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STABLE PALLADIUM(II) CARBONYL COMPLEXES CONTAINING PALLADIUM–CARBON σ-BONDS

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SUMMARY

Halo(2,*N-dihapto*-aromatic oxime)palladium(II) carbonyl compounds containing palladium–carbon σ-bonds have been synthesized by bridge-splitting reactions of di-μ-halobis(2,*N-dihapto*-aromatic oxime)dipalladium(II) (halogen = Cl, Br, or I) with carbon monoxide. These compounds are very stable in a dry atmosphere, and their structures, which include strong intramolecular hydrogen bonds, are discussed in terms of their IR spectra.

The CO and OH stretching frequencies show a marked dependence on the nature of the halogen; ν(CO), Cl- > Br- > I-complex and ν(OH), I- > Br- > Cl-complex. These variations are predominantly due to inductive effects.

INTRODUCTION

Although many studies have been reported on carbonyl complexes of transition metals, only a few rather unstable palladium derivatives are known. They are the anionic complexes $[Pd(CO)X_3]^{-}$[1], $[PdH(CO)Cl_2]^{-}$[2], and $[Pd(CO)(SnCl_3)_2Cl]^{-}$[3], a cationic complex, $[Pd(CO)(PEt_3)_2Cl]^{+}$[4], and neutral complexes, $[Pd(CO)(PPh_3)_3]$[5], $[Pd(CO)Cl]_n$[6], and $[Pd(CO)Cl_2]_n$[7]. In the palladium-catalyzed carbonylation reaction of olefins, acetylenes, and allylic compounds, it may reasonably be assumed that carbon monoxide coordinated to palladium is inserted into the palladium–carbon σ-bond[8,9]. Such carbonyl intermediates have, however, never been isolated.

In a previous paper[10], we reported the reaction of aromatic oximes with lithium tetrachloropalladate(II) to form di-μ-chlorobis(2,*N-dihapto*-aromatic oxime)dipalladium(II), and discussed the structures of the latter compounds which possess *ortho*-attached palladium–carbon σ-bonding and palladium–nitrogen coordinate bonding to the oxime groups.

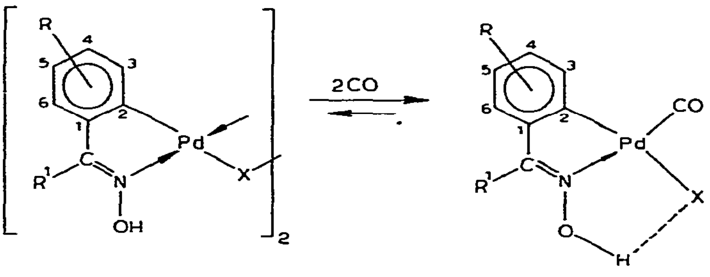
The above σ-complexes react with carbon monoxide to give new stable carbonyl complexes, *i.e.*, chloro(2,*N-dihapto*-aromatic oxime)palladium(II) carbonyls containing palladium–carbon σ-bonds. Bromo- and iodo-analogs may be similarly synthesized via the reaction of carbon monoxide with bromo- and iodo-bridged complexes.

The preparation, structure, and IR spectra of these new palladium(II) carbonyl complexes are discussed.

RESULTS AND DISCUSSION

When a chloroform solution of di-μ-chlorobis(2,*N*-*dihapto*-benzophenone oxime)dipalladium (Ia) was stirred under an atmosphere of carbon monoxide (1 atm), the initial yellow color of the solution paled and the theoretical amount (2 moles) of carbon monoxide was absorbed. The IR spectrum of the resulting solution was almost the same as that of the starting complex (Ia) with the exception of the appearance of ν(CO) (2134 cm^{-1}) and ν(OH) (3190 cm^{-1}) and the disappearance of ν(OH) (3340 cm^{-1}) of complex (Ia). No trace of a ν(CO) band corresponding to the acyl palladium group[9] was found in the 1700–1600 cm^{-1} region of the spectrum. From the solution chloro(2,*N*-*dihapto*-benzophenone oxime)palladium(II) carbonyl (VIa) was isolated as pale yellow crystals. Complexes (VIb) and (VIc) were prepared by the same way in chloroform, although complex (VIc) could not be separated. Complexes (IIa, b, c)–(Va, b, c) were insoluble in chloroform, but clear solutions, however, were obtained by stirring a suspension of (IIa, b, c)–(Va, b, c) in chloroform during the absorption of carbon monoxide, when the corresponding carbonyl complexes (VIIa, b, c)–(Xa, b, c) were obtained.

The complexes prepared and their IR data are summarized in Table 1.



(I), (VI) : R = H, $R^1 = C_6H_5$
(II), (VII) : R = H, $R^1 = CH_3$
(III), (VIII) ; R = 4-CH_3O , $R^1 = CH_3$
(IV), (IX) : R = 4-CH_3O , R^1 = H
(V), (X) ; R = 4,5-Benzo, $R^1 = CH_3$

a ; X = Cl
b ; X = Br
c ; X = I

The observed molecular weight* (506) of complex (VIa) was found to be intermediate in value between 366.1 [complex (VIa)] and 676.2 [complex (Ia)]. This may be attributed to the partial dissociation of complex (VIa) to complex (Ia) through the loss of carbon monoxide. In fact, the IR spectra of the solution showed two ν(OH)

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* The molecular weight was determined by the use of a Mechrolab 301 A osmometer using a chloroform solution (ca. 0.01 *M*) at 37°. Since the solution was prepared in air and since it was not possible with our instrument to conduct measurements under an atmosphere of carbon monoxide, the color of the solution became yellow during the period of stabilization (ca. 20 min).

absorptions at 3190 cm^{-1} [complex (VIa)] and 3340 cm^{-1} [complex (Ia)] respectively. Under an atmosphere of carbon monoxide the equilibrium in eqn. (1) lies to the right-hand side, but on passing argon gas into the chloroform solution of complex (VIa), the color of the solution became gradually yellow and ν(OH) (3340 cm^{-1}) of complex (Ia) began to appear after 5 min. The isolated complexes [(VIa, b)–(Xa, b, c)] are very stable in a dry atmosphere and may be stored unchanged in a desiccator for several months at room temperature. When heated, they gradually lose carbon monoxide above about 100°. The different stability of the palladium–carbonyl complexes in the solid state and in solution is most probably attributable to the increasing ease of the back reaction in eqn. (1) in solution.

According to Booth and Chatt[9], palladium–phenyl σ-bonds readily insert carbon monoxide at atmospheric pressure, but complexes (VIa, b, c)–(Xa, b, c) resisted further insertion of carbon monoxide presumably due to the rigid 5-membered chelate rings which are further strengthened by the presence of strong intramolecular hydrogen bonds.

Cleavage of chloride bridges by carbon monoxide is well known and has been used as a preparative method for metal carbonyl complexes. Although spectroscopic studies[11-13] have shown that chloride bridges of palladium complexes are cleaved by carbon monoxide, stable palladium carbonyl complexes have never been isolated; thus the characteristic ν(CO) band (2121 cm^{-1}) was observed in the reaction of [(2-methylallyl)PdCl]$_2$ with carbon monoxide, but the carbonyl complex could not be isolated. One carbonyl complex $[Pd(CO)(PEt_3)_2Cl]^+$ has, however, been isolated from the bridge-splitting reaction, but it is reported to be unstable in the solid state losing carbon monoxide[4].

As shown in Table 1, the IR spectra of the carbonyl complexes prepared in this

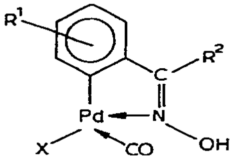
TABLE I

HALO(2,*N-dihapto*-AROMATIC OXIME)PALLADIUM(II) CARBONYL COMPLEXES

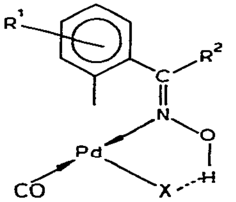
Compounds	Color	ν(CO)^a (cm^{-1})	ν(OH)^a (cm^{-1})	ν(OH)^a (cm^{-1})	Starting complex
(VIa)	Pale yellow	2136, 2122 (2129)^b	3194 (3147)^b	3343	(Ia)
(VIb)	Pale yellow	2133, 2120 (2127)^b	3210 (3190)^b	3345	(Ib)
(VIc)^c		(2122)^b	(3230)^b	3400	(Ic)
(VIIa)	White	2132	3200	3426	(IIa)
(VIIb)	Pale yellow	2129	3225	3423	(IIb)
(VIIc)	Pale yellow	2119	3245	3420	(IIc)
(VIIIa)	Yellow	2129	3263	3460, 3433	(IIIa)
(VIIIb)	Yellow	2119	3274	3430	(IIIb)
(VIIIc)	Yellow	2118	3286	3430	(IIIc)
(IXa)	Yellow	2126, 2121	3210	3415	(IVa)
(IXb)	Yellow	2121	3239	3425	(IVb)
(IXc)	Yellow	2115	3265	3430	(IVc)
(Xa)	White	2131	3170	3420	(Va)
(Xb)	Pale yellow	2125	3215	3380	(Vb)
(Xc)	Pale yellow	2108	3252	3430	(Vc)

[a] Measured in Nujol mulls. [b] Measured in CCl$_4$ solutions. [c]. Not isolated.

study exhibit strong ν(CO) absorptions in the 2108–2133 cm^{-1} region, while the ν(OH) frequencies observed in the 3170–3286 cm^{-1} region are shifted to lower wavelengths by about 150–200 cm^{-1} in comparison with the corresponding frequencies of the related starting halo-bridged materials. This behaviour is indicative of the presence of strong hydrogen bonds in the carbonyl complexes, either intermolecular [form (A)] or intramolecular [form (B)]. Hydrogen bonding to the carbonyl group probably does not occur, otherwise the ν(CO) (2108–2133 cm^{-1}) frequencies, which are characteristic for palladium(II) carbonyl complexes[4,11], would also be shifted to lower wavelengths.



(A)



(B)

The fact that the IR spectra of carbon tetrachloride solutions of complex (VIa) 0.05 *M* and 0.01 *M* and of complexes (VIb) and (VIc) 0.1 *M* and 0.01 *M*, respectively, exhibit only one ν(OH) absorption at 3147, 3190 and 3230 cm^{-1}, respectively, suggests the presence of intramolecular hydrogen bonds [form (B)]. A similar structure probably exists in the other complexes prepared, but in their cases IR measurements were not practicable owing to the low solubility of these complexes in carbon tetrachloride. Complexes (VIa), (VIb) and (IXa) have two ν(CO) absorptions in the solid state probably due to solid-state splitting.

Table 1 also shows the marked dependence of ν(CO) and ν(OH) frequencies on the nature of the halogen in each halo(2,*N-dihapto*-aromatic oxime)palladium(II) carbonyl compound.

The ν(OH) frequencies decreased in the order I- > Br- > Cl-complex indicating that the strength of the intramolecular hydrogen bonds is in the order Cl- > Br- > I-complex; this order is the same as that of the inductive effects of the halogen group.

Irving and Magnusson[14] have studied the effect of halogens on the ν(CO) frequencies of halo–platinum carbonyl complexes and have found that the ν(CO) frequencies decrease in the order Cl- > Br- > I-complex in each complex $Pt(CO)LX_2$ (X=Cl, Br, I; L=CO, pyridine, aniline, etc.). As shown in Table 1, the ν(CO) frequencies of the present carbonyl complexes exhibit the same order. Such an order can also be explained in terms of inductive effects; the effective nuclear charge on the palladium atom should decrease in the order Cl- > Br- > I-complex for each halo(2,*N-dihapto*-aromatic oxime)palladium(II) carbonyl complex and an increase in the nuclear charge should lead to a diminished back-donation from palladium to the antibonding π^* orbital of the CO group, *i.e.*, to a higher ν(CO) frequency.

EXPERIMENTAL

Melting points were determined on a Yanagimoto microstage apparatus and are reported uncorrected. Chloroform was purified by passing through a column packed with basic alumina (E. Merck, Grade 1). Carbon tetrachloride was dried over phosphorus pentoxide and redistilled. n-Hexane was refluxed with lithium aluminum hydride and re-distilled. IR spectra were recorded on a Nippon Bunko Model DS-403G Spectrometer, ammonia vapor, gaseous carbon monoxide, indene, or polystyrene being used for calibration. Di-μ-chlorobis(2,*N-dihapto*-aromatic oxime)-dipalladium(II) and bromo analogs were prepared as previously described[10].

Analyses, yields and melting points of new bromo- and iodo-bridged complexes are summarized in Table 2. Iodo-analogs were prepared as follows.

TABLE 2

DI-μ-HALOBIS(2,*N-dihapto*-AROMATIC OXIME)DIPALLADIUM(II) COMPLEXES

Compounds	Yield(%)	M.p.[a] (°C)	Analyses, found (calcd.) (%)	
			C	H
(Ic)	95.8	173–175	36.27 (36.35)	2.44 (2.35)
(IIc)	93.2	220–225	26.22 (26.15)	2.32 (2.20)
(IIIb)	95.7	246	30·92 (30.84)	2.62 (2.88)
(IIIc)	96.9	231–233	27.15 (27.19)	2.77 (2.54)
(IVb)	90.4	196–197	28.93 (28.55)	2.55 (2.40)
(IVc)	93.1	120	25.90 (25.06)	2.22 (2.11)
(Vb)	97.4	253–254	39.56 (38.89)	2.85 (2.73)
(Vc)	99.2	246–247	35.38 (34.52)	2.68 (2.42)

[a] All compounds decomposed with or without melting.

Preparation of di-μ-iodobis(2,N-dihapto-benzophenone-oxime)dipalladium(II) (Ic)

To a solution of di-μ-chlorobis(2,*N-dihapto*-benzophenone oxime)dipalladium(II) (Ia) (200 mg) in acetone (10 ml) was added a solution of potassium iodide (300 mg) in water (2 ml). After standing for 1 min, water was added dropwise to the solution. The precipitated yellow solids were filtered, washed with water and dried.

Other chloro-bridged complexes were insoluble in acetone, but clear solutions could be prepared by mixing with aqueous potassium iodide. As soon as clear solutions were obtained, they were worked up as above. Iodo-complexes were unstable in solution but stable in the solid state.

Reaction of di-μ-halobis(2,N-dihapto-aromatic oxime)dipalladium(II) with carbon monoxide. General procedure.

A chloroform solution or suspension of halo-bridged complexes was placed in a flask equipped with a magnetic stirrer bar and connected to a vacuum line. The system was evacuated, carbon monoxide introduced and stirring commenced. The absorption of carbon monoxide was completed in about 10 min and a clear solution (colorless to yellow) was obtained.

The stoichiometry of the reaction was confirmed by direct determination of the uptake of carbon monoxide, the volume of carbon monoxide taken up at 1 atm being followed by means of a gas-buret. The progress of the reaction was also confirmed by following the IR spectrum of the solution, samples of the solution were withdrawn periodically. The reaction was most conveniently followed by measuring the disappearance of the ν(OH) bands of the starting halo-bridged complexes.

Isolation of halo(2,N-dihapto-aromatic oxime)palladium(II) carbonyl

All reactions were carried out as above and the analytical data of the complexes obtained are summarized in Table 3. Some of these complexes when isolated contained small amounts of the corresponding starting complexes as judged from their IR spectra. In addition, the crystals of complexes (VIa) and (VIb) contained chloroform as confirmed by the presence of an absorption at 1223 cm^{-1} due to chloroform in their IR spectra. The typical procedure for their isolation is as follows.

TABLE 3

ANALYTICAL DATA FOR HALO(2,*N-dihapto*-AROMATIC OXIME)PALLADIUM(II) CARBONYL COMPLEXES

Compounds	Analyses, found (calcd.) (%)			
	C	H	Cl	Pd
(VIa)[a]	41.87 (41.53)	2.57 (2.52)	19.64 (19.42)	23.77 (23.63)
(VIb)[b]	38.25 (38.13)	2.39 (2.30)		
(VIIa)	35.88 (35.55)	2.66 (2.66)		
(VIIb)	31.04 (31.02)	2.41 (2.32)		
(VIIc)	27.62 (27.33)	2.10 (2.04)		
(VIIIa)	36.38 (35.95)	3.38 (3.02)		32.07 (31.85)
(VIIIb)	32.35 (32.59)	2.67 (2.74)		
(VIIIc)	28.64 (28.22)	2.55 (2.37)		
(IXa)	33.56 (33.77)	2.45 (2.52)	10.90 (11.08)	
(IXb)	29.96 (29.66)	2.27 (2.22)		
(IXc)	26.06 (26.27)	2.01 (1.96)		
(Xa)	43.99 (44.09)	2.94 (2.85)		30.11 (30.05)
(Xb)	39.34 (39.08)	2.48 (2.53)		
(Xc)	34.98 (35.04)	2.35 (2.27)		

[a] Contained 3/7 $CHCl_3$ per molecule. [b] Contained 1/3 $CHCl_3$ per molecule.

A solution of complex (Ia) (300 mg) in chloroform (5 ml) was stirred for 20 min under carbon monoxide. The solution was filtered through kieselguhr on sintered glass and the filtrate was again stirred under carbon monoxide. n-Hexane (40 ml) pre-saturated with carbon monoxide was added to the solution, whereupon pale yellow crystals were deposited. These were filtered, washed with n-hexane pre-saturated with carbon monoxide and dried *in vacuo* in a desiccator to give complex (VIa) (347 mg, 93.8%).

Measurement of the IR spectrum in carbon tetrachloride. Measurement of hydrogen bonds

A solution (0.005 *M*) of complex (Ia), (Ib) or (Ic) (0.1 mmole) in carbon tetrachloride (20 ml) was stirred under carbon monoxide for 20 min. The sample was withdrawn for the IR measurement.

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