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Rare Earth – Metal Bonding in Molecular Compounds. Recent Advances, Challenges, and Perspectives.

Mikhail V. Butovskii*^a and Rhatt Kempe*^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Metal–metal bonding in heterometallic complexes is of fundamental interest due to its implications to both bonding theory and new reactivities. In this review, all structurally authenticated molecular compounds with direct bonds between rare earth metals and transition or main group metals are summarized. Novel aspects of their syntheses, properties and reactivities are highlighted. Special attention is given to the synthetic challenges and the use of bond polarity as a tool for designing molecular intermetallics incorporating rare earth atoms and transition metals.

Introduction

Coordination and organometallic compounds containing metal–metal bonds supported or unsupported by virtue of bridging ligands have since long ago been a matter of extensive research.¹ In recent years a lot of enthusiasm was devoted to unusual metal–metal linkages.² Metal–metal bonds between f-elements and other metals are of fundamental interest in many regards. Among them unsupported bonds are the most attractive ones to study because ligand bridging is likely to alter the nature of the metal–metal bond.³ The f-elements, the footnotes of the periodic table, consist out of the actinoid series⁴ (= An) and the lanthanoid series⁵ (= Ln). The latter are often called rare earth atoms which include the group 3 metals scandium and yttrium⁵. Ln–metal, and especially Ln–TM (TM = transition metal), bonds are very interesting since the intermetallic compounds – which formally consist out of metal–metal bonds only – built up of these metal combinations are highly important with regard to many applications of our daily life. These intermetallic compounds are high-performance permanent magnets⁶ that account for approximately half of the world wide permanent magnet market,⁷ important hydrogen storage materials⁸ and the “heart” of batteries in, for instance, hybrid cars. Most rare earth–metal bonds are interesting due to their high bond polarity. This bond polarity allows a systematic approach towards highly aggregated systems^{9,3j} or intermetallics.¹⁰ These intermetallics close the gap between molecular heterometallic compounds and intermetallic solid state compounds.^{2c} In this review we summarize the state of the art in synthesis and structure (including electronic structures) of molecules having unsupported rare earth–metal bonds. Although f-element–metal bonding in molecular compounds was comprehensively reviewed a couple of times^{3d,f,i,j} the progress of recent years and continuous increase of publications necessitate regular reviewing. We hope, that this summary will help to attract the corresponding communities to synthesize more examples and

to start exploring their properties. In the following, a comprehensive list of all structurally authenticated molecular compounds featuring rare earth–metal bonds will be given; the compounds with Ln–MM (MM = main group metal)¹¹ are grouped with respect to the group of MM in the periodic table and Ln–TM are grouped according to the number of metal–metal bonds per Ln atom. The restriction to compounds characterized by X-ray diffraction studies (XRD) is provoked by the fact that there is a considerable body of work claiming metal–metal bonds which were not proven directly, but proposed based on plausibility considerations. While some references containing non-XRD proven results will shortly be mentioned in the respective sections, these studies will not be covered in full detail. Since a short metal–metal distance is not sufficient to prove an attractive interaction, as was shown for, e.g., Fe₂(CO)₉,¹² we restrict the discussion as much as possible to unsupported metal–metal contacts. However, when important for understanding of, e.g. the reactivity of metal–metal bonds, the compounds with ligand-supported metal–metal contacts will appear in the discussion. In addition, many of the studies given below feature theoretical calculations that support the formulation of metal–metal bonding.

Rare Earth–Main Group Metal Bonds (Ln–MM)

Rare Earth – Group 13 metal bonded compounds

The first complexes with unsupported bonds between 4f metals and a group 13 metal were described by Gamer *et al.*¹³ The adducts [Cp*₂LnAlCp*] (Ln = Eu, **1**; Yb, **2**; Figure 1) were obtained by heating a 1:4 mixture of [(η⁵-C₅Me₅)Al]₄ and solventfree [(η⁵-C₅Me₅)₂Ln] (Ln = Eu, Yb) in an evacuated ampoule at 120 °C for several days. The compounds are weakly bound (DFT calculations yielded binding energies of about 30 kcal·mol⁻¹) and had to be prepared in the absence of solvent as in solution decomplexation was observed. The metal–metal bond lengths amount to 336.52(10) pm (**1**) and 319.81(11) pm (**2**), respectively. In a subsequent study, Wiecko and Roesky¹⁴ reported on adduct formations using the higher homologue GaCp* that yielded the complexes [Cp*₂Eu(GaCp*)₂] (**3**, Figure 1) and [Cp*₂Yb(thf)GaCp*] (**4**, Figure 1). In contrast to the

^a Dr. M. V. Butovskii, Prof. Dr. R. Kempe Lehrstuhl Anorganische Chemie II Universität Bayreuth 95440 Bayreuth (Germany) Fax: (+ 49) 921-55-2157 E-mail: kempe@uni-bayreuth.de, mikhail.butovskiy@gmail.com

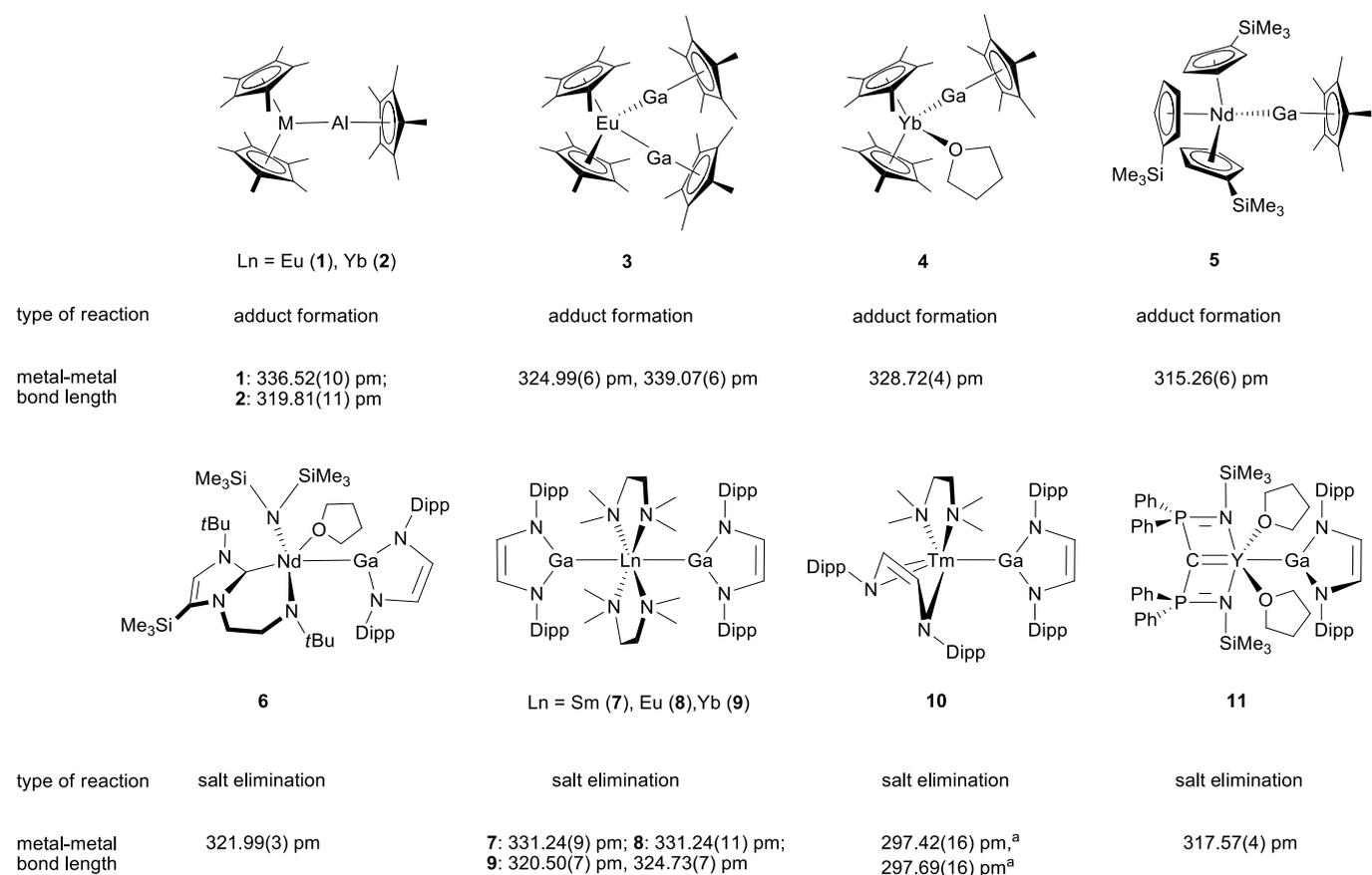


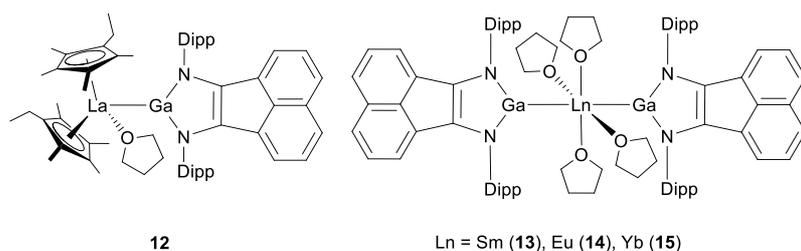
Figure 1. Structurally authenticated compounds containing Ln–MM bonds (MM = group 13 metal). [a] Two inequivalent molecules in the crystal structure.

related aluminium compounds, these reactions could be performed in toluene, indicating an unexpectedly higher stability of the gallium complexes. The metal–metal bond lengths were found to be 324.99(6) pm, 339.07(6) pm (**3**) and 328.72(4) pm (**4**), the differences in complexation patterns between **1** to **4** were rationalized in terms of (a) the greater radius of Ga^I compared to Al^I and (b) the smaller radius of Yb^{II} compared to Eu^{II}.

In two publications from Krinsky, Arnold and coworkers,¹⁵ the formation of labile adducts with the composition [(Cp^{TMS})₃NdMMCP*] (MM = Al; Ga, **5**; Figure 1) and [(Cp^{TMS})₃CeMMCP*] (MM = Al, Ga) is reported. All compounds except the gallium–neodymium complex (**5**) were only observed *in situ* by NMR spectroscopy, rare earth–Ga binding enthalpies were estimated to be $\Delta H_{NdGa} = -3.0(2)$ kcal·mol⁻¹ and $\Delta H_{CeGa} = -4.2(1)$ kcal·mol⁻¹. Comprehensive computational study of the model compounds Cp₃Ln–MMCP (MM = Al, Ga) supported the NMR experiments and indicated that covalency does exist in dative bonding with the formally trivalent Ln³⁺. The obtained crystal structure of **5** is the result of a co-crystallization of the title compound with [(Cp^{TMS})₂Nd]₂(μ-OH)₂, the metal–metal bond length is 315.26(6) pm.

The utility of gallium diyl, [Ga(NArCH)₂][K(tmeda)] (Ar = 2,6-Pr_iC₆H₃), an anionic gallium heterocycle which is valence isoelectronic to NHCs, in lanthanide chemistry was first demonstrated by Arnold and Jones *et al.*¹⁶ by the synthesis of the neodymium complex [(NHC^{NtBu})Nd{N(SiMe₃)₂}{Ga(dad)}(thf)] (**6**, Figure 1; NHC^{NtBu} = 1-(*tert*-butylamidoethyl)-3-*tert*-butyl-5-trimethylsilylimidazol-2-yl; Ga(dad) = [Ga(NArCH)₂]⁻). The neodymium atom in **6** adopts a distorted trigonal bipyramidal coordination sphere with the two neutral donors at the axial sites and a metal–metal bond length of 321.99(3) pm. Theoretical calculations on a simplified model complex yielded a Nd–Ga bond energy of about 92 kcal·mol⁻¹, which is significantly greater than the corresponding value for **1** and **2**, reflecting the charged nature of bonded fragments as well as a proposed covalent contribution in case of **6**.

Using the same gallium-containing precursor as above, Jones *et al.*¹⁷ reported on the synthesis of [(tmeda)₂Ln{Ga(dad)}₂] (Ln = Sm, **7**; Eu, **8**; Yb, **9**; Figure 1) by salt elimination from the respective lanthanoid diiodides in the presence of excess TMEDA. Proton NMR spectra of **9** suggested *cis/trans* isomerism, however, in the solid state only the *trans* configured products were observed. The isostructural solid state structures reveal a distorted octahedral lanthanoid environment with metal–metal bond lengths of 331.24(9) pm (**7**), 331.24(11) pm (**8**), and 322.6 pm (mean value, **9**), thus nicely reflecting the differences in the effective ionic radii of Sm^{II} (119 pm), Eu^{II} (117 pm) and Yb^{II} (102 pm).¹⁸ In an attempt to prepare the analogous thulium(II) compound, formal loss of one equivalent of gallium was observed, leading to the thulium(III)



difference in Sm–Ga bond length by about 10 pm. The fact that other bond distances within the molecules differ only slightly is in accordance with the weak nature of the Ln–Ga interaction, which is influenced by the packing. Secondly, the metal–metal bond distance of 312.95(5) pm in **15** is the shortest Yb–Ga bond distance reported so far.

Rare Earth – Group 14 metal bonded compounds

The first reported attempt to prepare a rare earth–group 14 metal bond in a molecular compound dates back to a paper from Schumann and Cygon in 1978,²² in which the synthesis of $[\text{Cp}_2\text{LnSnPh}_3]$ (Ln = Er, Yb) by salt elimination from $[\text{Cp}_2\text{LnCl}]$ and LiSnPh_3 was described. However, no metal–metal bond was proven by XRD. This initial report was followed by many others from different laboratories. When Lappert and Power²³ investigated the behavior of the heavy group 14 carbene analogues $\text{M}(\text{NR}_2)_2$ (M = Ge, Sn, or Pb; R = SiMe_3) with respect to Lewis acids, they claimed a scandium–adduct formulated as $[\text{Cp}_2\text{Sc}(\text{Me})\{\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2\}]$. The metal–metal bonded character of this compound was only postulated by comparison with other complexes. In the same year Wang *et al.*²⁴ published the synthesis and characterization of the diketonate complexes $[\{(\text{PhCO})_2\text{CH}\}_2\text{LnSnPh}_3]$ (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb) obtained by salt metathesis. Since all compounds are reported to exhibit the same colour and nearly identical proton NMR spectra the actual identity of the claimed substances seems to remain doubtful. The synthesis of $[(\text{dme})\text{Ln}\{\text{Sn}(\text{CH}_2\text{SiMe}_3)_3\}_3]$ (Ln = Pr, Nd) and $[(\text{MeOCH}_2\text{CH}_2\text{O})_2\text{LnSnEt}_3]$ (Ln = Pr, Nd) *via* amine elimination was reported by Razuvaev *et al.*²⁵ However, again, no direct metal–metal bond was proven. Inspired by this report the group of Bochkarev undertook the reactivity studies^{26a,b} of these DME adducts as well as investigated the reaction of Bu_3SnI with the metallic lanthanoids.^{26c} The products which were postulated as $[\text{ILnSnBu}_3]$ (Ln = Yb, Eu), however, lack XRD characterization. The first structurally authenticated complex with Ln–Sn bonds was published in 1990 by Bochkarev *et al.*,²⁷ it has the constitution $[(\text{thf})_4\text{Yb}(\text{SnPh}_3)_2]$ (**16**, Figure 3) and features a Yb–Sn bond length of 330.5(1) pm. In fact, this was the first molecular compound featuring Ln–MM unsupported bond as was revealed by X-ray structural analysis. The coordination sphere of ytterbium is distorted octahedral with the stannyl ligands arranged *trans* to each other. This compound was obtained by oxidative addition using naphthalenytytterbium and SnPh_4 ; subsequently, the preparation from other stannyl derivatives like Ph_3SnCl and $\text{Ph}_3\text{SnSnPh}_3$ was also described.²⁸ $[\text{YbCl}_2(\text{thf})_2]$ was found to catalyze these reactions. Surprisingly, the reaction of Ph_2SnCl_2 with ytterbium yielded, after recrystallization from DME, the ionic compound $[\{\text{Yb}(\text{dme})_3\}_2(\mu\text{-Cl})_2][\text{Sn}(\text{SnPh}_3)_3]_2$ that was also characterized by XRD measurements. This result illustrates the necessity of structural data in order to unequivocally prove direct metal–metal bonds in such systems. Further studies²⁹ showed the second main product resulting from the reduction of SnPh_4 and naphthalenytytterbium

Figure 2. Structurally authenticated compounds containing Ln–MM bonds (MM = group 13 metal) (continued). [a] data for two polymorphs.

complex $[(\text{tmeda})\text{Tm}\{\text{Ga}(\text{dad})\}(\text{dad})]$ (**10**, Figure 1) that features a doubly reduced DAD ligand directly bound to the lanthanoid in a η^4 coordination mode. The metal–metal bond length was found to be 297.42(16) pm.

While leaving the main group metal–fragment again unchanged, Liddle and Jones *et al.*¹⁹ presented another type of rare earth–Ga bonded compounds in 2009. The complex $[(\text{BIPM})\text{Y}(\text{thf})_2\{\text{Ga}(\text{dad})\}]$ (**11**, Figure 1) containing the bis(*N*-trimethylsilyl-*P,P*-diphenylimino-phosphorano)methandiide ligand BIPM^{2-} was formed by salt elimination and exhibits a (due to the bite angle of the chelate ligand) strongly distorted octahedral structure with the formal carbene moiety and the gallium center residing *trans* to each other. The Y–Ga bond length amounts to 317.57(4) pm. DFT calculations on a slightly simplified model complex led to the conclusion that the metal–metal bond is best described as a highly polarized covalent bond.

The synthesis of $[\text{Cp}^R_2\text{La}(\text{thf})\{\text{Ga}(\text{bian})\}]$ ($\text{Cp}^R = \text{Cp}^*$; $\text{C}_5\text{Me}_4\text{Et}$, **12**; Figure 2; bian^{2-} = dianion of 1,2-bis(2,6-di-*iso*-propylphenyl-imino)acenaphthene), reported by Fedushkin *et al.*²⁰ in 2011, resembles some common features with **6** to **11** in that both gallium-containing fragments rely on closely related, redox-active ligands (DAD and BIAN, respectively). The compounds were obtained by salt metathesis and the less symmetrically substituted derivative **12** could be characterized by XRD, showing a tetrahedral lanthanum coordination sphere with a La–Ga bond length of 301.34(8) pm. Shortly after **12** Fedushkin and Roesky²¹ published a series of divalent trimetallic complexes **13** to **15** (Figure 2) which is accessible by both synthetic strategies: 1) salt metathesis using $[(\text{dippBian})\text{GaK}(\text{thf})_5]$ and LnI_2 2) oxidative addition of $[(\text{dippBian})\text{Ga}]_2$ at Ln (Sm, Eu, and Yb). An attempt to extend the series with Tm and Dy analogues resulted in the opening and the reduction of one THF ring, thus forming the formal double negative charged anion $[\text{O}-(\text{CH}_2)_4]^{2-}$, which bridges lanthanide and gallium centers in the final product. The X-ray structural analysis of **13** to **15** has revealed two interesting features. Firstly, it was possible to characterize two polymorphs of **13**. These exhibited significant

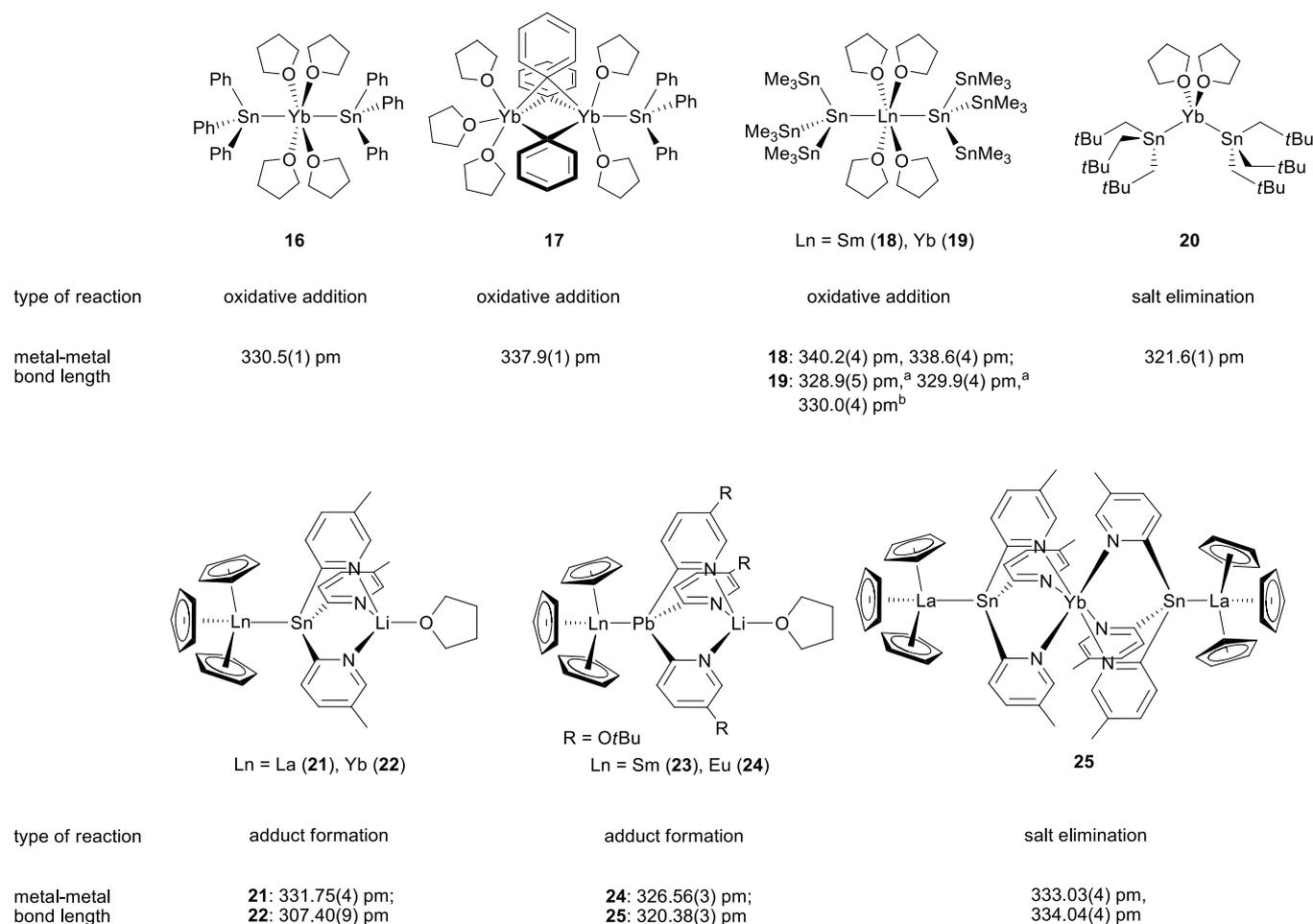


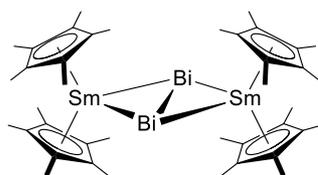
Figure 3. Structurally authenticated compounds containing Ln–MM bonds (MM = group 14 metal). [a] First modification. [b] Second modification.

to be $[(\text{thf})_2\text{Yb}(\mu\text{-Ph})_3\text{Yb}(\text{thf})_2\text{SnPh}_3]$ (**17**, Figure 3). The reported crystal structure contains two ytterbium atoms in a distorted octahedral environment each, bridged by three phenyl groups. The metal–metal bond distance (337.9(1) pm) is longer than in **16**, which was attributed to different steric bulk around the metal atoms of both compounds. In 1993,³⁰ the same working group reported on the isolation of $[(\text{thf})_4\text{Ln}\{\text{Sn}(\text{SnMe}_3)_3\}_2]$ (Ln = Sm, **18**; Yb, **19**; Figure 3) from the reaction of Me_3SnCl with the respective lanthanoid metal. The crystal structures are similar to those obtained for **16** in that the coordination sphere of the central atom is in both cases distorted octahedral with *trans* orientation of the ligands. The reported metal–metal bond lengths (**18**: 340.2(4) pm, 338.6(4) pm; **19**: 328.9(5) pm, 329.9(4) pm; a second modification of **19** exhibits 330.0(4) pm) are compatible with the one found in **16** (330.5(1) pm). Most interesting about this result is the major difference in the identity of products upon reaction of similar starting materials (Ph_2SnCl_2 vs. Me_3SnCl , *vide supra*).

Shortly after the report by Bochkarev *et al.*,²⁷ Cloke, Lawless and coworkers³¹ presented the somewhat similar ytterbium–tin complex $[(\text{thf})_2\text{Yb}\{\text{Sn}(\text{CH}_2\text{tBu})_3\}_2]$ (**20**, Figure 3) with an Yb–Sn bond length of 321.6(1) pm. In contrast to the abovementioned studies, salt elimination was employed as synthetic concept in this work. Apparently, the bulkier substituents in **20** as compared to those present in **16** to **19** lead to a smaller coordination number in this distorted tetrahedral complex. The ^{171}Yb NMR spectrum of **20** shows a single resonance ($\delta_{\text{Yb}} = 725$ ppm) with satellites due to coupling with ^{119}Sn ($^1J = 8627$ Hz) and ^{117}Sn ($^1J = 8254$ Hz) nuclei. Reactivity studies monitored by NMR showed **20** to react with Cp^*H and a substituted phenol yielding the corresponding ytterbium Cp^* and phenolate complexes, respectively, together with $\text{HSn}(\text{CH}_2\text{tBu})_3$.

Recently Zeckert *et al.*³² reported on the adducts $[\text{Cp}_3\text{Ln}\{\text{Sn}(\text{C}_5\text{H}_3\text{NMe}_3)\text{Li}(\text{thf})\}]$ (Ln = La, **21**; Yb, **22**; Figure 3). The lithium tris(2-pyridyl)stannate used as metal-centered ligand here may tentatively be regarded as intermediate between an anionic and a neutral donor. Consistent with this proposal, the formed products were found to be stable in THF solution. The solid state structures show distorted tetrahedral coordination of the lanthanoid with the stannate at the apical site, the metal–metal bond lengths were found to be 331.75(4) pm (**21**) and 307.40(9) pm

(22). The same research group reported the first examples of compounds with unsupported Pb–Ln bonds, obtained from the reactions of a lithiumtris(organo)plumbate $[\text{LiPb}(2\text{-py}^{\text{OtBu}})_3(\text{thf})]$ ($\text{py}^{\text{OtBu}} = \text{C}_5\text{H}_3\text{N-6-OtBu}$) with the trivalent lanthanocenes $[\text{Ln}(\text{Cp})_3(\text{thf})]$ ($\text{Ln} = \text{Sm}$, **23**; Eu , **24**; Figure 3).³³ The new compounds similarly exhibited distorted tetrahedral coordination of Sm and Eu as revealed by XRD studies, the metal–metal bond lengths were found to be 326.53(3) pm (**23**) and 320.38(3) pm (**24**). Interestingly, europium complex appears to be unstable in THF solutions and degrades over longer time into the hexa(2-pyridyl)diplumbane $[\text{Pb}(2\text{-py}^{\text{OtBu}})_3]_2$, the europocene(II) derivative $[\text{Eu}(\text{Cp})_2(\text{thf})]_n$ and LiCp. This redox reaction was the subject of spin-trapping EPR experiments that are consistent with a sterical-induced-reduction (SIR) route. Attempts to react stannate or plumbate precursors with $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OEt}_2)]$ ($\text{Ln} = \text{Yb}$, Eu) failed to yield Ln–MM bonded complexes but resulted in the loss of lithium and formation of bis($\kappa^3\text{N}$) sandwich compounds.^{33,34} However, when lanthanum bimetallic complex **21** was allowed to react with $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OEt}_2)]$ a pentametallic compound **25** was obtained in good yield.³⁵ The structure of **25** exhibits the Yb^{2+} cation encapsulated by two $[\text{Cp}_3\text{LaSn}(\text{C}_5\text{H}_3\text{NMe}_3)_3]$ units, the comparison of La–Sn bond distances in **21** and in **25** shows negligible difference.



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type of reaction	reductive coupling
metal-metal bond length	326.5(1) pm, 328.3(1) pm, 329.1(1) pm, 331.1(1) pm

Figure 4. Structurally authenticated compound containing Ln–MM bonds (MM = group 15 metal).

Rare Earth – Group 15 metal bonded compounds

In 1991, Evans *et al.*³⁶ reported the reaction of $[\text{SmCp}^*_2]$ with BiPh_3 to give the unexpected cluster compound $[\text{Cp}^*_2\text{Sm}(\mu\text{-}\eta^2\text{-}\eta^2\text{-Bi}_2)\text{SmCp}^*_2]$ (**26**, Figure 4). The four metal atoms are nearly coplanar with Sm–Bi bond lengths in the range of 326.5(1) pm to 331.1(1) pm and a Bi–Bi distance of 285.1(1) pm. The compound was found to be roughly comparable to its also structurally characterized lighter homologue $[\text{Cp}^*_2\text{Sm}(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)\text{SmCp}^*_2]$ ³⁷ and provides another example of the often unusual reduction

behavior of $[\text{SmCp}^*_2]$.³⁸ The bonding situation in **26** was analysed in detail by Ouddai and Bencharif.³⁹

Rare Earth–Transition Metal Bonds (Ln–TM)

Compounds with one Ln–TM bond

The start of Ln–TM metal-metal bonded chemistry is traditionally associated with the name of Beletskaya who was the first to publish unequivocally characterized molecular Ln–TM compound with direct metal-metal bond $[\text{Cp}_2\text{Lu}(\text{thf})\text{Ru}(\text{CO})_2\text{Cp}]$ ⁴⁰ (**27**, Figure 5). However, the research aimed at the synthesis of rare earth–transition metal bonded molecular compounds has already started in 1971 with the report from Marianelli and Durney,⁴¹ describing the reaction of erbium amalgam with $\text{Hg}[\text{Co}(\text{CO})_4]_2$ to form a product that was proposed to be $[(\text{thf})_4\text{Er}\{\text{Co}(\text{CO})_4\}_3]$. This initial report was followed by many others from different laboratories. The most common reactions involving transition metal carbonyl complexes and rare earth reagents include (a) salt elimination from alkali metal or thallium carbonylmetallates and (partly substituted and/or solvated) rare earth halides,⁴² (b) transmetalation as in the example stated above,^{41,43} (c) oxidative addition of rare earths or their amalgams to transition metal carbonyl halides,⁴⁴ (d) reduction of (partly substituted) transition metal carbonyls with rare earths or their amalgams.^{42c,45} The choice of transition metal fragments which contained carbonyl ligands in all early studies was guided by the assumption that the numerous stable metal carbonylates – effectively stabilized by the carbonyl ligand's ability to delocalize negative charges – could be suitable Lewis bases to form metal–metal bonds with the Lewis-acidic rare earth center. However, the presence of carbonyl ligands can also lead to a different type of interaction between the two metal-containing fragments, namely isocarbonyl linkages. This bridging mode of CO bonding was confirmed by XRD measurements for a variety of products resulting from the abovementioned experiments^{42,46} and surely is the most abundant type of product, the formation of ionic products was also established in some instances.⁴⁷ In studies not containing any crystal structures, these two competing classes of compounds were often sought to be differentiated from the metal–metal bonded target complexes by means of IR spectroscopy. However, this method proved not be sufficiently reliable as demonstrated for example by $[\text{SmI}_2(\text{thf})_2][\text{Co}(\text{CO})_4]$ which was at first proposed to contain metal–metal bonds⁴⁸ while later studies including XRD characterization^{47a} proved its ionic nature. In summary, the early reports on rare earth–transition metal bonds did not unequivocally prove the existence of a direct interaction between the two metal atoms; in many instances, the actual constitution of the reported products is of an isocarbonyl-bridged or ionic nature.

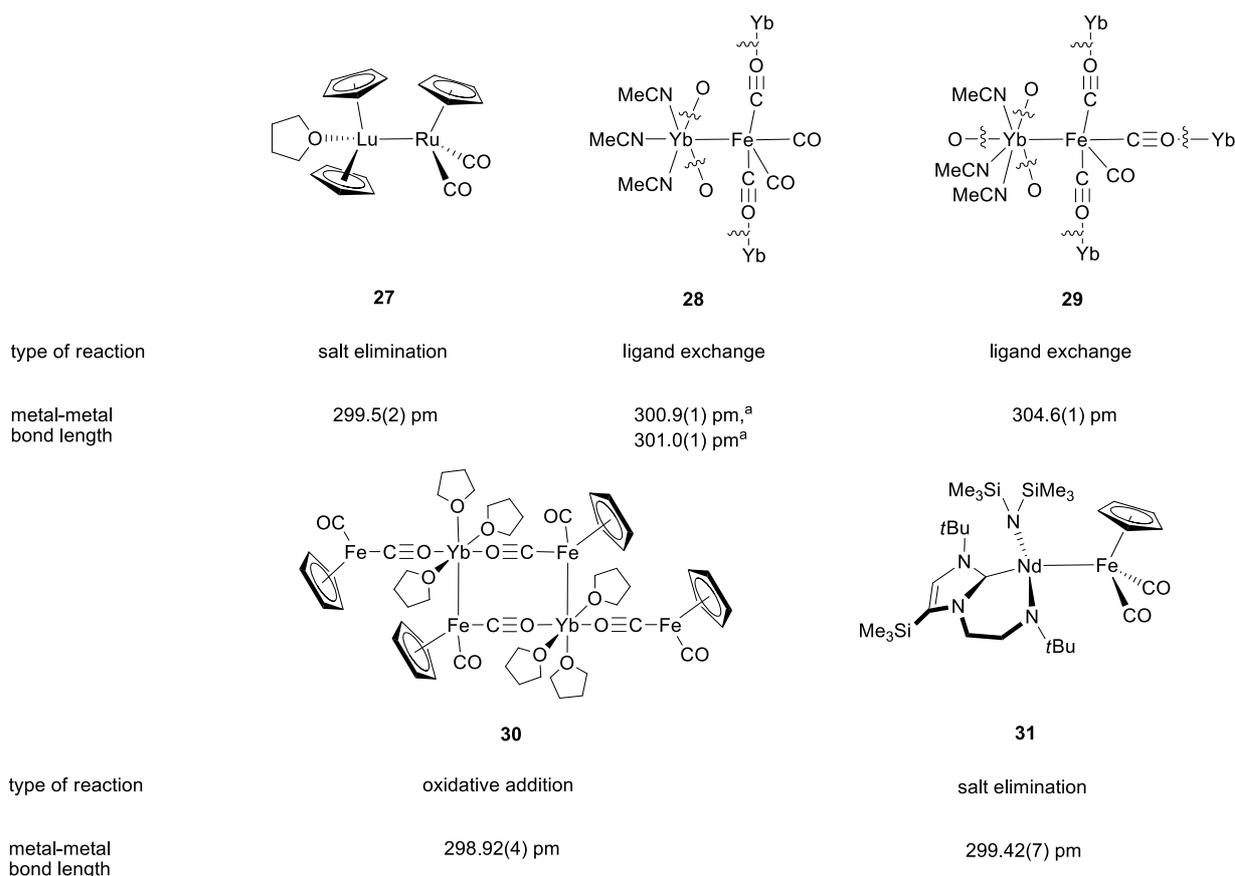


Figure 5. Structurally authenticated compounds containing one Ln–TM bond. [a] Two inequivalent formula units in the crystal structure.

Only two decades after the initial report of Marianelli and Durney, in 1990, Beletskaya and coworkers reported on the first structurally authenticated complex containing a rare earth–transition metal bond, **27** (Figure 5).⁴⁰ This compound was obtained by salt elimination; the lutetium atom reveals distorted tetrahedral coordination with a Lu–Ru bond length of 299.5(2) pm. Also by salt elimination, the related complexes $[(C_5H_3(SiMe_3)_2)_2Lu(thf)Ru(CO)_2Cp]$, $[Cp^*LuRu(CO)_2Cp]$ and $[(thf)_3LaLuRu(CO)_2Cp]$ were prepared, however, no structural data for these compounds was reported. Reactivity studies showed the complexes to react with water, hydrogen chloride and ketones by elimination of $[HRu(CO)_2Cp]$ together with the formation of hydroxo, chlorido and enolate lanthanoid complexes, respectively.

Following the report of Beletskaya, Shore and coworkers⁴⁹ published two studies on polymeric Yb–Fe compounds. Upon reaction of metallic ytterbium with $[Fe_3(CO)_{12}]$ in liquid ammonia, a product with the composition $(NH_3)_2YbFe(CO)_4$ was formed, which led to the crystallization of $[(MeCN)_3YbFe(CO)_4]_2 \cdot MeCN$ _∞ (**28**, Figure 5) and $[(MeCN)_3YbFe(CO)_4]_∞$ (**29**, Figure 5) when dissolved in acetonitrile. Both compounds feature direct metal–metal bonds as well as isocarbonyl linkages, the coordination sphere of iron can be described as roughly trigonal bipyramidal. While

28 is a one-dimensional polymer with ytterbium in a distorted octahedral environment, **29** consists of two-dimensional, polymeric sheets that are formed by additional isocarbonyl linkages as compared to **28**. The coordination sphere of ytterbium in **29** is thus expanded by an additional ligand, resulting in a pentagonal bipyramid. The metal–metal distances of both compounds are similar and amount to 300.9(1) pm, 301.0(1) pm (**28**) and 304.6(1) pm (**29**). Due to the more-dimensional structure the metal–metal bonds are not unsupported. In the style of the studies mentioned above, Blake *et al.*⁵⁰ reported on the preparation of $[(thf)_3Yb(Fe(CO)_2Cp)_2]_2$ (**30**, Figure 5) by reductive cleavage of $[Fe(CO)_2Cp]_2$ with ytterbium amalgam in THF. The obtained crystal structure is isostructural with the analogue calcium compound. The lanthanoid is situated in a distorted octahedral environment with a Yb–Fe bond length of 298.92(4) pm. Notably, the dimeric molecule features both metal–metal and isocarbonyl linkages, which underscores the difficulties in judging the reliability of early studies not containing any structural data based on XRD.

Using the same NHC neodymium precursor as in the synthesis of the Nd–Ga bonded complex **6**, Arnold and McMaster *et al.*⁵¹ reported on the synthesis of $[(NHC^{NBu})Nd\{N(SiMe_3)_2\}Fe(CO)_2Cp]$ (**31**, Figure 5) by salt elimination. The coordination sphere of neodymium is distorted tetrahedral with a Nd–Fe distance of 299.42(7) pm. Theoretical calculations showed the metal–metal bond to be strongly ionic in nature.

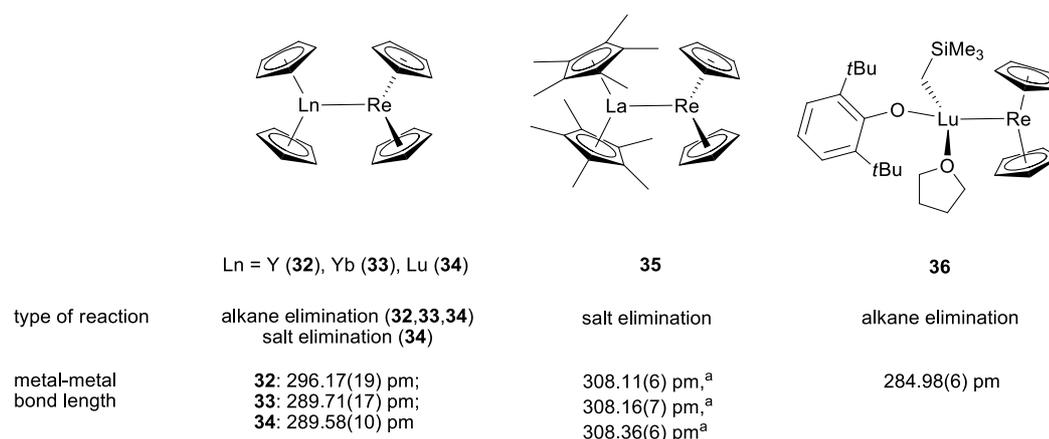
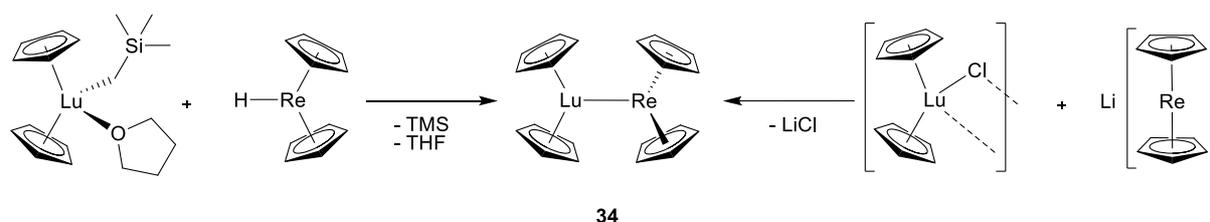


Figure 6. Structurally authenticated compounds containing one Ln–TM bond (continued). [a] The solid-state structure contains three independent molecules.

In 2008,⁵² our group showed that alkane elimination, a versatile synthetic methodology belonging to the armory of practically every organolanthanide chemist, can be used to selectively form rare earth–transition metal bonds. Thus the reaction of $[\text{Cp}_2\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{thf})]$ ($\text{Ln} = \text{Y}, \text{Yb}$) with $[\text{Cp}_2\text{ReH}]$ afforded the products $[\text{Cp}_2\text{LnReCp}_2]$ ($\text{Ln} = \text{Y}, \text{32}$; $\text{Yb}, \text{33}$; Figure 6, Scheme 1) that feature metal–metal bond lengths of 296.17(19) pm (**32**) and 289.71(17) pm (**33**) and distorted trigonal planar metal environments. Although both compounds were prepared using the same synthetic procedure, we noticed a drastic difference in yields (91 % for (**32**), 28 % for (**33**)). With the aim of preparing bismetallocenes for the largest and for the smallest member of the lanthanoid series (that is, for La and for Lu), we investigated the reactions of $[\text{Cp}^*\text{La}\{\text{CH}(\text{SiMe}_3)_2\}]$ (we had to use the bulkier Cp^* ligand instead of simple Cp due to the limitations of the synthesis of compounds of the type Cp_2LnX , where $\text{Ln} = \text{La}$ to Nd) and $[\text{Cp}_2\text{Lu}(\text{CH}_2\text{SiMe}_3)(\text{thf})]$ with the hydride complex of rhenium.⁵³ Taking the advantage of La and Lu as being diamagnetic in their trivalent states, NMR spectroscopic studies were performed that revealed not only low reaction rates in both cases, but also degradation pathways. In the case of lutetium it was possible identify the side product (Cp_3Lu) and its cause – THF, which is liberated from the monoalkyl precursor. The low

reaction rates together with the formation of side products precluded the isolation of pure samples of Lu and La bismetallocenes and made us think of alternative synthetic procedures. Similar to the preparation of **27**, but avoiding the clearly unsuitable solvent THF, we performed a salt elimination reaction of $[\{\text{Cp}_2\text{LuCl}_2\}]$ with $\text{Li}[\text{Cp}_2\text{Re}]$ in toluene and isolated analytically pure **34** in 40% yield (Figure 6, Scheme 1). The complexes **34** and **33** are isostructural and represent the same Cp rotation isomers. Since Lu and Yb are neighbors in the lanthanoid series, the metal–metal distances in both bismetallocenes (Lu–Re: 289.58(10) pm; Yb–Re: 289.71(17) pm) are identical within the error of the experiment. Similarly, salt elimination using $[\text{Cp}^*\text{La}(\text{Cl})(\text{thf})]$ and $\text{K}[\text{Cp}_2\text{Re}]$ afforded analytically pure $[\text{Cp}^*\text{LaReCp}_2]$ (**35**, Figure 6) in good yield. The crystal structure of **35** as determined by X-ray structural analysis features three independent molecules with very similar metrics. The most important structural aspect of the complex is the unsupported La–Re bond with a bond length of 308.11(6) to 308.36(6) pm, which is the longest Ln–Re bond in the bismetallocene family. DFT and ELI-D calculations were used to elaborate the nature of bonding which was found to be highly polarized. Position-space bonding analysis for **32**, **34**, and **35** on the basis of the QTAIM partitioning revealed the always positive effective charge of the metal atoms and covalent electron-sharing interactions between them. The obtained values of the delocalization index (position-space analogue of the covalent bond-order index) around 0.4 lie in the typical range for covalent single bonds between transition metals. The bismetallocenes **32** to **34** as well as the model complexes $[\text{Cp}_2\text{M–TMCP}_2]$ ($\text{M} = \text{La}, \text{Ac}$ and $\text{TM} = \text{Re}$; $\text{M} = \text{Th}$ and $\text{TM} = \text{Os}$) were also the subject of DFT and time-dependent DFT calculations performed by Arratia-Pérez *et al.*⁵⁴ The electronic structure calculated for respective pairs of



Scheme 1. Synthesis of bismetallocenes on the example of $[\text{Cp}_2\text{LuReCp}_2]$ (**34**).

metals allowed the authors to argue that the $[\text{Cp}_2\text{Re}]$ fragment is a good antenna chromophore due to the possibility of charge transfer transitions from this fragment to the f shell in lanthanide elements. Noteworthy is the observation of shifting of the absorption spectrum of around 100 nm of the $[\text{Cp}_2\text{Re}]$ fragment when is compared against the absorption spectrum of the entire complexes $[\text{Cp}_2\text{LnReCp}_2]$.

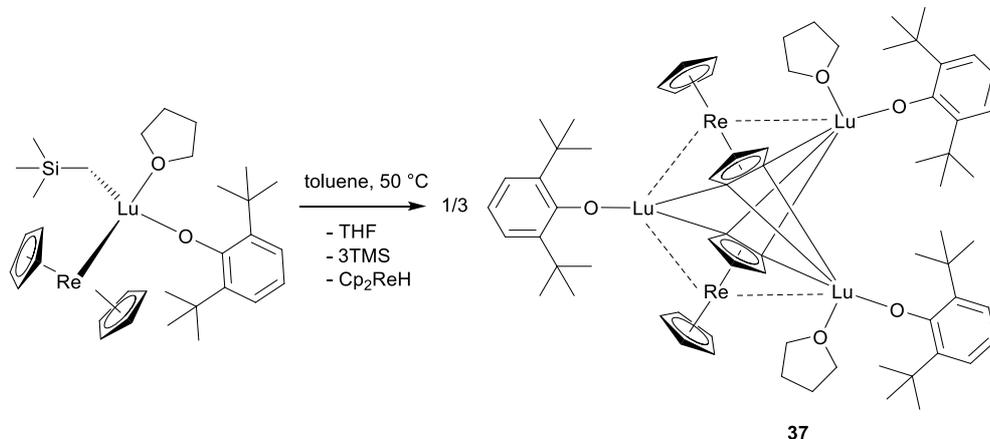
The reaction of dialkyl lutetium phenolate $[(2,6\text{-tBu}_2\text{C}_6\text{H}_3\text{O})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2]$ with 2 equivalents of $[\text{Cp}_2\text{ReH}]$, however, yielded the bimetallic complex with one Ln–Lu bond $[(2,6\text{-tBu}_2\text{C}_6\text{H}_3\text{O})\text{Lu}(\text{CH}_2\text{SiMe}_3)\text{ReCp}_2]$ (**36**, Figure 6) in good yield.⁵⁵ The lutetium coordination sphere is best described as tetrahedral with a metal–metal bond length of 284.98(6) pm. As this complex contains a reactive Ln–alkyl and a reactive Ln–TM bond in close proximity, it was particularly useful in identifying possible pathways of decomposition in systems with more than one metal–metal bond (*vide infra*).

With the aim to extend the armory of transition metal fragments for constructing Ln–TM bonded molecules we investigated also the reactions of the monoalkyl complexes $[\text{Cp}_2\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{thf})]$ (Ln = Y, Lu) with $[\text{HW}(\text{CO})_3\text{Cp}]$ and $[\text{HRu}(\text{dmpe})\text{Cp}]$ (dmpe = bis(dimethylphosphino)ethane). In the case of the tungsten hydride trinuclear complex $[\{\text{CpW}(\text{CO})_2(\mu\text{-CO})\}_2\text{YCp}(\text{thf})_3]$ was obtained in 88% yield.⁵⁶ The metal centers in this complex are bridged with isocarbonyl ligands. This outcome clearly shows that regardless the synthetic pathway, the presence of carbonyl ligands in a transition metal precursor is always accompanied with the danger of isocarbonyl linkage formation instead of metal–metal bonds.⁵⁷ Interestingly, the reaction of $[\text{Cp}_2\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{thf})]$ with the carbonyl-free ruthenium hydride $[\text{HRu}(\text{dmpe})\text{Cp}]$ led to the heterometallic hydrides $[\text{Cp}_2\text{Ln}(\mu\text{-H})(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Ru}(\text{dmpe})]$ (Ln = Y, Lu).⁵⁸ In order to determine the origin of the bridging hydride labeling experiment using $[\text{DRu}(\text{dmpe})\text{Cp}]$ was performed. It was found that the formation of these heterometallic products proceeds via direct attack of an aromatic C–H bond and the formation of transient unsupported Ln–Ru bonds is not relevant.

Compounds with two Ln–TM bonds per metal atom

After discovering that alkane elimination can give rise to high yields⁵² of Ln–TM bimetallics having an unsupported bond between the two metals our group became interested in using bis- and trisalkyl-Ln complexes to make intermetallics. It was assumed that the two or three alkyl functions could be formally replaced by Cp_2Re to produce molecules in which the lanthanoid is bonded by two or solely bonded by rhenium metal. Whereas the rhenium hydride failed to react with both alkyls of dialkyl lutetium phenolate (as described in previous section), the reaction with easily accessible $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ (Ln = Lu, Y) afforded insoluble precipitates that did not analyse as desired products. It was suspected that the presence of more than one Ln–carbon bonds in the starting material brings about side reactions of the Ln–TM bonds already formed, leading to polymeric materials. If one wants to understand (and later use such side reactions) a bis(alkyl) lanthanoid compound which allows the substitution of one of the two alkyl ligands by Cp_2Re -ligands should be exploited as a model system. Among the many monoanionic ligands which are able to stabilize bis(alkyl) Ln complexes deprotonated 2,6-di-*tert*-butylphenol proved to be a good choice.⁵⁵ The bimetallic complex **36**, described in the previous section, fulfills these requirements and indeed served as a good model system. Already at ambient temperature this compound displays limited stability and decomposes to **37** (Scheme 2, Figure 7). The structure of **37** has two interesting features, the double C–H-activated Cp ligands⁵⁹ and the nature of the metal–metal bonds. The polarity of the Re–Lu bond was determined, as in related investigations, employing the ELI-D/QTAIM-intersection procedure (in analogy ref. [60]). In this procedure the spatial region of the ELI-D bonding basin is partitioned between QTAIM atoms (atomic electron density basins) and the electronic population is divided correspondingly. It turns out that 81% of the population belongs to the Re atom and 8% belongs to each of the Lu atoms. Furthermore the bonding electrons seem to be split adequately between two Lu and one Re atom as indicated by the shape of the ELI-D/QTAIM intersection of lone pair basins.

These polar ReLu_2 three-center bonds sharing formally two electrons can be considered as a transition in terms of electron delocalization. A bimetallic complex has a localized two-center two-electron metal–metal bond. Metals or intermetallic compounds have a rather high degree of electron delocalization. In between might be two-electron multiple-center bonds as seen in **37**.



Scheme 2. Synthesis of **37**.

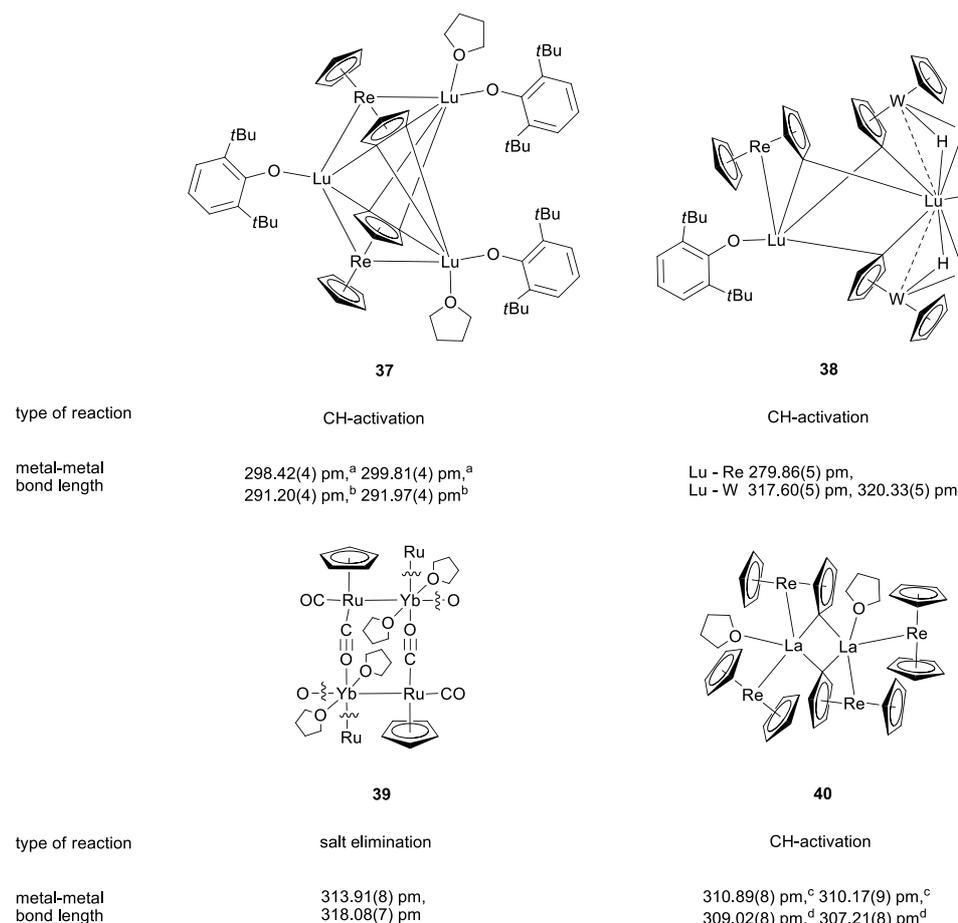


Figure 7. Structurally authenticated compounds containing more than one Ln–TM bond per metal atom containing additional bridging ligands. [a] Bonds involving "outer" Lu atoms. [b] Bonds involving "central" Lu atom. [c] Direct metal-metal bonds. [d] Metal-metal bonds with accompanying ($\eta^5:\eta^1$ -Cp) bridge.

Although the complex **36** failed to react with $[\text{Cp}_2\text{MH}_2]$ ($M = \text{W}, \text{Mo}$) to yield the trimetallic polyhydride cluster compounds (Figure 7, **38**, $M = \text{W}$).⁶¹ To the best of our knowledge, compound **38** is the first example of a Ln-metal polyhydride cluster featuring three different metals, as was revealed by XRD and NMR studies. One of the lutetium centers in **38** is five coordinate by one phenolate ligand, three C–H-activated Cp rings, and a rhenium atom. The other lutetium center has the coordination number ten containing a phenolate ligand, three C–H-activated Cp ligands, and two tungsten atoms each bridged by two μ_2 -hydrides. The Lu–Re bond length is 279.86(5) pm, which is way shorter than the sum of the covalent radii of rhenium and lutetium (338 pm) based on Alvarez and coworkers data,⁶² shorter than the sum of the atomic radii in crystals (310 pm) based on Slater,⁶³ and even shorter than the bond lengths in **34**, **36**, and in $[\text{Lu}(\text{Cp}_2\text{Re})_3]^{2c}$ (**44**, Figure 11) (*vide infra*). The method of ELI-D/QTAIM basin intersection revealed polar Re–Lu bond and

W–H...Lu interactions, in which the hydride atoms are polar-covalently coordinated to W, and the interaction with Lu is very ionic. Notably, inside the quadrilateral W–H–Lu1–H a region with negative values of the Laplacian of ELI-D was found, which indicates a covalent direct interaction W–Lu.

Though it was interesting to discover C–H-activation in Ln–TM bimetallics, it precluded the synthesis of the compounds with two unsupported Ln–TM bonds via alkane elimination synthetic strategy. However, we were able to obtain these compounds via salt elimination route. The reaction of two equivalents

$\text{Na}(\text{thf})[\text{CpRu}(\text{CO})_2]$ with the dihalide $[\text{YbI}_2(\text{thf})_4]$ in THF leads to the replacement of both iodide ligands with $[\text{CpRu}(\text{CO})_2]^-$ and the formation of a polymeric chain structure (**39**, Figure 7 and Figure 8).⁶⁴ Addition of 4-(*tert*-butyl)pyridine selectively

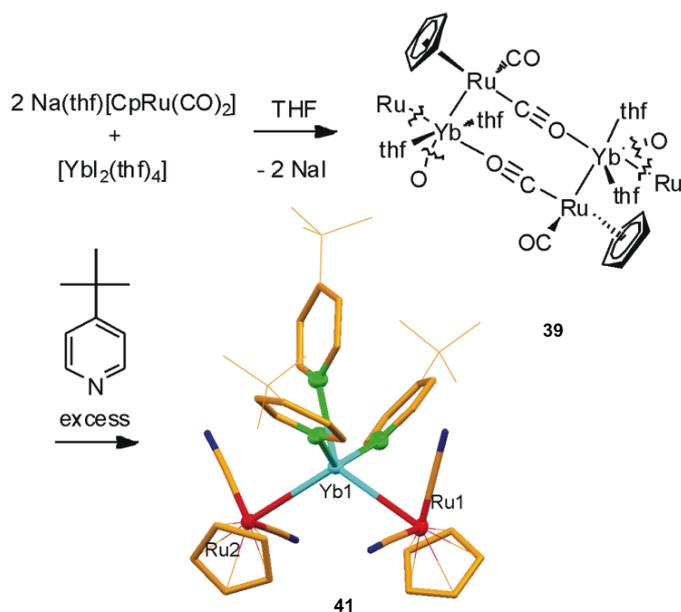
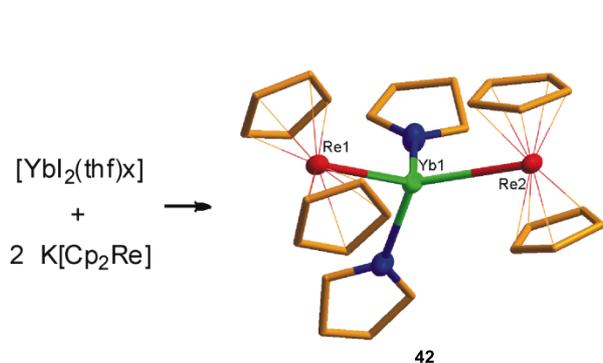


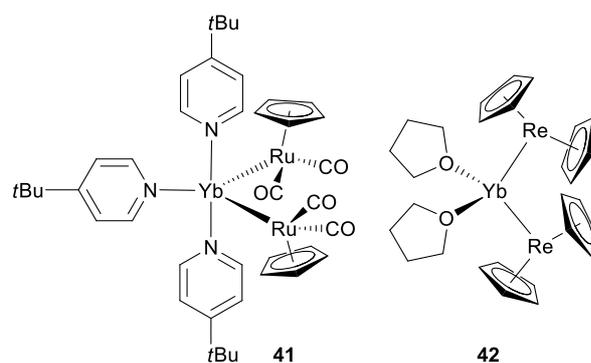
Figure 8. Synthesis of **41**.

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Figure 9. Synthesis of **42**.

cleaves the isocarbonyl linkage leaving metal–metal bonds intact and affords the molecular intermetalloid **41** (Figure 8, Figure 10). The ytterbium metal has a coordination number of five and is coordinated by three nitrogen atoms from the 4-tert-butylpyridines and two Ru atoms. The Yb–Ru bond lengths of 301.29(4) pm and 306.26(4) pm are significantly shorter than the Yb–Ru bond lengths of compound **39** due to the lower coordination number of the ytterbium metal and the lack of a polymeric ladder and thus increased flexibility of the monomeric compound **41**. Encouraged by the success with the synthesis of **41** the synthesis of a related Re complex was attempted. Salt elimination in THF-free environment using the same ytterbium dihalide and $K[Cp_2Re]$ indeed gave rise to trimetallic complex **42** (Figure 9, Figure 10). The ytterbium atom in **42** has a distorted tetrahedral coordination environment with angles ranging from 101° to 124°. The Yb–Re bond lengths of 302.08(7) pm and 303.66(7) pm are somewhat longer than the Yb–Re bond length of 289.7(2) in the trivalent compound $[Cp_2YbReCp_2]$ (**33**, Figure 6).



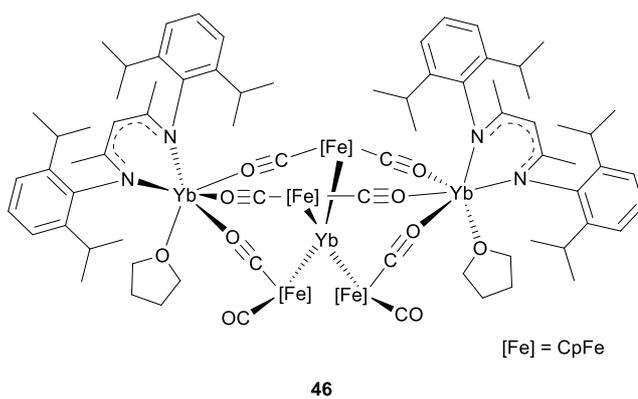
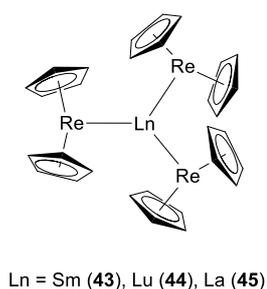
type of reaction	ligand exchange	salt elimination
metal-metal bond length	301.29(4) pm, 306.26(4) pm	302.08(7) pm, 303.66(7) pm

Figure 10. Structurally authenticated compounds containing two Ln–TM bonds per metal atom.

This is due to the fact of an increased ionic radius of divalent lanthanoids (102 pm for Yb^{II} compared to 86.8 pm for Yb^{III} with coordination number six).

Compounds with three and four Ln–TM bonds per metal atom.

It was found by us that THF is a problematic solvent in this bimetallic chemistry because it can favour side reactions leading to higher coordination numbers of low-coordinated Ln atoms. In consequence, for the synthesis of molecules in which the Ln is solely bonded by transition metals solvent-free trialkyls should be used. $[Ln\{CH(SiMe_3)_2\}_3]^{65}$ could be applied successfully to make compounds of the type $[Ln(ReCp_2)_3]^{2c}$ (**43–45**, Figure 11). These complexes are synthetically accessible for the whole lanthanoid series and are of suitable



type of reaction	alkane elimination	adduct formation
metal-metal bond length	43 : 296.00(10) pm, 297.92(9) pm, 298.09(10) pm; 44 : 287.73(8) pm, 288.99(7) pm, 289.13(8) pm; 45 : 303.15(9) pm, 305.42(9) pm, 305.77(8) pm	299.61(5) pm; 297.58(5) pm; 314.98(5) pm; 317.02(5) pm;

Figure 11. Structurally authenticated compounds containing three and four Ln–TM bond per metal atom.

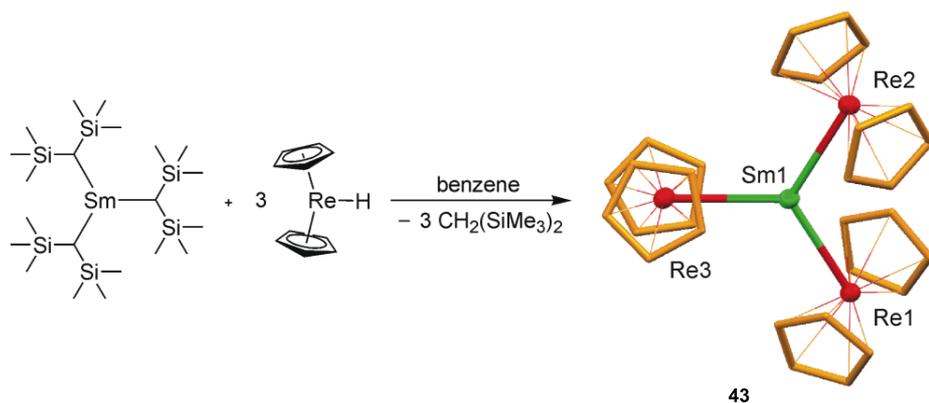


Figure 12. Synthesis of **43**. Reproduced with permission from Ref. [2c] Copyright 2010 Nature Publishing Group, London.

thermal stability. The complex $[\text{Sm}(\text{ReCp}_2)_3]$ (**43**, Figure 11) was isolated from the reaction of $[\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ with $[\text{Cp}_2\text{ReH}]$ as exceedingly air and moisture sensitive orange crystals in 34 % yield (Figure 12). Virtually, the reaction is extendable to all lanthanoids which was confirmed by preparing the Lu and La derivatives (**44** and **45**, Figure 11), albeit in lower yields. In the intermetallic compounds the motif of a lanthanoid in a triangular environment made up by TM is often to be found, for instance, in Y_2ReB_6 .⁶⁶ Comparison of the distribution of ELI-D for both the organometallic and the intermetallic compound reveals marked similarities in bonding despite the huge difference in their chemical nature. In this way the intermetalloids $[\text{Ln}(\text{ReCp}_2)_3]$ represent the missing link in the conceptual evolution from Ln–TM organometallic or coordination complexes to intermetallic compounds. Molecules of the type $[\text{Ln}(\text{ReCp}_2)_3]$ are highly reactive, for instance the La derivative reacts fast and quantitatively with a few equivalents of THF, a common solvent in organometallic chemistry, to afford the compound **40** (Figure 7, Figure 13). However, $[\text{Lu}(\text{ReCp}_2)_3]$ is stable in THF and its NMR spectra can be recorded in that solvent. It seems that the smaller Lu ion is much better shielded and the “THF danger” originates from its

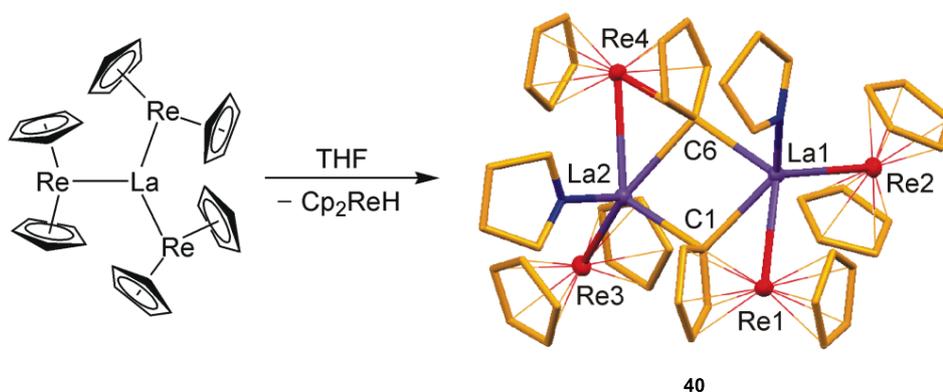


Figure 13. Synthesis of **40**. Reproduced with permission from Ref. [2c] Copyright 2010 Nature Publishing Group, London.

ability to coordinate Ln ions strongly, thereby increasing the coordination number.

The tendency of rare earth ions to form ‘ate’ complexes is well known. In this regard one may think of the complex compounds with four Ln–TM bonds per Ln atom e.g. $[\text{RE}\{\text{TM}\}_4]^-$ or $[\text{RE}\{\text{TM}\}_4]^{2-}$, where Ln is trivalent or divalent, respectively, and {TM} denotes anionic transition metal complex fragment. Since in molecular compounds with Ln–TM bonds transition metal always bears stabilizing ligands, the steric bulk of

the whole TM complex fragment may argue against the existence of such pentametallic ‘ate’ complexes. However, recently Mountford *et al.*⁶⁷ reported on the fascinating heptametallic ytterbium compound **46** (Figure 11) which was synthesized by reaction of $[\text{Yb}(\text{NacNac})\{\text{Fe}(\text{CO})_2\text{Cp}\}(\text{thf})_2]_2$ (NacNac = (2,6-diisopropyl-phenyl)((2Z,4E)-4-(2,6-diisopropylphenylimino)pent-2-en-2-yl)amide) with $[\{(\text{thf})_3\text{Yb}\{\text{Fe}(\text{CO})_2\text{Cp}\}_2\}]_2$ (**30**, Figure 4) in 74% yield. The compound **46** formally contains two $[\text{Yb}(\text{NacNac})(\text{thf})]^+$ cations bridged by an unprecedented $[\text{Yb}\{\text{Fe}(\text{CO})_2\text{Cp}\}_4]^{2-}$ anion. Two NacNac-bound Yb atoms are six-coordinate and bound only to N and O atoms, however, the third (central) Yb atom is four-coordinate and bonded solely to Fe atoms. The geometry at this Yb atom is approximately tetrahedral and the Yb–Fe distances are 297.58(5) pm, 299.61(5) pm, 314.98(5) pm, 317.02(5) pm. Although these bond lengths are all within the sum of the covalent radii (319 pm)⁶², we notice that the distances to the iron atoms featuring two isocarbonyl linkages are substantially longer, whereas the first pair compare well with the Yb–Fe bond length found in the starting complex **30** (298.92(4) pm).

Conclusions and perspectives

A variety of metal complex moieties were successfully linked to rare earths using synthetic methodologies like, for instance, salt elimination, alkane elimination, amine elimination or Roesky’s simple addition reactions. In terms of the variety of synthetic protocols significant progress has been made in recent years. The nature of the metal–metal bonds was investigated by a variety of theoretical approaches and is rather well understood at this stage. The metal–metal bonds in these bimetallic compounds are highly polar and highly reactive.

So far the reactivity towards the activation of small molecules has been rarely investigated and significant effort needs to be

put in such studies. Applications, for instance in catalysis, may result from this studies. The concept of connecting electrophilic and nucleophilic metal centres selectively to form larger aggregates, called here intermetaloids, works but has not left the proof-of-principle stage. Carbonyl complexes are not ideal since isocarbonyl linkage can be a problem. Cp ligands tend to undergo C–H-activation due to the relatively high acidity of that bond. The realm of Ln–MM compounds is dominated by Ln–Ga, Ln–Sn complexes, whereas Ln is unconquerable leader among transition metals. This fact underscores the need to enrich the armoury of metal fragments which can be linked to rare earths. With the discovery of new suitable MM and TM precursors one can envisage potential applications, for instance Ln luminescent complexes sensitized by TM or MM organometallic chromophores can be interesting candidates for optical technologies. In light of the finding that bonding situation in molecular Ln–TM compounds reflects the one of Ln–TM intermetallic solids, it is of interest to investigate the strength of *d-f* exchange interaction in molecular Ln–TM compounds comprising paramagnetic TM fragments. The design of single molecule magnets with Ln–TM bonds may be interesting in connection with the development of magnetic memory. It has been shown that a Ln metal atom can be solely bound by transition metal atoms. What about the capability of TM to link more than one Ln ions? If suitable complex environments can be found compounds like structured metals or intermetallics may become feasible and due to their structuring even (micro)porosity. The rare earth–metal bonding chemistry is still in its infancy but impressive progress has been made in very recent years and many fascinating discoveries can be done in future.

Acknowledgements

The authors gratefully acknowledge ongoing support by the Deutsche Forschungsgemeinschaft (DFG)

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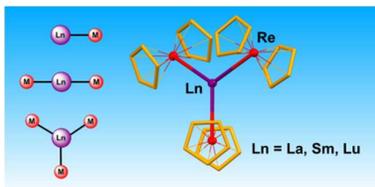
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Entry for the Table of Contents

Metal–Metal Bonding

*M. V. Butovskii**, *R. Kempe**
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**Rare Earth – Metal Bonding in
Molecular Compounds. Recent
Advances, Challenges, and
Perspectives.**



In this review, all structurally authenticated molecular compounds with direct bonds between rare earth metals and transition or main group metals are summarized. Novel aspects of their syntheses, properties and reactivities are highlighted.