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CYANO-ORGANOPALLADATE COMPLEXES AND THEIR CYANO-BRIDGED DERIVATIVES

R. USÓN *, J. FORNIÉS, P. ESPINET and A. ARRIBAS

Department of Inorganic Chemistry, University of Zaragoza, Zaragoza (Spain)

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Summary

The preparations of anionic complexes of the types $Q_2[(C_6F_5)_xPd(CN)_{4-x}]$ (x = 1, 2(*cis* and *trans*), 3; Q = ammonium or phosphonium cation) and $(N\text{-}n\text{-}Bu_4)[(\eta^3\text{-}C_3H_5)Pd(CN)_2]$ are described. Their reactions with palladium perchlorato complexes give polynuclear neutral, anionic or cationic cyano-bridged derivatives. The proposed structures of the new complexes are based on their IR spectra.

Introduction

In contrast to the great attention paid to systems of the type $[M(CN)_xL_y]^{2-}$ [1], the chemistry of cyano complexes containing organic radicals attached to the metal atom through a carbon atom has been little studied. The previously known cyano-organopalladium complexes are limited to: $[Pd(CN)(all)]_4$ (all = methylallyl, 1,2,3-trimethylallyl; 1,1,3,3-tetramethylallyl) [2], [Pd(CN)(all)L] (all = methylallyl; L = PPh_3, PMe_2Ph, $AsPh_3$) [2], $[Pd(CN)(C_6F_5)L_2]$ (L = PPh_3 [3], $AsPh_3$ [4]) and to the anionic complexes $[Pd(CN)_2(all)]^-$ (all = methylallyl [2]), $[Pd(CN)_3(C_6H_5)]^{2-}$ [5] and $[Pd(CN)_2(C{\equiv}CR)_2]^{2-}$ [6]. Moreover, polynuclear cyano-organopalladium complexes in which each two metal atoms are bridged by a CN-group have recently been reported [7,8], while the formation of polynuclear cyano-organopalladium complexes have been postulated as intermediates in the addition of HCN to olefines [9] and to olefinic silanes [10] catalyzed by palladium(0) complexes.

We describe below the preparation of anionic cyano-organopalladium complexes which, when treated with perchlorato complexes of palladium, behave as Lewis bases and form polynuclear cyano-bridged compounds.

The IR absorptions due to the CN and C_6F_5 groups along with those of the neutral ligands allow reasonable assignments of the structures of the new complexes.

Results and discussion

Anionic complexes

The cyano-organopalladium complexes were obtained by addition of KCN(aq) to the appropriate precursors [11], according to eq. 1—5.

$$[(C_6F_5)_3Pd(tht)]^- + CN^- \rightarrow [(C_6F_5)_3Pd(CN)]^{2-} + tht \qquad (1)$$

$$\tfrac{1}{2}[(C_6F_5)_4Pd_2(\mu\text{-}Br)_2]^{2-} + 2\,CN^- \rightarrow cis\text{-}[(C_6F_5)_2Pd(CN)_2]^{2-} + Br^- \qquad (2)$$

$$trans\text{-}[(C_6F_5)_2Pd(tht)_2] + 2\,CN^- \rightarrow trans\text{-}[(C_6F_5)_2Pd(CN)_2]^{2-} + 2\,tht \qquad (3)$$

$$\tfrac{1}{2}[(C_6F_5)_2Pd_2(\mu\text{-}Cl)_2(tht)_2] + 3\,CN^- \rightarrow [Pd(C_6F_5)(CN)_3]^{2-} + Cl^- + tht \qquad (4)$$

$$\tfrac{1}{4}[(\eta^3 - C_3H_5)Pd(\mu\text{-}CN)]_4 + CN^- \rightarrow [(\eta^3\text{-}C_3H_5)Pd(CN)_2]^- \qquad (5)$$

The stability of cyano-palladium complexes is revealed, for example, by the high stability constant of $[Pd(CN)_4]^{2-}$ [12]. In accordance with this, the reaction with the cyano group gives rise to the substitution of the halide group (as in reactions 2 and 4), to the cleavage of bridges (as in reactions 2, 4 and 5), or to the displacement of the neutral tetrahydrothiophen group (as in reactions 1, 3 and 4). However, no displacement of the aryl group C_6F_5 takes place in any of the reactions, not even when processes 1 and 3 are carried out with an excess of KCN.

The complexes were isolated from their acetone solutions as salts of tetra-n-butylammonium or benzyltriphenylphosphonium (in the case of reaction 2). All of them show a strong tendency to form oils, but after repeated washing with diethyl ether and/or hexane these can eventually be transformed into solids.

In contrast to the tricyanophenyl palladate described in the literature [5], the cyanopentafluorophenyl palladates show a remarkable thermal stability. In the solid state, however, the allyl derivative turns black after several hours standing at room temperature, and must therefore be stored at low temperature.

It is noteworthy that the *cis* or, respectively, *trans* configuration of the C_6F_5 groups is conserved during reactions 2 and 3. The resistance to isomerization seems to be characteristic for palladium complexes containing C_6F_5 [13].

The IR absorptions in two regions are of structural interest: those due to $\nu(C{\equiv}N)$ located at 2200—2000 cm^{-1} and the X-sensitive modes [13,14] of the C_6F_5 groups observed at 800—750 cm^{-1}. The corresponding IR active stretch-

TABLE 1

POINT GROUPS AND IR ACTIVE STRETCHING MODES FOR THE ANIONIC COMPLEXES

	Point group	$\nu(C{\equiv}N)$	C_6F_5-X-sensitive
$[(C_6F_5)_3Pd(CN)]^{2-}$	C_{2v}	A_1	$2\,A_1 + B_1$
cis-$[R_2Pd(CN)_2]^{x-\,a}$	C_{2v}	$A_1 + B_1$	$A_1 + B_1$
trans-$[(C_6F_5)_2Pd(CN)_2]^{2-}$	D_{2h}	B_{2u}	B_{2u}
$[(C_6F_5)Pd(CN)_3]^{2-}$	C_{2v}	$2\,A_1 + B_1$	A_1

[a] $R_2 = 2C_6F_5$, $x = 2$; $R_2 = \eta^3\text{-}C_3H_5$, $x = 1$.

TABLE 2

RELEVANT INFRARED DATA OF THE COMPLEXES [a]

		$\nu(C\equiv N)$	(Predicted)	C_6F_5-X sensitive	(Predicted)	Neutral ligand
I	$[(\eta^3\text{-}C_3H_5)Pd(CN)(PPh_3)]$	2114s	(1)	—	—	530s, 511s, 502s
II	$Q_2[(C_6F_5)_3Pd(CN)]$	2117s	(1)	778m, 765(sh), 760s	(3)	—
III	$Q'_2[\textit{cis}\text{-}(C_6F_5)_2Pd(CN)_2]$	2112s(br)	(2)	775s, 766s [b]	(2)	—
IV	$Q_2[\textit{trans}\text{-}(C_6F_5)_2Pd(CN)_2]$	2110s	(1)	760s	(1)	—
V	$Q_2[(C_6F_5)Pd(CN)_3]$	2124(sh), 2118s	(3)	772s	(1)	—
VI	$Q[(\eta^3\text{-}C_3H_5)Pd(CN)_2]$	2122(sh), 2112s	(2)	—	—	—
VII	$Q\{(C_6F_5)_3Pd[(\mu\text{-}CN)E]\}$	2140s	(1)	788m, 774m, 760s	(4)	526s, 518s, 497s
VIII	$\textit{cis}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E]_2\}$	2155m, 2143s	(2)	790m, 785(sh), 773m	(3)	523s, 515s, 500m
IX	$\textit{trans}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E]_2\}$	2153s	(1)	793s, 763s	(2)	525s, 513s, 500s
X	$\textit{trans}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E']_2\}$	2198s	(1)	795s, 765m(sh)	(2)	760s
XI	$\textit{trans}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E'']_2\}$	2170s	(1)	798s, 788(sh)	(2)	765s
XII	$\{(C_6F_5)Pd(CN)[(\mu\text{-}CN)E]_2\}$	2170s(br), 2130w	(3)	795s, 785s(sh)	(2)	532s, 528(sh), 516s, 499s
XIII	$\{(\eta^3\text{-}C_3H_5)Pd(PPh_3)[(\mu\text{-}CN)E''']\}ClO_4$	2150s	(1)	—	—	530s, 512s, 500s
XIV	$\{(\eta^3\text{-}C_3H_5)Pd[(\mu\text{-}CN)E''']_2\}ClO_4$	2150s	(2)	—	—	531s, 513s, 500s

[a] $[Q]^+ = [N\text{-}n\text{-}Bu_4]^+$; $[Q']^+ = [P(C_6H_5)_3(CH_2C_6H_5)]^+$; E = *trans*-$[Pd(C_6F_5)(PPh_3)_2]$; E' = *trans*-$[Pd(C_6F_5)(py)_2]$; E'' = $[Pd(C_6F_5)(bipy)]$; E''' = $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)]$.

[b] Assignment uncertain due to absorptions of the cation in this range.

ing modes for the anionic complexes are listed in Table 1. On comparing the expected (Table 1) with the recorded number of absorptions (Table 2) it is seen that they are in perfect agreement for the X-sensitive vibrations. However, the number of absorptions due to $\nu(C{\equiv}N)$ is not as expected, although a sharp band is observed where a single band has been predicted while a broad band or bands with shoulders are to be seen where two or three absorptions were expected. Coincidence of the various $\nu(C{\equiv}N)$ vibrations has previously been reported for the similar complexes $[(C_6H_5)Pd(CN)_3]^{2-}$ [5], and we think that the non-observation of the expected multiplicity in our case can also be attributed to the same reason.

The analytical results for the novel complexes (listed in Table 3) are in good agreement with the proposed stoichiometries (the calculated values are given in parentheses). The measured molar conductivities also coincide with the literature values for 1/1 and 2/1 electrolytes [15].

CN-bridged complexes

Since the CN group is capable of acting as a bidentate ligand [16] metal com-

TABLE 3

ANALYSES AND CONDUCTIVITIES OF THE COMPLEXES [a]

		Analysis (Found (calcd.) (%))			Λ_{max} (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
I	$[(\eta^3\text{-}C_3H_5)Pd(CN)(PPh_3)]$	61.39 (60.64)	4.95 (4.63)	3.40 (3.21)	n.c.
II	$Q_2[(C_6F_5)_3Pd(CN)]$	54.07 (54.76)	6.21 (6.49)	3.75 (3.76)	181 [b]
III	$Q'_2[cis\text{-}(C_6F_5)_2Pd(CN)_2]$	63.41 (64.09)	3.82 (3.70)	2.52 (2.34)	164 [b]
IV	$Q_2[trans\text{-}(C_6F_5)_2Pd(CN)_2]$	57.17 (56.52)	7.46 (7.42)	5.60 (5.73)	146 [b]; 141 [c]
V	$Q_2[(C_6F_5)Pd(CN)_3]$	59.49 (58.88)	8.60 (8.68)	8.44 (8.37)	156 [b]; 143 [c]
VI	$Q[(\eta^3\text{-}C_3H_5)Pd(CN)_2]$	56.63 (57.07)	9.27 (9.35)	9.38 (9.51)	124 [b]
VII	$Q\{(C_6F_5)_3Pd[(\mu\text{-}CN)E]\}$	55.08 (55.24)	3.92 (3.97)	1.71 (1.67)	81 [b]
VIII	$cis\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E]_2\}$	56.41 (56.36)	2.80 (2.90)	1.26 (1.34)	n.c.
IX	$trans\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E]_2\}$	55.62 (56.36)	3.03 (2.90)	1.29 (1.34)	n.c.
X	$trans\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E']_2\}$	40.49 (40.75)	1.83 (1.49)	6.36 (6.20)	n.c.
XI	$trans\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)E'']_2\}$	41.38 (40.87)	1.69 (1.19)	6.22 (6.22)	n.c.
XII	$\{(C_6F_5)Pd(CN)[(\mu\text{-}CN)E]_2\}$	57.00 (57.34)	3.18 (3.11)	2.25 (2.16)	n.c.
XIII	$\{(\eta^3\text{-}C_3H_5)Pd(PPh_3)[(\mu\text{-}CN)E''']\}ClO_4$	54.81 (54.65)	4.61 (4.27)	1.73 (1.48)	134 [b]
XIV	$\{(\eta^3\text{-}C_3H_5)Pd[(\mu\text{-}CN)E''']_2\}ClO_4$	49.94 (50.47)	4.61 (4.06)	2.74 (2.50)	134 [b]

[a] $[Q]^+ = [N\text{-}n\text{-}Bu_4]^+$; $[Q']^+ = [P(C_6H_5)_3(CH_2C_6H_5)]^+$; E = *trans*-$[Pd(C_6F_5)(PPh_3)_2]$; E′ = *trans*-$[Pd(C_6F_5)(py)_2]$; E″ = $[Pd(C_6F_5)(bipy)]$; E‴ = $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)]$. [b] Acetone. [c] Nitromethane.

plexes containing terminal cyano groups remain potential ligands. Thus, the above-described organic cyano complexes react with palladium complexes containing a perchlorato group with displacement of the latter group and formation of polynuclear cyano-bridged palladium complexes. For example, $(N\text{-n-Bu}_4)_2$-$[\textit{trans}\text{-}(C_6F_5)_2Pd(CN)_2]$ reacts according to eq. 6 and 7.

$$Q_2[\textit{trans}\text{-}(C_6F_5)_2Pd(CN)_2] + 2(O_3ClO)Pd(C_6F_5)(PPh_3)_2$$
$$\rightarrow \textit{trans}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_2\} + 2\ QClO_4 \qquad (6)$$
$$Q_2[\textit{trans}\text{-}(C_6F_5)_2Pd(CN)_2] + 2\ [(C_6F_5)Pd(acetone)L_2]ClO_4$$
$$\rightarrow \textit{trans}\text{-}\{(C_6F_5)_2Pd[(\mu\text{-}CN)Pd(C_6F_5)L_2]_2\} + 2\ QClO_4 + 2\ \text{acetone} \qquad (7)$$
$$([Q]^+ = [N\text{-n-Bu}_4]^+\ ; \quad L_2 = 2\ \text{py, bipy})$$

It is of interest that when reaction 7 is carried out with equimolecular amount ($L = PPh_3$) the product does not contain a CN-bridging group along with a terminal CN group but half of the anionic complex remains unreacted while the rest forms the double-cyano-bridged compound, which is also obtained in reaction 6. Similarly, $(N\text{-n-Bu}_4)_2[(C_6F_5)Pd(CN)_3]$ forms bridges with two of its three CN groups, but the single-cyano-bridged complex could not be synthesized. These observations suggest that the coordinating capacity of the nitrogen of a second CN group is increased by the presence of a cyano-bridging group.

Treatment of the tricyano complex (V) with a large excess of $(O_3ClO)(C_6F_5)Pd(PPh_3)_2$ does not lead to the triple-cyano-bridged compound. In fact, if a benzene solution of $(O_3ClO)(C_6F_5)Pd(PPh_3)_2$ is added to a solution of $\{(C_6F_5)Pd(CN)[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_2\}$ in the same solvent (both reagents are used in $\sim 1.2 \times 10^{-3}$ M concentration) the conductivity of the resulting solution is zero. This excludes the formation of a third bridge, which would only be possible if an ionic complex were formed (eq. 8).

$$\{(C_6F_5)Pd(CN)[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_2\} + (O_3ClO)(C_6F_5)Pd(PPh_3)_2$$
$$\rightarrow \{(C_6F_5)Pd[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_3\}\ (ClO_4) \qquad (8)$$

The analytical results and molar conductivities for the novel complexes agree satisfactorily with the proposed stoichiometries, as may be seen from Table 3.

The IR absorptions which are of structural interest, i.e. the $\nu(C{\equiv}N)$ stretching and the X-sensitive C_6F_5 frequencies along with some absorptions due to the PPh_3 and py-groups, are listed in Table 2. The $\nu(C{\equiv}N)$ stretching frequencies of complexes VII—XIV are clearly shifted toward higher energies relative to their locations in the parent compounds I—VI. All these bands are above 2140 cm^{-1}, as expected for cyano-bridging groups [17]. Complex XII also shows a band at 2130 cm^{-1} assignable to its terminal CN group.

A more detailed study of the IR spectra reveals that the geometry around the palladium atoms in the parent compounds is conserved in every case during the bridge-forming reactions. Thus, if the geometry around the central palladium atoms remains unchanged the number of the $\nu(C{\equiv}N)$ IR active vibrations of the resulting complexes must be that of the parent compounds (Table 1) increased by one, because of the attached $Pd(C_6F_5)L_2$-groups, for which one

C_6F_5-X-sensitive absorption can be predicted. As seen from Table 2, the observed spectra agree satisfactorily with the calculated ones, though a decrease of the expected multiplicities is again observed in a few cases. For complexes VIII—XI (the only one which could show *cis—trans*-isomerism) the coincidence is fortunately exact.

Relative to the entering groups, for $Pd(\eta^3\text{-}C_3H_5)(PPh_3)$ or for $Pd(C_6F_5)L_2$ when L_2 = bipy only one configuration is possible. For L_2 = 2py two absorptions at approx. 760 cm^{-1} may be expected for two mutually *cis*-pyridine groups, whilst a single band is expected for the *trans*-configuration [18]; the recorded IR spectrum shows that the pyridine groups are actually mutually *trans*, as they were in the parent compound. Finally, for L_2 = 2 PPh_3 a strong band could be expected for two mutually *cis*-phosphine groups [19] but all the novel complexes show the typical pattern of two mutually *trans*-PPh_3 groups, as were in the precursor perchlorato complex.

The geometry of complex XII, whose CN-bridging groups could be either *cis* or *trans*, could not be decided, since both isomers would show the same number of absorptions. If our suggestion that the bridge-forming tendency is increased by the presence of an existing bridge is correct, this effect should operate on the *trans*-site and the CN-bridging groups would thus be mutually *trans*.

Experimental

C, H and N analyses were determined with a Perkin—Elmer 240 microanalyzer; conductivities were measured in approx. 5×10^{-4} *M* solution with a Philips PW 9501/01 conductimeter; IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin—Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets.

Preparation of $(O_3ClO)Pd(\eta^3\text{-}C_3H_5)(PPh_3)$ in solution

Benzene solutions of $(O_3ClO)Pd(\eta^3\text{-}C_3H_5)(PPh_3)$ were obtained by stirring (30 min) $ClPd(\eta^3\text{-}C_3H_5)(PPh_3)$ [20] with stoichiometric amounts of $AgClO_4$ with exclusion of daylight, and after removal of the formed AgCl the solutions were used without further isolation of the perclorato complex.

Solutions of $(O_3ClO)Pd(C_6F_5)(PPh_3)_2$ and $(ClO_4)[(C_6F_5)Pd(acetone)L_2]$ (L_2 = 2py or 2,2-bipyridine) were prepared similarly in benzene or acetone.

Preparation of $(\eta^3\text{-}C_3H_5)Pd(CN)(PPh_3)$ (I)

To a solution of $ClPd(\eta^3\text{-}C_3H_5)(PPh_3)$ (250 mg, 0.562 mmol) in 50 ml of dichloromethane was added a stoichiometric amount of freshly prepared wet AgCN. After 8 h stirring with exclusion of daylight and removal of the precipitated AgCl the filtrate was dried with anhydrous $MgSO_4$ and evaporated to dryness. The resulting colourless oil was stirred with 15 ml of diethyl ether to give white crystals of I (70% yield).

Preparation of $(N\text{-}n\text{-}Bu_4)_2[(C_6F_5)_3Pd(CN)]$ (II)

To a solution of $(N\text{-}n\text{-}Bu_4)[(C_6F_5)_3Pd(tht)]$ (720 mg, 0.767 mmol) in 50 ml of acetone were added 100.7 mg (1.546 mmol) of KCN in 30 ml of water. The mixture was stirred for 8 h, after which $N\text{-}n\text{-}Bu_4Br$ (247 mg, 0.767 mmol) was added and the acetone was evaporated off. The residue was extracted with 100 ml of dichloromethane, the dichloromethane layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness. The resulting colourless oil was repeatedly stirred with 10 ml of n-hexane to remove the tht which was liberated during the reaction, and a white solid was finally obtained (II: 86% yield).

Preparation of $[P(C_6H_5)_3(CH_2\text{-}C_6H_5)]_2[cis\text{-}(C_6F_5)_2Pd(CN)_2]$ (III)

51.2 mg (0.786 mmol) of KCN in 25 ml of water were added to 300 mg (0.196 mmol) of $(N\text{-}n\text{-}Bu_4)_2[(C_6F_5)_4Pd_2Br_2]$ in 25 ml of acetone and the mixture was stirred for 3 h. After addition of 306 mg (0.786 mmol) of $P(C_6H_5)_3(CH_2C_6H_5)Cl$, 30 min stirring and evaporation of the acetone, the required complex was extracted as before with 100 ml of dichloromethane. The colourless oil obtained was repeatedly treated with diethyl ether and vacuum-evaporated to give the white complex III (60% yield).

Preparation of $(N\text{-}n\text{-}Bu_4)_2[trans\text{-}(C_6F_5)_2Pd(CN)_2]$ (IV)

To a solution of 1.111 g (1.80 mmol) of $(C_6F_5)_2Pd(tht)_2$ in 50 ml of warm acetone were added 258.1 mg (3.96 mmol) of KCN in 30 ml of water. Refluxing for 3 h, evaporation of the acetone, addition of 1.4521 g (4.50 mmol) of $N\text{-}n\text{-}Bu_4Br$, and stirring led to precipitation of the white complex IV (92% yield).

Preparation of $(N\text{-}n\text{-}Bu_4)_2[(C_6F_5)Pd(CN)_3]$ (V)

To a solution of 300 mg (0.378 mmol) of $(C_6F_5)_2Pd_2Cl_2(tht)_2$ in 20 ml of acetone were added 147.2 mg (2.26 mmol) of KCN in 10 ml of water. After 4 h refluxing, addition of 487.1 mg (1.511 mmol) of $BrN\text{-}n\text{-}Bu_4$, and evaporation of the acetone the work-up was continued as for II, giving a colourless oil, which was repeatedly stirred with n-hexane and finally with diethyl ether (complex V: 95% yield).

Preparation of $(N\text{-}n\text{-}Bu_4)[(\eta^3\text{-}C_3H_5)Pd(CN)_2]$ (VI)

To a stirred suspension of 160 mg (0.23 mmol) of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}CN)]_4$ in 40 ml of acetone and 297 mg (0.92 mmol) of $N\text{-}n\text{-}Bu_4Br$ was added dropwise a solution of 60 mg (0.92 mmol) of KCN in 20 ml of water. After 3 h stirring, filtration, and evaporation of the acetone the work-up was carried as for II. The resulting colourless oil was stirred with diethyl ether to give the white complex VI (88% yield).

Synthesis of the cyano-bridged complexes VII—XI, XIII and XIV

All these complexes were prepared in the same way as $\{(C_6F_5)_3Pd[(\mu\text{-}CN)(C_6F_5)Pd(PPh_3)_2]\}$ using the appropriate precursors.

A solution of 0.209 mmol of $(O_3ClO)(C_6F_5)Pd(PPh_3)_2$ in 50 ml of dichloromethane and 234 mg (0.209 mmol) of $(N\text{-}n\text{-}Bu_4)_2[(C_6F_5)_3Pd(CN)]$ was stirred for 2 h and evaporated to dryness. Upon addition of ethanol the required complex separated as a white solid (70% yield).

Complexes VIII and IX were obtained similarly in 50 or 75% yields, respectively. Complex IX can also be synthesized by use of a 1/1 molar ratio (34% yield).

Complexes X and XI were prepared in acetone solution since the respective perchlorato starting compounds are insoluble in non-coordinating solvents (yields: 50% or 70%, respectively).

Complex XIII was prepared in benzene and separated spontaneously (65% yield).

Complex XIV was also prepared in benzene and $(N\text{-}n\text{-}Bu_4)[(\eta^3\text{-}C_3H_5)Pd(CN)_2]$ was added in 10 ml of chloroform (60% yield).

Preparation of $\{(C_6F_5)Pd(CN)[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_2\}$ (XII)

To a solution of 0.19 mmol of $(O_3ClO)(C_6F_5)Pd(PPh_3)_2$ in 50 ml of benzene was added 80 mg (0.095 mmol) of $(N\text{-}n\text{-}Bu_4)_2[(C_6F_5)Pd(CN)_3]$; 3 h stirring and evaporation to dryness gave a white residue, which was washed with 25 ml of ethanol and recrystallized from benzene (52% yield).

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