A Novel Zwitterionic *ortho*-Metallated Ruthenium(II) Phenolate

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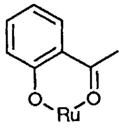
Decarbonylative metallation of the dialdehyde **2b** by $[Ru(PPh_3)_3Cl_2]$ affords the unusual complex $[Ru(MeL)(CO)(PPh_3)_2(Cl)]$ **4** which has been characterised by X-ray crystallography and in which the $Ru^{II}P_2C_2ClO$ coordination unit bears a single net negative charge; the Ru(MeL) (**3**, R = Me) fragment incorporates a four-membered *C,O*-chelated phenolato function with a neighbouring monoprotonated azomethine moiety.

Ruthenium(II and III) are readily *O,O*-chelated by salicylaldehyde to form **1**.[1] While exploring the possible binucleation of the dialdehyde **2a** we have observed the formation of an unprecedented four-membered *C,O*-chelated phenolato function having a neighbouring protonated azomethine moiety as in **3**, Ru(MeL).

Brief boiling of equimolecular proportions of **2a** and $[Ru(PPh_3)_3Cl_2]$ in ethanol or benzene in the presence of 1 mol. equiv. of a primary amine (RNH_2; the amine is essential for the reaction) affords a dark violet diamagnetic nonelectrolytic (in MeCN) complex in near-quantitative yield (based on Ru). With ethanol as solvent, the complex crystallises out directly, but evaporation is necessary with benzene as solvent. Identical results are obtained by using the preformed Schiff's base **2b** in place of **2a** + RNH_2. Evidently the active species is **2b**.

The dark violet complex is $[Ru(RL)(CO)(PPh_3)_2(Cl)]$. Complex **4**,† R = Me, is representative of the family with R = Me, Et, Bu^n, Ph, or p-C_6H_4Me, and its X-ray structure‡ is shown in Fig. 1. The RuP_2C_2ClO coordination unit is severely distorted from octahedral geometry; the two phosphorus ligands are *trans*, and the ring and carbonyl carbon atoms *cis*. The Ru(MeL) fragment, without the azomethine unit, is nearly planar (mean deviation of 0.05 Å), and the azomethine function is tilted with respect to this plane by ≈10°. No authentic Ru^{II} phenolate has been structurally characterised so far, although Ru^{II} semiquinonates[2] and Ru^{III} phenolates[1,3] are known. The Ru^{II}–O (phenolato) distance is estimated to be ≈2.07 Å by interpolation from Ru^{III}–O (phenolato),[1] 1.981(2) Å; Ru^{II}–O(H_2O),[4] 2.122(16) Å; Ru^{III}–O (H_2O),[4] 2.029(7) Å. Four-membered chelation makes the Ru^{II}–O (phenolato) bond in **4** relatively long, 2.205(16) Å. The Ru–Cl distance, 2.470(6) Å, is also longer than normal (2.40 Å) since C(37) is *trans* to Cl.[5]

The protonation of the azomethine function in **3** is revealed by IR data [$\nu(NH^+)$ 3020 cm^{-1}] and is confirmed by ^1H NMR spectra in $CDCl_3$. The NH^+ proton is observed[6] as a very broad peak at δ 11.65 which, as expected, disappears upon D_2O treatment. The proton may be weakly hydrogen-bonded to the phenolic oxygen as shown in **3**. Thus [Ru(MeL)-



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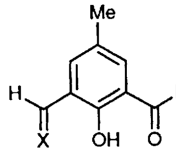
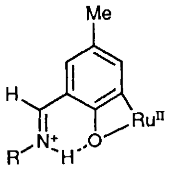


2a, X = O
2b, X = NR



Ru(RL)
3

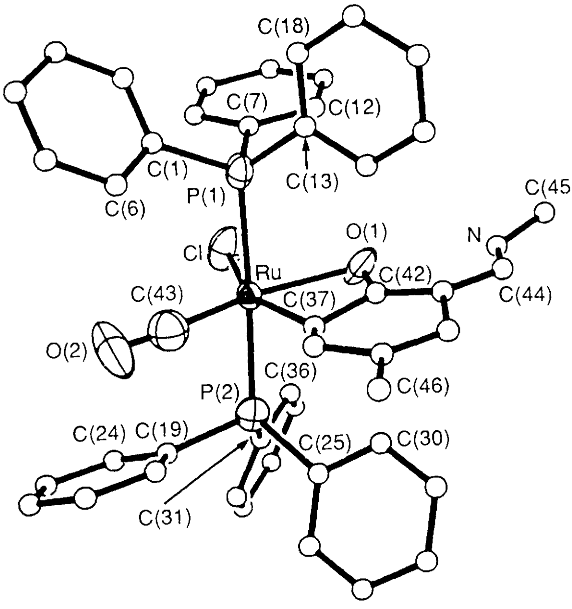


Fig. 1 ORTEP plot and labelling scheme for [Ru(MeL)-(CO)$(PPh_3)_2$(Cl)]. Pertinent distances (Å) and angles (°): Ru–Cl, 2.470(6); Ru–P(1), 2.408(6); Ru–P(2), 2.364(7); Ru–O(1), 2.205(16); Ru–C(37), 2.117(22); Ru–C(43), 1.778(28); Cl–Ru–P(1), 77.9(3); Cl–Ru–P(2), 102.2(3); P(1)–Ru–P(2), 177.4(3); P(1)–Ru–O(1), 79.8(5); Cl–Ru–C(37), 156.7(6); P(2)–Ru–C(37), 82.5(6); Cl–Ru–C(43), 108.0(10); P(2)–Ru–C(43), 74.1(9); C(37)–Ru–C(43), 95.2(11); Cl–Ru–O(1), 93.2(4); P(2)–Ru–O(1), 102.8(5); P(1)–Ru–C(37), 98.4(6); O(1)–Ru–C(37), 63.6(7); P(1)–Ru–C(43), 103.4(9); O(1)–Ru–C(43), 158.8(10).

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† Satisfactory elemental analyses were obtained; λ_{max}/nm (CH_2Cl_2) 480 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 3950), 360 (5280) and 290 (16 260); ν/cm^{-1} (KBr disc): ν_{RuCl} 330, ν_{CO} 1885, ν_{NH^+}, 3020 cm^{-1}; ^1H NMR ($CDCl_3$): phenolic ArH, δ 5.96 and 5.79; PPh_3 δ 7.23 and 7.64; CMe, δ 1.67; NMe, δ 2.93; azomethine CH, δ 7.10, NH^+, δ, 11.65 (all singlets except PPh_3); E^0_{298} for Ru^{III}/Ru^{II} 0.56 V *vs.* standard calomel electrode (SCE) in CH_2Cl_2 (0.1 mol dm^{-3} NEt_4ClO_4) at a platinum electrode.

‡ *Crystal data* for **4**: $C_{46}H_{40}ClNO_2P_2Ru$, M = 837.3, monoclinic, space group Pn, $Z = 2$, $a = 9.958(5)$, $b = 13.166(6)$, $c = 15.627(7)$ Å, $\beta = 91.72(4)°$, $V = 2047.8(16)$ Å^3, $T = 295$ K, $D_c = 1.358$ g cm^{-3}, μ(Mo-Kα) = 5.54 cm^{-1}, crystal dimensions 0.14 × 0.22 × 0.18 mm^3. Data were collected in the range $2.0 \leqslant 2\theta \leqslant 50.0°$ on a Nicolet R3m/V four circle diffractometer. 3672 independent reflections were collected by the ω-scan technique; the 1769 reflections with $I > 5\sigma(I)$ were used for structure solution. An empirical absorption correction was done on the basis of azimuthal scans. All calculations for data reduction, structure solution and refinement were done using the SHELXTL-Plus[9] program package. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares procedures. The phosphine phenyl rings displayed considerable disorder and were refined in the 'Affixed' condition. All Ru, Cl, P, O and N nonhydrogen atoms were refined anisotropically; C and H isotopically. Hydrogen atoms were included at calculated positions with U values of 0.08 Å^2. The structure refined to R = 6.59 and R_w = 7.80%. The highest difference Fourier peak was 0.34 e Å^{-3} near the metal atom. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$(CO)(PPh_3)_2(Cl)]$ is zwitterionic, the negative charge residing in the metal coordination sphere.

The moiety **3** evidently originates *via* decarbonylation of the aldehyde unit in **2**. Significantly, CO in **4** is coordinated *cis* to the metallated carbon which originally held the formyl function. Aldehyde decarbonylation by transition metal species[7] usually involves oxidative addition followed by reductive elimination. A simplified sequence is in eqn. (1). (M^z is the metal moiety of oxidation state z). According to this scheme the reaction between **2** and $[Ru(PPh_3)_3Cl_2]$ would generate a Ru^{IV} species in step I. Step II may not take place readily owing to the stability of the *ortho*-metallated system. However, reductive elimination can proceed by H^+ dissociation from the Ru^{IV}–H fragment with assistance from the azomethine nitrogen which is essential for the reaction. There is precedent for base-promoted reductive H^+ elimination from hydridic Ru^{IV} organometallics.[8]

$$M^z + R'CHO \xrightarrow{I} M^{(z+2)}(R')(CO)(H) \xrightarrow{II} M^z(CO) + R'H \quad (1)$$

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