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Chiral metal architectures in aminopyridinato complexes of zirconium†

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Optically pure 2-alkylaminopyridines (HL) are synthesised readily from bromopyridines and chiral amines [(*S*)-1,2,3,4-tetrahydro-1-naphthylamine and (*S*)-(−)-α-methylbenzylamine] using palladium-catalysed amination. Protonolysis reactions of these proligands with ZrX_4 (X = NMe_2, CH_2Ph, CH_2Bu^t) yield zirconium aminopyridinates, usually of the type $[ML_2X_2]$, some of which have been characterised by X-ray crystallography. Control of absolute configuration at the metal centre is pursued by investigation of the effects of chiral amine substituent, substitution at the pyridine rings and the identity of co-ligands. Surprisingly the conformationally flexible α-methylbenzyl based aminopyridinato ligands promote much better control of chirality-at-zirconium than do the cyclic tetrahydronaphthyl analogues. One complex of the former class displays complete control of stereochemistry at 193 K; only one diastereomer out of eight possible structures is observed. It is found that there is an excellent correlation between observed selectivities and calculated diastereomer energy differences from DFT. All the complexes studied are in dynamic exchange between diastereomers. The rate of these processes ($\Delta H^{\ddagger}$ *ca.* 40 kJ mol^{-1}) as studied by Selective Polarisation Transfer–Selective Inversion Recovery experiments (SPT-SIR) and lineshape analyses are significantly faster than those for aminopyridines containing bulkier amido substituents ($\Delta H^{\ddagger}$ *ca.* 70 kJ mol^{-1}). This type of dependence on steric effects, and the impact of the *trans* effect, is consistent with an *N*-dissociative mechanism, *i.e.* conversion from six- to five-coordinate structure followed by rapid intramolecular scrambling.

Introduction

When a metal coordination sphere includes one or more chiral non-racemic ligands, the metal center may itself become stereogenic as a result of diastereoselective interactions.[1,2] While the concept of chirality-at-metal has been of interest for some time,[3] the realisation that such chiral metal centers are present in many enantioselective catalyses[4] is promoting more intense study of methods by which the absolute stereochemistry at the metal may be predetermined.[1] Studies in this area are complicated by the great structural variety possible in organometallic and coordination compounds and also the range in kinetic stabilities of coordination environments. Accordingly, most studies on chiral metal complexes have involved later transition elements where the rates of topographical exchange are generally slow enough to be studied on convenient experimental timescales. For the early transition metals and f elements, where the rates of exchange are greater, very high levels of thermodynamic discrimination are needed in order to make systems that are of practical value.

The real challenge, for systems containing any type of metal, is to produce complexes in which not only is the metal stereochemistry selected efficiently, but also by virtue of the presence of one or more labile ligand sites is the complex suitable for catalytic applications. Traditionally, this has been achieved through the use of multidentate ligands, although the design and synthesis of such coordination environments presents different synthetic challenges.[5] Bidentate ligands are more readily available and more diverse in nature than multidentate systems. If the aim is to produce chiral metal catalysts then, for example Group 4 metals, this points us toward octahedral complexes of the type $[M(AB)_2X_2]$, where AB is a chiral bidentate monoanionic ligand. While this class of complex can in principle form eight diastereomers (*e.g.* Fig. 1), we have recently shown that it is quite possible to design highly diastereoselective systems.[6] In this contribution we describe our studies toward the control stereochemistry at zirconium using the system AB = aminopyridinato.[7] This work is informed by our recent studies on methods by which structure can be controlled in achiral aminopyridinate systems.[8,9] While we do not necessarily expect this ligand type to be of great use in applications to *e.g.* enantioselective catalysis, it has the advantage that a wide range of analogues can be made rapidly and the effects on structure and selectivity studied by standard techniques.

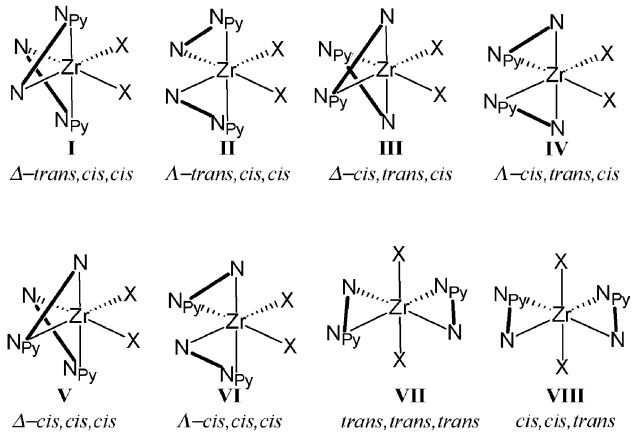

Fig. 1 Six-coordinate isomers of the compounds [Zr(aminopyridinate)$_2$X$_2$] (N = amido ligand atom). The stereochemical descriptors are based on the CIP priority sequence N_{Py} > N > X, which is true for X = alkyl.

Results and discussion

The aminopyridines HL[1–4] were synthesised from the corresponding bromopyridine and commercially available chiral non-racemic amines *via* palladium catalysed amine arylation

† Electronic supplementary information (ESI) available: Details of NOESY and SPT-SIR NMR spectra, rotatable structure files for X-ray and DFT output. See http://www.rsc.org/suppdata/dt/b4/b413023e/

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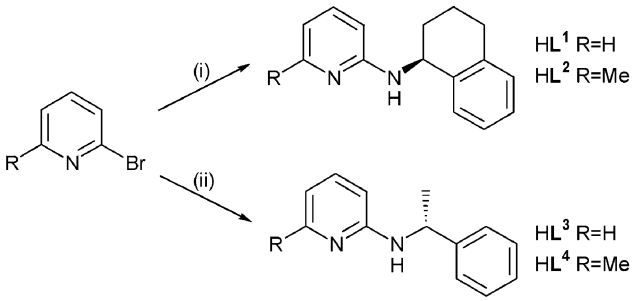
(Scheme 1).[10] HL^1 was recrystallised from pentane to give a pale yellow solid. Proligands HL^{2-4} were isolated from the crude reaction mixtures *via* distillation under reduced pressure. Upon cooling HL^2 gave a colourless crystalline solid whereas $HL^{3,4}$ gave colourless oils. Our expectation was that the cyclic structure present in L^1 and L^2 would provide for more efficient control of stereochemistry at metal than would L^3 and L^4, although the opposite was eventually shown to be the case.



Scheme 1 Synthesis of aminopyridines [conditions; toluene, 90 °C, 24 h]; (i) (*S*)-1,2,3,4-tetrahydro-1-naphthylamine, cat. binap/$[Pd_2(dba)_3]$, 30–50%; (ii) (*S*)-(−)-α-methylbenzylamine, cat. dppp/$[Pd_2(dba)_3]$, *ca.* 70%.

Zirconium complexes of $L^{1,2}$

The proligand HL^1 was treated with $[Zr(NMe_2)_4]$, $[Zr(CH_2Ph)_4]$ and $[Zr(CH_2Bu^t)_4]$ in various metal/ligand ratios. Each reaction gave very soluble yellow solids for which ^{1}H NMR spectra showed many products. We have previously shown that the presence of a 2-methyl group at the pyridine ring can have a profound effect on the chemistry of such ligands,[8] and correspondingly treatment of $[Zr(NMe_2)_4]$ with two equivalents of HL^2 yielded the complex $[ZrL^2_2(NMe_2)_2]$. The ^{1}H spectrum of this compound in C_6D_6 at 298 K showed a single set of ligand resonances. The pyridine methyl group appeared as a singlet at 2.11 ppm and the dimethylamido groups appeared as a broad singlet at 2.96 ppm; the resonances had a ratio 1 : 2 indicating the stoichiometry of the complex. The broadness of some of the resonances indicated a degree of fluxionality in the complex. The spectrum in d^6-benzene at 343 K was significantly sharper, but on cooling only further broadening occurred down to the viscosity limit of the solvent.

HL^2 was treated with $[Zr(CH_2Ph)_4]$ to yield the complex $[ZrL^2_2(CH_2Ph)_2]$. The benzyl CH_2 groups appear as a broad singlet resonance at 2.45 ppm in the ^{1}H NMR spectrum. Since the system is inherently chiral, notwithstanding the presence of any exchange processes, we expect the Zr–CH_2 groups to behave as AB spin systems, and indeed upon heating to 343 K this peak sharpens to give the expected pair of AB doublets. Upon cooling, the resonances broaden extensively then sharpen again at 203 K. The spectrum at this temperature is consistent with the presence of at least one C_2-symmetric and one C_1-symmetric species in the ratio *ca.* 2 : 1, although the appearance of additional broad minor resonances, possibly arising from other diastereomers, prevents a confident assessment of diastereoselection. Suffice to say that there is little control of stereochemistry with respect to the metal coordination sphere.

The treatment of HL^2 with one equivalent of $[Zr(CH_2Bu^t)_4]$ yielded the yellow oil $[ZrL^2(CHBu^t)_3]$. When higher ratios of ligand to metal were tried the same major product was isolated.

The above studies indicate that while the tetrahydronaphthylamine-based ligands $HL^{1,2}$ may form complexes with the appropriate stoichiometry, there seems to be little control in terms of diastereoselection of chirality-at-zirconium.

Zirconium complexes of L^3

Treatment of $[Zr(NMe_2)_4]$ with two equivalents of HL^3 gave a mixture of compounds, with the major product being $[ZrL^3_3(NMe_2)]$ as judged by NMR spectroscopy. Accordingly, treatment of $[Zr(NMe_2)_4]$ with three equivalents of the same ligand led to the isolation of this compound. A similar benzyl complex $[ZrL^3_3(CH_2Ph)]$ was isolated, but $[ZrL^3_2(CH_2Ph)_2]$ was inaccessible. In contrast, the reaction of $[Zr(CH_2Bu^t)_4]$ with two equivalents of HL^3 yielded $[ZrL^3_2(CH_2Bu^t)_2]$.

The molecular structure of this compound, determined by X-ray crystallography (Fig. 2, Table 1) showed a C_2-symmetric Λ-*trans*,*cis*,*cis*-isomeric structure corresponding to structure **II** (Fig. 1) with the α-methylbenzyl aryl groups pointing towards the back of the molecule. The structure has mutually *cis* neopentyl groups [C(32)–Zr(1)–C(27) = 98.2(3)°] with the pyridine nitrogen atoms mutually *trans* [N(1)–Zr(1)–N(3) = 172.0(2)°]. The bond lengths and angles are otherwise unremarkable.[8,11]

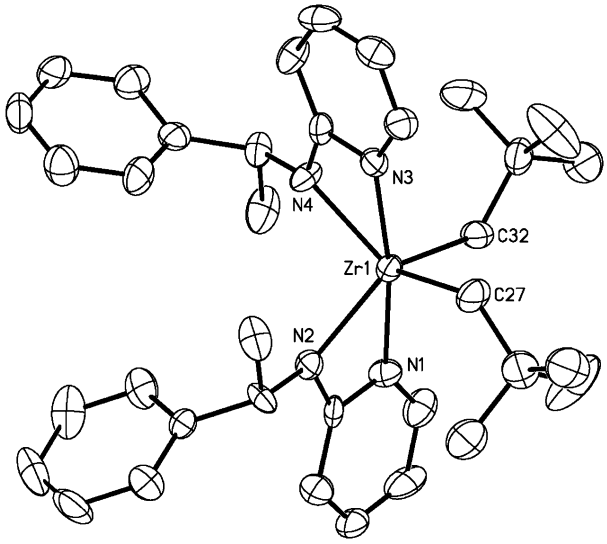


Fig. 2 Thermal ellipsoid plot of the molecular structure of Λ-*trans*,*cis*,*cis*-$[ZrL^3_2(CH_2Bu^t)_2]$ (H atoms omitted).

The ^{1}H NMR spectrum of this compound at 298 K (Fig. 3) showed a single set of aminopyridinato resonances, for example the quartet (a) for the α-methylbenzyl methine group at *ca.* 4.25, and two well-resolved pyridine C–H resonances (b) and (c) at *ca.* 6.0 and 6.4 ppm. The neopentyl CH_2 resonances appear as a pair of AB doublets at *ca.* 1.60 ppm. At 343 K (not shown) the CH_2 resonances sharpened, but there were no other significant changes in the spectrum. The spectrum broadened on lowering the temperature to 223 K then began to sharpen as the temperature was reduced. By 193 K peaks for major and minor components were resolved. The multiplets (a)–(c) have each split into two resonances in the ratio *ca.* 88 : 12, consistent with the presence of two diastereomers (both C_2 symmetric) in this ratio. NOESY NMR studies† established that the minor product was linked in an exchange process with the major product.

While this diastereoselection is far from perfect, it does give us an ideal opportunity to test the predictive power of DFT

Table 1 Selected bond lengths [Å] and angles [°] for $[ZrL^3_2(CH_2Bu^t)_2]$

Zr(1)–N(1)	2.334(5)	Zr(1)–N(4)	2.189(6)
Zr(1)–N(2)	2.210(6)	Zr(1)–C(27)	2.282(8)
Zr(1)–N(3)	2.360(5)	Zr(1)–C(32)	2.277(8)
N(1)–Zr(1)–N(3)	172.0(2)	N(4)–Zr(1)–C(27)	135.0(3)
N(2)–Zr(1)–N(1)	58.0(2)	N(4)–Zr(1)–C(32)	97.8(3)
N(2)–Zr(1)–N(3)	116.1(2)	C(27)–Zr(1)–N(1)	108.3(3)
N(2)–Zr(1)–C(27)	98.0(3)	C(27)–Zr(1)–N(3)	77.0(3)
N(2)–Zr(1)–C(32)	135.7(3)	C(32)–Zr(1)–N(1)	77.8(3)
N(4)–Zr(1)–N(1)	116.0(2)	C(32)–Zr(1)–N(3)	107.7(3)
N(4)–Zr(1)–N(2)	99.2(2)	C(32)–Zr(1)–C(27)	98.2(3)
N(4)–Zr(1)–N(3)	58.1(2)		

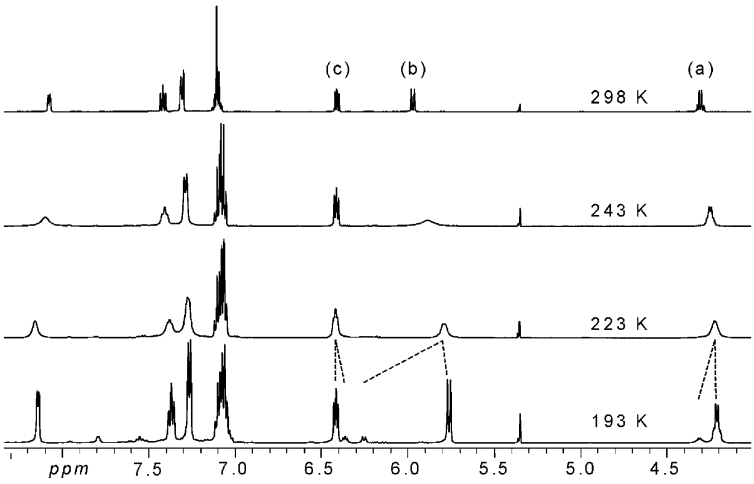


Fig. 3 Variable temperature NMR spectra of $[ZrL^3(CH_2Bu^t)_2]$.

calculations with respect to thermodynamic diastereoselection; the complexes are six-coordinate isomers of one-another in a poorly-coordinating low polarity medium, and so the issue of solvation is unlikely to be of importance. Using the X-ray crystallography data as a starting point, the structure of Λ-*trans*,*cis*,*cis*-$[ZrL^3_2(CH_2Bu^t)_2]$ was calculated using DFT. The converged output structure [Fig. 4(a)] was found to be superimposable on the X-ray crystallographic structure (Fig. 2). The seven remaining diastereomers of $[ZrL^3_2(CH_2Bu^t)_2]$ were investigated also; the only energetically feasible diastereomer Δ-*trans*,*cis*,*cis* [Fig. 4(b)] was found to be 4 kJ mol^{-1} higher in energy than the crystallographically-observed structure. Assuming that this is a difference in Gibbs free energy, it corresponds to a ratio of 92 : 8 in good agreement with the experimental value of 88 : 12.

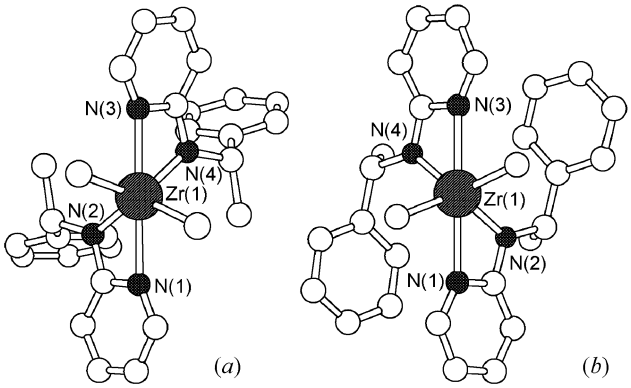


Fig. 4 Chem3D representations (neopentyl Bu^t groups removed) of the DFT-optimised structures of (a) Λ-*trans*,*cis*,*cis*-$[ZrL^3_2(CH_2Bu^t)_2]$ and (b) the diastereomer closest in energy Δ-*trans*,*cis*,*cis*-$[ZrL^3_2(CH_2Bu^t)_2]$.

It may be apparent from Fig. 4, or indeed from the chirality descriptors, that the major Λ-*trans*,*cis*,*cis* diastereomer (a) and the minor Δ-*trans*,*cis*,*cis* diastereomer (b) are related by simple inversion of chirality of the inner coordination spheres (compare **II** and **I**, Fig. 1). We note also that in both structures the α-methylbenzyl substituents are oriented (*via* rotation about the C–N bonds) so that the methyl and phenyl substituents avoid the pyridine 3-H atom. In the observed diastereomer (a) with Λ helicity at zirconium, this orients a phenyl group into a region of steric space at the back of the complexes as shown in Fig. 5(a). For the Δ diastereomer (b) the methyl groups occupy this position and the phenyl groups are caused to interact with the pyridine rings of the aminopyridinate ligand opposite Fig. 5(b). While this is sterically unfavourable, there will be an attractive contribution from π–π interactions, which is perhaps

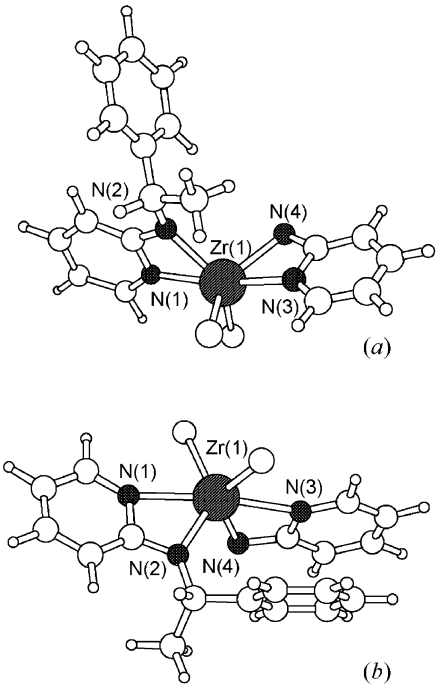


Fig. 5 Chem3D representation (some atoms removed for clarity) of the two diastereomers of $[ZrL^3_2(CH_2Bu^t)_2]$ (Fig. 4), showing the α-methylbenzyl group orientations.

responsible for bringing the energy of this structure relatively close to the crystallographically observed Λ-*trans*,*cis*,*cis*-isomer.

We wished to explore the exchange process between diastereomers, and since standard variable temperature NMR coalescence experiments are inappropriate for this system, the method of Selective Polarisation Transfer–Selective Inversion Recovery (SPT-SIR)[12] was used.† Observed rates k for exchange between diastereomers of 5.36 s^{-1} and 12.64 s^{-1} were obtained for two independent experiments, corresponding to a value of $\Delta G^{\ddagger}_{193} = 43 \pm 3$ kJ mol^{-1}. As may be apparent from the spectra in Fig. 3 it was not possible to perform SPT-SIR experiments over a sufficient range of temperatures in to allow determination of $\Delta H^{\ddagger}$.

Zirconium complexes of L^4

Treatment of $[Zr(NMe_2)_4]$ with two equivalents of HL^4 in pentane followed by cooling to −4 °C overnight yielded a yellow crystalline solid $[ZrL^4_2(NMe_2)_2]$. The ^{1}H NMR spectrum showed a single set of resonances at room temperature. High and low temperature NMR studies (343–183 K) showed no significant

Table 2 Selected bond lengths [Å] and angles [°] for $[Zr\mathbf{L}^4_2(NMe_2)_2]$

Zr(1)–N(1)	2.405(3)	Zr(1)–N(4)	2.216(3)
Zr(1)–N(2)	2.205(3)	Zr(1)–N(5)	2.040(4)
Zr(1)–N(3)	2.381(3)	Zr(1)–N(6)	2.048(4)
N(2)–Zr(1)–N(1)	57.91(13)	N(5)–Zr(1)–N(3)	158.39(15)
N(2)–Zr(1)–N(3)	92.37(12)	N(5)–Zr(1)–N(4)	101.21(17)
N(2)–Zr(1)–N(4)	141.00(11)	N(5)–Zr(1)–N(6)	97.7(2)
N(3)–Zr(1)–N(1)	79.67(11)	N(6)–Zr(1)–N(1)	157.66(14)
N(4)–Zr(1)–N(1)	89.99(13)	N(6)–Zr(1)–N(2)	101.99(16)
N(4)–Zr(1)–N(3)	57.73(13)	N(6)–Zr(1)–N(3)	92.59(14)
N(5)–Zr(1)–N(1)	96.84(16)	N(6)–Zr(1)–N(4)	103.64(17)
N(5)–Zr(1)–N(2)	103.90(16)		

change in the spectra, indicating that the system is probably in the fast exchange regime within this range of temperatures.

The molecular structure of $[Zr\mathbf{L}^4_2(NMe_2)_2]$ (Fig. 6, Table 2) corresponds to the type **IV** (Fig. 1, X = NMe_2). The structure obtained is approximately C_2-symmetric with *cis* dimethylamido units [N(5)–Zr(1)–N(6) = 97.7(2)°]. The pyridine units are approximately *trans* to the dimethylamido groups [N(6)–Zr(1)–N(1) = 157.66(14) and N(5)–Zr(1)–N(3) = 158.39(15)°]; hence like the two lowest energy isomers of $[Zr\mathbf{L}^3_2(CH_2Bu^t)_2]$, this structure follows the *trans* influence series $N_{amide} > C_{alkyl} > N_{py}$.[8] Unlike the alkyl complex structure(s) however the pyridine units in $[Zr\mathbf{L}^4_2(NMe_2)_2]$ are at the 'back' of the complex. This has a profound effect on the issue of chirality at zirconium in that the α-methylbenzyl substituents are placed in an area of relative steric freedom and thus their chirality is only poorly expressed in the complex architecture.

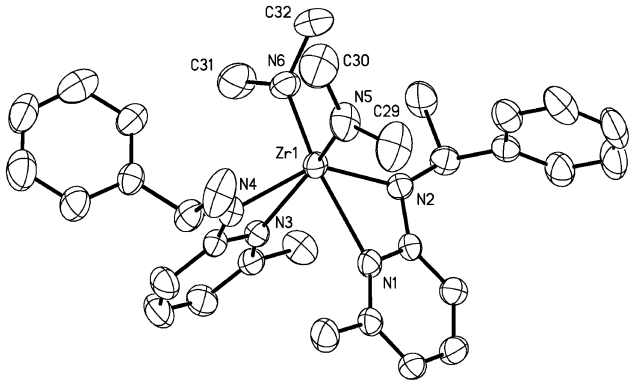


Fig. 6 Thermal ellipsoid plot of the molecular structure of $[Zr\mathbf{L}^4_2(NMe_2)_2]$ (H atoms omitted).

Treatment of $[Zr(CH_2Ph)_4]$ with two equivalents of $H\mathbf{L}^4$ in toluene followed by cooling to 4 °C yielded a orange/yellow crystalline solid $[Zr\mathbf{L}^4_2(CH_2Ph)_2]$. The molecular structure (Fig. 7, Table 3) corresponds to the Λ-*cis*,*cis*,*cis* diastereomer **VI** (Fig. 1). Hence unlike the structures described above, the aminopyridinato ligands are oriented 'head to tail' to give a C_1-symmetric structure. This might on first sight seem to disobey the *trans* influence series described above, particularly in that one pyridine unit at N(3) is nominally opposite an alkyl ligand at C(36), but at 144.81(7)°, C(36)–Zr(1)–N(3) is rather low to be considered a *trans* angle. The benzyl ligand at C(36) is η^2 coordinated, as is frequently observed for electron-deficient zirconium benzyls, with Zr(1)–C(36)–C(37) of 88.92(12)° and Zr–C_{ipso} distance of 2.6943(18) Å.

The ^{1}H NMR spectrum of $[Zr\mathbf{L}^4_2(CH_2Ph)_2]$ in the slow exchange regime at 203 K (Fig. 8) is consistent with such a C_1-symmetric structure. The alkyl region shows two slightly broadened peaks for the α-methylbenzyl methyl at 1.42 and 1.47 ppm, with the 6-methylpyridine singlets at 1.88 and 2.04 ppm. The benzyl CH_2 groups, which appear as two pairs of AB doublets at *ca.* 2.29 ppm and at 2.76 ppm have been shown by NOESY experiments at the same temperature to be in mutual

Table 3 Selected bond lengths [Å] and angles [°] for $[Zr\mathbf{L}^4_2(CH_2Ph)_2]$

Zr(1)–N(1)	2.3767(17)	Zr(1)-C(29)	2.338(2)
Zr(1)–N(2)	2.1767(16)	Zr(1)–C(36)	2.280(2)
Zr(1)–N(3)	2.3119(16)	Zr(1)–C(37)	2.6951(18)
Zr(1)–N(4)	2.1753(18)		
N(2)–Zr(1)–N(1)	58.37(6)	N(4)–Zr(1)–C(29)	106.39(7)
N(2)–Zr(1)–N(3)	91.57(6)	N(4)–Zr(1)–C(36)	87.70(7)
N(2)–Zr(1)–C(29)	146.86(7)	C(29)–Zr(1)–N(1)	89.89(7)
N(2)–Zr(1)–C(36)	104.63(8)	C(36)–Zr(1)–N(1)	119.59(6)
N(3)–Zr(1)–N(1)	95.54(6)	C(36)–Zr(1)–N(3)	144.81(7)
N(3)–Zr(1)–C(29)	81.56(7)	C(36)–Zr(1)–C(29)	99.22(9)
N(4)–Zr(1)–N(1)	145.98(6)	C(30)–C(29)–Zr(1)	109.62(14)
N(4)–Zr(1)–N(2)	97.32(6)	C(37)–C(36)–Zr(1)	88.92(12)
N(4)–Zr(1)–N(3)	58.98(6)		

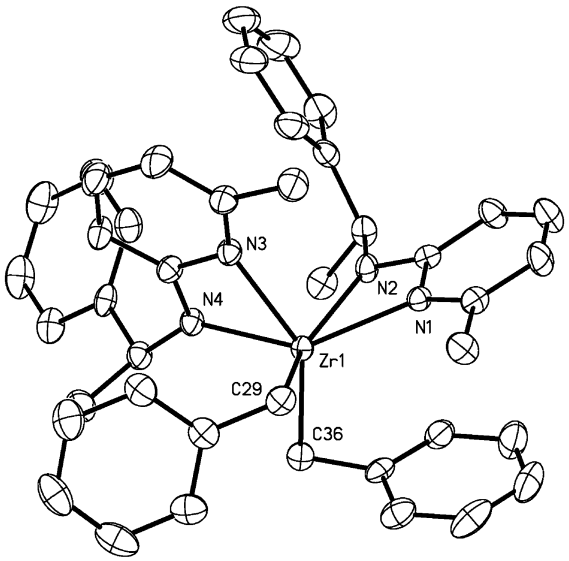


Fig. 7 Thermal ellipsoid plot of the molecular structure of Λ-*cis*,*cis*,*cis*-$[Zr\mathbf{L}^4_2(CH_2Ph)_2]$ (H atoms omitted).

exchange.† This confirms that the complex is one C_1-symmetric compound rather than two species in a 50 : 50 mixture. At 263 K these resonances coalesce to one AB system and at 298 K they sharpen somewhat and the AB 'quartet' structure is resolved. Over the same temperature range, resonances for the pyridine methyl groups (*ca.* 1.90 ppm) and benzylic CH groups (*ca.* 1.54 ppm) undergo similar processes. A NMR lineshape analysis (Win-Dyna software, Bruker) was undertaken in the range 203–263 K using the well-resolved pyridine methyl group resonances. This led *via* a standard Eyring plot to a value of $\Delta H^{\ddagger} = 42.4 \pm 4.7$ kJ mol^{-1}. We also note here the corresponding $\Delta S^{\ddagger} = -32 \pm 20$ J K mol^{-1}, but since this is obtained by extrapolating a line constructed over a relatively narrow temperature range to $1/T = 0$ we do not attach any great significance to this value or the calculated error.[13]

NMR studies on a closely related (achiral) aminopyridinato complex $[Zr(\eta^2\text{-PyNAd})_2(CH_2Bu^t)_2]$ (Ad = adamantyl) led to values $\Delta H^{\ddagger} = 71.7 \pm 2.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 30 \pm 9$ J K^{-1} mol^{-1} for inversion of chirality at the metal.[8] The complex $[Zr\mathbf{L}^4_2(CH_2Ph)_2]$, and indeed $[Zr\mathbf{L}^3_2(CH_2Bu^t)_2]$ above thus have much lower barriers to inversion of chirality at the metal than does $[Zr(\eta^2\text{-PyNAd})_2(CH_2Bu^t)_2]$. This observation is consistent with an *N*-dissociative mechanism for topographical exchange; we would expect pyridine dissociation to become less favourable as the steric demand of R is increased, simply because the aminopyridine ligand must pivot about the amido atom as the Zr–N_{Py} distance increases (Fig. 9). *N*-Dissociation is the proposed mechanism in related systems.[14–16]

Most importantly, however, the diastereoselection of the single chiral-at-metal isomer Λ-*cis*,*cis*,*cis*-$[Zr\mathbf{L}^4_2(CH_2Ph)_2]$ appears to be essentially complete (>95 : 5) since no other diastereomer is

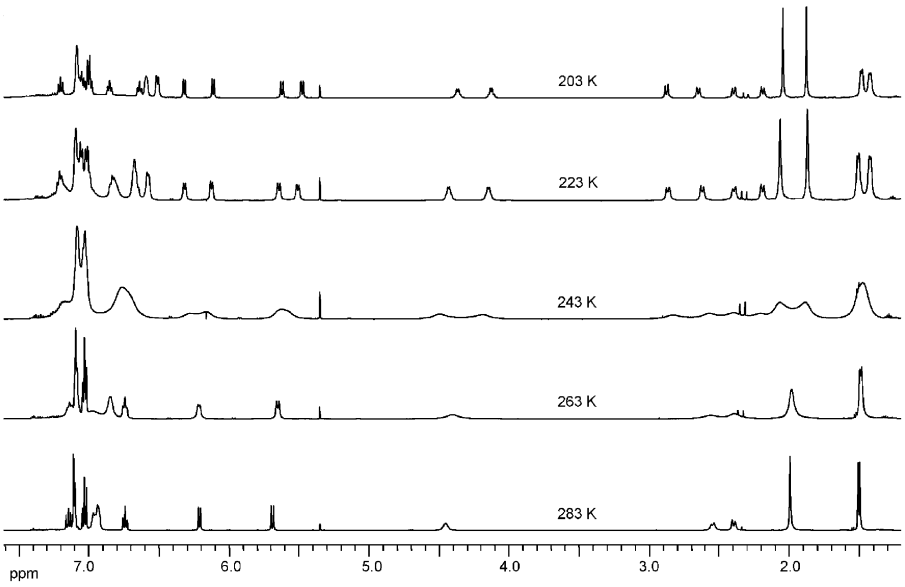


Fig. 8 Results of low temperature NMR spectroscopic experiments on $[ZrL^4{}_2(CH_2Ph)_2]$.

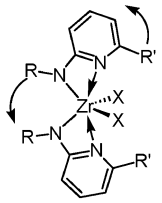


Fig. 9 Pyridine *N*-dissociation in zirconium aminopyridinato complexes.

observed. The origins of this excellent diastereoselectivity appear to be similar to those for $[ZrL^3{}_2(CH_2Bu^t)_2]$ above although the emergence of an unsymmetrical diastereomer as the lowest energy species is perhaps surprising. It was attempted to build models of all eight diastereomers of $[ZrL^3{}_2(CH_2Bu^t)_2]$, but the two with *trans* alkyl ligands were judged to be sterically unfeasible. The structures of the remaining six diastereomers were calculated using DFT. The crystallographically observed Λ-*cis*,*cis*,*cis* diastereomer, for which the calculated structure was essentially superimposable on the crystallographic structure is the more stable, the others being 24–74 kJ mol^{-1} higher in energy.† This confirms that the single C_1 symmetric diastereomer observed by NMR spectroscopy is indeed the same as that in the solid state, *i.e.* Λ-*cis*,*cis*,*cis*-$[ZrL^4{}_2(CH_2Ph)_2]$.

Unfortunately we are unable to compare the diastereoselectivity induced by L^3 and L^4 for the same co-ligands since $[ZrL^3{}_2(CH_2Bu^t)_2]$ is inaccessible; treatment of HL^4 with one equivalent of $[Zr(CH_2Bu^t)_4]$ in pentane gave the complex $[ZrL^4(CH_2Bu^t)_3]$ as a sticky yellow oil.

Conclusions

Surprisingly, the conformationally flexible α-methylbenzyl based aminopyridinato ligands promote much better control of chirality-at-zirconium (diastereoselectivity) in this organometallic system than do the tetrahydronaphthyl analogues. For example, several diastereomers of the complex $[ZrL^2{}_2(CH_2Ph)_2]$ were detected, while $[ZrL^3{}_2(CH_2Bu^t)_2]$ exists as a *ca.* 90 : 10 mixture of two isomers only. The complex $[ZrL^4{}_2(CH_2Ph)_2]$ displays excellent control of stereochemistry (>95 : 5) at 193 K although perhaps surprisingly the observed diastereomer is unsymmetrical. As we commented previously,[9] the factors that control structure in these complexes are subtle, but it does appear that there is an excellent correlation between observed selectivities and calculated energy differences from DFT.

All the complexes studied are in dynamic exchange between diastereomers *via* an *N*-dissociative mechanism, *i.e.* conversion from six- to five-coordinate structure followed by rapid intramolecular scrambling. The rate of this process is highly dependent on steric effects, but it is also interesting to note the effect of the geometry on both this exchange rate and the thermodynamic diastereoselection. We mentioned above that as a result of the *trans* influence, the stereogenic substituents in $[ZrL^4{}_2(NMe_2)_2]$ are oriented such that they have little influence on the complex architecture (Fig. 6). In addition, *N*-dissociation is promoted in this type of structure since the pyridine *N*-atoms are *trans* to amide, a strong *trans* effect ligand.

Hence although it is feasible to control chiral architecture in early transition metal complexes of the form $[M(AB)_2X_2]$, significant challenges remain. As a result of the observations made here, our current work is focussed on the development of chiral ligands with strong *trans* influence donor atoms A and B, and in which the anionic charge is delocalised more across the AB unit.

Experimental

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 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 (4Å).

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.* 0.7%, despite the use of high combustion temperatures and combustion aids. This can be ascribed to carbide formation.[17] 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.

Syntheses

Pyridin-2-yl-(1,2,3,4-tetrahydronaphthalen-1-yl)-amine HL[1]. Toluene (30 mL) was added to a Schlenk vessel charged with [$Pd_2(dba)_3$] (311 mg, 0.3 mmol), $NaOBu^t$ (4.57 g, 0.05 mol) and (±)-BINAP (423 mg, 0.7 mmol). Toluene (10 mL) was added to a vessel charged with (*S*)-1,2,3,4-tetrahydro-1-naphthylamine (5.00 g, 0.03 mol) and 2-bromopyridine (5.5 g, 0.03 mol) and degassed. The solutions were mixed and heated to 90 °C for 48 h. On cooling to room temperature the resultant red solution was treated with activated charcoal and passed through silica and the silica washed with diethyl ether (75 ml). The pale yellow solution was then dried over $MgSO_4$ and the solvent removed under reduced pressure. The solid pale yellow product was recrystallised from Et_2O (3.2 g, 48%). ^{1}H NMR (293 K, d_6-benzene) δ 1.47–1.68 (m, 2H, cyclohexyl-CH_2), 1.78–1.90 (m, 2H, cyclohexyl-CH_2), 2.62–2.46 (m, 2H, cyclohexyl-CH_2), 4.53 (d, 1H, NH, $^3J_{HH} = 8$ Hz), 5.30 (qt, 1H, CHN, $^3J_{HH} = 8$ Hz), 5.98 (d, 1H, Py-CH, $^3J_{HH} = 8$ Hz), 6.39 (t, 1H, Py-CH, $^3J_{HH} = 8$ Hz), 6.98 (d, 1H, Ar-CH, $^3J_{HH} = 8$ Hz), 7.01–7.12 (m, 3H, Ar-CH/Py-CH), 7.35 (d, 1H, Ar-CH, $^3J_{HH} = 8$ Hz), 8.21 (d, 1H, Py-CH, $^3J_{HH} = 8$ Hz). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 20.5, 30.1, 30.3 (ring CH_2), 49.6 (CHN), 108.1, 113.1 (Py-CH), 126.8, 127.6, 129.6, 130.0 (Ar-CH), 137.3 (Py-CH) 138.1 (Ar-Cq), 139.1 (Ar-Cq), 149.2 (Py-CH), 159.0 (Py-Cq). IR (neat, cm^{-1}): 3211, 3017, 2940, 2921, 1596, 1575, 1524, 1488, 1455, 1439, 1340, 1322, 1290, 1270, 1203, 1171, 1153, 1117, 1088, 988, 763, 736. Anal. Calcd. for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.25; N, 7.23; H, 12.45%. MS (EI) *m/z* 224 (M^+).

(6-Methylpyridin-2-yl)-(1,2,3,4-tetrahydronaphthalen-1-yl)-amine HL[2]. Toluene (30 mL) was added to a Schlenk vessel charged with [$Pd_2(dba)_3$] (311 mg, 0.3 mmol), $NaOBu^t$ (4.57 g, 0.05 mol) and (±)-BINAP (423 mg, 0.7 mmol). Toluene (10 mL) was added to a vessel charged with (*S*)-1,2,3,4-tetrahydro-1-naphthylamine (5.00 g, 0.03 mol) and 2-bromo-6-methylpyridine (5.9 g, 0.03 mol) and degassed. The solutions were mixed and heated to 90 °C for 48 h. On cooling to room temperature the resultant red solution was treated with activated charcoal and passed through silica and the silica washed with diethyl ether (75 ml). The pale yellow solution was then dried over $MgSO_4$ and the solvent removed under reduced pressure. The mixture was the distilled using Kugelrohr apparatus at 120 °C. The first fraction was unreacted bromopyridine and the second was the required product, a clear oil (2.29 g, 32%). ^{1}H NMR (293 K, d_6-benzene) δ 1.45–1.69 (m, 2H, cyclohexyl-CH_2), 1.73–1.93 (m, 2H, cyclohexyl-CH_2), 2.45 (s, 3H, Py-CH_3), 2.48–2.60 (m, 2H, cyclohexyl-CH_2), 4.28 (br d, 1H, NH, $J = 11$ Hz), 5.32 (br qt, 1H, cyclochexyl-CH, $^3J_{HH} = 8$ Hz), 5.89 (d, 1H, Py-CH, $^3J_{HH} = 11$ Hz), 6.36 (d, 1H, Py-CH, $^3J_{HH} = 11$ Hz), 6.95–7.14 (m, 4H, Ar-CH/Py-CH), 7.38 (d, 1H, Ar-CH, $^3J_{HH} = 12$ Hz). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 20.6 (ring CH_2), 25.1 (Py-CH_3), 30.1, 30.5 (ring CH_2), 49.5 (CH), 104.9, 112.3 (Py-CH), 126.8, 127.5, 129.5, 129.8 (Ar-CH), 137.9 (Py-CH), 138.0, 139.3 (Ar-Cq), 157.7 (Py-NCqN), 158.5 (Py-Cq-CH_3). IR (neat, cm^{-1}): 3414, 3019, 2927, 2860, 1593, 1489, 1458, 1386, 1331, 1271, 1222, 1156, 1100, 1034, 987, 949, 884, 850. Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.37; N, 7.56; H, 11.72%. MS (EI) *m/z* 238 (M^+).

(1-Phenylethyl)-pyridin-2-yl-amine HL[3]. Toluene (50 ml) was added to a large Schlenk vessel charged with (*S*)-(−)-α-methylbenzylamine (2.0 g, 16.5 mmol), 2-bromopyridine (3.0 g, 19.0 mmol), $Pd_2(dba)_3$ (200 mg, 0.22 mmol), dppp (200 mg, 0.48 mmol) and $NaOBu^t$ (2.4 g, 25.0 mmol). The resulting deep orange mixture was heated at 100 °C overnight with stirring. On cooling to room temperature the resultant red solution was treated with activated charcoal and passed through silica and the silica washed with diethyl ether (75 ml). The yellow/orange solution was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting yellow oil was eluted through a silica column using pentane : diethyl ether (5 : 1). The first two compounds eluted were impurities, the column was then flushed with dichloromethane to give the product as an opaque oil (2.85 g, 75%). ^{1}H NMR (293 K, d_6-benzene) δ 1.26 (d, 3H, CH_3, $^3J_{HH} = 7$ Hz), 4.79 (m, 2H, NH/CH), 6.04 (d, 1H, Py-CH, $^3J_{HH} = 8$ Hz), 6.40 (t, 1H, Py-CH, $^3J_{HH} = 8$ Hz), 7.06 (t, 1H, Py-CH, $^3J_{HH} = 8$ Hz), 7.20 (m, 5H, Ar-CH), 8.31 (d, 1H, Py-CH, $^3J_{HH} = 8$ Hz). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 24.3 (CH_3), 52.1 (CH), 107.4, 113.5 (Py-CH), 126.6, 127.4 (Ar-CH), 129.2, 137.4, 149.2 (Py-CH). IR (neat, cm^{-1}): 3408, 3246, 3024, 2970, 2927, 2868, 1597, 1572, 1482, 1442, 1335, 1290, 1208, 1155, 1095, 985, 769, 700, 632. Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.62; H, 7.17; N, 14.03%. MS (EI) *m/z* 198 (M^+), 183 ($M^+ - CH_3$).

(6-Methyl-pyridin-2-yl)-(1-phenyl-ethyl)-amine HL[4]. Toluene (50 ml) was added to a large Schlenk vessel charged with (*S*)-(−)-α-methylbenzylamine (2.0 g, 16.5 mmol), 2-bromo-6-methyl pyridine (3.0 g, 17.4 mmol), $Pd_2(dba)_3$ (200 mg, 0.22 mmol), dppp (200 mg, 0.48 mmol) and $NaOBu^t$ (2.3g, 23.9 mmol). The resulting deep orange mixture was heated at 100 °C overnight with stirring. On cooling to room temperature the resultant red solution was treated with activated charcoal and passed through silica and the silica washed with diethyl ether (75 ml). The yellow/orange solution was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting yellow oil was eluted through a silica column using pentane : diethyl ether (5 : 1). The first two compounds eluted were impurities, the column was then flushed with dichloromethane to give the product as an opaque oil (2.4 g, 69%). ^{1}H NMR (293 K, d_6-benzene) δ 1.20 (d, 3H, CH_3, $^3J_{HH}$), 2.41 (s, 3H, Py-CH_3), 4.66 (qn, 1H, CH, $^3J_{HH}$), 4.76 (s, 1H, NH), 5.88 (d, 1H, Py-CH, $^3J_{HH}$), 6.29 (d, 1H, Py-CH, $^3J_{HH}$), 6.99 (t, 1H, Py-CH, $^3J_{HH}$), 7.15 (m, 5H, Ar-CH). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 24.5 (CH_3), 24.9 (Py-CH_3), 52.2 (CH), 104.2, 112.7 (Py-CH), 126.6, 127.4, 129.2 (Ar-CH), 138.0 (Py-CH), 145.9 (Ar-Cq), 157.6 (Py-NCqN), 158.5 (Py-Cq). IR (neat, cm^{-1}): 3406, 3027, 2967, 2925, 2868, 1594, 1494, 1464, 1373, 1334, 1215, 1148, 779, 700, 632. Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.29; H, 7.59; N, 13.12%. MS (EI) *m/z* 212 (M^+), 197 ($M^+ - CH_3$).

[$ZrL^2_2(NMe)_2$]. Pentane (20 ml) was added to a Schlenk vessel charged with HL^2 (300 mg, 1.26 mmol) and [$Zr(NMe_2)_4$] (170 mg, 0.64 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane, filtered and the solvent volume reduced. Upon cooling to −30 °C the yellow solid [$ZrL^2(NMe_2)_2$] precipitated (263 mg, 64%). ^{1}H NMR (293 K, d_6-benzene) δ 1.79 (m, 2H), 1.94 (m, 2H), 2.04 (m, 2H, ring CH_2), 2.11 (s, 6H, Py-CH_3), 2.17 (m, 2H), 2.72 (m, 2H), 2.86 (m, 2H, ring CH_2), 2.96 (br s, 12H, NMe_2), 4.88 (br m, 2H, ring CH), 5.79 (d, 2H, Py-CH, $^3J_{HH} = 7$ Hz), 5.85 (br d, 2H, Py-CH, $^3J_{HH} = 8$ Hz), 6.84 (t, 2H, Py-CH, $^3J_{HH} = 7$ Hz), 7.11 (m, 6H, Ar-CH), 7.62 (d, 2H, Ar-CH, $^3J_{HH} = 6$Hz). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 22.6 (Py-CH_3), 23.0, 30.4, 30.8 (ring CH_2), 42.8 (NMe_2), 56.5 (ring

CH), 102.6, 107.4 (Py-CH), 125.8, 126.2, 128.9, 137.2 (Ar-C), 139.5 (Py-CH), 140.9 (Py-C), 154.1 (NCN). Anal. Calcd. for $C_{36}H_{46}N_6Zr$: C, 66.11; H, 7.09; N, 12.85. Found: C, 65.36; H, 6.98; N, 12.72%. MS (EI) *m/z* 608 ($M^+ - NMe_2$), 564 ($M^+ - 2NMe_2$).

[ZrL$^2_2$(CH$_2$Ph)$_2$]. Toluene (20 ml) was added to a Schlenk vessel charged with H**L**^{2} (230 mg, 0.97 mmol) and [Zr(CH$_2$Ph)$_4$] (220 mg, 0.48 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane (10 mL), filtered and the solvent volume reduced. Upon cooling to −30 °C a yellow powder precipitated. The product was isolated by filtration *via* cannula (222 mg, 62%). ^{1}H NMR (293 K, d$_6$-benzene) δ 1.19–1.35 (m, 2H), 1.58–1.69 (m, 2H), 1.76–1.87 (m, 4H, ring CH$_2$), 1.96 (s, 6H, Py-CH$_3$), 2.45 (br s, 4H, Bn-CH$_2$), 2.57–2.78 (m, 4H, ring CH$_2$), 4.98 (br s, 2H, ring CH), 5.48 (d, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 5.89 (d, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 6.70 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 6.87–7.18 (m, 18H, Ar-CH). ^{1}H NMR (343 K, d$_6$-benzene) δ 1.23–1.35 (m, 2H), 1.59–1.70 (m, 2H), 1.76–1.88 (m, 4H, ring CH$_2$), 1.99 (s, 6H, Py-CH$_3$), 2.48 (q, 4H, *J* = 10 Hz, Bn-CH$_2$), 2.58–2.78 (m, 4H, ring CH$_2$), 5.01 (br t, 2H, *J* = 8 Hz, ring CH), 5.52 (d, 2H, *J* = 8 Hz), 5.90 (d, 2H, *J* = 8 Hz), 6.74 (t, 2H, *J* = 8 Hz, Py-CH), 6.85 (t, 2H, *J* = 7 Hz, Bn-CH), 6.92–7.14 (m, 16H, Ar-CH). ^{13}C{^{1}H} NMR (293 K d$_6$-benzene) δ 23.0 (Py-CH$_3$), 23.3, 29.2, 30.4, 58.2 (ring CH), 72.8 (Bn-CH$_2$), 104.8, 110.8 (Py-CH), 122.5 (Bn-CH), 126.6, 126.7, 127.5, 128.6, 128.7 (Ar-CH), 137.7, 139.9 (cyclohexyl-Cq), 140.6 (Py-CH), 155.0 (Py-NCqN), 170.2 (Py-Cq-CH$_3$). Anal. Calcd. for $C_{46}H_{48}N_4Zr$: C, 73.85; H, 6.47; N, 7.49. Found: C, 73.27; H, 6.35; N, 7.43%. MS (EI) *m/z* 655 ($M^+ - Bn$).

[ZrL^2(CH$_2$Bu^t)$_3$]. Pentane (20 ml) was added to a Schlenk vessel charged with H**L**^{2} (230 mg, 0.97 mmol) and [Zr(CH$_2$Bu^t)$_4$] (363 mg, 0.97 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane (10 mL), filtered and the solvent removed under reduced pressure. A yellow thick oil was obtained and determined to be [Zr**L**^{2}(CH$_2$Bu^t)$_3$] by NMR spectroscopy. ^{1}H NMR (293 K, d$_6$-benzene) δ 1.24 (s, 27H, Bu^t), 1.48 (dd, 6H, Np-CH, *J* = 12 Hz), 1.60–1.88 (m, 2H), 1.92–2.15 (m, 2H, ring CH$_2$), 2.16 (s, 3H, Py-CH$_3$), 2.60–2.89 (m, 2H, ring CH$_2$), 5.12 (br s, 1H, ring CH), 5.66 (d, 1H, $^3J_{HH}$ = 8 Hz), 5.84 (d, 1H, $^3J_{HH}$ = 8 Hz), 6.75 (t, 1H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.02 (d, 1H, $^3J_{HH}$ = 7 Hz), 7.08 (t, 1H, $^3J_{HH}$ = 7 Hz), 7.17 (t, 1H, $^3J_{HH}$ = 7 Hz), 7.74 (d, 1H, $^3J_{HH}$ = 7 Hz, Ar-CH). ^{13}C{^{1}H} NMR (293 K d$_6$-benzene) δ 23.2 (ring CH$_2$), 23.4 (Py-CH$_3$), 30.7 (ring CH$_2$), 35.46 (Bu^t), 36.4 (ring CH$_2$), 99.1 (Np-CH$_2$), 101.1, 110.7 (Py-CH), 127.1, 127.1, 129.8 (Ar-CH), 142.3 (Py-CH), 154.9 (Py-NCqN), 168.8 (Py-Cq-CH$_3$).

[ZrL$^3_3$(NMe$_2$)]. Pentane (20 ml) was added to a Schlenk vessel charged with H**L**^{3} (400 mg, 2.03 mmol) and [Zr(NMe$_2$)$_4$] (181 mg, 0.68 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane (10 mL), filtered and the solvent volume reduced. Upon cooling to −30 °C a yellow powder precipitated which was then isolated by filtration *via* cannula. The residual solvent was removed under reduced pressure and the resulting yellow solid was determined to be [Zr**L**$^3_3$(NMe$_2$)] (348 mg, 71%). ^{1}H NMR (293 K, d$_6$-benzene) δ 1.66 (d, 9H, $^3J_{HH}$ = 7 Hz, CH$_3$), 3.14 (s, 6H, NMe$_2$), 4.68 (q, 3H, $^3J_{HH}$ = 7 Hz, CH), 5.87 (t, 3H, $^3J_{HH}$ = 8 Hz), 5.95 (d, 3H, $^3J_{HH}$ = 8 Hz), 6.79 (t, 3H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.08 (m, 9H), 7.27 (d, 6H, $^3J_{HH}$ = 7 Hz, Ar-CH), 7.62 (d, 3H, $^3J_{HH}$ = 8 Hz, Py-CH). ^{13}C{^{1}H} NMR (293 K, d$_6$-benzene) δ 23.2 (CH$_3$), 41.8 (N(*C*H$_3$)$_2$), 56.6 (CH), 107.1, 107.9 (Py-CH), 126.1, 126.8, 128.5 (Ar-CH), 138.9, 143.4 (Py-CH), 146.8 (Ar-Cq), 170.1 (Py-NCqN). Anal. Calculated for $C_{41}H_{45}N_7Zr$ C, 67.73; H, 6.24; N, 13.49. Found: C, 67.09; H, 6.18; N, 13.38%. MS (EI) *m/z* 681 ($M^+ - NMe_2$), 528 ($M^+ - L$).

[ZrL$^3_3$(CH$_2$Ph)]. Toluene (20 ml) was added to a Schlenk vessel charged with H**L**^{3} (250 mg, 1.27 mmol) and [Zr(CH$_2$Ph)$_4$] (220 mg, 0.64 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane (10 mL) and filtered and the solvent volume reduced. Upon cooling to −30 °C a yellow powder precipitated. The product was isolated by filtration *via* cannula and residual solvent removed under reduced pressure (223 mg, 68%). ^{1}H NMR (293 K, d$_6$-benzene) δ 1.57 (d, 9H, $^3J_{HH}$ = 7 Hz, CH$_3$), 2.87 (d, 1H, $^3J_{HH}$ = 10 Hz), 3.12 (d, 1H, $^3J_{HH}$ = 10 Hz, Bn-CH$_2$), 4.53 (q, 3H, $^3J_{HH}$ = 7 Hz, CH), 5.85 (m, 6H), 6.74 (t, 3H, $^3J_{HH}$ = 7 Hz, Py-CH), 6.92 (t, 3H, $^3J_{HH}$ = 8Hz), 7.03–7.21 (m, 17H, Ar-CH), 7.58 (d, 3H, $^3J_{HH}$ = 7 Hz, Py-CH). ^{13}C{^{1}H} NMR (293 K, d$_6$-benzene) δ 22.4 (CH$_3$), 55.7 (CH), 66.5 (Bn-CH$_2$), 106.0, 107.4 (Py-CH), 118.7 (Bn-Cq), 125.0, 127.4 (Ar-CH), 138.8, 142.1 (Py-CH), 145.1 (Ar-Cq), 170.2 (Py-NCqN). Anal. Calculated for $C_{46}H_{46}N_6Zr$ C, 71.37; H, 5.99; N, 10.86. Found: C, 70.84; H, 5.87; N, 10.80%. MS (EI) *m/z* 773 (M^+), 681 ($M^+ - Bn$).

[ZrL$^3_2$(CH$_2$Bu^t)$_2$]. Toluene (20 ml) was added to a Schlenk vessel charged with [Zr(CH$_2$Bu^t)$_4$] (467 mg, 1.25 mmol) and H**L**^{3} (493 mg, 2.5 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed under reduced pressure and the residue was redissolved in pentane (5 ml) and filtered. Cooling overnight at −30 °C afforded orange crystals (452 mg, 58%). ^{1}H NMR (293 K, d$_6$-benzene) δ 1.31 (s, 18H, Np-Bu^t), 1.56 (bq, 4H, Np-CH$_2$), 1.66 (d, 6H, $^3J_{HH}$ = 7 Hz, CH$_3$), 4.35 (q, 2H, $^3J_{HH}$ = 7 Hz, CH), 5.85 (d, 2H, $^3J_{HH}$ = 8 Hz), 5.98 (t, 2H $^3J_{HH}$ = 8 Hz), 6.85 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.03 (m, 6H), 7.34 (m, 4H, Ar-CH), 8.05 (d, 2H, Py-CH, $^3J_{HH}$ = 8 Hz). ^{1}H NMR (343 K, d$_6$-benzene) δ 1.24 (s, 18H, Np-Bu^t), 1.52 (q, 4H, $^3J_{HH}$ = 14 Hz, Np-CH$_2$), 1.65 (d, 6H, $^3J_{HH}$ = 7 Hz, CH$_3$), 4.41 (q, 2H, $^3J_{HH}$ = 7Hz, CH), 5.92 (d, 2H, $^3J_{HH}$ = 8 Hz), 6.03 (t, 2H, $^3J_{HH}$ = 8 Hz), 6.93 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 6.99–7.08 (m, 6H), 7.34 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-CH), 8.02 (d, 2H, $^3J_{HH}$ = 8 Hz, Py-CH). ^{13}C{^{1}H} NMR (293 K, d$_6$-benzene) δ 24.6 (Np-Bu^t), 34.9 (Cq), 35.1 (CH$_3$), 57.4 (Ar-CH), 87.7 (CH$_2$), 106.7, 109.0 (Py-CH), 126.6, 126.7, 128.4 (Ar-CH), 142.2, 142.3 (Py-CH), 145.6, 171.9 (Cq). Anal. Calculated for $C_{36}H_{48}N_4Zr$ C, 68.85; H, 7.70; N, 8.92. Found: C, 68.21; H, 7.58; N, 8.83%. MS (EI) *m/z* 556 ($M^+ - Np$).

[ZrL$^4_2$(NMe$_2$)$_2$]. Pentane (20 mL) was added to a Schlenk vessel charged with H**L**^{4} (350 mg, 1.65 mmol) and [Zr(NMe$_2$)$_4$] (220 mg, 0.83 mmol) at room temperature. The colour of the reaction mixture immediately turned yellow and was stirred at ambient temperature for 1 h. Cooling overnight to 4 °C afforded yellow crystals (152 mg, 30%). ^{1}H NMR (293 K, d$_6$-benzene) δ 1.73 (d, 6H, $^3J_{HH}$ = 7 Hz), 2.08 (bs, 6H, CH$_3$), 3.19 (bs, 12H, NMe$_2$), 4.44 (q, 2H, $^3J_{HH}$ = 7 Hz, CH), 5.74 (d, 2H, $^3J_{HH}$ = 8 Hz), 5.87 (d, 2H, $^3J_{HH}$ = 8 Hz), 6.77 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.17 (t, 2H, $^3J_{HH}$ = 7 Hz), 7.27 (m, 4H), 7.59 (m, 4H, Ar-CH). ^{13}C{^{1}H} NMR (293 K d$_6$-benzene) δ 22.5 (CH$_3$), 27.0 (Cq), 44.4 (NMe$_2$), 58.6 (CH), 103.4, 108.9 (Py-CH), 126.9, 127.0, 129.2 (Ar-CH), 136.9 (Cq), 140.5 (Py-CH), 149.1 (Cq). ^{1}H NMR (343 K, d$_6$-benzene) δ 1.73 (d, 6H, $^3J_{HH}$ = 7 Hz, CH$_3$), 2.08 (s, 6H, Py-CH$_3$), 3.17 (s, 12H, NMe$_2$), 4.51 (q, 2H, $^3J_{HH}$ = 7 Hz, CH), 5.77 (d, 2H, $^3J_{HH}$ = 8 Hz), 5.88 (d, 2H, $^3J_{HH}$ = 8 Hz), 6.82 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.13 (t, 2H, $^3J_{HH}$ = 7 Hz), 7.27 (t, 4H, $^3J_{HH}$ = 7 Hz), 7.51 (d, 4H, $^3J_{HH}$ = 7 Hz, Ar-CH). Anal. Calculated for $C_{32}H_{42}N_6Zr$ C, 63.85; H, 7.03; N, 13.96. Found: C, 63.07; H, 6.94; N, 13.86%. MS (EI) *m/z* 600 (M^+).

[ZrL$^4_2$(CH$_2$Ph)$_2$]. Toluene (20 ml) was added to a Schlenk vessel charged with H**L**^{4} (250 mg, 1.18 mmol) and [Zr(CH$_2$Ph)$_4$] (275 mg, 0.60 mmol) at room temperature. The reaction mixture

Table 4 Experimental data for the X-ray diffraction studies

	$[ZrL^3_2(CH_2Bu^t)_2]$	$[ZrL^4_2(NMe_2)_2]$	$[ZrL^4_2(CH_2Ph)_2]$
Molecular formula	$C_{36}H_{48}N_4Zr$	$C_{32}H_{42}N_6Zr$	$C_{42}H_{44}N_4Zr$
Formula weight	628.00	601.94	696.03
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a/Å	10.7595(3)	9.2445(4)	9.9881(7)
b/Å	12.7065(2)	15.8682(7)	18.2656(13)
c/Å	25.2894(4)	11.4990(5)	19.6287(14)
β/°	—	110.592(4)	—
Cell volume/Å^3	3457.46(12)	1579.06(12)	3581.0(4)
T/K	180(2)	180(2)	180(2)
Z	4	2	4
μ/mm^{-1}	0.346	0.378	0.342
Total reflections	17938	10721	23492
Independent reflections	6081	6657	8707
$R1$,[a] $wR2$[b] $[I>2\sigma(I)]$	0.0779, 0.1163	0.0467, 0.0918	0.0331, 0.0673

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for all data.

was stirred overnight at ambient temperature in the absence of light under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane and filtered and the solvent volume reduced. Upon cooling to a yellow solid was obtained (242 mg, 30%). ^{1}H NMR (293 K, d_6-benzene) δ 1.54 (d, 6H, $^3J_{HH}$ = 7 Hz, CH_3), 1.90 (s, 6H, Py-CH_3), 2.60 (d, 2H, $^3J_{HH}$ = 11 Hz), 2.81 (d, 2H, $^3J_{HH}$ = 11 Hz, Bn-CH_2), 4.48 (br qn, 2H, NCH), 5.67 (d, 2H, $^3J_{HH}$ = 8 Hz), 5.87 (d, 2H, $^3J_{HH}$ = 8 Hz), 6.73 (t, 2H, $^3J_{HH}$ = 8 Hz, Py-CH), 6.83 (t, 2H, $^3J_{HH}$ = 7 Hz), 7.05–7.12 (m, 18H, Ar-CH). ^{1}H NMR (193 K, d_2-dichloromethane) δ 1.43 (br s, 3H), 1.47 (br s, 3H, CH_3), 1.88 (s, 3H), 2.04 (s, 3H, Py-CH_3), 2.18 (d, 1H, $^3J_{HH}$ = 8 Hz), 2.39 (d, 1H, $^3J_{HH}$ = 8 Hz), 2.65 (d, 1H, $^3J_{HH}$ = 8 Hz), 2.87 (d, 1H, $^3J_{HH}$ = 8 Hz, Py-CH_2), 4.12 (br qt, 1H), 4.34 (br qt, 1H, CH), 5.46 (d, 1H, $^3J_{HH}$ = 7 Hz), 5.61 (d, 1H, $^3J_{HH}$ = 7 Hz), 6.10 (d, 1H, $^3J_{HH}$ = 7 Hz), 6.32 (d, 1H, $^3J_{HH}$ = 7 Hz, Py-CH), 6.48–6.64 (m, 5H), 6.84–7.08 (m, 15H, Ar-CH), 7.20 (t, 1H, $^3J_{HH}$ = 7 Hz, Py-CH). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 23.2 (Py-CH_3), 27.3 (CH_3), 58.5 (NCH), 74.2 (Bn-CH_2), 104.7, 111.5 (Py-CH), 122.2 (Ar-Cq), 126.9, 127.0 - 129.0 (Ar-CH), 140.7 (Py-CH), 146.7 (Ar-Cq), 159.8 (Py-NCqN), 168.9 (Py-Cq-CH_3). ^{13}C{^{1}H} NMR (193 K d_2-dichloromethane) δ 22.8, 24.9 (Py-CH_3), 27.8 (CH_3), 57.9, 73.7 (CH), 72.1, 73.7 (Bn-CH_2), 103.4, 105.2, 112.0, 113.4 (Py-CH), 120.7, 125.4, 126.3, 126.7, 126.9, 127.2, 129.0, 129.3, 129.6, 132.0, 135.8, 140.7, 141.7, 148.4, 150.5, 154.2, 155.7 (Ar-CH), 169.7, 169.9 (Py-CH). Anal. Calcd. for $C_{42}H_{44}N_4Zr$: C, 72.47; H, 6.37; N, 8.05. Found: C, 71.64; H, 6.34; N, 8.12%. MS (CI) m/z 619 (M^+ − Ph).

$[ZrL^4(CH_2Bu^t)_3]$. Pentane (20 ml) was added to a Schlenk vessel charged with HL^4 (200 mg, 0.95 mmol) and $[Zr(CH_2Bu^t)_4]$ (356 mg, 0.95 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature in the absence of light under argon. The solvent was removed under reduced pressure. The yellow solid was redissolved in pentane (10 mL) and filtered and the solvent removed. A thick yellow oil was obtained. ^{1}H NMR (293 K, d_6-benzene) δ 1.24 (s, 27H, Bu^t), 1.59 (s, 6H, CH_2), 1.76 (d, 3H, $^3J_{HH}$ = 7 Hz, CH_3), 2.16 (s, 3H, Py-CH_3), 4.99 (q, 1H, $^3J_{HH}$ = 7 Hz, CH), 5.72 (d, $^3J_{HH}$ = 8 Hz), 5.84 (d, 1H, $^3J_{HH}$ = 8 Hz), 6.74 (t, 1H, $^3J_{HH}$ = 8 Hz, Py-CH), 7.12 (m, 1H), 7.26 (t, 2H, $^3J_{HH}$ = 7 Hz), 7.53 (d, 2H, $^3J_{HH}$ = 7 Hz, Ar-CH). ^{13}C{^{1}H} NMR (293 K d_6-benzene) δ 21.2 (Ar-CH_3), 23.1 (CH_3), 35.1 (Np-Bu^t), 36.1 (Np-Cq), 56.1 (CH), 98.8 (Np-CH_2), 103.2, 110.7 (Py-CH), 126.8, 126.9, 128.7 (Ar-CH), 141.9 (Py-CH),144.8 (Ar-Cq), 154.4 (Py-Cq), 168.3 (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[18]). Structures were solved by direct methods (SHELXS[19]) 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[20] (control), SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics. See Table 4 for crystallographic data.

CCDC reference numbers 248563–248565.

See http://www.rsc.org/suppdata/dt/b4/b413023e/ for crystallographic data in CIF or other electonicformat.

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