

Single-Bridged Halide or Pseudohalide Complexes of Palladium(II)

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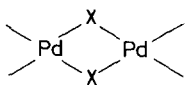
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The synthesis of cationic binuclear palladium complexes of the type $\{\mu\text{-X}\}[\text{Pd}(\text{C}_6\text{F}_5)_2\text{L}_2][\text{Pd}(\text{C}_6\text{F}_5)_2\text{L}'_2]\text{ClO}_4$ ($\text{L} = \text{N}$ or P donors) is described. X can be a pseudohalide, such as CN , SCN or N_3 , or a halide when L_2 is a bidentate N -ligand, such as *bipy*. Trinuclear complexes of the type $\{(\text{PPh}_3)_2\text{-Pd}\}(\mu\text{-X})_2[\text{Pd}(\text{C}_6\text{F}_5)_2\text{L}_2]_2\text{ClO}_4$ have only been obtained for $\text{X} = \text{CN}$. For $\text{X} = \text{other pseudohalide or halide}$, rearrangement reactions render binuclear double-bridged species along with binuclear single-bridged species of the above-mentioned type. The preparation of a pentanuclear complex $\{[\text{Pd}(\mu\text{-CN})_4] - [\text{Pd}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]_4\}(\text{ClO}_4)_2$ is also described.

Introduction

Most of the hitherto-known binuclear palladium(II) complexes [1] with halogen or pseudohalogens (X) contain the moiety



whose two square planar Pd atoms are double-bridged by two groups X . The preparation of neutral as well as anionic binuclear pentafluoro- and pentachlorophenyl palladium(II) complexes of this structure, *i.e.* with two groups X double-bridging the palladium atoms, has previously been described [2, 3].

The cyanide ligand shows a different behaviour. Since this group seemingly does not favour the establishment of bent bonds, the enforced linearity of the $-\text{C}\equiv\text{N}-$ group imposes the formation of bi- or polynuclear single-bridged derivatives [4–7].

In the present paper we describe the results of a study on the synthesis of bi- and polynuclear single-bridged palladium(II) complexes with other bridging

groups X , halogens or pseudohalogens, as well as cyanide.

Part of this research has been the subject of a preliminary communication [8].

Experimental

C, H and N analyses were determined with a Perkin-Elmer 240 microanalyzer; IR spectra were recorded ($4000\text{--}200\text{ cm}^{-1}$) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in approx. $5 \times 10^{-4}\text{ M}$ acetone solutions with a Philips PW 9501/01 conductimeter.

$\text{PdCl}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L} = \text{PPh}_3$, $\text{L}_2 = \text{bipy}$, *phen*) was prepared by reacting (in acetone) the binuclear complex $[\text{Pd}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ [2] with a slight excess of the respective neutral ligand.

$\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ was prepared by reacting (in benzene) stoichiometric amounts of $\text{PdCl}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ and AgClO_4 [9]. The resulting solution was filtered to remove the precipitated AgCl and the filtrate was used without further isolation of the perchlorato complex.

$\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ [10] was prepared by reacting (in acetone) $\text{PdCl}(\text{C}_6\text{F}_5)(\text{bipy})$ with AgClO_4 (1:1 molar ratio). The precipitated AgCl was filtered off, the filtrate was evaporated to dryness and the $[\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})(\text{acetone})]\text{ClO}_4$ obtained was heated overnight to 110°C to give $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)\text{bipy}$.

$\text{Pd}(\text{X})(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{X} = \text{Br}$, I , CN , SCN , N_3 , CH_3COO) were prepared by metathetical reaction in acetone between $\text{PdCl}(\text{C}_6\text{F}_5)_2\text{L}_2$ and KBr , KI , KCN , KSCN , AgN_3 or, respectively, NaCH_3COO . $\text{Pt}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PET}_3)_2$ was prepared as described elsewhere [11].

$\{\mu\text{-X}\}[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]_2\text{ClO}_4$ ($\text{X} = \text{CN}$ (1), SCN (2), N_3 (3))

To a solution of $\text{PdX}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2$ ($\text{X} = \text{CN}$, SCN or N_3) (0.5 mmol) in 50 ml of benzene was

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added drop by drop a solution of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.5 mmol) in 50 ml of benzene and stirred for 5 h at room temperature. The microcrystalline solid formed was filtered off, washed with benzene, and air-dried. (Yield: 1, 0.58 g (68%); 2, 0.65 g (75%); 3, 0.52 g (60%).)

No reaction could be observed when $\text{PdX}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CNO}$ or CH_3COO) was treated with $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ under analogous conditions. No precipitation took place, whilst evaporation of the solution rendered a mixture of the unchanged starting compounds.

$\{\mu\text{-X}\}[\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})]_2\text{ClO}_4$ ($\text{X} = \text{CN}(4), \text{SCN}(5), \text{Cl}(6), \text{Br}(7)$)

To a suspension of $\text{PdX}(\text{C}_6\text{F}_5)(\text{bipy})$ ($\text{X} = \text{CN}, \text{SCN}, \text{Cl}$ or Br) (0.5 mmol) in 30 ml of CH_2Cl_2 was added $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ (0.5 mmol) and the mixture was stirred overnight at room temperature. The resulting precipitate was filtered off and washed with benzene. (Yields: 4 (88%), 6 (93%), 7 (90%).)

Under these conditions complex (5) was obtained as an oily product which had to be treated with 2×10 ml of benzene and 2×10 ml of hexane to give a pale yellow solid (80% yield).

$\{\mu\text{-CN}\}[\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2][\text{Pt}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]\text{ClO}_4$ (8)

$\text{Pd}(\text{CN})(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ was reacted with $\text{Pt}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PEt}_3)_2$ (1:1 molar ratio) as for complex 1 and complex 8 was obtained in 75% yield.

Reaction of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ with $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$

To a solution of $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.171 g, 0.2 mmol) in 20 ml of benzene was added $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ (0.106 g, 0.2 mmol) in 20 ml of acetone and stirred overnight at room temperature. Concentration to ca. 10 ml and addition of 40 ml of benzene gave rise to the formation of a white precipitate, which was filtered off, washed with benzene, and dried. Complex 9: 0.115 g, (73%) yield. The filtrate was concentrated almost to dryness, 10 ml of ethanol was added and the formed white solid was filtered off and washed with ethanol. Complex 10: 0.040 g, 68% yield.

Reaction of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ with $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{bipy})$

$\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.25 mmol) in 60 ml of CHCl_3 was reacted with $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{bipy})$ (0.122 g, 0.25 mmol) in 20 ml of CHCl_3 at room temperature for 48 h. The solution was concentrated to 10 ml and the formed complex was carefully washed with 50 ml of benzene to isolate 9: 0.180

g, 91% yield. The benzene filtrate was concentrated to a few ml and ethanol was added to separate complex 10: 0.060 g, 81% yield.

Reaction of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ with $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{dpe})$

To a suspension of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{bipy})$ (0.211 g, 0.4 mmol) in 20 ml of CHCl_3 was added a solution of $\text{Pd}(\text{SCN})(\text{C}_6\text{F}_5)(\text{dpe})$ (0.292 g, 0.4 mmol) in 30 ml of CHCl_3 . After overnight stirring at room temperature the solution was concentrated to 5 ml and benzene was added to separate a pale-yellow oil. The oil was recrystallized from CHCl_3 /diethyl-ether to give a white solid, which was filtered off and dried. (11: 0.4 g, 81% yield).

Reaction of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ with $\text{Pd}(\text{CN})_2(\text{PPh}_3)_2$

To a solution of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.66 mmol) in 40 ml of benzene was added a solution of $\text{Pd}(\text{CN})_2(\text{PPh}_3)_2$ (0.22 g, 0.33 mmol) in 125 ml of CH_2Cl_2 and the mixture was stirred for 30 min, whilst the formation of a white precipitate could be observed almost instantaneously. The solution was concentrated to 40 ml, the formed white compound was filtered off, washed with benzene, and dried. (16: 1.67 g, 82% yield).

Reaction of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ with $\text{PdX}_2(\text{PPh}_3)_2$ ($\text{X} = \text{SCN}, \text{N}_3$ or I)

To a solution of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.5 mmol) in 50 ml of benzene was added a solution of $\text{PdX}_2(\text{PPh}_3)_2$ (0.25 mmol) ($\text{X} = \text{SCN}$ or N_3) in 80 ml of CH_2Cl_2 . After overnight stirring at room temperature a yellow precipitate separated, which was filtered off, washed with benzene, and dried. It was identified as complex 12 (0.17 g, 86% yield) or, respectively, complex 13 (0.19 g, 98% yield).

In the case of $\text{X} = \text{SCN}$ the filtrate was concentrated to 10 ml and allowed to cool; the resulting yellow crystals were filtered off and identified spectroscopically as a mixture of 12 and 2. The remaining filtrate was evaporated to dryness to give a white solid identified as 2. In the case of $\text{X} = \text{N}_3$ the filtrate was evaporated to dryness, the residue was stirred with 50 ml of benzene and the remaining pale-yellow solid was filtered off, dried, and identified as 3.

In the case of $\text{X} = \text{I}$ a solution of $\text{PdI}_2(\text{PPh}_3)_2$ (0.221 g, 0.25 mmol) in 125 ml of CH_2Cl_2 was added to a solution of $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ (0.5 mmol) in 50 ml of benzene. After 3 h stirring at room temperature the solution was concentrated to 30 ml giving rise to the crystallization of an orange-coloured solid, which was filtered off and washed with benzene (14): 0.173 g, 81% yield.

Reaction of Pd(OCIO₃)(C₆F₅)(PPh₃)₂ with Pd(N₃)₂(dpe)

To a solution of Pd(OCIO₃)(C₆F₅)(PPh₃)₂ (0.66 mmol) in 70 ml of benzene was added Pd(N₃)₂(dpe) (0.194 g, 0.33 mmol) in 30 ml of CH₂Cl₂ and stirred for 1 h (at room temperature). The resulting white precipitate was filtered off, washed with benzene, dried, and identified as 15: 0.20 g, 95% yield.

The filtrate was concentrated to 10 ml and the formed yellow solid was filtered off, washed with benzene, and dried. Complex 3: 0.45 g, 78% yield.

Reaction of Pd(OCIO₃)(C₆F₅)(PPh₃)₂ with [Pd(CN)₄](NBu₄)₂

To a solution of [Pd(CN)₄](NBu₄)₂ (0.135 g, 0.194 mmol) in 50 ml of CH₂Cl₂ was added Pd(OCIO₃)(C₆F₅)(PPh₃)₂ (0.78 mmol) in 100 ml of benzene and stirred for 2 h (room temperature). The solution was evaporated to 40 ml at room temperature and the stirring was continued whilst the formation of a white precipitate could be observed. After 5 days the solid was filtered off, washed with benzene, and air-dried. (17: 56% yield).

Reaction of Pd(OCIO₃)(C₆F₅)(bipy) with [Pd(SCN)₄](NBu₄)₂

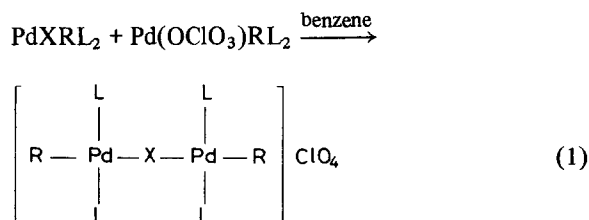
To a solution of Pd(OCIO₃)(C₆F₅)(bipy) (0.367 g, 0.693 mmol) in 50 ml of acetone was added [Pd(SCN)₄](NBu₄)₂ (0.142 g, 0.172 mmol) in 25 ml of acetone, whilst an almost instantaneous formation of an orange-red precipitate could be observed. After 1 h stirring (room temperature) the precipitate was filtered off and identified as [Pd(SCN)₂]_x.

The filtrate was concentrated to ~5 ml and ethanol was added to precipitate 5 (59% yield).

Results and Discussion

a) Binuclear Complexes

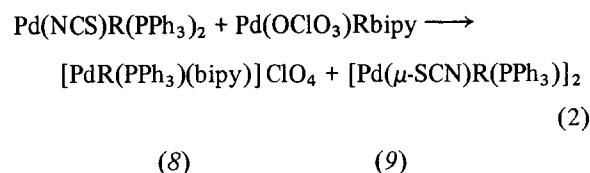
Our approach to the synthesis of single-bridged binuclear halo- or pseudohalo complexes of palladium(II) is based on the reaction, in a non-donor solvent, between mononuclear complexes. Of these one has a potential bridging ligand, whilst the other contains a poorly coordinating, *i.e.* a readily displaceable group, which on leaving vacates a site in the coordination sphere of the palladium atom that is to be occupied by the prospective bridging ligand of the first complex, as shown in eqn. 1:



R = C₆F₅, X = halogen or pseudohalogen, bridge not necessarily linear. When L = PPh₃ (*trans*-isomer) and X = a pseudohalogen the process takes place as represented in eqn. 1 and the binuclear complexes (X = CN(1), SCN(2) or N₃(3)) precipitate (see Table I). Moreover, no reaction could be observed for X = Cl, Br or I, and the unchanged starting complexes were recovered. In these cases the coordinated halogens of the starting complexes seemingly are only poor donors and lack the ability to displace the perchlorato ligand of the used compound. The same lack of reactivity could also be observed for X = CNO⁻ or CH₃COO⁻.

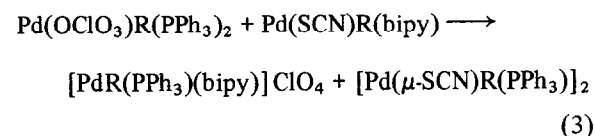
The election of a different system, however, increases the versatility of process (1). If a bidentate N-donor, such as 2,2'-bipyridine (bipy), is used instead of the two unidentate phosphorus ligands PPh₃, the binuclear complexes {(μ-X)[Pd(R)(bipy)]₂}-ClO₄ are obtained, not only in the cases of X = CN(4) or SCN(5), but also in those of X = Cl(6) or Br(7). To the best of our knowledge, complexes (6) and (7) are the only hitherto-reported palladium derivatives with a single halide bridge.

The synthesis of other binuclear single-bridged complexes with their two palladium atoms carrying different ligands has also been attempted. Nevertheless, owing to rearrangements such processes may take another course, leading to complexes of different kinds: *e.g.* the reaction (1:1) between Pd-(NCS)R(PPh₃)₂ (with N-bonded-NCS) and Pd(OCIO₃)R(bipy), according to eqn. (2):

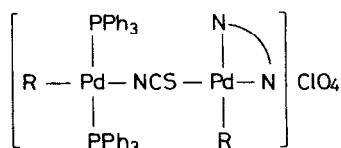


leads to a mixture of complexes 8 and 9, apparently because one mol of PPh₃ dissociates and withdraws the perchlorate ligand from the other complex thus giving rise to the formation of the cationic complex 8, whilst the remaining coordinatively-unsaturated species Pd(SCN)R(PPh₃) dimerizes giving the double-bridged 9.

The reaction between Pd(OCIO₃)R(PPh₃)₂ and Pd(SCN)R(bipy) (with S-bonded-SCN) renders the same end products, (eqn. 3):

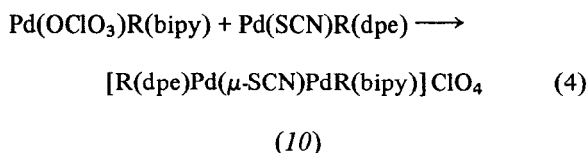


We think that this reaction may lead primarily to the formation of the expected single-bridged dimeric (non isolable) complex

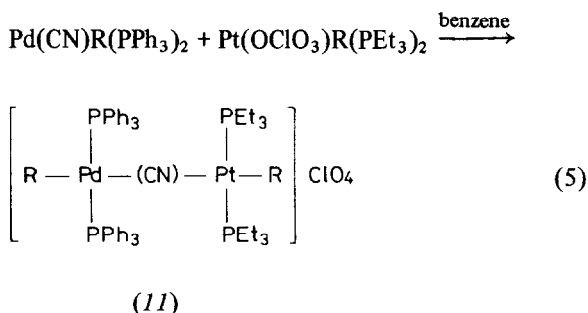


whilst subsequently some dissociated PPh_3 cleaves the S—Pd bond to give complex 8 and the fragment $(\text{Pd}(\text{NCS})\text{R}(\text{PPh}_3))$, which again dimerizes to form 9.

The desired monobridged dimeric complex 10 can be obtained by choosing a system which precludes the dissociation of a monodentate neutral ligands, since both reaction partners contain chelate ligands (eqn. 4):



Moreover, an appropriate choice of the reactants also allows the synthesis of bimetallic single-bridged complexes, as may be seen from eqn. 5:

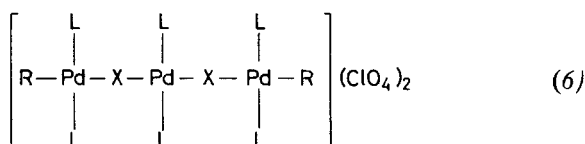
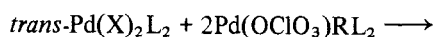


thus illustrating the overall generality of this synthetic approach, provided the careful selection of suitable reagents.

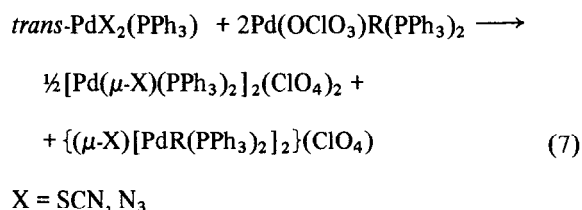
The leaving poor-coordinating ligand must not necessarily be an anionic group, such as perchlorato. Bimetallic anionic single bridged complexes of the types $[\text{RAuXPdR}_2\text{L}]^-$ or $[(\text{RAuX})_2\text{PdR}_2]^{2-}$ can be prepared if a neutral poor coordinating ligand (e.g. tetrahydrothiophen in gold complexes) can be found [12].

b) Polynuclear Complexes

The above described synthetic approach can easily be extended to the preparation of complexes of higher nuclearity. Thus, the reaction between one mol of a bifunctional palladium derivative and two moles of a perchlorato complex could lead to trinuclear complexes (eqn. 6):

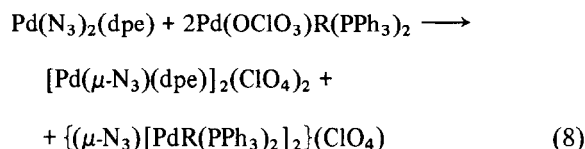


However, as may be expected, other parallel reactions can interfere leading to mixtures. Thus, in the case of $\text{R} = \text{C}_6\text{F}_5$, $\text{L} = \text{PPh}_3$ and $\text{X} = \text{SCN}$ or N_3 a mixture of $[\text{Pd}(\mu\text{-X})(\text{PPh}_3)_2]_2(\text{ClO}_4)_2$ ($\text{X} = \text{SCN}$ (12), N_3 (13) and $\{(\mu\text{-X})[\text{PdR}(\text{PPh}_3)_2]_2\}(\text{ClO}_4)$ ($\text{X} = \text{SCN}$ (2), N_3 (3) is obtained, according to eqn. 7:



For $\text{X} = \text{I}$ only the double-bridged binuclear complex 14, along with the mononuclear derivatives $\text{PdIR}(\text{PPh}_3)_2$ and $\text{Pd}(\text{OCIO}_3)\text{R}(\text{PPh}_3)_2$, can be isolated.

In order to elucidate the possible pathway of this process we have studied the reaction between $\text{Pd}(\text{N}_3)_2(\text{dpe})$ and $\text{Pd}(\text{OCIO}_3)\text{R}(\text{PPh}_3)_2$ (1:2 ratio), according to eqn. 8:



which leads to a mixture of the double-bridged $[\text{Pd}(\mu\text{-N}_3)(\text{dpe})]_2(\text{ClO}_4)_2$ (15) and the single bridged $\{(\mu\text{-N}_3)[\text{PdR}(\text{PPh}_3)_2]_2\}(\text{ClO}_4)$ (3) complexes.

This shows that the R and dpe groups are retained on the original palladium atom, and that the overall process involves mobilization of only the O_3ClO^- and N_3^- groups.

Reaction between the same starting compounds, but in a 1:1 molar ratio, renders as expected a mixture of $[\text{Pd}(\mu\text{-N}_3)(\text{dpe})]_2(\text{ClO}_4)_2$ and $\text{Pd}(\text{N}_3)\text{-R}(\text{PPh}_3)_2$.

Nonetheless, single-bridged trinuclear complexes can be obtained if potentially binuclear, firmly-attached X groups are used. In this case the process represented in eqn. 6 renders the trinuclear complex (16)

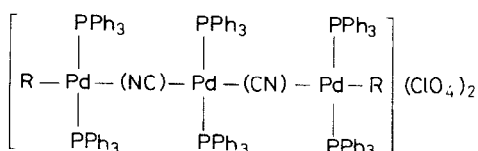


TABLE I. Analytical Results, Conductivities and Melting Points of the Complexes.^a

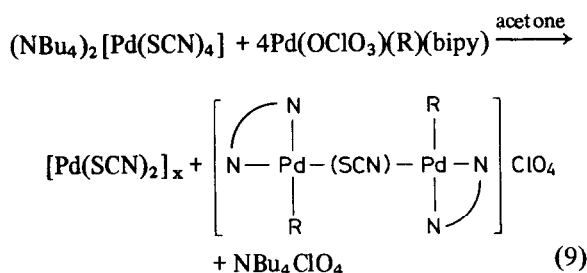
	C	N	H	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	M.P. (°C)
$[(\mu\text{-CN})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2\}_2]\text{ClO}_4$ (1)	58.94 (59.32)	0.82 (0.82)	3.65 (3.51)	129	209(d)
$[(\mu\text{-SCN})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2\}_2]\text{ClO}_4$ (2)	58.10 (58.23)	0.85 (0.80)	3.50 (3.45)	132	221(d)
$[(\mu\text{-N}_3)\{\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2\}_2]\text{ClO}_4$ (3)	58.37 (58.07)	2.51 (2.41)	3.56 (3.48)	130	220(d)
$[(\mu\text{-CN})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})\}_2]\text{ClO}_4$ (4)	40.85 (40.25)	7.01 (7.11)	1.63 (1.90)	128	300
$[(\mu\text{-SCN})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})\}_2]\text{ClO}_4$ (5)	39.17 (38.98)	7.08 (6.89)	1.80 (1.59)	129	176
$[(\mu\text{-Cl})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})\}_2]\text{ClO}_4$ (6)	38.32 (38.66)	5.88 (5.64)	1.62 (1.69)	137	212(d)
$[(\mu\text{-Br})\{\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})\}_2]\text{ClO}_4$ (7)	36.88 (37.00)	5.41 (5.39)	1.59 (1.55)	136	205(d)
$\{(\mu\text{-CN})[(\text{PPh}_3)_2(\text{C}_6\text{F}_5)\text{Pd}][\text{Pt}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]\}\text{ClO}_4$ (8)	49.16 (48.14)	0.90 (0.92)	3.89 (3.97)	131	180(d)
$[\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})(\text{PPh}_3)]\text{ClO}_4$ (9)	51.60 (51.60)	3.61 (3.54)	2.98 (2.92)	131	235
$[\text{Pd}(\mu\text{-SCN})(\text{C}_6\text{F}_5)(\text{PPh}_3)]_2$ (10)	50.41 (50.56)	2.35 (2.36)	2.77 (2.54)	0	245(d)
$\{(\mu\text{-SCN})[\text{Pd}(\text{C}_6\text{F}_5)(\text{dpe})][\text{Pd}(\text{C}_6\text{F}_5)(\text{bipy})]\}\text{ClO}_4$ (11)	46.80 (46.74)	3.37 (3.34)	2.95 (2.56)	126	155
$[(\mu\text{-SCN})_2\{\text{Pd}(\text{PPh}_3)_2\}_2](\text{ClO}_4)_2$ (12)	55.33 (56.35)	1.91 (1.78)	3.67 (3.87)	230	226(d)
$[(\mu\text{-N}_3)_2\{\text{Pd}(\text{PPh}_3)_2\}_2](\text{ClO}_4)_2$ (13)	55.66 (55.98)	5.10 (5.43)	3.91 (4.05)	218	190(d)
$[(\mu\text{-I})_2\{\text{Pd}(\text{PPh}_3)_2\}_2](\text{ClO}_4)_2$ (14)	49.52 (49.48)		3.51 (3.52)	232	240(d)
$[(\mu\text{-N}_3)_2\{\text{Pd}(\text{dpe})\}_2](\text{ClO}_4)_2$ (15)	48.12 (48.32)	6.35 (6.50)	3.58 (3.74)	210	210(d)
$\{(\mu\text{-CN})_2[(\text{PPh}_3)_2\text{Pd}][\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2]\}(\text{ClO}_4)_2$ (16)	56.66 (57.36)	1.48 (1.55)	3.89 (3.36)	202	186(d)
$\{[\text{Pd}(\mu\text{-CN})_4][\text{Pd}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2]_4\}(\text{ClO}_4)_2$ (17)	56.99 (57.36)	1.65 (1.56)	3.87 (3.35)	240	174(d)

^aCalculated values in parentheses.

Furthermore, the reaction (1:4) of $(\text{NBu}_4)_2\text{-}[\text{Pd}(\text{CN})_4]$ with $\text{Pd}(\text{OCIO}_3)_2 \cdot \text{R}(\text{PPh}_3)_2$ allows the synthesis of a pentanuclear complex $\{\text{Pd}(\mu\text{-CN})_4\text{-}[\text{PdR}(\text{PPh}_3)_2]_4\}(\text{ClO}_4)_2$ (17), which is similar to that formerly obtained by the reaction between $\text{K}_2[\text{M}(\text{CN})_4]$ ($\text{M} = \text{Pd}$ or Pt) and perchlorate tin complexes [5]. The influence of other ligands present in the complex is not to be minimized: thus the reaction of $(\text{NBu}_4)_2[\text{PdR}(\text{CN})_3]$ with $\text{Pd}(\text{OCIO}_3)_2 \cdot \text{R}(\text{PPh}_3)_2$ affords only a trinuclear complex, since the third CN group does not react, even if an excess of the perchlorate complex is being used [6].

On the other hand, the reaction (1:4) between $(\text{NBu}_4)_2[\text{Pd}(\text{SCN})_4]$ and $\text{Pd}(\text{OCIO}_3)_2 \cdot \text{R}(\text{bipy})$ leads to immediate precipitation of the reddish-brown $[\text{Pd}(\text{SCN})_2]_x$, which is filtered off. Vacuum-

evaporation of the filtrate and addition of EtOH renders the pale-yellow $\{(\mu\text{-SCN})[\text{PdRbipy}]_2\}\text{ClO}_4$ (5). The process is represented in eqn. 9:



The C, H and N analyses are in good agreement with the proposed formulae (see Table I). Complex 10 is non-conducting in solution. The conductivities

TABLE II. I.R. Relevant Data (cm^{-1}).

	a	C_6F_5	Neutral ligands
(1)	2139(2130)	1505, 1060, 950, <u>797</u> , <u>790</u>	525, 520, 498 ^b
(2)	2105(2070)	1500, 1057, 950, <u>805</u> , <u>796</u>	527, 518, 500 ^b
(3)	2098(2052)	1502, 1056, 950, <u>790</u>	530, 519, 502 ^b
(4)	2195(2140)	1505, 955, <u>794</u> (br)	1602, 768 ^c
(5)	2162(2112)	1502, 1060, 955, <u>795</u> (br)	1601, 766 ^c
(6)	320(350)	1505, 1050, 955, <u>790</u> (br)	1600, 768 ^c
(7)	—	1500, 1045, 953, <u>790</u> (br)	1600, 770 ^c
(8)	2155(2130)	1505, 1049, 957, 950, <u>800</u> , <u>780</u>	522, 513, 493 ^b
(9)	—	1500, 1055, 955, <u>795</u>	1600, 760 ^c , 540, 518, 498 ^b
(10)	2148(2070)	1505, 1060, 955, <u>798</u>	540, 515, 498 ^d
(11)	2153(2121)	1502, 1060, 955, <u>798</u> , <u>770</u>	1604, 772 ^c , 533, 480 ^e
(12)	2158(2093)	—	538, 526, 513, 495 ^b
(13)	2075(2040)	—	535, 520, 513, 495 ^b
(14)	—	—	533, 521, 512, 496 ^b
(15)	2074(2015)	—	530, 480 ^e
(16)	2157(2120)	1503, 1060, 955, <u>798</u>	528, 525, 497 ^b
(17)	2170(2115)	1500, 1060, 955, <u>790</u>	520, 512, 494 ^b

^aX-group absorptions sensitive to the terminal or bridging character of the X group. In parentheses, the values for the corresponding starting materials where X acts as terminal group. ^bAssigned to PPh_3 . ^cAssigned to bipy [24]. ^dIn agreement with data reported in ref. [25]. ^eAssigned to dpe.

of complexes 1, 2, 3, 4, 5, 6, 7, 8, 9 and 11 are those of 1:1 electrolytes, whilst complexes 12, 13, 14, 15, 16 and 17 behave as 1:2 electrolytes [13].

c) IR Spectra

All the cationic complexes exhibit absorptions at *ca.* 1100(vs,br) and 620 cm^{-1} , characteristic of the ClO_4^- anion (T_d) [14].

The cyanide derivatives (1, 4, 8, 16 and 17) show the $\nu(\text{CN})$ stretching vibration in the 2100 cm^{-1} region displaced towards higher energies relative to their location in the starting compound with terminal CN ligands, thus indicating that the ligand is acting as a bridging group [15] (Table II lists the recorded absorptions along with those of the starting compound). The same shift is observed for the thiocyanate complexes (2, 5, 10, 11 and 12) whose $\nu(\text{CN})$ absorptions of the SCN ligand in the 2100 cm^{-1} region are also observed at higher energies, as expected for SCN groups bridging two metal centres [16, 17].

The azido complexes (3, 13 and 15) show an absorption at 2100–2070 cm^{-1} (Table II), assignable to the $\nu_{\text{as}}(\text{N}_3)$ stretching, which, as expected, is also shifted towards higher energies, relative to its location in the precursor [18]. The stretching vibration $\nu(\text{Pd}-\text{Cl})$ in $[(\mu-\text{Cl})\{\text{Pd}(\text{R})(\text{bipy})\}_2]\text{ClO}_4$ (6) appears at 320 cm^{-1} , whilst for $\text{PdCl}(\text{C}_6\text{F}_5)(\text{bipy})$ it is observed at 350 cm^{-1} [19, 20].

Table II lists also some absorptions arising from the neutral ligands L, along with those due to the

C_6F_5 group [21]. The absorption or absorptions at 800 cm^{-1} (underlined in Table II) are noteworthy. They are assignable to an X-sensitive mode of the C_6F_5 group [22] and behave like a $\nu(\text{M}-\text{C})$ stretching vibration. Thus, complex 1 (C_{2v} , provided that the square planar environments of both palladium atoms lie on the same plane) shows two absorptions ($\nu(\text{M}-\text{C})$ $2A_1$, both IR active). Complex 2, whichever its overall geometry (since the bent coordination of the SCN decreases its symmetry) should show two $\nu(\text{M}-\text{C})$ absorptions, both IR active, in accordance with the observed bands. Complex 3 shows a single band, since of the two normal stretching modes $\nu(\text{M}-\text{C})$ ($A_g + B_{1u}$) only the latter is IR active (D_{2d} symmetry, under the same suppositions as for complex 1). The binuclear complexes containing bipy should also present two absorptions in this region, which in not every case could be observed. Complex 8 with C_6F_5 groups attached to different metal atoms (Pd and Pt) shows two absorptions at *ca.* 950 cm^{-1} , along with two bands in the 800 cm^{-1} region.

The trinuclear complex 16 exhibits a single band assignable to the X-sensitive mode of the pentafluorophenyl group (at 798 cm^{-1}) along with another one assignable to $\nu(\text{CN})$ (at 2157 cm^{-1}); this suggests that the CN groups are linked to the central palladium *via* the same atom (probably *via* the C atom). In this case the D_{2h} symmetry of the complex leads to two stretching modes ($A_g + B_{1u}$) for both the $\nu(\text{Pd}-\text{C}_6\text{F}_5)$ and the $\nu(\text{C}\equiv\text{N})$ vibrations, but only the B_{1u}

mode is IR active. A ($-\text{NC}-\text{Pd}-\text{NC}-$) arrangement should cause a descent of the symmetry of the molecule to C_{2v} and the two above modes (now 2 A_1) should be IR active, and is therefore discounted.

The pentanuclear complex 17 (D_{4h}) shows only one absorption assignable to the X-sensitive mode along with another one assignable to the $\nu(\text{C}\equiv\text{N})$ stretching vibration (Table II).

Complexes 1, 2, 3, 16 and 17 exhibit three absorptions at $530\text{--}500 \text{ cm}^{-1}$, assignable to internal vibrations of the ligand PPh_3 . This suggests that each palladium centre should have two mutually *trans* PPh_3 groups, whilst 12, 13 and 14 show four absorptions in this region, thus indicating that the molecules are mutually *cis* [23].

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