C_2-symmetric Schiff-base complexes of zirconium; structural analogues of the *ansa*-metallocenes

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The first *cis*-oriented C_2-symmetric quadridentate Schiff-base complex displays clean reactivity at both zirconium and ligand centres, giving a range of derivatives including a complex containing a tetraanionic N_2O_2 ligand.

C_2-symmetric *ansa*-metallocenes of the group 4 metals [*e.g.* Fig. 1(*a*)] have been successfully developed as catalysts for tacticity-controlled polymerisation,[1] and for enantioselective processes as varied hydrogenation,[2] kinetic resolution,[3] Diels–Alder cycloadditions[4] and hydrosilylation.[5] There is world-wide interest in the design and synthesis of non-cyclopentadienyl alternatives to these catalysts, using for example imido,[6] amido[7] and Schiff-base[8] ligands.

Most quadridentate Schiff-base complexes have the *trans*-structure **I** [Fig. 1(*b*)], although a few examples with the unsymmetric *cis*-structure **II** are known.[9,10] Molecular- modelling studies suggested to us that biaryldiamine-bridged ligands, previously used only in late-transition-metal complexes,[11] would have a strong preference for the hitherto unknown *cis* C_2-symmetric structure **III**; the non-planar coordination is enforced by the geometry of the biaryl fragment. We describe here the successful synthesis and structural characterisation of this type of complex, along with some preliminary studies of metal- and ligand-centred reactivity.

The new Schiff-base proligand (±)-H_2L^1 **1** (Scheme 1) was synthesised from 2,2′-diamino-6,6′-dimethylbiphenyl[12] and 3,5-di-*tert*-butylsalicylaldehyde[13] and was converted cleanly to its disodium salt **2** with sodium hydride in thf. Reaction of **2** with $[ZrCl_4(thf)_2]$ followed by either recrystallisation from toluene or sublimation at 250–300 °C (10^{-6} mbar) gave analytically pure *cis*-(±)-$[ZrL^1Cl_2]$ **3** in 93% yield.†

Single crystals of **3** grown by heating a sample to 250 °C in an evacuated glass tube were subjected to an X-ray crystallographic investigation.‡ The molecular structure is shown in Fig. 2. The unique non-planar orientation of the Schiff-base ligand is characterised by the fact that the planes defined by O, Zr, O′ and N, Zr, N′ are nearly orthogonal. The two chloro ligands are *cis*-oriented, the Cl–Zr–C′ angle being 103.56(3)°. Jordan and coworkers have reported the structures of some quadridentate Schiff-base complexes in which the X–Zr–X angle is as low as 130°.[8] However, since the N_2O_2 framework in these compounds is essentially planar, they are best described as having distorted class **I** structures [Fig. 1(*b*)]. The overall structure of **3** is analogous to that of *ansa*-metallocene complexes such as *rac*-ethylenebis(tetrahydroindenyl)dichlorozirconium[14] [Fig. 1(*a*)]. A prochiral ligand in either of two *cis* auxiliary coordination sites would experience the same enantiofacial steric differentiation. Fig. 3 is a stereoview of the molecular structure of **3** viewed along the crystallographic C_2-axis.

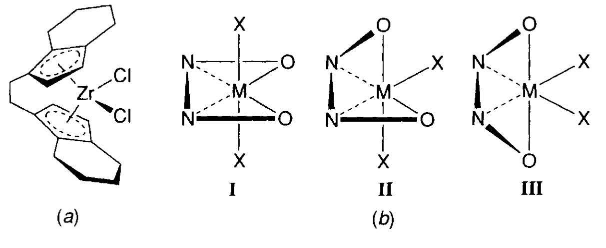
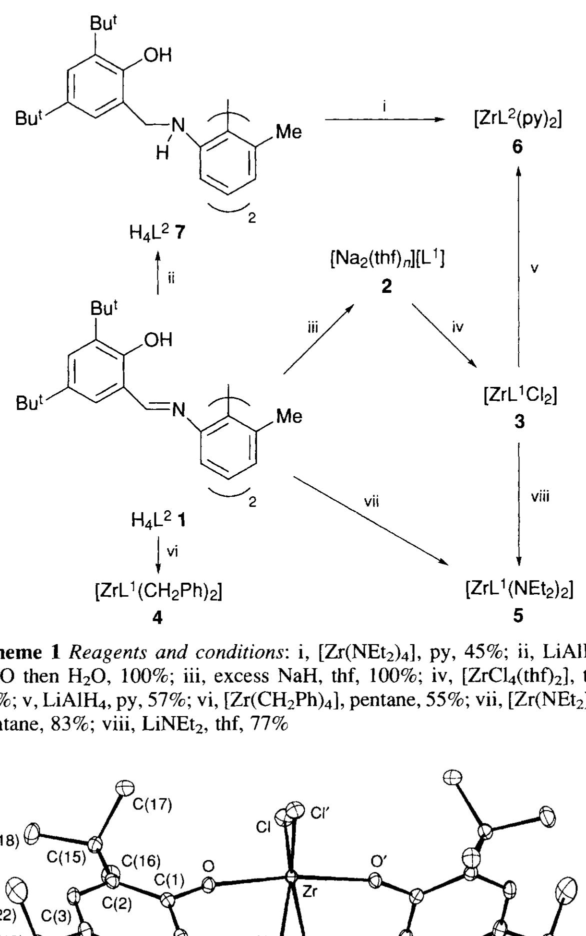


Fig. 1 (*a*) A prototypical *ansa*-metallocene and (*b*) three structural classes of (quadridentate Schiff-base)MX_2 complexes

Complex **3** is, to our knowledge, the first example of a class **III** Schiff-base complex. NMR data are consistent with this structure being retained in solution; no species with the



Scheme 1 *Reagents and conditions*: i, $[Zr(NEt_2)_4]$, py, 45%; ii, $LiAlH_4$, Et_2O then H_2O, 100%; iii, excess NaH, thf, 100%; iv, $[ZrCl_4(thf)_2]$, thf, 93%; v, $LiAlH_4$, py, 57%; vi, $[Zr(CH_2Ph)_4]$, pentane, 55%; vii, $[Zr(NEt_2)_4]$, pentane, 83%; viii, $LiNEt_2$, thf, 77%

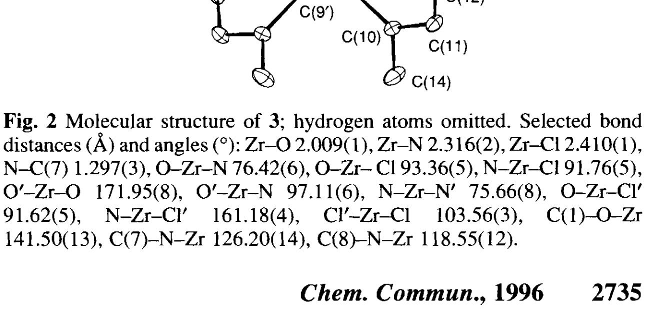


Fig. 2 Molecular structure of **3**; hydrogen atoms omitted. Selected bond distances (Å) and angles (°): Zr–O 2.009(1), Zr–N 2.316(2), Zr–Cl 2.410(1), N–C(7) 1.297(3), O–Zr–N 76.42(6), O–Zr– Cl 93.36(5), N–Zr–Cl 91.76(5), O′–Zr–O 171.95(8), O′–Zr–N 97.11(6), N–Zr–N′ 75.66(8), O–Zr–Cl′ 91.62(5), N–Zr–Cl′ 161.18(4), Cl′–Zr–Cl 103.56(3), C(1)–O–Zr 141.50(13), C(7)–N–Zr 126.20(14), C(8)–N–Zr 118.55(12).

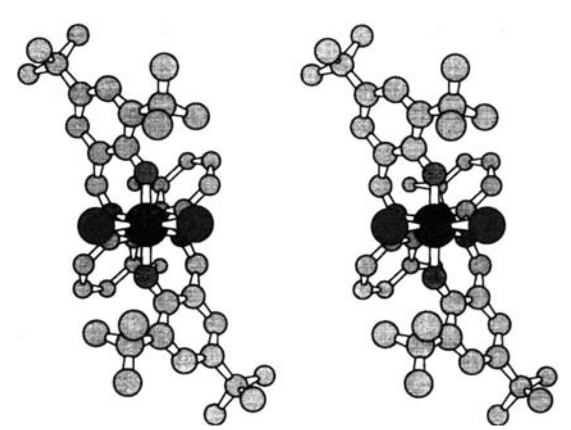


Fig. 3 Stereoview of **3** viewed along the crystallographic C_2 axis

unsymmetric structure (**II**) could be detected at accessible temperatures.

Our initial attempts to synthesise derivatives [ZrL^{1}R$_2$] from **3** using a variety of alkylating agents have been unsuccessful, presumably because of the electrophilicity of the coordinated imine groups (*vide infra*). However, reaction of H$_2$L^1 **1** with [Zr(CH$_2$Ph)$_4$] in pentane gave an orange microcrystalline precipitate for which ^{1}H NMR and mass spectra indicate the formula (±)-[ZrL^1(CH$_2$Ph)$_2$] **4** (55%); the ligand L^1 displays similar resonances to that in **3** and the diastereotopic benzyl CH$_2$ groups give rise to an AB quartet at δ *ca.* 3.0. The thermal- and light-sensitivity of this species have thus far frustrated further analysis.

Reaction of **3** with Li(NEt$_2$) in thf gave the amido derivative (±)-[ZrL^1(NEt$_2$)$_2$] **5** in 77% yield. This compound, which can also be prepared directly from **1** and [Zr(NEt$_2$)$_4$] in pentane (83%), is much more stable than the benzyl derivative **4** and will hopefully provide us with a convenient entry into the little explored area of enantio- or diastereo-selective M–N insertion and σ-bond metathesis chemistry of chiral metal amides.[15]

Reaction of **1** with LiAlH$_4$ in pyridine (py) gives (±)-[ZrL^2(py)$_2$] **6**, presumably *via* nucleophilic attack by hydride at the exposed imine carbon atoms [C(7) in Fig. 1] and elimination of LiCl. The protonated form of the novel chiral quadridentate tetraanionic N$_2$O$_2$ ligand contained in **6**, *i.e.* H$_4$L^2 **7**, can be prepared quantitatively on a large scale by reduction of **1** with LiAlH$_4$ followed by hydrolysis. This compound reacts directly with [Zr(NEt$_2$)$_4$] in pyridine or other solvents eliminating HNEt$_2$ to give complexes such as **6**, thus providing a convenient route to the chiral Lewis-acidic [ZrL^2] system.

We have developed rigid Schiff-base complexes of zirconium with the novel *cis* C_2-symmetric orientation, giving structures that are analogous to those observed in the technologically important *ansa*-metallocenes. While the instability of alkyl derivatives such as **4** would determine that **3** is unlikely to be a catalyst precursor for single-site Ziegler–Natta polymerisation, its facile conversion to dialkylamido compounds like **5** and diamidodiphenoxido derivative **6** indicates that this system will have an extensive chemistry. Given the ready electronic and steric manipulation of this type of ligand, we envisage a number of avenues for study in enantioselective reactivity and catalysis studies. Our current work in this area includes the chemistry of group 5, manganese and f-element derivatives.

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Footnotes

† *Selected NMR data* (^{1}H, 300 MHz, 298 K, [^{2}H$_6$]benzene): **3**, δ 7.86 (s, 2 H, N=CH), 7.75 (d, 2 H, phenolic ArH), 7.05 (d, 2 H, biaryl H), 6.90 (m, 4 H, biaryl H and phenolic ArH), 6.68 (d, 2 H, biaryl H), 1.73 (s, 24 H, Bu^t and Ar*Me*), 1.13 (s, 18 H, Bu^t).

5, δ 7.70 (s, 2 H, N=C*H*), 7.56 (d, 2 H, phenolic ArH), 7.27 (d, 2 H, biaryl H), 6.93 (t, 2 H, biaryl H), 6.76 (d, 2 H, phenolic ArH), 6.50 (d, 2 H, biaryl H), 3.91 (2 × q, 4 H, CH$_2$), 3.61 (2 × q, 4 H, CH$_2$), 1.76 (s, 24 H, Bu^t and Ar*Me*), 1.15 (s, 18 H, Bu^t), 0.99 (dd, 12 H, Me).

6, δ 8.38 (d, 4 H, pyridine H), 7.37 (s, 2 H) and 7.29 (d, 2 H, phenolic H), 6.77 (t, 2 H) and 6.57 (m, 4 H, biaryl H), 6.25 (m, 6 H, pyridine H), *ca.* 4.55 (AB q, 4 H, NCH$_2$), 1.94 (s, 6 H, Me), 1.54 (s, 18 H) 1.32 (s, 18 H, Bu^t).

‡ *Crystallographic details*: $C_{44}H_{54}Cl_2N_2O_2Zr$, M = 805.0, monoclinic, space group $C2/c$ (no. 15), a = 25.135(3), b = 10.722(2), c = 15.917(3) Å, β = 102.31(2)°, U = 4191.0(12) Å^3, Z = 4, D_c = 1.28 g cm^{-3}, $F(000)$ = 1688. Yellow air-stable block (0.60 × 0.50 × 0.50 mm) in oil, λ = 0.710 73 Å, μ(Mo-Kα) = 0.43 mm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer in θ–2θ mode using graphite- monochromated Mo-Kα radiation at 173(2) K. A total of 7149 reflections were measured ($2 < \theta < 25°$), 3698 unique [R_{int} = 0.0409 after absorption correction (T_{max} = 1.00, T_{min} = 0.91)], giving 3224 with $I > 2\sigma(I)$. All atoms were located by direct methods (SHELXS-86) and refined by full-matrix least squares on all F^2 with anisotropic thermal parameters (non-H atoms) (SHELXL-93) and scattering factors from ref. 16. H atoms included in riding mode with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl groups. The C(14) methyl group was fixed at idealised geometry but disordered equally over the two orientations related by rotation of 60° about C(10)–C(14). Final $R1$, $wR2$ and S were 0.031, 0.079 and 1.079. The structure of the Hf analogue has been fully refined and is isomorphous with **3**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/296.

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