Reactivity of Tetra-n-butylammonium Di-μ-chloro-bis[bis(pentafluorophenyl)palladate(II)]. A General Method for the Synthesis of *cis* Isomers of Neutral and Anionic Palladium(II) Complexes

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The reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with L (L = N, P, As, or Sb donor ligand) leads to the synthesis of novel anionic palladium complexes of the type $[NBu^n_4][PdCl(C_6F_5)_2L]$, which react with L to give the neutral complexes $[Pd(C_6F_5)_2L_2]$. Both families of compounds are the *cis* derivatives. Moreover, replacement of Cl by SCN or CN, and of L ($SbPh_3$ or $AsPh_3$) by PPh_3, takes place without a change in configuration, giving again *cis* isomers.

THE synthesis of the chloro-bridged binuclear compound $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with two C_6F_5 groups *cis* bonded to each palladium atom has recently been reported by us.[1] It seemed reasonable to expect that cleavage of the bridge by neutral ligands would lead to a hitherto unknown type of anionic organopalladium(II) complex, $[NBu^n_4][PdCl(C_6F_5)_2L]$, and that the addition of further quantities of the ligand would give rise to the neutral compound $[Pd(C_6F_5)_2L_2]$.

Moreover, if the geometry of the complexes is retained during the reactions with L, the resulting complexes would also be the *cis* isomers. This feature would be of particular interest since most of the hitherto known organopalladium(II) complexes have had *trans* configurations.[2]

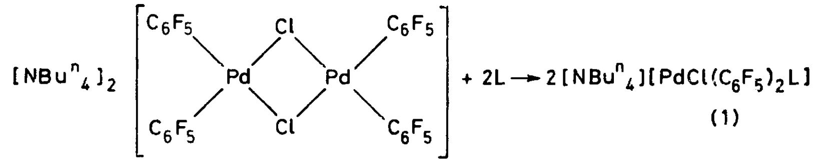
In fact, although in the unique case of $[PdMe_2L_2]$ the *cis* derivatives have initially been obtained, they gradually isomerize to give the *trans* form.[3] Pentafluorophenyl complexes of the types $[PdX(C_6F_5)L_2]$ and $[Pd(C_6F_5)_2L_2]$ [4,5] are generally *trans* although in two cases (L = PEt_3 [6] and $AsPh_3$ [4]) mixtures of the *cis* and *trans* compounds have been prepared, which, however, contain only small amounts of the former.

Evidence for several *cis*-$[PdCl_2L_2]$ complexes in the solid state has been advanced.[7] Some $[PdCl_2L_2]$ complexes, which are *trans* in the solid state, form *cis–trans* equilibrium mixtures in solution,[7,8] and it even seems that in all the tested solvents (except *m*-dichlorobenzene and deuteriochloroform) *cis*-$[PdCl_2(PMePh_2)_2]$ is thermodynamically more stable than its *trans* isomer.[9] Nevertheless, the arylation of *cis*-$[PdCl_2(PMePh_2)_2]$ with $Li[C_6F_5]$ leads to *trans*-$[Pd(C_6F_5)_2(PMePh_2)_2]$.[10]

Our preparative method leads in each case to *cis*-pentafluorophenylpalladium(II) complexes. This emphasizes the importance of the reaction path in influencing the configuration of the resulting complex.

RESULTS AND DISCUSSION

The (1 : 2) reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with neutral ligands L [L = PPh_3, $PMePh_2$, PEt_3, $P(OPh)_3$, $P(OMe)_3$, or NH_2CH_2Ph], in acetone or methanol solution, gives rise to the cleavage of the chloro-bridges and to the formation of anionic mononuclear compounds [equation (1)] which react with further amounts of the same ligand L (except NH_2CH_2Ph) or with L = pyridine (py), $AsPh_3$, or $SbPh_3$ to give neutral derivatives [equation (2)].



(1)

$$[NBu^n_4][PdCl(C_6F_5)_2L] + L \longrightarrow [NBu^n_4]Cl + [Pd(C_6F_5)_2L_2] \quad (2)$$

The latter can also be obtained directly by treating $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with L in a 1 : 4 mol ratio.

In some cases (L = py, $AsPh_3$, or $SbPh_3$) the reaction cannot be interrupted at the formation of the anionic intermediate complex, and the less soluble neutral complex is obtained directly, whilst the solution contains some anionic $[PdCl(C_6F_5)_2L]^-$, together with some unreacted binuclear complex. However, reaction with L = NH_2CH_2Ph always leads to the anionic intermediate, regardless of the excess of ligand used, since NH_2CH_2Ph is not capable of displacing the halogen to give the neutral complex.

Finally, not every ligand reacts according to equations (1) and (2). Thus, no reaction is observed with *e.g.* tetrahydrothiophen, tetrafluorophthalonitrile, and cycloocta-1,5-diene.

The analytical data, conductivities, melting points, and structurally relevant i.r. absorptions in the 750—800 cm^{-1} region (see below) for the novel complexes are listed in Table 1, whilst the reaction conditions for their syntheses are summarized in Table 2.

Structure.—The structural assignments are based on ^{31}P n.m.r. and i.r. spectroscopy.

The ^{31}P n.m.r. spectra of the complexes of type $[Pd(C_6F_5)_2L_2]$ (L being a P donor) under conditions of proton decoupling consist of a single and featureless signal due to the coupling with the ^{19}F of the C_6F_5 group. The δ values for *cis* and *trans* isomers differ by 3.4—7.5 p.p.m. (see Experimental section) and since the signals span no more than 1.5 p.p.m. at their bases, overlap does not occur. All our complexes show only a single signal, thus indicating that equilibrium is not established in chloroform solution.

TABLE 1

Analytical data, melting points, conductivities, and some i.r. data for the complexes

Complex	Found [a] (%)			Λ_M/ S cm^2 mol^{-1}	M.p. (θ_c/°C)	I.r. data	
	C	H	N			C_6F_5 (*X*-sensitive) [b]	ν(Pd–X)
(1) *cis*-$[NBu_4][PdCl(C_6F_5)_2(PPh_3)]$	55.45 (56.35)	5.55 (5.20)	1.35 (1.40)	81	143 (decomp.)	788, 769s	300m
(2) *cis*-$[NBu_4][PdCl(C_6F_5)_2(PMePh_2)]$	54.2 (53.6)	5.50 (5.55)	1.55 (1.50)	88	114	789, 769s	297m
(3) *cis*-$[NBu_4][PdCl(C_6F_5)_2(PEt_3)]$	49.4 (48.8)	6.10 (6.10)	1.65 (1.65)	105	137	785, 768s	291m
(4) *cis*-$[NBu_4][PdCl(C_6F_5)_2\{P(OPh)_3\}]$	53.9 (53.7)	5.05 (4.95)	1.40 (1.35)	90	98	*c*	302m
(5) *cis*-$[NBu_4][PdCl(C_6F_5)_2(NH_2CH_2Ph)]$	50.1 (50.90)	4.95 (5.45)	3.20 (3.40)	104	108	788, 776s	295s
(6) *cis*-$[NBu_4][Pd(CN)(C_6F_5)_2(PPh_3)]$	58.2 (58.1)	5.30 (5.25)	3.00 (2.50)	91	146	784, 774s	2 170m [d]
(7) *cis*-$[NBu_4][Pd(SCN)(C_6F_5)_2(PPh_3)]$	55.9 (56.25)	4.50 (5.10)	2.95 (2.80)	88	153 (decomp.)	783, 771s	2 114s [d]
(8) *cis*-$[Pd(C_6F_5)_2(PPh_3)_2]$	60.05 (59.75)	3.60 (3.10)		nil	159 (decomp.)	780, 771s (768)	
(9) *cis*-$[Pd(C_6F_5)_2(PMePh_2)_2]$	54.1 (54.25)	3.10 (3.10)		nil	185 (decomp.)	780, 771s (770)	
(10) *cis*-$[Pd(C_6F_5)_2(PEt_3)_2]$	43.15 (42.6)	4.15 (4.45)		nil	162 (decomp.) [e]	*c*	
(11) *cis*-$[Pd(C_6F_5)_2\{P(OPh)_3\}_2]$	54.45 (54.35)	3.00 (2.80)		nil	139 (decomp.)	*c*	
(12) *cis*-$[Pd(C_6F_5)_2\{P(OMe)_3\}_2]$	31.9 (31.4)	2.65 (2.60)		nil	135	*c*	
(13) *cis*-$[Pd(C_6F_5)_2(AsPh_3)_2]$	55.25 (54.75)	2.95 (2.85)		nil	163 (decomp.)	782, 772 (770)	
(14) *cis*-$[Pd(C_6F_5)_2(py)_2]$	44.05 (44.1)	1.75 (1.65)	4.35 (4.70)	nil	212 (decomp.)	790, 780 (768)	
(15) *cis*-$[Pd(C_6F_5)_2(SbPh_3)_2]$	49.55 (50.25)	2.70 (2.60)		nil	147 (decomp.)	782, 772 (771)	

[a] Calculated values are given in parentheses. [b] The corresponding absorptions for the *trans* derivatives are given in parentheses. [c] Assignment precluded due to the presence of internal vibration of L in this range. [d] ν(CN). [e] Literature value 153—154 °C.[6]

TABLE 2

Reaction conditions for the preparation of complexes

Complex	L	Reagent/mmol [a] (A)	(B)	Solvent/ cm^3	Yield/ %
(1)	PPh_3	0.190	0.381	30 [b]	63
(2)	$PMePh_2$	0.139	0.278	30 [b]	40
(3)	PEt_3	0.139	0.278	30 [b]	86
(4)	$P(OPh)_3$	0.139	0.278	30 [b]	86
(5)	NH_2CH_2Ph	0.104	0.626	30 [b]	58
(8)	PPh_3	0.139	0.557	30 [b]	75
(9)	$PMePh_2$	0.139	0.557	40 [b]	86
(10)	PEt_3	0.139	0.835	70 [c]	56
(11)	$P(OPh)_3$	0.139	0.557	30 [b]	70
(12)	$P(OMe)_3$	0.310	1.242	60 [c]	52
(13)	$AsPh_3$	0.139	0.557	40 [b]	56
(14)	py	0.139	0.557	40 [b]	70
(15)	$SbPh_3$	0.138	0.557	40 [b]	72

[a] (A) $[NBu_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$, (B) ligand L. [b] Acetone. [c] Methanol.

The i.r. spectra of the *cis* complexes of palladium and platinum $[Pd(C_6F_5)_2(L{-}L)]$, $[Pt(C_6F_5)_2L_2]$, and $[Pt(C_6F_5)_2(L{-}L)]$ (C_{2v}) have been previously shown[5] to exhibit two bands in the 750—800 cm^{-1} region whilst the *trans* isomers (D_{2h}) show only one and this appears to be a useful feature for distinguishing them. These absorptions (*X*-sensitive mode) must be related to the skeletal symmetry of the entire molecule,[11] and behave as ν(M–C) bands ($A_1 + B_1$ i.r. active for the *cis* isomers, B_{2u} i.r. active for the *trans* ones).

Of those under discussion, only the anionic complexes $[NBu^n_4][PdCl(C_6F_5)_2L]$ are hitherto known derivatives of this type. They all show a double band around 800 cm^{-1} in the i.r. Since the corresponding *trans* isomers are still unknown it is obviously not possible to compare the i.r. pattern. However for both symmetries (C_s for the *cis* isomers and C_{2v} for the *trans* isomers) group theory predicts two i.r.-active modes ($2A'$ and $A_1 + B_1$ respectively). We assign the *cis* structure to our anionic complexes [(1)—(7)] because their reactions with L lead, in every case, to neutral *cis* isomers [equation (2)].

cis Isomers are also obtained on replacing the Cl^- of $[NBu^n_4][PdCl(C_6F_5)_2(PPh_3)]$ by CN^- or SCN^-, and by treating *cis*-$[Pd(C_6F_5)_2L_2]$ (L = $AsPh_3$ or $SbPh_3$) with PPh_3.

Table 1 lists the two *X*-sensitive i.r. absorptions of the prepared complexes and the ν(Pd–Cl) vibrations for the anionic derivatives along with the ν(CN) vibrations of the cyano- and thiocyanato-complexes [(6) and (7)]. The internal standard ratio in the thiocyanato-complex (relative to salicylic acid)[12] is 0.56, which indicates Pd–S bonding of this group.

EXPERIMENTAL

The instrumentation and general experimental techniques were described earlier.[1] Phosphorus-31 n.m.r. spectra were run on a JEOL PFT-100 spectrometer at 40.48 MHz with proton noise decoupling. Chemical shifts are reported on the δ scale (positive values to high frequencies) with respect to 85% orthophosphoric acid. The values for the *cis* and *trans* isomers of $[Pd(C_6F_5)_2L_2]$ are: L = PPh_3, 18.6 and 22.0; L = $PMePh_2$, 3.1 and 8.9; L = PEt_3, −4.3 and −9.5; L = $P(OMe)_3$, 121.5 and 116.5; L = $P(OPh)_3$, 104.3 and 96.8 p.p.m. respectively.

The complex $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ was prepared as reported elsewhere.[1] The *trans*-$[Pd(C_6F_5)_2L_2]$ derivatives, used in comparing the ^{31}P n.m.r. spectra with those of the *cis* isomers, were obtained by refluxing acetone solutions of *trans*-$[Pd(C_6F_5)_2(tht)_2]$[1] (tht = tetrahydrothiophen) with an excess of the ligand, L, and their purity checked by analysis.

The quantities of reagents and solvents used for the reactions and the yields obtained are summarized in Table 2.

Reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ *with* L (1: *ca.* 4), L = PPh_3 (8), $PMePh_2$ (9), PEt_3 (10), $P(OPh)_3$ (11), $P(OMe)_3$ (12), $AsPh_3$ (13), py (14), NH_2CH_2Ph (5), *or* $SbPh_3$ (15).—To an acetone or methanol solution of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ was added the respective ligand L in a roughly 1 : 4 mol ratio. The mixture was stirred at room temperature for 30—60 min and afterwards evaporated to dryness. The oily residue was dissolved in ethanol and the *cis*-$[Pd(C_6F_5)_2L_2]$ complexes [(8)—(15)] reprecipitated as white crystals.

The reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with a large excess of NH_2CH_2Ph (1 : 8) leads only to the monosubstituted complex (5).

Reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ *with* L (1 : 2).—If the above reaction was carried out with smaller amounts of the ligands (1 : 2 mol ratio), evaporation of the solutions to dryness led again to oily residues which were treated with Pr^iOH (*ca.* 10 cm^3) and crystallized by partial evaporation [complex (1)]. For L = $PMePh_2$, treatment of the residue with n-butanol led to the crystallization of the neutral complex *cis*-$[Pd(C_6F_5)_2(PMePh_2)_2]$ (10% yield), and addition of hexane to the n-butanol solution gave rise to the crystallization of complex (2). Complexes (3) (L = PEt_3) and (4) [L = $P(OPh)_3$] were crystallized analogously.

If the reaction of the binuclear palladium complex with L = NH_2CH_2Ph (1 : 2 ratio) was carried out as above, addition of n-butanol to the residue led to the crystallization of 60% of the starting complex, whilst evaporation of the filtrate and addition of a few cm^3 of hexane yielded complex (5) (28% yield). Increasing the amount of NH_2CH_2Ph (1 : 5 mol ratio) and treating the residue with diethyl ether–hexane led to complex (5) (60% yield) but none of the disubstituted complex, *cis*-$[Pd(C_6F_5)_2(NH_2CH_2Ph)_2]$, could be obtained, although the proportions of reagents were appropriate.

The reaction of $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ with L = $AsPh_3$, py, or $SbPh_3$ (1 : 2 mol ratio) did not lead to isolation of the anionic mononuclear complexes, but gave mixtures of the unreacted starting compounds and the disubstituted neutral complexes. No reaction was observed between $[NBu^n_4]_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ and $[NBu^n_4]Cl$.

cis-$[NBu^n_4][PdX(C_6F_5)_2(PPh_3)]$, X = CN (6) *or* SCN (7).—A solution of complex (1) and K[CN] or K[SCN] (*ca.* 1 : 1.1 mol ratio) was stirred at room temperature [methanol, 30 min (6); acetone, 4 h (7)]. Evaporation of the solution to dryness and extraction of the residue with CH_2Cl_2 led, after evaporation almost to dryness and addition of diethyl ether, to complex (6) (45% yield). Partial evaporation of the solution after filtration and addition of n-butanol–hexane gave (7) (74% yield).

Reaction of cis-$[Pd(C_6F_5)_2L_2]$, L = $AsPh_3$ (13) *or* $SbPh_3$ (15), *with* PPh_3.—A solution of complex (13) or (15) (0.25 mmol) in acetone (30 cm^3) and PPh_3 (0.50 mmol) was stirred for 3 h at room temperature. Evaporation almost to dryness and addition of Pr^iOH (15 cm^3) gave complex (8) which was washed with n-hexane (yield *ca.* 80% in both cases).

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