# **CHEMISTRY** A European Journal



# Accepted Article

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To be cited as: Chem. Eur. J. 10.1002/chem.201704383

Link to VoR: http://dx.doi.org/10.1002/chem.201704383

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# Lanthanoid pseudo-Grignard reagents – a major untapped resource

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#### Abstract

Pseudo-Grignard reagents PhLnI (Ln = Yb, Eu) readily prepared by the oxidative addition of iodobenzene to ytterbium or europium metal at -78 °C in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), react with a range of bulky N,N'bis(aryl)formamidines to form an extensive series of Ln<sup>II</sup> or more rarely Ln<sup>III</sup> complexes, namely [Eu(DippForm)I(thf)<sub>4</sub>].thf (1),  $[{EuI_2(dme)_2}_2]$ (2),[Eu(XylForm)I(dme)<sub>2</sub>].0.5dme  $[Eu(XylForm)I(dme)(\mu-dme)]_n$ (3a),(3b),[{Eu(XylForm)I( $\mu$ -OH)(thf)<sub>2</sub>}] [Yb(DippForm)I(thf)<sub>3</sub>].thf (4), (5a), [Yb(DippForm)I<sub>2</sub>(thf)<sub>3</sub>].2thf (**5b**), [{Yb(MesForm)I(thf)<sub>2</sub>}<sub>2</sub>] (6), [{Yb(XylForm)I(thf)<sub>2</sub>}<sub>2</sub>] (7a), [Yb(XylForm)<sub>2</sub>I(dme)].dme (7b) {(Form (ArNCHNAr) = XylForm (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), MesForm (Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), DippForm (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)  $iPr_2C_6H_3$ . Repeatedly PhEuI and MesFormH in DME gave 2 and with XylFormH in THF gave 4. Europium complexes 1 and 3a are seven-coordinate divalent monomers, whilst **3b** is a seven-coordinate dme bridged polymer. Complex **5a** of the smaller  $Yb^{II}$ is a six-coordinate monomer, but related 6 and 7a are six-coordinate iodide bridged dimers. 4 is a trivalent seven-coordinate hydroxide bridged dimer, whereas complexes

**5b** and **7b** are seven-coordinate monomeric Yb<sup>III</sup> derivatives. A characteristic structural feature is that iodide ligands are *cisoid* to the formamidinate.

To illustrate the synthetic scope of the pseudo-Grignard reagents, [Yb(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>]  $(Ph_2pz = 3,5-diphenylpyrazolate)$  was oxidized with 1,2-diiodoethane giving the sevencoordinate monomeric pyrazolatoytterbium(III) iodide [Yb(Ph<sub>2</sub>Pz)I<sub>2</sub>(thf)<sub>3</sub>] (8) in high yield whilst metathesis between  $[Yb(Ph_2pz)I(thf)_4]$ and NaCp gave  $[Yb(C_5H_5)Ph_2pz)(thf)]_n$  (9), a nine-coordinate  $\eta^5:\eta^5$ -Cp-bridged coordination polymer. Reaction of the pseudo-Grignard MeYbI with KN(SiMe<sub>3</sub>)<sub>2</sub> gave  $[K(dme)_4][Yb{N(SiMe_3)_2}_3]$  (10) with a charge separated three-coordinate homoleptic  $[Yb{N(SiMe_3)_2}_3]$  anion, and the complex was obtained in high yield by a deliberate synthesis from YbI<sub>2</sub> and KN(SiMe<sub>3</sub>)<sub>2</sub> in DME.

*Keywords:* Pseudo-Grignard reagents; organolanthanoid complexes; LnLX type complexes; formamidines; X-ray diffraction.

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#### Introduction

Free rare earth metals are an emerging source of rare earth metal-organic compounds as an alternative to the commonly used metathesis reactions of rare earth halides.<sup>[1,2]</sup> Rare earth pseudo-Grignard reagents "RLnX", from reactions of the free metals with organic halides were discovered in the 1970s,<sup>[3,4]</sup> but remain a largely undeveloped resource of great potential for the synthesis of lanthanoid metal organic compounds. These organolanthanoid species "RLnI" (e.g. Ln = Eu, Sm and Yb; R = Me, Ph or 2,6- $Me_2C_6H_3$ <sup>[3-6]</sup> are termed *pseudo-Grignard* reagents because of their apparent stoichiometry and analogous reactivity towards acids and electrophiles to the wellknown Mg-based reagents.<sup>[7,8]</sup> However, there are some significant differences between the behaviour of pseudo-Grignard species and RMgI species.<sup>[7,8]</sup> For example, the reactivity of "PhYbI" with esters is higher than with ketones in sharp contrast to the behaviour of Grignard reagents enabling the preparation of ketones from esters.<sup>[7]</sup> These "RLnI" reagents have been investigated in a number of organic and inorganic transformations during the past years.<sup>[5,6,8-10]</sup> Due to the low thermal stability of the Ln-C  $\sigma$ -bond,<sup>[11]</sup> isolation of pseudo-Grignard products derived from the iodides has been a challenge, but has been assisted by use of bulky ligands. Only a few complexes have been structurally characterised. Dimeric prepared and  $[Yb{C(SiMe_3)_2(SiMe_2X)}]I(OEt_2)]_2$  (X = CH=CH<sub>2</sub>, OMe, Me) compounds, reported by Smith and co-workers, were prepared by the addition of C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>X)I to ytterbium metal in diethyl ether<sup>[12,13]</sup> and notably monomeric cis-[Yb(C<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)I(thf)<sub>3</sub>] was isolated.<sup>[14]</sup> The chemistry of "RLnX" is complicated by oxidation to  $Ln^{III}$  for Ln = Sm, Eu, Yb and the existence of Schlenk equilibria in both oxidation states.<sup>[15,16]</sup> Of the alkaline earth metal ions,  $Ca^{2+}$  has comparable ion size to  $Yb^{2+}$  (CN = 6: Yb<sup>2+</sup>: 1.02 Å; Ca<sup>2+</sup>: 1.00 Å)<sup>[17]</sup> and often displays analogous chemistry.<sup>[18]</sup> Thus,

there have been several studies on the preparation and isolation of Ca pseudo-Grignard reagents (ArCaX, X = I, Cl) and homoleptic CaAr<sub>2</sub> species during the past years. The chemistry is simplified by the absence of Ca<sup>2+</sup> redox chemistry.<sup>[19-24]</sup>

Treatment of ytterbium with iodobenzene in thf yields a red solution described as "PhYbI"(thf)<sub>x</sub>.<sup>[25]</sup> Although written as divalent ytterbium, the mixture contains trivalent species, as proposed by Evans *et al.* from magnetic susceptibility measurements<sup>[3,4]</sup> and exemplified by isolation of [YbPh<sub>3</sub>(thf)<sub>3</sub>] from THF and [Yb<sup>II</sup>(dme)<sub>4</sub>][Yb<sup>III</sup>Ph<sub>4</sub>(dme)]<sub>2</sub> from DME.<sup>[25]</sup> Recently, the synthetic potential of the pseudo-Grignard reagents was indicated by preparation of lanthanoid pyrazolate analogues of the pseudo-Grignard reagents namely, [Ln(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>] (Ln = Eu, Yb; Ph<sub>2</sub>pz = 3,5-diphenylpyrazolate) in high yield by the brief sonication of the metal powders with iodobenzene, followed by cooling to -78 °C, (Equation **1**, (i)) and addition of the 3,5-dphenylpyrazole ((ii)).<sup>[25]</sup>



#### Scheme 1

We now report reactions of "PhYbI" with some formamidines, XylFormH, MesFormH, DippFormH (ArNCHNAr; Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> respectively) giving both Yb<sup>II</sup> and Yb<sup>III</sup> products and <sup>171</sup>Yb NMR studies of reaction mixtures, thereby illustrating the complexity of Schlenk equilibria in the solutions. In addition, oxidation and metathesis reactions of [Yb(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>] illustrate the value of pseudo-Grignard reagents in further synthesis. Some reactions of "MeYbI" are also discussed. The isolation of charge separated  $[K(dme)_4]^+[Yb\{(N(SiMe_3)_2\}_3]^-$  with a homoleptic three-coordinate tris(bis(trimethylsilyl)amido)ytterbate(II) anion is a highlight.

#### **Results and Discussion**

#### Syntheses

A mixture of Eu or Yb metal and iodobenzene in THF or DME was cooled to -78 °C and briefly sonicated until a dark red or red-brown colour was observed in the solutions. Immediate addition of the proligands, XylFormH, DippFormH and MesFormH to this mixture formed Eu<sup>II or III</sup> and Yb<sup>II or III</sup> species (Scheme 2(a), (b)). All compounds shown in Scheme 2(a), (b) were isolated from the reaction mixture by fractional crystallisation from concentrated filtered THF ([Eu(DippForm)I(thf)<sub>4</sub>] 1, [{Eu(XylForm)I((µ-OH)(thf)<sub>2</sub> $_2$ ] 4, [Yb(DippForm)I(thf)<sub>3</sub>].thf 5a, [Yb(DippForm)I<sub>2</sub>(thf)<sub>3</sub>].thf 5b, [{Yb(MesForm)I(thf)<sub>2</sub>}<sub>2</sub>] and [{Yb(XylForm)I(thf)<sub>2</sub>}<sub>2</sub>] DME 6, 7a) or  $\left(\left[\left\{\text{EuI}_2(\text{dme})_2\right\}_2\right]\mathbf{2}, \left[\text{Eu}(\text{Xy}|\text{Form})I(\text{dme})_2\right].1/2\text{dme}\mathbf{3a}, \left[\text{Eu}(\text{Xy}|\text{Form})I(\text{dme})(\mu-\text{dme})\right]_n\right)$ **3b** and [Yb(XylForm)<sub>2</sub>I(dme)].dme (**7b**) solutions. Divalent europium species were isolated in all cases except for the formation reproducible (four times) of the hydroxidebridged dimer [{Eu(XylForm)I( $\mu$ -OH)(thf)<sub>2</sub>}] (4). All attempts to isolate [Eu(XylForm)I(thf)<sub>x</sub>] failed, and recrystallisation of [Eu(XylForm)I(dme)<sub>2</sub>]·0.5dme (3a), from THF also led to the isolation of 4. It is unlikely to be derived from adventitious water. A similar problem was encountered in attempted synthesis of  $[Yb(o-TolForm)_3(thf)]$  from Yb,  $Hg(C_6F_5)_2$  and o-TolFormH when [Yb(o-TolForm)<sub>2</sub>( $\mu$ -OH)(thf)]<sub>2</sub> was consistently obtained.<sup>[26]</sup> In reactions with ytterbium metal, quantities of solvated ytterbium diiodide precipitated from the mother liquor before isolation of the (formamidinato)ytterbium species owing to Schlenk equilibria and the lower solubility of solvated YbI<sub>2</sub>. Likewise the [PhEuI(dme)<sub>n</sub>] species with MesFormH in DME led to crystallisation solely of  $[{EuI_2(dme)_2}_2]$  2. In two cases, **5a,b**, **7a,b**, trivalent species accompanied the divalent iodo products  $[Ln(Form)I(solv)_x]$ 

and were separated by fractional crystallisation, leading to reduced yields of Yb<sup>II</sup> complexes. The highest yield of 46% was obtained for [Eu(DippForm)I(thf)<sub>4</sub>]·thf (**1**). These syntheses are more complex than the high yield isolation of [Ln(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>] (Ln = Eu, Yb),<sup>[25]</sup> and this difference may be attributed to the lower acidity of formamidines<sup>[27a]</sup> than 3,5-diphenylpyrazole,<sup>[27b]</sup> enabling competition from Schlenk equilibria and oxidation reactions. Despite these problems, a rich chemistry has resulted (Scheme 2(a), (b)).



Scheme 2(a): Synthesis of (formamidinato)europium halide complexes (lattice solvents not shown) All reactions initially at -78°C

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Scheme 2(b): Synthesis of (formamidinato)ytterbium halide complexes (lattice solvents not shown) All reactions initially at -78°C

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10.1002/chem.201704383

The divalent products in Schemes 2(a) and 2(b) arise from initial formation of the divalent, temperature-sensitive reagent "PhLnI(solv)<sub>n</sub>", followed by protolysis of Ph–Ln bonds with FormH and concomitant formation of PhH (Scheme 3).

 $PhLnI(solv)_n + FormH ----> [Ln(Form)I(solv)_m] + PhH$ 

**Scheme 3.** Formation of formamidinatolanthanoid compounds on protolysis of the pseudo-Grignard reagents.

The formation of **5b** arises from the protonation of "YbPhI<sub>2</sub>" formed by oxidation of PhYbI (Scheme 3). Similarly protolysis of oxidation product Ph<sub>2</sub>YbI yields **7b** (Scheme 4).



#### Scheme 4. Formation of trivalent complexes

Thus both divalent and trivalent ytterbium derivatives were collected after fractional crystallisation (Scheme 2), whereas predominantly divalent europium complexes were isolated from the europium reactions. This is in agreement with the redox potentials for  $Yb^{3+/2+}$  and  $Eu^{3+/2+}$  as well as observations of Evans of the relative distribution of

divalent and trivalent species in pseudo-Grignard products, based on magnetic measurements.<sup>[3,4]</sup>

#### <sup>171</sup>Yb NMR studies of reaction mixtures

To increase understanding of the organolanthanoid-halide system and the Schlenk equilibria in the Yb<sup>II</sup> state, <sup>171</sup>Yb NMR spectra of the reaction mixturse from Yb treated with PhI and then FormH in thf were recorded at various temperatures. In the case of the reaction with DippFormH, the <sup>171</sup>Yb NMR spectrum at 30 °C shows a doublet with a chemical shift of 552 ppm attributable to **5a**, as well as a sharp singlet at 460 ppm for [YbI<sub>2</sub>(thf)<sub>4</sub>] (Figure 1).<sup>[15,28]</sup> The coupling of the hydrogen on the backbone carbon (NC(H)N) with the  $^{171}$ Yb (spin  $\frac{1}{2}$ ) isotope gives rise to a doublet in the  $^{171}$ Yb NMR spectrum, with a coupling constant of 51 Hz, which is close to the coupling constant found in the <sup>1</sup>H NMR spectrum of isolated **5a** (44 Hz). Resonances were not observed for compound **5b** as it is paramagnetic. When the temperature was progressively reduced from 30 °C to -60 °C, both resonances moved to lower chemical shifts. At -60 °C, **5a** gave a broad singlet at 405 ppm and [YbI<sub>2</sub>(thf)<sub>4</sub>] a sharp singlet at 380 ppm (Figure ). Thus, two components of the Schlenk equilibrium, [YbI2(thf)4] and [Yb(DippForm)I(thf)<sub>3</sub>] thf, were observed in the <sup>171</sup>Yb NMR spectrum. The third component [Yb(DippForm)<sub>2</sub>(thf)<sub>2</sub>] is known<sup>[29]</sup> and shows a triplet with a chemical shift of 605 ppm at 30 °C. No resonances were detected in this region suggesting that [Yb(DippForm)<sub>2</sub>(thf)<sub>2</sub>] is not present in a significant amount or has oxidised to a Yb<sup>III</sup> species, e.g. [Yb(DippForm)<sub>2</sub>I(thf)<sub>n</sub>] (see e.g. isolation of **7b** for XylForm). Modifying the temperature does not seem to affect the solution composition significantly.



**Figure 1.** <sup>171</sup>*Yb NMR spectra of the reaction mixture from treatment of Yb with PhI and DippFormH at various temperatures (-60–50 °C)* 

In the case of the reaction with XylFormH, the <sup>171</sup>Yb NMR spectrum at 30 °C displays three discrete resonances: a broad signal at 655 ppm for  $[Yb(XylForm)_2(thf)_2]^{[29]}$  (not isolated from the reaction mixture); a doublet with a chemical shift of 552 ppm ( ${}^{3}J_{(YbH)}$ = 44 Hz) attributed to  $[Yb(XylForm)I(thf)_2]_2$  **7a**; and a sharp singlet at 460 ppm for  $[YbI_2(thf)_4]$  (Figure 2).<sup>[14,15,28]</sup> When the temperature was progressively lowered from 30 °C to -30 °C, at -15 °C the signal of  $[Yb(XylForm)_2(thf)_2]$  was split into a triplet ( ${}^{3}J_{(YbH)}$  = 40 Hz). On lowering the temperature, resonances of the solvated bis(formamidinato)ytterbium complex did not undergo any dramatic changes in the

chemical shifts (at -30 °C: a broad resonance at 677 ppm). However, both the resonance of **7a** and solvated ytterbium diiodide shift to lower  $\delta$  values. At -30 °C, **7a** gave a broad singlet at 455 ppm and [YbI<sub>2</sub>(thf)<sub>4</sub>] a sharp singlet at 380 ppm. The resonances of compound **7b** could not be detected due to the paramagnetism of Yb<sup>III</sup>. Thus, all three components of the Schlenk equilibrium (2Yb(XylForm)I  $\leftrightarrow$  Yb(XylForm)<sub>2</sub> + YbI<sub>2</sub>) were observed in the <sup>171</sup>Yb NMR spectrum. The spectra appear to remain similar on changing the temperature but, as the temperature increases, the amount of [Yb(XylForm)<sub>2</sub>(thf)<sub>2</sub>] is reduced somewhat.



**Figure 2.** <sup>171</sup>*Yb NMR spectra of the reaction mixture from Yb with PhI and XylFormH at various temperatures (-30 to 30 °C)* 

#### Characterisation

In general microanalyses were satisfactory for highly air- and water-sensitive compounds.  $[Eu(Xy|Form)I(dme)_2].0.5dme$  (**3a**) and  $[Eu(Xy|Form)I(dme)(\mu-dme)]_n$  (**3b**) deposited together and were identified by hand-picked single crystals, but the

microanalysis suggests the product was largely **3a**. In some cases loss of solvent of crystallisation and/or coordinated solvent was observed with the loss usually supported by <sup>1</sup>H NMR measurements. No satisfactory <sup>1</sup>H NMR spectra could be obtained for Eu complexes but paramagnetic Yb<sup>III</sup> complex **5b** gave an interpretable spectrum. Consistent <sup>1</sup>H NMR spectra for Yb<sup>II</sup> complexes were obtained and <sup>171</sup>Yb NMR spectra are discussed above.

#### **Structure Determinations**

#### Structures of PhLnI/formamidine reaction products

Complexes **1** and **3a** are seven coordinate pseudo-octahedral, monomeric Eu complexes (Figs. 3 and 4) with a chelating formamidinate ligand, either four thf or two



**Figure 3.** Molecular structure of **1** shown with 50% thermal ellipsoids. (Thf molecules are drawn as sticks and one thf molecule in the lattice and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Eu(1)-N(1) 2.656(3), Eu(1)-N(2) 2.600(3), Eu(1)-I(1) 3.2634(7), Eu(1)-O(1) 2.626(3), Eu(1)-O(2)

2.616(3), Eu(1)–O(3) 2.594(3), N(1)–C(backbone) 1.317(4), N(2)–C(backbone) 1.321(4); N(1)–Eu(1)–I(1) 115.14(6), N(2)–Eu(1)–I(1) 108.36(6), N(1)–C(backbone)– N(2) 120.6(3). C(backbone)<sup>---</sup>Eu(1)-I(1) 111.91(6), N(1)-Eu(1)-N(2) 51.68(8).



**Figure 4**. Molecular structure of **3a** shown with 50% thermal ellipsoids. (Hydrogen atoms and half of a dme molecule in the lattice have been omitted for clarity). Selected bond lengths (Å) and angles (°): Eu(1)–N(1) 2.573(3), Eu(1)–N(2) 2.562(3), Eu(1)–I(1) 3.2214(10), Eu(1)–O(1) 2.664(2), Eu(1)–O(2) 2.606(2), Eu(1)–O(3) 2.674(2), Eu(1)–O(4) 2.618(2); N(1)–Eu(1)–I(1) 105.34(7), N(2)–Eu(1)–I(1) 110.86(7), N(1)–C(backbone)–N(2) 121.2(3), C(backbone)<sup>…</sup>Eu(1)-I(1) 110.85(6), N(1)-Eu(1)-N(2) 53.41(8).

chelating dme ligands, and an iodide *cisoid* to the formamidinate. The structure of **1** is similar (coordination number and ligand array) to that of  $[Eu(Ph_2pz)I(thf)_4]$ .<sup>[25]</sup> However, the bite angle is much larger (51.68(8) vs 31.38(8)°) and all bond lengths are longer in **1** and **3a** than in the pyrazolate analogue, owing to the greater steric demands of formamidinate than pz ligands. Compound **3b** is a coordination isomer of **3a** and is a one-dimensional coordination polymer with two *transoid* oxygens (O(1)-Eu-O(1)# 148.27(12)°) of bridging dme ligands replacing one chelating dme of **3a** (Fig. 5). It appears that the DME of crystallisation in **3a** suppresses the formation of polymeric **3b**. Again, the Eu-I bond is *cisoid* to the chelating formamidinate. The bond



**Figure 5.** Molecular structure of **3b** shown with 50% thermal ellipsoids. (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Eu(1)–N(1) 2.592(3), Eu(1)–N(1)# 2.592(3), Eu(1)–I(1) 3.2216(6), Eu(1)–O(1) 2.661(2), Eu(1)–O(2) 2.619(4), Eu(1)–O(3) 2.602(3), N(1)–C(backbone) 1.322(3), N(1)#–C(backbone) 1.322(3); N(1)–Eu(1)–I(1) 114.99(6), N(1)–C(backbone)–N(2) 120.3(4), O(1)-Eu(1)-O(1#) 148.27(12), C(backbone)<sup>---</sup>Eu(1)-I(1) 114.41(9). Symmetry code for O1<sup>#</sup>: X, 1/2-Y, Z

distances are mainly comparable to those of **3a**, and the bridging Eu-O bond length is somewhat larger than the terminal bonds.

The structure of the ytterbium pseudo-Grignard derivative **5a** features a monomeric structure with six coordination of Yb arising from a chelating formamidinate ligand, a *cisoid* iodide, and three thf ligands (Fig. 6). The reduced coordination number from that of the seven coordinate Eu



**Figure 6.** Molecular structure of **5a** shown with 30% thermal ellipsoids. (Thf molecules are drawn as sticks and one thf molecule in the lattice and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°):Yb(1)–N(1) 2.4396(19), Yb(1)–N(2) 2.4247(18), Yb(1)–I(1) 3.0456(2), Yb(1)–O(1) 2.4194(17), Yb(1)–O(2) 2.4206(18), Yb(1)–O(3) 2.4354(16), N(1)–C(backbone) 1.316(3), N(2)–C(backbone) 1.314(3); N(1)–Yb(1)–I(1) 105.11(4), N(1)–Yb(1)–N(2) 55.66(6), N(1)–C(backbone)–N(2) 119.4(2), C(backbone)-Yb(1)-I(1) 107.06(4).

complex **1** is consistent with the reduced ionic radius of  $Yb^{2+}$ ,<sup>[17]</sup> but contrasts the Ph<sub>2</sub>pz pseudo-Grignard reagents [Ln(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>] (Ln = Eu, Yb)<sup>[25]</sup> which are isostructural reflecting the smaller size of Ph<sub>2</sub>pz compared with DippForm. By contrast, the other two ytterbium(II) pseudo-Grignard derivatives **6** and **7a** are both dimeric [{Yb(Form)( $\mu$ -I)(thf)<sub>2</sub>}] complexes with bridging iodide ligands (Figs. 7 and 8). Six



**Figure 7.** Molecular structure of **6** shown with 30% thermal ellipsoids. (Thf molecules are drawn as sticks and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.446(3), Yb(1)–N(2) 2.426(3), Yb(1)–I(1) 3.0971(13), Yb(1)–I(1)<sup>#</sup> 3.1777(7), Yb(1)–O(1) 2.387(3), Yb(1)–O(2) 2.446(3), N(1)–C(backbone) 1.321(5), N(2)–C(backbone) 1.319(5); N(1)–Yb(1)–I(1) 160.08(8), N(2)–Yb(1)–I(1) 97.55(8), N(1)–C(backbone)–N(2) 119.1(3), C(backbone)-Yb(1)-I(1) 132.64(8), I(1)–Yb(1)–I(1)<sup>#</sup> 88.99(3), Yb(1)-I(1)-Yb(1)<sup>#</sup> 91.01(2). Symmetry code for I1<sup>#</sup> and Yb1<sup>#</sup>: -X, 1-Y, 1-Z.



**Figure 8.** Molecular structure of **7a** shown with 30% thermal ellipsoids. (Thf molecules are drawn as sticks and hydrogen atoms have been omitted for clarity). Selected bond

lengths (Å) and angles (°):Yb(1)–N(1) 2.434(3), Yb(1)–N(2) 2.424(3), Yb(1)–I(1) 3.1695(6), Yb(1)–I(1)<sup>#</sup> 3.1346(7), Yb(1)–O(1) 2.417(3), Yb(1)–O(2) 2.409(3), N(1)–C(backbone) 1.322(5), N(2)–C(backbone) 1.324(5); N(1)–Yb(1)–I(1) 96.89(8), N(2)–Yb(1)–I(1) 93.23(8), N(1)–C(backbone)–N(2) 120.3(3), C(backbone)-Yb(1)-I(1) 95.99(7). I(1)–Yb(1)–I(1)<sup>#</sup> 90.074(14), Yb(1)-I(1)-Yb(1)<sup>#</sup> 89.927(14). Symmetry code for I1<sup>#</sup> and Yb1<sup>#</sup>: -X, 1-Y, 2-Z

coordination is maintained by elimination of coordinated thf compared with monomeric 5a. It is surprising that 5a with the bulkiest Form ligand prefers the extra thf ligand which has greater steric demand than iodide.<sup>[30]</sup> As in the monomeric complexes 1, 3a, 5a the iodide ligands are *cisoid* to the formamidinate ligands. The two pseudo-Grignard ytterbium(III) co-products [Yb(DippForm)I<sub>2</sub>(thf)<sub>3</sub>] 5b (Fig. 9) and  $[Yb(XylForm)_2I(dme)]$  7b (Fig. 10) are both monomeric and seven coordinate with one and two chelating Form ligands and two and one iodide ligands respectively. The former has three thf co-ligands and the latter one dme. Despite the smaller size of Yb<sup>3+</sup> than  $Yb^{2+}$ ,<sup>[17]</sup> these complexes can sustain a higher coordination number than **5a** and **7a** owing to the higher oxidation state. Again, the iodide ligands are *cisoid* to the Form



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**Figure 9.** Molecular structure of **5b** shown with 30% thermal ellipsoids. (Thf molecules and isopropyl groups are drawn as sticks and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.361(7), Yb(1)–N(2) 2.349(8), Yb(1)–I(1) 2.922(2), Yb(1)–I(2) 2.9993(7), Yb(1)–O(1) 2.333(7), Yb(1)–O(2) 2.409(7), Yb(1)–O(3) 2.350(7), N(1)–C(backbone) 1.324(10), N(2)–C(backbone) 1.333(10); I(1)–Yb(1)–I(2) 168.79(5), N(1)–Yb(1)–N(2) 57.0(2), C(backbone)-Yb(1)-I(1) 92.86(19), C(backbone)-Yb(1)-I(2) 96.32(18).



Figure 10. Molecular structure of 7b shown with 30% thermal ellipsoids. (DMEmolecules are drawn as sticks and hydrogen atoms and one DME molecule in the latticehave been omitted for clarity). Selected bond lengths (Å) and angles Yb(1)-N(1)2.397(3), Yb(1)-N(2) 2.339(3), Yb(1)-I(1) 2.9498(3), Yb(1)-O(1) 2.384(3), Yb(1)-O(2) 2.360(3), N(1)-C(backbone) 1.318(5), N(3)-C(backbone) 1.326(5); N(1)-Yb(1)-I(1) 91.80(8), N(3)-Yb(1)-I(1) 103.29(8), N(1)-C(backbone)-N(2) 118.1(3), N(3)-C(backbone)-N(4)C(backbone)-N(4)117.5(4), C(backbone(C9))-Yb(1)-I(1)93.36(8), C(backbone(C26))-Yb(1)-I(1) 97.85(8).

ligands. Complex **5b** has a similar structure to **8** (below), the product of oxidation of  $[Yb(Ph_2pz)I(thf)_4]$  with iodine.

The products  $[{Eu(dme)_2I(\mu-I)}_2]$  (2) (Fig. 11) and  $[{Eu(MesForm)I(\mu-OH)(thf)_2}_2]$ (4) (Fig. 12) are seven coordinate iodide- and hydroxo-bridged dimers respectively. In the latter the iodide ligand is *cis* to the MesForm.



**Figure 11.** Molecular structure of **2** shown with 50% thermal ellipsoids. (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Eu(1)–I(1) 3.1944(9), Eu(1)–I(2) 3.3026(9), Eu(1)–O(1) 2.605(5), Eu(1)–O(2) 2.589(5), Eu(1)–O(3) 2.634(5), Eu(1)–O(4) 2.589(5), I(1)–Eu(1)–I(2) 97.553(15), I(2)–Eu(1)–I(2)# 81.906(14), Eu(1)-I(2)-Eu(1)<sup>#</sup> 98.092(14), O(1)–Eu(1)–O(2) 64.38(14), O(3)–Eu(1)–O(4) 64.71(16). Symmetry code for I2<sup>#</sup> and Eu1<sup>#</sup>: 1-X, 1-Y, 1-Z



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**Figure 12**. Molecular structure of **4** shown with 50% thermal ellipsoids. (Thf molecules are drawn as sticks and hydrogen atoms (except for H(3') and H(3')<sup>#</sup> have been omitted for clarity). Selected bond lengths (Å) and angles (°): Eu(1)–N(1) 2.574(3), Eu(1)–N(2) 2.447(3), Eu(1)–I(1) 3.0940(6), Eu(1)–O(1) 2.438(3), Eu(1)–O(2) 2.502(2), Eu(1)–O(3) 2.280(3), N(1)–C(backbone) 1.319(4), N(2)–C(backbone) 1.325(4); Eu(1)–O(3)–Eu(1)# 111.78(11), N(1)–Eu(1)–I(1) 95.46(6), N(1)–C(backbone)–N(2) 117.3(3) C(backbone)-Eu(1)-I(1) 97.16(7). Symmetry code for Eu1<sup>#</sup>, H3<sup>\*\*</sup> and O3<sup>#</sup>: 1-X, -Y, 1-Z

#### Reactions of [Yb(Ph2pz)I(thf)4]

To illustrate the synthetic potential of pseudo-Grignard derivatives LYbI derived from PhYbI, two representative reactions of  $[Yb(Ph_2pz)I(thf)_4]^{[25]}$  were carried out (Scheme (Scheme 5). Thus oxidation by iodine led to  $[Yb(Ph_2pz)I_2(thf)_3]$  (8), and a metathesis reaction with NaCp (Cp = cyclopentadienide) led to the formation of  $[YbCp(Ph_2pz)(thf)]$  (9) without oxidation in excellent and good yields respectively.



Scheme 5: Reactions of [Yb(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>]

These reactions indicate the synthetic potential of products of the cleavage of PhYbI with various protic reagents. Further **8** and **9** can be used in further syntheses, e.g. metathesis for **8** and oxidation for **9**. The chemistry of **1**, **3a**, **5a**, **6**, **7a** could be developed in a similar manner. Complexes **8** and **9** gave satisfactory microanalyses, the latter for loss of thf of crystallisation and a <sup>1</sup>H NMR spectrum of **9** in d<sub>8</sub>-THF confirmed the 1:1 Cp:Ph<sub>2</sub>pz ratio.

#### **Reactions of MeYbI**

Preliminary reactions of MeYbI and MeEuI, prepared as for PhLnI (Ln = Eu, Yb) with Ph<sub>2</sub>pzH gave [Ln(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>], the same products as obtained from reactions of PhLnI with Ph<sub>2</sub>pzH, though the Eu derivative was contaminated with EuI<sub>2</sub>. Attempted preparation of MeYb(N(SiMe<sub>3</sub>)<sub>2</sub>) by reaction of MeYbI with KN(SiMe<sub>3</sub>)<sub>2</sub> in dme led to isolation of a few crystals of the charge separated [K(dme)4][Yb(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>], (**10**) which was characterised by X-ray crystallography. A deliberate synthesis of this compound was then carried out by metathesis between YbI<sub>2</sub> and KN(SiMe<sub>3</sub>)<sub>2</sub>.

```
3KN(SiMe_3)_2 + YbI_2 ----> [K(dme)_4][[Yb(N(SiMe_3)_2)_3] + 2KI
```

The isolated  $[Yb(N(SiMe_3)_2)_3]^-$  ion has not been previously reported though the bimetallic  $[LiYb(N(SiMe_3)_2)_3]$ , with two ligands bridging Li and Yb is known,<sup>[31]</sup> as is the Na analogue.<sup>[32]</sup> In the case of the reaction with MeYbI, YbI<sub>2</sub> from the Schlenk equilibrium reacts with KN(SiMe\_3)<sub>2</sub> faster than MeYbI. For  $[K(dme)_4][Yb(N(SiMe_3)_2)_3]$ , a <sup>1</sup>H NMR spectrum immediately on isolation was consistent with the single crystal composition, but the later microanalysis (transported to London) indicated loss of two dme molecules (*cf.* the isolation of  $[LiYb(N(SiMe_3)_2)_3]$ ).<sup>[31]</sup>

## Table 1 Crystallographic data for compounds 1, 2, 3a, 3b, 4, 5a and 5b.

Compound	1	2	3a	3b	4	5a	5b*
formula	$C_{45}H_{75}IN_2O_5Eu$	$C_8H_{20}EuI_2O_4$	$C_{27}H_{44}IN_2O_5Eu$	$C_{25}H_{39}IN_2O_4Eu$	$C_{50}H_{72}I_2N_4O_6Eu_2$	$C_{41}H_{67}IN_2O_4Yb$	$C_{37}H_{59}N_2O_3I_2Yb$
fw	1002.93	586.00	755.50	710.44	1382.84	951.91	1006.70
crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_{1}/c$	$P2_{1}/n$	P1, <sup>-</sup>	Pnma	$P2_{1}/n$	$P2_{1}/n$	Pbca
a, Å	16.326(3)	8.5150(17)	8.7430(17)	9.2620(19)	12.975(3)	13.9097(6)	19.3860(10)
b, Å	16.752(3)	16.055(3)	11.059(2)	15.766(3)	15.145(3)	19.2629(8)	18.8272(10)
<i>c,</i> Å	17.069(3)	12.265(3)	16.623(3)	19.263(4)	13.953(3)	15 9698(7)	24.1161(10)
$\alpha$ , deg	90.00	90	92.39(3)	90.00	90.00	90.00	90.00
$\beta$ , deg	91.62(3)	105.31(3)	94.39(3)	90.00	105.72(3)	91.328(2)	90.00
γ, deg	90.00	90	105.49(3)	90.00	90.00	9û.00	90.00
$V, Å^3$	4666.4(16)	1617.2(6)	1541.1(5)	2812.9(10)	2639.3(9)	4.27,7.8(3)	8802.0(7)
Ζ	4	4	2	4	4	4	8
<i>Т</i> , К	100(2)	100(2)	100(2)	100(2)	100(2)	123(1)	123(1)
no. of rflns collected	76290	9529	51174	26873	30779	72870	56265
no. of indep rflns	7968	2720	7055	3320	4637	9701	7732
R <sub>int</sub>	0.0371	0.0951	0.0756	0.0789	0.0349	·û.û418	0.0591
Final $R_1$ values $(I > 2\sigma(I))$	0.0293	0.0459	0.0330	0.0323	0.0246	5.0227	0.0574
Final $wR(F^2)$ values $(I >$	0.0705	0.1155	0.0873	0.0767	0.0577	0.0482	0.1696
$2\sigma(I)$						Τ	
Final $R_1$ values (all data)	0.0332	0.0481	0.0341	0.0351	0.0273	0 0323	0.0800
Final $wR(F^2)$ values (all data)	0.0722	0.1172	0.0880	0.0780	0.0587	0.0520	0.1855
GOOF (on $F^2$ )	1.111	1.027	1.086	1.087	1.102	1.943	1.104

\* Refinements were applied with Platon/Squeeze which accounts for about two thf molecules in the lattice and they were not included in the formula.

Compound	6	7a	7b	8	9	10
formula	$C_{27}H_{39}N_2O_2IYb$	$C_{50}H_{70}I_2N_4O_4Yb_2$	$C_{42}H_{58}IN_4O_4Yb$	$C_{27}H_{35}I_2N_2O_3Yb$	$C_{28}H_{32}N_2O_2Yb$	C34H94KN3O8Si6Yb
fw	723.54	1390.98	982.86	862.41	601.60	1053.80
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> -1	$P2_{1}/c$	P1, <sup>-</sup>	C2/c	$P2_{1}/c$	$P2_{1}/c$
<i>a</i> , Å	10.923(2)	14.818(3)	9.3028(5)	15.3186(9)	15.8812(9)	15.7037(7)
b, Å	11.924(2)	15.302(3)	14.8084(8)	12.0671(8)	16.2231(11)	16.7502(8)
<i>c</i> , Å	13.169(3)	13.158(3)	15.8244(9)	31.115(2)	20.4511(11)	22.5476(10)
$\alpha$ , deg	66.31(3)	90.00	80.122(3)	90.00	90.00	90.00
$\beta$ , deg	65.54(3)	115.90(3)	83.611(3)	98.185(4)	110.977(2)	104.493(2)
γ, deg	69.06(3)	90.00	81.823(3)	90.00	90.00	90.00
$V, Å^3$	1391.7(7)	2683.8(11)	2117.4(2)	5693.1(6)	4922.3(5)	5742.2(5)
Ζ	2	2	2	8	8 0)	4
<i>Т</i> , К	100(2)	100(2)	123(2)	123(2)	123(2)	123(2)
no. of rflns collected	27980	27389	50663	33390	54882	50042
no. of indep rflns	7714	6688	9709	5002	1119û	13176
R <sub>int</sub>	0.0689	0.0558	0.0226	0.0727	0.120)	0.0419
Final $R_1$ values $(I > 2\sigma(I))$	0.0398	0.0298	0.0291	0.0894	0.0002	0.0361
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1031	0.0717	0. 0809	0.1794	0.1238	0.0754
Final $R_1$ values (all data)	0.0405	0.0364	0. 0328	0.1066	0.1042	0.0577
Final $wR(F^2)$ values (all data)	0.1036	0.0764	0. 0947	0.1868	0.1521	0.0846
GOOF (on $F^2$ )	1.063	1.088	1.229	1.215	1.042	1.022

## Table 2 Crystallographic data for compounds 6, 7a, 7b, 8, 9 and 10.

#### X-ray crystal structures of 8-10

#### [Yb(Ph<sub>2</sub>Pz)I<sub>2</sub>(thf)<sub>3</sub>] (8)

The structure of  $[Yb(Ph_2Pz)I_2(thf)_3]$  (8) has seven-coordination for the ytterbium atom with one  $\eta^2$  -Ph<sub>2</sub>pz ligand, two *trans* iodide donors which are *cis* to the pyrazolate and three thf ligands arranged in a distorted pseudo-octahedral array (Fig. 13). The structure is very similar to that of  $[Yb(Ph_2pz)I(thf)_4]$ ,[25] with one thf replaced by I, and the bond lengths are 0.10-0.18 Å shorter than those of the divalent precursor in accord with ionic radii differences.<sup>[17]</sup> The structure is also reminiscent of trivalent compound **5b** (above) where the pyrazolate group replaces the chelating DippForm ligand. The Yb–O and the Yb–N bond lengths are very similar to those of  $[Yb(Ph_2pz)_3(thf)_2] \cdot 2C_6D_6$ .<sup>[33]</sup> The bite angle N(1)-Yb(1)-N(2) 35.2(4)° is typically small, but slightly larger than in the divalent precursor,<sup>[25]</sup> but much more acute as expected than in **5b** (57.0(2)°).



**Figure 13.** Molecular structure of **8** shown with 50% thermal ellipsoids. (Thf molecules are drawn as sticks and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.244(15), Yb(1)–N(2) 2.254(14), Yb(1)–I(1) 2.9706(13), Yb(1)-I(2) 3.0126(14), Yb(1)–O(1) 2.303(12), Yb(1)–O(2) 2.358(12), Yb(1)–O(3) 2.308(13), N(1)–N(2) 1.37(2); I(1)–Yb(1)–I(2) 170.39(4), N(1)–Yb(1)–

N(2) 35.4(5), N(1)–Yb–O(2) 162.0(5), C(backbone)-Yb(1)-I(1) 95.42, C(backbone)-Yb(1)-I(2) 94.03.

#### [Yb(C5H5)(Ph2Pz)(thf)]n.nthf (9)

The structure of the ytterbium complex  $[Yb(C_5H_5)(Ph_2Pz)(thf)]_n.nthf (9)$  is a divalent ytterbium coordination polymer (Fig. 14). The ytterbium atom is formally ninecoordinate and is bridged to two neighbours by  $\mu$ - $\eta^5$ : $\eta^5$ -Cp (Cp = cyclopentadienyl) ligands and bound by an  $\eta^2$ -Ph<sub>2</sub>pz and a thf ligand. There is an inversion centre which is at the midpoint of the Yb(1)····Yb(2) vector, and the Yb(1)-centroid(Cp)-Yb(2) angle is near linear. The arrangement about Yb is pseudo-tetrahedral – two Cp centroids, a N-N centroid and oxygen(thf).

In **9** the Yb–C(Cp) bond lengths range between 2.665(16)- 2.717(18) Å. Subtraction of the ionic radius for nine coordinate Yb<sup>3+</sup> gives 1.62 - 1.68 Å towards the higher end of the range (1.64±0.04 Å) of the Cp- ionic radius.<sup>[34]</sup> The bite angle N(1)–Yb(1)–N(2) 33.2(2) is comparable to N(11)–Yb(1)–N(12) 32.7(2) of  $[Yb(Ph_2pz)_2(dme)_2]$ ,<sup>[29]</sup> or in the precursor  $[Yb(Ph_2pz)I(thf)_4]^{[25]}$  (33.02(15)°).



**Figure 14.** Molecular structure of **9** (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.418(7), Yb(1)–N(2) 2.408(7), Yb–C(Cp) 2.665(16)- 2.717(18), Yb(1)–O(1) 2.420(6), N(1)–N(2) 1.377(8); Yb(1)– C(26)–Yb(2) 129.9(4), N(1)–Yb(1)–N(2) 33.2(2), N(1)–Yb–O(1) 119.0(2). Yb(1)centroid(Cp1)-Yb(2) 177.8(2), centroid(Cp1)-Yb(1)-centroid(Cp2) 125.1(2), cnttroid(Cp1)-Yb(2)-centroid(Cp3) 125.5(2). Symmetry code for Yb1<sup>#</sup>: -X, -Y, 1-Z; Yb2<sup>#</sup>: 1-X, -Y, 1-Z

#### [K(dme)4][Yb{N(SiMe3)2}3] (10)

The charge separated structure of the ytterbium-potassium complex  $[K(dme)_4]$  $[Yb{N(SiMe_3)_2}_3]$  (10) is displayed in Fig. 15. Being charge separated, it contrasts the molecular bimetallics  $[LiYb(N(SiMe_3)_2)_3]^{[31]}$  and  $NaYb[N(SiMe_3)_2]_3^{[32]}$  (and the Eu analogue).<sup>[32]</sup> There is a somewhat related charge separated heteroleptic complex  $[Na(12-crown4)_2][M{N(SiMe_3)_2}_3(OSiMe_3)].^{[35]}$  Complex **10** has three near equal Yb-N bond lengths (Fig. 15) with close to triangular ytterbium stereochemistry. This contrasts for example  $[LiYb(N(SiMe_3)_2)_3]$  where the Yb-N bond distances are dissimilar and the N-Yb-N angles show considerable variation owing to bridging of two  $N(SiMe_3)_2$  ligands between Yb and Li.<sup>[31]</sup> The terminal Yb-N bond is slightly shorter than the three Yb-N bonds of **10**. The potassium ion is eight coordinate with four chelating dme molecules. One of the  $\kappa^2$ -dme ligands showed signs of being disordered.

There are also three Yb<sup>...</sup>C agostic interactions (Fig. 15 legend), with typical values for such interactions<sup>[15]</sup> but these are ca 0.3 Å larger than the two short agostic Yb-C bonds of  $[LiYb(N(SiMe_3)_2)_3]$ .<sup>[31]</sup> Thus, the charge separated  $[Yb(N(SiMe_3)_2)_3]^-$  ion shows unique features from previous heterobimetallic molecules.



**Figure 15.** Molecular structure of **10** shown with 30% thermal ellipsoids. (Disordered moieties and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.348(2), Yb(1)–N(2) 2.331(3), Yb(1)–N(3) 2.334(2), Yb(1)···C(1) 3.131(6), Yb(1)···C(7) 3.091(5), Yb(1)···C(13) 3.160(5), K(1)-O(1A) 2.815(13), K(1)-O(2A) 2.836(12), K(1)–O(3) 2.833(2), K(1)–O(4) 2.784(2), K(1)-O(5)

2.757(3), K(1)-O(6) 2.863(3), K(1)-O(7) 2.822(2), K(1)O(8) 2.781(3); N(1)–Yb(1)– N(2) 116.47(9), N(1)–Yb(1)–N(3) 115.49(9), O(3)–K–O(4) 60.58(7).

#### Conclusions

The value of the readily accessible pseudo Grignard reagents  $[PhLnI(solv)_n]$  (Ln = Eu, Yb) as synthons has been enhanced by their reactions with bulky formamidines yielding [Ln<sup>II</sup>(Form)I(solv)<sub>n</sub>] complexes, accompanied in two cases by Yb<sup>III</sup> analogues from oxidation reactions. Studies of reaction mixtures by <sup>171</sup>Yb NMR spectroscopy showed evidence for Schlenk equilibria in the divalent state, thereby illustrating the value of the technique, though Yb<sup>III</sup> species cannot be detected. Dominant structural outcomes were monomers with seven (Eu) or six (Yb) coordination (as influenced by ion size) and cisoid Form and I ligands. However, two Yb complexes (6, 7a) were iodide bridged dimers, but the difference from monomeric 5a does not correlate with steric effects. Complexes 3a and 3b exhibit coordination isomerism and their crystallisation as Eu<sup>II</sup> species from DME contrasts the reaction of PhEuI with XylFormH in THF which consistently gave [ $\{Eu^{III}(Xy|Form)I(\mu-OH)(thf)_2\}_2$ ] **4**. To illustrate the potential pseudo-Grignard derivatives, the previously prepared synthetic use of  $[Yb(Ph_2pz)I(thf)_4]$  was oxidised to  $[Yb^{III}(Ph_2pz)I_2(thf)_3]$  by  $C_2H_4I_2$  with little structural change, and underwent metathesis with NaCp to give the coordination polymer  $[Yb(Ph_2pz)(\mu-Cp)(thf)]_n$  with  $\mu-\eta^5:\eta^5-Cp$  ligands. An attempt to convert MeYbI into MeYb(N(SiMe<sub>3</sub>)<sub>2</sub>) gave instead charge-separated [K(dme)<sub>4</sub>][Yb(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>] with an unique discrete three-coordinate anion.

#### **Experimental Section**

General information: All the lanthanoid metals and lanthanoid(II) and (III) products are highly air- and moisture-sensitive, hence operations were carried out under purified nitrogen using standard Schlenk line and glovebox techniques. All solvents were dried and deoxygenated by refluxing over and distillation from sodium benzophenone ketyl under nitrogen. Iodobenzene (Aldrich) was degassed before use. Formamidine compounds (XylFormH, MesFormH and DippFormH) were prepared by literature methods<sup>[36,37]</sup>. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory, Science Centre, London Metropolitan University, England or by the Campbell Microanalytical Laboratories, University of Otago, New Zealand, on samples sealed under argon or nitrogen. Infrared spectra (4000-650 cm<sup>-1</sup>) were obtained using Nujol mulls between NaCl plates with a Perkin-Elmer 1600 FTIR spectrometer. Room temperature (30 °C) NMR spectra were recorded on a Bruker DPX 300 instrument with dry degassed *perdeutero*-benzene  $(C_6D_6)$  as the solvent, and resonances were referenced to the residual <sup>1</sup>H resonances of the deuterated solvent. Where <sup>1</sup>HNMR spectra are not listed for Eu<sup>II, III</sup> and Yb<sup>III</sup> compounds, satisfactory spectra could not be obtained owning to paramagnetism. <sup>171</sup>Yb NMR spectra at various temperatures were recorded at 52.55 MHz using a Bruker DPX 300 spectrometer and referenced against  $[Yb(Cp^*)_2(thf)_2] (\delta = 0 \text{ ppm}).$ 

#### **Reaction of in situ generated PhLnI**

[Eu(DippForm)I(thf)4].thf (1): Eu metal filings (0.25 g, 1.60 mmol) were suspended in thf (20 ml) and at -78 C°, PhI (0.27 g, 1.30 mmol) was added. The mixture was sonicated for 10 s developing a red-brown colour. Solid DippFormH (0.48 g, 1.30 mmol) was added and the mixture stirred at -78 °C for another 3 h and at room temperature overnight. The resulting mixture was filtered through a pad of Celite to

remove the residual metal and the filtrate evaporated under vacuum to 5 ml and cooled at -25 °C. Large yellow crystals were collected after 2 days (0.60 g, 46 %).

m.p. 246-248 °C; Elemental analysis calcd for C<sub>45</sub>H<sub>75</sub>N<sub>2</sub>O<sub>5</sub>I<sub>1</sub>Eu<sub>1</sub> (1002.96 g.mol<sup>-1</sup>): C, 53.88; H, 7.54; N, 2.79. Found: C, 53.49; H, 7.40; N, 2.90. IR (Nujol, cm<sup>-1</sup>): 1519 s, 1295 s, 1260 m, 1190 w, 1096 w, 1034 m, 936 w, 918 m, 883 w, 800 m, 767 m, 756 w, 722 m, 666 w.

[{EuI<sub>2</sub>(dme)<sub>2</sub>]<sub>2</sub>](2): Eu metal filings (0.25 g, 1.60 mmol) were added to a Schlenk flask with dry dme (~20 ml) and at -78 °C, PhI (0.27 g, 1.30 mmol) was added. The mixture immediately developed a red-brown colour. Solid MesFormH (0.36 g, 1.30 mmol) was added and the mixture was stirred at -78 °C for another 3 h and then at room temperature for two days. The resulting red-brown solution was filtered through a pad of Celite to remove the residual metal and concentrated under vacuum to ca. 5 ml. Instead of isolated the desired pseudo-Grignard [Eu(MesForm)<sub>n</sub>I<sub>n</sub>] compound, small colourless crystals of (2) (0.08 g, 10 %) grew upon standing for one week and was identified by a full structural determination as [EuI( $\mu$ –I)(dme)<sub>2</sub>]<sub>2</sub>.

m.p. 105-107 °C; Elemental analysis calcd for  $[EuI(\mu-I)(dme)_2]_2$  (C<sub>16</sub>H<sub>40</sub>Eu<sub>2</sub>I<sub>4</sub>O<sub>8</sub>: 1172.03 g.mol<sup>-1</sup>): C, 16.40; H, 3.44. Calcd for C<sub>8</sub>H<sub>20</sub>Eu<sub>2</sub>I<sub>4</sub>O<sub>4</sub>: 991.79 g.mol<sup>-1</sup> (loss of two dme molecules): C, 9.69; H, 2.03. Found: C, 9.24; H, 2.01. IR (Nujol, cm<sup>-1</sup>): 2496 w, 2397 m, 2131 w, 1849 w, 1466 w, 1345 s, 1197 m, 761 w. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.27, s, 12H, CH<sub>3</sub>, dme (coord); 0.90, s, 6H, CH<sub>3</sub>, dme (free); 1.33, s, 8H, CH<sub>2</sub> (coord); 2.10, s, 4H, CH<sub>2</sub>, dme (coord); 3.12, s, 6H, CH<sub>3</sub>, dme (free); 3.35, s, 4H, CH<sub>2</sub>, dme (free).

[Eu(XylForm)I(dme)<sub>2</sub>].0.5dme (3a) and [Eu(XylForm)I(dme)(μ-dme)] (3b): Eu metal filings (0.25 g, 1.60 mmol) were suspended in dme (20 ml) and at -78 °C PhI

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(0.27 g, 1.30 mmol) was added. The mixture was sonicated for 10 s, developing a redbrown colour. Solid XylFormH (0.33 g, 1.30 mmol) was added and the mixture stirred at -78 °C for another 3 h and at room temperature overnight. The resulting mixture was filtered through a pad of Celite to remove the residual metal and the filtrate evaporated under vacuum to 5 ml and cooled at -25 °C. Large yellow crystals of a mixture of **3a** and **3b** were collected after 2 days (0.45 g).

**3a**: m.p. 130-134 °C; Elemental analysis calcd for  $C_{25}H_{39}N_2O_4IEu.C_2H_5O$  (755.52 g.mol<sup>-1</sup>): C, 42.92; H, 5.87; N, 3.71; calcd for  $C_{25}H_{39}N_2O_4IEu$  (710.46 g.mol<sup>-1</sup>): C, 42.26; H, 5.53; N, 3.94. Found: C, 42.96; H, 5.79; N, 3.53 suggesting **3a** is the bulk material. IR (Nujol, cm<sup>-1</sup>): 1537 s,1279 s, 1261 w, 1201 w, 1196 m, 1155 w, 1108 m, 1070 m, 1014 w, 978 w, 930 w, 909 m, 859 m, 801 w, 780 m, 722 m, 670 w.

[{**Eu**(**XylForm**)**I**(**OH**)(**thf**)<sub>2</sub>}<sub>2</sub>] (**4**): Following the same method for **3a** and using dry thf (20 ml) as solvent yielded dark orange crystals of **4** (0.30 g, 23 %).; dec.temp. 240-242 °C; Elemental analysis calcd for  $C_{50}H_{72}O_6Eu_2I_2N_4$  (1002.96 g.mol<sup>-1</sup>): C, 43.43; H, 5.25; N, 4.05. Found: C, 43.19; H, 5.17; N, 3.99. IR (Nujol, cm<sup>-1</sup>): 1578 s, 1261 m, 1171 w, 1156 w, 1090 w, 1071 w, 1020 m, 915 w, 868 m, 800 m, 722 m, 668 w.

The reaction was repeated four times with a similar outcome upon crystallisation. Recrystallisation of yellow **3a** from thf yielded orange crystals of **4**.

[**Yb**(**DippForm**)**I**(**thf**)<sub>3</sub>].**thf** (**5a**) **and** [**Yb**(**DippForm**)**I**<sub>2</sub>(**thf**)<sub>3</sub>].**2thf** (**5b**): Yb metal filings (0.28 g, 1.60 mmol) were suspended in thf (20 ml) and at -78 C° PhI (0.27 g, 1.30 mmol) was added. The mixture was sonicated for 10 s developing a red-brown colour. Solid DippFormH (0.48 g, 1.30 mmol) was added and the mixture stirred at -78 C° for another 3 h and at room temperature overnight. The resulting mixture was filtered through a pad of Celite to remove the residual metal and evaporated under vacuum to

5 ml. Upon storage at -25 °C overnight yellow crystals of [YbI<sub>2</sub>(thf)<sub>4</sub>] (unit cell identification: a = 8.30(10), b = 9.76(13), c = 13.55(18) Å,  $\alpha = 80.87(19)^{\circ}$ ,  $\beta = 87.43(17)^{\circ}$ ,  $\gamma = 87.4(2)^{\circ}$ , V = 1082(7) Å<sup>3</sup>)<sup>[38]</sup> formed. Fractional crystallisation from the mother liquor resulted in large orange crystals of **5a** (0.20 g, 16 %) and then **5b** (0.23 g, 17 %).

**5a**: m.p. 138-140 °C; Elemental analysis calcd for C<sub>41</sub>H<sub>67</sub>N<sub>2</sub>O<sub>4</sub>IYb (951.93 g.mol<sup>-1</sup>) C, 51.73; H, 7.09; N, 2.94. Found: C, 51.52; H, 6.88; N, 2.82. IR (Nujol, cm<sup>-1</sup>): 1667 m, 1591 w, 1519 s, 1317 m, 1286 m, 1187 w, 1098 w, 1032 m, 877 m, 801 m, 768 m, 756 w, 721 w, 667 w. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C):  $\delta$  = 1.16 (d, 24H, CH<sub>3</sub>), 1.40 (m, 16H, thf), 3.69 (m, 16H, thf), 3.88 (sep, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 4H, CH), 7.07–7.02 (m br, 6H, Ar), 8.03 (s, <sup>171</sup>Yb satellites, <sup>3</sup>*J*<sub>(YbH)</sub> = 44 Hz, 1H, NC(H)N) ppm; <sup>13</sup>C NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C):  $\delta$  = 24.9 (CH<sub>3</sub>), 25.6 (CH), 28.1 (CH<sub>2</sub>, thf), 68.7 (CH<sub>2</sub>, thf), 123.1 (Ar-CH), 123.5 (Ar-CH), 143.3 (Ar-C), 148.6 (Ar-C), 167.4 (NC(H)N) ppm.

**5b**: m. p. 170-172 °C; Elemental analysis calcd for C<sub>45</sub>H<sub>75</sub>N<sub>2</sub>O<sub>5</sub>I<sub>2</sub>Yb (1150.94 g.mol-1): C, 46.96; H, 6.57; N, 2.43., calcd for C<sub>37</sub>H<sub>59</sub>N<sub>2</sub>O<sub>3</sub>I<sub>2</sub>Yb (loss of 2 thf molecules of crystallisation) (1006.72 g.mol-1): C, 44.14; H, 5.91; N, 2.78. Found: C, 43.97; H, 5.81; N, 2.72; IR (Nujol, cm-1): 1667 w, 1591 w, 1529 s, 1321 m, 1270 m, 1183 w, 1099 w, 1072 m, 1016 m, 864 m, 804 m, 772 w, 758 w, 729 w, 673 w. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C): δ = -0.55 (s br, 4H, CH), -0.15 (s br, 6H, Ar), 0.30 (s br, 24H, CH<sub>3</sub>), 4.02 (s br, 12H, thf), 6.37 (s br, 12H, thf), 24.39 (s br, 1H, NC(H)N) ppm. Both the <sup>1</sup>H NMR spectrum and the microanalysis results indicate loss of thf of crystallisation.

Following the procedure described for the synthesis of **5**, Yb metal filings (0.28 g, 1.60 mmol), PhI (0.27 g, 1.30 mmol) and DippFormH (0.48 g, 1.30 mmol) gave a dark brown solution. <sup>171</sup>Yb NMR spectrum of the reaction mixture (52.55 MHz, 30 °C):  $\delta$  = 460 (br

s,  $[YbI_2(thf)_4]^{[28]}$ ), 552 (br d,  ${}^3J_{YbH} = 51$  Hz; NC(H)NYb, **5a**). Due to the paramagnetism of the corresponding Yb<sup>3+</sup> species in the solution, the spectrum was broad.

[{**Yb**(**MesForm**)**I**(**thf**)<sub>2</sub>}<sub>2</sub>] (6): Ytterbium metal filings (0.27 g, 1.60 mmol) were added to a Schlenk flask with dry thf (~20 ml) and at -78 °C, PhI (0.27 g, 1.30 mmol) was added. The mixture was immediately developing a red-brown colour. Solid MesFormH (0.36 g, 1.30 mmol) was added and the mixture was stirred at -78 °C for another 3h and then at room temperature for one week gave a a red-brown solution that was filtered through a pad of Celite to remove the residual metal and concentrated under vacuum to ca. 5 ml. Small yellow crystals of **6** (0.15 g, 41 %) were separated from yellow crystals of [YbI<sub>2</sub>(thf)<sub>4</sub>] (full structure determination, unit cell: triclinic, a = 8.4268(17), b =9.805(2), c = 13.646(3) Å,  $\alpha = 80.18(3)^\circ$ ,  $\beta = 87.58(3)^\circ$ ,  $\gamma = 86.97(3)^\circ$ , V = 1108.8(4)Å<sup>3</sup>) [<sup>38]</sup>, through fractional crystallisation and grew upon standing for two days.

**6**: m. p. 168-170 °C. Elemental analysis calcd for C<sub>54</sub>H<sub>78</sub>N<sub>4</sub>O<sub>4</sub>I<sub>2</sub>Yb<sub>2</sub> (1447.11 g.mol<sup>-1</sup>): C, 44.82; H, 5.43; N, 3.87. Found: C, 44.12; H, 4.94; N, 3.60; IR (Nujol, cm<sup>-1</sup>): 2484 s, 2404 s, 2025 s, 1907 s, 1835 s, 1768 s, 1646 m, 1528 w, 1280 m, 1195 m, 1086 s, 880 s, 757 m, 728 s. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C):  $\delta = 0.95$  (br s, 16H; CH<sub>2</sub>, thf), 1.16 (s, 24H, *o*-CH<sub>3</sub>), 1.22 (s, 12H, *p*-CH<sub>3</sub>), 3.29 (m, 16H, OCH<sub>2</sub>, thf), 7.02-7.07 (br m, 8H, Ar), 8.03 (s, 2H, NC(H)N) ppm.

[{Yb(XylForm)I(thf)<sub>2</sub>}<sub>2</sub>] (7a) and [Yb(XylForm)<sub>2</sub>I(dme)].dme (7b): Yb metal filings (0.28 g, 1.60 mmol) were suspended in thf (20 ml) and at -78 C° PhI (0.27 g, 1.30 mmol) was added. The mixture was sonicated for 10 s developing a red-brown colour. Solid XylFormH (0.33 g, 1.30 mmol) was added and the mixture stirred at -78 °C for another 3 h and at room temperature overnight. The resulting mixture was filtered through a pad of Celite to remove the residual metal and evaporated under vacuum to

5 ml. Upon storage at -25 °C overnight yellow crystals of  $[YbI_2(thf)_4]$  (unit cell identification)<sup>[38]</sup> formed. Fractional crystallisation from the mother liquor resulted in yellow crystals of **7a** (0.05 g, 5 %). The residual solution was evaporated to dryness and a mixture of dme and toluene (7:3 v/v) was added to the residue. Single crystals of **7b** were isolated from a mixture of products (0.03 g, 3 %).

**7a**: m. p. 250-254 °C: Elemental analysis calcd for C<sub>50</sub>H<sub>70</sub>N<sub>4</sub>O<sub>4</sub>I<sub>2</sub>Yb<sub>2</sub> (1391.0 g.mol<sup>-1</sup>): C, 43.17; H, 5.07; N, 4.03. Calcd for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>I<sub>2</sub>Yb<sub>2</sub> 1102.58 g.mol<sup>-1</sup> (loss all thf ligands): C, 37.04; H, 3.47; N, 5.08. Found: C, 36.88; H, 3.19; N, 4.98. IR (Nujol, cm<sup>-1</sup>): 1647 w, 1589 w, 1560 s, 1279 m, 1261 m, 1204 w, 1153 w, 1092 m, 1070 m, 1028 m, 978 w, 918 w, 918 w, 872 m, 799 m, 766 w, 722 m, 669 w. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C) (loss of 3 thf) :  $\delta$  = 0.93 (s, br, 4H; CH<sub>2</sub>, thf), 1.75 (s, 24H, CH<sub>3</sub>), 3.55 (s, br, 4H; OCH<sub>2</sub>, thf), 6.48-7.02 (m, 12H, Ar), 8.08 (s, 2H, NC(H)N) ppm.

**7b**: m. p. 258-262 °C: IR (Nujol, cm<sup>-1</sup>1654 w, 1595 w, 1534 s, 1279 s, 1261 w, 1203 w, 1193 w, 1158 w, 1094 m, 1034 m, 1013 w, 974 w, 941 w, 915 w, 858 w, 801 w, 763 m, 722 m, 670 w. A <sup>1</sup>H NMR spectrum could not be obtained owning to paramagnetism. Insufficient material was obtained for further characterisation.

Following the procedure described for the synthesis of **7a** and **7b**, Yb metal filings (0.28 g, 1.60 mmol), PhI (0.27 g, 1.30 mmol) and XylFormH (0.33 g, 1.30 mmol) gave a dark brown solution. <sup>171</sup>Yb NMR of the reaction mixture (52.55 MHz, 30 °C):  $\delta = 460$  (br s, [YbI<sub>2</sub>(thf)<sub>4</sub>]<sup>[28]</sup>), 530 (br d, <sup>3</sup>*J*<sub>YbH</sub> = 44 Hz; NC(H)NYb, **7a**), 655 (br, [Yb(XylForm)<sub>2</sub>(thf)<sub>2</sub>])<sup>[29]</sup>. <sup>171</sup>Yb NMR of the reaction mixture (52.55 MHz, -15 °C):  $\delta = 400$  (br s, [YbI<sub>2</sub>(thf)<sub>4</sub>]), 502 (br d, <sup>3</sup>*J*<sub>YbH</sub> = 44 Hz; NC(H)NYb, **7a**), 677 (br t, <sup>3</sup>*J*<sub>YbH</sub> = 40 Hz; NC(H)NYb, [Yb(XylForm)<sub>2</sub>(thf)<sub>2</sub>]). Due to the paramagnetism of the corresponding Yb<sup>3+</sup> species in the solution, the signals were broad.

#### Reactions of [Yb(Ph2pz)I(thf)3]

#### [Yb(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>]: was prepared as reported.<sup>[25]</sup>

**[Yb(Ph<sub>2</sub>pz)I<sub>2</sub>(thf)<sub>3</sub>] (8):** In 20 ml thf was dissolved [Yb(Ph<sub>2</sub>pz)I(thf)<sub>4</sub>] (0.16 g, 0.20 mmol) and at ~ 0 °C 1,2-diiodoethane (0.28 g, 0.10 mmol) was added. After 5 min a colour change from orange to yellow was observed and the solution was warmed to room temperature. Slow concentration to ~10 ml resulted in the formation of bright yellow crystals suitable for X-ray diffraction. Subsequent complete removal of the solvent *in vacuo* gave (0.17 g, 99 %) of **8** as a pale yellow solid.

dec.temp. 100 °C (darkens). Elemental analysis calcd for C<sub>27</sub>H<sub>35</sub>I<sub>2</sub>N<sub>2</sub>O<sub>3</sub>Yb (862.41 g/mol): C 37.60, H 4.09, N 3.25. Found C 37.16, H 4.16, N 3.24. IR (Nujol): 1654 (m), 1224 (w), 1055 (m), 1007 (s), 850 (s), 770(s), 767 (s).

 $[Yb(CsH_5)(Ph_2pz)(thf)]_n$  (9): NaCp (0.88 g, 1.00 mmol) and  $[Yb(Ph_2pz)I(thf)_4]$  (0.80 g, 1.00 mmol) were dissolved in 15 ml of thf. After stirring overnight, 3 ml of *n*-hexane were added and the mixture filtered from some colourless precipitate (presumably NaI) giving a red solution. The solvent was removed *in vacuo*, the residue was redissolved in 5 ml of thf and layered with 10 ml of *n*-hexane. Overnight **9** crystallised as a red mass on the side of the vessel and was decanted from a simultaneously formed white precipitate of NaI. Yield (0.28 g, 53 %).

dec.temp. 80 °C (darkens). Elemental analysis calcd for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>OYb (529.51 g.mol<sup>-1</sup>) (loss of thf of crystallization): C 54.44, H 4.57, N 5.29. Found C 55.13, H 4.64, N 5.01. IR (Nujol): 1654 w, 1600 m, 1304 m, 1217 w, 1154 m, 1057 m, 1031 s, 969 m, 890 m, 753 s. <sup>1</sup>H NMR (d<sub>8</sub>-THF): 5.70-6.03 (br, 5 H, Cp-H), 6.90 (s, 1 H, pz-H), 7.08 (m, 2 H, *p*-H), 7.25 (m, 4 H, *m*-H), 7.86 (br, 4 H, *o*-H). <sup>13</sup>C NMR (d8-thf): 83.5 (Cp), 123.0, 123.3, 126.3, 135.1 (Ph).

#### A reaction of MeYbI

[K(dme)4][Yb{N(SiMe3)2}3] (10): MeI (0.28 g, 2.00 mmol) was added by syringe to a suspension of Yb metal (0.43 g, 2.50 mmol) in 15 ml of dme at -78°C. The mixture was sonicated for 10 sec. and stirred at -78 °C. A colour change to yellow and formation of yellow-green precipitate was observed. After 3 h, KN(SiMe3)2 (0.40 g, 2.00 mmol) in toluene (4 ml) was added and the mixture turned dark blue. After stirring overnight the dark mixture was filtered giving a dark blue solution which was concentrated to ~ 5 ml and layered with 10 ml of *n*-hexane. A few blue crystals of 10 (< 5 % yield) suitable for X-ray diffraction and a sticky brown oil formed overnight. Deliberate synthesis of 10: YbI<sub>2</sub>(dme)<sub>3</sub> (0.69 g, 1.00 mmol) was dissolved in dme (10 ml). KN(SiMe<sub>3</sub>)<sub>2</sub> (0.62 g, 3.10 mmol) in toluene was added at room temperature and the dark blue mixture was stirred overnight and filtered. Concentration to 5 ml and layering with *n*-hexane (10 ml) gave dark blue crystals of pure 10 (0.85 g, 91 %).

m.p. ~ ambient temperature. Elemental analysis calcd for  $C_{26}H_{74}KN_3O_4Si_6Yb$  (873.55 g.mol<sup>-1</sup>) (**10** – 2dme): C 35.75 H 8.54 N 4.81. Found C 34.62, H 7.73, N 4.03. IR (Nujol): 2354 w, 1473 m, 1240 s, 1208 w, 1192 m, 1161 m, 1127 m, 1089 s, 1061 s, 1019 m, 987 m, 874 m, 822 m, 760 w, 661 w. <sup>1</sup>H NMR ( $C_6D_6$ ): 0.08 (s, 18 H, SiCH<sub>3</sub>), 0.27 (s, 9 H, SiCH<sub>3</sub>), 0.34 (s, 18 H, SiCH<sub>3</sub>), 0.58 (s, 9 H, SiCH<sub>3</sub>), 4.80 (br, 16 H, dme) 5.90 (br, 24 H dme). <sup>13</sup>C NMR ( $C_6D_6$ ): 1.0 (SiCH<sub>3</sub>), 2.2 (SiCH<sub>3</sub>), 5.1 (SiCH<sub>3</sub>), 5.8 (SiCH<sub>3</sub>), 61.3 (O-CH<sub>2</sub>), 73.8 (O-CH<sub>3</sub>).

#### Crystal and refinement data

Single crystals coated with viscous hydrocarbon oil were mounted on loops. Data were obtained at -173 °C (100 K) on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia (Compounds 1, 2, 3a, 3b, 4, 6, 7a),

or at  $-150 \,^{\circ}$ C (123 K) on a Bruker X8 APEX II CCD diffractometer (Compounds **5a**, **5b**, **7b**, **8**, **9**, **10**) equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). Data collection and integration on the MX1: Macromolecular Crystallography beamline was done using Blu-Ice<sup>[39]</sup> and the XDS software package.<sup>[40]</sup> Data collected on the Bruker X8 APEX II CCD were empirically corrected for absorption (SADABS)<sup>[41]</sup> then merged. The structures were solved using SHELXS<sup>[42]</sup> and refined by full-matrix least-squares on all  $F^2$  data using SHELX2014<sup>[42]</sup> in conjunction with the X-Seed graphical user interface.<sup>[43]</sup> All hydrogen atoms were placed in calculated positions using the riding model. Data collection and refinement details are collated in Table 1. CCDC-1574631 (1), 1574620 (2), 1574627 (3a), 1574622 (3b), 1574624 (4), 1574622 (9), 1574623 (5b), 1574625 (6), 1574626 (7a), 1574628 (7b), 1574629 (8), 1574632 (9), 1574630 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic

#### Acknowledgements

We gratefully acknowledge support from the Australian Research Council (ARC Discovery Grants: DP 130100152, DP160101640). Shima Hamidi was partially supported by a Monash University Dean's Scholarship. Safaa Ali gratefully acknowledges the Higher Committee for Education Development in Iraq (HCED) for sponsored his PhD study at James Cook University. Part of this research was undertaken on the MX1 and MX2 beamlines at the Australian Synchrotron, Victoria, Australia. A Deutsche Forschungsgemeinschaft Fellowship for Michal Wiecko is acknowledged.

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# **GRAPHICAL ABSTRACT**

#### Lanthanoid pseudo-Grignard reagents – a major untapped resource

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Pseudo-Grignard reagents PhLnX (Ln = Yb, Eu X = I) have been prepared by treatment of iodobenzene with lanthanoid metals (ytterbium or europium metal). These PhLnX reagents react with a range of the readily prepared and sterically tunable N,N'bis(aryl)formamidines to form an extensive series of the  $Ln^{II}/Ln^{III}$  mixed valent complexes.

