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CHELATING *C*-METALLATION OF SOME ORGANIC NITROGEN COMPOUNDS WITH HEXACHLOROTETRAKIS(TRI-n-BUTYLPHOSPHINE)-DIRHODIUM(III)

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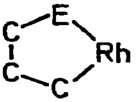
Summary

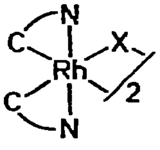
Hexachlorotetrakis(tri-n-butylphosphine)dirhodium(III), $Rh_2Cl_6(PBu_3)_4$, in refluxing xylene, metallates the organic nitrogen compounds (N—CH) to yield $RhCl_2$(N—C)(PBu_3); N—CH is acetophenoneoxime, *p*-methylacetophenoneoxime, *p*-methylbenzaldoxime, 8-methylquinoline, 2-phenylpyridine, *N*-phenylpyrazole, and benzo[*h*]quinoline. $RhCl_2$(N—C)(PBu_3) reacts with one mole of PBu_3 to give $RhCl_2$(N—C)$(PBu_3)_2$. Some bromo and iodo analogs of these compounds were also prepared. These newly prepared complexes were characterized by means of IR and PMR spectra, and probable structures are proposed.

Introduction

Rhodium(III) has the ability to metalate some organic compounds (E—CH), containing potential donor atoms (E) such as N, P, or As, to form a rhodocycle (I). Several nitrogen compounds (E=N) are known to be susceptible to such *C*-metallation by rhodium(III) halides; examples are azobenzene [1], aromatic ketoximes [2], 2-phenylpyridine [3], benzo[*h*]quinoline [3,4], or *N*-phenylpyrazole [5], etc. *C*-metallation with rhodium(III) complexes other than the halides has received little attention. The effect of the nature of coordinating ligands on metallation is of interest [6]. In this study we investigated *C*-metallation of several organic nitrogen compounds with $Rh_2X_6(PBu_3)_4$ (X = Cl, Br), where PBu_3 is tri-n-butylphosphine [7]. The reaction gives mono-rhodocyclic


I

complexes (I) which is different from the action of rhodium(III) halides, as in this case the di-rhodocyclic complexes (II) are formed [1-5].

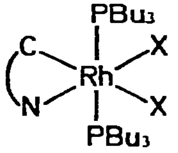


II

Results and discussion

Organic nitrogen compounds metallated by $Rh_2X_6(PBu_3)_4$ (X = Cl, Br) [7] are shown in Fig. 1 together with the abbreviations used in this paper. The analytical data and melting points for the newly prepared complexes are given in Table 1 using these abbreviations.

In a preliminary communication on the early stages of this investigation [8] were reported the results for metallation of complexes of *p*-methylacetophenoneoxime (Hatm). The $RhX_2(atm)(PBu_3)_2$ (X = Cl, Br, I) complexes produced were presumed to have a *trans*-$(PBu_3)_2$ configuration (III) on the basis of the PMR and



III

infrared spectral data (Table 2). The chloride showed two strong bands at 215 and 313 cm^{-1} which disappeared upon replacement of Cl with Br or I. Considering the *trans* influence of donor atoms [9], we can assign the higher frequency band to the Rh—Cl bond *trans* to the oxime-N and the lower one to that *trans* to the metallated-C atom. Acetophenoneoxime (Hapm) and *p*-methylbenzaldehydeoxime (Hftm)* are similarly metallated with $Rh_2Cl_6(PBu_3)_4$ to yield $RhCl_2$-(N—C)(PBu_3), where N—C is apm and ftm (Table 1). Their spectral data (Table 2) show that the two complexes have structures similar to that of the corresponding atm complex.

The PMR spectrum of $RhCl_2(bhq)(PBu_3)$ (Table 3) reveals that the 10-H of benzo[*h*]quinoline (Hbhq) has been lost [3] and the infrared spectra of RhX_2-(bhq)(PBu_3) (X = Cl, Br) show a few halogen-sensitive bands in the region below 400 cm^{-1} indicating coordination of halogens. However, assignment of ν(Rh—Cl) was difficult because of complicated band changes occuring upon exchange of halogens. The halogen-dependent chemical shifts of the 2-H and 9-H of RhX_2-(bhq)$(PBu_3)_2$ (X_2 = Cl_2, Br_2, ClI) (Table 3) indicate that both the 2-H and the 9-H are located in the proximity of halogens [10]. If we examine the trends of the shifts, it can be found that the positions of the 2-H resonance shifts to lower

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* An aromatic aldoxime has been reported not to be metallated with rhodium(III) chloride hydrate [2].

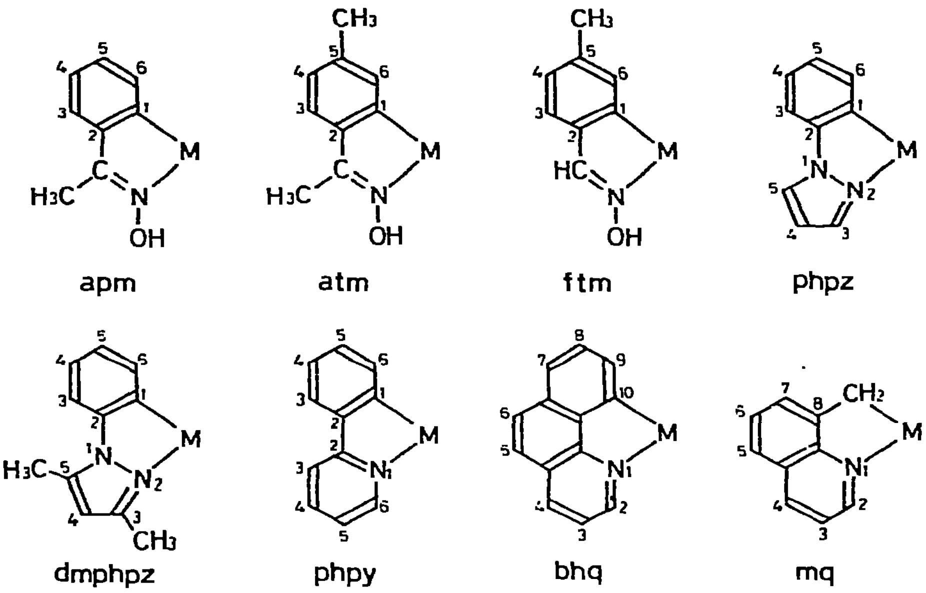
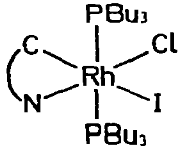


Fig. 1. Structures of ligands to M (M = tributylphosphine-rhodium complex) and their abbreviations.

frequency in the order of X_2: $Cl_2 > Br_2 > ClI$, while the chemical shifts of the 9-H are irregular with respect to this order (Table 3). The trend found for the 2-H is very similar to that reported previously for the phenyl ring 6-H of $RhX_2(atm)(PBu_3)_2$ (X = Cl, Br, I) (Table 2) [8]. Therefore, the halogen atoms adjacent to the 2-H seem to be Cl, Br, and I, while those adjacent to the 9-H seem to be Cl, Br, and Cl, respectively, in $RhCl_2(bhq)(PBu_3)_2$, $RhBr_2(bhq)(PBu_3)_2$, and $RhCl(I)(bhq)(PBu_3)_2$.

The two strong bands at 225 and 308 cm^{-1} of $RhCl_2(bhq)(PBu_3)_2$ disappeared upon replacement of the two Cl atoms with two Br atoms. The higher frequency band is assigned to the Rh—Cl bond *trans* to the bhq-N atom and the lower one to that *trans* to the metallated-C atom [9]. In the infrared spectrum of $RhCl(I)(bhq)(PBu_3)_2$ a strong band was observed at 308 cm^{-1}. This band is assigned to ν(Rh—Cl), the position of which suggests that the Cl atom is at the *trans* position to the bhq-N atom. The structure shown below (IV) is, therefore,



IV

proposed. This structure is also supported by the above PMR spectral data (Table 3).

When $RhCl_2(bhq)(PBu_3)_2$ was treated with two molar equivalents of sodium iodide, only the chloride *trans* to the metallated-C atom was exchanged for io-

TABLE 1

MELTING POINTS AND ANALYTICAL DATA

Complex	M.p. (°C)	Analysis, Found (calcd.) (%)			
		C	H	N	Other
$\mathrm{RhCl_2(apm)(PBu_3)}$	232-242[a]	47.12 (47.08)	7.12 (6.91)	2.79 (2.74)	Cl 14.00 (13.90)
$\mathrm{RhCl_2(atm)(PBu_3)}$	238-251[a]	47.94 (48.11)	7.13 (7.11)	2.87 (2.67)	
$\mathrm{RhBr_2(atm)(PBu_3)}$	255(dec.)	41.03 (41.13)	5.97 (6.08)	2.08 (2.28)	
$\mathrm{RhI_2(atm)(PBu_3)}$	238-243	35.86 (35.67)	5.21 (5.27)	2.02 (1.98)	
$\mathrm{RhCl_2(ftm)(PBu_3)}$	248-251	46.94 (47.08)	6.83 (6.91)	2.63 (2.74)	
$\mathrm{RhCl_2(phpz)(PBu_3)}$	270(dec.)	48.10 (48.57)	6.64 (6.60)	5.70 (5.39)	
$\mathrm{RhBr_2(phpz)(PBu_3)}$	292-293	41.58 (41.47)	5.68 (5.63)	4.94 (4.61)	Br 27.17 (26.28)
$\mathrm{RhCl_2(dmphpz)(PBu_3)}$	251-253	50.10 (50.47)	6.94 (7.00)	4.92 (5.12)	
$\mathrm{RhCl_2(phpy)(PBu_3)}$	305(dec.)	52.14 (52.09)	6.71 (6.84)	2.78 (2.64)	
$\mathrm{RhCl_2(bhq)(PBu_3)}$	305(dec.)	54.37 (54.17)	6.44 (6.36)	2.73 (2.53)	Cl 12.91 (12.79)
$\mathrm{RhBr_2(bhq)(PBu_3)}$	295(dec.)	46.82 (46.68)	5.45 (5.40)	2.44 (2.13)	
$\mathrm{RhCl_2(mq)(PBu_3)}$	268-270	50.93 (50.98)	6.67 (6.81)	2.84 (2.70)	
$\mathrm{RhCl_2(atm)(PBu_3)_2}$	177-178	54.57 (54.55)	8.77 (8.88)	1.98 (1.93)	Cl 10.11 (9.76)
$\mathrm{RhBr_2(atm)(PBu_3)_2}$	173-175	48.78 (48.60)	7.96 (7.91)	2.05 (1.72)	
$\mathrm{RhI_2(atm)(PBu_3)_2}$	155-156	43.31 (43.58)	7.07 (7.09)	1.49 (1.54)	
$\mathrm{RhCl_2(phpz)(PBu_3)_2}$	255(dec.)	54.93 (54.93)	8.55 (8.52)	3.73 (3.88)	
$\mathrm{RhCl_2(phpy)(PBu_3)_2}$	265(dec.)	57.15 (57.38)	8.53 (8.67)	1.83 (1.91)	
$\mathrm{RhCl_2(bhq)(PBu_3)_2}$	268(dec.)	58.45 (58.73)	8.40 (8.26)	1.83 (1.85)	P 8.04 (8.19)
$\mathrm{RhBr_2(bhq)(PBu_3)_2}$	260(dec.)	52.62 (52.56)	7.39 (7.39)	1.98 (1.66)	
$\mathrm{RhClI(bhq)(PBu_3)_2}$	236(dec.)	52.32 (52.40)	7.21 (7.37)	1.36 (1.65)	

[a] Melts with decomposition.

dide. This may be due to the fact that the *trans* effect of a metallated-C atom is higher than that of a heteroaromatic-N atom. A similar argument was recently presented for a related organorhodium(III) complex [11].

2-Phenylpyridine (Hphpy), *N*-phenylpyrazole (Hphpz), 3,5-dimethyl-1-phenylpyrazole (Hdmphpz), and 8-methylquinoline (Hmq) were similarly metallated with $\mathrm{Rh_2X_6(PBu_3)_4}$ to give $\mathrm{RhX_2(N—C)(PBu_3)}$. The PMR spectral data are given in Table 3. As was mentioned above, assignment of ν(Rh—Cl) of the complexes of the type $\mathrm{RhX_2(N—C)(PBu_3)}$ is difficult. For the complexes of the

TABLE 2

INFRARED AND 60 MHz PMR SPECTRA OF THE OXIME COMPLEXES

Complex	Infrared spectra (cm^{-1})			PMR spectra (δ ppm from TMS)						
	ν(C=N)	ν(O–H)	δ(O–H)[a]	Solvent	CH_3	3- and 4-H[b]			6-H	O–H
						δ_A	δ_B	J_{AB}[c]		
$RhCl_2(atm)(PBu_3)$	1614	3101	437	dmso-d_6	2.40	7.40	7.07	7.5	7.70	10.90
$RhBr_2(atm)(PBu_3)$	1613	3265	369	dmso-d_6	2.39	7.42	7.11	7.5	7.88	10.32
$RhI_2(atm)(PBu_3)$	1620	3300	338	dmso-d_6	2.39	7.39	7.06	7.5	8.10	9.66
$RhCl_2(atm)(PBu_3)_2$	1633	3025	650	$CDCl_3$	2.38	7.12	6.92	7.5	7.83	11.21
$RhBr_2(atm)(PBu_3)_2$	1631	3090	610(sh)	$CDCl_3$	2.36	7.12	6.93	7.5	8.02	10.72
$RhBr_2(atm)(PBu_3)_2$[d]	1630	2302	442							
$RhI_2(atm)(PBu_3)_2$	1632	3123	553	$CDCl_3$	2.40	7.15	6.96	7.5	8.31	10.09
$RhCl_2(apm)(PBu_3)$	1610	3178	443	dmso-d_6	2.43	[e]			7.87	10.96
$RhCl_2(ftm)(PBu_3)$	1610	3180	446	dmso-d_6	2.40	7.43	7.08	7.5	7.63	10.71[f]

[a] Tentative assignment. [b] Signals due to 3-H and 4-H exhibited an AB quartet, and the higher field doublet component showed an additional coupling ($J < 1.5$ Hz). [c] Hz. [d] The oxime-hydrogen was deuterated. [e] Signals due to 3-H, 4-H, and 5-H were observed in the region δ 7.2-7.7 ppm as a complicated multiplet. [f] The methine proton of —CH=N—OH appeared at δ 8.45 ppm.

type $RhCl_2(N—C)(PBu_3)_2$, ν(Rh—Cl) are assigned as follows: 222 and 305 cm^{-1} for $RhCl_2(phpy)(PBu_3)_2$, 219 and 311 for $RhCl_2(phpz)(PBu_3)_2$, and 218 and 318 for $RhCl_2(mq)(PBu_3)_2$. The structure III is also borne out by these data.

When $RhCl_2(mq)(PBu_3)$ was dissolved in dmso-d_6, isomers might be produced, since in the PMR spectrum, three peaks due to the metallated methylene group were observed between 3.7-4.5 ppm [12], and the 2-H resonance seems to split into, at least, two broad signals at 9.57(d) and 9.73(d) ppm. The integration ratios of all the signals indicate metallation at the methyl group of Hmq. The whole infrared and PMR spectra of $RhCl_2(mq)(PBu_3)_2$ are identical to those

TABLE 3

PMR SPECTRA OF THE COMPLEXES

Complex	Solvent	Frequency (MHz)	δ ppm from TMS (assignment[a]/intensity)
$RhCl_2(bhq)(PBu_3)$	dmso-d_6	60	9.71d(2-R/1) 8.62d(4-H/1) 8.21d(9-H/1) 7.4-7.9m(other/5)
$RhCl_2(bhq)(PBu_3)_2$	$CDCl_3$	100	10.02d(2-H/1) 8.33d(4-H/1) 8.47d(9-H/1) 7.4-8.0m(other/5)
$RhBr_2(bhq)(PBu_3)_2$	$CDCl_3$	100	10.25d(2-H/1) 8.32d(4-H/1) 8.69(br)d(9-H/1) 7.4-8.0m(other/5)
$RhCl(I)(bhq)(PBu_3)_2$	$CDCl_3$	100	10.48d(2-H/1) 8.34d(4-H/1) 8.51m(9-H/1) 7.4-8.0m(other/5)
$RhCl_2(dmphpz)(PBu_3)$	dmso-d_6	60	8.07dd(ph 6-H/1) 6.31s(pz 4-H/1) 2.76s(3,5-CH_3/6) 6.9-7.6m(other/3)
$RhCl_2(phpz)(PBu_3)$	dmso-d_6	60	8.90d(pz 3-H/1) 8.04d(pz 5-H/1) 6.73t(pz 4-H/1) 7.0-8.0m(other/4)
$RhCl_2(phpz)(PBu_3)_2$	$CDCl_3$	100	8.23m(pz 3-H, pz 5-H, ph 6-H/3) 6.60t(pz 4-H/1) 7.0-7.4m(ph 3,4,5-H/3)
$RhCl_2(phpy)(PBu_3$	dmso-d_6	60	9.53d(py 6-H/1) 6.9-8.2m(other/7)
$RhCl_2(phpy)(PBu_3)_2$	$CDCl_3$	60	9.90d(py 6-H/1) 8.32m(ph 6-H/1) 6.8-7.9m(other/6)
$RhCl_2(mq)(PBu_3)$	dmso-d_6	60	9.73d, 9.57d(2-H/1) 8.61d(4-H/1) 3.7-4.5(CH_2/2) 7.5-8.1m(other/4)

[a] ph = phenyl ring, pz = pyrazolyl ring, and py = pyridyl ring. s = singlet, d = doublet, t = triplet, m = multiplet, and (br) = broad.

of "$RhCl_2(mq)(PBu_3)_2$" reported in a previous paper [12]. Therefore, $RhCl_2(mq)(PBu_3)_2$ should have the same structure as that previously reported (III).

In the infrared spectra of Hphpz, Hphpy, and Hapm, the aromatic C—H out-of-plane deformation bands (ca. 690, 760 cm^{-1}) for the free ligands are replaced by one such band in the complexes (ca. 770 cm^{-1}). Metallation at the *ortho* position of a phenyl ring (Fig. 1) is also confirmed. The infrared spectra of the other ligands (N—CH) and complexes are complicated in the aromatic C—H out-of-plane deformation vibration region, so that unambiguous assignments are difficult.

Some other organic nitrogen compounds such as azobenzene, *N,N*-dimethylbenzylamine, and *N,N*-dimethylallylamine, which seem to be capable of being metallated [13], were also examined under similar conditions. Up to the present time, however, we have not isolated any pure complexes with *C*-metallated ligands. As has been reported [1-5], metallation with rhodium(III) halides in alcoholic solvents gave usually bis-chelate type complexes (II) $[RhX(C—N)_2]_2$, while metallation with the PBu_3 complexes used in this study yielded only mono-chelate type complexes $RhX_2(N—C)(PBu_3)$. Coordination of PBu_3 to rhodium(III) appears to decrease the ability of rhodium(III) to metallate organic nitrogen compounds. This interesting point is now under detailed investigation.

Experimental

Measurements

Measurements were carried out as described previously [3,12].

Preparations

Dimeric complexes $[RhX_3(PBu_3)_2]_2$ used as starting materials were prepared by the methods reported in the literature [7]. The following procedures are typical for preparing the *C*-metallated complexes.

$RhCl_2(bhq)(PBu_3)$ To a solution of 0.5 mmol (0.61 g) of $[RhCl_3(PBu_3)_2]_2$ in 50 ml of xylene was added 1 mmol (0.18 g) of Hbhq and the mixture refluxed for 8 h with stirring. The mixture was then concentrated to half the volume and cooled to room temperature. The resulting fine yellow crystals were filtered, washed with xylene, and dried in air. The yield was 0.32 g (58%). The product was recrystallized from dichloromethane.

$RhCl_2(bhq)(PBu_3)_2$. To a suspension of 1 mmol (0.55 g) of $RhCl_2(bhq)(PBu_3)$ in 30 ml of dichloromethane was added 1 mmol (0.20 g) of PBu_3 and the mixture heated until it had become clear. To the solution was added 30 ml of methanol and the mixture concentrated to a small volume to precipitate yellow crystals. The product was washed with methanol and dried in air. The yield was 0.50 g (66%).

The two iodo complexes, $RhI_2(atm)(PBu_3)_2$ and $RhCl(I)(bhq)(PBu_3)_2$ were prepared by reaction of the corresponding chloride with excess sodium iodide in acetone/dichloromethane.

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