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Chemistry of a New Family of Carboxyl-Chelated Ruthenium and Osmium Aryls Incorporating the Imine−Phenol Motif

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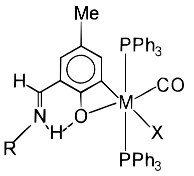
The reaction of carbonylhalo[4-methyl-6-(NR-iminiomethyl)phenolato-*C*^{2},*O*]bis(triphenylphosphine)metal(II), $M^{II}(\eta^2\text{-RL})(PPh_3)_2(CO)X$ (M = Ru, Os; X = Cl, Br; R = Ph, p-MeC_6H_4), **1**, with sodium carboxylates has afforded carbonyl(carboxylato)[4-methyl-6-(NR-iminomethyl)phenol-*C*^{2}]bis(triphenylphosphine)metal(II), $M^{II}(\eta^1\text{-RL})(PPh_3)_2(CO)(\eta^2\text{-R}'CO_2)$ (R′ = Me, Ph), **2**. The reaction is believed to proceed via initial associative cis attack on halide by carboxylate. The reaction **2** → **1** occurs upon treatment of **2** with excess halide. Spectral (UV−vis, IR, ^{1}H NMR) and electrochemical (metal redox) data for **2** are reported. Structure determination of $Ru(\eta^1\text{-}MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ and $Ru(\eta^1\text{-}MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)\cdot C_6H_6$ has revealed trans $(PPh_3)_2$ geometry, the MeC_6H_4L ligand being bonded via an aromatic carbon atom lying cis to the CO molecule. In the H-bonded phenol−imine function the bond parameters for the acetate complex are as follows: O1−H, 1.14(3) Å; N···H, 1.52(3) Å; O1···N, 2.592(10) Å; O1−H···N, 156(1)°. In the **1** → **2** interconversion, iminium−phenolate to imine−phenol tautomerization and a sterically controlled change in rotational conformation are involved.

Introduction

Recently it was demonstrated that decarbonylative metalation of 4-methyl-2,6-diformylphenol by $M(PPh_3)_3X_2$ in the presence of primary amines (RNH_2) affords organometallics of type **1** incorporating the zwitterionic iminium−phenolato motif.[1] The reactivity of these compounds is being examined. The coordinated X^- ligand is found to be replaceable by other anions. The present work concerns replacement of X^- by carboxylates $R'CO_2^-$. New organometallics of type **2** have thus been synthesized and their structures determined. A route for the reverse transformation **2** → **1** has also been worked out. Of special interest are the tautomeric and conformational changes associated with the interconversion of the two species.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M = Os, X = Br

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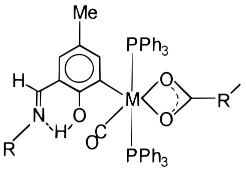
M = Ru, Os

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Results and Discussion

A. Synthesis. The complexes **1** and **2** will be abbreviated as $M(\eta^2\text{-RL})(PPh_3)_2(CO)X$ and $M(\eta^1\text{-RL})(PPh_3)_2(CO)(\eta^2\text{-R}'CO_2)$, respectively (R = Ph, p-MeC_6H_4; R′ = Me, Ph).

For M = Ru, the synthetic procedure consisted of slow addition of excess aqueous sodium carboxylate to $Ru(\eta^2\text{-RL})(PPh_3)_2(CO)Cl$ in dichloromethane−acetone mixture. The reaction of eq 1 took place at room temperature and was associated with a color change from violet to yellow. The $Ru(\eta^1\text{-RL})(PPh_3)_2(CO)(\eta^2\text{-R}'CO_2)$ complexes were isolated in high yields as bright yellow crystalline solids. In the case of osmium, carboxylate chelation occurred in poorer yields and that too under more drastic reaction conditions like a larger excess of carboxylate and boiling the reaction mixture.

$$M(\eta^2\text{-RL})(PPh_3)_2(CO)X + NaR'CO_2 \rightarrow M(\eta^1\text{-RL})(PPh_3)_2(CO)(\eta^2\text{-R}'CO_2) + NaX \quad (1)$$

B. Characterization. The complexes synthesized are listed in Table 1 along with selected characterization data. These are uniformly diamagnetic consistent with the metal oxidation state of +2. In dichloromethane solution 2 displays two characteristic allowed bands near 400 and 330 nm. The C≡O stretch (KBr disk) follows the order Ru > Os. The symmetric and asymmetric carboxyl stretches are observed near 1460 and 1520 cm^{-1}, respectively—the small separation between the two suggesting chelation.[2]

In ^{1}H NMR (Table 2) the singlets due to 42-H (~6.2 ppm), 41-Me (~2.0 ppm), and 54-Me (~0.7 ppm) occur at relatively high fields. Structural work (see below) shows that these protons lie in the shielding cones of phosphine rings.[1,3,5] The ring current shifts estimated

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(2) (a) Kavanagh, B.; Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 327. (b) Tocher, D. A.; Gould, R. O.; Stephenson, T. A.; Bennet, M. A.; Ennet, J. P.; Matheson, T. W.; Sawyer, L.; Shah, U. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1571. (c) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (d) Moore, D. S.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 2307. (e) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

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Table 1. Cyclic Voltammetric Reduction Potentials and IR and UV−Vis Spectral Data

complex	M(III)−M(II) $E_{1/2}$,[a] V (ΔE_p, mV)	IR data[b] ν_{max}, cm^{-1} C=N	C≡O	(OCO)$_{sy}$	(OCO)$_{asy}$	UV−vis data[c] λ_{max}, nm (ϵ,[d] M^{-1} cm^{-1})
Ru(η^1-PhL)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)	0.61 (180)	1585	1920	1460	1530	410 (5952), 330 (18 214)
Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)	0.60 (170)	1580	1920	1450	1525	400 (4875), 330 (19 501)
Ru(η^1-PhL)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	0.63 (170)	1585	1920	1480	1510	400 (3333), 330 (14 666)
Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	0.63 (160)	1590	1920	1480	1510	400 (2970), 330 (14 258)
Os(η^1-PhL)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)	0.55 (160)	1590	1910	1470	1530	395 (3385), 330 (14 948)
Os(η^1-PhL)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	0.54 (160)	1590	1910	1480	1510	400 (4097), 330 (18 753)
Os(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	0.54 (180)	1590	1910	1485	1510	400 (4208), 330 (20 692)

[a] Conditions: solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, ~10^{-3} M; $E_{1/2} = 0.5(E_{pa} + E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$. [b] In Kbr disk. [c] Solvent is dichloromethane. [d] Extinction coefficient.

Table 2. ^{1}H NMR Data in CDCl$_3$[a,b]

compd	δ, ppm 42-H^s	44-H^s	O-H^s	41-Me^s	48-Me^s	54-Me^s
Ru(η^1-PhL)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)	6.18	8.06	12.69	2.03		0.66
Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)	6.17	8.07	12.79	2.02	2.39	0.66
Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	6.23	8.08	12.70	2.03	2.39	
Os(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)	6.18	8.07	12.71	2.02	2.39	

[a] Atom numbering is as in Figures 1 and 2. [b] Aryl protons, 6.90−7.70^m; s = singlet and m = multiplet.

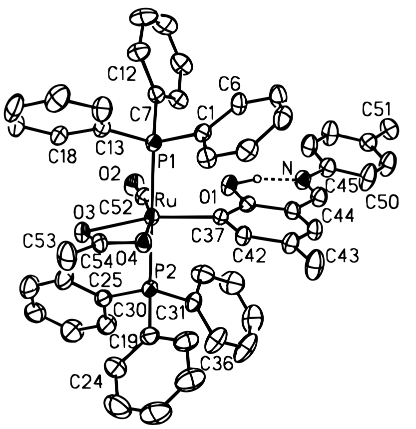

Figure 1. ORTEP plot (40% probability ellipsoids) and atom-labeling scheme for Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$).

Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$)

Distances			
Ru−O3	2.258(4)	Ru−O4	2.215(4)
Ru−P1	2.387(2)	Ru−P2	2.373(2)
Ru−C37	2.060(6)	Ru−C52	1.822(6)
O2−C52	1.150(7)	N−C44	1.286(8)
O3−C54	1.256(7)	O4−C54	1.250(7)
O1−H	1.14(3)	O1···N	2.592(10)
Angles			
P1−Ru−P2	178.0(1)	P1−Ru−O3	92.0(1)
P1−Ru−O4	84.6(1)	P1−Ru−C37	89.4(2)
P1−Ru−C52	93.7(2)	P2−Ru−O3	87.0(1)
P2−Ru−O4	93.5(1)	P2−Ru−C37	90.8(2)
P2−Ru−C52	88.2(2)	O3−Ru−C37	156.3(2)
O3−Ru−O4	58.2(2)	O3−Ru−C52	107.4(2)
O4−Ru−C37	98.4(2)	O4−Ru−C52	165.3(2)
C37−Ru−C52	96.2(3)	Ru−C52−O2	173.6(6)
Ru−O3−C54	89.7(3)	Ru−O4−C54	91.8(3)
O3−C54−O4	120.3(5)	O1−H···N	156(1)

from crystallographic data and isoshielding ρ−z plots[4] in the case of Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$) are as follows: 42-H, 0.50 ppm; 41-Me, 0.42 ppm; 54-Me, 1.26 ppm. The acetate methyl (54-Me) is subject to especially large shielding consistent with the observed chemical shift. In the absence of ring currents the acetate methyl chemical shift should be around 1.7 ppm.[5]

Solutions of **2** in dichloromethane display a characteristic quasi-reversible one-electron cyclic voltammetric response (Table 1) presumably corresponding to M^{III}/M^{II} redox. It has however not been possible to isolate the oxidized complexes. The $E_{1/2}$ values depend on R (alkyl < aryl) and M (Os < Ru). The values are systematically lower than those of 1.[1]

C. Structure of Acetates. a. Geometrical Features. Determination of the X-ray structure of a representative member, viz., Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$), has authenticated the binding mode shown in **2**. A molecular view is shown in Figure 1, and selected bond parameters are collected in Table 3. All the hydrogen atoms in this structure were directly located in difference Fourier maps.

The acetate ligand is chelated to the metal atom, and the two PPh$_3$ ligands lie in trans positions (P1−Ru−P2 angle, 178.0(1)°). The MeC$_6$H$_4$L ligand is bonded to the metal only at C37, the phenolic oxygen lying too far away (Ru···01, 3.448(5) Å) for significant binding. The coordinated carbon monoxide molecule lies cis to C37. The RuC$_2$P$_2$O$_2$ coordination sphere is severely distorted from octahedral geometry as can be seen from the angles at the metal center. The most deviated cis angle is O3−Ru−O4, 58.2(2)°, which is unexceptional for an acetate bite.[5,6] The extreme acuteness of this angle makes some other cis angles obtuse, especially O3−Ru−C52, 107.4(2)°. For the same reason the trans angles involving O3 and O4 deviate considerably from 180°, the most deviated angle being O3−Ru−C37, 156.3(2)°.

The four-membered carboxylate ring as well as the methyl carbon lie on a plane (e.g. A) while the metalated benzene ring along with Ru, C43, C44, O1, and N makes another plane (e.g. B) (mean deviation, 0.04 Å). The dihedral angle between planes A and B is 10.0°. The

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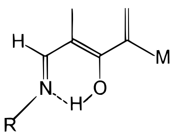
mean deviation of plane through Ru, C37, C52, O3, and O4 is 0.04 Å. The P1−Ru−P2 axis is nearly perpendicular to plane B. Otherwise at least one phenyl ring of each PPh_3 approaches plane B too closely.[7]

b. Bond Lengths. From covalent radii values the Ru^{II}−C(sp^2) length is estimated to be 2.06 Å.[8] Observed values span the range 1.96−2.16 Å.[9] In our complex the Ru−C37 distance is 2.060(6) Å. In the Ru(η^2-MeC_6H_4L)(PPh_3)$_2$(CO)Cl precursor the corresponding length is slightly shorter, 2.043(6) Å.[10] The Ru^{II}−CO length, 1.822(6) Å, is normal[9a,11] and is consistent with Ru−CO back-bonding and the trend of carbon radius C(sp^2) > C(sp). Due to the trans effect of the carbanionic C37 site the Ru−O3 bond is longer than the Ru−O4 bond by 0.04 Å (Table 3). In chelated acetates the Ru^{II}−O lengths usually lie in the range 2.14−2.28 Å.[5,6]

There is a contact of length 3.332(5) Å between carbonyl O2 of one molecule and the p-tolyl C49 of an adjacent symmetry-related molecule. The CH···O length, 2.36 Å, is significantly shorter than the sum of van der Waals radii (2.60 Å)[8] suggesting the presence of weak hydrogen bonding.

c. Imine−Phenol Motif. A notable feature of the structure is the presence of the phenolic hydrogen, the O−H distance being 1.14(3) Å corresponding to the imine−phenol motif **3**. The H···N length is 1.52(3) Å.



3

The hydrogen bonding is thus very unsymmetrical. The O···N length and O−H···N angle are respectively 2.592(10) Å and 156(1)°. Certain spectral features characteristic of **3** will be noted in a later section.

D. Structure of Benzoates. The benzene solvate Ru(η^1-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-$PhCO_2$)·C_6H_6 afforded satisfactory single crystals. A molecular view (without C_6H_6) is shown in Figure 2, and selected bond parameters are listed in Table 4. The gross features of the structure are similar to those of the acetate complex.

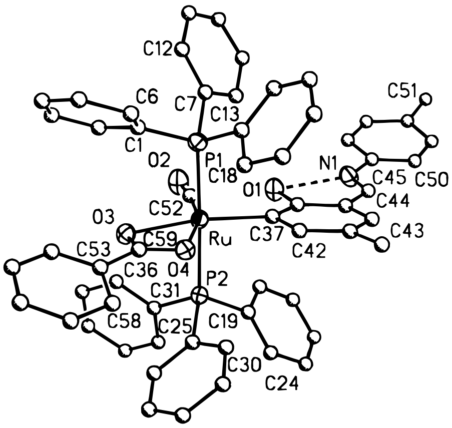


Figure 2. Perspective view and atom-labeling scheme for Ru(η^1-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-$PhCO_2$)·C_6H_6 (excluding C_6H_6).

Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Ru(η^1-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-$PhCO_2$)·C_6H_6

Distances			
Ru−O3	2.214(9)	Ru−O4	2.222(7)
Ru−P1	2.404(4)	Ru−P2	2.381(4)
Ru−C37	2.091(16)	Ru−C52	1.827(11)
O2−C52	1.143(14)	N1−C44	1.273(17)
O3−C59	1.279(14)	O4−C59	1.280(19)
N1···O1	2.607(20)		
Angles			
P1−Ru−P2	174.8(1)	P1−Ru−O3	90.2(2)
P1−Ru−O4	85.5(2)	P1−Ru−C37	90.8(4)
P1−Ru−C52	93.0(4)	P2−Ru−O3	86.7(2)
P2−Ru−O4	89.4(2)	P2−Ru−C37	90.9(4)
P2−Ru−C52	91.7(4)	O3−Ru−C37	163.1(3)
O3−Ru−O4	59.1(3)	O3−Ru−C52	102.0(5)
O4−Ru−C37	104.2(4)	O4−Ru−C52	161.0(5)
C37−Ru−C52	94.7(6)	Ru−C52−O2	171.2(13)
Ru−O3−C59	91.9(8)	Ru−O4−C59	91.5(6)
O3−C59−O4	117.5(10)		

The benzene of crystallization occurs in a general position and does not display any bonding with any other group in the complex.

The $RuC_2P_2O_2$ coordination sphere is again a highly distorted octahedron, the benzoate bite angle being 59.1(3)°. The trans-coordinated phosphine ligands make the angle P1−Ru−P2 = 174.8(1)°. The P1−Ru−P2 axis is nearly perpendicular to the metalated aromatic ring, which along with Ru, C43, C44, O1, and N1 makes a good plane (mean deviation 0.04 Å). The carboxylate chelate ring is nearly perfectly planar (mean deviation 0.003 Å). In this structure hydrogen atoms were not resolved in difference Fourier maps. However the N1···O1 length, 2.607(20) Å, is the same within the experimental error as that in the acetate complex implying the presence of the imine−phenol motif **3**.

The close similarity of spectral and other features (vide infra) of the various type **2** complexes is consistent with the presence of the same gross structure irrespective of M, R, and R′.

E. Phenomena Related to the Transformation 1 → 2. The gross process in this transformation is the displacement of the M−X and M−O(phenol) bonds due to $R'CO_2^-$ chelation. There are certain subtle but noteworthy structural differences between **1** and **2**.

a. Tautomerization. In **2** the uncoordinated salicylaldimine (imine−phenol) function **3** is present while **1** contains the zwitterionic iminium−phenolate function

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(6) (a) Sanchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Marquez-Silla, R.-L.; Schollhorn, H.; Klein, H.-P.; Fontal, B. *Inorg. Chem.* **1986**, *25*, 1097. (b) Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* **1974**, 390. (c) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556. (d) Boyar, E. B.; Harding, P. A.; Robinson, S. D.; Brock, C. P. *J. Chem. Soc., Dalton Trans.* **1986**, 1771. (e) Ashworth, T. V.; Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2184.

(7) In Ru(η^1-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-$MeCO_2$) the distance between the centroid of the metalated benzene ring with the centroids of phosphine phenyl rings are as follows: P(1)Ph_3, 4.15, 5.99, 7.23 Å; P(2)Ph_3, 4.28, 5.72, 7.22 Å.

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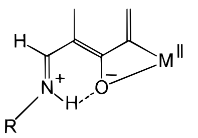
4 in which the metal is bonded at the oxygen site. In $Ru(\eta^2\text{-}MeC_6H_4L)(PPh)_2(CO)Cl$,[10] the relevant parameters of **4** are as follows: N−H, 0.99(6) Å; O···H, 1.75(5) Å; N···O, 2.665(12) Å; N−H···O, 144(1)°. Between motifs **4** and **3** the proton shifts from azomethine nitrogen to phenolic oxygen as the latter gets detached from the metal.



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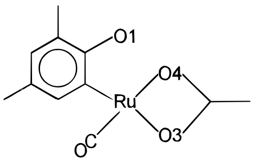
The motifs **3** and **4** have distinctive IR and ^1H NMR (Table 2) features. Thus the C═N stretching frequency in **3** (∼1590 cm^{-1}; Table 1) is significantly lower than that in **4** (∼1620 cm^{-1})[1] as expected.[12,13] Also expected is the large low-field shift of the aldimine CH resonance in the ^1H NMR of **3** (∼8.1 ppm; Table 2) compared to that in **4** (∼7.5 ppm).[1] The O−H resonance of **3** occurs near 12.7 ppm (Table 2) as a relatively sharp peak (width at half-height ∼0.1 ppm) compared to the nitrogen-quadrupole broadened (width at half height ∼0.5 ppm) N^+−H resonance of **4** at ∼13 ppm.[1]

b. Conformation. In both **1** and **2** the carbon monoxide molecule lies cis to the metalated carbon. However, it is positioned trans and cis to the phenolato oxygen in **1** and **2**, respectively. Between the two structures the RL fragment is effectively rotated by ∼180° around the M−C axis. Scrutiny of structural modes has revealed that imposition of conformation **1** on the carboxylate complex affords motif **5** 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.[8] The conformation **5** is thus precluded.



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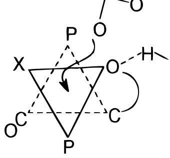
A plausible pathway[14] for the conversion of **1** to **2** consists of cis attack of halide by carboxylate as depicted in **6**. The anchored carboxylate as in **7** displaces the phenolic oxygen achieving the carboxyl chelation with concomitant tautomerization and conformational adjustments leading to **8**.



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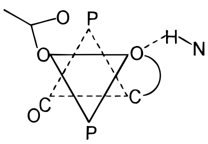

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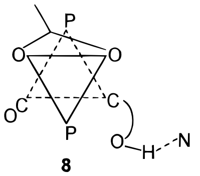

8

c. Reverting 2 to 1. The above mechanism suggests that it should be possible to go in the reverse direction via halide attack on **8**. This has been demonstrated in the case of $Ru(\eta^1\text{-}MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$. Upon treatment of it with excess tetraethylammonium chloride in acetone−alcohol mixture, $Ru(\eta^2\text{-}MeC_6H_4L)(PPh_3)_2(CO)Cl$ is produced. The interconversion reaction is stated in eq 2. The forward reaction is especially favored in acid media, and the acetate is best converted to the chloride by hydrochloric acid treatment.

$$Ru(\eta^1\text{-}MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2) \underset{MeCO_2^-}{\overset{Cl^-}{\rightleftharpoons}} Ru(\eta^2\text{-}MeC_6H_4L)(PPh_3)_2(CO)Cl \quad (2)$$

The tautomerization between the imine−phenol (**3**) and the iminium−phenolato (**4**) functions and conformational reorganization of the kind noted earlier are inherent in the processes of eq 2. Interestingly, this can be considered to be a distant analog of the imine−iminium tautomerization and olefinic geometrical isomerization in rhodopsins.[12]

Concluding Remarks

It is demonstrated that $M(\eta^2\text{-}RL)(PPh_3)_2(CO)X$ (M = Ru, Os), **1**, undergoes facile substitution of halide (X = Cl^-, Br^-) by aliphatic and aromatic carboxylates ($R'CO_2$; R′ = Me, Ph) affording a new family of organometallics, $M(\eta^1\text{-}RL)(PPh_3)_2(CO)(\eta^2\text{-}R'CO_2)$, **2**. Representative structure determination has revealed that in going from **1** to **2** the hapticity of RL changes from η^2 to η^1 as the iminium−phenolate function tautomerizes to the imine−phenol function. Further, steric repulsion between carboxylate and phenolic oxygen atoms enforces a conformational change of the $Ru(PPh_3)_2(CO)(\eta^2\text{-}R'CO_2)$ fragment with respect to RL. These transformations can be reversed by treating **2** with excess halide whereupon **1** is regenerated. An associative reaction mode involving attack of the entering group cis to the leaving group is consistent with the observed interconversion.

Experimental Section

Materials. The starting materials $Ru(PPh_3)_3Cl_2$,[15] $Os(PPh_3)_3Br_2$,[16] and $M(\eta^2\text{-}RL)(PPh_3)_2(CO)X$[1] were prepared by reported methods. The purification of dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as described in the previous work.[17] All other chemicals and solvents were of analytical grade and used as received.

Physical Measurements. Electronic and IR spectra were recorded with Hitachi 330 and Perkin-Elmer 783 IR spectrophotometers. For ^1H NMR spectra a Bruker 270-MHz FT NMR spectrometer was used (tetramethylsilane is the internal standard). Magnetic behavior was examined on a PAR 155

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vibrating-sample magnetometer fitted with a Walker Scientific magnet. Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer. Electrochemical measurements were performed under nitrogen atmosphere on a PAR 370-4 electrochemistry system as reported earlier.[17] 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 acetates M(η^1-RL)-$(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ were synthesized by reacting M(η^2-RL)-$(PPh_3)_2(CO)X$ with $NaMeCO_2 \cdot 3H_2O$. The benzoates M(η^1-RL)$(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$ were similarly prepared using $NaPhCO_2$. Yields were generally 80−85% on the basis of M(η^2-RL)$(PPh_3)_2(CO)X$ for M = Ru and 50−60% for M = Os. Details are given for representative cases.

Carbonyl(acetato)[4-methyl-6-(*N*-p-tolyliminomethyl)-phenol-*C*^{2}]bis(triphenylphosphine)ruthenium(II), Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$. To a vigorously stirring solution of Ru(η^2-$MeC_6H_4L)(PPh_3)_2(CO)Cl$ (50 mg, 0.05 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added dropwise an aqueous solution of $NaMeCO_2 \cdot 3H_2O$ (50 mg, 0.35 mmol). The mixture was stirred until the original violet color became yellow. The organic solvents were then removed under reduced pressure leaving an aqueous suspension of a yellow residue, which was isolated by filtration, washed repeatedly with water, and dried in vacuo. Anal. Calcd for $RuC_{54}H_{47}NO_4P_2$: C, 69.19; H, 5.06; N, 1.49. Found: C, 69.12; H, 5.08; N, 1.57.

The complex Ru(η^1-PhL)$(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ was similarly prepared. Anal. Calcd for $RuC_{53}H_{45}NO_4P_2$: C, 68.95; H, 4.92; N, 1.52. Found: C, 69.01; H, 4.89; N, 1.47.

Carbonyl(benzoato)[4-methyl-6-(*N*-p-tolyliminomethyl)phenol-*C*^{2}]bis(triphenylphosphine)ruthenium(II), Ru-(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$. This complex was prepared by the same procedure as above using $NaPhCO_2$ in place of $NaMeCO_2 \cdot 3H_2O$. Anal. Calcd for $RuC_{59}H_{49}NO_4P_2$: C, 70.91; H, 4.95; N, 1.40. Found: C, 70.85; H, 4.85; N, 1.47.

The complex Ru(η^1-PhL)$(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$ was similarly prepared. Anal. Calcd for $RuC_{58}H_{47}NO_4P_2$: C, 70.70; H, 4.81; N, 1.42. Found: C, 70.75; H, 4.88; N, 1.47.

Carbonyl(acetato)[4-methyl-6-(*N*-phenyliminomethyl)-phenol-*C*^{2}]bis(triphenylphosphine)osmium(II), Os(η^1-PhL)$(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$. To a solution of Os($\eta^2$-PhL)-$(PPh_3)_2(CO)Br$ (50 mg, 0.05 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added an aqueous solution (10 mL) of $NaMeCO_2 \cdot 3H_2O$ (200 mg, 1.4 mmol). The reaction mixture was then heated to reflux (6−7 h) until the violet solution turned yellow. The organic solvents were removed under reduced pressure. The aqueous suspension of the yellow residue was filtered out, washed repeatedly with water, and dried in vacuo. The yield was 60% on the basis of the bromo precursor. Anal. Calcd for $OsC_{53}H_{45}NO_4P_2$: C, 62.87; H, 4.48; N, 1.38. Found: C, 62.80; H, 4.52; N, 1.34.

Carbonyl(benzoato)[4-methyl-6-(*N*-phenyliminomethyl)phenol-*C*^{2}]bis(triphenylphosphine)osmium(II), Os(η^1-PhL)$(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$. This complex was prepared by the same procedure as above using $NaPhCO_2$ in place of $NaMeCO_2 \cdot 3H_2O$. Anal. Calcd for $OsC_{58}H_{47}NO_4P_2$: C, 64.83; H, 4.41; N, 1.30. Found: C, 64.89; H, 4.44; N, 1.23.

The complex Os(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$ was similarly prepared. Anal. Calcd for $OsC_{59}H_{49}NO_4P_2$: C, 65.09; H, 4.54; N, 1.29. Found: C, 65.01; H, 4.53; N, 1.35.

Conversion of Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ to Ru(η^2-$MeC_6H_4L)(PPh_3)_2(CO)Cl$. To a stirred solution of Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ (10 mg) in acetone (5 mL)−dichloromethane (2 mL) mixture were added two drops of 0.3 N HCl solution in acetone. The solution immediately changed from yellow to violet. Stirring was continued for another 10 min. The solvent was then removed under vacuo, water was added to the violet residue, and the suspension was stirred. This solid was collected by filtration. It was washed repeatedly with water and dried in vacuo. The yield was 7.5 mg (80%). Anal. Calcd for $RuC_{52}H_{44}NO_2P_2Cl$: C, 68.35; H, 4.85; N, 1.53. Found: C, 68.31; H, 4.80; N, 1.50. The complex was characterized with the help of spectra and other features.[1]

Table 5. Crystal, Data Collection, and Refinement Parameters for Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ and Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2) \cdot C_6H_6$

	Ru(η^1-$MeC_6H_4L)$-$(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$	Ru(η^1-$MeC_6H_6H_4L)$-$(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2) \cdot C_6H_6$
mol formula	$C_{54}H_{47}NO_4P_2Ru$	$C_{65}H_{55}NO_4P_2Ru$
mol wt	936.9	1077.1
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.079(2)	13.308(9)
b, Å	12.349(5)	14.638(8)
c, Å	18.486(8)	15.446(9)
α, deg	96.99(4)	100.61(5)
β, deg	94.10(3)	113.86(4)
γ, deg	101.82(3)	90.94(5)
V, Å^3	2445(1.6)	2691(2.5)
Z	2	2
D_{calcd}, g cm^{-3}	1.273	1.329
temp, °C	22	22
radiation	Mo Kα (graphite monochromated)	Mo Kα (graphite monochromated)
λ, Å	0.710 73	0.710 72
scan technique	ω	ω
μ, cm^{-1}	4.32	4.01
transm coeff	0.8262−0.9063	0.8052−0.9122
R,[a] %	4.81	6.44
R,[b] %	5.09	6.65
GOF[c]	1.04	1.30

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2|F_o| + g|F_o|^2$; $g = 0.0005$. [c] 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.

X-ray Structure Determination. A single crystal (0.28 × 0.12 × 0.36 mm^3) of Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ grown (at 298 K) by slow diffusion of hexane into benzene solution was used. The Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2)$ compound was initially nonsolvated, but the single crystals grown by slow diffusion of hexane into benzene solution contain one molecule of benzene as a solvent of crystallization. A single crystal of size 0.10 × 0.22 × 0.38 mm^3 for this compound was used. Cell parameters were determined by least-squares fit of 30 machine-centered reflections (rotation photo) for both the cases. Data were collected by the ω-scan technique in the range $2° \leq 2\theta \leq 50°$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction in any cases. All data were corrected for Lorentz−polarization effects, and an empirical absorption correction[18] was done on the basis of an azimuthal scan of six reflections for each crystal. Of the 9051 (Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)$-$(\eta^2\text{-}MeCO_2)$) and 10 012 (Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}PhCO_2) \cdot C_6H_6$) reflections collected, 8571 and 9404 were respectively unique of which 4531 and 2975 satisfying $I > 3\sigma(I)$ were respectively used for structure solutions and refinement. There were no systematic absences, and the structures were successfully solved in the space group $P\bar{1}$.

In each case the metal atom was located from Patterson maps, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least-squares procedures. All the non-hydrogen atoms of Ru(η^1-$MeC_6H_4L)(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ were refined anisotropically, and the hydrogen atoms were located by difference maps and refined with a fixed U = 0.08 Å^2 using a riding model. All the non-hydrogen atoms except two PPh_3

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carbons of the Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)·C$_6$H$_6$ were refined anisotropically, and the hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2. The highest residuals were 0.54 e Å^{-3} (Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$) and 0.66 e Å^{-3} (Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)·C$_6$H$_6$). All calculations were done on a MicroVaxII computer using the SHELXTL-PLUS program package.[19] Significant crystal data are listed in Table 5.

Computer Generation of Motif 5. The relative positions of CO and the carboxylate chelate are retained as in Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$) and Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)·C$_6$H$_6$, but the phenolic oxygen (O1) (the phenolic C−O lengths are 1.369 and 1.362 Å for the respective complexes) is shifted so as to correspond to the relative position in **1**. The O1···O4 distances are then found to be 2.16 and 2.45 Å for the acetate and benzoate motifs, respectively.

Computation of Chemical Shift Due to PPh$_3$ Ring Currents. The parameters taken from the crystallographic data for Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$) are (i) distance of the concerned proton from the centroid (G) of each 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 parameters the cylindrical coordinates[20] ρ and z of the concerned proton were calculated in units of the radius of the benzene hexagon.[4] The ρ and z values were then used to compute the shift with the help of available isoshielding plots.[4] The net shift was calculated by summing up individual contributions.

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Supporting Information Available: For Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-MeCO$_2$) and Ru(η^1-MeC$_6$H$_4$L)(PPh$_3$)$_2$(CO)(η^2-PhCO$_2$)·C$_6$H$_6$, tables of complete bond distances (Tables S1 and S6) and angles (Tables S2 and S7), anisotropic thermal parameters (Tables S3 and S8), hydrogen atom positional parameters (Tables S4 and S9), and non-hydrogen atomic coordinates and U values (Tables S5 and S10) (15 pages). Ordering information is given on any current masthead page.

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