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A Family of Ruthenium Aryls Incorporating an η^2-Bonded Nitrite or Nitrate and a Pendant Imine−Phenol Function

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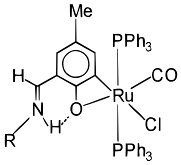
The reaction of carbonylchloro[4-methyl-6-(NR-iminio)phenolato-*C*^{2},*O*]bis(triphenylphosphine)ruthenium(II), $\mathrm{Ru^{II}}(\eta^2\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})\mathrm{Cl}$ (R = Ph, *p*-$\mathrm{MeC_6H_4}$), **1**, with NaY (Y = $\mathrm{NO_2}$, $\mathrm{NO_3}$) has afforded new organometallics of the type carbonyl(nitrito or nitrato)[4-methyl-6-(NR-imino)phenol-*C*^{2}]bis(triphenylphosphine)ruthenium(II), $\mathrm{Ru^{II}}(\eta^1\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-Y})$ (**2**, Y = $\mathrm{NO_2}$; **3**, Y = $\mathrm{NO_3}$). The transformation probably occurs via associative cis attack on chloride by $\mathrm{Y^-}$. The reconversion **2** (**3**) → **1** is achievable by treating **2** (**3**) with excess halide. The X-ray structures of $\mathrm{Ru}(\eta^1\text{-PhL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_2})$ and $\mathrm{Ru}(\eta^1\text{-PhL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_3})$ have revealed the presence of (i) *O,O′*-chelated $\mathrm{Y^-}$, (ii) monodentate PhL binding via an aromatic carbon atom lying cis to the CO molecule, and (iii) O(phenolic)···N(imine) hydrogen bonding. The interconversion between **1** and **2** (**3**) is attended with iminium−phenolate to imine−phenol tautomerization and a change in the rotational conformation of the RL ligand. Crystal data for the complexes are as follows. $\mathrm{Ru}(\eta^1\text{-PhL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_2})$: crystal system, monoclinic; space group, $P2_1/c$; $a = 18.597(9)$ Å, $b = 11.947(7)$ Å, $c = 20.362(5)$ Å, $\beta = 101.15(3)°$; $V = 4439(4)$ Å^3; $Z = 4$; $R = 0.0427$; $R_w = 0.0458$. $\mathrm{Ru}(\eta^1\text{-PhL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_3})$: crystal system, monoclinic; space group, $P2_1/c$; $a = 18.726(11)$ Å, $b = 11.857(4)$ Å, $c = 20.443(8)$ Å, $\beta = 102.77(4)°$; $V = 4426(3)$ Å^3; $Z = 4$; $R = 0.0654$; $R_w = 0.0659$.

Introduction

A few years ago a family of ruthenium organometallics of type **1** incorporating the zwitterionic iminium−phenolato motif was discovered in this laboratory as the product of decarbonylative metalation of 4-methyl-2,6-diformylphenol by $\mathrm{Ru(PPh_3)_3Cl_2}$ in the presence of a primary amine ($\mathrm{RNH_2}$).[1] It has now been found that the chloride atom in **1** is subject to facile replacement by certain other anions, the process being attended with interesting secondary structural changes.



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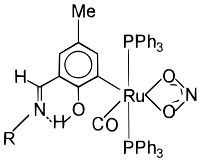
Herein we disclose the findings on the reaction of **1** with sodium nitrite and nitrate. Chloride is displaced, and in each case the entering anion binds the metal in the chelating O,O-mode, which is very rare in ruthenium(II)−nitrite/nitrate coordination chemistry. The displacement of chloride is associated with concomitant changes in the binding mode, tautomeric state, and rotameric conformation of the Schiff base ligand. These transformations are scrutinized and rationalized in the light of spectral and bond parametric data. The X-ray structures of two representative examples are reported.

Results and Discussion

(A) Synthetic Reactions. Complex **1** will be abbreviated as $\mathrm{Ru}(\eta^2\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})\mathrm{Cl}$ and the nitrite and nitrate complexes as $\mathrm{Ru}(\eta^1\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_2})$, **2**, and $\mathrm{Ru}(\eta^1\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-NO_3})$, **3**. The treatment of the solution of **1** in a dichloromethane−acetone mixture with excess aqueous sodium nitrite results in a color change from violet to yellow. From the reaction mixture **2** is isolated in high yields as a bright yellow crystalline solid. The reaction of **1** with sodium nitrate proceeds similarly, affording **3**. The syntheses are summerized in eq 1.



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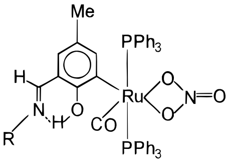

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$$\underset{\mathbf{1}}{\mathrm{Ru}(\eta^2\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})\mathrm{Cl}} + \mathrm{NaY} \longrightarrow \underset{\substack{\mathbf{2},\ \mathrm{Y} = \mathrm{NO_2}\\ \mathbf{3},\ \mathrm{Y} = \mathrm{NO_3}}}{\mathrm{Ru}(\eta^1\text{-RL})(\mathrm{PPh_3})_2(\mathrm{CO})(\eta^2\text{-Y})} + \mathrm{NaCl} \qquad (1)$$

The organometallics synthesized in the present work (R = Ph and *p*-$\mathrm{MeC_6H_4L}$) are listed in Table 1. All of these are diamagnetic, consistent with the ruthenium(II) description.

(B) Characterization. The complexes display two characteristic allowed electronic transitions at 390 and 320 nm, the latter being more intense (Table 1). The yellow color of **2** and **3** is to be contrasted with the violet color of **1** associated with an allowed band near 530 nm.[1] The $\mathrm{Ru^{II}}(\eta^1\text{-RL})$ (**2** and **3**) and $\mathrm{Ru^{II}}(\eta^2\text{-RL})$ (**1**) chromophores are thus easily distinguishable from their spectra in the UV−vis region. The infrared spectra (Table 1) of **2** and **3** are consistent with the chelation of $\mathrm{NO_2^-}$ and $\mathrm{NO_3^-}$ and with the imine−phenol hydrogen-bonding mode within RL; *vide infra.*

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Table 1. Electronic, IR Spectral Data, and Reduction Potentials

compound	UV−vis data[a] λ_{max} (ϵ,[b] M^{-1} cm^{-1}), nm	IR data,[c] cm^{-1} NO_2^-/NO_3^-			C≡O	C=N	reducn potentials[d] $E_{1/2}$ (ΔE_p, mV), V
2, R = Ph	390 (4810), 320 (16230)	1270 (m)	1195 (s)	860 (m)	1920 (vs)	1580 (s)	0.77 (170)
2, R = *p*-MeC_6H_4	390 (4730), 320 (16100)	1270 (m)	1200 (s)	855 (m)	1920 (vs)	1590 (s)	0.69 (180)
3, R = Ph	390 (4090), 320 (16140)	1520 (vs)	1255 (s)	1010 (m)	1925 (vs)	1580 (s)	0.74 (160)
3, R = *p*-MeC_6H_4	390 (3840), 320 (15920)	1520 (vs)	1255 (s)	1010 (m)	1925 (vs)	1590 (s)	0.66 (140)

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

Table 2. ^1H NMR Data in $CDCl_3$[a−c]

compound	δ, ppm 42-H[s]	40-H[s]	44-H[s]	0-H[s]	41-Me[s]	48-Me[s]
2, R = *p*-MeC_6H_4	6.29	7.04	8.10	12.62	1.97	2.39
3, R = *p*-MeC_6H_4	6.26	6.84	8.09	12.86	1.92	2.39

[a] Atom numbering is as in Figures 1 and 2. [b] TMS is used as internal standard. [c] Aryl protons, 7.10−7.40[m]. [s] singlet. [m] multiplet.

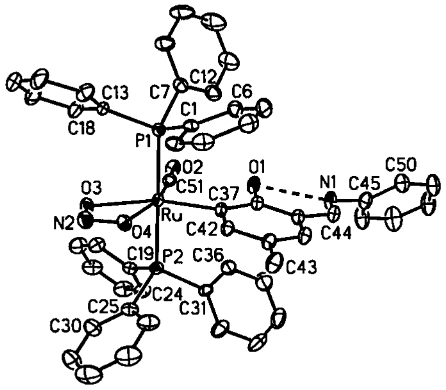

Figure 1. ORTEP plot (40% probability ellipsoids) and atom-labeling scheme for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2).

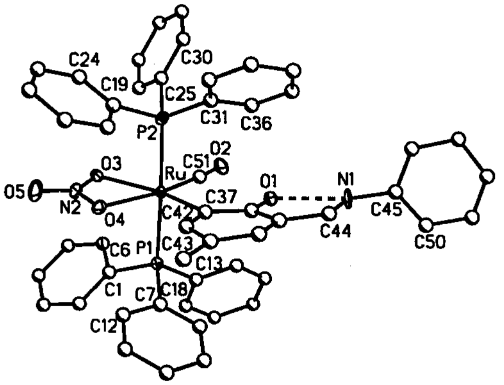

Figure 2. Perspective view and atom-labeling scheme for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3).

Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2)

Distances			
Ru−P1	2.391(2)	Ru−P2	2.397(2)
Ru−O3	2.239(4)	Ru−O4	2.196(4)
Ru−C37	2.062(5)	Ru−C51	1.811(6)
O2−C51	1.155(6)	N1−C44	1.274(7)
O3−N2	1.268(7)	O4−N2	1.270(7)
O1···N1	2.610(12)		
Angles			
P1−Ru−P2	178.5(1)	P1−Ru−O3	92.7(1)
P1−Ru−O4	85.4(1)	P1−Ru−C37	89.8(2)
P1−Ru−C51	93.9(2)	P2−Ru−C37	90.2(2)
P2−Ru−O4	93.2(1)	P2−Ru−O3	86.6(1)
P2−Ru−C51	87.6(2)	O3−Ru−C37	154.9(2)
O3−Ru−O4	56.3(1)	O3−Ru−C51	108.4(2)
O4−Ru−C37	99.1(2)	O4−Ru−C51	164.5(2)
C37−Ru−C51	96.3(2)	Ru−C51−O2	174.1(5)
Ru−O3−N2	95.3(3)	Ru−O4−N2	97.3(3)
O3−N2−O4	111.1(5)		

The high-resolution ^1H NMR spectra of two representative complexes ($CDCl_3$, 270 MHz) have been assigned (Table 2). Using the atom numbering schemes of Figures 1 and 2 (see below), we note that the singlets due to 40-H (~7 ppm), 41-Me (~2 ppm), and 42-H (~6 ppm) occur at relatively high fields. The X-ray structures described in the next section reveal that these protons indeed lie well within the shielding cones at phosphine phenyl rings.[1c,2] The extent of upfield shift due to this effect has been estimated from crystallographic data and available isoshielding ρ-z plots[3] in the case of **2** (R = Ph): 42-H, 0.97; 40-H, 0.75; 41-Me, 0.61 ppm. The nature and shift of ^1H signals of protons within the hydrogen-bonded RL ligand will be considered in a later section.

In dichloromethane solution, **2** displays a quasireversible one-electron response assigned to the Ru^{III}/Ru^{II} couple. The behavior of **3** is similar. The oxidized complexes are however unstable and could not be isolated. For a given *R* and $E_{1/2}$ (Table 1) values do not differ significantly between the nitrite and nitrate complexes.

(C) Structure of Nitrites. (1) Geometry and Bond Parameters. The X-ray structure of Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) has authenticated the binding mode **2**. A view of the molecule is displayed in Figure 1, and selected bond parameters are listed in Table 3. The nitrite ligand is chelated and the two PPh_3 donors lie in trans positions, the P1−Ru−P2 angle being 178.5(1)°. The Ru^{II}−P lengths, 2.391(2) and 2.397(2) Å, are normal.[4] The PhL ligand is coordinated to the metal only at the C37 site, the phenolic oxygen being too far away for significant coordination, Ru···O1, 3.441(10) Å. The coordinated carbon monoxide is located cis to C37.

On the basis of covalent radii, the Ru^{II}−C(sp^2) length has been estimated to be 2.06 Å.[5] Depending on ligands, the

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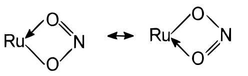
experimental values span the range 1.96−2.16 Å.[4h,6] In the nitrite complex, however, the Ru−C37 length has a near-ideal value, 2.062(5) Å. Because of the radius trend C(sp^2) > C(sp) and Ru−CO back-bonding, the Ru^{II}−CO(Ru−C51) length is expected to be much shorter than the Ru−C37 length, and so it is at 1.811(6) Å which is normal for ruthenium(II) carbonyls.[4h,i,7] In Ru(η^2-MeC_6H_4L)($(PPh_3)_2$)(CO)Cl, the two Ru−C lengths are 2.043(6) and 1.800(7) Å.[1a]

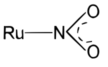
(2) Nitrite Chelation and Related Parameters. The nitrite chelation bite angle is 56.3(1)° and because of this extreme acuteness some other cis angles become obtuse, e.g., O3−Ru−C51, 108.4(2)°. Similarly trans angles involving nitrite O3 or O4 deviate considerably from the ideal 180°, such as O3−Ru−C37, 154.9(2)°. In effect, the $RuC_2P_2O_2$ coordination sphere in the complex is severely distorted from the model octahedral geometry.

The four-membered Ru(η^2-NO_2) chelate ring is nearly perfectly planar (plane A, mean deviation 0.001 Å). The Ru-(η^1-PhL) fragment minus the pendant Ph group also makes a good plane (plane B, mean deviation 0.06 Å) to which the Ph group makes a dihedral angle of 52°. The inclination between planes A and B is 9.9°. The metal center along with the coordinated carbon and oxygen atoms (C37, C51, O3, O4) defines a good plane (mean deviation 0.05 Å). Interestinghly the P1−Ru−P2 axis is nearly perpendicular to plane B. Otherwise, at least one phenyl ring of each PPh_3 ligand would approach the plane too closely. The observed distances of the centroids of the PPh_3 phenyl rings from the centroid of the metallated benzene ring are 4.11, 5.94, and 7.31 Å for P(1)Ph_3 and 4.10, 5.94, and 7.12 Å for P(2)Ph_3.

In the Ru(η^2-NO_2) fragment the Ru−O3 distance, 2.239(4) Å, is significantly longer than the Ru−O4 distance, 2.196(4) Å, due to the trans influence of the carbanionic C37 site. The two N−O distances, 1.268(7) and 1.270(7) Å, are, however, equal within experimental error corresponding to virtually equal weightage of the resonance forms **4a** and **4b**. Ruthenium(II) is known to afford numerous η^1-NO_2 complexes, incorporating the N-bonded motif **5**.[8] The monodentate O-bonded motif **6** has been shown to be present in Ru(salen)(NO)(NO_2).[9]



4a **4b**



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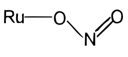

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The η^2-motif **4** characterized in this work does not appear to have been encountered before among ruthenium(II) complexes. The IR bands near 1270, 1200, and 860 cm^{-1} (Table 1) in the nitrite complexes are assigned to asymmetric N−O stretching, symmetric N−O stretching, and O−N−O bending, respectively.[10]

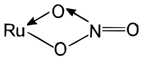
Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Ru(η^1-PhL)($(PPh_3)_2$)(CO)(η^2-NO_3)

Distances			
Ru−P1	2.384(6)	Ru−P2	2.386(7)
Ru−O3	2.262(14)	Ru−O4	2.179(12)
Ru−C37	2.057(15)	Ru−C51	1.790(16)
O2−C51	1.145(19)	N1−C44	1.246(21)
O3−N2	1.268(23)	O4−N2	1.276(20)
O1···N1	2.609(23)	O5−N2	1.217(27)

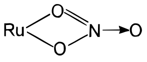
Angles			
P1−Ru−P2	177.2(2)	P1−Ru−O3	92.7(4)
P1−Ru−O4	85.1(4)	P1−Ru−C37	89.6(5)
P1−Ru−C51	94.7(6)	P2−Ru−C37	90.6(5)
P2−Ru−O4	92.1(4)	P2−Ru−O3	86.0(4)
P2−Ru−C51	88.1(6)	O3−Ru−C37	155.9(6)
O3−Ru−O4	57.9(4)	O3−Ru−C51	107.3(6)
O4−Ru−C37	98.5(5)	O4−Ru−C51	165.2(6)
C37−Ru−C51	96.4(7)	Ru−C51−O2	175.7(14)
Ru−O3−N2	91.5(11)	Ru−O4−N2	95.1(11)
O3−N2−O4	115.5(18)	O4−N2−O5	122.3(17)
O3−N2−O5	122.2(15)		

(D) Structure of Nitrates. Crystals of Ru(η^1-PhL)($(PPh_3)_2$)(CO)(η^2-NO_3) were weakly diffracting, and the final estimated standard deviations of bond parameters are relatively large (Table 4). The structure (Figure 2) is very similar to that of the nitrite complex. The PhL ligand is coordinated at C37 only. The Ru−P, Ru−C37, and Ru−C51 distances are comparable to those in the nitrite complex. The various planarity relationships and the distortions of the $RuC_2P_2O_2$ coordination sphere are also analogous for the two compounds.

The Ru(η^2-NO_3) fragment is highly planar (mean deviation 0.002 Å), and the bite angle is 57.9(4) Å. The Ru−O lengths are 2.262(14) and 2.179(12) Å—the longer distance being expectedly trans to C37. The N2−O3, 1.268(23) Å, and N2−O4, 1.276(20) Å, lengths are equal within experimental error, but the N2−O5 length, 1.217(27) Å, is significantly shorter. The resonance form of type **7a** is thus more important than that of type **7b**. This is not unusual in chelated nitrates.[11] However, no ruthenium(II) motif of type **7** appears to have been structurally characterized, although a ruthenium(IV) analogue has been.[11b] The present nitrate complexes display two strong bands at 1520 and 1255 cm^{-1} and one moderately strong band at 1010 cm^{-1}. These are assigned to N−O stretching modes, the band at 1520 cm^{-1} representing the uncoordinated N=O moiety.[10c,11]



7a



7b

(E) Tautomeric Shift between 2 (or 3) and 1. The distances between phenolic oxygen and Schiff base nitrogen, O1···N1 are 2.610(12) and 2.609(23) Å in the nitrite and nitrate

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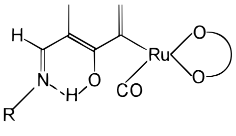
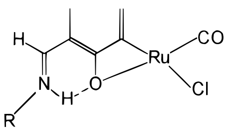
complexes, respectively. Hydrogen atoms could not be directly located in the present X-ray structural works, but charge balance consideration *vis-a-vis* spectral evidences leaves no doubt that hydrogen bonding of the imine−phenol type **8** is present in **2** and **3**. In contrast the parent chloro complexes, **1**, have the iminium−phenolate bonding in which the O···N length is significantly longer: 2.665(12) Å as in Ru(η^2-*p*-MeC_6H_4L)-$(PPh_3)_2(CO)Cl$.[1a] Between motifs **8** and **9** there is thus a prototropic shift from phenolic oxygen to azomethine nitrogen. This is very logical since metal binding to the phenolic function (as in **1**) is expected to promote proton dissociation from the function.



8

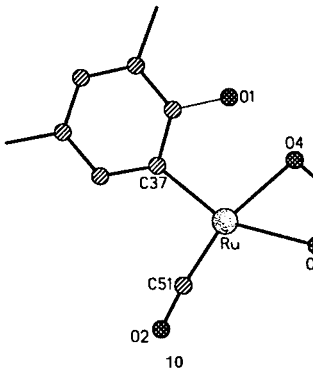


9

The two motifs **8** and **9** can be distinguished with the help of IR and ^{1}H NMR. The Schiff base C=N stretching frequency in the nitrite and nitrate complexes (motif **8**) occurs at 1580−1590 cm^{-1} (Table 1) which is significantly lower than that in motif **9** in **1** (~1620 cm^{-1}) as expected.[12] The ν_{OH} stretches in **2** and **3**, however, are too broad to be clearly observable in IR. The aldimine CH proton of the present complexes resonates at 8.1 ppm (Table 2) compared to 7.5 ppm in **1**.[1c] This high-field shift between **8** and **9** is as predicted.[12a,13] The phenolic O−H resonance of **2** and **3** occurs as a relatively sharp peak (width at half-height ~ 0.1 ppm) near 12.7 ppm (Table 2) compared to the N−H resonance of **1** near 13 ppm. The latter resonance is very broad (width at half-height ~ 0.5 ppm) presumably due to the nitrogen−quadrupole moment.

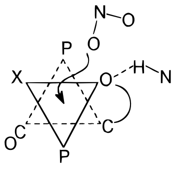
Finally we wish to note that the reaction of **1** with sodium acetate affords yellow colored complexes of the type Ru(η^1-RL)$(PPh_3)_2(CO)(\eta^2\text{-}MeCO_2)$ which are structural analogues of **2** and **3** with acetate replacing nitrite/nitrate. The IR and ^{1}H NMR characteristics of the RL ligand in the acetates are very alike those in **2** and **3**. More importantly X-ray structural characterization in one case (R = *p*-MeC_6H_4) has directly revealed the presence of motif **8**, including the crucial bridged H-atom.[1d] Here the N···O distance, 2.592(10) Å, compares very well with those in the nitrite and nitrate species. The acetate and other carboxylate complexes will be reported elsewhere.

(F) Conformational Reorganization. In **2** and **3** the carbon monoxide molecule lies cis to both the metallated carbon and phenolic oxygen as depicted in **8**. In **1** the corresponding locations are cis and trans, respectively; see **9**. The RL fragment is effectively rotated by ~180° around the Ru−C37 axis between the two structures. If a conformation of type **9** is imposed on the nitrite complex, we get a motif like **10**. Here the O1···O4 length is estimated to be 2.13 Å which represents a strongly repulsive interaction because the van der Waals radius of oxygen is 1.4 Å.[5] The situation for the nitrate complex is analogous; the O1···O4 distance in a conformation like **10**, being 2.10 Å.

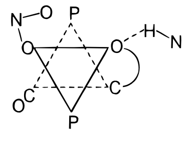


10

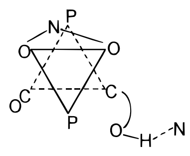
The conversion of **1** to **2** (or **3**), eq 1, can be rationalized[14] in terms of cis attack on chloride by nitrite (or nitrate). The anchored anion can then displace the phenolic oxygen, achieving chelation with concomitant conformational and tautomeric changes. These plausible events are depicted in **11**−**13** in the case of nitrite. Interestingly the prototropic and conformational reorganizations can be looked upon as distant analogues of the photochemical imine−iminium tautomerization in visual and bacterial rhodopsins, eq 2.[12a] This process is associated with an olefinic geometrical isomerization.



11



12



13

$$>C{=}N\cdots H{-}O{-} \xrightarrow{h\nu} >C{=}N{-}H\cdots O{-} \qquad (2)$$

(G) Interconversion. Treatment of **2** with excess tetraethylammonium chloride regenerates **1**. The two species are thus interconvertible, eq 3. The forward process is particularly

$$Ru(\eta^1\text{-}RL)(PPh_3)_2(CO)(\eta^2\text{-}NO_2) \underset{NO_2^-}{\overset{Cl^-}{\rightleftharpoons}} Ru(\eta^2\text{-}RL)(PPh_3)_2(CO)Cl \qquad (3)$$

favorable in acidic media, possibly due to initial proton attack on coordinated nitrite. The best method of converting **2** (or **3**) to **1** is to treat it with hydrochloric acid. The interconversion process, eq 3, is consistent with the proposed steps **11**−**13**. For example the replacement of nitrite (the forward reaction in eq 3) could begin by cis halide attack on the chelated nitrite in **13**.

Concluding Remarks

The new organometallic family, Ru(η^1-RL)$(PPh_3)_2$(CO)-(η^2-Y) (**2**, Y = NO_2; **3**, Y = NO_3) incorporating the unprecedented O,O′-chelated $Ru^{II}(\eta^2\text{-}NO_2$ or $\eta^2\text{-}NO_3)$ motif, has been synthesized by reacting Ru(η^2-RL)$(PPh_3)_2(CO)Cl$, **1**, with NaY. Apart from a change in the hapticity of the RL, the synthesis is associated with iminium−phenolate to imine−phenol tautomerization and sterically driven conformational reorganization of the RL fragment with reference to the rest of the molecule. An associative pathway is proposed, and expectedly the reverse reaction (nitrite or nitrate to chloride) is achievable in the presence of excess chloride. We are currently engaged in exploring the nature of the osmium and rhodium chemistry of the RL ligand system occurring in conjunction with carbon monoxide, triphenylphosphine, and an anion.

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Table 5. Crystallographic Data for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) and Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3)

	Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2)	Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3)
chem formula	$C_{51}H_{42}N_2O_4P_2Ru$	$C_{51}H_{42}N_2O_5P_2Ru$
fw	909.9	925.9
space group	$P2_1/c$	$P2_1/c$
a, Å	18.597(9)	18.726(11)
b, Å	11.947(7)	11.857(4)
c, Å	20.362(5)	20.443(8)
β, deg	101.15(3)	102.77(4)
V, Å^3	4439(4)	4426(3)
Z	4	4
T, °C	23	23
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.362	1.393
μ, cm^{-1}	4.72	4.78
transm coeff	0.7732−0.8212	
R,[a] %	4.27	6.54
R_w,[b] %	4.58	6.59
GOF[c]	1.30	1.33

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0003$ for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) and 0.0005 for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3). [c] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

Experimental Section

Materials. The starting materials Ru(PPh_3)$_3$$Cl_2$,[15] Os($PPh_3$)$_3$$Br_2$,[16] and Ru($\eta^2$-RL)($PPh_3$)$_2$(CO)Cl [1] complexes were prepared by reported methods. For electrochemical work the purification of dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) were done as described in the previous work.[17] Sodium nitrite, sodium nitrate, and other chemicals and solvents were of analytical grade and were used as received.

Physical Measurement. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer from 4000 to 200 cm^{-1}. An Hitachi 330 spectrometer was used to obtain electronic spectra. A Bruker 270 MHz FT NMR spectrometer was used to record ^{1}H NMR data (tetramethylsilane is the internal standard). Magnetic behavior was examined on a PAR 155 vibrating-sample magnetometer fitted with a Walker Scientific magnet. Microanalyses (C,H,N) data were obtained from a Perkin-Elmer 240 C elemental analyzer. All electrochemical measurements were performed under nitrogen atmosphere using a PAR 370-4 electrochemistry system as reported before.[17] All of the reported potentials in this work are uncorrected for junction contribution. Solution (~10^{-3} M) electrical conductivities were measured with the help of a Philips PR 9500 bridge.

Preparation of Complexes. The nitrito, Ru(η^1-RL)(PPh_3)$_2$(CO)(η^2-NO_2), and the nitrato, Ru(η^1-RL)(PPh_3)$_2$(CO)(η^2-NO_3), complexes were synthesized by reacting Ru(η^2-RL)(PPh_3)$_2$(CO)Cl with $NaNO_2$ and $NaNO_3$, respectively. Yields were 80−85% on the basis of Ru(η^2-RL)(PPh_3)$_2$(CO)Cl. Details are described for representative cases.

Carbonyl(nitrito-*O,O′*)[4-methyl-6-(phenylimino)phenol-*C*^{2}]bis(triphenylphosphine)ruthenium(II), Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2). To a vigorously stirring solution of Ru(η^2-PhL)(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 excess $NaNO_2$ (20 mg, 0.29 mmol). The stirring was continued until the dark violet solution turned yellow. The solvent was removed under reduced pressure, leaving an aqueous suspension of the yellow complex. This was filtered, washed repeatedly with water, and dried in vacuo. Anal. Calcd for $RuC_{51}H_{42}N_2O_4P_2$: C, 67.30; H, 4.65; N, 3.08. Found: C, 67.19; H, 4.69; N, 2.95.

The complex Ru(η^1-p-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-NO_2) was prepared similarly. Anal. Calcd for $RuC_{52}H_{44}N_2O_4P_2$: C, 67.58; H, 4.80; N, 3.03. Found: C, 67.65; H, 4.72; N, 3.10.

Carbonyl(nitrato-*O,O′*)[4-methyl-6-(phenylimino)phenol-*C*^{2}]bis(triphenylphosphine)ruthenium(II), Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3). This was prepared by the same procedure as that described above using $NaNO_3$ in place of $NaNO_2$. Anal. Calcd for $RuC_{51}H_{42}N_2O_5P_2$: C, 66.14; H, 4.57; N, 3.03. Found: C, 66.20; H, 4.50; N, 3.10.

The Ru(η^1-p-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-NO_3) complex was similarly prepared. Anal. Calcd for $RuC_{52}H_{44}N_2O_5P_2$: C, 66.42; H, 4.72; N, 2.98. Found: C, 66.49; H, 4.80; N, 2.95.

Conversion of Ru(η^1-*p*-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-NO_2) to Ru(η^2-*p*-MeC_6H_4L)(PPh_3)$_2$(CO)Cl. To a stirred solution of Ru(η^1-*p*-MeC_6H_4L)(PPh_3)$_2$(CO)(η^2-NO_2) (25 mg) in acetone (20 mL) and dichloromethane (5 mL) was added 3 drops of 0.3 N HCl in acetone. The yellow solution immediately turned violet, and the mixture was stirred for 0.5 h. The solvent was removed under reduced pressure, and the violet residue was washed thoroughly with water and finally filtered. The residue was dried in vacuo. Yield was 85% on the basis of the nitrite complex. Anal. Calcd for $RuC_{52}H_{44}NO_2P_2Cl$: C, 68.35; H, 4.85; N, 1.53. Found: C, 68.27; H, 4.80; N, 1.50. The complex was characterized with the help of spectra and other features.

X-ray Structure Determination. Single crystals (0.16 × 0.22 × 0.58 mm^3 for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) and 0.22 × 0.12 × 0.16 mm^3 for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3)) grown by slow diffusion of hexane into benzene solution in both cases were used. In each case cell parameters were determined by least-squares fit of 30 machine centered reflections (rotation photograph). Data were collected using the ω-scan technique in the range $3° \leq 2\theta \leq 50°$ for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) and $2° \leq 2\theta \leq 47°$ for Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3) on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Two check reflections measured after every 98 reflections showed no intensity reduction in any case. 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 the nitrite crystal. Total reflections collected, unique reflections, and used reflections for structure solution satisfying $I > 3\sigma(I)$ were as follows: (i) Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2), 8572, 7878, and 4395; (ii) Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3), 6168, 5600, and 1738. Systematic absences led to the space group $P2_1/c$ for both complexes.

In each case, the ruthenium atom was located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. In the case of Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3) the six phenyl rings of two PPh_3 displayed disorder and were refined in the "affixed" condition. The structures were refined by full-matrix least-squares procedures. All of the non-hydrogen atoms of Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2) and the ruthenium, phosphorus, oxygen, and nitrogen atoms of Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_3) were refined anisotropically. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in both cases. The highest residuals were 0.75 e Å^{-3} (Ru(η^1-PhL)(PPh_3)$_2$(CO)(η^2-NO_2)) and 0.55 e Å^{-3} (Ru(η^1-PhL)-

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$(PPh_3)_2(CO)(\eta^2\text{-}NO_3)$). All calculations were done on a MicroVax II computer using the SHELXTL-Plus program package.[19] Significant crystal data are listed in Table 5.

Computer Generation of Motif 10. Retaining the relative positions of CO and the nitrite chelate as in $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_2)$ the phenolic oxygen is shifted to the other ortho position of the metalated carbon to correspond to the relative position as in **1**. The phenolic C−O length is 1.369 Å. The O1···O4 distance is then found to be 2.13 Å. In the case of $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_3)$ the corresponding distance is 2.10 Å.

Computation of Chemical Shift Due to PPh_3 Ring Currents. The required parameters for this are the cylindrical coordinates (ρ, z)[20] of the concerned proton with respect to the centroids of PPh_3 phenyl rings. Using the crystallographic data of $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_2)$, these parameters were calculated from (i) the distance of the proton from the centroid (G) of each PPh_3 ring and (ii) the angle between the distance vector and the normal to the plane of the phenyl ring at G. Expressing the calculated ρ and z values in units of the radius of the benzene hexagon, the shifts were computed with the help of available isoshielding $\rho-z$ plots.[3] The net shift of a proton was obtained by summing up individual contributions.

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Supporting Information Available: For $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_2)$ and $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_3)$ tables of complete atomic coordinates (Tables S1 and S6), bond distances (Tables S2 and S7) and angles (Tables S3 and S8), anisotropic thermal parameters (Tables S4 and S9), and hydrogen atoms positional parameters (S5 and S10) and a figure of electronic spectra of $Ru(\eta^1\text{-}PhL)(PPh_3)_2(CO)(\eta^2\text{-}NO_2)$ and $Ru(\eta^2\text{-}PhL)(PPh_3)_2(CO)(Cl)$ (10 pages). Ordering information is given on any current masthead page.

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