Single-bridged Polynuclear Pseudohalide Complexes of Palladium(II) and/or Platinum(II)

R. USÓN*, J. FORNIÉS, M. A. USÓN and M. L. MAS

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza - C.S.I.C., 50009 Saragossa (Spain)

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Abstract

By reacting $MR_2(THF)_2$ or $PtR_2(CO)_2$ (M = Pd, Pt; R = C_6F_5; THF = OC_4H_8) containing two (THF) or, respectively, one (CO) readily displaceable ligands, with monomeric palladium(II) complexes containing one potentially bridging ligand (CN, SCN), homo- or hetero-, bi- or trinuclear single bridged complexes can be synthesized. The reactions take place with stereoretention around the metal centres. Some isomers of the above described complexes have also been obtained by alternative routes.

Introduction

A variety of synthetic methods can be used to prepare homo- or heteropolynuclear pentahalophenyl palladium(II) or platinum(II) complexes [1]. One of the newer ways uses $M(C_6X_5)_2(OC_4H_8)_2$ (M = Pd, Pt; X = F, Cl) precursors which have been prepared only recently [2] and their synthetic possibilities have therefore only scantily been studied. Alternatively, $Pt(C_6X_5)_2(CO)_2$ where only one carbon monoxide ligand is readily displaceable, can also be used.

In the present paper, we report the synthesis of single-bridged polynuclear pseudohalocomplexes of palladium(II) and/or platinum(II), based on reactions between two different complementary mononuclear complexes: one of them affording the terminal but potentially bridging group(s), whilst the other one contains one or two weakly coordinating ligands, ready to vacate the corresponding coordination sites. All these reactions proceed with stereoretention [2,3].

Experimental

The starting compounds *cis*-$M(C_6F_5)_2(OC_4H_8)_2$ (M = Pd, Pt) [2], *cis*-$Pt(C_6F_5)_2(CO)_2$ [2], *trans*-$Pd(X)(C_6F_5)(PPh_3)_2$ (X = CN, SCN, $OClO_3$) [4], (NBu_4)[*trans*-$PtCl(C_6F_5)_2(CO)$] [5] and *trans*-$Pd(CN)_2(PPh_3)_2$ [6] were prepared as reported elsewhere.

Infrared spectra were recorded, over the range 4000–200 cm^{-1}, on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets; NMR spectra on a Varian XL-200 as $CDCl_3$ solutions.

C, H and N analyses were performed with a Perkin-Elmer 240B microanalyser.

All reactions were carried out in solvents purified by standard procedures and, unless otherwise stated, at room temperature. Yields are given in Table 1.

Synthesis of $(NBu_4)_2$[cis-$Pd(CN)_2(C_6F_5)_2$]

A colourless solution containing *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ (0.2924 g, 0.5 mmol) in tetrahydrofuran (5 cm^3) was treated with an excess of KCN (0.0977 g, 1.5 mmol). After 1 h stirring, methanol (5 cm^3) was added, the solution was stirred for a further 15 min and $(NBu_4)Br$ (0.3869 g, 1.2 mmol) was added, before evaporating to dryness.

The obtained white mixture was washed with water (4 × 20 cm^3), dried *in vacuo* over P_2O_5 and extracted with dichloromethane. The solvent was again removed and the solid was stirred with hexane (5 cm^3), filtered off, washed with hexane (2 × 5 cm^3) and suction dried. Yield 93%.

Synthesis of cis-$(C_6F_5)_2M[(\mu$-NC)trans-$Pd(C_6F_5)(PPh_3)_2]_2$ (M = Pd (1), Pt (2))

The compound *trans*-$Pd(CN)(C_6F_5)(PPh_3)_2$ (0.1154 g, 0.14 mmol) was added to a solution containing the corresponding complex *cis*-$M(C_6F_5)_2(OC_4H_8)_2$ (0.07 mmol) in dichloromethane (10 cm^3), and stirred.

After 5 min for compound **1** (or 30 min for compound **2**) a white precipitate was formed. After 1 h stirring, the solvent was evaporated and diethyl ether (5 cm^3) was added.

The obtained white solid was filtered off, washed with Et_2O (2 × 2 cm^3) and dried *in vacuo* over P_2O_5.

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*Author to whom correspondence should be addressed.

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TABLE 1. Analyses and ^{19}F NMR data (*ortho* region) of the complexes

	C (%)	H (%)	N (%)	Yield (%)	δ	J_{om}	J_{Pt-F}	ν(C–N)	ν(CO)
$(C_6F_5)_2Pd[(\mu\text{-}NC)Pd(C_6F_5)(PPh_3)_2]_2$ (1)	56.75	3.09	1.17	82	−116.4	24		2185m,	
	(56.36)	(2.90)	(1.34)		−117.9	26		2170m	
$(C_6F_5)_2Pt[(\mu\text{-}NC)Pd(C_6F_5)(PPh_3)_2]_2$ (2)	54.68	3.03	1.47	79	−117.9	29		2190m,	
	(54.06)	(2.78)	(1.29)		−120.1	22	487	2175m	
$(C_6F_5)_2Pt[(\mu\text{-}NCS)Pd(C_6F_5)(PPh_3)_2]_2$ (3)	52.53	2.73	1.19	86	−118.3	22		2120vs,br	
	(52.51)	(2.70)	(1.25)		−118.4	28	457		
$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}CN)$*cis*-$Pt(C_6F_5)_2(CO)$ (4)	48.75	2.28	1.00	50	−118.1	28		2180s	2103vs
	(48.70)	(2.19)	(1.01)		−119.7	22	422		
					−121.0	26	371		
$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}SCN)Pt(C_6F_5)_2(CO)$ (5)	48.17	2.36	1.07	66	−118.7	28		2155vs	2090vs
	(47.59)	(2.14)	(0.99)		−119.2	21	391		
					−119.7	22	353		
$[(PPh_3)_2(C_6F_5)Pd(\mu\text{-}NC)]_2Pd(C_6F_5)_2$ (6)	55.77	2.97	1.16	76	−114.6	28		2148m,	
	(56.36)	(2.90)	(1.34)		−118.9	28		2138s	
$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}CN)$*trans*-$Pt(C_6F_5)_2(CO)$ (7)	48.80	2.56	0.97	75	−118.3	28		2185s	2105vs
	(48.70)	(2.19)	(1.01)		−119.6	29	254		

Synthesis of cis-$(C_6F_5)_2M[(\mu\text{-}NCS)$*trans-*$Pd(C_6F_5)(PPh_3)_2]_2$ *(3)*

To a stirred solution containing *trans*-$Pd(SCN)(C_6F_5)(PPh_3)_2$ (0.1199 g, 0.14 mmol) in 10 cm^3 of dichloromethane, was added *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ (0.0471 g, 0.07 mmol).

After 90 min, the solvent was evaporated under reduced pressure and methanol (2 cm^3) was added, affording a white solid which was filtered off, washed with MeOH (1 cm^3) and suction dried.

Synthesis of trans-$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}CN)$*cis-*$Pt(C_6F_5)_2(CO)$ *(4)*

Reaction of a dichloromethane solution (10 cm^3) of *cis*-$Pt(C_6F_5)_2(CO)_2$ (0.0585 g, 0.1 mmol) with *trans*-$Pd(CN)(C_6F_5)(PPh_3)_2$ (0.0824 g, 0.1 mmol) gave a colourless solution which, after partial evaporation (to *c.* 1 cm^3) and addition of diethyl ether (3 cm^3) yielded a white solid which was filtered off, washed with ether (2 × 1 cm^3) and suction dried.

Synthesis of trans-$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}SCN)$*cis-*$Pt(C_6F_5)_2(CO)$ *(5)*

Reaction of *cis*-$Pt(C_6F_5)_2(CO)_2$ (0.0585 g, 0,1 mmol) with *trans*-$Pd(SCN)(C_6F_5)(PPh_3)_2$ (0.0856 g, 0.1 mmol) in dichloromethane (10 cm^3) gave a colourless solution.

After 1 day stirring, the solvent was evaporated under reduced pressure and methanol (3 cm^3) was added, yielding a white solid which was filtered off, washed with MeOH (2 × 1 cm^3) and dried *in vacuo* over P_2O_5.

Synthesis of cis-$(C_6F_5)_2Pd(\mu\text{-}CN)$*trans-*$Pd(C_6F_5)(PPh_3)_2]_2$ *(6)*

To an *in situ* prepared solution containing *trans*-$Pd(OClO_3)(C_6F_5)(PPh_3)_2$ (0.2 mmol) in benzene (40 cm^3) was added the stoichiometric amount of $(NBu_4)_2$[*cis*-$Pd(CN)_2(C_6F_5)_2$] (0.0977 g, 0.1 mmol).

After 90 min stirring, the solution was evaporated under reduced pressure, treated with methanol (4 cm^3) and the white solid was filtered off, washed with MeOH (2 × 3 cm^3) and suction dried. The compound was recrystallized from dichloromethane/methanol.

Synthesis of trans-$(PPh_3)_2(C_6F_5)Pd(\mu\text{-}CN)$*trans-*$Pt(C_6F_5)_2(CO)$ *(7)*

A solution containing (NBu_4)[*trans*-$Pt(OClO_3)(C_6F_5)_2(CO)$] was obtained by reaction of the stoichiometric amount of $AgClO_4$ (0.0207 g, 0.1 mmol) and (NBu_4)[*trans*-$PtCl(C_6F_5)_2(CO)$] (0.0835 g, 0.1 mmol) in 10 cm^3 of tetrahydrofuran. After 20 min stirring, the solvent was evaporated and the solid was extracted (10 cm^3) and washed (2 × 2 cm^3) with diethyl ether.

The collected filtrate and washings were evaporated to dryness and the obtained oil was dissolved in dichloromethane (10 cm^3) and stirred with *trans*-$Pd(CN)(C_6F_5)(PPh_3)_2$ (0.0824 g, 0.1 mmol) for 2 h.

The solvent was removed under reduced pressure, and methanol (2 cm^3) was added giving a white solid which was filtered off, washed with MeOH (2 × 1 cm^3) and suction dried.

Results and Discussion

The (2:1) reaction between *trans*-$Pd(CN)(C_6F_5)(PPh_3)_2$ and a complex containing two labile tetrahydrofuran ligands, *cis*-$M(C_6F_5)_2(OC_4H_8)_2$ ($M = Pd$, Pt), leads to cyanide single-bridged trinuclear compounds, according to eqn. (1).

$$\textit{cis}\text{-}M(C_6F_5)_2(OC_4H_8)_2 + 2\textit{trans}\text{-}Pd(CN)(C_6F_5)(PPh_3)_2 \xrightarrow{-2OC_4H_8} \textit{cis}\text{-}(C_6F_5)_2M[(\mu\text{-}NC)\textit{trans}\text{-}Pd(C_6F_5)(PPh_3)_2]_2 \quad (1)$$

M = Pd (1), Pt (2)

Table 1 lists elemental analyses and spectroscopic data for complexes 1 and 2.

The infrared spectra of compounds 1 and 2 show two absorptions in the 2200–2000 cm^{-1} region, assignable to the $\nu(C{\equiv}N)$ vibrations, supporting the *cis* geometry around the M centre (local symmetry C_{2v}, IR active vibrations $A_1 + B_2$). In comparison with their location in the starting material, these absorptions are shifted towards higher energies which, since a weakly antibonding $\sigma(C–N)$ orbital is used for donation, is indicative [6, 7] of a change in the rôle played by the pseudohalide ligand, from terminal in the mononuclear reagent to bridging in the products.

Generally, it should be possible to assign the geometry around the two palladium centres linked by a cyanide bridge to the central M atom from the number of bands observed in the 550–480 cm^{-1} region (four absorptions due to the PPh_3 ligands being expected [8] for a *cis* configuration, but only three for a *trans* one) but the coincidence in the same region of the bands arising from the $\nu(M–C)$ vibrations precludes any meaningful assignation. Nevertheless, the ^{31}P NMR spectra of both compounds (1 and 2) show only one signal (at $\delta = 25.0$ or 24.8 ppm, respectively); this fact confirms the retention of the *trans* geometry around the palladium centres.

The presence of the pentafluorophenyl groups is shown by their characteristic absorptions at ~1500 and ~950 cm^{-1} (the last one has been assigned to $\nu(C–F)$ and its exact position is dependent on the nature of the metal to which the C_6F_5 ligand is bonded [9]); correspondingly, one band is observed for complex 1, but two for complex 2, which contains four C_6F_5 groups, two of them bonded to platinum and the other two each bonded to a palladium centre.

From the X-sensitive mode [10] of the pentafluorophenyl ligands, (820–760 cm^{-1} region), three bands (or for complex 1 two, one of them broad) arise, in agreement with that expected for compounds containing two C_6F_5 groups linked in mutually *cis* positions to a central metal atom which is CN-bridged to two other metal centres, each containing one C_6F_5 ligand.

The ^{19}F NMR spectra of complexes 1 and 2 show in the *ortho* fluorine region (−110 to −120 ppm), two doublets (one of them with 195-platinum satellites, in the case of compound 2) as expected for the proposed geometry.

The reactions of *cis*-$M(C_6F_5)_2(OC_4H_8)_2$ with *trans*-$Pd(SCN)(C_6F_5)(PPh_3)_2$ follow different paths, depending on the nature of M. For M = Pt, a trinuclear complex (3), similar to the above described ones, is obtained (eqn. (2)).

$$\textit{cis}\text{-}Pt(C_6F_5)_2(OC_4H_8)_2 + 2\textit{trans}\text{-}Pd(SCN)(C_6F_5)(PPh_3)_2 \xrightarrow{-2OC_4H_8} \textit{cis}\text{-}(C_6F_5)_2Pt[(\mu\text{-}NCS)\textit{trans}\text{-}Pd(C_6F_5)(PPh_3)_2]_2 \quad (2)$$

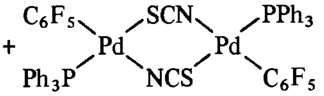
The infrared spectrum of complex 3 shows a single band in the $\nu(C{\equiv}N)$ region (2200–2000 cm^{-1}), displaced to higher energies than that in the mononuclear starting compound, supporting the bridging character of the sulphocyanide group [11]. This band is a broad one, ($\Delta\nu_{1/2} \sim 50$ cm^{-1}), possibly enveloping the two absorptions expected for a *cis* geometry around the platinum metal centre. Moreover, two absorptions (one of them broad) are observed in the 820–760 region (X-sensitive mode of the pentafluorophenyl ligand) as required by the *cis* geometry.

The ^{19}F NMR spectrum of complex 3 shows (in the range assignable to the *ortho* fluorine substituents) two partially overlapping doublets which integrate for an equal number of nuclei. Their assignment is made possible (Table 1) by the 195-platinum satellites observed for the C_6F_5 ligands bonded to the central platinum atom.

When M = Pd, however, a different reaction (eqn. (3)) takes place and a binuclear palladium complex with a double sulphocyanide bridge is formed, as a consequence of the ability of the SCN ligands to form 'bent' bridges in comparison with the linear ones formed by the cyanide groups (complexes 1 and 2).

$$\textit{cis}\text{-}Pd(C_6F_5)_2(OC_4H_8)_2 + 2\textit{trans}\text{-}Pd(SCN)(C_6F_5)(PPh_3)_2 \xrightarrow{-2OC_4H_8}$$

trans-$Pd(C_6F_5)_2(PPh_3)_2$ +



(3)

This different behaviour is not in the least surprising: the same binuclear compound has previously been obtained from the reactions of *trans*-Pd(SCN)-$(C_6F_5)(PPh_3)_2$ with other PPh_3 abstracting substrates [12, 13].

Reactions between equimolecular amounts of *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ and a bis(cyano) compound such as *trans*-$Pd(CN)_2(PPh_3)_2$ seem very promising for the synthesis of complexes of higher nuclearity (eqn. (4)).

$$\textit{cis}\text{-}Pd(C_6F_5)_2(OC_4H_8)_2 + \textit{trans}\text{-}Pd(CN)_2(PPh_3)_2 \xrightarrow{-2OC_4H_8} 1/x[\mu\text{-}(NC)Pd(PPh_3)_2(\mu\text{-}CN)M(C_6F_5)_2]_x \quad (4)$$

The white solid which can be isolated from this reaction analyses correctly for the proposed stoichiometry, shows one infrared absorption in the $\nu(C{\equiv}N)$ region, shifted to higher energies than that of the starting material. Nevertheless, the broadness of that band points to a mixture of complexes (with x spanning a range of different values) containing bridging cyanide groups in similar but not identical environments. In support of this proposal, the ^{19}F NMR spectrum of the solid shows very broad bands, resulting from superimposed signals.

The starting complex *cis*-$Pt(C_6F_5)_2(CO)_2$ behaves differently, since only one of the carbon monoxide ligands is readily displaced by either neutral or anionic nucleophiles, the second CO group being displaced in reactions with chelating ligands [2].

The reactions between the dicarbonyl complex and pseudohalo complexes have been monitored by infrared spectroscopy in the 2200–2000 cm^{-1} region, where both $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$ appear. Formation of the pseudohalide bridge is expected to result in an increase of the energy of $\nu(C{\equiv}N)$ (see above) together with a frequency decrease of $\nu(C{\equiv}O)$, if the monocarbonyl compound is formed [2, 7].

The (1:1) reaction between *cis*-$Pt(C_6F_5)_2(CO)_2$ and a pseudohalo complex of palladium (eqn. (5)) yields white solids which analyse correctly for the proposed stoichiometry (see Table 1).

$$\textit{cis}\text{-}Pt(C_6F_5)_2(CO)_2 + \textit{trans}\text{-}Pd(X)(C_6F_5)(PPh_3)_2 \xrightarrow[-CO]{CH_2Cl_2} \longrightarrow \textit{trans}\text{-}(PPh_3)_2(C_6F_5)Pd(\mu\text{-}X)\textit{cis}\text{-}Pt(C_6F_5)_2(CO) \quad (5)$$

X = CN (**4**), SCN (**5**)

Their infrared spectra show two bands in the 2200–2000 cm^{-1} region, one of them at higher frequency than that of the terminal X ligand in the starting material, therefore assignable to the bridging group, and the second one at lower energies than that observed in the *cis*-dicarbonyl complex, corresponding to the terminal CO ligand.

Two absorptions (or, for complex **5**, a broad one) are observed in the 950 cm^{-1} region, as required for a compound containing C_6F_5 groups attached to both a platinum and a palladium centre, while three bands (or, respectively, two for the SCN derivative) appear in the 820–760 cm^{-1} region, which are assignable to the X-sensitive mode of the pentafluorophenyl ligands.

The *cis* geometry around the platinum centre is proved by the ^{19}F NMR spectra, which show in the −110 to −120 ppm range (*ortho* fluorine) three groups of signals (1:1:1 integral), two of them along with the corresponding 195-platinum satellites.

Synthesis of Isomers

(i) A linkage isomer of complex **1** can be obtained (eqn. (6)) by the (1:2) reaction between the anionic $(NBu_4)_2[\textit{cis}\text{-}Pd(CN)_2(C_6F_5)_2]$ and the perchlorato complex $Pd(OClO_3)(C_6F_5)(PPh_3)_2$, where the $OClO_3$ group is readily displaceable.

$$(NBu_4)_2[\textit{cis}\text{-}Pd(CN)_2(C_6F_5)_2] + 2\textit{trans}\text{-}Pd(OClO_3)(C_6F_5)(PPh_3)_2 \longrightarrow (C_6F_5)_2Pd[(\mu\text{-}CN)Pd(C_6F_5)(PPh_3)_2]_2 + 2(NBu_4)ClO_4 \quad (6)$$

The desired compound **6** can be isolated as a white solid, whose infrared spectrum shows two absorptions in the 2200–2000 cm^{-1} region, thereby confirming the expected configuration retention around the central palladium atom. These bands appear at higher frequencies than those observed in the starting material, as expected for the change from terminal to bridging cyanide groups.

Two bands and a shoulder are found in the 820–760 cm^{-1} region (X-sensitive mode of the pentafluorophenyl moiety) in good agreement with that expected for a compound containing two mutually *cis* C_6F_5 ligands coordinated to a palladium centre, together with the other two C_6F_5 groups, each linked to a terminal metal centre.

The ^{19}F NMR spectrum shows (in the *ortho* fluorine range) two doublets which integrate for an equal number of nuclei, while a single peak in the ^{31}P NMR spectrum confirms the *trans* coordination of the triphenylphosphine ligands.

An analogous linkage isomer of complex **2** has not been prepared since the necessary starting compound

$(NBu_4)_2$[*cis*-$Pt(CN)_2(C_6F_5)_2$] could not be synthesized.

(ii) The all *trans* isomer of complex 4 can be prepared (eqn. (7)) using instead of the dicarbonyl derivative its own precursor [2] which readily undergoes displacement of the labile perchlorato ligand to afford the desired CN-bridged heterobinuclear complex (7). Its infrared spectrum shows two absorptions in the 2200–2000 cm^{-1} region: the one at 2185 cm^{-1} is assignable to the bridging CN group, the other at 2105 cm^{-1} to the terminal CO group (see above).

$$(NBu_4)[\textit{trans}\text{-}Pt(OClO_3)(C_6F_5)_2(CO)] + \textit{trans}\text{-}Pd(CN)(C_6F_5)(PPh_3)_2 \longrightarrow \textit{trans}\text{-}(PPh_3)_2(C_6F_5)Pd(\mu\text{-}CN)\textit{trans}\text{-}Pt(C_6F_5)_2(CO) + NBu_4(ClO_4) \quad (7)$$

Two absorptions at 958 and 952 cm^{-1} confirm the presence of pentafluorophenyl ligands linked to both palladium and platinum centres. A broad band with a shoulder observed in the 820–760 cm^{-1} region should be the envelope of the two expected signals (one for the two mutually *trans* C_6F_5 groups linked to the platinum atom and one for the C_6F_5 group attached to palladium).

The ^{19}F NMR spectrum shows two groups of signals (which integrate 1:2) in the *ortho* fluorine region, the doublet at lower field showing 195-platinum satellites.

Other Attempted Reactions

The (1:2) reaction between *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ and *trans*-$Pt(CN)(C_6F_5)(PEt_3)_2$ was studied (in CH_2Cl_2 at room temperature or at reflux, in refluxing $CHCl_3$ or refluxing 1,2-dichloroethane), without any conclusive result. No perceptible interaction seemed to take place in solution.

The preparation of trinuclear complexes by the (2:1) reaction of *cis*-$Pt(C_6F_5)_2(CO)_2$ and *trans*-$M(CN)_2(PPh_3)_2$ (M = Pd, Pt) was attempted but, when M = Pd, a solid with a N content higher than the expected one was obtained. When M = Pt, both the dicyano starting product and the reaction product gave low C, H and N analyses, although the ^1H and ^{19}F NMR spectra show the expected peaks.

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