

Metal complexes of a chiral quadridentate Schiff base†

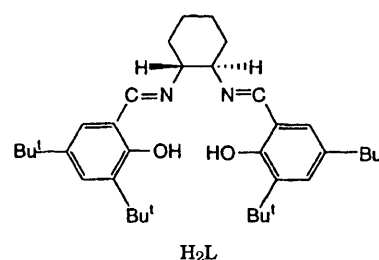
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Chiral metal Schiff-base complexes [AlL(Et)], [TiLCl₂], [VO(L)], [(FeL)₂O], [CoL], [NiL], [CuL], [ZrLCl₂], [RuL(CO)₂] and *trans*-[RuL(NO)Cl] ([H₂L = (*R,R*)-(–)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine] were synthesized and 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 AgBF₄ afforded air-stable [NiL]BF₄, 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 H₂L (or Jacobsen's catalyst) are capable of catalysing epoxidation of unfunctionalized alkenes in excellent enantiomeric excesses.¹ More recently, Jacobsen and co-workers² 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 (H₂L).

Experimental

Solvents were dried and distilled prior to use. The NMR spectra were recorded on a JEOL EM 400 spectrometer at 400 (¹H) and 104.2 (²⁷Al) MHz. Chemical shifts (δ) are reported with reference to SiMe₄ and [Al(OH)₂]³⁺ for ¹H and ²⁷Al 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 CHCl₃ solutions were determined by the Evans method⁴ 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.



Materials

The compound H₂L 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 Na₂L was prepared by reaction of H₂L with 2 equivalents of NaH in tetrahydrofuran (thf); [TiCl₄(thf)₂], [ZrCl₄(thf)₂],⁶ [(Ru(CO)₂Cl₂)]_n⁷ and [Ru(NO)Cl₃(PPh₃)₂]⁸ were prepared by the literature methods.

Preparations

[AlL(Et)] 1. To a solution of H₂L (0.5 g, 0.9 mmol) in toluene (20 cm³) was added 1 equivalent of AlEt₃ (1 cm³ 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 CH₂Cl₂–hexane to give yellow prisms (yield 0.43 g, 80%). NMR (CDCl₃): ¹H, δ –0.39 (q, 2 H, CH₂CH₃), 0.70 (t, 3 H, CH₂CH₃), 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_e), 7.03 (d, *J* = 2.5 Hz, 1 H, H_e), 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); ²⁷Al, δ 60 (half width = 4690 Hz, *T*₂ = 67.88 s) (Found: C, 77.5; H, 7.4; N, 4.9. C₃₈H₄₀AlN₂O₂ requires C, 78.2; H, 6.9; N, 4.8%).

[TiLCl₂] 2. To a solution of Na₂L (2.3 g, 3.68 mmol) in thf (20 cm³) was added [TiCl₄(thf)₂] (1.21 g, 3.68 mmol) under a stream of nitrogen and toluene (20 cm³). 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 CH₂Cl₂–

† Non-SI unit employed: μ_B ≈ 9.274 × 10⁻²⁴ J T⁻¹.

hexane (yield 0.54 g, 59%). $^1\text{H NMR}$ (CDCl_3): δ 1.33, 1.43 (s, 36 H, Bu¹), 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. $\text{C}_{36}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$ requires C, 65.1; H, 7.9; N, 4.2%).

[VO(L)] 3. To a solution of H₂L (1 g, 1.84 mmol) in dimethylformamide (dmf) (15 cm³) 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 CH₂Cl₂–hexane to give dark yellow crystals (yield: 0.67 g, 60%). IR (cm⁻¹): 986 [$\nu(\text{V=O})$]. $\mu_{\text{eff}} = 1.8 \mu_{\text{B}}$ (Found: C, 69.8; H, 9.0; N, 4.7. $\text{C}_{36}\text{H}_{52}\text{N}_2\text{O}_2\text{V}$ requires C, 70.9; H, 8.8; N, 4.6%).

[(FeL)₂O] 4. To a suspension of H₂L (1 g, 1.84 mmol) in MeOH (30 cm³) was added 1 equivalent of FeCl₃·4H₂O (0.37 g, 1.85 mmol) and 10 equivalents of NEt₃ (2.5 cm³, 18.4 mmol) and the resultant mixture stirred at room temperature for 2 h. The orange precipitate was collected and dissolved in CH₂Cl₂, washed twice with water (20 cm³), and dried with Na₂SO₄. Addition of hexane and slow evaporation of the CH₂Cl₂ 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. $\text{C}_{72}\text{H}_{104}\text{Fe}_2\text{N}_4\text{O}_3$ requires C, 70.4; H, 8.7; N, 4.4%).

[CoL] 5. To H₂L (2 g, 3.67 mmol) in toluene (30 cm³) was added dropwise Co(O₂CMe)₂ (0.95 g, 3.67 mmol) in aqueous ethanol (30 cm³) 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 CHCl₃–hexane to give red crystals, which are suitable for X-ray diffraction study (yield: 1.7 g, 76%). $\mu_{\text{eff}} = 1.7 \mu_{\text{B}}$ (Found: C, 71.6; H, 8.1; N, 4.7. $\text{C}_{36}\text{H}_{52}\text{CoN}_2\text{O}_2$ requires C, 71.6; H, 8.6; N, 4.6%).

[NiL] 6. A mixture of NiCl₂ (1 g), H₂L (1 g), and NEt₃ (0.5 cm³) was heated at reflux in MeOH (25 cm³) for 2 h. The orange solid was collected, washed with MeOH, redissolved in CH₂Cl₂, and layered with hexane. The dark orange needles formed were collected (yield 40%). $^1\text{H NMR}$ (CDCl_3): δ 1.26, 1.41 (s, 36 H, Bu¹), 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. $\text{C}_{36}\text{H}_{52}\text{N}_2\text{NiO}_2$ requires C, 68.1; H, 8.2; N, 4.4%).

[NiL]BF₄ 7. To a solution of complex **6** (50 mg, 0.83 mmol) in CH₂Cl₂ (10 cm³) was added 1 equivalent of AgBF₄ (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 Et₂O, and layered with hexane at -10 °C. The dark green crystals were collected and washed with hexane (yield: 0.42 g, 75%). UV/VIS (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm}(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ 383 (3190). $\mu_{\text{eff}} = 1.6 \mu_{\text{B}}$. IR (cm⁻¹): 1575 [$\nu(\text{C=N})$] (Found: C, 62.3; H, 7.6; N, 4.0. $\text{C}_{36}\text{H}_{52}\text{BF}_4\text{N}_2\text{NiO}_2$ requires C, 62.6; H, 7.5; N, 4.1%). The SbF₆ salt was prepared similarly from **6** and AgSbF₆.

[CuL] 8. This complex was prepared as for **5** from CuCl₂ (0.5 g) and H₂L (1 g) in MeOH (yield: 70%). Mass spectrum (FAB): m/z 607 (M^+). $\mu_{\text{eff}} = 1.6 \mu_{\text{B}}$ (Found: C, 70.4; H, 8.9; N, 4.9. $\text{C}_{36}\text{H}_{52}\text{CuN}_2\text{O}_2$ requires C, 71.1; H, 8.6; N, 4.6%).

[ZrLCl₂] 9. This complex was prepared as for **2** from Na₂L (1 g, 1.84 mmol) and [ZrCl₄(thf)₂] (0.68 g, 1.84 mmol). The product was recrystallized from CH₂Cl₂–hexane as a yellow microcrystalline solid (yield 1.05 g, 81%). $^1\text{H NMR}$ (CDCl_3): 1.32, 1.43, 1.49, 1.57 (s, 36 H, Bu¹), 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. $\text{C}_{36}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_2\text{Zr}$ requires C, 61.2; H, 7.4; N, 4.0%).

cis-[RuL(CO)₂] 10. To a solution of Na₂L (1 g, 1.84 mmol) in thf (50 cm³) was added an excess of [$\text{Ru}(\text{CO})_2\text{Cl}_2$]_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 CH₂Cl₂. The filtrate was concentrated to 1 cm³ and loaded onto a column of Florisil. The product was eluted with Et₂O–CH₂Cl₂ (5:95) as a yellow band. Recrystallization from MeOH as 0 °C afforded air-sensitive yellow crystals (yield: 0.29 g, 24%). $^1\text{H NMR}$ (CDCl_3): 1.19, 1.29, 1.34, 1.50 (s, 36 H, Bu¹), 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 [$\nu(\text{C=O})$] (Found: C, 64.2; H, 8.1; N, 3.8. $\text{C}_{38}\text{H}_{52}\text{N}_2\text{O}_4\text{Ru}$ requires C, 65.0; H, 7.4; N, 4.0%).

trans-[RuL(NO)Cl] 11. To a solution of Na₂L (0.17 g, 0.3 mmol) in toluene (25 cm³) was added [Ru(NO)Cl₃(PPh₃)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 cm³ 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 CH₂Cl₂–hexane. $^1\text{H NMR}$ (CDCl_3): δ 1.28, 1.54 (s, 36 H, Bu¹), 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. $\text{C}_{36}\text{H}_{52}\text{ClN}_3\text{O}_3\text{Ru}$ requires C, 61.0; H, 7.3; N, 5.9%). IR (cm⁻¹): 1844 [$\nu(\text{N=O})$], 1629 [$\nu(\text{C=N})$].

X-Ray crystallography

A summary of crystal data and experimental details for complexes **5**·0.5CHCl₃ and **11**·0.5C₆H₁₄ are listed in Table 3. Diffraction measurements for **5**·0.5CHCl₃ and **11**·0.5C₆H₁₄ were made on Enraf-Nonius CAD-4 and Siemens P4 diffractometers, respectively. Lattice parameters for **5**·0.5CHCl₃ were obtained from 25 reflections with 2 θ 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**·0.5C₆H₁₄ were refined from setting angles of 30 reflections with 2 $\theta > 20^\circ$. 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 $d(\text{C-H}) = 0.96 \text{ \AA}$ and not located directly. The absolute configuration of the compound was confirmed by

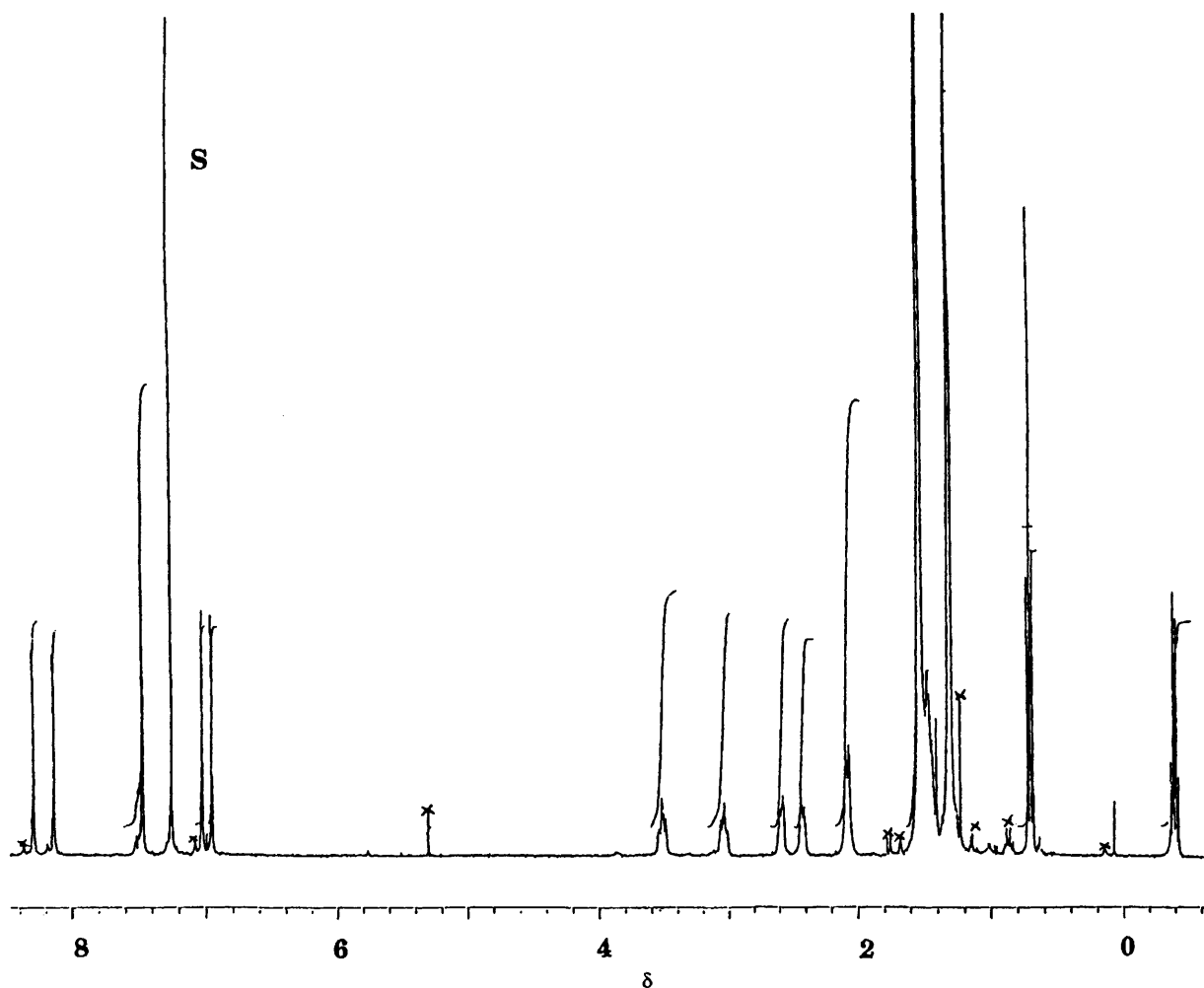


Fig. 1 Proton NMR (400 MHz) spectrum of $[AlL(Et)]$ in $CDCl_3$. x = Impurities; S = solvent

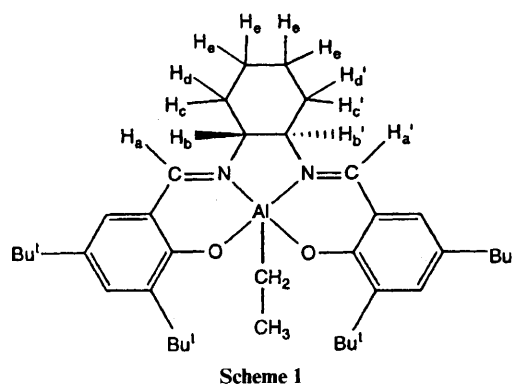
the Rogers test.¹⁰ The final atomic coordinates and selected bond lengths and angles for $11 \cdot 0.5C_6H_{14}$ are given in Tables 2 and 5, respectively.

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 $\delta -0.39$ (which probably is a doublet of quartets but could not be resolved at 400 MHz) and a triplet at $\delta 0.70$, 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 $\delta 2.07$ 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 $\delta 2.43$ 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 $\delta 3.03$ and 3.52 . The two doublets at $\delta 6.69$ and 7.03 assignable to the ortho phenyl protons H_o and H_o' are coupled to the *para* phenyl protons H_p



and H_p' , which are accidentally isochronous and appear as a doublet at $\delta 7.49$. The imine protons H_a and H_a' are diastereotopic and appear as doublets at $\delta 8.14$ 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 $\delta 60$ with half width 4690 Hz, which is typical for five-coordinate Al and comparable to that of the achiral analogue $[Al(salen)Et]$ [$H_2salen = N,N'$ -bis(salicylidene)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

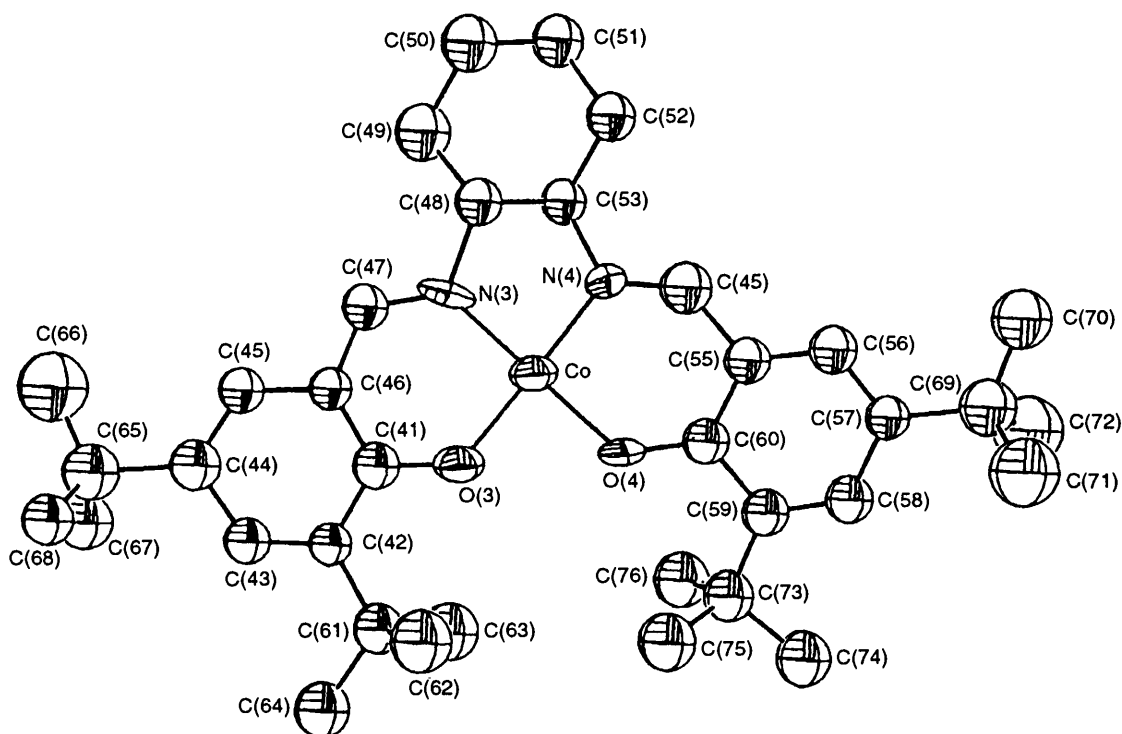


Fig. 2 Perspective view of complex **5**·0.5CHCl₃

prepared in high yields from the reactions of Na₂L with the chlorides [MCl₄(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 [MLCl₂] 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 azidoalcohols were isolated in each case.^{2,13}

Reactions of H₂L with [VO(acac)₂], Co(O₂CMe)₂, NiCl₂ and CuCl₂ in MeOH in the presence of NEt₃ 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]·0.5CHCl₃; 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)] [H₂bsalen = *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 FeCl₃ with H₂L in the presence of NEt₃ 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 oxidation¹⁸ and Diels–Alder reaction.¹⁹ The dicarbonyl complex *cis*-[RuL(CO)₂] **10** was prepared from [{Ru(CO)₂Cl₂}]_n with Na₂L 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)Cl₃(PPh₃)₂] with Na₂L 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,

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**·0.5CHCl₃

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**·0.5C₆H₁₄

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)

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**·0.5C₆H₁₄; 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)(OH₂)]SbF₆.¹⁹ 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 [AIL(Et)] and

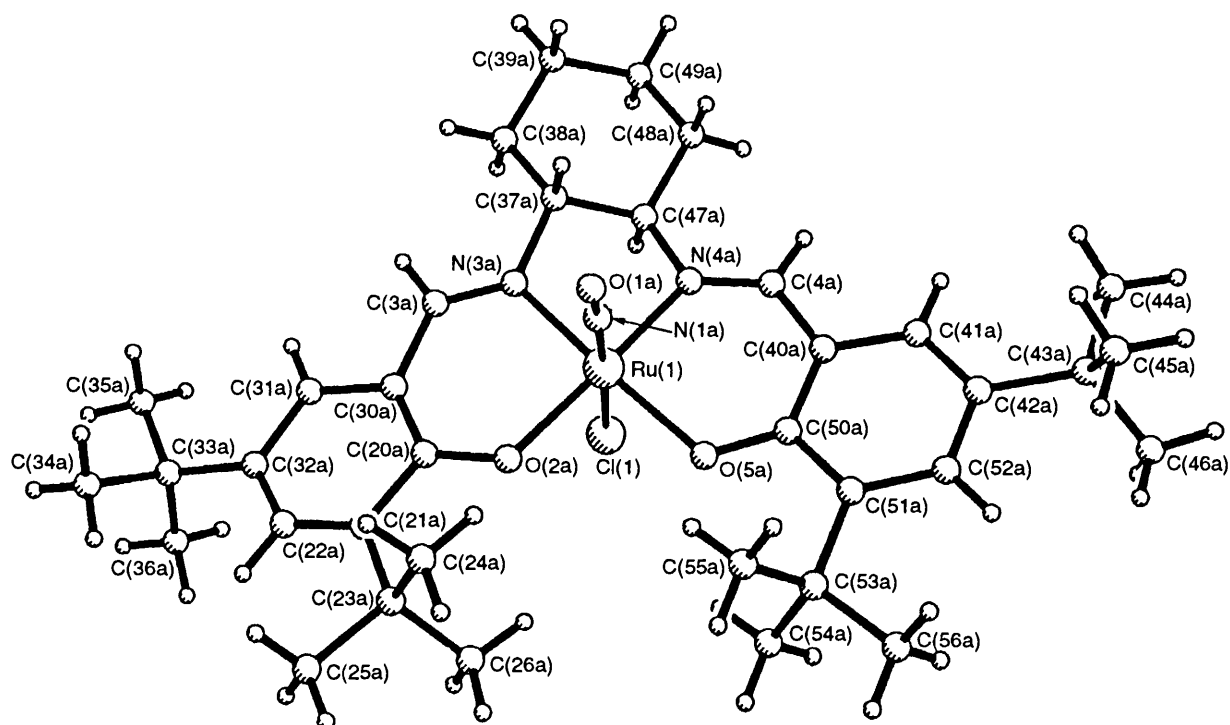


Fig. 3 Perspective view of complex $11 \cdot 0.5C_6H_{14}$

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

	$5 \cdot 0.5CHCl_3$	$11 \cdot 0.5C_6H_{14}$
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	$P2_12_12_1$	$P2_1$
$a/\text{\AA}$	26.463(6)	15.235(3)
$b/\text{\AA}$	26.881(6)	32.212(7)
$c/\text{\AA}$	10.306(8)	16.672(3)
$\beta/^\circ$		115.56(2)
$U/\text{\AA}^3$	7331(2)	8048(3)
Z	8	8
$D_c/\text{g cm}^{-3}$	1.202	1.245
T/K	298	198
μ/cm^{-1}	40.50	4.93
$2\theta/^\circ$	36.48–46.64	3.0–46.0
$F(000)$	2832	3192
Crystal dimensions/mm	$0.25 \times 0.30 \times 0.35$	$0.4 \times 0.3 \times 0.1$
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 $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R^a = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^b $[\sum w(F_o - F_c)^2]^{1/2} / (N_o - N_p)$, 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 [TiLCl₂] 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 trivalent 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 $E^\circ(M^{III} - M^{II})$ 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**-0.5CHCl₃

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(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(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** 0.5C₆H₁₄

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)				

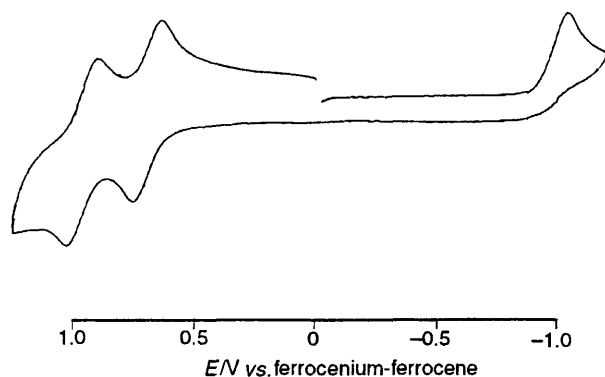


Fig. 4 Cyclic voltammogram of complex **11** in CH_2Cl_2 at a glassy carbon electrode. Scan rate = 100 mV s^{-1}

Table 6 Formal potentials (E°)^a for chiral Schiff-base complexes

Complex	$E^\circ/\text{V vs. ferrocenium-ferrocene}$
[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} $[\text{NBu}_4]\text{PF}_6$ 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 $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ couple. This potential is considerably more cathodic than that for $[\text{Ru}(\text{salen})\text{Cl}(\text{PPh}_3)]$,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 $[\text{ML}]^+$. Treatment of [CoL] and [NiL] with 1 equivalent of AgBF_4 yielded the stable cations $[\text{CoL}]^+$ and $[\text{NiL}]^+$, respectively, isolated as their BF_4 salts. The reaction of [CuL] with AgBF_4 gave only an intractable purple oil. The IR spectrum of $[\text{NiL}]^+$ is very similar to that for [NiL] except for the BF_4 band and a decrease in $\nu(\text{C}=\text{N})$ from 1600 to 1575 cm^{-1} . The EPR spectrum of $[\text{NiL}]^+$ at room temperature shows a broad isotropic signal with $g \text{ ca. } 2.007$, indicative of an organic cation radical. On the basis of EPR spectroscopy, we tentatively formulate $[\text{NiL}]^+$ as a nickel(II) complex of the Schiff-base cation radical. It seems likely that the oxidation of [NiL] initially generated $[\text{Ni}^{\text{III}}\text{L}]^+$ which subsequently underwent internal electron transfer to give the ligand-centred radical complex $[\text{Ni}^{\text{II}}(\text{L}^\bullet)]^+$. The ion $[\text{NiL}]^+$ is indefinitely

stable in the solid state but slowly decomposes to $[\text{NiL}]$ in solution. A study of the reactivity of this stable chiral radical species is underway.

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