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Review

Bis(pentafluorophenyl)mercury—a versatile synthon in organo-, organooxo-, and organoamido-lanthanoid chemistry

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Dedicated to the memory of Henry Gilman

Abstract

Diarylmercury(II) compounds, HgR_2 (particularly bis(pentafluorophenyl)mercury), which are easily prepared and are stable to air and moisture, are attractive reagents for the synthesis of highly reactive lanthanoid organometallics and complexes. Thus, reactions of HgR_2 ($R = C_6F_5$) with elemental lanthanoids in donor solvents generate organolanthanoid species that when subsequently treated with a protic reagent LH (e.g. C_5R_5H, ArOH, R_2NH) eliminate volatile RH giving cyclopentadienyl-, aryloxo- and organoamido-lanthanoids, respectively. Combining these two steps in a convenient 'one-pot' reaction between Ln metal, HgR_2 and LH provides a versatile synthetic method (redox transmetallation–ligand exchange) for a wide variety of lanthanoid complexes and exploits the high reactivity of the initially generated lanthanoid–carbon bond. The syntheses are possible even in instances where the intermediate organolanthanoid complex cannot be isolated or detected. The increasing scope of redox transmetallation–ligand exchange often makes it competitive with metathesis and its simplicity can make it superior. Previously unreported applications viz. to $[Ln(C_5H_5)_3(THF)]$ complexes, $[Yb(C_5H_5)_2(THF)_2]$ and $[Yb(C_5Me_5)_2(THF)_2]$ are included. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. General

The organometallic chemistry of the heavy main group elements mercury, lead, bismuth and thallium (as TlR_2X) is characterised by the inert behaviour of the metal–carbon bond to oxygen and water [1]. Consequently, many derivatives are easily prepared and manipulated without the need for specialised equipment or techniques and can be routinely performed in undergraduate laboratories. In contrast, organolanthanoid complexes and the corresponding organoamido- and organooxo-metallics are amongst the most highly reactive compounds currently known, being extremely air and moisture sensitive and, in some cases, thermally unstable [2–4]. However, such species have become highly significant through novel structural features, stabilisation of low coordination numbers and, recently, unusual oxidation states [5–8], and through their ability to rapidly transform small molecules, e.g. in olefin poylmerisation and in the activation of X–H (X = C, N, O) [2–4] and C–F bonds [9]. We now review the use of diarylmercury compounds[1], particularly bis(pentafluorophenyl)mercury, in the synthesis of lanthanoid organometallics, aryloxides and organoamides including pyrazolates.

1.2. Redox transmetallation

The synthesis of organolanthanoid complexes benefits from simple one-pot procedures combined with easy separation of the products. The redox transmetal-

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[1] Diarylmercury compounds are involatile at room temperature and have lower toxicity, and more facile breakdown than the notorious dialkylmercurials [10,11], and can be readily handled with appropriate precautions for non-volatile toxic reagents.

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lation reaction of elemental lanthanoids with diorganomercurials (Eq. (1)) meets these criteria and we have successfully prepared perfluoroaryllanthanoid(II) species from an appropriate diorganomercurial and metallic ytterbium or europium (Eq. (1), $R = C_6F_nH_m$) in a donor solvent, THF, at room temperature [12–15].

$$\mathrm{Ln} + \mathrm{HgR_2} \rightarrow \mathrm{LnR_2} + \mathrm{Hg} \qquad (1)$$

These complexes, e.g. $[Ln(C_6F_5)_2(THF)_n]$ ($Ln = Eu$, $n = 5$ [15]; $Ln = Yb$, $n = 4$ [13]) are examples of a very rare group of organolanthanoid complexes that do not have stabilising cyclopentadienyl or pseudo-cyclopentadienyl ligands (such as cyclooctatetraenides). Recent successful crystallisation of $[Eu(C_6F_5)_2(THF)_5]$, previously obtained only as a 'glue' [13], enabled the first structure of any fluorocarbon lanthanoid complexes to be determined. A pentagonal bipyramidal stereochemistry with long trans Eu–C bonds was observed [15] providing a basis for predicting the structure of $[Yb(C_6F_5)_2(THF)_4]$ (Fig. 1). Reactions between lanthanoid elements and $HgPh_2$ are harder to induce than those with $Hg(C_6F_5)_2$, and require activation of the metal ($HgCl_2$ or I_2) and heating [2]. Crystalline $[LnPh_3(THF)_3]$ ($Ln = Er$ or Ho) complexes have been isolated from such reactions (Eq. (2)) and have much higher thermal stability than the C_6F_5 analogues [16].

$$2\mathrm{Ln} + 3\mathrm{HgPh_2} \rightarrow 2\mathrm{LnPh_3} + 3\mathrm{Hg} \qquad (2)$$

However, the thermal stability is insufficient to sustain a solventless attempted synthesis [17]. It should be noted that reaction of naphthaleneytterbium $[Yb(C_{10}H_8)(THF)_2]$ [18], which can be viewed as activated Yb metal, reacts with $HgPh_2$ to give the remarkable mixed oxidation state $[Yb^{II}Yb^{III}Ph_5(THF)_4]$ [19]. Redox transmetallation syntheses of lanthanoid organoamides from mercuric amides (Eq. (3)) have also been achieved, e.g. for $R = SiMe_3$, $Ln = Yb$, Eu, Sm [20], $NR_2 = N(SiMe_3)(C_6H_3\text{-}2,6\text{-}Pr^i_2)$, $Ln = Sm$, Yb, [21] and $NR_2 =$ 3,5-diphenylpyrazolate (Ph_2pz) $Ln = Yb$ [22], and $Sn\{N(SiMe_3)_2\}_2$ has also been effective in an analogous venture [23].

$$\mathrm{Ln} + \mathrm{Hg(NR_2)_2} \rightarrow \mathrm{Ln(NR_2)_2} + \mathrm{Hg} \qquad (3)$$

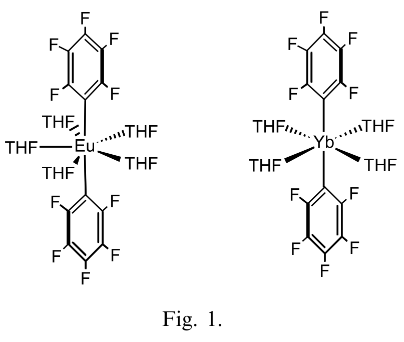


Fig. 1.

1.3. Redox transmetallation–ligand exchange

The high reactivity of the Ln–C bond in these complexes has been exploited in syntheses of cyclopentadienyl-, aryloxo- and organoamido-lanthanoids through ligand exchange reactions with a protic substrate (Eq. (4)).

$$\mathrm{Ln(C_6F_5)_2} + 2\mathrm{LH} \rightarrow \mathrm{Ln(L)_2} + 2\mathrm{C_6F_5H} \qquad (4)$$

Remarkably, these can be achieved even though the $Ln(C_6F_5)_2$ species are thermally unstable, decomposing by fluoride abstraction in hours or days (Yb, Eu) or minutes (Sm) at room temperature [13,14]. The trivalent $Ln(C_6F_5)_3$ derivatives have not yet been isolated and reaction mixtures that might generate such species undergo rapid decomposition into LnF_3 and complex organic products [14,24].

The synthetic utility of these perfluoroaryllanthanoids can best be realised by performing the reaction of metallic lanthanoids and $Hg(C_6F_5)_2$ in the presence of a protic reagent (Eqs. (5) and (6)).

$$\mathrm{Ln} + \mathrm{HgR_2} + 2\mathrm{LH} \rightarrow \mathrm{Ln(L)_2} + \mathrm{Hg} + 2\mathrm{RH} \qquad (5)$$

$$2\mathrm{Ln} + 3\mathrm{HgR_2} + 6\mathrm{LH} \rightarrow 2\mathrm{Ln(L)_3} + 3\mathrm{Hg} + 6\mathrm{RH} \qquad (6)$$

The in situ formed $Ln\text{–}C_6F_5$ species are then consumed immediately, thereby avoiding the problematic isolation of the $Ln(C_6F_5)_n$ ($n = 2$ or 3) complexes and the difficulties associated with their thermal instability [14,24]. These combined reactions represent an extremely simple 'one-pot' synthetic method and the review describes their application to the synthesis of a wide variety of lanthanoid complexes including organometallics, aryloxometallics and organoamidometallic (including pyrazolates). The bulk of the reported syntheses use bis(pentafluorophenyl)mercury because of its association with isolable organolanthanoids and the availability of an extremely facile synthesis. Mercuration of pentafluorobenzene under basic conditions (Eq. (7)) gives a near quantitative yield of the mercurial after 30 min reaction in aqueous *N*,*N*-dimethylformamide simply by pouring the reaction mixture into water [25].

$$\mathrm{HgBr_4^{2-}} + 2\mathrm{OH^-} + 2\mathrm{C_6F_5H} \rightarrow \mathrm{Hg(C_6F_5)_2} + 4\mathrm{Br^-} + 2\mathrm{H_2O} \qquad (7)$$

Recently the use of diphenylmercury has widened the scope of reactions (5) and (6) making them more versatile. Electrochemical measurements show $HgPh_2$ and $Hg(C_6F_5)_2$ lie at the extreme ends of the HgR_2 series in oxidising ability [26]. Thus, they provide an opportunity for selectivity in redox transmetallation–ligand exchange reactions.

On the basis of reaction (3) redox transmetallation–ligand exchange with Ln–$Hg(NR_2)_2$ and LH, paralleling reactions (5) and (6), could be envisaged. However, the air-sensitivity of many mercuric amides and their less easy syntheses than diarylmercurials makes them less satisfactory reagents. Although $Hg(Ph_2pz)_2$ is readily prepared and is air-stable, the relatively high acidity of Ph_2pzH greatly restricts the number of potential substrates LH that could be used in Ln–$Hg(Ph_2pz)_2$–LH reactions.

The review is conveniently arranged in terms of compound groups and includes some as yet unpublished results together with the appropriate Experimental justification.

2. Preparation of cyclopentadienyllanthanoid complexes

Initial studies involved preformed $Ln(C_6F_5)_2$ (Ln = Eu, Yb). Thus, solutions of $Ln(C_6F_5)_2$ (Ln = Eu, Yb) in THF react with cyclopentadienes (CpH), C_5H_6, C_9H_8 (indene), and $C_5H_5PPh_2$ to give the corresponding $LnCp_2$ complexes (Eq. (8)) [27–29].

$$Ln(C_6F_5)_2 + 2CpH \rightarrow LnCp_2 + 2C_6F_5H \quad (8)$$

The analogous reaction of $Yb(C_6F_5)_2$ with C_5H_5Me gave an explosive solid, although $Yb(C_5H_4Me)_2$ was detected in solution, and it is presumed the isolated compound is contaminated with a fluorocarbon–ytterbium impurity that detonates readily [27]. Addition of C_9H_8 to the unfiltered Yb–$Hg(C_6F_5)_2$ reaction mixture immediately upon initiation of the transmetallation reaction provided the first example of the a 'one-pot' procedure (Eq. (9), Ln = Yb, CpH = C_9H_8) and gave $[Yb(C_9H_7)_2(THF)_2]$ in good yield [27]. A high yield of $[Yb(C_5H_5)_2(THF)_2]$ results from Yb metal, $Hg(C_6F_5)_2$, and C_5H_6 in THF at room temperature (Eq. (9), Ln = Yb, CpH = C_5H_5) (Table 1).

$$Ln + Hg(C_6F_5)_2 + 2CpH \rightarrow LnCp_2 + Hg + 2C_6F_5H \quad (9)$$

An analogous reaction of Yb, $Hg(C_6F_5)_2$ and $C_5H_5PPh_2$ in THF–Et_2O was shown to give $[Yb(C_5H_4PPh_2)_2(THF)]$ (Eq. (9), Ln = Yb, CpH = $C_5H_5PPh_2$) in a higher yield than using preformed $Yb(C_6F_5)_2$ (Eq. (8), Ln = Yb, CpH = $C_5H_5PPh_2$) and could be readily carried out on large (10 g) scale [29]. The reaction of $Yb(C_6F_5)_2$ with C_5Me_5H does not give the well known $Yb(C_5Me_5)_2$ complex but instead a black material typical of decomposition of the starting organoytterbium species, thereby indicating that elimination of C_6F_5H had not occurred. This result is consistent with lower acidity of C_5Me_5H than C_6F_5H but the reaction may also be inhibited by the steric bulk of the C_5Me_5H. However, these problems can be conveniently overcome through replacement of $Hg(C_6F_5)_2$ with $HgPh_2$. The $C_6H_5^-$ anion is a considerably stronger base than $C_6F_5^-$ (pK_a C_6H_6 ~40; cf C_6F_5H ~26) [30], but $HgPh_2$ is less reactive with lanthanoid elements and requires heating to effect the transmetallation [2,16]. Since C_5Me_5H is thermally stable (cf dimerisation of C_5H_6 at room temperature), heating is possible and reactions of Yb, $HgPh_2$ and C_5Me_5H in refluxing THF readily give $[Yb(C_5Me_5)_2(THF)_2]$ (Eq. (10)) in good yield (Table 1).

$$Yb + HgPh_2 + 2C_5Me_5H \rightarrow Yb(C_5Me_5)_2 + Hg + 2PhH \quad (10)$$

The preparation of tris(cyclopentadienyl)lanthanoid(III) complexes by reaction of Ln metal (Ln = Eu, Yb) $Hg(C_6F_5)_2$ and C_5H_6 (Eq. (11), CpH = C_5H_6) in pyridine (py) has been reported giving the corresponding pyridine solvates $[Ln(C_5H_5)_3(py)]$ (Ln = Eu, Yb) [31].

$$2Ln + 3Hg(C_6F_5)_2 + 6CpH \rightarrow 2Ln(Cp)_3 + 3Hg + 6C_6F_5H \quad (11)$$

These results contrast the usual isolation of divalent products for these elements from this type of reaction.

Table 1
Syntheses of cyclopentadienyllanthanoid (II or III) complexes [a]

Ln (mmol)	HgR_2 R (mmol)	LH (mmol)	Solvent, time (h)	Product (% yield)
Yb (0.8)	C_6F_5 (0.8)	C_5H_6 (1.6)	THF, 5	$[Yb(C_5H_5)_2(THF)_2]$ (81)
Yb (10.0)	C_6H_5 (5.0)	C_5Me_5H (10.0)	THF [b], 48	$[Yb(C_5Me_5)_2(THF)_2]$ (60)
Ce (3.9)	C_6F_5 (3.9)	C_5H_6 (13.7)	THF, 9	$[Ce(C_5H_5)_3(THF)]$ (98)
Nd (4.6)	C_6F_5 (3.5)	C_5H_6 (8.5)	THF, 8	$[Nd(C_5H_5)_3(THF)]$ (86)
Sm (3.4)	C_6F_5 (3.4)	C_5H_6 (10.8)	THF, 10	$[Sm(C_5H_5)_3(THF)]$ (75)
Gd (2.9)	C_6F_5 (2.9)	C_5H_6 (6.3)	THF, 9	$[Gd(C_5H_5)_3(THF)]$ (73)
Dy (3.1)	C_6F_5 (3.4)	C_5H_6 (11.9)	THF, 7	$[Dy(C_5H_5)_3(THF)]$ (71)
Er (3.0)	C_6F_5 (3.0)	C_5H_6 (14.9)	THF, 8	$[Er(C_5H_5)_3(THF)]$ (86)
Tm (3.0)	C_6F_5 (3.0)	C_5H_6 (9.5)	THF, 9	$[Tm(C_5H_5)_3(THF)]$ (91)
Lu (2.9)	C_6F_5 (2.8)	C_5H_6 (14.3)	THF, 9	$[Lu(C_5H_5)_3(THF)]$ (40)

[a] Reactions at room temperature unless indicated otherwise.
[b] Reaction temperature 65 °C.

A stoichiometric 2:3 ratio of Ln:$Hg(C_6F_5)_2$ (Eq. (11)) presumably ensures that the final products are in the trivalent state. For Ln = Eu, intermediate formation of $Eu(C_5H_5)_2$ was detected [31]. In a more general application, the preparation of an extensive series of $[Ln(C_5H_5)_3(THF)]$ (Ln = Ce, Nd, Sm, Gd, Dy, Er, Tm, or Lu) complexes has also been achieved (Eq. (11)) using THF as the reaction solvent (Table 1). The products are obtained in good-excellent yields of 50–90% simply by evaporation of the solvent after decantation of the solution from precipitated mercury and the excess of Ln metal. This study demonstrates the use of the 'one-pot' method for elements for which the intermediate perfluoroaryllanthanoids cannot be isolated, and has been previously reported only in conference abstracts [32,33]. The reaction pathway to these lanthanoid(III) complexes is open to two interpretations. Most obvious is the initial formation of $Ln(C_6F_5)_3$ species (Eq. (12)) followed by rapid stepwise protolysis with C_5H_6 (Eq. (13)).

$$2Ln + 3Hg(C_6F_5)_2 \rightarrow 2Ln(C_6F_5)_3 + 3Hg \quad (12)$$

$$Ln(C_6F_5)_3 + 3C_5H_6 \rightarrow Ln(C_5H_5)_3 + 3C_6F_5H \quad (13)$$

However, for elements with an accessible divalent state (e.g. Eu, Sm, Yb and, as more recently demonstrated, La [8], Nd, and Tm [5–7]), the following reaction sequence is plausible (i) initial formation of $Ln(C_6F_5)_2$ (Eq. (1), R = C_6F_5); (ii) reaction with C_5H_6 giving $Ln(C_5H_5)_2$ (e.g. Eq. (4), LH = C_5H_6); (iii) oxidation by $Hg(C_6F_5)_2$ giving $Ln(C_5H_5)_2(C_6F_5)$ (Eq. (14)) and lastly (iv) further reaction with C_5H_6 yielding the isolated $Ln(C_5H_5)_3$ species (Eq. (15)).

$$2Ln(C_5H_5)_2 + Hg(C_6F_5)_2 \rightarrow 2Ln(C_5H_5)_2(C_6F_5) + Hg \quad (14)$$

$$2Ln(C_5H_5)_2(C_6F_5) + C_5H_6 \rightarrow Ln(C_5H_5)_3 + C_6F_5H \quad (15)$$

Step (iii) (Eq. (14)) has been independently demonstrated by reaction of $Yb(C_5R_5)_2$ (R = H, Me) complexes with $Hg(C_6F_5)_2$ yielding $Yb(C_5R_5)_2(C_6F_5)$ [34,35] which (R = H) has been shown to undergo protolysis [34] with the weaker acid PhCCH than C_5H_6, indicating the viability of reaction (15). In addition to demonstration of possible $Ln(C_6F_5)_2$ intermediacy by reaction (1) (Ln = Yb, Eu) [13–15], the formation of $Sm(C_6F_5)_2$ in the Sm–$Hg(C_6F_5)_2$ system (i.e. step (i)) has been inferred from trapping reactions with 2-phenylindole (see Section 4 below). Furthermore, traces of $[Yb(C_5H_5)_2(F)]_3$ were occasionally detected in preparations of $Yb(C_5H_5)_2$ and $Er_2(C_5H_5)_2(F)_2^+$ ions were observed in the mass spectra of $Er(C_5H_5)_3$ (Section 7). These fluoride species are conceivably derived from decomposition of $Ln(C_5H_5)_2(C_6F_5)$ by fluoride abstraction processes. Reactions of Ln–$Hg(C_6F_5)_2$ with other cyclopentadienes, C_5H_5Me, C_9H_8, gave clean products only for $[Sm(C_5H_4Me)_3(THF)]$ and $[Sm(C_9H_7)_3(THF)]$ (Eq. (11), Ln = Sm, CpH = C_5H_5Me or C_9H_8), in low yields (7–20%) [27], and with the cyclopentadiene added after the initiation of redox transmetallation. In all other cases intractable mixtures were obtained.

3. Preparation of aryloxolanthanoid complexes

Ligand exchange between phenols and bis(pentafluorophenyl)–europium(II) or –ytterbium(II) (Eq. (16)), prepared from the metals and $Hg(C_6F_5)_2$, and redox transmetallation–ligand exchange between europium or ytterbium, $Hg(C_6F_5)_2$ and phenols (Eq. (17)), were carried out initially to see if synthetic methods developed for cyclopentadienyls could be extended to aryloxides [36].

$$Ln(C_6F_5)_2 + 2HOAr \rightarrow Ln(OAr)_2 + 2C_6F_5H \quad (16)$$

$$Ln + Hg(C_6F_5)_2 + 2HOAr \rightarrow Ln(OAr)_2 + Hg + 2C_6F_5H \quad (17)$$

The first studies utilised the bulky ligands OAr = OC_6H_2-2,6-Bu^t_2-4-R, (R = H, Me, Bu^t) hence a further objective was to obtain low coordinate (CN ≤ 6) lanthanoid(II) complexes [37,38]. Success was achieved by both routes and complexes $[Ln(OC_6H_2\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}R)_2(THF)_n]$, (Ln = Yb or Eu; R = H, Me, Bu^t) were obtained in good yield from syntheses in THF and had distorted tetrahedral ($n = 2$) or square pyramidal ($n = 3$) stereochemistry. To this stage, the method has not been used to give trivalent complexes with these ligands. Detailed studies with elements normally giving Ln(III) complexes or with Sm, which might give either Sm(II) or Sm(III), have not been reported. However, pertinent studies with the ligand OAr = OC_6H_2-2,6-Bu^t_2-4-OMe are being completed and will be reported in due course. The trivalent analogues have been obtained by other synthetic methods such as metathesis and acidolysis [2–4] as well as by redox transmetallation with thallium aryloxides (which can also give Ln(II) complexes [37,38]) and by oxidation of $Ln(OAr)_2$ with Tl(OAr) [39].

By contrast, redox transmetallation–ligand exchange between lanthanoid elements, $Hg(C_6F_5)_2$ and 2,6-diphenylphenol (HOdpp) yields $Ln(Odpp)_3$ complexes (Eq. (18)), even for Ln = Yb or Sm, which might give Ln(II) complexes [40–42].

$$2Ln + 3Hg(C_6F_5)_2 + 6HOAr \rightarrow 2Ln(OAr)_3 + 3Hg + 6C_6F_5H \quad (18)$$

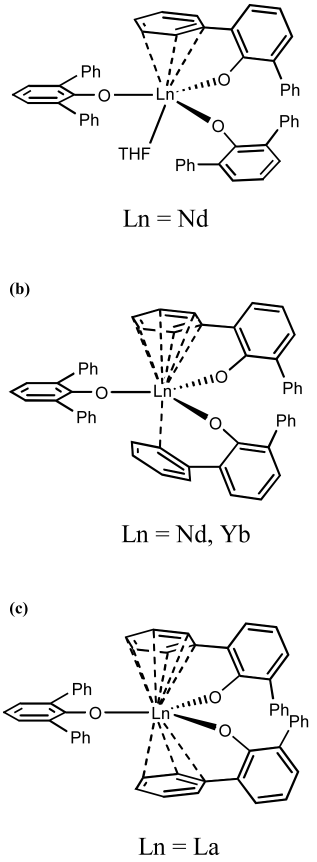
After syntheses in THF and a variety of workup and crystallisation procedures, a range of low coordination complexes were obtained viz. five-coordinate $[Ln(Odpp)_3(THF)_2]$, four-coordinate $[Nd(Odpp)_3(THF)]$ with an additional η^3-Ph···Nd intramolecular interaction (Fig. 2(a)), and formally three-coordinate

$[Ln(Odpp)_3]$ (Ln = Nd, Yb), which have additionally η^1- and η^6-Ph···Ln intramolecular coordination (Fig. 2(b)) [40,41]. The difficulty in accessing the Ln(II) oxidation state with the Odpp ligand required $Yb(Odpp)_2$ to be prepared by reduction of the trivalent complex with Yb(Hg) (Eq. (19)) and even this was incomplete [43].

$$2Yb(Odpp)_3 + Yb(Hg) \rightarrow 3Yb(Odpp)_2 \qquad (19)$$

One surprising development of Eq. (18) was to achieve reaction for Ln = La in toluene, thereby enabling a rare redox transmetallation–ligand exchange synthesis of a homoleptic aryloxide viz. $[La(Odpp)_3]$ which has an intramolecular π-Ph···La sandwich ($\eta^3 + \eta^6$) (Fig. 2(c)) [44].

A recent application of redox transmetallation–ligand exchange to lanthanoid 2,6-diphenylphenolates containing potentially buttressing 3,5-substituents has resulted in a new understanding of the capacity of the method. Use of reaction (18) with $Hg(C_6F_5)_2$ and $HOAr^R$ (Fig. 3) in THF led to isolation of $[Ln(OAr^{Bu})_3(THF)]\cdot THF$ (Ln = Yb, Sc), $[Yb(OAr^{Me})_3(THF)]$, and $[Sm(OAr^{Ph})_3(THF)_2]$, as well as the adventitiously prepared $[Yb(OAr^{Ph})_3(DME)]\cdot 1.5THF$ [45]. Isolation of four-coordinate Yb complexes in contrast to five-coordinate $[Yb(Odpp)_3(THF)_2]$ establishes that the bulk provided by the 3,5-substituents, presumably by buttressing the Ph groups, can lead to a reduction in the coordination number. By contrast, use of $HgPh_2$ in redox transmetallation–ligand exchange resulted in formation of $[Yb(OAr^{Me})_2(THF)_3]$ (Eq. (20)) [45].



Ln = Nd

Ln = Nd, Yb

Ln = La

Fig. 2.

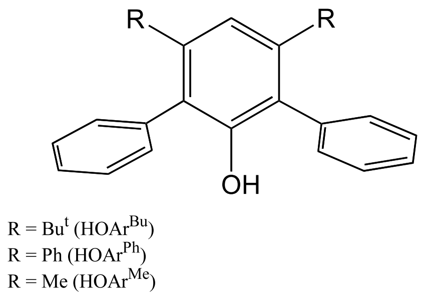


Fig. 3.

$$Yb + HgPh_2 + 2HOAr^{Me} \rightarrow Yb(OAr^{Me})_2 + Hg + 2PhH \qquad (20)$$

The development of oxidation state selectivity by choice of mercurial is an attractive addition to the synthetic weaponry. Electrochemical studies [26] as well as synthetic behaviour [34] show that $Hg(C_6F_5)_2$ is a superior oxidant to $HgPh_2$.

4. Preparation of organoamidolanthanoid complexes

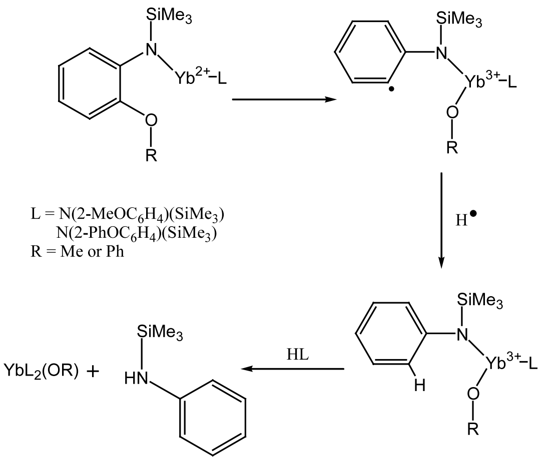
Further targeting low coordination number lanthanoid complexes led us to investigate the formation of organoamidolanthanoid derivatives, again utilising sterically demanding ligands. The most commonly used ligand is the bis(trimethylsilyl)amide ion, which gives complexes of the types $Ln(NR_2)_2(S)$ or $Ln(NR_2)_3$ (R = $SiMe_3$). However, the pK_a of $HN(SiMe_3)_2$ (~ 30) [46] is considerably higher than that of C_6F_5H (~ 26) [30] and accordingly mixtures of this amine and $Yb(C_6F_5)_2$ (Eq. (21)) did not undergo ligand exchange.

$$Yb(C_6F_5)_2 + 2HN(SiMe_3)_2 \not\rightarrow Yb\{N(SiMe_3)_2\}_2 + 2C_6F_5H \qquad (21)$$

To overcome this, the substitution of $HgPh_2$ for $Hg(C_6F_5)_2$ in the redox transmetallation–ligand exchange reaction provides a viable alternative since the pK_a of C_6H_6 (~ 40) is considerably higher than that of C_6F_5H [30]. Thus, reactions of Sm or Yb with $HgPh_2$ and $HN(SiMe_3)_2$ gave the corresponding $[Ln\{N(SiMe_3)_2\}_2(THF)_2]$ complexes (Eq. (22), Ln = Sm, Yb; R = $SiMe_3$) in good yields [21].

$$Ln + HgPh_2 + 2HN(SiMe_3)R \rightarrow Ln\{N(SiMe_3)R\}_2 + Hg + 2PhH \qquad (22)$$

These compounds are valuable precursors to other lanthanoid complexes [2–4] and the above reaction provides a very convenient 'one-pot' synthetic method.



Scheme 1.

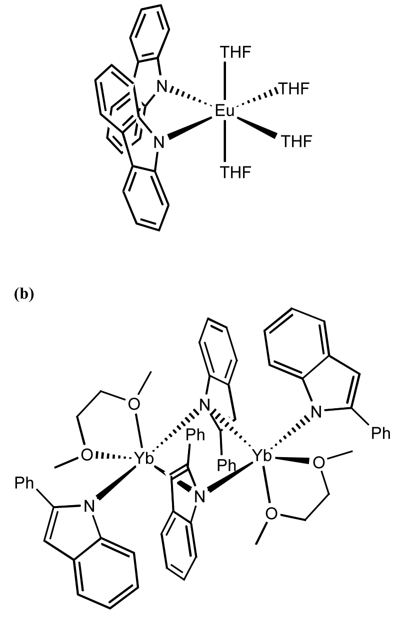


Fig. 4.

This procedure was further extended to aryltrimethylsilylamines, giving [Yb{N(SiMe$_3$)R}$_2$(THF)$_2$] (Eq. (22), Ln = Yb; R = 2,6-Pr$^i_2$C$_6$H$_3$) [21]. However, when the aryl group was substituted with an ether functionality (e.g. HN(2-ROC$_6$H$_4$)(SiMe$_3$), R = Me, Ph), the redox transmetallation–ligand exchange reactions of Yb, HgPh$_2$ and the amine gave unexpected Yb(III) products viz. [Yb{N(2-MeOC$_6$H$_4$)(SiMe$_3$)}$_2$(OMe)]$_2$ or [Yb{N(2-PhOC$_6$H$_4$)(SiMe$_3$)}$_2$(OPh)(THF)] [47]. These were considered to be derived from reduction of the organoamide ligand by intermediate Yb(II) complexes, [Yb{N(2-ROC$_6$H$_4$)(SiMe$_3$}$_2$(THF)$_2$] (Scheme 1), an example of which (R = Me) was independently synthesised by ligand exchange of [Yb{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] with HN(2-MeOC$_6$H$_4$)(SiMe$_3$) and shown to react with the free amine to give [Yb{N(2-MeOC$_6$H$_4$)(SiMe$_3$)}$_2$-OMe]$_2$ [47].

Reactions of bis(pentafluorophenyl)lanthanoids with the heterocyclic amines carbazole (cbzH), or 2-phenylindole (pinH) (Eq. (23)) or redox transmetallation–ligand exchange of lanthanoid elements, Hg(C$_6$F$_5$)$_2$ and pinH or 2,3,4,5 tetraphenylpyrrole (tppH) (Eq. (24)) gave the organoamidolanthanoid(II) complexes [Ln(NR$_2$)$_2$(THF)$_4$] (Ln = Sm, NR$_2$ = pin; Ln = Eu, NR$_2$ = cbz, pin, Ln = Yb, NR$_2$ = cbz, pin) and [Ln(tpp)$_2$(THF)$_3$] (Ln = Sm, Yb) [36,48].

$$\mathrm{Ln(C_6F_5)_2 + 2HNR_2 \rightarrow Ln(NR_2)_2 + 2C_6F_5H} \qquad (23)$$

$$\mathrm{Ln + Hg(C_6F_5)_2 + 2HNR_2 \rightarrow Ln(NR_2)_2 + Hg + 2C_6F_5H} \qquad (24)$$

Structural characterisation of [Eu(cbz)$_2$(THF)$_4$] revealed a monomeric distorted octahedral complex with the *N*-heterocyclic amides bound to europium solely through the nitrogen atoms (Fig. 4(a)) [48]. The bulky amide groups are in a *cisoid* arrangement. However stereochemical variability in these complexes was subsequently illustrated by the characterisation of both *cis*-[Sm(cbz)$_2$(THF)$_4$] and *trans*-[Sm(cbz)$_2$(Meim)$_4$] (Meim = *N*-methylimidazole) [49]. Further structural variation can be induced by limiting the availability of neutral donors leading to N-bridged species, e.g. five-coordinate [Yb(pin)(μ-pin)(DME)]$_2$ (Fig. 4(b)) [50].

The above reactions with Sm are particularly illustrative of variability in the oxidation state outcome in the redox transmetallation–ligand exchange reaction since for the first time high yields of Sm(II) products ([Sm(pin)$_2$(THF)$_4$], [Sm(tpp)$_2$(THF)$_3$]) were obtained [48,51]. Whilst these results parallel the syntheses of the analogous Yb(II) and Eu(II) organoamides, as well as the corresponding aryloxides and organometallics (see above), neither of the possible intermediate steps can be independently demonstrated for Sm. The redox transmetallation reaction of Sm with Hg(C$_6$F$_5$)$_2$ is extremely complex and gives a variety of products including Sm(C$_6$F$_5$)F$_2$, Sm(*o*-HC$_6$F$_4$) species, Sm(C$_{12}$F$_9$) species and complex fluorocarbon organic molecules. These are considered to be derived from decomposition of initially formed Sm(C$_6$F$_5$)$_n$ ($n = 2$ or 3) [14]. Previous attempts to trap the initial redox transmetallation product gave Sm(III) complexes (see above Section 2) implying the intermediate formation of Sm(C$_6$F$_5$)$_3$. A related route to the divalent product can be envisaged, viz. ligand exchange of Sm(C$_6$F$_5$)$_3$ with the amine giving Sm(NR$_2$)$_3$ (Eq. (25)) followed by reduction with the excess of Sm metal (Eq. (26)).

$$\mathrm{Sm(C_6F_5)_3 + 3HNR_2 \rightarrow Sm(NR_2)_3 + 3C_6F_5H} \qquad (25)$$

$$\mathrm{2Sm(NR_2)_3 + Sm \rightarrow 3Sm(NR_2)_2} \qquad (26)$$

The last reaction has a precedent in the formation of SmI$_2$ from SmI$_3$ and Sm [52] and the reduction of Yb(Odpp)$_3$ by amalgamated Yb metal (see above) [43]. However, it was shown that an independently prepared sample of [$\mathrm{Sm(pin)_3(THF)}$] was not reduced by Sm under the reaction conditions [51]. Thus, it appears that $\mathrm{Sm(C_6F_5)_2}$ is the initial product from the Sm–$\mathrm{Hg(C_6F_5)_2}$ redox transmetallation reaction (e.g. Eq. (1), Ln = Sm; R = $\mathrm{C_6F_5}$) and it reacts immediately with the amine to give $\mathrm{Sm(NR_2)_2}$. The isolated $\mathrm{Sm(pin)_2}$ complex will undergo oxidation–ligand exchange with $\mathrm{Hg(C_6F_5)_2}$ and pinH in THF solution yielding [$\mathrm{Sm(pin)_3(THF)}$] (Eq. (27)) [51].

$$\begin{aligned}&\mathrm{2Sm(pin)_2 + Hg(C_6F_5)_2 + 2pinH}\\&\quad\rightarrow \mathrm{2Sm(pin)_3 + Hg + 2C_6F_5H}\end{aligned}\qquad(27)$$

Therefore, the isolation of the divalent samarium amides from the redox transmetallation–ligand exchange reaction indicates that, in the presence of Sm metal, the transmetallation reaction (Eq. (1), Ln = Sm; R = $\mathrm{C_6F_5}$) predominates over the oxidation of the subsequently formed $\mathrm{Sm(NR_2)_2}$ complex (Eq. (27)). However, it is clear that these competing reactions of the organomercurial are finely balanced and the oxidation state outcome can be controlled through choice of lanthanoid, ligand or organomercury reagent.

5. Preparation of pyrazolatolanthanoid complexes

The redox transmetallation–ligand exchange reactions have been extensively explored for the preparation of pyrazolatolanthanoid complexes, which represent a special class of organoamides of these elements. The presence of two adjacent nitrogen atoms not only influences the behaviour of the ligands in these reaction but the resulting complexes have demonstrated a unique and highly novel structural chemistry. Consequently, these are discussed as a separate section, divided into two parts which highlight the differences in the uses of two different organomercurials, $\mathrm{Hg(C_6F_5)_2}$ and $\mathrm{HgPh_2}$.

5.1.1. Syntheses with bis(pentafluorophenyl)mercury

In the first example of a redox transmetallation–ligand exchange synthesis of a lanthanoid pyrazolate, Nd metal, $\mathrm{Hg(C_6F_5)_2}$ and 3,5-dimethylpyrazole ($\mathrm{Me_2pzH}$) were reacted in THF to give [$\mathrm{Nd(Me_2pz)_2(\mu\text{-}Me_2pz)(\mu\text{-}THF)}$]$_2$ (Eq. (28), Ln = Nd; $\mathrm{R_2pz = Me_2pz}$) [53].

$$\begin{aligned}&\mathrm{2Ln + 3Hg(C_6F_5)_2 + 6R_2pzH}\\&\quad\rightarrow \mathrm{2Ln(R_2pz)_3 + 3Hg + 6C_6F_5H}\end{aligned}\qquad(28)$$

The complex is interesting for having both μ-η^1:η^1 bridging pyrazolates, commonly observed in d-block chemistry, and also two terminal pyrazolate ligands, each with an η^2-coordination mode (Fig. 5(a)). The binding of both pyrazolate nitrogen atoms to the same lanthanoid presumably serves to relieve coordinative unsaturation of these large metal cations. In addition, bridging THF ligands are unusual. With bulkier 3,5-substituents which would inhibit η^1:η^1 bridging on the pyrazole, monomeric complexes having solely η^2 coordinated pyrazolates were achieved. The syntheses of such complexes have been extensively pursued utilising redox transmetallation–ligand exchange reactions with diphenylpyrazole ($\mathrm{Ph_2pzH}$) or di-*tert*-butylpyrazole ($\mathrm{Bu^t_2pzH}$) in THF solvent (Eq. (28), $\mathrm{R_2pz = Ph_2pz}$ or $\mathrm{Bu^t_2pz}$) yielding [$\mathrm{Ln(R_2pz)_3(THF)}_n$] complexes (e.g. Fig. 5(b)), encompassing virtually all of the lanthanoid elements as well as Y and Sc [54–57]. Notable in these syntheses was the exclusive formation of trivalent products, even for elements with accessible divalent states, e.g. Sm and Yb (overall divalent Yb complexes are a frequent outcome of redox transmetallation–ligand exchange reactions with this element (see above)). This aspect is further discussed below in conjunction with the syntheses of lanthanoid(II) pyrazolates using $\mathrm{HgPh_2}$, showing the flexibility of these reactions. A further feature of the redox transmetallation–ligand exchange reactions with $\mathrm{Hg(C_6F_5)_2}$ was the first use of a variety of solvents other than THF. Syntheses were carried out in DME or diethyl ether yielding the corresponding solvent complexes [$\mathrm{Ln(R_2pz)_3(S)}$] (S = DME or $\mathrm{OEt_2}$) [58,59]. More significantly, the solubility of the $\mathrm{Ln(Bu^t_2pz)_3}$ derivatives in petroleum spirit allowed the redox transmetallation–ligand exchange reactions to be achieved for the first time in this non-polar solvent. These gave either the solvent free homoleptic complex [$\mathrm{Nd(Bu^t_2pz)_3}$] [59] or complexes with both coordinated pyrazolate and pyrazole e.g. [$\mathrm{La(Bu^t_2pz)_3(Bu^t_2pzH)_2}$]

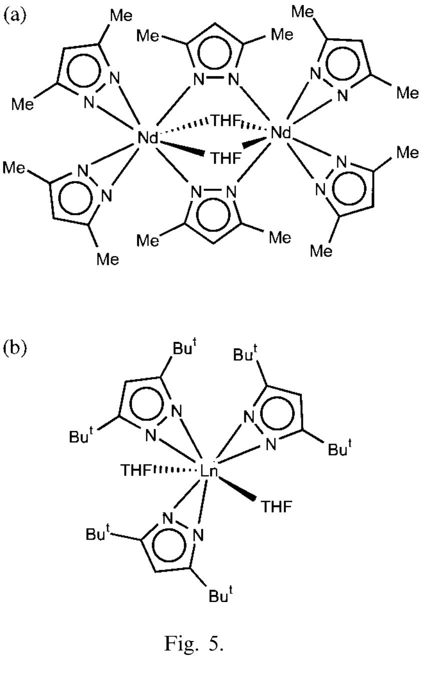


Fig. 5.

[59]. However, the former could not be obtained as single crystals, which had to await an alternative synthesis and work up [60,61].

5.1.2. Syntheses with diphenylmercury

Redox transmetallation–ligand exchange with diphenylmercury (Eq. (29)) provided one of the two routes used to give the first lanthanoid(II) pyrazolate (the other being redox transmetallation from thallium pyrazolates) [22,62].

$$\mathrm{Ln + HgPh_2 + 2R_2pzH \rightarrow Ln(R_2pz)_2 + Hg + 2PhH} \quad (29)$$

This contrasts the reaction utilising Yb, $Hg(C_6F_5)_2$ and Bu^t_2pzH giving $Yb(Bu^t_2pz)_3$ (above), and observation of gross decomposition in the corresponding reaction with Ph_2pzH. Subsequent investigation of the reaction between $Hg(C_6F_5)_2$ derived $Yb(C_6F_5)_2$ (reaction (1), Ln = Yb) and Ph_2pzH (Eq. (30)) showed that $Yb(Ph_2pz)_2$ could be obtained with a short reaction time.

$$\mathrm{Yb(C_6F_5)_2 + 2Bu^t_2pzH \rightarrow Yb(Bu^t_2pz)_2 + 2C_6F_5H} \quad (30)$$

Otherwise black decomposition products were obtained. The weaker oxidising ability of $HgPh_2$ vs. $Hg(C_6F_5)_2$ was further illustrated by the failure to convert $Yb(Ph_2pz)_2$ to $Yb(Ph_2pz)_3$ by oxidation–ligand exchange (Eq. (31)). In addition, it has been shown that the excess of Yb metal used in reaction (29) is unable to reduce $Yb(Ph_2pz)_3$ to $Yb(Ph_2pz)_2$ (Eq. (32)).

$$\mathrm{2Yb(Ph_2pz)_2 + HgPh_2 + 2Ph_2pzH \nrightarrow 2Yb(Ph_2pz)_3 + Hg + 2PhH} \quad (31)$$

$$\mathrm{2Yb(Ph_2pz)_3 + Yb \nrightarrow 3Yb(Ph_2pz)_2} \quad (32)$$

Redox transmetallation–ligand exchange was of greatest value in obtaining $Ln(Bu^t_2pz)_2$ (Ln = Yb, Eu) complexes since the inability to prepare $Tl(Bu^t_2pz)$ owing to thermal instability ruled out the thallium redox route [22]. Inability to crystallise the $[Yb(R_2pz)_2(THF)_n]$ complexes led to successful crystallisations of the reaction products from DME (Eq. (33)).

$$\mathrm{Yb(R_2pz)_2(THF)_{\mathit{n}} + 2DME \rightarrow Yb(R_2pz)_2(DME)_2 + \mathit{n}THF} \quad (33)$$

Both $[Yb(Ph_2pz)_2(DME)_2]$ and $[Eu(Bu^t_2pz)_2(DME)_2]$ were found to be eight-coordinate monomers with the R_2pz ligands mutually *cisoid* [22]. More remarkably crystallisation of $[Yb(Bu^t_2pz)_2(THF)_n]$ from hexane gave seven-coordinate $[Yb(Bu^t_2pz)_2(THF)]_2$ with the (then) new μ-η^2:η^2 pyrazolate binding mode, in which the N–N bond of the bridging pyrazolate is normal to the Yb···Yb axis instead of parallel in widespread μ-η^1:η^1-pyrazolate ligation (Fig. 6(a)) [62].

In contrast to the outcome from redox transmetallation–ligand exchange between Yb metal, $HgPh_2$, and Bu^t_2pzH in THF (reaction (29)), the same reagents in toluene for a prolonged period yielded the trivalent homoleptic complex $[Yb_3(Bu^t_2pz)_6]$ (Eq. (34)).

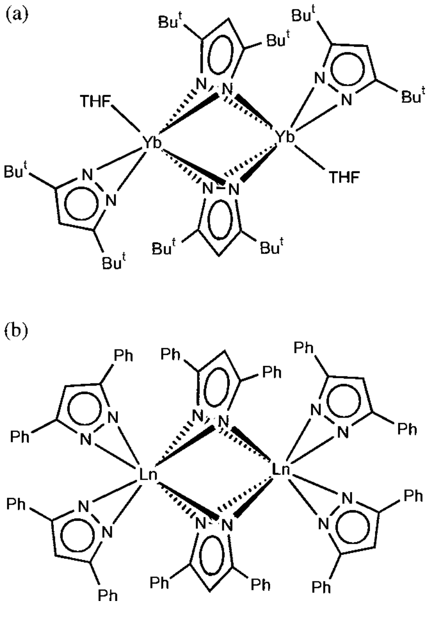


Fig. 6.

$$\mathrm{2Yb + 3HgPh_2 + 6Bu^t_2pzH \rightarrow Yb(Bu^t_2pz)_6 + 3Hg + 6PhH} \quad (34)$$

The complex has eight-coordinate Yb with terminal η^2-pyrazolate ligands and μ-η^2:η^2 bridging ligands (Fig. 6(b)). However, the initially detected product is the mixed oxidation state homoleptic complex $[Yb_2(Bu^t_2pz)_5]$ [60] (Eq. (35)), and this is oxidised by $HgPh_2$ with proton transfer by the pyrazole on longer reaction times (Eq. (36)).

$$\mathrm{4Yb + 5HgPh_2 + 10Bu^t_2pzH \rightarrow 2Yb(Bu^t_2pz)_6 + 5Hg + 10PhH} \quad (35)$$

$$\mathrm{2Yb_2(Bu^t_2pz)_5 + HgPh_2 + 2Bu^t_2pzH \rightarrow 2Yb_2(Bu^t_2pz)_6 + Hg + 2PhH} \quad (36)$$

Reaction (Eq. (36)) plausibly involves oxidation of $[Yb_2(Bu^t_2pz)_5]$ to $[Yb_2(Bu^t_2pz)_5Ph]$ which is then protolysed by the Bu^t_2pzH. The structure of the mixed oxidation state species, dinuclear with (formally) six-coordinate Yb(II) and eight-coordinate Yb(III) and μ-η^2:η^2 (or possibly μ-η^2:η^4) pyrazolates, has been determined for the product of an alternative synthesis [60]. Strikingly, it is not possible to obtain the divalent homoleptic complex by redox transmetallation–ligand exchange nor indeed by any other route. The outcome of these reactions suggests that $Yb(Bu^t_2pz)_3$ cannot be reduced by Yb metal in contrast to the reduction of $Yb(Odpp)_3$ by Yb metal in THF (above). Even the reaction of $[Yb_2(Bu^t_2pz)_5]$ with Yb(Hg) in molten

1,2,4,5-tetramethylbenzene at 350 °C did not provide the divalent complex.

6. Conclusions

This account demonstrates the value and significance of metal-based reactions utilising diarylmercurials, particularly $Hg(C_6F_5)_2$, in redox transmetallation–ligand exchange syntheses of lanthanoid organometallics (where new results are presented), aryloxides and organoamides. It has considerable potential for further exploration and exploitation, e.g. for phosphides, sulphides, alkoxides and more widely for amides.

7. Experimental

All manipulations, analyses and spectroscopic measurements were carried out as described previously [22,31,44]. Purification of solvents and sources of reagents have been given [22,31,44], apart from C_5Me_5H (Aldrich) which was dried and distilled from CaH_2 whilst C_5H_6 was prepared by cracking $(C_5H_6)_2$ over iron powder in a nitrogen atmosphere [63].

7.1. Preparations

Amounts of reagents and reaction conditions are given in Table 1 and characterisation of individual complexes are listed below.

7.1.1. [Yb(C$_5$Me$_5$)$_2$(THF)$_2$]

The reaction mixture was filtered through a Celite pad and intense purple filtrate was evaporated giving a red–purple solid. (Found: Yb, 30.0. $C_{28}H_{46}O_2Yb$ requires Yb, 29.4%). IR(Nujol): 1311w, 1294w, 1244w, 1170w, 1034s, 978w, 913w, 881s, 722m cm^{-1}. ^{1}H-NMR (C_6D_6): δ 1.34, br s, 8H, α-THF; 2.05, s, 30H, C_5Me_5; 3.38, br s, 8H, β-THF ppm. Vis. λ_{max} (ε) (THF): 519 (185). (PhMe): 441 (361), 506 (317) nm.

7.1.2. [Yb(C$_5$H$_5$)$_2$(THF)$_2$]

The reaction mixture was allowed to settle and the solution was decanted from the precipitated mercury and the excess of ytterbium metal. The volume was reduced to ca. 2 ml and the supernatant was removed by syringe. The resulting crystals were dried under vacuum yielding the title complex. IR, ^{1}H-NMR, and UV–vis–near IR spectra were in agreement with the reported data [64]. Mass spectrum, *m*/*z* (int): 902 [0.4%, $Yb_3(C_5H_5)_5F_3^+$]; 645 [0.1, $Yb_2(C_5H_5)_4F_2^+$]; 579 [0.8, $Yb_2(C_5H_5)_2F_2^+$]; 514 [0.2, $Yb_2(C_5H_5)_2F_2^+$]; 493 [0.05, $Yb_2(C_5H_5)_2F^+$]; 449 [0.2, $Yb_2(C_5H_5)F_2^+$]; 304 [22, $Yb(C_5H_5)_2^+$]; 239 [28, $Yb(C_5H_5)^+$]; 174 [8, Yb^+].

7.1.3. [Ln(C$_5$H$_5$)$_3$(THF)] general procedure

After the reaction was completed, the resulting mixtures were allowed to settle and the solutions were decanted from the precipitated mercury and excess of lanthanoid metal. The clear solutions were then evaporated to ca. 2 ml under vacuum giving crystals of the tris(cyclopentadienyl)(tetrahydrofuran)lanthanoid(III) complexes. The supernatant solutions were removed by syringe and the products were dried under vacuum.

7.1.4. Ln = Ce

IR, ^{1}H-NMR (C_6D_6), and UV–vis–near IR spectra were in agreement with reported data [64–66]. Mass spectrum, *m*/*z* (int): 335 [24%, $Ce(C_5H_5)_3^+$]; 294 [0.5, $CeC_{12}H_{10}^+$]; 270 [100, $Ce(C_5H_5)_2^+$]; 242 [7, $CeC_8H_6^+$]; 205 [32, $Ce(C_5H_5)^+$]; 180 [9, CeC_3H^+]; 165 [3, CeC_2^+]; 134.5 [4, $Ce(C_5H_5)_2^{2+}$]; 140 [1, Ce^+]; 102.5 [4, $Ce(C_5H_5)^{2+}$]; 73 [15, $C_4H_9O^+$]; 72 [14, $C_4H_8O^+$]; 66 [10, $C_5H_6^+$]; 65 [8, $C_5H_5^+$].

7.1.5. Ln = Nd

IR, ^{1}H-NMR (C_6D_6), UV–vis–near IR, and mass spectra were in agreement with reported data [64,67,68].

7.1.6. Ln = Sm

IR, ^{1}H-NMR (C_6D_6), UV–vis–near IR, and mass spectra were in agreement with reported data [64,67].

7.1.7. Ln = Gd

The IR spectrum was in agreement with the reported data [64]. Mass spectrum, *m*/*z* (int): 353 [8%, $Gd(C_5H_5)_3^+$]; 288 [28, $Gd(C_5H_5)_2^+$]; 260 [4, $GdC_8H_6^+$]; 247 [1, $Gd(C_7H_5)^+$]; 223 [7, $Gd(C_5H_5)^+$]; 195 [1, GdC_3H^+]; 176.5 [0.5, $Gd(C_5H_5)_3^{2+}$]; 144 [1, $Gd(C_5H_5)_2^{2+}$]; 73 [50, $C_4H_9O^+$]; 72 [4, $C_4H_8O^+$]; 66 [95, $C_5H_6^+$]; 65 [58, $C_5H_5^+$].

7.1.8. Ln = Dy

Mass spectrum was in agreement with reported data [69]. ^{1}H-NMR (C_6D_6): 152, v br, C_5H_5; 14.1, v br, THF. The resonances were too broad for satisfactory integration. UV–vis–near IR: 359, 362, 368, 803, 899, 905, 912, 975, 1076, 1089, 1095, 1110, 1115, 1120, 1156, 1237, 1244, 1258, 1266, 1271, 1284, 1301, 1322, 1327, 1335, 1343, 1355, 1404 nm.

7.1.9. Ln = Er

The IR, and UV–vis–near IR, spectra were in agreement with reported data [64,70]. ^{1}H-NMR (C_6D_6): 23.3, br s, C_5H_5; 2.74, br s, 4H, THF; 1.34, br s, 4H, THF. Mass spectrum, *m*/*z* (int): 563 [0.03%, $Er(C_{17}H_{15})^+$]; 497 [0.03, $Er_2(C_5H_5)_2F_2$]; 433 [0.02, $Er(C_5H_5)_3(C_4H_4O)^+$]; 404 [0.02, $Er(C_5H_5)_3(C_2H_3O)^+$]; 361 [15%, $Er(C_5H_5)_3^+$]; 296 [86, $Er(C_5H_5)_2^+$]; 231 [12, $Er(C_5H_5)^+$]; 180 [4, $Er(C_5H_5)_3^{2+}$]; 168 [8, Er^+]; 148 [2, $Er(C_5H_5)_2^{2+}$]; 73 [9, $C_4H_9O^+$]; 72 [1, $C_4H_8O^+$]; 66 [100, $C_5H_6^+$]; 65 [50, $C_5H_5^+$].

7.1.10. Ln = Tm

IR, ^{1}H-NMR (C_6D_6), and UV–vis–near IR spectra were in agreement with reported data [71,72]. Mass spectrum, *m*/*z* (int): 364 [24%, $Tm(C_5H_5)_3^+$]; 323 [0.5, $TmC_{12}H_{10}^+$]; 299 [100, $Tm(C_5H_5)_2^+$]; 271 [1, $TmC_8H_6^+$]; 234 [43, $Tm(C_5H_5)^+$]; 207 [2, TmC_3H^+]; 182 [2, $Tm(C_5H_5)_3^{2+}$]; 169 [30, Tm^+]; 73 [2, $C_4H_9O^+$]; 72 [6, $C_4H_8O^+$]; 66 [17, $C_5H_6^+$]; 65 [6, $C_5H_5^+$].

7.1.11. Ln = Lu

^{1}H-NMR (C_6D_6) spectrum was in agreement with reported data [67]. Mass spectrum, *m*/*z* (int): 370 [18%, $Lu(C_5H_5)_3^+$]; 305 [62, $Lu(C_5H_5)_2^+$]; 240 [8, $Lu(C_5H_5)^+$]; 185 [5, $Lu(C_5H_5)_3^{2+}$]; 175 [4, Lu^+]; 73 [1.5, $C_4H_9O^+$]; 72 [1, $C_4H_8O^+$]; 66 [100, $C_5H_6^+$]; 65 [49, $C_5H_5^+$].

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