Journal of Organometallic Chemistry, 263 (1984) 247–252
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BIS(PENTAFLUOROPHENYL) DERIVATIVES OF PALLADIUM(II) WITH *N*-DONOR LIGANDS

G. LOPEZ, G. GARCIA, C. DE HARO, G. SANCHEZ and M.C. VALLEJO
Department of Inorganic Chemistry, University of Murcia, Murcia (Spain)

(Received October 17th, 1983)

Summary

New bis(pentafluorophenyl) derivatives of palladium(II) have been prepared from *cis*-$Pd(C_6F_5)_2$(dioxane). The complexes with *o*- and *p*-aminophenol, *o*- and *p*-anisidine, *p*-phenylenediamine, 2- and 4-cyanopyridine, and allylamine are of the general formula *cis*-$Pd(C_6F_5)_2L_2$. Complexes of *o*-phenylenediamine and phthalonitrile have the stoichiometries *cis*-$Pd(C_6F_5)_2L$, where L acts as a chelating group. IR data show that the coordination is through the nitrogen atom of a NH_2 group or, in the cyanopyridine complexes, the pyridine nitrogen. ^{1}H NMR data to the allylamine compound are reported, and its condensation with acetone to give *cis*-$Pd(C_6F_5)_2(C_3H_5N{=}CMe_2)_2$ is described.

Introduction

Amine complexes of the type $M(C_6F_5)_2$(amine)$_2$ can be prepared by a general method based upon the arylation of the corresponding halo complexes, MX_2(amine)$_2$ [1]. The availability of the starting halo complex is obviously necessary for this method, and a separate arylation is needed for each amine derivative.

Recently, dioxane adducts of the type $M(C_6F_5)_2(Dx)_n$ (M = Ni [2], M = Pd [3], and M = Pt [4]; Dx = 1,4-dioxane) have been used as starting products for the preparation of complexes $M(C_6F_5)_2L_2$. The feasibility of the process comes from the easy replacement of dioxane in the coordination sphere of the metal atom. Since Smith and Tamborski [5] prepared some cobalt complexes from tetrahydrofuran solutions containing "$Co(C_6F_5)_2$", the method has been extended to nickel [2,6], palladium [3,7,8] and platinum [4].

This paper is concerned with the preparation of complexes $Pd(C_6F_5)_2L_n$ (n = 1,2), where L is one of the aforementioned N-donor Ligands, from *cis*-$Pd(C_6F_5)_2$Dx via the corresponding substitution reaction in either dichloromethane or diethyl ether as solvent.

0022-328X/84/$03.00

Results and discussion

The addition of the corresponding ligands to *cis*-$Pd(C_6F_5)_2Dx$ in CH_2Cl_2 leads to the formation of the expected organo complexes according to eq. 1:

$$cis\text{-}Pd(C_6F_5)_2Dx + 2L \rightarrow cis\text{-}Pd(C_6F_5)_2L_2 + Dx \qquad (1)$$

where L = *o*-$MeOC_6H_4NH_2$, *p*-$MeOC_6H_4NH_2$, *p*-$NH_2C_6H_4NH_2$, *o*-$OHC_6H_4NH_2$, *p*-$OHC_6H_4NH_2$, 2-CNC_5H_4N, 4-CNC_5H_4N and $C_3H_5NH_2$.

All attempts to isolate complexes with stoichiometries $(C_6F_5)_2Pd(LL)$ (LL = *o*-$MeOC_6H_4NH_2$, *o*-$OHC_6H_4NH_2$) or $[(C_6F_5)_2Pd(\mu\text{-}LL)]_2$ (LL = *p*-$MeOC_6H_4NH_2$, *p*-$OHC_6H_4NH_2$, *p*-$NH_2C_6H_4NH_2$) were unsuccesful. Thus the use of a ligand/Pd mol ratio of 1 always led to the isolation of solids containing varying amounts of both dioxane and the corresponding ligand. However, for LL = *o*-$NH_2C_6H_4NH_2$ and *o*-CNC_6H_4CN the stoichiometry $Pd(C_6F_5)_2(LL)$ was obtained. Elemental analyses of the compounds fit quite well the proposed formulae (Table 1).

The bis(pentafluorophenyl) derivatives of palladium(II) are white or pale yellow

TABLE 1. ELEMENTAL ANALYSES, DECOMPOSITION POINTS AND YIELDS OF PALLADIUM COMPLEXES

Compound	Colour	(Found (calcd.) (%))			Yields (%)	M.P. (°C)
		C	H	N		
$Pd(C_6F_5)_2(o\text{-}MeOC_6H_4NH_2)_2$ (I)	white	45.0 (45.4)	2.5 (2.6)	4.0 (4.1)	67	142
$Pd(C_6F_5)_2(p\text{-}MeOC_6H_4NH_2)_2$ (II)	white	45.7 (45.4)	2.4 (2.6)	4.4 (4.1)	80	136
$Pd(C_6F_5)_2(o\text{-}NH_2C_6H_4NH_2)$ (III)	pale yellow	39.9 (39.4)	1.5 (1.5)	5.5 (5.1)	76	162
$Pd(C_6F_5)_2(p\text{-}NH_2C_6H_4NH_2)_2$ (IV)	pale yellow	43.3 (43.8)	2.5 (2.4)	8.4 (8.5)	87	157
$Pd(C_6F_5)_2(o\text{-}OHC_6H_4NH_2)_2$ (V)	white	43.0 (43.7)	2.3 (2.1)	4.2 (4.3)	75	123
$Pd(C_6F_5)_2(p\text{-}OHC_6H_4NH_2)_2$ (VI)	pale yellow	44.0 (43.7)	2.3 (2.1)	4.1 (4.3)	70	110
$Pd(C_6F_5)_2(2\text{-}CNC_5H_4N)_2$ (VII)	pale yellow	44.0 (44.4)	1.3 (1.2)	8.5 (8.6)	86	157
$Pd(C_6F_5)_2(4\text{-}CNC_5H_4N)_2$ (VIII)	pale yellow	44.1 (44.4)	1.4 (1.2)	8.8 (8.6)	85	178
$Pd(C_6F_5)_2(o\text{-}CNC_6H_4CN)$ (IX)	white	42.9 (42.2)	0.7 (0.7)	4.9 (4.9)	76	155
$Pd(C_6F_5)_2(C_3H_5NH_2)_2$ (X)	white	37.8 (38.9)	2.2 (2.5)	5.3 (5.0)	64	120
$Pd(C_6F_5)_2(C_3H_5N{=}CMe_2)_2$ (XI)	white	44.3 (45.4)	4.0 (3.5)	4.4 (4.4)	60	97

solids stable in the air, but the 2- and 4-cyanopyridine compounds are hygroscopic and were kept in a P_4O_{10}-desiccator. They are soluble in THF, Et_2O, MeOH, EtOH, Me_2CO, CH_2Cl_2, and C_6H_6 and insoluble in hexane. They behave in acetone solutions as nonelectrolytes [9] ($\Lambda_M < 5$ cm^2 ohm^{-1} mol^{-1} for $c_M \simeq 10^{-4}$ M). However, the allylamine compound decomposes in solution slowly and progressively giving metallic palladium. The decomposition temperatures of the compounds are shown in Table 1.

Infrared spectra of all compounds show the characteristic absorptions of the C_6F_5 group [10] at ca. 1630m, 1600m, 1500vs, 1450vs, 1050vs, 950vs, and 800–780s cm^{-1}. The presence of two bands in the 800–780 cm^{-1} range has been used for assigning the *cis* configuration to the compounds (C_{2v} symmetry; two IR active vibrations for the X-sensitive mode of C_6F_5X molecules, which in metal complexes containing the C_6F_5 group is mainly a M–C stretching mode [3,11,12]).

Table 2 shows that the absorptions due to the N–H stretching vibrations of coordinated amines appear at frequencies lower than those observed for the free ligands. The number of infrared bands in this region is larger than the two bands expected for the asymmetric and symmetric vibrational modes of primary aromatic amines. However, such a pattern of infrared bands has also been observed for other *cis* complexes containing aromatic amines [8,13], and could be caused by partially hindered rotation of the coordinated amine about the nitrogen metal bond [14]. In fact, in the *o*-phenylenediamine compound, where such rotation would be completely hindered, only two bands are observed, which are compatible with its behaviour as chelating ligand. The compound containing *o*-aminophenol gives two additional bands at 3580 and 3550 cm^{-1}, attributed to free OH groups. Similarly, the complex with *p*-phenylenediamine also gives two bands at 3510 and 3420 cm^{-1}, which are assigned to a free amino group [13,15].

In 2- and 4-cyanopyridine both the nitrile group and the pyridine group are capable of coordinating with the metal ion. It is possible to determine the coordination site in the palladium compounds from the nitrile stretching, C–C and C–N (ring) stretching, and ring breathing frequencies of the free bases and the complexes. As the data in Table 3 show, the C≡N stretching frequency is virtually unaltered in the complex of 4-cyanopyridine, suggesting that in this complex the ligand is not nitrile bonded. On the other hand, it is known [16] that coordination of the nitrogen atom of the pyridine ring results in a blue shift of the four ring C–C and C–N

TABLE 2

INFRARED DATA ($\bar{\nu}$) FOR AMINE LIGANDS IN PALLADIUM COMPLEXES

Compound	$\nu(NH_2)$ (cm^{-1})	$\delta(NH_2)$ (cm^{-1})
$Pd(C_6F_5)_2$(*o*-$MeOC_6H_4NH)_2$	3360s, 3340sh, 3300s, 3280m	1595s, 1560m, 1550m
$Pd(C_6F_5)_2$(*p*-$MeOC_6H_4NH_2$)	3340m, 3300m, 3270s, 3240s 3160m	1585s, 1570m, 1510s
$Pd(C_6F_5)_2$(*o*-$NH_2C_6H_4NH_2$)	3340s, 3295s	1570s, 1550sh, 1585sh
$Pd(C_6F_5)_2$(*p*-$NH_2C_6H_4NH_2)_2$	3510m, 3420s, 3350-3340r,br 3260s, 3140m,br	1570m, 1510s
$Pd(C_6F_5)_2$(*o*-$OHC_6H_4NH_2)_2$	3370s, 3340s, 3310s, 3270s	1565s, 1550sh
$Pd(C_6F_5)_2$(*p*-$OHC_6H_4NH_2)_2$	3380sh, 3350s, 3290m, 3170m	1585s, 1570s, 1510s
$Pd(C_6F_5)_2(C_3H_5NH_2)_2$	3350m, 3300m	1595s

stretching vibrations, the highest frequency band giving the greatest shift. Since these features appear in the 4-cyanopyridine complex (see Table 3) the neutral ligand is bonded to palladium by the pyridine nitrogen. The 2-cyanopyridine complex is believed to be bonded at the pyridine ring since the C≡N stretching frequency is again almost unaffected by complex formation, although in this case the ring vibrations are little changed from the free ligand. However, this result has also been observed for other 2-cyanopyridine complexes of nickel(II), palladium(II), and platinum(II) and has been rationalized in terms of a π-bonding interaction [17] which reinforces the rather poor σ-donation from the 2-cyanopyridine.

In the phthalonitrile compound the elemental analysis and infrared spectrum indicate that the neutral ligand acts as a chelating group. Only one absorption is observed at 2275 cm^{-1}, a value which is ~ 40 cm^{-1} higher than that observed for the uncoordinated nitrile and is consistent with an end-on bonded nitrile.

The allylamine ligand in *cis*-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$ appears to be bonded to palladium through the nitrogen atom because the band at 1635 cm^{-1} from the C_6F_5 group shows a shoulder at 1645 cm^{-1}, which may be attributed to ν(C=C) (at 1642 cm^{-1} in free allylamine). In addition, bands at 1140s (C–N stretch), 990s, 930s, and 920s (CH out-of-plane bending) are also assignable to allylamine. The ^1H NMR spectrum of the allylamine compound (in $CDCl_3$ solution and TMS as internal standard) shows resonance signals for the allyl group at nearly the same δ's downfield from TMS as in free allylamine. Table 4 lists the observed peaks and their corresponding assignments. The apparent quartet observed for the CH_2 protons can be explained in terms of coupling with both the CH and NH_2 protons; this should produce six peaks, but two of the intermediate peaks are masked by the two central ones. The addition of D_2O resulted in the shortening and broadening of the triplet from NH_2 together with the transformation of the apparent quartet from CH_2 into the expected doublet structure arising from the coupling with CH only. It should be noted that incipient peaks are observed in the base line of the spectrum which are indicative of some interaction of palladium with the olefinic system of the allylamine.

TABLE 3

PRINCIPAL INFRARED BANDS OF 2-CYANOPYRIDINE, 4-CYANOPYRIDINE AND THEIR PALLADIUM COMPLEXES

Assignment	2-CNpy	*cis*-$Pd(C_6F_5)_2(2\text{-CNpy})_2$	4-CNpy	*cis*-$Pd(C_6F_5)_2(4\text{-CNpy})_2$
ν(C≡N)	2236w	2240w	2243w	2240s
	1582s	1595s	1592m-s	1610s
ν(CC) and ν(CN)	1573sh	1575w	1540m	1540s
	1430m	1435	1494w-m	[a]
				1420vs
Ring-breathing modes	1045m	[a]		
	990s	1030s	1081m	[a]
			988s	1030s
Out-of-plane deformation modes	776vs	775vs	826vs	850s
	736	740m	775m-s	830vs
				740m
	550m-w	550s	560s	565s
		440m		440m

[a] Spectral region masked by absorption from the C_6F_5 group.

TABLE 4

^{1}H NMR SPECTRUM OF *cis*-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$

	δ (ppm) [a]	J (Hz) [a]
CH	6.50–5.80(m)	J_{gem} 0, J_{cis} 12, J_{trans} 15
CH_2=	5.50(d), 5.25(d)	
CH_2	3.30(q)	$J(CH_2/CH)$ 7
NH_2	2.30(t)	$J(NH_2CH_2)$ 6

[a] All the values are approximate. Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet. The *gem*, *cis* and *trans* designations are obviously referred to the vinyl group.

On attempting to record the ^{1}H NMR spectrum of *cis*-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$ in acetone-d_6 as solvent a different spectrum was observed. Although the spectrum was not good enough to be analysed, it indicated clearly that the solvent had reacted with the palladium compound. The reactions between carbonyl compounds and amines in the presence of metal ions have been widely studied [18,19], but in the specific case of allylamine Kurosawa observed the occurrence of the condensation reaction of acetone with allylamine coordinated to platinum to give *trans*-$[PtH(PPh_3)_2(allylN{=}CMe_2)]^+$ from $PtH(ClO_4)(PPh_3)_2$ and $C_3H_5NH_2$ in acetone as solvent, a process which competes with the formation of the expected product, $[Pt(PPh_3)_2(\pi\text{-}C_3H_5)]^+$ [20]. With this result in mind, *cis*-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$ was treated with acetone, and this led to isolation of a white solid, characterized as *cis*-$Pd(C_6F_5)_2$ $(allylN{=}CMe_2)_2$ by its analytical data and IR spectrum. Thus the bands due to N–H and C–N stretching modes of allylamine had disappeared and a strong absorption at 1640 cm^{-1} (with a shoulder at 1645 cm^{-1}) had appeared, possibly attributable to $\nu(C{=}N)$. The CH out-of-plane bending vibrations of the vinyl group were observed as doublets at ca. 990m and 930m cm^{-1}. All attempts made to study the compound by ^{1}H NMR spectroscopy were unsuccesful because of its low solubility.

Experimental

cis-$Pd(C_6F_5)_2Dx$ was prepared according to ref. 3. The neutral ligands were commercial grade chemicals.

IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer as KBr discs. Conductivities were measured with a Phillips PW 9501/01 conductimeter. Melting points were determined on a Reichert microscope provided with heating plate. ^{1}H NMR spectra were recorded with Me_4Si as internal standard on a Varian EM360A spectrometer.

C, H, N analyses were performed with a Perkin–Elmer 240C microanalyzer.

Preparation of the complexes

cis-$Pd(C_6F_5)_2L_2$ (L = o-anisidine, p-anisidine, o-phenylenediamine, o-aminophenol, p-aminophenol, 2-cyanopyridine, and 4-cyanopyridine. In separate experiments ≃ 0.20 mmol of the appropriate ligand was added to 50 mg (0.095 mmol) of *cis*-$Pd(C_6F_5)_2Dx$ in dichloromethane (10 ml) and the solution was stirred for ca. 2 h at room temperature. The solution was then concentrated under vacuum and the addition of hexane determined the precipitation of the organo complex as a white or pale yellow solid, which was dried in the air. Table 1 gives the yield for each compound.

cis-$Pd(C_6F_5)_2(o\text{-}NH_2C_6H_4NH_2)$. The 1/1 mol ratio of the reagents (i.e., 0.095 mmol of *o*-phenylenediamine and 0.095 mmol of *cis*-$Pd(C_6F_5)_2Dx$) was used, and the work-up was similar to that for the above complexes. Yield 76%.

cis-$Pd(C_6F_5)_2(o\text{-}CNC_6H_4CN)$. A mixture of *cis*-$Pd(C_6F_5)_2Dx$ (50 mg; 0.095 mmol) and phthalonitrile (12.2 mg; 0.095 mmol) in diethyl ether (10 ml) was stirred for 1/2 h, then concentrated under vacuum. The addition of hexane precipitated the organo complex as a white solid, which was filtered off and dried in the air. Yield 76%.

cis-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$. 0.570 mmol (0.043 ml; density, 0.76 g/mol) of allylamine were added to 150 mg (0.285 mmol) of *cis*-$Pd(C_6F_5)_2Dx$ in dichloromethane (10 ml). The colourless solution was stirred for only 5 min to avoid the decomposition to metallic palladium, then concentrated under vacuum. Addition of hexane precipitated a white solid, which was filtered off and dried in the air. Yield, 64%.

cis-$Pd(C_6F_5)_2(allylN{=}CMe_2)_2$. A solution of 150 mg (0.285 mmol) of *cis*-$Pd(C_6F_5)_2(C_3H_5NH_2)_2$ in 5 ml of acetone was stirred for 15 h at room temperature. Hexane was then added until turbidity persisted, and was kept overnight in a refrigerator. The white precipitate was filtered off and dried in the air. Yield 60%.

References

1 R. Usón, J. Forniés, J. Gimeno, P. Espinet and R. Navarro, J. Organomet. Chem., 81 (1974) 115.
2 A. Arcas and P. Royo, Inorg. Chim. Acta, 30 (1978) 205.
3 G. Garcia and G. López, Inorg. Chim. Acta, 52 (1981) 87
4 G. López, G Garcia, N. Cutillas and J. Ruiz, J. Organomet. Chem., 241 (1983) 269.
5 C.F. Smith and C. Tamborski, J. Organomet. Chem., 32 (1971) 257.
6 A. Arcas and P. Royo, Inorg. Chim. Acta, 31 (1978) 97.
7 G. García, G. López and M.D. Santana, An. Quim., 79B (1983) 214.
8 G. García, G. López, G. Sánchez and M.D. Santana, An. Quim., in press.
9 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
10 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1955.
11 G.B. Deacon and J.H.S. Green, Spectrochim. Acta A, 24 (1968) 1125.
12 R. Usón, J. Forniés, P. Espinet, F. Martinez and M. Tomás, J. Chem. Soc. Dalton Trans., (1981) 463.
13 S. Haghighi, C.A. McAuliffe, W.E. Hill, H H. Kohl and M.E. Friedman, Inorg. Chim. Acta, 43 (1980) 113.
14 L.A. Duncanson and L.M. Venanzi, J. Chem. Soc., (1960) 3841.
15 A. Adeyemo, Y. Teklu and T. Williams, Inorg. Chim. Acta, 51 (1981) 19.
16 F. Farha and R.T. Iawamoto, Inorg. Chem., 4 (1965) 844.
17 R.A. Walton, J. Inorg. Nucl. Chem., 28 (1966) 2229.
18 J.W.L. Martin and N.F. Curtis, J. Chem. Soc. Dalton Trans., (1975) 87
19 J.M. Harrowfield, A.M. Sargeson, J. Springborg, M.R. Snow and D. Taylor, Inorg. Chem., 22 (1983) 186
20 H. Kurosawa, Inorg. Chem., 15 (1976) 120.