Journal of Organometallic Chemistry, 218 (1981) 409—416
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

A NEW TYPE OF PALLADIUM(0) COMPLEX HAVING BOTH ELECTRON-WITHDRAWING AND -DONATING SITES IN A LIGAND: 5,8-DIHYDRO- AND 5,8,9,10-TETRAHYDRO-1,4-NAPHTHOQUINONE COMPLEXES

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(Received March 5th, 1981)

Summary

A new type of palladium(0) complex, (5,8-dihydro-1,4-naphthoquinone)Pd-$(PPh_3)_2$ and (5,8,9,10-tetrahydro-1,4-naphthoquinone)Pd$(PPh_3)_2$, having both olefin and quinone or dihydro-quinone sites in a ligand molecule was prepared. IR and ^{1}H NMR spectroscopic studies of these complexes suggested that it is the quinone or dihydro-quinone C=C bond which is complexed to Pd. Ligand exchange reactions showed that the stability order of the olefinic quinone complexes was as follows: (1,4-naphthoquinone)Pd$(PPh_3)_2$ > (5,8-dihydro-1,4-naphthoquinone)Pd$(PPh_3)_2$ > (5,8,9,10-tetrahydro-1,4-naphthoquinone)Pd$(PPh_3)_2$.

Introduction

Studies on olefin complexes of palladium(0) have been relatively limited because of the low stability of such complexes and the lack of an appropriate route for their preparation. A few reports have appeared on [Pd(olefin)$(PPh_3)_2$] complexes (olefin = octafluoro-2-butene, dimethyl maleate, dimethyl fumarate, maleic anhydride, ethylene, and styrene) [1—4] and [Pd(quinone)$(L)_2$] type complexes (quinone = *p*-benzoquinones and 1,4-naphthoquinones; L = PPh_3, 1/2(*o*-phenanthroline), 1/2(2,2′-bipyridine), and 1/2(*N,N,N′,N′*-tetramethyl-

0022-328X/81/0000—0000/$02.50

ethylenediamine) [4—6]. A palladium(0) complex containing only an olefin as ligand, bis(dibenzylideneacetone)palladium(0) [7—10], has also been reported.

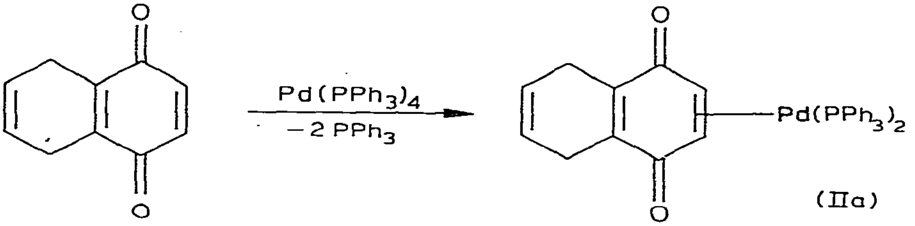
The complexes mentioned above contain a quinone or an electron-deficient olefin as a ligand, and seem to be stabilized by its electron-withdrawing effect. Pd^0 has a rather low affinity for usual olefin coordination, as was seen in the unsuccessful attempt to prepare the bis(1,5-cyclooctadiene) complex of Pd^0 using the procedure found to be successful for similar Ni^0 and Pt^0 compounds [2,10]. An exceptional Pd^0 complex which contains maleic anhydride as an electron-deficient ligand and 1,5-cyclooctadiene as an electron-donating ligand has been described by Itoh et al. [11].

However, palladium(0) complexes containing a ligand which has both an electron-donating olefin site and an electron-withdrawing quinone or dihydroquinone site in a ligand molecule have not been prepared. We report here the preparation and the properties of palladium(0) complexes of 5,8-dihydro-1,4-naphthoquinone and 5,8,9,10-tetrahydro-1,4-naphthoquinone, which are of particular interest since they contain a quinone (or dihydro-quinone) site and a dihydro- or tetrahydro-benzene-type olefin site in a ligand molecule. Therefore, this ligand has both oxidation and reduction sites.

Results and discussion

Preparation of the palladium(0) complexes

The reaction of $Pd(PPh_3)_4$ with 5,8-dihydro-1,4-naphthoquinone (Ia) in 1/1 molar ratio in benzene under argon afforded bis(triphenylphosphine)(5,8-dihydro-1,4-naphthoquinone)palladium(0) (IIa) in 83% yield (eq. 1). The reaction mixture initially was a homogeneous red-brown solution, and the Pd^0 complex (IIa) precipitated gradually as an orange powder.

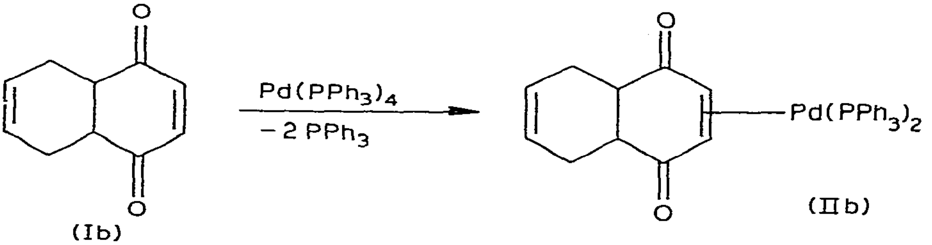


(1)

(Ia)

(IIa)

Similarly, 5,8,9,10-tetrahydro-1,4-naphthoquinone (Ib) reacted with an equimolar amount of $Pd(PPh_3)_4$ in benzene/diethyl ether to give bis(triphenylphosphine)(5,8,9,10-tetrahydro-1,4-naphthoquinone)palladium(0) (IIb) in 71% yield (eq. 2). This Pd^0 complex (IIb) was formed gradually as pale yellow powder during the reaction.



(2)

(Ib)

(IIb)

These two complexes appear to be fairly stable in air in the solid state. They decomposed gradually in usual organic solvents under atmosphere of air to precipitate metallic palladium. They are soluble in CH_2Cl_2 and $CHCl_3$, and complex IIb has higher solubility in organic solvents than the complex IIa. Table 1 summarizes decomposition points and elemental analyses of these new olefinic quinone complexes.

NMR and infrared spectra of the complexes

In order to obtain information on the structure of complexes IIa and IIb, the ^1H NMR and the infrared spectra were measured in $CDCl_3$ and in $CHCl_3$, respectively. Table 2 presents NMR and infrared data for complexes IIa and IIb. Both show signals at 4.60 and 4.29 ppm, respectively, in their NMR spectra which were much different from the corresponding signals of free ligands. These signals were assigned not to the isolated olefinic protons (H(3)) but to the conjugated olefinic protons (H(1)), because bis(triphenylphosphine)(1,4-naphthoquinone)-palladium(0) (IIc) showed the conjugated olefinic protons at 4.71 ppm in $CDCl_3$. In the NMR spectra of IIa and IIb, upfield shifts of the isolated olefinic proton (H(3)), the methylene proton (H(2)), and the methine proton (H(4)) signals of about 0.1—0.7 ppm also were observed. However, these shifts are rather small when they are compared with those of the conjugated olefinic protons (H(1)). Thus, palladium(0) appears to coordinate to a conjugated C=C group, i.e., the quinone site is more favorable than the isolated olefin site for coordination to palladium(0). The infrared spectroscopic data also support this postulated type of coordination.

In the infrared spectra, the frequencies of the ν(C=O) band of the olefinic quinones were decreased by 40—50 cm^{-1} by coordination to Pd^0. As was reported in the case of $[Mo(acrolein)_2(CO)_2]$ [12], where the ν(C=O) value of the conjugatively coordinated unsaturated carbonyl group was decreased by 150 cm^{-1}, the participation of both C=C and C=O bonds of the conjugated carbonyl ligand in bonding to a metal is assumed to cause a larger shift of ν(C=O) to lower frequency. Contrary to the case of such conjugated coordination, in the case of $[Pd(olefin)(PPh_3)_2]$ (olefin = dimethyl fumarate and dimethyl maleate), in which direct interaction between C=O group and Pd^0 does not occur [4], the lowering of ν(C=O) is small (about 30—35 cm^{-1}). The small frequency shifts of ν(C=O) of the present complexes then would indicate that

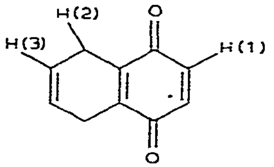
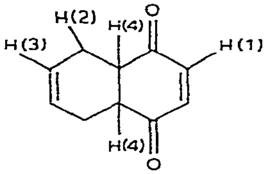
TABLE 1

DECOMPOSITION POINTS AND ANALYTICAL DATA IN $Pd(OLEFINIC\text{-}QUINONE)[P(C_6H_5)_3]_2$

No.	Complex Olefinic quinone	Yield (%)	Color	Dec. (°C)	Analyses found (calcd.) (%)	
					C	H
IIa	5,8-Dihydro-1,4-naphthoquinone	83	orange	171—176	69.82 (69.83)	4.85 (4.84)
IIb	5,8,9,10-Tetrahydro-1,4-naphthoquinone	71	pale-yellow	159—165	69.72 (69.66)	5.31 (5.08)

TABLE 2

^{1}H NMR AND IR DATA FOR FREE AND COMPLEXED OLEFINIC QUINONES

Olefinic quinone		Proton assign.	δ (ppm) (in $CDCl_3$)		ν(C=O) (cm^{-1}) (in $CHCl_3$)	
			Free	Complexed	Free	Complexed
	(Ia)	H(1)	6.71	4.60	1656	1619
		H(2)	3.06	2.65		
		H(3)	5.80	5.71		
		P—Ph	7.2(br) [a]	7.2(br)		
	(Ib)	H(1)	6.59	4.29	1692	1640 1655(sh)
		H(2)	2.25	2.0(br)		
		H(3)	5.65	5.47		
		H(4)	3.15	2.5(br)		
		P—Ph	7.2(br) [a]	7.2(br)		

[a] Datum for $Pd(PPh_3)_4$.

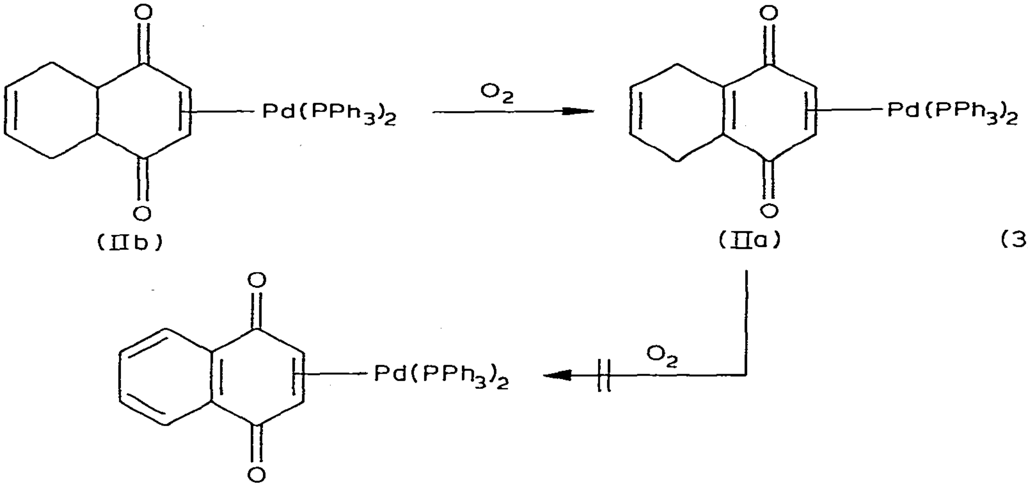
there is no or only weak interaction between the C=O group and Pd^0 in IIa and IIb.

These results thus suggest that coordination via the quinone or dihydroquinone C=C bond will be more important in complexation of the olefinic quinone ligands Ia and Ib to Pd^0 than that via the olefinic site in the dihydro- or tetrahydrobenzene portion of the ligand. However, Ib has a *cis*-structure (concerning the H(4) positions), and the coordination of the isolated olefin site to Pd^0 in IIb obtained from Ib cannot be excluded as yet, because of the observed upfield shift of the isolated olefinic proton signal (H(3)). X-ray structural analysis of the complexes clearly is required.

Reaction of the palladium(0) complexes with O_2 or chlorobenzene

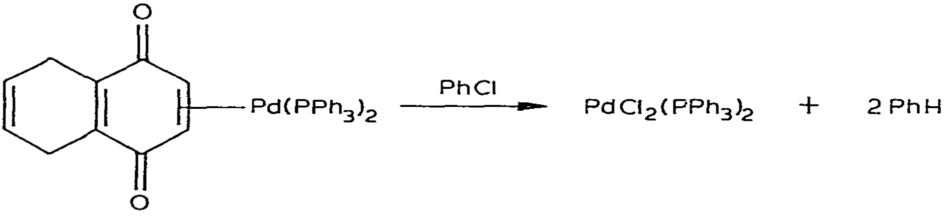
Neither 5,8-dihydro-1,4-naphthoquinone (Ia) or 5,8,9,10-tetrahydro-1,4-naphthoquinone (Ib) reacted with oxygen in CH_2Cl_2 for 2 h at room temperature, whereas (5,8,9,10-tetrahydro-1,4-naphthoquinone)$Pd(PPh_3)_2$ (IIb) reacted with oxygen under similar conditions (eq. 3), i.e., the reactivity of Ib with oxygen is increased by coordination to Pd^0. It is interesting that complex IIb reacted more readily with oxygen than IIa, which has a mobile hydrogen atom (H(2)) as part of its dihydrobenzene structure. This may suggest that the isolated olefin site interacts with Pd^0 as well as the quinone site to stabilize the dihydrobenzene moiety.

Complex IIa reacted with chlorobenzene in CH_2Cl_2 at reflux to give benzene and $PdCl_2(PPh_3)_2$ (eq. 4). 1,4-Naphthoquinone, which was expected as the dehydrogenation product, was not detected. Instead, an unidentified black solid, which presumably was formed from the unstable 5,8-dihydro-1,4-naphthoquinone ligand which dissociated, was obtained. (Note the reported oxidative addition of benzyl or alkyl halides to Pd^0 compelxes [13,14]).



(IIb) (IIa) (3)

(IIc)

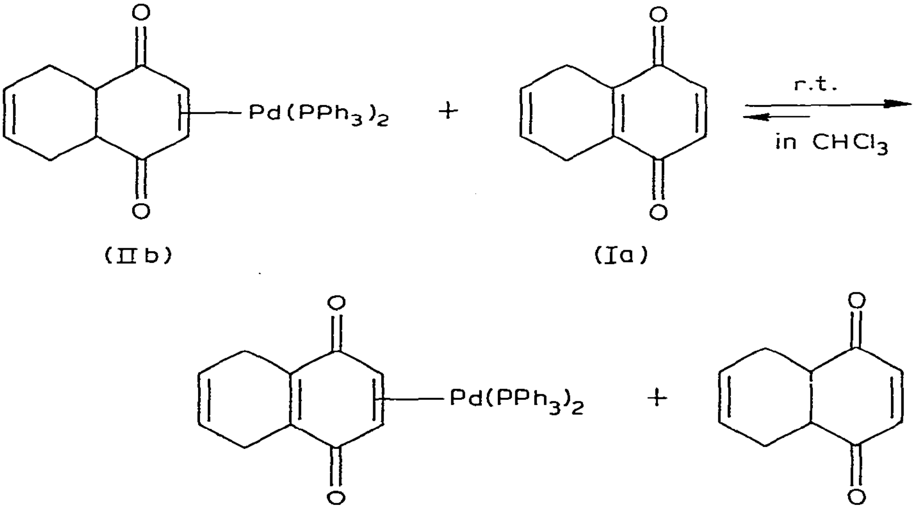


(4)

(IIa)

Ligand exchange reactions

In order to determine the relative stability of these new palladium(0) complexes, ligand exchange reactions were carried out. Complex IIb reacted with an equimolar amount of 5,8-dihydro-1,4-naphthoquinone (Ia) in $CHCl_3$ at room temperature under argon to give the unreacted complex IIb and complex IIa in a ratio of 5/9 (calculated from the areas of the NMR signals) (eq. 5).

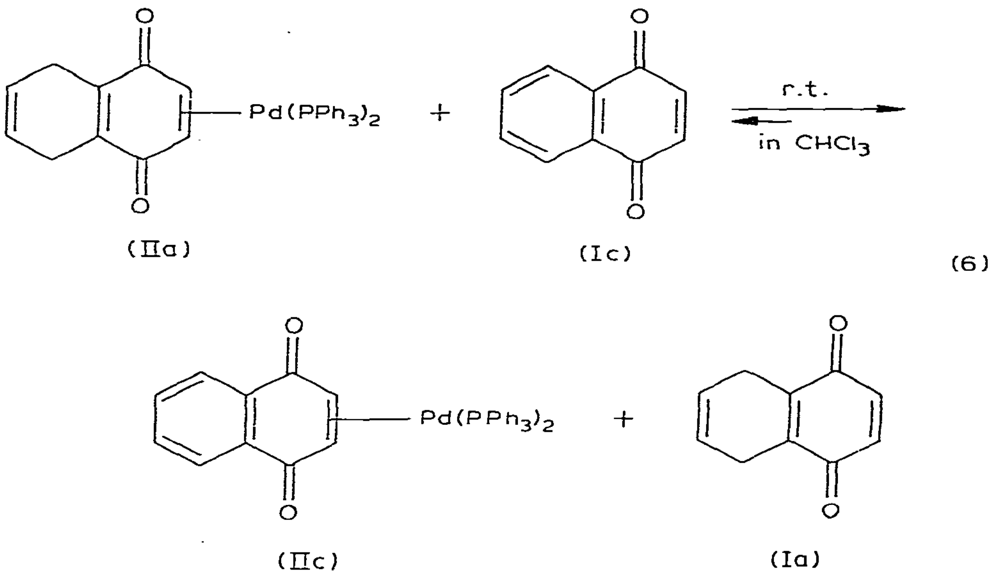


(IIb) (Ia)

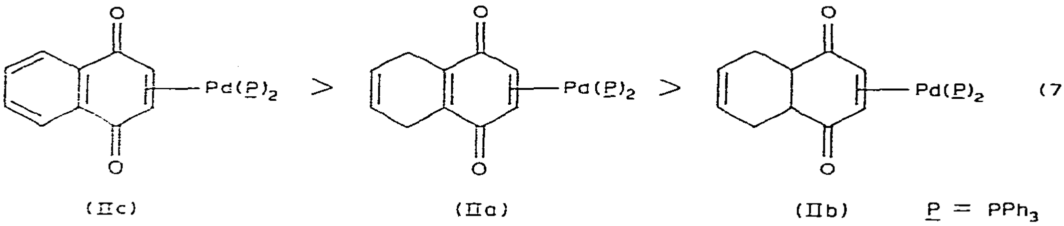
(5)

(IIa) (Ib)

Subsequently, complex IIa reacted also with an equimolar amount of 1,4-naphthoquinone (Ic) under similar conditions to give complex IIc (which was confirmed by the signal of the olefinic protons at 4.7 ppm and ν(C=O) at 1636 cm^{-1}), accompanied by the formation of free Ia. The NMR signals and the IR absorption bands assignable to complex IIa were not observed (eq. 6).



From these facts, the kinetic stability order of the olefinic quinone complexes is as shown in eq. 7. Such an order is not inconsistent with that of the usual electron-acceptor property or with the steric hindrance of the ligands.



However, this order differs from that of the reduction potentials of the corresponding olefinic quinones, which were measured by the polarographic method in CH_3CN using Ag/AgCl as a reference electrode, $E(1/2)$(V): Ia(—0.43, —1.03) > Ic(—0.50, —1.05) > Ib(—1.02, >—2.40). Studies on the characteristic behavior of these complexes (IIa—IIc) in oxidation-reduction processes are in progress and will be published at a later date.

Experimental

The infrared spectra were recorded on a Jasco IRA-1 spectrometer. The ^{1}H NMR spectra were measured on a Hitachi-Perkin-Elmer R24 spectrometer. The ^{1}H NMR signals are referred to internal tetramethylsilane. All manipulations were carried out under an atmosphere of argon. Solvents were dried in the usual manner, distilled, and stored under an atmosphere of nitrogen.

Materials

$Pd(PPh_3)_4$ and 5,8,9,10-tetrahydro-1,4-naphthoquinone (Ib) were prepared by literature methods [15] and [16]. 1,4-Naphthoquinone (1c) was commercially available and purified by recrystalization. 5,8-Dihydro-1,4-naphthoquinone was prepared by a following method. 5,8,9,10-Tetrahydro-1,4-naphthoquinone (Ib) (1.62 g, 10.0 mmol) was stirred for 10 min in dioxane (6.5 ml)/H_2O (4.0 ml) containing 0.25 *N* KOH at room temperature, followed by neutralization with dilute HCl to afford 5,8-dihydroxy-1,4-dihydronaphthalene (Id) (1.41 g, 87% yield); m.p. 208—210°C (lit. 212°C [16]). Subsequently, 5,8-dihydroxy-1,4-dihydronaphthalene (Id) (1.26 g, 7.77 mmol) was stirred for 1 h in dioxane (10 ml)/conc. HNO_3 (2.0 ml) at 0°C. The reaction mixture changed to a homogeneous yellow solution after a dark green precipitate appeared. Addition of a large excess of water to the reaction mixture afforded a yellow precipitate. The product was filtered, washed with cold water, and dried in vacuo to yield yellow crystals of 5,8-dihydro-1,4-naphthoquinone (Ia) (0.883 g, 71% yield); m.p. 105—107°C (lit. 109°C [16]).

Preparation of (5,8-dihydro-1,4-naphthoquinone)$Pd(PPh_3)_2$ (IIa)

5,8-Dihydro-1,4-naphthoquinone (Ia) (0.554 g, 3.46 mmol) and $Pd(PPh_3)_4$ (4.00 g, 3.46 mmol) were dissolved in benzene (80 ml) under argon at room temperature. The mixture was stirred for 5 h at room temperature to precipitate a red-brown powder, which was filtered, washed with diethyl ether, and dried in vacuo. The product was recrystallized from acetone to yield orange crystals of IIa (2.27 g, 83% yield).

Preparation of (5,8,9,10-tetrahydro-1,4-naphthoquinone)$Pd(PPh_3)_2$ (IIb)

Similar to the case of IIa, a mixture of 5,8,9,10-tetrahydro-1,4-naphthoquinone (Ib) and $Pd(PPh_3)_4$ was stirred in benzene/diethyl ether (1/1) to yield a pale-yellow powder of IIb (2.00 g, 71% yield).

Reaction of complex IIb with O_2

Oxygen was bubbled for 2 h at room temperature into a solution of complex IIb (0.200 g, 0.25 mmol) in dichloromethane (10 ml). The reaction solution changed from yellow to brown. After removal of solvent, the signals of the coordinated olefinic protons in the unreacted complex IIb and complex IIa were observed in a molar ratio of 4/1 (calculated from the areas of the NMR signals of the reaction mixture in $CDCl_3$).

Reaction of complex IIa with chlorobenzene

To a solution of complex IIa (0.200 g, 0.76 mmol) in dichloromethane (3 ml), chlorobenzene (0.085 g, 0.76 mmol) was added, and the mixture was heated at reflux for 24 h. After removal of solvent, the NMR signal of benzene was observed at 7.37 ppm (singlet) in the reaction trap. The formation of $PdCl_2(PPh_3)_2$, which was purified by recrystallization from acetone after removal of solvent, was also confirmed by decomposition point (260—265°C; lit. 259—

260°C [14]) and elemental analysis (found: C, 62.04; H, 4.44. $C_{36}H_{30}Cl_2P_2Pd$ calcd.: C, 61.61; H, 4.31%).

Ligand exchange reactions

To a solution of complex IIb (0.300 g, 0.38 mmol) in chloroform (10 ml), free Ia (0.060 g, 0.38 mmol) in chloroform (10 ml) was added at room temperature, and the mixture was stirred for 12 h. After removal of solvent, the signals of the coordinated olefinic protons in the unreacted complex (IIb) and complex IIa were observed in a molar ratio of 5/9, which was calculated from the areas of the NMR signals of the reaction mixture in $CDCl_3$.

The ligand exchange reaction of complex IIa with free Ic also was carried out under similar conditions. After removal of solvent, the NMR signals and the IR absorption bands of complex IIc and free Ia were observed.

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