Inorganica Chimica Acta, *187* (1991) 175–180

Anionic pentafluorothiophenolato complexes of palladium(II) or platinum(II)

R. Usón, J. Forniés, M. A. Usón and J. A. Apaolaza

Department of Inorganic Chemistry, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza — C.S.I.C., 50009 Saragossa (Spain)

(Received May 6, 1991)

Abstract

By reacting $Tl(SC_6F_5)$ with halide containing complexes of palladium(II) or platinum(II), mono- or binuclear compounds with terminal and/or bridging pentafluorothiophenolato groups can be obtained. Treatment of the latter ones with triphenylphosphine causes bridge-cleavage affording *cis*-mononuclear compounds.

Introduction

Pentafluorophenyl palladium or platinum complexes and their capability as starting products for the synthesis of polynuclear derivatives is the subject of our current research [1, 2] and only in a few cases has the pentafluorophenyl group been found to act as a bridging ligand [3].

As it is well known that thiolates tend to act as bridging ligands [4] and taking into account that the use of potentially good bridging ligands is in most cases a prerequisite for synthesizing polynuclear complexes, we, therefore, decided to explore the synthesis of pentafluorothiophenolato palladium or platinum derivatives.

In this paper we describe the preparation of mono- or polynuclear palladium or platinum complexes containing bridging and/or terminal $C_6F_5S^-$ groups, and mixed pentafluorophenyl and pentafluorobenzenethiolato derivatives and study their reactivity towards neutral mono- or bidentate ligands.

The structure of the obtained complexes is discussed on the bases of ^{19}F, ^{31}P NMR and IR data.

Experimental

The starting compounds $Tl(SC_6F_5)$ [5], $(NBu_4)_2[M(\mu\text{-}X)(C_6F_5)_2]_2$ (M = Pd, X = Br; M = Pt, X = Cl) [6, 7] and $(NBu_4)_2[Pt(C_6F_5)_4]$ [6] were prepared by previously published procedures.

IR spectra were recorded, over the range 4000–220 cm^{-1}, on a Perkin-Elmer 1730FT spectrophotometer, using Nujol mulls between polyethylene sheets; NMR spectra on a Varian XL-200 as hexadeuteroacetone solutions.

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

All reactions were carried out at room temperature, in solvents purified by standard procedures. Yields are given in Table 1; NMR and IR data in Tables 2 and 3, respectively.

Synthesis of $(NMe_4)_2[Pd(SC_6F_5)_4]$

$(NMe_4)_2[PdCl_4]$ (0.3965 g, 1 mmol) was suspended in 20 cm^3 of acetone and the addition of $Tl(SC_6F_5)$ (1.6140 g, 4 mmol) immediately gave rise to a deep red colour.

After 4 days, the formed TlCl was filtered off and, after partial evaporation (to *c*. 4 cm^3), the solid was filtered off and washed with acetone (1 cm^3).

Synthesis of $(NMe_4)_2[Pt(SC_6F_5)_4]$

The compound $(NMe_4)_2[PtCl_4]$ (0.0970 g, 0.2 mmol) was added to a solution containing $Tl(SC_6F_5)$ (0.3228 g, 0.8 mmol) in acetone (20 cm^3). The solution slowly turned yellow and, after 16 h stirring, the formed TlCl was filtered off and the solvent removed under vacuum.

Addition of isopropylic alcohol (7 cm^3) afforded a yellow solid which was filtered off, washed with ^iPrOH (1 cm^3) and suction dried.

Synthesis of $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$

A solution of $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$ (0.1526 g, 0.1 mmol) in acetone (20 cm^3) was treated with $Tl(SC_6F_5)$ (0.0807 g, 0.2 mmol) and a light yellow precipitate was formed immediately.

0020-1693/91/$3.50

TABLE 1. Elemental analysis, molar conductivity and yields

Compound	C (%)	H (%)	N (%)	$c \times 10^{-4}$	Λ_M	Yield
1 $(NBu_4)_2[Pd(SC_6F_5)_4]$	36.6 (36.7)	2.3 (2.3)	2.3 (2.7)	5.2	165.0	57
2 $(NMe_4)_2[Pt(SC_6F_5)_4]$	33.9 (33.7)	2.0 (2.1)	2.4 (2.5)	5.2	152.3	61
3 $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$	45.9 (46.3)	4.0 (4.1)	1.3 (1.6)	5.1	204.0	70
4 $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$	42.1 (42.1)	3.8 (3.7)	1.2 (1.4)	5.1	207.0	81
5 $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$	43.3 (43.2)	3.8 (3.8)	1.5 (1.5)	5.1	212.8	93
6 $(NMe_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$	30.5 (30.5)	1.1 (1.4)	1.6 (1.6)	5.1	195.6	85
7 (NBu_4)*cis*-$[Pd(SC_6F_5)(C_6F_5)_2(PPh_3)]$	54.4 (54.6)	4.3 (4.5)	1.2 (1.2)	5.1	95.1	92
8 (NBu_4)*cis*-$[Pt(SC_6F_5)(C_6F_5)_2(PPh_3)]$	50.4 (50.7)	4.1 (4.2)	1.2 (1.1)	5.9	93.1	84
9 $(NBu_4)[Pd(SC_6F_5)_3(PPh_3)]$	51.7 (51.7)	4.4 (4.3)	1.0 (1.2)	5.6	91.6	84
10 $(NEt_4)[Pt(SC_6F_5)_3(PPh_3)]$	44.4 (44.6)	3.0 (3.0)	1.2 (1.2)	5.1	140.2	69
11 $(NBu_4)_2[Pt_2(\mu\text{-}dppm)(SC_6F_5)_2(C_6F_5)_4]$	48.7 (48.0)	4.3 (4.1)	1.1 (1.2)	5.4	194.5	53
12 $(NBu_4)_2[Pt(SC_6F_5)_2(C_6F_5)_2]$	46.2 (45.6)	5.0 (4.9)	1.8 (1.9)	5.4	197.3	62

TABLE 2. ^{19}F and ^{31}P NMR data for complexes **1–12**

	C_6F_5			SC_6F_5		PR_3	
	δ	$J_{o\text{-}m}$	$J(Pt\text{-}F)$	δ	$J_{o\text{-}m}$	δ	$^1J(Pt\text{-}P)$
1				−130.8	23.0		
2				−131.4	22.5		
3	−115.3	29.3		−129.2	24.4		
4	−117.0	26.8	449	−129.0	21.4		
5				−131.3^a	23.9		
				−126.9^b	^{c}		
6				−129.1^a	20.3		
				−131.7^b	^{c}		
7	−112.3^d	26.8		−130.8	22.3	26.0	
	−112.9^e	32.3					
8	−115.1^d	^{c}	350	−130.4	21.7	24.1	2633
	−115.7^e	34.1	409				
9				−131.8^d	22.5	30.5	
				−132.2^e	24.1		
10				f	f	20.0	3440
11	−114.4^d	12.2	342	−129.7	22.3	13.1	2630
	−115.1^e	32.9	406				
12	−113.1	29.3	303	−130.1	23.3		

[a]Terminal ligand. [b]Bridging ligand. [c]Unresolved (broad signal). [d]*cis* to phosphine. [e]*trans* to phosphine. [f]Superimposing signals.

After 10 min stirring, the solid TlBr was filtered off, and the solution was evaporated to dryness. Addition of diethyl ether afforded a pale yellow solid, which was filtered off and washed with ether (2×1 cm^3).

Synthesis of $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$

To a solution containing $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.3233 g, 0.2 mmol) in acetone (10 cm^3), was added $Tl(SC_6F_5)$ (0.1614 g, 0.4 mmol); a white precipitate was immediately observed.

After 65 h stirring, the formed TlCl was filtered off and the solvent removed under reduced pressure. The remaining white solid was stirred with diethyl ether (3 cm^3), filtered off and washed with Et_2O (2×2 cm^3).

Synthesis of $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$

A suspension of $(NBu_4)_2[Pd(\mu\text{-}Br)Br_2]_2$ (0.2943 g, 0.25 mmol) in acetone (20 cm^3) was treated with $Tl(SC_6F_5)$ (0.6052 g, 1.5 mmol).

After 54 h stirring, the formed white TlCl was filtered off and the solvent was removed under vacuum. Addition of diethyl ether (7 cm^3) afforded an orange solid which was filtered off, washed with Et_2O (2×3 cm^3) and dried *in vacuo* over P_2O_5.

TABLE 3. Some characteristic IR absorptions of the fluorinated and phosphine ligands

	ν(C–S)	X-sensitive	ν(C–F)	ν(C–C)	Phosphine
1	858vs		954vs,sh, 973vs,br, 1014m	1627m 1076vs, 1095m,sh, 1123m	
2	856s		954w,sh, 972s,br, 1075s, 1126w	1510m,sh, 1628w	
3	850s	775s, 784s	952vs, 973vs, 1005m, 1056m 1080vs, 1093m, 1154vs	1605w, 1630s	
4	846s	788s, 799s	954s, 973s,br, 1005m 1058s,br, 1080s, 1152m	1601w, 1631w	
5	857s		972s, 1005w, 1081s, 1127w,sh	1506s,sh, 1626w	
6	856s,br		973s,br, 1085s,br, 1131w	1516m,sh, 1640w	
7	858s	771m, 781s	953vs,br, 970vs, 1000w 1044s, 1056s, 1080s	1500vs,sh, 1636w	496m, 509s, 528s 700s, 1099s, 1436vs,sh
8	855s	783m, 794s	954vs, 970vs, 1013w 1055s, 1079s, 1158w	1500s,sh, 1607w, 1636w	497m, 514s, 534s 699m, 1097s
9	855vs		970vs,br, 1001m,sh 1071s,sh, 1081vs, 1269m,br	1506vs,sh, 1621w	493m, 513s, 599s, 693s 704s, 753m,sh, 1093s, 1438vs,sh
10	855vs		778w, 971vs, 1002m 1077vs, 1130w, 1192m	1621w	493m, 519s, 539s, 705s, 744s 756m, 1097s, 1435vs,sh, 1440vs,sh
11	855s	780m, 794m	954s, 972s, 1057s, 1081s	1501s,sh, 1634w	483w, 509w, 696m,sh 1029w, 1095m,
12	853s	765m	952m, 969vs, 1042m 1055m, 1077s, 1152w	1501s,sh 1622w	

Synthesis of $(NMe_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$

To a suspension of $(NMe_4)_2[Pt(SC_6F_5)_4]$ (0.2850 g, 0.25 mmol) in methanol (20 cm^3) was added 1.08 cm^3 of concentrated hydrochloric acid/methanol (2:48); the solid turned slowly yellow.

After 5 days stirring, the solid was filtered off, washed with dichloromethane (1 cm^3) and suction dried.

Synthesis of $(NBu_4)[cis\text{-}Pd(SC_6F_5)(C_6F_5)_2PPh_3]$

To a solution containing $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ (0.8821 g, 0.5 mmol) in acetone (20 cm^3) was added PPh_3 (0.2623 g, 1.0 mmol).

After stirring for 80 h, the solvent was removed and the addition of diethyl ether (6 cm^3) gave a white solid, which was filtered off and washed with Et_2O (2×3 cm^3).

Synthesis of $(NBu_4)[cis\text{-}Pt(SC_6F_5)(C_6F_5)_2PPh_3]$

Triphenylphosphine (0.0367 g, 0.14 mmol) was added to a solution containing $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ (0.1359 g, 0.07 mmol) in acetone (15 cm^3).

After stirring for 6 days, the solvent was evaporated and the remaining white solid was treated with diethyl ether (2 cm^3), filtered off and dried *in vacuo* over P_2O_5.

Synthesis of $(NBu_4)_2[Pt_2(\mu\text{-}dppm)(SC_6F_5)_2(C_6F_5)_4]$

To a solution containing $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ (0.1359 g, 0.07 mmol) in acetone (15 cm^3) was added $Ph_2PCH_2PPh_2$ (0.0269 g, 0.07 mmol).

After 60 h stirring, the solvent was removed under vacuum and diethyl ether (3 cm^3) was added yielding a red solid which was filtered off, washed with Et_2O (2 cm^3) and dried *in vacuo* over P_2O_5.

Synthesis of $(NBu_4)[Pd(SC_6F_5)_3(PPh_3)]$

To a solution of $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ (0.0946 g, 0.05 mmol) in acetone (20 cm^3) was added PPh_3 (0.0262 g, 0.1 mmol).

After 80 h stirring, the solvent was removed and isopropyl alcohol (2 cm^3) was added. The orange solid was filtered off, washed with ^iPrOH (1 cm^3) and suction dried.

Synthesis of $(NEt_4)[Pt(SC_6F_5)_3(PPh_3)]$

An excess of PPh_3 (0.0315 g, 0.12 mmol) was added to a solution containing $(NEt_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ (0.0556 g, 0.03 mmol) in acetone (20 cm^3).

After stirring for 10 days, the solution was evaporated to dryness and the yellow solid was stirred with diethyl ether (3 cm^3), filtered off, washed with Et_2O (1 cm^3) and dried *in vacuo* over P_2O_5.

Synthesis of $(NBu_4)_2[trans\text{-}Pt(SC_6F_5)_2(C_6F_5)_2]$

The addition of $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.1348 g, 0.1 mmol) to a solution containing HSC_6F_5 (0.2 mmol, 0.0267 cm^3) in methanol (20 cm^3) immediately gave rise to a yellow colour.

After 24 h, the solvent was removed under vacuum and n-butyl alcohol (3 cm^3) was added. The yellow solid was filtered off, washed with ^{n}BuOH (2×1 cm^3) and suction dried.

Results and discussion

Dianionic mono- or dinuclear complexes

The tetrachlorometallate salts $(NMe_4)_2[MCl_4]$ (M = Pd, Pt) react (4:1) with $Tl(SC_6F_5)$ to give according to eqn. (1) the corresponding mononuclear thiolato complexes

$$(NMe_4)_2[MCl_4] + 4Tl(SC_6F_5) \longrightarrow 4TlCl\downarrow + (NMe_4)_2[M(SC_6F_5)_4] \qquad (1)$$

M = Pd (**1**), Pt (**2**)

whose synthesis had already been described [8, 9] although in lower yields.

The ^{19}F NMR spectra of these complexes show in the *ortho* fluorine region (−110 to −135 ppm) one doublet whose chemical shifts agree with those reported [8]. No coupling to ^{195}Pt is observed in the case of compound **2** (i.e. $^4J(F\text{–}Pt) \cong 0$).

Binuclear complexes with two bridging pentafluorothiophenolato ligands can readily be obtained as white stable solids, from the metathetical reaction (2:1) between $Tl(SC_6F_5)$ and the corresponding $[M(\mu\text{-}X)(C_6F_5)_2]_2$, according to eqn. (2).

$$(NBu_4)_2[M(\mu\text{-}X)(C_6F_5)_2]_2 + 2Tl(SC_6F_5) \longrightarrow 2TlX\downarrow + (NBu_4)_2[M(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2 \qquad (2)$$

M = Pd, X = Br (**3**); M = Pt, X = Cl (**4**)

Their ^{19}F NMR spectra show (in the range characteristic for *ortho* fluorine substituents) two doublets (2:1 integration), that at higher frequencies assignable to the pentafluorophenyl groups while that at higher fields corresponds to the pentafluorobenzenethiolato ligands. In the case of compound **4**, only the doublet arising from the C_6F_5 moieties shows ^{195}Pt satellites.

Reaction (1:6) between the binuclear $[Pd_2Br_6]^{2-}$ and thallium pentafluorothiophenolate in acetone yields the expected homoleptic compound (eqn. (3))

$$(NBu_4)_2[Pd(\mu\text{-}Br)Br_2]_2 + 6Tl(SC_6F_5) \longrightarrow (NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2 + 6TlBr\downarrow \qquad (3)$$

which can be isolated as a red solid **5**. On the other hand, treatment of the analogous $(NEt_4)_2[Pt(\mu\text{-}Cl)Cl_2]_2$ with thallium pentafluorothiophenolate gives a mixture of two compounds (in variable proportions) which could not be separated; the mixture is formed even in methylisobutylketone at reflux temperature. The desired compound **6** can best be obtained by treating a methanol solution of the mononuclear $(NMe_4)_2[Pt(SC_6F_5)_4]$ with an excess of hydrochloric acid.

$$2(NMe_4)_2[Pt(SC_6F_5)_4] + 2HCl \longrightarrow 2HSC_6F_5 + 2(NMe_4)Cl + (NMe_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2 \qquad (4)$$

The ^{19}F NMR spectra of these complexes show (in the *ortho* fluorine region) two groups of signals (which integrate 1:2): a broad resonance assigned to the bridging ligands and a doublet, at lower frequencies, which must correspond to the terminal thiolato groups.

The broadness of the signal at higher frequency must arise from a dynamic process, with a low rate at room temperature. Two different explanations seem possible: the bridging SC_6F_5 moieties might experience a rotation process around the $S\text{–}C_{ipso}$ bonds, hindered by an *o*-fluorine–metal interaction of the kind found in the solid state for some related compounds [10, 11]; or there might be an equilibrium between the *syn* and *anti*-planar geometries, through inversion at the sulfur centre [4, 12].

^{19}F NMR spectra of d^6-acetone solutions of complexes **5** and **6** were recorded at different temperatures, ranging from +55 to −85 °C. At +55 °C the broad signal becomes sharper but is not resolved yet; thus, fast exchange is not attained. On the other hand, at temperatures below 0 °C (*c.* −25 °C for compounds **5**, −55 °C for **6**) the signal further broadens and disappears in the baseline, although it can still be integrated; at even lower temperatures, the broad absorption resolves in two doublets.

The spectrum of **6** in CD_2Cl_2/acetone (2:1) at −95 °C clearly shows these two doublets, along with that assignable to the terminal thiolato groups. Since no coupling to ^{195}Pt is observed, the dynamic process is assumed to be an equilibrium between the *syn* and *anti*-planar isomers.

Bridge cleavage reactions

Thiolato ligands are known [4] for their tendency to act as a bridge between transition metal centres, so it seemed interesting to study the stability of the above described binuclear compounds towards neutral or anionic species.

No reaction takes place between $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ (**4**) and HCl in acetone/methanol even after one month stirring, as shown by ^{19}F NMR and IR spectroscopies. Again, treatment of $(NEt_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ (**5**) in acetone/methanol with aqueous concentrated hydrochloric acid renders the unchanged starting materials. This lack of reaction must be compared with the easy cleavage of the metal–carbon bonds in the case of $(NBu_4)_2[M(C_6F_5)_4]$ (M = Pd, Pt) [6] and of the metal–sulfur bonds in $[Pt(SC_6F_5)_4]^{2-}$ (see above, eqn. (4)) by HCl.

On the other hand, 2,2′-bipyridine does not react with $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ even after 18 days stirring, as shown by ^{19}F NMR and IR spectroscopies.

The binuclear thiolato-bridged $(NBu_4)_2[M(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ react (1:2) with triphenylphosphine to give (eqn. (5)) the desired mononuclear compounds

$$(NBu_4)_2[M(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2 + 2PPh_3 \longrightarrow 2(NBu_4)[cis\text{-}M(SC_6F_5)(C_6F_5)_2PPh_3] \quad (5)$$

M = Pd (**7**), Pt (**8**)

Their IR spectra show two absorptions in the 800–760 cm^{-1} region, assignable to the X-sensitive mode of the pentafluorophenyl ligands [13]. This does not allow us to distinguish *cis* from *trans* geometry, since two bands are theoretically expected for both configurations. However, previous studies on bis(pentafluorophenyl) complexes show that only one is observable for a *trans* arrangement [13, 14], so that complexes **7** and **8** should be the *cis* isomers.

Moreover, the ^{19}F NMR spectra of compounds **7** and **8** show (in the range characteristic of *ortho* fluorine substituents) three doublets (which integrate 1:1:1), proving the proposed *cis* configuration. The signals at higher frequencies (which in the case of complex **8** show platinum satellites) must be assigned to the C_6F_5 ligands, that *trans* to the phosphine displaying an unresolved coupling to ^{31}P.

Retention of configuration has been found for other bridge-cleavage processes on perhalophenyl dipalladium or diplatinum complexes [15, 16].

The ^{31}P NMR spectra show in every case a signal with an unresolved coupling to the fluorine nuclei of the *trans* pentafluorophenyl ligand, in the case of complex **8** along with the corresponding ^{195}Pt satellites.

The homoleptic $(NR_4)_2[M(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ also react (1:2) with triphenylphosphine (eqn. (6))

$$(NR_4)_2[M(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2 + 2PPh_3 \longrightarrow 2(NR_4)[M(SC_6F_5)_3(PPh_3)] \quad (6)$$

M = Pd, R = Bu (**9**); Pt, R = Me (**10**)

The ^{19}F NMR spectrum of the palladium derivative shows two doublets (that a lower field integrating for twice as many nuclei) in the *ortho* fluorine region, whereas for the platinum complex the doublets are almost superimposed and cannot be told apart.

The ^{31}P NMR spectra show a single signal, along with platinum satellites for compound **10**, as expected for all phosphine ligands being equivalent.

Bis(diphenylphosphino)methane reacts towards the binuclear complexes in a different way, depending on the substrate.

Thus, reaction (1:1) with $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ affords the expected diphosphine-bridged binuclear compound **11**, according to eqn. (7).

$$(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2 + dppm \longrightarrow cis,cis\text{-}(NBu_4)_2[(SC_6F_5)(C_6F_5)_2Pt(\mu\text{-}dppm)Pt(SC_6F_5)(C_6F_5)_2] \quad (7)$$

Its ^{19}F NMR spectrum shows (in the region assignable to *ortho* fluorine) a doublet and a broad peak (as a consequence of unresolved coupling to the *trans* phosphorus nucleus) both with platinum satellites and partly overlapping, arising from the pentafluorophenyl moieties, and a doublet at higher field with no satellite signals, assignable to the pentafluorothiophenolate ligand.

The ^{31}P NMR spectrum shows a single peak with platinum satellites, as expected. All three signals are somewhat broadened by coupling to the fluorine nuclei of the C_6F_5 group *trans* to the phosphine [17, 18].

The IR spectrum of compound **11** shows two absorptions for the X-sensitive vibration of the pentafluorophenyl moieties [3], in agreement with a *cis* configuration around the metal centres.

The reaction (1:1) of the homoleptic $(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ with bis(diphenylphosphino)methane takes a different route

$$(NBu_4)_2[Pt(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2 + dppm \longrightarrow (NBu_4)_2[Pt(SC_6F_5)_4] + [Pt(SC_6F_5)_2(P,P'\text{-}dppm)] \quad (8)$$

and asymmetric cleavage of the bridge takes place, as shown by ^{19}F and ^{31}P NMR, and IR spectroscopy.

On the other hand, reaction (1:1) of bis(diphenylphosphino)methane with $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ or $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ yields in both cases a complex mixture of unidentified compounds.

Reactions with pentafluorothiophenol

The homoleptic $[M(C_6F_5)_4]^{2-}$ complexes (M = Pd, Pt) are known to react with hydrochloric acid in methanol by cleavage of one or two of the metal–carbon bonds, depending on the metal and the ratio of the reactants [6].

In view of the acid character of pentafluorothiophenol, equimolecular amounts of HSC_6F_5 and $(NBu_4)_2[Pt(C_6F_5)_4]$ were stirred in methanol, leading to a mixture of the starting material and two other products. Reaction (2:1) yielded a single product (eqn. (9)), which is also present in the above mentioned mixture, as shown by ^{19}F NMR spectroscopy. Thus, the reaction must be a stepwise one, although the monosubstituted compound could not be isolated.

$$(NBu_4)_2[Pt(C_6F_5)_4] + 2HSC_6F_5 \longrightarrow$$

$$\text{‘}(NBu_4)_2[Pt(C_6F_5)_3(SC_6F_5)] + HSC_6F_5 + C_6F_5H \longrightarrow\text{’}$$

$$(NBu_4)_2[\textit{trans}\text{-}Pt(C_6F_5)_2(SC_6F_5)_2] + 2C_6F_5H \qquad (9)$$

In the ^{19}F NMR spectrum of the solid isolated from the 2:1 reaction, two doublets are observed in the *ortho* fluorine region, that at low field assignable to the pentafluorophenyl groups, since it shows platinum satellites. The IR spectrum of this compound shows only one absorption in the 800–760 cm^{-1} region, assigned to the X-sensitive mode of the pentafluorophenyl ligand [13], thus supporting a *trans* geometry around the platinum centre.

Reaction (1:2) between $(NBu_4)_2[Pd(SC_6F_5)_4]$ and pentafluorothiophenol gave a complex mixture which was not further investigated.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica and the Consejo Superior de Investigaciones Científicas for financial support (project PB88-0076).

References

1 R. Usón and J. Forniés, *Adv. Organomet. Chem., 28* (1988) 219.
2 R. Usón and M. A. Usón, in P. Braunstein (ed.), *Recent Advances in Di- and Polynuclear Chemistry, New J. Chem., 12* (1988) 707.
3 R. Usón, J. Forniés, M. Tomás, J. M. Casas and R. Navarro, *J. Chem. Soc., Dalton Trans.,* (1989) 169.
4 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev., 76* (1987) 121.
5 M. E. Peach, *Can. J. Chem., 46* (1968) 2699.
6 R. Usón, J. Forniés, M. Tomás and R. Fandos, *J. Organomet. Chem., 263* (1984) 253.
7 R. Usón, J. Forniés, F. Martinez and M. Tomás, *J. Chem. Soc., Dalton Trans.,* (1980) 888.
8 W. Beck, K. H. Stetter, S. Tadros and K. E. Schwarzhans, *Chem. Ber., 100* (1967) 3944.
9 R. S. Nyholm, J. F. Skinner, M. H. B. Stiddard, W. Ramsay and R. Forster, *J. Chem. Soc. A,* (1968) 38.
10 R. Usón, J. Forniés and M. Tomás, *J. Organomet. Chem., 358* (1988) 525.
11 R. Usón, J. Forniés, M. Tomás and I. Usón, *Angew. Chem., Int. Ed. Eng., 29* (1990) 1449.
12 E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem., 32* (1984) 1.
13 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A, 24* (1968) 1125.
14 R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics, 5* (1986) 1581, and refs. therein.
15 R. Usón, J. Forniés, P. Espinet, F. Martinez and M. Tomás, *J. Chem. Soc., Dalton Trans.,* (1981) 463.
16 R. Usón, J. Forniés, F. Martinez, M. Tomás and I. Reoyo, *Organometallics, 2* (1983) 1386.
17 R. Usón, J. Forniés, M. A. Usón, J. F. Yagüe, P. G. Jones and K. Meyer-Bäse, *J. Chem. Soc., Dalton Trans.,* (1986) 947.
18 R. Usón, J. Forniés, M. A. Usón and M. M. Carranza, *Inorg. Chim. Acta, 155* (1989) 71.