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Organotin Compounds as Reagents for the Synthesis of Lanthanoid Complexes by Redox Transmetallation Reactions

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Redox transmetallation reactions between trimethyltin compounds, $SnMe_3L$ [L = 3,5-diphenylpyrazolate (Ph_2pz), 2,6-di-*tert*-butyl-4-methylphenolate (OAr), or C_6F_5] and lanthanoid metals have yielded $[Ln(Ph_2pz)_2(DME)_2]$ (Ln = Eu, Yb), $[Ln(Ph_2pz)_3(DME)_2]$ (Ln = Y, La, Nd, Eu), $[Ln(Ph_2pz)_3(THF)_3]$ (Ln = Nd, Sm), $[Ln(Ph_2pz)_3(THF)_2]$ (Ln = Y, Yb), $[Sm(OAr)_3(THF)]$, $[Yb(OAr)_2(THF)_3]$, and $[Yb(C_6F_5)_2(THF)_4]$ complexes in yields generally competitive with those from other methods, and hexamethylditin. The crystal structures of $[Nd(Ph_2pz)_3(DME)_2]\cdot DME$, $[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$, and $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$ were determined. All have nine-coordination of the lanthanoid atom and three η^2-Ph_2pz ligands, the first two also having an η^1- and an η^2-DME ligand and the last having three THF ligands.

Introduction

Redox transmetallation reactions between lanthanoid metals and mercury or thallium compounds [Equations (1) and (2); n = 2, 3] have become an important route to rare earth organometallic compounds, organoamides, aryl oxides,[1] and thiolates.[2]

$$Ln + n/2\ HgL_2 \rightarrow Ln(L)_n + n/2\ Hg \quad (1)$$

$$Ln + n\ TlL \rightarrow Ln(L)_n + n\ Tl \quad (2)$$

On the other hand, there has been only one example of redox transmetallation between a tin reagent and a lanthanoid metal; viz formation of an ytterbium(II) organoamide from an Sn^{II} precursor,[3] despite the widespread use of tin reagents in *non-redox* transmetallations.[4] Trialkyltin compounds can be envisaged as potential redox transmetallation reagents for the preparation of lanthanoid complexes [Equation (3)].

$$Ln + n\ SnR_3L \rightarrow Ln(L)_n + n/2\ Sn_2R_6 \quad (3)$$

Encouragement that such syntheses may be possible comes from the oxidation of bis(*tert*-butylcyclopentadienyl)-samarium(II) by trimethyltin fluoride to give the corresponding organosamarium(III) fluoride [Equation (4)].[5]

$$6\ [Sm(\eta^5\text{-}C_5H_4tBu)_2(THF)_2] + 6\ SnMe_3F \rightarrow 2\ [Sm(\eta^5\text{-}C_5H_4tBu)_2F]_3 + 3\ Sn_2Me_6 \quad (4)$$

However, the reduction of hexaphenylditin and triphenyltin halide by ytterbium giving $[Yb(SnPh_3)_2]$[6] sends a note of warning especially if excess Ln metal is used, despite the high E_0 value (–2.9 V) for reduction of $Ph_3SnSnPh_3$.[7]

Lead(II) compounds have also been used as oxidants,[8] and an attempted use in redox transmetallation unexpectedly gave a Pb/La dimetallic compound.[9] We now report proof of concept of reaction according to Equation (3) by syntheses of a range of lanthanoid pyrazolates and aryl oxides generally in good yield from appropriate trimethyltin reagents. In addition, in situ formation of $Yb(C_6F_5)_2$ from $SnMe_3(C_6F_5)$ has been demonstrated.

Results and Discussion

The outcomes of the reactions of trimethyltin 3,5-diphenylpyrazolate [$SnMe_3(Ph_2pz)$],[10] trimethyltin 2,6-di-*tert*-butyl-4-methylphenolate [$SnMe_3(OAr)$] and trimethyl(pentafluorophenyl)tin with lanthanoid metals in 1,2-dimethoxyethane and tetrahydrofuran are summarised in Scheme 1. Reactions with $SnMe_3(Ph_2pz)$ gave both trivalent $[Ln(Ph_2pz)_3(DME)_2]$ (Ln = Y, La, Nd, Eu), $[Ln(Ph_2pz)_3(THF)_3]$ (Ln = Nd, Sm), $[Ln(Ph_2pz)_3(THF)_2]$ (Ln = Y, Yb) and divalent $[Ln(Ph_2pz)_2(DME)_2]$ (Ln = Eu, Yb) pyrazolate complexes [Equations (5) and (6); L = Ph_2pz; S = DME or THF].

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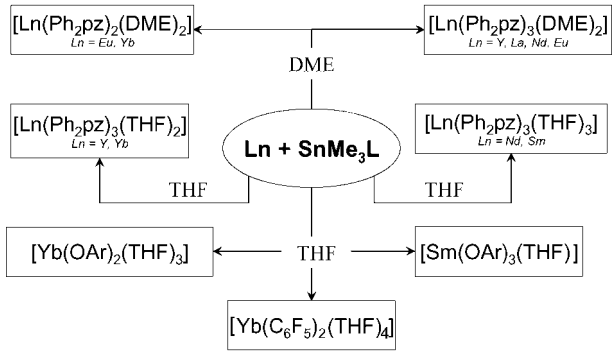
$$2\ Ln + 6\ SnMe_3L \xrightarrow{S} 2\ [LnL_3(S)_n] + 3\ Sn_2Me_6 \quad (5)$$

$$Ln + 2\ SnMe_3L \xrightarrow{S} [LnL_2(S)_n] + Sn_2Me_6 \quad (6)$$



Scheme 1. Redox transmetallation reactions between $SnMe_3L$ and Ln metals.

Similarly, $[Sm(OAr)_3(THF)]$ and $[Yb(OAr)_2(THF)_3]$ were obtained from analogous reactions of lanthanoid metals with $SnMe_3(OAr)$ in tetrahydrofuran [reactions according to Equations (5) and (6); Ln = Sm, Yb; L = OAr; S = THF]. Formation of hexamethylditin in all reactions was established by ^1H NMR spectroscopy[11] and in one case also by ^{119}Sn NMR spectroscopy.[12] Thus, the ^{119}Sn NMR spectrum of the filtrate after isolation of $[Yb(OAr)_2(THF)_3]\cdot THF$ showed the presence of a resonance attributable to Sn_2Me_6.[12] There was no resonance near δ = –95 ppm where the signal of the Yb–Sn-bonded species $[Yb\{Sn(CH_2tBu)_3\}_2(THF)_2]$ is observed,[13] suggesting significant amounts of $Yb(SnMe_3)_2$ are not formed despite the use of a large excess of Yb metal. Reactions were carried out with activation of the lanthanoid metal by Hg metal. Without activation, reactions occurred, but were slower. Initiation of reactions was faster in DME than in THF. Variation of the excess of europium metal in the reactions of $SnMe_3(Ph_2pz)$ in DME enabled either the Eu^{II} or Eu^{III} product to be obtained (Scheme 1) in good yield. On the other hand, the corresponding reaction of Yb metal has a solvent-dependent outcome, yielding a Yb^{II} complex in DME but a Yb^{III} complex in THF (Scheme 1), even though a greater excess of Yb metal was utilised for the latter. In THF, a deep orange-red colour suggestive of some Yb^{II} was observed after sonication, but the solution turned yellow after removal from the excess of Yb due to oxidation by $SnMe_3(Ph_2pz)$ [Equation (7)].

$$2\ Yb(Ph_2pz)_2 + 2\ SnMe_3(Ph_2pz) \rightarrow 2\ Yb(Ph_2pz)_3 + Sn_2Me_6 \quad (7)$$

Reactions according to Equations (5) and (6) generally give yields comparable with those of alternative routes (Table 1). However, $[Nd(Ph_2pz)_3(DME)_2]$, $[Nd(Ph_2pz)_3(THF)_3]$, and $[Sm(Ph_2pz)_3(THF)_3]$ are obtained in higher yield by the present method, but $[Ln(Ph_2pz)_3(THF)_2]$ (Ln = Y, Yb) in lower yield. In addition, $[Ln(Ph_2pz)_3(DME)_2]$ (Ln = Y, Eu), and $[Sm(Ph_2pz)_3(THF)_3]$ are new complexes, while $[Nd(Ph_2pz)_3(DME)_2]\cdot DME$ is a new solvate. The last complex has previously been isolated as an unsolvated powder[14] and as a C_6D_6 solvate.[15] Of special interest is the formation of $[Yb(Ph_2pz)_3(THF)_2]$ by reaction according to Equation (5), as attempts to prepare this complex from Yb metal, $Hg(C_6F_5)_2$ and Ph_2pzH led to gross decomposition,[16a] and the corresponding reaction using $HgPh_2$, and redox transmetallation between Yb metal and $Tl(Ph_2pz)$ both yielded Yb^{II} complexes.[16b] Thus, previous access to $[Yb(Ph_2pz)_3(THF)_2]$ required a two-step synthesis[17] (Table 1). Attempted reaction of Yb metal with $SnMe_3(C_6F_5)$ in tetrahydrofuran at room temperature for 2 d failed, but, after 1 d of ultrasonication, incomplete formation of $Yb(C_6F_5)_2$ [Equation (6); Ln = Yb; L = C_6F_5] was detected. By contrast, redox transmetallation between Yb and $Hg(C_6F_5)_2$ in tetrahydrofuran requires only a few minutes induction and is complete in 4 h.[1c]

Table 1. Comparison of yields of $Ln(L)_n$ complexes of the current study with literature methods.

$Ln(Ph_2pz)_n(S)_m$	Ln + $SnMe_3L$	Reported	Method
$[Y(Ph_2pz)_3(DME)_2]\cdot DME$	80	–	–
$[La(Ph_2pz)_3(DME)_2]$	82	77[a]	La/Ph_2pzH/$Hg(C_6F_5)_2$[a]
$[Nd(Ph_2pz)_3(DME)_2]\cdot DME$	79	17[a]	Nd/Ph_2pzH/$Hg(C_6F_5)_2$[a]
$[Eu(Ph_2pz)_2(DME)_2]$	88	90[b]	Eu/$Tl(Ph_2pz)$[b]
$[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$	70	–	–
$[Yb(Ph_2pz)_2(DME)_2]$	80	66[c]	several[c]
$[Y(Ph_2pz)_3(THF)_2]$	54	76[d]	Y/Ph_2pzH/$Hg(C_6F_5)_2$[d]
$[Nd(Ph_2pz)_3(THF)_3]\cdot THF$	97	69[e]	Nd/Ph_2pzH/$Hg(C_6F_5)_2$[e]
$[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$	96	72[f]	Sm/Ph_2pzH/$Hg(C_6F_5)_2$[f]
$[Yb(Ph_2pz)_3(THF)_2]$	51	64[g]	Yb/$Tl(Ph_2pz)$ + oxid. with $Tl(Ph_2pz)$[g]
$[Sm(OAr)_3(THF)]\cdot THF$	45	49[h]	metathesis[h]
$[Yb(OAr)_2(THF)_3]\cdot THF$	87	76[i]	several[i]

[a] Ref.[14] [b] Ref.[16a] [c] Ref.[16b] [d] Ref.[18] [e] Ref.[19] [f] This work. [g] Ref.[17] [h] Ref.[20] [i] Ref.[21]

Known complexes (Table 1) were characterised by lanthanoid metal analyses, IR spectroscopy and ^1H NMR spectroscopy, which confirmed the DME or THF/Ph_2pz or OAr ratio. However, 4-H(pz) and *o*-H(Ph) resonances of $[Nd(Ph_2pz)_3(THF)_3]\cdot THF$ were too broad for satisfactory integrations. Furthermore, single crystals of $[Nd(Ph_2pz)_3(THF)_3]\cdot THF$, $[Yb(Ph_2pz)_2(DME)_2]$ and $[Yb(OAr)_2(THF)_3]\cdot THF$ were grown, and their unit cells are in agreement with the reported data.[16,19,20] In the case of the known[16a] $[Eu(Ph_2pz)_2(DME)_2]$, fifteen of sixteen single crystals examined had unit cell data corresponding to that reported for *trans*-$[Eu(Ph_2pz)_2(DME)_2]$,[16a] the product of redox transmetallation between Eu metal and $Tl(Ph_2pz)$.[16a] However, the values for one crystal were close to those for *cis*-$[Yb(Ph_2pz)_2(DME)_2]$,[16b] and can be attributed to *cis*-$[Eu(Ph_2pz)_2(DME)_2]$. It previously seemed surprising that $[Eu(Ph_2pz)_2(DME)_2]$ crystallised with the Ph_2pz ligands mutually *transoid* when the complex of the

adjacent Sm was isolated *cisoid*[16a] as was *cis*-[Yb(Ph_2pz)$_2$(DME)$_2$].[16b] Although only one crystal of *cis*-[Eu(Ph_2pz)$_2$(DME)$_2$] was identified from the reaction according to Equation (6), its existence is established.

The composition of the new complex Y(Ph_2pz)$_3$(DME)$_3$ was established by microanalysis, metal analysis, and the DME/Ph_2pz ratio by ^{1}H NMR spectroscopy. Single crystals could not be obtained, but as Y^{3+} has a similar size to Er^{3+}, which gives a nine-coordinate [Er(Ph_2pz)$_3$(η^2-DME)(η^1-DME)][14] complex, it is likely the yttrium complex is a nine-coordinate mono-DME solvate [Y(Ph_2pz)$_3$(DME)$_2$]·DME. Besides characterisation by IR and NMR spectroscopy, and lanthanoid metal analyses, the new complexes [Eu(Ph_2pz)$_3$(DME)$_2$]·2DME, [Sm(Ph_2pz)$_3$(THF)$_3$]·3THF and the new solvate [Nd(Ph_2pz)$_3$(DME)$_2$]·DME were characterised by single-crystal X-ray structure determinations (below). For the Nd complex, both 4-H(pz) and *o*-H(Ph) resonances were severely broadened. The DME of solvation was readily lost from crystals of the Eu complex and the %Eu value for the dried complex corresponded to the composition [Eu(Ph_2pz)$_3$(DME)$_2$], whilst the ^{1}H NMR spectra from two separate preparations showed a DME/Ph_2pz ratio of 4:3, as in single crystals, and 3:3. Similarly, the dried product from one preparation of the samarium complex showed a THF/Ph_2pz ratio of 6:3 as in the single crystals, and the product from another a THF/Ph_2pz ratio of 5:3. No other products showed a similar loss of lattice solvent of crystallisation.

The structures of [Eu(Ph_2pz)$_3$(DME)$_2$]·2DME (Figure 1) and the new solvate [Nd(Ph_2pz)$_3$(DME)$_2$]·DME have nine-coordinate lanthanoid atoms with three η^2-Ph_2pz ligands, one chelating DME and one (less usual[22]) unidentate DME. Selected bond lengths and angles are given in Table 2. The complexes have similar connectivity to unsolvated [Er(Ph_2pz)$_3$(DME)$_2$][14] and [Nd(Ph_2pz)$_3$(DME)$_2$]·2C_6D_6,[15] but there are differences in the structural details. Notably, the uncoordinated end of the unidentate DME points away from the metal atom in the present complexes [Eu···O(2)$_{nonbonding}$ 5.47 Å, Nd···O(2)$_{nonbonding}$ 5.41 Å; Eu–O(1)···O(2) 162°, Nd–O(1)···O(2) 153°] more markedly than in the erbium complex (4.62 Å/122°) and the neodymium C_6D_6 solvate (4.92 Å/129°). Plausibly, packing effects associated with differing solvation in the crystals [2 DME (Eu), 1 DME (Nd) (this study); 0 DME (Er);[14] 2 C_6D_6 (Nd)[15]] affect the arrangements of the η^1-DME ligand. All Ph_2pz and η^2-DME ligands are nearly symmetrically chelating with only a small divergence in Ln–N (0.01–0.05 Å) and Ln–O (η^2-DME) (0.01–0.03 Å) bond lengths (Table 2). Nevertheless, the differences between Nd–N bond lengths of each chelating pair in the DME solvate (0.018, 0.054, 0.012 Å) (Table 2) are slightly larger than in the C_6D_6 solvate (0.008, 0.026, 0.005 Å).[15] For [Eu(Ph_2pz)$_3$(DME)$_2$]·2DME (Table 2) and [Nd(Ph_2pz)$_3$(DME)$_2$]·2C_6D_6,[15] the Ln–O (η^1-DME) distance lies between the values for Ln–O (η^2-DME), whereas for [Nd(Ph_2pz)$_3$(DME)$_2$]·DME (Table 2) and the Er complex[14] Ln–O (η^1-DME) is the shortest Ln–O distance. Moreover, the pairings here do not conform to the η^1-DME conformational pairings. Whilst the <Ln–N(O)> distances decline in the sequence Nd, Eu, Er as expected from the lanthanoid contraction, <Eu-N>

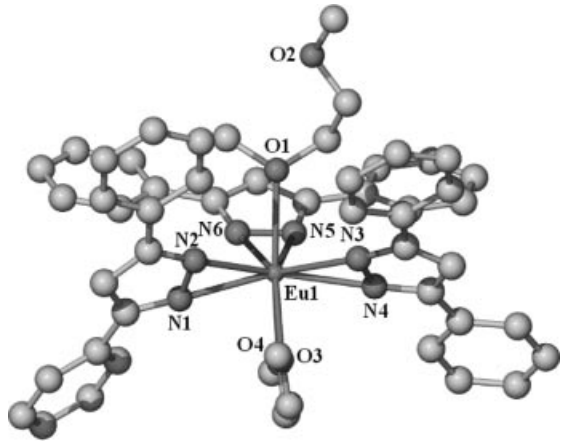


Figure 1. Molecular structure of [Eu(Ph_2pz)$_3$(DME)$_2$]·2DME. Selected bond lengths [Å] and angles [°] for this structure and the near isostructural Nd complex are given in Table 2. Only one disordered position of η^2-DME shown for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for the new Ln(Ph_2pz)$_n$ complexes.

	[Nd(Ph_2pz)$_3$(DME)$_2$]·DME	[Eu(Ph_2pz)$_3$(DME)$_2$]·2DME	[Sm(Ph_2pz)$_3$(THF)$_3$]·3THF			
Bond lengths			Molecule 1		Molecule 2	
Ln(1)–N(1)	2.452(3)	2.411(3)	Sm(1)–N(1)	2.428(4)	Sm(2)–N(7)	2.439(4)
Ln(1)–N(2)	2.470(3)	2.424(3)	Sm(1)–N(2)	2.463(4)	Sm(2)–N(8)	2.423(4)
Ln(1)–N(3)	2.485(3)	2.454(3)	Sm(1)–N(3)	2.435(4)	Sm(2)–N(9)	2.450(4)
Ln(1)–N(4)	2.430(3)	2.418(3)	Sm(1)–N(4)	2.418(4)	Sm(2)–N(10)	2.425(4)
Ln(1)–N(5)	2.451(2)	2.436(3)	Sm(1)–N(5)	2.415(4)	Sm(2)–N(11)	2.467(4)
Ln(1)–N(6)	2.462(2)	2.423(3)	Sm(1)–N(6)	2.460(4)	Sm(2)–N(12)	2.428(4)
Ln(1)–O(1)	2.526(2)	2.505(2)	Sm(1)–O(1)	2.507(3)	Sm(2)–O(4)	2.627(3)
Ln(1)–O(3)	2.558(2)	2.532(3)	Sm(1)–O(2)	2.588(3)	Sm(2)–O(5)	2.520(3)
Ln(1)–O(4)	2.576(2)	2.504(2)	Sm(1)–O(3)	2.517(3)	Sm(2)–O(6)	2.498(3)
Bond angles						
O(1)–Ln(1)–O(3)	140.87(7)	134.91(8)	O(1)–Sm(1)–O(2)	76.25(11)	O(4)–Sm(2)–O(5)	74.47(11)
O(1)–Ln(1)–O(4)	156.04(7)	160.42(8)	O(1)- Sm(1)–O(3)	159.00(12)	O(4)–Sm(2)–O(6)	131.23(11)
O(3)–Ln(1)–O(4)	63.05(7)	64.14(8)	O(2)–Sm(1)–O(3)	124.48(11)	O(5)–Sm(2)–O(6)	153.80(11)

exceeds <Er-N> by more (0.09 Å) than than expected (0.06 Å) from ionic radii,[23] whereas the corresponding <Ln–O> difference is less (0.03 Å) than expected.

$[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$ has nine-coordination for samarium with three η^2-Ph_2pz and three THF ligands (Figure 2). It is isostructural with $[Nd(Ph_2pz)_3(THF)_3]\cdot THF$, which was isolated as a mono-THF solvate,[19] whereas the present complex has two closely related independent molecules and six THF solvent molecules in the asymmetric unit. The Sm–O bond lengths are very similar to the Nd–O bond lengths,[23] despite the expectation of a 0.03 Å difference based on ionic radii.[23] Molecule 2 has almost identical O–Ln–O angles to those of the Nd complex, but molecule 1 shows some deviation. More symmetrical η^2-Ph_2pz bonding is observed in the present complex, and <Sm–N> is 0.02 Å shorter than <Nd–N>, near ionic radius expectations.[23]

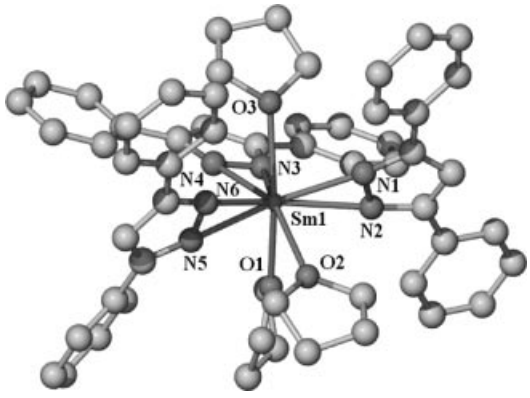


Figure 2. Molecular structure of $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$. One of the two independent but closely related molecules is displayed.

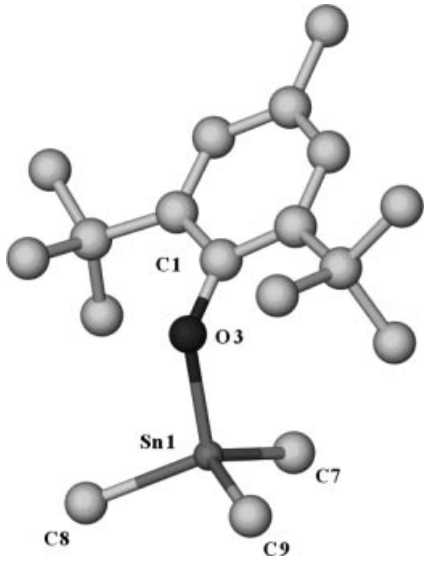


Figure 3. Molecular structure of $[SnMe_3(OAr)]$. Selected bond lengths [Å] and angles [°]: Sn(1)–O(3) 2.0082(15), O(3)–C(1) 1.363(3), Sn(1)–C(7) 2.127(2), Sn(1)–C(8) 2.139(3), Sn(1)–C(9) 2.127(3); C(1)–O(3)–Sn(1) 133.77(14), O(3)–Sn(1)–C(7) 105.56(9), O(3)–Sn(1)–C(8) 104.31(9), O(3)–Sn(1)–C(9) 106.44(9), C(7)–Sn(1)–C(8) 113.92(11), C(7)–Sn(1)–C(9) 117.10(11), C(8)–Sn(1)–C(9) 108.42(11).

An X-ray crystal structure was also obtained for the $[SnMe_3(OAr)]$ reagent (Figure 3). The compound is essentially isostructural with the known $[SiMe_3(OAr)]$.[24] The coordination environment around the tin atom is distorted tetrahedral. However, the C–O–Sn angle is significantly smaller than the C–O–Si angle within the silicon analogue,[24] presumably owing to reduced steric crowding by the *tert*-butyl groups due to the increased ionic radius of tin.

Conclusions

This study shows that organotin(IV) compounds can be used in redox transmetallation reactions with lanthanoid elements to provide metal–organic lanthanoid complexes [Equations (5) and (6)]. Although their initial reactivity is somewhat lower than that of the analogous Tl^I reagents or redox transmetallation with HgR_2 and LH, comparable or in some cases better yields have been obtained with the tin reagents (Table 1). Moreover, the different reactivity has enabled both Eu^{II} and Eu^{III} complexes to be isolated and a different Yb oxidation state outcome than with previous redox transmetallation methods. Besides variation of the alkyl groups, there is opportunity for considerable modulation of the tin reagents, e.g. (i) use of $SnMe_3Ar$ reagents with lanthanoid metals and protic reagents such as pyrazoles, phenols, and amines in redox transmetallation/ligand exchange, and (ii) exploration of $Sn^{VI} \rightarrow Sn^{II}$ reduction with the potentially more transfer efficient $SnMe_2L_2$ reagents. Evidence that Yb metal reacts with $SnMe_3(C_6F_5)$ to give $Yb(C_6F_5)_2$ in solution provides encouragement for the use of this compound in redox transmetallation/ligand exchange.

Experimental Section

General Remarks: All reactions were carried out under dry nitrogen using standard Schlenk and dry-box equipment. THF was freshly distilled from sodium/benzophenone, while DME was distilled from sodium. Infrared spectra (4000–650 cm^{-1}) were recorded as Nujol mulls with a Perkin–Elmer 1600 FTIR spectrophotometer. ^1H NMR spectra were recorded with a Bruker DPX 300 MHz spectrometer using dry degassed deuteriobenzene or deuteriotetrahydrofuran solvents at 25 °C; resonances were referenced to residual hydrogen from the solvent. ^{119}Sn NMR spectra were obtained with a Bruker DRX 400 spectrometer and were referenced to tetramethyltin. ^{19}F NMR spectra were recorded with a Bruker DPX 300 spectrometer and were referenced to external $CFCl_3$. ^1H NMR spectra of all solutions following reactions of lanthanoid metals with $SnMe_3L$ reagents showed the presence of Sn_2Me_6 (δ = 0.20 ppm; $J_{^{117}Sn-CH_3}$ = 46.4 Hz, $J_{^{119}Sn-CH_3}$ = 48.4 Hz).[11] Metal analyses of the lanthanoid complexes were performed by EDTA titration with xylenol orange indicator following digestion in concentrated nitric and sulfuric acids and buffering with hexamine.[16a] Microanalysis samples were sealed in glass ampoules under purified N_2 and were determined by the Campbell Microanalytical service, University of Otago, New Zealand. 3,5-Diphenylpyrazole and

$SnMe_3(Ph_2pz)$ were prepared as reported.[25,10] A modification (LiC_6F_5 instead of MgC_6F_5Br) of the reported method[26] was used to obtain $SnMe_3(C_6F_5)$, which was distilled under reduced pressure and had IR and ^{19}F NMR spectra as reported.[26] Bis(pentafluorophenyl)mercury $Hg(C_6F_5)_2$ was prepared by a literature method.[27]

(2,6-Di-*tert*-butyl-4-methylphenolato)trimethyltin(IV). Method (a): *n*-Butyllithium (11.2 mL, 1.6 M in hexanes, 18.0 mmol) was added dropwise to pre-dried 2,6-di-*tert*-butyl-4-methylphenol (3.30 g, 15.0 mmol) in Et_2O (50 mL), and the mixture was stirred for 1 h. Trimethyltin chloride (14.97 mL, 1.0 M in hexanes, 14.97 mmol) was then added dropwise. After stirring the reaction mixture overnight, the diethyl ether solution was filtered and the filtrate concentrated to crystallisation. Data of the crude product, which contained traces of lithium phenolate (NMR identification): IR: $\tilde{\nu}$ = 2726 w, 1603 w, 1418 vs, 1346 s, 1263 s, 1233 s, 1216 m, 1194 m, 1118 w, 1023 w, 918 w, 886 s, 861 m, 822 m, 772 m, 722 m cm^{-1}. ^1H NMR (C_6D_6): δ = 0.34 (s, $^2J_{H,^{117}Sn}$ = 53 Hz, $^2J_{H,^{119}Sn}$ = 57 Hz, 9 H, Me_3Sn), 1.51 (s, 18 H, *t*Bu), 2.32 (s, 3 H, Me), 7.20 (s, 2 H, 3,5-H) ppm. Extraction with hexane and concentration of the solvent yielded pure $SnMe_3OAr$ as colourless crystals (1.99 g, 35%), identified by X-ray crystallography (below). $^{119}Sn\{^1H\}$ NMR (149 MHz, C_6D_6, 25 °C): δ = 131.5 ppm. **Method (b):** Excess of $SnMe_3Cl$ (1.80 g; 9.05 mmol) was added to a solution of lithium 2,6-di-*tert*-butyl-4-methylphenolate (LiOAr) (1.33 g; 5.90 mmol) in Et_2O (50 mL), and the resulting solution was stirred at room temperature overnight. After filtration through a filter cannula, the Et_2O was removed under vacuum yielding a very fine crystalline material, which was washed with 3×10 mL of hexane to remove $SnMe_3Cl$. M.p. 138–140 °C;1.35 g, 55%. The ^1H NMR spectrum (C_6D_6) as above, was void of LiOAr resonances. $C_{18}H_{32}OSn$ (383.16): calcd. C 56.42, H 8.41; found C 56.56, H 8.22.

Redox Transmetallation Reactions

Preparation of Bis(3,5-diphenylpyrazolato)lanthanoid(II) and Tris(3,5-diphenylpyrazolato)lanthanoid(III) Complexes: DME or THF (50 mL) was added to excess lanthanoid metal (powder or filings), $SnMe_3(Ph_2pz)$ and 1–2 drops of mercury. The resulting mixture was stirred or sonicated at room temperature usually for 5 d. A colour change was observed for most reactions within 4 h (Yb: 1 h). The filtrate was collected by a filter cannula, and the solvent volume reduced to 15 mL. Crystalline or powdered $Ln(Ph_2pz)_n$ (n = 2,3) compounds were obtained by cooling of the concentrated solutions to –20 °C. In all cases, the ^1H NMR spectrum of the crude product was obtained to verify Sn_2Me_6 formation.[11] The product was then washed with hexane to remove Sn_2Me_6, and dried briefly under vacuum.

$[Y(Ph_2pz)_3(DME)_2]\cdot DME$: Y metal powder (0.59 g; 6.62 mmol) and $SnMe_3(Ph_2pz)$ (0.50 g; 1.32 mmol) in DME, stirred for 5 d, gave colourless crystals;0.36 g, 80%. IR: $\tilde{\nu}$ = 1603 m, 1512 w, 1420 w, 1260 m, 1225 w, 1192 w, 1154 w, 1130 w, 1107 m, 1072 m, 1057 s, 1026 m, 1000 w, 972 vs, 912 m, 872 s, 804 m, 794 m, 758 vs, 704 s, 696 vs, 688 s cm^{-1}. ^1H NMR (C_6D_6): δ = 2.98 (br. s, 18 H, CH_3-*DME*), 3.10 (br. s, 12 H, CH_2-*DME*), 7.04–7.07 (br. t, 6 H, *p*-H), 7.08 (s, 3 H, 4-H), 7.14 (br. s, 12 H, *m*-H), 7.90–7.93 (br. d, 12 H, *o*-H) ppm. $C_{57}H_{63}N_6O_6Y$ (1017.05): calcd. C 67.31, H 6.24, N 8.26, Y 8.74; found C 66.73, H 6.60, N 8.22, Y 8.91.

$[La(Ph_2pz)_3(DME)_2]$: La powder (1.03 g; 7.44 mmol) and $SnMe_3(Ph_2pz)$ (0.50 g; 1.31 mmol) in DME, stirred for 5 d, gave a white powder; 0.35 g, 82%. The IR spectrum is similar to that reported.[14] ^1H NMR (C_6D_6): δ = 3.02 (br. s, 12 H, CH_3-*DME*), 3.17 (br. s, 8 H, CH_2-*DME*), 7.01–7.12 (m, 21 H, *m*-H, *p*-H, 4-H), 7.86 (br. s, 12 H, *o*-H) ppm. $C_{53}H_{53}LaN_6O_4$ (976.93): calcd. La 14.22; found La 14.51.

$[Nd(Ph_2pz)_3(DME)_2]\cdot DME$: Nd metal powder (0.94 g; 6.55 mmol) and $SnMe_3(Ph_2pz)$ (0.52 g; 1.36 mmol) in DME, stirred for 5 d, gave lavender-blue crystals; 0.38 g, 79%. The IR spectrum is in agreement with that of $[Nd(Ph_2pz)_3(DME)_2]$.[15] ^1H NMR (C_6D_6): δ = –3.41 (br. s, 12 H, CH_2-*DME*), 0.29 (s, 18 H, CH_3-*DME*), 8.08-8.22 (m, 18 H, *m*-H, *p*-H), 12.4 (v. br. s, *o*-H), 17.8 (v. br. s, 4-H) ppm. $C_{57}H_{63}N_6NdO_6$ (1072.39): calcd. Nd 13.45; found Nd 13.71. X-ray crystallography established the composition $[Nd(Ph_2pz)_3(DME)_2]\cdot DME$.

$[Eu(Ph_2pz)_2(DME)_2]$: Eu metal filings (2.52 g, 16.6 mmol) and $SnMe_3(Ph_2pz)$ (0.60 g, 1.57 mmol) in DME, sonicated for 5 d, gave deep yellow crystals; 1.06 g, 88%. The IR spectrum is identical with that reported.[16a] ^1H NMR (C_6D_6): δ = 0.43 (br. s, 8 H, CH_2-*DME*), 0.92 (br. s, 12 H, CH_3-*DME*), 1.32–2.09 (br. m, 22 H, 4-H, *p*-, *m*-, *o*-H) ppm. $C_{38}H_{42}EuN_4O_4$ (770.73): calcd. Eu 19.73; found Eu 19.26. X-ray crystallographic examination of the yellow crystals gave *one* crystal: monoclinic, space group $P2_1/a$, a = 7.8740, b = 18.8715, c = 23.9260 Å; β = 91.042°, V = 3554.67 $Å^3$; isomorphous with *cis*-$[Yb(Ph_2pz)_2(DME)_2]$[16b] [monoclinic, space group $P2_1/a$, a = 7.882(4), b = 18.959(3), c = 24.080(14) Å; β = 91.03(2)°, V = 3598(3) $Å^3$] and *fifteen* crystals of *trans*-$[Eu(Ph_2pz)_2(DME)_2]$, monoclinic, space group $P2/c$, a = 14.9771, b = 12.5269, c = 19.6728 Å; β = 109.398°, V = 3481.40 $Å^3$, in agreement with reported data[16a] [monoclinic, space group $P2/c$, a = 19.746(3), b = 12.635(2), c = 15.396(2) Å; β = 110.12(1)°, V = 3607 $Å^3$].

$[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$: Eu metal chunks (0.73 g, 4.80 mmol) and $SnMe_3(Ph_2pz)$ (0.53 g, 1.38 mmol) in DME, stirred for 3 d, gave golden yellow crystals; 0.38 g, 70%. IR: $\tilde{\nu}$ = 1604 m, 1246 w, 1192 m, 1124 m, 1107 m, 1057 s, 1026 m, 971 s, 916 w, 865 m, 800 w, 758 vs, 724 w, 696 s, 684 s, 666 w cm^{-1}. ^1H NMR (C_6D_6): δ = 0.23 (s, 3 H, 4-H), 2.09-3.68 (br. s, 40 H, CH_3 and CH_2-DME), 7.01-8.56 (m, 30 H, *o*-, *m*-, *p*-H) ppm. Metal analysis on dried crystals for $C_{53}H_{53}EuN_6O_4$ (loss of DME of solvation) (989.99): calcd. Eu 15.35; found Eu 15.36. Single crystals were obtained from another preparation that involved sonication of the DME mixture of Eu metal chunks and $SnMe_3(Ph_2pz)$ for 3 d (yield <5%). X-ray crystallographic examination revealed the composition $[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$. The ^1H NMR spectrum in $[D_8]THF$ showed loss of 1DME of solvation (C_4D_8O): δ = 3.47–3.59 (m, 30 H, CH_3-, CH_2-*DME*), 5.16 (s, 3 H, 4-H), 7.35 (br. t, 18 H, *m*- and *p*-H), 7.84 (d, 12 H, *o*-H) ppm.

$[Yb(Ph_2pz)_2(DME)_2]$: Yb metal filings (1.20 g, 6.96 mmol) and $SnMe_3(Ph_2pz)$ (0.66 g, 1.72 mmol) in DME, sonicated for 5 d, gave deep red crystals; 0.54 g, 80%. The IR spectrum is in agreement with that reported.[16b] ^1H NMR (C_6D_6): δ = 3.12 (br. s, 20 H, CH_3, CH_2-*DME*), 7.22 (br. s, 6 H, *p*-H, 4-H), 7.33 (br. s, 8 H, *m*-H), 8.10 (br. s, 8 H, *o*-H) ppm (reasonable agreement with data for a solution in C_4D_8O).[16b] $C_{38}H_{42}N_4O_4Yb$ (791.80): calcd. Yb 21.85; found Yb 20.32. A unit cell, monoclinic, space group $P2_1/a$, a = 7.7214, b = 18.7327, c = 23.8207 Å; β = 91.03°, V = 3445.20 $Å^3$ is in agreement with that of *cis*-$[Yb(Ph_2pz)_2(DME)_2]$[16b] [monoclinic, space group $P2_1/a$, a = 7.882(4), b = 18.959(3), c = 24.080(14) Å; β = 91.03(2)°, V = 3598(3) $Å^3$].

$[Y(Ph_2pz)_3(THF)_2]$: Y metal powder (1.01 g; 11.36 mmol) and $SnMe_3(Ph_2pz)$ (0.61 g; 1.60 mmol) in DME, sonicated for 5 d, gave a white powder; 0.26 g, 54%. The IR spectrum is identical with that reported.[18] ^1H NMR (C_6D_6): δ = 1.36 (s, 8 H, CH_2-*THF*), 3.43 (br. s, 8 H, CH_2-*THF*), 6.91 (br. s, 6 H, *p*-H), 7.02 (br. t, 12 H, *m*-H), 7.17 (br. s, 3 H, 4-H), 7.71 (br. s, 12 H, *o*-H) ppm. $C_{53}H_{49}N_6O_2Y$ (890.90): calcd. Y 9.98; found Y 9.28.

$[Nd(Ph_2pz)_3(THF)_3]\cdot THF$: Nd metal powder (0.95 g; 6.57 mmol) and $SnMe_3(Ph_2pz)$ (0.57 g; 1.49 mmol) in THF, stirred for 5 d, gave

lavender-blue crystals; 0.51 g, 97%. The IR spectrum is identical with that reported.[19] ^{1}H NMR (C_6D_6): δ = –5.59 (br. s, 16 H, CH_2-*THF*), –2.78 (br. s, 16 H, CH_2-*THF*), 7.90–8.01 (br. s, 18 H, *m*-H, *p*-H), 12.37–12.62 (v. br. s, *o*-H), 17.95–17.98 (v. br. s, 4-H) ppm. $C_{61}H_{65}N_6NdO_4$ (1090.45): calcd. Nd 13.22; found Nd 13.58. A unit cell on the lavender blue crystals, orthorhombic, space group $P2_12_12_1$, a = 14.18(2), b = 16.26(1), c = 22.78(2) Å; V = 5254(8) Å^3 is identical with that of $[Nd(Ph_2pz)_3(THF)_3]\cdot THF$[19] [orthorhombic, space group $P2_12_12_1$, a = 14.009(9), b = 16.280(8), c = 22.640(16) Å; V = 5163(5) Å^3].

$[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$. Method (a). $SnMe_3(Ph_2pz)$ with Sm Metal in THF: Sm metal powder (1.59 g; 10.6 mmol) and $SnMe_3(Ph_2pz)$ (0.52 g; 1.36 mmol) in THF, stirred for 5 d, then sonicated for 1 d, gave a brownish/yellow precipitate; 0.54 g, 96%. IR $\tilde{\nu}$ = 1602 m, 1562 w, 1424 w, 1298 w, 1225 w, 1154 w, 1071 m, 1050 (sh), 1026 m, 970 s, 915 m, 869 m, 803 w, 757 s, 697 m, 669 w cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.91 (m, 24 H, CH_2-*THF*), 2.66 (m, 24 H, CH_2-*THF*), 7.29 (t, 6 H, *p*-H), 7.60 (t, 12 H, *m*-H), 7.83 (s, 3 H, 4-H), 9.48 (d, 12 H, *o*-H) ppm. $C_{69}H_{81}N_6O_6Sm$ (1240.78): calcd. Sm 12.12; found Sm 11.98. In a similar reaction, sonicating the same amounts of Sm and $SnMe_3(Ph_2pz)$ for 6 d, the filtrate, after isolation of the bulk product as a powder, was allowed to stand for a few months and deposited single crystals of $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$ (0.16 g, 30%). The IR spectrum and ^{1}H NMR chemical shifts agree with those of the above preparation, but the solid had lost 1THF of solvation. An X-ray structure determination of the colourless crystals found two $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$ molecules in the unit cell (see below). **Method (b):** Sm powder (0.22 g; 1.50 mmol), bis(pentafluorophenyl)mercury (0.80 g; 1.50 mmol) and 3,5-diphenylpyrazole (0.66 g; 3.00 mmol) were stirred in THF (30 mL) at room temperature for 5 d. After filtration through a diatomaceous earth pad, the pale yellow filtrate was concentrated to 2 mL. Petroleum spirit (20 mL) was added causing formation of a white precipitate, which was dried under vacuum for 3.5 h; 0.89 g, 0.72 mmol, 72%. The IR spectrum is as above. $C_{69}H_{81}N_6O_6Sm$ (1240.78): calcd. Sm 12.12; found Sm 12.30.

$[Yb(Ph_2pz)_3(THF)_2]$: Yb metal filings (1.36 g; 7.89 mmol) and $SnMe_3(Ph_2pz)$ (0.55 g; 1.44 mmol) in THF were sonicated for 5 d. The initial deep orange-red solution lightened to a yellow colour after filtration and concentration. A white powder was obtained after evaporation of THF; 0.24 g, 51%. The IR spectrum is similar to that reported.[17] $C_{53}H_{49}N_6O_2Yb$ (975.03): calcd. Yb 17.75; found Yb 18.34.

Preparation of (2,6-Di-*tert*-butyl-4-methylphenolato)lanthanoid(II) and 2,6-Di-*tert*-butyl-4-(methylphenolato)lanthanoid(III) Complexes

$[Sm(OAr)_3(THF)]\cdot THF$: THF (50 mL) was added to a mixture of Sm metal powder (1.52 g; 10.1 mmol), $SnMe_3(OAr)$ (0.89 g; 2.33 mmol) and 2 drops of Hg metal, and the resulting solution was sonicated for 5 d. The deep-coloured solution was filtered through a filter cannula, and THF was removed under vacuum. The precipitate was washed with hexane to remove Sn_2Me_6, giving a yellow powder; 0.33 g, 45%. IR $\tilde{\nu}$ = 1602 w, 1550 w, 1420 m, 1272 s, 1217 w, 1196 w, 1040 s, 918 m, 888 m, 862 m, 818 s, 802 s. 789 s, 722 w, 668 w cm^{-1}. ^{1}H NMR (C_6D_6): δ = 1.24 (br. s, 8 H, CH_2-*THF*), 1.71 (s, 54 H, *t*Bu), 2.43 (s, 9 H, Me), 3.19 (br. s, 8 H, CH_2-*THF*), 7.42 (s, 6 H, 3,5-H) ppm. $C_{53}H_{85}O_5Sm$ (952.60): calcd. Sm 15.78; found Sm 16.08.

$[Yb(OAr)_2(THF)_3]\cdot THF$: THF (50 mL) was added to a mixture of $SnMe_3(OAr)$ (1.10 g, 2.87 mmol), Yb metal filings (1.70 g, 9.82 mmol) and 2 drops of Hg metal, and the resulting mixture was ultrasonicated for 5 d. After allowing the suspension to settle, the deep orange supernatant solution was filtered and concentrated to 25 mL, resulting in golden-yellow crystalline $[Yb(OAr)_2(THF)_3]\cdot THF$; 1.12 g, 87%. The IR spectrum corresponds to that reported.[21b] $C_{46}H_{78}O_6Yb$ (900.15): calcd. Yb 19.22; found Yb 19.92. The unit cell, monoclinic, space group $P2_1$, a = 9.7489, b = 15.2423, c = 15.3858 Å; β = 95.62°, V = 2277.68 Å^3, is in agreement with that reported[21a] [monoclinic, space group $P2_1$, a = 15.393(4), b = 15.619(5), c = 9.859(2) Å; β = 95.62(2)°, V = 2359 Å^3]. A ^{119}Sn{^{1}H} NMR (149 MHz, C_6D_6, 25 °C) spectrum of the filtrate shows the presence of Sn_2Me_6: δ = –109.0 ppm (reported: δ = –108.7 ppm)[12] but no $SnMe_3(OAr)$ signal. The ^{1}H NMR spectrum (C_6D_6) of the concentrated solution shows phenolate resonances: δ = 2.18 (s, 6 H, Me), 7.42 (s, 4 H, 3,5-H) ppm (*t*Bu methyl resonances hidden by the residual THF solvent resonances).

$SnMe_3(C_6F_5)$ with Yb Metal in THF: $SnMe_3(C_6F_5)$ (1 mL, 8.03 mmol) was added under N_2 to a stirred mixture of Yb filings (1.14 g, 6.60 mmol) and 2 drops of Hg metal in THF (50 mL). After 2 d, no colour change was observed. The reaction mixture was ultrasonicated for 1 d resulting in a deep-coloured solution. A ^{19}F NMR spectrum (282 MHz, 25 °C) of the solution showed $[Yb(C_6F_5)_2(THF)_4]$[28] and $SnMe_3(C_6F_5)$[26] in a 2:1 ratio: δ = –108.3 (br. m, 8 F, *o*-F, $[Yb(C_6F_5)_2(THF)_4]$), –121.5 [m, 2 F, *o*-F, $SnMe_3(C_6F_5)$], –154.0 [m, 1 F, *p*-F, $SnMe_3(C_6F_5)$], –161.5 (m, 14 F, *m*-F, $SnMe_3(C_6F_5)$ and *m*-, *p*-F, $[Yb(C_6F_5)_2(THF)_4]$) ppm (in agreement with the respective reported data {$[Yb(C_6F_5)_2(THF)_4]$:[28] δ = –108.3 (*o*-F) and –161.4 (*m*-, *p*-F) ppm; $SnMe_3C_6F_5$:[26] δ = –122.2 (*o*-F), –153.9 (*p*-F), –161.4 (*m*-F) ppm}.

X-ray Crystallography: Crystalline samples of $SnMe_3(OAr)$, $[Nd(Ph_2pz)_3(DME)_2]\cdot DME$, $[Nd(Ph_2pz)_3(THF)_3]\cdot THF$, $[Eu(Ph_2pz)_2(DME)_2]$, $[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$, $[Yb(Ph_2pz)_2(DME)_2]$, $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$, and $[Yb(OAr)_2(THF)_3]\cdot THF$ were mounted on glass fibres in viscous hydrocarbon oil. Crystal data were collected using an Enraf–Nonius Kappa CCD instrument (Sn, Sm, Eu, Yb) or Bruker ApexII diffractometer (Nd) both equipped with monochromated Mo-K_α radiation, λ = 0.71073 Å. All data were collected at 123 K, maintained using an open flow of nitrogen from an Oxford Cryostreams cryostat. X-ray data were processed using the DENZO program (Nonius)[29] or SAINT package (Bruker).[30] Structural solution and refinement was carried out using SHELXL-97[31] and SHELXS-97[32] utilising the graphical interface X-Seed.[33] For $[Eu(Ph_2pz)_3(DME)_2]\cdot 2DME$ there was one disordered DME molecule in the lattice which was modelled over two sites. The η^2-DME contains two disordered positions of the C_2 backbone, also successfully modelled. For $[Sm(Ph_2pz)_3(THF)_3]\cdot 3THF$ there were three THF molecules in the lattice with varying degrees of disorder. These were refined isotropically and no hydrogen atoms were attached. For $[Nd(Ph_2pz)_3(DME)_2]\cdot DME$, one Ph_2pz phenyl group was successfully modelled as being disordered over two positions. The corresponding phenyl group of the same Ph_2pz ligand also showed signs of disorder but this could not be satisfactorily modelled. The μ_2-DME showed signs of being disordered in an analogous manner to that in the Eu complex but could not be modelled adequately. Crystal data and refinement parameters for all complexes are compiled below. CCDC-288000 to -288002 and -607830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for $SnMe_3(OAr)$: $C_{18}H_{32}OSn$, M = 383.16, 0.5 × 0.5 × 0.375 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 13.421(3), b = 15.265(3), c = 9.0962(18) Å, β = 93.34(3)°, V = 1860.5(6) Å^3, Z = 4, D_c = 1.368 g/cm^3, $F(000)$ = 792, $2\theta_{max}$ = 55.8°, 19949 reflections collected, 4416 unique (R_{int} = 0.0434). Final *GooF*

= 1.103, R_1 = 0.0316, wR_2 = 0.0851, R indices based on 3616 reflections with $I > 2\sigma(I)$ (refinement on F^2), 182 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.369 mm^{-1}. The complex is isostructural with $SiMe_3(OAr)$.[24]

Crystal Data for [Nd(Ph$_2$pz)$_3$(DME)$_2$]·DME: $C_{57}H_{63}N_6NdO_6$, M = 1072.39, blue block, 0.24×0.18×0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 12.3824(2), b = 16.0973(4), c = 26.7915(7) Å, β = 97.5260(10)°, V = 5294.2(2) Å^3, Z = 4, D_c = 1.345 g/cm^3, $F(000)$ = 2220, $2\theta_{max}$ = 55.0°, 42938 reflections collected, 12144 unique (R_{int} = 0.0263). Final *GooF* = 1.076, R_1 = 0.0413, wR_2 = 0.0963, R indices based on 10980 reflections with $I > 2\sigma(I)$ (refinement on F^2), 674 parameters, 9 restraints. Lp and absorption corrections applied, μ = 1.036 mm^{-1}.

Crystal Data for [Eu(Ph$_2$pz)$_3$(DME)$_2$]·2DME: $C_{61}H_{73}EuN_6O_8$, M = 1170.21, yellow block, 0.35×0.30×0.20 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 11.785(2), b = 25.600(5), c = 20.106(4) Å, β = 106.03(3)°, V = 5830(2) Å^3, Z = 4, D_c = 1.333 g/cm^3, $F(000)$ = 2432, $2\theta_{max}$ = 55.0°, 23569 reflections collected, 13230 unique (R_{int} = 0.0657). Final *GooF* = 0.951, R_1 = 0.0442, wR_2 = 0.0748, R indices based on 8144 reflections with $I > 2\sigma(I)$ (refinement on F^2), 711 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.134 mm^{-1}.

Crystal Data for [Sm(Ph$_2$pz)$_3$(THF)$_3$]·3THF: $C_{69}H_{81}N_6O_6Sm$, M = 1240.75, colourless block, 0.20×0.10×0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 13.343(3), b = 18.579(4), c = 25.270(5) Å, α = 76.58(3), β = 85.19(3), γ = 87.35(3)°, V = 6070(2) Å^3, Z = 4, D_c = 1.358 g/cm^3, $F(000)$ = 2588, $2\theta_{max}$ = 55.0°, 51382 reflections collected, 27663 unique (R_{int} = 0.0737). Final *GooF* = 1.018, R_1 = 0.0598, wR_2 = 0.1171, R indices based on 17199 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1471 parameters, 280 restraints. Lp and absorption corrections applied, μ = 1.025 mm^{-1}.

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