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FULL PAPER

Non-planar co-ordination of C_2-symmetric biaryl-bridged Schiff-base ligands: well expressed chiral ligand environments for zirconium †

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The C_2-symmetric Schiff-base proligand (H_2L^1) synthesized by condensation of 2,2′-diamino-6,6′-dimethylbiphenyl and 3,5-di-*tert*-butylsalicylaldehyde reacted in its deprotonated form with $[MCl_4(THF)_2]$ (M = Zr or Hf) to give $[ML^1Cl_2]$. The molecular structures of these complexes show that they belong to the hitherto unknown *cis-cis* class of quadridentate Schiff-base complex. Most importantly, the two chloride ligands occupy mutually *cis* co-ordination sites in a well expressed chiral ligand environment that is structurally analogous to that of the *ansa*-metallocenes. Alkylations of the zirconium complex were unsuccessful, but an unstable complex $[ZrL^1(CH_2Ph)_2]$ was synthesized from H_2L^1 and $Zr(CH_2Ph)_4$. Amido complexes $[ZrL^1(NR_2)_2]$ (R = Me or Et; $R_2 = HBu^t$) were synthesized by substitution reactions of $[ZrL^1Cl_2]$ and by reaction of H_2L^1 with $Zr(NR_2)_4$. The reactions of $[ZrL^1(NR_2)_2]$ (R = Me or Et) with $SiH(OEt)_3$ and $SiMe_3Cl$ gave $[ZrL^1(OEt)_2]$ and $[ZrL^1Cl_2]$ respectively. The reaction of $[ZrL^1Cl_2]$ with LiOPh gave $[ZrL^1(OPh)_2]$. The molecular structure of the latter confirms that it also has the *cis-cis* structure and also indicates the presence of edge–face arene interactions between the phenoxide ligands and the salicylidene units. The reaction of $[ZrL^1Cl_2]$ with $LiAlH_4$ in pyridine (py) led to reduction *in situ* of the imine groups and elimination of both chloride ligands to give a complex containing the quadruply deprotonated reduced form of L^1, *i.e.* $[ZrL^2(py)_2]$. This complex is also formed by reaction of H_4L^2 with $Zr(NR_2)_4$ in pyridine.

Introduction

In the mediation of reactions by metal complexes it is usually regarded as a requirement that substrate and reagent ligands occupy mutually *cis* co-ordination sites.[1] Indeed, one of the keys to the success of metallocene catalysts of the Group 4 metals, *e.g.* Fig. 1(*a*), is that co-ligands necessarily take up *cisoid* positions.[2] Dibasic quadridentate Schiff-base proligands such as salen [Fig. 1(*b*)] may provide alternative ligand sets to the familiar Cp_2 unit for the Group 4 elements,[3–16] but unfortunately most complexes incorporating this type of ligand adopt structure **I** [Fig. 1(*c*)] in which the N_2O_2 ligating atoms lie in a plane and the co-ligands X are forced to adopt mutually *trans* co-ordination sites. A few examples of the *cis-trans* structure **II** are known[17–21] but these are usually in some sort of equilibrium with structure **I**.[5] We set out to develop Schiff-base ligands in which the previously unknown metallocene-like structure **III** would be favoured. Molecular models, and reports of class **II** complexes based on propylenediamine ligands, confirmed that backbones longer than C_2 would be required,[17,18] but also that this would lead to unwanted structural flexibility. We therefore chose the conformationally constrained C_4 backbone provided by biaryldiamines such as 2,2′-diaminobinaphthyl **IV** and 2,2′-diamino-6,6′-dimethylbiphenyl **V**. The dihedral angle between the aryl rings should strongly enforce non-planar co-ordination, and in addition chiral non-racemic ligands and complexes could be synthesized as required. We chose in particular to use the diamine **V** since although **IV** is readily available in chiral non-racemic form the potent carcinogen 2-aminonaphthalene is co-produced in its synthesis.[22] Also, **V** was expected to confer more favourable physical properties such as solubility, crystallinity and volatility on subsequent complexes than would the relatively insoluble **IV**. Biarylamide complexes of zirconium[23] and more recently yttrium[24] based on **V** have been synthesized. During the course of our work, Schiff-base complexes derived from **IV** were reported in the search for new manganese catalysts for alkene epoxidation.[25,26]

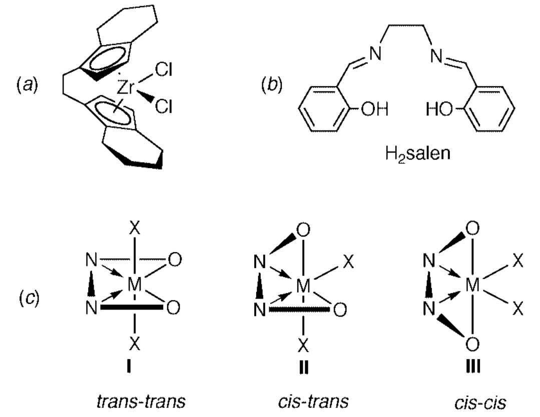
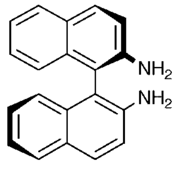
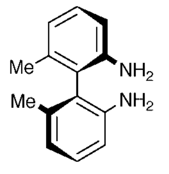


Fig. 1 The prototypical *ansa* metallocene (*a*), a quadridentate dibasic Schiff-base ligand (*b*) and structural classes of Schiff-base complex (*c*).



IV



V

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4069/

Quadridentate Schiff-base complexes of the Group 4 metals have potential for applications in alkene polymerisation[27,28] and in stereoselective catalysis, particularly where chiral non-racemic ligands are used.[19,29,30] We describe here the synthesis, structural characterisation and reactivity of chiral biaryl-bridged Schiff-base complexes of zirconium. A preliminary report of this work has appeared,[31] and we have described some related chemistry of niobium.[32]

Experimental

General

Unless otherwise stated, all manipulations were carried out under an atmosphere of dry argon using conventional Schlenk techniques and an MBraun glove box operating at <0.5 ppm of O_2/H_2O. All solvents were dried by refluxing for three days over an appropriate agent (sodium for toluene; potassium for THF and benzene; sodium–potassium alloy for diethyl ether, light petroleum (bp 40–60 °C), and pentane; calcium hydride for dichloromethane and pyridine). Deuteriated solvents were refluxed *in vacuo* over the appropriate agent (as above) before trap-to-trap distillation and storage in the glove box. NMR Samples were made up in the glove box in tubes sealed with Young's concentric stopcocks.

The NMR spectra were recorded on Bruker WM-360, AC-250, AC-400 or DMX-300 spectrometers and referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0.0), infrared spectra as Nujol mulls in an air tight holder on a Perkin-Elmer FT-IR spectrometer and EI mass spectra on a VG Autospec mass spectrometer by Dr. Ali Abdul-Sada at the University of Sussex. Elemental analyses were performed by Canadian Microanalytical Services Ltd, or Warwick Analytical Services.

The compounds $ZrCl_4$, $HfCl_4$, $LiNMe_2$, $LiCH(SiMe_3)_2$, LiPh, BCl_3, $AlMe_3$, EtMgBr, $SiH(OEt)_3$, NaOEt, $[NH_2Me_2]Cl$ and Me_3SiCl were purchased from Aldrich Chemical Company and used as supplied. Literature methods were used for the preparation of $[ZrCl_4(THF)_2]$,[5] $[Zr(CH_2Ph)_4]$[4] and $[Zr(NMe_2)_4]$.[6] Samples of $LiNEt_2$, $LiNHBu^t$ and LiOPh were prepared by the addition of a stoichiometric amount of $LiBu^n$ to a solution of the appropriate amine or phenol in pentane followed by collection and drying of the precipitated white solid.

Syntheses

H_2L^1. A 250 ml round bottomed flask was charged with 2,2′-diamino-6,6′-dimethylbiphenyl (2.97 g, 0.014 mol) and 3,5-di-*tert*-butylsalicylaldehyde (6.56 g, 0.028 mol). Methanol (100 ml) was added, and the mixture refluxed for 6 h. Over the course of this time the solution turned yellow, and a bright orange solid precipitated. The solid was collected on a frit, washed with cold methanol (3 × 20 ml) and dried at 60 °C under reduced pressure (7.72 g, 85%) (Found C, 81.90; H, 8.77; N, 4.30. $C_{22}H_{28}NO$ requires C, 81.94; H, 8.75; N, 4.34%). ^1H NMR ($CDCl_3$) δ 12.89 (s, 2 H, OH), 8.47 (s, 2 H, N=CH), 6.99–7.28 (m, 10 H, biaryl and phenolic), 2.03 (s, 6 H, Me), 1.29 (s, 18 H, Bu^t) and 1.22 (s, 18 H, Bu^t). ^{13}C-{^1H} NMR ($CDCl_3$) δ 162.10 (N=C), 157.92, 146.50, 139.42, 136.70, 136.26, 133.22, 127.89, 127.80, 127.02, 126.09, 117.81, 114.93 (aromatic), 34.63 , 33.70 (*C*Me$_3$), 31.06, 28.87, (C*Me*$_3$) and 19.50 (Me). IR (Nujol, cm^{-1}) 3424, 3388, 3305 (br), 3182, 2602, 1713, 1587, 1543, 1303m, 1255m, 1218, 1138m, 1088, 780, 753, 735, 721 and 675.

$[Na_2(THF)_n][L^1]$ 1. A solution of H_2L^1 (3.20 g, 4.96 mmol) in THF (50 ml) was added dropwise to solid NaH (357 mg, 14.9 mmol). A gas was evolved. The mixture was stirred for 4 h, filtered to remove the excess of NaH, and the solvent removed under reduced pressure to give bright yellow compound **1**. The amount of THF in the material was deduced by careful integration of a ^1H NMR spectrum recorded in deuteriated pyridine (yield 3.56 g, 93%). ^1H NMR (C_5D_5N) δ 8.53 (s, 2 H, N=CH), 6.51–7.46 (m, 10 H, biaryl and phenolic), 3.64 (m, variable, THF), 1.95 (s, 6 H, Me), 1.62 (m, variable, THF), 1.58 (s, 18 H, Bu^t), 1.33 (s, 18 H, Bu^t). ^{13}C-{^1H} NMR (C_5D_5N) δ 172.88 (N=C), 166.98, 153.00, 141.30, 138.05, 132.23, 130.37, 129.98, 128.18, 127.56, 125.84, 122.61, 119.37 (aromatic), 68.07 (THF), 35.96, 34.09 (*C*Me$_3$), 32.21, 30.19 (C*Me*$_3$), 26.04 (THF) and 20.69 (Me).

$[ZrL^1Cl_2]$ 2. Solid $[Na_2(THF)_{0.4}][L^1]$ (1.5 g, 2.1 mmol) and $[ZrCl_4(THF)_2]$ (0.69 g, 2.5 mmol) were loaded into a Schlenk tube and THF (30 ml) was added. The mixture was stirred for 12 h and the THF removed under reduced pressure. The solids were extracted into toluene (50 ml). The yellow solution was filtered through Celite, concentrated to *ca.* 20 ml *in vacuo* and cooled to −50 °C. This resulted in the precipitation of yellow, microcrystalline compound **2**. Alternatively, purification was achieved by sublimation of a crude sample at 300 °C and 10^{-6} mbar. Both methods resulted in approximately the same yield (1.38 g, 81%) (Found C, 65.80; H, 6.69; N, 3.41. $C_{44}H_{54}Cl_2N_2O_2Zr$ requires C, 65.65; H, 6.76; N, 3.48%). ^1H NMR (C_6D_6) δ 7.86 (s, 2 H, N=CH), 7.75 (d, 2 H, phenolic), 7.05 (d, 2 H, biaryl), 6.90 (m, 4 H, biaryl and phenolic), 6.68 (d, 2 H, biaryl), 1.73 (s, 24 H, Bu^t and Me) and 1.13 (s, 18 H, Bu^t). ^{13}C-{^1H} NMR (C_6D_6) δ 170.50 (C=N), 159.71, 149.58, 141.77, 139.36, 137.16, 132.46, 128.97, 128.88, 128.62, 128.51, 123.18, 122.15 (aromatic), 35.63, 34.20 (*C*Me$_3$), 31.28, 29.97 (C*Me*$_3$) and 19.77 (Me). IR (Nujol, cm^{-1}) 1607m, 1591m, 1557m, 1543m, 1299, 1274, 1254m, 1199, 1179, 1135, 1096, 1027, 981, 878, 847, 828, 778, 752 and 740. MS (EI) *m*/*z* 804 [*M*$^+$], 788, 771 [*M*$^+$ − Cl + 2], 751, 735 [*M*$^+$ − 2Cl + 3] and 360.

$[HfL^1Cl_2]$ 3. This compound was synthesized in an analogous manner to **2** to give a yellow microcrystalline solid which was purified by recrystallisation from toluene or by sublimation (260 °C, 10^{-6} mbar) (76%) (Found C, 59.10; H, 6.12; N, 3.01. $C_{44}H_{54}Cl_2HfN_2O_2$ requires C, 59.23; H, 6.10; N, 3.14%). ^1H NMR (C_6D_6) δ 7.81 (s, 2 H, N=CH), 7.70 (d, 2 H, phenolic), 6.90–6.45 (m, 6 H, phenolic and biaryl), 1.73 (s, 24 H, Bu^t and Me) and 1.10 (s, 18 H, Bu^t). MS (EI) *m*/*z* 892 [*M*$^+$], 877, 857 [*M*$^+$ − Cl], 841 and 644.

$[ZrL^1(NMe_2)_2]$ 5. A solution of H_2L^1 (1.21 g, 1.9 mmol) in diethyl ether (20 ml) was added dropwise to a solution of $Zr(NMe_2)_4$ (0.5 g, 1.9 mmol) in the same solvent (20 ml). The solution was stirred at room temperature for 5 h and an orange solid precipitated. Removal of the solvent and volatile side products under reduced pressure followed by extraction into diethyl ether and recrystallisation at −40 °C yielded yellow compound **5** (750 mg, 48%) (Found C, 69.95; H, 7.93; N, 6.69. $C_{48}H_{64}N_4O_2Zr$ requires C, 70.11; H, 8.09; N, 6.81%). ^1H NMR (C_6D_6) δ 7.80 (s, 2 H, N=H), 7.55 (d, 2 H, phenolic), 7.20 (d, 2 H, biaryl), 6.90 (t, 2 H, biaryl), 6.75 (d, 2 H, phenolic), 6.48 (d, 2 H, biaryl), 3.20 (s, 12 H, NMe_2), 1.75 (s, 18 H, Bu^t), 1.70 (s, 6 H, Me) and 1.15 (s, 18 H, Bu^t). ^{13}C-{^1H} NMR (C_6D_6) δ 168.45 (C=N), 162.18, 150.84, 139.21, 138.07, 136.69, 131.61, 130.32, 128.12, 127.89, 127.64, 121.96, 120.14, 105.65 (aromatic), 43.94 (NMe_2), 35.64, 33.95 (*C*Me$_3$), 31.43, 30.08 (C*Me*$_3$) and 19.89 (Me). IR (Nujol, cm^{-1}) 1610m, 1553, 1536, 1307, 1257, 1225, 1200, 1169, 1145, 972, 944, 873, 840, 824, 781, 770, 736, 722, 530 and 463. MS (EI) *m*/*z* 820 [*M*$^+$], 805 [*M*$^+$ − Me], 776 [*M*$^+$ − NMe_2] and 732 [*M*$^+$ − $2NMe_2$].

$[ZrL^1(NEt_2)_2]$ 6. *Method A.* The solids $[ZrL^1Cl_2]$ (490 mg, 0.609 mmol) and $LiNEt_2$ (106 mg, 1.34 mmol) were loaded into a Schlenk tube and diethyl ether (50 ml) was added. The solution was stirred for 16 h over which time a change occurred from yellow to orange. Removal of the solvent under reduced pressure followed by extraction of the solid with pentane and filtration through Celite gave an orange solution, which on concentration and cooling to −50 °C gave compound **6** as an orange powder (413 mg, 77%).

Method B. A solution of $Zr(NEt_2)_4$ (250 mg, 0.66 mmol) in toluene (10 ml) was added dropwise to a solution of H_2L^1 (425 mg, 0.66 mmol) in the same solvent (10 ml). The mixture turned orange over the course of the addition, and was stirred for 16 h. Removal of the solvent and liberated $NHEt_2$ under reduced pressure gave an orange solid which was recrystallised from pentane at −30 °C to give compound **6** (481 mg, 83%) (Found C, 70.85; H, 8.11; N, 5.98. $C_{52}H_{74}N_4O_2Zr$ requires C, 71.10; H, 8.49; N, 6.38%). ^{1}H NMR (C_6D_6) δ 7.96 (s, 2 H, N=CH), 7.55 (d, 2 H, phenolic), 7.27 (d, 2 H, biaryl), 6.93 (t, 2 H, biaryl), 6.76 (d, 2 H, phenolic), 6.50 (d, 2 H, biaryl), 3.91 (dq, 4 H, NCH_2CH_3), 3.61 (dq, 4 H, NCH_2CH_3), 1.76 (s, 24 H, Bu^t and Me), 1.15 (s, 18 H, Bu^t) and 0.99 (t, 12 H, NCH_2CH_3). ^{13}C-{^{1}H} NMR δ 167.93 (N=C), 161.42, 150.21, 138.05, 137.21, 135.68, 130.90, 129.31, 121.65, 119.25 (aromatic), 40.65 (NCH_2CH_3), 34.76, 33.11 (CMe_3), 30.60, 29.46 (CMe_3), 19.08 (Me) and 13.46 (NCH_2CH_3). IR (Nujol cm^{-1}) 1611m, 1538, 1305, 1259, 1202, 1169, 1000, 972, 875, 840, 825, 799, 770 and 737. MS (EI) *m*/*z* 849 [M^+ − Et + 2], 804 [M^+ − NEt_2], 733 [M^+ − $2NEt_2$] and 366.

[$ZrL^1(NHBu^t)_2$] 7. A solution of [ZrL^1Cl_2] (320 mg, 0.40 mmol) in diethyl ether (20 ml) was cooled to −80 °C and a slurry of $LiNHBu^t$ (94 mg, 1.20 mmol) in the same solvent (10 ml) added. The mixture was allowed to warm to room temperature with stirring over 12 h after which LiCl was removed by filtration through Celite. Reduction of the volume of the resultant solution under reduced pressure followed by cooling to −40 °C gave orange crystalline compound **7** (111 mg, 32%) (Found C, 71.02; H, 8.73; N, 6.16. $C_{52}H_{74}N_4O_2Zr$ requires C, 71.10; H, 8.49; N, 6.38%). ^{1}H NMR (C_6D_6) δ 7.65 (m, 4 H, N=CH and phenolic), 7.15 (m, 2 H, biaryl), 6.80 (m, 4 H, biaryl and phenolic), 6.50 (d, 2 H, biaryl), 5.05 (s, 2 H, NH), 1.81 (s, 18 H, Bu^t), 1.79 (s, 6 H, Me), 1.34 (s, 18 H, Bu^t) and 1.20 (s, 18 H, Bu^t). ^{13}C-{^{1}H} NMR (C_6D_6) δ 171.17 (C=N), 163.75, 152.66, 140.41, 140.33, 138.46, 134.02, 132.09, 129.21, 124.17, 122.30 (aromatic), 56.38 ($NCMe_3$), 37.41 (CMe_3), 36.88 ($NCMe_3$), 35.89 (CMe_3), 33.76, 32.26 (CMe_3) and 21.74 (Me). IR (Nujol, cm^{-1}) 3725, 3691, 1611, 1577, 1550, 1537, 1409, 1360, 1308, 1274, 1257, 1225, 1199, 1171, 1149, 1100, 1073, 1026, 975, 945, 917, 873, 843, 826, 782, 771, 729, 639, 593, 533 and 462. MS (EI) *m*/*z* 804 [M^+ − $NHBu^t$], 770, 751, 735 [M^+ − $2NHBu^t$].

[$ZrL^1(OEt)_2$] 8. Triethoxysilane (0.2 ml, excess) was added by syringe to a solution of [$ZrL^1(NMe_2)_2$] **5** (250 mg, 0.30 mmol) in THF (20 ml). The solution was stirred for 2 h over which time a change occurred from orange to pale yellow. Volatile components of the reaction mixture were removed under reduced pressure and the remaining solid was loaded into a sublimation tube. Pure compound **8** was sublimed at 230 °C and 10^{-6} mbar (215 mg, 87%) (Found C, 69.70; H, 7.82; N, 3.28. $C_{48}H_{64}N_2O_4Zr$ requires C, 69.94; H, 7.83; N, 3.40%). ^{1}H NMR (C_6D_6) δ 7.81 (s, 2 H, N=CH), 7.61 (d, 2 H, phenolic), 7.02 (s, 2 H, biaryl), 6.90 (t, 2 H, biaryl), 6.87 (d, 2 H, phenolic), 6.59 (d, 2 H, biaryl), 3.99 (s, 4 H, OCH_2), 1.79 (s, 6 H, Me), 1.77 (s, 18 H, Bu^t), 1.18 (s, 18 H, Bu^t) and 1.02 (t, 6 H, OCH_2CH_3). ^{13}C-{^{1}H} NMR (C_6D_6) δ 168.55 (C=N), 162.2, 154.49, 150.81, 139.33, 138.15, 136.87, 131.58, 130.34, 127.82, 127.64, 121.89, 121.05 (aromatic), 65.79 (OCH_2), 35.70, 34.03 (CMe_3), 31.50, 29.96 (CMe_3), 20.31, 19.93 (Me and OCH_2CH_3). IR (Nujol, cm^{-1}) 1610, 1551, 1536, 1310, 1273, 1257, 1226, 1200, 1158, 1134, 1072, 1027, 972, 946, 915, 873, 841, 824, 783, 770, 736, 692, 668, 641, 594 and 532. MS (EI) *m*/*z* 822 [M^+], 777 [M^+ − OEt] and 732 [M^+ − 2OEt].

[$ZrL^1(OPh)_2$] 9. The solids [ZrL^1Cl_2] **2** (250 mg, 0.31 mmol) and LiOPh (100 mg, 1.00 mmol) were loaded into a Schlenk tube and diethyl ether (20 ml) was added. Following stirring for 16 h the solvent was removed under reduced pressure and the solid extracted into pentane. Filtration through Celite gave an orange solution, which on concentration and cooling to −50 °C yielded compound **9**. Purification could also be achieved by sublimation at 230 °C and 10^{-6} mbar (240 mg, 84%) (Found C, 73.54; H, 7.25; N, 3.35. $C_{56}H_{64}N_2O_4Zr$ requires C, 73.08; H, 7.01; N, 3.04%). ^{1}H NMR (C_6D_6) δ 7.78 (s, 2 H, N=CH), 7.61(d, 2 H, phenolic), 7.05 (t, 2 H, biaryl), 6.96 (d, 2 H, biaryl), 6.70–6.81 (m, 12 H, OPh and phenolic), 6.54 (d, 2 H, biaryl), 1.74 (s, 6 H, Me), 1.69 (s, 18 H, Bu^t) and 1.17 (s, 18 H, Bu^t). ^{13}C-{^{1}H} NMR (C_6D_6) δ 169.38 (C=N), 163.01, 161.18, 149.72, 139.57, 139.11, 136.79, 131.20, 131.09, 128.79, 127.95, 122.18, 121.20, 119.70, 119.20 (aromatic), 35.50, 33.93 (CMe_3), 31.23, 29.68 (CMe_3) and 19.63 (Me). MS (EI) *m*/*z* 918 [M^+] and 825 [M^+ − OPh].

[$ZrL^1(CH_2Ph)_2$] 4. A slurry of H_2L^1 (425 mg, 0.66 mmol) in pentane (15 ml) was added dropwise to a solution of $Zr(CH_2Ph)_4$ (0.30 g, 0.66 mmol) in the same solvent (10 ml). The reaction mixture was stirred for 12 h with the exclusion of light. An orange solid was precipitated, collected and washed with pentane (2 × 5 ml) to yield slightly impure compound **4**. Complete purification was not possible due to the thermal- and light-sensitivity of this species (276 mg, 46%). ^{1}H NMR (C_6D_6) δ 7.27 (s, N=CH), 7.02–6.41 (m, phenolic and biaryl), 3.08 (d, CH_2Ph), 2.85 (d, CH_2Ph), 1.76 (s, Bu^t) and 1.20 (s, Bu^t).

[$ZrL^2(py)_2$] 10. *Method A.* A solution of [ZrL^1Cl_2] **2** (416 mg, 0.516 mmol) in pyridine (20 ml) was added dropwise to solid $LiAlH_4$ (115 mg, 3.03 mmol) with stirring. Over 12 h an orange colour developed. Removal of the pyridine under reduced pressure followed by extraction of the solid into light petroleum gave a pale orange solution, which on cooling to −50 °C gave compound **10** as an orange solid (223 mg, 56%).

Method B. A solution of $Zr(NMe_2)_4$ (100 mg, 0.37 mmol) in toluene (10 ml) was added dropwise to a solution of H_4L^2 (519 mg, 0.80 mmol) in toluene (20 ml) to which had been added pyridine (2 ml). The mixture slowly turned yellow on stirring for 16 h. Removal of volatile components of the reaction mixture under reduced pressure and extraction into pentane yielded a bright yellow solution, from which compound **10** was obtained by recrystallisation at −50 °C (238 mg, 72%) (Found C, 72.28; H, 7.40; N, 6.10. $C_{54}H_{66}N_4O_2Zr$ requires C, 72.52; H, 7.44; N, 6.26%). ^{1}H NMR (C_6D_6) δ 8.38 (d, 4 H, py), 7.37 (d, 2 H, phenolic), 7.28 (d, 2 H, phenolic), 6.76 (t, 2 H, biaryl), 6.54–6.60 (m, 4 H, biaryl and py), 6.22–6.27 (m, 6 H, biaryl and py), 4.78 (d, 2 H, CH_2), 4.33 (d, 2 H, CH_2), 1.94 (s, 6 H, Me), 1.53 (s, 18 H, Bu^t) and 1.32 (s, 18 H, Bu^t). ^{13}C-{^{1}H} NMR (C_6D_6) δ 157.93, 154.02, 148.34, 140.13, 137.84, 136.82, 136.12, 132.16, 131.69, 127.67, 124.73, 123.69, 122.28, 120.22, 112.07 (aromatic), 59.13 (CH_2), 35.46, 34.35 (CMe_3), 32.04, 30.55 (CMe_3) and 21.09 (Me). IR (Nujol, cm^{-1}) 1608, 1568, 1264m, 1238, 1218, 1168, 1130, 1079, 1044, 1013, 945, 912, 874, 834, 815, 782, 766, 748 and 697. MS (EI) (300 °C) *m*/*z* 734 [M^+ − 2py], 670 and 79 [py]$^+$

H_4L^2. A solution of H_2L^1 (1.00 g, 1.55 mmol) in diethyl ether was added dropwise to a slurry of $LiAlH_4$ (180 mg, 4.74 mmol) in the same solvent. After stirring for 16 h the mixture was cooled to 0 °C and cautiously hydrolysed with an excess of ice. The mixture was neutralised with solid ammonium chloride and transferred to a separating funnel. The aqueous layer was extracted with portions of diethyl ether (3 × 50 ml), and the organic portions combined. The solution was dried over $MgSO_4$ and the solvent removed under reduced pressure to yield compound H_4L^2 as an off-white solid (1.03 g, 100%) (Found C, 81.45; H, 9.59; N, 4.25. $C_{22}H_{30}NO$ requires C, 81.43; H, 9.32; N, 4.32%). ^{1}H NMR ($CDCl_3$) δ 8.68 (s, 2 H, OH), 7.09–7.46 (m, 10 H, aromatic), 4.56 (ABX, 4 H, CH_2), 3.77

(t, 2 H, NH), 2.15 (s, 6 H, Me), 1.60 (s, 18 H, Bu^t) and 1.50 (s, 18 H, Bu^t). ^{13}C-{^{1}H} (CDCl$_3$) δ 144.55, 141.29, 137.69, 136.22, 129.17, 124.26, 123.60, 123.56, 122.94, 121.95, 111.9 (aromatic), 49.35 (CH$_2$), 34.94, 34.20 (*C*Me$_3$), 31.60, 29.57 (C*Me*$_3$) and 19.55 (Me). IR (Nujol, cm^{-1}) 3357m (br), 1581, 1304, 1281, 1261, 1230m, 1163, 1098, 881, 772, 741 and 723.

Crystallography

Crystals of compounds **2**, **3** and **9** were coated with inert oil and transferred to the cold (173 K) N$_2$ gas stream on the diffractometer (Enraf-Nonius CAD4). Non-H atoms were located by heavy atom methods (SHELXS 86) and (for **2** and **3**) refined by full matrix least squares on all F^2 with anisotropic thermal parameters (SHELXL 93)[33] and scattering factors.[34] Compound H$_2$L^1 was treated similarly using a Siemens SMART three-circle diffractometer with CCD area detector and the structure refined using SHELXL 96.[35] Hydrogen atoms were included in the riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl groups. The C(14) methyl group in **2** was fixed at idealised geometry but disordered equally over two alternative orientations related by a rotation of 60° about the C(10)–C(14) bond. The structure of **3** contains a relatively large electron density hole (near Hf) which presumably arises from incomplete absorption correction for this plate-like crystal. For **9** only the Zr atom was set anisotropic. Attempts to refine the remaining non-hydrogen atoms resulted in many non-positive-definite thermal parameters. The reason for this was not clear and a second data set measured on another crystal gave similar problems. In both cases there were weak reflections which could not be indexed and the final difference map showed a string of weak residual density going through the Zr atom parallel to the *c* axis of the crystal.

CCDC reference number 186/1667.

See http://www.rsc.org/suppdata/dt/1999/4069/ for crystallographic files in .cif format.

Results and discussion

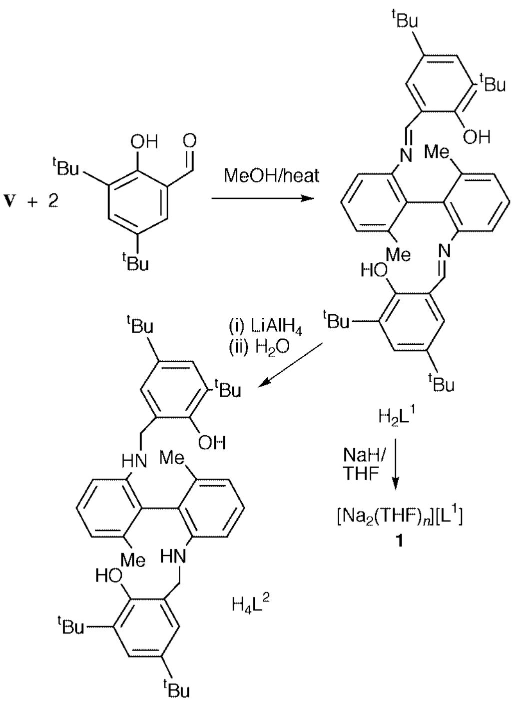
Synthesis and metallation of biaryl-bridged Schiff-base proligand H$_2$L^1

The new Schiff-base pro-ligand, 6,6′-dimethyl-2,2′-bis(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)biphenyl, H$_2$L^1, was synthesized from **V** and 3,5-di-*tert*-butylsalicylaldehyde (Scheme 1). Its molecular structure has been determined and will be discussed later. The phenolic OH groups are readily deprotonated by the addition of its solution in THF to an excess of NaH to give [Na$_2$(THF)$_n$][L^1] **1**. The quantity of THF incorporated into the solid varies at each preparation, but the stoichiometry can readily be determined by integration of the ^{1}H NMR spectrum recorded in d$_5$-pyridine. The dipotassium salt of L^1 may be prepared by an analogous reaction with KH.

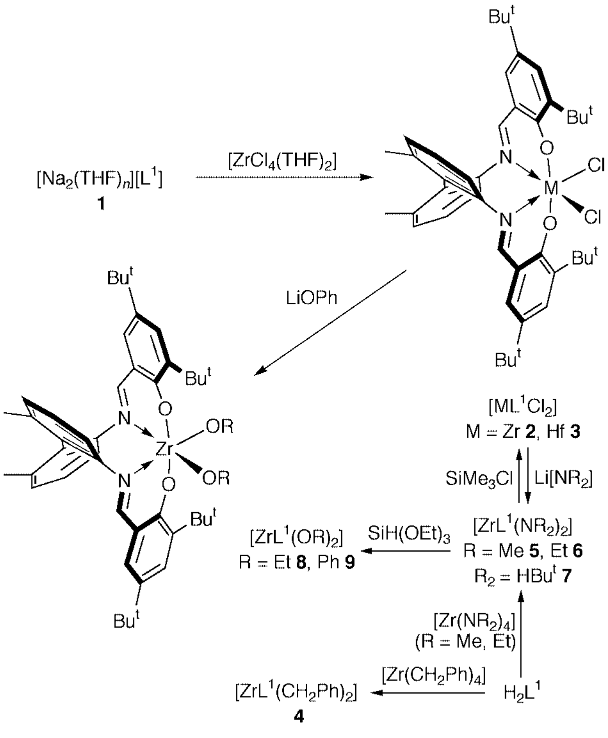
Synthesis and structural characterisation of the first class III Schiff-base complexes [ML^{1}Cl$_2$] (M = Zr 2 or Hf 3)

The complex [ZrL^{1}Cl$_2$] **2** was synthesized by a salt elimination reaction between **1** and [ZrCl$_4$(THF)$_2$] in THF (Scheme 2). Although **2** crystallises readily it may also be isolated by sublimation of the crude reaction residue at 300 °C and 10^{-6} mbar. Either method results in *ca.* 80% yield. There was no evidence for the formation of the complex [Zr(L^1)$_2$] when the synthesis was performed with an excess of **1**. In contrast, less bulky [Zr(Schiff base)$_2$] complexes are formed quite readily.[27,36] Samples of yellow **2** are indefinitely stable both in the solid state and in solution in the absence of oxygen and water, but hydrolyse slowly in moist air.

The ^{1}H and ^{13}C NMR spectra of compound **2** in d$_6$-benzene were assigned by standard one and two dimensional methods.



Scheme 1 Synthesis of the proligands H$_2$L^1 and H$_4$L^2.



Scheme 2 Synthesis and interconversion of complexes containing L^1.

The aliphatic region of the ^{1}H spectrum contains only two peaks, one assigned to two equivalent *tert*-butyl groups and one assigned to overlapping *tert*-butyl and methyl group resonances. Similarly, only one resonance is apparent for the imine protons. Hence, on these chemical shift timescales, **2** possesses a C_2 axis of rotation, and thus belongs either to the class **I** or class **III** structural type. No significant change in the spectrum was detected at accessible temperatures, or by recording the spectrum in a donor solvent (d$_5$-pyridine).

Single crystals of compound **2** suitable for X-ray crystallography (Table 1) were grown by heating a sample of the pure complex to 250 °C in an evacuated glass tube for 2 days, allowing the oven to cool slowly before removal of the tube for examination. The resultant molecular structure is shown in

Table 1 Experimental data for the X-ray diffraction studies of compounds H_2L^1, **2**, **3** and **9**

	H_2L^1	$[ZrL^1Cl_2]$ **2**	$[HfL^1Cl_2]$ **3**	$[ZrL^1(OPh)_2]$ **9**
Molecular formula	$C_{44}H_{56}N_2O_2$	$C_{44}H_{54}Cl_2N_2O_2Zr$	$C_{44}H_{54}Cl_2HfN_2O_2$	$C_{56}H_{64}N_2O_4Zr$
Formula weight	644.91	805.0	892.28	920.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$
a/Å	18.817(2)	25.135(3)	25.226(7)	13.210(10)
b/Å	11.504(2)	10.722(2)	10.762(10)	13.557(8)
c/Å	18.627(2)	15.917(3)	16.134(4)	15.287(7)
α/°	—	—	—	69.35(5)
β/°	105.337(5)	102.31(2)	102.13(2)	74.15(5)
γ/°	—	—	—	77.73(5)
Cell volume/Å^3	3888.6(9)	4191.0(12)	4282(4)	2444(3)
Z	4	4	4	2
μ/mm^{-1}	0.017	0.43	2.60	0.27
Total reflections	22684	7149	3844	4540
Independent reflections	9101 [R(int) = 0.0691]	3698 [R(int) = 0.0409]	3762 [R(int) = 0.0727]	4540 [R (int) = 0]
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0698, 0.1534	0.031, 0.079	0.047, 0.122	0.1186, 0.3364

Table 2 Selected bond distances (Å) and angles (°) for complexes **2** and **3**

	2	**3**
M–Cl	2.410(1)	2.394(2)
M–N	2.316(2)	2.294(2)
M–O	2.009(1)	2.003(5)
N–C(7)	1.297(3)	1.289(6)
C(1)–O	1.334(2)	1.333(7)
N–M–Cl	91.76(5)	91.56(12)
N–M–Cl′	161.18(4)	162.07(11)
N–M–O	76.42(6)	77.52(14)
Cl–M–Cl′	103.56(3)	103.10(10)
Cl′–M–N	161.18	162.07(11)
Cl–M–O	93.36(5)	93.99(13)
Cl′–M–O	91.62(5)	91.05(12)
O–M–O′	171.95(8)	171.9(2)
O′–M–N	97.11(6)	96.0(2)
N–M–N′	75.66(8)	76.2(2)
C(1)–O–M	141.50(13)	139.9(4)
C(7)–N–M	126.20(14)	126.4(4)
C(8)–N–M	118.55(12)	118.7(3)
C(7)–N–C(8)	114.7(2)	114.4(4)

Fig. 2. Selected bond lengths and angles are given in Table 2. The structure possesses a crystallographically imposed C_2 axis passing through Zr and the midpoint between C(9) and C(9′). A Chem3D representation of **2**, viewed along this axis, is given in Fig. 3. The metal centre has a distorted octahedral co-ordination environment. The imine nitrogen atoms occupy mutually *cis* sites, as do the chloride ligands, with the phenol oxygens in the remaining mutually *trans* sites. Thus, **2** belongs to the previously unknown class **III** of Schiff-base complexes, characterised by the fact that the planes containing O, Zr, O′ and N, Zr, N′ are almost orthogonal (*ca.* 97.1°). It is readily apparent that the overall structure is analogous to that of the *ansa*-metallocenes, *e.g.* Fig. 1(*a*).[2] A prochiral ligand in either of the two equivalent *cis* auxiliary co-ordination sites would experience the same enantiofacial steric differentiation. The *tert*-butyl groups in the 2 positions of the phenol rings which point forward over the metal centre are in a position which is stereochemically similar to the substituents β to the bridgehead atoms in *ansa*-metallocenes. These substituents play a crucial role in the stereoselectivity of α-olefin polymerisation catalysis by these compounds.[2] The bond angles and distances in **2** are similar to those observed in quadridentate Schiff-base complexes of zirconium.[5,17,27,36] The Zr–O distance of 2.009(1) Å and C–O–Zr angle of 141.50(13)° indicate some deviation from idealised sp^2 geometry at oxygen, in which the alkoxide is expected to act as a formal three electron LX ligand. However, the values fall some way short of those in a compound such as $[Li(OEt_2)_2][Zr(tritox)_2Cl_3]$ (tritox = $Bu^t{}_3CO$) in which the equivalent parameters are 1.889(8) Å and 171.9(6)° and the nearly linear C–O–Zr grouping can be regarded as a 6 electron, L_2X ligand.[37] The Zr–N(1) distance [2.316(2) Å] is typical of zirconium(IV) Schiff-base complexes. The structure and geometry suggest that **2** is best regarded as a 16 electron complex.

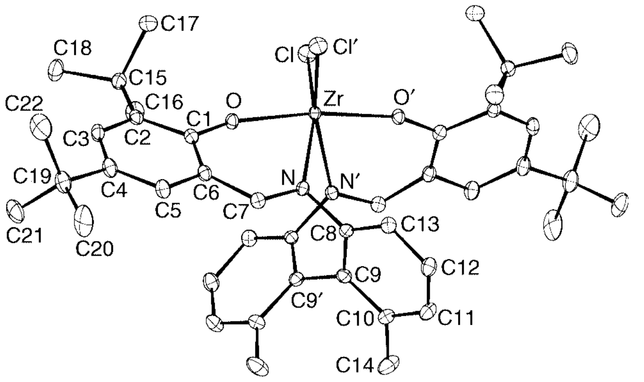


Fig. 2 Thermal ellipsoid plot of the molecular structure of $[ZrL^1Cl_2]$ **2** (non-hydrogen atoms). The hafnium analogue, complex **3**, is isostructural.

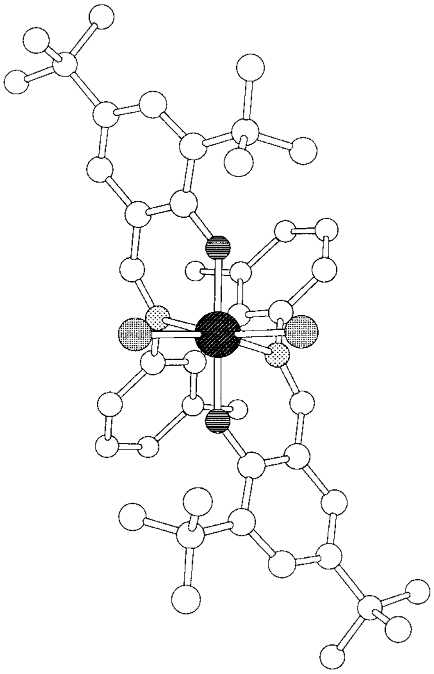


Fig. 3 Molecular structure of $[ZrL^1Cl_2]$ **2** (non-hydrogen atoms) viewed along the crystallographic C_2 axis.

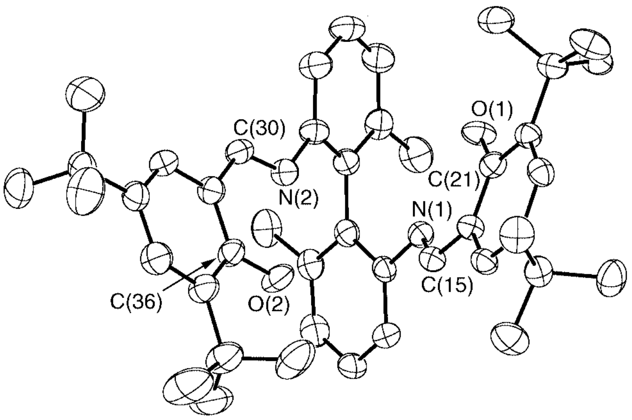


Fig. 4 Thermal ellipsoid plot of the molecular structure of H_2L^1

The hafnium analogue of **2**, $[HfL^1Cl_2]$ **3**, was synthesized in an analogous fashion and its structure was determined. It is isostructural with **2**, although with marginally shorter M–Cl, M–O, and M–N distances, consistent with the slightly smaller size of Hf^{IV} (85 pm) as compared to Zr^{IV} (86 pm).

The molecular structure of the proligand H_2L^1 shown in Fig. 4 has no unusual bond lengths in comparison to salicylideneimine compounds based on ethylenediamine or similar backbones.[38–40] The two imino bond lengths N(1)–C(15) and N(2)–C(30) of 1.277(3) and 1.282(3) Å increase slightly on co-ordination, to 1.297(3) and 1.289(6) Å in **2** and **3** respectively. The phenolic C(21)–O(1) and C(36)–O(2) bonds of 1.358(3) and 1.355(3) Å shorten slightly on metallation, to 1.334(2) and 1.333(7) Å in **2** and **3** respectively.

Attempts to synthesize alkyl derivatives $[ZrL^1R_2]$

The synthesis of alkyl derivatives of Schiff-base complexes is receiving attention[13,27,41] by virtue of the potential applications of these compounds in organic synthesis and catalysis. Reactions of **2** with reagents such as KCH_2Ph, LiMe, LiPh, EtMgBr, $LiCH(SiMe_3)_2$, and $AlMe_3$, employing a variety of solvents and reaction temperatures, were performed. In no case could a tractable product be isolated. The dichloride was consumed in each case, but the ^1H NMR spectra of the resultant materials were extremely complex. It is reasonable to assume that the failure to isolate alkyl derivatives of **2** by this method is due, at least in part, to the presence of the electrophilic imine carbon in the ligand backbone which may either be attacked directly by the alkylating agent, or to which the alkyl group may migrate from the metal centre. In a related system, Floriani and co-workers[7] have reported the migration of alkyl groups from zirconium to the imine carbon of a macrocyclic tetramethyldibenzotetraazaannulene ligand, a reaction which is promoted by the addition of a donor solvent. In an attempt to stabilise a possible alkyl-migrated product, the reaction of **2** and KCH_2Ph was conducted both in THF and in the presence of pyridine. In either case no well defined product could be isolated, although the ^1H NMR spectrum of the material from the reaction using pyridine contains resonances in the region δ 4–5 with J coupling consistent with a product in which one benzyl group had indeed become bonded to the imine carbon atom.

Dropwise addition of a slurry of H_2L^1 in light petroleum to one equivalent of $Zr(CH_2Ph)_4$ in the same solvent gives, in the absence of light, $[ZrL^1(CH_2Ph)_2]$ **4**. The product precipitates from the reaction mixture as an orange powder. The ^1H NMR spectrum contains similar ligand resonances to those of **2** and **3** together with a pair of AB doublets centred at δ 3.00 arising from diastereotopic benzyl CH_2 protons. Purification and thorough characterisation of this compound was severely hampered by its thermal and light sensitivity, and low solubility. Solutions of **4** decompose to a mixture of unidentified products in *ca.* 12 h even at −30 °C, making recrystallisation impractical. Decomposition occurs at room temperature over a period of weeks even in the solid state.

The stabilisation of metal–carbon σ bonds using Schiff-base ancillary ligands is well known in cobalt chemistry[42,43] but much less well so with other metals. Floriani *et al.*[6,11] have shown that alkylation of [Ti(acen)Cl(THF)] [acen = *N*,*N*′-ethylenebis(acetylacetoiminate) dianion] may be achieved by reaction with conventional nucleophilic alkylating agents, but the synthesis of titanium(IV) alkyl derivatives appears to be less straightforward. The migratory aptitude of alkyl groups supported by molybdenum Schiff bases is well defined.[41] These studies illustrate a fundamental point in the co-ordination/organometallic chemistry of Schiff bases; they are not inert spectator ligands, and indeed co-ordination of the imine nitrogen to an early transition metal centre not unexpectedly leads to increased electrophilicity of this group.

Synthesis of amido complexes $[ZrL^1(NR_2)_2]$

The reaction of compound **2** with $LiNMe_2$ followed by recrystallisation yields pale orange $[ZrL^1(NMe_2)_2]$ **5** in 70% yield (Scheme 2). Similarly, reaction of **2** with $LiNEt_2$ in diethyl ether gives $[ZrL^1(NEt_2)_2]$ **6** in 77% yield. The complexes **5** and **6** may also be synthesized by the reaction of H_2L^1 with the homoleptic zirconium amides $Zr(NR_2)_4$ (R = Me or Et). Their ^1H NMR spectra indicate that the C_2-symmetric structure present in **2** has been retained on substitution of the chloride ligands. All the NMe_2 protons of **5** are equivalent on the chemical shift timescale. The symmetry of **6** is also reflected in the appearance of the resonances for the amido ethyl groups; while the chemically equivalent methyl protons occur as a triplet at δ 0.99, the resonances for the diastereotopic methylene protons are observed as a two doublets of quartets, centred at δ 3.91 and 3.61. Observation of only two resonances for these methylene protons indicates that there is free rotation about the Zr–NEt_2 bonds.

The reaction of compound **2** with $LiNHBu^t$ gives another amido derivative $[ZrL^1(NHBu^t)_2]$ **7**. The target molecule in this instance was actually the *tert*-butyl imido complex $[ZrL^1({=}NBu^t)]$. Unfortunately **7** proved stable to the elimination of *tert*-butylamine even in refluxing toluene. A further attempt to access zirconium imido complexes containing L^1 by reaction of the disodium salt **1** with $[Zr({=}NR)Cl_2(py)_3]$ (R = 2,6-$Pr^i_2C_6H_3$) was made, following a synthetic methodology explored by Mountford,[44,45] but no well defined products could be isolated. We have recently characterised an imido derivative of niobium with supporting Schiff-base ligature.[32]

Reactions of $[ZrL^1(NR_2)_2]$

In order to establish whether compounds $[ZrL^1(NR_2)_2]$ have potential as ketone hydrosilation catalysts,[46–48] their reactions with triethoxysilane were investigated. Addition of an excess of $SiH(OEt)_3$ to **5** and **6** in diethyl ether resulted in a change from orange to pale yellow. After evaporation of volatiles, a yellow crystalline material was sublimed from the crude reaction product at 250 °C and 10^{-6} mbar. This was identified as $[ZrL^1(OEt)_2]$ **8**. ^1H NMR spectroscopy indicates that class **III** geometry is retained in solution. The formation of this very stable ethoxide derivative is not encouraging for the use of the amido precursors in hydrosilation catalysis.

Addition of an excess of trimethylsilyl chloride in pentane to a solution of compound **5** or **6** in diethyl ether at −78 °C gives, on warming to room temperature, a yellow precipitate of **2**. Such reactions of early transition metal amides are well established and have recently been used most effectively in the context of efficient synthesis of alkene polymerisation catalyst precursors.[49]

Jordan and co-workers[50] have demonstrated the use of $AlMe_3$ as a methylating agent in the conversion of zirconium

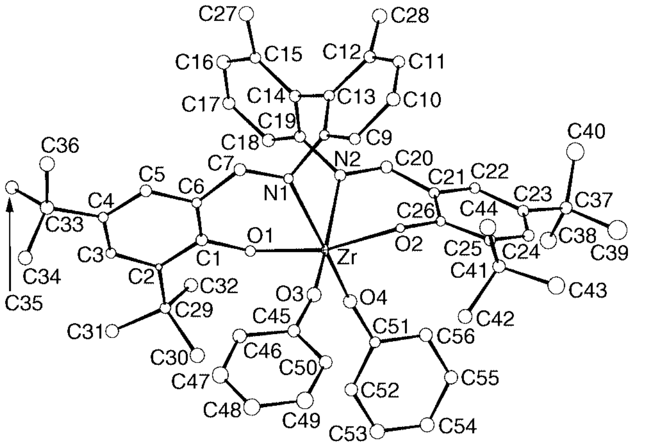


Fig. 5 Molecular structure of [ZrL^1(OPh)$_2$] **9** (non-hydrogen atoms). Only the Zr atom is anisotropic.

amido complexes into their methyl analogues. In the reaction of **5** or **6** with AlMe$_3$ the starting materials were consumed but no tractable products could be isolated.

Synthesis and structure of the phenoxide [ZrL^1(OPh)$_2$]

Initial attempts to produce alkoxide or aryl oxide derivatives of [ZrL^{1}Cl$_2$] **2** by reaction with NaOMe, LiOBut or LiOR′ (R′ = 2,6-*tert*-butyl-4-methylphenyl) led to the isolation of starting materials only. Also, an attempt to synthesize **8** from **2** and NaOEt led to no reaction, even in refluxing THF. However, reaction of **2** with two equivalents of freshly prepared LiOPh in diethyl ether at room temperature gives the pale yellow bis(alkoxide) complex [ZrL^1(OPh)$_2$] **9**. Sublimation of the filtered reaction product at 230 °C and 10^{-6} mbar gives pure **9** in 84% yield. It is not clear why LiOPh is the only alkoxide/aryl oxide reagent of those tried which reacts with **2**. Perhaps LiOBu^t and LiOR′ are too sterically demanding, and NaOMe and NaOEt may not react due to their polymeric nature.

The ^{1}H NMR spectrum of compound **9** indicates that the C_2-symmetric structure present in **2** is retained in solution. Single crystals of **9** were grown by heating a pre-sublimed sample in an evacuated glass tube at 200 °C and subjected to an X-ray crystallographic investigation. In this structure only the zirconium atom is anisotropic; attempts to refine the remaining non-H atoms anisotropic resulted in many non-positive definite thermal parameters. The reason for this problem was not clear, but two data collections on different crystals gave similar results. Hence the resulting molecular structure is of relatively low quality and a detailed discussion of bond lengths and angles would not be justified. It is however clear from the representation of the structure in Fig. 5 that the class **III** geometry is retained, with the phenoxide ligands occupying mutually *cis* positions in the distorted octahedral co-ordination environment at the metal centre. A further view of the structure, viewed down the approximate C_2 axis, is shown in Fig. 6. The arene rings of the phenoxide ligands are oriented towards the Schiff-base salicylidene rings, indicating the presence of edge-to-face interactions. The phenomenon of such non-covalent interactions between arene rings is well documented,[51] and for edge-to-face interactions the distances between the two ring centroids are found in the range 4.5–7.0 Å,[52] with a theoretical optimum distance of 5.2 Å.[53] In **9** the two centroid–centroid distances are *ca.* 5.5 and 4.9 Å. Jacobsen and co-workers[54] have postulated interactions of this nature as the possible origin of high stereoselectivities in aziridination reactions of olefins catalysed by a copper(I) Schiff-base complex.

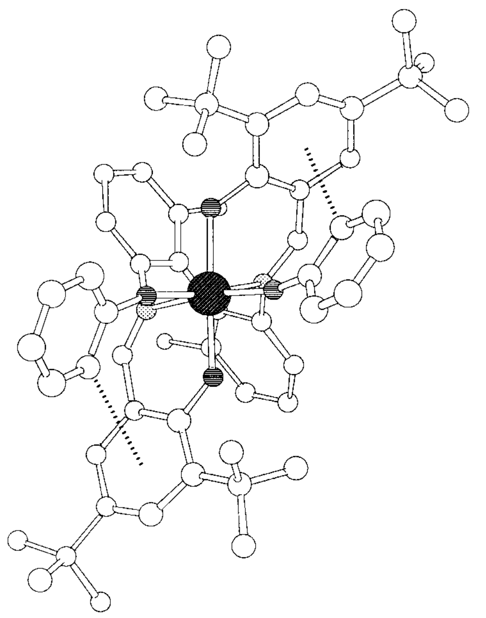
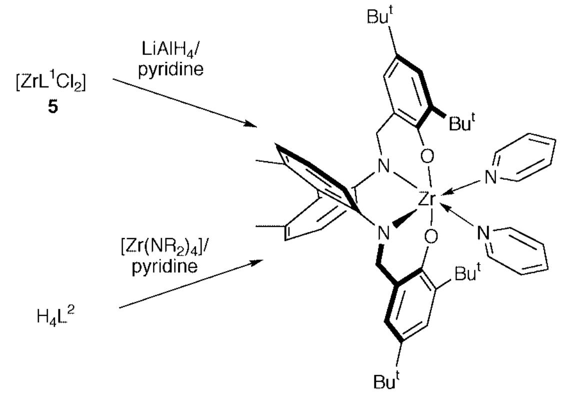


Fig. 6 Molecular structure of [ZrL^1(OPh)$_2$] **9** (non-hydrogen atoms) viewed along the approximate C_2 axis and indicating the arene edge–face interactions.

Synthesis of [ZrL^2(py)$_2$] 10

Treatment of a pyridine solution [ZrL^{1}Cl$_2$] with an excess of lithium aluminium hydride led to a change from yellow to orange over a period of several hours. Crystallisation of the products from light petroleum gave pale yellow, highly air and moisture sensitive **10** in 56% yield (Scheme 3). The ^{1}H NMR spectrum of this sample was found to contain no resonances attributable to imine N=CH protons. This, and further characterisation, led us to conclude that the lithium aluminium hydride had effected the reduction of the ligand imine groups, presumably *via* attack by hydride at the exposed imine carbon atoms and elimination of LiCl. The concomitant formation of Zr–N amido bonds leads to the tetraanionic "reduced" form of the ligand L^1, designated L^2 (Scheme 1).

The reaction of H$_2$L^1 in diethyl ether with an excess of LiAlH$_4$ followed by hydrolysis gives H$_4$L^2 quantitatively. The reaction of H$_4$L^2 with Zr(NR$_2$)$_4$ (R = Me or Et) in either neat pyridine or in light petroleum in the presence of an excess of pyridine causes deprotonation of both the phenol and amine functionalities of the ligand and the formation of compound **10** (Scheme 3). If either of the above synthetic routes to **10** are performed in a non co-ordinating solvent such as toluene, or in THF, no isolable products can be separated from the reaction mixture.



[ZrL^2(py)$_2$]
10

Scheme 3 Syntheses of [ZrL^2(py)$_2$] **10**.

The ^{1}H NMR spectrum of compound **10** contains two resonances assigned to *tert*-butyl groups (δ 1.53 and 1.32) and one resonance assigned to methyl groups (δ 1.94), indicating that the complex has a symmetrical structure which may belong to either the pseudo class **I** or class **III** structural type. Another key feature of the ^{1}H NMR spectrum is the resonance for the ligand methylene groups. The chiral environment of the complex renders these protons diastereotopic and they appear as a pair of AB doublets at *ca.* δ 4.78 and 4.33. The resonances for the protons of the co-ordinated pyridine groups occur at δ 8.38, 6.56 and 6.25. These chemical shifts differ markedly from those for free pyridine (δ 8.74, 7.54, and 7.22) indicating that the pyridine molecules are indeed co-ordinated to the metal centre rather than merely included in the crystal lattice. Further evidence for this is provided by the integrals of the relevant resonances, which correspond to exactly ten protons irrespective of the method of synthesis and history of a given sample.

Unfortunately, repeated attempts to grow crystals of compound **10** suitable for X-ray analysis have not proved fruitful, but nevertheless molecular modelling studies suggest a very strong preference for the adoption of the *cis-cis* (pseudo class **III**) structure as depicted in Scheme 3.

Conclusion

We have synthesized Schiff-base complexes of zirconium and hafnium with the hitherto unknown *cis-cis*, C_2-symmetric class **III** orientation. The structures formed are analogous to those of the technologically important *ansa*-metallocenes. The halide ligands of the parent complex [ZrL^{1}Cl$_2$] undergo clean reactions with hard nucleophiles such as amide and alkoxide, but softer nucleophiles such as organometallic carbon and hydride tend to attack the co-ordinated imine function. This is clearly an important issue with regard to the use of these complexes in catalysis. We are now engaged in the development of ligand sets similar to L^1 and L^2 for which this latter pathway is excluded and in which the well expressed chiral environment of *e.g.* **2** is retained.

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