Lanthanoid pseudo-Grignard reagents: A review☆

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ABSTRACT

This review covers the progress of the chemistry of divalent lanthanoid pseudo-Grignard, compounds, with E-Ln-X bonding (E = C, N, O; *X* = I, Br, Cl, F), especially since the 2002 review of Petrov et al. (2002)[1]. Emphasis is on synthetic pathways and the structures of these compounds. Their use in oxidation and metathesis reactions is discussed together with a consideration of interactions with organic substrates. The compounds appear to have considerable untapped potential.

1. Introduction

In a major breakthrough, Dennis Evans first showed that ytterbium metal reacts with alkyl and aryl iodides to form "RYbI" species in a manner reminiscent of the formation of Grignard reagents [2]. This was followed up by similar studies with europium and samarium metal [3]. Magnetic susceptibility measurements by the Evans NMR method showed the products were a mixture of divalent and trivalent complexes. Divalent complexes were most prevalent for Ln = Eu and less so for Ln = Yb and considerably less for Ln = Sm {Eu^{2+} (99 %), Yb^{2+} (85 %) and Sm^{2+} (50 %)} [3]. In the case of ytterbium, the highest proportion of Yb^{II} was achieved with 2,6-dimethyliodobenzene [2]. Given the versatility and prevalence of Grignard reagents, it might have been expected that this discovery would have led to a burgeoning chemistry, but in fact, developments have been slow. From the 1980s, Russian workers have sought to examine the scope of their formation, and Japanese workers have developed some organic chemistry, and, from the 1990s, limited structures utilising bulky ligand stabilisation emerged. The reason for the lack of interest is not easily understood, but perhaps cost and accessibility of lanthanoid metals may be a factor. However, groups studying lanthanoid metal reactions have been able to overcome this problem. Bochkarev's book on lanthanoid organometallics [4] provided an initial detailed account of this area, and Petrov's 2002 review in this journal provided a further and later account [1]. It is therefore timely to examine the field with an emphasis on recent developments.

We use the term pseudo-Grignard to embrace *divalent* lanthanoid compounds of the form L-Ln-X(solv)$_n$ where L is a monoanionic ligand bound to Ln by C, N, or O; Ln = Sm, Eu, Yb; *X* = F, Cl, Br, I; solv = donor solvent. We have limited the review to the classic divalent lanthanoid elements Sm, Eu, and Yb, as products of reactions of other Ln metals with organic halides are predominantly trivalent species. Trivalent species of the type LLnX$_2$ would open an enormous Pandora's box. Compounds of this type are mentioned solely when they are products of oxidation of LLnX species.

2. Synthesis and characterization—compounds with C-Ln-X (*X* = I, Br, Cl, F) bonding

Lanthanoid pseudo-Grignard reagents are mainly prepared by the direct reaction [1,4].

$$Ln + RX \xrightarrow{solv} RLnX(solv)_n \tag{1}$$

solv = tetrahydrofuran (thf), 1,2-methoxyethane (dme), diethyl ether etc.

R = alkyl, aryl, heteroaryl.

In terms of prevalence, *I* > Br >> Cl >> F, an order which reflects the increasing C-X bond strength, *I* < Br < Cl<F. In addition, alkyl iodides often have a slight iodine impurity, which can activate Ln metals [5]. In the main Ln = Sm, Eu, Yb, the traditional Ln^{II} forming elements, but analogous reactions of Ce have been reported in some cases [6], though the oxidation state is uncertain. The prices of the three Ln elements (e.g. from Strem in USD), Sm (280/25 g) Eu (818/5 g) Yb (570/25 g) *cf.* Mg

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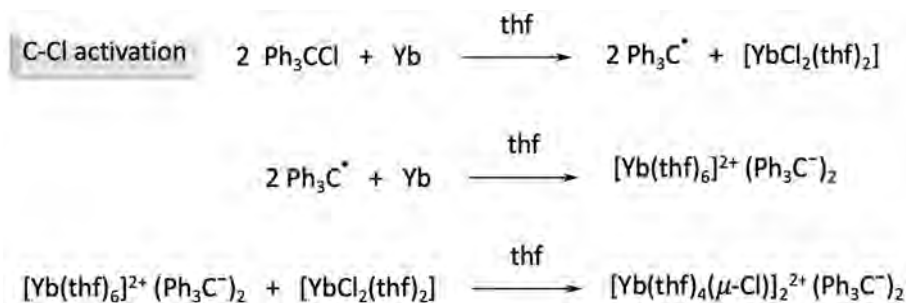
Scheme 1. Formation of an ionic pseudo-Grignard compound from Ph_3CCl and Yb metal.
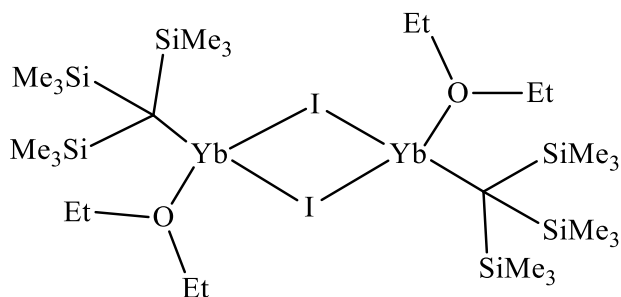
Fig. 2-1. Schematic of the X-ray structure of $[Yb\{C(SiMe_3)_3\}I(Et_2O)]_2$ (**1**) [10].

($<100/100$ g) are a deterrent, but bulk Ln metals as a piece (ca. 100 g which can be filed in an inert atmosphere dry-box) are available at cheaper prices from Treibacher Industrie AG, Austria.

The innovative Russian work of the 1980s has been reviewed [1,4], but some features should be mentioned. The carboranyllanthanoid pseudo-Grignard iodides were mainly prepared by metathesis between lithiocarboranes, but Yb and Eu derivatives were also obtained by the direct method (1) from iodocarboranes. The products were identified by reactions with trimethylsilyl chloride and acyl chlorides giving trimethylsilylcarboranes or carboranylketones [7]. Success in the direct reaction was also achieved with $C_8H_{17}X$ for $X = Cl$, Br, I and with the best performance surprisingly with the bromide [8]. 2-Thienyl and

pentafluorophenyl derivatives of Eu, Sm, Yb and Ce were also obtained by the direct method (1) from 2-iodothiophene and C_6F_5Br respectively, and were identified by reaction with triphenyltin chloride giving triphenyl(2-thienyl)tin and pentafluorophenyltriphenyltin respectively [6]. Of further interest, some were also prepared by an acidolysis reaction (Eq. (2)) with again organotin characterization.

$$PhLnI + C_6F_5H \rightarrow C_6F_5LnI + PhH \quad (2)$$

Three studies are of particular importance, as they have led to products characterized by X-ray crystallography. The first involves C—Cl activation of Ph_3CCl and appears to have led to the first structurally identified lanthanoid pseudo-Grignard reagent, albeit an ionic complex, *viz*. $\{[Yb(thf)_4(\mu\text{-Cl})]_2\}^{2+}(Ph_3C^-)_2$ [9]. A complex reaction path was proposed (Scheme 1).

The reaction only proceeds if a trace of $[YbCl_2(thf)_2]$ is present, in which case $[Yb(thf)_6]^{2+}$ $(Ph_3C^-)_2$ is formed rapidly, but the final pseudo-Grignard reagent formed slowly, and was obtained in good yield from the reaction between Yb metal powders and triphenylmethyl chloride in thf at room temperature for 15 h. $\{[Yb(thf)_4(\mu\text{-Cl})]_2\}^{2+}$ $(Ph_3C^-)_2$ was isolated as monoclinic crystals $P2_1/n$, where $[Yb_2(thf)_4(\mu\text{-Cl})_2]^{2+}$ is a centrosymmetric dimer bonded with two symmetric μ-Cl bridges. The anion is symmetrical planar with a triangular array of phenyl groups rotated by 26–34° out of the plane containing the central C atom [9].

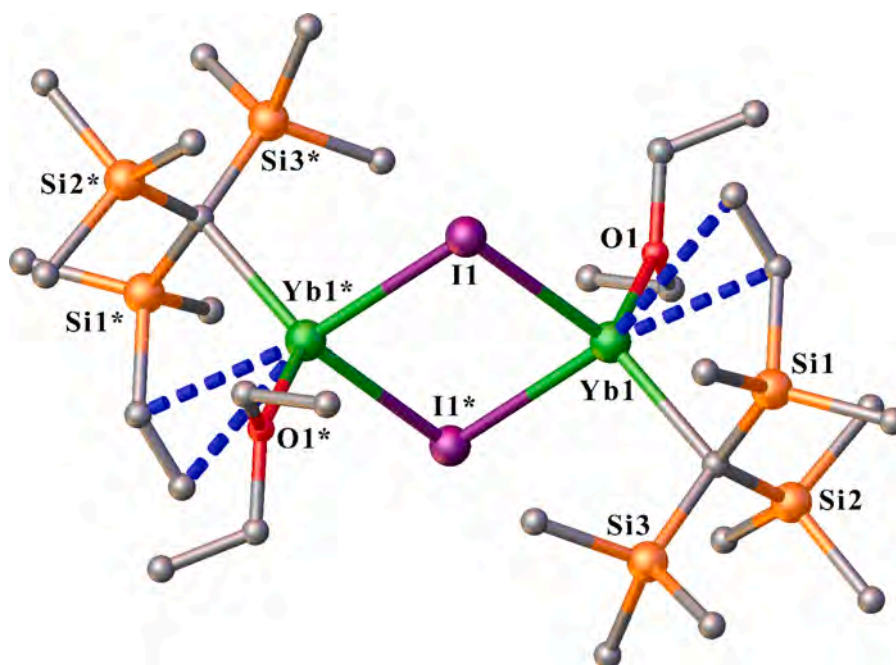A very important series of dimeric pseudo-Grignard compounds

Fig. 2-2. X-ray structure of $[Yb\{C(SiMe_3)_2(SiMe_2(CH{=}CH_2))\}I(Et_2O)]_2$ (**2**), Hydrogen atoms are omitted for clarity [10].
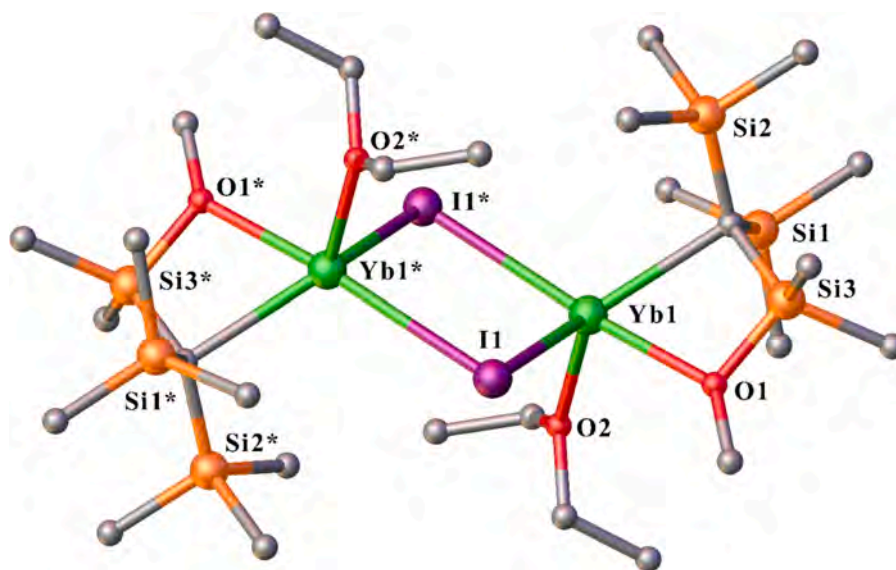
Fig. 2-3. X-ray structure of the of [Yb{C(SiMe$_3$)$_2$(SiMe$_2$(OMe))}I(Et$_2$O)]$_2$ (**3**), Hydrogen atoms are omitted for clarity [10].
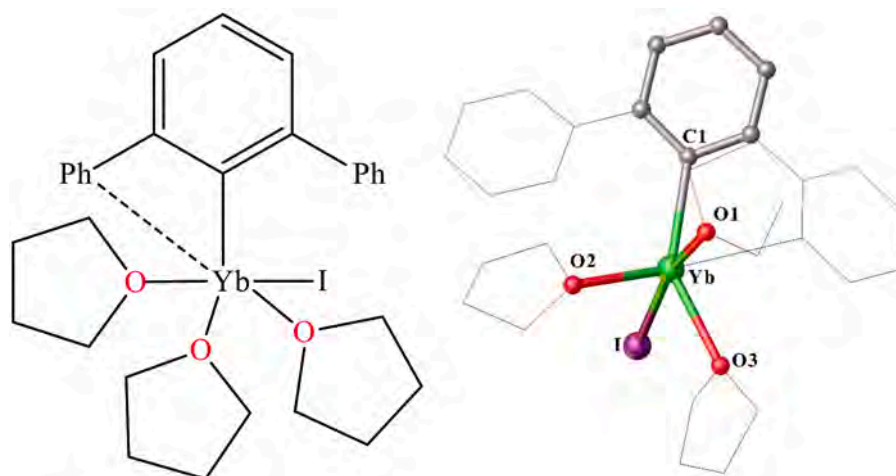
Fig. 2-4. Schematic and the X-ray structure of [Yb (2,6-Ph$_2$C$_6$H$_3$)I(thf)$_3$] (**5**). Hydrogen atoms are omitted and thf molecules and Ph groups are drawn as wireframe for clarity [12].

namely [Yb{C(SiMe$_3$)$_3$}I(Et$_2$O)]$_2$ (**1**), [Yb{C(SiMe$_3$)$_2$(Si-Me$_2$(CH=CH$_2$))}I(Et$_2$O)]$_2$ (**2**), [Yb{C(SiMe$_3$)$_2$(SiMe$_2$(OMe))}I(Et$_2$O)]$_2$ (**3**), [Yb{C(SiMe$_3$)$_2$(SiMe$_2$(Ph))}I(Et$_2$O)]$_2$ (**4**) have been prepared from the reaction between Yb metal with the corresponding {C(SiMe$_3$)$_2$(-SiMe$_2$R)}I (R = Me, CH=CH$_2$, MeO, Ph) oxidant in Et$_2$O at 25 °C [10], but (**1**) was initially obtained from the reaction of [Yb(C(SiMe$_3$)$_3$)$_2$] with methyl iodide or methylene diiodide [11]. Compound (**1**) (Fig. 2-1) crystallized in orthorhombic space group *Pbca* [11], whereas both compounds (**2**) (Fig. 2-2) and (**3**) (Fig. 2-3) are described as distorted

trigonal bipyramid with space group *P*2$_1$/*c* and *P*2$_1$/*n* respectively, [10]. In **2** and **3,** the structures are stabilised by intramolecular Yb·····(CH$_2$=CH$^-$) and Yb·····OMe bonding respectively.

The monomeric compound [Yb(2,6-Ph$_2$C$_6$H$_3$)I(thf)$_3$] (**5**) was isolated from the reaction between Yb metal powder and (2,6-Ph$_2$C$_6$H$_3$)I at room temperature in thf and was the first monomeric lanthanoid pseudo-Grignard reagent to be structurally identified [12]. The distorted tetragonal pyramidal compound [Yb(2,6-Ph$_2$C$_6$H$_3$)I(thf)$_3$] (**5**) (Fig. 2-4) crystallized in space group *P*2$_1$/*n*. The Yb atom in compound (**5**) is
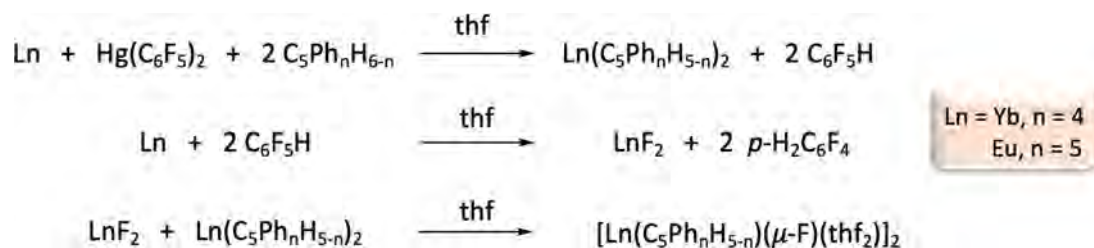
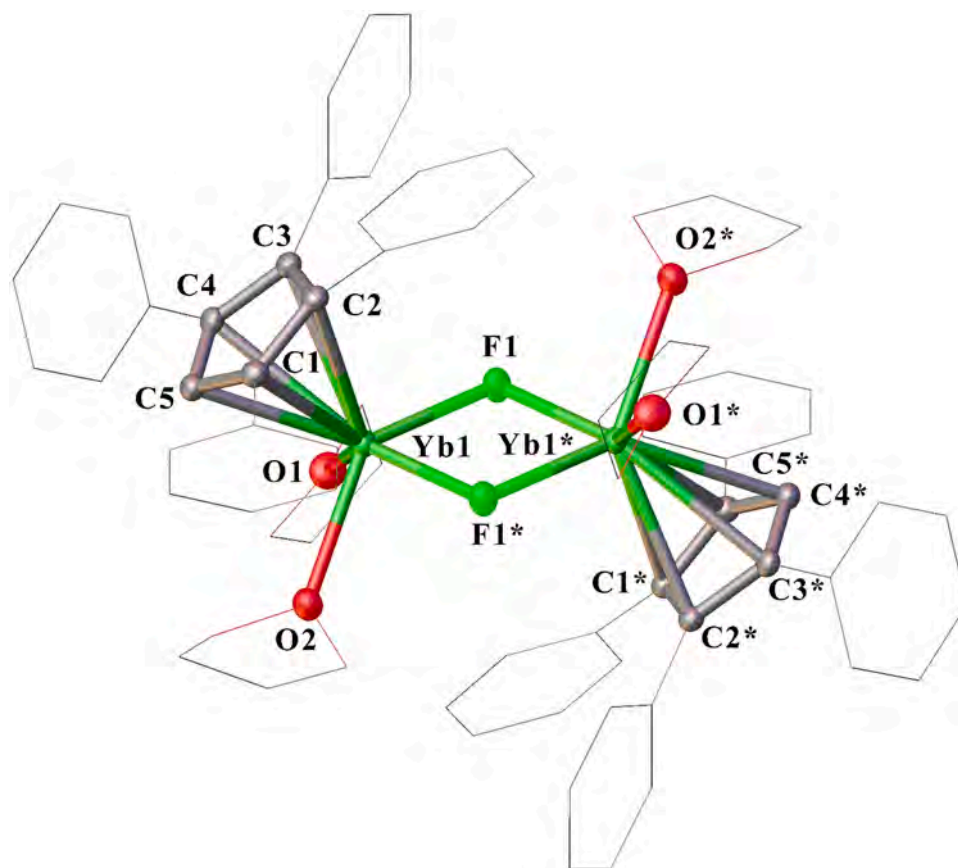**Scheme 2.** Formation of cyclopentadiene based lanthanoid pseudo-Grignard fluorides.

Fig. 2-5. X-ray structure of [Yb(C$_5$Ph$_4$H)(μ-F)(thf)$_2$]$_2$(**7**). Hydrogen atoms are omitted, coordinated thf molecules, Ph groups are drawn as wireframe for clarity [13].

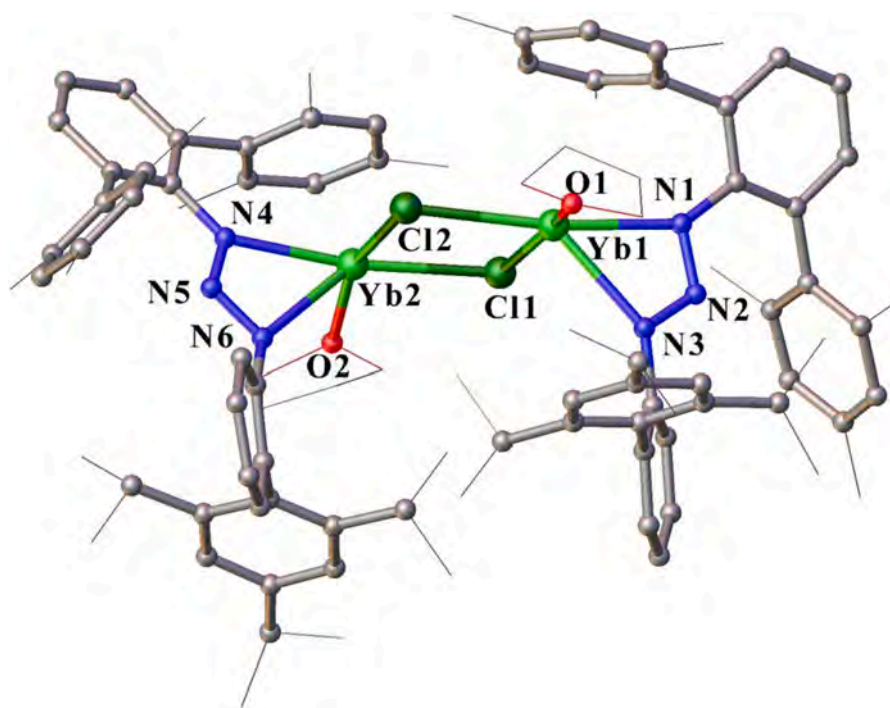**Fig. 2-6.** X-ray structure of [YbDmp(Tph)N$_3$Cl(thf)]$_2$ (**8**) {Dmp = 2,6-Mes$_2$C$_6$H$_3$, Tph = 2′,4′,6′-triisopropylbiphenyl-2-yl}. Hydrogen atoms are omitted, coordinated thf molecules, *i*Pr and CH$_3$ groups are drawn as wireframe for clarity [16].
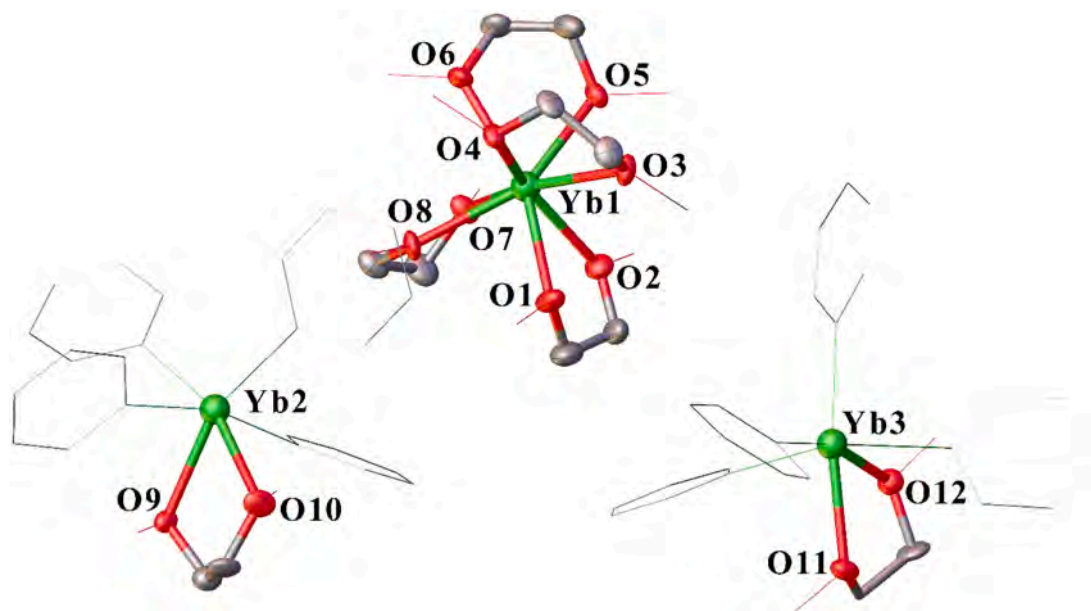
Fig. 2-7. X-ray structure of [Yb^{II}(dme)$_4$][Yb^{III}Ph$_4$(dme)]$_2$ (**9**). Hydrogen atoms are omitted, CH$_3$ and Ph groups are drawn as wireframe for clarity [18].

bound by the *ipso*-carbon of a phenyl group in addition to I, the phenyl C and three oxygens from thf ligands [12]. The ^{171}Yb NMR spectrum of **5** in D$_8$-thf showed not only a prominent resonance for **5** but also smaller equal intensity resonances attributable to YbI$_2$ and [Yb(2,6-Ph$_2$C$_6$H$_3$)$_2$] formed through a Schlenk equilibrium (see below) [12].

Two lanthanoid pseudo-Grignard fluorides [Eu(C$_5$Ph$_5$)(μ-F)(thf)$_2$]$_2$ and [Yb(C$_5$Ph$_4$H)(μ-F)(thf)$_2$]$_2$ have been isolated from reaction of Eu or Yb metal with Hg(C$_6$F$_5$)$_2$, and pentaphenyl- or tetraphenyl-cyclopentadiene in thf [13,14]. The formation is explained by the path shown in Scheme 2.

In each case the last step has independently been effected between in situ generated LnF$_2$(thf)$_n$ and the appropriate bis

(polyphenylcyclopentadienyl)lanthanoid complex [13,14]. An analogue of the last step has been used to prepare [Sm(C$_5$Ph$_4$H)I(thf)$_3$] [15], and is related to the final step in the synthesis of the triphenylmethyl pseudo-Grignard reagent (Scheme 1) [9]. [Eu(C$_5$Ph$_5$)(μ-F)(thf)$_2$]$_2$ (**6**) and [Yb(C$_5$Ph$_4$H)(μ-F)(thf)$_2$]$_2$ (**7**) are fluoride bridged dimeric pseudo-Grignard compounds [13,14]]. Compound [Eu(C$_5$Ph$_5$)(μ-F)(thf)$_2$]$_2$ (**6**) crystallized in the orthorhombic space group *Pbca*, where half of the dimer is generated by symmetry [13]. Compound [Yb(C$_5$Ph$_4$H)(μ-F)(thf)$_2$]$_2$ (**7**) crystallized in the monoclinic space group *P*2$_1$/*n* [14]. Both compounds (**6, 7**) have seven coordination, where the metal center is coordinated by one (η^5-C$_5$Ph$_5$ (**6**), C$_5$Ph$_4$H (**7**)) ring, two bridging fluorides and two thf molecules (Fig. 2-5) [13,14].
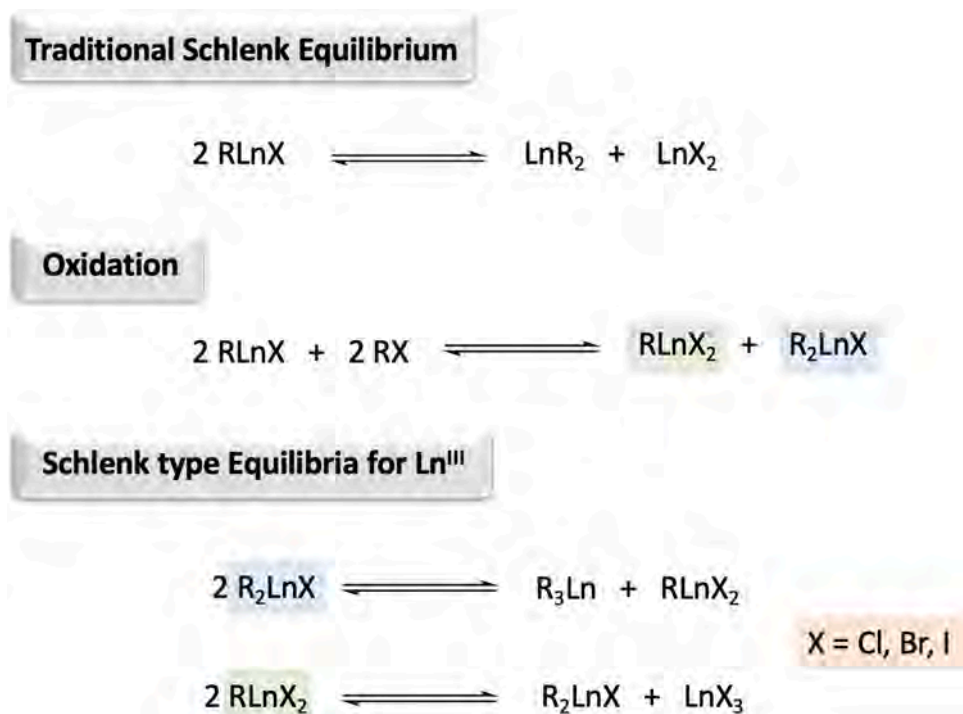
Scheme 3. Extended Schlenk equilibria and oxidation reactions accompanying lanthanoid pseudo-Grignard reagent formation.
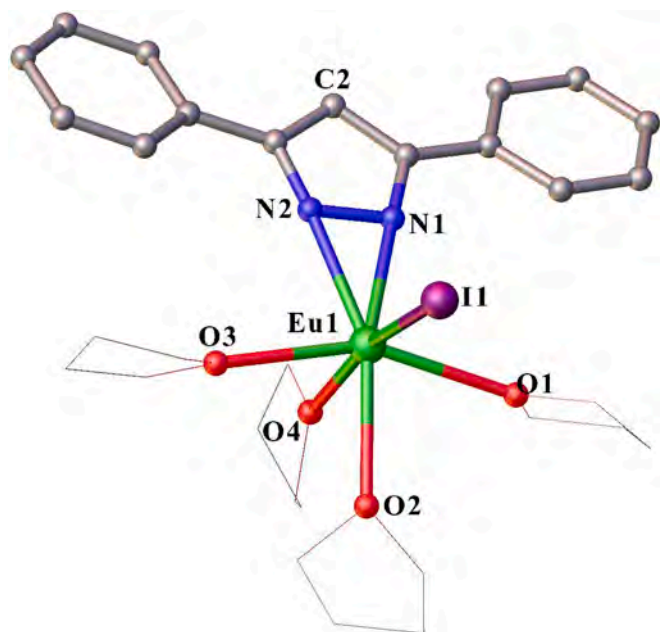
Fig. 3-1. X-ray structure of [Eu(Ph$_2$pz)I(thf)$_4$] (**10**). Hydrogen atoms are omitted and coordinated thf molecules are drawn as wireframe for clarity. The ytterbium analogue is isomorphous [18].

In an innovative approach, Niemeyer used redox transmetallation reactions of bulky triazenidomercuric chlorides to generate a pseudo-Grignard triazenidoytterbium chloride (**8**) (Eq. (3)) [16] (Figs. 2-6 and 2-7).

$$2\,Yb + 2\,ArAr'N_3HgCI \rightarrow [Yb(ArAr'N_3)CI(thf)_2 + 2\,Hg \qquad (3)$$
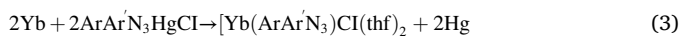
The dimeric compound (**8**) crystallizes in the triclinic space group $P\bar{1}$ and has tetragonal pyramidal coordination, where the metal atom is bonded by two chelating nitrogens from the triazenide (κ^2-bonded), two bridging chloride ligands and one oxygen atom from THF [16].

In an amplification of this synthesis, redox transmetallation/ protolysis reactions between ytterbium (or calcium), PhHgBr, and tetra-phenylcyclopentadiene gave [Yb(C$_5$Ph$_4$H)Br(thf)$_2$]$_2$ (or the Ca analogue) (Eq. (4)) [17].

$$2\,Yb + 2\,PhHgBr + 2\,C_5Ph_4H_2 \rightarrow \left[Yb(C_5Ph_4H)Br(thf)_2\right]_2 + 2\,Hg + 2\,PhH \qquad (4)$$
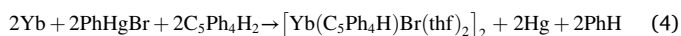
The unexpected isolation of a few crystals of the pseudo-Grignard reagent [Sm(C$_5$Ph$_5$)(μ-Br)(thf)$_2$]$_2$·6thf from a preparation of [Sm(C$_5$Ph$_5$)$_2$] has been attributed to a similar reaction arising from a PhHgBr impurity in a commercial sample of HgPh$_2$ [15].

The importance of using bulky ligands in isolation of crystalline stable divalent pseudo-Grignard reagents is well illustrated by attempts to crystallize PhYbI from thf and dme. In the former case, the products were [YbPh$_3$(thf)$_3$] and [YbI$_2$(thf)$_4$]. In the latter, after crystallization of [YbI$_2$(dme)$_3$], a low yield of the mixed valence species [Yb^{II}(dme)$_4$][Yb^{III}Ph$_4$(dme)]$_2$ (**9**) was obtained [18].

These outcomes reflect the intervention of oxidation to Ln^{III}, as mentioned in Evans' initial publications [2,3]. The oxidation leads to further species which can be involved in Schlenk-type equilibria analogous to that involving the initially formed RLnX pseudo-Grignard reagent. These reactions are summarized in Scheme 3.

In addition to the above complexity, there is the possibility of dimerisation of the above species as suggested by the structures of **2, 3,** and **7**.
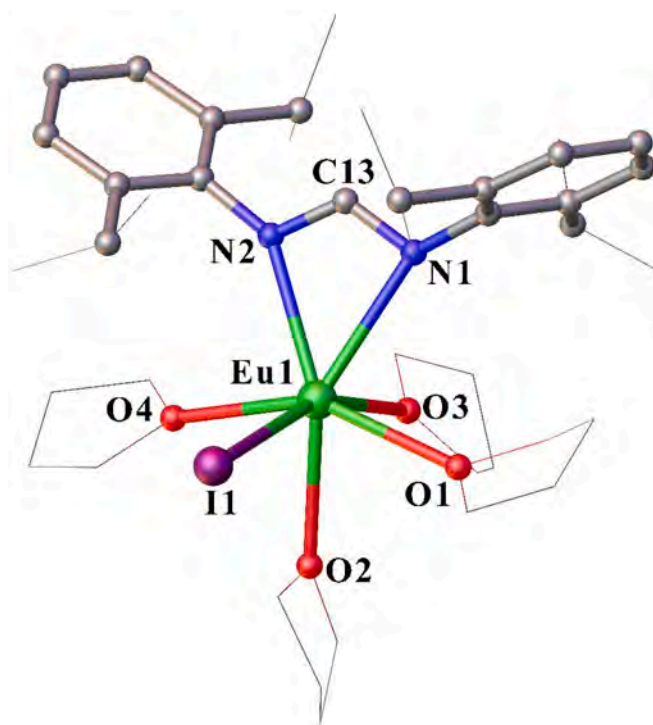

Fig. 3-2. X-ray structure of [Eu(DippForm)I(thf)$_4$] (**12**). Hydrogen atoms and lattice thf molecules are omitted, coordinated thf molecules and *i*Pr groups are drawn as wireframe for clarity [20].

3. Synthesis and characterization—compounds with N-Ln-X (*X* = Cl, Br, I, F) bonding

Lanthanoid pseudo-Grignard compounds, C-Ln-X, can be converted into divalent N-Ln bonded pseudo-Grignard reagent derivatives by protolysis reactions. In optimum cases, this is achieved despite the complexity of the Schlenk equilibria featured in Scheme 3. Thus, [Ln(Ph$_2$pz)I(thf)$_4$] (Ph$_2$pz = 3,5-diphenylpyrazolate, Ln = Eu **10**, (Fig. 3-1) Yb **11**) were obtained in high yield by reaction of PhLnI (Ln = Yb, Eu) with 3,5-diphenylpyrazole in thf at low temperature (Eq. (5)) [18].

$$PhLnI + Ph_2pzH \rightarrow Ln(Ph_2pz)I + PhH \qquad (5)$$

The monomeric structures contrast the more common dimeric structures of the C-Ln-X pseudo-Grignard complexes apart from **5**. The *cisoid* N-Ln-I array however resembles the analogous C-Ln-I array of the carbon based compounds.
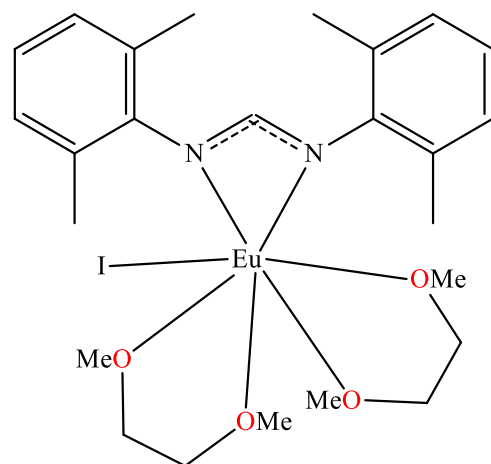

Fig. 3-3. Schematic of the X-ray structure of [Eu(XylForm)I(dme)$_2$] (**13**) [20].

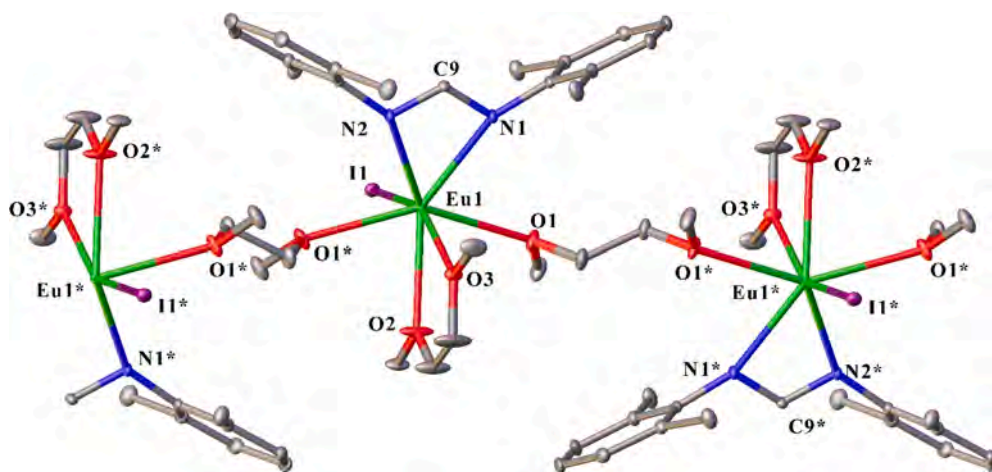**Fig. 3-4.** X-ray structure of [Eu(XylForm)I(dme)(μ-dme)]$_n$ (**14**) [20].
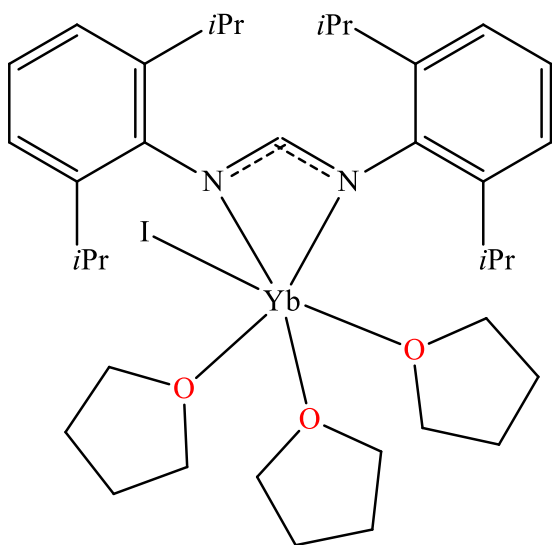
Fig. 3-5. Schematic of the X-ray structure of [Yb(DippForm)I(thf)$_3$] (**15**) [20].
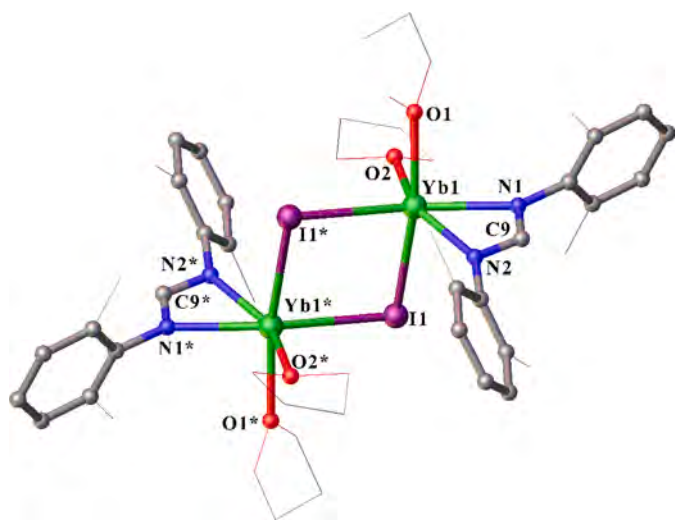
Fig. 3-6. X-ray structure of [{Yb(XylForm)I(thf)$_2$}$_2$] (**16**). Hydrogen atoms are omitted, coordinated thf molecules and CH$_3$ groups are drawn as wireframe for clarity [20].

When similar reactions were attempted with in situ generated PhLnBr, the outcomes were different. For Ln = Eu, the product was [Eu(Ph$_2$pz)$_2$(thf)$_4$], corresponding to protolysis of EuPh$_2$, a classic Schlenk equilibrium product (see Scheme 3, 1st step, *R* = Ph) (Eq. (6)) [19].

$$EuPh_2 + 2Ph_2pzH \rightarrow Eu(Ph_2pz)_2 + 2PhH \quad (6)$$

No crystalline product was obtained from the corresponding reaction of PhYbBr, whereas from PhSmBr, [Sm(Ph$_2$pz)$_3$(thf)$_3$] was crystallized, and also converted into [Sm(Ph$_2$pz)$_3$(dme)$_2$] by crystallization from dme. The formation of the former is attributed to protolysis of SmPh$_3$, an oxidation and redistribution product (Scheme 3 penultimate step), an outcome reflecting early conclusions about pseudo-Grignard reagent oxidation state behaviour (e.g., see Eq. (7)) [2,3].

$$SmPh_3 + 3Ph_2pzH \rightarrow Sm(Ph_2pz)_3 + 3PhH \quad (7)$$

When reactions of PhLnI (Ln = Eu, Yb) were extended to *N,N'*-diarylformamidines, the out- comes were more complex than the corresponding reactions with 3,5-diphenylpyrazole [20]. Six different divalent pseudo-Grignard compounds: [Eu(DippForm)I(thf)$_4$]·thf (DippForm = *N,N'*-bis(2,6-di-isopropylphenyl)formamidinate) (**12**) (Fig. 3-2), [Eu(XylForm)I(dme)$_2$]·0.5dme (XylForm = *N.N'*-bis(2,6-dimethylphenyl)formamidinate) (**13**) (Fig. 3-3), [Eu(XylForm)I(dme)(μ-dme)]$_n$ (**14**) (Fig. 3-4), [Yb(DippForm)I(thf)$_3$]·thf (**15**) (Fig. 3-5), [{Yb(XylForm)I(thf)$_2$}$_2$] (**16**) (Fig. 3-6) and [{Yb(MesForm)I(thf)$_2$}$_2$] (**17**) (MesForm = *N,N'*-bis(2,4,6-trimethylphenyl)formamidinate) were prepared by a similar procedure [20] and by changing solvent (using dme) for crystallizing (**13**) and (**14**) [20]. Pseudo-octahedral ([Eu(DippForm)I(thf)$_4$]·thf and [Eu(XylForm)I(dme)$_2$]·0.5dme are seven coordinate monomers having a chelating formamidinate ligand which is *cisoid* to the iodine ligand. In polymeric (**14**), two *transoid* oxygen atoms from bridging dme donors replace a chelating dme of (**13**), the compounds crystallizing as a mixture, though the microanalysis suggests (**13**) to be the dominant component [20], with iodine *cisoid* to the formamidinate in both. Not all Eu systems were satisfactory with MesFormH in dme yielding [EuI$_2$(dme)$_2$]$_2$ and XylFormH in thf [Eu(XylForm)I(thf)$_2$(OH)]$_2$ [20]. The ytterbium complexes are a six coordinate monomer (DippForm) (**15**) or iodide bridged dimers with the smaller XylForm (**16**) or MesForm (**17**). The steric bulk of iodide is less than that of thf [21]. However these reactions are far from simple with the DippFormH reaction also yielding the oxidation product [Yb(DippForm)I$_2$(thf)$_3$]·2thf, and with the XylFormH reaction giving the monomeric trivalent [Yb(XylForm)$_2$I(dme)]·dme after isolation of the Yb^{II} product (**16**), addition of dme, and further crystallization [20]. With the bulkier formamidines there is a reduction in coordination number from Eu to Yb in contrast to Ph$_2$pz. For the reaction of in situ generated PhYbI with DippFormH and with XylFormH, the reaction mixtures were
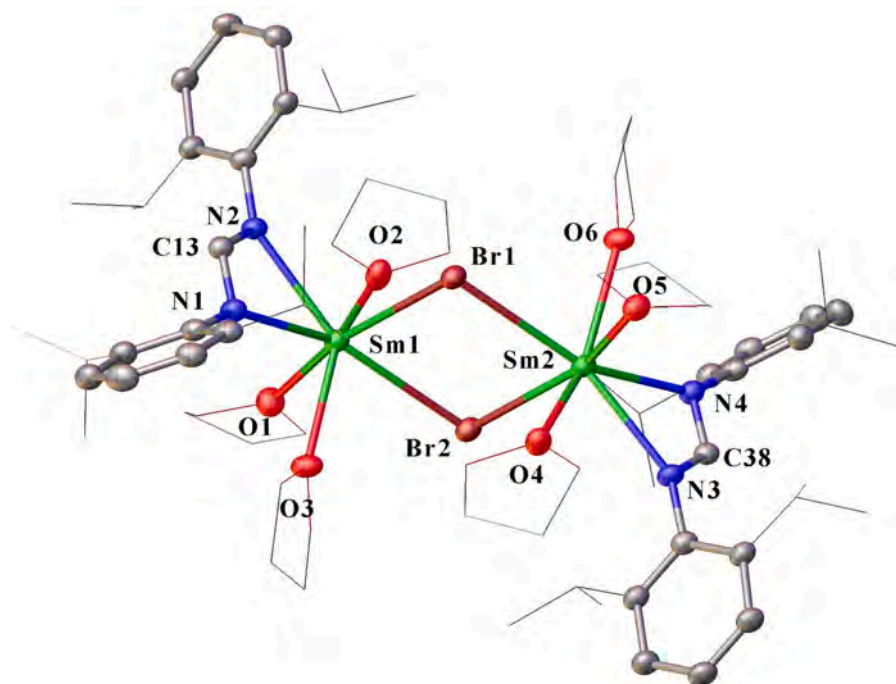
Fig. 3-7. X-ray structure of [Sm(DippForm)Br(thf)$_3$]$_2$·6thf (**18**). Hydrogen atoms and lattice thf molecules are omitted, coordinated thf molecules and *i*Pr groups are drawn as wireframe for clarity [19].
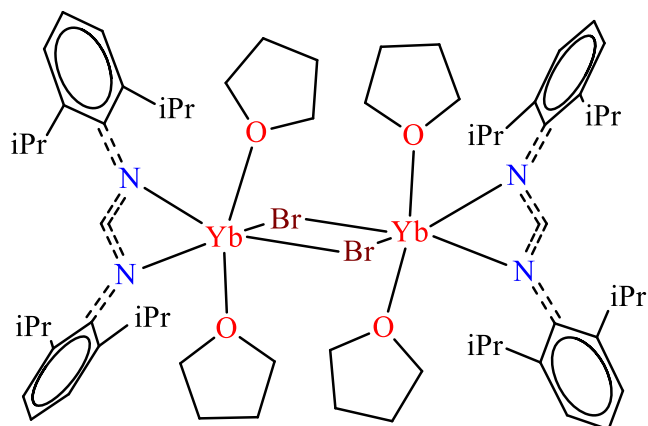

Fig. 3-8. Schematic of the X-ray structure of [Yb(DippForm)Br(thf)$_2$]$_2$·2thf (**20**) [19].

investigated by ^{171}Yb NMR spectroscopy. In the former case, both [Yb (DippForm)I(thf)$_3$I(thf)$_3$] (**15**) and YbI$_2$ were detected but not [Yb (DippForm)$_2$], the other component of the Schlenk equilibrium. Perhaps this had been oxidized to an NMR silent Yb^{III} (see e.g. Scheme 3, step 2). On the other hand, the XylFormH reaction mixture showed all three Schlenk equilibrium components, **16**, YbI$_2$, and [Yb(XylForm)$_2$] [20].

In view of Schlenk equilibria and oxidation state complexity in the reactions of PhLnBr with Ph$_2$pzH, and the formation of both divalent and trivalent formamidinatolanthanoid iodides in reactions of PhLnI with formamidines, the expectation would be that reactions of PhLnBr with formamidines would lead to both Ln^{II} and Ln^{III} products. To the contrary, three similar type lanthanoid(II) pseudo-Grignard compounds namely [Ln(DippForm)Br(thf)$_3$]$_2$·6thf (Ln = Sm **18** (Fig. 3-7) and Eu **19**) and [Yb(DippForm)Br(thf)$_2$]$_2$·2thf (**20**) (Fig. 3-8) were crystallized in 45–65 % yield from the reaction between the corresponding Grignard reagent (PhLnBr) and DippFormH [19]. The isolation of the Sm^{II} derivative is particularly noteworthy given the relative instability of this

oxidation state and earlier data on the Sm^{II}:Sm^{III} ratio in solutions of "PhSmI" [2,3]. Compounds (**18** and **19**) have seven coordinate metal centers, and both are bromine-bridged dimers with one chelating DippForm ligand *cis* to Br1 and *trans* to Br2. Compound ([Yb(DippForm) Br(thf)$_2$]$_2$·2thf **20**) is a six coordinate centrosymmetric dimer where half is generated from the Yb(1)···Yb(1)* vector. Compounds (**18** and **19**) crystallize in the monoclinic *P*2$_1$/*c* space group with distorted pentagonal bipyramidal stereochemistry and (**20**) in the triclinic *P*-1 space group (octahedral geometry). The lanthanoid contraction is very clear from the <Ln-N> values; Sm-N (2.64) ~ Eu-N (2.63)> Yb-N (2.46) [19]. A summary of reactions of PhLnX species with Ph$_2$pzH and with formamidines is given in Scheme 4.

A N—Yb—Cl pseudo-Grignard reagent (**8**) with a triazenide ligand has been prepared by redox transmetallation from the corresponding triazenidomercuric chloride (sections 2), and [Ln(Ap)I(thf)$_2$]$_2$ (Ln = Sm **21**, Yb **22**) were isolated from the reaction between KAp, and appropriate [LnI$_2$(thf)$_2$] ({ApH = (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine}) compounds in THF and crystallised from toluene or hexane. [Sm(Ap)I(thf)$_2$]$_2$ (**21**) (Fig. 3-9) crystallizes in monoclinic space group *P*2$_1$/*c* and [Yb(Ap)I(thf)$_2$]$_2$ (**22**) in triclinic space group *P*$\bar{1}$ [22]. Two isostructural divalent Eu compounds ([Eu (dpp-Bian)(µ-Cl)(dme)]$_2$ **23** and [Eu(dpp-Bian)(µ-Br)(dme)]$_2$ (**24**) (dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) were synthesized from the oxidation reaction between [Eu(dpp-Bian)(dme)$_2$] and [Sn(Ph)$_3$Cl] or [C$_2$H$_2$Br$_2$(Ph)$_2$]. The centrosymmetric distorted octahedral dimeric compounds ([Eu(dpp-Bian)(µ-X)(dme)]$_2$ (**23** and **24**) have triclinic crystal structures with space group *P*$\bar{1}$. The bite angle (N (1)-Eu(1)-N(2)) of these compounds is 66.60° and 66.92° respectively [23]. Divalent N-Ln-X pseudo-Grignard compounds are listed in Table 3.1.

4. Synthesis and characterization—compounds with O-Ln-X bonding

The divalent samarium pseudo-Grignard compound [Sm(ArO)(µ-I) (thf)$_3$]$_2$ (**25**) was synthesised in 91 % yield from the reaction of [Sm (OAr)$_2$(thf)$_3$] (Ar = C$_6$H$_2$Bu$^t_2$-2,6-Me-4) and SmI$_2$ (mole ratio 1:1) in
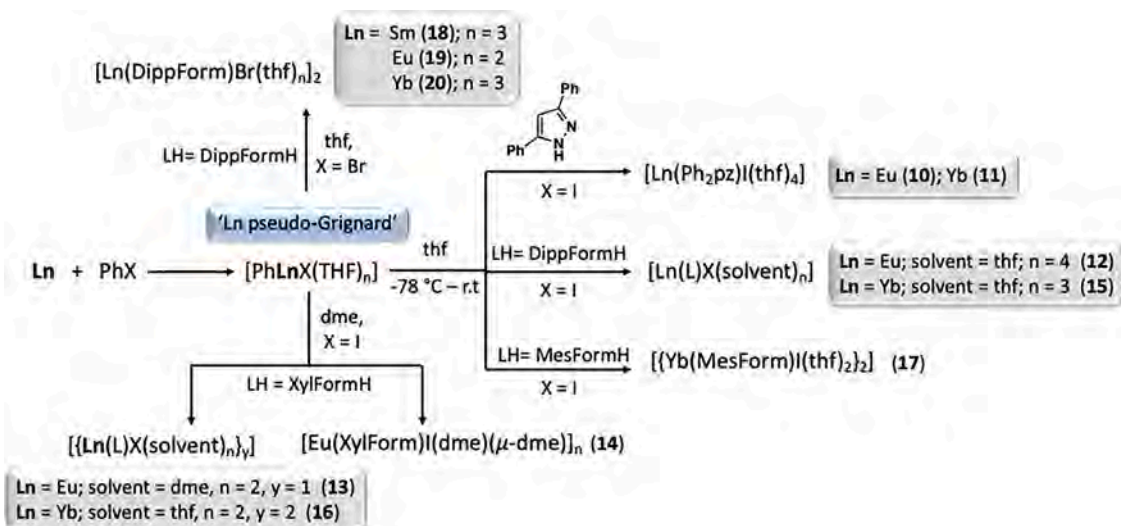
Scheme 4. Lanthanoid pseudo-Grignard compounds from the reactions of PhLnX species with Ph$_2$pzH and with formamidines.
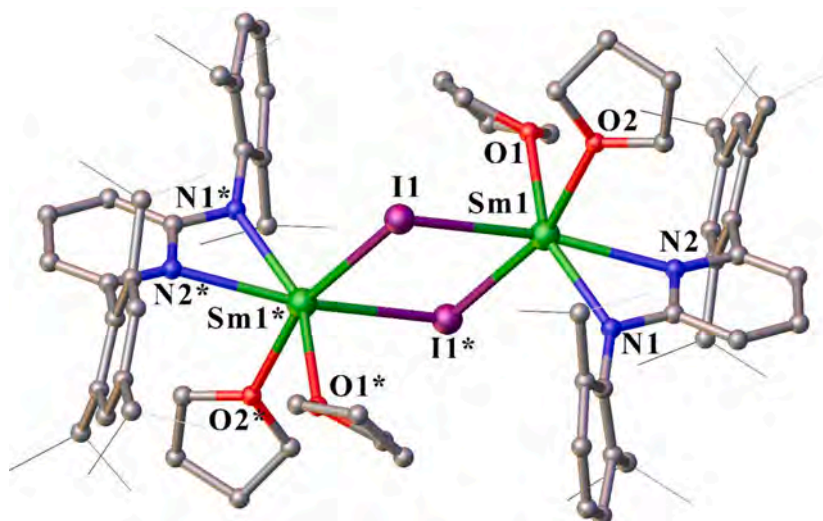

Fig. 3-9. X-ray structure of [Sm(Ap)I(thf)$_2$]$_2$(**21**). Hydrogen atoms are omitted and *i*Pr groups are drawn as wireframe for clarity [22].

THF. The six-coordinate distorted octahedral dimeric Sm^{II} complex (**25**) crystallized in monoclinic space group $P2_1/a$, with I(1)-Sm(1)-I(1*) 74.2 and Sm(1)-I(1)-Sm(1*) 105.8 [24] (Fig. 4-1).

5. Reactivity of divalent lanthanoid pseudo-Grignard compounds (N(O)-Ln-X) in oxidation and metathesis reactions

Oxidation and metathesis reactions of divalent lanthanoid pseudo-Grignard compounds expand their usefulness by providing access to new classes of complexes. Earlier reviews [1,4] have discussed use of protolysis reactions as well as metathesis reactions with trimethylsilyl chloride and triphenyltin chloride in characterization of divalent pseudo-Grignard reagents R-Ln-X and the metathesis reactions are mentioned in Section 2. The emphasis was on identification of the pseudo-Grignard reagents rather than on derived syntheses. Protolysis reactions of PhLnX are featured in Section 3 as a source of N-Ln-X pseudo-Grignard reagents.

Oxidation and metathesis reactions have led to new complexes (Scheme 5). Thus, [Yb(Ph$_2$Pz)I$_2$(thf)$_3$] (**26**) was isolated from the oxidation reaction of [Yb(Ph$_2$pz)I(thf)$_4$] with I$_2$ at 0 °C. The stereochemistry of compound (**26**) is a distorted pseudo-octahedron, with one

η^2-Ph$_2$pz ligand, two *trans* iodine donors (I(1)-Yb(1)-I(2) 170.39°), and three thf molecules resulting in seven-coordination [20]. Both iodine atoms are *cisoid* to the pyrazolate (C(backbone)-Yb(1)-I(1) 95.42° and C (backbone)-Yb(1)-I(2) 94.03°). The structure of the product is derived simply by replacement of a thf ligand of the reactant by iodine. Compound [Yb(C$_5$H$_5$)(Ph$_2$pz)(thf)]$_n$ (**27**) (Fig. 5-1) was isolated from the metathesis reaction between [Yb(Ph$_2$pz)I(thf)$_4$] and Na(C$_5$H$_5$) at room temperature (Scheme 5). Compound (**27**) is a nine coordinate divalent metal coordination polymer, where the Yb atoms are bridged by μ-η^5: η^5-Cp (Cp = C$_5$H$_5$) ligands. The pyrazolate ligands are chelating and it is perhaps surprising they are not bridging rather than Cp given the prevalence of the μ-1κ(N):2κ(N') bridging mode in pyrazolate chemistry. Compound [Sm(OAr)(C$_5$Me$_5$)(HMPA)$_2$] (**28**) was similarly prepared from the reaction of equimolar amounts of [Sm(ArO)(μ-I)(thf)$_3$]$_2$ and C$_5$Me$_5$K in THF/HMPA (HMPA = hexamethylphosphoramide) (Scheme 5). Complex (**28**) crystallizes in the triclinic space group $P\bar{1}$ and is distorted tetrahedral, where the angle of O(Ar)-Sm-C$_5$Me$_5$ ring center is 116° [24], paralleling the *cisoid* C(N)-Ln-I array of pseudo-Grignard complexes. The reaction between [MeYbI] and [KN(SiMe$_3$)$_2$] at −78 °C did not yield the targeted metathesis product [MeYbN(SiMe$_3$)$_2$]. Instead [K(dme)$_4$][Yb{N(SiMe$_3$)$_2$}$_3$] (**29**) (Fig. 5-2) was crystallized

Table 3.1
Divalent lanthanoid N-Ln-X pseudo-Grignard compounds.

Compound	Oxidant	Proligand	Yield %	Ref.
[YbDmp(Tph)N₃Cl(thf)]₂(**8**)	HgDmp(Tph)N₃Cl		77	[16]
[Eu(Ph₂pz)I(thf)₄](**10**)	PhI	Ph₂pzH	76	[18]
[Yb(Ph₂pz)I(thf)₄](**11**)			87	[18]
[Eu(DippForm)I(thf)₄]·thf (**12**)		DippFormH	46	[20]
[Eu(XylForm)I(dme)₂]·0.5dme (**13**)		XylFormH		[20]
[Eu(XylForm)I(dme)(μ-dme)]ₙ (**14**)				[20]
[Yb(DippForm)I(thf)₃]·thf (**15**)		DippFormH	16	[20]
[{Yb(XylForm)I(thf)₂}₂] (**16**)		XylFormH	5	[20]
[{Yb(MesForm)I(thf)₂}₂] (**17**)		MesForm	41	[20]
[Sm(DippForm)Br(thf)₃]₂·6thf(**18**)	PhBr	DippFormH	64	[19]
[Eu(DippForm)Br(thf)₃]₂·6thf(**19**)			48	[19]
[Yb(DippForm)Br(thf)₂]₂·2thf(**20**)			47	[19]
[Sm(Ap)I(thf)₂]₂(**21**)	–	ApH	26	[22]
[Yb(Ap)I(thf)₂]₂(**22**)	–		82	[22]
[Eu(dpp-Bian)(μ-Cl)(dme)]₂(**23**)	Ph₃SnCl		41	[23]
[Eu(dpp-Bian)(μ-Br)(dme)]₂(**24**)	Ph(Br)CHCH(Br)Ph		54	[23]

[20] (Scheme 5). It is unique in having an isolated triangular [Yb{N(SiMe₃)₂}₃] complex anion (Yb(1)-N(1) 2.348(2), Yb(1)-N(2) 2.331(3), Yb(1)-N(3) 2.334(2)) in contrast to alkali metal analogues in which silylamide ligands bridge Yb and the alkali metal leading to distortion of the stereochemistry around Yb. The reaction of divalent [Sm(dpp-Bian)I(dme)]₂ with 0.5 equivalent [(CH₃)₂NCS₂]₂ gave the oxidation product [Sm(dpp-Bian)I(S₂CN(CH₃)₂)(dme)] (**30**) (Scheme 5). The seven-coordinate compound (**30**) crystallizes in monoclinic space group *C*2/*c* [25] (Table 5.1).

6. Reactions of divalent pseudo-Grignard reagents with organic substrates

As part of the original characterization of PhYbI, Evans et al. treated the solutions with benzophenone and obtained triphenylmethanol after hydrolysis with hydrochloric acid [2,3]. Subsequently, a considerable

effort has been put into reactions with organic substrates, particularly directed to finding differences from the corresponding reactions of classical Grignard reagents. These studies are mainly covered by three previous reviews [1,4,26]. More recently there has been a dearth of interest perhaps owing to the complexity uncovered and the shortage of distinctive clean outcomes. Particular interest has focused on differences from Grignard reagent reactivity, as for similar reactivity, magnesium is much cheaper. Some of the more interesting results are mentioned in an attempt to stimulate further developments. Reactions of a number of ketones and aldehydes with PhYbI formed the corresponding alcohols after hydrolysis, whilst nitriles gave low yields of ketones [27]. However, esters gave a mixture of ketones and alcohols with the former favoured at low temperature (but far from completely selective), though differentiating from classical Grignard reagent behaviour. A competitive reaction between methyl benzoate and acetophenone favoured the ketone over alcohol in the product by 2:1. Further investigation of the behaviour of methyl benzoate showed that addition of PhYbI to the ester improved selectivity of ketone formation, but still far from specific [28]. In reactions of benzoyl chloride with PhYbI, Ph₂CO and Ph₃COH were both obtained together with a low yield of Ph₃CH. The addition of PhYbI to PhCOCl improved ketone selectivity, and this was virtually specific in the presence of ferric chloride [28].

Three publications from the Fujiwara group [29–31] reveal the increasing complexity of the reactions of Ph(Me)Yb-I with α, β-unsaturated ketones. In the first, it is shown that a set of these mostly gives exclusive 1,2-addition compared with the lower selectivity of classical Grignard reagents, though two of three comparison Grignard cases favour 1,2-addition without the specificity of PhYbI [29]. Next in response to a report from Sigalov et al. [32] of propene formation in such reactions, the group reported that whilst chalcone gave 1,2-addition on reaction with an equimolar amount of PhYbI, use of an excess (mainly 3:1) of the pseudo-Grignard reagent gave *trans*-stilbene, 1,1,3-triphenylpropene, and diphenylethanol together with, in some cases, the 1,2-addition product, 1,1,3-triphenylprop-2-en-1-ol [30]. These observations were further elaborated in a full paper detailing reactions of Ph(Me)YbI with α,β-unsaturated ketones and -alcohols [31]. The complexity of the products with a RYbI:substrate ratio of 3:1 tends to obscure the clean 1,2-addition with a 1:1 ratio. The intervention of deoxygenation in these reactions has also been observed in reactions with ketones, where for example, anthraquinone with PhYbI on a 1:4 mole ratio yields 9-phenylanthracene [32]. In a detailed study of the deoxygenation of benzophenone and 9-fluorenone with PhYbX (*X* = Br, I), it was found that the ratio of phenylmethane to phenylcarbinol was not affected by the halide but was increased by increasing the PhYbX: substrate ratio from 1:1 to 2:1, and reached near 100 % on addition of
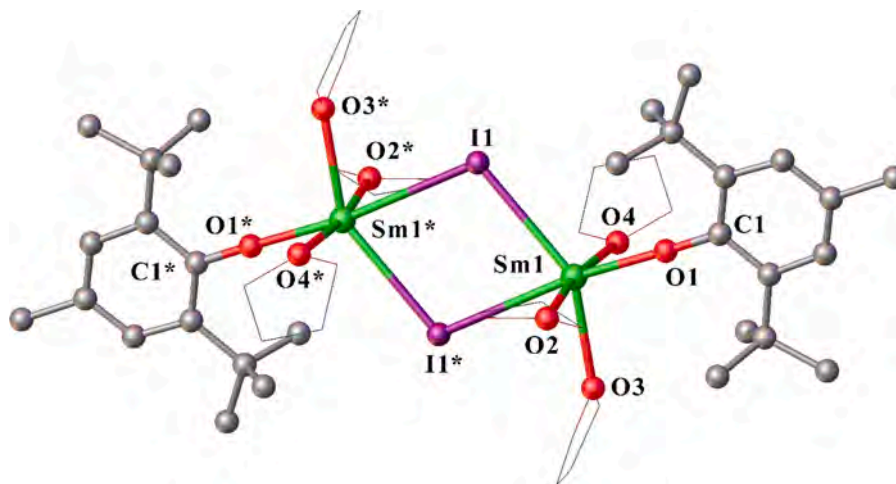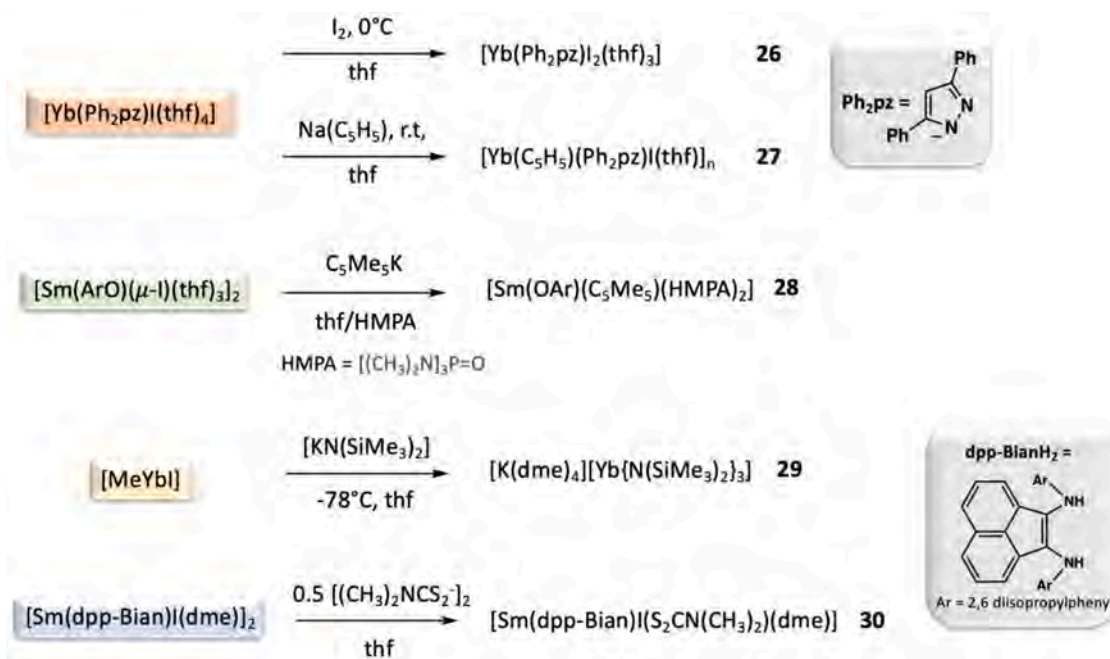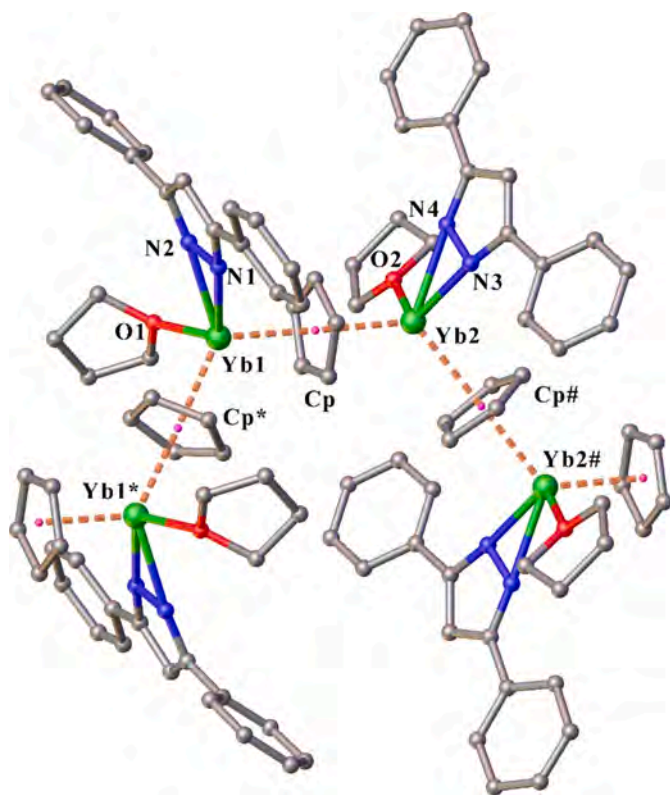

Fig. 4-1. X-ray structure of [Sm(ArO)(μ-I)(thf)₃]₂(**25**). Hydrogen atoms and lattice thf molecules are omitted, coordinated thf molecules are drawn as wireframe for clarity [24].

Scheme 5. Some reactions of N(O)-Ln-X divalent lanthanoid pseudo-Grignard reagents.

Fig. 5-1. X-ray structure of [Yb(C$_5$H$_5$)(Ph$_2$pz)(thf)]$_n$ (**27**). Hydrogen atoms and lattice thf molecule are omitted for clarity [20].

the co-reductant, biphenylyllithium [33]. On the other hand, the use of 2-thienyl- or 2-pyridyl-ytterbium iodide suppressed deoxygenation, and this was attributed to the stabilisation of the intermediate ytterbium carbinolate by intramolecular S(N)-Yb coordination.

Copper catalysed coupling of alkyl, benzyl, and styryl halides (RX) with PhYbI gave predominantly PhR rather than Ph$_2$, but coupling with

BuLi was less specific [34]. In a different study, a range of arylytterbium iodides was found to arylate dihydrosilanes to give monohydrosilanes many in near quantitative yield (Eq. (8)) [35].

$$ArYbI + RPhSiH_2 \rightarrow ArRPhSiH + \ ^{'}HYbI^{'} \tag{8}$$
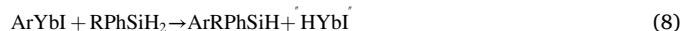
Although a specialist use, this may be one of the most straightforward of applications in organic synthesis. The corresponding alkylations were attempted, and gave a more variable outcome, from near quantitative formation of RPhMeSiH derivative (e.g. R = Me, *i*Bu) to low yields (e.g. R = *i*Pr, *cyclo*-C$_6$H$_{11}$) [35].

Overall, lanthanoid pseudo-Grignard reagents still have find a major role in organic synthesis.

7. Conclusions

The pseudo-Grignard compounds of divalent lanthanoid metals have been reviewed. By varying the steric and electronic effects of the ligands, the coordination number, structures and reactivity of the resulting complexes are changed. The scope of divalent pseudo-Grignard derivatives E-Ln-X (E = C, N, O; X = halide) has been enhanced by isolable derivatives with pyrazolate, formamidinate, and aryloxide ligands to add to the limited examples of isolable complexes with C-Ln-X bonding. The potential of these compounds and the few isolated divalent cyclopentadienyllanthanoid halides in subsequent chemistry, such as metathesis and oxidation reactions or treatment with organic substrates is little explored so far. These well-defined complexes have advantages over in situ generated RLnX (R = aryl or alkyl) species where Schlenk equilibria, including ones involving Ln^{III} compounds, raise issues of reproducibility and may account in part for the complexity of some reactions with organic substrates. The current review considers the effects of Schlenk equilibria on the species isolated when attempting to prepare N-Ln-X compounds. Although a number of interesting and unique reactions with organic substrates have been observed for in situ generated C-Ln-X species, they have yet to find a major role in organic synthesis, but there appears to be significant scope for expansion. However, given the much greater cost of Ln metals than Mg (or Ca), it requires a distinctive role, as found for SmI$_2$ [36].

On the basis of Ln^{3+} + e$^-$ → Ln^{2+} redox potentials, −1.55 (Sm), −1.15 (Yb), −0.35 (Eu) [37], the stability of the Ln pseudo-Grignards to
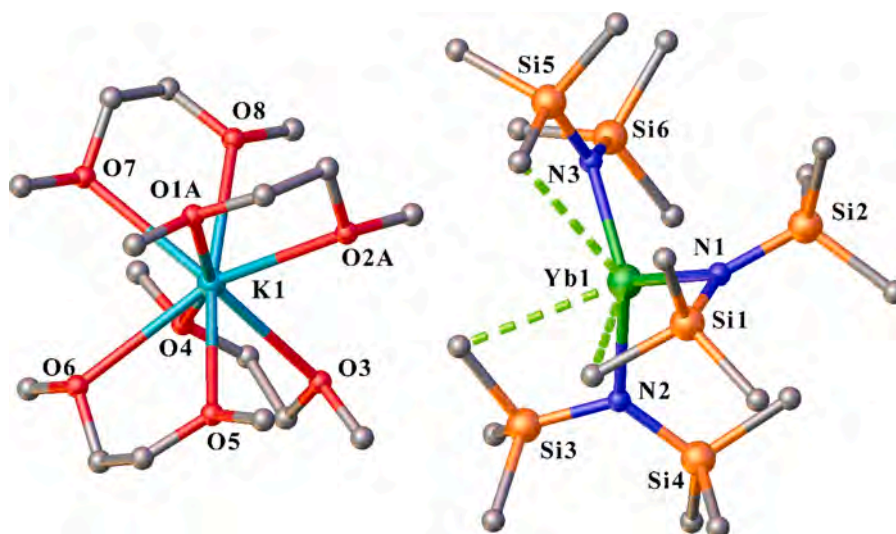
Fig. 5-2. X-ray structure of $[K(dme)_4][Yb\{N(SiMe_3)_2\}_3]$ (**29**). Disordered moieties and hydrogen atoms are omitted for clarity [20].

Table 5.1
Reactivity of divalent lanthanoid pseudo-Grignard compounds.

Reaction	Complex	Yield %	Ref.
$[Yb(Ph_2pz)I(thf)_4] + I_2$	$[Yb(Ph_2Pz)I_2(thf)_3]$ (**26**)	99	[20]
$[Yb(Ph_2pz)I(thf)_4] + NaC_5H_5$	$[Yb(C_5H_5)(Ph_2pz)(thf)]_n$(**27**)	53	[20]
$[Sm(ArO)(\mu\text{-}I)(thf)_3]_2 + C_5Me_5K$	$[Sm(OAr)(C_5Me_5)(HMPA)_2]$ (**28**)	11	[24]
$MeYbI + [KN(SiMe_3)_2]$	$[K(dme)_4][Yb\{N(SiMe_3)_2\}_3]$ (**29**)	<5	[20]
$[Sm(dpp\text{-}Bian)I(dme)]_2 + 0.5$ $[(CH_3)_2NCS_2^-]_2$	$[Sm(dpp\text{-}Bian)I(S_2CN (CH_3)_2)(dme)]$(**30**)	69	[25]

oxidation should be Eu>Yb>Sm, but if the triscyclopentdienyls [38] are a guide to organometallic behaviour, all may be 0.7–1.0 V less stable. This sequence accords with Evans' earlier magnetic measurements [2, 3]. With only three elements forming divalent lanthanoid pseudo-Grignards of significant stability and two with approximately the same size [39], the scope for studying the effect of Lewis acidity (related to ion size), electronegativity etc. on behaviour is limited. Europium and ytterbium pseudo-Grignard reagents with 3,5-diphenylpyrazolate are both seven-coordinate, with reduction in ion size having no effect on the coordination number [18], whereas with the larger *N,N'*-bis(2,6-diisopropylphenyl)formamidinate, the coordination number falls from seven to six from the Eu to the Yb complex (Section 3) [19, 20]. On the other hand, exploration of trivalent $RLnX_2$ compounds may prove rewarding in terms of Ln effect on properties, though these species are not divalent pseudo-Grignards.

CRediT authorship contribution statement

Md. Abdul Halim: Writing – review & editing, Writing – original draft, Investigation. **Zhifang Guo:** Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Victoria L. Blair:** Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Glen B. Deacon:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Conceptualization. **Peter C. Junk:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available on request.

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