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A New Route for the Synthesis of Binuclear Organometallic and Inorganic Palladium(II) Complexes

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A new generally applicable route for the preparation of binuclear organometallic palladium(II) complexes is described. Compounds of the general formula $[Pd(\mu\text{-}Cl)RL]_2$ *(R being* C_6F_5 *or* C_6Cl_5*; L being a neutral ligand with N, P, As, Sb or S as donor atom) have been obtained by the reaction of organometallic compounds of the* PdR_2L_2 *type with* $PdCl_2$ *in acetone solution at room temperature. The reaction with* $PdCl_2$ *has also been used for the synthesis of inorganic palladium(II) derivatives of the* $[PdCl_2L]_2$ *type.*

The structure of the novel organometallic complexes is discussed.

Introduction

Binuclear halogen-bridged complexes of the $[PdX_2L]_2$ type (X = halogen or pseudohalogen; L = neutral Vb or VIb group ligand) can be obtained, according to Mann and Purdie [1], by refluxing stoicheiometric amounts of the mononuclear complexes $PdCl_2L_2$ and $(NH_4)_2[PdCl_4]$ in aqueous–alcoholic solution:

$$PdCl_2L_2 + M_2[PdCl_4] \longrightarrow [PdCl_2L]_2 + 2\,MCl \qquad (1)$$

Thereafter Chatt and Venanzi reported [2] that if reaction (1) is carried out with ethanol or acetone solutions of $Na_2[PdCl_4]$ it can successfully be accomplished at room temperature. The reaction, which is seemingly of general application, except for L being olefin or amine, takes from a few hours to several days to go to completion.

Two routes described for the synthesis of chloro-bridged organometallic palladium(II) derivatives, (a) the reaction of $PdCl_2L_2$ with $(C_6F_5)_2TlBr$ [3], and (b) the arylation of $[PdCl_2L]_2$ with C_6F_5MgBr [4] lead only in a few cases to the desired results.

On trying to employ the method of Chatt and Venanzi for the preparation of organometallic compounds we found that the reaction of PdR_2L_2 (R = C_6F_5, C_6Cl_5; L = PPh_3, $AsPh_3$, tetrahydrothiophen = tht) with $Na_2[PdCl_4]$ in acetone at room temperature when L = PPh_3 yields the unchanged starting product PdR_2L_2, whilst when L = $AsPh_3$ it leads to a mixture of $PdCl_2L_2$ and $[Pd(\mu\text{-}Cl)(C_6F_5)L]_2$ which, having different solubility, can be separated. However the yields of the binuclear organometallic complex are considerably reduced by the formation of $PdCl_2L_2$.

Careful examination of eqn. (1) shows that $M_2[PdCl_4]$ does merely act as a carrier of $PdCl_2$, which is incorporated into the $PdCl_2L_2$ to form $[PdCl_2L]_2$. This consideration led us to expect that $PdCl_2$ could be used instead. By reacting organometallic compounds of the PdR_2L_2 type with $PdCl_2$ we have actually been able to obtain halogen-bridged binuclear pentafluorophenyl or pentachlorophenyl palladium(II) derivatives of the general formula $[Pd(\mu\text{-}Cl)(C_6X_5)L]_2$ (L being a neutral ligand with N, P, As, Sb or S as donor atom). Furthermore, $PdCl_2$ can also be used for the synthesis of inorganic palladium(II) derivatives of the $[PdCl_2L]_2$ type.

Experimental

The C, H, and N analyses were made with a Perkin-Elmer 240 microanalyzer. Cl analyses were performed as described by White [5], a few milligrams of sucrose being added to the samples to facilitate their combustion. For the determination of Pd the samples were either dissolved in fuming nitric acid and then in perchloric acid, whereupon the metal was precipitated with dimethylglyoxime [6]; or, in a few cases, the samples were incinerated (900 °C) and the resulting metallic Pd was weighed directly.

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. Melting points were obtained on a Reichert hot-stage microscope and are uncorrected.

TABLE I. Analytical Results, Molecular Weights, Conductivities and Melting Points for the Novel Complexes.

No.	Complex	Found (calcd) %						Λ_M ohm^{-1} cm^2 mol^{-1}	M.P. °C
		C	H	N	Pd	Cl	M.W.		
I	$Pd(C_6F_5)_2(AsPh_3)_2$	54.74 (54.75)	3.13 (2.87)					0.60	
II	$Pd(C_6F_5)_2(BzNH_2)_2$	47.05 (47.68)	2.67 (2.77)	4.09 (4.27)				0.35	
III	$Pd(C_6F_5)_2(PPh_3)_2$	59.30 (59.73)	3.31 (3.13)					0.70	
IV	$Pd(C_6F_5)_2(SbPh_3)_2$	51.11 (50.28)	2.52 (2.63)					0.40	
V	$[Pd(\mu\text{-}Cl)(C_6F_5)py]_2$	33.61 (34.05)	1.49 (1.30)	3.53 (3.60)	28.14 (27.42)	8.82 (9.14)	773 (776)	0.34	267(d)
VI	$[Pd(\mu\text{-}Cl)(C_6F_5)(PPh_3)]_2$	50.84 (50.46)	2.86 (2.65)		18.63 (17.85)	6.27 (6.21)	1133 (1142)	0.87	250(d)
VII	$[Pd(\mu\text{-}Cl)(C_6F_5)(AsPh_3)]_2$	46.78 (46.86)	2.65 (2.46)		16.89 (17.29)	5.94 (5.76)	1216 (1230)	0.40	210(d)
VIII	$[Pd(\mu\text{-}Cl)(C_6F_5)(SbPh_3)]_2$	44.10 (43.54)	2.55 (2.28)		16.43 (16.07)	5.25 (5.36)	1341 (1324)	5.40	148(d)
IX	$[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$	30.77 (30.24)	2.16 (2.01)		26.34 (26.80)	9.23 (8.93)	769 (794)	nil	267(d)
X	$[Pd(\mu\text{-}Cl)(C_6Cl_5)py]_2$	28.95 (28.09)	3.24 (2.98)	1.88 (2.12)	22.83 (22.62)	46.03 (47.01)	905 (940)	9.36	248(d)
XI	$[Pd(\mu\text{-}Cl)(C_6Cl_5)(BzNH_2)]_2$	31.07 (31.33)	1.72 (1.82)	2.72 (2.81)	21.60 (21.35)	42.99 (42.66)	985 (997)	0.47	219(d)
XII	$[Pd(\mu\text{-}Cl)(C_6Cl_5)(PPh_3)]_2$	44.97 (44.11)	2.70 (2.31)		15.65 (16.28)	32.08 (32.55)	1258 (1307)	2.94	251(d)
XIII	$[Pd(\mu\text{-}Cl)(C_6Cl_5)(AsPh_3)]_2$	42.30 (41.33)	2.31 (2.17)		15.00 (15.26)	31.06 (30.50)	1349 (1395)	0.47	282(d)
XIV	$[Pd(\mu\text{-}Cl)(C_6Cl_5)(SbPh_3)]_2$	38.93 (38.73)	2.15 (2.03)		13.46 (14.29)	28.29 (28.58)	1466 (1488)	0.75	165(d)
XV	$[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$	25.19 (25.05)	1.95 (1.68)		22.62 (22.20)	44.72 (44.41)	978 (958)	1.69	228(d)
XVI	$PdCl(C_6F_5)py_2$	40.26 (41.14)	2.06 (2.15)	5.80 (5.99)					
XVII	$PdCl(C_6F_5)(tht)_2$	34.13 (34.65)	3.13 (3.32)						
XVIII	$PdCl(C_6Cl_5)(tht)_2$	31.25 (31.40)	2.75 (3.01)						

[d] Decomposes.

The conductivities were measured in approx. 5×10^{-4} *M* solution with a Philips PW 9501/01 conductimeter. The molecular weights were determined with a Hitachi-Perkin-Elmer mod. 115 osmometer.

The analytical results, melting points, conductivities and molecular weights are collected in Table I.

Preparation of the Starting Compounds

All the bispentachlorophenyl palladium(II) derivatives were prepared as described in [7], $Pd(C_6F_5)_2py_2$ was obtained according to [8]. The synthesis of the other bispentafluorophenyl compounds was carried out as follows:

$Pd(C_6F_5)_2(AsPh_3)_2$ *(I) (*cis–trans*)*

trans-$PdCl_2(AsPh_3)_2$ [3] (1.25 g; 1.58 mmol) was added to a stirred solution of LiC_6F_5 [9] (6.20 mmol) in dry ether (60 ml) at −78 °C. After 15 min the mixture was allowed to warm to room temperature and the reaction was continued for 3 h. The excess of LiC_6F_5 was destroyed by addition of wet ether (50 ml) whereupon evaporation to dryness led to a residue which was extracted with acetone. The filtered solution was partially evaporated to crystallize (I). The obtained compound, a mixture of the *cis*- and the *trans*-isomer, was used for the reactions with $PdCl_2$ without further treatment (70% yield).

trans-$Pd(C_6F_5)_2(NH_2Bz)_2$ *(II)*

trans-$PdCl_2(NH_2Bz)_2$ [10] (0.9 g; 2.30 mmol) was added to a stirred solution of LiC_6F_5 (6.90 mmol) in dry ether (50 ml) at −78 °C, after which it was allowed to warm to room temperature while the reaction was continued overnight. Evaporation to dryness and extraction of the residue with warm dichloromethane followed by partial evaporation of the solvent and addition of methanol (a few ml) led to the crystallization of complex (II) (75% yield).

$Pd(C_6F_5)_2(PPh_3)_2$ *(III) (*cis–trans*)*

To a solution of complex (I) (*cis–trans*) (0.520 g; 0.494 mmol) in benzene (60 ml) was added PPh_3 (0.340 g; 1.3 mmol). The mixture was refluxed for 2 h and then the solvent was partially evaporated. The addition of warm ethanol gave rise to the crystallization of complex (III), which was identified as a mixture of the *cis*- and *trans*- isomer (60% yield).

trans-$Pd(C_6F_5)_2(SbPh_3)_2$ *(IV)*

To a solution of *trans*-$Pd(C_6F_5)_2(tht)_2$ [11] (0.400 g; 0.648 mmol) in benzene (50 ml) was added $SbPh_3$ (0.610 g; 1.73 mmol). The stirred solution was refluxed for 9 h and reacted for another 30 h at room temperature, whereupon the partial evaporation of the solvent and the addition of ether afforded complex IV (68% yield).

Preparation of the binuclear Complexes $[Pd(\mu\text{-}Cl)(C_6X_5)L]_2$ *(V–XV)*

All the complexes were obtained by reacting acetone solutions of $Pd(C_6X_5)_2L_2$ with stoicheiometric amounts of $PdCl_2$ until the latter was completely dissolved. Most reactions were carried out at reflux temperature and the respective reaction times varied between 3 h (XV) and 20 h (VI). For L being $SbPh_3$ the process had to be performed at room temperature (10 h (VIII); 30 h (XIV)), since the refluxing led after *ca.* 15 min to metallic Pd.

In a few cases the required compounds precipitated during the reaction and were separated by filtration; (V) did not precise recrystallization; (X) was extracted with chloroform and recrystallized by partial evaporation of the solvent and addition of ether; (XV) was recrystallized from benzene.

For (IX) the acetone solution was filtered and the filtrate was reduced to approx. 10 ml, whereupon the complex crystallized.

Complex (XIV) was obtained by addition of ether and recrystallized from benzene–ether.

In all the other cases the acetone solution was evaporated to dryness, the residue was extracted with benzene and the filtered solution was partially evaporated afterwards the complexes crystallized either after addition of ether ((VI), (XII) and (XIII)), or of hexane ((VII), (XI)) or, respectively, of ether–ethanol (VIII).

Table II lists the amounts of the reagents (mmol) and solvents (ml) along with the respective yields.

TABLE II. Reaction Conditions for the Preparation Complexes of the $[Pd(\mu\text{-}Cl)RL]_2$ Type.

Complex	Reagents, mmol[a] A	B	Solvent Acetone (ml)	Yield %
V	1.000	1.000	34	72
VI	0.269	0.270	80	69
VII	0.380	0.383	80	71
VIII	0.167	0.167	80	50
IX	1.090	1.090	50	75
X	0.327	0.327	50	65
XI	0.329	0.329	50	61
XII	0.239	0.288	80	71
XIII	0.206	0.218	80	78
XIV	0.119	0.129	80	68
XV	0.378	0.378	40	72

[a] A: $(C_6X_5)_2PdL_2$. B: $PdCl_2$.

Preparation of Mononuclear Complexes of the $PdCl(C_6X_5)L_2$ *Type (X =* C_6F_5*; L = py, tht) (XVI), (XVII); (X =* C_6Cl_5*; L = tht) (XVIII)*

The treatment of a suspension of the binuclear complexes (V), (IX) and (XV) in acetone with a slight excess of the respective ligand L (L = py or tht) causes the complexes to dissolve and leads to the mononuclear derivatives $PdCl(C_6X_5)L_2$, which were crystallized either by partial evaporation of the solvent (XVIII) or by evaporation to dryness and extraction with hexane (XVI, XVII). The analytical data of the compounds are collected in Table I.

Reactions of $Pd(C_6F_5)_2L_2$ with $Na_2[PdCl_4]$

Reaction of $Pd(C_6F_5)_2(AsPh_3)_2$ with $Na_2[PdCl_4]$

A solution of $Pd(C_6F_5)_2(AsPh_3)_2$ (0.4208 g; 0.4 mmol) and $Na_2[PdCl_4]$ (0.1176 g; 0.4 mmol) in acetone (80 ml) was stirred for 2 h at room temperature. The resulting yellow precipitate was filtered, washed with water to separate NaCl, and characterized as $PdCl_2(AsPh_3)_2$. The yellow filtrate afforded a pale-yellow solid which was identified as $[Pd(\mu\text{-}Cl)(C_6F_5)(AsPh_3)]_2$ ((VI): 22% yield).

Reaction of trans-*$Pd(C_6F_5)_2(tht)_2$ with $Na_2[PdCl_4]$*

A solution of $Pd(C_6F_5)_2(tht)_2$ (0.339 g, 0.55 mmol) and $Na_2[PdCl_4]$ (0.161 g; 0.55 mmol) in acetone (25 ml) was stirred for 2 h at room temperature and the precipitated NaCl was filtered off. Partial concentration of the filtrate led to the crystallization of a mixture of $PdCl_2(tht)_2$ and $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$, which can be separated by recrystallization from acetone (yield of the binuclear complex (IX) : 36%).

Reaction of trans-*$Pd(C_6F_5)_2(PPh_3)_2$ with $Na_2[PdCl_4]$*

A solution of $Pd(C_6F_5)_2(PPh_3)_2$ (0.289 g; 0.3 mmol) and $Na_2[PdCl_4]$ (0.0883 g; 0.3 mmol) in acetone (80 ml) was stirred for 5 h at room temperature, the precipitated NaCl was filtered off, and the filtrate was partially concentrated to crystallize a complex which was identified as the starting compound *trans*-$Pd(C_6F_5)_2(PPh_3)_2$.

Preparation of Binuclear Inorganic Complexes

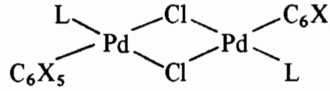
The refluxing for 2 h of stoicheiometric amounts of $PdCl_2L_2$ (L = PPh_3, $AsPh_3$, tht) and $PdCl_2$ in acetone solution leads in all the cases to the precipitation of the binuclear complex $[PdCl_2L]_2$. The yields are in each case over 90%.

Results and Discussion

Preparation of Complexes of the General Formula $[Pd(\mu\text{-}Cl)(C_6X_5)L]_2$

The reaction of stirred acetone solutions (or suspensions) of $Pd(C_6X_5)_2L_2$ ($C_6X_5 = C_6F_5$ or C_6Cl_5; L = PPh_3, $AsPh_3$, $SbPh_3$, tht (tetrahydrothiophen), py (C_5H_5N) or $BzNH_2$) with powdered $PdCl_2$ leads to the formation of binuclear complexes according to eqn. (2)

$$Pd(C_6X_5)_2L_2 + PdCl_2 \longrightarrow$$



(2)

The analytical data for the novel binuclear complexes are collected in Table I.

The reaction rates of process (2) are greatly influenced by the respective ligand L. Thus, when L = $SbPh_3$ or tht the reaction can be accomplished at room temperature; for L = $AsPh_3$ relatively short refluxing is sufficient, whereas for L = py, $BzNH_2$ or PPh_3 the refluxing must be prolongued up to 20 hours. It is noteworthy that for L = $BzNH_2$ the pentachlorophenyl derivative leads to the required binuclear compound whilst the pentafluorophenyl derivative does not react at room temperature and decomposes to metallic Pd when refluxed. When L = PEt_3 both the C_6Cl_5 and the C_6F_5 derivative decompose with formation of metallic Pd. The complexes with L = $SbPh_3$ are quite unstable at higher temperatures and therefore require prolongued treatment at room temperature.

If $Na_2[PdCl_4]$ is used for the synthesis of organometallic complexes it can clearly be seen that this reagent is manifestly inferior to $PdCl_2$. Thus, the reaction of $Pd(C_6F_5)_2L_2$ (L = PPh_3, $AsPh_3$ or tht) (which with $PdCl_2$ gives straightforwardly the bridged derivative as the only end product) leads with the sodium salt to the following results:

When L = PPh_3: although the expected precipitation of NaCl (according to eqn. (1)) can be observed, the unchanged starting product $Pd(C_6F_5)_2(PPh_3)_2$ is recovered whilst the very soluble $Na_2[Pd_2Cl_6]$ remains in the solution. Compounds of the $M_2[Pd_2X_6]$ type can be precipitated from aqueous solutions of $M_2[PdX_4]$ if the bridged anion is insolubilisized by a bulky cation, *e.g.* by addition of R_4NCl [13]. If the reaction is performed in acetone, where NaCl is little soluble, the equilibrium of the process can be displaced towards the right *via* the precipitation of this salt:

$$2Na_2[PdCl_4] \rightleftharpoons 2NaCl + Na_2[Pd_2Cl_6] \qquad (3)$$

When L = $AsPh_3$ or tht: after removing the precipitated NaCl, concentration of the filtrate leads to a mixture of $PdCl_2L_2$ and $[PdCl(C_6F_5)L]_2$. The former, being less soluble, is the first to separate during evaporation. It seems quite reasonable to assume that its formation takes place according to (4)

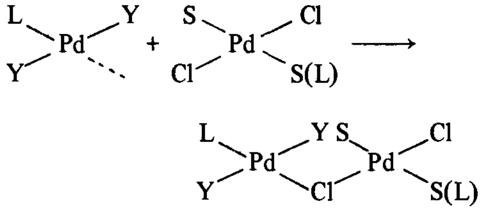
$$[PdCl_4]^{=} + 2L \longrightarrow PdCl_2L_2 + 2Cl^- \qquad (4)$$

and that the complex PdR_2L_2 should therefore be slightly dissociated according to (5)

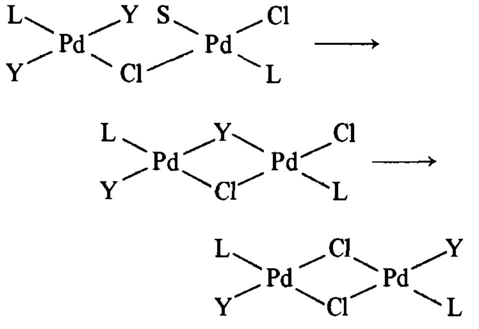
$$PdR_2L_2 \rightleftharpoons PdR_2L + L \qquad (5)$$

As may be expected, process (2) can be successfully used for the preparation of inorganic bridged derivatives from the corresponding $PdCl_2L_2$ complexes. We have actually obtained the required products for L = PPh_3, $AsPh_3$ or tht, whilst no reaction could be observed for L = py ($PdCl_2(py)_2$ and $Pd(C_6F_5)_2(py)_2$ do not react with $Na_2[PdCl_4]$ either, though the reaction of $Pd(C_6F_5)_2(py)_2$ with $PdCl_2$ progresses readily yielding $[PdCl(C_6F_5)(py)]_2$ (see Table I)).

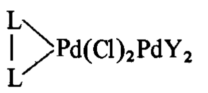
$PdCl_2$ is slightly soluble in acetone, probably in the form of $PdCl_2S_2$ (S = acetone). Thus, the above facts can be rationalized by assuming that process (2) takes place according to (6) between $PdCl_2S_2$ (or, respectively $PdCl_2SL$) and the moiety PdY_2L (Y = halogen or C_6X_5), present in the solution according to process (5) (this should also account for the minor reactivity with those PdY_2L_2 complexes which show less tendency to dissociate):


(6)

Thereafter, and probably *via* the displacement of the second S molecule, one of the Y groups is transferred to the second Pd atom:


(7)

The fact that no reaction can be observed if the starting products are of the $PdY_2(L–L)$ type (L–L = phen, diphosphine; Y = Cl or C_6F_5) is in accordance with the proposed mechanism. The feasibility of preparing assymmetric binuclear complexes of the


$\overset{L}{\underset{L}{|}}{>}Pd(Cl)_2PdY_2$

type, which until now have actually never been synthesized, should therefore be excluded.

We think that the method described herein is more adequate for the synthesis of binuclear organometallic complexes than all the hitherto reported routes. Thus, the reaction of $PdCl_2L_2$ and $(C_6F_5)_2TlBr$ leads [3] to a mixture of the mononuclear and binuclear organocomplexes $PdCl(C_6F_5)L_2$ and $[PdCl(C_6F_5)L]_2$, which must be separated, and takes place only in a few cases. On the other hand, the other method, the arylation of $[PdCl_2L]_2$ with RMgX, which leads to a unique end product, does also only take place in a few cases [4] and gives quite low yields (40–50%). Our new method surpasses the previously known routes since it is generally applicable and leads to a unique end product with yields which are generally of the order of 75–80%.

Conductivities and Melting Points

The results of the conductance studies in approx. 5×10^{-4} *M* solutions are shown in Table I. The very low conductivities confirm that the complexes are non-conductors [16].

The melting points of the novel binuclear complexes are also listed in Table I; all the compounds melt with decomposition. The data for the complexes which have been previously obtained by different methods coincide with those given in the literature [3].

Reactivity of the Binuclear Complexes

As may be expected, the reaction of the binuclear organometallic complexes with neutral ligands L leads to the cleavage of the halogen bridges and to the formation of mononuclear monosubstituted compounds

$$[Pd(\mu\text{-}Cl)(C_6X_5)L]_2 + 2L \longrightarrow 2PdCl(C_6X_5)L_2$$

Only those reactions which lead to hitherto non-isolated derivatives (L = py, tht, R = C_6F_5; L = tht, R = C_6Cl_5) are described (see Experimental), since other analogous processes have already been communicated in previous papers [3, 4].

Similarly [3, 4], the reaction of the novel binuclear complexes with salts of the XM type (LiBr, NaI, NaSCN) gives rise to the substitution of the chlorine-bridging atoms by others anions.

I. R. Spectra

All the pentafluorophenyl derivatives show the bands due to the C_6F_5 group [17] at 1635 (s), 1050 (s), 950 (s) and 800 (m) cm^{-1}, along with an absorption at 230 cm^{-1} which is not observed in the case of the analogous pentachlorophenyl compounds and which has hitherto not been assigned.

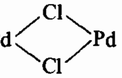
The binuclear palladium(II) complexes exhibit a single band in the 800 cm^{-1} region which confirms that each pentafluorophenyl group is attached to a different palladium atom [8], thus excluding the possibility of an assymmetric configuration of the complexes.

The pentachlorophenyl derivatives show the absorptions due to the C_6Cl_5 group at approx. 1330–1325 (s) and 1320–1312 (s), 1299–1289 (s), 1230–1220 (s) and 675–670 cm^{-1}, in good agreement with

TABLE III. Absorptions Assigned to the Neutral Ligands (cm^{-1}).

$[Pd(\mu\text{-}Cl)(C_6F_5)(PPh_3)]_2$	1098	690	540	518	495			[12]	[14]
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(PPh_3)]_2$	1100	690	538	518	498			[12]	[14]
$[Pd(\mu\text{-}Cl)(C_6F_5)(AsPh_3)]_2$	1580	1075	1000	688	485	472	462	a	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(AsPh_3)]_2$	1580	1075	1000	690	485	472	465	a	
$[Pd(\mu\text{-}Cl)(C_6F_5)py]_2$	1610	775	765	682				[15]	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)py]_2$	1609	772	768	691				[15]	
$[Pd(\mu\text{-}Cl)(C_6F_5)(SbPh_3)]_2$	689	459	448					a	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(SbPh_3)]_2$	690	460	448					a	
$[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$	1270							a	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$	1271							a	
$PdCl(C_6F_5)py_2$	1610	762	690	670				[15]	
$PdCl(C_6F_5)(tht)_2$	1270							[15]	

[a] Own observations.

TABLE IV. Absorptions Assigned to the PdPd moiety (cm^{-1}).

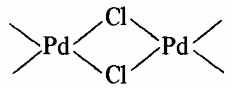
$[Pd(\mu\text{-}Cl)(C_6F_5)py]_2$	322 (s)	292 (s)	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)py]_2$	310 (br, m)	275 (br, m)	
$[Pd(\mu\text{-}Cl(C_6F_5)PPh_3]_2$	290 (s)	270 (s)	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)PPh_3]_2$	288 (br, s)	270 (s)	
$[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$	325 (m)	290 (br, s)	
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$	290 (s)	278 (s)	
$[Pd(\mu\text{-}Cl)(C_6F_5)(AsPh_3)]_2$	285 (sh)	276 (s)	264 (m)
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(AsPh_3)]_2$	285 (m)	274 (s)	
$[Pd(\mu\text{-}Cl)(C_6F_5)(SbPh_3)]_2$	*		
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(SbPh_3)]_2$	*		
$[Pd(\mu\text{-}Cl)(C_6Cl_5)(BzNH_2)]_2$	296 (s)	262 (s)	

*The presence of internal vibrations of the neutral ligand L ($SbPh_3$) prevents the assignment.

the literature data [18]. A further band located at 630–620 cm^{-1}, which is difficult to assign, can probably be attributed to the vibration [$\nu_{19}(E_u)$] of the C_6Cl_5 group, which for C_6Cl_6 is situated at 594 cm^{-1} according to the calculations of Scherer [19]. Morever, since this band cannot be observed in the spectra of the analogous pentafluoro derivatives we feel that it can unambiguously be assigned to the C_6Cl_5 group.

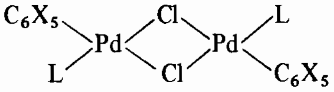
The presence of each ligand L is confirmed by the IR spectra. Some of the characteristic vibrations of the different ligands are collected in Table III.

The characteristic vibrations of the PPh_3 group are to be observed in the 540–495 cm^{-1} region and are somewhat shifted in the case of the mononuclear derivatives *trans*-$Pd(C_6F_5)_2(PPh_3)_2$, *trans*-$Pd(C_6Cl_5)_2(PPh_3)_2$ and *trans*-$PdCl(C_6F_5)(PPh_3)_2$; furthermore, the intense absorption at 550 ± 5 cm^{-1}, which according to Mastin [20] should correspond to the first overtone of the assymmetric bending mode PC_3, is not to be seen. This seemingly suggests that the two PPh_3 groups are not mutually *cis*, and does therefore rule out an assymmetric configuration of the complexes, as has already been indicated in the discussion of the band at ~800 cm^{-1}.

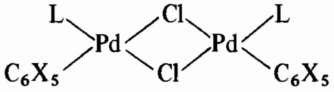


In the complexes described herein with C_{2h} symmetry the two absorptions assignable to the ν(Pd–Cl) frequencies of the moiety are located in the 300–250 cm^{-1} region (see Table IV), coinciding with the data reported in the literature [21–23] for analogous complexes. In some cases these absorptions are masked by internal vibrations of the neutral ligands (*e.g.* L = $SbPh_3$) and could therefore not be assigned.

The possibility of an assymmetric configuration of the binuclear derivatives can completely be ruled out both because of the IR data and because, in accordance with previous results [24], a structure of this type should be thermodynamically unstable since a molecule with such a high dipolar moment (≃20 D) must store a much too high amount of electrical energy. Though we do not dispose of the experimental evidence which would allow us to decide between the other two possibilities (a) or (b)



(a)



(b)

the previously reported data of other binuclear palladium complexes [2] allow us to expect that their structure should be *trans*-(a).

$Pd(C_6F_5)_2(AsPh_3)_2$ and $Pd(C_6F_5)_2(PPh_3)_2$ exhibit two bands in the 790–780 cm^{-1} region which seem to support a *cis*-symmetry of the complexes. $Pd(C_6F_5)_2(PPh_3)_2$ furthermore shows an intense band at 542 cm^{-1} which also points to a *cis*-configuration of the compound [20].

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