*Journal of Organometallic Chemistry*, 317 (1986) 105–119
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# SYNTHESES AND REACTIVITY OF PENTACHLOROPHENYLPALLADIUM(I) DERIVATIVES. MOLECULAR STRUCTURE OF $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$*

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(Received June 10th, 1986)

## Summary

The syntheses of $[XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ (X = Cl, $C_6Cl_5$) are described. Other neutral halogeno-pseudohalogeno-palladium(I) complexes $[XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ (X = Br, I, SCN or CNO) have been obtained from $[ClPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ by metathetical reactions, and $SnCl_2$ inserts into the Pd–Cl bond to give the Pd-$SnCl_3$ compound. The cationic derivatives $[LPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (L = $PPh_3$, $P(OPh)_3$, $AsPh_3$, $SbPh_3$, tht) have also been prepared. $SO_2$ or $RN_2^+$ insert into the Pd–Pd bond of $[ClPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ to give A-frame $Pd^{II}$ complexes, but do not react with $(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$. The nature of the products of the reactions of $XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ with RNC (R = t-Bu, Cy, *p*-Tol, $CNC_6H_4NC$) depend on the isonitrile used and the reaction conditions.

The molecular structure of $(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ has been established by a single crystal X-ray study. The crystals are triclinic, space group $P\bar{1}$, with 2 molecules of the 2 $CH_2ClCH_2Cl$ solvate in a cell of dimensions *a* 12.986(4), *b* 13.213(5), *c* 21.254(6) Å, $\alpha$ 90.49(3), $\beta$ 89.204(25), $\gamma$ 102.86(3)°, *V* 3554.8 Å$^3$. Of 9156 data collected on a four-circle diffractometer, 4474 observed reflections were used in the refinement ($R = 0.0902$). The complex has no crystallographically imposed symmetry, but overall is close to $D_{2d}$. The Pd–Pd bond length is 2.6704(21) Å.

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* Dedicated to Prof. Dr. R. Usón on the occasion of his 60th birthday.

## Introduction

We recently described the synthesis [1] and reactions [1,2] of some binuclear pentafluorophenylpalladium(I) derivatives with dppm as bridging ligand, and noted some differences in reactivity between these complexes $[XPd(\mu\text{-dppm})_2Pd(C_6F_5)]$ or $[(C_6F_5)Pd(\mu\text{-dppm})_2Pd(C_6F_5)]$ and the related halogeno derivatives $[XPd(\mu\text{-dppm})_2PdX]$ [3]. We describe here the synthesis of the related pentachlorophenylpalladium(I) derivatives $(XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$, $(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5))$ and their reactivity in the formation of cationic complexes and insertion of species such as RNC, CO, $SO_2$ and $N_2R^+$ into the Pd–Pd bond.

We also report the structure of $(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ as established by an X-ray diffraction study.

## Results and discussion

The pentachlorophenylpalladium(I) complexes $(XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$, X = Cl (**1**), $C_6Cl_5$ (**2**)) were prepared by a redox condensation between $Pd_2(dba)_3 \cdot CHCl_3$ and $PdX(C_6Cl_5)(\eta^1\text{-dppm})_2$ (X = Cl, $C_6Cl_5$) in oxygen-free dichloromethane (see Experimental), according to eq. 1.

$$Pd_2(dba)_3 \cdot CHCl_3 + 2\ PdX(C_6Cl_5)(\eta^1\text{-dppm})_2 \rightarrow 2\ XPd(\mu\text{-dppm})_2Pd(C_6Cl_5) + 3dba \quad (1)$$

(X = Cl (**1**), $C_6Cl_5$ (**2**))

The structure of complex **2** was established by a single crystal X-ray diffraction study as discussed later.

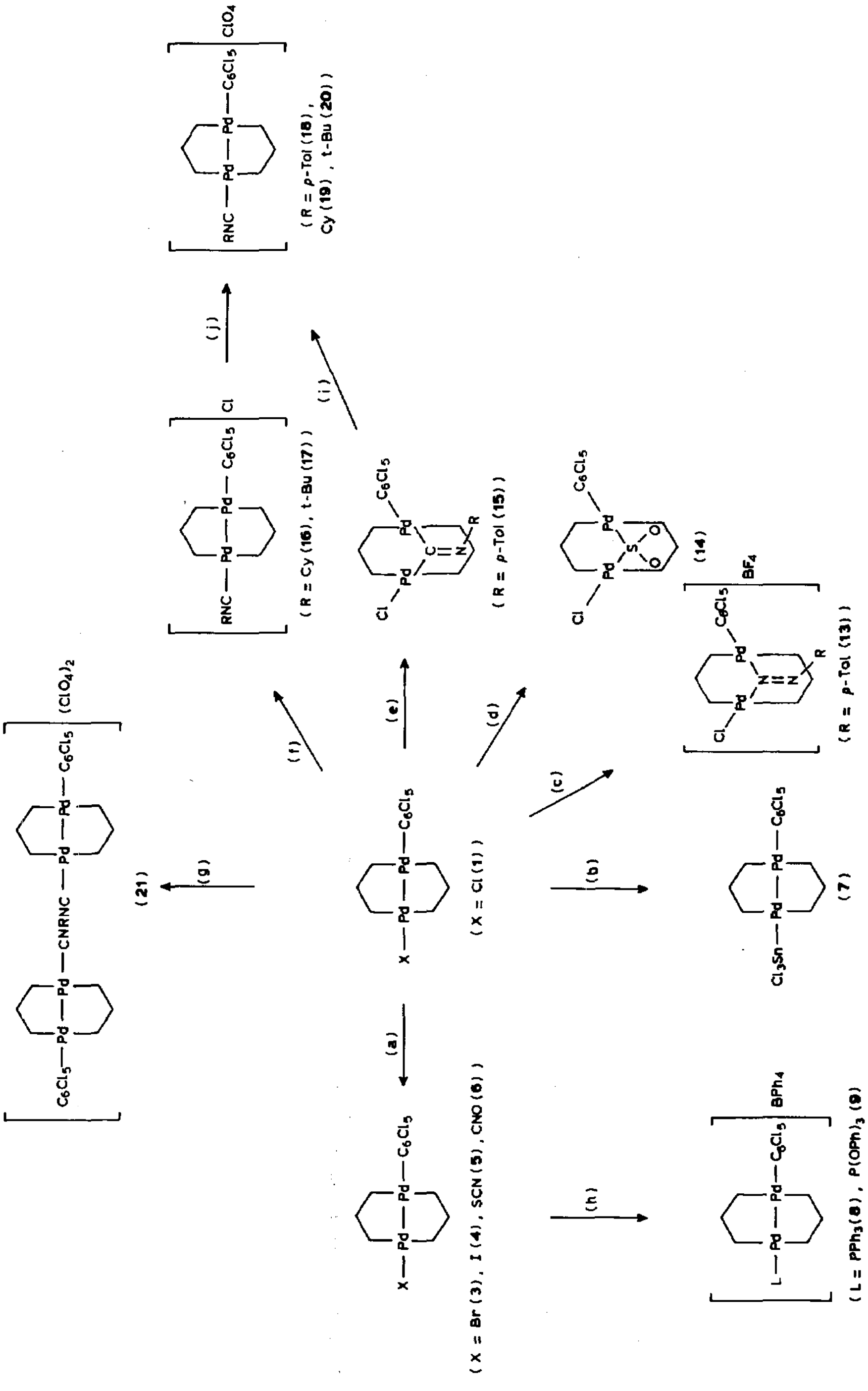
Scheme 1 shows the reactions of complex **1**, and analytical, and conductivity data are listed in Table 1.

Other pentachlorophenylpalladium(I) complexes (**3**–**6**) can be obtained by treating complex **1** with an excess of the corresponding salts (LiBr, NaI, KSCN, KOCN) in methanol/water (see Scheme 1(a)) at room temperature. Molecular weight determinations on some of these complexes are consistent with the proposed formulae (**1**, 1216 (1266); **2**, 1408 (1480); **3**, 1344 (1311); **4**, 1358 (1358)). The reaction between equimolecular amounts of complex **1** and $SnCl_2$ gives the $SnCl_3^-$ derivative (**7**) as a result of the insertion of $SnCl_2$ into the Pd–Cl bond (rather than into the Pd–Pd bond) as was observed with other $Pd^I$ [4] or $Pt^I$ [5] complexes.

Complex **1** is unreactive towards the formation of cationic complexes and treatment of $[ClPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ with an excess of L (L = P, As, S donor ligands) in methanol and $NaBPh_4$ (at room temperature or under reflux) leaves the starting material unchanged. This contrasts with the behaviour of $ClPd(\mu\text{-dppm})_2Pd(C_6F_5)$ [1] and $ClPt(\mu\text{-dppm})_2Pt(C_6F_5)$ [6] which in the presence of L (L = P, As, Sb, S donor) and $NaBPh_4$ readily give the cationic derivatives $(BPh_4)[LM(\mu\text{-dppm})_2M(C_6F_5)]$. Neither of the complexes **3** and **4** are useful for the preparation of cationic complexes, but complex **6** $(NCO)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ reacts in methanol at room temperature with equimolecular amounts of L and $NaBPh_4$ to give the corresponding cationic derivatives (L = $PPh_3$ (**8**), $P(OPh)_3$ (**9**), $AsPh_3$ (**10**), $SbPh_3$ (**11**) tht (**12**)) (see Scheme 1(h)).

All complexes show typical IR absorptions of the dppm and $C_6Cl_5$ [7] groups.

*(Continued on p. 110)*


X — Pd — Pd — C6Cl5
( X = Cl (1) )
(a)
( X = Br (3), I (4), SCN (5), CNO (6) )
(b)
Cl3Sn — Pd — Pd — C6Cl5
(7)
(c)
BF4
( R = p-Tol (13) )
(d)
(14)
(e)
( R = p-Tol (15) )
(f)
RNC — Pd — Pd — C6Cl5
Cl
( R = Cy (16), t-Bu (17) )
(g)
C6Cl5 — Pd — Pd — CNRNC — Pd — Pd — C6Cl5
(ClO4)2
(21)
(h)
L — Pd — Pd — C6Cl5
BPh4
( L = PPh3 (8), P(OPh)3 (9), AsPh3 (10), SbPh3 (11), tht (12) )
(i)
(j)
RNC — Pd — Pd — C6Cl5
ClO4
( R = p-Tol (18), Cy (19), t-Bu (20) )

SCHEME 1

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES ($ohm^{-1}\ cm^2\ mol^{-1}$) AND RELEVANT IR ABSORPTIONS ($cm^{-1}$)

| Complex | Analyses (Found (calcd.) (%)) | | | | $\Lambda_M$ [a] | $\nu(C\equiv N)$ | $\nu(C=N)$ | Other |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Cl | | | | |
| $ClPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**1**) | 53.0 | 3.8 | – | 16.5 | no cond. | – | – | 225 [b] |
| | (53.0) | (3.7) | | (16.8) | | | | |
| $(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**2**) | 50.4 | 3.1 | – | 24.0 | no cond. | – | – | – |
| | (50.3) | (3.0) | | (24.0) | | | | |
| $BrPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**3**) | 51.8 | 3.5 | – | [c] | Insol. | – | – | – |
| | (51.3) | (3.4) | | | | | | |
| $IPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**4**) | 49.1 | 3.2 | – | 13.3 | no cond. | – | – | – |
| | (49.5) | (3.3) | | (13.1) | | | | |
| $(SCN)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**5**) | 51.8 | 3.3 | 1.0 | 14.3 | no cond. | – | – | 2085 [d] |
| | (52.1) | (3.4) | (1.1) | (13.8) | | | | |
| $(OCN)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**6**) | 53.9 | 3.2 | 1.0 | 14.8 | no cond. | – | – | 2175 [e] |
| | (54.8) | (3.5) | (1.1) | (14.0) | | | | |
| $Cl_3SnPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (**7**) | 46.9 | 3.3 | – | [g] | no cond. | – | – | 307,285 [h] |
| | (46.2) | (3.0) | | | | | | |
| $[Ph_3PPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (**8**) | 64.5 | 4.1 | – | 9.5 | 74 | – | – | 610 [f] |
| | (64.8) | (4.4) | | (9.7) | | | | |
| $[(PhO)_3PPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (**9**) | 63.6 | 4.5 | – | 10.6 | 73 | – | – | 610 [f] |
| | (63.3) | (4.3) | | (9.5) | | | | |
| $[(Ph_3As)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (**10**) | 63.6 | 4.2 | – | 9.6 | 69 | – | – | 610 [f] |
| | (63.4) | (4.3) | | (9.5) | | | | |
| $[(Ph_3Sb)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (**11**) | 62.0 | 4.2 | – | 9.8 | 69 | – | – | 610 [f] |
| | (61.8) | (4.2) | | (9.3) | | | | |
| $[(tht)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)]BPh_4$ (**12**) | 61.8 | 4.2 | – | 9.8 | 73 | – | – | 610 [f] |
| | (61.6) | (4.4) | | (10.8) | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| [ClPd($\mu$-dppm)$_2$($\mu$-$p$-CH$_3$C$_6$H$_4$N$_2$)-Pd(C$_6$Cl$_5$)]BF$_4$ (**13**) | 51.1 | 3.6 | 1.9 | 15.1 | 139 | - | - | 1060 [i] |
| | (51.3) | (3.5) | (1.9) | (14.5) | | | | |
| ClPd($\mu$-dppm)$_2$($\mu$-SO$_2$)PdC$_6$Cl$_5$ (**14**) | 45.4 | 3.2 | - | 24.2 | no cond. | - | - | 1150,1018 [j],<br>270(m)$^{(b)}$ |
| | (45.5) | (3.2) | | (25.2) | | | | |
| ClPd($\mu$-dppm)$_2$($\mu$-CN-$p$-Tol)Pd(C$_6$Cl$_5$) (**15**) | 55.0 | 3.9 | 1.0 | 14.6 | 33 | - | 1615,1594 [k] | - |
| | (55.5) | (3.7) | (1.0) | (15.3) | | | | |
| [(CyNC)Pd($\mu$-dppm)$_2$Pd(C$_6$Cl$_5$)]Cl (**16**) | 54.8 | 4.1 | 1.1 | 15.0 | 66 | 2171 | - | - |
| | (55.0) | (4.0) | (1.0) | (15.5) | | | | |
| [(t-BuNC)Pd($\mu$-dppm)$_2$Pd(C$_6$Cl$_5$)]Cl (**17**) | 53.4 | 3.8 | 1.1 | 15.5 | 60 | 2165 | - | - |
| | (54.3) | (3.9) | (1.0) | (15.8) | | | | |
| [($p$-TolNC)Pd($\mu$-dppm)$_2$Pd(C$_6$Cl$_5$)]ClO$_4$ (**18**) | 53.4 | 3.4 | 0.9 | 14.5 | 123 | 2152 | - | 1100,620 [m] |
| | (53.1) | (3.5) | (1.0) | (14.7) | | | | |
| [(CyNC)Pd($\mu$-dppm)$_2$Pd(C$_6$Cl$_5$)]ClO$_4$ (**19**) | 52.8 | 3.7 | 1.3 | 14.0 | 125 | 2176 | - | 1100,620 [m] |
| | (52.6) | (3.8) | (1.0) | (14.7) | | | | |
| [($^t$BuNC)Pd($\mu$-dppm)$_2$Pd(C$_6$Cl$_5$)]ClO$_4$· 0.75(CH$_3$)$_2$CO (**20**) | 52.0 | 4.1 | 0.9 | 14.7 | 130 | 2168 [l] | - | 1100.620 [m] |
| | (52.1) | (4.0) | (1.0) | (15.0) | | | | |
| {($\mu$,$\mu'$-CNC$_6$H$_4$NC)[Pd($\mu$-dppm)$_2$-Pd(C$_6$Cl$_5$)]$_2$}(CLO$_4$)$_2$ (**21**) | 51.8 | 3.5 | 1.3 | 15.5 | 210 | 2131 | - | 1100,620 [m] |
| | (51.7) | (3.3) | (1.0) | (15.3) | | | | |

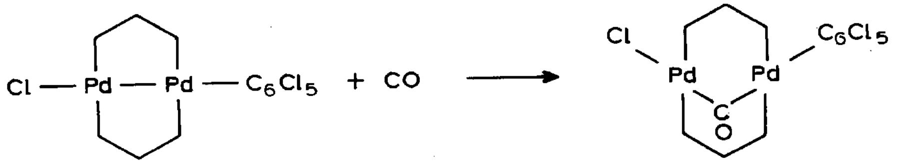
[a] In acetone solution, ca. $5\times10^{-4}$ *M*. [b] $\nu$(Pt–Cl). [c] The presence of Br$^-$ prevents determination of Cl$^-$. [d] $\nu$(C≡N), SCN group [11]; [e] $\nu_a$(NCO) [11]. [f] BPh$_4$. [g] No satisfactory chlorine analysis was obtained probably owing to difficulties in the combustion. [h] SnCl$_3^-$ [12]. [i] BF$_4^-$ [8]. [j] $\nu_{asym}$(SO)$_2$ and $\nu_{sym}$(SO$_2$) [10]. [k] Other bands in this region are probably due to the phenyl ring; their intensities increased upon insertion. We list both types of absorption. [l] $\nu$(CO) of acetone solvate at 1718 cm$^{-1}$. $^1$H NMR integration shows that 0.75 molecules of acetone are present. [m] ClO$_4^-$ [26].

Complex **1** shows a weak absorption at 225 $cm^{-1}$ assigned to $\nu$(Pd–Cl), in the range found for other palladium(I) derivatives [1], and clearly shifted to lower energies compared to those for the precursor $PdCl(C_6Cl_5)(\eta^1\text{-dppm})_2$ (302 $cm^{-1}$), suggesting a fairly high *trans*-influence of the Pd–Pd bond. The corresponding $\nu$(Pd–Br) or $\nu$(Pd–I) bands are expected to lie outside the range of our instrument.

Some relevant IR absorptions for complexes **1**–**12** are shown in Table 1.

*Insertion reactions*

Complex **1** reacts with the electrophilic species $[p\text{-}CH_3C_6H_4N_2]BF_4$ and $SO_2$ to give the asymmetric A-frame compounds **13** and **14** by insertion into the Pd–Pd bond (see Scheme 1(c,d)). Furthermore, when CO is bubbled through a solution of complex **1** in $CH_2Cl_2$ for 45 min, the presence of an inserted carbonyl compound (eq. 2) can be detected in the IR spectrum of the solution ($\nu$(CO) ~ 1708 $cm^{-1}$), but all attempts to isolate such a compound only gave the starting material, which is consistent with the usual lability of such palladium carbonyl derivatives [3d].



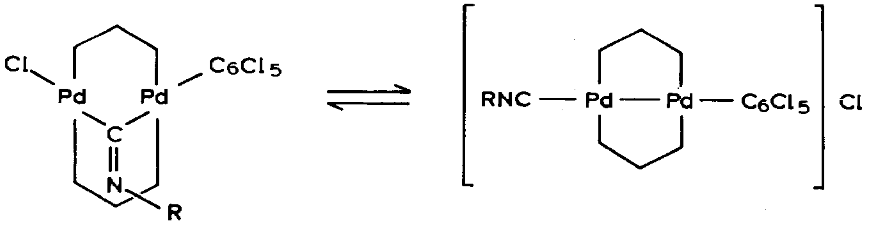
(2)

The insertion of $SO_2$ into the Pd–Pd bond is also reversible [3f], and although complex **14** is stable at room temperature it loses $SO_2$ at 100°C to regenerate complex **1**. Complex **14** crystallizes with $CH_2Cl_2$ ($^1H$ NMR), but when an orange sample of **14** is kept in an oven at 80°C the yellow complex **1** is re-formed.

The IR spectra of complex **13** shows a strong and broad absorption at 1060 $cm^{-1}$ due to the counterion $BF_4^-$ [8], and the $\nu$(Pd–Cl) band appears at 305 $cm^{-1}$, consistent with the increase of the formal oxidation state of the palladium [3f] and with the cationic nature of the compound [6]. Complex **14** shows two absorptions, at 1150s and 1018s [9] $cm^{-1}$, due to the symmetric and asymmetric $\nu$(S–O) stretching frequencies respectively [3f,10]; the increase in the $\nu$(Pd–Cl) stretching frequency to 270 $cm^{-1}$ for **14** compared with 225 $cm^{-1}$ for **1** is related to the increase of the formal oxidation state upon insertion of $SO_2$ into the Pd–Pd bond [3f,2].

Isonitriles can also be inserted into the metal–metal bond but the reaction of complex **1** with RNC is complicated, and either insertion, to give $[ClPd(\mu\text{-dppm})_2(\mu\text{-RNC})Pd(C_6Cl_5)]$, or coordination to give $[RNCPd(\mu\text{-dppm})Pd(C_6Cl_5)]Cl$, can occur depending on the nature of group R and of the solvent used for the reaction.

Complex **1** reacts in dichloromethane with a stoicheiometric amount of *p*-TolNC and the insertion product **15** can be isolated from the solution. However the IR



(3)

spectrum of the dichloromethane solution of **15** shows bands assignable to $\nu$(C=N) and to $\nu$(C≡N) (2146 $cm^{-1}$), thus suggesting that in the $CH_2Cl_2$ solution the insertion and the coordination species (eq. 3) are in equilibrium, but that only the insertion product **15** can be crystallized out. The conductivity of an acetone solution of **15** (30 $ohm^{-1}\,cm^2\,mol^{-1}$) is consistent with the existence of such an equilibrium.

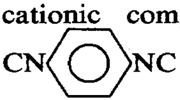
The isonitriles CyNC and t-BuNC react with complex **1** in benzene (which being a non-polar solvent should favour the formation of insertion products [6]) to mixtures of the coordinated complex and the starting material but not the insertion product. In order to complete the formation of the coordinated complexes **16** and **17** the reaction must be carried out in acetone and with an excess of the isonitrile. The reaction of complex **1** with RNC (R = Cy (**19**), t-Bu (**20**)) (molar ratio 1/1) in dichloromethane in the presence of an excess of $NaClO_4$ yields the corresponding cationic complexes $[RNCPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]ClO_4$. If the diisocyanide  is used the tetranuclear complex **21** is obtained. The insertion compound $[ClPd(\mu\text{-dppm})_2(\mu\text{-}p\text{TolNC})PdC_6Cl_5]$ (**15**) reacts with $NaClO_4$ in acetonitrile to give the cationic coordinated complex $[p\text{-TolNCPd}(\mu\text{-dppm})_2\text{-}Pd(C_6Cl_5)]ClO_4$ (**18**). (Scheme 1 (i)).

TABLE 2

CRYSTAL DATA FOR $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$

| | |
|---|---|
| Formula | $C_{62}H_{44}Cl_{10}P_4Pd_2 \cdot 2C_2H_4Cl_2$ |
| $M$ | 1678.18 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 12.986(4) |
| $b$ (Å) | 13.213(5) |
| $c$ (Å) | 21.254(6) |
| $\alpha$ (°) | 90.49(3) |
| $\beta$ (°) | 89.204(25) |
| $\gamma$ (°) | 102.86(3) |
| $V$ ($Å^3$) | 3554.8 |
| Diffractometer | Enraf–Nonius CAD 4 |
| $T$ (K) | 291 ± 1 |
| Radiation | Mo-$K_\alpha$ |
| $\bar{\lambda}$ (Å) | 0.71069 |
| $\mu$(Mo-$K_\alpha$) ($cm^{-1}$) | 9.5 |
| $\theta$-range (°) | 1-22 |
| Mode | $\omega - 2\theta$ scans |
| Data measured | 9156 |
| Data used | 4474 ($F \geqslant 6\sigma(F)$) |
| Solution | Patterson; $\Delta F$ syntheses |
| Refinement | Full-matrix least-squares |
| Model | Pd, P, Cl (not solvent) anisotropic. Rigid, planar hexagons. H atoms in calculated positions. Group $U$'s for H atoms (0.158 $Å^2$) and for solvent Cl atoms (0.237 $Å^2$). Solvent C atoms not located. |
| Weighting scheme | $w^{-1} = [\sigma^2(F) + 0.074F^2]$ |
| $R$ | 0.0902 |
| $R_w$ | 0.1013 |
| Variables | 287 |

TABLE 3

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS OF REFINED ATOMS IN $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Pd(1) | 0.26341(11) | 0.80501(10) | 0.22913(8) | 0.0377(10) |
| Pd(2) | 0.35419(11) | 0.67024(10) | 0.28784(8) | 0.0357(10) |
| P(1) | 0.1480(4) | 0.6625(4) | 0.1922(3) | 0.042(3) |
| P(2) | 0.3896(4) | 0.9371(4) | 0.2716(3) | 0.050(4) |
| P(3) | 0.5074(4) | 0.7731(4) | 0.2502(3) | 0.046(4) |
| P(4) | 0.1859(4) | 0.5814(4) | 0.3168(3) | 0.040(3) |
| Cl(1) | 0.2832(5) | 0.9345(5) | 0.0912(3) | 0.070(4) |
| Cl(2) | 0.1356(6) | 1.0715(6) | 0.0454(4) | 0.101(6) |
| Cl(3) | −0.0510(6) | 1.1042(6) | 0.1291(4) | 0.108(6) |
| Cl(4) | −0.0893(6) | 0.9988(6) | 0.2599(4) | 0.102(6) |
| Cl(5) | 0.0582(5) | 0.8618(5) | 0.3062(3) | 0.079(5) |
| Cl(6) | 0.4731(4) | 0.7492(4) | 0.4262(3) | 0.059(4) |
| Cl(7) | 0.6274(6) | 0.6451(6) | 0.4957(4) | 0.089(5) |
| Cl(8) | 0.6715(6) | 0.4370(6) | 0.4481(4) | 0.098(6) |
| Cl(9) | 0.5555(6) | 0.3322(5) | 0.3302(4) | 0.104(6) |
| Cl(10) | 0.4067(5) | 0.4382(4) | 0.2571(3) | 0.071(4) |
| C(1) | 0.0788(15) | 0.6011(15) | 0.2630(10) | 0.045(5) |
| C(2) | 0.5155(16) | 0.9043(15) | 0.2858(10) | 0.046(5) |
| C(3) | 0.1676 | 0.9043 | 0.1963 | 0.042(5) |
| C(4) | 0.1833 | 0.9512 | 0.1373 | 0.042(5) |
| C(5) | 0.1164 | 1.0133 | 0.1173 | 0.047(5) |
| C(6) | 0.0338 | 1.0287 | 0.1562 | 0.065(7) |
| C(7) | 0.0180 | 0.9819 | 0.2151 | 0.073(7) |
| C(8) | 0.0849(9) | 0.9197(9) | 0.2352(6) | 0.042(5) |
| C(9) | 0.4413 | 0.5850 | 0.3456 | 0.041(5) |
| C(10) | 0.4908 | 0.6306 | 0.3999 | 0.040(5) |
| C(11) | 0.5599 | 0.5827 | 0.4319 | 0.059(6) |
| C(12) | 0.5796 | 0.4892 | 0.4095 | 0.053(6) |
| C(13) | 0.5302 | 0.4436 | 0.3551 | 0.057(6) |
| C(14) | 0.4610(9) | 0.4915(9) | 0.3232(6) | 0.047(5) |
| C(16) | −0.0576 | 0.6919 | 0.1709 | 0.069(7) |
| C(17) | −0.1335 | 0.7229 | 0.1344 | 0.088(9) |
| C(18) | −0.1096 | 0.7548 | 0.0725 | 0.091(9) |
| C(19) | −0.0098 | 0.7557 | 0.0471 | 0.063(7) |
| C(20) | 0.0661 | 0.7247 | 0.0835 | 0.066(7) |
| C(15) | 0.0422(12) | 0.6928(13) | 0.1455(6) | 0.047(5) |
| C(22) | 0.0979 | 0.4827 | 0.1206 | 0.067(7) |
| C(23) | 0.1188 | 0.3958 | 0.0897 | 0.116(11) |
| C(24) | 0.2219 | 0.3814 | 0.0861 | 0.097(9) |
| C(25) | 0.3041 | 0.4539 | 0.1133 | 0.072(7) |
| C(26) | 0.2832 | 0.5408 | 0.1443 | 0.069(7) |
| C(21) | 0.1801(9) | 0.5552(13) | 0.1479(8) | 0.053(6) |
| C(28) | 0.5041 | 1.0696 | 0.1826 | 0.073(7) |
| C(29) | 0.5184 | 1.1525 | 0.1407 | 0.089(9) |
| C(30) | 0.4473 | 1.2177 | 0.1411 | 0.096(9) |
| C(31) | 0.3621 | 1.2000 | 0.1833 | 0.081(8) |
| C(32) | 0.3479 | 1.1172 | 0.2252 | 0.056(6) |
| C(27) | 0.4189(11) | 1.0520(12) | 0.2248(8) | 0.053(6) |
| C(34) | 0.2969 | 0.9273 | 0.3899 | 0.097(10) |
| C(35) | 0.2908 | 0.9611 | 0.4519 | 0.189(20) |
| C(36) | 0.3545 | 1.0554 | 0.4712 | 0.150(15) |
| C(37) | 0.4243 | 1.1157 | 0.4286 | 0.123(12) |

TABLE 3 (continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(38) | 0.4304 | 1.0819 | 0.3666 | 0.105(10) |
| C(33) | 0.3666(14) | 0.9876(13) | 0.3472(11) | 0.060(6) |
| C(40) | 0.6393 | 0.6408 | 0.2512 | 0.080(8) |
| C(41) | 0.7233 | 0.5999 | 0.2713 | 0.111(11) |
| C(42) | 0.7919 | 0.6521 | 0.3168 | 0.097(9) |
| C(43) | 0.7764 | 0.7453 | 0.3423 | 0.118(12) |
| C(44) | 0.6923 | 0.7862 | 0.3223 | 0.089(9) |
| C(39) | 0.6238(13) | 0.7340(13) | 0.2767(8) | 0.057(6) |
| C(46) | 0.4618 | 0.7863 | 0.1222 | 0.046(5) |
| C(47) | 0.4876 | 0.8195 | 0.0606 | 0.078(8) |
| C(48) | 0.5906 | 0.8712 | 0.0454 | 0.093(9) |
| C(49) | 0.6678 | 0.8897 | 0.0916 | 0.085(8) |
| C(50) | 0.6421 | 0.8565 | 0.1531 | 0.068(7) |
| C(45) | 0.5391(8) | 0.8048(11) | 0.1684(7) | 0.050(6) |
| C(52) | 0.1982 | 0.3991 | 0.3765 | 0.049(5) |
| C(53) | 0.1893 | 0.2924 | 0.3824 | 0.056(6) |
| C(54) | 0.1489 | 0.2258 | 0.3330 | 0.068(7) |
| C(55) | 0.1176 | 0.2658 | 0.2777 | 0.068(7) |
| C(56) | 0.1265 | 0.3725 | 0.2718 | 0.057(6) |
| C(51) | 0.1669(10) | 0.4391(9) | 0.3212(6) | 0.041(5) |
| C(58) | 0.1975 | 0.6737 | 0.4353 | 0.057(6) |
| C(59) | 0.1554 | 0.6975 | 0.4929 | 0.080(8) |
| C(60) | 0.0478 | 0.6622 | 0.5058 | 0.101(10) |
| C(61) | −0.0176 | 0.6033 | 0.4611 | 0.078(8) |
| C(62) | 0.0245 | 0.5795 | 0.4035 | 0.054(6) |
| C(57) | 0.1321(8) | 0.6148(11) | 0.3906(7) | 0.035(5) |
| Cl(11) | 0.2560(15) | 0.8810(15) | 0.6430(10) | 0.237 |
| Cl(12) | 0.1554(15) | 0.6345(15) | 0.7681(10) | 0.237 |
| Cl(13) | 0.3947(14) | 0.4423(15) | 0.9306(9) | 0.237 |
| Cl(14) | 0.2195(15) | 0.6683(15) | 0.9432(9) | 0.237(4) |

Finally, complex **1** reacts with an excess of *p*-TolNC in $CH_2Cl_2$ but only complex **15**, with inserted *p*-TolNC, can be isolated. If the reaction is carried out in acetonitrile and $NaClO_4$ then added (in order to facilitate the formation of the cationic complex) the complex $[p\text{-TolNCPd}(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})\text{Pd}(C_6Cl_5)]^+$ (**18**) which contains both coordinated and inserted isonitrile gives $[p\text{-TolNCPd}(\mu\text{-dppm})_2\text{Pd}(C_6Cl_5)]ClO_4$, containing only coordinated isonitrile.

The higher tendency of *p*-TolNC to give insertion products is in agreement with our previous observations on palladium(I) [1] or platinum(I) [6] pentafluorophenyl derivatives; in all these insertion processes the reactivity of the Pd–Pd bond is lower for the pentachlorophenyl than for the pentafluorophenyl derivatives, and thus *p*-TolNC or CyNC can be inserted into the M–M bond in either $ClPd(\mu\text{-dppm})_2Pd(C_6F_5)$ or $ClPt(\mu\text{-dppm})_2Pt(C_6F_5)$, although the CyNC complex of platinum is stable only at low temperature.

Table 1 lists some relevant IR absorptions which confirm the presence of coordinated ($\nu$(CN) at 2100–2200 $cm^{-1}$) or inserted ($\nu$(C=N) at 1550–1650 $cm^{-1}$) isonitriles.

$[(C_6Cl_5)Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)]$ does not react with CO, $SO_2$ or diazonium salts. Although complex **2** does react with *p*-TolNC we were unable to isolate pure products from the reaction mixture.

### *Structure of $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$*

The structure of complex **2** was determined by single crystal X-ray diffraction. Details of the crystallographic procedures are presented in Table 2. Atomic coordinates and bond distances and angles are listed in Tables 3 and 4 respectively. The molecular structure is shown in Fig. 1 and involves two palladium centers with a Pd–Pd bond (2.6704(21) Å) between them; two dppm ligands bridge the metal–metal bond and there is one $C_6Cl_5$ group per palladium atom. The environment around the palladium is almost square planar with small tetrahedral distortions (thus the dihedral angles between the planes Pd(2)Pd(1)P(2), P(1)Pd(1)C(3) and Pd(2)C(9)P(4), Pd(2)Pd(1)P(3) are 169.28(17) and 171.56(16)°, respectively. The angles between mutually *cis*-palladium–ligand bonds are in the range 83.9–97.5°, and the corresponding angles between mutually *trans*-palladium–ligand bonds are in the range 168.7–173.8° (see Table 4). The chain C(9)Pd(2)Pd(1)C(3) is not quite linear, and the C(9) and C(3) atoms lie respectively 0.363(8) and 0.408(8) Å away from the Pd(2)–Pd(1) line. The Pd–P distances are in the range of 2.27–2.32 Å, similar to those in $BrPd(\mu\text{-dppm})_2PdBr$ [13,14] or $ClPd(\mu\text{-dppm})_2Pd(SnCl_3)$ [4]. The distances Pd(1)–C(3) and Pd(2)–C(9) are 2.127(12) and 2.164(12) Å, respectively. The distance Pd(1)–Pd(2) is 2.6704(21) Å, somewhat shorter than that in the analogous $BrPd(\mu\text{-dppm})_2PdBr$ [13,14] although longer than those for other Pd–Pd bonds [15,16]. The two coordination planes around the palladium atoms are twisted about the Pd(1)–Pd(2) so that dihedral angle between them is 44.98(10)°. This angle is higher than for analogous palladium or platinum derivatives (cf. 39° for $BrPd(\mu\text{-dppm})_2PdBr$ [13,14] 38.6° for $ClPt(\mu\text{-dppm})_2PtCl$ [17] or 41.3° for $ClPd(\mu\text{-dppm})_2PdSnCl_3$ [4]), but lower than for other $Pd^I$–$Pd^I$ or $Pd^I$–$Pt^I$ bonds in complexes which do not contain any bridging ligands between the metal atoms (i.e. 86.4° for $[(CH_3NC)_6Pd_2]^{2+}$ [18,19], 85.3° for $[(CH_3NC)_4Pd_2I_2]$ [15], 60° for $[Pt_2(CO)_2Cl_4]^{2-}$ [20] or 79.8° for $Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2$ [21].

Complex **2** is the result of an oxidative addition of the Pd–$C_6Cl_5$ bond to the $Pd^0$ center to produce a Pd–Pd bond, this contrasts with the reaction of $Pt(PPh_3)_4$ with $C_6Cl_5AuPPh_3$ [22] which does not give a binuclear compound with a Pt–Au bond but instead gives $[(PPh_3)_2ClPt(\mu\text{-}3,4,5,6\text{-}C_6Cl_4)AuPPh_3]$ as a consequence of the reaction of $Pt(PPh_3)_4$ with the *ortho*-Cl–C bond of the pentachlorophenyl group.

## Experimental

The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Conductivities were determined with a Phillips PW 9501/01 conductimeter. Molecular weights were determined in $CHCl_3$ solution with a Knauer digital osmometer. IR spectra were recorded (in the range 4000–200 $cm^{-1}$) on a Perkin–Elmer 599 spectrophotometer, with Nujol mulls between polyethylene plates.

The complexes *trans*-$Pd(C_6Cl_5)_2(tht)_2$ [23], $[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$ [24] and $Pd_2(dba)_3CHCl_3$ [25] were prepared as described elsewhere.

The starting palladium(II) complexes were prepared as follows.

*$Pd(C_6Cl_5)_2(dppm)_2$.* A mixture of 1 g (1.27 mmol) of $Pd(C_6Cl_5)_2(tht)_2$ and 1.229 g (3.199 mmol) of dppm in 80 ml of toluene was refluxed for 3 h. The solution was evaporated to dryness and the residue was extracted in 20 ml of dichloromethane. The solution was evaporated to ~ 10 ml and the addition of ~ 15 ml of

TABLE 4

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$

| | | | |
|---|---|---|---|
| Pd(1)–Pd(2) | 2.6704(21) | P(3)–C(45) | 1.811(15) |
| Pd(1)–P(1) | 2.271(6) | P(4)–C(1) | 1.877(21) |
| Pd(1)–P(2) | 2.299(6) | P(4)–C(51) | 1.844(14) |
| Pd(1)–C(3) | 2.127(12) | P(4)–C(57) | 1.800(14) |
| Pd(2)–P(3) | 2.284(6) | Cl(1)–C(4) | 1.667(14) |
| Pd(2)–P(4) | 2.316(5) | Cl(2)–C(5) | 1.705(15) |
| Pd(2)–C(9) | 2.164(12) | Cl(3)–C(6) | 1.748(15) |
| P(1)–C(1) | 1.840(21) | Cl(4)–C(7) | 1.731(15) |
| P(1)–C(15) | 1.823(16) | Cl(5)–C(8) | 1.694(14) |
| P(1)–C(21) | 1.817(17) | Cl(6)–C(10) | 1.720(13) |
| P(2)–C(2) | 1.812(22) | Cl(7)–C(11) | 1.727(14) |
| P(2)–C(27) | 1.788(17) | Cl(8)–C(12) | 1.725(14) |
| P(2)–C(33) | 1.781(20) | Cl(9)–C(13) | 1.660(14) |
| P(3)–C(2) | 1.869(22) | Cl(10)–C(14) | 1.660(14) |
| P(3)–C(39) | 1.802(18) | | |

| | | | |
|---|---|---|---|
| Pd(2)–Pd(1)–P(1) | 85.51(15) | Pd(1)–C(3)–C(8) | 117.8(9) |
| Pd(2)–Pd(1)–P(2) | 88.32(16) | Cl(1)–C(4)–C(3) | 120.1(10) |
| Pd(2)–Pd(1)–C(3) | 168.7(3) | Cl(1)–C(4)–C(5) | 119.9(10) |
| P(1)–Pd(1)–P(2) | 173.82(21) | Cl(2)–C(5)–C(4) | 120.3(10) |
| P(1)–Pd(1)–C(3) | 91.4(4) | Cl(2)–C(5)–C(6) | 119.7(10) |
| P(2)–Pd(1)–C(3) | 94.8(4) | Cl(3)–C(6)–C(5) | 119.1(10) |
| Pd(1)–Pd(2)–P(3) | 83.90(15) | Cl(3)–C(6)–C(7) | 120.8(10) |
| Pd(1)–Pd(2)–P(4) | 87.39(14) | Cl(4)–C(7)–C(6) | 118.0(10) |
| Pd(1)–Pd(2)–C(9) | 169.6(3) | Cl(4)–C(7)–C(8) | 122.0(10) |
| P(3)–Pd(2)–P(4) | 171.22(20) | Cl(5)–C(8)–C(3) | 122.6(10) |
| P(3)–Pd(2)–C(9) | 91.3(4) | Cl(5)–C(8)–C(7) | 117.3(10) |
| P(4)–Pd(2)–C(9) | 97.5(3) | Pd(2)–C(9)–C(10) | 120.0(9) |
| Pd(1)–P(1)–C(1) | 104.5(7) | Pd(2)–C(9)–C(14) | 119.3(9) |
| Pd(1)–P(1)–C(15) | 113.7(5) | Cl(6)–C(10)–C(9) | 120.8(9) |
| Pd(1)–P(1)–C(21) | 126.8(6) | Cl(6)–C(10)–C(11) | 119.1(9) |
| C(1)–P(1)–C(15) | 103.5(8) | Cl(7)–C(11)–C(10) | 119.1(9) |
| C(1)–P(1)–C(21) | 104.2(9) | Cl(7)–C(11)–C(12) | 120.7(10) |
| C(15)–P(1)–C(21) | 101.7(7) | Cl(8)–C(12)–C(11) | 118.2(9) |
| Pd(1)–P(2)–C(2) | 114.8(7) | Cl(8)–C(12)–C(13) | 121.7(10) |
| Pd(1)–P(2)–C(27) | 113.8(6) | Cl(9)–C(13)–C(12) | 118.5(10) |
| Pd(1)–P(2)–C(33) | 119.3(7) | Cl(9)–C(13)–C(14) | 121.5(10) |
| C(2)–P(2)–C(27) | 105.7(9) | Cl(10)–C(14)–C(9) | 120.8(10) |
| C(2)–P(2)–C(33) | 99.3(10) | Cl(10)–C(14)–C(13) | 119.1(9) |
| C(27)–P(2)–C(33) | 101.9(8) | P(1)–C(15)–C(16) | 122.2(12) |
| Pd(2)–P(3)–C(2) | 106.1(7) | P(1)–C(15)–C(20) | 117.6(11) |
| Pd(2)–P(3)–C(39) | 113.1(6) | P(1)–C(21)–C(22) | 118.4(12) |
| Pd(2)–P(3)–C(45) | 126.2(5) | P(1)–C(21)–C(26) | 121.4(12) |
| C(2)–P(3)–C(39) | 104.9(9) | P(2)–C(27)–C(28) | 120.5(12) |
| C(2)–P(3)–C(45) | 101.8(8) | P(2)–C(27)–C(32) | 119.0(12) |
| C(39)–P(3)–C(45) | 102.6(7) | P(2)–C(33)–C(34) | 120.4(15) |
| Pd(2)–P(4)–C(1) | 114.5(7) | P(2)–C(33)–C(38) | 119.0(15) |
| Pd(2)–P(4)–C(51) | 115.4(5) | P(3)–C(39)–C(40) | 115.1(13) |
| Pd(2)–P(4)–C(57) | 118.2(5) | P(3)–C(39)–C(44) | 124.8(13) |
| C(1)–P(4)–C(51) | 104.0(8) | P(3)–C(45)–C(46) | 121.7(10) |
| C(1)–P(4)–C(57) | 99.3(8) | P(3)–C(45)–C(50) | 118.1(10) |
| C(51)–P(4)–C(57) | 103.2(6) | P(4)–C(51)–C(52) | 116.8(9) |
| P(1)–C(1)–P(4) | 105.2(10) | P(4)–C(51)–C(56) | 123.2(10) |
| P(2)–C(2)–P(3) | 106.4(11) | P(4)–C(57)–C(58) | 120.4(10) |
| Pd(1)–C(3)–C(4) | 122.2(9) | P(4)–C(57)–C(62) | 119.6(10) |

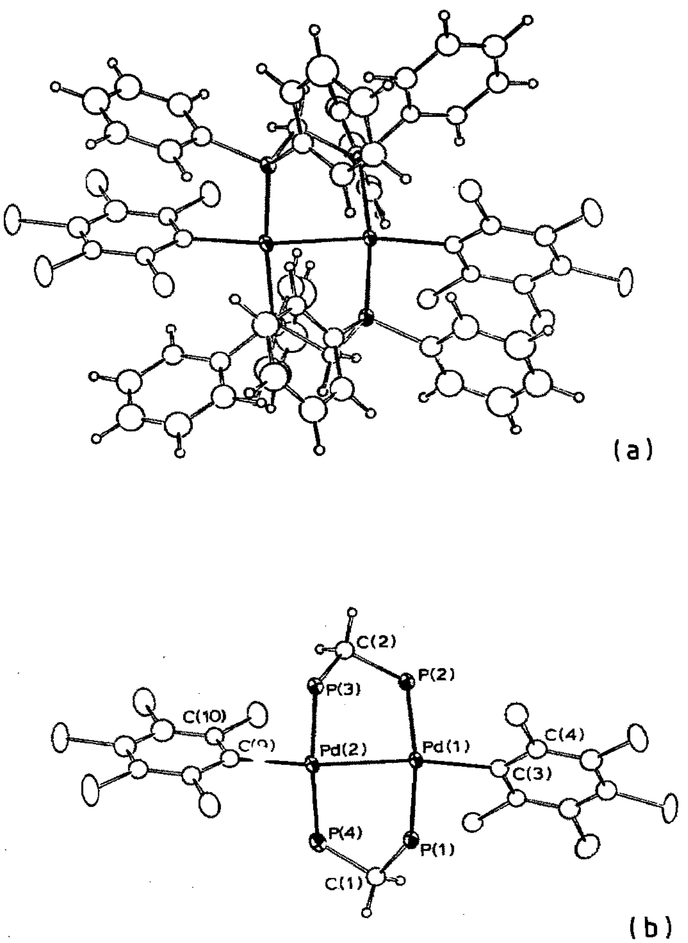


Fig. 1. Perspective views of $Pd_2(\mu\text{-dppm})_2(C_6Cl_5)_2$ (**2**): (a) Full molecule; (b) Central fraction with Ph rings removed, showing numbering of key atoms.

ethanol gave the white solid $Pd(C_6Cl_5)_2(dppm)_2$, which was washed with diethyl ether (73% yield).

*PdCl(C₆Cl₅)(dppm)₂*. This was made in a similar way from 1 g (1.04 mmol) of $[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$ and 2.0045 g (5.215 mmol) of dppm in 200 ml of toluene (Yield 74%).

Typical procedures for the synthesis of the complexes are given below.

*$XPd(\mu\text{-dppm})_2Pd(C_6Cl_5)$ (X = Cl (1), $C_6Cl_5$ (2))*

A mixture of $PdX(C_6Cl_5)(\eta^1\text{-dppm})_2$ (X = Cl, 1 g (0.862 mmol); X = $C_6Cl_5$, 0.6 g (0.436 mmol)) and $Pd_2(dba)_3 \cdot CHCl_3$ (X = Cl, 0.446 g (0.431 mmol), X = $C_6Cl_5$, 0.229 g (0.218 mmol)) in 80 ml of deoxygenated $CH_2Cl_2$ was refluxed under $N_2$ for 3 h. The solution was then evaporated to dryness and the residue was washed with 20 ml of $Et_2O$ to give respectively a yellow **1** (90%) or an orange complex **2** (77%). Complexes **1** and **2** crystallize with $CH_2Cl_2$, that can be removed by keeping the solid at 80°C for 4 h.

Crystals of **2** (as its $CH_2ClCH_2Cl$ solvate) suitable for the diffraction study were obtained by dissolving 0.050 g of the compound in $CH_2ClCH_2Cl$ (1 ml) and adding an upper layer of n-hexane (4 ml).

*$XPd(\mu\text{-}dppm)_2Pd(C_6Cl_5)$ (X = Br (**3**), I (**4**), SCN (**5**), CNO (**6**))*

To a suspension of 0.2 g (0.157 mmol) of complex **1** in 30 ml of ethanol was added a solution of 0.90 mmol of MX (MX = LiBr, NaI, KSCN, KCNO) in 1 ml of $H_2O$. The mixture was stirred for 6 h (22 h for the KCNO) at room temperature, then the solid was filtered off and washed successively with 4 × 10 ml of methanol, 10 ml of $H_2O$, and 10 ml of methanol. The resulting solid was dried at 80°C for 4 h (Yields 80–90%).

*$SnCl_3Pd(\mu\text{-}dppm)_2Pd(C_6Cl_5)$ (**7**)*

To 0.1 g (0.078 mmol) of **1** in 10 ml of $CH_2Cl_2$ was added $SnCl_2$ (0.014 g, 0.078 mmol) in 5 ml of ethanol, and the mixture was stirred for 1 h at room temperature then partially evaporated. Addition of 10 ml of diethyl ether produced orange crystals of **7** (78% yield).

*$[LPd(\mu\text{-}dppm)_2Pd(C_6Cl_5)]BPh_4$ (L = $PPh_3$ (**8**), $P(OPh)_3$ (**9**), $AsPh_3$ (**10**) $SbPh_3$ (**11**), tht (**12**))*

A mixture of 0.1 g (0.078 mmol) of complex **6** and 0.078 mmol of L ($PPh_3$, $P(OPh)_3$, $AsPh_3$, $SbPh_3$, tht) in 30 ml of methanol was stirred at room temperature for 15 min then 0.027 g (0.078 mmol) of $NaBPh_4$ was added and the mixture was stirred for 30 min. The suspension was filtered off and the resulting solid was washed successively with 10 ml of water, 2 × 10 ml of ethanol, and 10 ml of $Et_2O$.

The products were recrystallized from various solvents as follows: **8**, **11** from acetone/$Et_2O$; **9**, from dichloromethane/hexane; **10**, from dichloromethane/$Et_2O$. The crystals of complex **10** was heated at 80°C for 2 h to remove $CH_2Cl_2$. Yields: **6**, 75%; **9**, 51%; **10**, 50%; **11**, 67%; **12**, 50%.

*$[ClPd(\mu\text{-}dppm)_2(\mu\text{-}p\text{-}CH_3C_6H_4N_2)Pd(C_6Cl_5)]BF_4$ (**13**)*

To a solution of 0.1 g (0.078 mmol) of complex **1** in 50 ml of deoxygenated acetone at −20°C was added 0.0162 g (0.078 mmol) of $[p\text{-}CH_3C_6H_4N_2]BF_4$ and the mixture was stirred for 30 min, as the solution was allowed to warm to room temperature. The solution was then evaporated to ca. 5 ml and by 10 ml of diethyl ether was added to produce an orange precipitate, which was washed with 10 ml of $Et_2O$ then the compound recrystallized from acetone/$Et_2O$ and dried at 80°C for 5 h (86% yield).

*$ClPd(\mu\text{-}dppm)_2(\mu\text{-}SO_2)PdC_6Cl_5$ (**14**)*

$SO_2$ was bubbled for 30 min through a solution of **1** (0.15 g, (0.118 mmol)) in 5 ml of $CH_2Cl_2$. 10 ml of n-hexane were added to give a precipitate of **14**. Yield 96%.

*$ClPd(\mu\text{-}dppm)_2(\mu\text{-}CN\text{-}p\text{-}Tol)Pd(C_6Cl_5)$ (**15**)*

A solution of 0.150 g (0.118 mmol) of complex **1** and 15 μl (0.119 mmol) of *p*-TolNC in 40 ml of $CH_2Cl_2$ was stirred at room temperature for 2 h. The solution was partially evaporated and addition of n-hexane then gave complex **15** (86% yield).

### $[RNCPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]Cl$ *(R = Cy (16), t-Bu (17))*

A mixture of 0.230 g (0.182 mmol) of complex **1** and 0.248 mmol of CNR (R = Cy, t-Bu) in 30 ml of acetone was stirred at room temperature for 3 h, then the solution was evaporated to ca. 5 ml and 10 ml of diethyl ether were added. The precipitates were filtered off and washed with diethyl ether; complex **16** was obtained in 72% yield, and **17** was recrystallized from $CH_2Cl_2/Et_2O$ in the presence of some free isonitrile (to give a 62% yield).

### $[RNCPd(\mu\text{-dppm})_2Pd(C_6Cl_5)]ClO_4$

*R = p-Tol (18).* A mixture of 0.1 g (0.072 mmol) of $ClPd(\mu\text{-dppm})_2(\mu\text{-}CNTol)Pd(C_6Cl_5)$ (**15**) and 0.042 g (0.343 mmol) of $NaClO_4$ in 30 ml of acetonitrile was stirred for 1 h at room temperature. The solution was evaporated to ca. 2 ml and the yellow crystals obtained were washed with ethanol, water, and ethanol (to give **18**, 56% yield).

*R = Cy (19), ᵗBu (20).* A solution of 0.15 g (0.118 mmol) of complex **1** and 0.124 mmol of RNC (R = Cy, ᵗBu) in 30 ml of dichloromethane was stirred at room temperature for 15 min and then 0.040 g (0.326 mmol) of $NaClO_4$ in 3 ml of ethanol was added. The solution was stirred at room temperature for 30 min and then evaporated to ca. 2 ml. The complex (**19** or **20**) which separated was washed with water and ethanol to give **19** (70% yield) or **20**; the latter was recrystallized from acetone/$Et_2O$ (74% yield).

### $[\mu\text{-}CNRNC\{Pd(\mu\text{-dppm})_2Pd(C_6Cl_5)\}_2](ClO_4)_2$ *($R = p\text{-}C_6H_4$) (21)*

To a solution of 0.1 g (0.078 mmol) of complex **1** in 30 ml of $CH_2Cl_2$, 0.040 g (0.326 mmol) of $NaClO_4$ was added 0.005 g (0.039 mmol) of $p\text{-}C_6H_4(NC)_2$ and the mixture was stirred for 6 h at room temperature. The yellow solution was filtered then evaporated to ca. 5 ml and 10 ml of diethyl ether was added to give a yellow solid (**21**), which was recrystallized from acetone/n-hexane (40% yield).

## Acknowledgement

We thank the CAICYT (Spain) for financial support and the Scientific Office of NATO for a travel grant.

## References

1 R. Usón, J. Forniés, P. Espinet, F. Martínez, C. Fortuño and B. Menjón, J. Organomet. Chem., 256 (1983) 365.
2 R. Usón, J. Forniés, P. Espinet and C. Fortuño, Inorg. Chim. Acta, 87 (1984) 207.
3 (a) M.M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, J. Am. Chem. Soc., 99 (1977) 5502; (b) A.D. Rattray and D. Antton, Inorg. Chim. Acta, 27 (1978) L85; (c) L.S. Benner, M.M. Olmstead, H. Hope and A.L. Balch, J. Organomet. Chem., 153 (1978) C31; (d) L.S. Benner and A.L. Balch, J. Am. Chem. Soc., 100 (1978) 6099; (e) A.L. Balch, C.H.L. Lee, C.H. Lindsay and M.M. Olmstead, J. Organomet. Chem., 177 (1979) C22; (f) A.L. Balch, L.S. Benner and M.M. Olmstead, Inorg. Chem., 78 (1979) 2996.
4 M.M. Olmstead, L.S. Benner, H. Hope and A.L. Balch, Inorg. Chim. Acta, 32 (1979) 193.
5 M.G. Grossel, R.P. Moulding and K.R. Seddon, Inorg. Chim. Acta, 64 (1982) L275.
6 R. Usón, J. Forniés, P. Espinet and C. Fortuño. J. Chem. Soc., Dalton Trans., in press.
7 J. Casabó, J.M. Coronas and J. Sales, Inorg. Chim. Acta, 11 (1974) 5.
8 N.N. Greenwood, J. Chem. Soc., (1959) 3811.

9 It appears as a shoulder of an internal absorption of the dppm located at 1022 cm$^{-1}$.

10 D.M.P. Mingos, Trans. Met. Chem., 3 (1978) 1.

11 K. Nakamoto, Infrared spectra of Inorganic and Coordination Compounds 2nd Ed., Wiley-Interscience, New York, 1970, p. 187.

12 D.F. Schriver and M.P. Johnson, Inorg. Chem., (1967) 1265.

13 R.G. Holloway, B.R. Penfold, R. Colton and J. McCormick, J. Chem. Soc., Chem. Commun., (1976) 485.

14 R. Colton, M.J. McCormick and D. Pannan, Aust. J. Chem., 31 (1978) 1425.

15 N.M. Rutherford, M.M. Olmstead and A.L. Balch, Inorg. Chem., 23 (1984) 2833.

16 A. Ducruix, H. Felkin, C. Pascard and G.K. Turner, J. Chem. Soc., Chem. Commun., (1975) 615.

17 Lj. Manojlović-Muir, K.W. Muir and T. Solomun, Acta Cryst., B35 (1979) 1237.

18 D.J. Doonan, A.L. Balch, S.Z. Goldberg, R. Eisenberg and J.S. Miller, J. Am. Chem. Soc., 97 (1975) 1961.

19 S.Z. Goldberg and R. Eisenberg, Inorg. Chem., 15 (1976) 535.

20 A. Modinos and P. Woodward, J. Chem. Soc., Dalton Trans., (1975) 1516.

21 R. Usón, J. Forniés, P. Espinet, C. Fortuño, M. Tomás and A.J. Welch, unpublished results.

22 O. Rossell and J. Sales, Inorg. Chim. Acta, 64 (1981) L43.

23 R. Usón, J. Forniés, R. Navarro, M.P. García and B. Bergareche, Inorg. Chim. Acta, 25 (1977) 269.

24 R. Usón, J. Forniés, R. Navarro and M.P. García, Inorg. Chim. Acta, 33 (1979) 69.

25 T. Ukai, H. Kuwazura, Y. Ishii, J. Bonnet and J. Ibers, J. Organomet. Chem., 65 (1974) 253.

26 B.J. Hathaway and A.E. Underhill, J. Chem. Soc., (1961) 3091.