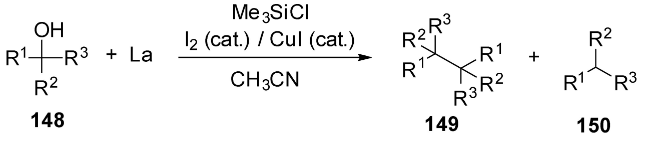
4.2. Late TM

As early as 1984, Fujiwara explored the cross-coupling reaction of ytterbium-Grignard reagents with alkyl and vinyl halides under Cu catalysis.[10]



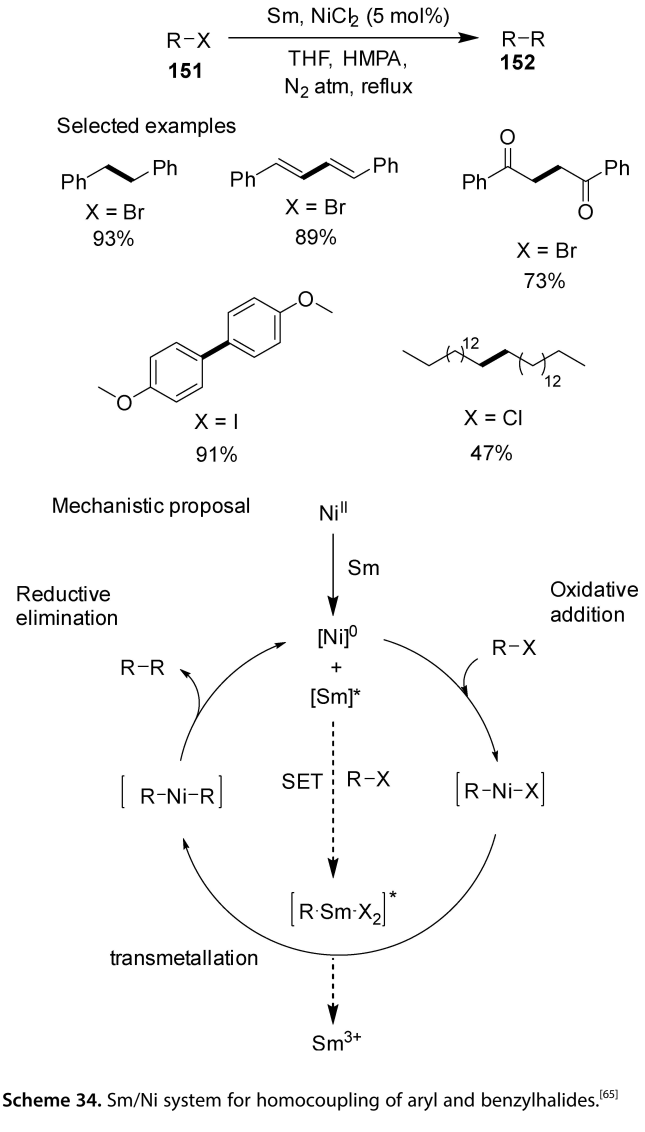
Scheme 32. Coupling of vinylsilane with alkynes using catalytic Cp_2ZrCl_2/Ln/$AlCl_3$ system.[63]

In 2002, the deoxygenative coupling of primary, secondary and tertiary alcohols **148** using a La/Me_3SiCl/I_2/CuI system was described (Scheme 33).[64] The coupling products **149** were obtained in moderate to good yields with small amounts of reduction products **150** present. The role of the lanthanide metal was presumably the initial formation of low-valent Cu species and their regeneration during the reaction process.



	149	150
R^1 = Ph, R^2 = R^3 = H	42%	15%
R^1 = 4-CH_3O-C_6H_4, R^2 = R^3 = H	67%	5%
R^1 = 4-CH_3-C_6H_4, R^2 = R^3 = H	59%	10%

Scheme 33. Deoxygenative coupling of alcohols using a La/Me_3SiCl/I_2/CuI system.[64]



Scheme 34. Sm/Ni system for homocoupling of aryl and benzylhalides.[65]

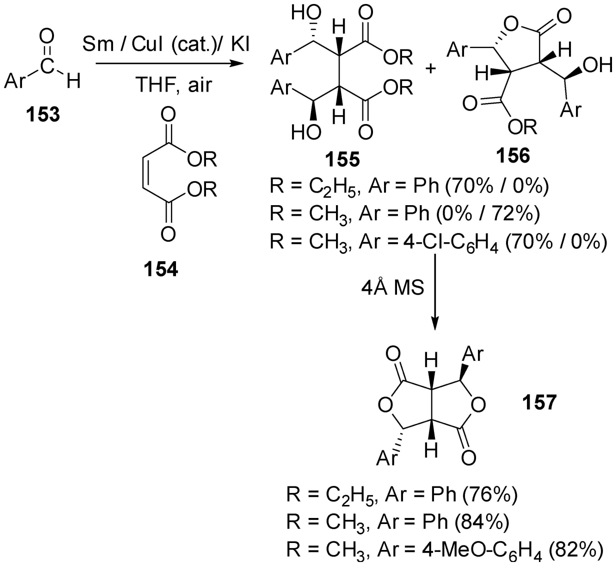
Recently, Ni and Cu salts have been employed in combination with Sm metal in the homocoupling of a wide range of alkyl, aryl and benzyl halides **151** (Scheme 34).[65,66] The role of Sm was postulated to be the formation of low-valent Ni or Cu species. An organosamarium intermediate derived from metal insertion into the R–X bond was also postulated in the mechanism.

The combination of Sm/CuI/KI was also applied for the synthesis of furofuran lignans **157** (Scheme 35).[67] Initial reaction of benzaldehyde derivatives **153** with maleates **154** in the presence of Sm and CuI in THF under air provided a mixture of bisaddition products **155** and **156**. Dehydration using molecular sieves afforded products **157** efficiently in good yields. The reaction worked also nicely with acrylates affording 2-hydroxylalkyl-γ-butyrolactones.[67]

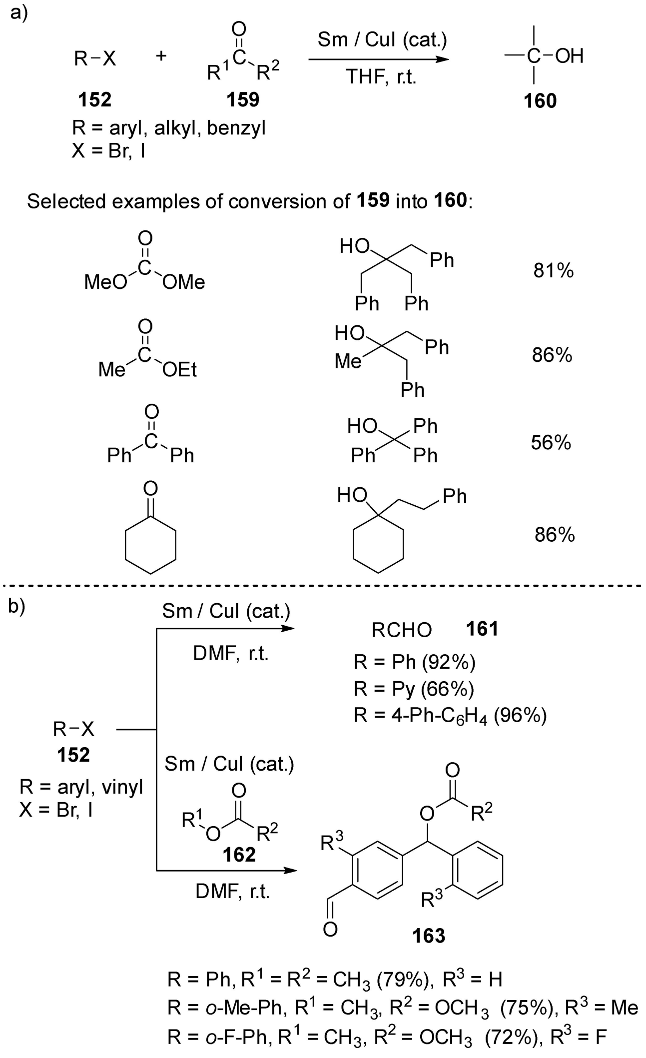
Very recently, the transformation of a large array of organic halides **158** (alkyl, allyl, benzyl and aryl halides) with different carbonyl compounds **159** was explored using catalytic CuI and Sm as a stoichiometric reducing agent (Scheme 36).[68,69] In THF, Grignard-like reactivity was observed leading to the formation of alcohols **160** (Scheme 36a). In contrast, in DMF formylation of a large variety of aryl halides was obtained providing aldehydes **161** in good yields.[68] Finally, a three-component reaction between aryl halides, DMF and esters **162** was reported yielding the unexpected synthesis of diarylmethanol derivatives **163** through a cascade process involving DMF cleavage and a C–H activation process (Scheme 36b).[69]

5. Conclusion

Over the last twenty years, the use of elemental lanthanides in organic synthesis has opened up to other metals than the dominating samarium and ytterbium metals. This has led to a broadening of the field of applications of these metals, such as



Scheme 35. Synthesis of furofuran lignans using a Sm/CuI system.[67]



Scheme 36. Reactions of alkyl, benzyl and aryl halides with carbonyl compounds using a Sm/CuI system a) in THF, b) in DMF.[68,69]

new radical processes, new dehalogenation reactions, especially C–F bond activation, and unprecedented bimetallic chemistry involving transition metals. In certain cases, a "lanthanide effect" was observed, leading to varying reactions outcomes depending on the metal used. No clear explanation has been found for this behavior so far. Even though mechanistic proposals have been put forward in many cases, structural information on organometallic intermediates is often lacking and more research on understanding lanthanide mediated processes is still required. Finally, the preparation and activation of the metal prior to the reaction should also not be neglected, as it might influence the outcome. Other forms of lanthanide metals such as the recently reported nanoparticles[70] or the use of lanthanide electrodes, in analogy to the inspiring work on Sm electrodes,[71] might be interesting for further investigations.

Acknowledgements

F.J. thanks all the students and coworkers who were involved in the research projects presented in this manuscript and whose names appear in the references. Financial support for this research from the CNRS, the Université de Reims Champagne-Ardenne, the Université de Montpellier, the Ecole Nationale Supérieure de Chimie de Montpellier, the Région Grand Est (France), the Indo-French Center for the Promotion of Advanced Research (CEFIPRA), the Agence Nationale de la Recherche (France) and the Australian Research Council is greatly acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Lanthanides · Grignard chemistry · Reduction · Radicals · Transition metals

[1] a) D. Evans, G. Fazakerley, R. Phillips, *J. Chem. Soc. Chem. Commun.* **1970**, 244–244; b) D. Evans, G. Fazakerley, R. Phillips, *J. Chem. Soc. A* **1971**, 1931–1934.
[2] a) K. Takaki, Y. Fujiwara, *Appl. Organomet. Chem.* **1990**, *4*, 297–310; b) G. A. Molander, *Chem. Rev.* **1992**, *92*, 29–68; c) P. G. Steel, *J. Chem. Soc. Perkin Trans. 1* **2001**, 2727–2751; d) B. K. Banik, *Eur. J. Org. Chem.* **2002**, *2002*, 2431–2444; e) E. S. Petrov, D. M. Roitershtein, L. F. Rybakova, *J. Organomet. Chem.* **2002**, *647*, 21–27; f) C. Liu, Y. Qi, Y. Liu, *Chin. J. Org. Chem.* **2021**, *41*, 2202–2216.
[3] a) M. Szostak, N. J. Fazakerley, D. Parmar, D. J. Procter, *Chem. Rev.* **2014**, *114*, 5959–6039; b) S. Maity, *Eur. J. Org. Chem.* **2021**, *2021*, 5312–5319.
[4] a) S. Cotton in *Lanthanide and Actinide chemistry*, John Wiley & Sons, Chichester, **2006**, Chapt. 2, pp. 9–19; b) N. N. Greenwood, A. Earnshaw in *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, **1997**, Chapt.20, pp. 944–953.
[5] a) S. Talukdar, J.-M. Fang, *J. Org. Chem.* **2001**, *66*, 330–333; b) Y. Liu, Y. Zhang, *Tetrahedron Lett.* **2003**, *44*, 4291–4294; c) S.-I. Fukuzawa, N. Nakano, T. Saitoh, *Eur. J. Org. Chem.* **2004**, *2004*, 2863–2867.
[6] T. Kumar, A. B. Hassine, A. Martinez, D. Harakat, S. Chevreux, F. Massicot, M. Taillefer, J.-B. Behr, J.-L. Vasse, F. Jaroschik, *J. Viz. Exp.– JoVE* **2018**, *137* e57948.
[7] Z. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo, H. Taniguchi, *J. Org. Chem.* **1987**, *52*, 3524–3528.
[8] a) O. P. Syutkina, L. F. Rybakova, M. N. Novgorodova, E. S. Petrov, *Russ. J. Gen. Chem.* **1997**, *67*, 76–78; b) L. F. Rybakova, O. P. Syutkina, E. S. Petrov, *Russ. J. Gen. Chem.* **2000**, *70*, 244–246.
[9] W.-S. Jin, Y. Makioka, T. Kitamura, Y. Fujiwara, *Chem. Commun.* **1999**, 955–956.
[10] K. Yokoo, T. Fukagawa, Y. Yamanaka, H. Taniguchi, Y. Fujiwara, *J. Org. Chem.* **1984**, *49*, 3237–3239.
[11] a) M. Wiecko, G. B. Deacon, P. C. Junk, *Chem. Commun.* **2010**, *46*, 5076–5078; b) S. H. Ali, G. B. Deacon, P. C. Junk, S. Hamidi, M. Wiecko, J. Wang, *Chem. Eur. J.* **2018**, *24*, 230–242.
[12] T. Nishino, T. Watanabe, M. Okada, Y. Nishiyama, N. Sonoda, *J. Org. Chem.* **2002**, *67*, 966–969.
[13] T. A. Starostina, L. F. Rybakova, E. S. Petrov, *Organomet. Chem. USSR* **1989**, *2*, 480–483.
[14] W.-D. Z. Li, B.-C. Ma, *Org. Lett.* **2005**, *7*, 271–274.
[15] a) T. Nishino, M. Okada, T. Kuroki, T. Watanabe, Y. Nishiyama, N. Sonoda, *J. Org. Chem.* **2002**, *67*, 8696–8698; b) Y. Nishiyama, M. Okada, T. Nishino, N. Sonoda, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 341–343.
[16] A. Prieto, F. Jaroschik, *Curr. Org. Chem.* **2022**, *26*, 6–41.
[17] Y. Tomisaka, A. Nomoto, A. Ogawa, *Tetrahedron Lett.* **2009**, *50*, 584–586.
[18] G. A. Molander, J. B. Etter, *J. Org. Chem.* **1987**, *52*, 3942–3944.
[19] J. M. Concellón, H. Rodríguez-Solla, C. Concellón, V. del Amo, *Chem. Soc. Rev.* **2010**, *39*, 4103–4113.

[20] a) X. Zhang, S. Zheng, S. Zhang, *RSC Adv.* **2017**, *7*, 54254–54257; b) Y. Wang, F. Huang, S. Zhang, *Eur. J. Org. Chem.* **2020**, *2020*, 5178–5181.

[21] a) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, M. Yokoyama, *J. Org. Chem.* **1984**, *49*, 3904–3912; b) S. Fukuzawa, N. Sumimoto, T. Fujinami, S. Sakai, *J. Org. Chem.* **1990**, *55*, 1628–1631.

[22] S. M. Rodrigues, V. Nardini, M. G. Constantino, G. V. J. da Silva, *Tetrahedron Lett.* **2012**, *53*, 6136–6137.

[23] J. W. Y. Zhang, W. Bao, *Synth. Commun.* **1996**, *26*, 2473–2477.

[24] R. Yanada, N. Negoro, M. Okaniwa, T. Ibuka, *Tetrahedron* **1999**, *55*, 13947–13956.

[25] a) Z. Li, Y. Zhang, *Tetrahedron* **2002**, *58*, 5301–5306; b) X. Liu, S. Zhang, J. Di, *Synthesis* **2009**, *2009*, 2749–2755; c) Y. Hu, T. Zhao, S. Zhang, *Chem. Eur. J.* **2010**, *16*, 1697–1705; d) Y. Li, Y.-Y. Hu, S.-L. Zhang, *Chem. Commun.* **2013**, *49*, 10635–10637; e) Y. Tu, L. Zhou, R. Yin, X. Lv, R. A. Flowers II, K. A. Choquette, H. Liu, Q. Niu, X. Wang, *Chem. Commun.* **2012**, *48*, 11026–11028; f) M. Shen, Y. Tu, G. Xie, Q. Niu, H. Mao, T. Xie, R. A. Flowers, X. Lv, X. Wang, *J. Org. Chem.* **2015**, *80*, 52–61; g) J. Li, Q. Niu, S. Li, Y. Sun, Q. Zhou, X. Lv, X. Wang, *Tetrahedron Lett.* **2017**, *58*, 1250–1253; h) B. You, M. Shen, G. Xie, H. Mao, X. Lv, X. Wang, *Org. Lett.* **2018**, *20*, 530–533; i) X. Wang, J. Li, T. Yuan, B. You, G. Xie, X. Lv, *J. Org. Chem.* **2018**, *83*, 8984–8994.

[26] P. Wang, X. Cao, S. Zhang, *Synthesis* **2021**, *53*, 3836–3846.

[27] a) S. Wu, Y. Li, S. Zhang, *J. Org. Chem.* **2016**, *81*, 8070–8076; b) F. Zhang, R. Wang, S. Wu, P. Wang, S. Zhang, *RSC Adv.* **2016**, *6*, 87710–87718.

[28] X. Y. Cao, F. Huang, S. Zhang, *Synlett* **2019**, *30*, 1437–1441.

[29] M. Gohain, B. J. Gogoi, D. Prajapati, J. S. Sandhu, *New J. Chem.* **2003**, *27*, 1038–1040.

[30] O. P. Syutkina, L. F. Rybakova, M. N. Novgorodova, E. S. Petrov, *Russ. J. Gen. Chem.* **1998**, *68*, 67.

[31] a) Y. Taniguchi, N. Fujii, K. Takaki, Y. Fujiwara, *Appl. Organomet. Chem.* **1995**, *9*, 377–384; b) Y. Taniguchi, N. Fujii, K. Takaki, Y. Fujiwara, *J. Organomet. Chem.* **1995**, *491*, 173–179; c) K. Takaki, Y. Itono, A. Nagafuji, Y. Naito, T. Shishido, K. Takehira, Y. Makioka, Y. Taniguchi, Y. Fujiwara, *J. Org. Chem.* **2000**, *65*, 475–481.

[32] W. Chen, K. Li, Z. Hu, L. Wang, G. Lai, Z. Li, *Organometallics* **2011**, *30*, 2026–2030.

[33] Z.-F. Li, Y. Tomisaka, A. Nomoto, Y. Zhang, A. Ogawa, *Chem. Lett.* **2009**, *38*, 16–17.

[34] Z. Zhu, J. Wang, Z. Zhang, X. Xiang, X. Zhou, *Organometallics* **2007**, *26*, 2499–2500.

[35] Y. Liu, F. Zhang, Y. Qi, Y. Zhang, S. Zhang, *Eur. J. Org. Chem.* **2008**, *2008*, 5470–5476.

[36] J. Mao, M. Wu, G. Xie, S. Ji, *Adv. Synth. Catal.* **2009**, *351*, 2101–2106.

[37] F. M. Moghaddam, R. Pourkaveh, M. Gholamtajari, A. Karimi, *ChemistrySelect* **2019**, *4*, 9618–9621.

[38] a) A. Ogawa, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1992**, *114*, 8729–8730; b) A. Ogawa, T. Nanke, N. Takami, M. Sekiguchi, N. Kambe, N. Sonoda, *Appl. Organomet. Chem.* **1995**, *9*, 461–466.

[39] M.-I. Lannou, F. Hélion, J.-L. Namy, *Tetrahedron* **2003**, *59*, 10551–10565.

[40] J. D. White, G. L. Larson, *J. Org. Chem.* **1978**, *43*, 4555–4556.

[41] B. K. Banik, M. Venkatraman, I. Banik, M. K. Basu, *Tetrahedron Lett.* **2004**, *45*, 4737–4739; B. K. Banik, I. Banik, S. Samajdar, R. Cuellar, *Tetrahedron Lett.* **2005**, *46*, 2319–2322; B. K. Banik, I. Banik, N. Aounallah, M. Castillo, *Tetrahedron Lett.* **2005**, *46*, 7065–7068.

[42] a) Z. Hou, K. Takamine, O. Aoki, H. Shiraishi, Y. Fujiwara, H. Taniguchi, *J. Chem. Soc. Chem. Commun.* **1988**, 668–670; b) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara, H. Taniguchi, *J. Chem. Soc. Chem. Commun.* **1992**, 722–724; c) Y. Makioka, Y. Taniguchi, Y. Fujiwara, K. Takaki, Z. Hou, Y. Wakatsuki, *Organometallics* **1996**, *15*, 5476–5478; d) Y. Makioka, S.-Y. Uebori, M. Tsuno, Y. Taniguchi, K. Takaki, Y. Fujiwara, *J. Org. Chem.* **1996**, *61*, 372–375; e) K. Takaki, M. Kurioka, T. Kamata, K. Takehira, Y. Makioka, Y. Fujiwara, *J. Org. Chem.* **1998**, *63*, 9265–9269; f) Z. Hou, Y. Wakatsuki in *Topics in Organometallic Chemistry; Lanthanides: Chemistry and Use in Organic Synthesis*, (Ed.: S. Kobayashi), Springer, Berlin, **1999**, *Vol. 2*, pp. 233–254.

[43] a) T. Nishino, Y. Nishiyama, N. Sonoda, *Heteroat. Chem.* **2000**, *11*, 81–85; b) T. Nishino, Y. Nishiyama, N. Sonoda, *Heteroat. Chem.* **2002**, *13*, 131–135.

[44] R. Umeda, M. Ninomiya, T. Nishino, M. Kishida, S. Toiya, T. Saito, Y. Nishiyama, N. Sonoda, *Tetrahedron* **2015**, *71*, 1287–1291.

[45] R. Yanada, K. Bessho, K. Yanada, *Chem. Lett.* **1994**, *23*, 1279–1282.

[46] H. Kawabata, T. Nishino, Y. Nishiyama, N. Sonoda, *Tetrahedron Lett.* **2002**, *43*, 4911–4913.

[47] Y. Nishiyama, H. Kawabata, T. Nishino, K. Hashimoto, N. Sonoda, *Tetrahedron* **2003**, *59*, 6609–6614.

[48] R. Umeda, T. Yuasa, N. Anahara, Y. Nishiyama, *J. Organomet. Chem.* **2011**, *696*, 1916–1919.

[49] a) M. Klahn, U. Rosenthal, *Organometallics* **2012**, *31*, 1235–1244; b) A. M. Träff, M. Janjetovic, L. Ta, G. Hilmersson, *Angew. Chem. Int. Ed.* **2013**, *52*, 12073–12076; *Angew. Chem.* **2013**, *125*, 12295–12298; c) W. Huang, P. L. Diaconescu, *Organometallics* **2017**, *36*, 89–96; d) Z. Guo, V. L. Blair, G. B. Deacon, P. C. Junk, *Chem. Eur. J.* **2022**, *28*, e202103865.

[50] a) G. B. Deacon, F. Jaroschik, P. C. Junk, R. Kelly, *Chem. Commun.* **2014**, *50*, 10655–10657; b) A. Shephard, A. Delon, R. Kelly, Z. Guo, S. Chevreux, G. Lemercier, G. B. Deacon, G. Dushenko, F. Jaroschik, P. Junk, *Aust. J. Chem.* **2022**, https://doi.org/10.1071/CH21324.

[51] a) T. Kumar, F. Massicot, D. Harakat, S. Chevreux, A. Martinez, K. Bordolinska, P. Preethalayam, R. Kokkuvayil Vasu, J.-B. Behr, J.-L. Vasse, *Chem. Eur. J.* **2017**, *23*, 16460–16465; b) T. Kumar, Y. Yang, S. Sghaier, Y. Zaid, X. Le Goff, E. Rousset, F. Massicot, D. Harakat, A. Martinez, M. Taillefer, *Chem. Eur. J.* **2021**, *27*, 4016–4021.

[52] a) Y. Zhang, Y. Yu, W. Bao, *Synth. Commun.* **1995**, *25*, 1825–1830; b) Y. Huang, Y. Zhang, *Synth. Commun.* **1996**, *26*, 2911–2915; c) Y. Huang, H. Guo, Y. Zhang, Y. Wang, *J. Chem. Research (S)* **1999**, 214–215; d) X. Jia, Y. Zhang, *J. Chem. Research (S)* **2003**, 540–541; e) X.-S. Jia, Y.-M. Zhang, *Chin. J. Chem.* **2005**, *23*, 303–304.

[53] G. Bousrez, I. Déchamps, J.-L. Vasse, F. Jaroschik, *Dalton Trans.* **2015**, *44*, 9359–9362.

[54] Y. Horikawa, M. Watanabe, T. Fujiwara, T. Takeda, *J. Am. Chem. Soc.* **1997**, *119*, 1127–1128.

[55] L. Zhang, X. Yu, L. Zhang, X. Zhou, Y. Lin, *Org. Chem. Front.* **2014**, *1*, 929–935.

[56] T. Takahashi, Y. Li, in *Titanium and Zirconium in Organic Synthesis*, (Ed.: I. Marek), Wiley-VCH, Weinheim, **2002**, Chapt. 2, pp.50–85.

[57] C. Denhez, S. Medegan, F. Helion, J.-L. Namy, J.-L. Vasse, J. Szymoniak, *Org. Lett.* **2006**, *8*, 2945–2947.

[58] G. Bousrez, F. Jaroschik, A. Martinez, D. Harakat, E. Nicolas, X.-F. Le Goff, J. Szymoniak, *Dalton Trans.* **2013**, *42*, 10997–11004.

[59] G. Bousrez, E. Nicolas, A. Martinez, S. Chevreux, F. Jaroschik, *Heteroat. Chem.* **2019**, 2596405.

[60] M. Soueidan, F. Hélion, J.-L. Namy, J. Szymoniak, *Organometallics* **2008**, *27*, 2074–2077.

[61] A. Joosten, M. Soueidan, C. Denhez, D. Harakat, F. Helion, J.-L. Namy, J.-L. Vasse, J. Szymoniak, *Organometallics* **2008**, *27*, 4152–4157.

[62] M. Soueidan, F. Hélion, J.-L. Namy, J. Szymoniak, *Tetrahedron Lett.* **2010**, *51*, 115–117.

[63] M. Soueidan, F. Hélion, J.-L. Namy, J. Szymoniak, *Tetrahedron Lett.* **2011**, *52*, 1348–1350.

[64] a) T. Nishino, Y. Nishiyama, N. Sonoda, *Tetrahedron Lett.* **2002**, *43*, 3689–3691; b) T. Nishino, Y. Nishiyama, N. Sonoda, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 635–641.

[65] Y. Liu, S. Xiao, Y. Qi, F. Du, *Chem. Asian J.* **2017**, *12*, 673–678.

[66] Y. Liu, D. Zhang, S. Xiao, Y. Qi, S. Liu, *Asian J. Org. Chem.* **2019**, *8*, 858–862.

[67] Y. Liu, G. Tian, J. Li, Y. Qi, Y. Wen, F. Du, *J. Org. Chem.* **2017**, *82*, 5932–5939.

[68] S. Xiao, C. Liu, B. Song, L. Wang, Y. Qi, Y. Liu, *Chem. Commun.* **2021**, *57*, 6169–6172.

[69] B. Song, D. Zhang, S. Xiao, C. Liu, H. Chen, Y. Qi, Y. Liu, *J. Org. Chem.* **2021**, *86*, 9854–9860.

[70] C. Schöttle, S. Rudel, R. Popescu, D. Gerthsen, F. Kraus, C. Feldmann, *ACS Omega* **2017**, *2*, 9144–9149.

[71] a) K. Sahloul, L. Sun, A. Requet, Y. Chahine, M. Mellah, *Chem. Eur. J.* **2012**,*18*, 11205–11209; b) S. Bazzi, E. Schulz, M. Mellah, *Org. Lett.* **2019**, *21*, 10033–10037.

Manuscript received: February 21, 2022
Revised manuscript received: April 18, 2022
Accepted manuscript online: April 21, 2022