Bis(pentachlorophenyl) Derivatives of Palladium(II)

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The preparation of $Pd(C_6Cl_5)_2L_2$ by reacting $PdCl_2L_2$ with LiC_6Cl_5 can be achieved for L being a N-, As- or S-ligand but not for L = phosphine. The As- or S- ligand can thereafter be replaced by other mono- or bidentate ligands, even by phosphines.

Introduction

The only hitherto known bis(pentachlorophenyl) derivatives of transition metal atoms are of the types $Fe(C_6Cl_5)_2L_2$, $Co(C_6Cl_5)_2L_2$ (L being a tertiary phosphine) [1] and $Pd(C_6Cl_5)_2bipy$ (bipy = 2,2'-bipyridine) [2]. The reaction of a large excess of $XMgC_6Cl_5$ or LiC_6Cl_5 with X_2PdL_2 (L being a phosphine) leads in every case to the monoaryl derivatives $Pd(C_6Cl_5)XL_2$ [3, 4].

Since kinetic more than steric [5] reasons do probably hinder a second C_6Cl_5 group from entering we have studied the reactions of X_2PdL_2 (L = N-, As-, or S- ligand) with an excess of LiC_6Cl_5 to establish the role played by the ancillary ligands. We have found that diaryl derivatives can readily be obtained when L = pyridine, triphenylarsine or tetrahydrothiophene. Except for the pyridine compound, the neutral ligand can thereafter be replaced by other groups, even by tertiary phosphines. Thus, we report the preparation of eleven novel complexes of the $Pd(C_6Cl_5)_2L_2$ type, L being tetrahydrothiophene(tht), pyridine(py), benzylamine(bam), triethylphosphine(PEt_3), triphenylphosphine(PPh_3), triphenylarsine($AsPh_3$), triphenylstibine($SbPh_3$), bis(diphenylarsino)methane (dam), or L_2 being 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), bis(diphenylphosphino)metane (dpm), 1,4-bis(diphenylphosphino)butane (dpb).

Experimental

The conductivities were measured in approx. 5×10^{-4} *M* solution with a Philips PW 9501/01 conductimeter. The melting points were determined with a Reichert (Austria) apparatus. The IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. C, H and N analyses were made with a Perkin–Elmer 240

microanalyzer. Cl analyses were performed as described by White [6] a few milligrams of sucrose being added to facilitate the combustion. The analytical results are collected in Table I.

$Pd(C_6Cl_5)_2L_2$ (L = tht, py, $AsPh_3$)

3 mmol of Cl_2PdL_2 (prepared according to [7–9]) were added to an ether solution of LiC_6Cl_5 (prepared according to [10] by reacting 15 mmol of C_6Cl_6 with 15 mmol of n-BuLi in 45 ml of dry ether at $-15\,°C$). While the yellow suspension was stirred for 24 h at room temperature it turned white. The resulting white solid was filtered off, washed with warm hexane and dissolved in either dichloromethane (L = tht, $AsPh_3$) or in dichloroethane (L = py). The white crystals of $Pd(C_6Cl_5)_2L_2$ were obtained by partial evaporation of the solution and addition of diethyl ether (50–60% yields).

$Pd(C_6Cl_5)_2(L–L)$ (L–L = bipy, phen, dpb, dpm)

To a suspension of 1 mmol (1.21 g) of $Pd(C_6Cl_5)_2(AsPh_3)_2$ in 50 ml of xylene (phen, bipy) or benzene (dpb, dpm) were added 2 mmol of the respective ligand L–L. The stirred mixture was refluxed for 6 h and the complete precipitation of $Pd(C_6Cl_5)_2(L–L)$ was achieved by partial evaporation and cooling. The resulting complex was washed with warm ethanol and ether (90–95% yields).

$Pd(C_6Cl_5)_2L_2$ (L = PEt_3, PPh_3, $AsPh_3$, bam, $SbPh_3$, dam)

To a solution of 0.3 mmol of $Pd(C_6Cl_5)_2(tht)_2$ in 80 ml of warm benzene was added 1 mmol of the respective ligand L. The stirred mixture was refluxed for 6 h. The complexes $Pd(C_6Cl_5)_2L_2$ were obtained after partial evaporation and addition of ethanol or ether. They were washed with the precipitating agent. (70–80% yields).

Results and Discussion

Preparation of the Complexes

Two different methods have essentially been used
i) The reaction of X_2PdL_2 (L = N-, As-, or S- ligand) with an excess of LiC_6Cl_5, according to eqn. (1):

TABLE I. Analytical Data.

	Found (calcd) (%)				M.P. °C
	C	H	N	Cl	
$Pd(C_6Cl_5)_2(tht)_2$	30.25 (30.74)	2.32 (2.06)		45.65 (45.37)	230
$Pd(C_6Cl_5)_2py_2$	34.16 (34.61)	1.35 (1.32)	3.46 (3.66)	45.92 (46.44)	250(d)
$Pd(C_6Cl_5)_2(bam)_2$	38.42 (38.12)	2.18 (2.21)	3.68 (3.42)	43.35 (43.27)	196
$Pd(C_6Cl_5)_2(bipy)$	33.32 (34.70)	1.12 (1.05)	3.46 (3.67)	45.56 (46.50)	334(d)
$Pd(C_6Cl_5)_2(phen)$	35.55 (36.70)	1.10 (1.02)	3.62 (3.56)	44.54 (45.13)	340(d)
$Pd(C_6Cl_5)_2(PEt_3)_2$	34.53 (34.26)	3.54 (3.59)		41.89 (42.14)	268
$Pd(C_6Cl_5)_2(PPh_3)_2$	51.30 (51.04)	2.92 (2.68)		31.67 (31.38)	214(d)
$Pd(C_6Cl_5)_2(dpm)$	44.36 (44.92)	1.99 (2.20)		34.82 (35.83)	280(d)
$Pd(C_6Cl_5)_2(dpb)$	46.40 (46.50)	3.06 (2.73)		33.63 (34.37)	310(d)
$Pd(C_6Cl_5)_2(AsPh_3)_2$ [a]	47.90 (47.37)	2.51 (2.48)		28.70 (29.19)	210(d)
$Pd(C_6Cl_5)_2(AsPh_3)_2$ [b]	46.65 (47.37)	2.69 (2.48)		29.32 (29.19)	210(d)
$Pd(C_6Cl_5)_2(SbPh_3)_2$	43.42 (43.96)	2.45 (2.31)		27.72 (27.04)	217(d)
$Pd(C_6Cl_5)_2(As-As)_2$	48.35 (48.05)	2.99 (2.86)		22.64 (22.88)	203

[a]From $Cl_2Pd(AsPh_3)_2$. [b]From $Pd(C_6Cl_5)_2(tht)_2$.

$trans\text{-}Cl_2PdL_2 + 2LiC_6Cl_5 \longrightarrow$

$$trans\text{-}Pd(C_6Cl_5)_2L_2 + 2LiCl \qquad (1)$$
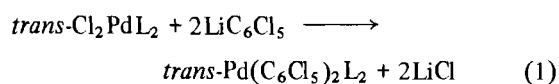
(L = py, AsPh$_3$, tht)

ii) The substitution of L (L = AsPh$_3$ or tht) in $trans$-Pd(C$_6$Cl$_5$)$_2$L$_2$ by other neutral ligands, according to eqn. (2):

$trans\text{-}Pd(C_6Cl_5)_2L_2 + 2L' \longrightarrow$

$$Pd(C_6Cl_5)_2L'_2 + 2L \qquad (2)$$
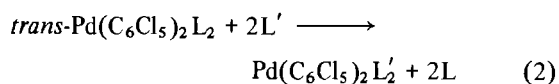
(for L = AsPh$_3$, 2L' = bipy, phen, dpm, dpb)
(for L = tht, L' = PEt$_3$, PPh$_3$, AsPh$_3$, bam, dam)

The substitution of AsPh$_3$ or tht by monodentate ligands must obviously be due to the higher formation enthalpy of the corresponding Pd–L bonds, whilst in the reaction with chelate ligands the chelate effect should have a decisive influence. It is noteworthy that (dam) behaves as a monodentate ligand to form Pd(C$_6$Cl$_5$)$_2$(dam)$_2$. The different behaviour

of (dam) and (dpm) must be attributed to the inability of a single methylene group to bridge the much larger arsenic atoms [11] in the chelate complex.

The analytical data and melting points of the novel compounds are listed in Table I.

Conductivities and Melting Points

All the complexes are essentially non-conducting. Their conductivities (in acetone or dichloromethane, depending on solubility) are very low ($\Lambda_M \sim 0{-}1$ ohm^{-1} cm^2 mol^{-1}).

All the complexes are thermally stable up to at least 200 °C. The decomposition point of Pd(C$_6$-Cl$_5$)$_2$(bipy) (334 °C) coincided with that reported in the literature (335 °C) [2].

IR Spectra

All the complexes show the absorptions due to the C$_6$Cl$_5$ group at 1330–1325 (s) and 1320–1312 (s) cm^{-1} (components of the ν_{13} mode) [12], at 1294–1289 (s) cm^{-1} (ν_6), and 1230–1215 (s) cm^{-1} (the

latter is in some cases difficult to assign because of the proximity of internal vibrations due to the respective ligand L). The band at $\sim$675–670 cm^{-1} is assigned to one of the components of the ν_{12} mode.

The disubstitution is evidenced by the absence of absorption bands in the 360–250 cm^{-1} region, which are characteristic for a Pd–Cl coordination.

The complex $Pd(C_6Cl_5)_2py_2$ shows a single band at 770 (s) cm^{-1} due to an internal vibration of pyridine. Since this absorption was observed as a single band in *trans*-X_2Mpy (M = Pd, Pt) and as a double one in *cis*-X_2Ptpy_2 [13] our complex should be the *trans*- isomer.

For complexes of the general formula PtX_2-$(PPh_3)_2$ it has recently been reported [14] that the intensity of the band at 550 ± 5 cm^{-1} (assigned as the first overtone of the assymetric PC_3 deformation mode) is directly related to the geometry of the compound: thus, the *cis*-isomer shows an intense band whilst the *trans*-isomer exhibits a weak one. The band at 548 (vw) cm^{-1} observed in our complex points to its *trans*- configuration.

The configuration of $Pd(C_6Cl_5)_2(PEt_3)_2$ cannot unambiguously be assigned from its IR spectrum. According to [15] the single absorption at 421 (m) cm^{-1} should confirm the *trans*- configuration of the compound, but Nakamoto [16], by using an isotopic interchange technique has assigned the Pd–P vibrations at below 250 cm^{-1}. On the other hand, the sample is not soluble enough for a ^{1}H NMR study, which could perhaps help to elucidate the *cis*- or *trans*- geometry. Nevertheless, we think that the problem would not have been solved by this method since in $Pt(C_6F_5)_2(PEt_3)_2$, for example, the chemical shift between the methylene and methyl resonances is small ($\delta_{AB} \sim 5$) giving rise to large secondary order effects which do not allow the elucidation of the structure [17].

Reaction with Chlorine

The treatment of some of our compounds with Cl_2 under mild conditions does not show any effect,

the prolonged treatment ($>$6h) leads to the cleavage of the Pd–C bonds. The presence of organometallic Pd(IV) complexes, however, could not be observed in any case, not even where positive results have previously been obtained with the homologous compounds $Pd(C_6F_5)_2(L–L)$ (L–L = bipy or phen) [18].

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