

# Decarbonylative Metalation of Diformylphenol Schiff Bases: New Osmium and Ruthenium Organometallics Incorporating the Iminium–Phenolato Zwitterionic Motif

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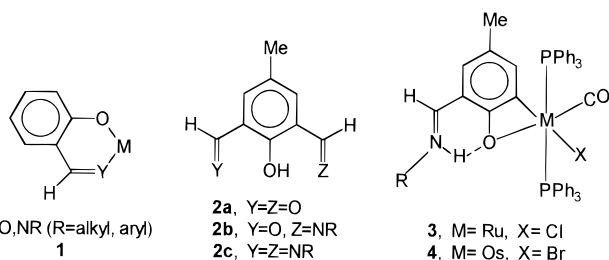
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The reaction of Schiff bases of 2,6-diformyl-4-methylphenol with  $M(\text{PPh}_3)_3\text{X}_2$  in ethanol has afforded carbonylhalo[4-methyl-6-(*N*-*R*-iminoethyl)phenolato-*C*<sup>2</sup>, *O*]bis(triphenylphosphine)metal(II) compounds,  $M^{\text{II}}(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{X}$  ( $M = \text{Os}$ ,  $\text{X} = \text{Br}$ ;  $M = \text{Ru}$ ,  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{alkyl, aryl}$ ). The process is believed to proceed via oxidative addition of the aldehydic  $\text{C}(\text{O})\text{—H}$  bond to the metal followed by  $\text{CO}$  extrusion and reductive proton elimination. The X-ray structure of  $\text{Os}(\text{EtL})(\text{PPh}_3)_2(\text{CO})\text{Br}\cdot\text{CH}_2\text{Cl}_2$  has revealed the presence of the distorted octahedral  $\text{OsC}_2\text{P}_2\text{BrO}$  coordination sphere. In the four-membered,  $\text{Os}(\text{C},\text{O})$  chelate ring, the metal atom is bonded to the carbon site to which an aldehyde group was attached in the parent ligand. The presence of the iminium–phenolato zwitterionic motif is consistent with the  $\text{N}\cdots\text{O}$  length as well as with IR and  $^1\text{H}$  NMR spectra. Bond parameters of the osmium and ruthenium systems are compared. Significant  $d\pi\text{—}p\pi$  back-bonding with the metalated aromatic ring occurs in the case of osmium. The complexes display a quasi-reversible one-electron cyclic voltammetric couple ( $E_{1/2} = 0.50\text{—}0.70$  V), but the oxidized congeners are too unstable to be isolated. Upon reaction of  $M(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{X}$  with carboxylates, the latter gets chelated, the  $\text{M—O}(\text{phenolato})$  linkage is cleaved, and the iminium–phenolato function tautomerizes to the imine–phenol function.

## Introduction

The salicyl chelate motif **1** has been documented for ruthenium<sup>1,2</sup> and osmium.<sup>3</sup> This prompted us to explore



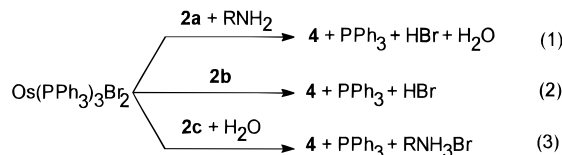
the possible binucleation<sup>4</sup> of ligands of type **2** by these metals. This objective has remained unrealized, but the endeavor has led to the discovery of new organometallics

of type **3** and **4**, incorporating the unprecedented four-membered C,O-chelate and an iminium function,  $\text{—CH= N}^+\text{HR}$ , ortho to the phenolato group. Iminium chemistry is of general interest in the context of visual and bacterial rhodopsins.<sup>5</sup>

In the present work we disclose the chemistry of the osmium family **4**. The results are compared and contrasted with those of ruthenium congeners, **3**, on which preliminary reports are available.<sup>6</sup>

## Results and Discussion

**A. Synthesis. a. Methods.** The complexes **3** and **4** will be generally abbreviated as  $M(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{X}$ . The osmium chelates were obtained in excellent yields by the stoichiometric reaction of  $\text{Os}(\text{PPh}_3)_3\text{Br}_2$  with the dialdehyde **2a** and the amine  $\text{RNH}_2$  in ethanol, eq 1.



The same result is achievable by using the preformed Schiff monobase **2b** in place of **2a** +  $\text{RNH}_2$ , eq 2. The Schiff dibase **2c** also affords **4** via hydrolysis by the water present in the solvent, eq 3. The reactions of eqs

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**Table 1.** IR and UV-Vis Spectral Data

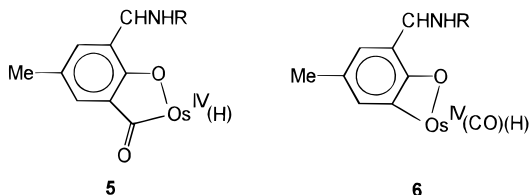
compd	IR data: $\nu_{\max}$ , $\text{cm}^{-1}$			UV-vis data: <sup>c</sup> $\lambda_{\max}$ , nm ( $\epsilon$ , $\text{d}^{\text{M}^{-1}} \text{cm}^{-1}$ )
	C=N <sup>a</sup>	N-H <sup>b</sup>	C≡O <sup>a</sup>	
Os(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	1630	3380	1860	500 (3234), 360 (5074)
Os(EtL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	1630	3380	1865	500 (3172), 360 (4991)
Os(PhL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	1630	3400	1870	560 (3211), 410 (9037), 325 (7478)
Os(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	1640	3400	1870	560 (3634), 415 (10 572), 335 (9140)
Ru(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	1630	3400	1885	480 (3950), 360 (5280)
Ru(EtL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	1630	3400	1885	480 (3900), 360 (6270)
Ru(PhL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	1630	3440	1920	535 (5650), 405 (13 900), 325 <sup>s</sup> (10 000) <sup>e</sup>
Ru(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	1630	3440	1900	530 (4560), 405 (11 430), 320 <sup>s</sup> (7700) <sup>e</sup>

<sup>a</sup> In KBr disk. <sup>b</sup> In hexachlorobutadiene. <sup>c</sup> Solvent is dichloromethane. <sup>d</sup> Extinction coefficient. <sup>e</sup> s = shoulder.

1–3 afford **3** when Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> is used in place of Os(PPh<sub>3</sub>)<sub>3</sub>Br<sub>2</sub>.

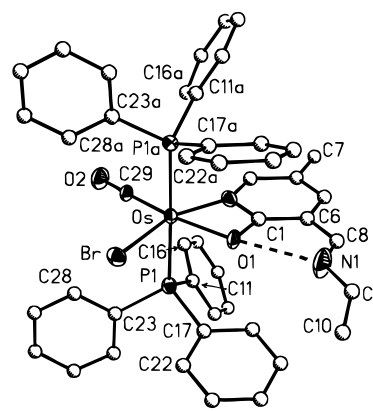
The complexes synthesized in this work are listed in Table 1. These are red (R = alkyl) or violet (R = aryl) diamagnetic (t<sub>2</sub><sup>6</sup>) solids which afford nonelectrolytic solutions in polar solvents.

**b. Reaction Path.** The synthesis of **4** constitutes a rare example of aldehyde decarbonylation by osmium. Decarbonylation promoted by ruthenium<sup>7</sup> and rhodium<sup>8</sup> usually proceeds via oxidative addition of the QC(O)–H bond to the metal site followed by CO extrusion and Q migration (Q = alkyl, aryl).<sup>9</sup> In the present system oxidative addition with concomitant phenolato chelation and azomethine protonation would afford the motif **5** (PPh<sub>3</sub> and Br not shown), which then undergoes Q migration: **5** → **6**.



The intermediacy of **5** is supported by the isolation and structural characterization of a rhodium(III) analog of **5**.<sup>10</sup> Since carbonyls of osmium(IV) are inherently unstable,<sup>11</sup> **6** could spontaneously transform to **4** via reductive proton elimination (Os<sup>IV</sup>(CO)(H) → Os<sup>II</sup>(CO)(H<sup>+</sup>)).<sup>12</sup>

**B. Structure. a. Geometry.** The X-ray structure of the dichloromethane adduct Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> has authenticated the bonding mode **4**. A view of the structure (CH<sub>2</sub>Cl<sub>2</sub> excluded) is shown in Figure 1, and selected bond parameters are listed in Table 2. We have here a structural situation that is unprece-

**Figure 1.** Perspective view and atom-labeling scheme for Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> (excluding CH<sub>2</sub>Cl<sub>2</sub>).**Table 2.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub>

Distances			
Os–Br	2.636(2)	Os–P1	2.379(2)
Os–C2	1.980(19)	Os–O1	2.151(10)
O2–C29	1.194(15)	Os–C29	1.846(12)
O1–C1	1.353(23)	N1–C8	1.253(34)
Angles			
Br–Os–P1	88.9(2)	Br–Os–C29	101.3(7)
Br–Os–C2	154.8(3)	C2–Os–C29	103.9(7)
P1–Os–C29	90.1(1)	P1–Os–O1	90.1(1)
Br–Os–O1	88.2(4)	O1–Os–C2	66.6(5)
P1–Os–C2	91.0(2)	O1–Os–C29	170.6(8)
P1–Os–P1A	177.8(3)	Os–C29–O2	178.1(19)

ented in osmium chemistry. Structurally characterized Os<sup>II</sup>–O(phenolato) systems are virtually unknown. Orthometalated Os<sup>II</sup>–C species are rare,<sup>13</sup> and the four-membered organometallic ring incorporating Os<sup>II</sup>(C,O) chelation is a novelty. The metal atom is bonded to C2 where the aldehyde group was originally attached in the parent ligand. The extruded carbon monoxide and the Br atom are coordinated in positions respectively cis and trans to C2. The non-hydrogen atoms of the EtL ligand as well as Br and CO lie on a crystallographic plane of symmetry along with the metal atom (0,0,0). The methyl group in Et displays 2-fold disorder with respect to the plane.

The OsC<sub>2</sub>P<sub>2</sub>BrO coordination sphere is severely distorted from octahedral geometry as can be seen from the angles at the metal center (Table 2). The angles due to atoms lying trans to each other span the range 177.8(3)–154.7(4)°. The cis angles have an even wider range, 66.6(5)–103.9(7)°. The minimum cis angle cor-

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Table 3.  $^1\text{H}$  NMR Data in  $\text{CDCl}_3^{a,b}$ 

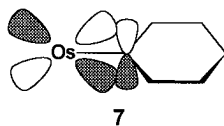
compd	$\delta$ , ppm				
	3-H <sup>s</sup>	5-H <sup>s</sup>	4-Me <sup>s</sup>	=N <sup>+</sup> H <sup>s</sup>	-CH=N <sup>+</sup> <sup>s</sup>
Os(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	5.78	6.34	1.76	10.90	7.06
Os(EtL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	5.78	6.21	1.74	10.90	7.11
Os(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	5.88	6.42	1.80	12.55	7.54
Ru(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	5.80	6.00	1.70	11.65	7.10
Ru(PhL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	5.89	6.03	1.69	13.17	c
Ru(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	5.88	6.02	1.69	13.19	7.58

<sup>a</sup> Atom numbering is as in Figure 1. <sup>b</sup> Other signals: aryl protons, 6.80–7.70<sup>m</sup>; aryl-Me, 2.40<sup>s</sup>; N-Me, 2.90<sup>s</sup>; N-Et, 3.11<sup>a</sup> and 1.17<sup>t</sup> ppm. Abbreviations: s = singlet; t = triplet; q = quartet; m = multiplet. <sup>c</sup> Nonresolvable peak.

responds to the four-membered chelate ring, and the maximum, to C2–Os–C29.

**b. Bond Length Trends.** The Os–P and Os–C29 lengths are unexceptional<sup>14,15</sup> while the Os–C2 length, 1.98(1) Å, is shorter than that (2.08 Å) in the ortho-metalated azobenzene complex.<sup>13</sup> Between the two Os–C bonds, Os–C29 is shorter (1.85(1) Å) in agreement with the expected size trend C2(sp<sup>2</sup>) > C29(sp) and with Os<sup>II</sup>–CO back-bonding. The trans effect of the carbanionic C2 atom lengthens the Os–Br bond to 2.636(2) Å (usual range, 2.50–2.60 Å).<sup>15a,16</sup> The Os–O1 length is 2.151(10) Å—no other Os<sup>II</sup>–O(phenolato) complex appeared to have been structurally characterized. In a catechol complex the average Os<sup>III</sup>–O length is 2.02 Å.<sup>17</sup>

The covalent radii of bivalent osmium and ruthenium are virtually the same, 1.33 Å.<sup>18</sup> The Os–O1 and Os–C2 lengths are however found to be shorter than the corresponding Ru–O and Ru–C lengths in Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl<sup>6</sup> by 0.09 and 0.06 Å respectively—as though the metalated ring is pulled closer to the metal in the case of osmium. The Os⋯i and Ru⋯i lengths in the complexes are 3.30 and 3.49 Å, respectively (i = center of gravity of the metalated benzene ring). The osmium atom is believed to be engaged in dπ–pπ back-bonding,<sup>19</sup> 7, with an aromatic π\* orbital such as the



realized e<sub>2</sub> of benzene.<sup>20</sup> Back-bonding of this type is expected to be much weaker in the case of ruthenium.

**c. The Iminium–Phenolato Zwitterionic Motif.** The N⋯O length in Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> is

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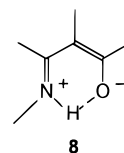
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2.654(20) Å. Here none of the hydrogen atoms of the structure could be resolved in difference Fourier maps. However in Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl the motif 8 is



directly observable: N–H, 0.99(6) Å; O⋯H, 1.75(5) Å; N⋯O, 2.665(12) Å; N–H⋯O, 144(1)°. The N–H⋯O bridge is highly unsymmetrical, and the weakness of the O⋯H hydrogen bond is consistent with the IR data (see below). The structure of the iminium function is of considerable interest in the context of rhodopsins, but in very few cases has the N<sup>+</sup>–H hydrogen been directly located.<sup>5,21</sup>

We note that the N⋯O length in Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> is same as that in the ruthenium complex within experimental error. This result taken collectively with IR and  $^1\text{H}$  NMR results (*vide infra*) demonstrates that 3 and 4 generally contain the iminium–phenolato motif, 8.

**C. Spectra.** Relevant UV–vis and IR spectral features are listed in Table 1, and  $^1\text{H}$  chemical shifts are set out in Table 3.

Two (R = alkyl) and three (R = aryl) allowed bands observed in the range 300–700 nm are diagnostic of the chelate chromophore in 3 and 4. The MLCT (t<sub>2</sub> → π\*) band near 500 nm is red-shifted in going from ruthenium to osmium as well as from R = alkyl to R = aryl. The significant effect of the R substituent is indicative of sizable iminium character of the acceptor π\* orbital.

In  $^1\text{H}$  NMR the aromatic 3-H and 5-H singlets occur at relatively high fields (5.8–6.4 ppm) and so does the 4-Me resonance of the metalated ring (1.7–1.8 ppm). The X-ray structure of Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> indeed reveals that these protons lie well within the shielding cones of phosphine phenyl rings.<sup>22</sup> The extent of upfield shifts due to this factor estimated from crystallographic data and isoshielding ρ–z plots<sup>23</sup> is as

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**Table 4. Cyclic Voltammetric Reduction Potentials<sup>a</sup> at 298 K**

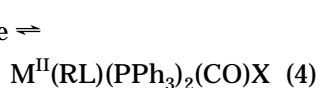
compd	$E_{1/2}[M(III)-M(II)]^b$ V( $\Delta E_p$ , mV)
Os(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	0.52 (160)
Os(EtL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	0.50 (120)
Os(PhL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	0.59 (180)
Os(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Br	0.57 (190)
Ru(MeL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	0.56 (100)
Ru(EtL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	0.54 (200)
Ru(PhL)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	0.68 (150)
Ru(MeC <sub>6</sub> H <sub>4</sub> L)(PPh <sub>3</sub> ) <sub>2</sub> (CO)Cl	0.65 (150)

<sup>a</sup> Conditions: solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration,  $\sim 10^{-3}$  M. <sup>b</sup>  $E_{1/2} = 0.5(E_{pa} + E_{pc})$  at scan rate 50 mV s<sup>-1</sup>, where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials respectively;  $\Delta E_p = E_{pa} - E_{pc}$ .

follows (ppm): 3-H, +0.4; 5-H, +0.5; 4-Me, +0.6. Ortho-metalation is expected to further augment the upfield shifts of the ring protons.<sup>24</sup>

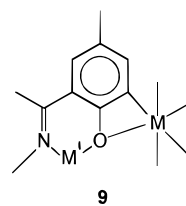
The presence of the iminium function **8** is revealed in both IR and <sup>1</sup>H NMR spectra. A broad band of medium intensity near 3400 cm<sup>-1</sup> is assigned to the N<sup>+</sup>-H stretch. The observed frequency is indicative of the presence of weak hydrogen bonding.<sup>5,25,26</sup> The relatively high ( $\sim 1620$  cm<sup>-1</sup>) C=N stretching frequency also consistent with nitrogen protonation.<sup>5,21</sup> The N<sup>+</sup>-H proton gives rise to a broad <sup>1</sup>H resonance of correct intensity in the range 10.9–12.6 ppm (Table 3). The signal disappears upon shaking with D<sub>2</sub>O. In free phenols of type **2b,c** the OH resonance occurs as a relatively sharp feature near 13 ppm. The aldimine CH proton in these phenols resonates near 8.7 ppm. The corresponding resonances in **3** and **4** lie in the region 0–7.6 ppm. A significant high-field shift of the aldimine CH is indeed expected upon protonation at nitrogen.<sup>27</sup>

**D. Reactivity. a. Metal Redox.** In dichloromethane solution the M(RL)(PPh<sub>3</sub>)<sub>2</sub>(CO)X species display a characteristic quasi-reversible one-electron cyclic voltammetric response corresponding to the M(III)–M(II) couple, eq 4. The  $E_{1/2}$  values (Table 4) follow the

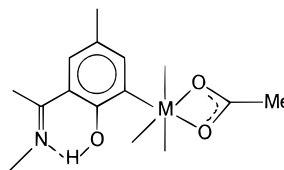


expected trend: Os < Ru (for fixed R) and alkyl < aryl (for fixed M). The oxidized complexes are unstable, and attempted synthesis in bulk concentration by constant-potential coulometry did not succeed.

**b. M–O Cleavage and Carboxylate Chelation.** In view of the presence of the motif **8**, it seemed possible that **3** and **4** might act as ligands for binding a second metal (M') at the N,O sites via proton displacement as in **9**. The high affinity of copper(II) for salicylaldimines<sup>28</sup> led us to try copper(II) as M'. The reaction of Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl with copper(II) acetate monohydrate in aqueous organic solvent yielded a

**9**

yellow colored solid in excellent yield. This however did not contain any copper but was found to have the composition Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)(MeCO<sub>2</sub>). Further scrutiny has revealed that here the acetate ion is chelated while the RL ligand is  $\eta^1$ -bonded via the aromatic carbon center, the phenolic oxygen being engaged in imine–phenol hydrogen bonding as shown in **10**, a tautomer of **8**. Families of ruthenium and

**10**

osmium complexes of type **10** have been synthesized by reacting **3** and **4** with metal carboxylates, and their detailed chemistry will be described elsewhere.

### Concluding Remarks

New families of organometallics, **3** and **4**, have been synthesized via decarbonylative metalation. The osmium complexes, **4**, constitute rare examples of Os<sup>II</sup>–O(phenolato) and ortho-metalated Os<sup>II</sup>–C binding. The four-membered Os(C,O) chelate ring is unprecedented. Other points of special interest include (i) osmium–aromatic d $\pi$ –p $\pi$  bonding as depicted in **7** and (ii) the conversion of **3** and **4** to **10** via reaction with carboxylates resulting in iminium–phenolato to imine–phenol tautomerization. Item ii as well as reactions of **3** and **4** with oxo anions like NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> are under scrutiny.

### Experimental Section

**Materials.** The starting materials Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>,<sup>29</sup> Os(PPh<sub>3</sub>)<sub>3</sub>Br<sub>2</sub><sup>30</sup> (from (NH<sub>4</sub>)<sub>2</sub>OsBr<sub>6</sub><sup>31</sup>), and 2,6-diformyl-4-methylphenol<sup>32</sup> were synthesized by literature methods. The purification of dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as before.<sup>33</sup> All other chemicals and solvents were of analytical grade and used as received. The Schiff bases **2b,c** were prepared by reacting 2,6-diformyl-4-methylphenol with the amine RNH<sub>2</sub> in 1:1 (in ethanol at 60 °C) and 1:2 (in boiling ethanol) ratios, respectively.

**Physical Measurements.** Spectra were recorded on the following equipments: UV–vis, Hitachi 330 spectrophotometer; IR, Perkin-Elmer 783 IR spectrophotometer; <sup>1</sup>H NMR, Bruker 270-MHz FT NMR spectrometer (tetramethylsilane is used as an internal standard). A Perkin-Elmer 240 C elemen-

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tal analyzer was used to collect microanalytical data (CHN). Magnetic susceptibilities of solids were measured with a Model 155 PAR vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrochemical measurements were performed under nitrogen atmosphere on a PAR 370-4 electrochemistry system as reported earlier.<sup>33</sup> All potentials reported in this work are uncorrected for junction contribution. Solution ( $\sim 10^{-3}$  M) electrical conductivities were measured with the help of a Philips PR 9500 bridge.

**Preparation of Complexes.** The complexes having R = aryl were synthesized by reacting  $M(\text{PPh}_3)_3\text{X}_2$  with the preformed Schiff monobases (**2b**), and those with R = alkyl were prepared from the dialdehyde (**2a**) in the presence of the corresponding primary amines. Yields were generally 90–95% on the basis of  $M(\text{PPh}_3)_3\text{X}_2$ . Details are given for representative cases.

**Carbonylbromo[4-methyl-6-(*N-p*-tolyliminomethyl)phenolato-*C*,*O*]bis(triphenylphosphine)osmium(II), Os(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br.** To a solution of 2-formyl-4-methyl-6-(*N-p*-tolyliminomethyl)phenol (40 mg, 0.15 mmol) in hot ethanol (25 mL) was added Os(PPh<sub>3</sub>)<sub>3</sub>Br<sub>2</sub> (115 mg, 0.10 mmol). The mixture was heated to reflux for 2 h. A violet solution was formed, from which a dark violet solid progressively deposited. The solution was cooled to complete the deposition. The solid was filtered out, washed thoroughly with ethanol, and dried in vacuo. Anal. Calcd for OsC<sub>52</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Br: C, 59.62; H, 4.24; N, 1.34. Found: C, 59.60; H, 4.28; N, 33.

The complex Os(PhL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br was similarly prepared. Anal. Calcd for OsC<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Br: C, 59.27; H, 4.10; N, 1.35. Found: C, 59.32; H, 4.04; N, 1.38.

**Carbonylbromo[4-methyl-6-(*N*-methyliminomethyl)phenolato-*C*,*O*]bis(triphenylphosphine)osmium(II), Os(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br.** To a solution of 2,6-diformyl-4-methylphenol (50 mg, 0.30 mmol) in warm ethanol was added a 40% aqueous solution of methylamine (25 mg). The resulting solution was heated to reflux for 0.5 h. Thereafter Os(PPh<sub>3</sub>)<sub>3</sub>Br<sub>2</sub> (250 mg, 0.22 mmol) was added to the hot solution and heating was continued for an additional 2 h. A red solid separated, and the mixture was then cooled and finally filtered. The solid residue was washed thoroughly with cold ethanol and dried in vacuo. Anal. Calcd for OsC<sub>46</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Br: C, 56.88; H, 4.15; N, 1.44. Found: C, 56.91; H, 4.10; N, 1.43.

The complex Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br was similarly synthesized. Anal. Calcd for OsC<sub>47</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Br: C, 57.28; H, 4.30; N, 1.42. Found: C, 57.22; H, 4.29; N, 1.43.

**Carbonylchloro[4-methyl-6-(*N-p*-tolyliminomethyl)phenolato-*C*,*O*]bis(triphenylphosphine)ruthenium(II), Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl.** To a solution of 2-formyl-4-methyl-6-(*N-p*-tolyliminomethyl)phenol (40 mg, 0.15 mmol) in hot ethanol (25 mL) was added Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (100 mg, 0.10 mmol). The mixture was heated to reflux for 0.5 h. Upon cooling, a dark violet solid separated, which was collected by filtration, washed thoroughly with cold ethanol, and dried in vacuo. Anal. Calcd for RuC<sub>52</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Cl: C, 68.35; H, 4.85; N, 1.53. Found: C, 68.49; H, 4.79; N, 1.49.

The complex Ru(PhL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl was similarly prepared. Anal. Calcd for RuC<sub>51</sub>H<sub>42</sub>O<sub>2</sub>P<sub>2</sub>Cl: C, 68.08; H, 4.70; N, 1.55. Found: C, 67.98; H, 4.67; N, 1.58.

**Carbonylchloro[4-methyl-6-(*N*-methyliminomethyl)phenolato-*C*,*O*]bis(triphenylphosphine)ruthenium(II), Ru(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl.** This complex was prepared by the same procedure as used in the case of Os(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br. Only Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (200 mg) was used in place of Os(PPh<sub>3</sub>)<sub>3</sub>Br<sub>2</sub>. Anal. Calcd for RuC<sub>46</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Cl: C, 65.96; H, 4.81; N, 1.67. Found: C, 65.88; H, 4.71; N, 1.63.

The complex Ru(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl was similarly prepared. Anal. Calcd for RuC<sub>47</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Cl: C, 66.28; H, 4.97; N, 1.64. Found: C, 66.23; H, 4.87; N, 1.58.

**Carbonyl(acetato)[4-methyl-6-(*N-p*-tolyliminomethyl)phenolato-*C*]bis(triphenylphosphine)ruthenium(II), Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)(MeCO<sub>2</sub>).** To a vigorously stirring

**Table 5. Crystal, Data Collection, and Refinement Parameters for Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub>**

mol formula	C <sub>48</sub> H <sub>44</sub> N <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Cl <sub>2</sub> BrOs
mol wt	1069.8
cryst syst	monoclinic
space group	<i>Cm</i>
<i>a</i> , Å	18.389(8)
<i>b</i> , Å	14.880(5)
<i>c</i> , Å	10.134(3)
$\beta$ , deg	123.13(3)
<i>V</i> , Å <sup>3</sup>	2322(1.5)
<i>Z</i>	2
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.530
temp, °C	22
radiation	Mo K $\alpha$ (graphite monochromated)
$\lambda$ , Å	0.710 73
scan technique	$\omega$
$\mu$ , cm <sup>-1</sup>	38.28
transm coeff	0.1953–0.2332
<i>R</i> , %	3.42
<i>R</i> <sub>w</sub> , %	3.81
GOF <sup>c</sup>	1.19

<sup>a</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w^{-1} = \sigma^2|F_o| + g|F_o|^2$ ;  $g = 0.0005$ . <sup>c</sup> The goodness of fit is defined as  $[\sum w(|F_o| - |F_c|)^2 / (n_o - n_v)]^{1/2}$ , where  $n_o$  and  $n_v$  denote the numbers of data and variables, respectively.

solution of Ru(MeC<sub>6</sub>H<sub>4</sub>L)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl (50 mg, 0.05 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added dropwise an aqueous solution of Cu(MeCO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (50 mg, 0.25 mmol). The mixture was stirred until the violet solution turned yellow. The organic solvents were then removed in vacuo leaving an aqueous suspension of a yellow residue which was isolated by filtration, washed repeatedly with water, and dried in vacuo. Anal. Calcd for RuC<sub>54</sub>H<sub>47</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 69.19; H, 5.06; N, 1.49. Found: C, 69.23; H, 5.00; N, 1.55.

**X-ray Structure Determination.** A single crystal (0.16 × 0.20 × 0.54 mm<sup>3</sup>) of Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> grown (at 298 K) by slow diffusion of hexane into dichloromethane solution was used. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ( $2\theta = 15$ – $30^\circ$ ). Data were collected by the  $\omega$ -scan technique in the range  $3^\circ \leq 2\theta \leq 55^\circ$  on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction. All data were corrected for Lorentz–polarization effects, and an empirical absorption correction was done on the basis of azimuthal scan of six reflections.<sup>34</sup> Of the 3036 reflections collected, 2950 were unique of which 2787 were taken as observed ( $I > 3\sigma(I)$ ) for structure solution and refinement. On the basis of systematic absences, possible space groups were *Cm*, *C2*, and *C2/m*. Successful structure solution was achieved in the *Cm* space group only.

The metal atom was located from Patterson maps, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structure was refined by full-matrix least-squares procedures. The Me group of the Et substituent is disordered with respect to the mirror plane. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added at calculated positions with fixed  $U = 0.08$  Å<sup>2</sup> in the final cycle of refinement. The highest residual was 1.20 e Å<sup>-3</sup> close to the metal atom. All calculations were done on a MicroVax II computer using the SHELXTL-PLUS program package.<sup>35</sup> Significant crystal data are listed in Table 5.

**Computation of Chemical Shift Due to PPh<sub>3</sub> Ring Currents.** The required parameters computed from crystallographic data of Os(EtL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br·CH<sub>2</sub>Cl<sub>2</sub> are (i) distance

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of the concerned proton from the centroid (G) of each  $\text{PPh}_3$  phenyl ring and (ii) the angle between each distance vector and the normal to the plane of the phenyl ring at G. From these distances and angles the cylindrical coordinates<sup>36</sup>  $\rho$  and  $z$  of the concerned proton were calculated in units of the radius of the benzene hexagon.<sup>23</sup> The  $\rho$  and  $z$  values were then used to compute the shift with the help of available isoshielding plots.<sup>23</sup> The net shift was calculated by summing up individual contributions. Further details are given in a dissertation.<sup>37</sup>

**Acknowledgment.** We are thankful to the Department of Science and Technology, New Delhi, for finan-

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**Supporting Information Available:** For  $\text{Os}(\text{EtL})(\text{PPh}_3)_2(\text{CO})\text{Br}\cdot\text{CH}_2\text{Cl}_2$ , tables of complete bond distances (Table S1) and angles (Table S2), anisotropic thermal parameters (Table S3), hydrogen atom positional and  $U$  parameters (Table S4), and non-hydrogen atomic coordinates and  $U$  values (Table S5) (5 pages). Ordering information is given on any current masthead page.

OM960018B

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