Metal complexes of a chiral quadridentate Schiff base†

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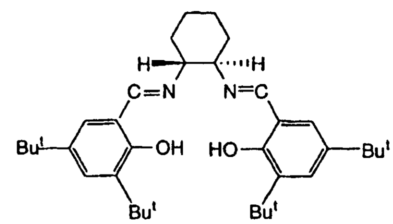
Chiral metal Schiff-base complexes [AlL(Et)], [TiLCl$_2$], [VO(L)], [(FeL)$_2$O], [CoL], [NiL], [CuL], [ZrLCl$_2$], [RuL(CO)$_2$] and *trans*-[RuL(NO)Cl] ([H$_2$L = (*R*,*R*)-(−)-*N*,*N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine] were synthesized and characterized. The structures of [CoL] and *trans*-[RuL(NO)Cl] have been established by X-ray crystallography. The former has a pseudo-square-planar geometry with Co–N and Co–O distances of 1.88 and 1.84 Å, respectively. The geometry around Ru in *trans*-[RuL(NO)Cl] is octahedral with Ru–N (nitrosyl) and Ru–Cl distances of 1.72(2) and 2.354(4) Å, respectively, and Ru–N–O 175(2)°. The cyclic voltammograms for the metal Schiff-base complexes show reversible M^{III}–M^{II} and ligand-centred oxidation couples. Treatment of NiL with AgBF$_4$ afforded air-stable [NiL]BF$_4$, which is formulated as a nickel(II) complex of the Schiff-base cation radical.

The application of metal Schiff-base complexes to asymmetric catalysis has attracted much attention since the discovery that manganese(III) complexes of chiral quadridentate Schiff bases such as H$_2$L (or Jacobsen's catalyst) are capable of catalysing epoxidation of unfunctionalized alkenes in excellent enantiomeric excesses.[1] More recently, Jacobsen and co-workers[2] reported that the chromium(III) complex [CrL(Cl)] also catalyses highly stereoselective ring opening of *meso*-epoxides such as cyclohexene oxide with trimethylsilyl azide. The nature of the transition state and origin of the asymmetric induction in Jacobsen's epoxidation and ring-opening reactions, however, remain controversial.[3] Given the easy availability and stereoelectronic flexibility of chiral quadridentate Schiff bases, chiral metal Schiff-base complexes are anticipated to have high potential in enantioselective catalysis. Rationally to design asymmetric transformation catalysed by chiral metal Schiff-base complexes, a knowledge of their redox and structural properties is desirable. Here we report the syntheses, electrochemistry and crystal structures of some metal complexes of Jacobsen's Schiff base (H$_2$L).

Experimental

Solvents were dried and distilled prior to use. The NMR spectra were recorded on a JEOL EM 400 spectrometer at 400 (^{1}H) and 104.2 (^{27}Al) MHz. Chemical shifts (δ) are reported with reference to SiMe$_4$ and [Al(OH$_2$)$_6$]$^{3+}$ for ^{1}H and ^{27}Al NMR spectra, respectively. The hydrogen-atom labelling scheme for the Schiff base ligand is shown in Scheme 1. Infrared spectra (Nujol mulls) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, mass spectra on a Kratos MS80R FAQ spectrometer and the EPR spectrum on a Varian E12 (X-band) spectrometer. Magnetic moments in CHCl$_3$ solutions were determined by the Evans method[4] at room temperature. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. Potentials were with respect to a Ag$^+$–Ag reference electrode in acetonitrile, but are reported with respect to the ferrocenium–ferrocene couple as measured in the same solution. Elemental analyses were performed by Medac Ltd., Brunel University, UK.

† *Non-SI unit employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.



H$_2$L

Materials

The compound H$_2$L was prepared by condensation of 1,2-diaminocyclohexane with 2 equivalents of 2,4-di-*tert*-butylsalicylaldehyde according to the literature procedure.[5] Triethylaluminium (1 mol dm^{-3} in hexanes) was obtained from Aldrich and used as received. The salt Na$_2$L was prepared by reaction of H$_2$L with 2 equivalents of NaH in tetrahydrofuran (thf); [TiCl$_4$(thf)$_2$], [ZrCl$_4$(thf)$_2$],[6] [{Ru(CO)$_2$Cl$_2$}$_n$][7] and [Ru(NO)Cl$_3$(PPh$_3$)$_2$][8] were prepared by the literature methods.

Preparations

[AlL(Et)] 1. To a solution of H$_2$L (0.5 g, 0.9 mmol) in toluene (20 cm^3) was added 1 equivalent of AlEt$_3$ (1 cm^3 of a 1 mol dm^{-3} solution in hexane). The resulting mixture was heated at reflux for 4 h and evaporated to dryness. The yellow solid was recrystallized from CH$_2$Cl$_2$–hexane to give yellow prisms (yield 0.43 g, 80%). NMR (CDCl$_3$): ^{1}H, δ −0.39 (q, 2 H, C*H$_2$*CH$_3$), 0.70 (t, 3 H, CH$_2$C*H$_3$*), 1.31, 1.52 (s, 36 H, Bu^t), 2.07 (br s, 1 H, H$_c$), 2.09 (br s, 1 H, H$_{c'}$), 2.43 (d, *J* = 5, 1 H, H$_d$), 2.58 (d, *J* = 8, 1 H, H$_{d'}$), 3.03 (t, *J* = 5, 1 H, H$_b$), 3.52 (t, *J* = 8, 1 H, H$_{b'}$), 6.69 (d, *J* = 2.5, 1 H, H$_o$), 7.03 (d, *J* = 2.5 Hz, 1 H, H$_{o'}$), 7.49 (d, *J* = 2.5, 2 H, H$_p$ and H$_{p'}$), 8.14 (d, *J* = 1.9, 1 H, H$_a$) and 8.29 (d, *J* = 1.9 Hz, 1 H, H$_a$); ^{27}Al, δ 60 (half width = 4690 Hz, T_2 = 67.88 s) (Found: C, 77.5; H, 7.4; N, 4.9. C$_{38}$H$_{40}$AlN$_2$O$_2$ requires C, 78.2; H, 6.9; N, 4.8%).

[TiLCl$_2$] 2. To a solution of Na$_2$L (2.3 g, 3.68 mmol) in thf (20 cm^3) was added [TiCl$_4$(thf)$_2$] (1.21 g, 3.68 mmol) under a stream of nitrogen and toluene (20 cm^3). The resultant mixture was heated at reflux overnight and filtered. The filtrate was evaporated to dryness *in vacuo* and washed with diethyl ether to give a red solid, which was further recrystallized from CH$_2$Cl$_2$–

hexane (yield 0.54 g, 59%). ^{1}H NMR ($CDCl_3$): δ 1.33, 1.43 (s, 36 H, Bu^t), 2.08 (d, J = 8, 2 H, H_c and $H_{c'}$), 2.57 (br s, 1 H, H_d) 2.60 (br s, 1 H, $H_{d'}$), 4.06 (d, J = 8 Hz, 2 H, H_b and $H_{b'}$), 7.33 (s, 2 H, H_p and $H_{p'}$), 7.59 (s, 2 H, H_o and $H_{o'}$) and 8.35 (s, 2 H, H_a and $H_{a'}$) (Found: C, 63.4; H, 8.0; N, 4.2. $C_{36}H_{52}Cl_2N_2O_2Ti$ requires C, 65.1; H, 7.9; N, 4.2%).

[VO(L)] 3. To a solution of H_2L (1 g, 1.84 mmol) in dimethylformamide (dmf) (15 cm^3) was added [$VO(acac)_2$] (acac = acetylacetonate) (0.5 g, 1.87 mmol). The reaction mixture was heated at reflux for 8 h. The solvent was pumped off and the residue recrystallized from CH_2Cl_2–hexane to give dark yellow crystals (yield: 0.67 g, 60%). IR (cm^{-1}): 986 [ν(V=O)]. μ_{eff} = 1.8 μ_B (Found: C, 69.8; H, 9.0; N, 4.7. $C_{36}H_{52}N_2O_2V$ requires C, 70.9; H, 8.8; N, 4.6%).

[(FeL)$_2$O] 4. To a suspension of H_2L (1 g, 1.84 mmol) in MeOH (30 cm^3) was added 1 equivalent of $FeCl_3{\cdot}4H_2O$ (0.37 g, 1.85 mmol) and 10 equivalents of NEt_3 (2.5 cm^3, 18.4 mmol) and the resultant mixture stirred at room temperature for 2 h. The orange precipitate was collected and dissolved in CH_2Cl_2, washed twice with water (20 cm^3), and dried with Na_2SO_4. Addition of hexane and slow evaporation of the CH_2Cl_2 extract afforded orange crystals (yield: 0.81 g, 70%). μ_{eff} (Evans method): 1.4 μ_B per Fe (Found: C, 71.0; H, 8.7; N, 4.4. $C_{72}H_{104}Fe_2N_4O_3$ requires C, 70.4; H, 8.7; N, 4.4%).

[CoL] 5. To H_2L (2 g, 3.67 mmol) in toluene (30 cm^3) was added dropwise $Co(O_2CMe)_2$ (0.95 g, 3.67 mmol) in aqueous ethanol (30 cm^3) heated in a water-bath at 100 °C. The pink solution turned brown and a copious amount of precipitate was formed. The solid was collected, washed with ethanol and recrystallized from $CHCl_3$–hexane to give red crystals, which are suitable for X-ray diffraction study (yield: 1.7 g, 76%). μ_{eff} = 1.7 μ_B (Found: C, 71.6; H, 8.1; N, 4.7. $C_{36}H_{52}CoN_2O_2$ requires C, 71.6; H, 8.6; N, 4.6%).

[NiL] 6. A mixture of $NiCl_2$ (1 g), H_2L (1 g), and NEt_3 (0.5 cm^3) was heated at reflux in MeOH (25 cm^3) for 2 h. The orange solid was collected, washed with MeOH, redissolved in CH_2Cl_2, and layered with hexane. The dark orange needles formed were collected (yield 40%). ^{1}H NMR($CDCl_3$): δ 1.26, 1.41 (s, 36 H, Bu^t), 1.9 (br s, 2 H, H_c and $H_{c'}$), 2.45 (br s, 2 H, H_d and $H_{d'}$), 2.95 (br s, 2 H, H_b and $H_{b'}$), 6.88 (d, J = 2, 2 H, H_p and $H_{p'}$), 7.30 (d, J = 2 Hz, 2 H, H_o and $H_{o'}$), and 7.39 (s, 2 H, H_a and $H_{a'}$). (Found: C, 67.6; H, 8.3; N, 4.2. $C_{36}H_{52}N_2NiO_2$ requires C, 68.1; H, 8.2; N, 4.4%).

[NiL]BF$_4$ 7. To a solution of complex **6** (50 mg, 0.83 mmol) in CH_2Cl_2 (10 cm^3) was added 1 equivalent of $AgBF_4$ (16 mg, 0.83 mmol) The resulting green solution was stirred for 30 min at room temperature and filtered. The filtrate was evaporated to dryness, the residue dissolved in Et_2O, and layered with hexane at −10 °C. The dark green crystals were collected and washed with hexane (yield: 0.42 g, 75%). UV/VIS (CH_2Cl_2): λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) 383 (3190). μ_{eff} = 1.6 μ_B. IR (cm^{-1}): 1575 [ν(C=N)] (Found: C, 62.3; H, 7.6; N, 4.0. $C_{36}H_{52}BF_4N_2NiO_2$ requires C, 62.6; H, 7.5; N, 4.1%). The SbF_6 salt was prepared similarly from **6** and $AgSbF_6$.

[CuL] 8. This complex was prepared as for **5** from $CuCl_2$ (0.5 g) and H_2L (1 g) in MeOH (yield: 70%). Mass spectrum (FAB): m/z 607 (M^+). μ_{eff} = 1.6 μ_B (Found: C, 70.4; H, 8.9; N, 4.9. $C_{36}H_{52}CuN_2O_2$ requires C, 71.1; H, 8.6; N, 4.6%).

[ZrLCl$_2$] 9. This complex was prepared as for **2** from Na_2L (1 g, 1.84 mmol) and [$ZrCl_4(thf)_2$] (0.68 g, 1.84 mmol). The product was recrystallized from CH_2Cl_2–hexane as a yellow microcrystalline solid (yield 1.05 g, 81%). ^{1}H NMR ($CDCl_3$): 1.32, 1.43, 1.49, 1.57 (s, 36 H, Bu^t), 2.10 (d, J = 8, 2 H, H_c), 2.43, (d, J = 8, 1 H, H_b) 2.62 (d, J = 8, 1 H, $H_{d'}$), 3.86 (d, J = 8, 2 H, H_b and $H_{b'}$), 7.34 (d, J = 3, 2 H, H_o and $H_{o'}$), 7.63 (d, J = 3 Hz, 2 H, H_p and $H_{p'}$), 8.46 (s, 1 H, H_a) and 8.51 (s, 1 H, $H_{a'}$) (Found: C, 61.2; H, 7.6; N, 3.3. $C_{36}H_{52}Cl_2N_2O_2Zr$ requires C, 61.2; H, 7.4; N, 4.0%).

***cis*-[RuL(CO)$_2$] 10.** To a solution of Na_2L (1 g, 1.84 mmol) in thf (50 cm^3) was added an excess of [{$Ru(CO)_2Cl_2$}$_n$] (0.84 g, 3.68 mmol) and the reaction mixture heated at reflux overnight. The solvent was distilled off *in vacuo* leaving an orange solid, which was dissolved in CH_2Cl_2. The filtrate was concentrated to 1 cm^3 and loaded onto a column of Florisil. The product was eluted with Et_2O–CH_2Cl_2 (5:95) as a yellow band. Recrystallization from MeOH as 0 °C afforded air-sensitive yellow crystals (yield: 0.29 g, 24%). ^{1}H NMR ($CDCl_3$): 1.19, 1.29, 1.34, 1.50 (s, 36 H, Bu^t), 1.97 (br s, 2 H, H_c and $H_{c'}$), 2.39 (br s, 1 H, H_d), 2.72 (br s, 1 H, $H_{d'}$), 3.49 (br s, 2 H, H_b and $H_{b'}$), 6.93 (d, J = 2, 2 H, H_p and $H_{p'}$), 7.41 (d, J = 2 Hz, 2 H, H_o and $H_{o'}$), 8.13 (s, 1 H, H_a) and 8.38 (s, 1 H, $H_{a'}$). IR (cm^{-1}) 1890, 1920 [ν(C≡O)] (Found: C, 64.2; H, 8.1; N, 3.8. $C_{38}H_{52}N_2O_4Ru$ requires C, 65.0; H, 7.4; N, 4.0%).

***trans*-[RuL(NO)Cl] 11.** To a solution of Na_2L (0.17 g, 0.3 mmol) in toluene (25 cm^3) was added [$Ru(NO)Cl_3(PPh_3)_2$] (0.24 g, 0.48 mmol) and the mixture heated under reflux overnight. The solvent was removed in a Rotavapor and the residue extracted with ether. The filtrate was concentrated to *ca.* 5 cm^3 and loaded onto a silica column. The product was eluted with ether–hexane (1:1 v/v) as a dark red band and crystallized from ether–hexane as dark red microcrystals (yield: 0.16 g, 40%). X-Ray-quality crystals were obtained by recrystallization from CH_2Cl_2–hexane. ^{1}H NMR ($CDCl_3$): δ 1.28, 1.54 (s, 36 H, Bu^t), 2.07 (t, J = 12, 2 H, H_d and $H_{d'}$), 2.73 (d, J = 12, 1 H, H_c), 2.87 (d, J = 12, 1 H, $H_{c'}$), 3.27 (t, J = 12, 1 H, H_b), 4.16 (t, J = 12, 1 H, $H_{b'}$), 7.00 (d, J = 2, 2 H, H_p and $H_{p'}$), 7.50 (d, J = 2 Hz, 2 H, H_o and $H_{o'}$), 8.16 (s, 1 H, H_a), and 8.24 (s, 1 H, $H_{a'}$) (Found: C, 61.2; H, 7.6; N, 5.4. $C_{36}H_{52}ClN_3O_3Ru$ requires C, 61.0; H, 7.3; N, 5.9%). IR (cm^{-1}): 1844 [ν(N≡O)], 1629 [ν(C=N)].

X-Ray crystallography

A summary of crystal data and experimental details for complexes **5**·0.5CHCl$_3$ and **11**·0.5C$_6$H$_{14}$ are listed in Table 3. Diffraction measurements for **5**·0.5CHCl$_3$ and **11**·0.5C$_6$H$_{14}$ were made on Enraf-Nonius CAD-4 and Siemens P4 diffractometers, respectively. Lattice parameters for **5**·0.5CHCl$_3$ were obtained from 25 reflections with 2θ angles in the range 36.48–46.64°. All reflections were corrected for Lorentz, polarization and absorption effects. Data reductions were performed using the NRCC-SDP-VAX packages.[9] The structure was solved by the Patterson method and refined by full-matrix least squares; all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the organic ligands were calculated in the idealized positions and were in the structure-factor calculation. The final atomic coordinates and selected bond lengths and angles are given in Tables 1 and 4, respectively. Unit-cell parameters for **11**·0.5C$_6$H$_{14}$ were refined from setting angles of 30 reflections with 2θ > 20°. Structure solution by direct methods revealed the positions of four independent Ru atoms in the asymmetric unit. Four molecules of the complex were subsequently found by Fourier-difference synthesis and refined (on F) by a combination of anisotropic and isotropic thermal parameters. Two solvent molecules were also revealed in the asymmetric unit. Fourier maps showed these to be disordered, but best modelled by hexane. The atoms of the two hexanes were given occupancies of 0.5 and refined with geometric restraints and common isotropic thermal parameters. Hydrogen atoms were added in calculated positions d(C–H) = 0.96 Å and not located directly. The absolute configuration of the compound was confirmed by

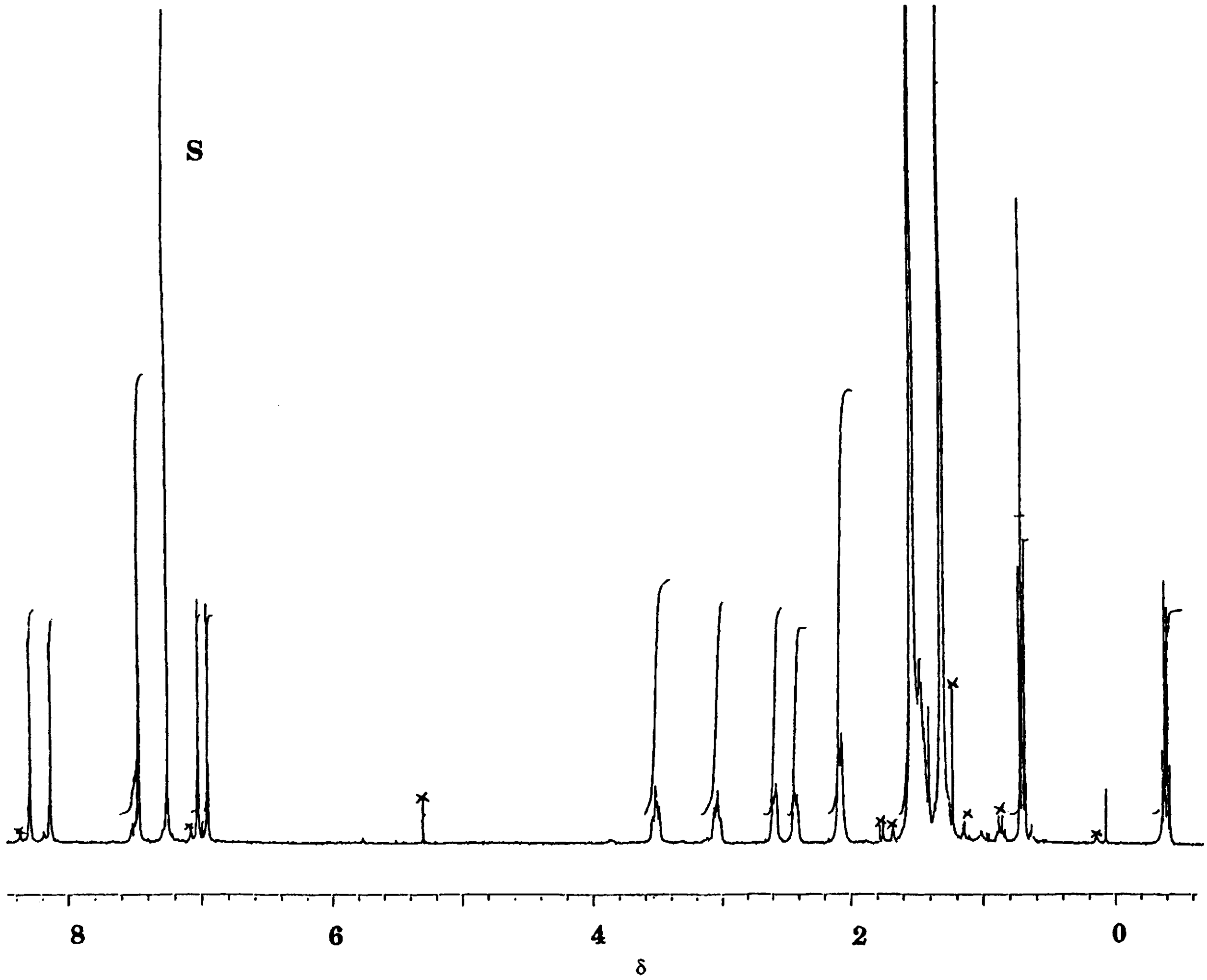


Fig. 1 Proton NMR (400 MHz) spectrum of [AlL(Et)] in $CDCl_3$. x = Impurities; S = solvent

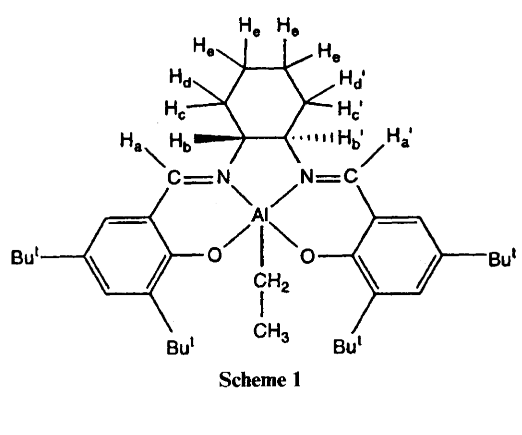
the Rogers test.[10] The final atomic coordinates and selected bond lengths and angles for **11**·$0.5C_6H_{14}$ are given in Tables 2 and 5, respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Syntheses

Reaction of $AlEt_3$ with H_2L in refluxing toluene gave the ethyl complex [AlL(Et)] **1** isolated as yellow crystals. Complex **1** is remarkably air-stable and remains intact even after recrystallization from wet CH_2Cl_2–hexane in air. The ^1H NMR spectrum (Fig. 1) shows a quartet at δ −0.39 (which probably is a doublet of quartets but could not be resolved at 400 MHz) and a triplet at δ 0.70, assignable to the methylene and methyl protons of the axial ethyl group, respectively. The four inequivalent Bu^t groups appear as two singlets presumably due to accidental overlap of the four signals. The two overlapping broad singlets at δ 2.07 and 2.09 are assigned to the equatorial cyclohexyl protons H_c and $H_{c'}$ that are β to the imine (see Scheme 1). The two doublets at δ 2.43 and 2.58 are assigned to the axial cyclohexyl protons H_d and $H_{d'}$ that are β to the imine group. The remaining four cyclohexyl protons H_e which were found to be coupled with H_c, $H_{c'}$, H_d and $H_{d'}$, are hidden by the large Bu^t signals. The cyclohexyl protons H_b and $H_{b'}$ that are α to the imine are inequivalent and were found at δ 3.03 and 3.52. The two doublets at δ 6.69 and 7.03 assignable to the ortho phenyl protons H_o and $H_{o'}$ are coupled to the *para* phenyl protons H_p



Scheme 1

and $H_{p'}$, which are accidentally isochronous and appear as a doublet at δ 7.49. The imine protons H_a and $H_{a'}$ are diastereotopic and appear as doublets at δ 8.14 and 8.29. The coupling between H_a and H_b is rather small and was not observed for some other Schiff-base complexes.

The ^{29}Al NMR spectrum of complex **1** shows a broad signal at δ 60 with half width 4690 Hz, which is typical for five-co-ordinate Al and comparable to that of the achiral analogue [Al(salen)Et] [H_2salen = *N,N'*-bis(salicyalidene)ethane-1,2-diamine].[11] Unlike [Al(salen)Et], however, no reactions between [AlL(Et)] and alcohols such as phenol were observed. The ethyl group can be removed by protonation of **1** with 1 equivalent of HBF_4, as evidenced by NMR spectroscopy. This protonated species, possibly a cationic Schiff-base complex,[12] is very reactive and we have not been able to obtain it pure.

The dichloride complexes [$MLCl_2$] (M = Ti or Zr) were

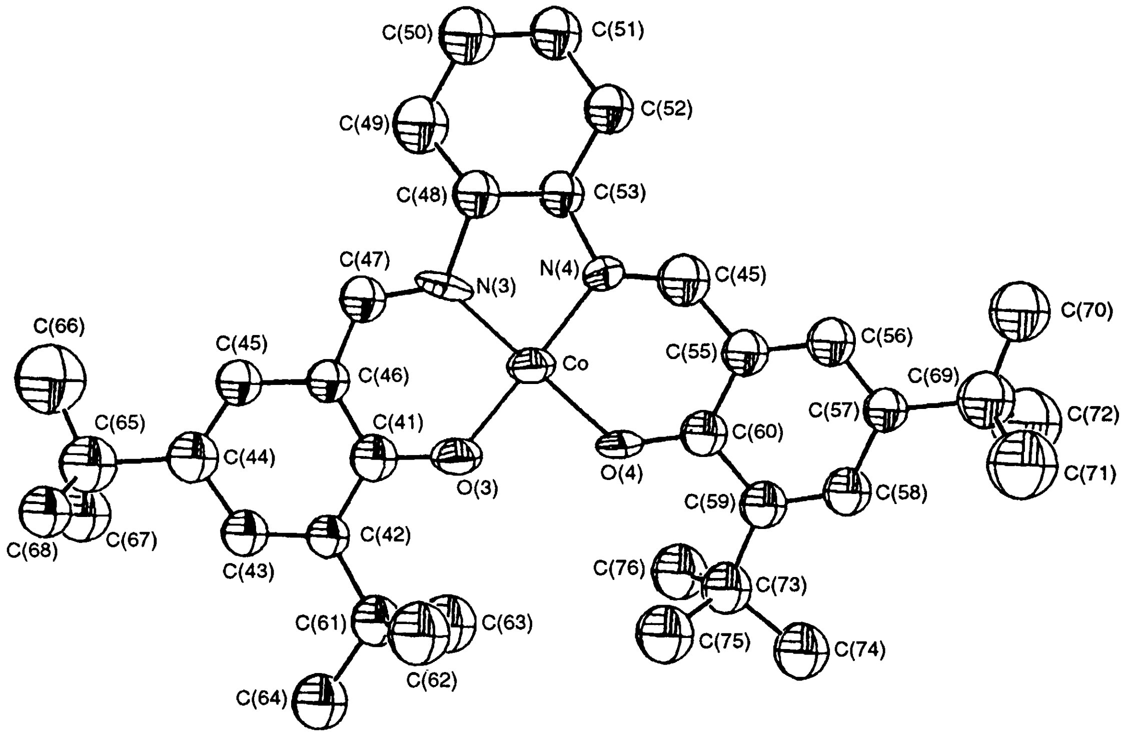


Fig. 2 Perspective view of complex **5**·0.5$CHCl_3$

prepared in high yields from the reactions of Na_2L with the chlorides $[MCl_4(thf)_2]$ and isolated as moderately air-sensitive solids. Unlike **1**, the ^1H NMR spectra for these two complexes show one signal only for H_b and $H_{b'}$. Preliminary studies showed that $[MLCl_2]$ are potent Lewis-acid catalysts. For example, they were found to catalyse ring opening of cyclohexene oxide by trimethylsilyl azide in good yields. However, only a racemic mixture of the azidohydrins were isolated in each case.[2,13]

Reactions of H_2L with $[VO(acac)_2]$, $Co(O_2CMe)_2$, $NiCl_2$ and $CuCl_2$ in MeOH in the presence of NEt_3 gave, respectively, [VO(L)], [CoL], [NiL] and [CuL]. The structure of [CoL] has been established by X-ray crystallography. Fig. 2 shows a perspective view of [CoL]·0.5$CHCl_3$; selected bond distances and angles are given in Table 1. The geometry around Co is pseudo-square planar with Co–N and Co–O distances of *ca.* 1.88 and 1.84 Å which are similar to those [1.855(3) and 1.853(2) Å respectively] found in the achiral analogue [Co(bsalen)] [H_2bsalen = *N*,*N'*-(3-*tert*-butylsalicylidene)tetramethylethane-1,2-diamine].[14] Complex **5** can be reduced by sodium amalgam to give exceedingly air-sensitive Na[CoL] which undergoes oxidative addition with a variety of alkyl halides to give cobalt(III) alkyls. Attempts to purify these chiral alkyls by chromatography were unsuccessful. Reaction of $FeCl_3$ with H_2L in the presence of NEt_3 gave the μ-oxo dimer $[(FeL)_2O]$. The measured magnetic moment of 1.4 μ_B per Fe is consistent with the antiferromagnetically coupled oxo-bridged structure as found for $[\{Fe(salen)\}_2O]$.[15–17]

Ruthenium–salen complexes are of special interest because they were found to catalyse a variety of organic transformations such as oxidation[18] and Diels–Alder reaction.[19] The dicarbonyl complex *cis*-$[RuL(CO)_2]$ **10** was prepared from $[\{Ru(CO)_2Cl_2\}_n]$ with Na_2L in refluxing thf. The observation of four Bu^t signals and only one H_b signal in the ^1H NMR spectrum (see later) as well as two ν(C≡O) bands is indicative of the *cis* disposition of the two carbonyls in **10**. Complex **10** is stable in the solid state but readily oxidized in air in solution to give a paramagnetic green species, presumably containing Ru^{III}. Treatment of $[Ru(NO)Cl_3(PPh_3)_2]$ with Na_2L in refluxing toluene afforded *trans*-[RuL(NO)Cl] **11** isolated as dark red crystals. The IR spectrum shows ν(N≡O) at 1844 cm^{-1}, suggestive of a linear co-ordination mode for the nitrosyl ligand. In contrast to **10**, complex **11** is stable in both the solid state and solution. Fig. 3 shows a perspective view of **11**·0.5C_6H_{14}; selected bond lengths and angles are given in Table 2. The geometry around Ru is octahedral with the NO and Cl as axial ligands. The Ru–N–O angle is almost linear (175°) consistent with the IR data. The Ru–N (nitrosyl) distance of 1.72(2) Å is comparable to those in [Ru(salen)(NO)(ONO)][20] and $[Ru(salen)(NO)(OH_2)]SbF_6$.[19] The Ru–Cl bond is longer than a normal Ru^{II}–Cl bond as a result of the *trans* influence of the nitrosyl ligand. In contrast to **10**, the imine protons H_b in **11** are inequivalent. Therefore it seems reasonable to speculate that the observation of two H_b resonant signals for the metal Schiff-base complexes may indicate that the Schiff-base ligand is 'flat' and the other two ligands of the metal are *trans* to each other, as in the cases of [AlL(Et)] and

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**·0.5 $CHCl_3$

Co–O(1)	1.84(1)	Co–N(1)	1.89(1)
Co–O(2)	1.84(1)	Co–N(2)	1.871(1)
O(1)–Co–O(2)	87.2(4)	O(1)–Co–N(1)	93.5(5)
O(1)–Co–N(2)	172.3(5)	O(2)–Co–N(1)	92.5(5)
N(1)–Co–N(2)	88.1(5)		

Table 2 Selected bond distances (Å) and angles (°) for complex **11**·0.5C_6H_{14}

Ru(1)–Cl(1)	2.354(4)	Ru(1)–N(1a)	1.72(2)
Ru(1)–O(2a)	2.03(1)	Ru(1)–O(5a)	2.027(9)
Ru(1)–N(4a)	2.02(2)	Ru(1)–N(3a)	2.00(1)
Cl(1)–Ru(1)–N(1a)	177.4(5)	Cl(1)–Ru(1)–O(2a)	86.6(3)
N(1a)–Ru(1)–O(2a)	90.9(6)	Cl(1)–Ru(1)–O(5a)	87.3(3)
N(1a)–Ru(1)–O(5a)	93.3(5)	O(2a)–Ru(1)–O(5a)	90.9(4)
Cl(1)–Ru(1)–N(4a)	87.0(3)	N(1a)–Ru(1)–N(4a)	95.5(6)
O(2a)–Ru(1)–N(4a)	172.8(4)	O(5a)–Ru(1)–N(4a)	91.9(4)
Cl(1)–Ru(1)–N(3a)	86.8(3)	N(1a)–Ru(1)–N(3a)	92.8(6)
O(2a)–Ru(1)–N(3a)	92.9(5)	O(5a)–Ru(1)–N(3a)	172.8(3)
N(4a)–Ru(1)–N(3a)	83.6(5)	Ru(1)–N(1a)–O(1a)	175(2)

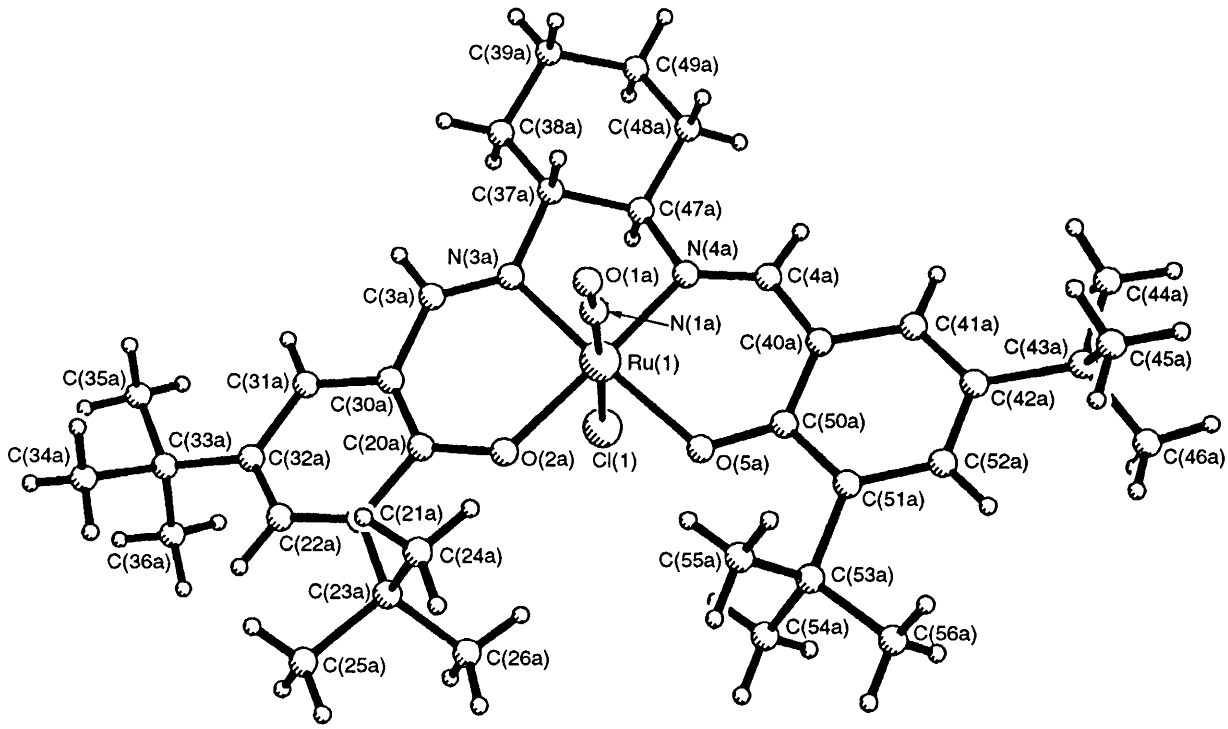


Fig. 3 Perspective view of complex **11**·$0.5C_6H_{14}$

Table 3 Summary of crystallographic data for complexes **5**·$0.5CHCl_3$ and **11**·$0.5C_6H_{14}$

	5·$0.5CHCl_3$	**11**·$0.5C_6H_{14}$
Formula	$C_{36.5}H_{52.5}Cl_{1.5}CoN_2O_2$	$C_{36}H_{52}ClN_3O_3Ru \cdot 0.5C_6H_{14}$
M_r	663.4	754.4
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a/Å	26.463(6)	15.235(3)
b/Å	26.881(6)	32.212(7)
c/Å	10.306(8)	16.672(3)
β/°		115.56(2)
U/Å^3	7331(2)	8048(3)
Z	8	8
D_c/g cm^{-3}	1.202	1.245
T/K	298	198
μ/cm^{-1}	40.50	4.93
2θ/°	36.48–46.64	3.0–46.0
F(000)	2832	3192
Crystal dimensions/mm	0.25 × 0.30 × 0.35	0.4 × 0.3 × 0.1
No. data collected	5077	10 301
No. unique reflections	5077	10 267
No. observed reflections	2227 [$F > 2.0\sigma(F)$]	8220 [$F > 3.0\sigma(F)$]
R, R' [a]	0.074, 0.067	0.0542, 0.0601
Weighting scheme, w	$1/\sigma^2(F_o)$	$1/[\sigma^2(F) + 0.001F^2]$
Goodness of fit [b]	2.46	1.13

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o - F_c)^2]^{\frac{1}{2}}/(N_o - N_p)$, where N_o = number of observations and N_p = number of parameters.

[RuL(NO)Cl]. The observation of a single resonant signal for H_b possibly suggests that the Schiff-base ligand is 'folded' and the other two ligands of the metal are *cis* to each other, as in the cases of [TiLCl_2] and [RuL$(CO)_2$].

Electrochemistry

Electrochemistry of metal complexes of Schiff bases such as salen has been well studied. The nature of the oxidation product of [M(salen)] (M = Co or Ni) is known to be solvent dependent.[21] In co-ordinating solvents such as dmf and pyridine the oxidation of [M(salen)] is metal-centred giving the respective tervalent cations $[M^{III}(salen)]^+$. However, in non-co-ordinating solvents the oxidation is ligand-centred leading to polymeric Schiff-base complexes *via* C–C coupling of the phenoxide anion radical.[22,23] The reduction potentials for the Schiff-base complexes [ML] (M = Co, Ni or Cu) and *trans*-[RuL(NO)Cl] have been determined by cyclic voltammetry and the results are given in Table 6. The cyclic voltammograms all display two reversible oxidation couples: the metal-centred M^{III}–M^{II} couple and the ligand-centred couple which occurs at *ca.* 0.6 V. Electropolymerization does not occur apparently because the steric bulk of *tert*-butyl substituents of L prevents C–C bond coupling of the phenoxide radical.[22a] The $E°(M^{III}$–$M^{II})$ values for Co, Ni and Cu were determined to be 0.0, 0.30 and 0.36 V *vs.* ferrocene–ferrocenium. These potentials are comparable to those for the [M(salen)] counterparts. The cyclic voltammogram of **11** shows reversible oxidation couples at 0.9

Table 4 Final atomic coordinates for complex **5**·$0.5CHCl_3$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.609 63(9)	0.723 71(9)	0.995 0(3)	O(4)	0.743 0(3)	0.771 1(4)	0.592 3(11)
Co(2)	0.699 23(9)	0.724 51(9)	0.520 0(3)	N(3)	0.655 4(4)	0.679 2(5)	0.445 6(13)
O(1)	0.549 2(3)	0.699 0(3)	0.934 5(11)	N(4)	0.642 8(4)	0.756 1(4)	0.581 0(13)
O(2)	0.572 8(4)	0.773 0(4)	1.075 0(10)	C(41)	0.759 4(6)	0.651 1(6)	0.387 5(16)
N(1)	0.648 6(4)	0.681 4(4)	0.888 7(13)	C(42)	0.807 5(6)	0.631 4(5)	0.350 1(16)
N(2)	0.669 5(4)	0.743 4(4)	1.076 3(13)	C(43)	0.808 7(6)	0.592 2(6)	0.275 4(16)
C(1)	0.542 9(6)	0.659 2(6)	0.868 4(16)	C(44)	0.765 3(6)	0.565 9(6)	0.222 7(17)
C(2)	0.489 7(6)	0.640 0(6)	0.852 3(17)	C(45)	0.719 5(6)	0.585 4(6)	0.263 1(16)
C(3)	0.481 9(6)	0.600 0(6)	0.774 3(18)	C(46)	0.715 5(5)	0.626 1(5)	0.347 9(16)
C(4)	0.520 7(6)	0.573 4(6)	0.708 8(16)	C(47)	0.666 0(6)	0.640 0(6)	0.376 4(17)
C(5)	0.568 9(6)	0.588 9(6)	0.724 2(17)	C(48)	0.601 0(5)	0.688 1(5)	0.487 8(17)
C(6)	0.580 2(6)	0.633 2(5)	0.801 2(16)	C(49)	0.560 5(6)	0.671 0(6)	0.384 2(18)
C(7)	0.631 1(5)	0.648 3(5)	0.818 3(16)	C(50)	0.508 6(6)	0.683 5(6)	0.453 2(18)
C(8)	0.702 6(5)	0.695 6(5)	0.899 0(14)	C(51)	0.502 3(6)	0.737 3(6)	0.484 4(19)
C(9)	0.739 3(6)	0.658 0(6)	0.854 9(17)	C(52)	0.546 5(6)	0.754 7(6)	0.577 3(16)
C(10)	0.794 2(6)	0.677 3(6)	0.867 0(17)	C(53)	0.596 5(5)	0.742 3(5)	0.507 3(18)
C(11)	0.804 2(6)	0.693 3(5)	1.001 6(18)	C(54)	0.644 2(6)	0.789 7(6)	0.665 8(18)
C(12)	0.766 5(6)	0.731 6(6)	1.052 4(16)	C(55)	0.684 8(6)	0.818 5(6)	0.727 0(16)
C(13)	0.711 8(5)	0.711 2(5)	1.036 3(16)	C(56)	0.675 9(6)	0.854 1(6)	0.818 0(17)
C(14)	0.677 3(5)	0.776 9(6)	1.168 0(16)	C(57)	0.713 8(5)	0.886 6(5)	0.849 4(16)
C(15)	0.637 1(6)	0.808 2(6)	1.205 9(16)	C(58)	0.763 0(6)	0.879 2(6)	0.791 6(17)
C(16)	0.651 1(5)	0.844 5(5)	1.296 2(15)	C(59)	0.773 8(6)	0.843 8(6)	0.703 1(17)
C(17)	0.617 0(6)	0.880 6(6)	1.340 4(18)	C(60)	0.733 7(5)	0.808 1(5)	0.670 7(16)
C(18)	0.569 4(6)	0.879 0(6)	1.279 2(17)	C(61)	0.854 7(6)	0.656 0(6)	0.396 8(17)
C(19)	0.553 5(6)	0.844 6(6)	1.194 0(17)	C(62)	0.858 0(7)	0.653 5(6)	0.541 8(19)
C(20)	0.588 7(6)	0.806 4(5)	1.158 8(16)	C(63)	0.856 3(6)	0.712 6(6)	0.362 0(19)
C(21)	0.445 9(6)	0.669 5(6)	0.917 1(18)	C(64)	0.904 6(6)	0.634 3(6)	0.337 6(18)
C(22)	0.442 4(7)	0.719 4(7)	0.868 2(20)	C(65)	0.773 0(6)	0.516 0(6)	0.135 2(19)
C(23)	0.453 9(6)	0.664 9(6)	1.065 8(17)	C(66)	0.723 8(7)	0.497 3(7)	0.087 3(22)
C(24)	0.395 9(7)	0.642 5(7)	0.899 7(20)	C(67)	0.804 5(6)	0.535 6(6)	0.015 4(19)
C(25)	0.511 5(7)	0.527 6(7)	0.621 4(20)	C(68)	0.801 4(6)	0.478 1(6)	0.206 7(17)
C(26)	0.483 6(9)	0.493 4(9)	0.701(3)	C(69)	0.704 5(6)	0.930 4(6)	0.942 8(18)
C(27)	0.469 1(8)	0.541 8(8)	0.526 3(23)	C(70)	0.652 3(6)	0.934 1(6)	0.998 2(19)
C(28)	0.555 1(9)	0.503 8(9)	0.574(3)	C(71)	0.740 9(7)	0.923 3(7)	1.061 4(21)
C(29)	0.633 0(6)	0.923 8(6)	1.429 7(17)	C(72)	0.716 2(7)	0.980 6(7)	0.876 6(22)
C(30)	0.594 9(7)	0.921 1(7)	1.544 3(19)	C(73)	0.824 4(6)	0.839 6(6)	0.632 4(17)
C(31)	0.626 2(6)	0.973 2(7)	1.357 8(20)	C(74)	0.858 7(6)	0.882 0(6)	0.681 6(19)
C(32)	0.687 3(6)	0.919 6(6)	1.486 0(19)	C(75)	0.851 5(6)	0.790 7(6)	0.663 6(18)
C(33)	0.500 4(6)	0.847 4(6)	1.131 7(18)	C(76)	0.818 5(6)	0.843 3(6)	0.487 4(19)
C(34)	0.471 0(7)	0.895 0(7)	1.180 7(19)	C	0.554 0(8)	0.537 4(8)	0.046 8(22)
C(35)	0.468 3(6)	0.802 3(6)	1.161 2(18)	Cl(1)	0.587 2(3)	0.583 4(3)	0.121 6(8)
C(36)	0.506 8(6)	0.853 9(6)	0.981 4(20)	Cl(2)	0.582 7(3)	0.488 1(3)	0.022 0(10)
O(3)	0.755 5(3)	0.690 1(3)	0.462 9(11)	Cl(3)	0.500 6(3)	0.527 8(3)	0.138 7(11)

Table 5 Atomic coordinates for complex **11** $0.5C_6H_{14}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.3538(1)	0.6179	0.0012(1)	C(25d)	0.6263(14)	0.6520(5)	0.6262(11)
Ru(2)	−0.1136(1)	0.6665(1)	0.1265(1)	C(26d)	0.6856(13)	0.5859(5)	0.6437(9)
Ru(3)	0.0101(1)	0.4709(1)	0.2941(1)	C(30d)	0.6132(10)	0.5889(4)	0.3546(8)
Ru(4)	0.5755(1)	0.5015(1)	0.4056(1)	C(31d)	0.6354(10)	0.6251(4)	0.3318(9)
Cl(3)	−0.1224(3)	0.5037(1)	0.2998(2)	C(32d)	0.6529(10)	0.6563(4)	0.3837(8)
Cl(1)	0.5237(3)	0.6128(1)	0.0826(2)	C(33d)	0.6803(14)	0.6955(4)	0.3605(11)
Cl(4)	0.4069(3)	0.5143(1)	0.3317(2)	C(34d)	0.6763(17)	0.6964(5)	0.2690(11)
Cl(2)	0.0262(3)	0.6339(1)	0.1384(2)	C(35d)	0.6198(12)	0.7264(4)	0.3720(12)
N(1a)	0.2305(11)	0.6229(4)	−0.0617(9)	C(36d)	0.7838(15)	0.7044(6)	0.4277(15)
O(1a)	0.1526(12)	0.6265(5)	−0.1071(11)	C(37d)	0.5969(11)	0.4942(4)	0.2411(8)
N(1b)	−0.2212(12)	0.6897(3)	0.1110(8)	C(38d)	0.5734(12)	0.5055(4)	0.1460(9)
O(1b)	−0.2909(10)	0.7050(4)	0.0969(8)	C(39d)	0.5898(13)	0.4710(5)	0.0974(10)
N(1c)	0.1055(13)	0.4465(4)	0.2915(10)	C(40d)	0.5497(11)	0.4125(4)	0.4512(8)
O(1c)	0.1670(14)	0.4286(5)	0.2932(12)	C(41d)	0.5557(13)	0.3729(4)	0.4724(10)
N(1d)	0.6971(11)	0.4929(3)	0.4559(8)	C(42d)	0.5616(13)	0.3598(5)	0.5512(11)
O(1d)	0.7796(10)	0.4875(4)	0.4870(9)	C(43d)	0.5732(16)	0.3174(5)	0.5721(12)
O(2a)	0.3811(7)	0.6425(3)	−0.0958(6)	C(44d)	0.4899(34)	0.3040(12)	0.5786(28)
O(2b)	−0.0361(7)	0.6803(3)	0.2567(5)	C(45d)	0.6717(35)	0.3147(13)	0.6622(29)
O(2c)	−0.0448(8)	0.4230(3)	0.3253(6)	C(46d)	0.5667(48)	0.2909(16)	0.4874(38)
O(2d)	0.5877(7)	0.5521(3)	0.4647(6)	C(44e)	0.6330(44)	0.2961(16)	0.5317(38)
O(5a)	0.3569(7)	0.5655(3)	−0.0482(6)	C(45e)	0.5789(31)	0.3053(11)	0.6631(26)
O(5b)	−0.0581(7)	0.7127(2)	0.0942(5)	C(46e)	0.4754(32)	0.2963(12)	0.4997(27)
O(5c)	−0.0748(8)	0.4634(2)	0.1637(6)	C(47d)	0.5306(11)	0.4612(4)	0.2400(8)
O(5d)	0.5492(7)	0.4758(3)	0.5014(5)	C(48d)	0.5427(13)	0.4268(4)	0.1915(10)
N(4a)	0.3433(8)	0.5957(3)	0.1084(7)	C(49d)	0.5296(14)	0.4374(5)	0.0985(10)

Table 5 (*contd.*)

Atom	x	y	z	Atom	x	y	z
C(4a)	0.3256(11)	0.5612(4)	0.1171(9)	C(50d)	0.5520(11)	0.4395(4)	0.5131(9)
N(4b)	−0.1748(8)	0.6468(3)	0.0019(7)	C(51d)	0.5453(11)	0.4264(4)	0.5920(9)
C(4b)	−0.1836(11)	0.6667(4)	−0.0666(8)	C(52d)	0.5538(11)	0.3877(5)	0.6068(10)
N(3a)	0.3643(8)	0.6672(3)	0.0643(6)	C(53d)	0.5342(13)	0.4543(5)	0.6571(10)
C(3a)	0.4022(11)	0.6974(4)	0.0497(10)	C(54d)	0.4409(14)	0.4779(5)	0.6108(11)
N(3b)	−0.1625(7)	0.6172(3)	0.1538(6)	C(55d)	0.6253(13)	0.4812(5)	0.6938(10)
C(3b)	−0.1401(9)	0.6054(3)	0.2340(8)	C(56d)	0.5293(14)	0.4344(5)	0.7374(10)
N(3c)	0.0854(9)	0.4847(3)	0.4232(7)	C(1s)	0.9283(33)	0.2031(13)	0.2218(25)
C(3c)	0.0683(11)	0.4705(4)	0.4849(8)	C(2s)	0.8836(35)	0.2173(11)	0.1259(25)
N(4c)	0.0578(8)	0.5216(3)	0.2729(7)	C(3s)	0.8153(31)	0.2463(12)	0.1220(27)
C(4c)	0.0473(10)	0.5346(4)	0.1970(8)	C(4s)	0.8021(30)	0.2727(12)	0.0469(28)
N(3d)	0.5887(8)	0.5243(3)	0.2998(7)	C(5s)	0.7213(33)	0.2967(12)	0.0305(26)
C(3d)	0.6022(11)	0.5596(4)	0.2902(9)	C(6s)	0.6755(31)	0.3138(13)	−0.0569(25)
N(4d)	0.5463(8)	0.4538(3)	0.3334(7)	C(7s)	0.7587(53)	0.8826(21)	0.5265(40)
C(4d)	0.5389(10)	0.4202(4)	0.3620(9)	C(8s)	0.7618(55)	0.8892(16)	0.4422(36)
C(20a)	0.4153(10)	0.6773(4)	−0.0912(9)	C(9s)	0.8120(43)	0.8549(19)	0.4256(31)
C(21a)	0.4297(11)	0.6902(4)	−0.1648(9)	C(10s)	0.7612(54)	0.8548(15)	0.3253(31)
C(22a)	0.4739(12)	0.7243(5)	−0.1553(12)	C(11s)	0.7752(50)	0.8158(16)	0.3000(36)
C(23a)	0.4009(12)	0.6657(5)	−0.2460(9)	C(12s)	0.6968(49)	0.8128(19)	0.2053(36)
C(24a)	0.4134(13)	0.6867(5)	−0.3202(11)	C(40b)	−0.1499(11)	0.7065(4)	−0.0656(8)
C(25a)	0.4579(13)	0.6289(5)	−0.2291(10)	C(41b)	−0.1770(12)	0.7231(5)	−0.1500(10)
C(26a)	0.2922(12)	0.6551(5)	−0.2854(9)	C(42b)	−0.1549(14)	0.7588(4)	−0.1599(10)
C(30a)	0.4320(11)	0.7021(4)	−0.0195(9)	C(43b)	−0.1878(17)	0.7780(6)	−0.2495(12)
C(31a)	0.4759(12)	0.7377(5)	−0.0180(12)	C(44b)	−0.2495(22)	0.7564(8)	−0.3246(19)
C(32a)	0.5013(14)	0.7502(5)	−0.0845(15)	C(45b)	−0.2599(27)	0.8105(9)	−0.2526(18)
C(33a)	0.5522(20)	0.7868(5)	−0.0817(16)	C(46b)	−0.1013(22)	0.7904(10)	−0.2611(15)
C(34a)	0.4953(16)	0.8099(6)	−0.1663(19)	C(47b)	−0.2041(10)	0.6073(3)	−0.0036(8)
C(35a)	0.6510(16)	0.7796(6)	−0.0788(17)	C(48b)	−0.2854(11)	0.5953(4)	−0.0901(8)
C(36a)	0.5622(24)	0.8109(7)	−0.0090(22)	C(49b)	−0.3077(13)	0.5531(5)	−0.0880(10)
C(37a)	0.3274(11)	0.6633(4)	0.1324(8)	C(50b)	−0.0907(11)	0.7254(4)	0.0134(8)
C(38a)	0.3513(14)	0.6951(4)	0.1981(10)	C(51b)	−0.0604(13)	0.7628(4)	0.0024(9)
C(39a)	0.3040(14)	0.6866(5)	0.2612(11)	C(52b)	−0.0948(14)	0.7781(4)	−0.0813(11)
C(40a)	0.3106(10)	0.5323(4)	0.0553(8)	C(53b)	−0.0017(14)	0.7864(4)	0.0856(10)
C(41a)	0.2789(9)	0.4967(4)	0.0733(8)	C(54b)	0.0924(16)	0.7666(5)	0.1435(12)
C(42a)	0.2601(11)	0.4660(4)	0.0210(10)	C(55b)	0.0256(17)	0.8249(5)	0.0624(12)
C(43a)	0.2213(13)	0.4282(4)	0.0385(10)	C(56b)	−0.0564(16)	0.7922(5)	0.1395(12)
C(44a)	0.2294(29)	0.4268(6)	0.1289(16)	C(20c)	−0.0487(12)	0.4189(4)	0.4029(10)
C(45a)	0.1175(17)	0.4260(6)	−0.0223(22)	C(21c)	−0.1053(11)	0.3883(4)	0.4095(9)
C(46a)	0.2612(17)	0.3941(5)	0.0191(18)	C(22c)	−0.1129(11)	0.3844(4)	0.4884(10)
C(47a)	0.3635(11)	0.6252(4)	0.1776(8)	C(23c)	−0.1514(13)	0.3595(5)	0.3334(11)
C(48a)	0.3219(11)	0.6175(4)	0.2436(9)	C(24c)	−0.2177(13)	0.3776(7)	0.2481(11)
C(49a)	0.3444(13)	0.6500(4)	0.3121(10)	C(25c)	−0.0682(14)	0.3397(5)	0.3184(13)
C(50a)	0.3255(11)	0.5357(4)	−0.0255(8)	C(26c)	−0.2078(20)	0.3267(7)	0.3522(14)
C(51a)	0.3060(10)	0.5026(4)	−0.0798(8)	C(30c)	0.0035(10)	0.4419(4)	0.4785(8)
C(52a)	0.2734(10)	0.4698(4)	−0.0561(9)	C(31c)	−0.0115(11)	0.4353(4)	0.5578(8)
C(53a)	0.3157(11)	0.5047(4)	−0.1686(8)	C(32c)	−0.0683(13)	0.4070(5)	0.5620(10)
C(54a)	0.4207(13)	0.5150(5)	−0.1492(10)	C(33c)	−0.0842(14)	0.4007(5)	0.6461(10)
C(55a)	0.2495(13)	0.5349(5)	−0.2270(10)	C(34c)	−0.1859(17)	0.4127(7)	0.6295(15)
C(56a)	0.2920(13)	0.4679(5)	−0.2178(10)	C(35c)	−0.0821(25)	0.3627(8)	0.6701(17)
C(20b)	−0.0339(10)	0.6594(3)	0.3233(8)	C(36c)	−0.0249(24)	0.4210(10)	0.7200(16)
C(21b)	0.0206(10)	0.6750(3)	0.4098(8)	C(37c)	0.1558(10)	0.5158(4)	0.4326(8)
C(22b)	0.0186(10)	0.6554(4)	0.4814(9)	C(38c)	0.2006(11)	0.5349(4)	0.5209(9)
C(23b)	0.0763(11)	0.7123(4)	0.4218(8)	C(39c)	0.2697(12)	0.5672(5)	0.5233(9)
C(24b)	0.0073(13)	0.7452(4)	0.3757(10)	C(40c)	−0.0035(11)	0.5138(4)	0.1147(9)
C(25b)	0.1301(14)	0.7235(5)	0.5190(10)	C(41c)	0.0009(10)	0.5324(4)	0.0380(9)
C(26b)	0.1514(12)	0.7086(4)	0.3822(10)	C(42c)	−0.0462(10)	0.5184(4)	−0.0450(8)
C(30b)	−0.0816(9)	0.6246(4)	0.3162(8)	C(43c)	−0.0382(11)	0.5384(4)	−0.1243(9)
C(31b)	−0.0801(10)	0.6061(3)	0.3926(8)	C(44c)	−0.0459(19)	0.5813(5)	−0.1206(13)
C(32b)	−0.0310(10)	0.6216(4)	0.4753(8)	C(45c)	0.0561(14)	0.5299(5)	−0.1257(12)
C(33b)	−0.0345(13)	0.6033(4)	0.5578(9)	C(46c)	−0.1169(14)	0.5258(6)	−0.2123(10)
C(34b)	−0.0775(18)	0.5647(5)	0.5378(11)	C(47c)	0.1054(11)	0.5439(4)	0.3567(8)
C(35b)	−0.0942(13)	0.6286(6)	0.5904(10)	C(48c)	0.1737(12)	0.5744(4)	0.3546(10)
C(36b)	0.0688(12)	0.6020(5)	0.6330(9)	C(49c)	0.2206(12)	0.5938(4)	0.4486(9)
C(37b)	−0.2318(10)	0.5992(4)	0.0728(8)	C(50c)	−0.0583(12)	0.4809(4)	0.1018(9)
C(38b)	−0.2487(11)	0.5571(4)	0.0771(8)	C(51c)	−0.1009(10)	0.4634(4)	0.0142(9)
C(39b)	−0.3292(12)	0.5427(4)	−0.0087(9)	C(52c)	−0.0918(11)	0.4843(4)	−0.0545(9)
C(20d)	0.6044(11)	0.5844(4)	0.4359(9)	C(53c)	−0.1567(13)	0.4256(4)	−0.0016(9)
C(21d)	0.6180(10)	0.6172(4)	0.4902(8)	C(54c)	−0.1837(12)	0.4116(4)	−0.0969(9)
C(22d)	0.6404(10)	0.6505(4)	0.4635(9)	C(55c)	−0.2515(13)	0.4318(5)	0.0096(11)
C(23d)	0.6077(12)	0.6138(5)	0.5787(9)	C(56c)	−0.0920(12)	0.3952(4)	0.0637(9)
C(24d)	0.5085(13)	0.6009(5)	0.5587(11)				

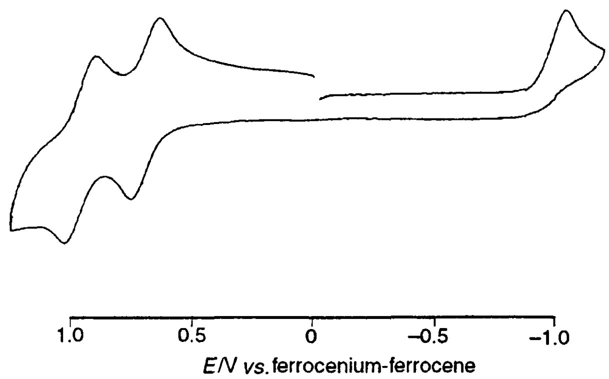


Fig. 4 Cyclic voltammogram of complex **11** in CH_2Cl_2 at a glassy carbon electrode. Scan rate = 100 mV s^{-1}

Table 6 Formal potentials ($E°$)[a] for chiral Schiff-base complexes

Complex	$E°$/V *vs.* ferrocenium-ferrocene
[CoL]	0, 0.61
[NiL]	0.30, 0.70
[CuL]	0.36, 0.66
[RuL(NO)Cl]	−1.02,[b] 0.60, 0.90

[a] Measured at a glassy carbon electrode in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n{}_4]PF_6$ as supporting electrolyte. Scan rate = 100 mV s^{-1}. [b] Irreversible.

and 0.6 V, and an irreversible reduction wave at −1.02 V (Fig. 4). The couple at 0.6 V is assigned to the ligand-centred oxidation, by comparison with the cobalt and nickel analogues. That at 0.9 V is assigned to the metal-centred Ru^{III}–Ru^{II} couple. This potential is considerably more cathodic than that for $[Ru(salen)Cl(PPh_3)]$,[17] demonstrating the stabilization of the ruthenium(II) state by NO^+. The irreversible wave at −1.02 V is assigned to the metal-centred reduction of Ru^{II}.

Oxidation of [ML]

The lipophilicity of L as well as its inability to undergo oxidative polymerization facilitates isolation of the oxidized species $[ML]^+$. Treatment of [CoL] and [NiL] with 1 equivalent of $AgBF_4$ yielded the stable cations $[CoL]^+$ and $[NiL]^+$, respectively, isolated as their BF_4 salts. The reaction of [CuL] with $AgBF_4$ gave only an intractable purple oil. The IR spectrum of $[NiL]^+$ is very similar to that for [NiL] except for the BF_4 band and a decrease in ν(C=N) from 1600 to 1575 cm^{-1}. The EPR spectrum of $[NiL]^+$ at room temperature shows a broad isotropic signal with *g ca.* 2.007, indicative of an organic cation radical. On the basis of EPR spectroscopy, we tentatively formulate $[NiL]^+$ as a nickel(II) complex of the Schiff-base cation radical. It seems likely that the oxidation of [NiL] initially generated $[Ni^{III}L]^+$ which subsequently underwent internal electron transfer to give the ligand-centred radical complex $[Ni^{II}(L^{\bullet})]^+$. The ion $[NiL]^+$ is indefinitely stable in the solid state but slowly decomposes to [NiL] in solution. A study of the reactivity of this stable chiral radical species is underway.

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References

1 W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1990, **112**, 2801; W. Zhang and E. N. Jacobsen, *J. Org. Chem.*, 1991, **56**, 2296; B. D. Brandes and E. N. Jacobsen, *J. Org. Chem.*, 1994, **59**, 4378; H. Sasaki, R. Irie, T. Hamada, K. Susuki and T. Katsuki, *Tetrahedron*, 1994, **50**, 11827.
2 L. E. Martinez, J. L. Leighton, D. H. Carsten and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1995, **117**, 5897.
3 E. N. Jacobsen, W. Zhang and M. L. Güller, *J. Am. Chem. Soc.*, 1991, **113**, 6703; E. N. Jacobsen, L. Deng, Y. Furukawa and L. E. Martinez, *Tetrahedron*, 1994, **50**, 4323; E. N. Jacobsen, in *Catalytic Asymmetric Syntheses*, ed. I. Ojima, New York, 1993, ch. 4.2.
4 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
5 J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie and C. M. Zepp, *J. Org. Chem.*, 1994, **59**, 1939.
6 L. E. Manzer, J. Deaton, P. Sharp and R. R. Schrock, *Inorg. Synth.*, 1981, **21**, 135.
7 F. A. Colton and R. H. Farthing, *Aust. J. Chem.*, 1971, **24**, 903.
8 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 1970, 2947.
9 NRCVAX, E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
10 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
11 P. L. Gurian, L. K. Cheatham, J. W. Ziller and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1991, 1449.
12 M. G. Davidson, C. Lambert, I. Lopez-Solera, P. R. Raithby and R. Snaith, *Inorg. Chem.*, 1995, **34**, 3765.
13 E. K. F. Chow, M. Phil Thesis, The Hong Kong University of Science and Technology, 1994.
14 R. S. Gall, J. F. Rogers, W. P. Schaefer and G. G. Christoph, *J. Am. Chem. Soc.*, 1976, **98**, 5135.
15 J. Lewis, F. E. Mabbs and A. R. Richards, *J. Chem. Soc. A*, 1967, 1014.
16 M. Gerloch, E. D. McKenzie and A. D. C. Towl, *J. Chem. Soc. A*, 1969, 2850.
17 W.-H. Leung, E. Y. Y. Chan and I. D. Williams, unpublished work.
18 W.-H. Leung and C.-M. Che, *Inorg. Chem.*, 1989, **28**, 4619.
19 W. Odenkirk, A. L. Rheingold and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 6392.
20 M. A. A. A. F de C. T. Carrondo, P. R. Rudolf, A. C. Skapski, J. R. Thornback and G. Wilkinson, *Inorg. Chim. Acta*, 1977, **24**, L95.
21 A. Kapturkiewicz and B. Behr, *Inorg. Chim. Acta*, 1983, **69**, 247.
22 (*a*) K. A. Goldsby, J. K. Blaho and L. A. Hoferkamp, *Polyhedron*, 1989, **8**, 113; (*b*) L. A. Hoferkamp and K. A. Goldsby, *Chem. Mater.*, 1989, **1**, 348.
23 A. Audebert, P. Capdevielle and M. Maumy, *New. J. Chem.*, 1991, **15**, 235 and refs. therein.

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