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Geometrical isomerism and redox behaviour in zirconium–Schiff base complexes: the formation of C−C bonds functioning as two-electron reservoirs †

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Two model compounds have been used for exploring the ligand-based redox chemistry of zirconium–Schiff base complexes, namely [Zr(salophen)Cl_2(thf)] **1** and [Zr(salophen)$_2$] **2** [salophen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine dianion, thf = tetrahydrofuran]. The latter occurs in two thermally non-interconvertible isomeric forms, **2A** and **2B**. Both contain eight-co-ordinate zirconium in a dodecahedral, **2A**, and in a square-antiprismatic environment, **2B**. The reduction of **1** with either Na or Mg led to the isolation of [$Zr_2LL'_2$] (L′ = thf **3** or pyridine **4**). The centrosymmetric dinucleating octaanionic ligand L, which contains two-fold coupled salophen units joined by two C−C bonds, arises from the intermolecular reductive coupling of four imino groups belonging to two Zr(salophen) units. In an attempt to perform intramolecularly the same transformation, complexes **2A** and **2B** were reduced with sodium. Both isomers gave complex [ZrL″Na_4(dme)$_4$] **5** (dme = 1,2-dimethoxyethane) containing a novel form of an hydrogenated coupled salophen ligand, L″, where the two salophen units are joined by a single C−C bond. The C−C bonds in the ligand L have been exploited as two-electron reservoirs in the reaction of **3** with $PhICl_2$ and 9,10-phenanthrenequinone. In this reaction the original salophen moiety is restored in its original form and the Zr(salophen) moiety present in **3** behaves as a source of masked zirconium(II).

The use of polydentate macrocyclic ligands has had a recent renaissance with the objective of moving to a new area of ancillary ligands in the organometallic chemistry of early transition metals.[1–4] In this context, relatively limited attention has been devoted to the tetradentate Schiff bases, which served in the past as ancillary ligands for a large number of complexes containing Co−C σ bonds.[5] The major limitation in the use of Schiff bases as ancillary ligands for high-valent early transition metals derives from the presence of metal-enhanced electrophilic imino groups, which react with alkylating agents or function as accepting groups in migratory insertion reactions.[1a,1d,2k] On the other hand, the redox chemistry of metal–Schiff base complexes, which received a lot of attention in the case of late transition metals,[5,6] is almost neglected for early transition metals. Taking advantage of the fact that the redox chemistry of transition metal–Schiff base complexes can be metal- or ligand-centred,[7] we decided to explore the rather unknown zirconium–Schiff base compounds,[1b] with the purpose of investigating the ligand-centred redox chemistry. We report here the redox chemistry of two model compounds, namely [Zr(salophen)Cl_2(thf)][1b] [H_2salophen = *N*,*N*-bis(salicylidene)-*o*-phenylenediamine, thf = tetrahydrofuran] and [Zr(salophen)$_2$],[8] the latter of which occurs in two distinct isomeric forms, and an investigation into their intermolecular and intramolecular ligand reductions. Such reactions have led to the formation of intraligand C−C bonds acting as two-electron reservoirs.[7]

Experimental

General

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Proton NMR and IR spectra were recorded on AC-200, DPX-400 Bruker, and Perkin-Elmer FT 1600 instruments, respectively. Activated metals have been prepared according to ref. 9.

Syntheses

[Zr(salophen)Cl_2(thf)] 1. A thf (250 cm^3) suspension of NaH (2.70 g, 112.4 mmol) was slowly added to an orange solution of H_2salophen (17.8 g, 56.2 mmol) in thf (250 cm^3). The resulting orange-yellow suspension was heated to 50 °C for 20 min and the excess of NaH removed. The compound [$ZrCl_4$(thf)$_2$] (21.2 g, 56.2 mmol) was then added and the mixture refluxed for 4 h. The yellow solid was filtered off, extracted with the mother-liquor to remove NaCl and the yellow suspension then concentrated to 50 cm^3. *n*-Hexane (150 cm^3) was added and the resulting yellow precipitate filtered off and dried *in vacuo* (24.5 g, 80%) (Found: C, 52.56; H, 3.95; N, 5.01. $C_{24}H_{22}Cl_2N_2O_3Zr$ requires C, 52.55; H, 4.04; N, 5.11%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.63 (s, 1 H, HC=N), 7.55 (m, 2 H, aryl), 7.43 (br s, 2 H, aryl), 6.96 (t, *J* = 7.2, 1 H, aryl), 6.83 (d, *J* = 8.4 Hz, 1 H, aryl), 4.41 (m, 2 H, thf) and 2.06 (m, 2 H, thf). ^{13}C-{^{1}H}NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 164.1 (d, *J* = 163.5), 163.5 (s), 145.3 (s), 137.7 (d, *J* = 159.5), 135.9 (d, *J* = 164.8), 129.6 (d, *J* = 166.3), 123.6 (s), 120.1 (d, *J* = 155.7), 119.5 (d, *J* = 153.8), 118.5 (d, *J* = 158.8), 70.86 (t, *J* = 145.6, thf) and 25.97 (t, *J* = 125.8 Hz, thf).

[Zr(salophen)$_2$] 2A. The compounds H_2salophen (40.32 g, 127.4 mmol) and [$ZrCl_4$(thf)$_2$] (24.0 g, 63.7 mmol) were added to toluene (1000 cm^3) and the resulting orange-red mixture refluxed for 3 d. The suspension was taken to dryness and the yellow solid added to CH_2Cl_2 (400 cm^3), filtered and extracted with the mother-liquor. The yellow mixture was again taken to dryness and *n*-hexane (350 cm^3) added. The yellow product was

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† Dedicated to Professor Sir Geoffrey Wilkinson, a ‘Maestro’ of organometallic chemistry.

filtered off and dried *in vacuo* (34.3 g, 75%) (Found: C, 66.50; H, 3.93; N, 7.78. $C_{40}H_{28}N_4O_4Zr$ requires C, 66.74; H, 3.92; N, 7.76%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.50 (s, 1 H, HC=N), 7.47 (m, 1 H, aryl), 7.41 (m, 1 H, aryl), 7.19 (dd, $J_o = 7.6$, $J_m = 1.8$, 1 H, aryl), 7.00 (ddd, $J_o = 8.6$, 7.6, $J_m = 1.8$, 1 H, aryl), 6.48 (td, $J_o = 7.6$, $J_m = 1.8$, 1 H, aryl) and 5.93 (d, $J = 8.6$ Hz, 1 H, aryl). $^{13}C-\{^1H\}$NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 166.0 (s), 160.7 (d, $J = 160.7$), 146.5 (s), 135.3 (d, $J = 157.2$), 134.5 (d, $J = 156.4$), 128.4 (d, $J = 162.8$), 123.0 (s), 120.4 (d, $J = 160.0$), 119.1 (d, $J = 154.1$) and 116.7 (d, $J = 162.1$ Hz).

[Zr(salophen)$_2$] 2B. A thf (200 cm^3) suspension of NaH (2.68 g, 112.0 mmol) was added slowly to an orange thf (200 cm^3) solution of H_2salophen (16.1 g, 50.9 mmol). The resulting orange-yellow suspension was heated at 50 °C and the excess of NaH filtered off. The compound ($ZrCl_4(thf)_2$] (9.59 g, 25.4 mmol) was then added and the mixture refluxed for 4 h. The yellow suspension was filtered and the yellow solid extracted with the mother-liquor for 1 d. This operation resulted in pure isomer **2B** and NaCl on the extraction filter and a mixture of isomers **2A** and **2B** (2:3) in the filtrate. The solid was then extracted with fresh thf (200 cm^3) for 1 week and the resulting suspension concentrated (50 cm^3) and *n*-hexane (150 cm^3) added. Crystals suitable for X-ray analysis were grown from a pyridine–hexane solution {Found: C, 66.70; H, 4.62; N, 6.85 [Zr(salophen)$_2$]·thf, $C_{44}N_{36}N_4O_5Zr$ requires C, 66.82; H, 4.59; N, 7.09%}. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.84 (s, 1 H, HC=N), 8.38 (s, 1 H, HC=N), 7.96 (d, $J = 7.6$, 1 H, aryl), 7.43 (t, $J = 7.6$, 1 H, aryl), 7.37 (d, $J = 8.4$, 1 H, aryl), 7.25 (d, $J = 8.4$, 1 H, aryl), 7.06 (t, $J = 7.4$, 1 H, aryl), 7.01 (t, $J = 8.4$, 1 H, aryl), 6.91 (t, $J = 8.4$, 1 H, aryl), 6.83 (d, $J = 7.4$, 1 H, aryl), 6.64 (t, $J = 8.4$, 1 H, aryl), 6.60 (t, $J = 8.4$, 1 H, aryl), 6.09 (d, $J = 8.4$, 1 H, aryl), 5.74 (d, $J = 8.4$, 1 H, aryl), 3.7 (m, 2 H, thf) and 1.8 (m, 2 H, thr). $^{13}C-\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 165.2 (s), 162.1 (s), 160.1 (d, $J = 165.5$), 159.6 (d, $J = 160.8$), 144.6 (s), 144.5 (s), 133.3 (d), $J = 153.1$), 132.8 (d, $J = 164.1$), 131.7 (d, $J = 155.9$, 2C), 126.0 (d, $J = 162.1$), 125.4 (d, $J = 161.2$), 120.6 (s), 119.6 (s), 119.1 (d, $J = 175.5$), 118.4 (d, $J = 167.7$), 116.1 (d, $J = 183.8$), 115.7 (d, $J = 171.2$), 115.0 (d, $J = 157.9$), 114.4 (d, $J = 153.8$), 67.4 (t, $J = 140.6$) and 25.2 (t, $J = 135.8$ Hz). IR (Nujol, $\tilde{\nu}_{max}$/cm^{-1}): 1607s, 1580s and 1537s. The mixture obtained from the first extraction and which contained isomers **2A** and **2B** (^1H NMR, 2:3 respectively) was taken to dryness and hexane (150 cm^3) added. The yellow solid was filtered off and then dried *in vacuo* (12.1 g, 60%) (Found: C, 66.57; H, 4.52; N, 6.90. $C_{40}H_{28}N_4O_4Zr$·thf requires C, 66.82; H, 4.59; N, 7.09%).

Reaction of compound 2 with [ZrCl$_4$(thf)$_2$]. The reaction of compound **2A** or **2B** (9.51 g, 13.2 mmol) and [$ZrCl_4(thf)_2$] (4.99 g, 13.2 mmol) in thf (300 cm^3) gave a yellow suspension which was refluxed for 1 d. The yellow solid, **1**, identified *via* microanalysis and IR and NMR spectra, was then collected and dried *in vacuo* (9.2 g, 64%).

Compound 3. *Method A*.—To a suspension of activated Mg[9] (1.26 g, 51.8 mmol) in thf (250 cm^3) was added compound **1** (9.18 g, 16.7 mmol). The yellow suspension was stirred overnight resulting in a change from yellow to deep red. Extraction of the reaction solids with the mother-liquor (to remove excess of Mg) gave a yellow solid crystallizing spontaneously from the solution. It was collected and dried *in vacuo* (5.9 g, 69%). Crystals suitable for X-ray analysis were grown from thf solution (Found: C, 60.72; H, 5.35; N, 5.15. **3**·thf, $C_{52}H_{52}N_4O_6Zr_2$ requires C, 60.79; H, 5.10; N, 5.45%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.17 (td, $J_o = 8$, $J_m = 1.6$, 2 H, aryl), 7.15 (dd, $J_o = 8$, $J_m = 1.6$, 2 H, aryl), 6.81 (td, $J_o = 8$, $J_m = 1.6$, 2 H, aryl), 6.56 (dd, $J_o = 8$, $J_m = 1.6$ Hz, 2 H, aryl), 6.36 (m, 2 H, aryl), 6.12 (m, 2 H, aryl), 4.77 (s, 2 H, HC−N), 3.90 (m, 4 H, thf$_a$), 3.68 (m, 2 H, thf$_b$), 1.82 (m, 2 H, thf$_b$) and 1.48 (m, 4 H, thf$_a$). $^{13}C-\{^1H\}$ NMR (50.33 MHz, CD_2Cl_2, 298 K): δ 160.0 (s, aryl), 137.8 (s, aryl), 129.7 (d, $J = 154.9$), 129.6 (s, aryl), 128.9 (d, $J = 155.7$, aryl), 120.9 (d, $J = 160.2$, aryl), 119.3 (d, $J = 163.3$, aryl), 117.4 (d, $J = 157.2$, aryl), 113.6 (d, $J = 164.8$, aryl), 73.1 (t, $J = 151.1$, thf$_a$), 69.2 (d, $J = 145.0$, HC−N), 68.2 (t, $J = 143.5$, thf$_b$), 26.0 (t, $J = 131.2$, thf$_b$) and 25.6 (t, $J = 135.8$ Hz, thf$_a$).

Method B.—To a sodium (1.73 g, 75.2 mmol)–mercury (40 cm^3) amalgam[10] in thf (250 cm^3) was added compound **1** (20.6 g, 37.6 mmol). The yellow suspension was stirred overnight resulting in a change from yellow to deep red. Mercury was separated and the red-brown suspension filtered and then extracted to remove NaCl. The resulting yellow microcrystalline solid (the filtrate was deep red) was collected and dried *in vacuo* (5.50 g, 28.5%).

Compound 4. Complex **3** recrystallized from neat pyridine (py) to give **4**·4py (Found: C, 65.69; H, 4.82; N, 10.46. $C_{70}H_{58}N_{10}O_4Zr_2$ requires C, 65.39; H, 4.55; N, 10.89%). ^1H NMR (CD_2Cl_2, 298 K): δ 8.57 (m, py), 7.67 (m, py), 7.31 (m, py), 7.20 (m, 8 H), 6.82 (dt, 4 H), 6.52 (dd, 4 H), 6.08 (m, 4 H), 5.88 (m, 4 H) and 4.93 (s, 4 H).

Compound 5. Compound **2A** or **2B** (10.6 g, 14.8 mmol) and Na (1.97 g, 85.7 mmol) were added to 1,2-dimethoxyethane (dme) (400 cm^3) and the mixture refluxed. The solution slowly changed from yellow to deep violet and then to brick red. After 2 d it was filtered to remove excess of Na, and the filtrate taken to dryness. To the light red residue was added *n*-hexane (200 cm^3) and stirred for 12 h. The resulting white solid was filtered off and dried *in vacuo* (14.2 g, 82%) (Found: C, 57.40; H, 6.09; N, 4.89. **5**·4dme, $C_{56}H_{76}N_4Na_4O_{12}Zr$ requires C, 57.27; H, 6.01; N, 4.77%). ^1H NMR (400 MHz, CD_3CN, 298 K): δ 7.20 (d, $J = 6.8$, 1 H, aryl), 7.08 (d, $J = 7.0$, 1 H, aryl), 6.92 (t, $J = 7.0$, 1 H, aryl), 6.69 (t, $J = 6.4$, 1 H, aryl), 6.50 (d, $J = 7.0$, 1 H, aryl), 6.44 (t, $J = 7.0$, 1 H, aryl), 6.29 (d, $J = 6.8$, 2 H, aryl), 6.17 (d, $J = 6.8$, 1 H, aryl), 6.08 (t, $J = 7.3$, 1 H, aryl), 5.92 (t, $J = 7.3$, 1 H, aryl), 5.86 (d, $J = 7.3$, 1 H, aryl), 4.99 (s, 1 H, HC−N), 4.91 (d, $J = 14.4$, 1 H, H_2C−N), 4.36 (d, $J = 14.4$ Hz, 1 H, H_2C−N), 3.44 (s, 4 H, dme) and 3.27 (s, 6 H, dme). ^{13}C NMR (100.6 MHz, CD_3CN, 298 K): δ 161.1, 151.1, 151.3, 138.1, 133.7, 131.3, 129.0, 127.6, 126.6, 121.7, 115.3, 113.9, 113.4, 112.9, 107.0, 105.1, 72.3 (dme), 59.2 (dme) and 50.2. Crystals suitable for X-ray analysis were obtained from a Et_2O–thf mixture.

Reaction of compound 3 with PhICl$_2$. Compound **3**·thf (1.50 g, 1.46 mmol) and $PhICl_2$[11] (0.80 g, 2.92 mmol) were added to thf (200 cm^3) and stirred overnight. The solution slowly changed from dark yellow to deep orange. The resulting solution was filtered and taken to dryness. Dichloromethane (100 cm^3) was added and the pale orange solution filtered and concentrated to 50 cm^3. Diethyl ether (40 cm^3) was then added and the yellow product **1** collected and dried *in vacuo* (0.76 g, 47.4%) (Found: C, 52.10; H, 3.90; N, 4.88%). The IR and NMR spectra were identical to those of an authentic sample.

Reaction of compound 3 with 9,10-phenanthrenequinone. A thf (100 cm^3) solution of 9,10-phenanthrenequinone (0.55 g, 2.66 mmol) was added dropwise to a yellow solution of [Zr_2(salophen)$_2$·2thf]·thf (1.36 g, 1.32 mmol) in thf (100 cm^3). The green suspension was refluxed for 3 d. The resulting bright blue solid, **7**, was collected and washed with CH_2Cl_2, then dried *in vacuo* (0.52 g, 39%) (Found: C, 66.60; H, 3.34. $C_{28}H_{16}O_4Zr$ requires C, 66.40; H, 3.19%). IR (Nujol, $\tilde{\nu}_{max}$/cm^{-1}) 1606w, 1584w and 1556m. NMR measurements were not possible due to the low solubility of the complex. The green solution was concentrated to 50 cm^3, Et_2O (70 cm^3) added, and the yellow precipitate **2A** collected and dried *in vacuo* (0.64 g, 30.5%).

Table 1 Experimental data for the X-ray diffraction studies on crystalline complexes **2B**, **4** and **5**

	2B	**4**	**5**
Formula	$C_{40}H_{28}N_4O_4Zr_2 \cdot C_5H_5N$	$C_{50}H_{38}N_6O_4Zr_2 \cdot 4C_5H_5N$	$C_{120}H_{148}N_8Na_8O_{19}Zr_2$
M	878.1	1285.7	2372.9
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	14.387(4)	15.178(2)	14.563(2)
b/Å	20.410(5)	15.264(2)	17.388(3)
c/Å	14.455(3)	12.828(2)	22.947(4)
β/°	104.88(2)	93.13(2)	99.51(2)
U/Å^3	4102.2(18)	2967.5(7)	5730.8(17)
Z	4	2	2
λ/Å	1.541 78	0.710 69	1.54178
D_c/g cm^{-3}	1.422	1.439	1.375
μ/cm^{-1}	26.44	4.02	23.65
Transmission coefficient range	0.880–1.000	0.929–1.000	0.900–1.000
Unique data used in refinement ($I > 0$), N_o	6703	5215	8786
Unique observed data [$I > 2\sigma(I)$]	4302	2084	4870
No. parameters refined, N_v	550	388	697
Overdetermination ratio $N_o : N_v$	12.2 : 1	13.4 : 1	12.6 : 1
R	0.055	0.036	0.061
$wR2$	0.168	0.060	0.182

$R = \Sigma|\Delta F|/\Sigma|F_o|$ calculated on the unique observed data [$I > 2\sigma(I)$], $wR2 = (\Sigma w|\Delta F^2|^2/\Sigma w|F_o^2|^2)^{\frac{1}{2}}$ calculated on the unique total data with $I > 0$.

X-Ray crystallography

Suitable crystals of complexes **2B**, **4** and **5** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[12] Crystal data and details associated with data collection are given in Table 1. Data were collected on a single-crystal diffractometer (Rigaku AFC6S for **2B** and **5** and Siemens AED for **4**) at 295 K for **2B** and **4** and at 133 K for **5**. For intensities and background the individual reflection profiles were analysed.[13] The structure amplitudes were obtained after the usual Lorentz-polarization corrections and the absolute scale was established by the Wilson method.[14] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complexes **2B** and **5**. Data for **2B** and **5** were then corrected for absorption using a semiempirical method.[15] The function minimized during the least-square refinements was $\Sigma w(\Delta F^2)^2$. Anomalous scattering corrections were included in all structure factor calculations.[16b] Scattering factors for neutral atoms were taken from ref. 16(*a*) for non-hydrogen atoms and from ref. 17 for H. Structure solutions were based on the observed reflections [$I > 2\sigma(I)$] while the refinements were based on the unique reflections having $I > 0$. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.[18] Refinements were done by full-matrix least-squares first isotropically and then anisotropically for all non-H atoms except for the disordered atoms in **5**. The hydrogen atoms were located in a Fourier difference map and introduced in the refinements as fixed contributions ($U_{iso} = 0.08$, 0.10 and 0.05 Å^2 for **2B**, **4** and **5**, respectively). The H atoms associated with the disordered carbon atoms were ignored. In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was applied with $a = 0.0997$, 0.000 and 0.0843 for **2B**, **4** and **5** respectively. All calculations were performed by using SHELXL 92.[19] The final difference maps showed no unusual features, with no significant peaks above the general background.

Refinements of complexes **2B** and **4** were straightforward. In complex **5** the high values of the thermal parameters associated with the C(45), C(46) carbon atoms of the thf molecule bonded to Na(2) [O(8),C(53)–C(56)] and with the oxygen and carbon atoms of the Et_2O molecule bonded to Na(4) indicate disorder. The atoms were then split over two positions, called A and B, isotropically refined with site occupation factors of 0.5. The C(56) methyl carbon atom was split over three positions A, B and C, isotropically refined with site occupation factors of 0.25, 0.5 and 0.25 respectively. The C(49)–C(52) carbon atoms of the thf molecule bonded to Na(3) were also found to be affected by disorder, which was solved by splitting the atoms over two positions A and B, isotropically refined with site occupation factors of 0.7 and 0.3 respectively. During the refinement the C−C bond distances within the disordered thf and Et_2O solvent molecules were constrained to be 1.54(1) Å. Some trouble was experienced in refining the second solvent molecule bonded to Na(3), which was interpreted in terms of a statistical distribution of dme and Et_2O molecules approximately sharing one methyl [C(57)] and one methylene [C(59)] carbon atom. The best fit was then obtained by allowing the C(57) and C(59) atoms to vary anisotropically and by splitting the O(9), C(58) and C(60) atoms over two positions (A and B) isotropically refined with site occupation factors of 0.5. The O(10) oxygen atom of the dme solvent molecule was also isotropically refined with a site occupation factor of 0.5.

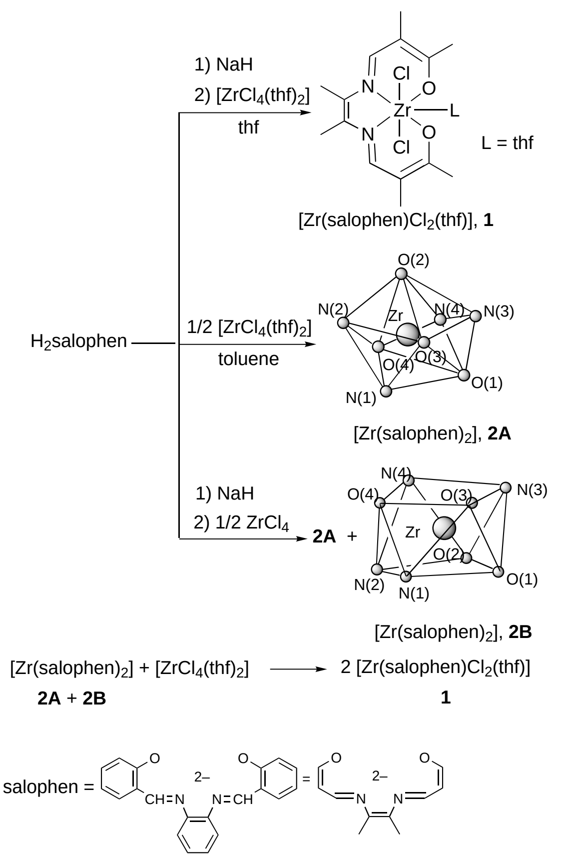
CCDC reference number 186/618.

Results and Discussion

Two compounds have been considered as starting materials for understanding the redox chemistry of zirconium–Schiff base complexes. Scheme 1 outlines the salophen derivatives used to illustrate the present work.

An improved synthesis is reported for compound **1**, which we structurally characterized several years ago.[1b] The co-ordination sphere of the metal approximates that of a pentagonal bipyramid with the equatorial plane defined by the N_2O_2 donor atom of the salophen ligand and a thf molecule, while the two chlorides are *trans* to each other.[1b] When the reaction between $ZrCl_4 \cdot 4thf$ and the salophen ligand is carried out with a 1 : 2 molar ratio all the chlorides around zirconium are replaced and the [Zr(salophen)$_2$] complex **2** is obtained. Complex **2**, however, occurs as two geometrical isomers **2A** and **2B**. The former was reported several years ago.[8] Depending on the reaction conditions, a single isomer, **2A**, can be obtained, or a mixture of **2A** and **2B**. When the reaction was carried out with H_2salophen the single known isomer **2A** was obtained,[8] while reactions performed using the corresponding sodium salt Na_2salophen gave a mixture of two isomers.

The co-ordination spheres of the two isomers with the numbering scheme used for the X-ray analysis are shown in Scheme 1 [N(1), N(2), O(1), O(2) and N(3), N(4), O(3), O(4) identifying the two salophen ligands]. The structure and the synthesis of isomer **2A** has been reported as the unique species derived from



Scheme 1

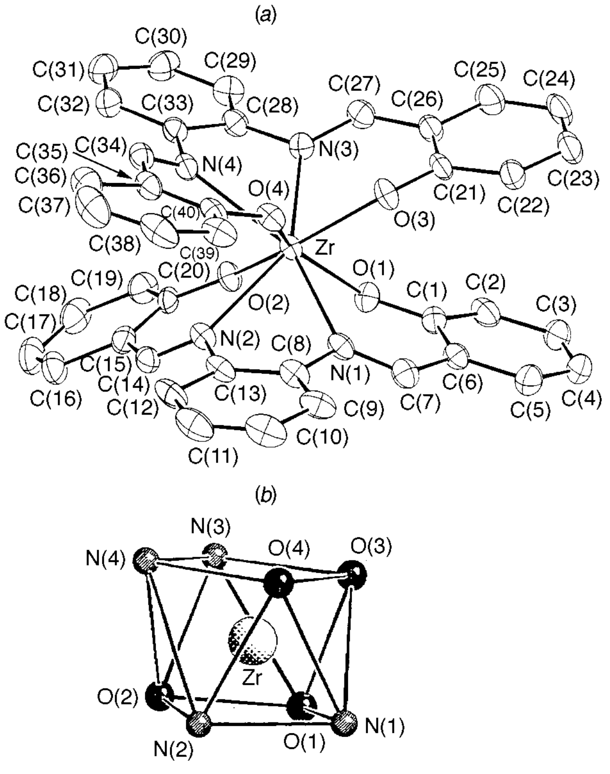


Fig. 1 (*a*) An ORTEP drawing of complex **2B** (30% probability ellipsoids). (*b*) A SCHAKAL[21] drawing of the co-ordination polyhedron around zirconium in **2B**

Table 2 Selected bond distances (Å) and angles (°) for complex **2B**

Zr–O(1)	2.086(4)	O(3)–C(21)	1.319(8)
Zr–O(2)	2.115(4)	O(4)–C(40)	1.317(7)
Zr–O(3)	2.106(5)	N(1)–C(7)	1.286(7)
Zr–O(4)	2.106(4)	N(1)–C(8)	1.425(8)
Zr–N(1)	2.380(5)	N(2)–C(13)	1.419(8)
Zr–N(2)	2.426(5)	N(2)–C(14)	1.291(8)
Zr–N(3)	2.379(5)	N(3)–C(27)	1.296(8)
Zr–N(4)	2.429(4)	N(3)–C(28)	1.405(7)
O(1)–C(1)	1.314(6)	N(4)–C(33)	1.432(8)
O(2)–C(20)	1.296(8)	N(4)–C(34)	1.283(7)
O(4)–Zr–N(4)	72.8(2)	Zr–O(3)–C(21)	133.1(4)
O(4)–Zr–N(3)	113.6(2)	Zr–O(4)–C(40)	135.9(4)
O(3)–Zr–N(4)	112.8(2)	Zr–N(1)–C(8)	114.7(4)
O(3)–Zr–N(3)	74.7(2)	Zr–N(1)–C(7)	126.4(4)
O(3)–Zr–O(4)	76.1(2)	C(7)–N(1)–C(8)	118.8(6)
O(2)–Zr–N(2)	73.3(2)	Zr–N(2)–C(14)	129.6(4)
O(2)–Zr–N(1)	116.0(2)	Zr–N(2)–C(13)	112.9(4)
O(1)–Zr–N(2)	110.2(2)	C(13)–N(2)–C(14)	117.3(5)
O(1)–Zr–N(1)	74.7(2)	Zr–N(3)–C(28)	114.1(4)
O(1)–Zr–O(2)	76.3(2)	Zr–N(3)–C(27)	126.4(4)
N(3)–Zr–N(4)	66.3(2)	C(27)–N(3)–C(28)	119.4(5)
N(1)–Zr–N(2)	65.6(2)	Zr–N(4)–C(34)	127.8(4)
Zr–O(1)–C(1)	133.3(4)	Zr–N(4)–C(33)	113.7(4)
Zr–O(2)–C(20)	142.1(4)	C(33)–N(4)–C(34)	118.4(5)

a template synthesis from [Zr(sal)$_4$] (sal = salicylaldehyde anion) and *o*-phenylenediamine.[8] Separation of the two isomers is straightforward as a result of their different solubilities in thf, **2A** being by far the more soluble. The two isomers have very distinct ^{1}H NMR spectra, **A** showing a singlet and **B** two singlets for the imino protons. The mixture **2A** + **2B** shows three singlets, the relative ratio of which does not change on heating. In separate experiments, using pure **2A** and **2B**, we did not observe any interconversion between the two isomers in solution. Except for the stoichiometric ratio, the synthesis of **1** and the isomeric mixture **2A** + **2B** occurs under the same experimental conditions. Therefore we cannot exclude that the first compound formed under these conditions is [Zr(salophen)$_2$], **2A** + **2B**. Both isomers, in fact, reacted with [ZrCl$_4$(thf)$_2$] in thf to give a ligand-disproportionation reaction and the formation of **1** (Scheme 1).

The isomers **2A** and **2B**, crystallized from thf and from pyridine–hexane respectively, gave crystals suitable for an X-ray analysis. The structure of **2A** which contains benzene of crystallization was reported several years ago,[8] while a crystallographic report on crystals containing toluene of crystallization has been deposited, the compound being identified as **S1**. The structural parameters are almost the same for the two different solvated forms. Hereafter we will refer to the structural parameters of **2A** containing toluene of crystallization, that is, to complex **S1**.

The structure of isomer **2B** contains pyridine of crystallization in a 1:2 molar ratio. An ORTEP[20] view of the complex is given in Fig. 1, selected bond distances and angles in Table 2. The eight-co-ordination around zirconium is provided by the nitrogen and oxygen atoms of two Schiff bases which are rotated so that the C(1)–C(6), C(8)–C(13), C(15)–C(20) aromatic rings from one ligand approximately overlap the C(21)–C(26), C(35)–C(40) and C(28)–C(33) rings of the second. The rotation of the salophen units [133.7(4)°] could be calculated from the average value of the dihedral angles formed by the corresponding O(1)···O(2) ∧ O(3)···O(4) and N(1)···N(2) ∧ N(3)···N(4) vectors. The resulting co-ordination polyhedron around zirconium could be described as a distorted square antiprism with the N_2O_2 cores of the two ligands defining the bases. The N_2O_2 cores are close to planarity [maximum displacement 0.064(5) and 0.0193(5) Å for O(1), O(2), N(1), N(2) and O(3), O(4), N(3), N(4) respectively] and nearly parallel to each other [dihedral angle 2.0(1)°]. The co-ordination environment of the metal is completely different from that observed in **2A**, where the N_2O_2 cores of the two Schiff bases intersect perpendicularly [dihedral angles of 89.9(1) and 89.2°] giving rise to a dodecahedral arrangement of the donor atoms with the nitrogen and oxygen atoms occupying the dodecahedral A and B positions respectively (see Fig. 2). The

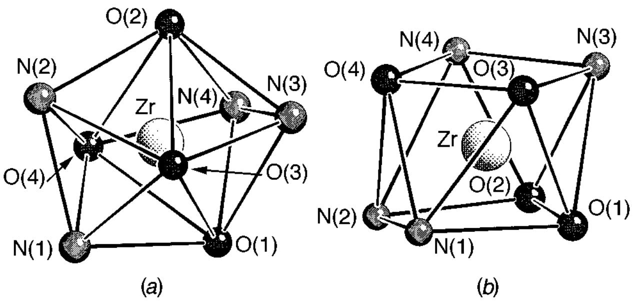
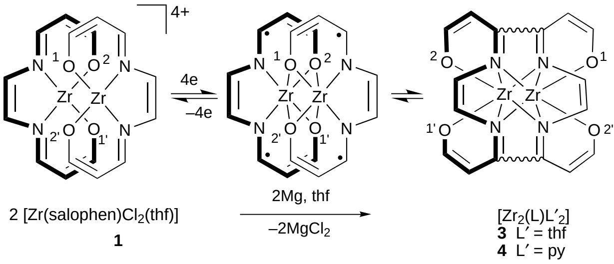


Fig. 2 A SCHAKAL drawing of the co-ordination polyhedron of zirconium in compounds **2A** (*a*) and **2B** (*b*)



Scheme 2

Zr–O and Zr–N bond distances are not affected by the different co-ordination geometries however, the narrow range of values found for **2B** [Zr–O 2.086(4)–2.115(4), Zr–N 2.379(5)–2.429(4) Å] being in good agreement with those found in complex **2A** [Zr–O 2.045(3)–2.087(3), Zr–N 2.389(4)–2.433(5) Å]. The salophen ligands assume an umbrella conformation, the dihedral angles between the peripheral phenolic rings being 40.6(2) and 23.8(2)° for C(1)···C(6) $\wedge$ C(15)···C(20) and C(21)···C(26) $\wedge$ C(35)···C(40) respectively. The six-membered chelate rings are folded along the O···N lines [dihedral angles: Zr,N(1),O(1) $\wedge$ O(1),C_3,N(1) 29.6(2), Zr,O(2),N(2) $\wedge$ O(2),C_3,N(2) 15.2(2), Zr,N(3),O(3) $\wedge$ O(3),C_3,N(3) 28.4(2), Zr,O(4),N(4) $\wedge$ O(4),C_3,N(4) 27.9(2)°] zirconium being displaced by 0.875(1), 0.477(1), 0.848(1) and 0.852(1) Å from the mean planes through the O(1)–C(1)–C(6)–C(7)–N(1), O(2)–C(20)–C(15)–C(14)–N(2), O(3)–C(21)–C(26)–C(27)–N(3) and O(4)–C(40)–C(35)–C(34)–N(4) atoms respectively. The five-membered chelate rings are also folded, the dihedral angles Zr,N(1),N(2) $\wedge$ N(1),C(8),C(13),N(2) and Zr,N(3),N(4) $\wedge$ N(3),C(28),C(33),N(4) being 33.4(3) and 31.4(2)° respectively.

Reduction of compound **1** with sodium metal or, better, with activated magnesium metal led to the results given in Scheme 2. The upper part of the scheme shows the structural consequences to the two salophen skeletons on reduction, while the lower part shows the corresponding chemical equation. The starting material **1** is drawn as two overlapping non-bonded monomeric cationic units; thf and Cl^- are omitted from the co-ordination sphere of the metal. In the two-electron reduction of **1** chloride is removed as NaCl or $MgCl_2$ and two electrons are introduced into each monomer; a reductive coupling between two pairs of imino groups occurs and a doubly C–C bonded dimer is formed. Such a coupling is accompanied by a change in the bonding mode of the salophen unit, which can be visualized by rotating all the oxygen arms in the opposite directions. At the same time the nitrogens bridge the two metals. The two-electron reduction results not only in C–C bond formation but also exchange of the two salophen skeletons between the two metal centres.

The second step in the reduction process proceeds either intramolecularly, as reported here for zirconium, or intermolecularly, as in the case of nickel, to give a C–C bridged polymer.[7b] The choice between the two pathways is controlled by the co-ordination sphere of the metal, which occurs in five- or six-co-ordinate forms in the case of V[7c] and Mn[7d,e] but unlike Ni[7b] which remains strictly planar four-co-ordinate in this environment.

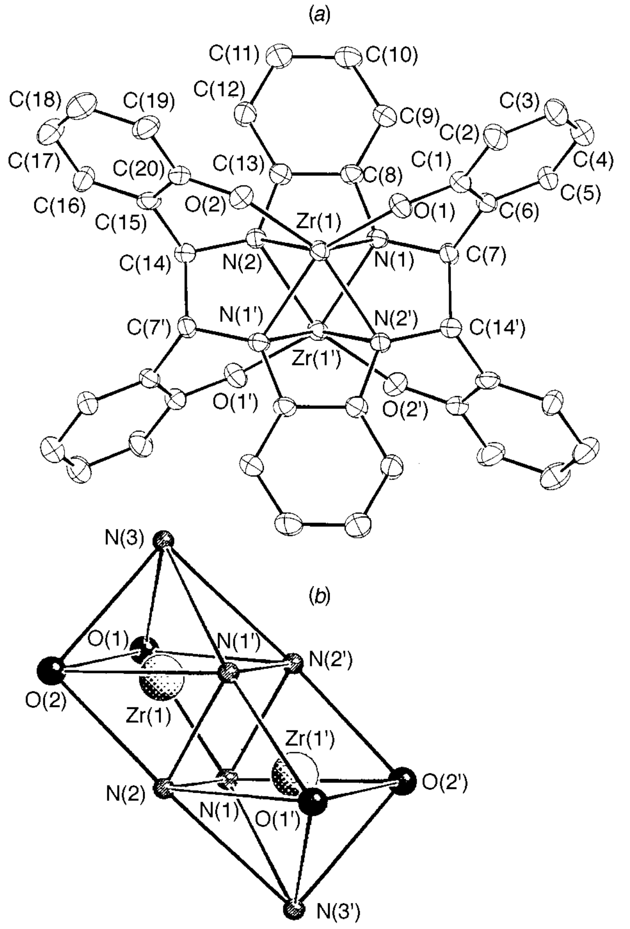


Fig. 3 (*a*) An ORTEP drawing of complex **4** (30% probability ellipsoids). The pyridine molecules bonded to zirconium have been omitted for clarity (prime denotes a transformation of $-x$, $-y$, $-z$). (*b*) A SCHAKAL drawing of the co-ordination polyhedra around the zirconium cations

The proposed structure for compounds **3** and **4** is supported by an X-ray analysis. Details are given for **4** [Fig. 3(*a*)], which contains pyridine of crystallization in a dimer : pyridine molar ratio of 1 : 4. Selected bond distances and angles are listed in Table 3. The two-fold coupled salophen moieties joined by two C–C bonds [C(7)–C(14′), C(14)–C(7′)] form the centrosymmetric dinucleating octaanionic ligand L, which has been drawn without the metal centres in Fig. 4. It contains an approximately planar 12-membered ring [maximum deviation 0.146(3) Å for N(2)] which is nearly coplanar with the *o*-phenylene ring C(8)–C(13) [dihedral angle 9.7(1)°]. The ring could be better described by two nearly planar N(1),N(2),C(7),C(8),C(13), C(14) and N(1′),N(2′),C(7′),C(8′),C(13′),C(14′) moieties [maximum displacement 0.098(4) Å for C(7)] which are parallel from symmetry requirements and stacked by 0.345(3) Å. At the centre of the 12-membered ring is a perfectly planar N_4 core shared on opposite sides by two centrosymmetric zirconium atoms. This results in a Zr_2N_4 octahedron of zirconium and nitrogen atoms, zirconium lying 1.520(1) Å from the N_4 core [Fig. 3(*b*)]. The seven-co-ordination around each zirconium is completed by the O(1) and O(2) oxygen atoms at the N_2O_2 core of the original Schiff base and by the N(3) nitrogen atom of a pyridine molecule. The two O(1),O(2),N(3) and O(1′),O(2′), N(3′) centrosymmetric (therefore parallel) planes define the dimer giving rise to a triple-decker complex, the dihedral angle between these planes and the N_4 core being 0.7(1)°. The Zr···Zr′ separation is 3.040(1) Å. The Zr–O bond distances [Zr(1)–O(1) 2.020(3), Zr(1)–O(2) 2.031(3) Å] are not significantly different and agree with those found in **1** and other

Table 3 Selected bond distances (Å) and angles (°) for complex **4**

Zr(1)–O(1)	2.020(3)	O(2)–C(20)	1.347(5)
Zr(1)–O(2)	2.031(3)	N(1)–C(7)	1.479(5)
Zr(1)–N(1)	2.282(3)	N(1)–C(8)	1.406(5)
Zr(1)–N(1′)	2.284(3)	N(2)–C(13)	1.406(5)
Zr(1)–N(2)	2.282(3)	N(2)–C(14)	1.478(4)
Zr(1)–N(2′)	2.294(3)	C(6)–C(7)	1.512(6)
Zr(1)–N(3)	2.356(3)	C(7)–C(14′)	1.608(5)
O(1)–C(1)	1.359(6)		
N(2′)–Zr(1)–N(3)	84.0(1)	Zr(1)–O(1)–C(1)	138.1(3)
N(2)–Zr(1)–N(3)	138.5(1)	Zr(1)–O(2)–C(20)	139.6(3)
N(2)–Zr(1)–N2′	96.7(1)	Zr(1)–N(1)–Zr(1′)	83.5(1)
N(1′)–Zr(1)–N(3)	80.4(1)	Zr(1′)–N(1)–C(8)	117.8(2)
N(1′)–Zr(1)–N(2′)	64.0(1)	Zr(1′)–N(1)–C(7)	113.5(2)
N(1′)–Zr(1)–N(2)	63.5(1)	Zr(1)–N(1)–C(8)	95.7(2)
N(1)–Zr(1)–N(3)	144.3(1)	Zr(1)–N(1)–C(7)	109.4(2)
N(1)–Zr(1)–N(2′)	63.3(1)	C(7)–N(1)–C(8)	124.8(3)
N(1)–Zr(1)–N(2)	64.2(1)	Zr(1)–N(2)–Zr(1′)	83.3(1)
N(1)–Zr(1)–N(1′)	96.5(1)	Zr(1′)–N(2)–C(14)	114.2(2)
O(2)–Zr(1)–N(3)	83.9(1)	Zr(1′)–N(2)–C(13)	117.4(2)
O(2)–Zr(1)–N(2′)	158.7(1)	Zr(1)–N(2)–C(14)	109.1(2)
O(2)–Zr(1)–N(2)	81.0(1)	Zr(1)–N(2)–C(13)	95.6(2)
O(2)–Zr(1)–N(1′)	96.7(1)	C(13)–N(2)–C(14)	124.7(3)
O(2)–Zr(1)–N(1)	131.6(1)	N(1)–C(7)–C(6)	115.9(3)
O(1)–Zr(1)–N(3)	85.0(1)	C(6)–C(7)–C(14′)	111.9(3)
O(1)–Zr(1)–N(2′)	92.6(1)	N(1)–C(7)–C(14′)	105.6(3)
O(1)–Zr(1)–N(2)	136.1(1)	N(2)–C(14)–C(7′)	105.0(3)
O(1)–Zr(1)–N(1′)	153.4(1)	C(7′)–C(14)–C(15)	112.7(3)
O(1)–Zr(1)–N(1)	82.6(1)	N(2)–C(14)–C(15)	115.9(3)
O(1)–Zr(1)–O(2)	103.8(1)		

Prime denotes a transformation of −*x*, −*y*, −*z*.

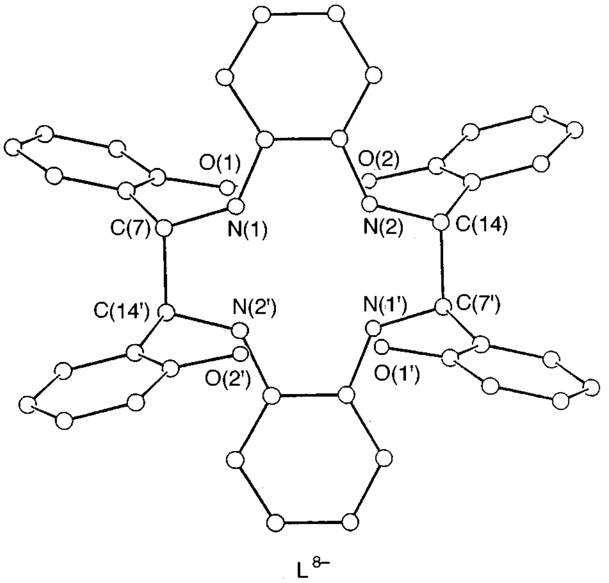
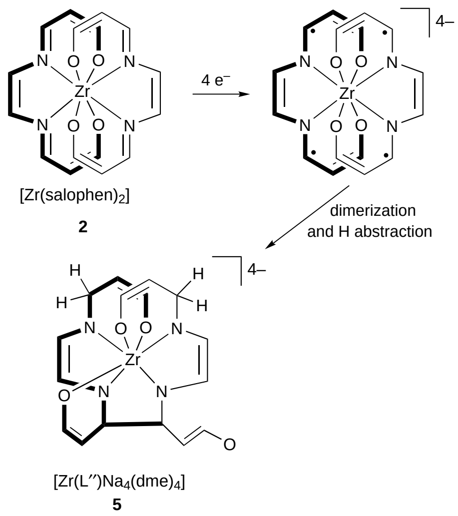


Fig. 4 A SCHAKAL view of the doubly C–C bond bridged salophen, L, in complex **4**



Scheme 3

zirconium–Schiff base complexes.[1b] The Zr–N bond distances [Zr(1)–N(1) 2.282(3), Zr(1)–N(2) 2.282(3), Zr(1)–N(1′) 2.284(3), Zr(1)–N(2′) 2.294(3) Å] are not significantly different from each other. They fall in the range observed for zirconium–Schiff base complexes and are significantly shorter than those observed in **1**, except for Zr(1)–N(3) [2.356(3) Å]. The co-ordinated pyridine molecule is oriented to give the following contacts between the α-hydrogen atoms and the N and O donor atoms: O(2)···C(21) 3.047(6), H(21)···O(2) 2.55, C(21)–H(21)···O(2) 109.7°; O(1)···C(25) 3.294(6) Å, H(25)···O(1) 2.87, C(25)–H(25)···O(1) 108.7°; N(2′)···C(25) 3.240(5), H(25)···N(2′) 2.73 Å, C(25)–H(25)···N(2′) 115.3°. The dihedral angles formed by the pyridine plane with the N_2O_2 and N_4 planes are 49.5(1) and 29.9(1)° respectively. The original salophen moiety loses its stereochemical rigidity and planarity in the dinucleating ligand L, thus the C(8)–C(13) aromatic ring is nearly perpendicular to the N_2O_2 core [dihedral angle 90.8(1)°] rather than parallel. The N_2O_2 core still remains almost planar showing small though significant tetrahedral distortions [maximum displacement 0.043(3) Å], the zirconium out-of-plane distance being 0.734(1) Å. The C(7)–C(14′) bond distance [1.608(5) Å] is significantly longer than the value expected for a C(sp^3)–C(sp^3) single bond, as has been found in sterically hindered environments.

In an attempt to achieve the reductive coupling across two salophen units bonded to the same metal, and thus to have redox processes (see below) occurring within the co-ordination sphere of a single metal centre, we undertook the reduction of compound **2**. It is important to recognize that the same product is obtained regardless of whether isomer **2A** or **2B** is employed. Reduction of **2**, carried out in thf using 4 equivalents of sodium metal per zirconium, led to **5** (Scheme 3). The final species is shown in the anionic form rather than associated with the sodium cations. The reduction of **2** by four electrons proceeds formally, as in the case of two molecules of **1** in Scheme 2, to give a tetraradical. In the present case, however, a single pair of radicals couple to form a C–C bond, while the other two abstract hydrogen from the solvent (see complex **5**). The latter reaction is, very probably, dictated by the steric constraints, derived from the arrangement of two salophens around a single metal, which prevents the second pair of radicals coupling. Complex **5** crystallized as a dimer from a mixture of solvents and the structure is shown in Fig. 5(*a*), with selected bond distances and angles in Table 4.

The structure of compound **5** consists of [ZrL″Na_3(thf)$_3$-(Et_2O)$_{1.5}$(dme)$_{0.5}$] anions linked into centrosymmetric dimers by two bridging sodium cations Na(1) and Na(1′), sharing asymmetrically O(4) and O(4′), which do not interact with zirconium [Na(1)–O(4) 2.249(5), Na(1)–O(4′) 2.332(5) Å; prime denotes a transformation of −*x*, −*y*, −*z*].

The two salophens are linked by a carbon–carbon bond [C(7)–C(34) 1.540(10) Å] in L″. Bonds distances and angles involving the C(7), C(14), C(27), C(34) imino carbon atoms are consistent with the sp^3 character of the atoms (Table 4). Seven-co-ordination around zirconium is provided by N(1), N(2), O(1), O(2) from one salophen moiety and by O(3), N(3), N(4) atoms from the other one. The resulting co-ordination polyhedron is a monocapped trigonal prism, the equatorial plane being defined by the O(1), O(2), N(1), N(3) donor atoms [see Fig. 5(*b*)]. Zirconium is displaced by 0.316(1) Å from the mean equatorial plane toward N(2) and O(3). The Zr–O and Zr–N distances are in the range observed in the present and related complexes. As a consequence of the sp^3 character of all imino

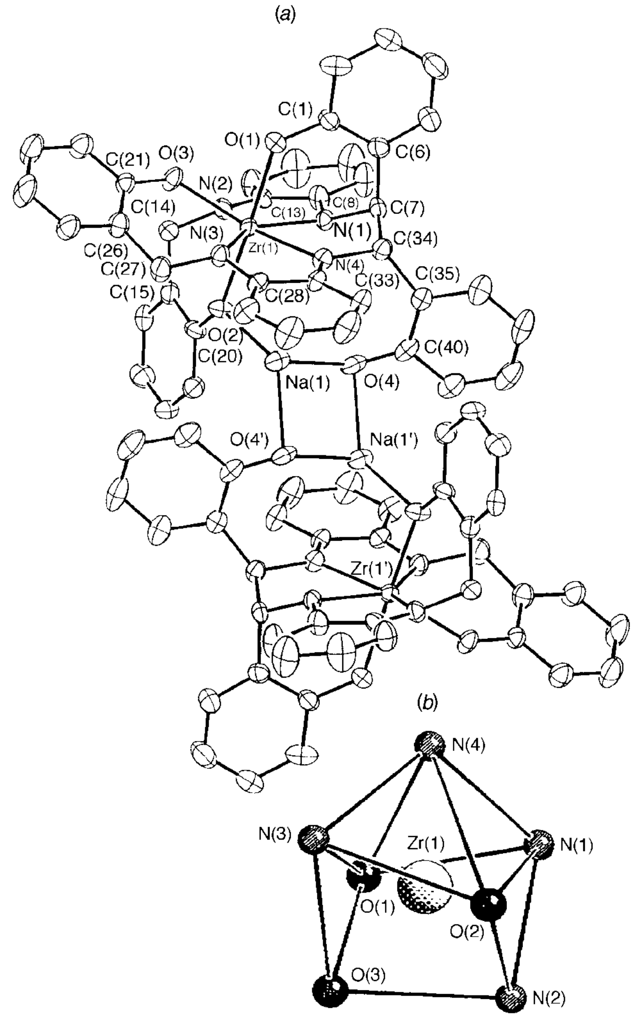


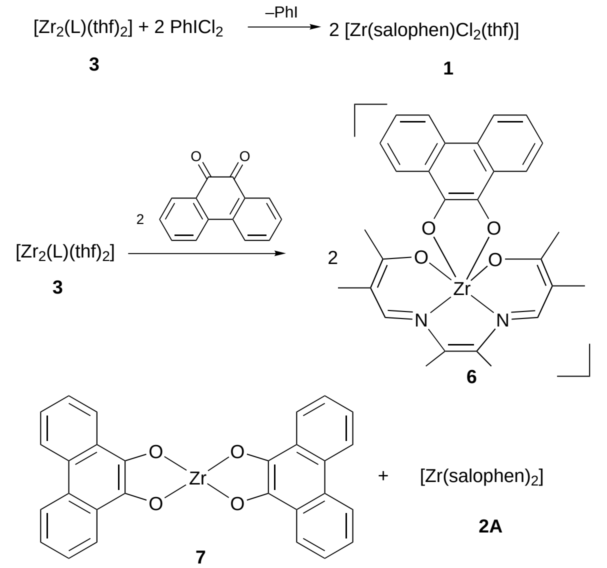
Fig. 5 (*a*) An ORTEP drawing of complex **5** (50% probability ellipsoids). The sodium cations Na(2), Na(3), Na(4) and associated thf, Et_2O and dme solvent molecules have been omitted for clarity (prime denotes a transformation of $-x$, $-y$, $-z$). (*b*) A SCHAKAL drawing of the co-ordination polyhedron of zirconium within the monomeric unit

Table 4 Selected bond distances (Å) and angles (°) for complex **5**

Zr(1)–O(1)	2.197(5)	N(1)–C(8)	1.394(8)
Zr(1)–O(2)	2.156(5)	N(2)–C(13)	1.391(8)
Zr(1)–O(3)	2.181(5)	N(2)–C(14)	1.461(9)
Zr(1)–N(1)	2.189(5)	N(3)–C(27)	1.471(9)
Zr(1)–N(2)	2.207(6)	N(3)–C(28)	1.406(9)
Zr(1)–N(3)	2.230(5)	N(4)–C(33)	1.387(8)
Zr(1)–N(4)	2.190(5)	N(4)–C(34)	1.464(8)
O(1)–C(1)	1.343(8)	C(6)–C(7)	1.542(11)
O(2)–C(20)	1.358(9)	C(7)–C(34)	1.540(10)
O(3)–C(21)	1.320(8)	C(14)–C(15)	1.505(10)
O(4)–C(40)	1.325(10)	C(26)–C(27)	1.485(11)
N(1)–C(7)	1.455(9)	C(34)–C(35)	1.547(10)
N(3)–Zr(1)–N(4)	71.3(2)	Zr(1)–O(3)–C(21)	137.5(4)
N(2)–Zr(1)–N(4)	140.4(2)	Na(1)–O(4)–C(40)	127.5(5)
N(2)–Zr(1)–N(3)	144.8(2)	Zr(1)–N(1)–C(8)	119.3(4)
N(1)–Zr(1)–N(4)	71.7(2)	Zr(1)–N(1)–C(7)	113.5(4)
N(1)–Zr(1)–N(3)	143.1(2)	C(7)–N(1)–C(8)	118.3(5)
N(1)–Zr(1)–N(2)	70.7(2)	Zr(1)–N(2)–C(14)	116.8(4)
O(3)–Zr(1)–N(4)	140.6(2)	Zr(1)–N(2)–C(13)	120.9(4)
O(3)–Zr(1)–N(3)	77.1(2)	C(13)–N(2)–C(14)	117.8(6)
O(3)–Zr(1)–N(2)	77.6(2)	Zr(1)–N(3)–C(28)	119.3(4)
O(3)–Zr(1)–N(1)	135.6(2)	Zr(1)–N(3)–C(27)	120.7(5)
O(2)–Zr(1)–N(4)	94.8(2)	C(27)–N(3)–C(28)	114.8(5)
O(2)–Zr(1)–N(3)	83.4(2)	Zr(1)–N(4)–C(34)	121.2(4)
O(2)–Zr(1)–N(2)	79.7(2)	Zr(1)–N(4)–C(33)	121.2(4)
O(2)–Zr(1)–N(1)	99.6(2)	C(33)–N(4)–C(34)	116.7(5)
O(2)–Zr(1)–O(3)	104.5(2)	N(1)–C(7)–C(6)	112.1(6)
O(1)–Zr(1)–N(4)	87.9(2)	C(6)–C(7)–C(34)	109.8(6)
O(1)–Zr(1)–N(3)	98.8(2)	N(1)–C(7)–C(34)	108.8(5)
O(1)–Zr(1)–N(2)	97.3(2)	N(2)–C(14)–C(15)	112.1(6)
O(1)–Zr(1)–N(1)	80.0(2)	N(3)–C(27)–C(26)	117.4(6)
O(1)–Zr(1)–O(3)	74.0(2)	N(4)–C(34)–C(7)	106.7(5)
O(1)–Zr(1)–O(2)	176.9(2)	C(7)–C(34)–C(35)	110.9(6)
Zr(1)–O(1)–C(1)	128.9(4)	N(4)–C(34)–C(35)	120.3(6)
Zr(1)–O(2)–C(20)	135.6(4)		

carbon atoms the salophen moieties assume a strongly distorted conformation as indicated by the loss of planarity of the N_2O_2 systems and by the dihedral angle between peripheral phenolic rings [C(1)–C(6) ∧ C(15)–C(20) 73.5(2), C(21)–C(26) ∧ C(35)–C(40) 72.9(3)°]. With respect to the plane of the phenylene rings the phenolic rings are oriented nearly perpendicular, the dihedral angles they form being C(1)–C(6) ∧ C(8)–C(13) 82.5(2), C(15)–C(20) ∧ C(8)–C(13) 77.5(2), C(21)–C(26) ∧ C(28)–C(33) 82.7(2), C(35)–C(40) ∧ C(28)–C(33) 89.9(2)°. The folding of the salophen moieties leaves the pairs of atoms O(1), O(2) and O(3), O(4) at bite distances of 4.351(7) and 6.195(8) Å respectively, with O(4) not interacting with zirconium. This conformation allows the anchoring of four sodium cations [Na(1), Na(2), Na(3), Na(4)], each bonded to two oxygen atoms from the salophen ligands [O(2), O(4) for Na(1); O(1), O(3) for Na(2) and Na(3); O(2), O(4) for Na(4). The co-ordination around each cation is completed by a nitrogen atom [N(4), N(2), N(3), and N(1) for Na(1), Na(2), Na(3) and Na(4) respectively] and by the oxygen atoms from the two thf molecules for Na(2), a thf molecule and a dme/Et_2O molecule for Na(3) and a Et_2O molecule for Na(4). The intramolecular contacts involving the sodium cation Na(1) and the carbon atoms C(28) and C(33) of a phenylene ring [Na(1)···C(28) 2.775(8), Na(1)···C(33) 2.622(8) Å] are consistent with a possible sodium–η^2-aromatic ring interaction.[22]

The C–C bonds in complexes **3**, **4** and **5** behave as two-electron reservoirs, without becoming at any stage the centre of reactivity. The metal centre assists the transfer of the electrons stored in the C–C bonds. This redox behaviour is illustrated in Scheme 4 by the reaction of **3** with $PhICl_2$ and 9,10-phenanthrenequinone. In the first reaction both C–C bonds are cleaved and the chlorine reduced to chloride, which in turn restores the original imino groups and forms the starting material **1**. In the second reaction electrons are transferred to 9,10-phenanthrenequinone, which is reduced to the corresponding dianion. The expected product **6** undergoes, however, a ligand disproportionation reaction to give **2A** and **7**, the isolation and characterization of which is reported in the Experimental section. The proposed structure of **6** is indirectly demonstrated



Scheme 4

by the isolation and X-ray structural characterization of the corresponding titanium analogue,[23] which does not, however, undergo any ligand disproportionation reaction. We should emphasize that in both reactions (Scheme 4) the reduction of the substrate occurs with the concomitant cleavage of the C−C bonds in **3**, which function as two-electron reservoirs, and the original salophen moiety is restored to its intact form. A significant feature of such systems, when functioning as reducing agents, is their ability to transfer electrons long distances from the storage site by the intermediacy of the transition metal. In the reactions shown in Scheme 4 the Zr(salophen) moiety behaves as a typical zirconium(II) complex in oxidative-addition reactions. This suggests that the reduction of salophen-type ligands can be used for masking or mimicking low oxidation states, mainly in the case of difficult to reduce metals, *i.e.* early transition metals.

Conclusion

The ligand-based redox chemistry of zirconium–salophen complexes allowed the discovery of a novel mode of storing and releasing electrons *via* the reductive coupling of imino groups of the ligand and the oxidative cleavage of the resulting C−C bonds. The C−C bond in such complexes functions as a two-electron shuttle, without being directly involved in any reactivity process, thus the metal mediates the electron transfer from the C−C bonds to the substrates. Although the metal does not change its oxidation state, namely zirconium(IV), the reduced form, namely Zr_2L, behaves as a source of the zirconium(II) fragment Zr(salophen). This result suggests an approach for masking low oxidation states of difficult to reduce metals such as early transition metals.

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