Action of HCl upon the Pt–C bonds in [NBu$_4$]$_2$[Pt(C$_6$Cl$_5$)$_4$] and [NBu$_4$]$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$]: synthesis of tris(pentachlorophenyl), [NBu$_4$][Pt(C$_6$Cl$_5$)$_3$L] and dichloro-monopentachlorophenyl-platinate(II), [NBu$_4$][PtCl$_2$(C$_6$Cl$_5$)L], complexes

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Abstract

The reaction of HCl on (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_4$] or (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] can be interrupted after the elimination of one C$_6$Cl$_5$ ligand in the presence of one molar proportion of a neutral ligand L, to give (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$L] or, (NBu$_4$)[PtCl$_2$(C$_6$Cl$_5$)L], respectively. When L is tetrahydrothiophene, it can be displaced by other neutral ligands, and this is of special value in the case of readily protonated ligands. When bidentate ligands (L–L = dppe, 4,4'-bipy) are used, the products are binuclear complexes. Finally, (NBu$_4$)[Pt(C$_6$X$_5$)$_3$(CO)] (X = F, Cl) can be obtained by a ligand rearrangement reaction between (NBu$_4$)$_2$[Pt(C$_6$X$_5$)$_4$] and *cis*-Pt(C$_6$X$_5$)$_2$(CO)$_2$.

Introduction

Under certain conditions [1] arylation of PtCl$_2$(tht)$_2$ (tht = SC$_4$H$_8$, tetrahydro-thiophene) with C$_6$F$_5$Li gives [Pt(C$_6$F$_5$)$_3$(tht)]$^-$, the tht ligand of which can be readily displaced by other neutral ligands. When C$_6$Cl$_5$Li is employed, only *trans*-Pt(C$_6$Cl$_5$)$_2$(tht)$_2$ is isolated.

The 1/1 reaction between (NBu$_4$)$_2$[Pt(C$_6$F$_5$)$_4$] and HCl gives (NBu$_4$)$_2$[PtCl-(C$_6$F$_5$)$_3$], from which other similar anions [PtX(C$_6$F$_5$)$_3$]$^{2-}$ (X = Br, I, CN, SCN) can be prepared [2]. With a 1/2 ratio, the binuclear (NBu$_4$)$_2$[Pt(μ-Cl)(C$_6$F$_5$)$_2$]$_2$ is obtained in good yield. The analogous 1/1 reaction starting from (NBu$_4$)$_2$[Pt-(C$_6$Cl$_5$)$_4$] gives a mixture of (NBu$_4$)$_2$[Pt(μ-Cl)(C$_6$Cl$_5$)$_2$]$_2$ [3], unchanged (NBu$_4$)$_2$-[Pt(C$_6$Cl$_5$)$_4$], and probably some (NBu$_4$)$_2$[PtCl(C$_6$Cl$_5$)$_3$], but the similar solubilities of all these species prevent isolation of the latter, if it is present at all. The

analogous 1/2 reaction gives only the binuclear derivative $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6\text{-}Cl_5)_2]_2$, in high yield ($\sim 85\%$).

The methods which lead to tris(pentafluorophenyl) anions of the types $[Pt(C_6F_5)_3L]^-$ or $[PtX(C_6F_5)_3]^{2-}$ are thus ineffective for the synthesis of tris(pentachlophenyl) complexes. Indeed, the only $(NBu_4)[Pt(C_6Cl_5)_3(PPh_3)]$ reported, was tris(pentachlorophenyl) platinate(II), obtained [4] by treatment of the platinum(III) complex $(NBu_4)[Pt(C_6Cl_5)_4]$ with an excess of PPh_3 (4 h, room temperature, 40% yield).

We thus decided to reexamine the action of HCl upon some anionic platinum precursors, namely $[Pt(C_6Cl_5)_4]^{2-}$ and $[trans\text{-}PtCl_2(C_6F_5)_2]^{2-}$. The study has led to the preparation of complexes containing the anions $[Pt(C_6Cl_5)_3L]^-$ or $[PtCl_2(C_6\text{-}Cl_5)L]^-$.

Results and discussion

(a) Reaction of $(NBu_4)_2[Pt(C_6Cl_5)_4]$ with one equivalent of HCl in the presence of a neutral ligand L

The action of HCl on $(NBu_4)_2[Pt(C_6Cl_5)_4]$ is known to lead to cleavage of two $Pt\text{-}C_6Cl_5$ bonds and formation of the binuclear $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ [3], but if the process takes place stepwise there should be a possibility of interrupting it after the cleavage of the first $Pt\text{-}C_6Cl_5$ bond if a neutral ligand is present. This has been shown to be the case (eq. 1) for L = PPh_3, PPh_2Me, $SbPh_3$, tht (tetrahydrothiophene), $NC_5H_5(py)$

$$(NBu_4)_2[Pt(C_6Cl_5)_4] + HCl + L \rightarrow$$

$$(NBu_4)[Pt(C_6Cl_5)_3L] + HC_6Cl_5 + NBu_4Cl \qquad (1)$$
$$(I\text{-}V)$$
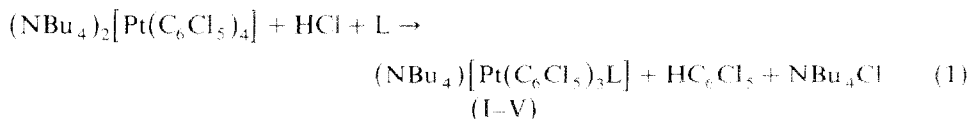
(L = PPh_3 (I), PPh_2Me (II), $SbPh_3$ (III), tht (IV), NC_5H_5 (V))

The complexes I–IV were isolated in 68–82% yields.

When L = py protonation of the ligand is likely to occur to some extent, and the yield of complex V is much lower ($\sim 15\%$).

(b) Displacement of tht from $(NBu_4)[Pt(C_6Cl_5)_3(tht)]$ by neutral ligands

The complex $(NBu_4)[Pt(C_6Cl_5)_3(tht)]$, can be used as a precursor for the synthesis of other complexes containing more basic neutral ligands, especially, those which can be partially protonated under the conditions described under above (sect. a) (eq. 2).

$$(NBu_4)[Pt(C_6Cl_5)_3(tht)] + L \rightarrow tht + (NBu_4)[Pt(C_6Cl_5)_3L] \qquad (2)$$

(L = py (V), PEt_3 (VI), CO (VII))

The reactions were carried out in refluxing toluene (V and VI) or in CH_2Cl_2 at room temperature (VII).

Binuclear complexes can be obtained by use of bidentate ligands (L–L) in suitable molar ratio (eq. 3)

$$2(NBu_4)[Pt(C_6Cl_5)_3(tht)] + L\text{-}L \rightarrow (NBu_4)_2[\{Pt(C_6Cl_5)_3\}_2(\mu\text{-}L\text{-}L)] \qquad (3)$$
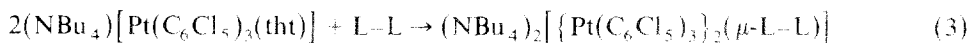
(L = dppe (VIII), 4,4′-bipy (IX))

(c) Reaction of (NBu₄)₂[trans-PtCl₂(C₆Cl₅)₂] with HCl (1 / 1)

The reaction between $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$ and HCl (molar ratio 1/1) results in the cleavage of only one Pt–C₆Cl₅ bond, and the formation of the binuclear $(NBu_4)_2[Pt(\mu\text{-}Cl)Cl(C_6Cl_5)]_2$ (X) (77% yield) (eq. 4)

$$(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2] + HCl \rightarrow (NBu_4)_2[Pt(\mu\text{-}Cl)Cl(C_6Cl_5)]_2 \qquad (4)$$
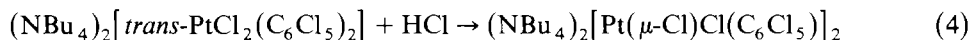
Complex X reacts with PPh₃ in acetone to give the mononuclear derivative $(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)(PPh_3)]$ (XII). Mononuclear complexes $(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)L]$ can also be obtained by treating $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$ with HCl in the presence of ligand L.

(d) Reaction of (NBu₄)₂[trans-PtCl₂(C₆Cl₅)₂] with HCl (1 / 1) in the presence of a neutral ligand L

The principles of the above proces (eq. 1) can also be extended to similar systems, and thus the 1/1 reaction of $(NBu_4)_2[PtCl_2(C_6Cl_5)_2]$ with HCl in dichloromethane solution in the presence of a neutral ligand L gave complexes of the type $(NBu_4)[PtCl_2(C_6Cl_5)L]$ (eq. 5).

$$(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2] + HCl + L \rightarrow$$

$$(NBu_4)[PtCl_2(C_6Cl_5)L] + HC_6Cl_5 + NBu_4Cl \qquad (5)$$
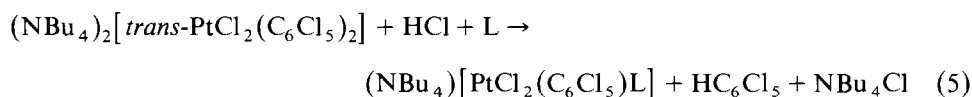
(L = tht (XI), PPh₃ (XII), SbPh₃ (XIII))

Complexes XI–XIII have a *trans*-structure as indicated by their IR spectra (see below), and thus these reactions (eq. 5) occur with stereoretention.

(e) Displacement of tht in (NBu₄)[trans-PtCl₂(C₆Cl₅)(tht)] by other neutral ligands

$(NBu_4)[PtCl_2(C_6Cl_5)(tht)]$ reacts with one equivalent of pyridine in refluxing toluene/dichloromethane (9/1) to give $(NBu_4)[PtCl_2(C_6Cl_5)(py)]$ (XIV). None of the chloride ligand is displaced, and the reaction occurs with stereoretention.

(f) Synthesis of (NBu₄)[Pt(C₆Cl₅)₃(CO)] by ligand rearrangement

The room temperature (1/1) reaction between $(NBu_4)_2[Pt(C_6Cl_5)_4]$ and *cis*-Pt-$(C_6Cl_5)_2(CO)_2$ [5] in dichloromethane solution affords a tris-arylated derivative (eq. 6).

$$(NBu_4)_2[Pt(C_6Cl_5)_4] + cis\text{-}Pt(C_6Cl_5)_2(CO)_2 \rightarrow 2(NBu_4)[Pt(C_6Cl_5)_3(CO)] \qquad (6)$$
$$(VII)$$
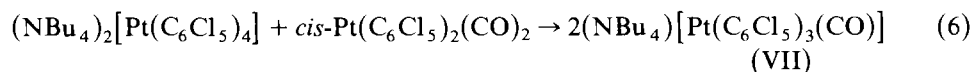
This reaction takes ca. 3 days for completion, and its course can be monitored by examining the IR spectrum of the solution, since the two $\nu(CO)$ bands at 2158 and 2123 cm^{-1}, due to *cis*-Pt(C₆Cl₅)(CO)₂, slowly disappear as a band at 2073 cm^{-1} due to $(NBu_4)[Pt(C_6Cl_5)_3(CO)]$ (VII) grows progressively, and is ultimately the only one present.

Other *cis*-Pt(C₆Cl₅)₂L₂ derivatives (e.g., L = tht) do not react with $(NBu_4)_2[Pt(C_6Cl_5)_4]$. On the other hand, the CO ligand in complex VII cannot be displaced by other neutral ligands (PPh₃ does not displace CO either at room temperature or in refluxing CH₂Cl₂).

Table 1

Analytical data, conductivities and melting points

Complex		Analyses (Found. (calcd.) (%))				Λ_M (ohm^{-1} cm^2 mol^{-1})	M.P. (°C)
		C	H	N	Cl		
$(NBu_4)[Pt(C_6Cl_5)_3(PPh_3)]$	(I)	43.49 (43.13)	3.49 (3.52)	0.88 (0.96)	37.52 (36.73)	80	201
$(NBu_4)[Pt(C_6Cl_5)_3(PMePh_2)]$	(II)	40.9 (40.7)	3.3 (3.5)	1.0 (1.0)	37.50 (38.37)	86	170
$(NBu_4)[Pt(C_6Cl_5)_3(SbPh_3)]$	(III)	41.0 (40.6)	3.3 (3.3)	0.9 (0.9)	34.35 (34.56)	86	190
$(NBu_4)[Pt(C_6Cl_5)_3(tht)]$	(IV)	36.2 (35.9)	3.4 (3.4)	1.2 (1.1)	42.50 (41.75)	97	176
$(NBu_4)[Pt(C_6Cl_5)_3(py)]$	(V)	37.0 (37.0)	3.1 (3.2)	2.5 (2.2)	42.00 (42.05)	83	192
$(NBu_4)[Pt(C_6Cl_5)_3(PEt_3)]$	(VI)	37.6 (36.8)	4.0 (3.9)	1.1 (1.0)	40.33 (40.79)	86	157
$(NBu_4)[Pt(C_6Cl_5)_3(CO)]$	(VII)	35.1 (34.6)	3.1 (3.0)	1.3 (1.2)	43.23 (43.82)	109	182(d)
$(NBu_4)_2[\{Pt(C_6Cl_5)_3\}_2(\mu\text{-dppe})]$	(VIII)	41.3 (40.8)	3.4 (3.5)	1.0 (1.0)	37.82 (38.40)	148	136
$(NBu_4)_2[\{Pt(C_6Cl_5)_3\}_2(\mu\text{-4,4'-bipy})]$	(IX)	37.2 (37.0)	3.0 (3.1)	2.2 (2.2)	41.58 (42.08)	168	232(d)
$(NBu_4)_2[Pt(\mu\text{-Cl})Cl(C_6Cl_5)]_2$	(X)	35.15 (34.85)	4.58 (4.75)	1.65 (1.84)	33.29 (32.74)	183	146
$(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)(tht)]$	(XI)	36.8 (36.9)	5.1 (5.2)	2.0 (1.6)	28.24 (29.33)	97	143
$(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)(PPh_3)]$	(XII)	47.5 (47.0)	4.8 (5.0)	1.4 (1.4)	23.53 (24.32)	83	171
$(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)(SbPh_3)]$	(XIII)	43.9 (43.2)	4.3 (4.6)	1.2 (1.3)	22.24 (22.34)	84	187(d)
$(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)(py)]$	(XIV)	38.1 (38.7)	4.6 (4.9)	3.4 (3.3)	29.61 (29.65)	95	177
$(NBu_4)[Pt(C_6F_5)_3(CO)]$	(XV)	43.72 (43.48)	3.82 (3.72)	1.69 (1.45)	–	110	134(d)

However $(NBu_4)[Pt(C_6F_5)_3(CO)]$ (XV) can be synthesized by the same procedure (eq. 5).

Analytical (C, H, N, Cl) and other data for complexes I–XV are listed in Table 1.

Infrared spectra

Characteristic absorptions of the new complexes are summarized in Table 2. All the pentachlorophenyl derivatives show absorptions near 1200 and in the range 600–700 cm^{-1} corresponding to internal vibrations of the C_6Cl_5 group, along with vibrations at ca. 800 cm^{-1} due to the X-sensitive mode [6] and at ca. 600 cm^{-1} due to $\nu(Pt–C)$ [7]. Three active absorptions (C_{2v}, $2A_1 + B_1$) due to the X-sensitive or $\nu(M–C)$ modes are expected for complexes of the type $(NBu_4)[Pt(C_6Cl_5)_3L]$, though these absorptions can actually be observed only in some cases (see Table 2), as was the case for $(NBu_4)[Pt(C_6F_5)_3L]$ complexes [1]. For the complexes $(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)L]$ only one absorption due to the X-sensitive mode and

another due to ν(Pt–C) were expected, and these were found. These complexes also show in the 350–320 cm^{-1} range a strong, absorption along with a weak one, due to ν(Pt–Cl) C_{2v}, $A_1 + B_1$). Since two absorptions are also expected for the *cis*-isomers (C_s, 2A′), there is some ambiguity, but the very different intensities of the two bands points out to the *trans* formulation [5].

Absorptions due to the neutral ligand L are also present (Table 2). For instance, in the spectra of the carbonyl derivatives, ν(CO) appears at 2.073 cm^{-1} for VII and 2084 cm^{-1} for XV, in accordance with earlier observations on other types of pentachloro- or pentafluoro-phenylcarbonylplatinum derivatives [5].

Experimental

Microanalyses (C, H, N) were carried out by Mr. F. Ortego and his staff in this Laboratory, with a Perkin–Elmer 240 microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in approx. 5×10^{-4} M acetone solutions with a Philips PW 9501/01 conductimeter. (NBu$_4$)$_2$[Pt(C$_6$X$_5$)$_4$] (X = F [1], X = Cl [3]) (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] [3] and *cis*-Pt(C$_6$X$_5$)$_2$(CO)$_2$ [5] were prepared as described previously.

Synthesis of (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$L] (L = PPh$_3$ (I), PMePh$_2$ (II), SbPh$_3$ (III), SC$_4$H$_8$ (IV), NC$_5$H$_5$ (V))

To a solution of (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_4$] (I: 0.7 g, (0.4173 mmol); II, III, IV: 0.5 g (0.298 mmol), V: 0.21 g (0.123 mmol)) in CH$_2$Cl$_2$ (20 ml) was added a molar equivalent of the ligand L (I: (PPh$_3$), 0.1094 g (0.4173 mmol); II: (PMePh$_2$) 57.2 μl, (0.298 mmol); III: (SbPh$_3$), 0.1032 g, (0.298 mmol), IV: (tht), 26.37 μl, (0.298 mmol); V: (py), 0.1 ml (1.23 mmol)) together with a solution of HCl in methanol (0.464 N) (I: 0.899 ml (0.4173 mmol); II, III, IV: 0.64 ml (0.298 mmol); V: 2.57 ml, (1.23 mmol)). The mixture was stirred at room temperature for 1 h, then evaporated to dryness, and the residue was treated with ^{i}PrOH. The resulting white solids were washed with n-hexane. Yields: I, 80%; II, 68%; III, 70%, IV, 82%, V, 15%.

Synthesis of (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$L] (L = NC$_5$H$_5$ (V), PEt$_3$ (VI), CO (VII))

Complexes V and VI. To a suspension of (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(tht)] (V: 0.38 g (0.298 mmol); VI: 0.15 g (0.117 mmol)) in 10 ml of toluene was added an equimolecular amount of ligand L (V: py 24 μl (0.298 mmol); VI: PEt$_3$, 17.39 μl (0.117 mmol)). The mixture was refluxed for 8 h, then evaporated to dryness, and the residue was treated with ^{i}PrOH (V) or hexane (VI). Complex V was recrystallized from CH$_2$Cl$_2$/^{i}PrOH. Yields: V, 72%; VI, 64%.

Complex VII. Carbon monoxide was bubbled at room temperature for 5 h through a solution of (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(tht)] (0.18 g (0.0141 mmol)) in 15 ml of CH$_2$Cl$_2$. The solution was evaporated to dryness and the white residue washed with n-hexane. Complex VII, 73% yield.

Synthesis of (NBu$_4$)$_2$[{Pt(C$_6$Cl$_5$)$_3$}$_2$(μ-L-L)] (L-L = dppe (VIII), 4,4′-bipy (IX))

To a solution of (NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(tht)] (VIII: 0.6 g (0.471 mmol); IX: 0.15 g (0.117 mmol)) in 18 ml of toluene and 2 ml of CH$_2$Cl$_2$ was added a 0.5 molar proportion of ligand L–L (VIII: 0.0938 g (0.235 mmol) of dppe; IX: 0.009 g (0.0589

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Table 2

Relevant ir absorption (cm^{-1})

		C_6X_5		others	L	$\nu(Pt-Cl)$
		(X-sensitive)	$\nu(M-C)$			
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(PPh$_3$)]	(I)	827(m)	615(2), 591(sh)	1211(s), 671(s)	1093(s), 756(s), 740(s), 705(s), 694(s), 530(s), 510(s), 490(s), 459(w), 426(w)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(PPh$_2$Me)]	(II)	822(m)	593(s)	1211(s), 671(s)	886(s), 882(s), 689(s), 515(s), 475(m), 440(m), 411(m)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(SbPh$_3$)]	(III)	824(m)	614(sh), 602(s), 594(s)	1210(s), 670(s)	693(s), 461(s), 452(m), 444(m), 268(m), 257(m)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(tht)]	(IV)	823(m)	615(sh), 602(s), 597(s)	1212(s), 669(s)	1204(s)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(py)]	(V)	823(m)	612(sh), 593(m)	1208(s), 669(s)	1602(m), 761(m), 696(m)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(PEt$_3$)]	(VI)	824(m)	591(s)	1208(s), 673(s)	767(m), 757(m)	
(NBu$_4$)[Pt(C$_6$Cl$_5$)$_3$(CO)]	(VII)	828(m)	604(m)	1212(s), 674(s)	2073(s)	
(NBu$_4$)$_2$[{Pt(C$_6$Cl$_5$)$_3$}$_2$(μ-dppe)]	(VIII)	824(m)	591(s)	1205(s), 673(s)	740(s), 699(s), 521(s), 494(w), 485(w), 445(m)	
(NBu$_4$)$_2$[{Pt(C$_6$Cl$_5$)$_3$}$_2$(μ-4,4'-bipy)]	(IX)	817(m)	590(m)	1212(s), 668(s)	1608(s)	
(NBu$_4$)$_2$[Pt(μ-Cl)CH(C$_6$Cl$_5$)]$_2$	(X)	845(w)	632(s)	1220(s), 673(s)		328(s), 308(s)
(NBu$_4$)[trans-Pt(Cl)$_2$(C$_6$Cl$_5$)(tht)]	(XI)	838(w)	626(s)	1220(m), 670(s)		350(m), 332(s)
(NBu$_4$)[trans-Pt(Cl)$_2$(C$_6$Cl$_5$)(PPh$_3$)]	(XII)	833(m)	615(m)	1224(m), 668(s)	1093(s), 747(s), 705(s), 691(s), 528(s), 508(s), 495(s)	348(vw), 325(s)
(NBu$_4$)[trans-Pt(Cl)$_2$(C$_6$Cl$_5$)(SbPh$_3$)]	(XIII)	836(m)	618(m)	1224(m), 669(s)	692(s), 627(s), 452(s), 262(s)	351(vw), 327(s)
(NBu$_4$)[trans-Pt(Cl)$_2$(C$_6$Cl$_5$)(py)]	(XIV)	840(w)	624(s)	1216(s), 667(s)	1598(s), 758(s), 690(s), 641(m)	351(vw), 324(s)
(NBu$_4$)[Pt(C$_6$F$_5$)$_3$(CO)]	(XV)	802(s), 791(m), 778(s)		1500(vs), 1059(vs), 955(vs)	2084(s)	

mmol) of 4,4'-bipy). The mixture was refluxed for 3 h (VIII) or 4 h (IX). The crystals which precipitated during the reaction were washed with toluene and n-hexane. Yields: VIII, 89%, IX, 76%.

Synthesis of (NBu$_4$)$_2$[Pt(μ-Cl)Cl(C$_6$Cl$_5$)]$_2$

(NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] (0.2 g, 0.10 mmol) in 20 ml of acetone was treated with 0.34 ml of HCl in MeOH (0.464 *N*), after 2 h at room temperature the solution was evaporated to dryness and the residue washed with 10 ml of ^{i}PrOH. Complex X, 77% yield.

Synthesis of (NBu$_4$)[trans-PtCl$_2$(C$_6$Cl$_5$)L] (L = tht (XI), PPh$_3$ (XII), SbPh$_3$ (XIII))

To a solution of (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] (XI: 0.5 g (0.4 mmol); XII, XIII: 0.2 g (0.16 mmol)) in 25 ml of CH$_2$Cl$_2$ were added, a molar proportion of ligand L (XI: 35.3 μl (0.4 mmol) of tht; XII; 0.042 g (0.16 mmol) of PPh$_3$; XIII: 0.0565 g, (0.16 mmol) of SbPh$_3$) and a solution of HCl in methanol (0.464 *N*) (XI: 0.862 ml (0.4 mmol); XII, XIII: 0.345 ml, (0.16 mmol)). The mixture was stirred at room temperature for 1 h, then evaporated to dryness, and the residue was treated with 5 ml of ^{i}PrOH. The resulting solids were washed with n-hexane. Yields: XI, 82%; XII, 79%; XIII, 76%.

Synthesis of (NBu$_4$)[trans-PtCl$_2$(C$_6$Cl$_5$)py] (XIV)

To a solution of (NBu$_4$)[*trans*-PtCl$_2$(C$_6$Cl$_5$)(tht)] (0.16 g, 0.189 mmol) in 18 ml of toluene and 2 ml of dichloromethane were added 15.26 μl (0.189 mmol) of py. The solution was refluxed for 6 h, then evaporated to dryness. The residue was washed with ^{i}PrOH and n-hexane (Yield: 57%).

Synthesis of (NBu$_4$)[Pt(C$_6$X$_5$)$_3$CO] (X = Cl (VII), F (XV))

A solution of (NBu$_4$)$_2$[Pt(C$_6$X$_5$)$_4$] (X = Cl, 0.137 g (0.082 mmol); X = F, 0.23 g (0.17 mmol)) and *cis*-Pt(C$_6$X$_5$)$_2$(CO)$_2$ (X = Cl, 0.061 g, (0.082 mmol); X = F, 0.1 g (0.17 mmol)) in 25 ml of CH$_2$Cl$_2$ was stirred at room temperature for 5 min (X = F) or 3 days (X = Cl). After filtration the solution was evaporated to ca. 5 ml, and slow diffusion of 40 ml of n-hexane at − 30 °C gave precipitates of complex VII (60%) or XV (97%).

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