

Organoamido- and Aryloxo-Lanthanoids, 19^[a]Synthesis and Structures of *cisoid* and *transoid* Bis(1,2-dimethoxyethane)bis(η^2 -pyrazolato)lanthanoid(II) ComplexesGlen B. Deacon,^{*[a]} Ewan E. Delbridge,^[a] Brian W. Skelton,^[b] and Allan H. White^[b]**Keywords:** Lanthanide(II) complexes / Ytterbium / Europium / Samarium / Redox transmetallation / Thallium / Diphenylmercury

The complexes [Yb(bind)₂(DME)₂], [Yb(MePhpz)₂(DME)₂], [Yb(azin)₂(DME)₂], and [Eu(Ph₂pz)₂(DME)₂] (bindH = 4,5-dihydro-2*H*-benz[*g*]indazole; MePhpzH = 3-methyl-5-phenylpyrazole; azinH = 7-azaindole; Ph₂pzH = 3,5-diphenylpyrazole; DME = 1,2-dimethoxyethane) have been prepared by redox transmetallation between ytterbium or europium metal and the corresponding thallium(I) pyrazolate in tetrahydrofuran (THF) in the presence of mercury metal, followed by work up with DME. The thallium reagents were obtained by treatment of the appropriate pyrazole with thallium(I) ethoxide. Both [Yb(Ph₂pz)₂(DME)₂] and [Sm(Ph₂pz)₂(DME)₂] have been prepared by metathesis from LnI₂(THF)₂ and K(Ph₂pz) in THF, whilst the former has also been obtained by redox transmetallation from [Hg(Ph₂pz)₂] and ytterbium metal and by reaction of 3,5-diphenylpyrazole with Yb(C₆F₅)₂, and the latter from protolysis of [Sm{N(SiMe₃)₂}(THF)₂] with Ph₂pzH, followed in each case by crystallisation of the crude product from DME.

Europium(II) 3,5-di-*tert*-butylpyrazolate was synthesised by a redox transmetallation/ligand exchange reaction between europium metal chunks, diphenylmercury(II), and 3,5-di-*tert*-butylpyrazole (*t*Bu₂pzH) in the presence of mercury metal in THF, and [Eu(*t*Bu₂pz)₂(DME)₂] was isolated on crystallisation of the crude product from DME. The X-ray crystal structures of [Ln(L)₂(DME)₂] (Ln = Yb, L = bind or azin; Ln = Eu or Sm, L = Ph₂pz; Ln = Eu, L = *t*Bu₂pz), each of a different crystallographic form, reveal eight-coordinate lanthanoid complexes with two η^2 -pyrazolate and two chelating DME ligands, but the structures differ in the relationship (*cisoid* or *transoid*) between the pyrazolate ligands. Thus cen–Ln–cen (cen = centre of the N–N bond) angles of 106.7° [Yb(bind)₂(DME)₂] (**3a**), 141.4° [Yb(azin)₂(DME)₂] (**3c**), 142.2° [Eu(Ph₂pz)₂(DME)₂] (**4a**), 107.4° [Eu(*t*Bu₂pz)₂(DME)₂] (**4b**), and 102.1° [Sm(Ph₂pz)₂(DME)₂] (**5**) are observed.

Introduction

Pyrazolate ligands have had an extensive role as bridging ligands particularly between d-block metals, and as chelating ligands, particularly to f-block metals.^[2] This chemistry is now being enlivened by a range of new features, such as the first homoleptic η^2 -pyrazolates,^[3a] the first η^2 -d block^[3a,3b] and main-group^[3c] pyrazolates, the use of pyrazolates in semiconductor doping,^[3d] and new modes of pyrazolate coordination (μ - η^2 : η^2 ^[3e] and combined η^2 and μ - η^1 : η^1 ^[3f]). Recent investigations have provided synthetic routes to a range of lanthanoid(III) pyrazolates.^[4–7] Structures of initially prepared compounds revealed cages and dimers with both bridging (μ - η^1 : η^1) and chelating (η^2) ligands.^{[4][5]} However, lanthanoid(III) complexes of bulky 3,5-disubstituted pyrazolates [Ln(R₂pz)₃(L)_{*n*}] (R = *t*Bu or Ph; L = tetrahydrofuran (THF), 1,2-dimethoxyethane

(DME), or Ph₃PO; *n* = 1–3) are monomeric with exclusively η^2 -bonding.^{[6][7]} Moreover, the preferred arrangements of the three η^2 -pyrazolate ligands, can induce unexpected coordination modes of the co-ligands, e.g. bridging DME ligands in [Nd(*t*Bu₂pz)₃(DME)]_∞, and novel unidentate DME in [Er(Ph₂pz)₃(DME)₂].^[7] Lanthanoid(II) pyrazolates appear less favoured since the redox transmetallation/ligand exchange reaction between Yb metal, Hg(C₆F₅)₂, and 3,5-di-*tert*-butylpyrazole yields [Yb(*t*Bu₂pz)₃(THF)₂] even when an excess of the highly reducing metal is used.^[6a,6c] However, recently we have prepared the first lanthanoid(II) pyrazolate complex [Yb(Ph₂pz)₂(DME)₂] by redox transmetallation between Yb metal and thallium(I) 3,5-diphenylpyrazolate, and also by redox transmetallation/ligand exchange between the lanthanoid element, HgPh₂, and 3,5-diphenylpyrazole.^[8] Subsequently, use of 3,5-di-*tert*-butylpyrazole in the latter synthetic method and crystallisation of the product from petroleum ether gave [Yb(*t*Bu₂pz)₂(THF)]₂, which contained the first example of a μ - η^2 : η^2 -bonded pyrazolate.^[3e] We now report a detailed study of the synthesis and structures of a range of bis(1,2-dimethoxyethane)bis(pyrazolato)lanthanoid(II) complexes, as well as the preparation and structure of the closely related [Yb(azin)₂(DME)₂] (azinH = 7-azaindole).

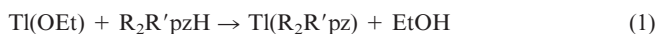
^[a] Chemistry Department, Monash University, Clayton, Victoria 3168, Australia
Fax: (internat.) + 61-3/9905-4597
E-mail: Glen.Deacon@sci.monash.edu.au

^[b] The Department of Chemistry, The University of Western Australia, Nedlands, Western Australia, 6907, Australia
Fax: (internat.) + 61-8/9380-1005

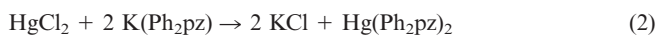
Results and Discussion

Synthesis

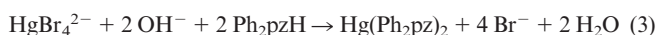
A key step in the route to lanthanoid(II) pyrazolates was the synthesis of the thallium(I) pyrazolates, Tl(bind) (**1a**) (bindH = 4,5-dihydro-2*H*-benz[*g*]indazole), Tl(MePhpz) (**1b**) (MePhpzH = 3-methyl-5-phenylpyrazole), Tl(azin) (**1c**), Tl(Ph₂pz)^[8] (**1d**), and Tl(MePh₂pz) (**1e**) (MePh₂pzH = 4-methyl-3,5-diphenylpyrazole).



However, Tl(*t*Bu₂pz) could not be prepared by this method and appeared thermally unstable. Consistent with pyrazolate formation, no ν(NH) absorption was observed in the infrared spectra of the complexes, which were additionally characterized by parent ions in their mass spectra and/or satisfactory ¹H-NMR spectra. Another possible redox transmetallation reagent, mercury(II) 3,5-diphenylpyrazolate (**2a**), was prepared both by metathesis (Equation 2),

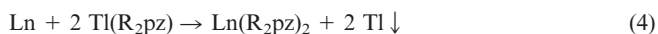


and by mercuration of diphenylpyrazole under alkaline conditions.

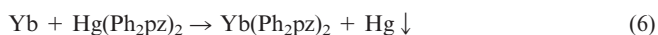
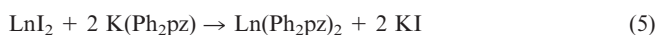


The complex could not be obtained analytically pure, but the identity was clear from an MH⁺ ion in the electrospray mass spectrum and the product was a viable source of Yb(Ph₂pz)₂ (below).

Several thallium(I) pyrazolates and Tl(azin) were found to undergo redox transmetallation with ytterbium and europium in tetrahydrofuran to give the corresponding divalent pyrazolates.



Crystallisation of the crude products from DME gave the complexes [Yb(bind)₂(DME)₂] (**3a**), [Yb(MePhpz)₂(DME)₂] (**3b**), [Yb(azin)₂(DME)₂] (**3c**), and [Eu(Ph₂pz)₂(DME)₂] (**4a**). The reported [Yb(Ph₂pz)₂(DME)₂], previously prepared by Equation 4 and by redox transmetallation/ligand exchange from Yb metal, HgPh₂, and Ph₂pzH,^[8] was prepared in modest to good yields by three further methods, viz. metathesis from ytterbium diiodide (Equation 5, Ln = Yb), redox transmetallation from impure Hg(Ph₂pz)₂ (Equation 6), and protolysis of bis(pentafluorophenyl)ytterbium(II) (Equation 7).

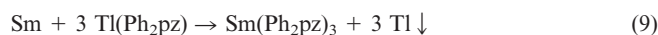


Only, a short reaction time was needed for successful isolation of Yb(Ph₂pz)₂ from Equation 7, otherwise a black unidentified solid was obtained, similar to the unsuccessful outcome of an attempted synthesis by redox transmetal-

lation/ligand exchange from Yb metal, Hg(C₆F₅)₂, and 3,5-diphenylpyrazole. Because of the failure to prepare Tl(*t*Bu₂pz), an alternative to Equation 4 was needed for Eu(*t*Bu₂pz)₂, and this was achieved by redox transmetallation/ligand exchange between europium metal, diphenylmercury, and 3,5-di-*tert*-butylpyrazole (Equation 8),



followed by isolation as [Eu(*t*Bu₂pz)₂(DME)₂] (**4b**). This synthetic method has previously been used for [Yb(Ph₂pz)₂(DME)₂] (**3d**)^[8] and [Yb(*t*Bu₂pz)₂(THF)₂]^[3e]. Since an attempt to prepare Sm(Ph₂pz)₂ by Equation 4 yielded instead Sm(Ph₂pz)₃ (Equation 9),^[8]



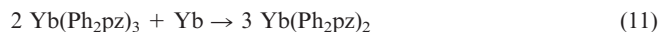
two alternative approaches were used to give the divalent target compound, viz metathesis (Equation 5) (Ln = Sm), and protolysis of bis[bis(trimethylsilyl)amido]samarium(II) by 3,5-diphenylpyrazole.



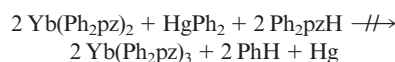
After workup with DME a much higher yield of [Sm(Ph₂pz)₂(DME)₂] (**5**) was obtained by the former method.

Equation 4 opens the use of thallium-based redox transmetallation as a route to lanthanoid organoamides. Redox transmetallation with thallium(I) reagents was a source of only cyclopentadienyls^[9] and phenolates,^[10] prior to our preliminary report.^[8] Mercury-based redox transmetallation (e.g. Equation 6) has previously been used for lanthanoid amides,^[9c,11] whilst use of diphenylmercury in redox transmetallation/ligand exchange (e.g. Equation 8), is a recent development^[11] by contrast with the extensive use of Hg(C₆F₅)₂.^[9a–9c]

The different outcomes of the reactions of ytterbium and samarium with thallium 3,5-diphenylpyrazolate (Equation 4; Ln = Yb; R = Ph and Equation 9) are explicable by the observation (Experimental Section) that samarium metal does not reduce Sm(Ph₂pz)₃ whereas ytterbium metal reduces Yb(Ph₂pz)₃.



Formation of Yb(Ph₂pz)₂, rather than a trivalent complex from redox transmetallation/ligand exchange between ytterbium metal, diphenylmercury, and 3,5-diphenylpyrazole,^[8] is guaranteed both by reduction (Equation 11), and also by the current finding that Yb(Ph₂pz)₂ does not undergo oxidation/ligand exchange with diphenylmercury and Ph₂pzH.



This further illuminates the contrasting formation of Yb(*t*Bu₂pz)₃ from synthesis with Hg(C₆F₅)₂^[6a,6c] but Yb(*t*-Bu₂pz)₂ with HgPh₂.^[3c] Synthetic consequences of the dif-

fering oxidising capacity of these mercurials have been previously observed in that YbCp_2 is converted by $\text{Hg}(\text{C}_6\text{F}_5)_2$ into $\text{YbCp}_2(\text{C}_6\text{F}_5)$, but is inert to diphenylmercury,^[12a] and electrochemical reduction is more facile for $\text{Hg}(\text{C}_6\text{F}_5)_2$ than for HgPh_2 .^[12b,12c]

Despite the high air and moisture sensitivity of $[\text{Ln}(\text{R}_2\text{pz})_2(\text{DME})_2]$ complexes and $[\text{Yb}(\text{azin})_2(\text{DME})_2]$, all complexes were obtained with acceptable C, H, N, and Ln analyses. No $\nu(\text{NH})$ absorptions were observed in the spectra, consistent with the formation of pyrazolatolanthanoid complexes. The ^1H -NMR spectra of the diamagnetic Yb^{II} complexes and of $[\text{Sm}(\text{Ph}_2\text{pz})_2(\text{DME})_2]$ were consistent with the proposed compositions, except for **3a** where the bind integrations were approximately half the expected intensity, and where all resonances, especially those of bind, were surprisingly broadened. This may be the source of the low integrations. A spectrum of a cooled solution showed the same features. No Yb^{III} impurities could be detected by electronic spectroscopy (Experimental Section), and the oxidation state is clear from spectroscopy, analysis and the X-ray crystallography. Not only was the ^1H -NMR spectrum of the paramagnetic Sm^{II} complex **5** clearly resolved and assigned (Experimental Section), but it was clearly distinguishable from that of the Sm^{III} analogue, $[\text{Sm}(\text{Ph}_2\text{pz})_3(\text{DME})_2]$.^[8] The ^{171}Yb resonance of the azin complex **3c** (Experimental Section) was very close to that ($\delta = 480$) of $[\text{Yb}(\text{Ph}_2\text{pz})_2(\text{DME})_2]$,^[8] consistent with our view of the azin ligand as a pseudo-pyrazolate. It is also at lower frequencies than the ^{171}Yb chemical shift of seven-coordinate $[\text{Yb}(\text{tBu}_2\text{pz})_2(\text{THF})]_2$ ($\delta = 536$).^[3e] There is some evidence that a higher frequency shift accompanies a decrease in coordination number in complexes with similar ligands,^{[11][13]} as in these examples, but **3c** and **3d** necessarily were examined in DME and $[\text{Yb}(\text{tBu}_2\text{pz})_2(\text{THF})]_2$ in PhMe. The visible/near-IR spectra of the complexes show moderately intense (for Ln complexes) features attributable to $\text{Ln} \rightarrow \text{L}$ charge transfer (Experimental Section). More notably near-infrared absorptions characteristic^[14] of Yb^{III} and Sm^{III} were absent from the spectra of the Yb^{II} and Sm^{II} compounds.

X-ray Structure Determinations

Single-crystal X-ray structure determinations have been carried out for **3a**, **3c**, **4a**, **4b**, and **5**. No complexes, including the analogous **3d** of the preliminary report,^[8] are isostructural, and all show crystallographically independent forms. These are displayed in Figures 1–6, attention being drawn to crystallographically significant features in the Figure captions and in the Experimental Section. Selected bond lengths and angles are in Tables 1 and 2. All $[\text{Ln}(\text{R}_2\text{pz})_2(\text{DME})_2]$ complexes have eight-coordinate monomeric structures with two chelating DME and two chelating (η^2)-pyrazolate or azin ligands. In each case the two nitrogen atoms bind nearly symmetrically to the metal centre such that the metal is approximately coplanar with the ligand plane (Figures 1–6). There are two different ster-

eochemical types. Thus, the $\text{cen}-\text{Ln}-\text{cen}$ angles (cen = centre of N–N bonds or, for azin, the centre of the $\text{N} \cdots \text{N}$ distance) (Table 3) are either in the range $101-108^\circ$ (**3a**, **3d**, **4b**, **5**; Figures 1–4) giving a *cisoid* disposition of the pyrazolate ligands, or $141-143^\circ$ (**3c**, **4a**; Figure 5, 6) giving a *transoid* array of Ph_2pz or azin ligands. A similar relationship is shown by the $\text{cen}'-\text{Ln}-\text{cen}'$ angles (cen' = mid-point of the $\text{O} \cdots \text{O}$ distance) (Table 3), with **3a**, **4b**, **5**, and **3d** having values of $85-98^\circ$ and a *cisoid* disposition of DME ligands. By contrast **3c** and **4a** have values of $138-143^\circ$ respectively, arising from *transoid* DME ligands, where the four oxygen donor atoms are nearly coplanar. All single crystals were obtained from concentrated DME solutions, hence the difference in arrangement seen in the Ph_2pz complexes **3d**, **4a**, and **5**, and especially between the complexes of the adjacent metals $\text{Ln} = \text{Eu}$ or Sm , is striking.

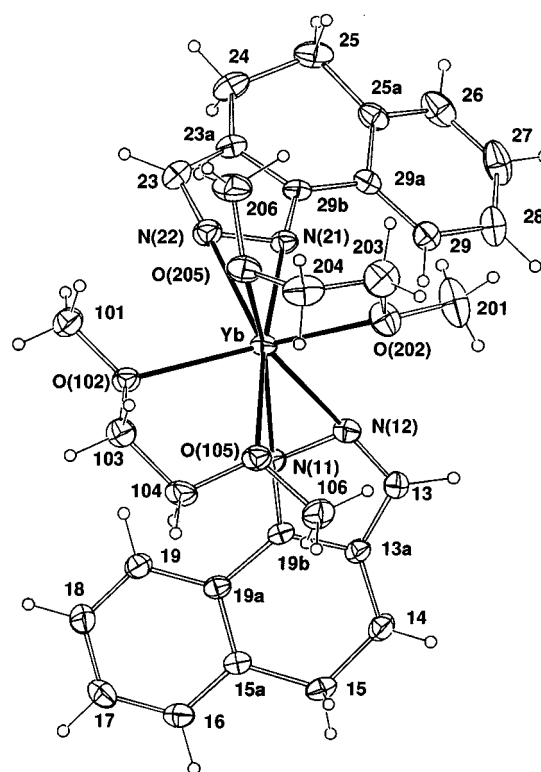


Figure 1. Molecular projection of $[\text{Yb}(\text{bind})_2(\text{DME})_2]$ (**3a**) down the quasi-2 axis; no disorder is present

Amongst the *cis* complexes, **4b**, **5**, and **3d** differ from **3a** in that the $\text{Ln}(\text{R}_2\text{pz})_2$ arrays have potential *mm* symmetry, one *m* bisecting the ligand and relating the two substituents. By contrast, the $\text{Yb}(\text{bind})_2$ array in **3a** is disposed as approaching 2 symmetry. In the *transoid* complexes, **3c** and **4a**, the Ph_2pz and azin ligand pairs are closely coplanar with each other and with the metal atom. In the diphenylpyrazolate complexes **4a**, **5**, and **3d**, each pyrazolate ring is almost coplanar with its phenyl substituents, regardless of whether the Ph_2pz groups are *cisoid* or *transoid*.

In **3a**, one molecule devoid of crystallographic symmetry, and of any complicating factors such as different bind ligand orientations (possible by reversal of the inequivalent

Table 1. Metal atom environments in *cisoid* **5**, **4b** (molecules 1 and 2), **3d**, **3a**; connectivity to (*r* [Å]) or via the metal centre (angles [°]); * values are for the disordered/symmetry-related O component

Atom*	<i>r</i> [Å]	5 N(11') 4b(1) N(112) 4b(2) N(212) 3d N(12) 3a N(12)	N(21) N(121) N(221) N(21) N(21)	N(21') N(122) N(222) N(22) N(22)	O(102) O(1102) O(2102) O(102) O(102)	O(105) O(1105) O(2105) O(105) O(105)	O(202) O(1202) O(2202) O(202) O(202)	O(205) O(1205) O(2205) O(205) O(205)
5 N(11)	2.556(3)	31.07(8)	105.47(8)	97.10(8)	91.1(1)	76.0(1)	118.7(1)	155.24(9)
4b(1) N(111)	2.53(1)	32.2(3)	112.8(3)	99.9(3)	92.3(3)	79.8(3)	123.4(3)	162.5(4)
4b(2) N(211)	2.51(1)	31.6(3)	110.7(3)	98.3(3)	94.9(3)	78.7(3)	124.1(4)	166.0(3)
3d N(11)	2.426(7)	32.7(2)	107.3(2)	95.5(2)	87.7(2)	91.2(2)	116.7(2)	174.7(2)
3a N(11)	2.465(3)	32.6(1)	101.5(1)	112.7(1)	91.80(9)	76.91(9)	112.9(1)	156.7(1)
5 N(11')	(2.556(3))		(97.10(8))	(105.47(8))	121.4(1)*	87.6(1)*	89.8(1)*	(155.24(9))
4b(1) N(112)	2.527(9)		103.5(3)	108.3(3)	122.0(3)	85.6(3)	96.3(3)	158.4(3)
4b(2) N(212)	2.54(1)		101.9(3)	107.4(3)	123.3(3)	83.8(3)	97.5(4)	158.8(3)
3d N(12)	2.414(7)		96.4(2)	102.8(2)	119.7(2)	97.9(2)	86.8(2)	150.9(2)
3a N(12)	2.440(3)		90.6(1)	117.2(1)	123.5(1)	85.2(1)	83.7(1)	147.1(1)
5 N(21)	2.538(3)			30.99(1)	112.9(1)	173.0(1)	92.2(1)	97.1(1)
4b(1) N(121)	2.54(1)			31.4(3)	118.7(3)	167.1(3)	96.7(3)	81.1(3)
4b(2) N(221)	2.533(9)			32.3(3)	120.7(3)	169.6(3)	98.0(3)	79.5(3)
3d N(21)	2.430(7)			32.5(2)	116.8(2)	161.2(2)	91.0(2)	77.3(2)
3a N(21)	2.399(3)			33.1(1)	118.77(9)	174.3(1)	95.3(1)	101.8(1)
5 N(21')	(2.538(3))				83.5(1)*	142.5(1)*	121.4(2)*	(97.1(1))
4b(1) N(122)	2.517(9)				92.2(3)	153.5(3)	125.6(4)	86.7(3)
4b(2) N(222)	2.511(9)				93.8(3)	154.0(3)	127.2(4)	85.3(3)
3d N(22)	2.424(7)				86.7(2)	151.2(2)	122.8(2)	87.1(2)
3a N(22)	2.459(3)				86.7(1)	152.6(1)	115.8(1)	87.1(1)
5 O(102)	2.720(7)					60.2(2)	134.8(2)	70.5(1)
4b(1) O(1102)	2.667(8)					61.4(3)	114.8(3)	71.2(4)
4b(2) O(2102)	2.693(8)					61.1(3)	110.4(3)	71.2(3)
3d O(102)	2.576(7)					65.6(2)	136.6(2)	87.9(2)
3a O(102)	2.519(3)					66.84(9)	133.26(9)	76.67(9)
5 O(105)	2.708(5)						93.0(2)	80.4(1)
4b(1) O(1105)	2.724(9)						72.9(3)	87.1(3)
4b(2) O(2105)	2.767(8)						72.4(3)	92.0(3)
3d O(105)	2.484(6)						77.8(2)	84.4(2)
3a O(105)	2.551(3)						80.5(1)	79.95(9)
5 O(202)	2.627(7)							69.5(1)
4b(1) O(1202)	2.69(1)							62.2(4)
4b(2) O(2202)	2.68(1)							61.5(4)
3d O(202)	2.502(6)							65.2(2)
3a O(202)	2.508(3)							65.1(1)
5 O(205)	2.551(4)							
4b(1) O(1205)	2.71(1)							
4b(2) O(2205)	2.73(1)							
3d O(205)	2.558(7)							
3a O(205)	2.577(3)							

N donor atoms), comprises the asymmetric unit. However, in **3c**, isomeric diversity arising from alternative azin orientations is manifested as disorder, although one of the four possible combinations is dominant, as is displayed in Figure 3a.

The pyrazolate and azin ligands are symmetrically coordinated with differences in Ln–N bond pairs ≤ 0.06 Å for all ligands and ≤ 0.03 Å for all but two. Even the largest differences, which, not surprisingly, are found for the unsymmetrical ligands bind and azin, are observed for only one ligand in each of **3a** and **3c**, respectively. Moreover, the maximum difference (0.06 Å) is less than those (0.07–0.10 Å) in some Ln^{III} complexes with Ph₂pz and *t*Bu₂pz.^[6b,7a] There is more asymmetry in the DME chelation with the largest pair of differences (0.10, 0.06 Å) in **3d** which has

highly symmetrical Ph₂pz coordination, but different conformations of the (non-disordered) DME ligands. Further, no unusual asymmetry in the DME coordination is found in complexes of the unsymmetrical ligands bind and azin. In **3a**, the two DME ligands have different conformations whilst in **3c** they are the same. When appropriate allowance is made for the differences in the ionic radii of eight coordinate Eu²⁺, Sm²⁺, and Yb²⁺^[15], the <Ln–N> bond distances of all complexes are very similar with sole exception of **3c**, where <Yb–N> is ca. 0.13 Å longer than values for the other two Yb^{II} complexes, **3a** and **3d**. Given that the 7-azindolate ligand is not a pyrazolate, it would be unwise at this stage to attach too much significance to this difference, but it can be argued that azin has more steric stress in the immediate vicinity of the donor atoms than R₂pz ligands

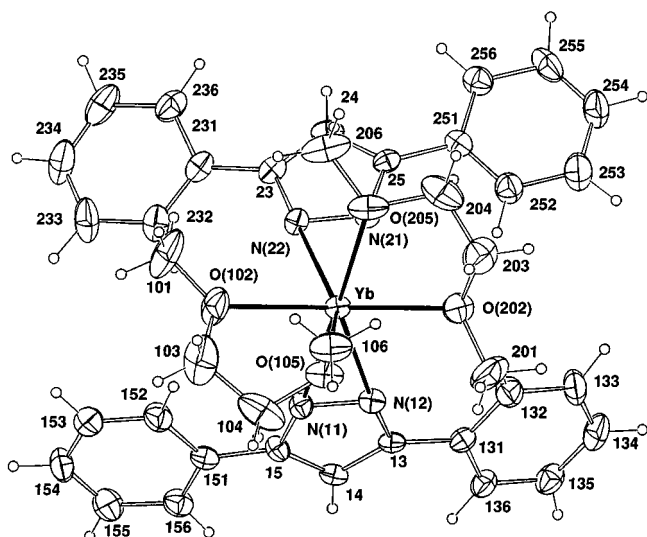


Figure 2. Molecular projection of $[\text{Yb}(\text{Ph}_2\text{pz})_2(\text{DME})_2]$ (**3d**) down the quasi-2 axis; no disorder is present

and the “bite” is also larger. Greater uniformity is seen in ionic radius adjusted $\langle \text{Ln}-\text{O} \rangle$ values (despite greater individual variation than for $\text{Ln}-\text{N}$), with a slight deviation in $\langle \text{Eu}-\text{O} \rangle$ of **4b**, which is ca. 0.05 Å longer than for other complexes. This may be a consequence of the bulky *tert*-butyl substituents of the *t*Bu₂pz ligand. For the azin complex **3c**, the Yb–O distances are similar to those of **3a** and **3d**, despite the longer Yb–N lengths. Comparison of bond lengths in *cisoid* and *transoid* Ph₂pz complexes **3d**, **5**, and **4a** reveals no significant differences after allowance for ionic radii differences. Subtraction of eight-coordinate Ln³⁺ radii^[15] from $\langle \text{Ln}-\text{N} \rangle$ values gives a residue of 1.28–1.32 Å, for all complexes except for the anomalous **3c** (1.42 Å), and these are at the low end of the range, 1.26–1.38 Å, for $[\text{Ln}(\text{R}_2\text{pz})_3\text{L}_n]$ (L = THF, *n* = 2 or 3; L = DME, *n* = 1 or 2) complexes.^[6,7a] The uniqueness of the azin coordination is further illustrated by the subtraction value, which lies outside the normal pyrazolatanlanthanoid range. Similar subtraction from $\langle \text{Ln}-\text{O} \rangle$ gives 1.38–1.40 Å with the exception of 1.45 Å for the *t*Bu₂pz complex **4b**. Values for Ln^{III} complexes $[\text{Ln}(\text{R}_2\text{pz})_3(\text{THF})_n]$ (*n* = 2 or 3) cover the range 1.35–1.38 Å,^[6] whilst $[\text{Er}(\text{Ph}_2\text{pz})_3(\eta^2\text{-DME})(\eta^1\text{-DME})]$ gives 1.35 Å for the η^1 -DME and 1.42 Å for the chelating DME.^[7a] These subtraction residues suggest that the $[\text{Ln}(\text{R}_2\text{pz})_2(\text{DME})_2]$ structures are not greatly crowded, especially given that analogous values for Ln–O(THF) in crowded, bulky aryloxides lie in the range 1.49–1.59 Å.^[10b,10c,16]

Experimental Section

General: The compounds described here are extremely air- and moisture-sensitive and consequently all operations were carried out in an inert atmosphere (purified argon or nitrogen). Unless indicated otherwise, handling methods and solvent purification were as described previously.^[17] Petroleum ether refers to the fraction boiling between 40 and 60 °C. – IR data (4000–650 cm^{−1}) were obtained for Nujol mulls sandwiched between NaCl plates with a Per-

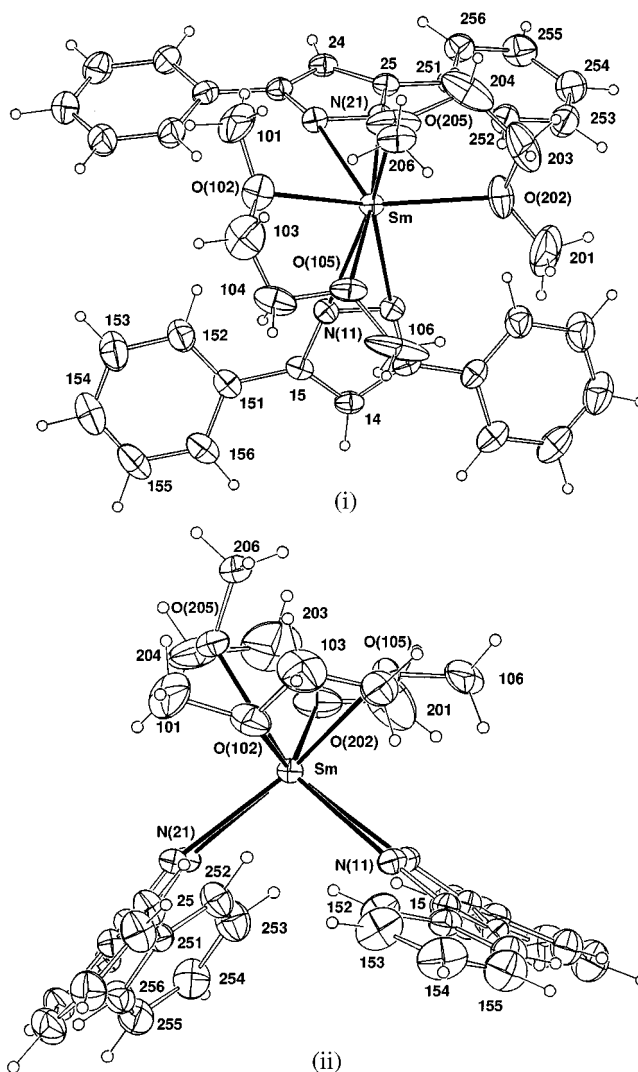


Figure 3. Molecular projections of $[\text{Sm}(\text{Ph}_2\text{pz})_2(\text{DME})_2]$ (**5**) (i) down and (ii) normal to the quasi-2 axis; as modelled, the molecule lies disposed to either side of a crystallographic mirror plane, passing through samarium and the mid-points of the N–N bonds of the pyrazolate ligands, i.e. normal to and vertical in the page in (i) and in the plane of the page in (ii); the DME ligands are necessarily disordered to either side of that plane, the two components having different conformations, only one of each type being shown

kin Elmer 1600 FTIR spectrometer. – Mass spectra were obtained with a VG Trio-1 GC mass spectrometer (Ln, Tl compounds) or a Micromass Platform Electrospray mass spectrometer $[\text{Hg}(\text{Ph}_2\text{pz})_2]$. Each listed *m/z* value for metal-containing ions (where the metal has more than one isotope) is the most intense peak of a cluster with an isotope pattern in good agreement with the calculated pattern. – Room-temperature (20 °C) NMR spectra were recorded with a Bruker AC 200 MHz (¹H, ¹³C) or AM 300 MHz (¹H, ¹⁷¹Yb) spectrometer. The chemical shift references were the residual solvent signals ($[\text{D}_6]$ benzene: $\delta_{\text{H}} = 7.15$, $\delta_{\text{C}} = 128.0$; $[\text{D}_8]$ THF: $\delta_{\text{H}} = 1.73$, 3.58, $\delta_{\text{C}} = 25.3$, 67.4; $[\text{D}_8]$ toluene: $\delta_{\text{H}} = 2.09$) or external $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{THF})_2]$ (0.15 M solution in THF) (¹⁷¹Yb: $\delta = 0.0$).^[13] Degrees of substitution for ¹³C nuclei were determined using ¹H/¹³C *J*-modulation pulse sequences. $[\text{D}_6]$ benzene (Cambridge Isotopes) was dried with sodium/potassium alloy and $[\text{D}_8]$ THF (Cambridge Isotopes) was dried with CaH₂. The deuterated solvents were then vacuum-transferred to greaseless Schlenk tubes and stored under purified argon. – Lanthanoid analyses were by

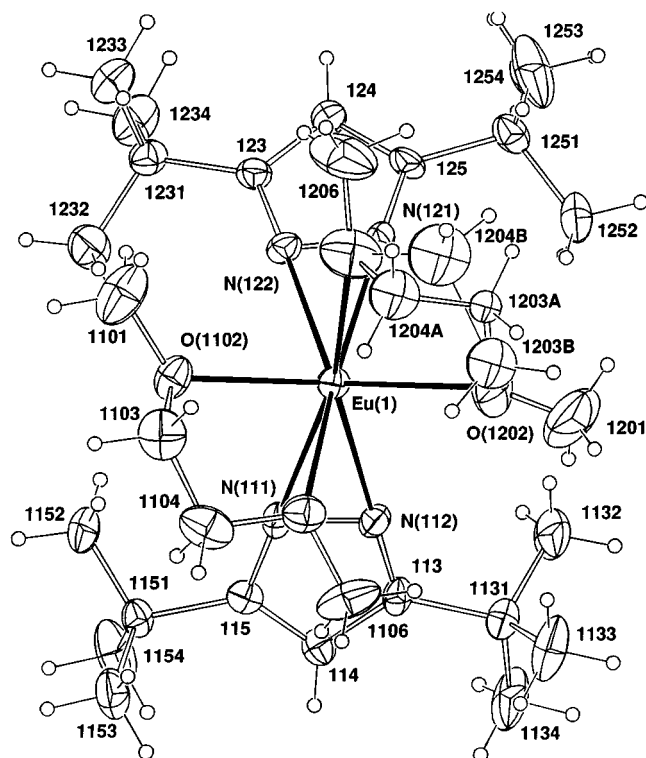


Figure 4. Molecular projection of $[\text{Eu}(\text{tBu}_2\text{pz})_2(\text{DME})_2]$ (**4b**) down the quasi-2 axis (molecule 1 only is shown, molecule 2 being pseudo-symmetrically related and therefore similar); one of the DME ligands is disordered over two conformations, the two components of the relevant atoms of the CH_2CH_2 group being shown

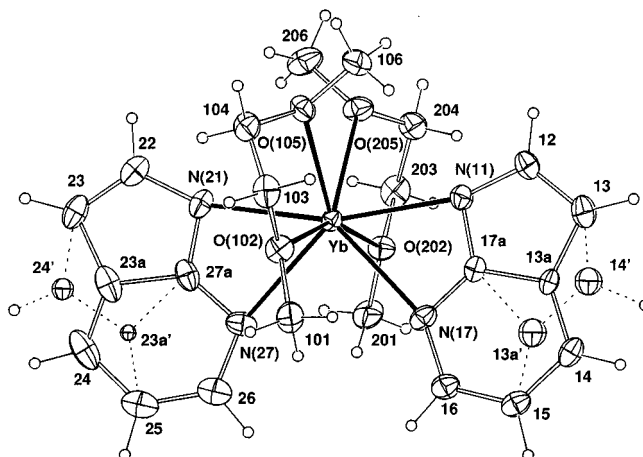
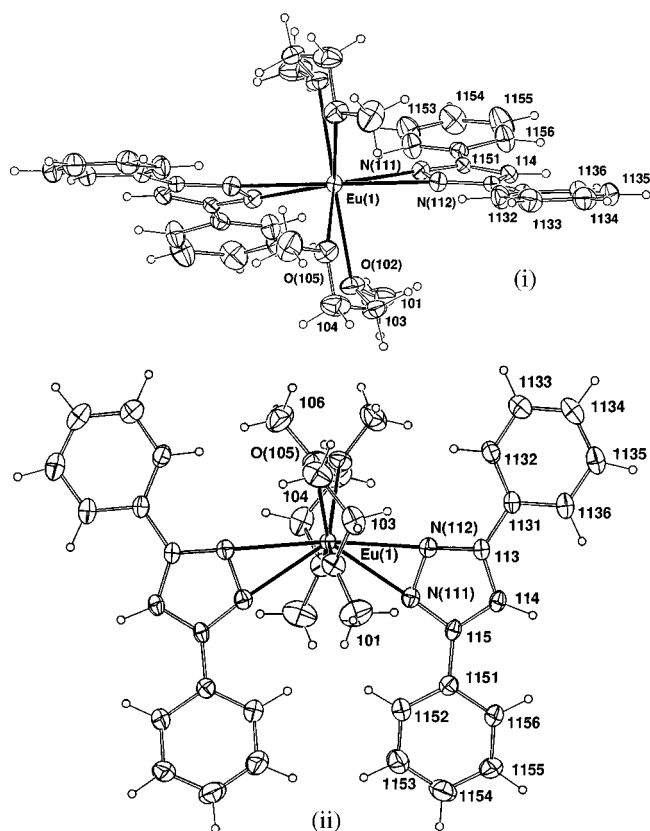


Figure 5. Molecular projection of $[\text{Yb}(\text{azin})_2(\text{DME})_2]$ (**3c**) normal to the the quasi-2 axis; minor disordered azin components being shown

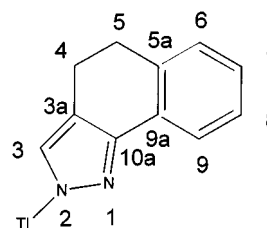
EDTA titration^[18] with xylenol orange indicator of solutions prepared by digestion of accurately weighed samples in concentrated HNO_3 /2% concentrated H_2SO_4 followed by dilution with water and buffering with hexamine. Thallium analyses were by potassium iodate titration^[19] of solutions prepared by digestion of accurately weighed samples in concentrated HNO_3 /2% concentrated H_2SO_4 . Once the HNO_3 was removed by heating, the residue was treated with excess Na_2SO_3 to reduce Ti^{3+} to Ti^+ , and the solution was boiled to expel excess SO_2 . — Microanalysis samples were sealed in glass ampoules under purified argon and were determined either by the Campbell Microanalytical Service, University of Otago, New

Table 2. Metal atom environments in *transoid* **3c**, **4a** (molecules 1 and 2); connectivity to (r [Å]) or via the metal centre (angles [°])

Atom	r [Å]	3c N(11) 4a(1) N(112) 4a(2) N(212)	N(27) N(111') N(211')	N(21) N(112') N(212')	O(102) O(102) O(202)	O(105) O(105) O(205)	O(202) O(102') O(202')	O(205) O(105') O(205')
3c N(17)	2.569(6)	54.3(2)	87.6(2)	141.8(2)	83.4(2)	124.7(2)	80.3(2)	125.4(2)
4a(1) N(111)	2.552(5)	31.0(2)	112.1(2)	141.4(2)	82.3(2)	123.1(2)	83.4(2)	107.6(2)
4a(2) N(211)	2.554(6)	31.0(2)	111.7(2)	140.4(2)	80.9(2)	115.5(2)	84.2(2)	115.1(2)
3c N(11)	2.547(6)		141.7(2)	163.9(2)	98.4(2)	85.3(2)	86.5(2)	81.4(2)
4a(1) N(112)	2.582(4)		(141.4(2))	172.2(2)	80.5(2)	96.1(2)	97.8(2)	89.8(2)
4a(2) N(212)	2.536(6)		(140.4(2))	171.1(2)	96.3(2)	99.8(2)	81.6(2)	87.0(2)
3c N(27)	2.596(6)			54.4(2)	77.7(2)	124.7(2)	83.7(2)	126.3(2)
4a(1) N(111')				31.0(2)	83.4(2)	107.6(2)	82.3(2)	123.1(2)
4a(2) N(211')				31.0(2)	84.2(2)	115.1(2)	80.9(2)	115.5(2)
3c N(21)	2.538(6)				85.1(2)	82.0(2)	96.7(2)	85.6(2)
4a(1) N(112')					(97.8(2))	(89.8(2))	(80.5(2))	(96.1(2))
4a(2) N(212')					(81.6(2))	(87.0(2))	(96.3(2))	(99.8(2))
3c O(102)	2.523(5)					65.2(2)	155.7(2)	138.8(2)
4a(1) O(102)	2.637(6)					63.5(2)	154.4(2)	141.6(2)
4a(2) O(202)	2.614(5)					62.9(2)	153.2(2)	143.9(2)
3c O(105)	2.565(5)						139.0(1)	73.8(2)
4a(1) O(105)	2.660(5)						(141.6(2))	80.9(2)
4a(2) O(205)	2.684(5)						(143.9(2))	81.0(2)
3c O(202)	2.508(5)							65.3(1)
4a(1) O(102')								(63.5(2))
4a(2) O(202')								(62.9(2))
3c O(205)	2.553(5)							



Zealand or by Chemical and Microanalytical Services Pty. Ltd, Belmont, Australia. – Lanthanoid elements as either powders or distilled metal ingots were obtained from Rhône-Poulenc. Thallium(I) ethoxide was purchased from Fluka or Merck and was filtered under argon to remove any thallium metal and stored at -20°C in the dark. 7-Azaindole and HgPh_2 were purchased from Aldrich. 4,5-Dihydro-2*H*-benz[*g*]indazole was synthesised by a reported method^[20]. Other pyrazoles were synthesised^[21] by treating the appropriate commercially available β -diketone with an equimolar



(4,5-Dihydro-2H-benz[glindazoloto]thallium(I) (1a): Thallium(I) ethoxide (0.35 mL, 1.25 g, 5.0 mmol) was added to a diethyl ether solution (30 mL) of 2H-benz[gl]-4,5-dihydroindazole (0.85 g, 5.0 mmol) giving a white precipitate, which was filtered from solution and washed twice with petroleum ether (2 × 20 mL) yielding 1.62 g (87%) of a white crystalline solid. – IR: $\tilde{\nu}$ = 1608 cm⁻¹ w, 1531 w, 1508 w, 1340 w, 1315 m, 1298 w, 1272 m, 1213 m, 1156 w, 1098 m, 1052 s, 1036 s, 1019 s, 1011 s, 960 s, 931 m, 887 m, 850 s, 762 vs, 732 s, 706 vs, 685 m, 659 w. – ¹H NMR (200 MHz, [D₈]THF): δ = 2.75 (t, 2 H, 4-H), 2.85 (t, 2 H, 5-H), 6.99–7.05 (m, 2 H, 6-H and 9-H), 7.15 (t, 1 H, 7-H), 7.44 (s, 1 H, 3-H), 7.62 (t, 1 H, 8-H). – ¹³C{¹H} NMR (200 MHz, [D₈]THF): δ = 21.0 (C-4), 31.7 (C-5), 118.0 (C-3a), 123.0 (C-9), 126.5 (C-8), 127.2 (C-7), 128.9 (C-3 and C-6), 132.5 (C-9a), 137.3 (C-5a), 151.7 (C-10a). – MS (70 eV, EI); *m/z* (%): 374 (20) [²⁰⁵Tl]M⁺, 205 (85) [²⁰⁵Tl]⁺, 170 (100) [C₁₁H₁₀N₂]⁺. – C₁₁H₉N₂Tl (373.6): calcd. Tl 54.71; found Tl 55.26.

(3-Methyl-5-phenylpyrazolato)thallium(I) (1b): Thallium(I) ethoxide (0.35 mL, 1.25 g, 5.0 mmol) was added to a THF solution (30 mL) of 3-methyl-5-phenylpyrazole (0.79 g, 5.0 mmol) giving a pale yellow solution. The THF was removed under vacuum giving **3** as an off-white solid which was recrystallised from CH₂Cl₂ and petroleum ether [1.40 g (77%)]. – IR: $\tilde{\nu}$ = 1599 cm⁻¹ m, 1292 w, 1261 m, 1154 vw, 1092 m, 1070 m, 1019 s, 962 m, 866 vw, 791 w, 759 vs, 716 s, 696 vs. – ¹H NMR (300 MHz, [D₈]THF): δ = 2.37 (s, 3 H, Me), 6.41 (s, 1 H, 4-H), 7.08–7.13 (m, 1 H, *p*-H), 7.17–7.23 (t, 2 H, *m*-H), 7.59 (d, 2 H, *o*-H). – MS (70 eV, EI); *m/z* (%): 362

Compound/molecule	3c <i>transoid</i>	4a/1 <i>transoid</i>	4a/2 <i>transoid</i>	3a <i>cisoid</i>	3d <i>cisoid</i>	4b/1 <i>cisoid</i>	4b/2 <i>cisoid</i>	5 <i>cicoid</i>
N ₁ –Ln–N ₂	141. ₄	142. ₂	141. ₂	106. ₇	101. ₄	107. ₄	105. ₈	102. ₁
N ₁ –Ln–O(102)	91. ₀	81. ₁	88. ₅	107. ₆	103. ₇	107. ₂	109. ₃	106. ₃
N ₁ –Ln–O(105)	105. ₀	109. ₈	108. ₂	80. ₇	94. ₇	82. ₄	81. ₀	81. ₅
N ₁ –Ln–O(202)	82. ₆	90. ₇	82. ₆	98. ₅	101. ₈	110. ₁	111. ₀	104. ₃
N ₁ –Ln–O(205)	104. ₁	98. ₉	101. ₂	156. ₄	166. ₉	168. ₆	171. ₂	160. ₅
N ₁ –Ln–O ₁	100. ₁	96. ₂	99. ₈	94. ₇	101. ₀	95. ₃	95. ₆	94. ₄
N ₂ –Ln–O ₂	94. ₀	95. ₆	92. ₃	129. ₆	134. ₈	140. ₇	141. ₉	135. ₉
N ₂ –Ln–O(102)	80. ₃	—	—	102. ₆	101. ₈	105. ₇	107. ₅	98. ₂
N ₂ –Ln–O(105)	104. ₂	—	—	168. ₉	161. ₇	166. ₂	168. ₄	157. ₉
N ₂ –Ln–O(202)	90. ₂	—	—	106. ₁	106. ₉	111. ₂	112. ₇	106. ₉
N ₂ –Ln–O(205)	107. ₁	—	—	94. ₅	81. ₉	83. ₇	82. ₁	97. ₄
N ₂ –Ln–O ₁	92. ₈	—	—	136. ₂	132. ₇	136. ₆	138. ₅	128. ₁
N ₂ –Ln–O ₂	100. ₃	—	—	102. ₁	94. ₉	98. ₄	98. ₁	104. ₉
O ₁ –Ln–O ₂	138. ₃	142. ₇	143. ₀	92. ₀	97. ₉	85. ₁	85. ₂	95. ₆

(40) $[(^{205}\text{Tl})\text{M}^+]$, 205 (15) $[(^{205}\text{Tl})^+]$, 158 (15) $[\text{C}_{10}\text{H}_{10}\text{N}_2^+]$. – $\text{C}_{10}\text{H}_9\text{N}_2\text{Ti}$ (361.6): calcd. Ti 56.52; found Ti 56.84.

(7-Azaindolato)thallium(I) (1c): Thallium(I) ethoxide (2.56 mL, 9.01 g, 36.1 mmol) was added to an ether solution (30 mL) of 7-azaindole (4.26 g, 36.1 mmol) giving a white precipitate and a pale yellow solution. The white precipitate was filtered from solution and washed with petroleum ether (2×30 mL) giving **1c** [11.61 g (65%)]. – IR: $\tilde{\nu} = 1582\text{ cm}^{-1}$ w, 1534 w, 1333 w, 1278 m, 1257 w, 1150 m, 1092 m, 1044 w, 898 m, 798 s, 766 vs, 746 s, 721 vs, 622 m. – ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$): $\delta = 6.39$ (s, 1 H, 3-H), 6.90 (dd, 1 H, 5-H) 7.30 (s, 1 H, 2-H), 7.87 (d, 1 H, 4-H), 8.05 (d, 1 H, 7-H). – $\text{C}_7\text{H}_5\text{N}_2\text{Ti}$ (321.5): calcd. Ti 63.57; found Ti 64.11.

(3,5-Diphenylpyrazolato)thallium(I) (1d): The preparation and properties have been given in a preliminary report.^[8]

(4-Methyl-3,5-diphenylpyrazolato)thallium(I) (1e): Thallium(I) ethoxide (0.35 mL, 1.25 g, 5.0 mmol) was added to a THF solution (30 mL) of 4-methyl-3,5-diphenylpyrazole (1.17 g, 5.0 mmol) giving a deep yellow solution. This was reduced in volume to ca. 5 mL and petroleum ether was added causing deposition of **1e** as a white solid, which was filtered off and dried under vacuum [1.80 g (82%)]. – IR: $\tilde{\nu} = 1601\text{ cm}^{-1}$ m, 1528 w, 1516 w, 1292 w, 1248 w, 1225 w, 1145 w, 1117 s, 1070 s, 1011 s, 994 w, 966 w, 916 m, 847 w, 771 vs, 718 s, 700 vs. – ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = 2.26$ (s, 3 H, CH_3), 7.20–7.26 (m, 2 H, *p*-H), 7.29–7.31 (m, 4 H, *m*-H), 7.44 (t, 4 H, *o*-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, $[\text{D}_8]\text{THF}$): $\delta = 12.2$ (Me), 111.9 (C-4, pz), 127.2 (C-4, Ph), 129.1 (C-2, C-6 and C-3, C-5, Ph), 136.2 (C-1, Ph), 153.1 (C-3, C-5, pz). – MS (70 eV, EI); *m/z* (%): 438 (40) $[(^{205}\text{Tl})\text{M}^+]$, 234 (90) $[\text{C}_{16}\text{H}_{14}\text{N}_2^+]$, 205 (15) $[(^{205}\text{Tl})^+]$, 130 (100) $[\text{C}_9\text{H}_8\text{N}^+]$. – $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Ti}$ (437.7): calcd. C 43.90, H 2.99, N 6.40; found C 44.00, H 3.08, N 6.21.

Bis(3,5-diphenylpyrazolato)mercury(II) (2)

Method A: 3,5-Diphenylpyrazole (1.00 g, 4.5 mmol) was treated with a THF solution (30 mL) of potassium hydride (0.18 g, 4.5 mmol) at 0°C . Gas evolution was observed and a slightly pale yellow solution formed. HgCl_2 (0.62 g, 2.3 mmol) was added causing formation of a white precipitate. The reaction mixture was stirred for 1 h and then was treated with water. The precipitated mercurial **2** was filtered off, washed with water, ethanol, and ether, and then dried under vacuum for 30 min giving 1.10 g (76%) of impure **2** as a white powder. – IR: $\tilde{\nu} = 1604\text{ cm}^{-1}$ m, 1542 w, 1400 m, 1236 w, 1321 w, 1296 w, 1274 m, 1236 m, 1157 m, 1128 m, 1074 s, 1026 m, 1001 w, 986 m, 958 w, 914 m, 844 w, 800 w, 758 vs, 696 vs. – MS (electrospray); *m/z* (%): 641 (100) $[(^{202}\text{Hg})\text{MH}^+]$, 549 (100) $[(^{202}\text{Hg})\text{C}_{23}\text{H}_{15}\text{N}_4^+]$, 467 (76) $[(^{202}\text{Hg})\text{C}_{17}\text{H}_{19}\text{N}_3^+]$. – $\text{C}_{30}\text{H}_{22}\text{N}_4\text{Hg}$ (639.1): calcd. C 56.38, H 3.47, N 8.77; found C 54.57, H 3.77, N 8.07.

Method B: HgBr_2 (1.80 g, 5.0 mmol) and NaBr (2.05 g, 20 mmol) were dissolved in *t*BuOH (80 mL). 3,5-Diphenylpyrazole (2.20 g, 10 mmol) and NaOH (0.80 g, 20 mmol) were added and the reaction mixture was refluxed for 4 h. The cream-coloured solution was poured into distilled H_2O (150 mL) giving bis(3,5-diphenylpyrazolato)mercury as a cream precipitate which was filtered from the solution and dried under vacuum. The infrared spectrum of this compound was in good agreement with that of the product from Method A and a yield of > 90% was obtained.

Bis(2H-benz[*g*]-4,5-dihydroindazolato)bis(1,2-dimethoxyethane)-ytterbium(II) (3a): A mixture of ytterbium powder (0.69 g, 4.0 mmol) and (2H-benz[*g*]-4,5-dihydroindazolato)thallium(I) (0.74 g, 2.0 mmol) in THF (30 mL) was subjected to ultrasonication for 24 h. The resulting deep red solution with grey suspended solids was allowed to stand for several hours, when a filter cannula was em-

ployed to separate the red solution from the deposited grey solids. The THF was removed under vacuum yielding a red solid which was dissolved in DME (40 mL) and allowed to stand for several days at room temperature during which time 0.54 g (78%) of large red crystals formed. – IR: $\tilde{\nu} = 1605\text{ cm}^{-1}$ m, 1528 w, 1509 w, 1297 w, 1275 w, 1240 w, 1224 w, 1210 w, 1191 w, 1121 m, 1097 s, 1073 s, 1045 w, 1028 w, 1009 m, 977 m, 954 m, 943 m, 884 m, 855 s, 818 s, 766 vs, 734 m, 716 vs, 686 m, 673 m. – ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = 2.73$ and 2.79 (br. d, overlapping signals, total integration 4 H, 4-H, 5-H), 3.31 (br. s, 12 H, MeO, DME), 3.48 (br. s, 8 H, CH_2 DME), 7.00 (br. m, 3 H, 6-H, 7-H, 9-H), 7.55 (br. s, 1 H, 3-H), 7.85 (br. s, 1 H, 8-H). Integration of the indazole protons showed approximately half the expected intensity. – Visible/near IR (THF): λ_{max} (ϵ): 430 (415) nm. – $\text{C}_{30}\text{H}_{38}\text{N}_4\text{O}_4\text{Yb}$ (691.7): calcd. C 52.09, H 5.54, N 8.10, Yb 25.02; found C 51.91, H 5.66, N 7.27, Yb 25.14.

Bis(1,2-dimethoxyethane)bis(3-methyl-5-phenylpyrazolato)-ytterbium(II) (3b): A mixture of ytterbium powder (1.73 g, 10.0 mmol), mercury metal (ca. 0.20 mL), and (3-methyl-5-phenylpyrazolato)thallium(I) (1.20 g, 2.31 mmol) in THF (30 mL) was subjected to ultrasonication for 48 h. The resulting deep red solution with grey suspended solids was allowed to stand for several hours until the suspension settled out. The reaction mixture was then filtered using a filter cannula. The filtrate was concentrated to dryness under vacuum yielding a red solid which was dissolved in DME which was subsequently removed under vacuum giving **3b** [0.48 g (62%)]. – IR: $\tilde{\nu} = 1602\text{ cm}^{-1}$ m, 1527 w, 1491 m, 1413 m, 1298 w, 1190 w, 1155 w, 1099 m, 1054 s, 1016 m, 964 m, 912 w, 888 m, 858 m, 762 vs, 712 m, 695 vs. – Visible/near IR (THF): λ_{max} (ϵ) = 389 nm (586). – ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = 2.22$ (br. s, 6 H, 3-Me), 3.20 (s, 12 H, MeO DME), 3.36 (s, 8 H, CH_2 DME), 6.30 (br. s, 2 H, 4-H), 6.96 (br. s, 2 H, *p*-H), 7.14 (br. s, 4 H, *m*-H), 7.72 (br. s, 4 H, *o*-H). – $\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_4\text{Yb}$ (667.7): calcd. Yb 25.92; found Yb 25.82.

Bis(7-azaindolato)bis(1,2-dimethoxyethane)ytterbium(II) (3c): A mixture of ytterbium powder (1.73 g, 10.0 mmol), mercury metal (ca. 0.20 mL), and (7-azaindolato)thallium(I) (0.64 g, 2.0 mmol) in THF (30 mL) was subjected to ultrasonication for 16 h. The resulting deep red solution with grey suspended solids was allowed to stand for several hours until the suspension settled out. The reaction mixture was then filtered using a filter cannula. The filtrate was concentrated to dryness under vacuum yielding a red solid which was recrystallised from DME giving **3c** [0.41 g (70%)]. – IR: $\tilde{\nu} = 1581\text{ cm}^{-1}$ m, 1542 m, 1402 w, 1335 w, 1321 m, 1295 s, 1258 m, 1193 m, 1153 s, 1118 m, 1060 m, 1020 m, 984 m, 951 w, 907 w, 896 w, 857 vs, 795 s, 771 s, 744 s, 718 vs, 617 m, 598 m. – Visible/near IR (THF): λ_{max} (ϵ) = 480 nm (259). – ^1H NMR (300 MHz, $[\text{D}_6]\text{benzene}$): $\delta = 2.79$ (s, 12 H, MeO DME), 2.83 (s, 8 H, CH_2 DME), 6.74 (m, 4 H, 2-H, 5-H), 7.88 (s, 2 H, 2-H), 7.97 (m, 4 H, 4-H, 7-H). – ^{171}Yb NMR (52.5 MHz, 0.04 M in DME): $\delta = 489$ ($\Delta\nu_{1/2} = 54$ Hz). – $\text{C}_{22}\text{H}_{30}\text{N}_4\text{O}_4\text{Yb}$ (587.6): calcd. C 44.97, H 5.15, N 9.54, Yb 29.45; found C 43.85, H 4.82, N 10.01, Yb 29.41.

Bis(1,2-dimethoxyethane)bis(3,5-diphenylpyrazolato)ytterbium(II) (3d)

Method A: A mixture of ytterbium powder (0.83 g, 4.8 mmol) and $\text{Hg}(\text{Ph}_2\text{pz})_2$ (1.00 g, 2.4 mmol) in THF (30 mL) was subjected to ultrasonication for 6 d. The resulting deep red solution with grey suspended solids was allowed to stand for several hours, and was then filtered. The THF was removed under vacuum giving a deep red sticky solid which was recrystallised from DME affording 1.10 g (58%) of large red crystals. – IR: identical with that reported.^[8] – $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_4\text{Yb}$ (791.8): calcd. Yb 21.85; found Yb 22.28, 22.04.

Method B: $\text{Yb}(\text{C}_6\text{F}_5)_2$, generated in situ from ytterbium metal (1.73 g, 10.0 mmol) and $\text{Hg}(\text{C}_6\text{F}_5)_2$ (1.07 g, 2.0 mmol) was treated with 3,5-diphenylpyrazole (0.88 g, 4.0 mmol) in THF (30 mL). After stirring at room temperature for 15 min, the THF was removed and the red solid was recrystallised from DME [0.34 g, (22%)]. – IR and visible/near IR (THF): identical with those reported.^[8]

Method C: 3,5-Diphenylpyrazole (0.59 g, 2.7 mmol) was treated with a THF solution (30 mL) of potassium hydride (0.11 g, 2.7 mmol) at 0°C. To the resulting solution $\text{YbI}_2(\text{THF})_2$ (0.77 g, 1.35 mmol) was added causing an formation of a red solution and a white precipitate. After stirring for 12 h, removal of THF gave a sticky orange solid which was extracted with in toluene (80 mL) giving a red/brown solution and a white precipitate. After filtration, the toluene solution was concentrated to dryness giving a red solid which was recrystallised from DME [0.40 g (37%)]. – IR: identical with that reported.^[8] – $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_4\text{Yb}$ (791.8): calcd. Yb 21.85; found Yb 21.52.

Bis(1,2-dimethoxyethane)bis(3,5-diphenylpyrazolato)europium(II) (4a): A mixture of europium metal chunks (0.61 g, 4.0 mmol), mercury metal (ca. 0.20 mL) and (3,5-diphenylpyrazolato)thallium(I) (0.85 g, 2.0 mmol) in THF (30 mL) was subjected to ultrasonication for 48 h. The resulting deep yellow solution with grey suspended solids was allowed to stand for several hours. Filtration, and evaporation of the THF yielded a yellow solid, which was recrystallised from DME giving 0.69 g (90%) of **4a** as large yellow crystals. – IR: $\tilde{\nu} = 1602\text{ cm}^{-1}$ m, 1157 w, 1120 w, 1193 w, 1115 m, 1096 m, 1069 s, 1057 s, 1025 m, 1016 m, 980 m, 968 s, 907 w, 852 s, 832 w, 794 w, 770 m, 750 vs, 697 s, 682 s. – $\text{C}_{38}\text{H}_{42}\text{EuN}_4\text{O}_4$ (770.7): calcd. C 59.22, H 5.49, Eu 19.72, N 7.27; found C 59.06, H 5.67, Eu 19.68, N 7.59.

Bis(3,5-di-*tert*-butylpyrazolato)bis(1,2-dimethoxyethane)europium(II) (4b): A mixture of europium metal chunks (1.52 g, 10.0 mmol), mercury metal (ca. 0.20 mL), diphenylmercury(II) (0.98 g, 2.78 mmol) and 3,5-di-*tert*-butylpyrazole (1.00 g, 5.56 mmol) in THF (30 mL) was heated (60°C) for 24 h. The resulting deep yellow solution with grey suspended solids was allowed to stand for several hours. Filtration, and evaporation of the THF yielded a yellow solid, which was recrystallised from DME giving 0.57 g (59%) of **4b** as large yellow crystals. – IR: $\tilde{\nu} = 1509\text{ cm}^{-1}$ m, 1404 w, 1354 m, 1318 w, 1248 s, 1218 m, 1195 m, 1158 w, 1123 m, 1103 m, 1078 s, 1032 m, 1010 s, 996 m, 860 vs, 769 vs, 722 vs. – Visible/near IR (THF): $\lambda_{\text{max}}(\epsilon) = 345\text{ nm}$ (477). – $\text{C}_{38}\text{H}_{42}\text{EuN}_4\text{O}_4$ (690.8): calcd. C 52.16, H 8.46, Eu 22.00, N 8.11; found C 51.28, H 8.39, Eu 22.02, N 8.88.

Bis(1,2-dimethoxyethane)bis(3,5-diphenylpyrazolato)samarium(II) (5)

Method A: 3,5-Diphenylpyrazole (0.27 g, 1.2 mmol) was treated with a THF solution (30 mL) of bis[bis(trimethylsilyl)-amido]bis(tetrahydrofuran)samarium(II) (0.38 g, 0.60 mmol). The resulting purple solution was stirred for 30 min, and the THF was then removed under vacuum yielding a purple solid which was washed twice with petroleum ether ($2 \times 30\text{ mL}$). The purple solid was recrystallised from DME (30 mL) giving 0.12 g (25%) of **5** as dark purple crystals. – IR: $\tilde{\nu} = 1602\text{ cm}^{-1}$ m, 1509 w, 1243 w, 1220 w, 1156 w, 1121 w, 1101 m, 1073 s, 1026 m, 1014 w, 967 s, 913 w, 860 m, 849 m, 793 w, 758 vs, 697 s, 685 s. – Visible/near IR (THF) $\lambda_{\text{max}}(\epsilon)$: ca. 600 br. (900) nm. – ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = -11.76$ (s, 2 H, H-4), 2.93 (d, 8 H, *o*-H), 3.48 (s, 12 H, MeO, DME), 3.54 (s, 8 H, CH_2 , DME), 5.84 (t, 4 H, *p*-H), 6.73 (t, 8 H, *m*-H). – $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_4\text{Sm}$ (769.2): calcd. C 59.34, H 5.50, N 7.28, Sm 19.55; found C 59.42, H 5.63, N 7.51, Sm 19.26.

Method B: $\text{SmI}_2(\text{THF})_2$ (0.54 g, 1.0 mmol) was added to a THF solution (30 mL) of (3,5-diphenylpyrazolato)potassium(I) (2.0 mmol) (generated in situ as described above in the synthesis of **3d**) causing formation of a dark purple solution and a white precipitate. This reaction mixture was stirred for 12 h followed by removal of THF to give a sticky purple solid, which was extracted with toluene (30 mL) giving a red/brown solution and a white precipitate. The toluene solution was filtered and concentrated to dryness yielding dark purple **5** which was recrystallised from DME [0.48 g (62%)]. – IR: identical with that of the product from Method A. – $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_4\text{Sm}$ (769.2): calcd. Sm 19.55; found Sm 19.90.

Reaction between 3d and HgPh_2 and Ph_2pzH : **3d** (0.40 g, 0.50 mmol), HgPh_2 (0.89 g, 0.25 mmol) and Ph_2pzH (0.55 g, 0.25 mmol) were stirred in DME (30 mL) at room temperature for 2 d. The reaction mixture remained red and there were no signs of precipitated metal. A visible/near-IR spectrum of the reaction mixture was identical to that reported^[8] for **3d**.

Reaction between (1,2-Dimethoxyethane)tris(3,5-diphenylpyrazolato)ytterbium(III) and Ytterbium Metal: A mixture of (1,2-dimethoxyethane)tris(3,5-diphenylpyrazolato)ytterbium(III)^[25] (0.46 g, 0.50 mmol), ytterbium metal (1.73 g, 10.0 mmol), and mercury metal (ca. 0.20 mL) in DME (30 mL) were subjected to ultrasonication for 24 h. The initially colourless solution turned deep red after sonication for 12 h. Separation of excess ytterbium and mercury followed by removal of DME yielded a red solid. Visible/near-IR and IR spectra were identical with those reported^[8] for **3d**.

Reaction between Bis(1,2-dimethoxyethane)tris(3,5-diphenylpyrazolato)samarium(III) and Samarium Metal: A mixture of bis(1,2-dimethoxyethane)tris(3,5-diphenylpyrazolato)samarium(III)^[8] (0.99 g, 1.0 mmol), samarium metal (1.50 g, 10.0 mmol), and mercury metal (ca. 0.20 mL) in DME (30 mL) were subjected to ultrasonication for 2 d. The initially colourless solution remained colourless after sonication for 2 d. A visible/near IR spectrum of the reaction mixture was identical with that reported^[8] for $[\text{Sm}(\text{Ph}_2\text{pz})_3(\text{DME})_2]$.

Attempted Reaction of Ytterbium Metal with $\text{Hg}(\text{C}_6\text{F}_5)_2$ and 3,5-Diphenylpyrazole: A mixture of ytterbium powder (1.73 g, 10.0 mmol), mercury metal (ca. 0.20 mL), bis(pentafluorophenyl)mercury(II) (0.53 g, 1.0 mmol), and 3,5-diphenylpyrazole (0.44 g, 2.0 mmol) in THF (40 mL) was stirred at room temperature for 4 d. On addition of THF an orange solution formed. This progressively darkened to a black solution over the course of the reaction. The resulting black solution with grey suspended solids was allowed to stand for several hours. Filtration and removal of THF under vacuum revealed a black solid which was insoluble in DME. The infrared spectrum of this black material was significantly different from that obtained for compound **3d**. – IR: $\tilde{\nu} = 1365\text{ cm}^{-1}$ m, 1303 w, 1246 m, 1193 m, 1112 br. s, 1028 m, 983 m, 940 m, 852 s, 763 vw, 723 vw.

Structure Determinations: Room-temperature single-counter/four-circle diffractometer data sets were measured on capillary-mounted specimens (2 θ / θ -scan mode; graphite-monochromated radiation, $\lambda = 0.71073\text{ \AA}$; $T \approx 295\text{ K}$), in most cases with symmetry equivalences, yielding N_{total} reflections, these being merged (R_{int} as specified) after absorption correction, yielding N (unique) data, N_{o} with $I > 2\sigma(I)$ being considered “observed” and used in the full-matrix least-squares refinement (n_{v} variables). Anisotropic thermal parameters were refined for the non-hydrogen atoms, (x , y , z , U_{iso})_H being included constrained at estimated values. Conventional residuals R , R_{w} [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})]$ on $|I|$ are quoted at convergence. Neutral atom complex scattering

factors were employed, the Xtal 3.4 program system^[26] being used. Individual abnormalities, variations in procedure and idiosyncrasies are noted as "variata"; in no case was there difference-map evidence for occluded solvent, although ligand disorder was evident in some cases (see below). In Figures 1–6, 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. In the case of **5** and **4a** pairs of molecular projections (Figures 3 and 6) are shown and provide views (i) down the actual or putative 2 axis of the molecule, so as to display that symmetry, and (ii) normal to that axis. The latter is provided to display better (a) any difference in conformation among the pair of DME ligands, (b) any ligand disorder, (c) any tendency to dodecahedral coordination about the metal atom [the (N₂)₂ ligand pair comprising one of the two intersecting planes and the (O₂)₂ the other]. Crystallographic data (excluding structure factors and including torsion angles describing the DME conformations) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101118 (**3d**)^[8] and -109937–109941. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal/Refinement Data

3a [Yb(bind)₂(DME)₂]: C₃₀H₃₈N₄O₄Yb, *M* = 691.7. Monoclinic, space group *P*2₁/*c* (*C*_{2h}⁵, no. 14), *a* = 15.570(2), *b* = 23.434(5), *c* = 8.052(3) Å, β = 94.98(2)°, *V* = 2927 Å³. *D*_{calcd.} (*Z* = 4) = 1.570 g cm⁻³; *F*(000) = 1392. μ_{Mo} = 32.4 cm⁻¹; specimen: 0.45 × 0.30 × 0.45 mm; *A**_{min,max} = 2.28, 3.85 (analytical correction). 2θ_{max} = 55°; *N* = 6476, *N*_o [*I* > 3σ(*I*)] = 4954; *R* = 0.026, *R*_w = 0.029; *n*_v = 333. |Δρ_{max}| = 1.13 e Å⁻³.

3c [Yb(azin)₂(DME)₂]: C₂₂H₃₀N₄O₄Yb, *M* = 587.6. Orthorhombic, space group *Pbca* (*D*_{2h}¹⁵, no. 61), *a* = 18.183(4), *b* = 16.567(6), *c* = 15.855(9) Å, *V* = 4776 Å³. *D*_{calcd.} (*Z* = 8) = 1.634 g cm⁻³; *F*(000) = 2336. μ_{Mo} = 39.5 cm⁻¹; specimen: 0.12 × 0.40 × 0.45 mm; *A**_{min,max} = 1.60, 4.2 (analytical correction). 2θ_{max} = 55°; *N*_{total} = 11095, *N* = 5483 (*R*_{int} = 0.028), *N*_o = 3229; *R* = 0.034, *R*_w = 0.038; *n*_v = 299. |Δρ_{max}| = 0.80 e Å⁻³.

Variata: Each azin ligand is capable of coordinating in two modes involving interchange of nitrogen atoms with various associated possibilities of isomerism; these modes are both observed for each ligand, C(4,4') [Figure 5: C(14), C(14') and C(24), C(24') of the respective ligands] of each being the only constituent atoms sufficiently displaced from overlap to permit meaningful refinement of the alternate fragments. Site occupancies (*x*, 1 – *x*) for the two ligands refined to *x* = 0.83, 0.77(3), isotropic thermal parameter forms being used for the minor fragments.

[M(Ph₂p_z)₂(DME)₂] (M = Yb, Eu, Sm): C₃₈H₄₂MN₄O₄.

[3d (M = Yb)] has been recorded elsewhere;^[8] a redeposition has been made, with atoms relabelled as shown in Figure 2, in conformity with present arrays, which conform to the quasi-2 symmetry of the system.]

4a (M = Eu): *M* = 770.7. Monoclinic, space group *P*2₁/*c* (*C*_{2h}⁴, no. 13), *a* = 19.746(3), *b* = 12.635(2), *c* = 15.396(2) Å, β = 110.12(1), *V* = 3607 Å³. *D*_{calcd.} (*Z* = 4) = 1.419 g cm⁻³; *F*(000) = 1572. μ_{Mo} = 17.8 cm⁻¹; specimen: 0.55 × 0.30 × 0.30 mm; *A**_{min,max} = 1.50, 1.82 (gaussian correction). 2θ_{max} = 50°; *N* = 6328, *N*_o = 4823; *R* = 0.046, *R*_w = 0.049; *n*_v = 427. |Δρ_{max}| = 0.85 e Å⁻³.

5 (M = Sm): *M* = 769.1. Orthorhombic, space group *Pnma* (*D*_{2h}¹⁶, no. 62), *a* = 7.9941(6), *b* = 24.263(3), *c* = 19.080(3) Å, *V* = 3701 Å³. *D*_{calcd.} (*Z* = 4) = 1.380 g cm⁻³; *F*(000) = 1568. μ_{Mo} = 16.3

cm⁻¹; specimen: 0.25 × 0.35 × 0.55 mm; *A**_{min,max} = 1.47, 1.72 (gaussian correction). 2θ_{max} = 60°; *N*_{total} = 8395, *N* = 3650 (*R*_{int} = 0.029), *N*_o = 2240; *R* = 0.042, *R*_w = 0.037; *n*_v = 270. |Δρ_{max}| = 1.04 e Å⁻³.

Variata: As modelled in the present space group, the DME moieties are disordered across the crystallographic mirror plane; meaningful refinement could not be achieved in a lower symmetry space group. An ordered component is shown in the Figures and Tables and has a crystallographic mirror plane passing through the metal atom and relating the two halves (including substituents) of each Ph₂p_z ligand. Despite similar Ln sizes, the M = Eu, Sm adducts **4a**, **5** are not isomorphous with each other, or with the Yb adduct **3d**.

4b [Eu(rBu₂p_z)₂(DME)₂]: C₃₀H₅₈EuN₄O₄, *M* = 690.8. Triclinic, space group *P*1̄ (*C*_i¹, no. 2), *a* = 22.791(4), *b* = 15.709(4), *c* = 10.289(3) Å, α = 89.38(2), β = 82.31(2), γ = 84.49(2)°, *V* = 3634 Å³. *D*_{calcd.} (*Z* = 4) = 1.263 g cm⁻³; *F*(000) = 1444. μ_{Mo} = 17.6 cm⁻¹; specimen: 0.40 × 0.50 × 0.50 mm; *A**_{min,max} = 1.60, 2.12 (gaussian correction). 2θ_{max} = 50°; *N*_{total} = 19495, *N* = 12765 (*R*_{int} = 0.047), *N*_o [*I* > 3σ(*I*)] = 6027; *R* = 0.057, *R*_w = 0.064; *n*_v = 700. |Δρ_{max}| = 1.45 e Å⁻³.

Variata: One of the DME groups is conformationally disordered in each molecule, discrete (CH₂)₂ carbon atoms being resolvable and refined (C thermal parameters isotropic) with site occupancies set at 0.5 after trial refinement. Crystal decomposition of 55% was evident during data collection (isotropic) and compensated by scaling.

Acknowledgments

We are grateful to the Australian Research Council for financial support and for the award of an Australian Postgraduate Award to E. E. D.

- [1] G. B. Deacon, C. M. Forsyth, P. C. Junk, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1998**, 1381–1388.
- [2] [2a] S. Trofimenko, *Chem. Rev.* **1972**, 72, 497–509. – [2b] S. Trofimenko, *Prog. Inorg. Chem.* **1986**, 34, 115–210. – [2c] A. P. Sadimenko, S. S. Bassoon, *Coord. Chem. Rev.* **1996**, 147, 247–297. – [2d] G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, 46, 151–238. – [2e] J. E. Cosgriff, G. B. Deacon, *Angew. Chem.* **1998**, 110, 298–299; *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 286–287.
- [3] [3a] I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1997**, 119, 2287–2288. – [3b] I. A. Guzei, G. P. A. Yap, C. H. Winter, *Inorg. Chem.* **1997**, 36, 1738–1739. – [3c] D. Pfeiffer, M. J. Heeg, C. H. Winter, *Angew. Chem.* **1998**, 110, 2674–2676; *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 2517–2519. – [3d] T. D. Culp, J. G. Cederberg, B. Bieg, T. F. Keuch, K. L. Bray, D. Pfeiffer, C. H. Winter, *J. Appl. Phys.* **1998**, 83, 4918–4927. – [3e] G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, 110, 2372–2373; *Angew. Chem. Int. Ed. Engl.* **1998**, 37, 2251–2252. – [3f] C. Yélamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, 37, 3892–3894.
- [4] H. Schumann, P. R. Lee, J. Loebel, *Angew. Chem.* **1989**, 101, 1073–1074; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 1033–1035.
- [5] [5a] H. Schumann, J. Loebel, J. Pickardt, C. Qian, Z. Xie, *Organometallics* **1991**, 10, 215–219. – [5b] G. B. Deacon, B. M. Gatehouse, S. Nickel, S. N. Platts, *Aust. J. Chem.* **1991**, 44, 613–621.
- [6] [6a] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling, H. Schumann, *Angew. Chem.* **1993**, 105, 906–907; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 874–875. – [6b] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, *Aust. J. Chem.* **1993**, 46, 1881–1896. – [6c] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling, H. Schumann, *Aust. J. Chem.* **1994**, 47, 1223–1235.

- [7] [7a] J. E. Cosgriff, G. B. Deacon, G. D. Fallon, B. M. Gatehouse, H. Schumann, R. Weimann, *Chem. Ber.* **1996**, *129*, 953–958. — [7b] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, P. R. Lee, H. Schumann, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1399–1403.
- [8] G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **1998**, 543–545.
- [9] [9a] H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986. — [9b] F. T. Edelmann, in *Comprehensive Organometallic Chemistry*, 2nd ed. (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1995**, chapter 2. — [9c] M. N. Bochkarov, L. N. Zakharov, G. S. Kalinina, *Organoderivatives of Rare Earth Elements*, Kluwer Academic Press, Dordrecht, **1995**. — [9d] G. B. Deacon, G. N. Pain, T. D. Tuong, *Inorg. Synth.* **1990**, *28*, 291–297. — [9e] G. B. Deacon, A. J. Koplick, G. N. Pain, T. D. Tuong, in *Herrmann-Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry*, 3rd ed. (Ed. W. A. Herrmann), G. Thieme, Stuttgart, **1997**, vol. 6, pp. 54–55, 86–87.
- [10] [10a] G. B. Deacon, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, P. MacKinnon, R. H. Newnham, *J. Chem. Soc., Chem. Comm.* **1989**, 935–937. — [10b] G. B. Deacon, T. Feng, S. Nickel, M. I. Ogden, A. H. White, *Aust. J. Chem.* **1992**, *45*, 671–683. — [10c] G. B. Deacon, T. Feng, P. MacKinnon, R. H. Newnham, S. Nickel, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1993**, *46*, 387–399.
- [11] G. B. Deacon, G. D. Fallon, C. M. Forsyth, H. Schumann, R. Weimann, *Chem. Ber.* **1997**, *130*, 409–415.
- [12] [12a] G. B. Deacon, D. L. Wilkinson, *Inorg. Chim. Acta.* **1988**, *142*, 155–159. — [12b] K. P. Butin, A. N. Kashin, I. P. Beleskaya, L. S. German, V. R. Polishchuk, *J. Organomet. Chem.* **1970**, *25*, 11–16. — [12c] K. P. Butin, I. P. Beleskaya, A. N. Kashin, O. A. Reutov, *J. Organomet. Chem.* **1967**, *10*, 197–210.
- [13] [13a] J. R. van den Hende, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1995**, 1435–1440. — [13b] A. G. Avent, M. A. Edelman, M. F. Lappert, G. A. Lawless, *J. Am. Chem. Soc.* **1989**, *111*, 3423–3425.
- [14] W. T. Carnell, in *The Absorption and Fluorescence Spectra of Rare Earth Ions in Solution in Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner, L. Eyring), North-Holland, Amsterdam, **1979**, vol. 3, chapter 24.
- [15] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.
- [16] G. B. Deacon, T. Feng, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1995**, *48*, 741–756.
- [17] G. B. Deacon, C. M. Forsyth, B. M. Gatehouse, A. Philosofo, B. W. Skelton, A. H. White, P. A. White, *Aust. J. Chem.* **1997**, *50*, 959–970.
- [18] J. L. Atwood, W. E. Hunter, A. L. Wayda, W. J. Evans, *Inorg. Chem.* **1981**, *20*, 4115–4119.
- [19] G. H. Jeffery, J. Basset, J. Mendham, R. C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed., Longman Scientific & Technical, New York, **1989**, p. 404.
- [20] A. L. Rheingold, R. L. Ostrander, B. S. Haggerty, S. Trofimenko, *Inorg. Chem.* **1994**, *33*, 3666–3676.
- [21] [21a] B. Sjollem, *Justus Liebigs Ann. Chem.* **1894**, *279*, 248–257. — [21b] M. S. R. Murthy, E. V. Rao, *Indian Drugs* **1985**, *22*, 462–464 (*Chem. Abstr.* **1986**, *105*, 6443e).
- [22] [22a] P. L. Watson, T. H. Tulip, I. Williams, *Organometallics* **1990**, *9*, 1999–2009. — [22b] J. L. Namy, P. Girard, H. B. Kagan, P. E. Caro, in *Herrmann-Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry*, 3rd ed. (Ed.: W. A. Herrmann), G. Thieme, Stuttgart, **1997**, vol. 6, pp. 26–27.
- [23] [23a] W. J. Evans, D. K. Drummond, H. Zhang, J. L. Atwood, *Inorg. Chem.* **1988**, *27*, 575–579. — [23b] W. J. Evans, D. K. Drummond, H. Zhang, J. L. Atwood, in *Herrmann-Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry*, 3rd ed. (Ed.: W. A. Herrmann), G. Thieme, Stuttgart, **1997**, vol. 6, pp. 28–29.
- [24] G. B. Deacon, J. E. Cosgriff, E. T. Lawrenz, C. M. Forsyth, D. L. Wilkinson, in *Herrmann-Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry*, 3rd ed. (Ed.: W. A. Herrmann), G. Thieme, Stuttgart, **1997**, vol. 6, pp. 48–50.
- [25] G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, unpublished results.
- [26] S. R. Hall, H. D. Flack, J. M. Stewart (Eds.), *The XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, **1992**.

Received November 17, 1998
[198398]