

New organometallic chemistry of ruthenium and osmium

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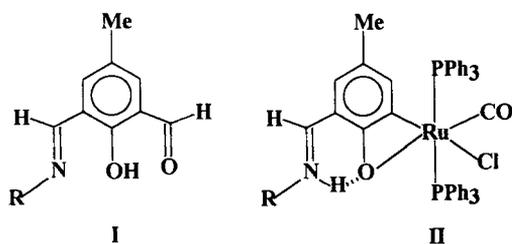
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Abstract. The reaction of Schiff monobases of 2,6-diformyl-4-methylphenol with ruthenium(II) and osmium(II) has afforded a new family of orthometalated organometallics. Synthesis, characterization and reactivity are briefly discussed in this article.

Keywords. Organometallics; decarbonylative orthometalation; iminium-phenolato zwitterion; conformational tautomerisation; alkyne insertion.

1. Introduction

Some years ago we became interested^{1,2} in ruthenium phenolates which constituted a relatively small family of compounds. While examining the possible binding of 2,6-diformyl-4-methylphenol and its Schiff bases as potential binucleating agent for the metal,



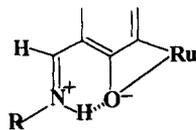
we discovered a new family of organometallics which have since received significant attention. Some of the main findings based on the Schiff monobase ligand **I** are summarized in this note.

2. The primary ruthenium system

The reaction of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ with the Schiff base **I** in boiling ethanol affords dark violet crystals of **II** in nearly quantitative yield³⁻⁵. The compounds with $\text{R} = \text{Et}$ and *p*-tolyl have been structurally characterized. The unprecedented four-membered metallacycle incorporating the phenolato function is excellently planar. The coordinated carbon monoxide is located *cis* to the ortho-metalated carbon to which the aldehyde function was attached before decarbonylative metalation.

An interesting feature is the presence of the iminium-phenolato zwitterionic motif **III**. Selected bond parameters are as follows: N-H , 0.99(6) Å; $\text{O}\cdots\text{H}$, 1.75(5) Å; $\text{N}\cdots\text{O}$, 2.665(12) Å; $\text{N-H}\cdots\text{O}$, 144(1)°. The $\text{N-H}\cdots\text{O}$ bridge is highly unsymmetrical. A broad

band of medium intensity near 3400 cm^{-1} is assigned to the $\text{N}^+\text{-H}$ stretch and the observed frequency is consistent with the presence of weak hydrogen bonding⁶. The relatively high

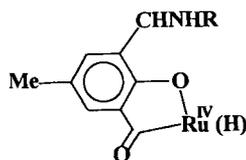


III

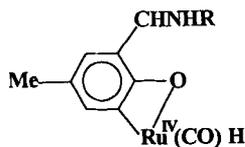
($\sim 1620\text{ cm}^{-1}$) $\text{C}=\text{N}$ stretching frequency agrees with nitrogen protonation^{6,7}. The $\text{N}^+\text{-H}$ proton gives rise to a broad ^1H resonance in the range 10.9–12.6 ppm. The aldimine C-H proton occurs at relatively high fields (7.0–7.6 ppm) consistent with protonation of nitrogen⁸.

3. Reaction path

Decarbonylation of aldehydes (QCHO ; $\text{Q} = \text{alkyl, aryl}$) by ruthenium usually proceeds *via* oxidative addition of the C-H bond to the metal site followed by CO extrusion and Q



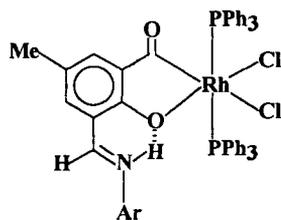
IV



V

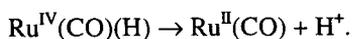
migration⁹⁻¹¹. In the present system oxidative addition with concomitant phenolato chelation and azomethine protonation would afford the motif **IV** (PPh_3 and Cl not shown). It then undergoes Q migration forming **V**.

The intermediacy of **IV** is supported by the isolation and structural characterization of rhodium(III) analogues of **IV** such as **VI**¹². Since carbonyls of ruthenium(IV) are



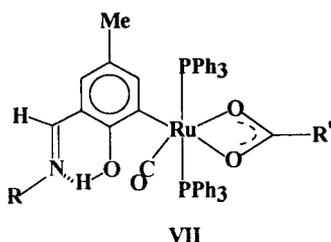
VI

unstable, **V** would spontaneously be transformed to **II** *via* reductive proton elimination¹³.

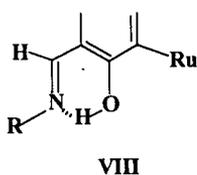


4. Carboxyl chelation

The slow addition of excess aqueous sodium carboxylates to **II** in dichloromethane-acetone mixture leads to a colour change from violet to yellow and from the reaction

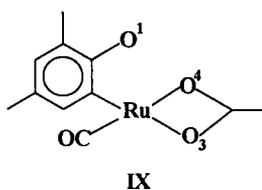


mixture organometallics of type **VII** are isolated in high yields as bright yellow crystalline solids¹⁴. Structure determination has confirmed the binding mode in the cases of R = tolyl, R' = Me and R = tolyl, R' = Ph. In **VII** the imine-phenol function **VIII** is present which is tautomeric with the iminium-phenolato function **III** present in **I**. The



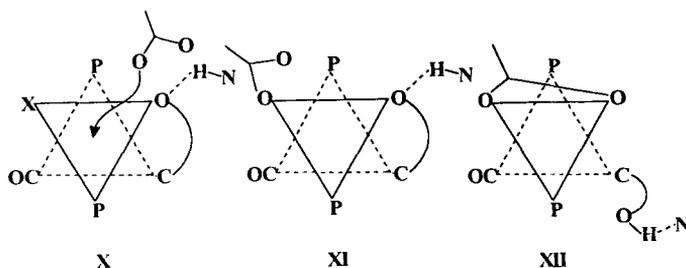
relevant bond parameters in **VIII** are: O–H, 1.14(3) Å; H...N, 1.52(3) Å; O...N, 2.592(10) Å and O–H...N, 156(1)°. The O–H ¹H-resonance of **VIII** occurs near 12.7 ppm as a relatively sharp peak in contrast to the nitrogen-quadrupole broadened N⁺–H resonance of **III** near 13 ppm.

In both **I** and **VII** the carbon monoxide molecule lies *cis* to the metalated carbon. However, it is positioned *trans* and *cis* to the phenolato oxygen in **I** and **VII**, respectively. Between the two structures the RL fragment is effectively rotated by ~ 180° around the Ru–C axis. Scrutiny of structural models has revealed that imposition of conformation **I** on the carboxylate affords moiety **IX** with an estimated O1...O4 distance



of ~2.3 Å. This is a strongly repulsive situation since the van der Waals radius of oxygen is 1.4 Å. The conformation **IX** is thus precluded.

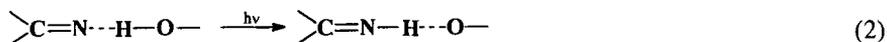
A plausible pathway¹⁵ for the conversion of **I** to **VII** consists of *cis* attack of halide by carboxylate as depicted in **X**. The anchored carboxylate as in **XI** displaces the phenolic oxygen completing carboxyl chelation with concomitant tautomerization and conformational adjustment leading to **XII**.



The above mechanism suggests that it should be possible to go in the reverse direction *via* halide attack on **XII**. In practice this is found to be the case. The interconversion is



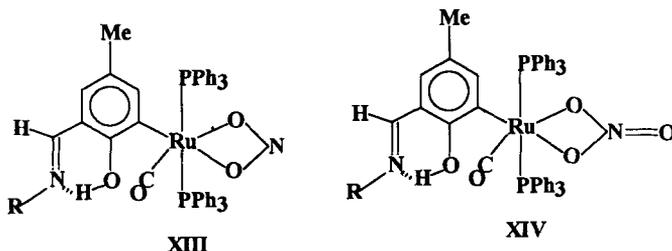
stated in (1). The tautomerization between the imine-phenol **VIII** and iminium-phenolato **III** functions and conformational reorganization of the kind noted earlier are inherent in the process of (1)⁶. Interestingly, this prototropic and conformational reorganization can be looked upon as a distant analog of the photochemical imine-iminium tautomerization in visual and bacterial rhodopsins⁶, (2). This process is



associated with an olefinic geometrical isomerization.

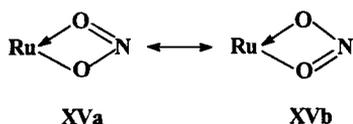
5. Nitrate and nitrite binding

These anions behave similarly to carboxylates. The reaction of **II** with sodium nitrite and

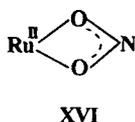


nitrate have afforded the yellow coloured species **XIII** and **XIV** which have been structurally characterized¹⁶.

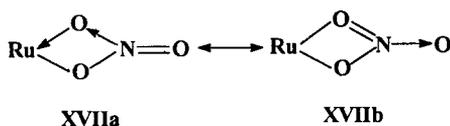
In the nitrite the two N-O distances are equal (1.27 Å) within experimental error corresponding to equal weightage of the resonance form **XVa** and **XVb**. Ruthenium(II) is



known to afford numerous mono-dentate N-bonded^{17,18} and one¹⁹ O-bonded NO₂ complexes. The chelating motif **XVI** described here has not been encountered before in ruthenium(II) chemistry.



In **XIV** the Ru(NO)₃ fragment is highly planar. Bond distance data show that the resonance form **XVIIa** is more important than **XVIIb**. No ruthenium(II) species

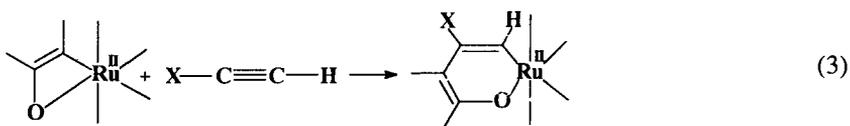


incorporating **XVII** appears to have been structurally characterized although a ruthenium(IV) analogue has been²⁰.

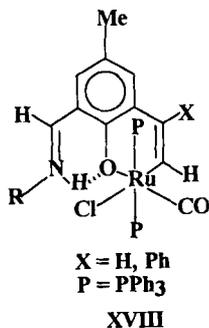
The tautomeric changes and conformational reorganisations accompanying the conversion of **II** to **XIII** and **XIV** are analogues to those occurring in the case **II** → **VII**.

6. Alkyne insertion

Alkyne insertion into metal-carbon bond is a potentially versatile tool for organometallic and organic synthesis²¹⁻²⁵. We have observed that species of type **II** undergo facile insertion of alkynes into the Ru-C bond expanding the four-membered metallacycle into a

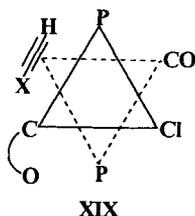


six-membered type, (3). In this manner the hitherto unknown organometallics of type **XVIII** have been synthesized²⁶. The alkynes used are acetylene and phenylacetylene. In previous studies only substituted acetylenes have been inserted into Ru-C bonds. Acetylene itself is successfully employed here for the first time²⁷. Two complexes *viz.*, **XVIII** (R = Et, X = H and R = X = Ph) have been structurally characterized. The reaction of (3) is not hindered by the presence of large excesses (10- to 50-fold) of either chloride (LiCl/Et₄NCl) or PPh₃ in the reaction solution. Therefore, the reaction does not appear to proceed *via* equilibrium dissociation of halide or phosphine ligands. Another crucial

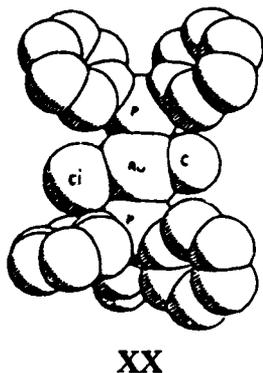


feature of the reaction is that phenylacetylene inserts regioselectively, the $\equiv CPh$ and $\equiv CH$ carbons adding respectively to the carbon and metal ends of the Ru–C bond of **II**. In this manner the Ph group which gets positioned *anti* to the metal site in **XVIII** is distanced from both PPh_3 and Cl. Interestingly, diphenylacetylene fails to insert into **II** under the conditions used for acetylene and phenylacetylene. These findings are indicative of a dominant steric control of the reaction path.

The Ru–O(phenolato) bond in **II** is known to be long ($\sim 2.24 \text{ \AA}$) being subject to facile reversible cleavage by ligands^{14,16}. The initial π -anchoring of the alkyne to the metal is



believed to be attended with Ru–O cleavage, as in **XIX**²⁸. Subsequent 2 + 2 alkyne addition to the Ru–C bond is subject to steric crowding from the Cl and PPh_3 ligands (see **XX**)^{29,30}. The bulky $\equiv CPh$ end of phenylacetylene therefore adds to the carbon site. After



insertion, the Ru–O bond is re-established as in **XVIII**. The inertness of diphenylacetylene to insertion is consistent with this model.

The organic ligand in **XVIII** is new, and we are trying to liberate it from **XVIII** *via* demetallation with the objective of developing its organometallic chemistry with other transition metals.

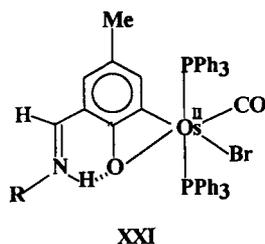
7. Metal redox

Organometallics incorporating trivalent ruthenium are scarce³¹ and this prompted us to explore the feasibility of generating ruthenium(III) congeners of species such as **II** and **XVIII**. The type **II** species display the ruthenium(II)-ruthenium(III) couple near 0.6 V and the corresponding couple in **XVIII** lie at lower potential near 0.4 *vs* SCE.

Coordination by the phenolato group, a hard donor, has been documented^{31,32} to stabilize trivalent ruthenium. The lowering of $E_{1/2}$ values of **XVIII** compared to those of **II** is associated with the strengthening of the Ru–O (phenolato) bond and formation of the Ru–C (vinyl) bond in going from **II** to **XVIII**. The oxidised species in both cases are however unstable for isolation *via* coulometry.

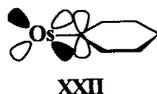
8. The case of osmium

The reaction of $\text{Os}(\text{PPh}_3)_3\text{Br}_2$ with **I** has afforded the metallacycle **XXI**, an osmium analogue of **II**. The structure of the R = Et compound has been determined. This is of



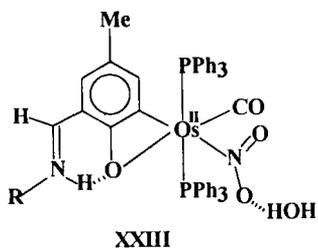
special interest because $\text{Os}^{\text{II}}\text{-O}(\text{phenolato})$ systems are virtually unknown, ortho-metallated $\text{Os}^{\text{II}}\text{-C}$ species are rare and the four-membered organometallic ring incorporating $\text{Os}^{\text{II}}(\text{C}, \text{O})$ chelation is a novelty. The iminium-phenolato N...O length in **XXI** is the same as that in **II**.

The covalent radii of bivalent osmium and ruthenium are virtually the same, 1.33 Å. The Os–O(phenolato) and Os–C(aryl) lengths in **XXI** are however shorter than those in **II** by 0.09 Å and 0.06 Å respectively – as though the metallated ring is pulled closer to the metal in the case of osmium. This is attributed to $d_{\pi}\text{-}p_{\pi}$ backbonding as in **XXII**.

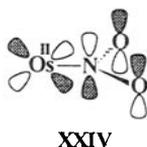


Backbonding of this type is expected to be much weaker in the case of ruthenium^{5,33}.

The metathesis of **XXI** with NaNO_2 affords the N-bonded nitrite **XXIII**, in sharp contrast to the (O, O) chelated ruthenium entity **XIII** formed from **II** and NaNO_2 . The structure of the R = Et compound has been determined. The MLCT band (475 nm) of **XXIII** is blue shifted with respect to the corresponding band (500 nm) of the bromo



precursor **XXI**. In effect, the metal t_2 shell lies lower in the nitro complex. A plausible reason is the superior π -accepting power of the nitro group leading to $d_{\pi}-p_{\pi}^*$ Os-NO₂



back bonding as depicted in **XXIV**. Significantly, the C≡O stretching frequency of **XXIII** is $\sim 30\text{ cm}^{-1}$ higher than that of the bromo complex.

The stronger binding of the Schiff base ligand to osmium(II) compared to ruthenium(II) (see previous section) is believed to be the major reason for the retention of the chelate mode of the ligand in going from **XXI** to **XXIII**. The required six-coordination of the metal ensures that nitrite is bonded in the monohapto fashion and softness trends favour Os-NO₂ bonding. In the case of **II** the weaker Ru-Schiff base chelation is superseded by nitrite chelation affording **XIII**.

Conclusion

We have demonstrated that the Schiff base **I** has a fascinating organometallic chemistry. The case of ruthenium has been emphasized and a brief reference to osmium has been made. This area is being developed with the particular reference to other metals such as rhodium and iridium and to the reactivity of the M-C bond towards unsaturated organics.

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28. To exclude steric repulsion between the entering ligand and the displaced phenolic oxygen, the cleavage is associated with a 180° rotation of I ligand around the Ru–C bond as implicated in **XIX**
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