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Biaryl-bridged Schiff base complexes of zirconium alkyls: synthesis structure and stability

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Abstract

Three substituted salicylaldimine derivatives H_2L^{1-3} of 2,2′-diamino-6,6′-dimethylbiphenyl give, under appropriate conditions, isolable alkyls of zirconium [$ZrL^{1-3}R_2$] (R = CH_2Ph, CH_2Bu^t). Two molecular structures confirm their *cis*-α geometry (C_2-symmetric with *cis* alkyl ligands). They decompose via 1,2-migratory insertion of an alkyl group to imine, followed in some instances by a second similar reaction. The dimeric molecular structure of one such doubly-inserted product is presented. The kinetics of decomposition by this process are studied briefly, and it is noted that the rate increases with increased steric demand of the salicylaldimine unit.

Keywords: Zirconium alkyls; Schiff base complexes; Synthesis

1. Introduction

Coates [1] and Fujita [2] have recently developed salicylaldimine (iminophenolate, IP) complexes of the Group 4 metals, [$M(IP)_2Cl_2$] (Fig. 1), which yield extremely active catalysts for the polymerisation of alkenes. It is assumed, quite reasonably, that metal alkyls are involved in these catalyses [1,2], but to our knowledge such species, [$M(IP)_2R_2$], have never been characterised. Indeed, Schiff base complexes of early transition metal alkyls are rather rare.

Floriani showed that alkylation of the Schiff base complex [Ti(acen)Cl(THF)] may be achieved by reaction with nucleophilic alkylating agents in THF solution with the loss of coordinated THF [3]. The alkylation of [$Ti(salen)Cl_2$] is less straightforward and found to be dependent on the alkylating agent involved [4,5]. Outcomes include dialkylation, monoalkylation with reduction of the titanium centre, and monoalkylation with reduction of a ligand imine group. These reactions highlight a fundamental issue in the chemistry of Schiff base complexes; the imine units are electrophilic, particularly so when coordinated to an early transition metal [6]. Jordan has explored the chemistry of zirconium complexes bearing acen ligands, and has exploited the method of introducing Schiff base ligands via protonolysis with a metal tetraalkyl [7]. This avoids the problem of using nucleophilic alkylating agents.

We have developed salicylaldimine proligands based on 2,2′-diamino-6,6′-dimethylbiphenyl (i.e. H_2L, Scheme 1). Our first reports in this area detailed the chemistry of various halide, amide and alkyl complexes of the zirconium system [8]. While these represented the first examples of *cis*-α N_2O_2 Schiff base complexes, it was found that the *cis*-dichloride complex (R = ^{t}Bu) was completely inactive as a catalyst precursor for alkene polymerisation. In order to understand why this is the case [9] we required the synthesis of the alkyls [$ZrLR_2$]. Attempts at the synthesis of alkyl complexes from the chlorides using conventional alkylating agents proved unsuccessful (c.f. Floriani) [3]. Reaction of H_2L (R = ^{t}Bu) with zirconium tetrabenzyl gave an orange precipitate, which was found to be an impure sample of

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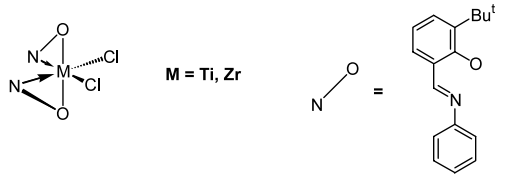


Fig. 1. Group IV iminophenolate complexes developed by Coates and Fujita.

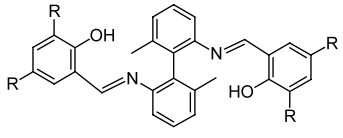
the desired dibenzyl complex. The complex was found to decompose readily in solution (< 12 h at −30 °C) to unidentified products [8]. A similar reaction of H_2L (R = H) with zirconium tetrabenzyl gave an orange material that was insoluble in all suitable solvents. Mass spectrometry and CHN analysis gave promising indications of this being the desired complex, $[ZrL(CH_2Ph)_2]$, but it could not be further characterised.

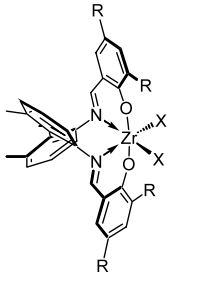
On the basis of these preliminary results we proposed to tune the ligand alkyl groups (R, Scheme 1), such that the complexes would be both sufficiently soluble and stable for analysis. The products of this work are currently being used in a detailed study of the mechanism of their decomposition, and some preliminary results have been communicated [9].

2. Results and discussion

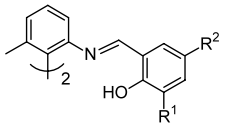
2.1. Synthesis of proligands, H_2L^{1-3}

The salicylaldehydes required for the synthesis of proligands H_2L^{1-3} (Fig. 2) are not commercially available and were accessed by formylation of the coresponding phenol. Many literature procedures for this reaction





Scheme 1. Biaryl bridged iminophenolate proligands and corresponding zirconium complexes [8].



H_2L^1 $R^1 = R^2 = Me$
H_2L^2 $R^1 = {}^iPr$, $R^2 = H$
H_2L^3 $R^1 = H$, $R^2 = {}^tBu$

Fig. 2. Numbering scheme for proligands.

type exist [10]. We found that the most efficient by some margin was that reported by Skattebøl and Hofsløkken [11].

2.2. Synthesis and structure of $[ZrL^{1-3}R_2]$

The reaction of stoichiometric amounts of $H_2\mathbf{L^1}$ and $[Zr(CH_2Ph)_4]$ in dichloromethane at −78 °C gave, according to the ^{1}H-NMR spectrum the desired dialkyl complex (vide infra) with impurities (ca. 15%). Purification by recrystallisation was attempted using various solvents and solvent combinations, but this generally gave poor yields of impure material, which was not surprising giving the thermally sensitive nature of the complex in solution. We found that the complex has very low solubility in acetonitrile, whilst the proligand and $[Zr(CH_2Ph)_4]$ are reasonably soluble at reduced temperatures. Accordingly, the reaction of H_2L^1 with a slight excess of $[Zr(CH_2Ph)_4]$ in acetonitrile at −50 °C gave an orange precipitate which was shown to be $[ZrL^1(CH_2Ph)_2]$ in reasonably high purity. The complex $[ZrL^2(CH_2Ph)_2]$ was synthesised in a similar manner. The reaction of $H_2\mathbf{L^3}$ with $[Zr(CH_2Ph)_4]$ in acetonitrile did not however produce the desired result since H_2L^3 is rather insoluble in acetonitrile. The reaction of H_2L^3 with $[Zr(CH_2Ph)_4]$ in dichloromethane at −78 °C yielded an orange solid which was found to be the desired complex $[ZrL^3(CH_2Ph)_2]$ in reasonable purity.

The ^{1}H-NMR spectrum of $[ZrL^2(CH_2Ph)_2]$, shown in Fig. 3, contains a single imine peak at δ 7.82 ppm. This and other features of the spectrum indicate that the complex is C_2-symmetric, consistent with the *cis*-α topography (vide infra). A pair of AB doublets at ca. δ 1.51 and 1.88 ppm is assigned to the diastereotopic CH_2Ph groups. In addition, the isopropyl methyl groups on the phenolic ring of the ligand are diastereotopic and are observed as a pair of doublets at δ 1.40 and 1.21 ppm. The above complexes were found to decompose in solution over a period of several hours.

Treatment of H_2L^1 with $[Zr(CH_2CMe_3)_4]$ in an NMR tube indicated clean formation of the desired C_2-symmetric product, $[Zr\mathbf{L^1}(CH_2CMe_3)_2]$. This was found to be thermally unstable in solution, although the apparent rate of decomposition was considerably reduced, occurring over a period of several days compared to hours for the similar benzyl complexes. The complex,

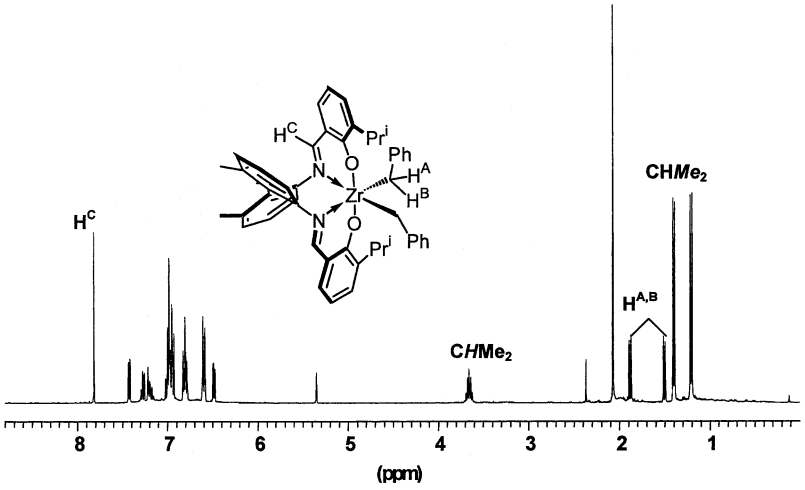


Fig. 3. ^{1}H-NMR spectrum of $[ZrL^2(CH_2Ph)_2]$ at 298 K in d_2-dichloromethane.

and similar derivatives of L^2 and L^3 were isolated successfully. NMR spectra were analogous to those recorded for the benzyl complexes.

The relative stability of these complexes allowed for recrystallisation from toluene, yielding samples of $[ZrL^1(CH_2CMe_3)_2]$ and $[ZrL^2(CH_2CMe_3)_2]$ suitable for X-ray crystallographic analysis. The structures obtained (Figs. 4 and 5) confirmed the *cis*-α geometry. The molecules have approximate C_2-symmetry as shown in Fig. 6. The Zr–O and Zr–N distances and O(1)–Zr–O(2) and N(1)–Zr–N(2) angles are similar in both complexes (Table 1). These angles and distances are in good agreement with the molecular structure of a similar chloride complex [8]. The Zr–C distances for the metal bound neopentyl groups are also similar in both complexes and are comparable with reported zirconium compounds [12]. The C–Zr–C′ angles are significantly different between the two complexes, being more acute in $[ZrL^2(CH_2CMe_3)_2]$ (ca. 107°) than in $[ZrL^1(CH_2CMe_3)_2]$ (ca. 115°). Also, the angles between the planes of O–Zr–O′ and C–Zr–C′ are 86.9(14) and 78.8(12)° for complexes $[ZrL^1(CH_2CMe_3)_2]$ and $[ZrL^2(CH_2CMe_3)_2]$, respectively. We suggest that these differences arise from the greater steric compression between phenolate *ortho*-alkyl substituents and the metal-bound alkyl groups for L^2 than for L^1.

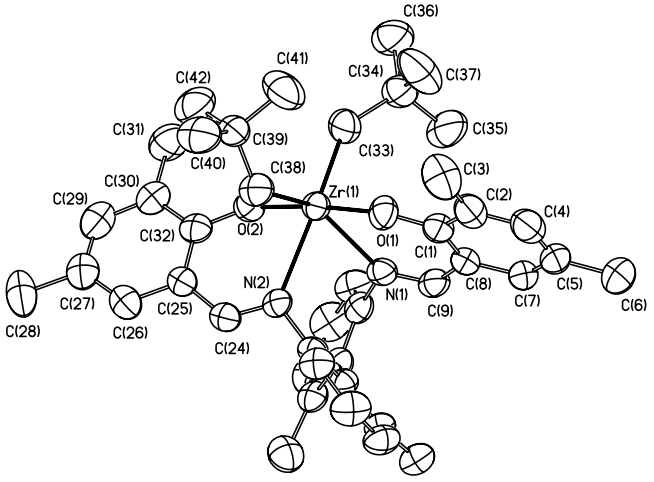


Fig. 4. X-ray crystallographic molecular structure of $[ZrL^1(CH_2CMe_3)_2]$.

2.3. Products of decomposition of $[ZrL^{1-3}R_2]$

NMR tubes were charged with solutions of the pure zirconium benzyl complexes of $\mathbf{L^{1-3}}$ at 298 K and ^{1}H-NMR spectra were recorded at intervals. In the case of $[ZrL^1(CH_2Ph)_2]$, after ca. 3 h the formation of one major product was noted. The NMR spectrum (Fig. 7) indicated that a diastereoselective 1,2-migratory insertion of a benzyl group to the ligand was occurring (Scheme 2). A new peak at δ 8.34 ppm corresponds to the imine hydrogen atom of the new complex (H^{D*}). The new peaks appearing at δ 5.64, 3.46 and 2.90 ppm (expanded for clarity in Fig. 7) correspond to the formation of a new stereogenic centre at the former imine carbon. The doublets of doublets at ca. δ 3.46 and 2.90 ppm are assigned to the migrated diastereotopic CH_2Ph group (H^{A*} and H^{B*}, Scheme 2) and the doublet of doublets at ca. δ 5.64 ppm are attributed to the hydrogen at the new chiral α-amido carbon (H^{C*}). The product formed from migratory insertion has C_1-symmetry, and a total of six new methyl resonances are observed. The remaining zirconium bound benzyl group is observed as a pair of AB doublets at δ 2.47 and 2.21 ppm, assigned with reference to COSY and HMQC experiments.

We have described a similar reaction to the above in a titanium benzyl complex [13], but here the 1,2-migratory insertion occurred at a similar rate to that of the complex formation, making analysis of the kinetics difficult. Also, unlike the titanium complex, the 1,2-

Table 1
Selected bond lengths and angles for molecular structures of $[ZrL^1(CH_2CMe_3)_2]$ and $[ZrL^2(CH_2CMe_3)_2]$

$[ZrL^1(CH_2CMe_3)_2]$		$[ZrL^2(CH_2CMe_3)_2]$	
Bond lengths			
Zr(1)–O(2)	2.023(3)	Zr(1)–O(2)	2.022(3)
Zr(1)–O(1)	2.026(3)	Zr(1)–O(1)	2.030(3)
Zr(1)–C(33)	2.271(5)	Zr(1)–C(35)	2.261(6)
Zr(1)–C(38)	2.287(5)	Zr(1)–C(40)	2.268(6)
Zr(1)–N(1)	2.418(4)	Zr(1)–N(1)	2.412(4)
Zr(1)–N(2)	2.425(4)	Zr(1)–N(2)	2.418(4)
Bond angles			
O(2)–Zr(1)–O(1)	175.04(14)	O(2)–Zr(1)–O(1)	176.04(14)
N(1)–Zr(1)–N(2)	71.33(12)	N(1)–Zr(1)–N(2)	70.92(12)
C(33)–Zr(1)–C(38)	115.53(19)	C(35)–Zr(1)–C(40)	107.2(2)

migratory insertion product from $[ZrL^1(CH_2Ph)_2]$ undergoes a further decomposition and the ^{1}H-NMR spectra become very complex. The disappearance of peaks in the imine region of the ^{1}H-NMR spectrum indicates that the remaining metal bound benzyl group undergoes migratory insertion to the second imine unit.

The decomposition of $[Zr\mathbf{L^2}(CH_2Ph)_2]$ was also followed by ^{1}H-NMR spectroscopy. This revealed that a 1,2-migratory insertion process, similar to that for $[Zr\mathbf{L^1}(CH_2Ph)_2]$, occurs and is followed again by a more complex 1,2-migratory insertion decomposition (Scheme 3). In this instance we were able to isolate a few crystals of a product $[\{ZrL^{2'}\}_2]$, which were analysed by X-ray crystallography (Fig. 8).

The four coordinate species resulting from the second 1,2-migratory insertion (Scheme 3), dimerises through bridging of one oxygen atom from each ligand to the two zirconium centres. Within the monomer unit the atropisomeric biaryl has (at least for the observed diastereomer) directed the stereochemistry of 1,2-migratory insertion for both benzyl groups in the same absolute sense. Thus, $[Zr\{(S)\text{-}L^2\}(CH_2Ph)_2]$ has given rise to (S,S) stereochemistry for the migrated benzyl groups on the α-amino carbon atoms and $[Zr\{(R)\text{-}L^2\}(CH_2Ph)_2]$ has given (R,R) configuration. The dimer which crystallised is however heterochiral, i.e. composed of both these enantiomers. Given that this and similar species have at least eight elements of chirality, the observation of a mixture of products in solution is not surprising.

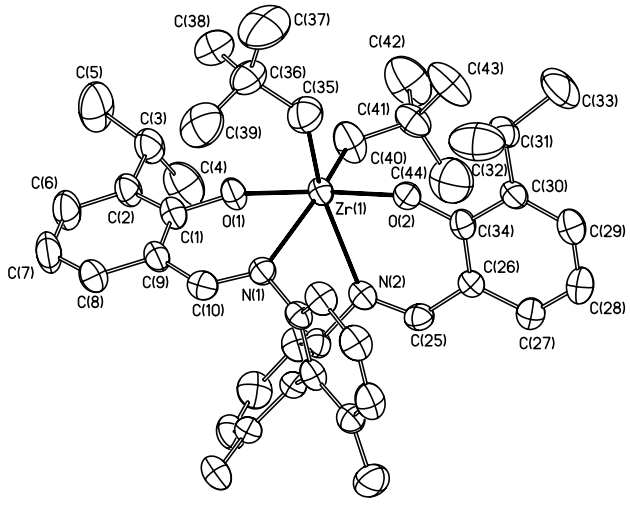
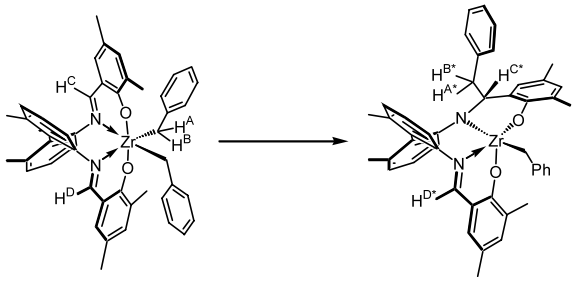


Fig. 5. X-ray crystallographic molecular structure of $[ZrL^2(CH_2CMe_3)_2]$.



Scheme 2. 1,2-Migratory insertion of a metal bound benzyl group to an imine carbon.

The decomposition of the complex $[ZrL^3(CH_2Ph)_2]$ was also followed by ^{1}H-NMR spectroscopy. Again the highly diastereoselective 1,2-migratory insertion of a benzyl group from metal centre to an imine carbon was observed, but unlike $[ZrL^{1,2}(CH_2Ph)_2]$, the product formed from this decomposition was stable with respect to the second migratory insertion reaction [13].

2.4. Rates of decomposition for $[ZrL^{1-3}(CH_2Ph)_2]$

Since the decomposition of complexes $[ZrL^{1-3}(CH_2Ph)_2]$ occurred over a period of ca. 12–24 h, ^{1}H-NMR spectroscopy provided an ideal means for obtaining kinetic data. The NMR solvent of choice was

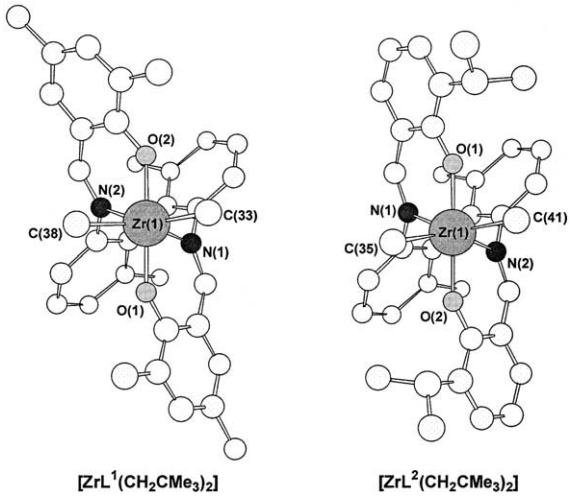


Fig. 6. Comparison of $[ZrL^1(CH_2CMe_3)_2]$ and $[ZrL^2(CH_2CMe_3)_2]$ highlighting the C_2-symmetry and *cis*-α geometry of the complexes (*tert*-butyl groups removed).

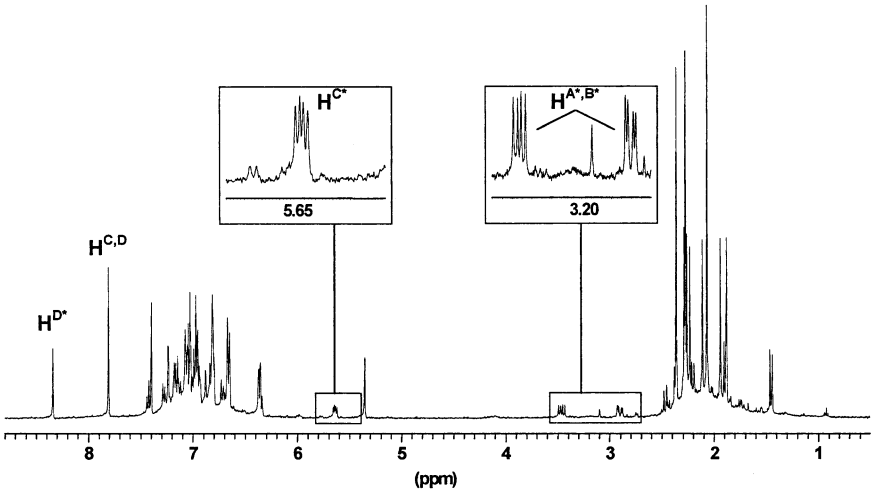


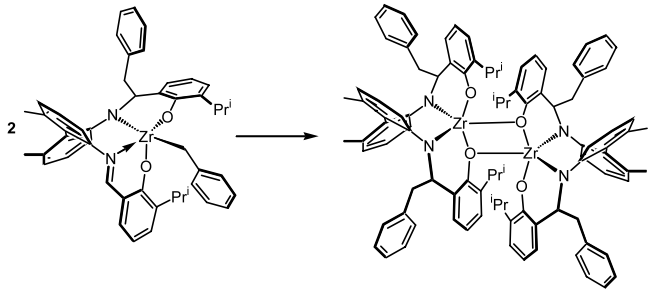
Fig. 7. ^{1}H-NMR spectrum of [ZrL^1(CH$_2$Ph)$_2$] at 298 K in d_2-dichloromethane after 3 h.

d_2-dichloromethane, as this was found to have a residual protio solvent resonance completely separated from peaks associated with all three complexes as well as their decomposition products. The complexes (ca. 15 mg) were dissolved in d_2-dichloromethane and ^{1}H-NMR spectra recorded at set time intervals over a period of several hours. The rate of loss of starting material was measured by comparison of the integral of the imine peak with the residual protio resonance of the solvent. The kinetic plots are shown in Fig. 9 and the relative rates of decomposition shown in Table 2.

These results show that there is very little difference in the decomposition rate for the initial 1,2-migratory insertion between H and Me groups at the R^1 position. Upon increasing steric bulk at R^1 to an isopropyl group a significant increase in the rate of decomposition is observed. It might then be expected that the more sterically demanding *tert*-butyl group would show an even greater increase in rate of decomposition, and indeed we have noted the rapid decomposition of such a compound [8].

3. Conclusion

It has been shown that by careful ligand and solvent choice it is possible to isolate biaryl-bridged Schiff base complexes of zirconium alkyls which have a predetermined *cis*-α geometry. However, the imine units are subject to a 1,2-migratory insertion of a metal bound alkyl group from the metal centre. Evidently, steric effects control these processes; increasing the size of the alkyl groups at the position *ortho* to the phenolate creates compression at the metal centre, which is alleviated upon migration of a metal-bound alkyl to the ligand. Given this instability, the lack of alkene polymerisation activity in the system is not surprising, although we have recently shown that with suitable modification a stable polymerisation system can be accessed [9].



Scheme 3. Secondary 1,2-migratory insertion and subsequent dimerisation.

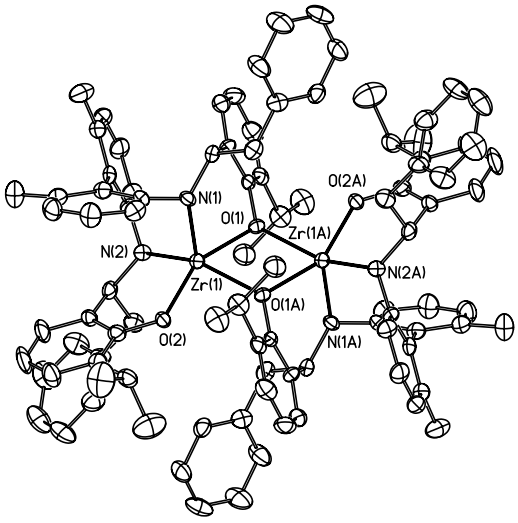


Fig. 8. X-ray crystallographic molecular structure of secondary decomposition product of [ZrL^2(CH$_2$Ph)$_2$]; hydrogen atoms omitted.

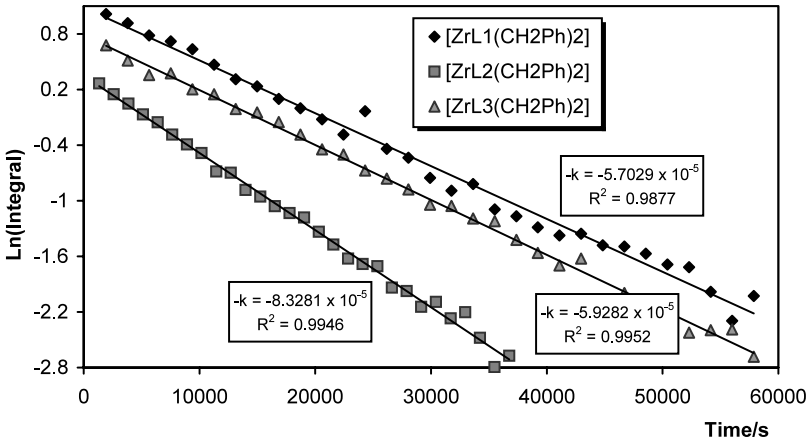


Fig. 9. Plot of ln(integral of imine peak) vs. time/s for $[ZrL^{1-3}(CH_2Ph)_2]$ at 298 K.

4. Experimental

4.1. General details

Unless stated otherwise, organic preparations were carried out in air. Organometallic manipulations were performed under an atmosphere of dry argon, using conventional Schlenk line techniques and an MBraun glove box (< 1 ppm O_2/H_2O). For organometallic preparations, hydrocarbon and ether solvents were pre-dried over sodium wire. These were then dried under reflux conditions over sodium (for toluene), potassium (THF and benzene), sodium–potassium alloy (diethyl ether, petroleum ether and pentane), then distilled and degassed before use. Dichloromethane and acetonitrile were dried under reflux conditions over calcium hydride then distilled and degassed. Deuterated solvents were degassed by the freeze-thaw method and dried over potassium (toluene, benzene and THF) or calcium hydride (dichloromethane and acetonitrile) before trap-to-trap distillation and storage in the glove box. NMR samples of air sensitive species were prepared in the glovebox in tubes sealed with Young's concentric stopcocks.

Unless stated otherwise, commercial chemical reagents were used as received. Chiral ligands and complexes were racemic mixtures unless stated otherwise.

NMR spectra were recorded at ca. 298 K on Bruker AC-250, DPX-300, DPX-400 or AC-400 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0.0$ ppm). Proton and carbon NMR assignments were confirmed routinely by $^1H-^1H$ (COSY) or $^1H-^{13}C$ (HMQC) experiments. NMR kinetic data were obtained using Bruker AC-400 or DPX-500 spectrometer with calibrated temperature probes. Infra-red spectra were carried out on sodium chloride plates in an airtight holder, and obtained as thin film (dichloromethane as solvent) or nujol mulls on a Perkin–Elmer FT-IR spectrometer. EI and CI mass spectra were obtained on a VG Autospec mass spectrometer. Elemental analyses were performed by Warwick Analytical Services. For many complexes, analyses of % C were found to be lower than calculated values; this is frequently the case in such systems [14].

Table 2
Rates of decomposition for $[ZrL^{1-3}(CH_2Ph)_2]$ at 298 K

Complex	R^1	k_{obs} 10^{-5} s^{-1}	k_{rel} [a]
$[ZrL^1(CH_2Ph)_2]$	Me	5.70 (±0.12)	1
$[ZrL^2(CH_2Ph)_2]$	Pr^i	8.33 (±0.12)	1.46
$[ZrL^3(CH_2Ph)_2]$	H	5.93 (±0.08)	1.04

[a] Relative rate constant, k_{rel}, vs. $[Zr\mathbf{L^1}(CH_2Ph)_2]$.

4.2. Synthesis of salicylaldehydes [11]

The reaction was performed under argon to prevent moist air from entering the reaction vessel. Acetonitrile and triethylamine were dried over CaH_2, paraformaldehyde dried over P_2O_5 and anhydrous $MgCl_2$ (98%) purchased from Aldrich was dried over P_2O_5 at 120 °C. A 1 l side arm round bottom flask with stirrer bar was placed under an argon atmosphere and charged with the appropriate phenol (100 mmol) and dry acetonitrile (500 ml). To this was added dry triethylamine (52.2 ml, 375 mmol), anhydrous $MgCl_2$ (14.28 g, 150 mmol) and the solution was stirred for 15 min. Dry paraformaldehyde (20.25 g, 675 mmol) was added and a wide bore condenser fitted to the round bottom flask. The solution was heated at reflux temperature under argon for ca. 2.5 h. The solution was allowed to cool to room temperature and added to 5% aq. HCl (800 ml) followed by stirring for 30 min. This was extracted with diethyl ether (7×100 ml portions) and the ether fractions collected together and washed with saturated $NaCl_{(aq)}$ (3×100 ml portions). The ether layer was dried over anhydrous

$MgSO_4$ followed by filtration. Volatiles were removed under reduced pressure to yield the corresponding salicylaldehydes, usually contaminated with the starting phenol. Purification prior to reaction with the biaryl diamine (vide infra) was found to be generally unnecessary, as the Schiff base product precipitates from the reaction solution. Samples of the products were nevertheless isolated and fully characterised, as described below.

4.2.1. 3,5-Dimethyl-2-hydroxybenzaldehyde

Using the above procedure with 2,4-dimethylphenol (12.21 g) the reaction mixture was heated at reflux temperature for 3 h. During this period the solution turned yellow. A yellow oil was obtained (14.21 g) which was found to contain 3,5-dimethyl-2-hydroxybenzaldehyde (94% by ^{1}H-NMR). A sample of the oil (2.00 g) was purified by column chromatography (hexane–diethyl ether 6:1).

Yield = 1.79 g, 90% (from 2 g of crude product).

Anal. Found (Calc. for $C_9H_{10}O_2$): C, 71.89 (71.99); H, 6.72% (6.71).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 11.07 (s, 1H, ArO*H*), 9.81 (s, 1H, *H*C=O), 7.20 (s, 1H, Ar*H*), 7.16 (s, 1H, Ar*H*), 2.29 (s, 3H, *Me*), 2.23 (s, 3H, *Me*).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 196.6 (H*C*=O), 157.8, 139.0, 130.8, 128.4, 126.4, 119.6 (Ar), 20.1 (*Me*), 14.8 (*Me*).

IR (CH_2Cl_2 Thin film): ν cm^{-1} 3163 (b, OH), 3103, 2923, 2845, 2740, 1652 (s, C=O), 1621, 1470, 1415, 1380, 1323, 1263 (s, C–O), 1214, 1165, 1036, 969, 953, 863, 788, 745, 711.

MS (EI) *m*/*z* 150 $[M]^+$, 149 $[M-H]^+$, 135 $[M-CH_3]^+$, 121 $[M-CHO]^+$.

4.2.2. 3-Isopropyl-2-hydroxybenzaldehyde

Using the general procedure, 2-isopropylphenol (13.60 g) was used as the reagent and the reaction mixture heated at reflux temperature for 2.5 h, during which time the solution turned yellow. A yellow oil was obtained (14.85 g) and analysis by ^{1}H-NMR spectroscopy revealed it to contain 3-isopropyl-2-hydroxybenzaldehyde (90%). A small sample of the product mixture (1.00 g) was purified by column chromatography (hexane–diethyl ether 4:1). Yield = 0.84 g, 84% (from 1 g of crude product).

Anal. Found (Calc. for $C_{10}H_{12}O_2$): C, 72.71 (73.15); H, 7.44% (7.37).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 11.37 (s, 1H, ArO*H*), 9.87 (s, 1H, *H*C=O), 7.46 (dd, 1H, Ar*H*, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 2$ Hz), 7.38 (dd, 1H, Ar*H*, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz), 6.97 (t, 1H, Ar*H*, $^3J_{HH} = 8$ Hz), 3.37 (m, 1H, C*H*Me$_2$, $^3J_{HH} = 7$ Hz), 1.24 (d, 6H, CH*Me*$_2$, $^3J_{HH} = 7$ Hz).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 196.7 (H*C*=O), 159.0, 136.9, 133.4, 131.1, 120.0, 119.4 (*Ar*), 26.0 (*C*HMe$_2$), 22.0 (CH*Me*$_2$).

IR (Thin film): ν cm^{-1} 3049 (w, OH), 2964, 2870, 2843, 2746, 2361, 2342, 1652 (s, C=O), 1616, 1439, 1386, 1363, 1308, 1265 (s, C–O), 1219, 1175, 1151, 1109, 1100, 1050, 1010, 968, 924, 878, 827, 790, 753, 697, 681, 668, 642.

MS (EI) *m*/*z* 164 $[M]^+$, 149 $[M-CH_3]^+$.

4.2.3. 5-tert-Butyl-2-hydroxybenzaldehyde

Using the general procedure with 4-*tert*-butylphenol (15.00 g), the mixture was heated at reflux temperature for 3 h, during which time the solution turned yellow. A yellow oil was obtained which ^{1}H-NMR spectra showed to be 5-*tert*-butyl-2-hydroxybenzaldehyde (99% purity).

Yield = 17.53 g, 98%.

Anal. Found (Calc. for $C_{11}H_{14}O_2$): C, 73.38 (74.13); H, 7.93% (7.92).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 10.86 (s, 1H, ArO*H*), 9.87 (s, 1H, *H*C=O), 7.57 (dd, 1H, Ar*H*, $^3J_{HH} = 9$ Hz, $^4J_{HH} = 3$ Hz), 7.50 (d, 1H, Ar*H*, $^4J_{HH} = 3$ Hz), 6.92 (d, 1H, Ar*H*, $^3J_{HH} = 9$ Hz), 1.31 (s, 9H, C*Me*$_3$).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 190.7 (H*C*=O), 159.3, 142.6, 134.6, 129.6, 119.8, 117.0 (*Ar*), 33.9 (*C*Me$_3$), 31.1 (C*Me*$_3$).

IR (Thin film): ν cm^{-1} 3197 (b, OH), 3077, 2963, 2909, 2869, 2743, 2396, 2254, 2064, 1917, 1730, 1700, 1657 (s, C=O), 1622, 1592, 1485, 1395, 1376, 1363, 1318, 1289, 1265 (s, C–O), 1230, 1185, 1136, 1106, 1025, 924, 890, 834, 775, 733, 654, 601.

MS (EI) *m*/*z* 178 $[M]^+$, 163 $[M-CH_3]^+$, 161 $[M-OH]^+$, 148 $[M-(CH_3)_2]^+$, 133 $[M-(CH_3)_3]^+$.

4.3. Synthesis of Schiff base proligands, H_2L^{1-3}

A 100 ml round bottom flask with stirrer bar was charged with the appropropiate salicylaldehyde and a stoichiometric amount of the amine 2,2′-diamino-6,6′-dimethylbiphenyl. The reactants were dissolved in ethanol or methanol (40–100 ml), and heated at reflux for ca. 18 h, using a condenser fitted with a drying tube containing $CaCl_2$. A precipitate generally formed during the reaction and the solid was isolated by vacuum filtration and washed with cold ethanol or methanol. All remaining volatiles were removed in vacuo.

4.3.1. H_2L^1

Following the general procedure, 3,5-dimethyl-2-hydroxybenzaldehyde (4.31 g, 28.54 mmol), 2,2′-diamino-6,6′-dimethylbiphenyl (3.05 g, 14.39 mmol) and ethanol (50 ml) were used. A bright orange solid was obtained.

Yield = 6.45 g, 95%.

Anal. Found (Calc. for $C_{32}H_{32}N_2O_2$): C, 80.69 (80.64); H, 6.80 (6.77); N, 6.00% (5.88).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 12.12 (s, 2H, ArO*H*), 8.32 (s, 2H, N=C*H*), 7.32 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.21 (d, 2H, Ar*H*, $^3J_{HH}$ = 7 Hz), 7.01 (d, 2H, Ar*H*, $^3J_{HH}$ = 7 Hz), 6.94 (s, 2H, Ar*H*), 6.82 (s, 2H, Ar*H*), 2.21 (s, 6H, *Me*), 2.12 (s, 6H, *Me*), 2.04 (s, 6H, *Me*).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 162.3 (N=*C*H), 157.0, 147.4, 137.0, 134.8, 133.2, 129.7, 128.4, 128.2, 126.9, 125.7, 118.1, 115.5 (*Ar*), 20.2 (*Me*), 19.8 (*Me*), 15.5 (*Me*).

IR (CH_2Cl_2 Thin film): ν cm^{-1} 2919, 2361, 1622 (s, N=C), 1598, 1569, 1470, 1435, 1379, 1362, 1324, 1283, 1266 (s, C–O), 1242, 1220, 1167, 1108, 1049, 1019, 975, 943, 860, 806, 788, 751, 738, 700.

MS (EI) *m*/*z* 476 $[M]^+$, 461 $[M-CH_3]^+$.

4.3.2. H_2L^2

Following the general procedure, 3-isopropyl-2-hydroxybenzaldehyde (4.50 g, 27.27 mmol), 2,2′-diamino-6,6′-dimethylbiphenyl (2.91 g, 13.73 mmol) and ethanol (50 ml) were used. A bright yellow solid was obtained.

Yield = 6.42 g, 93%.

Anal. Found (Calc. for $C_{34}H_{36}N_2O_2$): C, 80.88 (80.92); H, 7.17 (7.19); N, 5.60% (5.55).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 12.54 (s, 2H, ArO*H*), 8.42 (s, 2H, N=C*H*), 7.33 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.22 (d, 2H, Ar*H*, $^3J_{HH}$ = 7 Hz), 7.20 (dd, 2H, Ar*H*, $^4J_{HH}$ = 1 Hz), 7.05 (dd, 2H, Ar*H*, $^4J_{HH}$ = 1 Hz), 7.03 (d, 2H, Ar*H*, $^3J_{HH}$ = 7 Hz), 6.79 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 3.24 (m, 2H, C*H*Me$_2$, $^3J_{HH}$ = 7 Hz), 2.06 (s, 6H, *Me*$_i$), 1.16 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 7 Hz), 1.15 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 7 Hz).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 162.3 (N=*C*H), 158.5, 147.1, 137.0, 136.2, 133.3, 129.7, 129.2, 128.4, 128.3, 118.5, 118.2, 115.5 (*Ar*), 26.3 (*C*HMe$_2$), 22.3 (CH*Me*$_2$), 22.2 (CH*Me*$_2$), 19.8 (*Me*).

IR (CH_2Cl_2 Thin film): ν cm^{-1} 3058 (w, OH), 2961, 2869, 2360, 2341, 1613 (s, N=C), 1569, 1458, 1438, 1382, 1306, 1264 (m, C–O), 1218, 1176, 1151, 1108, 1097, 1051, 982, 944, 881, 826, 797, 771, 750 (s), 700, 668.

MS (EI) *m*/*z* 504 $[M]^+$, 489 $[M-CH_3]^+$.

4.3.3. Synthesis of H_2L^3

Following the general procedure, 5-*tert*-butyl-2-hydroxybenzaldehyde (8.00 g, 44.9 mmol), 2,2′-diamino-6,6′-dimethylbiphenyl (4.73 g, 22.3 mmol) and ethanol (100 ml) were used. An orange/yellow solid was obtained.

Yield = 10.96 g, 92%.

Anal. Found (Calc. for $C_{36}H_{40}N_2O_2$): C, 80.82 (81.17); H, 7.55 (7.57); N, 5.21% (5.26).

^{1}H-NMR 300 MHz ($CDCl_3$): δ ppm 12.15 (s, 2H, ArO*H*), 8.57 (s, 2H, N=C*H*), 7.39 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.31 (dd, 2H, Ar*H*, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 2 Hz), 7.28 (d, 2H, Ar*H*), 7.27 (d, 2H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.16 (d, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.80 (d, 2H, Ar*H*, $^3J_{HH}$ = 9 Hz), 2.07 (s, 6H, *Me*), 1.27 (s, 18H, C*Me*$_3$).

^{13}C{^{1}H}-NMR 75 MHz ($CDCl_3$): δ ppm 161.4 (N=*C*H), 158.5, 146.3, 141.2, 137.0, 133.9, 130.0, 130.0, 128.4, 128.3, 118.4, 116.5, 114.8 (*Ar*), 33.8 (*C*Me$_3$), 31.2 (C*Me*$_3$), 19.7 (*Me*).

IR (CH_2Cl_2 Thin film): ν cm^{-1} 3426 (b, OH), 2962, 2361, 1623 (s, N=C), 1566, 1490, 1461, 1394, 1364, 1289, 1265 (s, C–O), 1246, 1209, 1184, 1136, 1108, 1019, 978, 938, 886, 826, 809, 792, 750.

MS (EI) *m*/*z* 532 $[M]^+$, 517 $[M-CH_3]^+$.

4.4. Synthesis of zirconium benzyl complexes

4.4.1. $[ZrL^1(CH_2Ph)_2]$

A Schlenk vessel with stirrer bar was charged with H_2L^1 (246 mg, 0.52 mmol) and [Zr(CH$_2$Ph)$_4$] (252 mg, 0.55 mmol). The vessel was placed in an acetone/dry ice bath at −78 °C and acetonitrile (20 ml) added. This was transferred to an ice bath at 0 °C and allowed to stir for 20 min. An orange precipitate formed and was isolated by filtration at 0 °C, followed by washing with cold acetonitrile. The orange solid was dried in vacuo.

Yield = 251 mg, 65%.

Anal. Found (Calc. for $C_{46}H_{44}N_2O_2Zr$): C, 72.09 (73.86); H, 5.83 (5.93); N, 4.42% (3.74).

^{1}H-NMR 400 MHz (CD_2Cl_2): δ ppm 7.77 (s, 2H, N=C*H*), 7.20 (s, 2H, Ar*H*), 7.01 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.98 (d, 2H, Ar*H*), 6.93 (t, 4H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.78 (t, 2H, Ar*H*), 6.77 (s, 2H, Ar*H*), 6.63 (d, 4H, Ar*H*, $^3J_{HH}$ = 7 Hz), 6.34 (dd, 2H, Ar*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 2.33 (s, 6H, *Me*), 2.24 (s, 6H, *Me*), 2.04 (s, 6H, *Me*), 1.87 (d, 2H, C*H*$_2$Ph, $^2J_{HH}$ = 8 Hz), 1.44 (d, 2H, C*H*$_2$Ph, $^2J_{HH}$ = 8 Hz).

^{13}C{^{1}H}-NMR 75 MHz (CD_2Cl_2): δ ppm 168.8 (N=*C*H), 160.0, 150.0, 144.2, 138.2, 137.0, 132.1, 131.2, 128.7, 128.5, 128.2, 128.1, 127.2, 127.2, 121.2, 121.2, 119.9 (*Ar*), 60.8 (*C*H$_2$Ph), 20.4 (*Me*), 19.9 (*Me*), 17.2 (*Me*).

IR (Nujol): ν cm^{-1} 2729, 2360, 1615 (s, N=C), 1591, 1557, 1295, 1264 (s, C–O), 1218, 1173, 1098, 1054, 1028, 973, 965, 942, 899, 848, 825, 802, 759, 749, 737, 698.

MS (EI) *m*/*z* 656 $[M-CH_2Ph]^+$, 565 $[M-(CH_2Ph)_2]^+$, 550 $[M-\{(CH_2Ph)_2$ and $CH_3\}]^+$.

4.4.2. $[ZrL^2(CH_2Ph)_2]$

Using the same procedure as Section 4.4.1, H_2L^2 (302 mg, 0.60 mmol) and [Zr(CH$_2$Ph)$_4$] (296 mg, 0.65 mmol) gave an orange/yellow solid.

Yield = 358 mg, 77%.

Anal. Found (Calc. for $C_{48}H_{48}N_2O_2Zr$): C, 72.40 (74.28); H, 6.09 (6.23); N, 3.14% (3.61).

^{1}H-NMR 400 MHz (CD_2Cl_2): δ ppm 7.82 (s, 2H, N=C*H*), 7.42 (dd, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.00 (t, 2H, Ar*H*), 6.99 (dd, 2H, Ar*H*), 6.98 (d, 2H, Ar*H*), 6.95 (t, 4H, Ar*H*), 6.81 (t, 2H, Ar*H*, $^3J_{HH}$ = 8

Hz), 6.80 (t, 2H, Ar*H*, $^3J_{HH}=7$ Hz), 6.60 (d, 4H, Ar*H*, $^3J_{HH}=7$ Hz), 6.49 (dd, 2H, Ar*H*, $^3J_{HH}=8$ Hz, $^4J_{HH}=2$ Hz), 3.66 (m, 2H, C*H*Me$_2$, $^3J_{HH}=7$ Hz), 2.07 (s, 6H, *Me*), 1.88 (d, 2H, C*H*$_2$Ph, $^2J_{HH}=9$ Hz), 1.51 (d, 2H, C*H*$_2$Ph, $^2J_{HH}=9$ Hz), 1.40 (d, 6H, CH*Me*$_2$, $^3J_{HH}=7$ Hz), 1.21 (d, 6H, CH*Me*$_2$, $^3J_{HH}=7$ Hz).

^{13}C{^{1}H}-NMR 75 MHz (CD_2Cl_2): δ ppm 169.0 (N=CH), 160.3, 150.0, 144.0, 138.7, 137.1, 132.5, 132.2, 131.5, 128.6, 128.5, 128.1, 127.9, 122.0, 121.4, 119.9, 118.4 (*Ar*), 60.7 (*C*H$_2$Ph), 26.5 (*C*HMe$_2$), 24.1 (CH*Me*$_2$), 22.2 (CH*Me*$_2$), 20.0 (*Me*$_i$).

IR (Nujol): ν cm^{-1} 2283, 1604 (s, N=C), 1555, 1321, 1264 (m, C–O), 1233, 1215, 1149, 1106, 1050, 1022, 981, 944, 890, 852, 794, 751, 698.

MS (EI) *m*/*z* 760 [M−Me]$^+$, 745 [M−(Me)$_2$]$^+$, 689 [M−(Pr^i)$_2$]$^+$, 684 [M−(CH$_2$Ph)]$^+$, 669 [M−(CH$_2$Ph and Me)]$^+$, 598 [M−{CH$_2$Ph and (Pr^i)$_2$}].

4.4.3. [ZrL^3(CH$_2$Ph)$_2$]

A Schlenk vessel with stirrer bar was charged with H_2L^3 (504 mg, 0.94 mmol) and [Zr(CH$_2$Ph)$_2$] (450 mg, 0.99 mmol). The vessel was placed in a dry ice/acetone bath at −78 °C and dichloromethane (30 ml) was added. This was stirred for 30 min and then filtered at −78 °C, followed by removal of solvent under reduced pressure. The orange solid obtained was then washed with acetonitrile, filtered and dried in vacuo.

Yield = 601 mg, 79%.

Anal. Found (Calc. for $C_{50}H_{52}N_2O_2Zr$): C, 72.30 (74.68); H, 6.06 (6.52); N, 3.28% (3.48).

^{1}H-NMR 400 MHz (d_6-benzene): δ ppm 7.72 (s, 2H, N=C*H*), 7.23 (dd, 2H, Ar*H*, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz), 7.21 (t, 4H, Ar*H*, $^3J_{HH}=8$ Hz), 7.14 (d, 4H, Ar*H*, $^3J_{HH}=7$ Hz), 7.01 (t, 2H, Ar*H*, $^3J_{HH}=7$ Hz), 6.94 (d, 2H, Ar*H*, $^4J_{HH}=3$ Hz), 6.93 (d, 2H, Ar*H*, $^3J_{HH}=9$ Hz), 6.81 (t, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 6.58 (d, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 6.57 (d, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 2.31 (d, 2H, C*H*$_2$Ph, $^2J_{HH}=8$ Hz), 1.91 (d, 2H, C*H*$_2$Ph, $^2J_{HH}=8$ Hz), 1.82 (s, 6H, *Me*), 1.16 (s, 18H, C*Me*$_3$).

^{13}C{^{1}H}-NMR 100 MHz (d_6-benzene): δ ppm 168.5 (N=*C*H), 161.9, 149.8, 144.1, 140.6, 136.2, 134.2, 131.0, 130.2, 129.6, 128.6, 128.3, 128.1, 121.8, 121.5, 120.5, 119.6 (*Ar*), 61.1 (*C*H$_2$Ph), 31.8 (*C*Me$_3$), 31.3 (C*Me*$_3$), 19.7 (*Me*).

IR (Nujol): ν cm^{-1} 2726, 1614 (s, N=C), 1590, 1541, 1363, 1307, 1266 (m, C–O), 1208, 1180, 1143, 1127, 1026, 952, 882, 837, 771, 748, 700, 668.

MS (EI) *m*/*z* 804 [M$^+$], 789 [M$^+$−CH$_3$], 774 [M$^+$−(CH$_3$)$_2$], 759 [M$^+$−(CH$_3$)$_3$], 747 [M$^+$−Bu^t], 690 [M$^+$−(Bu^t)$_2$].

4.5. Synthesis of zirconium neopentyl complexes

4.5.1. [ZrL^1(CH$_2$CMe$_3$)$_2$]

A Schlenk vessel with stirrer bar was charged with H_2L^1 (511 mg, 1.07 mmol) and [Zr(CH$_2$CMe$_3$)$_4$] (410 mg, 1.09 mmol). This was cooled to −78 °C and dichloromethane (30 ml) added, with stirring of the solution. The solution was allowed to warm to room temperature and stirring was continued for a further 30 min, during which time the solution turned from yellow to orange. This was then filtered and the solvent removed under reduced pressure to yield a yellow/orange solid which was dried in vacuo. The product was recrystallised from toluene to yield crystals suitable for X-ray analysis. The product was also precipitated from pentane (100 ml) at −30 °C to yield a yellow/orange solid.

Yield = 646 mg, 85%.

Anal. Found (Calc. for $C_{42}H_{52}N_2O_2Zr$): C, 68.75 (71.24); H, 6.95 (7.40); N, 3.60% (3.96).

^{1}H-NMR 300 MHz (CD_2Cl_2): δ ppm 7.79 (s, 2H, N=C*H*), 7.21 (s, 2H, Ar*H*), 7.09 (t, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 7.01 (d, 2H, Ar*H*, $^3J_{HH}=7$ Hz), 6.91 (d, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 6.75 (s, 2H, Ar*H*), 2.38 (s, 6H, *Me*), 2.24 (s, 6H, *Me*), 2.12 (s, 6H, *Me*), 1.12 (d, 2H, C*H*$_2$CMe$_3$, $^2J_{HH}=13$ Hz), 0.92 (d, 2H, C*H*$_2$CMe$_3$, $^2J_{HH}=13$ Hz), 0.88 (s, 18H, CH$_2$C*Me*$_3$).

^{13}C{^{1}H}-NMR 75 MHz (CD_2Cl_2): δ ppm 170.3 (N=*C*H), 163.9, 150.4, 137.8, 137.2, 131.6, 131.6, 128.4, 127.7, 126.6, 120.9, 119.3 (*Ar*), 86.2 (*C*H$_2$CMe$_3$), 35.0 (CH$_2$*C*Me$_3$), 34.5 (CH$_2$C*Me*$_3$), 20.2 (*Me*), 19.9 (*Me*), 16.9 (*Me*).

IR (Nujol): ν cm^{-1} 2733, 1732, 1617 (s, N=C), 1597, 1557, 1300, 1264 (s, C–O), 1218, 1171, 1138, 1097, 1058, 1014, 980, 962, 942, 894, 862, 830 (s), 772, 760, 738.

MS (EI) *m*/*z* 707 [M]$^+$, 693 [M−CH$_3$]$^+$, 651 [M−(CH$_2$=CMe$_2$)]$^+$.

4.5.2. Synthesis of [ZrL^2(CH$_2$CMe$_3$)$_2$]

This complex was prepared in an analogous procedure to Section 4.5.1 using H_2L^2 (572 mg, 1.13 mmol) and [Zr(CH$_2$CMe$_3$)$_4$] (444 mg, 1.18 mmol). Recrystallisation from toluene yielded crystals suitable for X-ray analysis.

Yield = 699 mg, 84%.

Anal. Found (Calc. for $C_{44}H_{56}N_2O_2Zr$): C, 68.35 (71.52); H, 7.06 (7.54); N, 4.23% (3.88).

^{1}H-NMR 300 MHz (CD_2Cl_2): δ ppm 7.83 (s, 2H, N=C*H*), 7.42 (dd, 2H, Ar*H*, $^3J_{HH}=8$ Hz, $^4J_{HH}=2$ Hz), 7.04 (t, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 6.97 (d, 2H, Ar*H*), 6.95 (dd, 2H, Ar*H*, $^3J_{HH}=8$ Hz, $^4J_{HH}=2$ Hz), 6.93 (dd, 2H, Ar*H*, $^4J_{HH}=1$ Hz), 6.78 (t, 2H, Ar*H*, $^3J_{HH}=8$ Hz), 3.82 (m, 2H, C*H*Me$_2$, $^3J_{HH}=7$ Hz), 2.12 (s, 6H, *Me*), 1.33 (d, 6H, CH*Me*$_2$, $^3J_{HH}=7$ Hz), 1.28 (d, 2H, C*H*$_2$Bu^t), 1.24 (d, 6H, CH*Me*$_2$, $^3J_{HH}=7$ Hz), 0.93 (d, 2H, C*H*$_2$CMe$_3$, $^2J_{HH}=12$ Hz), 0.86 (s, 18H, CH$_2$C*Me*$_3$).

^{13}C{^{1}H}-NMR 75 MHz (CD_2Cl_2): δ ppm 170.6 (N=*C*H), 160.5, 150.3, 139.2, 137.3, 132.0, 131.9, 131.8, 127.6, 127.5, 121.7, 119.3, 118.0 (*Ar*), 86.9 (*C*H$_2$CMe$_3$),

35.2 (CH_2CMe_3), 34.5 (CH_2CMe_3), 26.6 ($CHMe_2$), 23.6 ($CHMe_2$), 21.9 ($CHMe_2$), 19.9 (Me).

IR (Nujol): ν cm^{-1} 2360, 1605 (s, N=C), 1555,1321, 1283 (m, C–O), 1208, 1148, 1109, 1050, 1017, 978, 942, 888, 851, 804, 751, 728, 710, 668, 651.

MS (EI) m/z 737 $[M]^+$, 679 $[M-CHMe_3]^+$, 666 $[M-CH_2CMe_3]^+$.

4.5.3. $[ZrL^3(CH_2CMe_3)_2]$

This complex was prepared in an analogous procedure to Section 4.5.1, using H_2L^3 (420 mg, 0.79 mmol) and $[Zr(CH_2CMe_3)_4]$ (308 mg, 0.82 mmol). Removal of volatiles under reduced pressure yielded an orange/yellow solid. This was dissolved in pentane and the solution was filtered, concentrated and kept at −30 °C overnight to yield a yellow precipitate, which was isolated by filtration and dried in vacuo.

Yield = 325 mg, 54%.

Anal. Found (Calc. for $C_{46}H_{60}N_2O_2Zr$): C, 70.46 (72.05); H, 7.37 (7.79); N, 3.76% (3.73).

^{1}H-NMR 300 MHz (d_6-benzene): δ ppm 7.78 (s, 2H, N=CH), 7.28 (dd, 2H, ArH, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz), 7.21 (d, 2H, ArH, $^3J_{HH}=9$ Hz), 7.16 (d, 2H, ArH, $^3J_{HH}=7$ Hz), 6.94 (d, 2H, ArH, $^4J_{HH}=2$ Hz), 6.79 (t, 2H, ArH, $^3J_{HH}=8$ Hz), 6.59 (d, 2H, ArH, $^3J_{HH}=8$ Hz), 1.83 (s, 6H, Me), 1.59 (d, 2H, CH_2CMe$_3$, $^2J_{HH}=13$ Hz), 1.51 (s, 18H, CH_2CMe_3), 1.40 (d, 2H, CH_2CMe$_3$, $^2J_{HH}=13$ Hz), 1.14 (s, 18H, CMe_3).

^{13}C{^{1}H}-NMR 75 MHz (d_6-benzene): δ ppm 170.1 (N=CH), 162.0, 150.3, 140.5, 136.7, 134.5, 131.3, 130.1, 128.2, 127.9, 121.3, 120.1, 119.8 (Ar), 87.0 (CH_2CMe_3), 35.5 (CH_2CMe_3), 34.9 (CH_2CMe_3), 33.8 (CMe_3), 31.3 (CMe_3), 19.8 (Me).

IR (Nujol): ν cm^{-1} 1613 (s, N=C), 1591, 1542, 1362, 1307, 1267 (m, C–O), 1257, 1232, 1208, 1178, 1146, 1100, 1024, 978, 949, 885, 837, 773, 759, 737, 704, 668.

MS (EI) m/z 764 $[M]^+$, 707 $[M-CMe_3]^+$.

4.6. Crystallography

Crystals were coated with inert oil and transferred to the cold (180 K) N_2 gas stream on the diffractometer (Bruker-AXS SMART three-circle with CCD area detector). Graphite monochromated Mo–K_α radiation $\lambda = 0.71073$ Å was used. Absorption correction was performed by multi-scan (SADAB). The structures were solved by direct methods using SHELXS [15] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The structures were refined using SHELXL-96 [16]. Experimental data is given in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 208943–208945 for $[ZrL^1(CH_2CMe_3)_2]$, $[ZrL^2(CH_2CMe_3)_2]$ and $[\{ZrL^{2'}\}_2]$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-

Table 3
Experimental data for the X-ray diffraction studies

	$[ZrL^1(CH_2CMe_3)_2]$	$[ZrL^2(CH_2CMe_3)_2]$	$[\{ZrL^{2a}\}_2]$
Molecular formula	$C_{42}H_{52}N_2O_2Zr$	$C_{58}H_{72}N_2O_2Zr$	$C_{48}H_{48}N_2O_2Zr$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Colour	Yellow	Yellow	Yellow
Habit	Block	Block	block
a (Å)	11.2609(13)	12.047(2)	12.633(3)
b (Å)	13.7172(16)	13.818(3)	12.953(3)
c (Å)	14.3272(17)	17.511(4)	14.956(3)
α (°)	92.709(3)	78.04(3)	83.2180(10)
β (°)	102.194(3)	75.21(3)	65.6150(10)
γ (°)	113.220(3)	71.06(3)	62.3870(10)
Cell volume (Å^3)	1966.8(4)	2641.2(9)	1967.1(7)
Z	2	2	2
μ (mm^{-1})	0.314	0.471	0.321
Total reflections	14 884	19 551	8214
Independent reflections	9040 ($R_{int}=0.0520$)	12 195 ($R_{int}=0.0532$)	5087 ($R_{int}=0.0542$)
R_1, wR_2 [$I>2\sigma(I)$]	0.0860, 0.1772	0.0842, 0.1631	0.0701, 0.1330

336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Note added in proof

Coates has reported a new class of phenoxyketimine ligand which form the stable benzyl complexes of titanium: S. Reinartz, A.F. Mason, E.B. Lobkovsky, G.W. Coates, Organometallics 22 (2003) 2542.

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