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ortho-METALATION REACTIONS OF AROMATIC KETOXIMES BY RHODIUM(I) AND -(III) COMPOUNDS

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SUMMARY

Aromatic ketoximes and their *O*-methyl derivatives have been found to be *ortho*-metalated by rhodium(III) salts to give complexes having five-membered chelate rings; the structures of these complexes have been discussed on the basis of IR, far-IR, and NMR data. The same complexes have also been prepared by the reaction with low-valent rhodium(I) complexes such as chlorocyclooctadienerhodium-(I), chlorodiethylenerhodium(I), and chlorodicyclooctenerhodium(I) dimer.

INTRODUCTION

The facile intramolecular *ortho*-metalation of azobenzene and its structurally related compounds has recently been shown to occur with metal complexes of Groups VI, VII, and VIII[1-12]. Though dioximes, especially dimethylglyoxime, have been studied as chelating agents for various transition metals, only complexes with platinum and palladium were reported for monoximes[13-15].

Previously[16] we reported that aromatic oximes react with lithium tetrachloropalladate(II) to form di-μ-chlorobis-(2,*N*-*dihapto*-aromatic oxime)dipalladium(II) (I) having five-membered chelate rings.

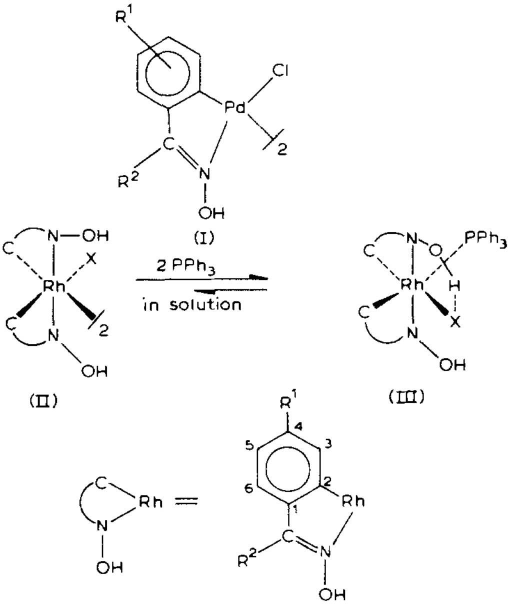
In this paper, we report the reaction of aromatic ketoximes with rhodium compounds to form the *ortho*-metalated rhodium complexes analogous to an above palladium complex and discuss their structures in terms of IR, far-IR, and NMR data.

RESULTS AND DISCUSSION

When a 90% ethanol solution of $RhCl_3 \cdot 3H_2O$ and acetophenone oxime was heated, the initial red-brown color of the solution became lighter in color and yellow-brown solids were deposited, which could be separated into a brown powder, insoluble in dichloromethane, and soluble yellow crystals (IIa). The structure of complex (IIa) will be discussed in detail later. The brown powder shows almost the same IR spectrum as that of complex (IIa). This may be probably polymeric but further studies were not carried out.

The same reaction in the presence of NaCl gave only complex (IIa). This procedure was successfully applied to several aromatic ketoximes, involving benzophenone, propiophenone, n-butyrophenone and *p*-t-butylacetophenone oxime★.

The complexes obtained are summarized in Table 1. The corresponding bromo-bridged complexes were prepared by the reaction of aromatic ketoximes with $RhCl_3 \cdot 3H_2O$ in the presence of excess NaBr or by the metathetic reaction of chloro-bridged complexes with NaBr in acetone.



That two aromatic oximes are bonded to each rhodium atom is shown by analytical data. Complexes derived from acetophenone and benzophenone oxime are almost insoluble in chloroform, but the molecular weights of the other complexes confirm the halo-bridged dimeric structure. The proton NMR spectrum of complex (IIi) from *p*-t-butylacetophenone oxime is in agreement with the proposed structure, showing a singlet at 9.27 (OH, 1H), a multiplet at 7.20–6.99 (aromatic, 3H), a singlet at 2.53 (CH_3, 3H) and a singlet at 1.17 ppm (t-C_4H_9, 9H). The C–H out-of-plane bending modes characteristic for the *ortho*-substituted aromatic ring are observed at ca. 720 cm^{-1} in complexes (IIa–h)[19]. The ν(OH) absorptions are found in the range 3300–3390 cm^{-1} both in the solid state and in solution and these low values indicate the structure with intramolecular hydrogen bonds with the bridging halogen atoms; this is appropriate for the proposed structure. Further evidence for (II) comes from the far-IR data. Only one ν(RhCl) band is observed in each chloro complex in the range of 208–220 cm^{-1} in accord with the symmetrical structure with chlorine *trans* to the Rh–C

★ We have tried, without success, the reaction of dibenzylketone oxime with $RhCl_3 \cdot 3H_2O$ in accord with the literature reports[17,18] that the reaction to form a six-membered chelate ring is less sterically favorable than that to form a five-membered ring. We also have failed to isolate the corresponding complexes from aromatic aldoximes in contrast to the palladium complexes[16].

TABLE I

AROMATIC KETOXIME–RHODIUM(III) COMPLEXES

Compound	R^1	R^2	*X*	$\nu(OH)$ $(cm^{-1})^a$	$\nu(RhCl)$ $(cm^{-1})^a$	*Mol. wt.* *found (calcd.)*
IIa	H	CH_3	Cl	3390(sh), 3330	211	
IIb	H	CH_3	Br	3380(sh), 3340		
IIc	H	C_6H_5	Cl	3300	220	
IId	H	C_6H_5	Br	3300		
IIe	H	C_2H_5	Cl	3340	215	831(869.5)
IIf	H	C_2H_5	Br	3340		940(958.4)
IIg	H	n-C_3H_7	Cl	3330	215	928(925.6)
IIh	H	n-C_3H_7	Br	3330		1020(1014.6)
IIi	t-C_4H_9	CH_3	Cl	3365	208	1002(1037.9)
IIj	t-C_4H_9	CH_3	Br	3375		1100(1126.8)

[a] Measured in Nujol mulls.

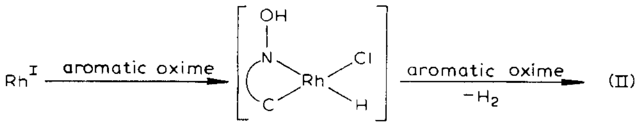
σ-bonds. The terminal ν(RhCl) vibration[20,21] *trans* to alkyl is reported to appear at ca. 240 cm^{-1} and the bridging one[22] is about 20–40 cm^{-1} lower than the former.

The halo-bridged complexes (II) reacted with triphenylphosphine to afford complex (III). For example, complex (IIIa) (R^1=H, R^2=CH_3, X=Cl) and (IIIb) (R^1=H, R^2=CH_3, X=Br) were prepared from corresponding complexes (IIa) and (IIb), respectively. The IR spectra of these complexes appear as a superposition of the spectrum of triphenylphosphine on the spectrum of the original dimer except for the region of ν(OH) frequencies. The IR spectrum of complex (IIIb) in the solid state exhibits two ν(OH) absorptions at 3500 and 3135 cm^{-1} presumably due to a free and intramolecular hydrogen bond, respectively. Similarly, the IR spectrum of complex (IIIa) exhibits two bands at 3510 and ca. 3110 (sh) cm^{-1}, the latter overlapped with the ν(C=C) bands. The trend of Cl > Br complex for the strength of an intramolecular hydrogen bond was also observed in the palladium complexes[23]. In solution, complex (III) is partly dissociated into triphenylphosphine and the original halo-bridged dimer. The IR spectrum of complex (IIIb) in chloroform shows three ν(OH) absorptions at 3500, 3340 and 3135 cm^{-1}; an absorption at 3340 cm^{-1} due to complex (IIb) disappears when additional triphenylphosphine is added to the solution.

Lithium aluminum hydride reduction of complex (II) gave corresponding amines similar to the case of complex (I)[16]. However, the mixture of complex (II) and lithium aluminum hydride in tetrahydrofuran turned yellow on heating under argon and rhodium metal was deposited only when water was added. Lithium aluminum deuteride reduction of complex (IIa) gave deuterated α-phenylethylamine. Although one deuterium atom should be added at the original Rh–C position in the benzene ring, additional deuterium atoms were shown to be involved. The proton NMR spectrum of its acetyl derivative showed that 2.5 deuterium atoms were contained in the benzene ring, four singlets at 7.28 (aromatic proton, 2.5H), 6.27 (NH), 1.92 ($COCH_3$, 3H) and 1.45 ppm (CH_3, 3H). To examine the position of incorporated deuterium atoms, the amine was oxidized to acetophenone under mild conditions by the use of 3,5-di-t-butyl-1,2-benzoquinone, followed by hydrolysis[24] at pH 4. Its proton NMR spectrum contains no signals at 7.91 ppm where the signals due to *ortho*-hydrogens should appear, but a multiplet at 7.47 (*meta* and *para* hydrogens) and a singlet at 2.57 ppm (CH_3), the relative integral intensity ratio being 60/70. The ratio indicates that part of *meta* and *para* hydrogens, probably *meta* hydrogens, are deuterated. Moreover, it was determined by mass spectrometry that it contains 8% of d_1, 67% of d_2, 16% of d_3, 7% of d_4 and 2% of d_5 species. It can be easily calculated that 2.5 deuterium atoms, on the average, are incorporated in the benzene ring.

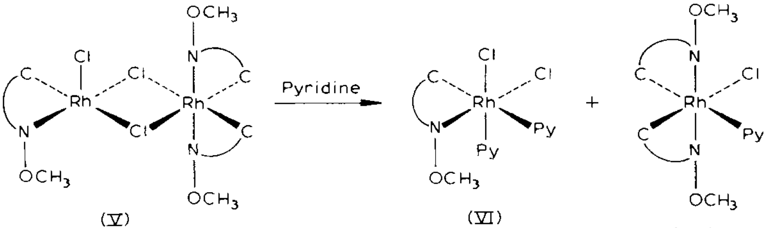
The H–D exchange at the *ortho*-positions of aniline and phenol with D_2O on metal surfaces[25] and triphenylphosphine or triphenylphosphite coordinated to low-valent Rh, Ir, Co and Ru complexes[1,26] with D_2 was reported. In our case, the structure of the intermediate of the reduction is not clear but it seems probable that α-phenylethylamine formed undergoes a successive intramolecular oxidative-addition reaction by a low-valent rhodium atom followed by the reduction of a Rh–C σ-bond.

It is thus suggested that reaction between α-phenylethylamine and low-valent rhodium complexes gives an *ortho*-metalated complex. However, a stable complex could not be isolated, since it was presumably unstable if formed. Instead, reaction between aromatic ketoximes and low-valent rhodium complexes such as chlorocyclooctadienerhodium(I), chlorodiethylenerhodium(I), and chlorodicyclooctenerhodium(I) dimer gave the expected complexes, *i.e.*, complexes (IIa) and (IIe) from acetophenone and propiophenone oxime, respectively. A mechanism has been suggested involving oxidative-addition of aromatic oxime after displacement of coordinated olefin or diene, although the postulated hydride (IV) has not been isolated.

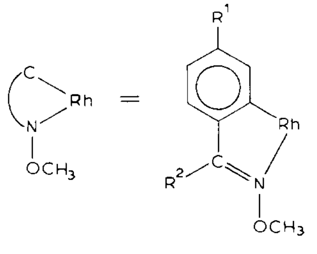


(IV)

Reaction between *O*-methyl oximes and lithium tetrachloropalladate(II) yielded predominantly dichlorobis(*O*-methyl oxime)palladium(II)[16]. On the other



(V) (VI) (VII)



a: $R^1 = H, R^2 = C_6H_5$

b: $R^1 = t-C_4H_9$, $R^2 = CH_3$

hand, *ortho*-metalated complexes (V) were isolated from the reaction of *O*-methyl derivatives of benzophenone and *p*-t-butylacetophenone oxime with $RhCl_3 \cdot 3H_2O$. The occurrence of *ortho*-metalation was confirmed by the IR spectrum of complex (Va), *i.e.*, the absorption at 728 cm^{-1} due to the C–H out-of-plane bending mode of the *ortho*-substituted benzene ring[19]. Although it has not been possible to determine the absolute configuration, analytical and molecular weight data and reaction products with pyridine confirmed the chloro-bridged structure. The terminal ν(RhCl) absorption was found at 344 and 337 cm^{-1} for complexes (Va) and (Vb), respectively, but no definite bridging ν(RhCl) absorptions were identified. In addition, the low solubility of (V) in common solvents precluded the recording of their proton NMR spectra.

By the bridge-splitting reaction of complex (Vb) with pyridine, equimolar quantities of complexes (VIb) and (VIIb) were obtained.

EXPERIMENTAL

Spectroscopic studies and molecular weight measurements were carried out using the instruments described elsewhere[2]. Tetrahydrofuran was refluxed with lithium aluminum hydride and distilled before use. Lithium aluminum deuteride was obtained from Alpha Inorganics. Chlorocyclooctadienerhodium(I)[27], chlorodiethylenerhodium(I)[28] and chlorodicyclooctenerhodium(I) dimer[29] were prepared according to described methods. Proton NMR spectra were measured in $CDCl_3$.

Preparation of complexes (II)

When a 90% ethanol solution (20 ml) of acetophenone oxime (0.81 g, 6 mmoles), $RhCl_3 \cdot 3H_2O$ (0.53 g, 2 mmoles) and excess NaCl was refluxed on a water bath for 5 min, the color of the solution changed from red-brown to red-yellow and yellow crystals began to precipitate. After standing for 24 h, the crystals were collected by filtration, washed with ethanol and water, and dried *in vacuo* to give complex (IIa) (0.76 g, 93%). The same reaction in presence of NaBr instead of NaCl yielded complex (IIb).

TABLE 2

YIELDS, MELTING POINTS AND ANALYSES

Compounds	*Yield* (%)	*M.p.* (°C)	*Analyses, found (calcd.) (%)*		
			C	*H*	*Cl*
IIa	93	291–296	47.40(47.25)	3.93(3.97)	8.89(8.82)
IIb	92	295–299	42.65(42.59)	3.72(3.58)	
IIc	99	>300	58.56(58.82)	3.84(3.81)	7.15(6.68)
IId	89	>300	54.40(54.28)	3.67(3.51)	
IIe	86	>300	49.71(49.72)	4.70(4.65)	8.46(8.15)
IIf	84	>300	45.72(45.11)	4.35(4.22)	
IIg	83	248–255	52.07(51.90)	5.31(5.24)	7.79(7.66)
IIh	74	256–260	47.92(47.35)	4.77(4.78)	
IIi	77	>300	55.40(55.54)	6.20(6.23)	7.06(6.83)
IIj	90	280–	51.10(51.16)	5.60(5.74)	

Similar complexes were obtained from benzophenone, propiophenone, n-butyrophenone and *p*-t-butylacetophenone oxime.

Yields, melting points and analyses of complexes obtained are summarized in Table 2. They are pale yellow to yellow-brown in color and can be recrystallized from dichloromethane-n-hexane.

Reaction of complexes (IIa) and (IIb) with triphenylphosphine

A suspension of complex (IIa) (100 mg) in dichloromethane (1 ml) became homogeneous on adding triphenylphosphine (100 mg). Addition of n-hexane to the solution yielded complex (IIIa) as pale yellow crystals (145 mg, 88%), m.p. 205–207°. Found: C, 60.53; H, 4.44; N, 4.23. $C_{34}H_{31}N_2O_2ClPRh$ calcd.: C, 61.04; H, 4.68; N, 4.18%.

Complex (IIb) gave in a similar way complex (IIIb) (90%), m.p. 186–187°. Found: C, 57.27; H, 4.33; N, 3.91. $C_{34}H_{31}N_2O_2BrPRh$ calcd.: C, 57.23; H, 4.39; N, 3.93%.

Lithium aluminum deuteride reduction of complex (IIa)

To a stirred mixture of complex (IIa) (500 mg) in tetrahydrofuran (20 ml) was added lithium aluminum deuteride (300 mg) in small portions under argon. After refluxing for 30 min, the reaction mixture was cooled and worked up by careful addition of deuterium oxide (2 ml) followed by the addition of anhydrous sodium sulfate. The mixture was filtered and washed with tetrahydrofuran. A colorless oil (260 mg), crude α-phenylethylamine, was obtained by removal of tetrahydrofuran and oxidized to acetophenone according to Corey's method[24].

Reaction of acetophenone and propiophenone oxime with low-valent rhodium (I) complexes

A mixture of chlorocyclooctadienerhodium(I) dimer (0.59 g, 1 mmole) and acetophenone oxime (0.54 g, 4 mmoles) in *o*-dichlorobenzene (2 ml) was refluxed under argon for 2 h and n-hexane was added to the solution, whereupon yellow solids precipitated. These were recrystallized from dichloromethane-n-hexane to give complex (IIa) (250 mg, 62%).

Complexes (IIa) and (IIe) were also prepared in moderate yields by treatment of acetophenone and propiophenone oxime, respectively, with chlorodiethylene-rhodium(I) or chlorodicyclooctenerhodium(I) dimer.

Reaction of O-methyl derivatives of benzophenone and p-tertbutylacetophenone oxime with $RhCl_3 \cdot 3H_2O$

A solution of *O*-methyl benzophenone oxime (1.06 g, 5 mmoles) and $RhCl_3 \cdot 3H_2O$ (0.53 g, 2 mmoles) in 80% ethanol (20 ml) was refluxed for 20 min. The color of the solution changed from red-brown to red-yellow and yellow solids (0.32 g), after standing for 24 h, were deposited. The filtrate was diluted with water and extracted with dichloromethane. More yellow solids (0.38 g) were obtained by addition of n-hexane to the extract. The combined yellow solids were recrystallized from dichloromethane-n-hexane to give complex (Va) as a yellow solid (0.60 g, 64%), m.p. >300°. Found: C, 54.00; H, 3.84; N, 4.10; Cl, 11.01; mol. wt., 958. $C_{42}H_{36}N_3O_3Cl_3Rh_2$ calcd.: C, 53.49; H, 3.86; N, 4.46; Cl, 11.28%; mol. wt., 943.0.

Similarly, complex (Vb) was obtained from *O*-methyl *p*-t-butylacetophenone oxime as yellow solids (80%), m.p. >300°. Found: C, 50.67; H, 5.89; Cl, 11.13. $C_{39}H_{54}N_3O_3Cl_3Rh_2$ calcd.: C, 50.64; H, 5.89; Cl, 11.50%.

Reaction of complex (Vb) with pyridine

Pyridine (0.1 ml) was added to a suspension of complex (Vb) (374 mg) in dichloromethane (1 ml). The resulting solution was evaporated and the residue was chromatographed on silica gel (30 g). Ethylacetate/dichloromethane (5/95) eluted yellow-brown crystals (218 mg, 100 %), which were recrystallized from dichloromethane-n-hexane to give analytically pure complex (VIb), m.p. 239–242°. Its proton NMR spectrum shows four singlets at 3.35 (OCH_3), 2.60 (CH_3), 1.24 (t-C_4H_9) and 5.27 ppm (CH_2Cl_2, solvent of recrystallization) in addition to signals due to aromatic protons. Found: C, 50.92; H, 5.38; Cl, 14.31; mol. wt., 552. $C_{23}H_{28}N_3OCl_2Rh\cdot\frac{1}{10}CH_2Cl_2$ calcd.: C, 50.92; H, 5.23; Cl, 14.50%; mol. wt., 536.4.

Ethylacetate/dichloromethane (20/80) eluted complex (VIIb) as yellow crystals (251 mg, 99%), m.p. 227–229°. Its proton NMR spectrum shows three singlets at 3.93 (OCH_3, broad), 2.47 (CH_3) and 1.21 (t-C_4H_9) in addition to signals due to aromatic protons. Found: C, 59.39; H, 6.63; Cl, 6.18; mol. wt., 630. $C_{31}H_{41}N_3O_2RhCl$ calcd.: C, 59.46; H, 6.61; Cl, 5.66%; mol. wt., 626.1.

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