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Synthesis and molecular structure of di- and mono-nuclear Schiff-base phenolate complexes: facile formation of cyclometallated ruthenium complexes

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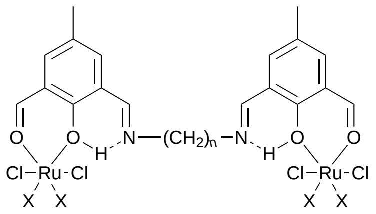
Condensation of 2,6-diformyl-4-methylphenol with aliphatic diamines, $NH_2(CH_2)_nNH_2$ ($n = 2$–4) in the presence of $[Ru(dmso)_4Cl_2]$ (dmso = dimethyl sulfoxide) resulted in acyclic dinuclear six-co-ordinate ruthenium(II) complexes $[Ru_2L(dmso)_4Cl_4]$. The crystal structure of a representative complex was determined. However these reactions in the presence of PPh_3 gave four-membered cyclometallated dinuclear complexes $[Ru_2L'(PPh_3)_4(CO)_2Cl_2]$. Compounds formed by condensation of 2,6-diformyl-4-methylphenol with aromatic monoamines reacted with $[Ru(dmso)_4Cl_2]$–PPh_3 to give cyclometallated mononuclear ruthenium(II) complexes. The structure of a representative complex was determined. The facile formation of cyclometallated ruthenium complexes is rationalised.

Formation of macrocyclic dinuclear complexes by the template condensation of 2,6-diformyl-4-methylphenol with alkyldiamines like 1,3-diaminopropane in 2:2 ratio in the presence of 3d ions is well documented.[1] However such condensation reactions with monoamines in 1:2 ratio provide acyclic ligands.[2] The dinucleating ability of these compounds originates from the readiness of the phenolic group to deprotonate and bridge two metal ions in close proximity. The homo- and hetero-dinuclear complexes of 3d metal ions have been investigated in detail.[3,4]

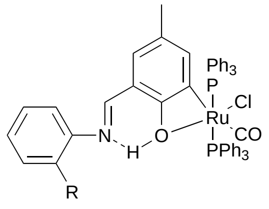
However, the role of ruthenium as a template ion in such condensation reactions is not well understood. One example of cyclometallation in the presence of ruthenium ions involving acyclic dinucleating ligands has been reported.[5] Hence we have now studied the condensation reactions of 2,6-diformyl-4-methylphenol with different diamines and monoamines in the presence of ruthenium salts in order to determine the pattern of product formation. Under appropriate conditions acyclic dinuclear ruthenium complexes **1**–**3** are obtained. They have been structurally characterised. These complexes were then converted into the analogous cyclometallated complexes **9**–**11** by varying the reaction conditions. Under different conditions, mononuclear cyclometallated ruthenium complexes **4**–**8** are obtained which have also been structurally characterised. The facile formation of cyclometallated ruthenium complexes is rationalised from the experimental data.

Experimental

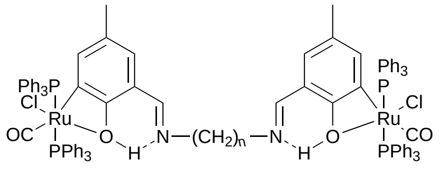
Ruthenium trichloride was obtained from Sisco chemicals and activated by treatment with concentrated hydrochloric acid and evaporating to dryness two or three times. The adduct $[Ru(dmso)_4Cl_2]$[6] (dmso = dimethyl sulfoxide) and 2,6-diformyl-4-methylphenol[4] were prepared according to the literature. The compounds L^1–L^8 were synthesized by known procedures.[2,7] All the solvents were dried prior to use by standard procedures. Dichloromethane was purified by treatment with $NaHCO_3$ and anhydrous calcium chloride. Triphenylphosphine was recrystallised from hexane. The amines were purified by distillations. All other solvents and chemicals were of reagent grade and used without further purification.



1 $n = 2$, L^1 X = dmso
2 $n = 3$, L^2
3 $n = 4$, L^3



4 R = H, L^4
5 R = Me, L^5
6 R = OMe, L^6
7 R = F, L^7
8 R = Cl, L^8



9 $n = 2$, L^9
10 $n = 3$, L^{10}
11 $n = 4$, L^{11}

Syntheses

Complexes 1–3. These complexes were synthesized by following a general method. Details are given for a representative complex (**2**).

To a solution of 2,6-diformyl-4-methylphenol (0.082 g, 0.5 mmol) in dry methanol (20 cm^3) was added $[Ru(dmso)_4Cl_2]$ (0.242 g, 0.5 mmol) under dry nitrogen and the reaction mixture was stirred for 10 min. 1,3-Diaminopropane (0.037 g, 0.5 mmol) in dry methanol (10 cm^3) was added and the reaction mixture was refluxed for 4 h. Cooling to room temperature resulted in deposition of a red microcrystalline solid (**2**). This was washed with small quantities of cold methanol and dried in vacuum. Yields 50–60%.

Complexes **1**–**3** were also obtained by reaction of the pre-formed pro-ligands (L^1–L^3, prepared by condensation of 2,6-diformyl-4-methylphenol with various diamines in 2 : 1 ratio in dry ethanol) with [Ru(dmso)$_4$Cl$_2$]. To a solution of L (0.5 mmol) in dry methanol (25 cm^3) was added [Ru(dmso)$_4$Cl$_2$] (1 mmol) and the mixture was refluxed for 4 h under dry nitrogen. It was then cooled to room temperature and the red microcrystalline solid was filtered off, washed with small quantities of cold methanol and dried in vacuum for 4 h.

Complexes 4–8. These complexes were synthesized as follows. To a solution of L^4 (0.215 g) in dry methanol (30 cm^3) was added [Ru(dmso)$_4$Cl$_2$] (0.242 g, 0.5 mmol) and PPh$_3$ (1 mmol) and the mixture was refluxed for 1 h by which time a red microcrystalline solid had separated in quantitative yield.

Complexes 9–11. The general procedure for the synthesis of these complexes was as follows. To a solution of L^2 (0.183 g, 0.5 mmol) in dry methanol (30 cm^3) were added [Ru(dmso)$_4$Cl$_2$] (0.484 g, 1 mmol) and PPh$_3$ (0.524 g, 2 mmol) under nitrogen and the mixture was refluxed for 2 h by which time an orange microcrystalline solid had separated. It was filtered off, washed repeatedly with warm hexane to remove any excess of triphenylphosphine and dried in vacuum for 3 h. Yields 55–65%.

Physical measurements

The carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrophotometer as KBr pellets, electronic absorption spectra on a JASCO model 7800 UV/VIS spectrophotometer. Magnetic susceptibility measurements were carried out on a CAHN magnetic balance set-up. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol as matrix. Cyclic voltammograms were recorded on a Cypress systems model CS-1090/CS-1087 computer-controlled electroanalytical system. All the experiments were performed under dry nitrogen in dichloromethane as solvent; 1 × 10^{-3} mol dm^{-3} solutions were used with 0.1 mol dm^{-3} NBu$_4$ClO$_4$ as supporting electrolyte, a platinum working electrode, Ag–AgCl electrode as reference and platinum wire as auxiliary electrode. The ferrocene–ferrocenium couple was used as the redox standard.

Crystallography

[Ru$_2$L^2(dmso)$_4$Cl$_4$]·CH$_2$Cl$_2$. A red plate of dimensions 0.04 × 0.20 × 0.20 mm obtained by diffusion of diethyl ether into a dichloromethane solution was mounted on a fibre. 8850 Reflections were measured with a Rigaku RAXIS IIc diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å, $2\theta_{max} = 55°$). An empirical absorption correction was applied[8] (transmission factors 0.747, 1.040). The structure was solved using Siemens SHELXTL PLUS (PC version)[9,10] by direct methods in orthorhombic space group *Pbca* (no. 61) with eight molecules in the unit cell and refinement was based on *F*. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The carbon atoms of two dmso ligands were disordered and were refined with site occupation factor 0.5. 5233 Reflections with $F > 6\sigma(F)$ were used for structure solution. Refinement converged at $R = 0.040$, $R' = 0.047$ (509 variable parameters). The crystallographic parameters are summarised in Table 3.

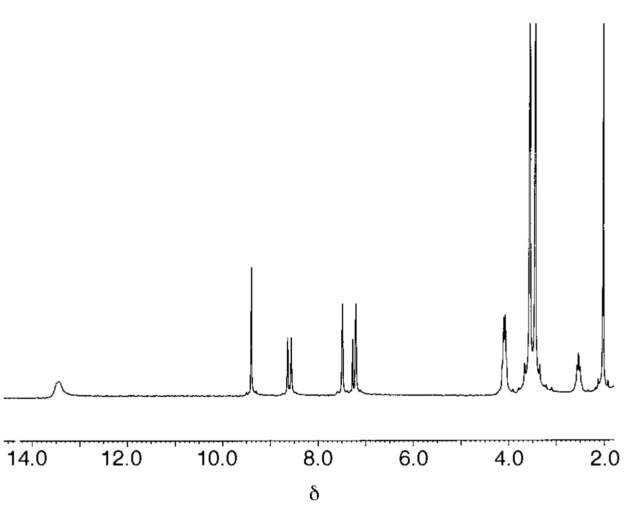


Fig. 1 Proton NMR spectrum of a representative ruthenium(II) complex **2**

[RuL^5(PPh$_3$)$_2$(CO)Cl]. A red prism of dimensions 0.25 × 0.33 × 0.33 mm obtained by diffusion of hexane into a dichloromethane solution was mounted on a fibre. 7073 Reflections were measured with a Rigaku AFC7S diffractometer using graphite-monochromated Mo-Kα radiation ($2\theta_{max} = 47°$). An empirical absorption correction was applied (transmission factors 0.9044, 1.00). Cell constants and the orientation matrix for data collection, obtained from a least-squares refinement (based on *F*) using the setting angles of 25 carefully centred reflections in the range $15.18 < 2\theta < 26.96°$ corresponded to a C-centred monoclinic cell. All calculations were performed using TEXSAN[11] and solved by direct methods[12,13] in space group *C*2/*c* (no. 15) with eight molecules in the unit cell. The phenyl ring on one of the PPh$_3$ is disordered and was refined as such. In the final cycles all non-hydrogen atoms were refined anisotropically except those in the disordered phenyl ring and all hydrogen atoms were fixed at idealised positions. The anisotropic displacement parameters for carbons C(47)–C(56) were not calculated due to disorder. There were 6935 unique reflections of which 4644 with $F > 6\sigma(F)$ were used for structure solution. Refinement converged at $R = 0.045$ and $R' = 0.052$ (518 variable parameters).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/450.

Results and Discussion

Acyclic dinuclear ruthenium(II) complexes

To examine the role of ruthenium in template condensations, reactions of 2,6-diformyl-4-methylphenol with aliphatic diamines such as 1,2-diaminoethane (L^1), 1,3-diaminopropane (L^2) and 1,4-diaminobutane (L^3) in 2 : 2 ratio in the presence of [Ru(dmso)$_4$Cl$_2$] were investigated. These reactions yielded red microcrystalline products.

The IR spectra of the complexes exhibit a C=N stretching band at 1616 cm^{-1}. The C=O stretching frequency of 2,6-diformyl-4-methylphenol at 1680 cm^{-1} is shifted to 1655 cm^{-1} for the complexes indicating the presence of a co-ordinated C=O group. The relevant bands are presented in Table 1. The ^{1}H NMR spectrum of a representative complex **2** is shown in Fig. 1. The aldehydic proton signal at δ 10.4 of 2,6-diformyl-4-methylphenol is shifted upfield to δ 9.4 and appears as a singlet (2 H). The azomethine protons give two signals each corresponding to one proton. The broad signal in the range δ 13.3–13.7 is due to phenolic hydrogen bonded to

Table 1 Analytical and selected IR data for ruthenium(II) complexes **1–11**

	Analysis* (%)			IR (cm^{-1})		
Complex	C	H	N	C=O	C=N	C≡O
1 $[Ru_2L^1(dmso)_4Cl_4]$	33.0 (33.3)	4.2 (4.4)	2.6 (2.8)	1655	1616	
2 $[Ru_2L^2(dmso)_4Cl_4]$	33.9 (34.1)	4.4 (4.3)	2.5 (2.7)	1655	1616	
3 $[Ru_2L^3(dmso)_4Cl_4]$	34.6 (34.7)	4.3 (4.6)	2.5 (2.7)	1649	1618	
4 $[RuL^4(PPh_3)_2(CO)Cl]$	67.6 (68.1)	4.7 (4.7)	1.4 (1.6)		1630	1905
5 $[RuL^5(PPh_3)_2(CO)Cl]$	68.5 (68.4)	4.9 (4.8)	1.4 (1.5)		1628	1907
6 $[RuL^6(PPh_3)_2(CO)Cl]$	66.5 (67.2)	4.6 (4.7)	1.6 (1.5)		1628	1907
7 $[RuL^7(PPh_3)_2(CO)Cl]$	65.8 (66.8)	4.2 (4.5)	1.7 (1.5)		1618	1910
8 $[RuL^8(PPh_3)_2(CO)Cl]$	66.8 (65.6)	4.9 (4.4)	1.3 (1.5)		1618	1908
9 $[Ru_2L^9(PPh_3)_4(CO)_2Cl_2]$	65.9 (66.1)	4.6 (4.7)	1.7 (1.7)		1630	1907
10 $[Ru_2L^{10}(PPh_3)_4(CO)_2Cl_2]$	66.0 (66.2)	4.8 (4.8)	1.6 (1.7)		1630	1911
11 $[Ru_2L^{11}(PPh_3)_4(CO)_2Cl_2]$	65.8 (66.4)	4.8 (4.8)	1.7 (1.7)		1633	1898

* Calculated values in parentheses.

Table 2 The NMR, electronic spectral and cyclic voltammetric data for the ruthenium(II) complexes

	NMR[a] (δ)		UV/VIS[b]	$E_{\frac{1}{2}}$/V (ΔE/mV)
Complex	^1H	^{31}P	λ_{max} (ε/dm^3 mol^{-1} cm^{-1})	Ru^{II}–Ru^{III}[c]
1	13.7 (br, 2 H), 9.4 (s, 2 H), 8.3 (d, 2 H), 7.6 (d, 2 H), 7.5 (d, 2 H), 4.1 (s, 4 H), 3.6 (s, 12 H), 3.4 (s, 12 H), 2.1 (s, 6 H)	—	470 (6890), 407 (11 070), 310 (2850)	0.900 (66)
2	13.4 (br, 2 H), 9.4 (s, 2 H), 8.6 (d, 2 H), 7.5 (d, 2 H), 7.2 (d, 2 H), 4.1 (t, 4 H), 3.6 (s, 12 H), 3.4 (s, 12 H), 2.6 (q, 2 H), 2.0 (s, 6 H)	—	480 (6775), 407 (10 815), 314 (3690)	0.876 (100)
3	13.4 (br, 2 H), 9.4 (s, 2 H), 8.6 (d, 2 H), 7.4 (d, 2 H), 7.3 (d, 2 H), 3.9 (m, 4 H), 3.5 (s, 12 H), 3.4 (s, 12 H), 2.2 (m, 4 H), 2.0 (s, 6 H)	—	476 (7175), 406 (12 090), 313 (3970)	0.845 (75)
4	12.6 (br, 1 H), 7.7 (m, 12 H), 7.6 (s, 1 H), 7.2 (m, 18 H), 7.2 (d, 2 H), 7.0 (d, 2 H), 6.9 (s, 1 H), 6.0 (2 s, 2 H), 1.7 (s, 3 H)	37.70	538 (4580), 411 (11 330)	0.648 (77)
5	12.6 (br, 1 H), 7.8 (m, 12 H), 7.6 (s, 1 H), 7.2 (m, 18 H), 7.2 (m, 2 H), 7.0 (m, 2 H), 6.0 (2 s, 2 H), 2.4 (s, 3 H), 1.7 (s, 3 H)	36.9	539 (4360), 412 (11 080)	0.639 (93)
6	12.5 (br, 1 H), 7.7 (m, 12 H), 7.5 (s, 1 H), 7.2 (m, 18 H), 7.1 (s, 2 H), 7.0 (s, 2 H), 5.8 (2 s, 2 H), 4.1 (s, 3 H), 1.7 (s, 3 H)	36.70	531 (5475), 419 (12 050)	0.591 (84)
7	12.7 (br, 1 H), 7.7 (m, 12 H), 7.5 (s, 1 H), 7.2 (m, 18 H), 7.0 (m, 4 H), 6.0 (2 s, 2 H), 1.7 (s, 3 H)	37.20	548 (3480), 414 (9535)	—
8	11.5 (br, 1 H), 7.7 (m, 12 H), 7.5 (m, 18 H), 7.4 (s, 1 H), 7.2 (m, 4 H), 6.0 (s, 1 H), 5.9 (s, 1 H), 1.7 (s, 1 H)	36.40	555 (4290), 419 (12 525)	0.649 (93)
9	*d*	*d*	504 (6810), 374 (9890)	0.688 (62)
10	11.4 (br, 2 H), 7.7 (m, 12 H), 7.5 (s, 2 H), 7.2 (m, 18 H), 6.0 (s, 2 H), 5.9 (s, 2 H), 2.8 (t, 4 H), 1.8 (m, 2 H), 1.7 (s, 6 H)	37.21	495 (6485), 370 (10 145)	0.663 (71)
11	*d*	*d*	490 (4950), 370 (6025)	0.651 (78)

[a] In $CDCl_3$. [b] In CH_2Cl_2. [c] Cyclic voltammetry was carried out in CH_2Cl_2 at 298 K using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte at a platinum electrode with Ag–AgCl as reference electrode. [d] Not recorded (partially soluble).

nitrogen (N···O···H). The two aromatic protons of 2,6-diformyl-4-methylphenol appear as two separate signals for the complex. In addition to these, resonances due to co-ordinated dmso molecules are seen as two sharp singlets at δ 3.6 and 3.4 corresponding to twelve protons each indicating the presence of four dmso molecules in two different environments. The relevant data are presented in Table 2. The IR and the ^1H NMR data suggest the presence of both C=N and C=O groups in the ruthenium complexes. This implies that the condensation has proceeded in a 2 : 1 fashion with two molecules of 2,6-diformyl-4-methylphenol and one of diamine resulting in an acyclic system.

The analytical data (C, H, N) (Table 1) show the composition of the complexes to be $[Ru_2L(dmso)_4Cl_4]$. The presence of dmso molecules was inferred from the ^1H NMR signals. The FAB mass spectrum of complex **2** ($C_{29}H_{46}Cl_4N_2O_8Ru_2S_4$: *M* 1022) shows a molecular-ion peak at *m*/*z* 1022. In addition to this several prominent fragments are seen at *m*/*z* 987, 944, 909, 860, 830, 790, 753 and 640. The species with *m*/*z* 987 is assigned to the loss of one chloride ion and that with *m*/*z* 944 to loss of one dmso molecule. The other fragments correspond to progressive loss of dmso or chloride units. Room-temperature magnetic susceptibility measurements show that the complexes are diamagnetic with a t_{2g}^6 ground state. The electronic spectra of the complexes in CH_2Cl_2 exhibit high-intensity charge-transfer transitions[14] at *ca.* 480 and at 400 nm besides a band at ≈315 nm of the ligand. Data are collected in Table 2.

Based on these data, the complexes are assigned a dimeric structure as shown. Each ruthenium(II) ion is co-ordinated by aldehydic and phenolic oxygens, two chloride ions and two molecules of dmso in an octahedral fashion. Owing to the bulky groups around the ruthenium centres, the metal ions will move away facilitating the arrangements shown. Flexibility of the bridging diamine helps this. The complexes do not co-ordinate further $Ru(dmso)_4Cl_2$ *via* phenolate and azomethine nitrogen. Also further condensation of co-ordinated aldehyde groups in these complexes with aromatic monoamines was unsuccessful.

Cyclic voltammetric profiles of complexes **1**–**3** in CH_2Cl_2 show an oxidation peak at ≈0.92 V and a corresponding reduction peak at ≈0.82 V at a scan rate of 100 mV s^{-1} [Fig. 2(*a*)]. The anodic and cathodic peak heights are equal and the peak-to-

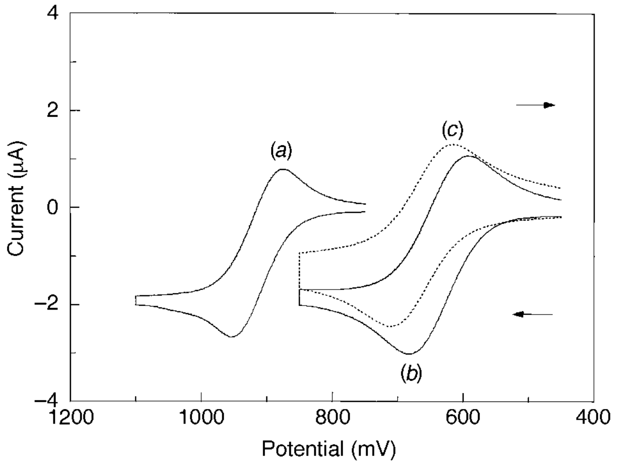


Fig. 2 Cyclic voltammograms at 298 K in CH_2Cl_2 (0.1 mol dm^{-3} NBu_4ClO_4) at a platinum electrode of complexes **2** (*a*), **5** (*b*) and **10** (*c*) at a scan rate of 100 mV s^{-1}

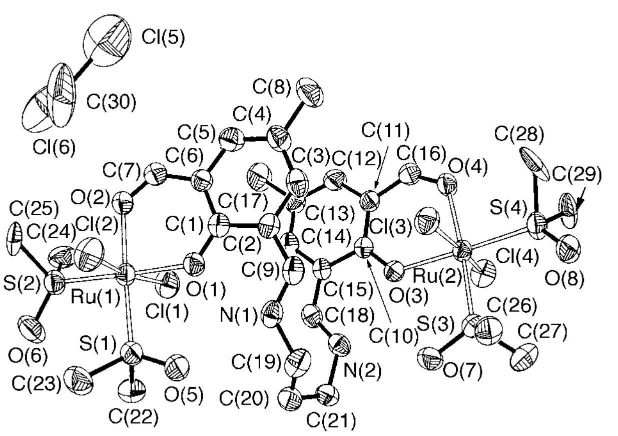


Fig. 3 An ORTEP drawing of the molecular structure of $[Ru_2L^2(dmso)_4Cl_4]\cdot CH_2Cl_2$ showing thermal ellipsoids at the 35% probability level and the atom numbering scheme. Atoms C(24), C(25), C(28) and C(29) are disordered, site occupation factor 0.5

Table 3 Crystallographic data for $[Ru_2L^2(dmso)_4Cl_4]\cdot CH_2Cl_2$ and $[RuL^5(PPh_3)_2(CO)Cl]$

Formula	$C_{30}H_{48}Cl_6N_2O_8Ru_2S_4$	$C_{52}H_{43}ClNO_2P_2Ru$
M	1107.816	912.39
Space group	*Pbca* (no. 61)	*C*2/*c* (no. 15)
a/Å	15.070(1)	34.263(10)
b/Å	23.112(1)	9.855(7)
c/Å	25.240(1)	26.710(7)
β/°	—	102.67(2)
U/Å^3	8791(4)	8799(6)
Z	8	8
D_c/g cm^{-3}	1.692	1.377
T/°C	21	24.0
μ(Mo-Kα)/cm^{-1}	12.88	5.32
F(000)	4576	3752
Transmission coefficients	0.747–1.04	0.90–1.00
R^a	0.040	0.045
R'^b	0.047	0.052

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + 0.0000F^2$.

Table 4 Selected bond distances (Å) and bond angles (°) in $[Ru_2L^2(dmso)_4Cl_4]\cdot CH_2Cl_2$

Ru(1)–Cl(1)	2.386(2)	Ru(1)–Cl(2)	2.418(2)
Ru(1)–S(1)	2.211(2)	Ru(1)–S(2)	2.228(2)
Ru(1)–O(1)	2.076(4)	Ru(1)–O(2)	2.081(4)
Ru(2)–Cl(3)	2.389(2)	Ru(2)–Cl(4)	2.389(2)
Ru(2)–S(3)	2.225(2)	Ru(2)–S(4)	2.221(2)
Ru(2)–O(3)	2.066(4)	Ru(2)–O(4)	2.095(4)
O(1)–C(1)	1.274(7)	O(2)–C(7)	1.232(8)
O(3)–C(10)	1.280(7)	O(4)–C(16)	1.245(7)
N(1)–C(9)	1.290(8)	N(1)–C(19)	1.468(8)
N(2)–C(18)	1.294(8)	N(2)–C(21)	1.474(7)
Cl(1)–Ru(1)–Cl(2)	170.6(1)	Cl(1)–Ru(1)–S(1)	93.0(1)
Cl(2)–Ru(1)–S(1)	91.3(1)	Cl(1)–Ru(1)–S(2)	92.7(1)
Cl(2)–Ru(1)–S(2)	95.3(1)	S(1)–Ru(1)–S(2)	95.0(1)
Cl(1)–Ru(1)–O(1)	85.4(1)	Cl(2)–Ru(1)–O(1)	86.4(1)
S(1)–Ru(1)–O(1)	87.9(1)	S(2)–Ru(1)–O(1)	176.7(1)
Cl(1)–Ru(1)–O(2)	87.1(1)	Cl(2)–Ru(1)–O(2)	88.2(1)
S(1)–Ru(1)–O(2)	177.2(1)	S(2)–Ru(1)–O(2)	87.8(1)
O(1)–Ru(1)–O(2)	89.4(2)	Cl(3)–Ru(2)–Cl(4)	171.0(1)
Cl(3)–Ru(2)–S(3)	92.0(1)	Cl(4)–Ru(2)–S(3)	93.1(1)
Cl(3)–Ru(2)–S(4)	92.2(1)	Cl(4)–Ru(2)–S(4)	94.8(1)
S(3)–Ru(2)–S(4)	94.3(1)	Cl(3)–Ru(2)–O(3)	87.2(1)
Cl(4)–Ru(2)–O(3)	85.6(1)	S(3)–Ru(2)–O(3)	87.6(1)
S(4)–Ru(2)–O(3)	178.1(1)	Cl(3)–Ru(2)–O(4)	87.3(1)
Cl(4)–Ru(2)–O(4)	87.1(1)	S(3)–Ru(2)–O(4)	175.9(1)
S(4)–Ru(2)–O(4)	89.8(1)	O(3)–Ru(2)–O(4)	88.3(2)

peak separation (ΔE_p) lies in the range of 70–100 mV suggesting a nearly reversible redox process which corresponds to metal oxidation $Ru^{II} \longrightarrow Ru^{III} + e^-$. The $E_{\frac{1}{2}}$ values for the complexes are given in Table 2.

Crystal structure of $[Ru_2L^2(dmso)_4Cl_4]\cdot CH_2Cl_2$

To confirm the proposed dinuclear structure the crystal structure of a representative complex **2** was solved.

An ORTEP[15] drawing of the molecule **2** and the atom numbering scheme is displayed in Fig. 3. Selected bond parameters are listed in Table 4. The asymmetric unit consists of two ruthenium ions bridged by the Schiff-base ligand. The metal ions are in identical environments. The Schiff-base ligand acts as a tetradentate O_4 donor, each ruthenium being co-ordinated by a phenolate and carbonyl oxygen, two sulfur atoms from dimethyl sulfoxide and two chloride ions in *trans* fashion. The metal co-ordination sphere is almost octahedral. Slight deviation in the bond angles results because of the bulky dmso molecules. Atoms Ru(1), O(1), O(2), S(1), S(2); Ru(1), S(2), O(1), Cl(1), Cl(2) and Ru(1), O(2), S(1), Cl(1), Cl(2), separately define three least-squares planes with no atom deviating by >0.09 Å and the maximum deviation between the planes is 1.39°. Similar deviations from least-squares planes were observed for the three orthogonal planes around the other ruthenium centre.

The average Ru–O (phenolate) distance is 2.071(4) Å and the average Ru–O (carbonyl) length 2.088(4) Å. Ruthenium(II)–oxygen (carbonyl) distances are close to 2.12 Å.[16] In $Ru^{III}(sal)_3$ (sal = salicylaldehyde)[14] complexes the average Ru–O (phenolate) distance is 1.981(2) Å and the average Ru–O (carbonyl) length 2.031(2) Å. The near equivalence in the Ru–O (carbonyl) and Ru–O (phenolate) bond lengths in the present complexes suggests electron delocalisation involving these centres. In *cis*-$[Ru(dmso)_4Cl_2]$ the mean Ru–S distance is 2.268(1) Å[17,18] and is the result of d_π–d_π back donation from the central metal to the sulfur atom. In *trans*-$[Ru(dmso)_4Cl_2]$ the average Ru–S (dmso) distance is close to 2.35 Å[18,19] and the increase in the bond length is explained by the greater *trans* influence of S compared to Cl and the greater π-bonding competition among the dmso ligands. The shorter Ru–S (dmso) bond lengths (2.221 Å) in the present complex indicate greater d_π–d_π back bonding. The average Ru–Cl bond length of 2.395(2) Å is comparable to the Ru–Cl bond lengths in octahedral complexes with *trans* chlorides.[18] The distance between O(1)–N(1) and O(3)–N(2) is 2.62 and 2.61 Å respectively indicating N···H···O interaction involving hydrogen atoms on O(1) and O(3). The hydrogens, though not located on the difference map, are calculated to be 0.85 Å from the O atoms. An analogous hydrogen-bonding interaction of phenolic hydrogen with adjacent nitrogen in a ruthenium complex has been crystallographically established.[5]

The molecular geometry of the non-disordered dmso ligands is identical to that in $[\mathrm{Ru(dmso)_4Cl_2}]$[17] and free dmso.[20] The average C–S–O (106.3°), C–S–C angles (99.3°) in the present complex are comparable to the average C–S–O and C–S–C angles in $[\mathrm{Ru(dmso)_4Cl_2}]$ (106.6, 99°) and free dmso molecule (107, 98°). The mean C–S bond lengths are also comparable. In the disordered dmso molecules a 2–3° deviation is observed for the average C–S–C angles. Deviations in the bond lengths are within the standard deviations.

The crystal structure of complex **2** supports the proposed generalised structure shown. It is clear that condensation has proceeded in a 2 : 1 fashion (aldehyde : amine) to provide an acyclic dinuclear complex. This is in contrast to 2 : 2 condensation in the presence of 3d metal ions which results in dinuclear macrocyclic complexes. The preference of ruthenium for oxygen co-ordination might have directed the condensation reaction in this fashion.

Cyclometallated mononuclear ruthenium(II) complexes

2,6-Diformyl-4-methylphenol is known to condense with substituted anilines in 1 : 2 ratio to give corresponding Schiff bases (HL) which form dinuclear complexes of composition $[\mathrm{M_2L_2}]^{2+}$ with 3d metal ions.[2,21] Structural deviations of ruthenium complexes compared to the 3d metal complexes as discussed in the previous section prompted us to explore the structural features of the ruthenium complexes of $\mathrm{L^4}$–$\mathrm{L^8}$. These compounds were obtained as mixtures of mono- and di-condensed Schiff bases. Efforts to complete the condensation of both carbonyl groups or separate the two products were unsuccessful. Hence the mixtures were used as such for further complexation.

Reaction of $[\mathrm{Ru(dmso)_4Cl_2}]$ with a slight excess of these mixtures in dry methanol gave dark red microcrystalline products. However it was not possible to assign structures to these complexes based on analytical and spectral data. Attempts to grow single crystals of these complexes were also unsuccessful. However, reactions of these mixtures with $[\mathrm{Ru(dmso)_4Cl_2}]$ in the presence of triphenylphosphine yielded complexes **4**–**8**. Their analytical data do not correspond to dinuclear structures. The IR spectra show an intense band at ≈1900 $\mathrm{cm^{-1}}$ indicating the presence of a carbonyl group, besides the characteristic bands due to C=N stretching. Absorptions due to co-ordinated triphenylphosphine molecules at ≈1500, 1480, 740 and 690 $\mathrm{cm^{-1}}$ are present. All the complexes are diamagnetic which indicates t_{2g}^{6} ground-state configurations. The ^{1}H NMR spectra show the phenolic ring protons shifted to δ 6.0–5.8. The azomethine proton is also shifted upfield from the usual δ 8.5–7.5. Two complex sets of signals at δ 7.2 and 7.7 are observed due to co-ordinated triphenylphosphine units. The ^{31}P NMR spectra of the complexes show a sharp singlet at δ 37 indicating the phosphines to be in *trans* position. The electronic spectra recorded in dichloromethane show high-intensity charge-transfer bands at 530 and 410 nm.

The cyclic voltammograms of the complexes in dichloromethane solvent at a platinum electrode show one-electron nearly reversible couples in the range 0.6–0.65 V at a scan rate of 100 mV $\mathrm{s^{-1}}$ [Fig. 2(*b*)] corresponding to the metal oxidation $\mathrm{Ru^{II}} \longrightarrow \mathrm{Ru^{III}} + e^-$. At this scan rate the anodic and cathodic peak heights are equal. On increasing the scan rate the anodic response becomes progressively prominent and the cathodic response appears with a diminished height. The spectral and electrochemical data are presented in Table 2.

The analytical and spectral data indicate the formation of cyclometallated ruthenium complexes.

Crystal and molecular structure of $[\mathrm{RuL^5(PPh_3)_2(CO)Cl}]$

The crystal structure of a representative complex **5** was solved to establish the structures of complexes **4**–**8**.

An ORTEP drawing of the molecule **5** and the atom numbering scheme is displayed in Fig. 4. Selected bond lengths and bond angles are given in Table 5. The geometry around $\mathrm{Ru^{II}}$ is distorted octahedral. The ruthenium ion is co-ordinated by phenolate oxygen O(1) and carbon C(2) to form a planar four-membered metallacycle. In addition to this it is bonded to carbonyl carbon [C(16)], which is *cis* to C(2), and a chloride ion. The two phosphines are co-ordinated *trans* to each other. The $\mathrm{Ru^{II}}$–O (phenolate) distance in the four-membered chelate ring is longer than that in five-membered rings[22] and ruthenium(II) semiquinonates.[23] The O(1)–Ru–C(2) and Cl–Ru–C(2) angles deviate from optimum values.

Table 5 Selected bond distances (Å) and bond angles (°) in $[\mathrm{RuL^5(PPh_3)_2(CO)Cl}]$

Ru–Cl	2.484(2)	Ru–P(1)	2.377(2)
Ru–P(2)	2.381(2)	Ru–O(1)	2.246(4)
Ru–C(2)	2.040(5)	Ru–C(16)	1.805(6)
C(1)–O(1)	1.316(6)	C(16)–O(2)	1.158(6)
N–C(7)	1.317(7)	N–C(8)	1.427(7)
Cl–Ru–P(1)	88.54(5)	Cl–Ru–P(2)	94.71(6)
Cl–Ru–O(1)	91.22(10)	Cl–Ru–C(2)	155.3(1)
Cl–Ru–C(16)	103.6(2)	P(1)–Ru–P(2)	176.75(6)
P(1)–Ru–O(1)	88.2(1)	P(1)–Ru–C(2)	87.8(2)
P(1)–Ru–C(16)	91.8(2)	P(2)–Ru–O(1)	91.79(10)
P(2)–Ru–C(2)	89.2(2)	P(2)–Ru–C(16)	87.4(2)
O(1)–Ru–C(2)	64.2(2)	O(1)–Ru–C(16)	165.2(2)
C(2)–Ru–C(16)	100.9(2)	C(7)–N–C(8)	125.2(5)

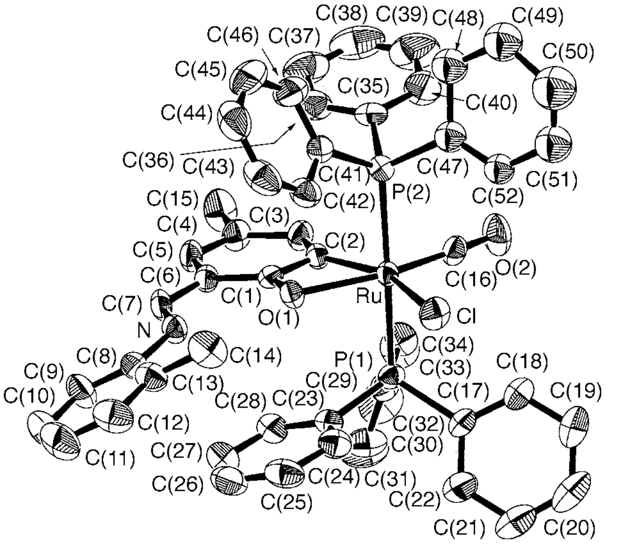
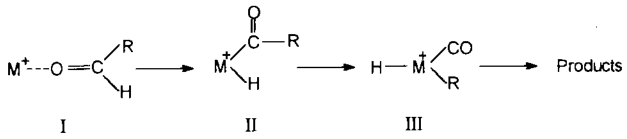


Fig. 4 An ORTEP drawing of the molecular structure of $[\mathrm{RuL^5(PPh_3)_2(CO)Cl}]$ **5** showing thermal ellipsoids at the 50% probability level and the atom numbering scheme



Scheme 1

From the structure of the complex it appears that the reaction proceeds *via* decarbonylation of the aldehyde group resulting in cyclometallation of the phenyl ring and formation of a four-membered metallacycle. The proposed mechanism[24] of cyclometallation proceeds through the intermediates shown in Scheme 1. These reaction steps involve oxidative addition followed by reductive elimination. In the present reaction the product formed after the oxidative addition step is a stable orthometallated phenolate chelate ring and hence reductive elimination proceeds by $\mathrm{H^+}$ elimination assisted by the azomethine nitrogen.[25]

The preference of ruthenium for oxygen co-ordination is the key factor in the formation of intermediate **I** with ligands L^4–L^8 which in turn provide the cyclometallated ruthenium complexes as the final product.

Cyclometallated dinuclear ruthenium(II) complexes

The results of the previous section clearly indicate the facile formation of cyclometallated ruthenium complexes *via* $M^+\cdots O{=}CR$ intermediates. The dinuclear ruthenium complexes **1**–**3** have been shown to contain two ruthenium centres of the type $Ru\cdots O{=}CR$ which is recognised as the prerequisite for cyclometallation reaction. Therefore *in situ* cyclometallation reactions of L^1–L^3 were attempted to test the product formation.

Reaction of $[Ru(dmso)_4Cl_2]$ with L^1–L^3 in the presence of triphenylphosphine yielded orange microcrystalline complexes **9**–**11**. The IR spectra show characteristic absorptions at 1630 cm^{-1} corresponding to C=N stretching and a sharp absorption at ≈1910 cm^{-1} corresponding to C≡O. In addition, absorptions due to co-ordinated triphenylphosphine are seen at 1500, 1480, 740 and at 690 cm^{-1}.

The ^1H NMR spectra of the complexes show sharp singlets at δ 6.0 and 5.8 in addition to a singlet due to the azomethine protons at δ 7.5, all of them corresponding to two protons each. Two complex sets of signals at δ 7.2 and 7.7 corresponding to the protons of the triphenylphosphine are observed. No signals due to co-ordinated dmso molecules are present. The upfield shift of the ring protons is similar to that observed in the case of complexes **4**–**8**. A sharp signal at δ ≈37 is observed in the ^{31}P NMR spectra indicating PPh_3 to be in the *trans* position. The ^1H and ^{31}P NMR data are presented in Table 2. The absence of dmso signals and emergence of PPh_3 NMR signals indicate that dmso has been replaced by PPh_3 groups.

The analytical data (C, H, N) show the composition of the complexes to be $[Ru_2L'(PPh_3)_4(CO)_2Cl_2]$. The FAB mass spectrum of complex **10** ($C_{93}H_{80}Cl_2N_2O_4P_4Ru_2$; *M* 1685) exhibits the molecular-ion peak at *m*/*z* 1685. Intense fragments at *m*/*z* 1650, 1614, 1388, 1126 and 1090 are due to progressive loss of chloride or triphenylphosphine units. The spectral and analytical data for complexes **9**–**11** are quite different from those of **1**–**3** and in many respects comparable to those of cyclometallated complexes **4**–**8**. The structure shown was deduced by comparison with that of cyclometallated $[RuL^5(PPh_3)_2(CO)Cl]$ (see above). Each Ru^{II} is six-co-ordinated and the two phosphines are *trans* to each other; the other positions are occupied by the phenyl ring carbon, phenolic oxygen, CO and Cl^-.

Complexes **9**–**11** are obtained only when the Schiff bases are treated with $[Ru(dmso)_4Cl_2]$ and PPh_3 in stoichiometric ratio. The active reagent in the reaction mixture can be presumed to be $[Ru(PPh_3)_2Cl_2]$ which is known to initiate cyclometallation. Addition of PPh_3 in the later stages of the reaction leads to the formation of a mixture of complexes **1**–**3** and **9**–**11**. Once formed, **1**–**3** do not react further with PPh_3 implying that the latter does not replace the co-ordinated dmso molecules.

The electronic spectra of the complexes show bands at ≈495 and at ≈370 nm. These low-energy transitions with high intensities are due to metal-to-ligand charge-transfer transitions. Magnetic susceptibility measurements indicate the complexes to be diamagnetic and thus confirm the +2 oxidation state for ruthenium. The complexes undergo one-electron reversible redox processes in the range 0.66–0.69 V in dichloromethane at a platinum electode. The ΔE_p values lie in the range 60–80 mV. The redox potentials are comparable with those of complexes **4**–**8** but quite separated from those of $[Ru_2L(dmso)_4Cl_4]$ **1**–**3**. This further supports the structural similarity of complexes **9**–**11** and **4**–**8**. The electrode process corresponds to metal oxidation to Ru^{3+}. The cyclic voltammetry profile of a representative complex **10** is shown in Fig. 3(*c*) and the data are presented in Table 2.

Conclusion

Template Schiff-base condensations of dicarbonyl systems in the presence of ruthenium salts like $[Ru(dmso)_4Cl_2]$ involves one carbonyl group while the second is co-ordinated generating acyclic dinuclear complexes. When the reactions are performed in the presence of PPh_3 the active species is $[Ru(PPh_3)_2Cl_2]$ and cyclometallated complexes are the final products. The facile formation of cyclometallated mono- and di-nuclear ruthenium complexes is rationalised.

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