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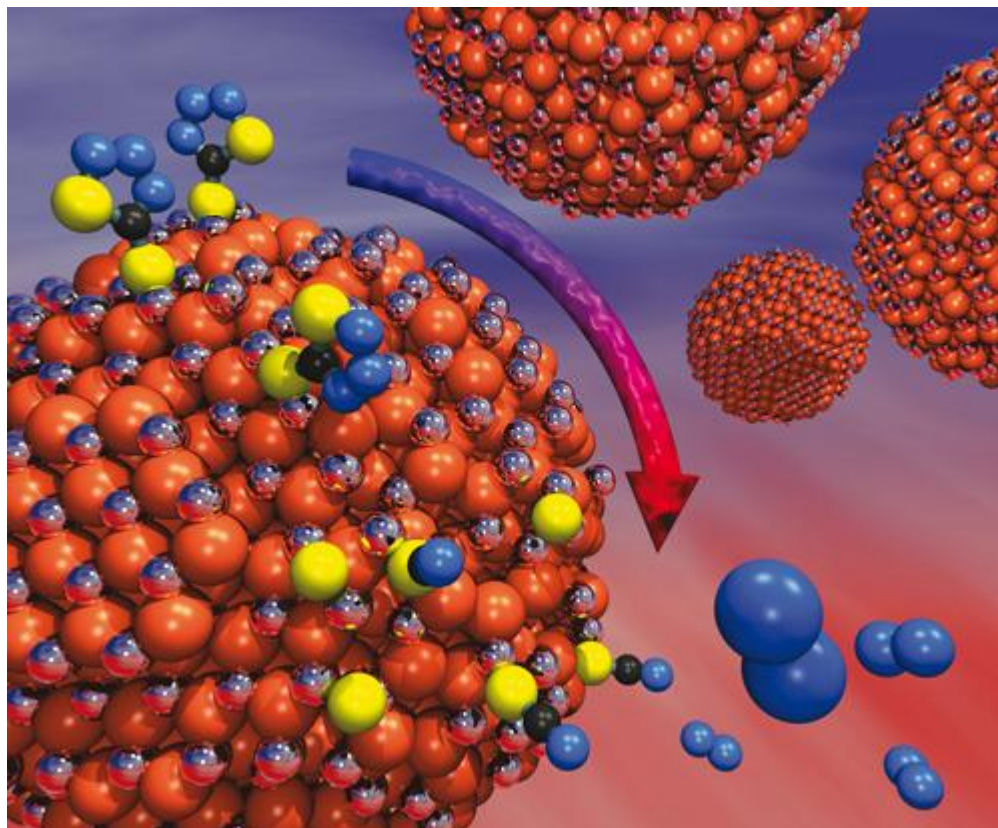Published in issue 26, 2012 of *Dalton Transactions*

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COMMUNICATION

Thermally stable rare earth dialkyl complexes supported by a novel bis(phosphinimine)pyrrole ligand†

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A novel bis(phosphinimine)pyrrole based ligand (HL) and its synthesis are reported. Rare earth dialkyl complexes of the ligand, LLn(CH$_2$SiMe$_3$)$_2$ (Ln = Er, Lu, Sc), have been prepared and found to exhibit high thermal stability in solution. The protio-ligand and dialkyl lanthanide complexes (Ln = Er, Lu) have been characterised by single crystal X-ray diffraction studies.

The last decade has been witness to a surge in the development of non-carbocyclic scaffolds for supporting highly reactive rare earth metal species.[1] The novel ligands that have arisen throughout this "post-metallocene" era have often proven to be attractive frameworks for catalytic transformations due to their high degree of tunability. This inherent property allows for rational and convenient adjustment of ligand steric and/or electronic properties and, hence, reaction chemistry of the resultant metal complexes. Of particular interest to us is the preparation of rare earth alkyl complexes stabilized by non-carbocyclic ancillaries as they often play prominent roles as catalysts or pre-catalysts in important industrial transformations, such as olefin polymerisation,[2] lactone polymerisation[3] and hydroamination.[4]
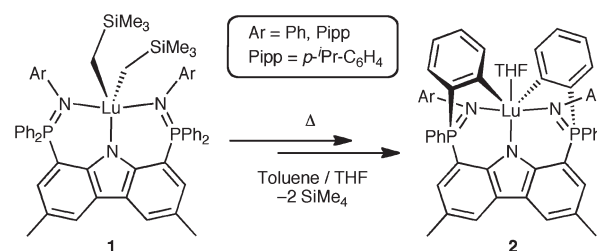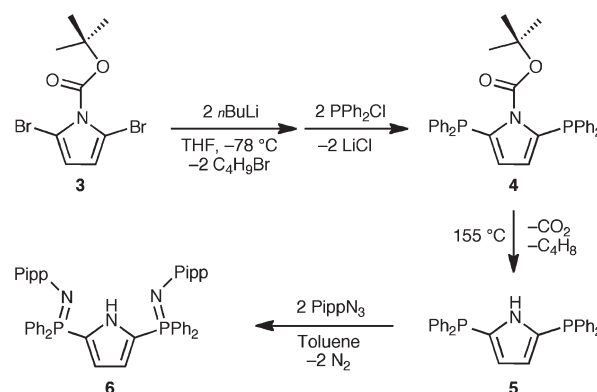
We recently reported a family of bis(phosphinimine)carbazole ligands and their utility in the synthesis of organolutetium complexes, *e.g.* **1**.[5] Unfortunately, dialkyl lanthanide complexes supported by this ligand were found to be highly thermally sensitive and, as a result, susceptible to a rapid intramolecular metalative alkane elimination process. The resultant products of this metalative degradation were lutetium complexes that were coordinated by the ligand in a κ^5 bonding mode *via* three nitrogen atoms and two *ortho*-metalated *P*-phenyl rings, **2** (Scheme 1).[5] Additionally, we have recently demonstrated that this ligand framework is susceptible to *ortho*-metalation of the *N*-aryl rings.[6]

In an attempt to mitigate the *ortho*-metalation difficulties encountered with our bis(phosphinimine)carbazole pincer, we elected to modify the geometry of the ligand. As seen in **1**, tridentate coordination of the original scaffold forms two six-membered chelate rings. As such, it was reasoned that if coordination to a metal instead formed two five-membered rings, the ligand bite angle would be enlarged.[7] To this end, we have incorporated pyrrole into the ligand framework in place of carbazole.

Synthesis of the target bis(phosphinimine)pyrrole ligand was achieved in high yield over 3 steps from the *N*-Boc protected derivative of 2,5-dibromopyrrole, **3**,[8] as outlined in Scheme 2. Lithium halogen exchange of **3** with ^{n}BuLi in THF,[9] followed by reaction with chlorodiphenylphosphine, afforded the Boc-protected bis(phosphine), **4**. Thermal removal of the Boc group was performed at 155 °C to liberate 2,5-bis(diphenylphosphino)-1*H*-pyrrole, **5**. Finally, the phosphinimine functionality was installed *via* a Staudinger reaction between **5** and *para*-isopropylphenyl (Pipp) azide, with concomitant loss of N$_2$, to afford **6** in 60% overall yield.

Protio-ligand **6** contains chemically equivalent phosphorus nuclei in solution and exhibits a single resonance in its ^{31}P{^{1}H} NMR spectrum at δ −8.1 (benzene-d$_6$). The ^{1}H and ^{13}C{^{1}H}

Scheme 1 Double metalative alkane elimination reaction of **1**.

Scheme 2 Synthesis of bis(phosphinimine)pyrrole ligand **6**.

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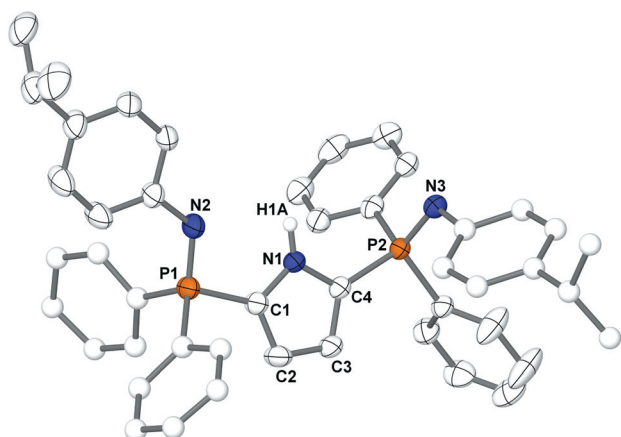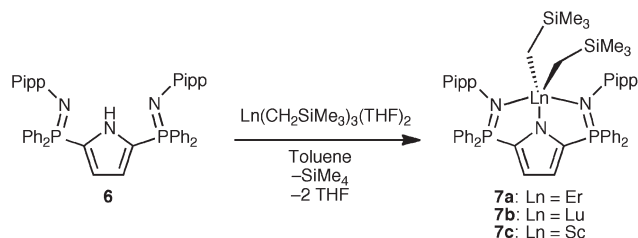
Fig. 1 Thermal ellipsoid plot (50% probability) of HL (**6**) with hydrogen atoms (except H1A) omitted for clarity. Disordered atoms are depicted as spheres of an arbitrary radius.

NMR spectra corroborate the expected ligand connectivity. Single crystals of **6** suitable for an X-ray diffraction experiment were obtained from a concentrated toluene solution at ambient temperature and the molecular structure is depicted in Fig. 1 as a thermal ellipsoid plot.[10]

Tridentate pincer ligand **6** has been designed to chelate metals in a meridional fashion *via* N1, N2 and N3. As such, when coordinated to a metal, it would be expected that the pincer arms (N2 and N3) would occupy a common plane with the pyrrole backbone. In the solid-state, N2 is close to the plane of the pyrrole backbone (N2–P1–C1–N1 torsion angle = 23.3(3)°). Conversely, N3 lies significantly further out of this plane with an N3–P2–C4–N1 torsion angle of 54.6(3)°. This rotation is influenced by intermolecular contacts in the crystal structure.[11] Other metrical parameters of interest in ligand **6** include the phosphinimine P–N bond lengths of 1.562(2) Å (P(1)–N(2)) and 1.572(2) Å (P(2)–N(3)). These values correlate well with other examples in the literature whereby the phosphinimine functionality exhibits a strong P=N double bond character.[5,12]

Protio-ligand **6** reacts readily with organometallic reagents at ambient temperature. For example, dialkyl lanthanide complexes of the ligand were prepared *via* an alkane elimination reaction of **6** (HL) with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Er, Lu, Sc; Scheme 3). When these reactions were followed *in situ* on an NMR tube scale in benzene-d$_6$, they proceeded rapidly with formation of the desired metal dialkyl complexes, one equivalent of SiMe$_4$ and two equivalents of liberated THF. Upon scale-up of the reactions in a toluene solution, the dialkyl products, LLn(CH$_2$SiMe$_3$)$_2$ (Ln = Er, **7a**; Lu, **7b**; Sc, **7c**), were obtained in high yield (81%, 82% and 81%, respectively) after recrystallization.

In the ^{31}P{^{1}H} NMR spectra (benzene-d$_6$), a significant downfield shift of the phosphinimine resonance was observed upon complexation of **6** with diamagnetic rare earth metals (**7b** δ 25.0; **7c**, δ 23.8). Despite the paramagnetic nature of erbium, the broad ^{31}P{^{1}H} NMR resonance of **7a** (δ −0.29, benzene-d$_6$) also proved to be a diagnostic indicator of ligand coordination. The ^{1}H NMR spectra (benzene-d$_6$) of **7b** and **7c** revealed the corresponding –CH$_2$SiMe$_3$ methylene (δ −0.20, **7b**; 0.55, **7c**) and

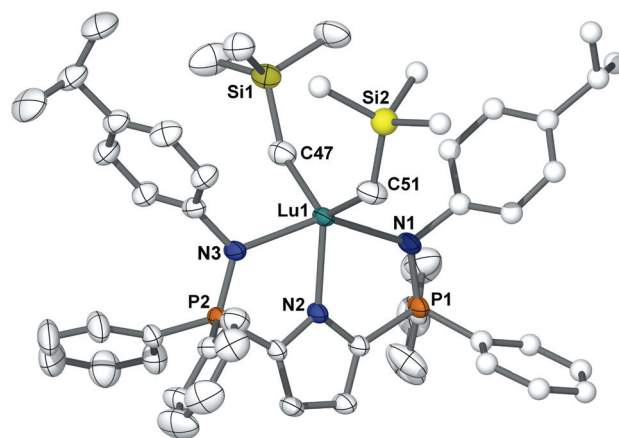**Scheme 3** The synthesis of dialkyl rare earth complexes.

Fig. 2 A thermal ellipsoid plot (50% probability) of LLu(CH$_2$SiMe$_3$)$_2$ (**7b**) with hydrogen atoms omitted for clarity. The solid-state structure of LEr(CH$_2$SiMe$_3$)$_2$ (**7a**) is isostructural to that of **7b**. Disordered atoms are depicted as spheres of an arbitrary radius.

methyl signals (δ 0.18, **7b**; 0.11, **7c**) as sharp singlets, integrating as 4H and 18H, respectively.

Notably, the dialkyl rare earth complexes were all base-free and the lutetium and scandium derivatives exhibited high thermal stability in both the solid and solution states. For example, complexes **7b** and **7c** can be left in benzene-d$_6$ solution at ambient temperature for at least one week with no apparent decomposition (as evidenced by ^{1}H and ^{31}P NMR spectroscopy). This is a dramatic improvement compared to the analogous carbazole-based dialkyl lutetium complex **1** that exhibited a half-life at ambient temperature (22.6 °C) of only 1160 s.[5] Perhaps even more significant is the fact that preliminary experiments indicate **7b** is stable in solution at 60 °C with no sign of decomposition over 4.5 hours.

In order to unambiguously establish the connectivity of the rare earth dialkyl complexes, X-ray diffraction analyses were performed. Single crystals of **7a** and **7b** were obtained from concentrated toluene–THF mixtures and their molecular structures were determined.[13] Complexes **7a** and **7b** were found to be isostructural; a representative thermal ellipsoid plot of **7b** is depicted in Fig. 2. While we did not obtain a solid-state structure of **7c**, it is reasonable to assume that it would possess an isostructural geometry to that of the lutetium and erbium derivatives.

The lanthanide complexes **7a** and **7b** are monomeric with five-coordinate metal centres that are bound to the pincer ligand in a κ^3 fashion through the three nitrogen atoms. The geometry is best described as distorted trigonal bipyramidal with the

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equatorial plane defined by N2 and the alkyl groups (C47 and C51). The phosphinimine donors (N1 and N3) occupy the apical sites. The bond angles about the equatorial plane in each complex are close to the ideal value of 120° (N2–Er1–C47 = 115.8(1)°, N2–Er1–C51 = 117.0(1)°, C47–Er1–C51 = 127.3(2)°, **7a**; N2–Lu1–C47 = 117.2(1)°, N2–Lu1–C51 = 116.0(1)°, C47–Lu1–C51 = 126.8(1)°, **7b**); however, the apical bond angle (N1–Ln–N3) deviates significantly from 180° (142.4(1)°, **7a**; 144.3(1)°, **7b**). The Ln–C–Si bond angles fall within the normal range for rare earth trimethylsilylmethyl complexes (129.5(3)°, 136.6(2)°, **7a**; 130.7(2)°, 136.9(2)°, **7b**). The Er–C bond lengths in **7a** (2.375(6) Å and 2.397(5) Å) agree well with other recently structurally characterised organoerbium complexes, such as (nacnac)Er(CH_2SiMe_3)$_2$ (2.342(3) Å and 2.380(2) Å)[14] and (Czx)Er(CH_2SiMe_3)$_2$ (2.398(3) and 2.404(3) Å),[15] where nacnac = 2,6-^{i}Pr-C_6H_3 substituted β-diketiminate and Czx = carbazole-bis(oxazoline). Complex **7b** exhibits slightly shorter Lu–C bond lengths (2.347(4) Å and 2.355(4) Å) than the corresponding contacts in the erbium congener, but the distances fall within the range expected for typical Lu–CH_2SiMe_3 bonds.[16]

In **7a** and **7b**, the metal sits in the centre of the ancillary ligand binding pocket. Both of the complexes exhibit Ln–pyrrole distances that are significantly shorter than the Ln–phosphinimine lengths (Er1–N2 = 2.338(3) Å *cf.* Er1–N1 = 2.360(3) Å and Er1–N3 = 2.396(3) Å, **7a**; Lu1–N2 = 2.297(2) Å *cf.* Lu1–N3 = 2.332(3) Å and Lu1–N1 = 2.364(2) Å, **7b**). The P–N bonds in the dialkyl complexes (ranging from 1.606(4) to 1.610(3) Å) are elongated by *ca.* 3% compared to those in the free protio-ligand, suggesting strong donation from the phosphinimine functionality to the rare earth metal.

Preliminary reactivity studies of **7b** (on an NMR tube scale in benzene-d$_6$) have revealed rich reaction chemistry. For instance, addition of one equivalent of the oxonium acid, [H(OEt$_2$)$_2$]$^+$ [B(C_6F_5)$_4$]$^-$,[17] to **7b** proceeded at ambient temperature over 4.5 h to liberate the expected cationic species as a diethyl ether adduct, [LLu(CH_2SiMe_3)(OEt$_2$)$_2$]$^+$[B(C_6F_5)$_4$]$^-$, **8**, with loss of one equivalent of SiMe$_4$. Alternatively, reaction of **7b** with one equivalent of Mes*NH$_2$ (Mes* = 2,4,6-^{t}Bu$_3$-C_6H_2) in the presence of 4-dimethylaminopyridine (DMAP) at 100 °C (over 1.5 h) resulted in the clean formation of the DMAP adduct of the mixed alkyl–anilide complex, LLu(CH_2SiMe_3)(NHMes*) (DMAP), **9**. The neutral (**7a–c**) and cationic (**8**) complexes are of interest to us as catalysts for various applications (*e.g.* lactone and olefin polymerisation) and we are currently evaluating their efficacy for mediating such processes. We are also interested in exploring the chemistry of **9** as it may provide fundamental insight into the structure and reactivity of lanthanide alkyl–anilide complexes, as well as serving as a useful hydroamination catalyst precursor.

In conclusion, we have prepared and characterised a new ancillary ligand comprised of a modular bis(phosphinimine) pyrrole framework (**6**). We have demonstrated the versatility of this ligand in that it can readily be complexed to lanthanide metals *via* an alkane elimination protocol to generate thermally robust rare earth dialkyl species. Current efforts are underway to investigate the small molecule reactivity of complexes **7a–c** in order to exploit the full range of their utility.

Acknowledgements

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10 Structure **6**: $C_{46}H_{45}N_3P_2$, $P\bar{1}$, a = 12.9263(2) Å, b = 14.5326(2) Å, c = 14.8331(3) Å, α = 112.587(1)°, β = 103.521(1)°, γ = 108.770(1)°, N = 36845, N_{ind} 10 171, R_1 = 0.0709 ($I > 2\sigma(I)$) and wR_2 = 0.1723 ($I > 2\sigma(I)$), GOF = 1.045.
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