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Dimethyltin(IV) Bis(3,5-diphenylpyrazolate) as a Synthetic Reagent in the Preparation of Rare-Earth Pyrazolate Complexes

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Reaction of $SnMe_2Cl_2$ with $[Li(Ph_2pz)]$ (Ph_2pz = 3,5-diphenylpyrazolate) in diethyl ether in a 1:2 ratio afforded the new transmetallation reagent $[SnMe_2(Ph_2pz)_2]$. Treatment of $[SnMe_2(Ph_2pz)_2]$ with Ln metals in either 1,2-dimethoxyethane (dme) or tetrahydrofuran (thf) provided a new route to the divalent $[Ln(Ph_2pz)_2(dme)_2]$ (Ln = Sm, Eu, Yb) and the trivalent $[La(Ph_2pz)_3(dme)_2]$ and $[Yb(Ph_2pz)_3(thf)_2]$ complexes in comparable yields to those from alternative methods. These reactions enabled isolation of the highly reactive $[Sm(Ph_2pz)_2(dme)_2]$ complex in good yield, in addition to the new *cis* isomer of $[Eu(Ph_2pz)_2(dme)_2]$, thereby establishing a rare case of geometric isomerism in lanthanoid chemistry. ^1H and ^{119}Sn NMR spectral studies and EDAX measurements were performed on the reaction mixture and/or residue to identify the tin-containing products and suggest formation of $SnMe_4$, Sn_2Me_6, tin metal and two other $SnMe_3$ species, which plausibly result from decomposition of unstable "$SnMe_2$". Treatment of $[Yb(Ph_2pz)_2(dme)_2]$ with $[SnMe_2(Ph_2pz)_2]$ or $[Tl(Ph_2pz)]$ resulted in the isolation of $[Yb(Ph_2pz)_3(thf)_2]\cdot 2C_6D_6$ and $[Yb(Ph_2pz)_3(dme)]\cdot 0.5dme$ complexes, the structures of which have eight-coordinate Yb atoms and contrast nine-coordination observed for previous $[Ln(Ph_2pz)_3(thf\ or\ dme)_n]$ complexes.

Introduction

Redox transmetallation reactions provide simple halide-free reaction routes to both divalent and trivalent rare-earth complexes.[1] The use of organomercurial[1–4] and thallium[4–6] reagents is now well established for the synthesis of various metal–organic lanthanoid derivatives [Equations (1)–(3)].

As an alternative approach, trimethyltin(IV) compounds have recently been shown to be effective reagents in redox transmetallation reactions with Ln metals in the synthesis of both trivalent [Equation (4)] and divalent [Equation (5)] metal–organic lanthanoid complexes,[7] by utilisation of the $Sn^{IV} \rightarrow Sn^{III}$ reduction.

Earlier, Lappert had provided a single example of the use of the $Sn^{II} \rightarrow Sn^0$ reduction in redox transmetallation.[8] The new use of organotin reagents in redox transmetallation with lanthanoid elements contrasts their common use as non-redox metathesis reagents.[9]

$$Ln + HgR_2 \longrightarrow LnR_2 + Hg \qquad (R = C_6F_5;\ Ln = Eu, Yb) \qquad (1)$$

$$2\ Ln + 3\ HgR_2 \longrightarrow 2\ LnR_3 + 3\ Hg \qquad (R = Ph;\ Ln = Ho, Er) \qquad (2)$$

$$Ln + n\ TlL \longrightarrow Ln(L)_n + n\ Tl \qquad (L = R_2pz, OAr, Cp;\ n = 2, 3) \qquad (3)$$

$(R_2pz$ = 3,5-disubstituted pyrazolates)

$$2\ Ln + 6\ SnMe_3L \xrightarrow{solv.} 2\ [Ln(L)_3(solv)_n] + 3\ Sn_2Me_6 \qquad (4)$$

$$Ln + 2\ SnMe_3L \xrightarrow{solv.} [Ln(L)_2(solv)_n] + Sn_2Me_6 \qquad (5)$$

L = 3,5-diphenylpyrazolate (Ph_2pz), 2,6-di-*tert*-butyl-4-methylphenolate (OAr), C_6F_5;
solv. = thf, dme; $n = 2, 3$

In a recent study by Westerhausen,[10] treatment of the dimethyltin(IV) reagent $[SnMe_2(N\{SiMe_3\})_2]_2$ with Ca metal in a redox transmetallation reaction resulted in the preparation of $[Ca(N\{SiMe_3\}_2)_2(thf)_2]$ [Equation (6)].

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$$16\,Ca + 15\,SnMe_2[N(SiMe_3)_2]_2 \xrightarrow{thf} 15\,[Ca(N\{SiMe_3\}_2)_2(thf)_2] + [Ca(Sn\{SnMe_3\}_3)_2(thf)_2] + 3\,SnMe_4 + 4\,Sn \quad (6)$$

This raises the possibility of use of dimethyltin(IV) compounds in the redox transmetallation synthesis of lanthanoid complexes, though Ln elements [E^0 ($Ln^{3+} + 3e \rightarrow Ln$) = –2.38→–2.30 V] are less electropositive than Ca [E^0 ($Ca^{2+} \rightarrow Ca + 2e$) = –2.87 V].[11] We now report the successful preparation of both divalent and trivalent lanthanoid 3,5-diphenylpyrazolate complexes $[Ln(Ph_2pz)_n(solv)_m]$ (n = 2, 3; solv = dme, thf; m = 2, 3) by treating the newly synthesised $[SnMe_2(Ph_2pz)_2]$ reagent with an excess of Ln metal. With two Ph_2pz groups per tin atom, $[SnMe_2(Ph_2pz)_2]$ is potentially a more effective pyrazolate transfer reagent than $[SnMe_3(Ph_2pz)]$. The study provides proof of concept for a new general synthetic method in lanthanoid metal–organic chemistry.

Results and Discussion

Synthesis and Structure of the $[SnMe_2(Ph_2pz)_2]$ Reagent

The air- and moisture-sensitive $[SnMe_2(Ph_2pz)_2]$ complex was obtained by a metathesis reaction between $[Li(Ph_2pz)]$ and $SnMe_2Cl_2$ in Et_2O [Equation (7)].

The ^1H NMR spectrum in C_6D_6 shows the expected 6:22 ratio for Me/Ph_2pz protons. A single resonance at δ = 0.48 ppm is observed for the $SnMe_2$ moiety and shows two sets of tin satellites corresponding to the two tin isotopes, with the smaller coupling constant (J = 69 Hz) assigned to ^{117}Sn and the larger (J = 72 Hz) to ^{119}Sn. The $^{119}Sn\{^1H\}$ NMR spectrum is consistent with the ^1H NMR spectrum, shows a single tin resonance at –8.1 ppm attributable to $[SnMe_2(Ph_2pz)_2]$ and suggests a monomeric four-coordinate Sn^{IV} species.[12–16] The IR spectrum is void of an NH stretching absorption attributable to Ph_2pzH at 3150–3300 cm^{-1}.

Crystals of $[SnMe_2(Ph_2pz)_2(thf)]$ were obtained by recrystallisation from tetrahydrofuran. An X-ray crystal-structure determination shows a monomeric complex (Figure 1). The five-coordinate Sn^{IV} atom adopts a distorted trigonal-bipyramidal geometry, binding η^1 to two pyrazolate ligands [N(1) and N(3)], two carbon atoms of the methyl groups [C(37) and C(38)] and O(1) of the thf solvent molecule. Although the apical N(1)–Sn(1)–O(1) angle is near 180° (Table 1), the equatorial angles (Σ = 352.28°) deviate considerably from 120°. The Sn(1)–N(1)/N(3) bond lengths of 2.142(3) and 2.092(2) Å, respectively, are close to the Sn–N bond length of four-coordinate $SnMe_3(Ph_2pz)$ [2.102(5) Å][12] and to the Sn–N bond lengths reported for Sn compounds containing various N-heterocycles (for example some pyrazoles,[17] tetrazolates,[13] triazolates[16] and thiodiazolates[18]). Although Sn(1)···N(2) [2.986(2) Å] and Sn(1)···N(4) [2.913(2) Å] are within the sum of van der Waals radii of tin and nitrogen (3.6 Å), they are considered non-bonding and their proximity is solely due to the N–N connectivity of the pyrazolate ligand. This is supported by the N(2)–N(1)–Sn(1) [114.28(18)°] and N(4)–N(3)–Sn(1) [112.59(17)°] bond angles, both of which are close to the N(2)–N(1)–Sn(1) bond angle in $[SnMe_3(Ph_2pz)]$ [115.7(4)°],[12] in which Ph_2pz is also considered unidentate. Further, both pseudo bite angles N(1)–Sn(1)···N(2)

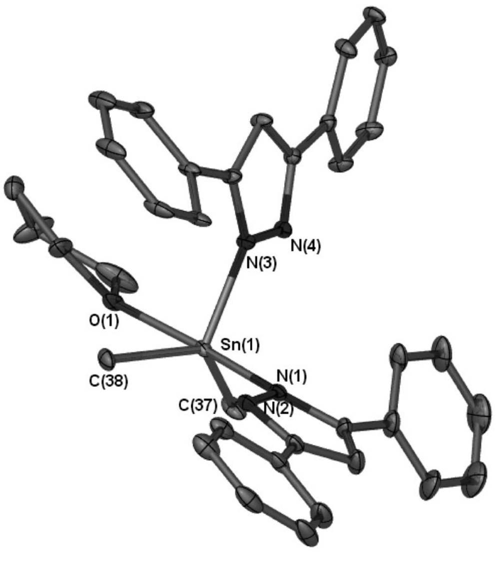

Figure 1. Molecular structure of $[SnMe_2(Ph_2pz)_2(thf)]$; ellipsoids are shown with 35% probability; hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°] for this structure are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for $[SnMe_2(Ph_2pz)_2(thf)]$.

Bond lengths	
Sn(1)–N(1)	2.142(3)
Sn(1)–N(2)[a]	2.986(2)
Sn(1)–N(3)	2.092(2)
Sn(1)–N(4)[a]	2.913(2)
Sn(1)–C(37)	2.104(3)
Sn(1)–C(38)	2.111(3)
Sn(1)–O(1)	2.524(3)
Bond angles	
N(3)–Sn(1)–N(1)	98.59(10)
N(3)–Sn(1)–C(37)	109.19(12)
N(3)–Sn(1)–C(38)	115.28(11)
C(37)–Sn(1)–N(1)	101.69(14)
C(38)–Sn(1)–N(1)	97.41(12)
N(1)–Sn(1)–O(1)	175.18(10)
C(37)–Sn(1)–C(38)	127.81(13)
N(2)–N(1)–Sn(1)	114.28(18)
N(3)–Sn(1)–O(1)	78.90(11)
C(37)–Sn(1)–O(1)	83.06(14)
C(38)–Sn(1)–O(1)	80.12(12)

[a] Considered nonbonding.

$$2\,[Li(Ph_2pz)] + SnMe_2Cl_2 \xrightarrow{Et_2O} [SnMe_2(Ph_2pz)_2] + 2\,LiCl \quad (7)$$

[24.88(7)°] and N(3)–Sn(1)···N(4) [25.90(6)°] are much smaller than the bite angles for η^2-pyrazolate bonding, which are in the range 31–35°.[4,6,7,12,19–21] The differences between the Sn(1)–N(1)/N(2) distance and the Sn(1)–N(3)/N(4) distance, 0.84 and 0.82 Å respectively, are higher than the upper limit proposed for unsymmetrical η^2 coordination.[22] The Sn(1)–O(1) bond length of 2.524(3) Å is rather long for a typical Sn–O bond, but is not unusual.[23] The ^{119}Sn NMR spectrum of the thf complex in C_6D_6 indicates dissociation of thf in solution.

Redox Transmetallation Reactions

Syntheses

$[SnMe_2(Ph_2pz)_2]$ was treated with the rare-earth metals La, Sm, Eu and Yb in either dme [Equation (8)] or thf [Equation (9)] at room temperature to yield both divalent $[Ln(Ph_2pz)_2(dme)_2]$ (Ln = Sm, Eu, Yb) and trivalent $[Ln(Ph_2pz)_3(solv)_2]$ (Ln = La; solv = dme, Ln = Yb; solv = thf) complexes [Equation (8) and (9)].

Reactions of Sm and Eu metals required 3 d of stirring and/or sonication, respectively, and activation by mercury metal. An analogous reaction of Eu without activation by mercury gave a low yield. Reactions of Yb metal with $[SnMe_2(Ph_2pz)_2]$ in thf or dme with Hg activation were complete in 1 and 2 h, respectively, at room temperature. Without Hg activation, it was necessary to stir for 24 h followed by sonication for 3 and 1 h, respectively, for complete reaction. As an alternative to the use of mercury, activation with iodine[2,24] was examined in the reaction between $[SnMe_2(Ph_2pz)_2]$ and La metal in dme, and complete reaction giving $[La(Ph_2pz)_3(dme)_2]$ was achieved in 4 d at room temperature *without stirring* and indicates the viability of this approach. In general, syntheses from $[SnMe_2(Ph_2pz)_2]$ and Ln metals [Equation (8) and (9)] gave good yields (60–80%), comparable with those from redox transmetallation reactions between Ln metals and $[SnMe_3(Ph_2pz)]$ or $[Tl(Ph_2pz)]$ and from other methods (Table 2). Transfer of two Ph_2pz groups per heavy metal is an advantage over $[SnMe_3(Ph_2pz)]$ or $[Tl(Ph_2pz)]$, as is the faster reaction of Yb metal with $[SnMe_2(Ph_2pz)_2]$ than with the other two reagents.[4,7]

There were some differences in outcomes between the present reactions [Equation (8) and (9)] and redox transmetallation reactions of $[SnMe_3(Ph_2pz)]$ or $[Tl(Ph_2pz)]$.[6,7] Most notably, only crystals of *cis*-$[Eu(Ph_2pz)_2(dme)_2]$ were obtained from the reaction of Eu metal with $[SnMe_2(Ph_2pz)_2]$ (Table 2), whereas reactions with $[Tl(Ph_2pz)]$ or $[SnMe_3(Ph_2pz)]$ gave only or predominantly (14 out of 15 crystals) *transoid*-$[Eu(Ph_2pz)_2(dme)_2]$, respectively,[4,6,7] {termed *transoid* rather than *trans* as cen[N(1)/N(2)]–Eu–cen[N(3)/N(4)] and cen[O(1)/O(2)]–Eu–cen[O(3)/O(4)] angles (cen[N/N′] and cen[O/O′] are centres of Ph_2pz N–N′ bonds and dme O···O′ vectors, respectively} are ca. 140° rather than 180°). Thus, this provides a rare example of geometric isomerism in lanthanoid chemistry (the first example of lanthanoid geometric isomers is *cis*- and *trans*-$[SmI_2(diglyme)_2]$ [diglyme = bis(2-methoxyethyl) ether[25]), where the lability of lanthanoid complexes militates against their formation. Reactions of Sm metal with $[Tl(Ph_2pz)]$[6] and $[SnMe_3(Ph_2pz)]$[7] in thf yield $[Sm(Ph_2pz)_3(thf)_3]$, whereas the present synthesis in dme yields $[Sm(Ph_2pz)_2(dme)_2]$ (Table 2), previously obtained only by metathesis or protolysis from divalent precursors.[6]

The formation of a Yb^{II} complex in dme and Yb^{III} in thf suggested that $[Yb(Ph_2pz)_2(dme)_2]$ could be oxidised by $[SnMe_2(Ph_2pz)_2]$ in thf [Equation (10)], and this reaction was carried out at room temperature.

$$\mathrm{Ln} + n/2\ [\mathrm{SnMe_2(Ph_2pz)_2}] \xrightarrow{\mathrm{dme}} [\mathrm{Ln(Ph_2pz)}_n\mathrm{(dme)_2}] + n/2\ \text{"SnMe}_2\text{"} \qquad (8)$$

$$\mathrm{Yb} + 3/2\ [\mathrm{SnMe_2(Ph_2pz)_2}] \xrightarrow{\mathrm{thf}} [\mathrm{Yb(Ph_2pz)_3(thf)_2}] + 3/2\ \text{"SnMe}_2\text{"} \qquad (9)$$

$$[\mathrm{SnMe_2(Ph_2pz)_2}] + 2\ [\mathrm{Yb(Ph_2pz)_2(dme)_2}] \xrightarrow{\mathrm{thf}} 2\ [\mathrm{Yb(Ph_2pz)_3(thf)_2}] + \text{"SnMe}_2\text{"} \qquad (10)$$

Table 2. Comparison of yields of $[Ln(Ph_2pz)_n(solv)_m]$ (n, m = 2, 3; solv = thf, dme) obtained from $[SnMe_2(Ph_2pz)_2]$ with yields from literature methods.[a]

$[Ln(Ph_2pz)_n(solv)_m]$	Activation	Yield [%] from this work	Yield [%] from Ln + $SnMe_3(Ph_2pz)$ (Hg activated)[7]	Yield [%] from other reported methods	Reported method
$[La(Ph_2pz)_3(dme)_2]$	I_2	79	82[7]	77[20]	$La/Ph_2pzH/Hg(C_6F_5)_2$[20]
$[Sm(Ph_2pz)_2(dme)_2]$	Hg	77	–	62[6]	$[K(Ph_2pz)]/SmI_2(thf)_2$[6]
$[Eu(Ph_2pz)_2(dme)_2]$	none	33[b][c]	88[7][d]	90[6][d]	$Eu/Tl(Ph_2pz)$[6]
	Hg	77[c]	88[7][d]	90[6][d]	$Eu/Tl(Ph_2pz)$[6]
$[Yb(Ph_2pz)_2(dme)_2]$	none	71	80[7]	66[4]	several[6]
	Hg	73			
$[Yb(Ph_2pz)_3(thf)_2]$	none	58	51[7]	64[26b]	$Yb/Tl(Ph_2pz)$+oxid. with $Tl(Ph_2pz)$[26b]
	Hg	74			

[a] Syntheses in dme, except for the last two reactions, which were performed in thf. [b] Incomplete reaction. [c] *cis* isomer. [d] *transoid* isomer.

$$[\mathrm{Tl(Ph_2pz)}] + [\mathrm{Yb(Ph_2pz)_2(dme)_2}] \xrightarrow[\text{(ii) dme}]{\text{(i) thf}} [\mathrm{Yb(Ph_2pz)_3(dme)}]\cdot 0.5(\mathrm{dme}) + \mathrm{Tl} \qquad (11)$$

$$2[\mathrm{Yb(Ph_2pz)_2(dme)_2}] + [\mathrm{Hg(C_6F_5)_2}] + 2\,\mathrm{Ph_2pzH} \xrightarrow[\text{(ii) dme}]{\text{(i) thf}} 2[\mathrm{Yb(Ph_2pz)_3(dme)}]\cdot 0.5(\mathrm{dme}) + 2\mathrm{C_6F_5H} + \mathrm{Hg} \qquad (12)$$

In unpublished work by Delbridge,[26a] a similar result was obtained when $[\mathrm{Yb(Ph_2pz)_2(dme)_2}]$ was treated with $[\mathrm{SnMe_3(Ph_2pz)}]$. Repeating the reported oxidation of $[\mathrm{Yb(Ph_2pz)_2(dme)_2}]$ with $[\mathrm{Tl(Ph_2pz)}]$[26b] in thf [Equation (11)], followed by recrystallisation of $[\mathrm{Yb(Ph_2pz)_3(thf)_2}]$ from dme, afforded $[\mathrm{Yb(Ph_2pz)_3(dme)}]\cdot 0.5\mathrm{dme}$ in good yield. The same product was also obtained after $[\mathrm{Yb(Ph_2pz)_2(dme)_2}]$ was treated with stoichiometric amounts of $[\mathrm{Hg(C_6F_5)_2}]$ and $\mathrm{Ph_2pzH}$ in thf followed by recrystallisation from dme [Equation (12)].

Characterisation of the Lanthanoid Pyrazolate Complexes

Infrared data for all compounds confirm the absence of the NH functional group, with no absorption bands between 3150 and 3300 cm^{-1}, consistent with previously reported examples.[4,6,7] For complexes for which NMR spectra were feasible, the NH resonance at ca. 10 ppm was absent. For the diamagnetic $\mathrm{La^{3+}}$ and $\mathrm{Yb^{2+}}$ species, the chemical shifts are in agreement with those reported.[4,7] The ^{1}H NMR spectrum of the $[\mathrm{Sm(Ph_2pz)_2(dme)_2}]$ complex in $\mathrm{C_6D_6}$ shows the presence of both divalent and trivalent Sm–pyrazolate species, although the divalent complex is predominant and it is likely that the extremely air-sensitive $[\mathrm{Sm(Ph_2pz)_2(dme)_2}]$ oxidised slightly during preparation and handling of the solution. The identity of the divalent compound is supported by a unit cell determination and a UV/Vis spectrum, both consistent with reported values,[6] and a Sm metal analysis. The ^{1}H NMR spectrum of *cis*-$[\mathrm{Eu(Ph_2pz)_2(dme)_2}]$ is similar to that recorded for the *transoid* isomer[7] and suggests a single species in solution or fast exchange between the isomers. The IR spectrum of $[\mathrm{Yb(Ph_2pz)_3(thf)_2}]$ is in agreement with those reported for structurally uncharacterised $[\mathrm{Ln(Ph_2pz)_3(thf)_2}]$ (Ln = Gd, Er, Y, Yb, Lu) complexes.[27] A satisfactory ^{1}H NMR spectrum of the paramagnetic compound could not be obtained (grossly broadened), but single crystals of $[\mathrm{Yb(Ph_2pz)_3(thf)_2}]\cdot 2\mathrm{C_6D_6}$ deposited and the structure was determined. The IR spectrum of the new complex $[\mathrm{Yb(Ph_2pz)_3(dme)}]\cdot 0.5\mathrm{dme}$ is similar to those of the $[\mathrm{Ln(Ph_2pz)_3(dme)_2}]$ (Ln = La, Nd, Eu, Er)[7,20] complexes, while the visible/near IR spectrum shows a weak absorption at 975 nm (ε = 15), which is consistent with $\mathrm{Yb^{III}}$. No absorption band is seen near 350 nm, in contrast to the intense absorption band at 410 nm (ε = 744) for $[\mathrm{Yb(Ph_2pz)_2(dme)_2}]$.[4] Satisfactory analyses were obtained, and the structure was established by X-ray crystallography. The structures of the two Yb complexes, $[\mathrm{Yb(Ph_2pz)_3(thf)_2}]\cdot 2\mathrm{C_6D_6}$ and $[\mathrm{Yb(Ph_2pz)_3(dme)}]\cdot 0.5\mathrm{dme}$, are of importance, since they contrast previous structurally characterised thf and dme complexes of $\mathrm{Ln(Ph_2pz)_3}$, which have the composition $[\mathrm{Ln(Ph_2pz)_3(dme)_2}]$ (Ln = La, Nd, Eu, Er)[7,20] and $[\mathrm{Ln\ (Ph_2pz)_3(thf)_3}]$ (Ln = La, Nd, Sm),[7,21] respectively, in which the Ln metals are nine coordinate. Complexes with the composition $[\mathrm{Ln\ (Ph_2pz)_3(thf)_2}]$ have been obtained with the rare-earth metals (Ln = Sc, Gd, Er, Y, Yb, Lu),[26b,27] but no structures have been determined.

The Sn Coproduct(s)

The ^{1}H NMR spectra of the crude products from reactions with La, Sm, Eu and Yb metals display multiple resonances corresponding to methyltin derivatives at around 0.66, 0.81–0.90 and 1.23–1.83 ppm, though the integrations are low when compared with those of the lanthanoid complexes. Comparison of the chemical shifts with those reported for plausible methyltin products (Table 3) suggests that species with $\mathrm{SnMe_3}$ and $\mathrm{SnMe_2}$ groups may be present.[28,29] No resonances attributable to $[\mathrm{SnMe_2(Ph_2pz)_2}]$ were present, hence the reactant is fully consumed. After a separate reaction between Yb metal and $[\mathrm{SnMe_2(Ph_2pz)_2}]$, a sample of the reaction mixture diluted with $\mathrm{C_6D_6}$ was examined by ^{119}Sn{^{1}H} NMR spectroscopy. Four distinct resonances are observed, namely 1.8, –95.5, –97.4 and –108 ppm, which supports the presence of several products as indicated by the ^{1}H NMR spectra. The resonances at 1.8 and –108 ppm can be attributed to $\mathrm{SnMe_4}$ and $\mathrm{Sn_2Me_6}$ (confirmed by GC/MS), respectively,[14,30] (Table 3). The resonances at –95.5 and –97.4 ppm are near the value (–95 ppm) reported for a Sn–Yb bonded complex, $[\mathrm{Yb\{Sn(Nep)_3\}_2(thf)_2}]$ (Nep = 2,2-dimethylpropyl).[31] A corresponding resonance in the ^{171}Yb NMR spectrum near ca. 725 ppm was not observed, the sole signal being at δ = 488 ppm, which corresponds to $[\mathrm{Yb(Ph_2pz)_2(dme)_2}]$.[4] However, there may be a problem with detection, as the more sensitive ^{119}Sn{^{1}H} resonances are of weak intensity. The chemical shifts at –95 and –97 ppm are also close to resonances for *SnMe*$_3$ reported for $[\mathrm{SnMe_3]_2SnMe_2}$ or $\mathrm{(SnMe_3)_3SnMe}$ (–99.5 and –89.5 ppm, respectively)[32,33] (Table 3). However, despite a prolonged scan time (17 h), the corresponding $\mathrm{SnMe_2}$ or SnMe resonances were not observed, nor were resonances attributable to $\mathrm{(SnMe_2)_6}$[34] (–231 and/or –241 ppm). An energy dispersive analysis by X-rays (EDAX) on the metallic residue detected the presence of elemental Sn, in addition to excess Yb metal. The products are consistent with the transitory existence and decomposition of molecular $\mathrm{SnMe_2}$ [Equation (13)],[9a,9b] the putative initial product of reactions (8) and (9), and they resemble those from reaction of Ca metal with $[SnMe_2(N(SiMe_3)_2)_2]$ [Equation (6)].

$$n\text{"}(SnMe_2)\text{"} \longrightarrow SnMe_4 + Sn_2Me_6 + SnMe_3X + SnMe_3Y + Sn \qquad (13)$$

Table 3. ^{1}H NMR and ^{119}Sn{^{1}H} NMR chemical shifts [ppm] of some organotin(IV) compounds [^{119}Sn(^{1}H) chemical shifts relative to external $SnMe_4$].

	$\delta(^1H)$	$\delta(^{119}Sn\{^1H\})$
This work	0.63	–1.8
Ln +$[SnMe_2(Ph_2pz)_2]$	0.81–0.90	–95.5
	1.23–1.83	–97.4
		–108.0
Sn_2Me_6	0.20[46]	–108.0[32]
$(SnMe_2)_n$	1.15–1.36[29]	
$(SnMe_2)_6$	0.63 (conc.)[34]	–231.04 and/or –241[34]
	0.53 + 0.63 (dil.)[34]	
$[SnMe_3]_4Sn$		–80 and –739[32]
$[SnMe_3]_3SnMe$		–89.5 and –489[32]
$[SnMe_3]_2SnMe_2$		–99.5 and –261[32]

The well documented pyrolysis of polymeric diethyltin gives similar products, viz. $SnEt_4$, Sn_2Et_6, Sn and other species with $SnEt_n$ [(n = 1–3) groups].[35]

Single-Crystal X-ray Studies – The Structures of *cis*-$[Eu(Ph_2pz)_2(dme)_2]$, $[Yb(Ph_2pz)_3(dme)]{\cdot}0.5dme$ and $[Yb(Ph_2pz)_3(thf)_2]{\cdot}2C_6D_6$

Single crystals of $[Sm(Ph_2pz)_2(dme)_2]$ and $[Yb(Ph_2pz)_2(dme)_2]$ were grown, and their unit cells (as determined by single-crystal X-ray diffraction) are in agreement with reported data[4,6] (see Experimental Section). Although a crystalline product was obtained for $[La(Ph_2pz)_3(dme)_2]{\cdot}dme$, the material was not satisfactory for an X-ray crystallographic structure determination. However, the structures of the new Eu^{II} isomer *cis*-$[Eu(Ph_2pz)_2(dme)_2]$, $[Yb(Ph_2pz)_3(dme)]{\cdot}0.5dme$ and $[Yb(Ph_2pz)_3(thf)_2]{\cdot}2C_6D_6$ were determined.

The structure of *cis*-$[Eu(Ph_2pz)_2(dme)_2]$ has an eight-coordinate Eu atom with two chelating dme ligands and two chelating (η^2) pyrazolate ligands (Figure 2) and is isotypic with the reported $[Yb(Ph_2pz)_2(dme)_2]$ analogue.[4] The cen[N(1)/N(2)]–Eu–cen[N(3)/N(4)] (cen = centre of the N–N bond of the pyrazolate ligand) angle of 102.09° corresponds to a *cis* disposition of the pyrazolate ligands and is consistent with values (103–108°) observed for the *cis* Ln^{II} complexes $[Yb(Ph_2pz)_2(dme)_2]$,[4] $[Sm(Ph_2pz)_2(dme)_2]$,[6] $[Eu(tBu_2pz)_2(dme)_2]$[6] and $[Yb(bind)_2(dme)_2]$ (tBu$_2$pz = 3,5-di-*tert*-butylpyrazolate; bind = 4,5-dihydro-2*H*-benz[*g*]-indazolate).[6] In comparison, *transoid* Ln^{II} cen–Ln–cen angles are in the range 141–143°.[6] Similarly, the present cen[O(1)/O(2)]–Eu–cen[O(3)/O(4)] angle is 95° and contrasts 140° for the *transoid* isomer. Both Ph_2pz ligands are nearly symmetrically chelating in the *cis* isomer with only a small divergence in Ln–N distances (0.01 and 0.05 Å). The η^2-dme ligands have a slightly larger difference in Eu–O distances (0.05 and 0.07 Å), possibly because of steric hindrance imposed by the phenyl rings and the *cis* arrangement. Table 4 provides a comparison of selected key bond lengths and angles of the structures of the four divalent $[Ln(Ph_2pz)_2(dme)_2]$ complexes. Crystallisation of *cis*-$[Eu(Ph_2pz)_2(dme)_2]$ means that this isomer is established for all three normal divalent elements. However, Eu now provides a rare example of geometric isomerism for labile lanthanoid complexes. The Ln–N bond lengths in $[Sm(Ph_2pz)_2(dme)_2]$[6] and the two $[Eu(Ph_2pz)_2(dme)_2]$ isomers are comparable, whilst that of $[Yb(Ph_2pz)_2(dme)_2]$ is smaller owing to the smaller ionic radius of Yb.[36] Generally, the differ-

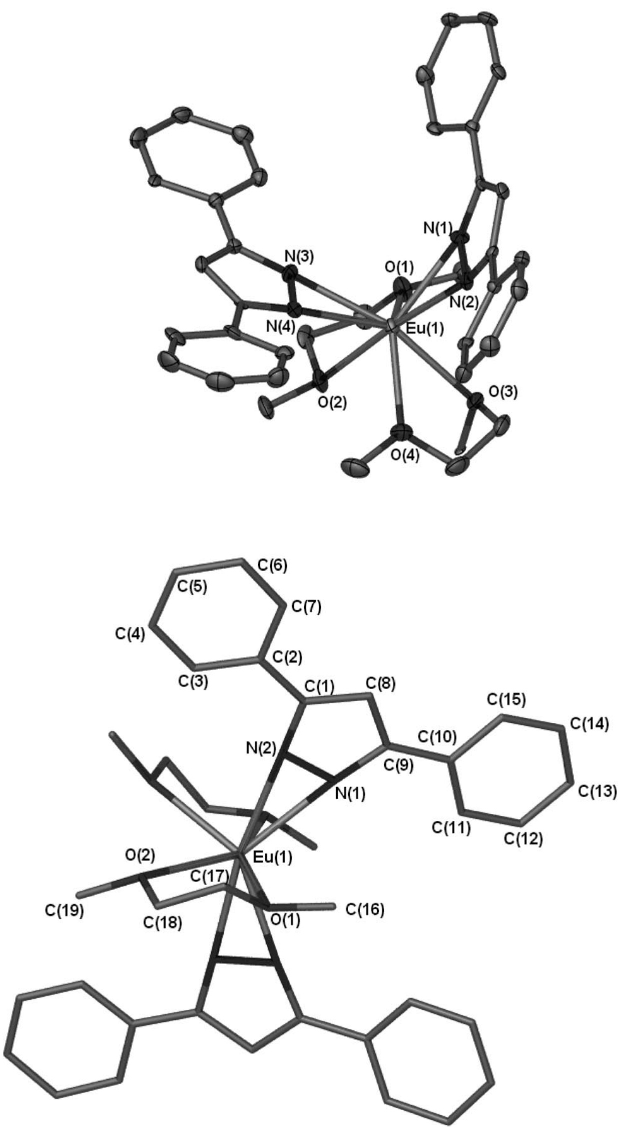

Figure 2. (top) X-ray crystal structure of *cis*-$[Eu(Ph_2pz)_2(dme)_2]$; ellipsoids shown at 40% probability; hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°] for this structure are given in Table 4; (bottom) X-ray crystal structure of *transoid*-$[Eu(Ph_2pz)_2(dme)_2]$;[6] hydrogen atoms and Me groups of dme molecules are removed for clarity.

Table 4. Selected bond lengths [Å] and angles [°] for *cis*-[Ln(Ph_2pz)$_2$(dme)$_2$] and *transoid*-[Eu(Ph_2pz)$_2$(dme)$_2$].[a]

	cis-[Sm(Ph_2pz)$_2$(dme)$_2$][6]	*transoid*-[Eu(Ph_2pz)$_2$(dme)$_2$][6]	*cis*-[Eu(Ph_2pz)$_2$(dme)$_2$]	*cis*-[Yb(Ph_2pz)$_2$(dme)$_2$][4]
Ln–N				
N1	2.556(3)	2.552(5)	2.520(7)	2.426(7)
N2	2.556(3)	2.582(4)	2.532(6)	2.414(7)
N3	2.538(3)	2.554(6)	2.512(7)	2.424(7)
N4	2.538(3)	2.536(6)	2.559(7)	2.430(7)
Ln-O				
O1	2.720(7)	2.637(6)	2.606(5)	2.502(6)
O2	2.708(5)	2.660(5)	2.671(5)	2.558(7)
O3	2.551(4)	2.614(5)	2.575(4)	2.484(6)
O4	2.627(7)	2.684(5)	2.623(6)	2.576(7)
N–Ln-N				
N1–Ln–N2	31.07(8)	31.0(2)	31.55(15)	32.7(2)
N3–Ln–N4	30.99(10)	31.0(2)	31.34(16)	32.5(2)
O–Ln-O				
O1–Ln–O2	60.2(2)	63.5(2)	62.71(16)	65.2(2)
O3–Ln–O4	69.5(2)	62.9(2)	64.41(17)	65.6(2)

[a] N1–N4 and O1–O4 are generalised atom labels for literature compounds – Sm: N(11), N(11′), N(21), N(21′), O(102), O(105), O(202), O(205); *transoid*-Eu: N(111), N(112), N(211), N(212), O(102), O(105), O(202), O(205); Yb: N(11), N(12), N(21), N(22), O(31), O(31′), O(41), O(41′).

ence is close to that expected,[36] but in the case of Ln–O(4), the difference is only 0.05 Å. Although the two [Eu(Ph_2pz)$_2$(dme)$_2$] isomers have similar Eu–N and Eu–O bond lengths (Table 4), the average Eu–N and Eu–O bond lengths for the *cis* isomer (2.53(2) and 2.62(4) Å, respectively) may be marginally shorter than those for the *transoid* [2.56(2) and 2.65(3) Å]. The overall position with the two isomers is that the *cis* isomer is somewhat distorted towards *trans* and the *transoid* isomer is considerably distorted towards the *cis* isomer. Thus, the geometric isomerism contrasts [SmI_2(diglyme)$_2$], which forms normal *cis*- and *trans* isomers.

The Yb^{3+} ions in both [Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6 (Figure 3) and [Yb(Ph_2pz)$_3$(dme)]·0.5dme (Figure 4) are eight coordinate and are bonded in an η^2-fashion by three pyrazolate ligands and two *transoid* thf molecules or a chelating dme molecule, respectively. The eight-coordinate Yb complexes contrast the previously reported nine-coordinate [Ln(Ph_2pz)$_3$(dme)$_2$] (Ln = Nd, Eu, Er)[7,20,37] and ([Ln(Ph_2pz)$_3$(thf)$_3$] Ln = Nd[21] or Sm[7]) complexes and reflect the lanthanoid contraction. It is thus likely that [Ln(Ph_2pz)$_3$(thf)$_2$] (Ln = Y, Er and Lu)[27] complexes have a similar structure to [Yb(Ph_2pz)$_3$(thf)$_2$]. In contrast to the nine-coordinate [Ln(Ph_2pz)$_3$(dme)$_2$] complexes of the light lanthanoids, eight coordination is observed in the polymeric [Nd(tBu_2pz)$_3$(μ-dme)]$_n$ complex,[20] owing to the bulkier pyrazolate ligand.

The Yb–N bond lengths of [Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6 and [Yb(Ph_2pz)$_3$(dme)]·0.5dme are remarkably similar (Table 5), given the contrasting nature of the two coordinating neutral ligands. η^2-Pyrazolate binding is reasonably symmetric, with Yb–N bond length differences ranging from 0.014–0.087 {[Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6} and 0.09–0.093 Å {[Yb(Ph_2pz)$_3$(dme)]·0.5dme}. The average Yb–N bond lengths, 2.310 {[Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6} and 2.305 Å {[Yb(Ph_2pz)$_3$(dme)]·0.5dme}, are 0.12 and 0.13 Å, respectively, shorter than the average Nd–N bond length of the eight-coordinate [Nd(tBu_2pz)$_3$(μ-dme)]$_n$ complex[20] and are very close to ionic radii differences.[36] The O(1)–Yb–O(2) angle of 153.45(7)° in [Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6 is close to that of O(1)–Nd–O(3)[21] in [Nd(tBu_2pz)$_3$(μ-dme)]$_n$ [153.5(2)°],[20] but is much larger than that of O(1)–Er–O(2) [140.1(4)°] in [Er(tBu_2pz)$_3$(thf)$_2$].[38]

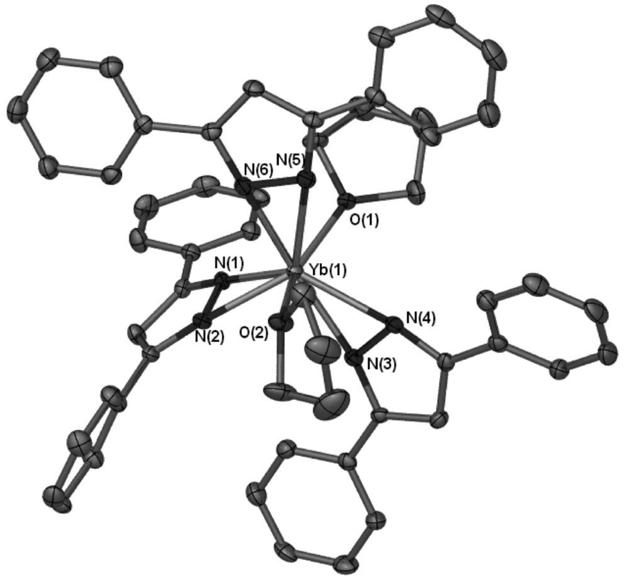

Figure 3. X-ray crystal structure of [Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6; ellipsoids shown at 50% probability; hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°] for this structure are given in Table 5.

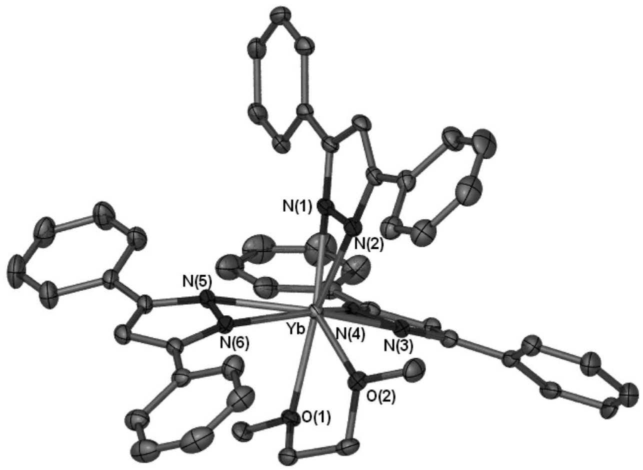

Figure 4. X-ray crystal structure of [Yb(Ph_2pz)$_3$(dme)]·0.5dme; ellipsoids shown at 20% probability. Selected bond lengths [Å] and angles [°] for this structure are given in Table 5.

Table 5. Selected bond lengths [Å] and angles [°] for [Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6 and [Yb(Ph_2pz)$_3$(dme)]·0.5dme.

	[Yb(Ph_2pz)$_3$(thf)$_2$]·2C_6D_6	[Yb(Ph_2pz)$_3$(dme)]·0.5dme
Bond lengths		
Yb–N(1)	2.291(2)	2.251(4)
Yb–N(2)	2.305(2)	2.347(4)
Yb–N(3)	2.274(2)	2.337(4)
Yb–N(4)	2.361(2)	2.282(4)
Yb–N(5)	2.352(2)	2.356(4)
Yb–N(6)	2.280(2)	2.266(4)
Yb–O(1)	2.3260(19)	2.404(3)
Yb–O(2)	2.357(2)	2.342(3)
Bond angles		
N(1)–Yb–N(2)	34.90(8)	34.44(12)
N(3)–Yb–N(4)	34.50(8)	34.80(13)
N(6)–Yb–N(5)	34.38(8)	34.28(12)
O(1)–Yb–O(2)	153.45(7)	68.33(11)

Observation of a Reaction Intermediate

A feature of reactions (8) and (9) is that they appear to proceed via an "intermediate" stage, where a white precipitate is formed 5–30 min after solvent addition. This "intermediate" then redissolved within 1 h [Yb/dme; Hg activation], 1 d [Yb/thf or Yb/dme; no Hg activation] or 3 d {La [I_2 activation, Eu and Sm (Hg activation)]}, which signifies reaction completion. Attempts were made to identify the "intermediate" species formed during the preparation of [Eu(Ph_2pz)$_2$(dme)$_2$] and during the preparation of [La(Ph_2pz)$_3$(dme)$_2$]·dme. Lack of crystallinity and near insolubility in suitable NMR solvents hindered structural evaluation. The ^{1}H NMR spectra suggest the presence of SnMe and Ph_2pz moieties, but adsorption of soluble species in the precipitate is possible. The IR spectrum of the precipitate from the reaction with Eu differs from those of [$SnMe_2$(Ph_2pz)$_2$] and [Eu(Ph_2pz)$_2$(dme)$_2$], but shows features indicative of Ph_2pz and SnMe groups. An EDAX measurement on this product indicates the presence of Sn and Eu (2:1). It is possible that a dimetallic Sn/Ln intermediate is formed and then reacts further. In the redox transmetallation reaction between Ca and [$SnMe_2$(N{$SiMe_3$}$_2$)$_2$], a Ca/Sn complex [Ca{Sn($SnMe_3$)$_3$}$_2$(thf)$_2$] was obtained in addition to the target [Ca(N{$SiMe_3$}$_2$)$_2$(thf)$_2$] compound[10,39] [Equation (6)]. The very low solubility of this intermediate in any solvent suggests that it is polymeric in nature. An attempt to prepare a Sn/Ln pyrazolate dimetallic without redox, by reaction of [$SnMe_2$(Ph_2pz)$_2$] with [Nd(Ph_2pz)$_3$(thf)$_3$]·thf, was not successful.

Conclusions

This study further highlights the efficacy of organotin(IV) reagents in redox transmetallation reactions for the synthesis of rare-earth complexes. Treatment of the new reagent [$SnMe_2$(Ph_2pz)$_2$] with Ln metals (Ln = La, Sm, Eu and Yb) enables the preparation of both divalent and trivalent Ln-pyrazolate complexes. A second geometric isomer (*cis*) of [Eu(Ph_2pz)$_2$(dme)$_2$] was characterised. This work complements the success of [$SnMe_3$(Ph_2pz)] in the synthesis of Ln(Ph_2pz)$_n$ (n = 2, 3) complexes.[7] The yields of products obtained were comparable to those obtained from [$SnMe_3$(Ph_2pz)] and from other literature methods. However, reactions involving [$SnMe_2$(Ph_2pz)$_2$] occur faster than those of [$SnMe_3$(Ph_2pz)] and even [Tl(Ph_2pz)], especially with Yb metal, and have the advantages of transferring two Ph_2pz groups per Sn atom. The organotin product undergoes decomposition to form tin metal, Sn_2Me_6, $SnMe_4$, in addition to two other species. From oxidation reactions of [Yb(Ph_2pz)$_2$(dme)$_2$], the new crystallographically characterised [Yb(Ph_2pz)$_3$(thf)$_2$] and [Yb(Ph_2pz)$_3$(dme)] complexes were obtained.

Experimental Section

General Remarks: All reactions were carried out under dry nitrogen by using standard Schlenk and dry box equipment. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone, while 1,2-dimethoxyethane was distilled from sodium. Infrared spectra (4000–650 cm^{-1}) were recorded as Nujol mulls with a Perkin–Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker DPX 300 MHz spectrometer by using dry degassed deuterated benzene, and resonances were referenced to residual hydrogen from the solvent. ^{119}Sn NMR spectra were obtained by using a Bruker DRX 400 spectrometer, and resonances were referenced to tetramethyltin. Metal analyses of the lanthanoid complexes were performed by EDTA titration with Xylenol Orange indicator following digestion in concentrated nitric and sulfuric acids unless indicated otherwise and buffering with hexamine.[6] Microanalysis samples were sealed in glass ampoules under purified N_2 and were determined by the Campbell Microanalytical service, University of Otago, New Zealand. EDAX (Energy Dispersive Analysis by X-rays) was used to qualitatively determine the presence of lanthanoid and tin metals in specific samples. Measurements were carried out by using a Joel JSM 840A scanning microscope in EDS mode. GC Mass spectra were obtained by using the Agilent 5973 spectrometer. Dimethyltin dichloride was purchased from Aldrich and used as is. 3,5-Diphenylpyrazole[40] and bis(pentafluorophenyl)mercury[41] were prepared by literature methods.

Preparation of [$SnMe_2(Ph_2pz)_2$]: [$SnMe_2Cl_2$] (1.50 g; 6.86 mmol) was added to a solution of [$Li(Ph_2pz)$] (3.09 g; 13.7 mmol) in Et_2O (50 mL), causing formation of a milky white suspension, which was stirred at room temperature overnight. After filtration through a filter cannula, the Et_2O was removed under vacuum. The white product was washed with hexane (40 mL). Yield: 2.91 g (72%). IR: $\tilde{\nu}$ = 1602 (m), 1538 (w), 1268 (m), 1158 (m), 1111 (m), 1071 (m), 1026 (m), 955 (m), 798 (m), 758 (vs), 698 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.48 (s, $^2J_{H,117Sn}$ = 69, $^2J_{H,119Sn}$ = 72 Hz, 6 H, Me_2Sn), 6.79 [s, 2 H, H4 (pz)], 7.12 (t, 4 H, *p*-H), 7.34 (br. t, 8 H, *m*-H), 7.79 (br. s, 8 H, *o*-H). $^{119}Sn\{^1H\}$ NMR (149 MHz, C_6D_6, 25 °C): δ = –8.1 ppm. Crystals of [$SnMe_2(Ph_2pz)_2$(thf)] were obtained after recrystallisation from thf. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.49 (s, $^2J_{H,117Sn}$ = 69, $^2J_{H,119Sn}$ = 72 Hz, 6 H, Me_2Sn), 1.25–1.30 (m, 4 H, CH_2-thf), 3.34–3.47 (m, 4 H, OCH_2-thf), 6.74 [s, 2 H, H4(pz)], 7.12 (t, 4 H, *p*-H), 7.34 (br. t, 8 H, *m*-H), 7.77 (br. s, 8 H, *o*-H) ppm. $^{119}Sn\{^1H\}$ NMR (149 MHz, C_6D_6, 25 °C): δ = –9.3 ppm. For [$SnMe_2(Ph_2pz)_2$(thf)]: $C_{36}H_{36}N_4OSn$ (659.38): calcd. C 65.57, H 5.50, N 8.49; found C 63.13, H 5.12, N 8.85. For unsolvated [$SnMe_2(Ph_2pz)_2$]: $C_{32}H_{28}N_4Sn$ (587.30): calcd. C 65.44, H 4.81, N 9.54; found C 63.13, H 5.12, N 8.85.

Redox Transmetallation Reactions with La, Sm and Eu

[$La(Ph_2pz)_3(dme)_2$]·dme

(a) Activation by I_2: dme (50 mL) was added by a cannula to a mixture of La metal filings (1.11 g; 8.03 mmol), [$SnMe_2(Ph_2pz)_2$] (1.14 g; 1.94 mmol) and I_2 (≈ 0.1 g). The resulting deep-orange solution was allowed to stand at room temperature. Within 1 h of standing, the solution lightened to a light yellow, and after 6 h this colour was pale orange-yellow with crystalline white material forming. This product then redissolved after 4 d of standing when the solution was again deep orange. The filtrate was collected by a filter cannula, and the dme was concentrated to 15 mL, resulting in deep orange-yellow (microcrystalline) material. Yield 1.09 g (79%). The IR spectrum was identical with that reported for [$La(Ph_2pz)_3(dme)_2$],[7] and the ^1H NMR spectrum was also in agreement with that reported for [$La(Ph_2pz)_3(dme)_2$]·dme in C_6D_6.[7] $C_{57}H_{63}LaN_6O_6$ (1067.05): calcd. La 13.02; found La 12.74.

(b) Activation by Hg: dme (40 mL) was added by a cannula to a mixture of La metal filings (0.55 g; 3.97 mmol), [$SnMe_2(Ph_2pz)_2$] (0.51 g; 0.87 mmol) and 1–2 drops of Hg. The resulting colourless solution was stirred at room temperature. A white precipitate appeared after 20 min and was still visible after 5 h. Approximately 5 mL of "intermediate suspension" was collected by a cannula, and dme was concentrated to 1 mL. ^1H NMR (300 MHz, diluted by C_6D_6, 25 °C): δ = 0.31–1.81 (multiple resonances) 7.15–7.19 (t, *p*-H), 7.24–7.30 (tr, *m*-H), 8.00–8.02 (br. d, *o*-H) ppm. ^1H NMR spectrum of sample exposed to air (300 MHz, 3:1 CD_3CN/C_6D_6, 25 °C): δ = 2.26 (br. s, H_2O), 3.27–3.38 (br. s, *CH_3*-dme), 3.52–3.53 (br. s, *CH_2*-dme), 7.09 (s, H4), 7.44–7.71 (m, *p*-H, *m*-H), 7.82–8.01 (br. d, *o*-H), 11.62 (br. s, NH) ppm. The bulk reaction mixture was stirred for 2 d, after which time the precipitate had redissolved. The dme filtrate was collected by a filter cannula, and dme was concentrated to 5 mL, resulting in a white precipitate. The IR and ^1H NMR (in C_6D_6) spectra were consistent with that reported for [$La(Ph_2pz)_3(dme)_2$]·dme.[7].

[$Sm(Ph_2pz)_2(dme)_2$]: dme (40 mL) was added by a cannula to a stirring mixture of [$SnMe_2(Ph_2pz)_2$] (0.24 g; 0.42 mmol), Sm metal powder (0.49 g; 3.25 mmol) and 1–2 drops of Hg. The pale-yellow solution was stirred for 1 h, whereby after 15 min reaction time a precipitate had formed. The mixture was then placed in a sonication bath for a further 1 h and 30 min, but the precipitate was still present. The mixture was then stirred at room temperature for 2 d, resulting in a deep-yellow solution. After standing for 3 d, the solution had darkened to a deep colour. The filtrate was collected by a filter cannula, and the dme solution was concentrated to ca. 3 mL, yielding a dark sludgy precipitate, amongst which were a few single crystals. The IR spectrum was in agreement with that reported for [$Sm(Ph_2pz)_2(dme)_2$].[6] Visible/near IR (thf): λ_{max} (ε) = 545 (841, br.) nm. The ^1H NMR spectrum showed the presence of both trivalent [$Sm(Ph_2pz)_3(dme)_2$][4] and divalent [$Sm(Ph_2pz)_2(dme)_2$][6] species, with the latter dominant (300 MHz, C_6D_6, 25 °C): δ = for [$Sm(Ph_2pz)_2(dme)_2$]: –9.67 (v br. s, H4), –4.43 (v br. s, *o*-H) (resonances too broad owing to paramagnetism for meaningful integration), 3.73 (br. s, 20 H, CH_2 and CH_3-dme), 5.22 (br. s, 4 H, *p*-H), 5.91 (br. s, 8 H, *m*-H) ppm; for $Sm(Ph_2pz)_3$ the pyrazolate resonances are: 7.46–7.96 (br. m, *p*- and *m*-H), 8.30 (br. s, H4), 9.12 (br. s, *o*-H). A unit cell for the purple crystals [orthorhombic, a = 8.02(2), b = 24.39(14), c = 19.22(5) Å; V = 3762(10) $Å^3$] was consistent with formation of [$Sm(Ph_2pz)_2(dme)_2$][6] [orthorhombic, *Pnma*, a = 7.9941(6), b = 24.263(3), c = 19.080(3) Å; V = 3701 $Å^3$]. The metal analysis of the samarium complex was performed by EDTA titration with Xylenol Orange indicator following degradation with 4 M HCl and buffering with hexamine. $C_{38}H_{42}N_4O_4Sm$ (769.12): calcd. Sm 19.54; found Sm 18.70 [For trivalent $C_{53}H_{53}N_6O_4Sm$ (988.38): calcd. Sm 15.22; found Sm 18.70].

cis-[$Eu(Ph_2pz)_2(dme)_2$]

(a) Without Activation by Mercury: dme (40 mL) was added by a cannula to a mixture of Eu metal pieces (0.77 g; 5.09 mmol) and [$SnMe_2(Ph_2pz)_2$] (0.33 g; 0.56 mmol). After 30 min of sonication, a murky peach-coloured solution was observed and a precipitate began to deposit. After 2 d of sonication, a yellow colour was observed with the precipitate still visible. The yellow solution was filtered by a filter cannula, and the precipitate was collected. The yellow filtrate was concentrated under reduced pressure, yielding yellow crystalline material (0.14 g, 33%). X-ray analysis on five crystals showed formation of the *cis*-[$Eu(Ph_2pz)_2(dme)_2$] species. The IR spectrum agreed with that reported for *transoid*-[$Eu(Ph_2pz)_2(dme)_2$].[6] ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.28 (br. m, 12 H, *CH_3*-dme), 0.63 (br. s, 8 H, *CH_2*-dme), 0.92 (br. s, 4 H, *p*-H), 1.34 (br. s, 18 H, H4, *o*-H,*m*-H) ppm. The precipitate was only barely soluble in available deuterated solvents (C_6D_6, $CD_3C_6D_5$, C_2D_6OS, C_4D_8O), with the resulting NMR spectra inconclusive. However, no starting material [$SnMe_2(Ph_2pz)_2$] was present. The IR was different from those of both starting material and the target [$Eu(Ph_2pz)_2(dme)_2$] complex: $\tilde{\nu}$ = 1600 (s), 1536 (m), 1512 (m), 1427 (s), 1400 (s), 1319 (w), 1295 (w), 1276 (w), 1224 (w), 1189 (m), 1152 (w), 1121 (w), 1078 (s), 1062 (vs), 1026 (s), 1000 (w), 980 (vs), 961 (s), 912 (s), 869 (m), 846 (w), 807 (m), 758 (vs), 707 (s), 682 (vs), 658 (w) cm^{-1}. EDAX showed 2:1 Sn/Eu ratio.

(b) With Activation by Mercury: dme (50 mL) was added by a cannula to a mixture of Eu metal pieces (0.87 g; 5.76 mmol), [$SnMe_2(Phpz)_2$] (0.40 g; 0.68 mmol) and two Hg drops. An instant golden-yellow solution was obtained, with all [$SnMe_2(Ph_2pz)_2$] dissolved. After 5 min of stirring at room temperature, a precipitate was seen, and the solution was a lemon-yellow colour. The mixture was stirred at room temperature for 2 d, after which time all the precipitate had redissolved giving a golden-yellow solution. Concentrating the filtrate resulted in crystalline material of [$Eu(Ph_2pz)_2(dme)_2$]. Yield: 0.40 g (77%). The IR and ^1H NMR spectra were as above for the [$Eu(Ph_2pz)_2(dme)_2$] complex.[6] $C_{38}H_{42}EuN_4O_4$

(770.73): calcd. Eu 19.72; found Eu 20.05. Single-crystal X-ray determination on three representative crystals of the bulk yellow crystals showed formation of the *cis*-[Eu$(Ph_2pz)_2(dme)_2$] isomer.

[Yb$(Ph_2pz)_2(dme)_2$]

(a) Activation by Hg: dme (40 mL) was added by a cannula to a mixture of [$SnMe_2(Ph_2pz)_2$] (0.62 g; 1.06 mmol), Yb metal filings (0.91 g; 5.26 mmol) and 2 drops of Hg. An orange colour was observed immediately. After 10 min of stirring, the initial orange colour lightened to a light-orange hue as a white precipitate began to form. This precipitate redissolved into solution after 2 h of stirring, causing the solution to deepen into a deep orange/red colour. The deep-coloured filtrate was collected by a filter cannula, and the dme solution was concentrated under vacuum to ca. 10 mL, resulting in deep-red crystalline material. Yield: 0.61 g (73%). A unit cell of these crystals [monoclinic, $P2_1/c$, a = 24.12(8), b = 18.53(6), c = 7.63(3) Å; β = 95.6(2)°, V = 3394(5) Å^3] was in agreement with that reported for [Yb$(Ph_2pz)_2(dme)_2$][4] [monoclinic, $P2_1/a$, a = 7.882(4), b = 18.959(3), c = 24.080(14) Å; β = 91.03(2)°, V = 3598(3) Å^3]. This was also confirmed by the ^{1}H NMR and IR spectra, which were identical with those reported.[4] $C_{38}H_{42}N_4O_4Yb$ (791.80): calcd. Yb 21.85; found Yb 21.51.

(b) Without Activation by Hg: dme (40 mL) was added by a cannula to a mixture of Yb metal filings (0.67 g; 3.89 mmol) and [$SnMe_2(Ph_2pz)_2$] (0.48 g; 0.82 mmol). A golden-yellow solution was observed after 5 min. As with mercury activation, a white precipitate appeared with progression of the reaction. The mixture was stirred overnight, after which time the colour had deepened to an orange colour with some precipitate still observed. The mixture was sonicated for 1 h, causing the remaining precipitate to dissolve, and the solution was orange-red. The filtrate was collected by a filter cannula and dme was concentrated to 10 mL, resulting in deep-red crystalline material. Yield 0.65 g (71%). The IR and ^{1}H NMR spectra of these crystals were identical with those reported for [Yb$(Ph_2pz)_2(dme)_2$].[4] A unit cell on these crystals [monoclinic, $P2_1/a$, a = 7.827(3), b = 18.835(6), c = 24.005(7) Å; β = 91.17(3)°, V = 3538(1) Å^3] was in agreement with that reported for [Yb$(Ph_2pz)_2(dme)_2$].[4] $C_{38}H_{42}N_4O_4Yb$ (791.80): calcd. Yb 21.85; found Yb 22.44.

Analysis of [Yb$(Ph_2pz)_2(dme)_2$] Reaction Mixture (for Identification of Sn Coproducts): dme (15 mL) was added by a cannula to a mixture of Yb metal filings (0.98 g; 5.68 mmol), [$SnMe_2(Ph_2pz)_2$] (0.59 g; 1.01 mmol) and 1–2 drops of Hg. The resulting solution was stirred for 2 h, resulting in a deep-red solution. Samples of the reaction mixture were collected in the drybox for ^{119}Sn and ^{171}Yb NMR spectroscopy. ^{119}Sn{^{1}H} NMR (149 MHz, C_6D_6, 25 °C): δ = 1.8, –95.5, –97.4, –108.0 ppm. ^{171}Yb NMR: δ = 488.6 ppm. GC/MS of the reaction mixture indicated formation of hexamethylditin (*m*/*z* 326, most intense peak of cluster with the correct isotope pattern).

[Yb$(Ph_2pz)_3(thf)_2$]

(a) Activation by Hg: thf (40 mL) was added by a cannula to a mixture of Yb metal filings (0.66 g; 3.81 mmol), [$SnMe_2(Ph_2pz)_2$] (0.54 g; 0.93 mmol) and Hg (2 drops). An instant deep-orange colour was observed. The mixture was stirred for 1 h, after which time the resulting deep orange-red solution was filtered by a filter cannula. Upon concentration of the filtrate, the deep-coloured solution lightened gradually to a yellow solution, and very fine yellow crystalline material formed. These crystals were unsuitable for X-ray determination. The solvent thf was removed under vacuum, yielding a pale-yellow precipitate (0.43 g; 74%). The IR spectrum agreed with that of [Yb$(Ph_2pz)_3(thf)_2$].[27] $C_{53}H_{49}N_6O_2Yb$ (975.03): calcd. Yb 17.74; found Yb 18.59. For loss of one thf molecule $C_{49}H_{41}N_6OYb$ (902.92): calcd. 19.16; found 18.59.

(b) Without Activation by Hg: thf (40 mL) was added by a cannula to a mixture of Yb metal filings (0.76 g; 4.40 mmol) and [$SnMe_2(Ph_2pz)_2$] (0.42 g; 0.72 mmol). No colour change was observed after 5 min. The solution was stirred overnight, after which time a white precipitate was observed. The mixture was placed in the sonication bath for 3 h. After 2 h of sonication, a deep-yellow colour was obtained, which deepened to deep orange-red after 3 h. The deep-coloured solution was allowed to settle and was then filtered by a filter cannula. As the solution was concentrated, the colour lightened to an orange colour. No crystals formed, and thf was removed under vacuum, yielding pale orange-yellow precipitate (0.27 g; 58%). The IR spectrum was in agreement with that of [Yb$(Ph_2pz)_3(thf)_2$].[27] For $C_{53}H_{49}N_6O_2Yb$ (975.03): calcd. Yb 17.74; found Yb 17.76.

[Yb$(Ph_2pz)_3(thf)_2$]·$2C_6D_6$: thf (10 mL) was added to [Yb$(Ph_2pz)_2(dme)_2$] (0.14 g; 0.18 mmol) and [$SnMe_2(Ph_2pz)_2$] (0.08 g; 0.13 mmol), and an instant orange-red solution was observed. The solution was stirred at room temperature for 2 d, after which time an orange solution was obtained. Concentration of the thf solution resulted in an orange precipitate. The IR spectrum of the orange precipitate was different to both starting materials and was similar to other reported [Ln$(Ph_2pz)_3(thf)_2$][27,41] complexes: $\tilde{\nu}$ = 1601 (m), 1574 (w), 1537 (w), 1511 (w), 1401 (m), 1294 (w), 1099 (br. s), 1059 (br. s), 1020 (br. s), 976 (m s), 915 (m), 866 (m), 792 (br. s), 754 (s), 706 (m), 688 (s), 668 (m) cm^{-1}. The ^{1}H NMR spectrum was attempted in C_6D_6. However, due to the paramagnetic nature of Yb^{3+}, a spectrum could not be obtained due to excessive broadening and shifting of the resonances. The NMR solution was returned to the dry box, and crystalline product [Yb$(Ph_2pz)_3(thf)_2$]·$2C_6D_6$ was obtained after allowing the C_6D_6 solution to slowly evaporate over time.

[Yb$(Ph_2pz)_3$(dme)]·0.5dme

(a) Oxidation with [Tl(Ph_2pz)]: [Tl(Ph_2pz)] (0.42 g; 1.00 mmol) was added to a thf solution (30 mL) of [Yb$(Ph_2pz)_2(dme)_2$] (0.79 g; 1.00 mmol), causing an immediate colour change from deep red to pale yellow and suspension of a grey solid. The solid was isolated and thf was removed under reduced pressure to give an off-white solid. The precipitate was recrystallised from dme to give yellow crystals of [Yb$(Ph_2pz)_3$(dme)]·0.5dme (0.74 g; 77%). IR: $\tilde{\nu}$ = 3060 (m), 3036 (m), 1605 (m), 1512 (m), 1422 (w), 1408 (w), 1250 (w), 1191 (w), 1124 (m), 1108 (m), 1092 (m), 1072 (w), 1047 (s), 1021 (m), 974 (s), 909 (w), 861 (s), 803 (m), 761 (vs), 694 (vs), 683 (vs) cm^{-1}. Visible/near IR (thf): λ_{max} (ε) = 975 (15) nm. $C_{51}H_{48}N_6O_3Yb$ (966.0): calcd. C 63.41, H 5.01, N 8.70, Yb 17.91; found C 62.74, H 5.28, N 8.56, Yb 17.50.

(b) Treatment with Ph_2pzH and [Hg$(C_6F_5)_2$]: Ph_2pzH (0.33 g; 1.50 mmol) and [Hg$(C_6F_5)_2$] (0.41 g; 0.75 mmol) were successively added to a thf solution (30 mL) of [Yb$(Ph_2pz)_2(dme)_2$] (1.19 g; 1.5 mmol) causing an immediate colour change (on addition of [Hg$(C_6F_5)_2$]) from deep red to pale yellow and suspension of a grey solid. After filtration thf was removed under reduced pressure to give an off-white solid, which was recrystallised from dme to give large yellow crystals of [Yb$(Ph_2pz)_3$(dme)]·0.5dme (1.16 g; 80%). The IR spectrum was the same as that obtained in method a. $C_{51}H_{48}N_6O_3Yb$ (966.0): calcd. Yb 17.91; found Yb 17.50. Single crystals suitable for X-ray were grown at –20 °C from a saturated solution in dme.

Reaction of [Nd$(Ph_2pz)_3(thf)_3$]·thf with [$SnMe_2(Ph_2pz)_2$] in thf: thf (10 mL) was added by a cannula to a mixture of [$SnMe_2(Ph_2pz)_2$]

(0.13 g; 0.22 mmol) and $[Nd(Ph_2pz)_3(thf)_3]\cdot thf$ (0.44 g; 0.40 mmol), and the resulting mixture was stirred at room temperature for 1 h. Concentration of the thf solution resulted in pale-blue crystalline material. A unit cell of these crystals [orthorhombic, $P2_12_12_1$, a = 14.13(2), b = 16.11(1), c = 22.61(2) Å; V = 5147(8) Å^3] was in agreement with that of $[Nd(Ph_2pz)_3(thf)_3]\cdot thf$[21] [orthorhombic, $P2_12_12_1$, a = 14.009(9), b = 16.280(8), c = 22.640(16) Å; V = 5163(5) Å], indicating no reaction. The IR and ^{1}H NMR spectra both agreed with data for $[Nd(Ph_2pz)_3(thf)_3]\cdot thf$.[21]

X-ray Crystallography: Crystalline samples of $[SnMe_2(Ph_2pz)_2(thf)]$, $[Eu(Ph_2pz)_2(dme)_2]$, $[Yb(Ph_2pz)_2(dme)].0.5dme$ and $[Yb(Ph_2pz)_3(thf)_2]\cdot 2C_6D_6$ were mounted on glass fibres in viscous hydrocarbon oil. Crystal data were collected by using the Bruker ApexII diffractometer, equipped with monochromated Mo-K_α radiation, λ = 0.71073 Å. All data were collected at 123 K, maintained by using an open flow of nitrogen from an Oxford Cryostreams cryostat. X-ray data were processed by using the SAINT[42] package (Bruker). Structural solution and refinement was carried out by using SHELXS-97[43] and SHELXL-97[44] utilising the graphical interface X-Seed.[45] For $[SnMe_2(Ph_2pz)_2(thf)]$, the thf molecule showed signs of disorder and was successfully modelled over two positions. Crystal data and refinement parameters for all complexes are compiled below. CCDC-676346, -676347, -676348 and -676463 contains 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.

$[SnMe_2(Ph_2pz)_2(thf)]$: $C_{36}H_{36}N_4OSn$, M = 659.38, colourless block, $0.25\times 0.18\times 0.16$ mm, monoclinic, space group $P2_1/n$ (No. 14), a = 11.3424(3), b = 17.1623(4), c = 16.4613(3) Å, β = 102.7590(10)°, V = 3125.26(12) Å^3, Z = 4, D_c = 1.401 g/cm^3, $2\theta_{max}$ = 55.0°, 80348 reflections collected, 7176 unique (R_{int} = 0.0353). Final $GooF$ = 1.12, R_1 = 0.042, wR_2 = 0.083, R indices based on 6810 reflections with $I > 2\sigma(I)$ (refinement on F^2), 382 parameters, 0 restraints. L_p and absorption corrections applied, μ = 0.85 mm^{-1}.

***cis*-$[Eu(Ph_2pz)_2(dme)_2]$:** $C_{38}H_{42}EuN_4O_4$, M = 770.72, yellow block, $0.20\times 0.15\times 0.12$ mm, monoclinic, space group $P2_1/c$ (No. 14), a = 23.894(4), b = 18.840(3), c = 7.8584(13) Å, β = 90.163(5)°, V = 3537.7(10) Å^3, Z = 4, D_c = 1.447 g/cm^3, $2\theta_{max}$ = 55.0°, 62824 reflections collected, 8129 unique (R_{int} = 0.0633). Final $GooF$ = 1.248, R_1 = 0.048, wR_2 = 0.105, R indices based on 7686 reflections with $I > 2\sigma(I)$ (refinement on F^2), 425 parameters, 24 restraints. L_p and absorption corrections applied, μ = 1.82 mm^{-1}.

$[Yb(Ph_2pz)_3(thf)_2]\cdot 2C_6D_6$: $C_{65}H_{61}N_6O_2Yb$, M = 1131.24, colourless block, $0.10\times 0.08\times 0.07$ mm, monoclinic, space group $P2_1/c$ (No. 14), a = 15.5107(3), b = 10.1644(2), c = 34.8291(6) Å, β = 100.9280(10)°, V = 5391.48(18) Å^3, Z = 4, D_c = 1.394 g/cm^3, $2\theta_{max}$ = 55.0°, 64783 reflections collected, 12379 unique (R_{int} = 0.0414). Final $GooF$ = 1.085, R_1 = 0.034, wR_2 = 0.063, R indices based on 10378 reflections with $I > 2\sigma(I)$ (refinement on F^2), 667 parameters, 0 restraints. L_p and absorption corrections applied, μ = 1.79 mm^{-1}.

$[Yb(Ph_2pz)_3(dme)]\cdot 0.5dme$: $C_{51}H_{48}N_6O_3Yb$, M = 965.99, yellow prism, $0.52\times 0.48\times 0.28$ mm, monoclinic, space group $P2_1/c$ (No. 14), a = 11.401(11), b = 14.769(8), c = 27.594(18) Å, β = 102.74(6)°, V = 4532(6) Å^3, Z = 4, D_c = 1.416 g/cm^3, $2\theta_{max}$ = 50°, 7962 unique reflections measured. Final $GooF$ = 1.14, $R1$ = 0.033, $wR2$ = 0.100, R indices based on 6938 reflections with $I > 2\sigma(I)$ (refinement on F^2), 581 parameters, 0 restraints. L_p and absorption corrections applied, μ = 2.1 mm^{-1}. *Variata*: A unique data set was acquired at ca. 293 K by using a single counter instrument.

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