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Diazaallyls of group 4 metals based on *trans*-1,2-diaminocyclohexane

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Abstract

Amination of 1-bromo-2-methylpyridine with *trans*-1,2-diaminocyclohexane gives the corresponding bis(aminopyridine) $H_2\mathbf{L^1}$. Conversion of the same diamine to the *N*,*N*′-bis(amino-4,4-dimethylthiazoline) $H_2\mathbf{L^2}$ is also completed in three steps. The analogous aminooxazoline is however inaccessible, although the aminocyclohexane analogue is prepared readily. The proligand $H_2\mathbf{L^1}$ forms bis(aminopyridinato) alkyl complexes of the type $[Zr\mathbf{L^1}R_2]$ (R = CH_2Ph, CH_2Bu^t). The molecular structure of the neopentyl complex shows that the chiral backbone leads to a puckering of the N_4Zr coordination sphere, which contrasts with the related cyclohexyl-bridged Schiff-base complexes which are essentially planar. $[Zr\mathbf{L^2}(CH_2Bu^t)_2]$ – the first aminothiazolinato complex – is formed similarly. A comparison of the structures of $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ and $[Zr\mathbf{L^2}(CH_2Bu^t)_2]$ indicates that the latter has a fully delocalised N–C–N system, rather similar to a bis(amidinate). Reaction of $H_2\mathbf{L^2}$ with $[Ti(NMe_2)_4]$ gives $[Ti\mathbf{L^2}(NMe_2)_2]$ which appears to be C_2-symmetric like the above complexes according to NMR spectra, but has one uncoordinated thiazoline unit in the solid state. This is a result of increased ring strain at the smaller titanium metal centre.

Keywords: NCN; Chiral; Titanium; Zirconium; Amidinate

1. Introduction

We have recently reported work on the synthesis, structural and dynamic properties of group 4 metal complexes of bidentate aminopyridinato ligands **I** [1–3]. This has been concerned with control of stoichiometry and structure for both achiral [1] and chiral [2] systems. Related tetradentate ligands are quite rare [3,4], but we have prepared biphenyl-bridged **II** that cleanly forms C_2-symmetric complexes of the type *cis*-[Ti(**II**)X_2] [5], the chirality of the biaryl backbone being expressed efficiently in the structure of the complex [6]. We wished to investigate the synthesis of related cyclohexyl-bridged systems, which despite the availability of potentially suitable proligands [7,8], are unknown. We were interested in what effects the constrained ligand geometry would have on structure and stability in comparison to, e.g., complexes of the Schiff-base ligand system **III** [9,10]. We have also taken opportunity here to explore the possibility of synthesis of the related proligands based on our recently reported aminooxazolinato unit **IV** (E = O) [11,12] and the hitherto unknown ligand type aminothiazolinato **IV** (E = S). The formal negative charge on these latter diazaallyl systems should be more extensively delocalised than it is in aminopyridinato ligands and hence, like the amidinates, they may be suitable for coordination to a much wider range of metals.

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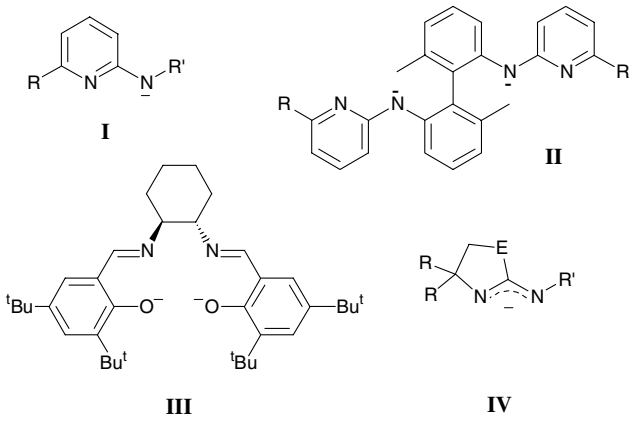


2. Results and discussion

2.1. Synthesis of proligands

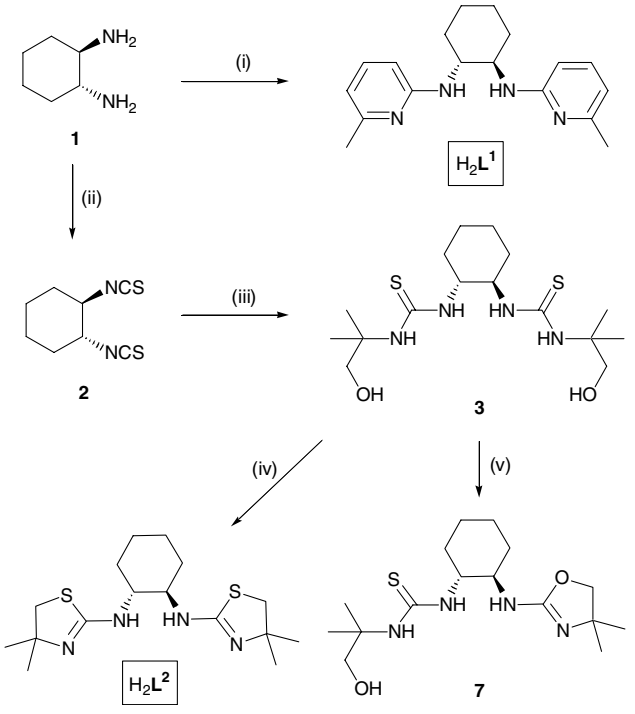
The preparation of H_2L^1 was carrying out using palladium catalysed amine arylation [13] as shown in Scheme 1. No *meso* product was detected, indicating that epimerisation of the stereogenic C centres does not occur to a significant degree under these conditions. Cabanal-Duvillard and Mangeney [14] made a similar observation in related diaminoethane-based compounds. Buchwald and coworkers [15] reported the arylation of **1** with 2-bromopyridine to give a *tri*-substituted product.

H_2L^2 was produced in three steps (Scheme 1). Treatment of racemic *trans*-1,2-cyclohexylamine **1** with 1,1′-thiocarbonyldi-2(1*H*)-pyridone [16] gave the diisothiocyanate product **2** in 47% isolated yield after filtration through silica gel. Following the work of Kim et al. on 2-phenylamino-2-oxazolines [17], the reaction of **2** with 2-amino-2-methyl-1-propanol was attempted. NMR analysis showed that addition of the amino alcohol to one isothiocyanate group was complete after stirring overnight at ambient temperature. The second isothiocyanate addition was complete only after a further 2 d of heating at reflux temperature in the presence of an excess amino alcohol. Washing with hexane and cooling the mixture gave **3** in sufficient purity for our purposes; an analytically pure sample was isolated by recrystallisation from chloroform. The thiourea **3** was treated with concentrated hydrochloric acid [18] and heated to 95 °C for 4 h to give the thiazoline (H_2L^2), which was separated by dilution with water and neutralisation with sodium carbonate (77% yield).

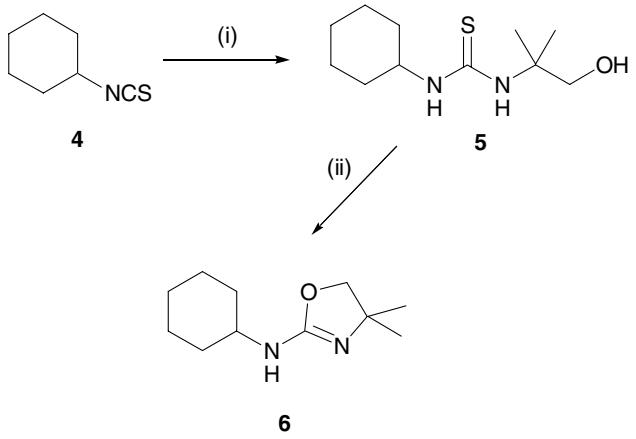
Although the model aminooxazoline **6** was synthesised readily by the route shown in Scheme 2, the attempted NaOH/TsCl mediated double ring-closure [17] of **3** (Scheme 1) to give the oxazoline analogue of H_2L^2 proceeded only with one ring closure per molecule, despite the use of forcing condition, giving the product **7**. This could be a result of steric crowding or a stabilising H-bonding effect in the latter.

2.2. Zirconium complexes of L^1

While treatment of H_2L^1 with $[Zr(NMe_2)_4]$ in pentane yielded a mixture of compounds, a similar reaction with the sterically more demanding (and perhaps less



Scheme 1. Synthesis of proligands $H_2L^{1,2}$ and **7**: conditions (i) 2-bromo-6-methylpyridine, cat. binap/$[Pd_2(dba)_3]$, toluene, 90 °C, 24 h, 60%; (ii) 1,1′-Thiocarbonyldi-2(1*H*)-pyridone (2.2 eq.), DCM, 47%; (iii) 2-amino-2-methyl-1-propanol (5 eq.), THF, 53%; (iv) HCl, 95 °C, 77%; (v) TsCl (2.2 eq.), NaOH (5 eq.), THF/H_2O.



Scheme 2. Synthesis of aminooxazoline **6**: conditions (i) 2-amino-2-methyl-1-propanol (5 eq.), THF, 85%; (ii) TsCl (2.2 eq.), NaOH (5 eq.), THF/H_2O, 72%.

reactive) $[Zr(CH_2Ph)_4]$ yielded the target complex $[Zr\mathbf{L^1}(CH_2Ph)_2]$ in 62% yield. The ^1H NMR spectrum of this compound is slightly broad between 183 and 293 K, but these spectra and that at 343 K indicate that the complex has C_2-symmetry. The resonances for the benzyl CH_2 groups appear as a pair of AB doublets at ca. 2.51 ppm.

The treatment of $H_2\mathbf{L^1}$ with $[Zr(CH_2Bu^t)_4]$ yielded the desired complex $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ in 54% yield after crystallisation. The ^1H NMR spectrum at 293 K (d_6-benzene) featured some slightly broadened resonances but was consistent with the presence of a C_2-symmetric complex. The neopentyl CH_2 groups gave rise to a pair of AB doublets at ca. 1.71 ppm.

The molecular structure of $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ was determined by X-ray crystallography and is shown in Fig. 1 (see also Tables 1 and 2). The bond lengths Zr(1)–N(2) and Zr(1)–N(3) at the cyclohexyl unit [2.1794(18) and 2.1654(18) Å] are significantly shorter than the usual range [2.198(5)–2.228(6) Å] for aminopyridinates [19]. For the pyridine ligands, Zr(1)–N(1) and Zr(1)–N(4) [2.3681(18) and 2.3943(17) Å] are in the upper range of those previously recorded [2.299(5)–2.372(6) Å] [2,19]. These two observations are in accord with expectations given the nature of the ligand, particularly that coordination of the pyridine rings is likely to cause ring-strain in the backbone. The pyridine N atoms are essentially *trans* to one another [N(1)–Zr(1)–N(4) = 173.73(6)°], while in [Ti(**III**)Cl_2] [10] the analogous O–Ti–O angle is ca. 110.4°. It is also of interest that for the co-ligands, [C(19)–Zr(1)–C(24)] is 112.44(8)° (Fig. 2(a), upper) compared with Cl–Ti–Cl of ca. 191.8° in [Ti(**III**)Cl_2] (Fig. 2(b), upper).

The N_4Zr coordination sphere in $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ is twist distorted from planarity as a result of the presence

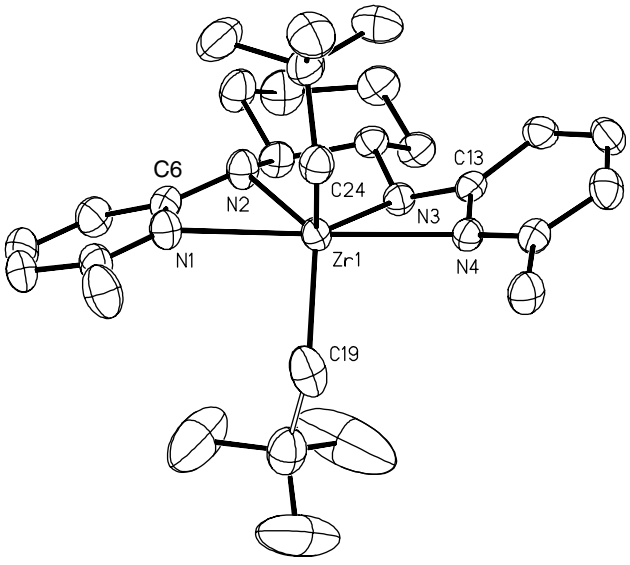


Fig. 1. Thermal ellipsoid plot of the molecular structure of $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ (H atoms omitted).

of the cyclohexane ring (Fig. 2(a), lower); the distances of N(2) and N(3) from the plane N(1)–Zr(1)–(N4) are 1.6264(34) and 1.7930(25) Å, respectively. In [Ti(**III**)Cl_2] the N_2O_2 unit is planar within experimental error. This effect is amplified in the orientation of the pyridine rings in $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ which project away from the N(1)–Zr(1)–(N4) plane.

Our attempts to synthesise titanium complexes of $\mathbf{L^1}$ via salt metathesis and protonolysis routes led to complex mixtures of products.

2.3. Metal complexes of $\mathbf{L^2}$

Treatment of $H_2\mathbf{L^2}$ with $[Zr(NMe_2)_4]$ yielded a mixture of compounds, and the product of the reaction between $H_2\mathbf{L^2}$ and one equivalent of $[Zr(CH_2Ph)_4]$ appeared to be thermally unstable. The corresponding aminopyridinato complex $[Zr\mathbf{L^1}(CH_2Ph)_2]$ is stable in solution at elevated temperatures (vide supra).

Treatment of $H_2\mathbf{L^2}$ with one equivalent of $[Zr(CH_2Bu^t)_4]$ yielded yellow $[Zr\mathbf{L^2}(CH_2Bu^t)_2]$, the first complex of this new ligand class, in 67% isolated yield. The ^1H NMR spectrum of the compound indicates C_2-symmetry. The thiazoline CH_2 groups appear as a pair of AB doublets at ca. 2.89 ppm. Low temperature NMR studies showed no significant change in the spectra down to 183 K.

The molecular structure of this compound (see Fig. 3 and Table 3) shows the neopentyl groups C(17)–Zr(1)–C(22) at an angle of 111.44(10)° and the thiazolinyl N atoms *trans* to one another with N(1)–Zr(1)–N(4) = 176.72(8)°. The cyclohexyl N–Zr bonds at 2.221(2) and 2.225(2) Å are significantly longer than those in $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ [2.1794(18) and 2.1654(18) Å]. In contrast the thiazolinyl N–Zr bonds [2.307(2) and 2.327(2) Å] are shorter than the pyridine N–Zr bonds in that compound [2.3681(18) and 2.3943(17) Å]. Notably also for the present compound the cyclohexyl N–Zr bonds are only slightly shorter than the thiazolinyl N–Zr bonds. The diazaallyl C–N bond lengths (all 1.32 ± 0.01 Å) are shorter than the analogous distances in the aminopyridinato complex $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ above (1.36 ± 0.01 Å). All these observations are consistent with the anticipated delocalisation of charge in the diazallyl systems of $[Zr\mathbf{L^2}(CH_2Bu^t)_2]$.

As with the aminopyridinato complex $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ the N_4Zr coordination sphere is puckered, the deviations of N(2) and N(3) from the plane N(1)–Zr(1)–N(4) are 0.3384(33) and 0.4278(33) Å, respectively, i.e., significantly less than was observed for $[Zr\mathbf{L^1}(CH_2Bu^t)_2]$ (1.6–1.8 Å). In other words, the chirality of the cyclohexyl unit is less well expressed in the coordination sphere of the complex.

When $H_2\mathbf{L^2}$ was treated with $[Ti(NMe_2)_4]$, the yellow compound $[Ti\mathbf{L^2}(NMe_2)_2]$ was formed in 52% isolated yield. The molecular structure (Fig. 4 and Table 4)

Table 1
Experimental data for the X-ray diffraction studies

	$[ZrL^1(CH_2Bu^t)_2]$	$[ZrL^2(CH_2Bu^t)_2]$	$[TiL^2(NMe_2)_2]$
Colour	Yellow	Yellow	Yellow
Habit	Block	Block	Plate
Molecular formula	$C_{28}H_{44}N_4Zr$	$C_{26}H_{48}N_4S_2Zr$	$C_{20}H_{38}N_6S_2Ti$
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
Unit cell dimensions			
a (Å)	9.659(3)	10.8923(9)	24.7653(12)
b (Å)	11.639(3)	14.8473(12)	9.6230(5)
c (Å)	12.911(4)	19.4594(16)	21.7278(10)
α (°)	102.937(7)	75.602(3)	–
β (°)	91.201(7)	88.123(2)	104.8030(10)
γ (°)	91.323(6)	87.698(2)	–
Cell volume (Å^3)	1413.7(7)	3044.9(4)	5006.2(4)
Z	2	4	8
μ (mm^{-1})	0.410	0.518	0.527
Total reflections	12176	20327	16149
Independent reflections	6613	14087	6024
R_1, $wR_2[I > 2\sigma(I)]$	0.0348, 0.0862	0.0415, 0.0890	0.0737, 0.1609

shows a five coordinate titanium centre, with one thiazoline ring uncoordinated [Ti(1)–S(1) = ca. 3.5 Å cf. a bound Ti–S bond length ca. 2.67 Å] [20]. This difference in behaviour in comparison with the zirconium compounds above probably arises from increased strain in the cyclohexyl bridged system at the smaller titanium atom; we note that titanium complexes of the less flexible aminopyridinate system $\mathbf{L^1}$ appear to be completely inaccessible (vide supra). The dimethylamido units in $[TiL^2(NMe_2)_2]$ are at an angle of 109.13(15)° [N(3)–Ti(1)–N(4)] to one another. The distances Ti(1)–N(1) and Ti(1)–N(2) [2.068(3) and 2.097(3) Å] are similar to amino N–Ti bond lengths in aminopyridinates (ca. 2.03 Å) [21], despite the coordination of only one thiazoline unit. The dimethylamido units are oriented off the perpendicular of the cyclohexyl backbone and away from the coordinated thiazoline. The η^2-bound aminothiazolinato ligand has similar N–C distances to those found in the zirconium complex $[ZrL^2(CH_2Bu^t)_2]$, but for the η^1 fragment N(6)–C(11) is essentially a double bond at 1.282(5) Å while N(1)–C(11) at 1.368(5) Å is a single bond.

Table 2
Selected bond lengths [Å] and angles [°] for $[ZrL^1(CH_2Bu^t)_2]$

Zr(1)–N(1)	2.3681(18)
Zr(1)–N(2)	2.1794(18)
Zr(1)–N(3)	2.1654(18)
N(3)–C(13)	1.355(3)
N(4)–C(13)	1.364(3)
Zr(1)–N(4)	2.3943(17)
Zr(1)–C(19)	2.173(2)
Zr(1)–C(24)	2.285(2)
N(2)–C(6)	1.350(3)
N(1)–C(6)	1.371(3)
N(1)–Zr(1)–N(4)	173.73(6)
N(2)–Zr(1)–N(1)	57.83(7)
N(2)–Zr(1)–N(4)	126.34(7)
N(2)–Zr(1)–C(24)	113.51(8)
N(3)–Zr(1)–N(1)	127.33(6)
N(3)–Zr(1)–C(19)	111.69(7)
N(3)–Zr(1)–N(2)	70.41(7)
N(3)–Zr(1)–N(4)	57.90(6)
N(3)–Zr(1)–C(24)	122.67(8)
C(19)–Zr(1)–N(1)	88.29(8)
C(19)–Zr(1)–N(2)	120.57(8)
C(19)–Zr(1)–N(4)	92.63(8)
C(19)–Zr(1)–C(24)	112.44(8)
C(24)–Zr(1)–N(1)	88.52(7)
C(24)–Zr(1)–N(4)	85.39(7)

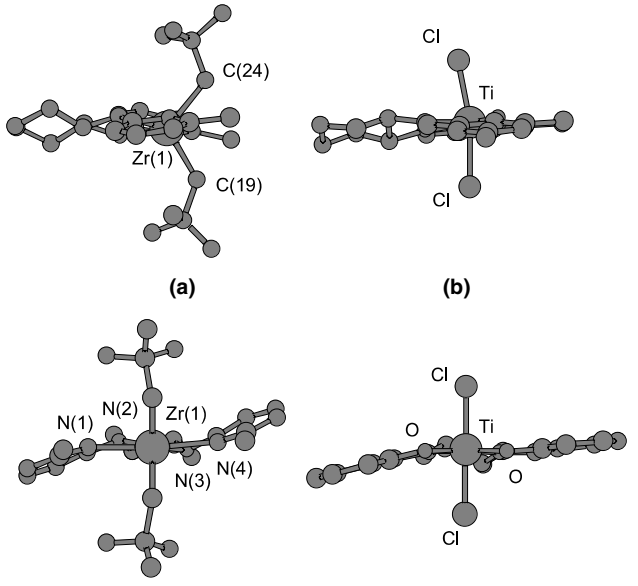


Fig. 2. Chem3D representations of (a) $[ZrL^1(CH_2Bu^t)_2]$ and (b) $[Ti(\mathbf{III})Cl_2]$ (alkyl groups removed for clarity) comparing (upper) the orientations of the co-ligands and (lower) the twist distortions in the cyclohexyl-bridged ligands.

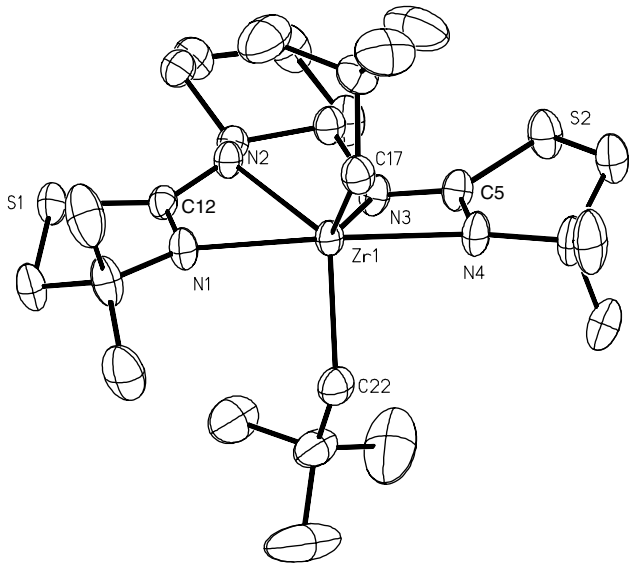


Fig. 3. Thermal ellipsoid plot of the molecular structure of $[Zr\mathbf{L}^{2}(CH_2Bu^{t})_2]$ (H atoms omitted).

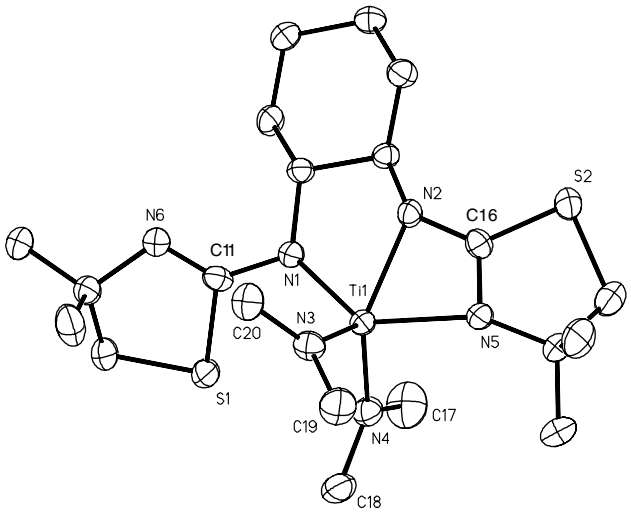


Fig. 4. Thermal ellipsoid plot of the molecular structure of $[Ti\mathbf{L}^{2}(NMe_2)_2]$ (H atoms omitted).

The ^{1}H NMR spectrum of $[Ti\mathbf{L}^{2}(NMe_2)_2]$ indicates that the complex has average C_2-symmetry in solution with resonances for the thiazoline methyl groups at 1.30 and 1.31 ppm and dimethylamido units at 3.16 ppm. The resonances for the thiazoline CH_2 groups appear as a singlet at 2.83 ppm (293 K). Low temperature NMR data showed no apparent lowering of symmetry to match the molecular structure although significant broadening of resonances was observed. This is consistent with facile intramolecular exchange of coordination for the thiazoline units.

3. Conclusion

Despite the strain introduced by use of the 1,2-diaminocyclohexane backbone, bis(aminopyridinato) and bis(aminothiazolinato) complexes of $\mathbf{L}^{1}$ and $\mathbf{L}^{2}$, respectively, may be formed at zirconium. The quadridentate

Table 3
Selected bond lengths [Å] and angles [°] for $[Zr\mathbf{L}^{2}(CH_2Bu^{t})_2]$

Zr(1)–N(1)	2.327(2)
Zr(1)–N(2)	2.221(2)
Zr(1)–N(3)	2.225(2)
N(1)–C(12)	1.317(3)
N(2)–C(12)	1.333(3)
S(1)–C(12)	1.768(3)
Zr(1)–N(4)	2.307(2)
Zr(1)–C(17)	2.259(3)
Zr(1)–C(22)	2.258(3)
N(3)–C(5)	1.329(3)
N(4)–C(5)	1.316(3)
S(2)–C(5)	1.772(3)
N(2)–Zr(1)–N(1)	59.16(8)
N(2)–Zr(1)–N(3)	68.59(8)
N(2)–Zr(1)–N(4)	124.12(8)
N(2)–Zr(1)–C(17)	108.81(9)
N(2)–Zr(1)–C(22)	126.46(9)
N(3)–Zr(1)–N(1)	123.84(8)
N(3)–Zr(1)–N(4)	59.05(8)
N(3)–Zr(1)–C(17)	127.78(9)
N(3)–Zr(1)–C(22)	109.36(10)
N(4)–Zr(1)–N(1)	176.72(8)
C(17)–Zr(1)–N(1)	89.20(9)
C(17)–Zr(1)–N(4)	89.79(9)
C(22)–Zr(1)–N(1)	87.54(9)
C(22)–Zr(1)–N(4)	89.92(10)
C(22)–Zr(1)–C(17)	111.44(10)

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

Ti(1)–N(1)	2.068(3)
Ti(1)–N(2)	2.097(3)
Ti(1)–N(3)	1.867(3)
N(2)–C(16)	1.323(5)
N(5)–C(16)	1.328(5)
S(2)–C(16)	1.772(4)
Ti(1)–N(4)	1.910(3)
Ti(1)–N(5)	2.134(3)
N(1)–C(11)	1.368(5)
N(6)–C(11)	1.282(5)
S(1)–C(11)	1.810(4)
N(1)–Ti(1)–N(2)	75.60(12)
N(1)–Ti(1)–N(5)	134.08(12)
N(1)–Ti(1)–C(16)	102.44(12)
N(2)–Ti(1)–N(5)	63.34(12)
N(2)–Ti(1)–C(16)	32.36(12)
N(3)–Ti(1)–N(1)	106.24(13)
N(3)–Ti(1)–N(2)	109.42(14)
N(3)–Ti(1)–N(4)	109.13(15)
N(3)–Ti(1)–N(5)	106.07(14)
N(3)–Ti(1)–C(16)	118.25(14)
N(4)–Ti(1)–N(1)	101.00(13)
N(4)–Ti(1)–N(2)	140.61(14)
N(4)–Ti(1)–N(5)	98.23(13)
N(4)–Ti(1)–C(16)	117.34(14)
N(5)–Ti(1)–C(16)	32.46(12)

units encompass only around half of the coordination plane, the outermost N atoms being approximately *trans* to one-another. This leads to a distortion of the co-ligands in the two remaining coordination sites away from the *trans* arrangement found in the analogous cyclohexyl-salen complexes. For the smaller titanium, the aminopyridinates appear to be inaccessible, and [Ti$\mathbf{L^2}$(NMe$_2$)$_2$] has one uncoordinated thiazoline unit. It would appear that these classes of cyclohexyl-bridged diazaallyls are better suited for coordination to larger metals.

With regard to the design of chiral tetradentate ligands based on aminothiazolinates and the analogous aminooxazolinates [11,12] we note that the cyclohexyl unit in $\mathbf{L^2}$ has a small but significant effect on the coordination arrangement in the region of co-ligand sites (Fig. 5), the thiazolinyl 4-methyl groups at (a) are oriented away from the coordination sphere while those at (b) are oriented towards it. This effect would be amplified by the use of chiral non-racemic aminoalcohols in the synthesis of the proligand (Scheme 1). A simplifying approach here would be to use an achiral backbone such as that based on 1,2-ethylenediamine (en), but our efforts in this regard have been hampered by the instability of the en and other primary analogues of isothiocyanate **2**.

Our current efforts are directed toward the synthesis of later transition metal complexes of aminothiazoline proligands such as $\mathbf{L^2}$ and the possibility of applications to enantioselective catalysis.

4. Experimental

4.1. General details

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). 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 (4 Å).

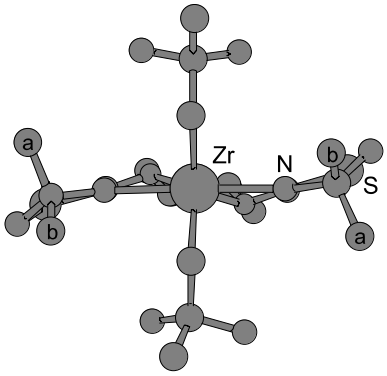


Fig. 5. Chem3D representation of the molecular structure of [Zr$\mathbf{L^2}$(CH$_2$Bu^t)$_2$] showing the distinction between diastereotopic thiazolinyl 4-substituents.

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 (δ = 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 analyses for zirconium compounds were consistently low by ca. 0.5%, despite the use of high combustion temperatures and combustion aids. This can be ascribed to carbide formation [22]. 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.

4.2. Synthesis of proligands

4.2.1. *N,N′-bis(6-methylpyridin-2-yl)cyclohexane-1,2-diamine [$H_2\mathbf{L^1}$]*

Toluene (50 mL) was added to a large Schlenk vessel charged with (±)-*trans*-1,2-diaminocyclohexane (1.0 g, 8.8 mmol), 2-bromo-6-methyl pyridine (3.0 g, 18 mmol), (±)-BINAP (218 mg, 0.35 mmol), [Pd$_2$(dba)$_3$] (160 mg, 0.18 mmol) and NaOBu^t (2.4 g, 25 mmol). The resulting deep red/brown mixture was heated for 4 h at 80 °C with stirring. After cooling to room temperature, diethyl ether (50 mL) was added. The resultant yellow mixture was washed with brine (2 × 30 mL), dried over MgSO$_4$ and the solvent removed by evaporation under reduced pressure. The yellow product was recrystallised from pentane/diethyl ether (yield: 1.72 g, 60%).

^{1}H NMR (293 K, d_6-benzene) δ 1.25 (m, 4H), 1.58 (m, 2H), 2.30 (m, 2H, Cy-CH$_2$), 2.52 (s, 6H, Py-CH$_3$),

4.05 (m, 2H, Cy-CH), 5.39 (s, 2H, NH), 5.97 (d, $^3J_{HH}$ = 7 Hz, 2H), 6.34 (d, $^3J_{HH}$ = 7 Hz, 2H), 7.06 (t, $^3J_{HH}$ = 7 Hz, 2H, Py-CH).

$^{13}C\{^1H\}$ NMR (293 K, d_6-benzene) δ 25.1 (Py-CH_3), 25.6, 33.6 (Cy-CH_2), 56.5 (Cy-CH), 105.9, 111.6, 137.6 (Py-CH), 157.0 (Py Cq CH_3), 159.3 (Py NCqN).

IR (nujol, cm^{-1}): 3292, 2726, 2669, 1605, 1582, 1519, 1336, 1295, 1226, 1153, 1115, 1099, 1029, 986, 948, 933, 778, 728.

Anal. Calc. for $C_{18}H_{24}N_4$: C, 72.94; H, 8.16; N, 18.90. Found: C, 73.06; H, 8.09; N, 18.86.

MS (CI): m/z = 297 (M^+), 202 ($M^+ - PyCH_3$), 187 (M^+ − NH and $PyCH_3$), 109 ($M^+ - 2 \times PyCH_3$).

4.2.2. Trans-1,2-diisothiocyanatocyclohexane (2)

Trans-1,2-diaminocyclohexane (**1**) (1.00 g, 8.76 mmol) was measured into a round bottomed flask and dichloromethane (100 mL) was added. 1,1′-Thiocarbonyldi-2(1*H*)-pyridone (4.40 g 18.94 mmol) was added slowly and the reaction mixture was stirred overnight. The solution was washed with water (200 mL) and the aqueous layer extracted with dichloromethane (100 mL). The combined organic solution was then washed with brine (100 mL) and dried over $MgSO_4$. The dichloromethane was evaporated under reduced pressure to leave a thick red oil with an orange solid. Hexane:ethyl acetate (2:1, 5 mL) was then added and the mixture was heated gently to encourage dissolution. A sparingly soluble orange solid remained. The solution was then eluted through a silica column with hexane:ethyl acetate (2:1). The appropriate fractions were combined to give an off white low melting point solid (yield: 0.810 g, 47%).

^1H NMR (293 K, d_1-chloroform) δ 1.33 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 2.13 (m, 2H, CH_2), 3.67 (m, 2H, CH).

$^{13}C\{^1H\}$ NMR (293 K, d_1-chloroform) δ 22.9 (CH_2), 31.5 (CH_2), 60.0 (CH), 134.9 (Cq).

IR (nujol, cm^{-1}): 2946, 2863, 2362, 2341, 2046, 1448, 1363, 1347, 1305, 956, 721, 669.

Anal. Calc. for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.08; N, 14.13. Found: C, 48.59; H, 4.95; N, 13.92.

MS (EI): m/z = 198 (M^+).

4.2.3. 1-(2-Hydroxy-1,1-dimethylethyl)-3-{2-[3-(2-hydroxy-1,1-dimethylethyl)thioureido]cyclohexyl} thiourea (3)

2-Amino-2-methyl-1-propanol (0.795 g, 8.92 mmol) was placed in a Schlenk vessel and purged with argon. THF (20 mL) was added and the Schlenk vessel was degassed. The isothiocyanate **2** (0.800 g, 4.04 mmol) was dissolved THF and then added to the solution, which was then heated to reflux (75 °C) for 72 h under static vacuum. The THF was evaporated under reduced pressure to leave a sticky white solid. The compound was washed with warm hexane, cooled and the solid filtered. The isolated solid was then was used without further purification. For purposes of obtaining a sample for analysis the following work up procedure was performed: Hexane (100 mL) was added and the mixture heated with stirring to remove the excess amino alcohol. The solid was then isolated by filtration and residual solvent removed by evaporation under reduced pressure. The white solid was redissolved in chloroform and the solution left in a freezer overnight to crystallise. The white solid was then filtered off and any residual ether removed under reduced pressure (yield: 53%, 0.800 g).

^1H NMR (293 K, d_1-chloroform) δ 1.14 (s, 6H, CH_3), 1.28 (m, 4H, Cy-CH_2), 1.31 (s, 6H, CH_3), 1.70 (m, 2H), 1.99 (m, 2H, Cy-CH_2), 3.39 (d, $^3J_{HH}$ = 12 Hz, 2H, CH_2,), 3.69 (d, 2H), 4.16 (m, 2H, Cy-CH), 5.86 (s, 2H, NH), 9.34 (s, 2H, NH).

$^{13}C\{^1H\}$ NMR (293 K, d_1-chloroform) δ 21.1 (CH_3), 24.7 (Cy-CH_2), 27.3 (CH_3), 32.7 (Cy-CH_2), 57.9 (NCq), 59.8 (Cy-CH), 69.7 (CH_2), 178.4 (NCqN).

IR (DCM layer, cm^{-1}): 3240, 3072, 2930, 2857, 1594, 1527, 1462, 1411, 1369, 1259, 1230, 1051, 915, 731, 631.

Anal. Calc. for $C_{16}H_{32}N_4S_2O_2$: C, 51.03; H, 8.56; N, 14.88. Found: C, 50.87; H, 8.52; N, 14.78.

MS (EI): m/z = 376 (M^+).

4.2.4. 1-Cyclohexyl-3-(2-hydroxy-1,1-dimethylethyl) thiourea (5)

To a Schlenk vessel charged with 2-amino-2-methyl-1-propanol (6.6 g, 74.1 mmol) in dry THF (20 mL) was added cyclohexyl isothiocyanate 4 (5.0 g, 35.4 mmol) in THF (10 mL). The solution was stirred overnight to yield an off-white precipitate which was isolated by filtration and washed with cold chloroform. Residual solvent was then removed by evaporation under reduced pressure (yield: 6.92 g, 85%).

^1H NMR (293 K, d_5-pyridine) δ 1.06 (m, 2H), 1.36 (m, 2H, Cy-CH_2), 1.47 (s, 6H, CH_3), 1.59 (m, 2H), 2.15 (m, 2H, Cy-CH_2), 3.80 (s, 2H, CH_2), 4.62 (m, 2H, Cy-CH), 5.07 (s, 1H, OH), 7.95 (br s, 1H, NH), 9.26 (br s, 1H, NH).

$^{13}C\{^1H\}$ NMR (293 K, d_5-pyridine) δ 26.6 (CH_3), 26.9, 27.9, 34.9 (Cy-CH_2), 55.9 (Cy-CH), 59.3 (Me_2Cq), 72.8 (CH_2), 183.7 (NCqN).

IR (Thin film, cm^{-1}): 3225, 3072, 2995, 2975, 2927, 2852, 1599, 1530, 1447, 1424, 1370, 1346, 1303, 1270, 1259, 1234, 1189, 1167, 1152, 1114, 1054, 986, 888, 854, 820, 787, 758, 673.

Anal. Calc. for $C_{11}H_{22}N_2SO$: C, 57.35; H, 9.63; N, 12.16. Found: C, 57.26; H, 9.59; N, 12.17.

MS (EI): m/z = 230 (M^+).

4.2.5. Cyclohexyl-(4,4-dimethyloxazolin-2-yl)amine (6)

A Schlenk vessel containing the cyclohexyl thiourea 5 (2.0 g, 8.68 mmol) was dissolved in THF (20 mL) and purged with argon. An emulsion of NaOH (0.87 g, 0.2 mol) in water (3 mL) and *p*-toluenesulfonyl chloride (1.83 g, 9.60 mmol) in THF (7 mL) was added slowly

(20 min). The solution was then left to stir overnight. The product was then extracted with dichloromethane and dried over magnesium sulfate. The solvent was then removed by evaporation under reduced pressure to yield a white solid (yield: 1.22 g, 72%).

^{1}H NMR (293 K, d_1-chloroform) δ 1.11 (m, CH_2, 2H), 1.23 (s, 6H, CH_3), 1.35 (m, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 3.37 (m, 1H, CH), 3.64 (br s, 1H, NH).

^{13}C{^{1}H} NMR (293 K, d_1-chloroform) δ 24.7, 25.5, 28.2 (Cy-CH_2), 28.8 (CH_3), 33.5 (Cy-CH_2), 51.2 (Cy-CH), 65.0 (Me_2Cq), 78.8 (CH_2), 158.3 (NCqN).

IR (Thin film, cm^{-1}): 3192, 2928, 2854, 1655, 1609, 1553, 1451, 1350, 1319, 1293, 1247, 1202, 1165, 1119, 1027, 974, 891, 703, 673.

Anal. Calc. for $C_{11}H_{20}N_2O$: C, 67.31; H, 10.27; N, 14.27. Found: C, 67.22; H, 10.24; N, 14.21.

MS (EI): m/z = 196 (M^+).

4.2.6. Trans-N,N′-bis(4,4-dimethylthiazolin-2-yl) cyclohexane-1,2-diamine ($H_2\mathbf{L^2}$)

The thiourea **3** (3.18 g, 8.46 mmol) was placed in a round bottom flask (250 mL) and conc. HCl (100 mL) was added slowly. The solution was then heated to 95 °C for 4 h. The solution was then diluted to 250 mL and placed in a conical flask (500 mL). Sodium carbonate was added slowly until effervescence ceased and a white precipitate had formed. The precipitate was then filtered and washed with water (20 mL). The white solid was dissolved in chloroform and washed with water (2×10 mL). The organic layer was then dried over magnesium sulfate and the solvent removed to leave a white solid (yield: 2.20 g, 77%).

^{1}H NMR (293 K, d_6-benzene) δ 0.92 (m, 2H), 1.02 (m, 2H, Cy-CH_2), 1.33 (s, 6H, CH_3), 1.39 (m, 2H, Cy-CH_2), 1.51 (s, 6H, CH_3), 2.17 (m, 2H, Cy-CH_2), 2.82 (d, $^3J_{HH}$ = 11 Hz, 2H, CH_2), 2.93 (d, $^3J_{HH}$ = 11 Hz, 2H, CH_2), 3.69 (m, 2H, Cy-CH), 5.82 (br s, 2H, NH).

^{13}C{^{1}H} NMR (293 K, d_6-benzene) δ 25.2 (Cy-CH_2), 28.4, 29.5 (CH_3), 32.7 (Cy-CH_2), 47.0 (CH_2), 59.8 (Cy-CH), 74.3 (Cq-CH_3), 158.3 (NCqN).

IR (DCM layer, cm^{-1}): 3192, 2961, 2920, 2855, 1597, 1538, 1448, 1358, 1268, 1220, 1163, 973, 927, 899, 624.

Anal. Calc. for $C_{16}H_{28}N_4S_2$: C, 56.43; H, 8.29; N, 16.45. Found: C, 56.35; H, 8.22; N, 16.41.

MS (EI): m/z = 340 (M^+).

4.3. Metal complexes

4.3.1. [Zr$\mathbf{L^1}$(CH_2Ph)$_2$]

Toluene (20 mL) was added to a Schlenk charged with $H_2\mathbf{L^1}$ (200 mg, 0.67 mmol) and [Zr(CH_2Ph)$_4$] (310 mg, 0.68 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed by evaporation under reduced pressure to give a yellow solid. The solid was then redissolved in pentane (10 mL) and cooled to −30 °C. The resulting precipitate was isolated by filtration and the residual solvent was removed by evaporation under pressure (yield: 236 mg, 62%).

^{1}H NMR (293 K, d_6-benzene) δ 1.17–1.29 (m, 4H), 1.59–1.60 (m, 2H), 2.00–2.03 (m, 2H, Cy-CH_2), 2.34–2.37 (s + d, 8H, Py-CH_3 + CH_2Ph), 2.64–2.68 (m, 4H, Cy-CH + CH_2Ph), 5.79 (d, $^3J_{HH}$ = 8 Hz, 2H, Py-CH), 6.03 (d, $^3J_{HH}$ = 8 Hz, 2H, Py-CH), 6.65 (d, $^3J_{HH}$ = 7 Hz, 4H, CHPh), 6.79 (t, $^3J_{HH}$ = 7 Hz, 2H, CHPh), 6.99–7.04 (m, 6H, Py-CH + CHPh).

^{13}C{^{1}H} NMR (293 K, d_6-benzene) δ 23.2 (Py-CH_3), 25.6 (cyclohexyl-CH_2), 33.2 (cyclohexyl-CH_2), 68.8 (Bn-CH_2), 69.3 (cyclohexyl-CH), 104.4 (Py-CH), 110.4 (Py-CH), 121.5 (Bn-CH), 127.5 (Bn-CH), 128.9 (Bn-CH), 142.9 (Py-CH), 144.3 (Bn-Cq), 155.3 (Py-Cq-CH3), 164.5 (Py-NCqN).

^{1}H NMR (343 K, d_6-benzene) δ 1.22–1.27 (m, 4H), 1.61–1.63 (m, 2H), 2.03–2.05 (m, 2H, Cy-CH_2), 2.30 (d, $^3J_{HH}$ = 10 Hz, 2H, CH_2Ph), 2.38 (s, 3H, Py-CH_3), 2.57 (d, $^3J_{HH}$ = 10 Hz, 2H, CH_2Ph), 2.72–2.74 (m, 2H, Cy-CH), 5.83 (d, $^3J_{HH}$ = 8 Hz, 2H, Py-CH), 6.05 (d, $^3J_{HH}$ = 8 Hz, 2H, Py-CH), 6.65 (d, $^3J_{HH}$ = 7 Hz, 4H, CHPh), 6.74 (t, $^3J_{HH}$ = 7 Hz, 2H, CHPh), 6.96 (t, $^3J_{HH}$ = 7 Hz, 4H, CHPh), 7.05 (t, $^3J_{HH}$ = 7 Hz, 2H, Py-CH).

Anal. Calc. for $C_{32}H_{36}N_4Zr$: C, 67.68; H, 6.39; N, 9.87. Found: C, 67.19; H, 6.38; N, 9.90.

MS (EI): m/z = 475 (M^+ − Bn).

4.3.2. [Zr$\mathbf{L^1}$(CH_2Bu^t)$_2$]

Et_2O (20 mL) was added to a Schlenk vessel charged with $H_2\mathbf{L^1}$ (200 mg, 0.67 mmol) and [Zr(CH_2Bu^t)$_4$] (253 mg, 0.67 mmol) at room temperature. The reaction mixture was stirred for 2 d at ambient temperature under argon. The solvent was removed by evaporation under reduced pressure to give a yellow solid. The solid was then redissolved in ether (10 mL) and crystallised upon cooling to 4 °C overnight. The resulting crystals were isolated by filtration and the residual solvent was removed by evaporation under reduced pressure (yield: 205 mg, 54%).

^{1}H NMR (293 K, d_6-benzene) δ 1.05 (s, 18H, Bu^t), 1.48 (d, 2H), 1.79 (d, 2H, Np-CH_2), 1.5–2.5 (br m, 8H, Cy-CH_2), 2.49 (s, 6H, Py-CH_3), 3.38 (br. m, 2H, Cy-CH), 6.11 (2d, 4H, Py-CH), 7.10 (t, $^3J_{HH}$ = 8 Hz, 2H, Py-CH).

^{13}C{^{1}H} NMR (293 K, d_6-benzene) δ 25.7 (Cy-CH_2), 32.0 (Py-CH_3), 35.5 (Cy-CH_2), 34.9 (Bu^t), 69.2 (Cy-CH), 83.6 (Np-CH_2), 104.4, 110.9, 142.7 (Py-CH), 156.0 (Py-CqN), 164.3 (Py-NCqN).

^{1}H NMR (343 K, d_6-benzene) δ 0.98 (s, 18H, Bu^t), 1.05 (d, $^3J_{HH}$ = 12 Hz, 2H, Np-CH), 1.30–1.57 (m, 6H, Cy-CH_2 + Np-CH), 1.69–1.71 (br m, 2H, Cy-CH_2), 2.24–2.27 (br m, 2H, CY-CH_2), 2.51 (s, 6H, Py-CH_3),

3.37–3.39 (br d, $^3J_{HH}$ = 8 Hz, 2H, Cy-CH), 6.11–6.15 (m, 4H), 7.14 (t, $^3J_{HH}$ = 8 Hz, 2H, Py-CH).

Anal. Calc. for $C_{28}H_{44}N_4Zr$: C, 63.71; H, 8.40; N, 10.61. Found: C, 63.25; H, 8.18; N, 10.34.

MS (EI): m/z = 528 (M^+).

4.3.3. [Zr**L**^{2}(CH_2Bu^t)$_2$]

Pentane (20 mL) was added to a Schlenk vessel charged with H_2**L**^{2} (200 mg, 0.59 mmol) and [Zr(CH_2Bu^t)$_4$] (225 mg, 0.60 mmol) at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed by evaporation under reduced pressure to give a yellow solid. The solid was then redissolved in pentane (10 mL) and then cooled to 4 °C. The resulting crystals were isolated by filtration and the residual solvent was removed by evaporation under reduced pressure (yield: 225 mg, 67%).

^{1}H NMR (293 K, d_6-benzene) δ 1.06 (m, 2H, Cy-CH_2), 1.23 (m, 20H, CH_2Bu^t + Bu^t), 1.34 (m, 8H, CY-CH_2 + Np-CH_3), 1.46 (m, 2H, Cy-CH_2), 1.48 (d, 2H, CH_2Bu^t, 12 Hz), 1.62 (s, 6H, CH_3), 2.18 (m, 2H, Cy-CH_2), 2.71 (d, $^3J_{HH}$ = 11 Hz, 2H, CH_2) 2.94 (d, $^3J_{HH}$ = 11 Hz, 2H, CH_2), 3.28 (m, 2H, Cy-CH).

^{13}C{^{1}H} NMR (293 K, d_6-benzene) δ 24.4 (Cy-CH_2), 28.1 (CH_3), 28.7 (CH_3), 32.4 (Cy-CH_2), 35.0 (Bu^t), 35.4 (Cq^{t}Bu), 46.7 (CH_2), 67.9 (Cy-CH), 69.9 (N*Cq*CH_3), 82.9 (*CH2* Bu^t), 175.6 (N*Cq*N).

Anal. Calc. for $C_{26}H_{48}N_4S_2Zr$: C, 54.59; H, 8.46; N, 9.79. Found: C, 54.10; H, 8.45; N, 9.77.

MS (EI): m/z = 570 (M^+).

4.3.4. [Ti**L**^{2}(NMe_2)$_2$]

Pentane (20 mL) was added to a Schlenk vessel charged with H_2**L**^{2} (300 mg, 0.88 mmol). A 0.1 M solution of [Ti(NMe_2)$_4$] (9 mL, 202 mg, 0.90 mmol) was then added slowly at room temperature. The reaction mixture was stirred overnight at ambient temperature under argon. The solvent was removed by evaporation under reduced pressure to give a yellow solid. The solid was then redissolved in pentane (10 mL) and cooled to −30 °C. The resulting crystals were isolated by filtration and the residual solvent was removed by evaporation under reduced pressure (yield: 217 mg, 52%).

^{1}H NMR (293 K, d_6-benzene) δ 1.30 (s, 6H, CH_3), 1.31 (s, 6H, CH_3), 1.44 (m, 4H), 1.72 (m, 2H, Cy-CH_2), 2.83 (s, 4H, CH_2), 2.98 (m, 2H, Cy-CH_2), 3.16 (s, 12H, NMe_2), 3.85 (m, 2H, Cy-CH).

^{13}C{^{1}H} NMR (293 K, d_6-benzene) δ 25.7 (Cy-CH_2), 28.5 (CH_3), 29.1 (CH_3), 32.8 (Cy-CH_2), 43.7 (NMe_2), 47.0 (CH_2), 71.8 (*Cq*CH_3), 72.0 (Cy-CH), 166.9 (N*Cq*N).

Anal. Calc. for $C_{20}H_{39}N_6S_2Ti$: C, 50.51; H, 8.27; N, 17.67. Found: C, 50.34; H, 8.00; N, 17.67.

MS (EI): m/z = 475 (M^+).

4.4. Crystallography

Crystals were coated in an inert oil prior to transfer to a cold nitrogen gas stream on Bruker-AXS SMART three circle area detector diffractometer system equipped with Mo Kα radiation (λ = 0.71073 Å). Data were collected with narrow (0.3° in ω) frame exposures. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). Structures were solved by direct methods (SHELXS) with additional light atoms found by Fourier methods. Anisotropic displacement parameters were used for all non-H atoms, except the disordered *tert*-butyl group (C20–C23) of [Zr**L**^{1}(CH_2Bu^t)$_2$] which was refined isotopically. This *tert*-butyl group was modelled as disordered over two positions in a ratio 47:53. All structures were refined on F^2 values for all unique data. Table 1 gives further details. All H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs used were Bruker AXS SMART (control), SAINT (integration) and SHELXTL [23] for structure solution, refinement, and molecular graphics.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 249213–249215 for [Zr**L**^{1}(CH_2CMe_3)$_2$], [Zr**L**^{2}(CH_2CMe_3)$_2$] and [Ti**L**^{2}(NMe_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 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web http://www.ccdc.cam.ac.uk.

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