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Contrasting Binding Modes in Lanthanoid Pyrazolate and Pseudo-pyrazolates Prepared by Oxidation of Lanthanoid(II) Complexes and Lanthanoid Metals with Thallium(I) Reagents

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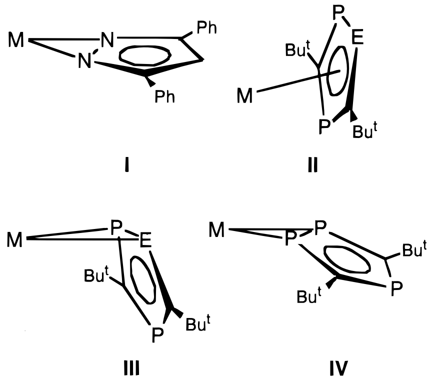
Oxidation of Yb(C_5Me_5)$_2$ with [Tl(Ph_2pz)] and [Tl(azin)] (Ph_2pz = 3,5-diphenylpyrazolate, azin = 7-azaindolate) yields [Yb(C_5Me_5)$_2$(Ph_2pz)] (**1**) and [Yb(C_5Me_5)$_2$(azin)] (**2**). X-ray crystal structures of **1** and **2** reveal monomeric eight-coordinate complexes with η^2-Ph_2pz or azin ligands. Treatment of neodymium metal with [Tl(Ph_2pz)] yields [Nd(Ph_2pz)$_3$(dme)$_2$] (**3**), which is a nine-coordinate monomer with three η^2-pyrazolate ligands and a chelating and a unidentate dme ligand. Oxidation of Sm(C_5Me_5)$_2$ with [Tl(1,4,2-$P_2SbC_2Bu^t{}_2$)]/[Tl(1,2,4-$P_3C_2Bu^t{}_2$)] (approximately 4:1) gave a mixture of [Sm(C_5Me_5)$_2$(1,2,4-$P_3C_2Bu^t{}_2$)] (**4**) and [Sm(C_5Me_5)$_2$(1,4,2-$P_2SbC_2Bu^t{}_2$)]. The former was shown to be a nine-coordinate monomer with novel pseudo-pyrazolate η^2-(P_2)-[1,2,4-$P_3C_2Bu^t{}_2$] coordination of the triphosphacyclopentadienide ligand. After metathesis routes to Ln(1,4,2-$P_2SbC_2Bu^t{}_2$)$_n$ complexes failed, redox transmetalation between ytterbium metal and [Tl(1,4,2-$P_2EC_2Bu^t{}_2$)] (E = Sb, P) containing a substantial impurity of [Li(tmeda)$_2$][1,4,2-$P_2EC_2Bu^t{}_2$] yielded the first lanthanoid diphosphastibacyclopentadienide complex in a mixture with [1,2,4-$P_3C_2Bu^t{}_2$] species. An X-ray investigation of single crystals containing an isomerically diverse mixture enabled the structure of [Li(thf)$_4$]-[Yb(1,4,2-$P_2SbC_2Bu^t{}_2$)$_3$] (**5**) to be determined, and it was shown to contain a π-η^2 and two η^5-[1,4,2-$P_2SbC_2Bu^t{}_2$] ligands. In the series **1**, **4**, and **5**, the η^2-ring varies from edge-on to side-on, reflecting a progression from σ to π coordination. [Li(tmeda)$_2$][1,4,2-$P_2SbC_2Bu^t{}_2$] (**6**) has been successfully crystallized from a [Li(tmeda)$_2$][$P_2EC_2Bu^t{}_2$] mixture and structurally characterized.

Introduction

Since 1996, pyrazolate coordination has been transformed by the discovery of new binding modes.[1] In lanthanoid complexes, the σ-η^2 binding mode, with the ring edge-on to the metal and coplanar with it (**I**), is dominant[1a−c,2] (Scheme 1). However, μ-η^1:η^1 bonding is also known,[2] while the μ-η^2:η^2 mode has recently been discovered.[1a,b]

Scheme 1. Some Coordination Modes of Pyrazolate and Pseudo-pyrazolate Ligands



It is of interest to compare coordination of lanthanoids by pyrazolates (≡1,2-diazacyclopentadienides) with coordination by heavier group 15-substituted cyclopenta-

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dienides [1,4,2-$P_2EC_2Bu^t{}_2$] (E = P^{3-5} or Sb^5), which can be viewed as pseudo-pyrazolates. The latter are π-bonded to other metals, with η^5 (**II**), μ-η^5:η^5, μ-η^5:η^1, and η^1 ligation observed,[3−5] but σ-η^2 (analogous to **I**) and π-η^2 (**III**) can be envisaged if the pyrazolate analogy is valid. Although lanthanoid complexes of P- and As-substituted cyclopentadienyl ligands are known,[3] only one lanthanoid complex of [1,4,2-$P_2EC_2Bu^t{}_2$] ligands is known, viz., an η^5-bonded [1,2,4-$P_3C_2Bu^t{}_2$] derivative of the unexpected Sc(I) oxidation state.[4] Accordingly, we now report the synthesis and structures of some lanthanoid complexes with the 3,5-diphenylpyrazolate (Ph_2pz), the 7-azaindolate (azin), and [1,4,2-$P_2EC_2Bu^t{}_2$] ligands and a comparison of their binding modes. We also report the structure of the of the commonly used[5] reagent [Li(tmeda)$_2$][1,4,2-$P_2SbC_2Bu^t{}_2$], crystals having been obtained from a mixture with [Li(tmeda)$_2$][1,2,4-$P_3C_2Bu^t{}_2$] by fractional crystallization. The syntheses feature oxidation of Ln(II) complexes and lanthanoid metals by the recently prepared [Tl(Ph_2pz)],[6] [Tl(azin)],[6] and [Tl(1,4,2-$P_2EC_2Bu^t{}_2$)].[5d] The first two complexes have recently been introduced as redox transmetalation reagents for the synthesis of lanthanoid(II) pyrazolate and azaindolate complexes (eq 1),[6] while [Tl(1,4,2-$P_2SbC_2Bu^t{}_2$)] and [Tl(1,2,4-$P_3C_2Bu^t{}_2$)] are obtained as an inseparable mixture on a preparative scale by the organolithium route.[5d]

$$2\mathrm{Tl}(\mathrm{R_2pz\ or\ azin}) + \mathrm{Ln} \rightarrow \mathrm{Ln}(\mathrm{R_2pz\ or\ azin})_2 + 2\mathrm{Tl} \qquad (1)$$

$$\mathrm{Ln} = \mathrm{Eu\ or\ Yb}$$

Results and Discussion

Synthesis and Characterization. [Yb(C_5Me_5)$_2$(thf)] has been oxidized by either [Tl(Ph_2pz)] or [Tl(azin)] in dme or thf to yield the heteroleptic complexes [Yb(C_5Me_5)$_2$(Ph_2pz)] (**1**) or [Yb(C_5Me_5)$_2$(azin)] (**2**), respectively, and thallium metal (eq 2).

$$\mathrm{Yb(C_5Me_5)_2} + \mathrm{TlL} \xrightarrow{\mathrm{S}} [\mathrm{Yb(C_5Me_5)_2(L)}] + \mathrm{Tl}\downarrow \qquad (2)$$

$$\mathrm{L = Ph_2pz,\ S = dme;\ L = azin,\ S = thf}$$

In both cases the redox reaction was nearly instantaneous, as evidenced by the precipitation of thallium metal and the change in the solution color from orange to deep purple. Both **1** and **2** were obtained in good yield with satisfactory analyses for unsolvated compositions [Yb(C_5Me_5)$_2$L] (L = Ph_2pz or azin), which were confirmed by X-ray crystallography (below). Their mass spectra showed progressive loss of C_5Me_5 groups followed by Ph_2pz or azin ligands and were less complex than observed for [Ln(C_5H_4Me)$_3$].[7] Compounds **1** and **2** have similar electronic spectra. A broad intense peak near 510 nm has intensity similar to a corresponding band of [YbCp$_3$][8] or [Yb(C_5Me_5)$_2$Cl][9] attributable to ligand → metal charge transfer. Absorption bands at 930−980 nm are attributable to 4f → 4f transitions,[8] and the molar absorption coefficients are similar to those observed for YbCp$_3$ and [Yb(C_5Me_5)$_2$Cl] in this region.[8,9] However the molar absorption coefficients (ca. 200) for the bands near 1000 nm are more intense than those observed for [YbCp$_3$][8] or [Yb(C_5Me_5)$_2$Cl][9] complexes (ca. 30 and 80, respectively) and perhaps have some contribution from charge transfer in addition to 4f → 4f transitions.

Redox transmetalation between lanthanoid metals and thallium(I) 3,5-diphenylpyrazolate [Tl(Ph_2pz)] has now been shown to be a route to trivalent lanthanoid pyrazolate complexes since treatment of neodymium metal with [Tl(Ph_2pz)] in thf and recrystallization from dme afforded [Nd(Ph_2pz)$_3$(dme)$_2$] (**3**) in good yield (eq 3). Thallium 3,5-diphenylpyrazolate has previously been used only to give divalent lanthanoids by redox transmetalation (eq 1), apart from isolation of impure [Sm(Ph_2pz)$_3$(dme)$_2$] from an attempt to prepare the Sm(II) derivative by eq 1 (Ln = Sm).[6]

$$\mathrm{Nd} + 3\mathrm{Tl(Ph_2pz)} \rightarrow \mathrm{Nd(Ph_2pz)_3} + 3\mathrm{Tl}\downarrow \qquad (3)$$

Unequivocal characterization of **3** was provided by an X-ray crystallography study (below). Compound **3** has been prepared previously[10] by redox transmetalation/ligand exchange in dme (eq 4).

$$2\mathrm{Nd} + 3\mathrm{Hg(C_6F_5)_2} + 6\mathrm{Ph_2pzH} \rightarrow 2\mathrm{Nd(Ph_2pz)_3} + 6\mathrm{C_6F_5H} + 3\mathrm{Hg}\downarrow \qquad (4)$$

The chemistry of the 1,4,2-diphosphastibacyclopentadienide ligand is bedevilled by its synthesis as an (normally) inseparable mixture with the 1,2,4-triphosphacyclopentadienide species.[5,11] Accordingly, a [Tl($P_2EC_2Bu^t{}_2$)] (E = Sb, P) mixture was used in syntheses. The structure of the former has been determined on a serendipitously isolated single crystal, but separation was impossible on a preparative scale.[5d] Oxidation of [Sm(C_5Me_5)$_2$(thf)$_2$] by [Tl($P_2EC_2Bu^t{}_2$)] in thf afforded thallium metal and a mixture of samarium(III) complexes, [Sm(C_5Me_5)$_2$($P_2EC_2Bu^t{}_2$)(thf)] (eq 5), which were obtained in low yield on crystallization from light petroleum.

$$[\mathrm{Sm(C_5Me_5)_2(thf)_2}] + [\mathrm{Tl(P_2EC_2Bu^t{}_2)}] \rightarrow [\mathrm{Sm(C_5Me_5)_2(P_2EC_2Bu^t{}_2)(thf)}] + \mathrm{thf} + \mathrm{Tl} \qquad (5)$$

$$\mathrm{E = P,\ Sb}$$

The products are a new class of heteroleptic tris-

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(cyclopentadienyl)lanthanoid complex. The ^{1}H NMR spectrum of the mixture revealed paramagnetically broadened overlapping signals precluding satisfactory integration and assignment of some peaks. However, a resonance at 0.35 ppm was assigned to the C_5Me_5 protons, while singlets at 0.85, 1.15, and 1.25 ppm were indicative of three different types of Bu^t group arising from the presence of both $[P_2SbC_2Bu^t{}_2]$ and $[P_3C_2Bu^t{}_2]$ ligands. Only a single thf resonance could be located. The ^{31}P NMR spectrum had four resonances, as expected for a mixture of $[P_2SbC_2Bu^t{}_2]$ and $[P_3C_2Bu^t{}_2]$ ligands. While the signals were not greatly shifted from those of the diamagnetic $[Li(tmeda)_2][P_2EC_2Bu^t{}_2]$ (E = Sb, P) compounds,[11] the signals were considerably broadened by Sm(III) paramagnetism such that coupling constants could not be determined and integrations provided only a qualitative guide. Approximately equal intensity resonances at 279 and 281 ppm were assigned to P4 and P1, respectively, of the $[P_2SbC_2Bu^t{}_2]$ ligand, while unequal resonances at 287 and 308 ppm were assigned to P1,2 and P4, respectively, of the $[P_3C_2Bu^t{}_2]$ ligand. Estimation of the relative amounts of the two ligands was problematical due to the exceptional broadness of the signal at 308 ppm. However, there appeared to be more $[P_3C_2Bu^t{}_2]$ than $[P_2SbC_2Bu^t{}_2]$ ligands present in the sample, by contrast with the composition of the thallium(I) reactant mixture but consistent with the low yield of the product. Slow fractional crystallization of the $[Sm(C_5Me_5)_2(P_2EC_2Bu^t{}_2)(thf)]$ mixture from light petroleum gave single crystals of pure $[Sm(C_5Me_5)_2(P_3C_2Bu^t{}_2)(thf)]$, consistent with a larger proportion of $[P_3C_2Bu^t{}_2]$ than $[P_2SbC_2Bu^t{}_2]$ in the bulk reaction product. Possibly the minor component $[Tl(P_3C_2Bu^t{}_2)]$ is a better oxidant than $[Tl(P_2SbC_2Bu^t{}_2)]$ for $Sm(C_5Me_5)_2$ leading to $[Sm(C_5Me_5)_2(P_3C_2Bu^t{}_2)(thf)]$ as the main product but in low yield.

The failure to isolate an X-ray characterizable complex containing the [1,4,2-$P_2SbC_2Bu^t{}_2$] ligand or the [1,4,2-$P_2EC_2Bu^t{}_2$] mixture from eq 5 led to alternative approaches to this objective. Metathesis reactions between $NdCl_3$ or $[YbI_2(thf)_2]$ and $[Li(tmeda)_2][P_2EC_2Bu^t{}_2]$ were attempted, but surprisingly no reaction was observed. Redox transmetalation between ytterbium metal and $[Tl(P_2EC_2Bu^t{}_2)]$ afforded thallium metal and an ytterbium(II) complex identified by X-ray crystallography as $[Li(thf)_4][Yb(1,4,2\text{-}P_2EC_2Bu^t{}_2)_3]$ (E = Sb:P = 2:1). Clearly a very significant amount of $[Li(tmeda)_2][P_2EC_2Bu^t{}_2]$, the reactant in the preparation of $[Tl(P_2EC_2Bu^t{}_2)]$, was present in the thallium reagent and was a major factor in obtaining a crystallizable product. Subsequent examination of a sample of $[Tl(P_2EC_2Bu^t{}_2)]$ from another preparation showed the presence of lithium by ^{7}Li NMR spectroscopy, but no ^{31}P resonances independent of those of $[Tl(P_2EC_2Bu^t{}_2)]$ and certainly none corresponding to $[Li(tmeda)_2][P_2EC_2Bu^t{}_2]$ were observed. Given that the sample used in the redox transmetalation reaction showed only ^{31}P resonances attributable to $[Tl(P_2SbC_2Bu^t{}_2)]$ and $[Tl(P_3C_2Bu^t{}_2)]$, it appears that lithium may be present as a thallate complex, e.g., $[Li(tmeda)_2][Tl(P_2EC_2Bu^t{}_2)_2]$, which has ^{31}P resonances indistinguishable from those of $[Tl(P_2EC_2Bu^t{}_2)]$. (The possibility that the bulk $[Tl(P_2EC_2Bu^t{}_2)]$ originally obtained, and for which ^{31}P NMR data were reported, was in fact a thallate complex seems unlikely, as the ^{13}P NMR resonances of single crystals of $[Tl(P_2SbC_2Bu^t{}_2)]$ corresponded to those of the major component of the bulk material.) Previously, an analogous thallate complex, $[Li(pmdeta)][TlCp_2]$ (pmdeta = $(Me_2NCH_2CH_2)_2NMe$), was isolated.[12] ^{1}H and ^{31}P resonances of the single crystals were in the normal range and thus were consistent with the diamagnetic Yb^{II} oxidation state. Four peaks were observed in the latter spectrum, with the two highest frequency peaks corresponding to the phosphorus atoms of the $[P_2SbC_2Bu^t{}_2]$ ligand (1:1 ratio). The signal at highest δ value (315 ppm) is attributed to the phosphorus adjacent to the relatively electrophilic and quadrupolar antimony center, and the other signal (283 ppm) corresponds to P4. The other two signals in the ^{31}P NMR spectrum arise from the phosphorus atoms in the $[P_3C_2Bu^t{}_2]$ ring system, where the lowest frequency signal (246 ppm) is assigned to P1 and P2, being twice the intensity of the peak at 263 ppm (P4). The overall 2:1 ratio of the $[P_2SbC_2Bu^t{}_2]/[P_3C_2Bu^t{}_2]$ ligands found in this spectrum corresponds to the ratio established in the structure refinement for this complex (see below). It was impossible to confirm the relative amounts of the $[P_2SbC_2Bu^t{}_2]$ and $[P_3C_2Bu^t{}_2]$ ligands from the ^{1}H NMR spectrum owing to broadening of the resonances. The spectrum did however display three different Bu^t resonances, consistent with the presence of the two ligands as well as peaks attributable to the α and β thf protons. Peaks at 1045 and 889 cm^{-1} in the infrared spectrum of the complex are assigned to ν(C−O−C) of coordinated thf and are lowered from free ligand values 909 and 1070 cm^{-1}.[13] The EI mass spectrum of the complex (scan range 0−1000 amu) revealed a number of ytterbium-containing fragments, but no lithium species were observed. Fragmentation patterns were consistent with the predicted formulation since the highest m/z value of 818 corresponded to $[Yb(P_2SbC_2Bu^t{}_2)_2]^+$ and clusters at m/z 726 and 636 corresponded to the mixed species $[\{Yb(P_2SbC_2Bu^t{}_2)(P_3C_2Bu^t{}_2)\}-H]^+$ and the triphospholyl species $[Yb(P_3C_2Bu^t{}_2)_2]^+$, respectively.

$[Li(tmeda)_2][P_2EC_2Bu^t{}_2]$ alone does not react with ytterbium metal, but crystallization from the ensuing mixture realized pure $[Li(tmeda)_2][P_2SbC_2Bu^t{}_2]$ (**6**) free from any triphosphacyclopentadienyl ligands.

X-ray Discussion. Structure Determination of 1 and 2. The X-ray crystal structures of **1** and **2** have shown both to be eight-coordinate monomers with the C_5Me_5 ligands η^5 bound to the ytterbium atom and the diaza ligand chelating edge-on through the nitrogen atoms (Figure 1). Dinuclear structures with bridging (μ-η^1:η^1) pyrazolates have been proposed for the related $[Y(C_5Me_5)_2(RR'pz)]$ (R = R′ = H, Me; R = H, R′ = Me) since $[\{Ln(O(CH_2CH_2C_5H_4)_2)\}_2(\mu\text{-}Me_2pz)(\mu\text{-}OH)]$[14] and $[Nd(\eta^2\text{-}Me_2pz)_2(\mu\text{-}Me_2pz)(\mu\text{-}thf)]_2$[15] are dimeric with μ-η^1:η^1 pyrazolate ligands. It is possible that the increased steric bulk of the Ph_2pz and azin ligands over Me_2pz and pz makes adoption of a bridging arrangement less favorable. The steric coordination number is smaller for

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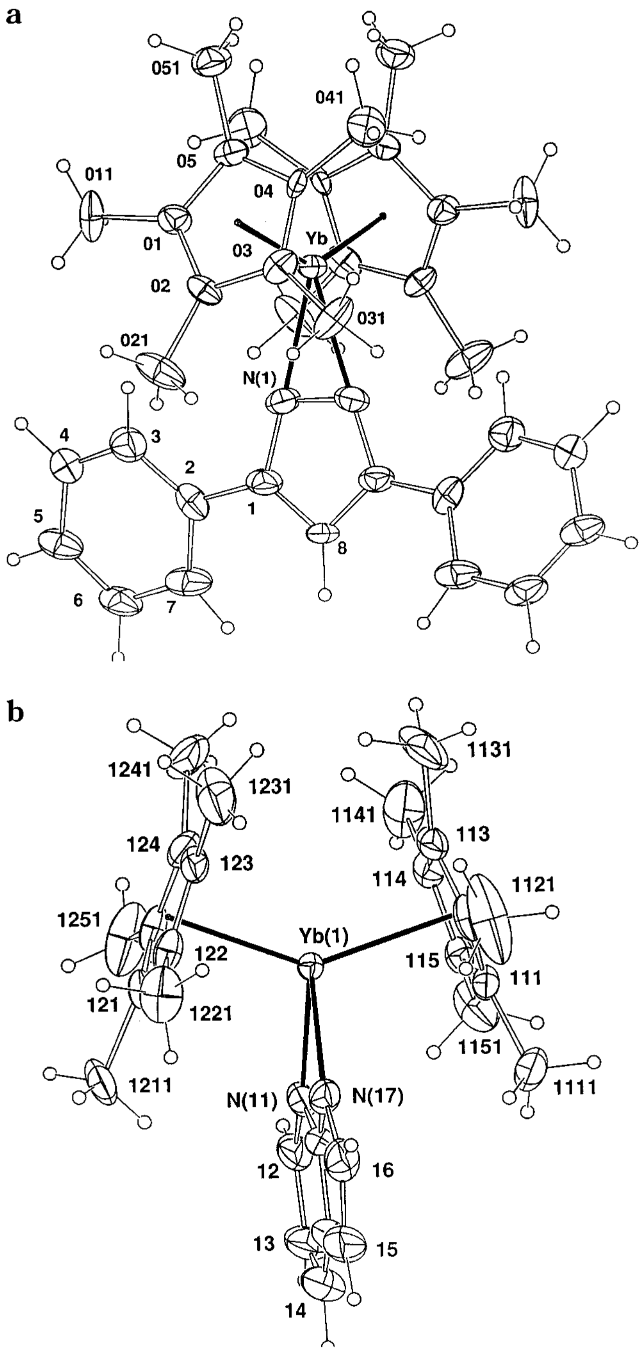

Figure 1. Projections of the ytterbium(III)/diazaligand complexes, **1** and **2**, showing 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Carbon atoms are designated by numbers without letters. A zero precedes the number for C_5Me_5 carbons in (a). (a) **1** projected normal to the molecular (crystallographic) *2*-axis. (b) **2** (molecule 1 (the nondisordered molecule)), projected normal to its approximate *2*-axis.

a chelating Me_2pz than two bridging Me_2pz ligands at a metal center.[15] These compounds are the first structurally characterized bis(cyclopentadienyl)pyrazolato- or azaindolatolanthanoid complexes. There is a high degree of crystallographic symmetry in **1** (Table 1), with only one C_5Me_5 ligand and half the Ph_2pz ligand comprising the asymmetric unit, with the rest of the molecule being generated by the appropriate symmetry operation. In **2** two molecules are in the asymmetric unit, one having disorder arising from the two different possible orientations of the low-symmetry azin ligand (refined in a 1:1 occupancy) (molecule 2) and the other having no isomeric diversity (molecule 1). Only the data from molecule 1 are discussed here. Analysis of the Yb−C bond lengths of **1** and **2** indicates symmetrical binding of the C_5Me_5 ligands to ytterbium, with average Yb−C bond lengths of 2.59 and 2.60 Å, respectively (Table 2). These bond lengths are typical of eight-coordinate $[Yb(C_5Me_5)_2XY]$ complexes.[16] Subtraction of the ionic radius[17] for eight-coordinate ytterbium from ⟨Yb−C⟩ gives a typical[18] 1.61 Å. The Yb−cen distances (cen = centroid of the C_5Me_5 ligand) are 2.30 Å for **1** and 2.31 and 2.30 Å for **2**. In **2**, the Yb−N bond lengths (Table 2) of **1** and **2** are 2.25(2) and 2.279(8) Å (for the amide nitrogen of the azin ligand), respectively. The Yb(1)−N(17) bond distance of 2.362(8) Å is significantly longer, which is expected since N(17) is a pyridine-type nitrogen. The (C_5Me_5)cen−Yb−cen(C_5Me_5) angles of **1** and **2** are 142° and 141°, respectively, which are at the extreme end of those for other eight-coordinate bis(cyclopentadienyl)ytterbium(III) complexes[19] and approach the large value (143°) in seven-coordinate $[Sc(C_5Me_5)_2]_2C_2$.[20] Because of the planar nature of the Ph_2pz (dihedral angle of the phenyl substituents to the C_3N_2 (pz) ring, 17°) and azin ligands and their small bite angles (34.5(6)° (**1**) and 60.0(3)° (**2**)), there is abundant space for wide separation of the C_5Me_5 rings. The Yb−N bond lengths for **1** and the Yb−N(amide) length for **2** (Table 2) approach closely values for $[Er(Bu^t{}_2pz)_3(thf)_2]$[21] and $[Nd(Bu^t{}_2pz)_3(\mu\text{-}dme)]_n$[10], where differences in ionic radii are considered. Ytterbium is approximately coplanar with the C_5Me_5 ring centroids and the center of the N−N bond (or vector) of **1** or **2**.

It is apparent from these two crystal structures that the diaza ligands bind in an edge-on fashion (η^2-σ, **I**, Scheme 1) and not side-on or face-on (π) to the ytterbium center. This is exemplified by the angle (180°) between Yb−cen(N−N) (the center of the N−N bond of Ph_2pz) and the pyrazolate ring plane for **1**, and the angle of (175.8°) for **2**. For exact end-on binding, the angle should be 180°. This type of bonding contrasts that found in phosphorus- and antimony-substituted cyclopentadienyl ligands (see below).

Structure Determination of 3. Single crystals of **3** as a C_6D_6 solvate were shown to contain a nine-coordinate neodymium atom with three chelating pyrazolate ligands and a chelating and a unidentate dme. Since the complex has the same molecular structure as $[Er(Ph_2pz)_3(dme)_2]$[10] (Table 1), no diagram is displayed. Bond distances and angles (provided in Supporting Information) are comparable with those reported[10] for the erbium complex when differences in ionic radii[17] are

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Table 1. Crystallographic Data (1−6)

	1[b]	**2**[c]	**3**[d]	**4**[e]	**5**[f]	**6**[g]
formula	$C_{35}H_{41}N_2Yb$	$C_{27}H_{35}N_2Yb$	$C_{65}H_{53}D_{12}N_6NdO_4$	$C_{34}H_{56}OP_3Sm$	$C_{46}H_{86}LiO_4P_{7.07}Sb_{1.93}Yb$	$C_{22}H_{50}LiN_4P_2Sb$
M_r	662.8	560.6	1150.6	724.1	1337.5	561.3
cryst syst	tetragonal	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group (no.)	$P4_12_12$ (#92)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (# 14)
a (Å)	10.137(4)	15.448(1)	8.917(6)	15.574(4)	12.184(1)	13.955(2)
b (Å)		8.504(3)	13.625(8)	13.083(1)	24.220(3)	14.118(2)
c (Å)	29.95(1)	38.524(5)	23.599(19)	17.4910(6)	20.650(2)	16.583(2)
α (deg)			83.28(6)			
β (deg)		95.311(9)	89.20(6)	101.05(1)	104.28(1)	111.484(2)
γ (deg)			83.97(5)			
V (Å^3)	3078	5039	2831	3498	5905	3040
D_c (g cm^{-3})	1.43_0	1.45_8	1.35	1.37_5	1.48_8	1.22_9
Z (f.u.)	4	8	2	4	4	4
$F(000)$	1340	2248	1178	1500	2686	1176
μ_{Mo} (cm^{-1})	30.6	37.3	9.7	18.4	26.3	$10._3$
specimen (mm)	0.18 × 0.30 × 0.28	0.18 × 0.50 × 0.40	0.15 × 0.25 × 0.15	0.15 × 0.20 × 0.18	0.25 × 0.30 × 0.20	0.40 × 0.30 × 0.20
$T_{min,max}$	0.51, 0.64	0.35. 0.60	0.81, 1.0			0.71, 0.84
N_{total}	6049 (quadrant)	18 894 (hemisphere)	10 428	13 126	22 983	34 742 (sphere)
N (R_{int})	2686(0.071)	8829 (0.037)	9070 (0.045)	5033 (0.079)	8823 (0.11)	7611 (0.023)
N_o ($I > n\sigma(I)$)	1555 ($n = 3$)	6348 ($n = 3$)	6020 ($n = 3$)	3480 ($n = 2$)	2919 ($n = 2$)	5766
R	0.052	0.044	0.045	0.037	0.036	0.038
R_w/wR_2[a]	0.052	0.051	0.032	0.040	0.032	0.048

[a] $R = \sum\Delta|F|/\sum|F_o|$, $R_w = (\sum w\Delta|F|^2/\sum w|F_o|^2)^{1/2}$ for **1**−**3**; for **4**, **5**, $wR_2 = \{\sum w(\Delta F^2)/\sum w(\Delta(F^2))^2\}^{1/2}$. [b] The absolute structure parameter (x_{abs}) refined to −0.05(6). [c] The azaindole chelate of molecule 2 was disordered over the two possible orientations, modeled in the refinement as superimposed rigid bodies (site occupancies set as 0.5 after trial refinement) with isotropic thermal parameter forms. Unresolved concomitant disorder is also suggested in the thermal envelopes of the peripheral C_5Me_5 substituents. [d] The asymmetric unit contains two molecules of C_6D_6. The complex has the same molecular structure as $[Er(Ph_2pz)_3(dme)_2]$.[10] [e] The coordinated thf exhibited high "thermal motion", suggestive of unresolved disorder for the peripheral carbon atoms; similarly, anomalously high "thermal motion" was observed in the peripheral methyl substituent atoms of the other moieties, particularly Cp (1), in a manner suggestive of rotation about the Sm−centroid "bond". [f] While atom E at position 4 of all three ligands was modeled agreeably in terms of total E = P occupancy (and set as such), sites 1,2 for all ligands appeared to be composites of P and Sb components. With the constraint of occupancy of unity for the sum of the fragments, P (=x), Sb (=1−x) occupancies were refined for each of the six sites across the three ligands, yielding, for sites 11, 12, 21, 22, 31, 32, x = 0.488(5), 0.714(5); 0.501(5), 0.908(4); 0.679(4), 0.776(4) with P···Sb separations correspondingly of 0.42(4), 0.49(4); 0.33(6), 0.32(6); 0.15(3), 0.38(2) Å, a total P occupancy of 4.0_7, cf. Sb 1.9_3, total 6, tempting the inferences that sites 11,21 are equally occupied and that overall the P:Sb ratio is essentially 2:1. Despite measurement of data at 150 K, apparent "thermal motion" throughout the structure is high, presumably as a consequence of pervasive unresolved disorder among the non-E components of the structure. [g] P, Sb components of sites 1,2 were refined initially without constraint, total occupancies not being significantly different from occupancy of unity for each type; refinement was continued with stoichiometric constraint of P_1Sb_1, x(P(1)), refining to 0.856(1) with other occupancies ensuing. P(1)···Sb(1), as modeled, refines to 0.108(6), with P(2)···Sb(2) 0.46(2) Å.

considered. In addition the Nd−N and Nd−O distances are in good agreement with those of nine-coordinate $[Nd(Ph_2pz)_3(thf)_3]$.[22] Unidentate dme bonding is relatively unusual,[10,23,24] but is known for lanthanoids[10,24] and indicates that the lanthanoid(III) center is unable to accommodate two chelating dme ligands.

Structure Determination of 4. The X-ray crystal structure **4** revealed a samarium(III) compound that was free from antimony (Figure 2a). This compound is the first lanthanoid complex in a normal oxidation state containing the $[P_3C_2Bu^t_2]$ ion. A novel scandium(I) complex that contains two $[P_3C_2Bu^t_2]$ ligands in a triple-decker sandwich complex has been reported.[4] In this monomeric complex, samarium is formally nine-coordinate, with the $[P_3C_2Bu^t_2]^-$ ion ligated through adjacent phosphorus atoms (P(1) and P(2)), two η^5-C_5Me_5 groups, and a thf oxygen. The C_5Me_5 ligands are bound symmetrically to samarium, as indicated by the Sm−C bond lengths, which range closely between 2.702(8) and 2.742(8) Å, with an average value of 2.72 Å (Table 2). This average is well within the range found for the numerous crystallographically characterized nine-coordinate $[Sm(C_5Me_5)_2XYZ]$ complexes.[25] Subtraction of the ionic radius for nine-coordinate Sm^{3+} gives a typical value[18] of 1.59 Å.

The Sm−P bond lengths are rather long at 3.135(2) and 3.164(2) Å and, after subtraction of the ionic radius of nine-coordinate Sm^{3+} (1.13_2 Å), give values of 2.002 and 2.033 Å, respectively. A corresponding subtraction from either a related eight-coordinate samarium(II) π-benzophospholyl complex or a nine-coordinate σ-bonded tris(bis(diphenylphosphino)methanido)samarium(III) gives a value of 1.81 or 1.72 Å, respectively. Presumably the large steric bulk of the $[P_3C_2Bu^t_2]$ ligand (the related 1,3-$(Me_3Si)_2C_5H_3$ ligand has a large steric coordination number of 2.60[26]) accounts for the relatively long Sm−P bond lengths for η^2-bonding of the $[P_3C_2Bu^t_2]$ ligand to samarium.

Remarkably, the η^2-$[P_3C_2Bu^t_2]$ ligand binds to samarium midway (**IV**, Scheme 1) between edge-on (**I**) and side-on (**III**) (Figure 2a) and contrasting with the edge-on binding of the diaza ligands in **1** and **2**. This is exemplified by the angle between Sm(1)−cen(PP) (center of the P−P bond) and the $[P_3C_2Bu^t_2]$ ring planes, viz., 143.8°, which differs from the corresponding angles (ca. 180°) of **1** and **2**, but is much larger than 90° for

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Table 2. Selected Geometries (1, 2, 4, and 5)[a]

1: Primed Atoms Are Related by the Intramolecular Crystallographic *2*-Axis[b]

atom	*r*	C(0)	N(1′)	C(0′)
N(1)	2.25(2)	109.$_4$	34.5(6)	107.$_1$
C(0)	2.3$_0$			141.$_8$

2: Values for (the Two Disordered Components of) Molecule 2 Lie below Those for Molecule 1[c]

atom	*r*	N(7)	C(10)	C(20)
N(1)	2.362(8)	60.0(3)	105.$_6$	107.$_9$
	(2.325(8)/2.298(10))	(62.7(3)/65.4(3))	106.$_9$/107.$_1$	108.$_2$/106.$_8$
N(7)	2.279(8)		106.$_8$	106.$_5$
	(2.569(10)/2.425(11))		(105.$_5$/104.$_4$))	(104.$_9$/106.$_4$)
C(10)	2.32$_2$			141.$_3$
	2.30$_7$			141.$_3$
C(20)	2.30$_3$			
	2.29$_6$			

4[d]

atom	*r*	P(2)	C(10)	C(20)	O(101)
P(1)	3.135(2)	38.71(5)	112.$_8$	108.$_4$	82.9(1)
P(2)	3.164(2)		95.$_7$	104.$_8$	120.8(1)
C(10)	2.46$_5$			134.$_4$	101.$_1$
C(20)	2.44$_8$				102.$_4$
O(101)	2.496(4)				

5: For Ligand 3; the Major Components of E(31,32) Are Given

atom	*r*	P(32)	C(01)	C(02)
Sb(31)	3.24(3)	41.8(4)	115.$_4$	104.$_0$
P(32)	3.09(2)		111.$_9$	108.$_4$
C(10)	2.61			137.$_3$
C(20)	2.65			

[a] Metal atom environments are presented in matrix form, *r* (Å) being the metal−ligand distance, the other entries being the angles (deg) subtended at the metal by the relevant atoms at the head of the row and column. C(*n*0) is the ring center of ligand *n*. [b] Yb−C(01−05) range between 2.57(2) and 2.62(2) Å. Yb is obligate coplanar with the C_3N_2 (pz) ring; the dihedral angle of the latter to the associated C_6 phenyl plane is 17(1)°. [c] Yb(*n*)−C(*nm*1−5) range between 2.551(9) and 2.616(8) Å. Yb lies 0.15(1); 0.03(1)/0.01(1) Å out of the associated azaindolate skeletal planes. [d] In $C_5Me_5(n)$, Sm−C(*nm*) (*m* = 1−5) are (*n* = 1) 2.742(8), 2.724(9), 2.72(1), 2.736(8), 2.740(8); (*n* = 2), 2.709(7), 2.734(7), 2.735(7), 2.734(8), 2.702(8) Å. P(1)−P(2) is 2.088(3) Å.

face-on coordination. Thus the bonding can be viewed as midway between σ (nine-coordinate) and π (eight-coordinate).

Structure Determination of 5. The X-ray structure of **5** revealed a charge-separated complex with a $[Li(thf)_4]^+$ cation (frequently a counterion in lanthanoid "ate" complexes[27]) and a $[Yb(1,4,2\text{-}P_2SbC_2Bu^t_2)_3]^-$ anion, in which the ytterbium center is surrounded by one side-on η^2-$[P_2SbC_2Bu^t_2]$ (**III**) and two η^5-$[P_2SbC_2Bu^t_2]$ (**II**) ligands (Figure 2b). The one other example of an X-ray-characterized complex containing a Ln−Sb bond has the Zintl ion Sb^{3-} coordinated to three samarium centers, viz., $[\{Sm(C_5Me_5)_2\}_3(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}Sb_3)(thf)]$.[28] The bonding arrangement of the η^2-$[P_2SbC_2Bu^t_2]$ ligand has not previously been observed and is different from the η^2-pyrazolate (**I**), η^2-azindolate (**I**), or η^2-$[P_3C_2Bu^t_2]$ (**IV**) coordination described above for **1**, **2**, or **4**. In $[Yb(P_2SbC_2Bu^t_2)_3]^-$, the η^2-$[P_2SbC_2Bu^t_2]$ ligand appears to be π-bound to the ytterbium(II) center since Yb(1)−cen(SbP) (cen(SbP) = center of the P(5)−Sb(3) bond) makes an angle of 112.$_8$° to the plane of the η^2-bonded ring. Thus ytterbium is formally seven-coordinate. Presumably the coordination sphere around ytterbium(II) is sterically saturated and thus unable to allow the third $[P_2SbC_2Bu^t_2]$ ligand to bind η^3, η^4, or η^5 to the ytterbium center or to accommodate a donor solvent molecule as in **4**.

There is disorder in this complex due, first, to the isomeric diversity arising from the two different arrangements, which each of the low-symmetry $[P_2SbC_2Bu^t_2]$ ligands can adopt, and also due to cocrystallization of species with the related triphosphacyclopentadienyl ligand. It was found from the refinement that sites Sb(1), Sb(2), and Sb(3) (Figure 2b) have partial phosphorus occupancies of 50, 50, and 70%, respectively, while P(1), P(3), and P(5) have partial antimony occupancies of 25, 10, and 20%, respectively. The optimum refinement corresponded to an approximately 2:1 ratio of $[P_2SbC_2Bu^t_2]$ to $[P_3C_2Bu^t_2]$, in agreement with the ratio from ^{31}P NMR spectroscopy (see above). Because of the disorder, no detailed discussion of bond distances and angles is warranted. However, Yb(II)−C bond lengths (2.97(1)−3.07(1) Å) of the η^5-bonded ligands do appear significantly lengthened from those of seven-coordinate $[Yb(C_5Me_5)_2(thf)]$[29] (average 2.66 Å) owing to the combined effects of the large P/Sb substituents and the bulky Bu^t groups.

Structure Determination of 6. Slow crystallization of $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ (E = P, Sb) from petroleum spirit afforded large yellow single crystals, which X-ray crystallography established as the charge-separated [Li-

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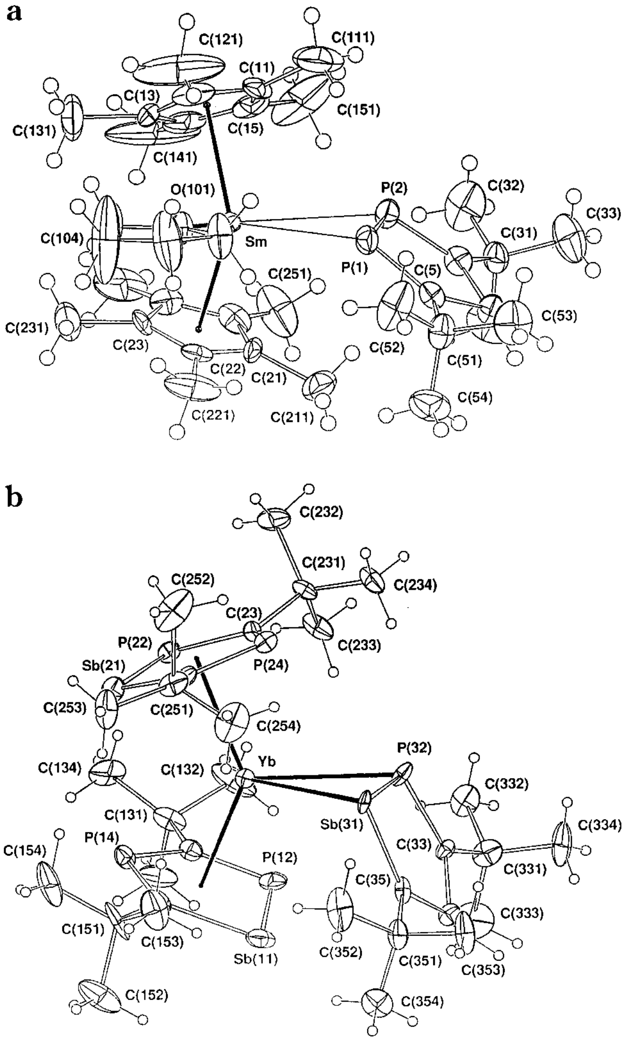

Figure 2. Projections of the [$P_2EC_2Bu^t{}_2$] (E = P, Sb) complex **4** and anion of **5** similarly but showing 50% thermal ellipsoids for the non-hydrogen atoms. (a) **4** approximately through the P(1)−P(2) line, i.e., the thf/Sm/P_2-ring "plane", (b) anion of **5** similarly.

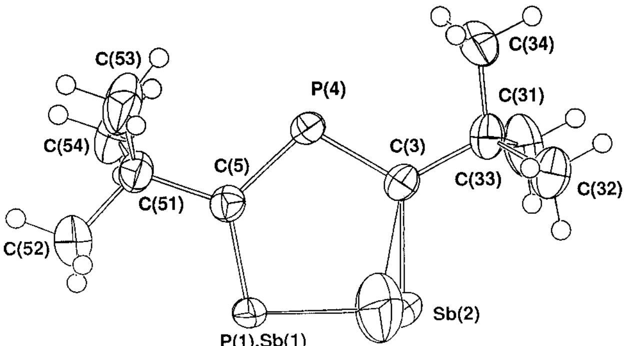

Figure 3. Projection of the anion of **6** normal to the ring plane.

(tmeda)$_2$][$P_2SbC_2Bu^t{}_2$] **6** (Figure 3). The structure solution established that only the [$P_2SbC_2Bu^t{}_2$]$^-$ anion was present and that it is essentially planar. There is positional disorder arising from the two possible arrangements adopted by the [$P_2SbC_2Bu^t{}_2$] ligand in the structure. This results in the Sb(1) site having partial phosphorus occupancy (denoted P(1)) and the P(2) site having partial antimony occupancy (denoted Sb(2)) (site occupancies of Sb(1) and P(1) refined to 85:13 and Sb-(2) and P(2) refined to 12:84) (Figure 3). Consequently, it would be unwise to comment in detail on the bond lengths and angles in [$P_2SbC_2Bu^t{}_2$]$^-$. Although [Li(12-crown-4)$_2$][$P_2EC_2Bu^t{}_2$] (E = Sb, P) has previously been structurally characterized, it contained both [$P_2SbC_2Bu^t{}_2$] and [$P_3C_2Bu^t{}_2$] ligands. As a result, that structure solution had complications additional to those arising from disorder in the P1 and Sb2 ring positions.

Conclusions. The present reactions demonstrate the versatility of [Tl(Ph_2pz)] and [Tl(azin)] as oxidants in the synthesis of lanthanoid(III) Ph_2pz and azin complexes and have provided the first X-ray-characterized lanthanoid(II or III) complexes of the novel [$P_3C_2Bu^t{}_2$]$^-$ and [$P_2SbC_2Bu^t{}_2$]$^-$ ligands. There is an intriguing variation in the η^2-bonding of the Ph_2pz^-, [$P_3C_2Bu^t{}_2$]$^-$, and [$P_2SbC_2Bu^t{}_2$]$^-$ ligands from σ, through σ/π, to π, respectively. The increasingly diffuse nature of the lone pairs on the heteroatoms in the sequence N, P, Sb makes them increasingly less suitable for electrostatic interaction with the hard Ln^{3+} ions. Thus there is a switch to π-bonding with Sb incorporation, consistent with the quasi-cyclopentadienyl nature of [$P_2SbC_2Bu^t{}_2$]$^-$.

Experimental Section

General Procedures. 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.[6] Melting points are uncorrected, with air-sensitive samples being sealed in capillaries under argon. IR data (4000−650 cm^{-1}) were obtained for Nujol mulls sandwiched between NaCl plates with a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were obtained with a VG Trio-1 GC mass spectrometer. 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 on a Bruker AC 200, AM 300, WM 250, or AC 400 spectrometer. The chemical shift references were the residual solvent signals ([D$_6$] benzene δ_H 7.15, δ_C 128.0; [D$_8$] THF δ_H 1.73, 3.58, δ_C 25.3, 67.4; [D$_8$] toluene δ_H 2.09) or external 85% H_3PO_4 (^{31}P δ = 0.0). Degrees of substitution for ^{13}C nuclei were determined using ^{1}H/^{13}C *J*-modulation pulse sequences. Deuterated solvents (Cambridge Isotopes) were dried over either sodium/potassium alloy or CaH_2 and were then vacuum transferred to greaseless Schlenk tubes and stored under purified argon. Visible/near-infrared spectra (350−1400 nm) were obtained using either a Cary 17 or a Cary 5G spectrophotometer with solutions sealed in a 1 mm silica glass cell fitted with a Rotaflo tap. Lanthanoid analyses were by EDTA titration[30] 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. Microanalysis samples were sealed in glass ampules under purified argon and were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Lanthanoid elements as either powders or distilled metal ingots were obtained from Rhône-Poulenc. Unless stated otherwise, all commercially available reagents were used without any further purification. Thallium(I) chloride was purchased from Avocado Chemicals. Bis(pentamethylcyclo-

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pentadienyl)bis(tetrahydrofuran)samarium(II),[31] bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II)·0.5(toluene),[29] 3,5-diphenylpyrazolatothallium(I),[6] 7-azaindolatothallium(I),[6] and the inseparable mixtures of $[Li(tmeda)_2][P_2EC_2Bu^t_2]$[11] and $[Tl(P_2EC_2Bu^t_2)]$[5d] (E = P and Sb) were synthesized by the indicated methods. The inseparable mixtures were identified by ^{31}P NMR spectroscopy and used without any further purification.

Synthesis of $[Yb(C_5Me_5)_2(Ph_2pz)]$, 1. $Tl(Ph_2pz)$ (0.38 g, 0.89 mmol) was added to a dme solution (30 mL) of $[Yb(C_5Me_5)_2(thf)]·0.5(C_7H_8)$ (0.50 g, 0.89 mmol), causing an immediate color change from orange to deep purple in addition to formation of a gray suspended solid, which was filtered from the solution. The dme was removed under vacuum to give a pink solid, which was then recrystallized from light petroleum to give large purple crystals of $[Yb(Ph_2pz)(C_5Me_5)_2]$ (0.50 g, 85%). IR: $\nu = 1605$ cm^{-1} m, 1179 w, 1070 w, 1037 m, 1025 m, 968 s, 904 w, 830 w, 802 w, 752 vs, 722 w, 702 m, 692 m, 680 vs, 665 w. Visible/near-IR (thf) λ_{max} (ϵ): 513 br (236), 933 (34), 975 (3), 1004 (205) nm. MS (70 eV, EI) *m/z* (%): 663 (15) [M^+], 528 (35) [$Yb(C_5Me_5)(Ph_2pz)^+$], 393 (35) [$Yb(Ph_2pz)^+$], 174 (35) [Yb^+], 135 (55) [$C_5Me_5^+$], 119 (100) [$C_9H_{11}^+$], 105 (70) [$C_8H_9^+$], 91 (45) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$]. Anal. Calcd for $C_{35}H_{41}N_2Yb$ (662.7): C 63.43, H 6.24, N 4.23, Yb 26.11. Found: C 62.93, H 5.37, N 4.38, Yb 25.72. Single crystals suitable for X-ray analysis were grown at −20 °C from a saturated solution in light petroleum.

Synthesis of $[Yb(C_5Me_5)_2(azin)]$, 2. Similar treatment of $[Yb(C_5Me_5)_2(thf)]·(C_7H_8)_{0.5}$ (0.84 g, 1.49 mmol) in thf (30 mL) with Tl(azin) (0.48 g, 1.49 mmol) and a similar purification gave large purple crystals of $[Yb(azin)(C_5Me_5)_2]$ (0.62 g, 74%). IR: $\nu = 1588$ cm^{-1} m, 1415 m, 1328 m, 1286 s, 1260 m, 1201 w, 1170 vs, 1115 w, 1064 w, 1023 m, 916 s, 900 w, 793 s, 769 vs, 743 m, 726 vs, 625 m. Visible/near-IR (thf) λ_{max} (ϵ): 510 br (296), 953 (64), 980 (60), 1000 (219) nm. MS (70 eV, EI) *m/z* (%): 561 (25) [M^+], 426 (70) [$Yb(C_5Me_5)(azin)^+$], 291 (100) [$Yb(azin)^+$], 174 (20) [Yb^+], 135 (18) [$C_5Me_5^+$], 119 (35) [$C_9H_{11}^+$], 105 (33) [$C_8H_9^+$], 91 (38) [$C_7H_7^+$], 77 (25) [$C_6H_5^+$]. Anal. Calcd for $C_{27}H_{35}N_2Yb$ (560.6): C 57.85, H 6.29, N 5.00, Yb 30.87. Found: C 56.58, H 6.39, N 5.24, Yb 30.79. Single crystals of **2**, suitable for X-ray analysis, were grown at −20 °C from a saturated solution in light petroleum.

Synthesis of $[Nd(Ph_2pz)_3(dme)_2]$, 3. $Tl(Ph_2pz)$ (0.42 g, 1.0 mmol) and neodymium metal (0.30 g, 2.1 mmol) in thf (30 mL) were subjected to ultrasonication for 3 days, after which time gray solids had deposited from a blue solution. Filtration of the precipitate followed by removal of the thf and recrystallization of the residue from dme afforded the blue crystalline $[Nd(Ph_2pz)_3(dme)_2]$ (0.23 g, 71%). Spectroscopic data were identical with those reported.[10] Single crystals of **3**·(C_6D_6) suitable for X-ray analysis were grown at room temperature from a C_6D_6 solution of the product.

Synthesis of $[Sm(C_5Me_5)_2(P_2EC_2Bu^t_2)(thf)]$ (E = P, Sb). $[Tl(P_2EC_2Bu^t_2)]$ (0.67 g, 1.27 mmol) and $[Sm(C_5Me_5)_2(thf)_2]$ (0.71 g, 1.27 mmol) in thf (30 mL) were stirred at room temperature for 2 h, giving a red-orange solution and a gray precipitate of thallium, which was filtered off. Removal of thf under vacuum gave a sticky red residue, which was extracted with light petroleum. Slow cooling of the solution afforded a red crystalline material containing both $[Sm(C_5Me_5)_2(P_2SbC_2Bu^t_2)(thf)]$ and $[Sm(C_5Me_5)_2(P_3C_2Bu^t_2)(thf)]$ (0.09 g, 10%), mp 215 °C. IR: $\nu = 1652$ cm^{-1} s, 1641 s, 1355 vs, 1224 m, 1010 m, 858 m, 722 w. ^1H NMR (250 MHz; C_6D_6): δ 0.35 (br s, C_5Me_5), 0.85 (br m, Bu^t), 1.15 (br m, Bu^t), 1.25 (br s, Bu^t), 2.25 (br m, thf). Very broad, overlapping signals precluded satisfactory integration and assignment of the Bu^t resonances, and the broadness of the signals prevented resolution of two thf resonances. ^{31}P NMR (101 MHz; C_6D_6): δ 279 (s, ($P_2SbC_2Bu^t_2$)), 281 (s, ($P_2SbC_2Bu^t_2$)), 287 (br s, ($P_3C_2Bu^t_2$)), 308 (vbr s, ($P_3C_2Bu^t_2$)). Very broad signals precluded satisfactory integration, but it was evident that the [$P_3C_2Bu^t_2$] species was in excess over the [$P_2SbC_2Bu^t_2$]. A small number of single crystals suitable for X-ray analysis were grown at −30 °C from a saturated solution in light petroleum and were found to be solely the $[Sm(C_5Me_5)_2(P_3C_2Bu^t_2)(thf)]$ complex **4**.

Synthesis of $[Li(thf)_4][Yb(P_2EC_2Bu^t_2)_3]$ (E = P, Sb), 5. $[Tl(P_2EC_2Bu^t_2)]$ (1.05 g, 2.0 mmol) (which presumably also contained a substantial amount of a lithium-containing species) and ytterbium metal (1.73 g, 10.0 mmol) in thf (30 mL) were stirred at room temperature under argon for 2 h followed by ultrasonication for 48 h to give a green/yellow solution. The precipitated thallium and excess ytterbium were filtered off and thf was removed to give a sticky black residue, which was extracted with light petroleum (bp 60−80 °C). Slow cooling of the solution afforded black crystals, suitable for X-ray analysis, of $[Li(thf)_4][Yb(P_2EC_2Bu^t_2)_3]$, which also contained species with ($P_3C_2Bu^t_2$) rings (0.48 g, 35%), mp 116 °C dec. IR: $\nu = 1358$ cm^{-1} s, 1293 w, 1261 w, 1218 m, 1045 vs, 916 w, 889 m, 800 w, 722 w. ^1H NMR (250 MHz; C_7D_8): δ 1.00 (vbr s, β-thf) 1.25 (br s, Bu^t), 1.52 (br s, Bu^t), 2.03 (br s, Bu^t), 3.51 (vbr s, α-thf). Very broad, overlapping signals precluded satisfactory integration and assignment of the Bu^t resonances. ^{31}P NMR (101 MHz; C_7D_8): δ 246 (br s, 2P, P1 and P2 ($P_3C_2Bu^t_2$)), 263 (br s, 1P, P4 ($P_3C_2Bu^t_2$)), 283 (br s, 1P, P4 ($P_2SbC_2Bu^t_2$)), 315 (br s, 1P, P1 ($P_2SbC_2Bu^t_2$)). Ratio [$P_2SbC_2Bu^t_2$] rings to [$P_3C_2Bu^t_2$] rings = ∼2:1. MS (70 eV, EI): *m/z* (%): 818 (20) [$Yb(P_2SbC_2Bu^t_2)_2^+$], 726 (30) [$(Yb(P_2SbC_2Bu^t_2)(P_3C_2Bu^t_2))-H)^+$], 636 (20) [$Yb(P_3C_2Bu^t_2)_2^+$], 405 (20) [$Yb(P_3C_2Bu^t_2)^+$], 321 (40) [$P_2SbC_2Bu^t_2{}^+$], 231 (35) [$P_3C_2Bu^t_2{}^+$], 169 (85) [$PC_2Bu^t_2{}^+$], 69 (100) [$Bu^tC^+$].

Attempted Reaction between $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ (E = P, Sb) and Ytterbium Metal. $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ (1.08 g, 2.0 mmol), ytterbium metal (1.73 g, 10.0 mmol), and mercury metal (ca. 0.2 mL) in thf (30 mL) were subjected to ultrasonication for 2 days, after which time the yellow solution remained unchanged. Filtration of the unreacted ytterbium metal and concentration of the thf solution yielded a yellow solid, which was extracted with light petroleum. Concentration of the light petroleum solution afforded yellow crystals, suitable for X-ray analysis, of $[Li(tmeda)_2][P_2SbC_2Bu^t_2]$, **6**.

Reaction between $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ and $NdCl_3$. $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ (1.08 g, 2.0 mmol) and $NdCl_3$ (0.25 g, 1.0 mmol) in thf (30 mL) were stirred for 12 h at room temperature, after which time unreacted $NdCl_3$ remained. A ^{31}P NMR spectrum of the reaction mixture revealed unreacted $[Li(tmeda)_2][P_2EC_2Bu^t_2]$.

Reaction between $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ and $[YbI_2(thf)_2]$. $[Li(tmeda)_2][P_2EC_2Bu^t_2]$ (1.08 g, 2.0 mmol) and $[YbI_2(thf)_2]$ (0.57 g, 1.0 mmol) in dme (30 mL) were stirred at room temperature for 12 h. A ^{31}P NMR spectrum of the brown reaction mixture revealed unreacted $[Li(tmeda)_2][P_2EC_2Bu^t_2]$.

Structure Determinations. These were executed at three venues with the following local conditions: **1**−**2**, University of Western Australia, single counter/sequential instrument, *T* ca. 295 K, capillary mounted specimens, Gaussian absorption correction, Xtal 3.2 program package;[32] **3**, Monash University, Nicolet (Siemens) R3m/V four-circle diffractometer *T* ca. 173 K; teXsan crystallographic software package;[33] **4**, **5**, University of Cardiff, FAST area-detector instrument, *T* ca. 150 K, SHELX program system[34] (final cycles Xtal), no absorption correction; **6**, UWA, Bruker AXS CCD area-detector instrument, *T* ca. 153 K, "empirical" absorption correction, Xtal

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3.2 program package. In all venues, Mo Kα radiation was employed ($\lambda = 0.7107_3$ (**1**, **2**, **6**), 0.7106_9 Å (**3**−**5**), $2\theta_{max}$ being 50° for all determinations (**6** excepted: 58°). For **3**, a unique data set was measured; for the others redundant equivalents ($N_{t(otal)}$ reflections) merging, after absorption correction, to N unique (R_{int} quoted), N_o of these with $I > n\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinements. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Residuals as in Table 1 are quoted at convergence, statistical weights being employed. Neutral atom complex scattering factors were used. Pertinent results are given in the figures and tables, individual variations in procedure being noted in the footnote to Table 1.

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