ON THE EXISTENCE OF ORGANOMETALLIC PALLADIUM(IV) COMPLEXES

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Summary

The reactions of palladium(II) compounds of the type Cl_2PdL_2 with bromobis(pentafluorophenyl)thallium(III) has been reexamined. The reported preparation of the organo palladium(IV) complex $Cl_2Pd(C_6F_5)_2(PPh_3)_2$ could not be repeated, and instead mixtures of binuclear palladium(II) compounds, $Cl_2Pd(C_6F_5)_2L_2$, and mononuclear palladium(II) compounds were obtained. The binuclear are transformed into the mononuclear complexes on addition of an excess of ligand L.

The chlorine bridging atoms of the binuclear complexes can be replaced by other halogens or pseudohalogens by treatment with salts of the MX type (X = Br, I, SCN).

Introduction

Nyholm and Royo [1,2] reported that $BrTl(C_6F_5)_2$ can be used for the oxidation of transition metal complexes by converting them into organometallic complexes whose central atom has both its oxidation number and its coordination number increased by two.

$$X_2ML_2 + BrTl(C_6F_5)_2 \rightarrow X_2M(C_6F_5)_2L_2 + TlBr \tag{1}$$
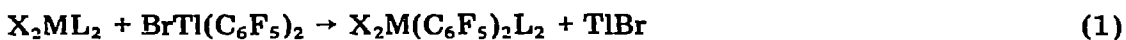
They stated that $Cl_2Pd(PPh_3)_2$ gives the corresponding hexacoordinated palladium(IV) complex obtained according to eqn. 1, and Nyholm furthermore claimed that $Cl_3Pd(C_6F_5)(PPh_3)_2$ is apparently produced by direct chlorination of $ClPd(C_6F_5)(PPh_3)_2$ [3].

The products mentioned are the only reported organometallic palladium(IV) complexes, and so their preparation was quickly noted in specialist literature [4,5]. However, the procedure for preparing $Cl_3Pd(C_6F_5)(PPh_3)_2$ was never published, and we have observed that the reaction of chlorine with $ClPd(C_6F_5)(PPh_3)_2$ always leads to breaking of the Pd—C bond even under

very mild conditions (with diluted halogen solutions, at room temperature). This left $Cl_2Pd(C_6F_5)_2(PPh_3)_2$ as the only apparent example of an organometallic palladium(IV) compound, but the existence of this complex would be rather surprising, since it is known that square planar complexes of d^8 ions of the third transition series are more likely to undergo oxidative addition reactions than are those of the second series and even so we could not detect any platinum(IV) product from the reaction of the corresponding platinum(II) complex Cl_2PtL_2 with $BrTl(C_6F_5)_2$ [6]. It thus seemed desirable to reexamine the supposed preparation of $Cl_2Pd(C_6F_5)_2(PPh_3)_2$. The results which are discussed below show that $BrTl(C_6F_5)_2$ does not oxidize compounds of the Cl_2-PdL_2 type (L = PPh_3, PPh_2Me, $AsPh_3$), and that no palladium(IV) complex could have been prepared by such a route. The reactions are, nevertheless, of value for the synthesis of Cl-bridged organopalladium(II) compounds of the $Cl_2Pd_2(C_6F_5)_2L_2$ type and of mononuclear complexes of the $ClPd(C_6F_5)L_2$ type.

Results and discussion

(a) Preparative results

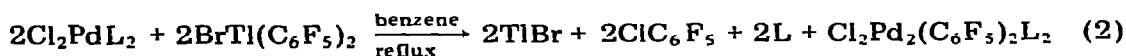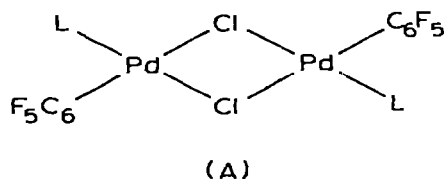When benzene solutions of stoichiometric amounts of Cl_2PdL_2 (L = PPh_3, PPh_2Me, $AsPh_3$) and $BrTl(C_6F_5)_2$ are refluxed the initially orange-red or reddish solution gradually turns pale yellow as TlBr is separated over 4-6 hours.

When the TlBr is removed by filtration and the yellow solution set aside (L = PPh_3) or eventually concentrated and set aside (L = PPh_2Me, $AsPh_3$), yellow crystals separated and their analyses are shown in Table 1. It is evident that no palladium(IV) complex can be obtained, although it may be formed as an intermediate. The stoichiometry of the products obtained agrees with that expected for the binuclear palladium(II) complexes of type A,

TABLE 1

ANALYTICAL RESULTS FOR $Cl_2Pd_2(C_6F_5)_2L_2$, $ClPd(C_6H_5)L_2$ AND $X_2Pd_2(C_6F_5)_2(PPh_3)_2$

Complex	Analysis found (calcd.) (%)				
	C	H	Cl	N	Pd
$Cl_2Pd_2(C_6F_5)_2(PPh_3)_2$ (I)	50.61	2.74	6.46		18.03
	(50.46)	(2.64)	(6.20)		(18.62)
$Cl_2Pd_2(C_6F_5)_2(PPh_2Me)_2$ (V)	44.85	2.90	6.36		20.47
	(44.81)	(2.55)	(6.96)		(20.89)
$Cl_2Pd_2(C_6F_5)_2(AsPh_3)_2$ (III)	47.45	3.06	5.43		16.57
	(46.86)	(2.44)	(5.76)		(17.29)
$ClPd(C_6F_5)(PPh_3)_2$ (II)	60.24	3.25	4.17		12.89
	(60.52)	(3.62)	(4.25)		(12.76)
$ClPd(C_6F_5)(PPh_2Me)_2$ (VI)	53.86	3.74	4.13		14.68
	(54.18)	(3.66)	(4.99)		(14.99)
$ClPd(C_6F_5)(AsPh_3)_2$ (IV)	54.25	3.34	3.85		10.36
	(54.74)	(3.28)	(3.84)		(11.54)
$Br_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VII)	47.02	2.44			
	(46.81)	(2.43)			
$I_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VIII)	43.42	2.60			
	(43.48)	(2.26)			
$(SCN)_2Pd_2(C_6F_5)_2(PPh_3)_2$ (IX)	50.79	2.66		2.32	
	(50.56)	(2.52)		(2.32)	

which are formed according to the overall eqn. 2.

(A)

$$2Cl_2PdL_2 + 2BrTl(C_6F_5)_2 \xrightarrow[\text{reflux}]{\text{benzene}} 2TlBr + 2ClC_6F_5 + 2L + Cl_2Pd_2(C_6F_5)_2L_2 \quad (2)$$

Mixtures of crystals of the binuclear complex and of $ClPd(C_6F_5)L_2$ are obtained when ethanol is added to benzene solution (which in some cases must also be concentrated by partial evaporation) from which the binuclear complex has previously been removed by filtration. They are either a direct product of the reaction (see below) or are the result of the breaking of the halogen bridges by the ligand L, liberated according to eqn. 2.

$$Cl_2Pd_2(C_6F_5)_2L_2 + 2L \rightarrow 2ClPd(C_6F_5)L_2 \quad (3)$$
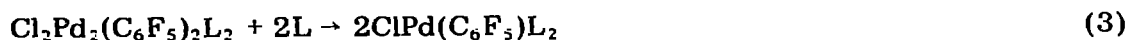
When L = PPh_3 the mixture can easily be resolved by fractional crystallization (see Experimental section).

If an excess of ligand L is added to the mixture of crystals resulting from process 2 or to pure samples of the binuclear complexes, reaction 3 occurs quantitatively and the pure mononuclear complexes may be isolated (the analyses are shown in Table 1).

It is clear that while it can give binuclear complexes of the $Cl_2Pd_2(C_6F_5)_2L_2$ type and mononuclear complexes of the $ClPd(C_6F_5)L_2$ type (which are difficult to prepare by other procedures) $BrTl(C_6F_5)_2$ does not convert Pd^{II} to Pd^{IV} compounds, or, alternatively that $Cl_2Pd(C_6F_5)_2(PPh_3)_2$ is formed but is not stable under the published conditions [1,2].

When stoichiometric amounts of Cl_2PdL_2 and $BrTl(C_6F_5)_2$ are stirred at room temperature, the solution remains yellow after six hours and no thallium-(I) bromide is precipitated. If after 6 h the solution is concentrated under reduced pressure, without warming, yellow crystals separate whose analyses are consistent with the formation of a binuclear complex.
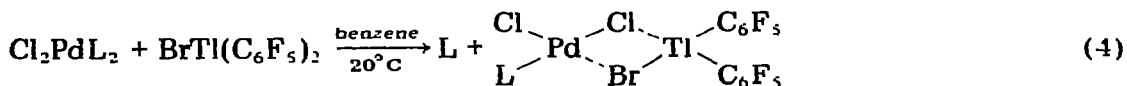

In the overall process represented by eqn. 2, when the solution is being refluxed a C_6F_5 group is presumably transferred to the palladium atom, with splitting of the bridge, and this is followed by the formation of ClC_6F_5 and the precipitation of TlBr.

The coordinatively unsaturated fragment B can attain stabilization by dimerizing to a binuclear complex $Cl_2Pd_2(C_6F_5)_2L_2$ or by taking up the ligand L, previously set free in reaction 4. Thus the reaction gives rise to mixtures of binuclear and mononuclear complexes. If an excess of ligand L is present from the beginning the only complex which is formed is the mononuclear one, which can then be readily separated in pure form.

(5)

(B)
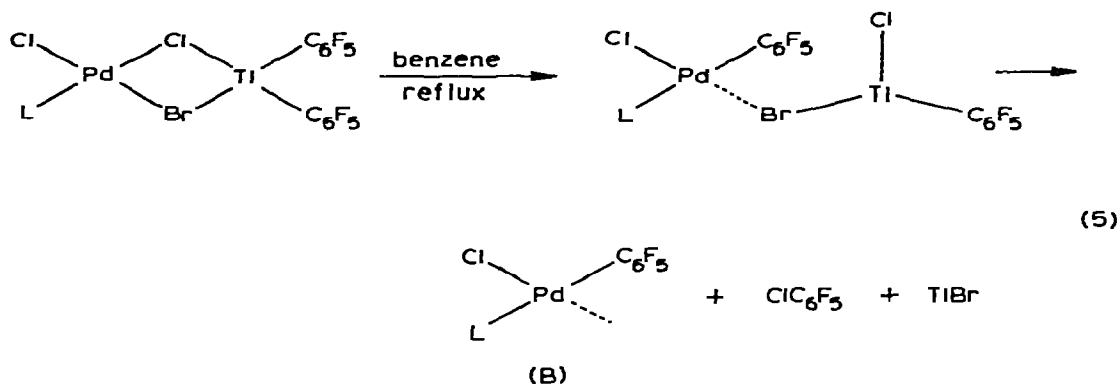
(b) Substitution reactions of the binuclear complex $Cl_2Pd_2(C_oF_5)_2(PPh_3)_2$

The chlorine atoms of the binuclear complexes $Cl_2Pd_2(C_6F_5)_2L_2$ can be replaced by other anions without the bridge being split. So, the complex Cl_2-$Pd_2(C_6F_5)_2(PPh_3)_2$ undergoes substitution reactions as in eqn. 6. Details of the products are shown in Table 1.

$$Cl_2Pd_2(C_6F_5)_2(PPh_3)_2 + 2MX \rightarrow X_2Pd_2(C_6F_5)_2(PPh_3)_2 + 2MCl \qquad (6)$$
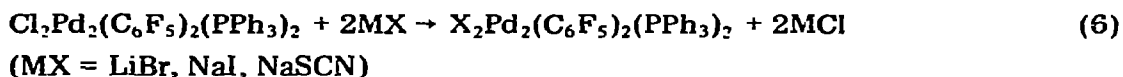
(MX = LiBr, NaI, NaSCN)

The substitution takes place increasingly readily in the sequence LiBr < NaI < NaSCN i.e. with the increasing nucleophilic character of the anion X. Thus with LiBr it is necessary to work at reflux temperature for some hours, whilst with NaI and NaSCN the reaction occurs readily at room temperature. This agrees with the expected trend.

(c) Conductivities and melting points

Only one of the complexes melts without decomposition. The results of the conductance studies in approx. $5 \times 10^{-4} M$ solutions are shown in Table 2. The very low conductivities show that both the binuclear and the mononuclear complexes are non-conductors [7].

TABLE 2

MOLAR CONDUCTIVITIES AND MELTING POINTS

Complex	λ_{max}(ohm^{-1} cm^2 mol^{-1})	M.p.(^{o}C)
$Cl_2Pd_2(C_6F_5)_2(PPh_3)_2$ (I)	3.8[a]	251(dec.)
$Cl_2Pd_2(C_6F_5)_2(PPh_2Me)_2$ (V)	7.8[b]	220(dec.)
$Cl_2Pd_2(C_6F_5)_2(AsPh_3)_2$ (III)	0.6[c]	210(dec.)
$Br_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VII)	nil[c]	285(dec.)
$I_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VIII)	3.4[c]	294(dec.)
$(SCN)_2Pd_2(C_6F_5)_2(PPh_3)_2$ (IX)	2.0[c]	245(dec.)
$ClPd(C_6F_5)(PPh_3)_2$ (II)	1.2[a]	230(dec.)
$ClPd(C_6F_5)(PPh_2Me)_2$ (V₁)	1.4[c]	192
$ClPd(C_6F_5)(AsPh_3)_2$ (VI)	3.2[c]	250(dec.)

[a] Solvent: N,N-dimethylformamide. [b] Solvent: nitromethane. [c] Solvent: acetone.

(d) IR spectra

All the complexes show bands due to the ligand L along with those of the C_6F_5 group. Thus bands are observed near 1600-1635 m, 1490-1510 vs, 1050 -1070 vs, 950-960 vs, 780-800 s and 610 m cm^{-1}, in good agreement with literature data [8].

Mononuclear complexes. The band at 310 cm^{-1}, due to ν(Pd—Cl) can only be clearly observed when L = PPh$_3$. The internal vibrations of the ligands (or other unidentified vibrations) in the region of 350 - 300 cm^{-1} prevent a reliable assignation of ν(Pd—Cl) in the cases of L = PPh$_2$Me and AsPh$_3$.

Binuclear complexes. The ν(Pd—Cl) frequencies are influenced by all the other ligands, and especially by that *trans* to the Cl bridging atom. Two bands are observed when each chlorine is *trans* to a different ligand. In previously described complexes, none of which had a C_6F_5 group as a ligand, the band at higher frequency was in the range 337 - 280 cm^{-1} [9]. The vibrations due to ν(Pd—Br) and ν(Pd—I) should, of course, be found at lower frequencies. With our spectrophotometer (range 4000 - 250 cm^{-1}) we were only able to observe the beginning of a band at 260 cm^{-1}, in the case of L = PPh$_3$ and PPh$_2$Me, probably due to ν(Pd—Cl) for chlorine *trans* to C_6F_5. In all the other cases no bands due to ν(Pd—X) were observed.

The thiocyanate complex shows a very intense band at 2148 cm^{-1}. The other internal vibrations of the SCN group are being masked by the vibrations of other ligands. This single vibration at 2148 cm^{-1} which appears in a region free from other bands, provides reliable indication of the symmetrical arrangement of the thiocyanate bridging group (structure C) [10].

(C)
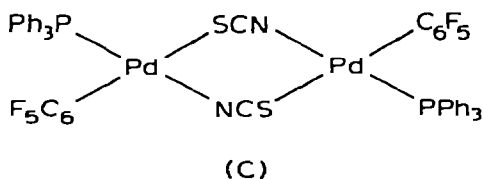
Experimental

The IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000 - 250 cm^{-1}) using Nujol mulls between polyethylene sheets. The conductivities were measured in approx. 5 × 10^{-3} M solutions with a Philips PW 9501/01 conductimeter. The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer.

For determination of Pd, the samples were dissolved in fuming nitric acid and then in perchloric acid, and the metal was precipitated with dimethyl-glyoxime [11]. Quantitive Cl analyses were performed as described by White [12], a few milligrams of sucrose being added to the sample to facilitate its combustion. The analytical results are given in Table 1.

$Cl_2Pd(PPh_3)_2$ and $Cl_2Pd(AsPh_3)_2$ were prepared by mixing stoichiometric amounts of aqueous ethanolic solutions of $K_2(PdCl_4)$ with ethanolic solutions of the ligand. The resulting yellow solids were recrystallized from dichloromethane and afterwards warmed to 100°C in a dry-oven to remove the trapped

dichloromethane. The purity of both products was confirmed by C and H analyses. The preparation of $Cl_2Pd(PPh_2Me)_2$ was carried out as described by Rausch and Tibbetts [13].

$Cl_2Pd_2(C_6F_5)_2(PPh_3)_2$ (I)

A mixture of $BrTl(C_6F_5)_2$ (1.249 g, 2.0 mmol) and $Cl_2Pd(PPh_3)_2$ (1.40 g, 2.0 mmol) in benzene (40 ml) was stirred at reflux temperature for 4 hours, then the precipitated TlBr was separated by centrifugation and the solution was set aside for 24 hours. The resulting yellow crystals were filtered off and washed with diethyl ether to give 0.46 g of I (41% yield). I is soluble in benzene, chloroform and acetone, and insoluble in ethanol, diethylether, petroleum ether, and water.

Further crystallizations of the benzene solutions yield mixtures of I and II.

$ClPd(C_6F_5)(PPh_3)_2$ (II)

A mixture of I and II, prepared as above, was refluxed with an excess of PPh_3 for 30 minutes. The solution gradually became colourless and a white product crystallized after partial evaporation and addition of ethanol. The crystalls were filtered off and treated with ether to give 0.79 g (80%) of the known [2] complex II.

$Cl_2Pd_2(C_6F_5)_2(AsPh_3)_2$ (III)

A magnetically-stirred mixture of $BrTl(C_6F_5)_2$ (1.24 g, 2.0 mmol) and $Cl_2Pd(AsPh_3)_2$ (1.58 g, 2 mmol) in benzene (50 ml) was refluxed for 4 hours, and centrifuged to remove the TlBr formed. Partial evaporation and cooling of the solution gave yellow crystals, which were filtered and repeatedly washed with petroleum ether to yield 0.3 g (25% yield) of complex III. III is soluble in benzene and acetone, and insoluble in methanol, ethanol, petroleum ether and water.

Partial evaporation of the remaining solution and the addition of ethanol resulted in crystallization of mixtures of III and IV.

$ClPd(C_6F_5)(AsPh_3)_2$ (IV)

A mixture of III and IV obtained as above was dissolved in benzene or dichloromethane and refluxed with an excess of $AsPh_3$ for 30 minutes. The solution gradually became colourless and partial evaporation and addition of ethanol gave yellowish-white crystals which were filtered off and washed with petroleum ether to give 1.24 g (90% yield) of complex IV. It is soluble in chloroform, dichloromethane, benzene and acetone, and insoluble in petroleum ether, hexane, methanol, ethanol and water.

$Cl_2Pd_2(C_6F_5)_2(PPh_2Me)_2$ (V)

A solution of $BrTl(C_6F_5)_2$ (1.18 g, 1.9 mmol) and $Cl_2Pd(PPh_2Me)_2$ (1.11 g, 1.9 mmol) in benzene (40 ml) was stirred at reflux temperature for 4 hours. The resulting TlBr was removed by centrifugation, and the solution was concentrated and left standing at room temperature for 24 hours. The yellow crystals formed were filtered and repeatedly washed with petroleum ether

to give 0.36 g (38% yield) of complex V. It is soluble in benzene and acetone, and insoluble in methanol, ethanol and petroleum ether.

Partial evaporation of the remaining solution and the addition of ethanol resulted in crystalline mixtures of V and VI.

$ClPd(C_6F_5)(PPh_2Me)_2$ (VI)

When a mixture of V and VI, obtained by procedure V, was treated with an excess of PPh_2Me, the solution immediately became colourless and slightly turbid. The centrifuged solution was partially evaporated, and complex VI (0.59 g, 70% yield) separated on addition of ethanol. VI is soluble in chloroform, dichloromethane, and benzene, slightly soluble in methanol and ethanol and insoluble in petroleum ether, hexane and water.

$Br_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VII)

A magnetically stirred mixture of complex I (1.56 g, 1.5 mmol) and LiBr (0.28 g, 3.2 mmol) in acetone (100 ml) was refluxed for 6 hours, and afterwards concentrated to approx. one third of its original volume. The precipitated NaCl was filtered off and the yellow solution was partially evaported. Upon addition of ethanol, yellow crystals were obtained which were filtered off, repeatedly washed with water, ethanol, and petroleum ether, and finally vacuum-dried (70% yield).

$I_2Pd_2(C_6F_5)_2(PPh_3)_2$ (VIII)

A solution of complex I (1.56 g, 1.5 mmol) and NaI (0.48 g, 3.2 mmol) in acetone (100 ml) was stirred at room temperature for 6 hours. The volume was reduced to approx. one third and the precipitated NaCl was removed by filtration. Ethanol was added to the partially evaporated yellow solution to precipitate yellow crystals which were filtered off, washed and dried as for VII (70% yield).

$(SCN)_2Pd_2(C_6F_5)_2(PPh_3)_2$ (IX)

A mixture of complex I (1.56 g, 1.5 mmol) and SCNNa (0.26 g, 3.2 mmol) in acetone (100 ml) was stirred at room temperature for five hours, concentrated to one third of its volume and filtered to remove the precipitated NaCl. Light-yellow crystals of complex IX were obtained upon partial evaporation of the light-yellow solution and adding ethanol. The subsequent work-up was as in VII (60% yield).

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