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Arylaminopyridinato complexes of zirconium†

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Received 10th May 2004, Accepted 10th June 2004
First published as an Advance Article on the web 29th June 2004

A range of 2-arylaminopyridines (H**L**) are synthesised readily from bromopyridines and amines using palladium-catalysed amination. Protonolysis reactions of these proligands with ZrX_4 (X = NMe_2, CH_2Ph, CH_2Bu^t) yield zirconium complexes of the type $[ML_nX_{4-n}]$, several of which have been characterised by X-ray crystallography. Control of metal/ligand stoichiometry and structure is pursued by investigation of the effects on substitution patterns of the pyridine and aryl rings. Some distinct patterns emerged; (i) the 6-methyl position on the pyridine appears to be particularly important with regards to control of stoichiometry, although there are co-ligand effects; (ii) structures of the metal alkyl derivatives $[ZrL_n(CH_2R)_{4-n}]$ are dominated by aromatic π–π stacking, even when bulky arene substituents are employed at **L**. This leads to the complexes adopting a C_{2v}-symmetric core; (iii) the amides $[ZrL_2(NMe_2)_2]$ have structures for which aromatic π–π stacking is unfeasible, and correspondingly C_2-symmetric or similar structures are adopted. All the structural data presented is consistent with a *trans* influence order at zirconium Me_2N > RCH_2 > py.

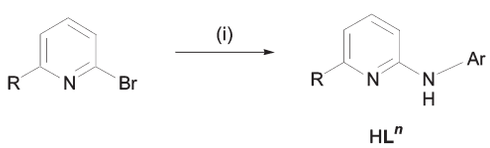
Introduction

Complexes of the amidinate ligand **I** have an extensive chemistry.[1–3] In particular, Sita has developed a class of cyclopentadienyl/amidinate complexes **II** that support catalysis of the polymerisation of vinylcyclohexane[4] and 1-hexene,[5,6] and have potential for the development of reagents for asymmetric hydrozirconation.[7] In comparison to these amidinates, the related aminopyridinates **III** are much less well developed in their catalytic[8] and stoichiometric chemistry.[9] Aminopyridinato (APy) complexes of the later transition metals where the substituent R is relatively small show a tendency to form bi-[10] or polynuclear[11,12] complexes. For the early transition metals, bimetallic structures have also been identified.[9a,13] Kempe *et al*. have employed aminopyridines such as **IV** incorporating bulkier (trimethylsilyl) substituents at the amido N and has synthesised many complexes including the group 4 systems $[M(APy)_nX_{4-n}]$ (X = *e.g.* halide, alkyl, amide).[14] Of this type of complex the $[M(APy)_2X_2]$ class[15,16,20] is arguably the most important because of its structural similarity to the metallocenes Cp_2MX_2. Unfortunately, these compounds are relatively difficult to synthesise without resorting to the use of bis(aminopyridine) proligands.[17–19] For example, treatment of $[Zr(NEt_2)_2Cl_2]$ with aminopyridine **IV** gave complexes with one or three (but not two) aminopyridinato ligands, depending on the substitution of the pyridine. We have previously shown that despite its similar steric demand to Kempe's trimethylsilylated aminopyridinates, **III** (R = adamantyl, R′ = H) readily formed complexes of the type $[M(APy)_2X_2]$ (X = Cl, NMe_2, CH_2Ph, CH_2Bu^t).[20] This suggests that the proton acidity of the parent aminopyridine is an important factor in determining metal–ligand stoichiometry.

These latter complexes provide a moderately active alkene polymerisation system. Also we were surprised to find that the barrier to inversion of chirality-at-metal in the C_2-symmetric complexes $[Zr(APy)_2(CH_2R)_2]$[20] is as high as *ca*. 60 kJ mol^{-1}. Hence we were interested to develop further proligands **III** (R = alkyl, aryl) for potential applications in polymer and stereoselective synthesis. In this paper we describe the synthesis and structural characterisation of a number of aminopyridines **III** (R = aryl) and their zirconium complexes.

Results and discussion

Kempe and Arndt,[15] and Polamo and Leskelä[9a,21] have used the aminopyridine **III** (R′ = H, R = Ph) to synthesise group 4 complexes of the type $[M(APy)_2X_2]_n$. The advent of Pd catalysed arylation of amines[22] opens the way for the synthesis of a much wider range of sterically-demanding aminopyridines than have hitherto been available from commercial sources. A range of aminopyridines (HL^1–HL^6) was thereby synthesised (Scheme 1).



HL^1 (R = H, Ar = 3,5-$C_6H_3Me_2$)
HL^2 (R = H, Ar = 3,5-$C_6H_3Bu^t_2$)
HL^3 (R = Me, Ar = 2,4-$C_6H_3Me_2$)
HL^4 (R = Me, Ar = 2-$C_6H_4Pr^i$)
HL^5 (R = H, Ar = 2,4,6-$C_6H_2Me_3$)
HL^6 (R = Me, Ar = 2,4,6-$C_6H_2Me_3$)

Scheme 1 Synthesis of *N*-aryl aminopyridines (conditions; $ArNH_2$, cat. dppp/$[Pd_2(dba)_3]$, toluene, 90 °C, 24 h, 60–80%).

Complexes of L^1 and L^2

Treatment of $[Zr(NMe_2)_4]$, $[Zr(CH_2Ph)_4]$ and $[Zr(CH_2{}^tBu)_4]$ with two equivalents of HL^1 in pentane gave, according to NMR spectra a mixture of compounds with varying metal to ligand ratios. The use of three equivalents gave a similar mixture, while four equivalents of HL^1 gave the clean formation of $[ZrL^1_4]$. Polamo[21] reported a hafnium complex using the unsubstituted aminopyridine **III** (R′ = H, R = Ph) with stoichiometry $[M(APy)_4]$. The ^{1}H NMR spectrum of

† Electronic supplementary information (ESI) available: Rotatable 3-D crystal structure diagrams and NMR spectra. See http://www.rsc.org/suppdata/dt/b4/b407008a/

DOI: 10.1039/b407008a

Table 1 Experimental data for the X-ray diffraction studies

	[Zr**L**$^2_4$]	[Zr**L**$^3_2$(NMe$_2$)$_2$]	[Zr**L**$^4_2$(NMe$_2$)$_2$]	[Zr**L**$^5_3$(CH$_2$Ph)]	[Zr**L**$^6_2$(NMe$_2$)$_2$]	[Zr**L**$^6_2$(CH$_2$Ph)$_2$]
Molecular formula	$C_{152}H_{200}N_{16}Zr_2{\cdot}C_5H_{12}$	$C_{32}H_{42}N_6Zr$	$C_{34}H_{46}N_6Zr$	$C_{49}H_{52}N_6Zr{\cdot}C_5H_{12}$	$C_{34}H_{46}N_6Zr$	$C_{44}H_{48}N_4Zr$
Formula weight	2505.87	601.94	629.99	888.33	629.99	724.08
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*Pna*2(1)	*P*2(1)/*n*	*P*2(1)/*c*	$P\bar{1}$	$P\bar{1}$	*Pbca*
a/Å	42.2168(13)	18.233(5)	20.017(3)	11.43920(10)	9.5430(18)	12.1162(15)
b/Å	21.6512(7)	9.202(3)	11.6567(19)	13.9372(3)	9.681(4)	17.401(2)
c/Å	16.5244(5)	19.792(6)	14.995(2)	14.9971(3)	18.882(4)	35.707(5)
α/°	90	90	90	85.4960(10)	98.120(15)	90
β/°	90	111.862(5)	111.197(4)	89.2130(10)	100.776(16)	90
γ/°	90	90	90	88.76	98.72(3)	90
Cell volume/Å^3	15104.0(8)	3082.0(15)	3262.0(9)	2382.88(7)	1667.8(8)	7528.4(17)
Z	4	4	4	2	2	8
μ/mm^{-1}	0.190	0.387	0.369	0.273	0.361	0.328
Total reflections	59679	23222	20984	15699	12703	47058
Independent reflections	18707 (R_{int} = 0.1511)	7661 (R_{int} = 0.1260)	7912 (R_{int} = 0.1393)	11236 (R_{int} = 0.0414)	7899 (R_{int} = 0.0182)	9457 (R_{int} = 0.0343)
*R*1[a], *wR*2[b] [$I > 2\sigma(I)$]	0.0730, 0.1316	0.0695, 0.1135	0.0632, 0.0905	0.0526, 0.1067	0.0307, 0.0763	0.0371, 0.0817

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [c] GoF = $[\sum w(F_o^2 - F_c^2)^2/$(no. unique reflns − no. of params)$]^{1/2}$.

Table 2 Selected bond lengths [Å] and angles [°] for [Zr**L**$^2_4$]

Zr(1)–N(1)	2.218(6)	Zr(1)–N(5)	2.213(6)
Zr(1)–N(2)	2.341(7)	Zr(1)–N(6)	2.372(7)
Zr(1)–N(3)	2.228(6)	Zr(1)–N(7)	2.210(7)
Zr(1)–N(4)	2.349(7)	Zr(1)–N(8)	2.365(8)
N(1)–Zr(1)–N(2)	58.5(3)	N(5)–Zr(1)–N(1)	143.0(3)
N(1)–Zr(1)–N(3)	86.1(2)	N(5)–Zr(1)–N(2)	85.2(2)
N(1)–Zr(1)–N(4)	80.5(3)	N(5)–Zr(1)–N(3)	95.5(3)
N(1)–Zr(1)–N(6)	155.9(3)	N(5)–Zr(1)–N(4)	131.3(3)
N(1)–Zr(1)–N(8)	76.7(3)	N(5)–Zr(1)–N(6)	57.3(3)
N(2)–Zr(1)–N(4)	124.5(2)	N(5)–Zr(1)–N(8)	88.1(3)
N(2)–Zr(1)–N(6)	133.7(2)	N(7)–Zr(1)–N(1)	96.6(3)
N(2)–Zr(1)–N(8)	75.2(2)	N(7)–Zr(1)–N(2)	132.0(3)
N(3)–Zr(1)–N(2)	80.9(3)	N(7)–Zr(1)–N(3)	142.4(3)
N(3)–Zr(1)–N(4)	58.8(3)	N(7)–Zr(1)–N(4)	84.5(3)
N(3)–Zr(1)–N(6)	77.3(2)	N(7)–Zr(1)–N(5)	103.9(3)
N(3)–Zr(1)–N(8)	155.5(3)	N(7)–Zr(1)–N(6)	86.4(3)
N(4)–Zr(1)–N(6)	76.0(2)	N(7)–Zr(1)–N(8)	58.4(3)
N(4)–Zr(1)–N(8)	133.0(3)	N(8)–Zr(1)–N(6)	123.9(2)

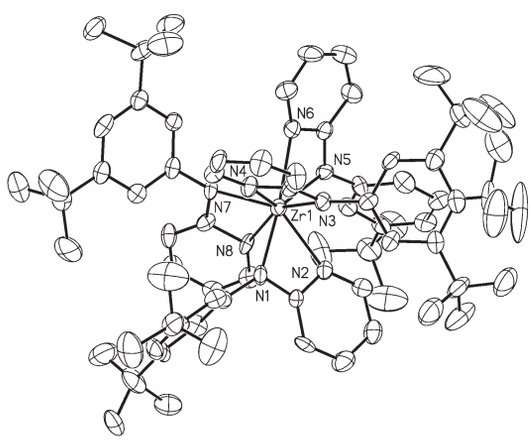


Fig. 1 Thermal ellipsoid plot of the molecular structure of [Zr**L**$^2_4$] (H atoms omitted).

[Zr**L**$^1_4$] at 293 K showed one set of aminopyridinato resonances only, indicating high symmetry or a system in rapid flux on this timescale. The ligand **L**^{2} gave a similar complex [Zr**L**$^2_4$] despite the increased steric bulk. The ^{1}H NMR spectrum of this compound at 293 K showed eight equivalent ^{t}Bu groups at 1.32 ppm. Some of the aryl CH resonances were broadened, probably due to hindered rotation about the N–C$_{aryl}$ bond since on raising the temperature to 343 K the spectrum sharpened to give the expected four pyridine and two aryl peaks between 5.95 and 7.29 ppm.

The molecular structure of eight-coordinate [Zr**L**$^2_4$] was determined by X-ray crystallography and is shown in Fig. 1, with experimental details and selected bond lengths and angles in Tables 1 and 2. The aminopyridinato ligands in approximately *trans* positions to one another are oriented 'head to tail' such as to avoid collision of the bulky arene units. The bond lengths for the Zr–N$_{amide}$ [2.213(6)–2.228(6) Å] and Zr–N$_{pyridine}$ [2.341(7)–2.372(7) Å] are comparable to those found by Kempe *et al.*[23] and ourselves,[20] despite the high coordination number.

Complexes of L^3

H**L**^{3}, which contains a 2-methyl substituent at the aryl group, was treated with [Zr(NMe$_2$)$_4$] to give the yellow complex [Zr**L**$^3_2$(NMe$_2$)$_2$] in 56% yield. Evidently, increasing the steric bulk in the arylamido *ortho* position has facilitated some control over metal/ligand stoichiometry. The molecular structure determined by X-ray structure crystallography (Fig. 2) showed a C_2-symmetric complex with mutually *cis* amides [N(6)–Zr(1)–N(5) = 100.47°(16)]. In contrast to the structure of a related dialkyl complex [Zr(APy)$_2$(CH$_2$Ph)$_2$] for which *trans* orientation of the pyridine units was observed, [Zr**L**$^3_2$(NMe$_2$)$_2$] has adopted an orientation with *cis* pyridine units at the "back" of the complex and *trans* to the dimethylamido co-ligands [N(1)–Zr(1)–N(5) = 150.58(16)° and N(3)–Zr(1)–N(6) = 152.14(15)°]. Other parameters are comparable with literature values[23] and [Zr**L**$^2_4$].

The reaction of H**L**^{3} with [Zr(CH$_2$Ph)$_4$] followed by crystallisation from pentane gave yellow [Zr**L**$^3_2$(CH$_2$Ph)$_2$] in 71% yield. The ^{1}H NMR spectrum at 293 K showed slight broadening of peaks, particularly the Zr–CH$_2$ resonance at 2.50 ppm. At 333 K all the resonances sharpen giving a singlet for the benzyl CH$_2$ at 2.53 ppm. The neopentyl complex [Zr**L**$^3_2$(CH$_2$^{t}Bu)$_2$] was formed similarly, and in 64% yield. Variable temperature ^{1}H studies showed similar results to that of the benzyl complex. Single crystals of [Zr**L**$^3_2$(CH$_2$^{t}Bu)$_2$] were analysed by X-ray crystallography, but the relatively poor quality data allowed only partial refinement. The structure elucidated for [Zr**L**$^3_2$(CH$_2$^{t}Bu)$_2$] is depicted in Scheme 2 (related molecules are described later in more detail). The unexpected presence of an approximate mirror plane containing the two pyridine rings, and an accompanying arene π–π interaction motif explains the symmetry indicated by the NMR spectra. Polamo and Leskelä have reported a dimeric zirconium dichloride complex that we have found to exhibit similar π–π stacking.[9a]

Complexes of L^4

The proligand H**L**^{4} was synthesised to explore the effect increasing the size of the single *ortho* substituent present in H**L**^{3}. The ^{1}H NMR spectrum of the subsequent amide complex [Zr**L**$^4_2$(NMe$_2$)$_2$] is consistent with the presence of two independent ligands **L**^{4} in that two sets of arene and methyl resonances are observed. The ^{i}Pr methyl

Table 3 Selected bond lengths [Å] and angles [°] for [Zr**L**$^3_2$(NMe$_2$)$_2$]

Zr(1)–N(1)	2.398(4)	Zr(1)–N(4)	2.262(4)
Zr(1)–N(2)	2.238(4)	Zr(1)–N(5)	2.038(4)
Zr(1)–N(3)	2.385(4)	Zr(1)–N(6)	2.034(4)
N(2)–Zr(1)–N(1)	57.60(14)	N(5)–Zr(1)–N(3)	93.45(14)
N(2)–Zr(1)–N(3)	98.74(14)	N(5)–Zr(1)–N(4)	107.64(15)
N(2)–Zr(1)–N(4)	148.19(14)	N(6)–Zr(1)–N(1)	94.05(15)
N(3)–Zr(1)–N(1)	85.00(13)	N(6)–Zr(1)–N(2)	104.21(15)
N(4)–Zr(1)–N(1)	96.35(14)	N(6)–Zr(1)–N(3)	152.14(15)
N(4)–Zr(1)–N(3)	57.76(13)	N(6)–Zr(1)–N(4)	94.84(15)
N(5)–Zr(1)–N(1)	150.58(16)	N(6)–Zr(1)–N(5)	100.47(16)
N(5)–Zr(1)–N(2)	93.84(16)		

Table 4 Selected bond lengths [Å] and angles [°] for [Zr**L**$^4_2$(NMe$_2$)$_2$]

Zr(1)–N(1)	2.369(3)	Zr(1)–N(4)	2.258(3)
Zr(1)–N(2)	2.249(3)	Zr(1)–N(5)	2.023(4)
Zr(1)–N(3)	2.390(3)	Zr(1)–N(6)	2.035(4)
N(1)–Zr(1)–N(3)	79.09(10)	N(5)–Zr(1)–N(3)	93.57(13)
N(2)–Zr(1)–N(1)	57.99(12)	N(5)–Zr(1)–N(4)	103.45(13)
N(2)–Zr(1)–N(3)	100.28(12)	N(5)–Zr(1)–N(6)	104.11(15)
N(2)–Zr(1)–N(4)	153.85(12)	N(6)–Zr(1)–N(1)	98.72(13)
N(4)–Zr(1)–N(1)	101.12(11)	N(6)–Zr(1)–N(2)	104.24(13)
N(4)–Zr(1)–N(3)	57.42(12)	N(6)–Zr(1)–N(3)	149.42(14)
N(5)–Zr(1)–N(1)	144.97(14)	N(6)–Zr(1)–N(4)	93.82(14)
N(5)–Zr(1)–N(2)	90.48(13)		

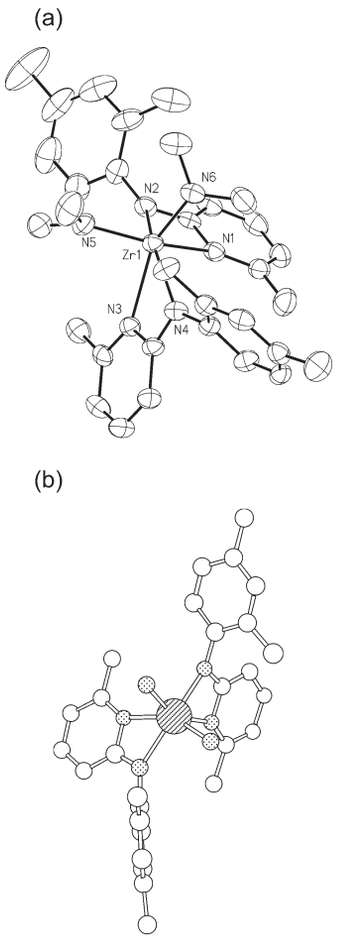
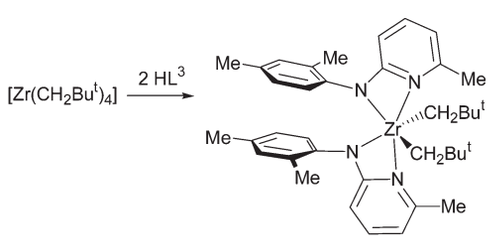


Fig. 2 Molecular structure of [Zr**L**$^3_2$(NMe$_2$)$_2$] (H atoms omitted) (a) thermal ellipsoid plot and (b) Chem3D representation, viewed along the approximate C_2 axis.



Scheme 2 Synthesis of [Zr**L**$^3_2$(CH$_2$Bu^t)$_2$] showing the structure with coplanar pyridine units and π-stacked arene groups.

region is unusual in that one apparent doublet and one apparent triplet is observed, however these are interpreted as arising from a completely overlapping and partially overlapping pair of doublets respectively. In support of this, each composite resonance correlates with two ^{13}C resonances in the HMQC spectrum. The *iso*-propyl CH groups overlap to give a complex grouping at *ca.* 3.4 ppm. The amide NMe$_2$ resonances most surprisingly appear as 3 singlets in the ratio 3 : 6 : 3 at *ca.* 2.6–3.0 ppm. These spectra are consistent with one amide group only suffering from restricted rotation. We postulate that the structure in solution is similar to that of [Zr**L**$^6_2$(NMe$_2$)$_2$] (*vide infra*). Variable temperature NMR studies on this system gave very complicated spectra and we are only able to conclude that the complex was undergoing a number of exchange processes between different diastereomers.

The molecular structure of this complex [Zr**L**$^4_2$(NMe$_2$)$_2$] (Fig. 3) sheds no light on this isomer problem given that it is approximately C_2-symmetric in the solid state. The structure is very similar to that of [Zr**L**$^3_2$(NMe$_2$)$_2$] (Fig. 2) with *cis*oid dimethylamides [N(5)–Zr(1)–N(6) = 104.11(15)°]. The pyridine moieties are approximately *trans* to the above amides, leaving the unsymmetrically-substituted 2-isopropylphenyl groups projecting to the 'front' of the molecule alongside the dimethylamido co-ligands.

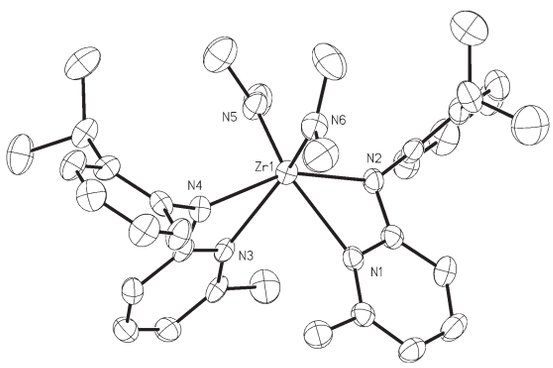


Fig. 3 Thermal ellipsoid plot of the molecular structure of [Zr**L**$^4_2$(NMe$_2$)$_2$] (H atoms omitted).

The reaction of H**L**^{4} with [Zr(CH$_2$Ph)$_4$] followed by crystallisation from pentane gave yellow [Zr**L**$^4_2$(CH$_2$Ph)$_2$] in 61% yield. The ^{1}H NMR spectrum at 293 K was rather broad, and this situation was not alleviated at higher temperatures. Treatment of H**L**^{4} with [Zr(CH$_2$^{t}Bu)$_4$] followed by crystallisation from pentane gave yellow [Zr**L**$^4_2$(CH$_2$^{t}Bu)$_2$] (49%) which had similar NMR properties to the benzyl complex. On the basis of the results presented later we propose that these complexes have the π-stacked structure such as that shown for [Zr**L**$^3_2$(CH$_2$^{t}Bu)$_2$] in Scheme 2.

Zirconium complexes of L^5

Treatment of [Zr(NMe$_2$)$_4$] and [Zr(CH$_2$Ph)$_4$] with two equivalents of H**L**^{5} yielded mixtures of complexes, but in this case analysis of NMR spectra indicated that [Zr**L**$^5_3$X] was the predominant stoichiometry. The two complexes (X = NMe$_2$, CH$_2$Ph) were synthesised using 3 equivalents of H**L**^{5}.

^{1}H NMR spectra of the benzyl complex [Zr**L**$^5_3$(CH$_2$Ph)] in d$_2$-dichloromethane gave integral ratios showing only one benzyl CH$_2$ singlet, and interestingly two types of aminopyridinato ligand in the ratio 2 : 1.

The molecular structure determined by X-ray crystallography (Fig. 4) is very unusual; for two of the aminopyridinato units, the bulky mesityl groups are face-to-face parallel and the pyridine rings are mutually coplanar [Fig. 4(b)]. The presence of this π–π interaction, also proposed for the alkyls [Zr**L**$^3_2$(CH$_2$^{t}Bu)$_2$] (Scheme 2) and [Zr**L**$^4_2$(CH$_2$R)$_2$] (R = ^{t}Bu, Ph), is rather surprising given the rather

Table 5 Selected bond lengths [Å] and angles [°] for [Zr**L**$^5_3$(CH$_2$Ph)]

Zr(1)–N(1)	2.209(2)	Zr(1)–N(5)	2.208(2)
Zr(1)–N(2)	2.371(2)	Zr(1)–N(6)	2.312(3)
Zr(1)–N(3)	2.217(2)	Zr(1)–C(43)	2.297(3)
Zr(1)–N(4)	2.314(2)		
N(1)–Zr(1)–N(2)	58.19(8)	N(5)–Zr(1)–N(1)	106.74(9)
N(1)–Zr(1)–N(3)	101.50(8)	N(5)–Zr(1)–N(2)	135.13(9)
N(1)–Zr(1)–N(4)	87.54(8)	N(5)–Zr(1)–N(3)	87.30(9)
N(1)–Zr(1)–N(6)	88.00(9)	N(5)–Zr(1)–N(4)	145.83(9)
N(3)–Zr(1)–N(2)	134.92(8)	N(5)–Zr(1)–N(6)	58.80(9)
N(3)–Zr(1)–N(4)	59.12(8)	N(6)–Zr(1)–N(2)	77.63(9)
N(3)–Zr(1)–N(6)	146.05(9)	N(6)–Zr(1)–N(4)	154.69(9)
N(4)–Zr(1)–N(2)	78.86(8)		

heavily substituted aryl rings. The rings are aligned almost face-to-face rather than the frequently observed offset structure (*vide infra*).[24] The distance between mesityl ring centroids is *ca.* 3.69 Å, perhaps at the upper end of the expected range, but the shortest inter-ligand distance [C(20)–C(34)] is *ca.* 3.43 Å. The third aminopyridinato unit and the benzyl ligand occupy the remaining coplanar coordination sites in the open face of the complex thereby generated.

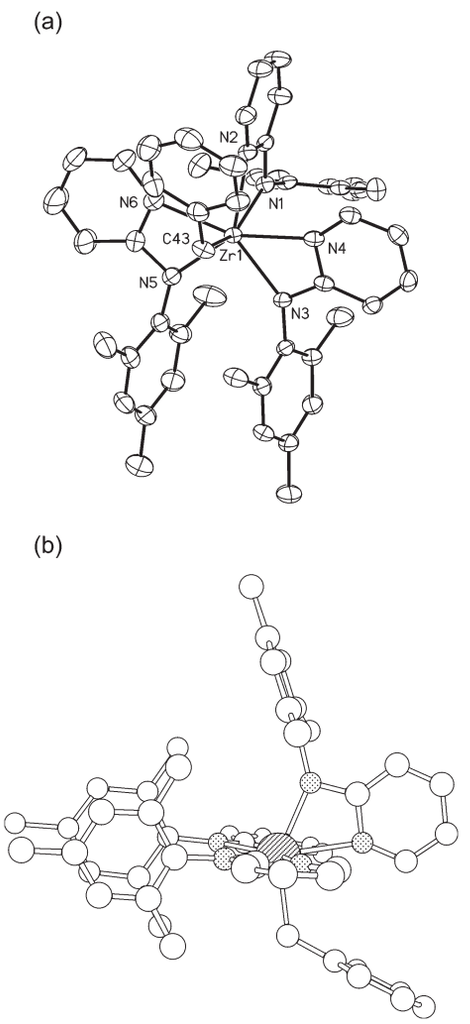


Fig. 4 Molecular structure of [Zr**L**$^5_3$(CH$_2$Ph)] (H atoms omitted); (a) thermal ellipsoid plot and (b) Chem3D projection showing the parallel pyridine units and arene π-stacking motif.

In contrast to the above, reaction of [Zr(CH$_2$^{t}Bu)$_4$] with two equivalents of H**L**^{5} yielded the desired [Zr**L**$^5_2$(CH$_2$^{t}Bu)$_2$] in 69% yield. In the ^{1}H NMR spectrum, the presence of a singlet for the neopentyl CH$_2$ group at 1.88 is consistent with the presence of a mirror plane (a structure similar to those in Scheme 2 and Fig. 4) or with a C_2-symmetric compound in rapid exchange between other structural isomers on the ^{1}H-NMR chemical shift timescale.

Table 6 Selected bond lengths [Å] and angles [°] for [Zr**L**$^6_2$(NMe$_2$)$_2$]

Zr(1)–N(1)	2.3776(15)	Zr(1)–N(4)	2.3031(15)
Zr(1)–N(2)	2.1980(16)	Zr(1)–N(5)	2.0729(16)
Zr(1)–N(3)	2.3254(16)	Zr(1)–N(6)	2.0230(16)
N(2)–Zr(1)–N(1)	58.37(5)	N(5)–Zr(1)–N(3)	95.63(6)
N(2)–Zr(1)–N(3)	142.45(5)	N(5)–Zr(1)–N(4)	152.44(6)
N(2)–Zr(1)–N(4)	97.22(5)	N(6)–Zr(1)–N(1)	152.60(6)
N(3)–Zr(1)–N(1)	88.44(5)	N(6)–Zr(1)–N(2)	94.26(6)
N(4)–Zr(1)–N(1)	82.25(5)	N(6)–Zr(1)–N(3)	116.88(6)
N(4)–Zr(1)–N(3)	58.10(5)	N(6)–Zr(1)–N(4)	101.71(6)
N(5)–Zr(1)–N(1)	89.42(6)	N(6)–Zr(1)–N(5)	97.73(7)
N(5)–Zr(1)–N(2)	100.64(6)		

Zirconium complexes of L^6

The molecular structure of [Zr**L**$^5_3$(CH$_2$Ph)] above indicated that a 6-methyl group on the pyridine ring would point into the area occupied by the third ligand in that complex and therefore possibly promote the formation of [M(APy)$_2$X$_2$] compounds.

The reaction of H**L**^{6} with [Zr(NMe$_2$)$_4$] followed by crystallisation from toluene gave yellow [Zr**L**$^6_2$(NMe$_2$)$_2$] in 74% yield. ^{1}H NMR spectra of this complex indicated that the two aminopyridinato ligands are spectroscopically equivalent in the range 193–298 K. An X-ray crystallographic study however indicated a rather unusual structure (Fig. 5); the aminopyridinato ligands are "head to tail", *i.e.* one ligand presents its amido N atom and one its pyridine ring toward the "front" of the complex. Hence one dimethylamido unit is *trans* to a pyridine [N(6)–Zr(1)–N(1) = 152.60(6)°] and the other is *trans* to arylamido [N(5)–Zr(1)–N(4) = 152.44(6)°]. The dimethylamido units are mutually *cis* [N(6)–Zr(1)–N(5) = 97.73(7)°]. Interestingly, steric compression between C(33) and the mesityl ring C(7)–C(14) appears to have led to an unusually large angle Zr(1)–N(6)–C(33) [143.09(14)°]. Angle Zr(1)–N(6)–C(34) is correspondingly small at [105.35(13)°]. A similar phenomenon has been reported by Kempe *et al.*[23]

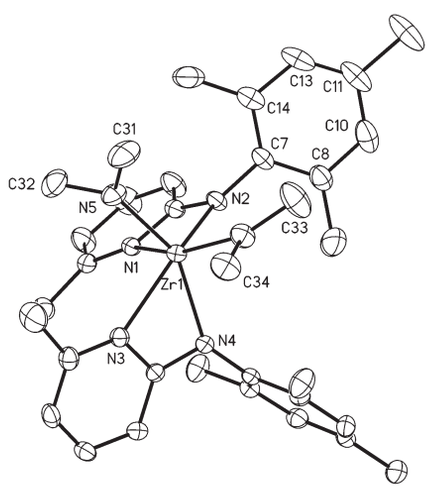


Fig. 5 Thermal ellipsoid plot of the molecular structure of [Zr**L**$^6_2$(NMe$_2$)$_2$] (H atoms omitted).

The adoption of this rather sterically compressed structure is surprising given the C_2-symmetric structure of [Zr**L**$^3_2$(NMe$_2$)$_2$] (Fig. 2); evidently the situation is rather finely balanced. For the overall structure of [Zr**L**$^6_2$(NMe$_2$)$_2$] we propose that the apparent symmetry indicated by the NMR spectra results from the complex being in rapid flux on the ^{1}H NMR chemical shift timescale between structures such as that in Fig. 5 rather than there being a more symmetrical structure (*i.e.* C_2-symmetry) adopted in solution.

Reaction of H**L**^{6} with [Zr(CH$_2$Ph)$_4$] gave the yellow, heat and light sensitive product [Zr**L**$^6_2$(CH$_2$Ph)$_2$] in 65% yield. The ^{1}H NMR spectrum, which indicated the presence of two equivalent aminopyridinato ligands, contains rather broad peaks including a singlet CH$_2$ peak at 2.95 ppm for two benzyl ligands. The spectra showed little change except further broadening of all peaks down to

Table 7 Selected bond lengths [Å] and angles [°] for [Zr**L**$^6_2$(CH_2Ph)$_2$]

Zr(1)–N(1)	2.3747(16)	Zr(1)–N(4)	2.1665(15)
Zr(1)–N(2)	2.1667(16)	Zr(1)–C(31)	2.289(2)
Zr(1)–N(3)	2.3258(16)	Zr(1)–C(38)	2.285(2)
N(2)–Zr(1)–N(1)	58.81(6)	N(4)–Zr(1)–N(2)	90.19(6)
N(2)–Zr(1)–N(3)	150.01(6)	N(4)–Zr(1)–N(3)	59.83(6)
N(3)–Zr(1)–N(1)	151.15(6)	C(38)–Zr(1)–C(31)	121.75(8)
N(4)–Zr(1)–N(1)	148.98(6)		

193 K. Fig. 6 and Fig. 7 show the X-ray crystallographic structure of [Zr**L**$^6_2$(CH_2Ph)$_2$], with coplanar pyridines and parallel mesityl groups as for [Zr**L**$^5_3$(CH_2Ph)] (Fig. 4). The distance between centroids of the mesityl rings is *ca.* 3.65 Å with the shortest [C(7)–C(22)] contact of *ca.* 3.44 Å. It is also apparent from Fig. 7 that as a result of this interaction the two aminopyridinato units are pulled together toward one side of the Zr(N–C–N)$_2$ coordination plane; the inter-ligand distance between pyridine methyl group H atoms is > 4 Å, indicating that steric compression at this side of the coordination plane is not responsible for the distortion. The benzyl ligand CH_2 carbon atoms are distorted from a mutually *trans* arrangement [C(38)–Zr(1)–C(31) = 121.75°(8)] at least partially as a result of the above distortion, and also as a result of the steric demand of the mesityl 2,6-substituents. The benzyl phenyl groups are rotated back toward the mesityl substituents in order to avoid the pyridine methyls. Overall, given the strong possibility that the above structural features will lead to restricted rotation of *e.g.* the benzyl groups it is not surprising that the ^{1}H NMR spectrum contains rather broad peaks. This also goes some way to explaining the similar NMR spectra for [Zr**L**$^5_2$(CH_2Bu^t)$_2$] above.

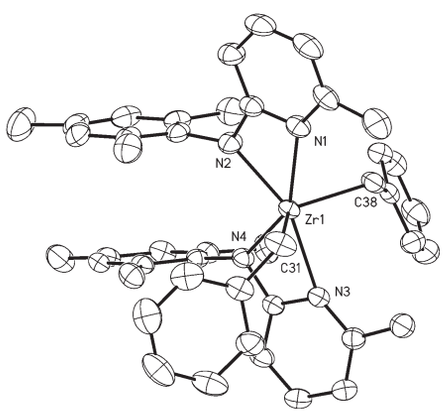


Fig. 6 Thermal ellipsoid plot of the molecular structure of [Zr**L**$^6_2$(CH_2Ph)$_2$] (H atoms omitted).

In contrast to the above reaction of H**L**^{6} with [Zr(CH_2Ph)$_4$], the reaction with [Zr(CH_2Bu^t)$_4$] gave only [Zr**L**^{6}(CH_2Bu^t)$_3$]. Presumably, this complex is too sterically crowded to react with a second aminopyridine to give the desired [M(APy)$_2$X$_2$].

Conclusions

While we have previously shown that certain alkylaminopyridine proligands readily form complexes [Zr(APy)$_2$X$_2$] with well-defined C_2-symmetric structures,[20] the arylaminopyridines described here present considerable structural diversity. Firstly, significant steric bulk in the aryl substituent, and more importantly a 6-methyl substitution at the pyridine, is required to furnish control of metal/ligand stoichiometry. Secondly, the structures are highly dependent on the identity of the co-ligands X; the amido compounds (X = NMe_2) give *cis*-C_2-symmetric or similar complexes while the alkyls (X = CH_2Ph, CH_2Bu^t) adopt the unexpected π-stacked C_{2v} structures with an almost *trans* arrangement of X. Thirdly, there are a number of discrepancies between the structures adopted in the solid state and those in solution, especially for the amido compounds. Evidently the factors that control structure in these compounds are rather finely balanced, and apart from the formation of the π-stacked motif in the alkyls, are rather difficult to predict.

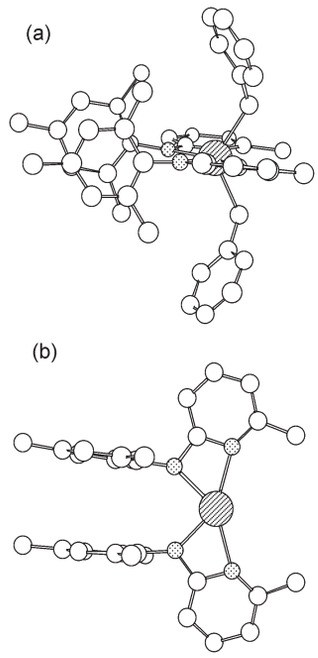
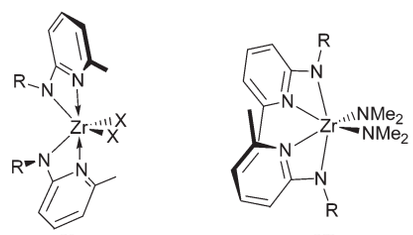


Fig. 7 Chem3D representations of [Zr**L**$^6_2$(CH_2Ph)$_2$] (a) showing the coplanarity of pyridine units and (b) parallel orientation of mesityl groups; benzyl ligands in the latter removed for clarity.



V **VI**

There seems to be a pattern emerging (i) that alkyls[20] adopt structure similar to **V** (which in the case R′ = aryl allows formation of the arene π–π interaction) and (ii) that the amides adopt a structure similar to **VI** (which in the case R′ = aryl does not lead to a π–π interaction simply because the arene units are not appropriately oriented). This structural pattern leads us to the conclusion that the *trans* influence at zirconium for the ligands used here is in the order Me_2N > Ar(Py)N > $PhCH_2$ > py; the strongest *trans* influence ligand is to be found opposite py. In particular for the series of compounds described here, dialkylamido avoids being *trans* to dialkylamido.‡ While the ordering of aminopyridinate amido unit [Ar(Py)N] lower than dialkyl amido is not surprising, given that in the former the negative charge is substantially delocalised, the ordering of alkyl lower than both amido units is perhaps unexpected. We will address this issue in future studies.

Experimental details

General comments

Where necessary, procedures were carried out under an inert atmosphere of argon by using a dual manifold vacuum/argon line and standard Schlenk techniques, or in an MBraun dry box. Solvents were dried by refluxing for three days under dinitrogen over the appropriate drying agents (sodium for toluene; potassium for THF and benzene; sodium–potassium alloy for diethyl ether, petroleum ether, and pentane; calcium hydride for dichloromethane) and degassed before use. Solvents were stored in glass ampoules under argon. All glassware and cannulae were stored in an oven (>373 K) and flame dried immediately prior to use. Most chemicals and reagents were purchased from either Aldrich Chemical Company, Acros Chemical

‡ The structure of [Zr**L**$^6_2$(NMe_2)$_2$] is a minor exception in that it suggests Me_2N ~ Ar(Py)N [one py (the weakest *trans* ligand) is *trans* to dimethylamido and the other is *trans* to arylamido].

Company, Lancaster or Strem and used without further purification. Deuterated solvents were freeze–thaw degassed and dried by heating to their normal boiling points over potassium (or calcium hydride for d_2-dichloromethane) *in vacuo* for three days before vacuum distilling (trap-to-trap) to a clean, dry Young's tap ampoule and being stored in the dry box. Deuterated chloroform was dried in the bottle over molecular sieves (4 Å).

NMR spectra were recorded on Bruker ACF-250, DPX-300, DPX-400, AV-400 and DRX-500 spectrometers and the spectra were referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). EI/CI mass spectra were obtained on a VG Autospec mass spectrometer. Infrared spectra were obtained either as Nujol mulls using a Perkin-Elmer Paragon 1000 FTIR spectrometer, or directly using an Avatar 320 FTIR instrument. Elemental analyses were performed by Warwick Analytical Services. Carbon analysis for these compounds were consistently low by *ca.* 1%, despite the use of high combustion temperatures and combustion aids. This can be ascribed to carbide formation.[25] NMR spectra are deposited as ESI† as evidence of purity. Flash chromatography was performed with a FlashMaster Personal chromatography system and a selection of pre-packed disposable columns. Thin-layer chromatography was performed using Merck 0.25 mm silica layer foil-backed plates.

(3,5-Dimethylphenyl)pyridin-2-ylamine HL[1]. Toluene (30 mL) was added to a Schlenk vessel charged with 3,5-dimethylaniline (2.02 g, 16.67 mmol), 2-bromopyridine (2.08 g, 13.16 mmol), $[Pd_2(dba)_3]$ (204 mg, 0.22 mmol), dppp (204 mg, 0.49 mmol) and NaOBu^t (1.73 g, 18.00 mmol). The resulting deep red/brown mixture was heated overnight at 90 °C with stirring. After cooling to ambient temperature the solution was passed though silica and the silica was washed with diethyl ether (75 mL). The resultant red mixture was treated with activated charcoal overnight and passed through $MgSO_4$. The pale yellow solution was then concentrated *in vacuo*. The resulting white product was isolated by filtration and washed with cold pentane (yield 2.57 g, 78%).

^{1}H NMR (293 K, d_6-benzene) δ 2.17 (s, 6H, CH_3), 6.41 (t, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 6.61 (s, 1H, Ar–CH), 6.64 (d, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 6.67 (br s, 1H, NH), 6.92 (s, 2H, Ar–CH), 7.06 (t, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 8.31 (d, 1H Py–CH, $^3J_{HH} = 8$ Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 21.8 (Ar–CH_3), 108.8 (Py–CH), 115.0 (Py–CH), 118.9 (Ar–CH), 125.0 (Ar–CH), 137.7 (Py–CH), 139.1 (Ar–CCH_3), 149.2 (Py–CH), 151.5 (Ar–CN), 157.4 (Py–NCN).

IR (thin film, cm^{-1}) 3228, 3012, 2914, 1579, 1530, 1468, 1439, 1334, 1150, 989, 833, 767.

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.78; H, 7.12; N, 14.25.

MS (EI) *m*/*z* 197 (M$^+$)

(3,5-Di-tert-butylphenyl)pyridin-2-ylamine HL[2]. Toluene (30 mL) was added to a Schlenk vessel charged with 3,5-di-*tert*-butylaniline (2.0 g, 9.74 mmol), 2-bromopyridine (1.6 g, 10.13 mmol), $[Pd_2(dba)_3]$ (200 mg, 0.22 mmol), dppp (200 mg, 0.49 mmol) and NaOBu^t (1.3 g, 13.53 mmol). The resulting deep red/brown mixture was heated overnight at 90 °C with stirring. After cooling to ambient temperature the solution was passed though silica and the silica was washed with diethyl ether (75 mL). The resultant red mixture was stirred with activated charcoal overnight and passed through $MgSO_4$. The pale yellow solution was then concentrated *in vacuo*. The resulting yellow product was isolated by filtration and washed with cold pentane (yield 2.04 g, 74%).

^{1}H NMR (293 K, d_6-benzene) δ 1.34 (s, 18H, ^{t}Bu), 6.42 (m, 1H, Py–CH), 6.79 (d, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 7.09 (m, 1H, Py–CH), 7.30 (m, 3H, Ar–CH), 7.47 (br s, 1H, NH), 8.34 (m, 1H, Py–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 31.6 (^{t}Bu–CH_3), 35.0 (^{t}Bu–Cq), 107.8 (Py–CH), 114.5 (Py–CH), 116.0 (Ar–CH), 117.1 (Ar–CH), 137.4 (Py–CH), 140.8 (^{t}Bu Ar–Cq), 149.0 (Py–CH), 152.0 (Ar–CqN), 157.5 (NCqN).

IR (DCM layer, cm^{-1}) 2961 (NH), 1582, 1537, 1468, 1431, 1333, 1247, 1153, 995, 768, 712.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.93; H, 9.25; N, 9.89.

MS (EI) *m*/*z* 282 (M$^+$)

(2,4-Dimethylphenyl)(6-methylpyridin-2-yl)amine HL[3]. Toluene (50 mL) was added to a Schlenk vessel charged with 2,4-dimethylaniline (2.0 g, 17 mmol), 2-bromo-6-methylpyridine (3.0 g, 17.4 mmol), $[Pd_2(dba)_3]$ (200 mg, 0.22 mmol), dppp (200 mg, 0.48 mmol) and NaOBu^t (2.2 g, 22.9 mmol). The resulting deep red/brown mixture was heated overnight at 90 °C with stirring. After cooling to ambient temperature the solution was passed though silica and the silica was washed with diethyl ether (75 mL). The resultant red mixture was treated with activated charcoal and passed through $MgSO_4$. The pale yellow solution was then concentrated *in vacuo*. The resulting white crystalline product was isolated by filtration, washed with cold pentane and dried *in vacuo*. (yield 2.15 g, 61%).

^{1}H NMR (293 K, d_6-benzene): δ 2.02 (s, 3H, Ar–CH_3), 2.16 (s, 3H, Ar–CH_3), 2.39 (s, 3H, Py–CH_3), 6.32 (d, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 6.36 (d, 1H, Py–CH, $^3J_{HH} = 7$ Hz), 6.74 (s, 1H, NH), 6.88 (d + s, 2H, Ar–CH), 7.04 (t, 1H, Py–CH, $^3J_{HH} = 8$ Hz), 7.28 (d, 1H, Ar–CH, $^3J_{HH} = 8$ Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene): δ 18.2 (Ar–CH_3), 21.3 (Ar–CH_3), 24.8 (Py–CH_3), 104.2 (Py–CH), 113.8 (Py–CH), 125.2 (Ar–CH), 128.0 (Ar–CH), 132.3 (Ar–CH), 133.1 (Ar–Cq), 134.5 (Ar–Cq), 137.1 (Ar–Cq), 138.3 (Py–CH), 158.1 (Py–Cq).

IR (nujol, cm^{-1}): 3172 (NH), 2728, 1595, 1583, 1519, 1333, 1265, 1238, 1224, 1156, 1123, 1092, 1030, 992, 880, 802, 787, 723, 616.

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.28, H, 7.57, N, 12.81.

MS (EI) *m*/*z* 212 (100%, M$^+$), 197 (M$^+$ − CH_3).

(2-Isopropylphenyl)(6-methylpyridin-2-yl)amine HL[4]. Toluene (30 mL) was added to a Schlenk vessel charged with 2-isopropylaniline (2.25 g, 16.7 mmol), 2-bromo-6-methylpyridine (3.0 g, 17.4 mmol), $[Pd_2(dba)_3]$ (200 mg, 0.22 mmol), dppp (200 mg, 0.49 mmol) and NaOBu^t (2.25 g, 23.4 mmol). The resulting deep red/brown mixture was heated overnight at 90 °C with stirring. After cooling to ambient temperature the solution was passed though silica and the silica was washed with diethyl ether (75 mL). The resultant red mixture was treated with activated charcoal and passed through $MgSO_4$. The pale yellow solution was then concentrated *in vacuo*. The resulting white crystalline product was isolated by filtration and washed with cold pentane (yield 2.18 g, 58%).

^{1}H NMR (293 K, d_6-benzene) δ 1.04 (s, 3H, ^{i}Pr–CH_3), 1.06 (s, 3H, ^{i}Pr–CH_3), 2.40 (s, 3H, Py–CH_3), 3.08 (heptet, 1H, ^{i}Pr–CH, $^3J_{HH} = 7$ Hz), 7.02 (t, 1H, Py–H, $^3J_{HH} = 8$ Hz), 7.05–7.35 (m, 4H, Ar–CH), 7.15 (s, 1H, NH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 23.6 (^{i}Pr–CH_3), 24.7 (Py–CH_3), 28.5 (^{i}Pr–CH), 104.0 (Py–CH), 113.8 (Py–CH), 126.3 (Ar–CH), 126.7(Ar–CH), 126.9 (Ar–CH), 127.2 (Ar–CH), 138.4 (Py–CH), 144.5 (Ar–CqN), 158.0 (Py–CqN), 158.8 (Py–NCqN).

IR (nujol, cm^{-1}): 3188, 1591, 1520, 1487, 1338, 1280, 1262, 1235, 1158, 1087, 1033, 990, 780, 759, 723, 638.

Anal. Calcd. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.47; H, 7.98; N, 12.22.

MS (EI) *m*/*z* 226 (90%, M$^+$).

Pyridin-2-yl(2,4,6-trimethylphenyl)amine HL[5]. Toluene (30 mL) was added to a Schlenk vessel charged with 2,4,6-trimethylaniline (2.6 g, 19.0 mmol), 2-bromopyridine (3.0 g, 19.0 mmol), $[Pd_2(dba)_3]$ (200 mg, 0.11 mmol), dppp (200 mg, 0.25 mmol) and NaOBu^t (2.6 g, 26.5 mmol). The resulting deep red/brown mixture was heated overnight at 90 °C with stirring. After cooling to ambient temperature the solution was passed though silica and the silica was washed with diethyl ether (75 mL). The resultant red mixture was treated with activated charcoal and passed through $MgSO_4$. The pale yellow solution was then concentrated *in vacuo*. The resulting white crystalline product was isolated by filtration and washed with cold pentane (yield 2.00 g, 51%).

^{1}H NMR (293 K, d_6-benzene) δ 2.17 (s, 6H, Ar–CH_3), 2.20 (s, 3H, Ar–CH_3), 5.96 (d, 1H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.32 (t, 1H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.84 (s, 2H, Ar–H), 6.99 (t, 1H, Py–CH, $^3J_{HH}$ = 8 Hz), 7.48 (s, 1H, NH), 8.15 (d, 1H, Py–CH, $^3J_{HH}$ = 8 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 18.7 (Ar–CH_3), 21.4 (Ar–CH_3), 105.8 (Py–CH), 113.7 (Py–CH), 129.9 (Ar–CH), 135.3 (Ar–Cq), 136.5 (Ar–CN), 137.3 (Ar–Cq), 138.1 (Py–CH), 149.2 (Py–CH) 159.6 (Py–NCN).

IR (nujol, cm^{-1}): 3154, 3088, 1594, 1575, 1518, 1325, 1292, 1252, 1241, 1227, 1152, 1100, 1034, 1011, 993, 852, 819, 697, 614.

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.24; H, 7.58; N, 13.08.

MS (EI) *m*/*z* 212 (M^+), 197 ($M^+ - CH_3$).

(6-Methylpyridin-2-yl)(2,4,6-trimethylphenyl)amine HL^6. Toluene (30 mL) was added to a Schlenk vessel charged with 2,4,6-trimethylaniline (1.0 g, 7.5 mmol), 2-bromo-6-methylpyridine (1.0 g, 5.9 mmol), [Pd_2(dba)$_3$] (101 mg, 0.11 mmol), dppp (102 mg, 0.25 mmol) and NaOBu^t (0.85 g, 8.9 mmol). The resulting deep red/brown mixture was heated overnight at 100 °C with stirring. After cooling to ambient temperature diethyl ether (50 mL) was added. The resultant dark red mixture was washed with brine (2 × 30 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting white product was precipitated by trituration with *n*-hexane from the initial yellow oil (yield 0.78 g, 59%).

^{1}H NMR (293 K, d_6-benzene) δ 2.18 (s, 6H, Ar–CH_3), 2.30 (s, 3H, Ar–CH_3), 2.40 (s, 3H, Py–CH_3), 5.75 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.05 (s, 1H, NH), 6.47 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.94 (s, 2H, Ar–CH), 7.23 (t, 1H, Py–CH, $^3J_{HH}$ = 8 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 18.7 (Ar–CH_3), 21.3 (Ar–CH_3), 24.7 (Ar–CH_3), 102.6 (Py–CH), 113.3 (Py–CH), 129.6 (Ar–CH), 134.3 (Ar–Cq), 136.7 (Ar–CqN), 137.1 (Ar–Cq), 138.5 (Py–CH), 157.6 (Py–Cq), 158.0 (Py–NCqN).

IR (nujol, cm^{-1}): 3189, 2728, 1594, 1582, 1515, 1456, 1377, 1335, 1261, 1234, 1154, 1092, 1033, 990, 860, 820, 788, 722, 621.

Anal. Calcd. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.55; H, 8.01; N, 12.40.

MS (EI) *m*/*z* 226 (100%, M^+), 211 ($M^+ - CH_3$).

[Zr$\mathbf{L^1}_4$]. Pentane (20 mL) was added to a Schlenk vessel charged with H**L^1** (250 mg, 1.27 mmol) and [Zr(CH$_2$^{t}Bu)$_4$] (120 mg, 0.32 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solution was then filtered and concentrated under reduced pressure. Upon cooling to −4 °C a yellow precipitate was obtained (yield 608 mg, 56%).

^{1}H NMR (293 K, d_6-benzene) δ 2.24 (s, 24H, Ar–CH_3), 5.93 (t, 4H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.38 (d, 4H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.51 (s, 8H, Ar–CH), 6.72 (s, 4H, Ar–CH), 6.83 (t, 4H, Py–CH, $^3J_{HH}$ = 8 Hz), 7.08 (d, 4H, Py–CH, $^3J_{HH}$ = 8 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 21.8 (Ar–CH_3), 106.5 (Py–CH), 109.0 (Py–CH), 123.2 (Ar–CH), 125.2 (Ar–CH), 138.7 (Ar–CCH_3), 139.4 (Py–CH), 143.5 (Py–CH), 149.2 (Ar–CN), 171.1 (Py–NCN).

Anal. Calcd. for $C_{52}H_{52}N_8Zr$: C, 70.95; H, 5.95; N, 12.73. Found: C, 69.87; H, 5.90; N, 12.19.

MS (EI) *m*/*z* 878 (M^+)

[Zr$\mathbf{L^2}_4$]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L^2** (500 mg, 1.77 mmol) and [Zr(CH$_2$^{t}Bu)$_4$] (170 mg, 0.45 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solution was then filtered and the solvent removed under reduced pressure. The resulting yellow solid was then redissolved in a minimum of diethyl ether. Upon cooling to −4 °C a yellow crystalline product was obtained (yield 1.13 g, 52%).

^{1}H NMR (293 K, d_6-benzene) δ 1.32 (s, 72H, ^{t}Bu–CH_3), 5.97 (br s, 4H, Py–CH), 6.35 (d, 4H, Py–CH, $^3J_{HH}$ = 9 Hz), 6.70 (br m, 8H, Ar–CH), 6.91 (br m, 4H, Py–CH), 7.09 (br m, 4H, Py–CH), 7.33 (s, 4H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 31.9 (^{t}Bu–CH_3), 35.0 (^{t}Bu–Cq), 105.7 (Py–CH), 115.7 (Ar–CH), 117.4 (Ar–CH), 119.9 (Py–CH), 139.1 (Py–CH), 143.5 (Py–CH), 148.6 (Ar–CqN), 151.6 (NCqN).

^{1}H NMR (343 K, d_6-benzene) δ 1.32 (s, 72H, ^{t}Bu–CH_3), 5.95 (br t, 4H, Py–CH, $^3J_{HH}$ = 6 Hz), 6.28 (d, 4H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.73 (s, 8H, Ar–CH), 6.94 (br t, 4H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.14 (br d, 4H, Py–CH, $^3J_{HH}$ = 4 Hz), 7.29 (s, 4H, Ar–CH).

Anal. Calcd. for $C_{76}H_{100}N_8Zr$: C, 75.01; H, 8.28; N, 9.21. Found: C, 74.06; H, 8.30; N, 8.81.

MS (EI) *m*/*z* 1215 (M^+)

[Zr$\mathbf{L^3}_2$(NMe$_2$)$_2$]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L^3** (250 mg, 1.2 mmol) and [Zr(NMe$_2$)$_4$] (158 mg, 0.6 mmol). The reaction mixture was stirred for 1 h at ambient temperature under argon. The solvent was removed *in vacuo* to give a yellow solid. The solid was then dissolved in pentane (10 mL) and the solution was filtered. After cooling to −30 °C overnight a yellow crystalline product was isolated by filtration (yield 168 mg, 56%).

^{1}H NMR (293 K, d_6-benzene) δ 2.32 (s, 6H, Py–CH_3), 2.39 (s, 6H, Ar–CH_3), 2.45 (s, 6H, Ar–CH_3), 3.15 (s, 12H, NMe), 5.96 (m (d + d), 4H, Py–CH), 6.94 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.12–7.30 (m, 6H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 17.1 (Py–CH_3), 19.6 (Ar–CH_3), 21.2 (Ar–CH_3), 41.3 (NMe), 101.7 (Py–CH), 107.4 (Py–CH), 124.5 (Ar–CH), 126.2 (Ar–CH), 130.7 (Ar–CH), 131.5 (Ar–C), 131.9 (Ar–C). 138.7 (Py–CH), 143.3 (Ar–Cq–N), 152.8 (Py–NCqN), 166.9 (pyridine-Cq–CH_3).

MS (EI) *m*/*z* 600 (100%, M^+), 556 ($M^+ - NMe_2$), 512 ($M^+ - 2NMe_2$), 301 (Zr**L^3**).

Anal. Calcd. for $C_{32}H_{42}N_6Zr$: C, 63.85; H, 7.03; N, 13.96. Found: C, 62.93; H, 6.91; N, 13.72.

[Zr$\mathbf{L^3}_2$(CH$_2$Ph)$_2$]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L^3** (300 mg, 1.4 mmol) and [Zr(CH$_2$Ph)$_4$] (322 mg, 0.86 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure. The resulting yellow solid was redissolved in pentane and the solution filtered and concentrated under reduced pressure. Upon cooling to −4 °C a yellow crystalline product was obtained (yield 379 mg, 71%).

^{1}H NMR (293 K, d_6-benzene) δ 1.85 (s, 6H, Ar–CH_3), 2.08 (s, 6H, Py–CH_3), 2.19 (s, 6H, Ar–CH_3), 2.50 (br s, 4H, Bn–CH_2), 5.52 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.96 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.31 (d, 2H, Ar–CH, $^3J_{HH}$ = 8 Hz), 6.87–6.82 (m, 8H, Ar–CH + Py–CH), 7.05 (d, 4H, Bn–CH, $^3J_{HH}$ = 7 Hz), 7.16 (t, 4H, Bn–CH, $^3J_{HH}$ = 7 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 18.0 (Ar–CH_3), 21.1 (Ar–CH_3), 24.6 (Py–CH_3), 104.0 (Py–CH), 113.7 (Py–CH), 124.9 (Ar–CH), 127.8 (Ar–CH), 132.1 (Ar–CH), 132.8 (Ar–Cq), 134.3 (Ar–Cq), 137.0 (Ar–CqN), 138.1 (Py–CH), 157.9 (Py–CqN).

^{1}H NMR (333 K, d_6-benzene) δ 1.86 (s, 6H, Ar–CH_3), 2.13 (s, 6H, Py–CH_3), 2.19 (s, 6H, Ar–CH_3), 2.53 (s, 4H, Bn–CH_2), 5.51 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.99 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.33 (d, 2H, Ar–CH, $^3J_{HH}$ = 6 Hz), (m (s + d + t), 6H, Ar–CH (s + d), Bn–CH (t)), 6.86 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.01 (d, 4H, Bn–CH, $^3J_{HH}$ = 6 Hz), 7.12 (t, 4H, Bn–CH, $^3J_{HH}$ = 6 Hz).

^{13}C{^{1}H} NMR (333 K d_6-benzene) δ 18.6 (Ar–CH_3), 21.5 (Ar–CH_3), 23.1 (Py–CH_3), 75.9 (Bn–CH_2), 103.8 (Py–CH), 111.7 (Py–CH), 122.7 (Bn–CH), 127.0 (Ar–CH), 128.3 (Bn–CH), 130.0 (Bn–CH), 132.2 (Ar–CH), 134.0 (Ar–Cq), 134.5 (Ar–Cq), 141.2 (Bn–Cq), 142.0 (Py–CH), 144.6 (Ar–CqN), 154.9 (Py–CqN), 170.0 (Py–NCqN).

Anal. Calcd. for $C_{42}H_{44}N_4Zr$: C, 72.47; H, 6.37; N, 8.05. Found: C, 71.55, H, 6.46, N, 7.87.

MS (EI) *m*/*z* 605 ($M^+ - CH_2Ph$), 514 ($M^+ - 2 \times CH_2Ph$), 303 (Zr**L^3**).

[Zr$\mathbf{L^3}_2$(CH$_2$^{t}Bu)$_2$]. Pentane (20 mL) was added to a Schlenk vessel charged with H**L^3** (300 mg, 1.4 mmol) and [Zr(CH$_2$^{t}Bu)$_4$] (266 mg, 0.7 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The

yellow solution was filtered and concentrated under reduced pressure to 15 mL. Upon cooling to −4 °C a yellow crystalline product was obtained (yield 298 mg, 64%).

^{1}H NMR (293 K, d_6-benzene) δ 1.20 (s, 18H, Np–^{t}Bu), 1.75 (br s, 4H, Np–CH_2), 2.21 (s, 6H, Ar–CH_3), 2.27 (br s, Ar–CH_3), 2.43 (br s, 6H, Py–CH_3), 5.62 (d, Py–CH, $^3J_{HH}$ = 4 Hz), 5.95 (d, 2H, Py–CH, $^3J_{HH}$ = 4 Hz), 6.80 (t + br m, 6H, Py–CH + Ar–CH), 7.05 (br m, 2H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 19.3 (Ar–CH_3), 21.4 (Ar–CH_3), 23.2 (Py–CH_3), 35.3 (Np–^{t}Bu), 82.0 (Np–CH_2), 103.2 (Py–CH), 111.6 (Py–CH), 142.1 (Py–CH).

^{1}H NMR (343 K, d_6-benzene) δ 1.15 (s, 18H, Np–^{t}Bu), 1.73 (s, 4H, Np–CH_2), 2.22 (s, 6H, Ar–CH_3), 2.26 (s, 6H, Ar–CH_3), 2.43 (br s, 6H, Py–CH_3), 5.61 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.99 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.79 (br d + s, 4H, Ar–CH), 6.85 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.06 (br d, 2H, Ar–CH, $^3J_{HH}$ = 6 Hz).

^{13}C{^{1}H} NMR (343 K d_6-benzene) δ 18.9 (Ar–CH_3), 20.9 (Ar–CH_3), 22.8 (Py–CH_3), 35.0 (Np–^{t}Bu), 103.1 (Py–CH), 111.2 (Py–CH), 127.0 (Ar–CH), 127.7 (Ar–CH), 131.7 (Ar–CH), 133.3 (Ar–Cq), 133.9 (Ar–Cq), 141.5 (Py–CH), 143.9 (Ar–CqN), 153.8 (Py–CqN), 169.2 (Py–NCqN).

Anal. Calcd. for $C_{38}H_{52}N_4Zr$: C, 69.57; H, 7.99; N, 8.54. Found: C, 68.71; H, 7.75; N, 8.64.

MS (EI) *m*/*z* 583 ($M^+ - CH_2{}^t$Bu), 512 ($M^+ - 2 \times CH_2{}^t$Bu), 301 (Zr**L**^{3}).

[ZrL$^4_2$(NMe$_2$)$_2$]. Toluene (50 mL) was added to a Schlenk vessel charged with H**L**^{4} (250 mg, 1.1 mmol) and [Zr(NMe_2)$_4$] (148 mg, 0.55 mmol). The reaction mixture was stirred for 2 d at ambient temperature under argon. The solvent was removed under reduced pressure to give a yellow solid. The solid was then dissolved in pentane (10 mL) and then filtered. Upon cooling to −4 °C a yellow crystalline product was obtained (yield 236 mg, 68%).

^{1}H NMR (293 K, d_6-benzene) δ 0.99–1.02 (m (d + d), 6H, ^{i}Pr–CH_3), 1.10–1.12 (m (d + d), 6H, ^{i}Pr–CH_3), 1.94 (s, 3H, Py–CH_3), 1.98 (s, 3H, Py–CH_3), 2.68 (s, 3H, NMe), 2.82 (s, 6H, NMe), 2.94 (s, 3H, NMe), 3.40 (m, 2H, ^{i}Pr–CH), 5.64 (m (d + d), 4H, Py–CH), 6.49–7.22 (m, 8H, Ar–CH), 6.61 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 20.8 (Py–CH_3), 21.2 (Py–CH_3), 21.8 (^{i}Pr–CH_3), 22.6 (^{i}Pr–CH_3), 23.4 (^{i}Pr–CH_3), 23.8 (^{i}Pr–CH_3), 26.3 (^{i}Pr–CH), 39.5 (NMe), 41.2 (NMe), 42.7 (NMe), 101.5 (Py–CH), 102.1 (Py–CH), 107.0 (Py–CH), 107.4 (Py–CH), 123.4 (Ar–CH), 124.6 (Ar–CH), 124.8 (Ar–CH), 125.1 (Ar–CH), 125.3 (Ar–CH), 138.9 (Py–CH), 143.5 (Ar–Cq–^{i}Pr), 144.7 (Ar–CqN), 152.7 (Py–Cq–CH_3), 167.9 (Py–NCqN).

Anal. Calcd. for $C_{34}H_{46}N_6$: C, 64.82; H, 7.36; N, 13.34. Found: C, 63.11; H, 7.15; N, 13.38.

MS (EI) *m*/*z* 628 (M^+), 584 ($M^+ - NMe_2$), 540 ($M^+ - 2\ NMe_2$).

[ZrL$^4_2$(CH$_2$Ph)$_2$]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L**^{4} (200 mg, 0.88 mmol) and [Zr(CH_2Ph)$_4$] (205 mg, 0.45 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure to give a yellow solid. The solid was then dissolved in pentane (10 mL) and the solution filtered. The solvent was then removed under reduced pressure (yield 392 mg, 61%).

^{1}H NMR (343 K, d_6-benzene) δ 0.99 (s, 6H, ^{i}Pr–CH_3), 1.00 (s, 6H, ^{i}Pr–CH_3), 2.04 (s, 6H, Py–CH_3), 2.34 (br s, 4H, Bn–CH_2), 3.04 (sept, 2H, ^{i}Pr–CH), 5.55 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.99 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.31 (d, 2H, Ar–CH, $^3J_{HH}$ = 6 Hz), 6.85 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.86 (br s, 2H, Bn–CH), 7.04 (br s, 4H, Bn–CH), 7.07 (m, 4H, Ar–CH), 7.04–7.10 (br t, 4H, Bn–CH), 7.27 (d, 2H, Ar–CH, $^3J_{HH}$ = 6 Hz).

^{13}C{^{1}H} NMR (343 K d_6-benzene) δ 22.5 (Py–CH_3), 27.8 (^{i}Pr–CH), 103.8 (Py–CH), 111.4 (Py–CH), 125.6 (Ar–CH), 126.4 (Ar–CH), 126.6 (Bn–CH), 127.1 (Bn–CH), 129.7 (Bn–CH), 141.2 (Py–CH), 145.0 (Ar–Cq), 146.1 (Ar–NCq), 154.8 (Py–C).

Anal. Calcd. for $C_{44}H_{48}N_4Zr$: C, 72.98; H, 6.68; N, 7.74. Found: C, 71.84; H, 6.52; N, 7.76.

MS (EI) *m*/*z* 647 ($M^+ - Ph$).

[ZrL$^4_2$(CH$_2{}^t$Bu)$_2$]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L**^{4} (200 mg, 0.88 mmol) and [Zr($CH_2{}^t$Bu)$_4$] (166 mg, 0.44 mmol). The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure to give a yellow solid. The solid was then dissolved in pentane (10 mL) and the solution filtered. The solvent was then removed under reduced pressure to give a yellow solid (yield 295 mg, 49%).

^{1}H NMR (343 K, d_6-benzene) δ 1.08 (s, 18H, Np–^{t}Bu), 1.29 (br s, 6H, ^{i}Pr–CH_3), 1.78 (s, 4H, Np–CH_2), 2.27 (br s, 6H, Py–CH_3), 3.77 (br sept, 2H, ^{i}Pr–CH), 5.74 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.93 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.85 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.13–7.17 (m, 6H, Ar–CH), 7.36–7.38 (m, 2H, Ar–CH).

^{13}C{^{1}H} NMR (343 K d_6-benzene) δ 22.6 (Py–CH_3), 27.9 (^{i}Pr–CH_3), 35.0 (Np–^{t}Bu), 103.8 (Py–CH), 110.8 (Py–CH), 125.7 (Ar–CH), 127.0 (Ar–CH), 127.2 (Ar–CH), 141.5 (Py–CH), 145.0 (Ar–CqN), 153.9 (Py–Cq), 170.6 (Py–NCqN).

Anal. Calcd. for $C_{40}H_{56}N_4Zr$: C, 70.23; H, 8.25; N, 8.19. Found: C, 69.85; H, 8.05; N, 7.61.

MS (EI) *m*/*z* 613 ($M^+ - CH_2{}^t$Bu), 542 ($M^+ - 2 \times CH_2{}^t$Bu), 317 (Zr**L**^{4}).

[ZrL$^5_3$(NMe$_2$)]. Diethyl ether (30 mL) was added to a Schlenk vessel charged with H**L**^{5} (250 mg, 1.16 mmol) and [Zr(NMe_2)$_4$] (155 mg, 0.58 mmol). The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure to give a yellow solid. The yellow solid was then redissolved in a minimum of diethyl ether and cooled to give a white crystalline product, which was isolated by filtration and identified by ^{1}H NMR to be unreacted proligand. The remaining yellow solution was then concentrated to precipitate a yellow crystalline product (yield 106 mg, 35%).

^{1}H NMR (293 K, d_6-benzene) δ 1.80 (s, 6H, Ar–CH_3), 1.89 (s, 6H, Ar–CH_3), 2.23 (s, 6H, Ar–CH_3), 2.25 (s, 3H, Ar–CH_3), 2.27 (s, 6H, Ar–CH_3), 3.26 (s, 6H, NMe_2), 5.64 (d, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 5.82 (d, 1H, Py–CH, $^3J_{HH}$ = 8 Hz), 5.84 (t, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.15 (t, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.57 (s, 2H, Ar–CH), 6.47 (s, 2H, Ar–CH), 6.76 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.89 (s, 2H, Ar–CH), 6.93 (t, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.25 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 7.90 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 15.0 (Ar–CH_3), 18.3 (Ar–CH_3), 19.3 (Ar–CH_3), 19.4 (Ar–CH_3), 21.4 (Ar–CH_3), 25.4 (Ar–CH_3), 46.1 (NMe_2), 90.4 (Ar–CH), 106.6 (Py–CH), 106.9 (Py–CH), 107.7 (Py–CH), 108.0 (Py–CH), 108.7 (Py–CH), 129.0 (Ar–CH), 129.8 (Ar–CH), 139.9 (Py–CH), 141.0 (Py–CH), 142.8 (Py–CH), 143.3 (Py–CH), 164.6 (Py–NCN).

Anal. Calcd. for $C_{44}H_{51}N_7Zr$: C, 68.71; H, 6.68; N, 12.75. Found: C, 66.37; H, 7.06; N, 12.47.

MS (EI) *m*/*z* 767 (M^+), 723 ($M^+ - NMe_2$), 512 (Zr**L**$^2_2$), 301 (Zr**L**^{5}).

[ZrL$^5_3$(CH$_2$Ph)]. Toluene (20 mL) was added to a Schlenk vessel charged with H**L**^{5} (250 mg, 1.16 mmol) and [Zr(CH_2Ph)$_4$] (267 mg, 0.98 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure to give a yellow solid. The yellow solid was then redissolved in pentane (20 mL), filtered and cooled to −4 °C. The yellow crystalline product obtained was then isolated by filtration (yield 118 mg, 36%).

^{1}H NMR (293 K, d_2-dichloromethane) δ 1.41 (s, 6H, Ar–CH_3), 1.52 (s, 6H, Ar–CH_3), 2.16 (s, 12H, Ar–CH_3), 2.22 (s, 3H, Ar–CH_3), 2.83 (s, 2H, Bn–CH_2), 5.60 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.69 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.27–6.30 (m, 3H, Py–CH), 6.32 (s, 2H, Ar–CH), 6.48 (s, 2H, Ar–CH), 6.53 (br d, 1H, Py–CH), 6.68 (d, 2H, Bn–CH, $^3J_{HH}$ = 7 Hz), 6.71 (s, 2H, Ar–CH), 6.78 (t, 1H, Bn–CH, $^3J_{HH}$ = 7 Hz), 7.09 (t, 2H, Bn–CH, $^3J_{HH}$ = 7 Hz), 7.28–7.33 (m, 5H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_2-dichloromethane) δ 16.2 (Ar–CH_3), 17.7 (Ar–CH_3), 18.6 (Ar–CH_3), 19.7 (Ar–CH_3), 64.4 (Bn–CH_2), 104.7 (Py–CH), 105.0 (Py–CH), 108.5 (Bn–CH), 108.7 (Bn–CH), 118.3 (Bn–CH), 124.7 (Bn–CH), 126.9 (Ar–CH), 127.2 (Ar–CH), 127.9

(Ar–CH), 139.2 (Py–CH), 140.1 (Py–CH), 141.9 (Py–CH), 142.9 (Py–CH), 151.3 (Ar–CqN), 167.5 (Py–NCqN), 171.0 (Py–NCqN).

Anal. Calcd. for ($C_{49}H_{52}N_6Zr$): C, 72.11; H, 6.42; N, 10.30. Found: C, 71.47; H, 6.38; 10.14.

MS (EI) *m*/*z* 422 ($M^+ - \mathbf{L}^5_2$), 331 ($Zr\mathbf{L}^5$).

[$ZrL^5_2(CH_2{}^tBu)_2$]. Toluene (30 mL) was added to a Schlenk vessel charged with H$\mathbf{L}^5$ (250 mg, 1.16 mmol) and [$Zr(CH_2{}^tBu)_4$] (222 mg, 0.98 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure to give a yellow solid. The yellow solid was then redissolved in a minimum of pentane and cooled to give a yellow precipitate which was isolated by filtration (yield 230 mg, 69%).

^{1}H NMR (293 K, d_6-benzene) δ 1.25 (s, 18H, Np–^{t}Bu), 1.88 (s, 4H, Np–CH_2), 2.22 (s, 6H, Ar–CH_3), 2.24 (s, 12H, Ar–CH_3), 5.54 (d, 2H, Py–CH, $^3J_{HH}$ = 6 Hz), 6.01 (t, 2H, Py–CH, $^3J_{HH}$ = 6 Hz), 6.62 (s, 4H, Ar–CH), 6.76 (t, 2H, Py–CH, $^3J_{HH}$ = 6 Hz), 7.96 (d, 2H, Py–CH, $^3J_{HH}$ = 6 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 20.1 (Ar–CH_3), 21.4 (Ar–CH_3), 35.3 (Np–^{t}Bu), 94.0 (Np–CH_2), 106.0 (Py–CH), 110.2 (Py–CH), 129.5 (Ar–CH), 142.0 (Py–CH), 144.9 (Py–CH), 169.5 (Py–NCqN).

Anal. Calcd. for ($ZrC_{38}H_{52}N_4$): C, 69.57; H, 7.99; N, 8.54. Found: C, 68.73; H, 7.83; N, 8.42.

MS (EI) *m*/*z* 583 ($M^+ - CH_2{}^tBu$).

[$ZrL^6_2(NMe_2)_2$]. Toluene (50 mL) was added to a Schlenk vessel charged with H$\mathbf{L}^6$ (200 mg, 0.89 mmol) and [$Zr(NMe_2)_4$] (119 mg, 0.44 mmol). The reaction mixture was stirred for 30 min at ambient temperature under argon. The solution was concentrated under reduced pressure to give a yellow crystalline solid isolated by filtration (yield 413 mg, 74%).

^{1}H NMR (293 K, d_6-benzene) δ 2.07 (s, 12H, Ar–CH_3), 2.18 (s, 6H, Py–CH_3), 2.26 (s, 6H, Ar–CH_3), 2.92 (s, 12H, NMe_2), 5.59 (d, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.86 (d, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.79 (t, 2H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.93 (s, 4H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 18.4 (Ar–CH_3), 21.4 (Ar–CH_3), 22.5 (Py–CH_3), 42.4 (4C, NMe_2), 103.6 (Py–CH), 108.2 (Py–CH), 133.3 (Ar–CH), 134.6 (Ar–CH), 141.0 (Py–CH), 154.3 (Py–$CqCH_3$), 168.8 (Py–CqN).

Anal. Calcd. for $C_{34}H_{46}N_6Zr$: C, 64.82; H, 7.36; N, 13.34. Found: C, 63.50; H, 7.19; N, 13.17.

MS (CI) *m*/*z* 630 (100%, M^+), 585 ($M - NMe_2$).

[$ZrL^6_2(CH_2Ph)_2$]. Toluene (20 mL) was added to a Schlenk vessel charged with H$\mathbf{L}^6$ (250 mg, 1.1 mmol) and [$Zr(CH_2Ph)_4$] (251 mg, 0.55 mmol). The reaction mixture was stirred for 1 h at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure to give a yellow solid. The solid was then washed in pentane (10 mL) and recrystallised from diethyl ether (yield 227 mg, 65%).

^{1}H NMR (293 K, d_6-benzene) δ 1.85 (s, 12H, Ar–CH_3), 2.18 (s, 6H, Ar–CH_3), 2.35 (s, 6H, Py–CH_3), 2.89 (s, 4H, Bn–CH_2), 5.40 (d, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.01 (d, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.46 (s, 4H, Ar–CH), 6.80 (t, 2H, Py–CH, $^3J_{HH}$ = 8 Hz), 6.85 (m, 2H, Bn–CH), 6.88 (d, 4H, Bn–CH, $^3J_{HH}$ = 7 Hz), 7.10 (t, 4H, Bn–CH, $^3J_{HH}$ = 7 Hz).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 19.4 (Ar–CH_3), 21.4 (Ar–CH_3), 23.1 (Py–CH_3), 72.1 (Bn–CH_2), 102.8 (Py–CH), 111.9 (Py–CH), 121.9 (Bn–CH), 122.0 (Bn–Cq), 127.2 (Ar–Cq), 128.1 (Bn–CH), 128.8 (Ar–CH), 128.8 (Bn–CH), 129.7, (Ar–CqN), 133.6 (Ar–Cq), 142.4 (Py–CH), 148.7 (Py–Cq–CH_3), 161.2 (Py–NCqN).

Anal. Calcd. for $C_{44}H_{48}N_4Zr$: C, 72.98; H, 6.68; N, 7.74. Found: C, 71.91; H, 6.60; N, 7.63.

MS (EI) *m*/*z* 633 (50%, $M^+ - CH_2Ph$), 542 (100%, $M^+ - 2 \times CH_2Ph$).

[$ZrL^6(CH_2{}^tBu)_3$]. Toluene (20 mL) was added to a Schlenk vessel charged with H$\mathbf{L}^6$ (250 mg, 1.1 mmol) and [$Zr(CH_2{}^tBu)_4$] (208 mg, 0.54 mmol). The reaction mixture was stirred overnight at ambient temperature, under argon and in the absence of light. The solvent was removed under reduced pressure to give a yellow solid. The solid was dissolved in a minimum of pentane and cooled overnight. The resulting white solid was isolated by filtration and was found to be unreacted proligand. The yellow pentane solution was reduced to dryness under reduced pressure to give a thick yellow oil and determined to be [$Zr\mathbf{L}^1(CH_2{}^tBu)_3$] *via* ^{1}H NMR.

^{1}H NMR (293 K, d_6-benzene) δ 1.22 (s, 27H, Np–^{t}Bu), 1.63 (s, 6H, Np–CH_2), 2.23 (s, 3H, Py–CH_3), 2.24 (s, 3H, Ar–CH_3), 2.42 (s, 6H, Ar–CH_3), 5.45 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 5.86 (d, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.76 (t, 1H, Py–CH, $^3J_{HH}$ = 7 Hz), 6.94 (s, 2H, Ar–CH).

^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 19.8 (Ar–CH_3), 21.3 (Py–CH_3), 23.4 (Ar–CH_3), 35.2 (Np–^{t}Bu), 36.6 (Np–Cq), 83.7 (Np–CH_2), 102.5 (Py–CH), 111.1 (Py–CH), 130.1 (Ar–CH), 133.9 (Ar–Cq), 134.7 (Ar–Cq), 142.9 (Py–CH), 144.0 (Ar–CqN), 154.5 (Py–Cq), 169.2 (Py–NCqN).

Crystallography

Crystals were coated in an inert oil prior to transfer to a cold nitrogen gas stream on a Bruker-AXS SMART three circle CCD area detector diffractometer system equipped with Mo Kα radiation (λ = 0.71073 Å). Data were collected using narrow (0.3° in ω) frame exposures. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). Structures were solved by direct methods (SHELXS) or by the location of heavy atom sites by Patterson interpretation of ΔF-data with additional light atoms found by Fourier methods. All non-hydrogen atoms were refined anisotropically. All H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs used were Bruker AXS SMART (control), SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.

CCDC reference numbers 238254–238259.

See http://www.rsc.org/suppdata/dt/b4/b407008a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

PS thanks the University of Warwick for a studentship (to EJC) and EPSRC for support.

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