A New Family of Acylrhodium Organometallics

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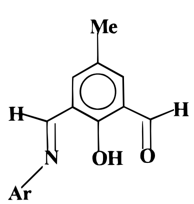
Received September 3, 1998

The Schiff mono bases of 2,6-diformyl-4-methylphenol, **1**, react with $RhCl_3 \cdot 3H_2O$ and PPh_3 in ethanol, affording dichloro[4-methyl-6-((arylimino)methyl)phenolato-*C*[1],*O*]bis(triphenylphosphine)rhodium(III), $Rh(XL_{sb})(PPh_3)_2Cl_2$ (**5**; X = H, Me, OMe, Cl). Organometallics of the type (carboxylato)[4-methyl-6-formylphenolato-*C*[1],*O*]bis(triphenylphosphine)rhodium(III), $Rh(L_{al})(PPh_3)_2(RCO_2)$ (**6**; R = H, Me, Et, Ph), have been synthesized by oxidative addition of **1** to $RhCl(PPh_3)_3$ in the presence of dilute RCO_2H in ethanol. Replacement of RCO_2H by dilute HNO_3 has afforded the nitrate analogue $Rh(L_{al})(PPh_3)_2(NO_3)$ (**7**). Species of type **5** are susceptible to aldiminium → aldehyde hydrolysis in a dichloromethane−acetone−water mixture with concomitant chloride dissociation, furnishing $Rh(L_{al})(PPh_3)_2Cl$ (**8a**), from which the N-bonded nitrite $Rh(L_{al})(PPh_3)_2(NO_2)$ (**8b**) has been generated metathetically. The four types of species **5**−**8** are interconvertible, and a possible reaction pathway involving pentacoordinate intermediates is proposed. The X-ray structures of $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (**5b**; bis(dichloromethane) adduct), $Rh(L_{al})(PPh_3)_2(MeCO_2)$ (**6b**), $Rh(L_{al})(PPh_3)_2(NO_3)$ (**7**), and $Rh(L_{al})(PPh_3)_2(NO_2)$ (**8b**) have been determined. Among these, **5b**, **6b**, and **7** are pseudooctahedral—the bonds *trans* to the acyl function being longer by 0.2−0.4 Å compared to those *trans* to phenolato oxygen. Complex **8b** is square pyramidal, there being no ligand *trans* to the acyl function. In **5b** iminium−phenolato (N···O, 2.66(1) Å) and in the remaining species aldehyde−phenolato (C···O, 2.86(1) Å) hydrogen bonding is present. Internal charge balance is crucial for the stability of the present organometallics.

Introduction

The reaction of $Ru(PPh_3)_3Cl_2$ with the Schiff mono base of 2,6-diformyl-4-methylphenol, **1**, has been shown to afford organometallics of type **2**.[1,2] The unusual four-



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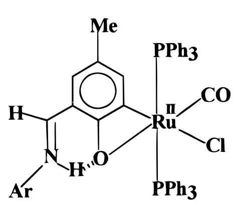

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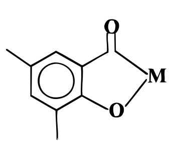

3 M = Ru^{IV}

4 M = Rh^{III}

membered metallacycle has been proposed to arise from reductive (Ru(IV) → Ru(II)) decarbonylation of an elusive acyl intermediate incorporating the ring **3** formed *via* oxidative (Ru(II) → Ru(IV)) aldehyde addition. The richness of the chemistry[1−5] of **2** has prompted us to search for organorhodium species based on **1**, with special reference to the status of the acylrhodium moiety **4**.

In the present work we have scrutinized the reaction of **1** with $RhCl(PPh_3)_3$. Aldehydes are usually decarbonylated[6−9] by $RhCl(PPh_3)_3$ (eq 1), a reaction that finds use

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10.1021/om980748e CCC: $18.00
Publication on Web 03/20/1999

in organic synthesis (*Q* = alkyl, aryl).[10,11] Acyl inter-

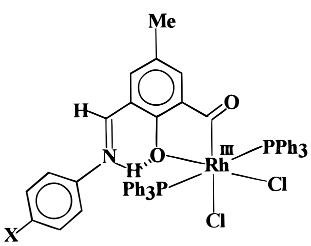
$$\mathrm{QCHO + Rh^{I}Cl(PPh_3)_3 \rightarrow QH + \mathit{trans}\text{-}Rh(CO)Cl(PPh_3)_2} \quad (1)$$

mediates formed *via* oxidative (Rh(I) → Rh(III)) addition are implicated, but these are generally very unstable with respect to reductive (Rh(III) → Rh(I)) decarbonylation. Instances of isolation and characterization of such intermediates are therefore rare.[12,13]

If decarbonylation would prevail in our reaction also, the only products would be a salicylaldimine and *trans*-Rh(CO)Cl(PPh_3)$_2$. No rhodium(I) analogue of **2** is anticipated, since the low-spin d^8 metal is already coordinatively saturated in *trans*-Rh(CO)Cl(PPh_3)$_2$. In practice, the reaction of **1** with RhCl(PPh_3)$_3$ proceeded smoothly in acidic media *without* decarbonylation, affording stable acylrhodium species incorporating motif **4**. The structure and properties of the new family of organometallics generated *via* this route are reported in this present work.

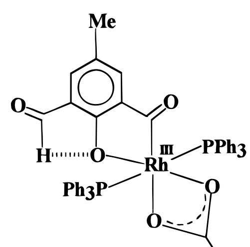
Results and Discussion

A. Synthesis. a. The Family. The title family consists of three pseudooctahedral and one distorted square pyramidal acylrhodium system. These are abbreviated as Rh(XL_{sb})(PPh_3)$_2$$Cl_2$ (**5**), Rh(L_{al})(PPh_3)$_2$(RCO_2) (**6**), Rh(L_{al})(PPh_3)$_2$(NO_3), (**7**), and Rh(L_{al})(PPh_3)$_2$(Y) (**8**).



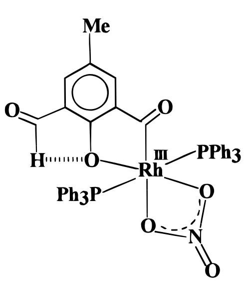
Rh(XL_{sb})(PPh_3)$_2$$Cl_2$

	X
5a	H
5b	Me
5c	OMe
5d	Cl

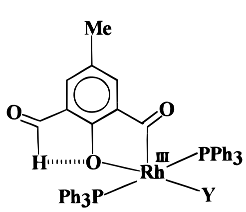


Rh(L_{al})(PPh_3)$_2$(RCO_2)

	R
6a	H
6b	Me
6c	Et
6d	Ph



Rh(L_{al})(PPh_3)$_2$(NO_3)
7



Rh(L_{al})(PPh_3)$_2$(Y)

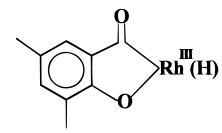
	Y
8a	Cl
8b	NO_2

b. Rh(XL_{sb})(PPh_3)$_2$$Cl_2$, 5. The type **5** organometallics are afforded in excellent yields upon reacting the Schiff mono base **1** with RhCl(PPh_3)$_3$ in boiling ethanol in the presence of dilute hydrochloric acid. The reaction is shown in eq 2. The synthesis can be conveniently

$$\mathrm{RhCl(PPh_3)_3 + \mathbf{1} + HCl \rightarrow \mathbf{5} + PPh_3 + H_2} \quad (2)$$

carried out as a single-pot process involving **1**, $RhCl_3$·$3H_2O$, and PPh_3, the last two generating RhCl(PPh_3)$_3$ and HCl *in situ*.[14,15]

In the absence of HCl the reaction of RhCl(PPh_3)$_3$ and **1** affords only *trans*-Rh(CO)Cl(PPh_3)$_2$, presumably formed *via* reductive decarbonylation of a hydridoacyl intermediate incorporating motif **9**. The acid (here HCl) is



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believed to facilitate rapid proton-assisted displacement of hydride from **9** by chloride. The acid also sustains the cationic aldiminium moiety, which helps to stabilize the system (*vide infra*). Upon using 2,6-diformyl-4-methylphenol in place of **1** in eq 2, rapid decarbonylation occurs and only *trans*-Rh(CO)Cl(PPh_3)$_2$ is isolated.

c. Rh(L_{al})(PPh_3)$_2$(RCO_2) (6) and Rh(L_{al})(PPh_3)$_2$(NO_3) (7). The reaction (eq 3) of RhCl(PPh_3)$_3$ with **1** in the presence of dilute carboxylic acids proceeds in a manner similar to that of eq 2 but with concomitant hydrolysis of the aldimine function affording **6** in excellent yields. Upon replacing RCO_2H by HNO_3, the

$$\mathrm{Rh^{I}Cl(PPh_3)_3 + \mathbf{1} + RCO_2H + H_2O \rightarrow \mathbf{6} + PPh_3 + XC_6H_4NH_2{\cdot}HCl + H_2} \quad (3)$$

nitrate **7** is obtained. We have been able to isolate **6** and **7** only *via* this substitution-cum-hydrolysis route.

Use of 2,6-diformyl-4-methylphenol in place of the Schiff base **1** in eq 3 leads to decarbonylation, affording *trans*-Rh(CO)Cl(PPh_3)$_2$. This prompts us to propose that in the present synthesis the cation $[Rh(XL_{sb})(PPh_3)_2(RCO_2)]^+$ incorporating the aldiminium function is first formed in the same manner as **5** is formed in eq 2. It is, however, subject to facile nucleophilic water attack

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furnishing electroneutral **6** *via* rapid aldiminium → aldehyde hydrolysis.

d. Rh(L_{al})(PPh_3)$_2$(Y) (8). Aldimine → aldehyde hydrolysis occurs in the case of **5** also upon boiling its solution in a dichloromethane–acetone mixture with water. The process is associated with concomitant dissociation of a chloride ligand, affording electroneutral **8a** (eq 4). In **5** the Rh–Cl bond *trans* to the acyl function

$$\mathbf{5} + H_2O \rightarrow \mathbf{8a} + XC_6H_4NH_2{\cdot}HCl \qquad (4)$$

is reletively weak (*vide infra*), and it is this bond that undergoes ionic dissociation. The synthesis of **8b** involves metathesis between **8a** with $NaNO_2$ (eq 5).

$$\mathbf{8a} + NaNO_2 \rightarrow \mathbf{8b} + NaCl \qquad (5)$$

e. Stability. The Rh–C(acyl) bond in the present complexes is stabilized by chelate formation involving phenolato oxygen. All members in the family **5**–**8** are indefinitely stable in the solid state and in dry halocarbon (CH_2Cl_2, $CHCl_3$) solutions. The type **5** complexes are sparingly soluble in ethanol, and dissolution in boiling ethanol is associated with reductive decarbonylation to *trans*-Rh(CO)Cl(PPh_3)$_2$. In the synthesis of **5** it is therefore necessary to optimize the reaction time so that *trans*-Rh(CO)Cl(PPh_3)$_2$ remains only a minor byproduct. In contrast to **5**, **6**–**8** have good solubility in ethanol and the solutions are thermally stable.

Internal charge balance is a crucial stabilizing factor in this family of organometallics. In this context we note the intimate relationship between the charge of the anion(s) bonded to the metal and the state of the remote side chain on the phenolato–acyl ligand. Thus, when two chloride ligands are present, electroneutrality is achieved in the form of **5**, where the side chain is in the aldiminium form. In **8** only one chloride ligand is present and the side chain becomes aldehydic (**6** and **7** are similar). We have not succeeded in isolating cationic species such as $[Rh(XL_{sb})(PPh_3)_2(RCO_2)]^+$, which was implicated as a hydrolytically unstable intermediate in the synthesis of **6**; neither have we been able to prepare an anionic system such as $[Rh(L_{al})(PPh_3)_2Cl_2]^-$.

The aldehyde function in **6**–**8** is a potential site of further oxidative addition to $RhCl(PPh_3)_3$. In practice, however, no reaction occurs even on prolonged boiling in ethanol. The formyl function in **6**–**8** is deactivated by the existing acyl moiety and the bulk of the neighboring Rh(PPh_3)$_2$ fragment.

B. Spectra. The colors of type **5** (orange-yellow) and type **6**–**8** (yellow) are due to MLCT($t_2 \rightarrow \pi^*$) absorption occurring near 500 and 425 nm, respectively. The acyl C=O stretch[13b,16] is observed as a strong band near 1700 cm^{-1}. Two well-separated Rh–Cl stretch (near 320 and 350 cm^{-1}) occur in **5**, consistent with the *cis*-$RhCl_2$ configuration having two Rh–Cl bonds of unequal lengths. Significantly, the single Rh–Cl stretch in **8a** is at 350 cm^{-1}. The two carboxyl vibrations[3,13e,17] in **6**, the three nitrate vibrations[4,18] in **7**. and the three nitrite vibrations[18e,19] in **8b** are consistent with the designated bonding modes.

Table 1. Ring Current Shifts (ppm)[a] of ^{1}H NMR Signals of 5b, 6b, 7, and 8b[b]

compd	3-H	5-H	4-Me	9-H	10-Me
5b	1.00 (0.90)	*c*	0.24 (0.30)		
6b	1.33 (0.90)	0.50 (0.20)	0.50 (0.20)	0.60 (0.70)	0.94 (1.35)
7	1.20 (1.40)	0.58 (0.53)	0.43 (0.45)	0.71 (0.68	
8b	0.91 (0.90)	0.29 (0.36)	0.44 (0.34)	0.83 (0.50)	

[a] Calculated shifts are in parentheses. [b] The atom-numbering scheme is the same as in X-ray structures (see Figures 1–4). [c] Not individually resolved; lies within a complex multiplet of aromatic protons (7–8 ppm).

A characteristic feature of the ^{1}H NMR spectra of the present organometallics is the significant upfield shift of several proton signals of chelated XL_{sb} and L_{al} ligands relative to **1** and 2,6-diformyl-4-methylphenol. The X-ray structural results (*vide infra*) revealed that ring currents due to phosphine phenyl rings can be the primary origin of such shifts. Using structural parameters and isoshielding ρ–z plots[20] the expected shifts due to ring current have been estimated in the case of **5b**, **6b**, **7**, and **8b**. These are listed in Table 1 along with the corresponding observed shifts. The agreement is generally satisfactory. The most shifted protons are 3-H (all cases), 9-H (**6b**, **7**, **8b**), and 10-Me[21] (**6b**).

C. Structure. a. Geometrical Features. The X-ray structures of **5b** (bis(dichloromethane) adduct), **6b**, **7**, and **8b** have been determined. Molecular views are shown in Figures 1–4, and selected bond parameters are listed in Tables 2–4. To our knowledge, instances where acyl complexes have been isolated by the reaction of $RhCl(PPh_3)_3$ with aldehydes followed by X-ray structural characterization are rare, probably unknown. The present structures are of particular significance in this context. The structures of a few rhodium acyl complexes formed *via* other routes have been documented.[13a–f]

In **5b**, **6b**, and **7** the coordination spheres are severely distorted from idealized octahedral geometry. In **5b** the Rh(MeL_{sb})Cl_2 fragment defines a crystallographic plane of symmetry (x, $^1/_4$, z). The Rh(L_{al}) fragments in **6b** and **7** constitute good planes (plane A, mean deviation ≤0.05 Å), and the carboxylate (**6b**) and nitrate (**7**) chelate rings are nearly perfectly planar (plane B, mean deviation ≤0.01 Å). The dihedral angle between A and B is 11.7° in **6b** and 4.0° in **7**. Thus, the bulk of the equatorial region increases in the order **5b** < **7** < **6b**, and this is attended by a corresponding increase in the P–Rh–P angle in the same order.

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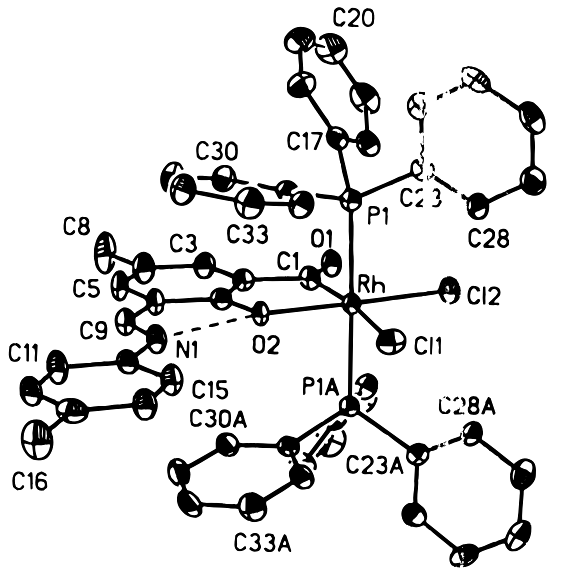

Figure 1. ORTEP plot (30% probability ellipsoids) and atom-labeling scheme for **5b**·$2CH_2Cl_2$.

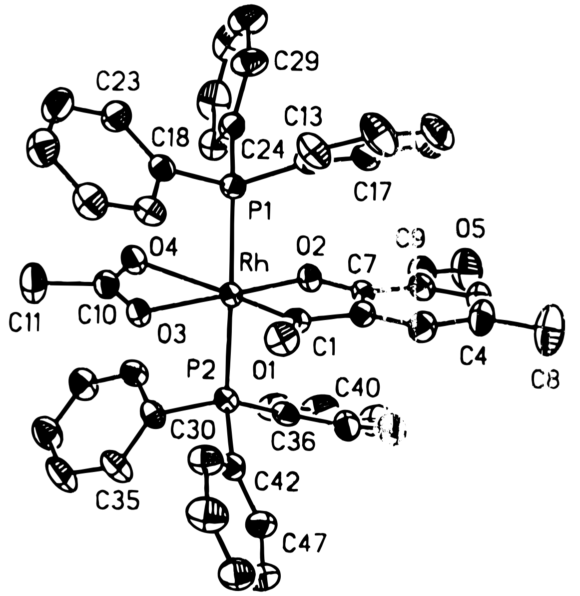

Figure 2. ORTEP plot (30% probability ellipsoids) and atom-labeling scheme for **6b**.

In **8b** the coordination sphere has distorted-square-pyramidal geometry. The donor atoms P1, P2, O2, and N1 constitute an excellent equatorial plane (mean deviation 0.02 Å), from which the metal atom is shifted by 0.15 Å toward the acyl carbon atom. The $Rh(NO_2)$ plane (mean deviation 0.02 Å) makes a dihedral angle of 86.1° with the equatorial plane and 12.8° with the $Rh(L_{al})$ plane (mean deviation 0.06 Å).

b. Bond Lengths. The observed Rh−C(acyl), C=O(acyl), and Rh−P lengths fall within reported ranges—1.94−1.99 Å,[13a−d] 1.18−1.22 Å,[13a−d] and 2.30−2.40 Å,[22] respectively. The Rh−N distance in **8b** (1.997(5) Å) is shorter than that in $Rh(NO_2)_6^{3-}$ (2.06 Å).[23]

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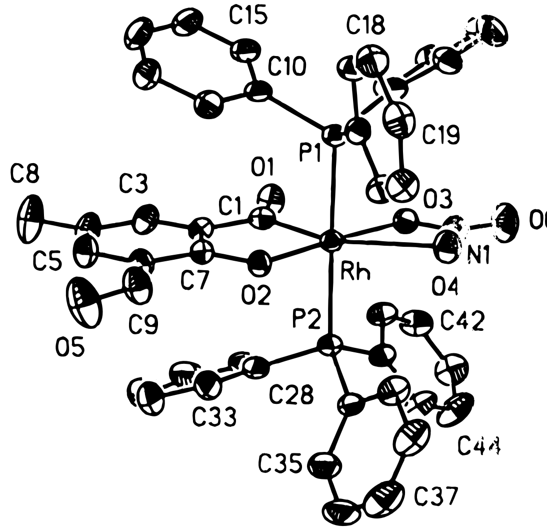


Figure 3. ORTEP plot (30% probability ellipsoids) and atom-labeling scheme for **7**.

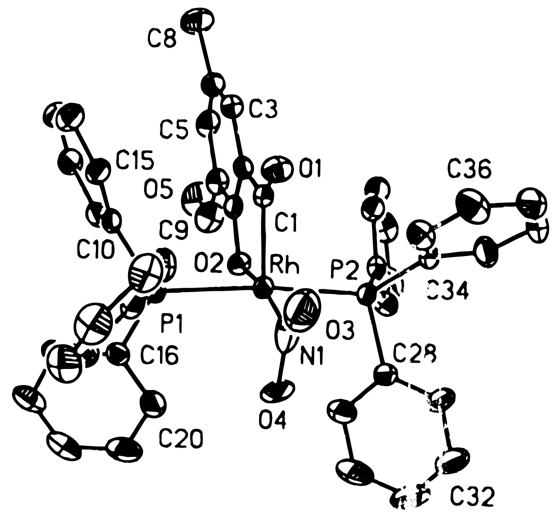


Figure 4. ORTEP plot (30% probability ellipsoids) and atom-labeling scheme for **8b**.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 5b·$2CH_2Cl_2$

	Distances		
Rh−C1	1.983(9)	Rh−Cl2	2.365(3)
Rh−O2	2.070(6)	Rh−Pl	2.367(2)
Rh−Cl1	2.552(3)	Rh−PlA	2.367(2)
Cl−O1	1.203(11)	N1···O2	2.663(1)
	Angles		
C1−Rh−O2	83.8(3)	O2−Rh−Cl1	86.8(2)
Cl1−Rh−Cl2	96.2(1)	Cl2−Rh−Cl	93.2(3)
Pl−Rh−P1A	173.4(1)	Cl−Rh−Cl1	170.6(3)
O2−Rh−Cl2	177.0(2)	P1−Rh−Cl	92.6(1)
P1−Rh−O2	88.2(1)	P1−Rh−Cl1	87.1(1)
P1−Rh−Cl2	91.9(1)		

The structures provide an unique opportunity for observing the strong *trans* influence of the acyl function. The two Rh−Cl distances in **5b**, Rh−O(acetate) distances in **6b**, and Rh−O(nitrate) distances in **7** differ by ~0.2, ~0.3, and ~0.4 Å, respectively. In each case the longer and shorter bonds lie respectively *trans* to the acyl and phenolato functions.

The C−O(acetate), N−O(nitrate), and N−O(nitrite) distances in **6b**, **7**, and **8b** are consistent with the

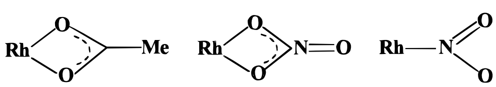
Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 6b and 7

	6b	7		6b	7
Distances					
Rh−C1	1.955(5)	1.965(7)	C10−O3	1.261(6)	
Rh−O2	2.045(3)	2.038(4)	C10−O4	1.237(7)	
Rh−O3	2.089(4)	2.077(4)	N1−O3		1.278(8)
Rh−O4	2.402(4)	2.495(6)	N1−O4		1.246(7)
Rh−P1	2.368(2)	2.359(2)	N1−O6		1.206(8)
Rh−P2	2.368(2)	2.370(2)	C9···O2	2.861(1)	2.860(1)
C1−O1	1.226(6)	1.194(7)			
Angles					
C1−Rh−O2	82.7(2)	83.9(2)	P1−Rh−O2	91.0(1)	88.4(1)
O2−Rh−O4	115.2(1)	120.2(2)	P1−Rh−O4	83.0(1)	84.4(1)
O4−Rh−O3	57.3(1)	55.0(2)	P1−Rh−O3	91.6(1)	91.1(1)
O3−Rh−Cl	105.3(2)	100.9(2)	P2−Rh−Cl	91.2(1)	91.4(1)
P1−Rh−P2	178.2(1)	176.4(1)	P2−Rh−O2	90.8(1)	89.8(1)
Cl−Rh−O4	160.4(2)	155.3(2)	P2−Rh−O4	96.2(1)	93.7(1)
O2−Rh−O3	171.6(1)	175.2(2)	P2−Rh−O3	86.6(1)	90.4(1)
P1−Rh−C1	89.1(1)	91.6(1)			

Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 8b

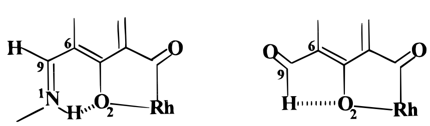
Distances			
Rh−C1	1.975(5)	Rh−O2	2.059(3)
Rh−N1	1.997(5)	Rh−P1	2.369(2)
Rh−P2	2.376(2)	N1−O3	1.094(8)
N1−O4	1.334(7)	C1−O1	1.205(6)
		O9···O2	2.860(1)
Angles			
C1−Rh−O2	83.3(2)	C1−Rh−N1	106.5(2)
C1−Rh−P1	90.1(1)	C1−Rh−P2	95.7(1)
O2−Rh−N1	170.1(2)	P1−Rh−P2	173.8(1)

approximate valence-bond structures **10**, **11**, and **12**, respectively. The length of the shorter N−O bond (1.094(3) Å) in **8b** approaches that of nitric oxide and the complex is thus a potentially good candidate for oxo-transfer activity.[19a,24]



10 **11** **12**

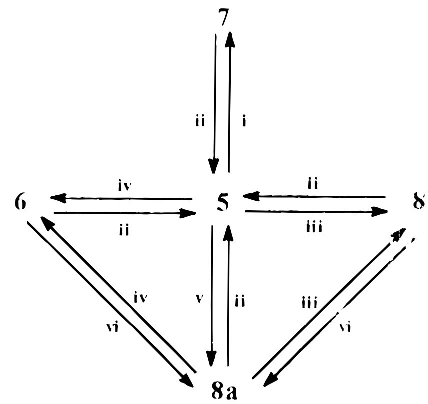
c. Aldiminium−Phenolato and Aldehyde−Phenolato Moieties. The nonhydrogen atoms of the aldiminium−phenolato moiety **13** present in **5b** define a virtually perfect plane. The observed N1···O2 length,



13 **14**

2.663(11) Å, is the same as that, 2.665(12) Å, in the ruthenium complex **2** (Ar = *p*-tolyl), where the iminium hydrogen was directly located.[2] The iminium N−H stretch in **5** occurs near 3400 cm^{-1},[25] and in ^1H NMR the iminium proton resonates near 14 ppm, giving rise to a relatively broad signal which disappears upon shaking with D_2O. Further, the presence of the aldiminium function in **5** is consistent with relatively high C=N stretching frequency[25,26] (~1635 cm^{-1}) and a high-field shift[27] of the C−H proton signal (~7.3 ppm; 8.7 ppm in **1**).

Scheme 1



Reagents:

i = $NaNO_3$, ii = $MeArNH_2.HCl$, iii = $NaNO_2$
iv = $NaMeCO_2$, v = H_2O , vi = HCl

Reaction media:

CH_2Cl_2-Me_2CO-H_2O: i , iii , iv , v
EtOH-H_2O: ii ,vi

The nearly perfectly planar aldehyde−phenolato moiety **14** is present in **6b**, **7**, and **8b**. All hydrogen atoms were resolved in difference Fourier maps in the case of **8b**. The C9···O2 distance is 2.86(1) Å in all the species. The rotameric conformations of **13** and **14** around the C6−C9 axis differ by 180°, consistent with the presence of hydrogen bonding.

d. Interconversion. (i) Species 5−8. The four groups of organometallics reported in this work are readily interconvertible upon treatment with appropriate reagents. Some of the interconversions centered around **5** are shown in Scheme 1. Thus, when **5** is reacted with excess carboxylates or free carboxylic acids, **6** is obtained in excellent yields and the reverse reaction occurs on treating **6** with $XC_6H_4NH_2{\cdot}HCl$ (excess) and HCl (eq 6).

$$\mathbf{5} + RCO_2H + H_2O \underset{EtOH}{\overset{CH_2Cl_2-Me_2CO-H_2O}{\rightleftharpoons}} \mathbf{6} + XC_6H_4NH_2{\cdot}HCl + HCl \quad (6)$$

In the conversion of **5** to the other species the reaction medium always contains water. In view of the facile nature of the reaction **5** → **8a**, it is plausible that the conversions of **5** to the other species proceed through pentacoordinated **8a**. For example, the reaction **5** → **6** can proceed *via* occupation of the vacant site by a carboxyl oxygen followed by displacement of chloride ligand and completion of chelate ligation (Scheme 2).

(ii) Comparison with Ruthenium. The pair **5** and **6** provides a contrast to the ruthenium pair **2** and **15**,

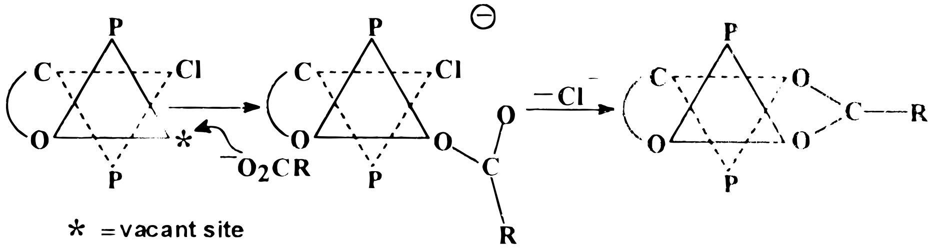
(24) Sieker, F.; Blake, A. J.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1996**, 1419.

(25) (a) Sandorfy, C.; Vocelle, D. *Mol. Phys. Chem. Biol.* **1989**, *IV*, 195. (b) Chevalier, P.; Sandorfy, C. *Can. J. Chem.* **1960**, *38*, 2524. (c) Favrot, J.; Vocelle, D.; Sandorfy, C. *Photochem. Photobiol.* **1979**, *30*, 417.

(26) Bohme, H.; Haake, M. In *Advances in Organic Chemistry*; Bohme, H., Viehe, H. G., Eds.; Interscience: New York, 1976; Part 1, Vol. 9, p 1.

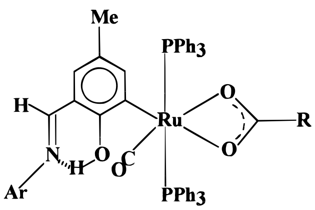
(27) Sharma, G. M.; Roels, O. A. *J. Org. Chem.* **1973**, *38*, 3648.

Scheme 2



8a **6**

which are also interconvertible. In the **5**, **6** pair substi-



15

tution of chloride by carboxylate occurs in the ratio 2:1, but in the **2**, **15** pair this ratio is 1:1. Electroneutrality thus remains unaffected by the substitution in the latter case and there is no aldiminium hydrolysis in the conversion **2** → **15**, unlike in **5** → **6**. Chelation by RCO_2^- is accommodated in **15** by sacrificing the Ru−O(phenolato) bond present in **2**. The process is attended with aldiminium−phenolato → aldimine−phenol tautomerization and a rotameric transformation around the Ru−C(aryl) axis.[3]

The case of nitrites provides another notable rhodium−ruthenium contrast, highlighting the qualitative effect of the acyl trans influence on the binding of ligands. In the case of rhodium a pentacoordinated structure, **8b**, with a strong $Rh-NO_2$ bond is preferred to a hexacoordinated situation involving O,O-chelation weakened by acyl *trans* influence. For ruthenium this effect is absent and nitrite is chelating (as in **15** with RCO_2^- replaced by NO_2^-).

Concluding Remarks

Organometallics of type **5**−**7** incorporating acyl−phenolate chelation have been synthesized *via* oxidative addition of the Schiff mono base **1** to $RhCl(PPh_3)_3$ in acidic media. These are rare instances where the aldehyde−$RhCl(PPh_3)_3$ reaction gets arrested prior to reductive decarbonylation. In **5**−**7** the metal is hexacoordinated, the bond trans to the acyl function being strongly elongated (by 0.2−0.4 Å). This bond is prone to ionization, thus providing access to square-pyramidal species of type **8**. The intermediacy of pentacoordination forms a plausible basis for the observed interconversion among species of types **5**−**8**.

Internal charge balance is a crucial stabilizing factor, and there is an intimate relationship between the charge of the anion(s) bonded to the metal and the state of the remote side chain of the phenolato−acyl ligand. Thus, in **5** the side chain is aldiminium in nature and in **6**−**8** it is aldehydic. The rotameric conformations of the two functions get spontaneously adjusted to promote NH···O or CH···O hydrogen bonding.

The **5**, **6** pair provides a contrast with the ruthenium pair **2**, **15**, where chelation by RCO_2^- is accommodated by sacrificing the Ru−O(phenolato) bond. The strong *trans* influence of the acyl function promotes monodentate $Rh-NO_2$ bonding in **8b**, while in the nitrite analogue of **15**, NO_2^- is O,O-chelating. In view of the large asymmetry of N−O bond lengths, we are scrutinizing the possible oxo transfer behavior of **8b**.

Experimental Section

Materials. $RhCl(PPh_3)_3$ was prepared by a reported method.[28] The purification of dichloromethane was done as described before.[29] All the other chemicals and solvents were of analytical grade and were used as received. The Schiff bases **1** were prepared by reacting 2,6-diformyl-4-methylphenol with the amine $XC_6H_4NH_2$ in a 1:1 (in hot ethanol) ratio.

Physical Measurements. Electronic and IR spectra were recorded with Hitachi 330 and Perkin-Elmer 783 IR spectrophotometers. For ^1H NMR spectra a Bruker 300 MHz FT NMR spectrophotometer was used (tetramethylsilane is the internal standard). Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer.

Preparation of Complexes. The $Rh(XL_{sb})(PPh_3)_2Cl_2$ (**5**), $Rh(L_{al})(PPh_3)_2(RCO_2)$ (**6**), $Rh(L_{al})(PPh_3)_2(NO_3)$ (**7**), $Rh(L_{al})(PPh_3)_2Cl$ (**8a**), and $Rh(L_{al})(PPh_3)_2(NO_2)$ (**8b**) complexes were synthesized by using the same general procedures. Details are given for representative cases.

$Rh(HL_{sb})(PPh_3)_2Cl_2$ (5a). a. From $RhCl(PPh_3)_3$. To a solution of 2-formyl-4-methyl-6-((phenylimino)methyl)phenol (**1**; X = H) (13 mg, 0.05 mmol) in hot ethanol (25 mL) was added $RhCl(PPh_3)_3$ (50 mg, 0.05 mmol) and 2 N HCl (5 mL). The mixture was heated to reflux for 0.5 h. Upon cooling, a bright orange-yellow crystalline solid separated, which was collected by filtration, washed thoroughly with cold ethanol, and dried *in vacuo*. The crude product was purified by washing with benzene (30 mL), which removes the small amount of $Rh(CO)Cl(PPh_3)_2$ formed as a byproduct. Yield: 45 mg (89%). Anal. Calcd for $RhC_{51}H_{42}NO_2P_2Cl_2$: C, 65.38; H, 4.48; N, 1.49. Found: C, 65.30; H, 4.46; N, 1.50. ^1H NMR ($CDCl_3$; δ): 6.81 (s, 1H, arom), 7.13−7.86 (m, 32H arom), 7.35 (d, 2H, arom, J_{HH} = 8.7 Hz), 7.40 (d, 2H, arom, J_{HH} = 8.8 Hz), 2.16 (s, 3H, CH_3), 7.30 (s, 1H, $-CH{=}N^+$), 14.00 (s, 1H, $=N^+H$). IR (KBr; cm^{-1}): ν(C=N) 1630; ν(C=O(acyl)) 1680; ν(Rh−Cl) 320, 350; ν(N−H, hexachlorobutadiene) 3420. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 500 (11 600), 310 (23 300).

b. From $RhCl_3 \cdot 3H_2O$. To a solution of 2-formyl-4-methyl-6-((phenylimino)methyl)phenol (45 mg, 0.18 mmol) in hot ethanol (25 mL) was added an ethanolic solution (25 mL) of $RhCl_3 \cdot 3H_2O$ (50 mg, 0.18 mmol) and PPh_3 (100 mg, 0.38 mmol). The mixture was heated to reflux for 0.5 h. Upon cooling, a

(28) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

(29) (a) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; ELBS and Longman Group: Harlow, U.K., 1965; Chapter 2, pp 176−177. (b) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; p 212.

bright orange-yellow crystalline solid separated, which was collected by filtration, washed with cold ethanol, and dried *in vacuo*. This crude product was purified by washing with benzene (30 mL). Yield: 155 mg (88%).

$Rh(MeL_{sb})(PPh_3)_2Cl_2$ (5b). Yield: 89%. Anal. Calcd for $RhC_{52}H_{44}NO_2P_2Cl_2$: C, 65.68; H, 4.63; N, 1.47. Found: C, 65.62; H, 4.61; N, 1.48. ^1H NMR ($CDCl_3$; δ): 6.80 (s, 1H, arom), 7.14−7.86 (m, 31H, arom), 7.33 (d, 2H, arom, J_{HH} = 9.0 Hz), 7.38 (d, 2H, arom, J_{HH} = 8.9 Hz), 2.17 and 2.46 (2s, 6H, $2CH_3$), 7.28 (s, 1H, $-CH{=}N^+$), 13.98 (s, 1H, $=N^+H$). IR (KBr; cm^{-1}): ν(C=N) 1645; ν(C=O(acyl)) 1690; ν(Rh−Cl) 320, 355; ν(N−H, hexachlorobutadiene) 3440. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 500 (11 300), 310 (22 600).

$Rh(MeOL_{sb})(PPh_3)_2Cl_2$ (5c). Yield: 90%. Anal. Calcd for $RhC_{52}H_{44}NO_3P_2Cl_2$: C, 64.59; H, 4.55; N, 1.44. Found: C, 64.61; H, 4.57; N, 1.42. ^1H NMR ($CDCl_3$; δ): 6.75 (s, 1H, arom), 7.11−7.81 (m, 31H, arom), 6.93 (d, 2H, arom, J_{HH} = 8.7 Hz), 7.15 (d, 2H, arom, J_{HH} = 7.3 Hz), 2.13 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 7.28 (s, 1H, $-CH{=}N^+$), 14.02 (s, 1H, $=N^+H$). IR (KBr; cm^{-1}): ν(C=N) 1635; ν(C=O(acyl)) 1680; ν(Rh−Cl) 315, 350; ν(N−H, hexachlorobutadiene) 3440. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 505 (10 800), 315 (21 900).

$Rh(ClL_{sb})(PPh_3)_2Cl_2$ (5d). Yield: 91%. Anal. Calcd for $RhC_{51}H_{41}NO_2P_2Cl_3$: C, 63.06; H, 4.22; N, 1.44. Found: C, 63.10; H, 4.24; N, 1.45. ^1H NMR ($CDCl_3$; δ): 6.82 (s, 1H, arom), 7.13−7.83 (m, 31H, arom), 7.19 (d, 2H, arom, J_{HH} = 7.2 Hz), 7.42 (d, 2H, arom, J_{HH} = 8.7 Hz), 2.17 (s, 3H, CH_3), 7.34 (s, 1H, $-CH{=}N^+$), 14.01 (s, 1H, $=N^+H$). IR (KBr; cm^{-1}): ν(C=N) 1630; ν(C=O(acyl)) 1685; ν(Rh−Cl) 310, 350; ν(N−H, hexachlorobutadiene) 3440. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (11 600), 320 (22 400).

$Rh(Lal)(PPh_3)_2(HCO_2)$ (6a). To a solution of 2-formyl-4-methyl-6-((*p*-tolylimino)methyl)phenol (20 mg, 0.07 mmol) in hot ethanol (25 mL) was added $RhCl(PPh_3)_3$ (50 mg, 0.05 mmol) and 0.3 N HCOOH (10 mL). The mixture was heated to reflux for 1.5 h, affording a yellow solution. The solvent was removed under reduced pressure, leaving a yellow residue. This was isolated by filtration and washed with water and dried *in vacuo*. Yield: 41 mg (92%). Anal. Calcd for $RhC_{46}H_{37}O_5P_2$: C, 66.18; H, 4.43. Found: C, 66.02; H, 4.32. ^1H NMR ($CDCl_3$; δ): 6.876 (d, 1H, arom, J_{HH} = 1.7 Hz), 7.01 (d, 1H, arom, J_{HH} = 1.9 Hz), 7.34−7.61 (m, 31H, arom and HCO_2), 1.93 (s, 3H, CH_3), 9.50 (s, 1H, −CHO). IR (KBr; cm^{-1}): ν(C=O(acyl, formyl)) 1670; ν(OCO) 1455 (sym), 1545 (asym). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 435 (6450).

$Rh(L_{al})(PPh_3)_2(MeCO_2)$ (6b). Yield: 93%. Anal. Calcd for $RhC_{47}H_{39}O_5P_2$: C, 66.50; H, 4.59. Found: C, 66.40; H, 4.61. ^1H NMR ($CDCl_3$; δ): 6.52 (d, 1H, arom, J_{HH} = 1.8 Hz), 7.01 (d, 1H, arom, J_{HH} = 2.0 Hz), 7.31−7.56 (m, 30H, arom), 1.91 and 0.76 (2s, 6H, $2CH_3$), 9.89(s, 1H, −CHO). IR (KBr; cm^{-1}): ν(C=O(acyl, formyl)) 1670; ν(OCO) 1450 (sym), 1550 (asym). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 430 (6830).

$Rh(L_{al})(PPh_3)_2(EtCO_2)$ (6c). Yield: 94%. Anal. Calcd for $RhC_{48}H_{41}O_5P_2$: C, 66.82; H, 4.75. Found: C, 66.92; H, 4.82. ^1H NMR ($CDCl_3$; δ): 6.48 (d, 1H, arom, J_{HH} = 1.8 Hz), 6.98 (d, 1H, arom, J_{HH} = 2.1 Hz), 7.32−7.55 (m, 30H, arom), 0.96 (q, 2H, Et), 0.17 (t, 3H, Et), 1.90 (s, 3H, CH_3), 9.88 (s, 1H, −CH=O). IR (KBr; cm^{-1}): ν(C=O(acyl, formyl)) 1665; ν(OCO) 1450 (sym), 1550 (asym). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 430 (6520).

$Rh(L_{al})(PPh_3)_2(PhCO_2)$ (6d). Yield: 94%. Anal. Calcd for $RhC_{52}H_{41}O_5P_2$: C, 68.57; H, 4.50. Found: C, 68.63; H, 4.61. ^1H NMR ($CDCl_3$; δ): 6.52 (d, 1H, arom, J_{HH} = 1.8 Hz), 7.02 (d, 1H, arom, J_{HH} = 2.0 Hz), 7.11−7.58 (m, 31H, arom), 6.66 (d, 2H, arom, J_{HH} = 7.8 Hz), 6.93 (t, 2H, arom, J_{HH} = 6.7 Hz), 1.91 (s, 3H, CH_3), 9.96 (s, 1H, −CH=O). IR (KBr; cm^{-1}): ν(C=O(acyl, formyl)) 1670; ν(OCO) 1457 (sym), 1555 (asym). UV−vis (CH_2Cl_2;, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 430 (7200).

$Rh(L_{al})(PPh_3)_2(NO_3)$ (7). To a solution of 2-formyl-4-methyl-6-((*p*-tolylimino)methyl)phenol (20 mg, 0.07 mmol) in hot ethanol (25 mL) was added $RhCl(PPh_3)_3$ (50 mg, 0.05 mmol) and 0.4 N HNO_3 (10 mL). The mixture was heated to reflux for 1 h, affording a yellow solution. The solvent was removed under reduced pressure, leaving a yellow residue. This was isolated by filtration, washed with water, and dried *in vacuo*. Yield: 42 mg (92%). Anal. Calcd for $RhC_{45}H_{36}NO_6P_2$: C, 63.45; H, 4.23. Found: C, 63.48; H, 4.19; N, 1.62. ^1H NMR ($CDCl_3$; δ): 6.65 (d, 1H, arom, J_{HH} = 3 Hz), 6.93 (d, 1H, arom, J_{HH} = 3 Hz), 7.33−7.51 (m, 30H, arom), 1.97 (s, 3H, CH_3), 9.84 (s, 1H, −CHO). IR (KBr; cm^{-1}): ν(C=O(acyl)) 1705; ν(C=O(formyl)) 1670; ν(N=O) 1500; $\nu(NO_2)$ 1000 (sym), 1200 (asym). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 420 (4250).

$Rh(L_{al})(PPh_3)_2Cl$ (8a). To a solution of $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (50 mg, 0.05 mmol) in dichloromethane (20 mL) and acetone (20 mL) was added water (15 mL). The heterogeneous mixture was then heated to reflux for 0.5 h, affording a yellow solution. The organic solvents were removed under reduced pressure, leaving a suspension of the yellow residue in water. The solid was isolated by filtration, washed with water, and dried *in vacuo*. Yield: 40 mg (93%). Anal. Calcd for $RhC_{45}H_{36}O_3ClP_2$: C, 65.49; H, 4.36. Found: C, 65.51; H, 4.38. ^1H NMR ($CDCl_3$, δ): 6.87 (d, 1H, arom, J_{HH} = 2.1 Hz), 7.01 (d, 1H, arom, J_{HH} = 2.1 Hz), 7.33−7.51 (m, 30H, arom), 2.00 (s, 3H, CH_3), 9.51 (s, 1H, −CHO). IR (KBr; cm^{-1}): ν(C=O(acyl)) 1705; ν(C=O(formyl)) 1675; ν(Rh−Cl) 350. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 425 (5200).

$Rh(L_{al})(PPh_3)_2(NO_2)$ (8b). To a stirred solution of $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (50 mg, 0.005 mmol) in dichloromethane−acetone (1:1) (30 mL) was added an aqueous solution of $NaNO_2$ (40 mg, 0.57 mmol). Stirring was continued for 0.5 h, and the orange color of the solution changed to yellow. The resulting solution was evaporated under reduced pressure. A yellow suspension of the complex was obtained, which was isolated by filtration and then washed repeatedly with water. The crystalline solid was dried *in vacuo*. Yield: 41 mg (94%). Anal. Calcd for $RhC_{45}H_{36}NO_5P_2$: C, 64.67; H, 4.31; N, 1.67. Found: C, 64.61; H, 4.40; N, 1.65. ^1H NMR ($CDCl_3$; δ): 6.94 (d, 1H, arom, J_{HH} = 3.2 Hz), 7.22 (d, 1H, arom, J_{HH} = 2.8 Hz), 7.37−7.65 (m, 30H, arom), 1.96 (s, 3H, CH_3), 9.72 (s, 1H, −CHO). IR (KBr; cm^{-1}): ν(C=O(acyl)) 1705; ν(C=O(formyl)) 1670; ν(N−O) 1280 (sym), 1310 (asym); ν(O−N−O) 830. UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 420 (5120).

Interconversions. a. $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (5b) to $Rh(L_{al})(PPh_3)_2(MeCO_2)$ (6b). To a stirred solution of $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (50 mg, 0.05 mmol) in 1:1 dichloromethane−acetone (40 mL) was added an aqueous solution of $NaCO_2Me\cdot 3H_2O$ (50 mg, 0.36 mmol). The solution instantly changed from orange to yellow. Stirring was continued for 0.5 h. The organic solvents were removed under reduced pressure, leaving an aqueous suspension of a yellow residue of **6b**. This was isolated by filtration, washed with water, and dried *in vacuo*. Yield: 93%.

b. $Rh(L_{al})(PPh_3)_2(MeCO_2)$ (6b) to $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (5b). To a stirred solution of $Rh(L_{al})(PPh_3)_2(MeCO_2)$ (10 mg) in ethanol (5 mL) were added $MeArNH_2\cdot HCl$ (10 mg) and 0.3 N HCl solution (2 mL). The solution immediately changed from yellow to orange. Stirring was continued for another 15 min. The solvent was then removed under reduced pressure, and water was added to the orange residue of **5b**. The suspension was stirred, and the orange solid was collected by filtration, washed with water, and dried *in vacuo*. Yield: 79%.

c. $Rh(L_{al})(PPh_3)_2Cl$ (8a) to $Rh(MeL_{sb})(PPh_3)_2Cl_2$ (5b). To a stirred solution of $Rh(L_{al})(PPh_3)_2Cl$ (10 mg) in ethanol (20 mL) was added $MeC_6H_4NH_2\cdot HCl$ (10 mg) and 0.3 N HCl solution (5 mL). Stirring was continued for 0.5 h. After the organic solvent was evaporated, the residue of **5b** was washed with ethanol dried *in vacuo*. Yield :94%.

d. $Rh(L_{al})(PPh_3)_2Cl$ (8a) to $Rh(L_{al})(PPh_3)_2(RCO_2)$ (6b). To a stirred solution of $Rh(L_{al})(PPh_3)_2Cl$ (50 mg, 0.06 mmol) in a 1:1 dichloromethane−acetone mixture (25 mL) was added an aqueous solution of $NaCO_2Me$ (30 mg, 0.24 mmol). Stirring was continued for 0.5 h. After the organic solvents were

Table 5. Crystal, Data Collection, and Refinement Parameters for 5b·2CH₂Cl₂, 6b, 7, and 8b

	5b·$2CH_2Cl_2$	**6b**	**7**	**8b**
mol formula	$C_{54}H_{49}Cl_6NO_2P_2Rh$	$C_{47}H_{39}O_5P_2Rh$	$C_{45}H_{36}NO_6P_2Rh$	$C_{45}H_{36}NO_5P_2Rh$
mol wt	1121.5	848.6	851.6	835.6
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	18.560(7)	10.967(4)	21.086(10)	17.885(10)
b, Å	18.230(6)	31.117(16)	10.216(6)	9.930(3)
c, Å	15.182(4)	11.698(6)	21.309(7)	22.060(9)
β, deg		93.02(4)	118.70(3)	94.43(4)
V, Å^3	5137(3)	3987(3)	4026(3)	3904(3)
Z	4	4	4	4
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
μ, cm^{-1}	7.49	5.56	5.54	5.67
D_{calcd}, g cm^{-3}	1.450	1.414	1.408	1.422
temp, °C	22	22	22	22
R,[a] %	3.79	4.10	4.12	3.63
R,[b] %	4.36	4.99	4.58	4.22
GOF[c]	1.29	1.32	1.06	1.03

[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 = 0.004 for **5b**·$2CH_2Cl_2$, 0.002 for **6b**, 0.0002 for **7**, and 0.0003 for **8b**. [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.

evaporated. the yellow aqueous suspension of **6b** was filtered, washed with water, and dried *in vacuo*. Yield: 98%.

e. Rh(L$_{al}$)(PPh$_3$)$_2$Cl (8a) to Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_3$) (7). Use of $NaNO_3$ instead of $NaCO_2Me$ in the above procedure afforded **7**. Yield: 94%.

f. Rh(L$_{al}$)(PPh$_3$)$_2$Cl (8a) to Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) (8b). Use of $NaNO_2$ in place of $NaCO_2Me$ in procedure **d** above furnished **8b**. Yield: 98%.

g. Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) (8b) to Rh(L$_{al}$)(PPh$_3$)$_2$Cl (8a). To a stirred solution of Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) (50 mg, 0.05 mmol) in ethanol (20 mL) was added 0.3 N aqueous HCl (5 mL). The stirring was continued for 0.5 h. After the organic solvent was evaporated, the residue **8a** was extracted with water and finally isolated by filtration. It was washed repeatedly with water and dried *in vacuo*. Yield: 95%.

h. Rh(L$_{al}$)(PPh$_3$)$_2$(MeCO$_2$) (6b) to Rh(L$_{al}$)(PPh$_3$)$_2$Cl (8a). This was achieved by using Rh(L$_{al}$)(PPh$_3$)$_2$(MeCO$_2$) in place of Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) in procedure **g**. Yield: 97%.

i. Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_3$) (7) to Rh(L$_{al}$)(PPh$_3$)$_2$Cl (8a). Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_3$) was used instead of Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) in procedure **g**. Yield: 98%.

Reaction of 1 (X = OMe) with RhCl(PPh$_3$)$_3$ in the Absence of HCl. To a solution of 2-formyl-4-methyl-6-((*p*-methoxyimino)methyl)phenol (22 mg, 0.08 mmol) in hot ethanol (25 mL) was added RhCl(PPh$_3$)$_3$ (50 mg, 0.05 mmol). The mixture was heated to reflux for 0.5 h. Upon cooling, bright yellow crystalline *trans*-Rh(CO)Cl(PPh$_3$)$_2$ separated out. It was collected by filtration, washed thoroughly with cold ethanol, and dried *in vacuo*. Yield: 36 mg (98%). The same result was obtained irrespective of the X substituent.

X-ray Structure Determinations. Single crystals of **5b**·$2CH_2Cl_2$ (0.40 × 0.30 × 0.25 mm^3) and **6b** (0.50 × 0.40 × 0.35 mm^3), **7** (0.20 × 0.30 × 0.30 mm^3), and **8b** (0.20 × 0.20 × 0.35 mm^3) were grown by slow diffusion of hexane into dichloromethane and benzene solutions, respectively. To avoid loss of solvent and crystallinity **5b**·$2CH_2Cl_2$ was mounted in a sealed capillary over mother liquor. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ = 15−30°). Data were collected by the ω-scan technique in the ranges 3° ≤ 2θ ≤ 46° for **5b**·$2CH_2Cl_2$, 3° ≤ 2θ ≤ 45° for **6b**, 3° ≤ 2θ ≤ 48° for **7**, and 3° ≤ 2θ ≤ 45° for **8b** 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 198 reflections showed no significant intensity reduction in all cases. All data were corrected for Lorentz−polarization effects, and an empirical absorption correction[30] was done on the basis of an azimuthal scan of six reflections for each crystal.

In each case the metal atom was located from a Patterson map; 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 were refined anisotropically, and the hydrogen atoms of **5b**·$2CH_2Cl_2$, **6b**, and **7** were added at calculated positions with fixed U = 0.08 Å^2. All the hydrogen atoms of **8b** were located by difference Fourier maps and refined with a fixed U = 0.08 Å^2 using a riding model. The highest residuals were 0.33 e Å^{-3} (**5b**·$2CH_2Cl_2$), 0.92 e Å^{-3} (**6b**), 0.94 e Å^{-3} (**7**), and 0.50 e Å^{-3} (**8b**) near the metal atom. All calculations were done on a MicroVax II computer using the SHELXTL-PLUS program package.[31] Significant crystal data are listed in Table 5.

Computation of Chemical Shift Due Ring Currents. The parameters taken from the crystallographic data of **5b**·$2CH_2Cl_2$, **6b, 7**, and **8b** 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[32] ρ and z of the proton involved were calculated in units of the radius of the benzene hexagon. With the help of isoshielding plots[20] and ρ, z values the shifts were calculated. The net shifts were obtained after summation of the individual contributions. Further details are given in a dissertation.[33]

Acknowledgment. We are thankful to the Indian National Science Academy, New Delhi, India, the Department of Science and Technology, New Delhi, India, and the Council of Scientific and Industrial Research, New Delhi, India, for financial support. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged.

Supporting Information Available: For Rh(MeL$_{sb}$)(PPh$_3$)$_2$Cl$_2$·$2CH_2Cl_2$ (**5b**·$2CH_2Cl_2$), Rh(L$_{al}$)(PPh$_3$)$_2$(MeCO$_2$) (**6b**), Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_3$) (**7**), and Rh(L$_{al}$)(PPh$_3$)$_2$(NO$_2$) (**8b**) all bond distances (Tables S1, S6, S11, and S16) and angles (Tables

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S2, S7, S12, and S17), anisotropic thermal parameters (Tables S3, S8, S13, and S18), hydrogen atom positional parameters (Tables S4, S9, S14, and S19), and non-hydrogen atomic coordinates and *U* values (Tables S5, S10, S15, and S20). This material is available free of charge via the Internet at http://pubs.acs.org.

OM980748E