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SYNTHESIS OF NEUTRAL AND CATIONIC PENTAFLUOROPHENYLPALLADIUM(I) DERIVATIVES. INSERTION VERSUS COORDINATION OF ISOCYANIDES IN BINUCLEAR PALLADIUM(I) COMPLEXES

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Summary

Reaction between $PdX(C_6F_5)(dpm)_2$ (dpm = bis(diphenylphosphino)methane; X = Cl, Br, I, CNO or C_6F_5) and $Pd_2(dba)_3CHCl_3$ (dba = dibenzylideneacetone) gives, the pentafluorophenyl palladium(I) derivatives $[XPd(\mu\text{-dpm})_2Pd(C_6F_5)]$. Treatment of $[ClPd(\mu\text{-dpm})_2Pd(C_6F_5)]$ with an excess of the ligand L, and in the presence of $NaBPh_4$ gives the cationic complexes $[LPd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$ (L = PPh_3, $P(OPh)_3$, pyridine or tetrahydrothiophene (tht)). Reaction with isocyanides RNC leads to three different types of compounds: (a) products with the isocyanide groups inserted into the Pd–Pd bond $[(\mu\text{-RNC})\{XPd(\mu\text{-dpm})_2Pd(C_6F_5)\}]$ (X = C_6F_5; R = *p*-tolyl; X = Cl, R = *p*-tolyl or Cy); (b) cationic complexes with terminal isocyanides $[(RNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]X$ (X = Cl; R = t-Bu; X = BPh_4, R = *p*-tolyl, Cy or t-Bu), and (c) complexes which contain both bridging and terminal isocyanides, $[(\mu\text{-RNC})\{(RNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)\}BPh_4]$ (R = *p*-tolyl or cyclohexyl). Addition of $NaBPh_4$ to solutions of complexes of type a (X = Cl) results in deinsertion of the isocyanide to give complexes of type b. IR spectroscopy reveals that $[(\mu\text{-CyNC})\{ClPd(\mu\text{-dpm})_2Pd(C_6F_5)\}]$ isomerizes in CH_2Cl_2 to give $[(CyNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]Cl$, which upon recrystallization regenerates the former complex, showing that in this case the insertion–deinsertion process is reversible.

Introduction

Binuclear palladium(I) complexes containing a Pd–Pd metal bond, two bridging dpm ligands, and a single terminal X ligand attached to each palladium atom have recently been prepared [1–6]. So far, only neutral complexes have been described, and no complex in which each palladium atom is linked to a different ligand X, or in which X is a σ-Pd–C bonded organic ligand has hitherto been reported.

In the present paper we describe similar neutral binuclear complexes with C_6F_5 as

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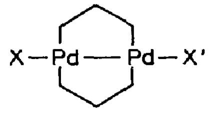

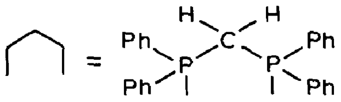

one of the substituents and X' = Cl, Br, I, CNO or C_6F_5, and also the cationic complexes in which X = C_6F_5, X' = PPh_3, $P(OPh)_3$, Py, tht, t-BuNC, *p*-TolNC or CyNC, with BPh_4 as anion *. The insertion of isocyanides into the Pd–Pd bond of the neutral complexes has also been studied.

(1) Synthesis of the palladium(II) precursors $Pd(C_6F_5)X(dpm)_2$ (X = Cl, Br, I, CNO or C_6F_5)

$PdCl(C_6F_5)(dpm)_2$ (I) can be prepared in refluxing benzene by cleaving the bridge of the binuclear complex $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [7] with a slight excess over the theoretical amount (1/4) of dpm. Complex I reacts in acetone with LiBr, KI, or KCNO to give the corresponding $PdX(C_6F_5)(dpm)_2$ (II, X = Br; III, X = I, IV, X = NCO). When dpm is added to *trans*-$Pd(C_6F_5)_2(tht)_2$ (2/1 ratio) $Pd(C_6F_5)_2(dpm)_2$ (V) can be isolated.

Table 1 lists the analytical and other data for complexes I–V. Their IR spectra show the absorptions characteristic of the C_6F_5 group [8–10] at 1650(m), 1500(m,s), 1050(m,s), 950(m,s) and 770(m,s) cm^{-1}, along with those arising from the dpm group. In I the ν(Pd–Cl) stretching vibration is located at 320 cm^{-1}, while for II and III it would be expected to appear outside the range of our instrument. The cyanato complex IV shows a band at 2233(s) cm^{-1} due to ν_{as}(NCO) [11].

(2) Synthesis of binuclear palladium(I) complexes $[XPd(\mu\text{-}dpm)_2Pd(C_6F_5)]$ (X = Cl, Br, I, CNO or C_6F_5)

Reaction of complexes I–V with $Pd_2(dba)_3 \cdot CHCl_3$ [12] in oxygen free dichloromethane gives yellow or brownish-orange neutral binuclear palladium(I) complexes (see Scheme 1 (a)) VI–X (see Table 1). These are stable as solids and in solution in the absence of light. Their IR spectra show the absorptions characteristic of the dpm ligand along with those of the pentafluorophenyl group (see above). It is noteworthy that the band at ca. 950 cm^{-1} is shifted [13,14] towards lower wavelengths relative to its position in the palladium(II) precursors, as expected for a decrease of the formal oxidation state of the metal (see Table 2). The ν(Pd–Cl) stretching vibration appears at 251(m,w) cm^{-1}. (249(w) cm^{-1} was reported for $Pd_2(\mu\text{-}dpm)_2Cl_2$ [1]). Complex IX exhibits an absorption at 2195(s) cm^{-1} assignable to ν_{as}(CNO).

(3) Synthesis of the cationic complexes $[LPd(\mu\text{-}dpm)_2Pd(C_6F_5)]BPh_4$ (L = t-BuNC, PPh_3, $P(OPh)_3$, Py or tht)

Addition of a neutral ligand L to complex VI in methanol suspension (or dichloromethane solution) leads to complete dissolution and to the formation of

(Continued on p. 369)

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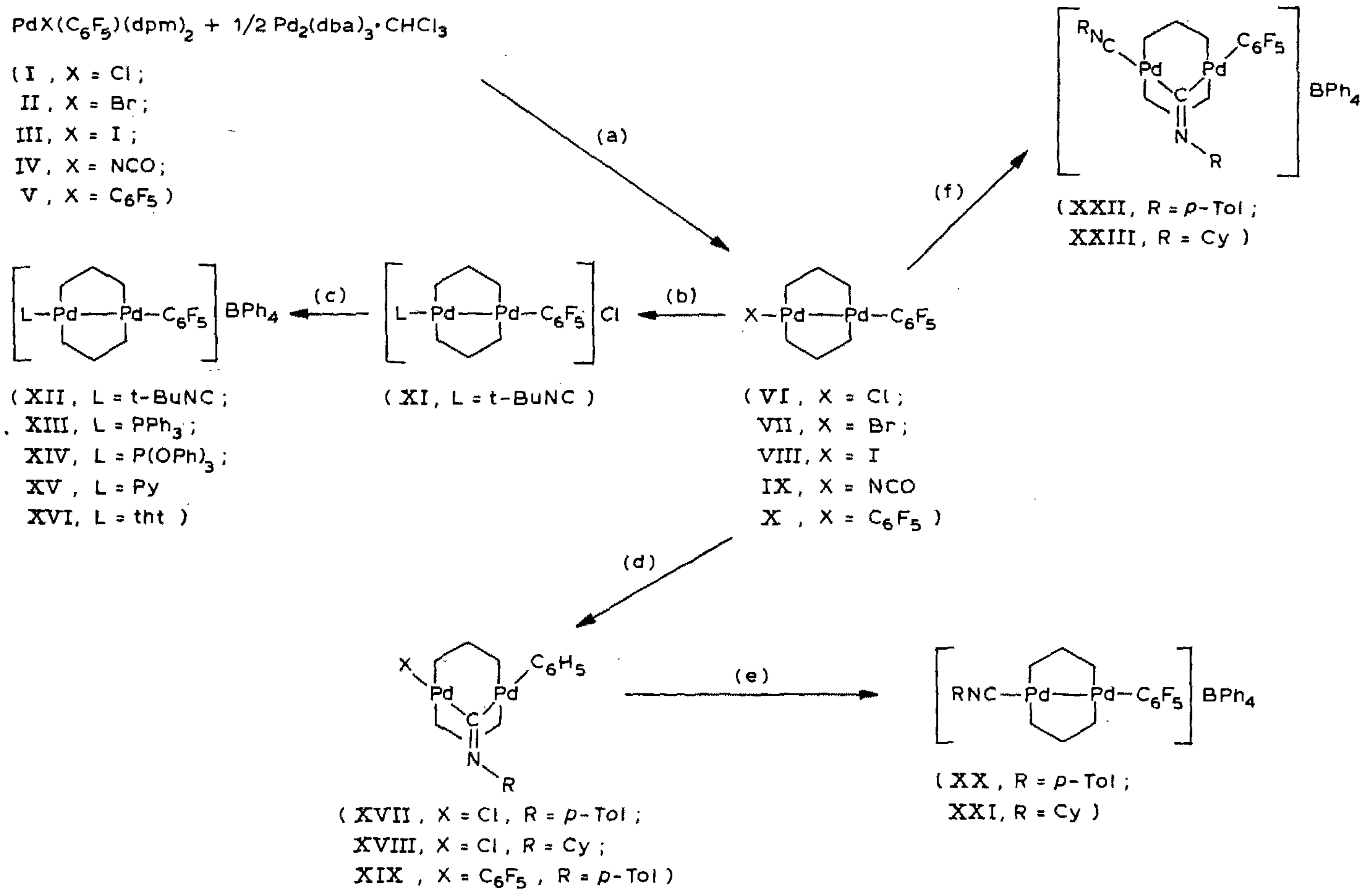
* Py = pyridine, tht = tetrahydrothiophene, Tol = tolyl, Cy = cyclohexyl, dpm = bis(diphenylphosphino)methane, dba = dibenzylindeneacetone.

TABLE 1

ANALYTICAL DATA, COLOUR AND CONDUCTIVITIES

Complex	Analysis (Found (calcd.) (%))			Colour	Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N		
PdCl(C_6F_5)(dpm)$_2$ (I)	62.08 (62.41)	4.37 (4.11)	–	white	3.9
PdBr(C_6F_5)(dpm)$_2$ (II)	60.49 (59.94)	4.28 (3.95)	–	white	5.8
PdI(C_6F_5)(dpm)$_2$ (III)	57.62 (57.53)	3.90 (3.79)	–	pale-yellow	12.6
Pd(NCO)(C_6F_5)(dpm)$_2$ (IV)	63.26 (63.14)	4.75 (4.09)	1.38 (1.29)	white	3.4
Pd(C_6F_5)$_2$(dpm)$_2$ (V)	60.95 (61.59)	4.36 (3.66)	–	white	2.2
ClPd(μ-dpm)$_2$Pd(C_6F_5) (VI)	56.85 (56.80)	3.89 (3.74)	–	yellow	4.9
BrPd(μ-dpm)$_2$Pd(C_6F_5) (VII)	54.52 (54.75)	3.90 (3.61)	–	yellow	6.2
IPd(μ-dpm)$_2$Pd(C_6F_5) (VIII)	52.48 (52.73)	3.74 (3.48)	–	ochreous-orange	1.8
(OCN)Pd(μ-dpm)$_2$Pd(C_6F_5) (IX)	57.80 (57.50)	4.26 (3.72)	1.35 (1.18)	yellow	1.2
(C_6F_5)Pd(μ-dpm)$_2$Pd(C_6F_5) (X)	56.10 (56.60)	3.26 (3.37)	–	yellow	14
[(t-BuNC)Pd(μ-dpm)$_2$Pd(C_6F_5)]Cl (XI)	57.22 (57.82)	4.30 (4.21)	1.23 (1.10)	yellow	72
[(t-BuNC)Pd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XII)	65.71 (65.82)	4.81 (4.74)	1.23 (0.90)	yellow	80
[(PPh$_3$)Pd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XIII)	67.47 (68.03)	4.99 (4.60)	–	ochreous-orange	84
[P(OPh)$_3$Pd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XIV)	66.28 (66.19)	5.00 (4.47)	–	ochreous-orange	70
[PyPd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XV)	65.33 (65.99)	4.47 (4.49)	0.98 (0.93)	yellow	85
[thtPd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XVI)	64.70 (64.53)	5.13 (4.66)	–	reddish-orange	75
(μ-TolNC){ClPd(μ-dpm)$_2$Pd(C_6F_5)} (XVII)	59.36 (59.07)	4.42 (3.95)	1.03 (1.08)	orange	3.7
(μ-CyNC){ClPd(μ-dpm)$_2$Pd(C_6F_5)} (XVIII)	58.68 (58.51)	4.76 (4.29)	1.09 (1.08)	orange	44
(μ-*p*-TolNC){C_6F_5)Pd(μ-dpm)$_2$Pd(C_6F_5)} (XIX)	58.70 (58.68)	3.54 (3.38)	0.82 (0.98)	orange	5.1
[(*p*-TolNC)Pd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XX)	66.20 (66.68)	4.44 (4.51)	1.08 (0.88)	yellow	80
[(CyNC)Pd(μ-dpm)$_2$Pd(C_6F_5)]BPh$_4$ (XXI)	66.04 (66.26)	4.71 (4.79)	1.05 (0.89)	yellow	80
[(μ-*p*-TolNC){(*p*-TolNC)Pd(μ-dpm)$_2$Pd(C_6F_5)}]BPh$_4$ (XXII)	68.24 (67.74)	5.46 (4.62)	1.67 (1.64)	reddish-orange	82
[(μ-CyNC){(CyNC)Pd(μ-dpm)$_2$Pd(C_6F_5)}]BPh$_4$ (XXIII)	66.78 (66.95)	5.39 (5.14)	1.54 (1.66)	orange	90



SCHEME 1. (a) CH_2Cl_2, room temperature or reflux; (b) X = Cl, addition of t-BuNC (1/1); (c) X = Cl, addition of 1 mol L and 1 mol BPh_4Na; (d) Addition of RNC (1/1 molar ratio), X = Cl, in CH_2Cl_2; (e) When X = Cl, addition of BPh_4Na in CH_3CN; (f) X = Cl addition of an excess of RNC and $NaBPh_4$.

TABLE 2

SOME RELEVANT IR ABSORPTIONS

	Complex	ν(cm^{-1})		
		[a]	[b]	[c]
I	$PdCl(C_6F_5)(dpm)_2$	952		
II	$PdBr(C_6F_5)(dpm)_2$	951		
III	$PdI(C_6F_5)(dpm)_2$	949		
IV	$Pd(CNO)(C_6F_5)(dpm)_2$	953		
V	$Pd(C_6F_5)_2(dpm)_2$	949		
VI	$ClPd(\mu\text{-dpm})_2Pd(C_6F_5)$	941		
VII	$BrPd(\mu\text{-dpm})_2Pd(C_6F_5)$	940		
VIII	$IPd(\mu\text{-dpm})_2Pd(C_6F_5)$	942		
IX	$(OCN)Pd(\mu\text{-dpm})_2Pd(C_6F_5)$	942		
X	$(C_6F_5)Pd(\mu\text{-dpm})_2Pd(C_6F_5)$	943		
XI	$[(t\text{-BuNC})Pd(\mu\text{-dpm})_2Pd(C_6F_5)]Cl$	944	2177	
XII	$[(t\text{-BuNC})Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	945	2176	
XIII	$[(PPh_3)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	949		
XIV	$[P(OPh)_3Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	945		
XV	$[PyPd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	945		
XVI	$[thtPd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	947		
XVII	$(\mu\text{-}p\text{-TolNC})\{ClPd(\mu\text{-dpm})_2Pd(C_6F_5)\}$	948	1623–1593	
XVIII	$(\mu CyNC)\{ClPd(\mu\text{-dpm})_2Pd(C_6F_5)\}$	941	1651	
XIX	$(\mu\text{-}p\text{-TolNC})\{(C_6F_5)Pd(\mu\text{-dpm})_2Pd(C_6F_5)\}$	945 938	1609–1585	
XX	$[(p\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	943	2151	
XXI	$[(cyNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$	946	2165	
XXII	$[(\mu\text{-}p\text{-TolNC})\{p\text{-TolNC})Pd(\mu\text{-dpm})_2Pd(C_6F_5)\}]BPh_4$	943	2154	1630(br)
XXIII	$[(\mu\text{-CyNC})\{(CyNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)\}]BPh_4$	944	2184	1653

[a] Due to C_6F_5 group. [b] $\nu(C\equiv N)$ terminal isocyanide. [c] $\nu(C=N)$ bridging isocyanide. $\nu(C\equiv N)$ free isocyanide: t-BuNC (2143); *p*-TolNC (2132); CyNC (2143).

$[LPd(\mu\text{-dpm})_2Pd(C_6F_5)]Cl$, which can be isolated when L = t-BuNC (XI) (Scheme 1 (b)). Subsequent addition of $NaBPh_4$ permits the isolation of $[LPd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$ (XII, L = t-BuNC; XIII, L = PPh_3; XIV, L = $P(OPh)_3$; XV, L = py; XVI, L = tht) (see Scheme 1 (c)).

Complexes XI–XVI behave as 1/1 electrolyts in ~ 5×10^{-4} *M* acetone solution [15] (see Table 1).

Their IR spectra show an absorption at 610(s) cm^{-1} due to the anion BPh_4^-. XIV exhibits bands at 1210(m), 1180(m) and 1160(m) cm^{-1} characteristic of the $P(OPh)_3$ ligand; XV presents absorptions at 1600(m) and 765(m) cm^{-1}, due to the Py ligand [16], while XVI shows a weak absorption at 1270 cm^{-1} arising from the tht group [7].

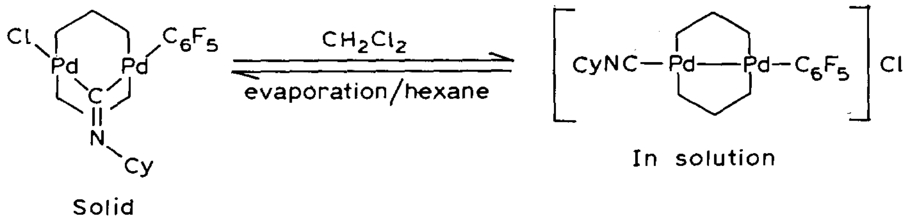
(4) Reaction with isocyanides RNC

Isocyanides react with the dpm-bridged binuclear palladium(I) complexes $[Pd_2(\mu\text{-dpm})_2X_2]$ [1] to give the products of insertion into the metal–metal bond, but an excess of the isocyanide causes the displacement of the terminal halogens or pseudohalogens to give the cationic complexes $[(\mu\text{-RNC})\{(RNC)Pd(\mu\text{-dpm})_2PdCl\}Cl]$ or $[(\mu\text{-RNC})\{(RNC)Pd(\mu\text{-dpm})_2Pd(CNR)\}Cl_2]$.

Our studies of the reactions of the pentafluorophenyl palladium(I) derivatives with *p*-tolyl isocyanide (*p*-TolNC), cyclohexyl isocyanide (CyNC) and t-butyl isocyanide (t-BuNC) have shown that the outcome depends upon both the substrate and the isocyanide. Thus, while $[ClPd(\mu\text{-dpm})_2Pd(C_6F_5)]$ (VI) reacts (Scheme 1 (d)) with stoicheiometric amounts of *p*-TolNC and CyNC to give the insertion products XVII and XVIII, in the case of $[(C_6F_5)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]$ only insertion of *p*-TolNC occurs to give XIX. As mentioned above, addition of t-BuNC to VI results only in its coordination as a terminal ligand (XI, XII).

Addition of $NaBPh_4$ to acetonitrile solutions of XVII or XVIII yields the cationic complexes $[(RNC)Pd(\mu\text{-dpm})_2Pd(C_6F_5)]BPh_4$ (XX, R = *p*-Tol; XXI, R = Cy) by deinsertion of the bridging RNC, which coordinates to one of the metal centres as a terminal ligand. This process, which to the best of our knowledge is unprecedented in the chemistry of palladium, parallels observations on platinum(I) carbonyls [17,18].

In the case of complex XVIII the insertion–deinsertion is reversible. In dichloromethane solution the IR spectrum (vide infra) shows the coordination of CyNC as terminal ligand, whereas upon evaporation of the solvent and addition of n-hexane the solid XVIII with inserted isocyanide is recovered.



This reversible interconversion of two linkage isomers is without precedent in the chemistry of palladium. Complex XVII does not behave in this way, and the deinsertion requires addition of $NaBPh_4$ (see above).

The results show that in the case of palladium(I) complexes with $X = X' = C_6F_5$ the insertion of isocyanide is not favoured, although it may occur with the reactive *p*-TolNC. For complexes with $X = Cl$ and $X' = C_6F_5$ the tendency for insertion decreases in the sequence *p*-TolNC > CyNC > t-BuNC, as found for the insertion of isocyanides into M–C bonds [19,20].

Addition of an excess of isocyanide to an acetonitrile solution of equimolecular amounts of $[ClPd(\mu\text{-dpm})_2Pd(C_6F_5)]$ and $NaBPh_4$ leads to complexes of the type $[(\mu\text{-CNR})\{(RNC)Pd(dpm)_2Pd(C_6F_5)\}BPh_4]$ (XXII, R = *p*-Tol; XXIII, R = Cy), which contain terminal as well as bridging isocyanides (Scheme 1 (f)).

The presence of the isocyanide and its situation in the complex can be inferred from the IR data. Complexes XI, XII, XX and XXI which only contain terminal isocyanide show an absorption assignable to the $\nu(C\equiv N)$ stretching vibration at higher wavelengths relative to the free isocyanide (see Table 2), whilst complexes XVII, XVIII and XIX show absorptions in the 1600 cm^{-1} region (see Table 2) due to the $\nu(C{=}N)$ stretching vibration of the bridging isocyanide. The *p*-TolNC complexes also show absorptions in this region, which are probably due to the phenyl ring. Their intensities are increased by the insertion and this prevents rigorous assignments. Both types of absorptions are listed in Table 2. Finally, complexes XXII and XXIII with both terminal and bridging isocyanides show bands in the

2150 and 1600 cm^{-1} regions, assignable to each type (Table 2). All the complexes show vibrations characteristic of the pentafluorophenyl group; those around 950 cm^{-1} are listed in Table 2.

It is noteworthy that the complexes with Pd–Pd bonds, as well as those resulting from the isocyanide insertion, XVII, XVIII, XIX, XXII and XXIII, exhibit this C_6F_5 band at very similar wavelengths, in agreement with the X-ray photoelectron spectra data reported by Balch and col. [21], which show that insertion of isocyanide into other palladium(I) complexes does not perceptibly modify the electron density around the metal.

The conductivities (Table 1) are in accordance with the expected values. The conductivity of XVIII is the expected consequence of the insertion–coordination equilibrium discussed above.

Experimental

For C, H and N analyses a Perkin–Elmer 240 microanalyzer was used. IR spectra were recorded (over the range 4000–200 cm^{-1}) on a Perkin–Elmer 599 spectrophotometer, using Nujol mulls between polyethylene plates. Conductivities were determined with a Phillips PW 9501/01 conductimeter.

The complexes *trans*-$Pd(C_6F_5)_2(tht)_2$ [22], $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [7] and $Pd_2(dba)_3CHCl_3$ [12] were prepared as described elsewhere.

Synthesis of $PdX(C_6F_5)(dpm)_2$ (I, X = Cl, II, X = Br, III, X = I; IV, X = NCO, V, X = C_6F_5)

$PdCl(C_6F_5)(dpm)_2$ (I). To a solution of $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (0.746 g, 0.938 mmol) in 50 ml of benzene was added a solution of dpm (1.5 g, 3.90 mmol) in 20 ml of benzene. The mixture was refluxed for 1 h. Evaporation to dryness, extraction with 50 ml of CH_2Cl_2, addition of 20 ml of ethanol, and partially evaporation led to the crystallization of I in 87% yield.

The reaction between *trans*-$Pd(C_6F_5)_2(tht)_2$ (1.61 g, 2.6 mmol) and dpm (2.006 g, 5.2 mmol) was carried out similarly and gave a solid, which was heated for 17 h to 80°C, to give V (80% yield).

$PdBr(C_6F_5)(dpm)_2$ (II). Lithium bromide (0.144 g, 1.658 mmol) was added to a solution of $PdCl(C_6F_5)(dpm)_2$ (0.3 g, 0.28 mmol) in 70 ml of warm acetone. The mixture was refluxed for 3 h, then evaporated to dryness. The residue was extracted with 50 ml of CH_2Cl_2 and the solution was dried ($MgSO_4$), then filtered. The filtrate was evaporated to ~ 5 ml and n-hexane was added to precipitate complex II in 87% yield.

Complexes III (77% yield) and IV (80% yield) were obtained similarly by prolonged reaction (~ 20 h) at room temperature.

Synthesis of $XPd(\mu\text{-}dpm)_2Pd(C_6F_5)$ (VI, X = Cl; VII, X = Br; VIII, X = I; IX, X = NCO; X, X = C_6F_5)

$ClPd(\mu\text{-}dpm)_2Pd(C_6F_5)$ (VI). To a solution of I (0.300 g, 0.278 mmol) in 40 ml of CH_2Cl_2 (deoxygenated) under nitrogen was added $Pd_2(dba)_3 \cdot CHCl_3$ (0.144 g, 0.139 mmol). Refluxing for 25 min gave an orange-coloured solution, which was evaporated to dryness. The residue was washed with 2 × 15 ml of diethyl ether and air-dried. Complex VI: 68% yield.

Similar procedures but with slightly different reaction times, gave the following complexes: VII: 66% yield; 2 h, room temperature; VIII: 40% yield, 45 min room temperature; IX: 75% yield, 2 h, room temperature; X: 91% yield, 7 min refluxing.

[LPd(μ-dpm)$_2$Pd(C$_6$F$_5$)]X (XI, X = Cl, L = t-BuNC; XII–XVI, X = BPh$_4$; XII, L = t-BuNC; (XIII, L = PPh$_3$; XIV, L = P(OPh)$_3$; XV, L = Py; XVI, L = tht)

[(t-BuNC)Pd(μ-dpm)$_2$Pd(C$_6$F$_5$)]Cl (XI). To a solution of ClPd(μ-dpm)$_2$Pd(C$_6$F$_5$) (0.180 g, 0.152 mmol) in 30 ml of CH_2Cl_2 was added t-BuNC (16.7 μl, 0.152 mmol). After 6 h stirring at room temperature the solution was concentrated to a small volume and hexane was dropwise added to precipitate crystalline XI (80% yield).

[(t-BuNC)Pd(μ-dpm)$_2$Pd(C$_6$F$_5$)]BPh$_4$ (XII). This was obtained by a similar procedure except that a slight excess of $NaBPh_4$ (1/1.2 molar ratio) was present from the start. After filtration of the dichloromethane solution, the solution was partially evaporated and ethanol was added to crystallize XII (73% yield).

[(PPh$_3$)Pd(μ-dpm)$_2$Pd(C$_6$F$_5$)]BPh$_4$ (XIII). Triphenylphosphine (0.022 g, 0.084 mmol) was added to a suspension of VI (0.1 g, 0.084 mmol) in 20 ml of methanol and stirring at room temperature for 5 min resulted in complete dissolution. After addition of $NaBPh_4$ (0.03 g, 0.087 mmol) in 10 ml of methanol the stirring was continued for 15 min. Evaporation left an oily residue, which was washed with 2-propanol and n-hexane. The resulting microcrystalline compound was washed with H_2O and vacuum-dried. Complex XIII: 80% yield.

The same procedure gave XIV (70% yield), XV (75% yield), and XVI (86% yield).

(μ-CNR)[XPd(μ-dpm)$_2$Pd(C$_6$F$_5$)] (XVII, X = Cl, R = p-Tol; XVIII, X = Cl, R = Cy; XIX, X = C$_6$F$_5$, R = p-Tol)

(μ-p-TolNC)[ClPd(μ-dpm)$_2$Pd(C$_6$F$_5$)] (XVII). To a solution of VI (0.180 g, 0.152 mmol) in 30 ml of CH_2Cl_2 (deoxygenated) under nitrogen was added *p*-TolNC, (19.1 μl, 0.152 mmol). The yellow solution turned orange. After 6 h stirring the solution was concentrated to ~ 2 ml and hexane was slowly added with stirring to crystallize XVII: 60% yield.

A similar procedure gave complex XVIII: 51% yield.

A similar procedure for reaction of $Pd_2(dpm)_2(C_6F_5)_2$ (X) in benzene with *p*-TolNC gave XIX (84% yield).

No reaction took place under these conditions with t-BuNC or CyNC.

[(RNC)Pd(μ-dpm)$_2$Pd(C$_6$F$_5$)]BPh$_4$ (XX, R = p-Tol; XXI, R = Cy)

XX, R = p-Tol. To a solution of XVII (0.150 g, 0.115 mmol) in 25 ml of CH_3CN under nitrogen was added $NaBPh_4$ (0.100 g, 0.292 mmol). The colour of the solution ligthened and a slight turbidity was observed. The mixture was stirred for 1 h, filtered, and concentrated to ~ 10 ml. Addition of ethanol and subsequent evaporation gave crystals of XX, which were filtered off and washed with H_2O and ethanol (74% yield).

Complex XXI was obtained similarly (70% yield).

[(μ-CNR){(RNC)Pd(μ-dpm)$_2$Pd(C$_6$F$_5$)}]BPh$_4$ (XXII, R = p-Tol; XXIII, R = Cy)

XXII, R = p-Tol. An excess of *p*-TolNC was added to a stirred solution of VI (0.208 g, 0.175 mmol) and $NaBPh_4$ (0.075 g, 0.219 mmol) in 50 ml of CH_3CN under nitrogen. The yellow solution turned an intense orange. Stirring was continued at room temperature for 6 h. After filtration the solution was concentrated to ca. 10 ml. Addition of ethanol and partial evaporation gave crystals of XXII: 65% yield.

XXIII was obtained analogously: 60% yield.

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