Synthesis and Reactivity of Binuclear Perhalogenophenyl Derivatives of Platinum(I). Molecular Structure of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]\cdot 0.4CHCl_3$ *

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Binuclear complexes of platinum(I) $[Pt_2(C_6X_5)_2L_2(PPh_3)_2]$ (X = F, L = CO, p-MeC_6H_4NC, $C_6H_{11}NC$, or Bu^tNC; X = Cl, L = CO or p-MeC_6H_4NC) have been prepared by a redox condensation reaction between *cis*-$[Pt(C_6X_5)_2L_2]$ and $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$. The reactivity of these binuclear complexes towards phosphines, isocyanides, MeI, and I_2 has been studied. The structure of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ has been determined by single-crystal *X*-ray diffraction; space group $C2/c$, a = 18.272(4), b = 16.006(3), c = 17.787(5) Å, β = 101.046(19)°, Z = 4, R = 0.0378 for 3 449 unique reflections with $F \geqslant 6\sigma(F)$. The structure consists of two $Pt(C_6F_5)(CO)(PPh_3)$ fragments linked by a Pt–Pt bond [2.599(1) Å].

Most platinum(I) derivatives are binuclear complexes with metal-to-metal bonds supported by other bridging ligands such as $Ph_2PCH_2PPh_2$,[1] $Ph_2AsCH_2AsPh_2$,[2] $Ph_2PCH_2AsPh_2$,[3] o-$C_5H_4N(PPh_2)$,[4] $Ph_2PCH_2NEt_2$,[5] allyl or cyclopentadienyl,[6] CO,[7,8] S or Se[9–14] and complexes, mainly CO[15,16] or isocyanide[17] derivatives, containing a Pt–Pt bond unsupported by bridging ligands have been described only rarely. Much attention has been paid to the structures and reactivity of these complexes. Their reactivity is strongly dependent on the type of complex.

This paper deals with the synthesis of some binuclear pentafluoro- or pentachloro-phenyl platinum(I) derivatives containing Pt–Pt bonds unsupported by any bridging ligand $[Pt_2(C_6X_5)_2L_2(PPh_3)_2]$ (X = F or Cl; L = CO or CNR) and the study of their reactivity towards PR_3, CNR, MeI, and I_2. The molecular structure of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ has been established by a single-crystal *X*-ray study.

Recently[18] $[Pt_2Cl_2(CO)_2(PBu^t_2Ph)_2]$ was prepared by treating $[Pt_3(CO)_3(PBu^t_2Ph)_3]$ either with HCl at −50 °C or with Cl_2 and its molecular structure has been established.

Results and Discussion

The synthesis of the binuclear perhalogenophenyl platinum (I) derivatives has been carried out by a redox condensation reaction between *cis*-$[Pt(C_6X_5)_2L_2]$ and $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ in oxygen-free tetrahydrofuran (thf) solutions at reflux temperature [equation (1); X = F, L = CO (**1**), p-MeC_6H_4NC (**2**), $C_6H_{11}NC$ (**3**), or Bu^tNC (**4**); X = Cl, L = CO (**5**) or p-MeC_6H_4NC (**6**)].

$$cis\text{-}[Pt(C_6X_5)_2L_2] + [Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2] \longrightarrow [Pt_2(C_6X_5)_2L_2(PPh_3)_2] + C_2H_4 \quad (1)$$

However this process is not a general one since when X = F, L = PPh_3 or OC_4H_8 and X = Cl, L = PPh_3, $C_6H_{11}NC$, or Bu^tNC no reaction takes place even by refluxing the corresponding solutions for 1 h. Moreover, if longer reaction times are used partial decomposition occurs and most of the platinum(II) starting material is recovered.

Analytical results and molecular weights in $CHCl_3$ for complexes (**1**)—(**6**) are collected in Table 1. The i.r. spectra of these complexes show typical absorptions due to the C_6F_5[19] or C_6Cl_5[20] groups. The pentafluorophenyl derivatives show an absorption near 950 cm^{-1} (see Table 1) which is shifted to lower wavelengths relative to the platinum(II) starting materials (see Table 1), in accordance with previous observations for other pentafluorophenyl complexes of Pd^I or Pt^I.[21,22] Absorptions due to $\nu(C{\equiv}O)$ or $\nu(C{\equiv}N)$ in the 2 200—2 000 cm^{-1} region appear at lower wavelengths than for the corresponding platinum(II) starting materials as for other platinum(I) derivatives.[22,23] No absorptions in the 1 850—1 600 cm^{-1} region are observed so that the presence of bridging CO or CNR can be ruled out.

Structure of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ (**1**).—The structure of complex (**1**) has been determined by single-crystal *X*-ray diffraction (see Experimental section). Single crystals were grown by slow diffusion (*ca.* 10 d) of n-hexane into a $CHCl_3$ solution of the complex at −30 °C so that $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]\cdot 0.4CHCl_3$ was obtained. Positional parameters and selected bond distances and angles are given in Tables 2 and 3 respectively. The molecular structure is shown in Figure 1 and consists of two $Pt(C_6F_5)(CO)(PPh_3)$ fragments fused by a direct Pt–Pt′ bond unsupported by any bridging ligand. The molecule has crystallographically required C_2 symmetry, the two-fold axis bisecting the Pt–Pt bond.

The Pt–Pt′ distance is 2.599(1) Å, similar to that found in $[Pt_2Cl_4(CO)_2]^{2-}$ [2.584(2) Å] and shorter than that in $[Pt_2Cl_2(CO)_2(PBu^t_2Ph)_2]$ [2.628(1) Å][18] or in other bridged binuclear platinum(I) complexes $[Pt_2X_2(\mu\text{-}CO)(PPh_3)_2]$ (X = Cl, 2.634(3) Å;[8] Br, 2.654(1) Å][7] and $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (2.651(1) Å].[24]

The environment around each platinum atom is almost square planar with both PPh_3 ligands in positions *trans* to the Pt–Pt′ bond, so that the P–Pt–Pt′–P′ system is nearly linear. The P–Pt–Pt′ angle is 174.1(1)°. The corresponding angles Cl(1)–Pt(1)–Pt(2) and Pt(1)–Pt(2)–Cl(2) in $[Pt_2Cl_4(CO)_2]^{2-}$ are 177.1(2) and 173.7(2)° respectively.[25] The distance Pt–P is 2.313(2) Å similar to other Pt–P lengths *trans* to a Pt–Pt

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* Bis[carbonyl(pentafluorophenyl)(triphenylphosphine)platinum] (*Pt–Pt*)-chloroform (5/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical results, molecular weights, and relevant i.r. absorptions (in parenthesis absorptions due to the Pt(II) starting materials)

Complex	Analysis[a]/%			M[a]	I.r. bands (cm^{-1})[b]	
	C	H	N		$\nu(C_6F_5)$	ν(C≡O), ν(C≡N)
(1) $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]\cdot C_6H_6$[c]	48.70	2.70		1 480	951	2 054, 2 036
	(48.65)	(2.60)		(1 304)	(961)	(2 174, 2 143)
(2) $[Pt_2(C_6F_5)_2(CNC_6H_4Me\text{-}p)_2(PPh_3)_2]$	51.55	3.15	1.85	1 612	948	2 122br
	(51.85)	(3.00)	(1.90)	(1 483)	(956)	(2 216, 2 186)
(3) $[Pt_2(C_6F_5)_2(CNC_6H_{11})_2(PPh_3)_2]$	51.00	3.50	1.85	1 475	950	2 166, 2 151
	(50.75)	(3.55)	(1.90)	(1 467)	(958)	(2 239, 2 216)
(4) $[Pt_2(C_6F_5)_2(CNBu^t)_2(PPh_3)_2]$	49.35	3.35	1.85	*d*	948	2 171br
	(49.25)	(3.40)	(2.00)	(1 415)	(958)	(2 236, 2 215)
(5) $[Pt_2(C_6Cl_5)_2(CO)_2(PPh_3)_2]$	41.00	2.15		1 562		2 054, 2 032
	(40.85)	(2.05)		(1 469)		(2 160, 2 126)
(6) $[Pt_2(C_6Cl_5)_2(CNC_6H_4Me\text{-}p)_2(PPh_3)_2]$	46.35	2.65	1.80	1 706		2 144, 2 122
	(46.65)	(2.70)	(1.70)	(1 647)		(2 206, 2 180)
(7) $[Pt(C_6F_5)I(CO)(PPh_3)]$	38.35	1.90		793	960	2 111
	(38.55)	(1.95)		(779)		
(8) $[Pt(C_6F_5)I(CNC_6H_4Me\text{-}p)(PPh_3)]$	44.30	2.60	1.90	923	957	2 195
	(44.25)	(2.55)	(1.60)	(862)		
(9) $[Pt(C_6Cl_5)I(CO)(PPh_3)]$	34.95	1.85		881		2 095 (2 101sh)
	(34.85)	(1.75)		(793)		2 099[e]
(10) $[Pt(C_6Cl_5)I(CNC_6H_4Me\text{-}p)(PPh_3)]$	40.40	2.35	1.45	1 010		2 190
	(40.40)	(2.35)	(1.45)	(951)		

[a] Calculated values in parentheses. [b] Values in parentheses are due to the platinum(II) starting materials. [c] Benzene can be eliminated by heating the sample at 80 °C for 6 h. [d] Not soluble enough for molecular weight determination. [e] In CH_2Cl_2 solution.

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses for $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$

Atom	x	y	z
Pt	683(1)	369(1)	2 389(1)
P	1 916(1)	247(1)	2 296(1)
F(2)	970(3)	−1 575(3)	2 596(3)
F(3)	571(3)	−2 901(3)	1 711(3)
F(4)	−316(3)	−2 707(4)	314(3)
F(5)	−798(3)	−1 149(4)	−174(3)
F(6)	−379(3)	181(3)	700(3)
C(1)	332(4)	−627(5)	1 685(4)
C(2)	551(4)	−1 436(5)	1 909(5)
C(3)	339(5)	−2 136(6)	1 441(6)
C(4)	−108(5)	−2 038(5)	758(6)
C(5)	−340(5)	−1 247(6)	508(5)
C(6)	−120(5)	−580(5)	984(5)
C(7)	837(4)	1 251(6)	3 105(5)
O	927(4)	1 761(4)	3 548(4)
C(8)	2 299(3)	1 067(3)	1 772(3)
C(9)	1 873(3)	1 768(3)	1 510(3)
C(10)	2 176(3)	2 402(3)	1 128(3)
C(11)	2 907(3)	2 336(3)	1 008(3)
C(12)	3 333(3)	1 634(3)	1 270(3)
C(13)	3 029(3)	1 000(3)	1 652(3)
C(14)	2 486(3)	192(4)	3 227(2)
C(15)	3 113(3)	688(4)	3 475(2)
C(16)	3 484(3)	651(4)	4 236(2)
C(17)	3 228(3)	118(4)	4 750(2)
C(18)	2 600(3)	−378(4)	4 502(2)
C(19)	2 229(3)	−341(4)	3 741(2)
C(20)	2 140(3)	−666(3)	1 753(3)
C(21)	2 521(3)	−1 351(3)	2 124(3)
C(22)	2 602(3)	−2 077(3)	1 713(3)
C(23)	2 303(3)	−2 117(3)	931(3)
C(24)	1 922(3)	−1 431(3)	560(3)
C(25)	1 841(3)	−706(3)	971(3)
Cl(1)	5 829(18)	−1 367(21)	3 922(19)
Cl(2)	5 034(20)	80(23)	3 309(20)
Cl(3)	4 420(19)	−1 335(21)	3 456(19)

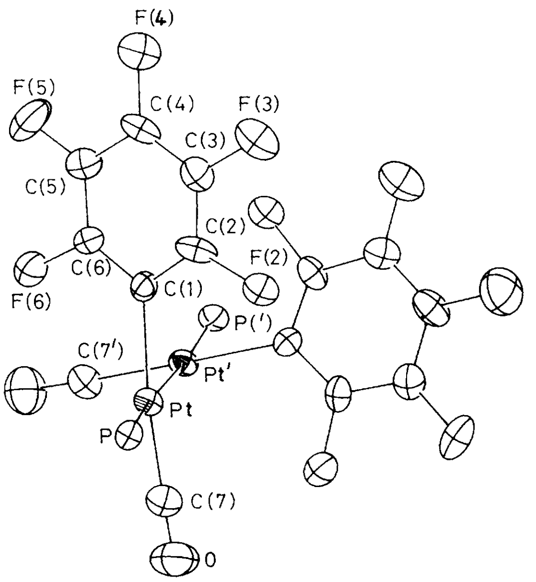

Figure 1. Molecular structure of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ showing the atom-labelling scheme. Phenyl rings of PPh_3 have been omitted for clarity

bond.[26–28] The pentafluorophenyl and the CO ligands bonded to the same platinum atom are in *trans* positions. The Pt–CO [Pt–C(7)] distance is 1.887(9) Å and the Pt–C_6F_5 [Pt–C(1)] distance is 2.053(8) Å, the latter being similar to those found in other pentafluorophenylplatinum derivatives.[29–31] The mean planes of the ligands around each Pt atom are rotated so that the angle between the two planes is 78.6(2)°. A similar situation is observed in other complexes of Pd^I or Pt^I, *i.e.* $[Pt_2Cl_4(CO)_2]^{2-}$,[25] $[Pd_2I_2(CNMe)]_4$,[32] and $[Pd_2(CNMe)_6]^{2+}$,[33,34] whose angles are 60, 85.3, and 86.4° respectively. Finally it is observed that the carbonyl or the pentafluorophenyl groups take up the cisoid sites on the adjacent metal atom. The corresponding torsion angles C(7)–Pt–Pt′–C′(7) and C(1)–Pt–Pt′–C′(1) are 82.7(4) and 77.3(3)° respectively.

N.M.R. Spectra.—The ^{31}P n.m.r. spectra of complexes (**1**)—

Table 3. Selected bond distances (Å) and angles (°) in $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2$

Pt′–Pt′	2.599(1)	P–Pt	2.313(2)
C(1)–Pt	2.053(8)	C(7)–Pt	1.887(9)
C(8)–P	1.796(4)	C(14)–P	1.821(5)
C(20)–P	1.813(4)	C(3)–F(3)	1.355(10)
C(2)–F(2)	1.331(10)	C(5)–F(5)	1.344(10)
C(4)–F(4)	1.341(9)	C(2)–C(1)	1.391(11)
C(6)–F(6)	1.367(10)	C(3)–C(2)	1.405(12)
C(6)–C(1)	1.360(11)	C(5)–C(4)	1.382(13)
C(4)–C(3)	1.336(13)	O–C(7)	1.123(10)
C(6)–C(5)	1.373(12)		
Pt′–Pt–P	174.1(1)	Pt′–Pt–C(1)	84.1(2)
Pt′–Pt–C(7)	85.5(3)	C(7)–Pt–P	95.9(2)
C(1)–Pt–P	94.2(2)	C(8)–P–Pt	117.5(2)
C(7)–Pt–C(1)	169.2(3)	C(14)–P–C(8)	106.8(3)
C(14)–P–Pt	108.1(2)	O–C(7)–Pt	178.0(8)
C(20)–P–Pt	115.7(2)	C(6)–C(1)–Pt	125.4(6)
C(20)–P–C(8)	101.1(3)	C(1)–C(2)–F(2)	120.1(7)
C(20)–P–C(14)	106.9(3)	C(6)–C(1)–C(2)	113.9(8)
C(2)–C(1)–Pt	120.7(6)	C(3)–C(2)–C(1)	122.7(8)
C(3)–C(2)–F(2)	117.2(7)	C(4)–C(3)–F(3)	121.5(8)
C(2)–C(3)–F(3)	118.6(8)	C(3)–C(4)–F(4)	119.9(9)
C(4)–C(3)–C(2)	119.8(8)	C(5)–C(4)–C(3)	119.7(8)
C(5)–C(4)–F(4)	120.5(9)	C(6)–C(5)–F(5)	121.6(9)
C(4)–C(5)–F(5)	119.8(8)	C(1)–C(6)–F(6)	119.6(7)
C(6)–C(5)–C(4)	118.6(8)	C(5)–C(6)–C(1)	125.2(8)
C(5)–C(6)–F(6)	115.2(8)	C(19)–C(14)–P	116.1(2)
C(9)–C(8)–P	120.5(2)	C(21)–C(20)–P	122.3(2)
C(13)–C(8)–P	119.5(2)	C(25)–C(20)–P	117.3(2)
C(15)–C(14)–P	123.8(2)		

* Primed atoms related by symmetry: $\bar{x}, y, 0.5 - z$.

Table 4. ^{31}P N.m.r. spectra (δ referred to 85% H_3PO_4, *J* in Hz; solvent $CDCl_3$)

Complex	δ/p.p.m.	^3J(P–P)	^1J(Pt–P)	^2J(Pt–P)
(**1**)	31.5	165.3	2 143.2	628.7
(**2**)	27.1	187.0	2 060.0	726.6
(**3**)	25.7	197.2	2 009.4	779.7
(**4**)	25.8	200.6	2 005.2	774.0
(**5**)	28.1	153.8	2 167.9	681.1
(**6**)	23.7	167.7	2 087.1	764.4

(**6**) in $CDCl_3$ show a similar pattern. The spectrum of complex (**1**) is shown in Figure 2 and data for complexes (**1**)—(**6**) are collected in Table 4.

As a consequence of the natural abundance of ^{195}Pt (33.7%), these binuclear complexes are a mixture of the following three isotopomers: (A) P–Pt–Pt–P (44%), (B) P–^{195}Pt–Pt–P (45%), and (C) P–^{195}Pt–^{195}Pt–P (11%). The ^{31}P n.m.r. spectrum must be the superimposed spectra of the three isotopomers, and consist of a central singlet due to the A_2 spin system (isotopomer A), eight signals (two doublets of doublets) due to the AA′ part of the AA′X spin system (isotopomer B) from which the parameters ^3J(P–P), ^2J(Pt–P), and ^1J(Pt–P) can be extracted; finally the isotopomer C is an AA′XX′ spin system and must present for the AA′ part ten signals, the two external more intense and separated by $N = {}^1J(\text{Pt–P}) + {}^2J(\text{Pt–P})$ being the only ones detected in our spectrum.

Reactivity.—We have studied the reactivity of complex (**1**) towards differing nucleophiles and electrophiles. When CH_2Cl_2 solutions of complex (**1**) are treated at room temperature or at reflux with an excess of PPh_3 or dppm, in order to displace the CO groups, no reaction is observed and the corresponding starting materials are recovered. A similar behaviour has been reported by Goodfellow *et al.*[7] for the anion $[Pt_2X_4(CO)_2]^{2-}$ which reacts with phosphine affording a variety of phosphine carbonyl derivatives but where none of the carbonyl groups has been substituted by phosphine. Complex (**1**) reacts at room temperature in CH_2Cl_2 with *p*-tolyl isocyanide (molar ratio 1:2) giving a yellow solid (**2**) [equation (2)] where the CO ligands have been displaced by CNC_6H_4Me-*p*; however no insertion of the isocyanide into the Pt–Pt bond is observed in contrast with the usual insertion of CNR observed in [ClPt(μ-dppm)$_2$PtX] (X = Cl, I,[35] or C_6F_5[22]). The treatment of refluxing CH_2Cl_2 solutions of complex (**1**) with $SnCl_2$ leaves the starting material unchanged and no insertion of the $SnCl_2$ into the Pt–Pt bond has been noted. This contrasts with the behaviour of $[Pt_2Cl_4(CO)_2]^{2-}$ which reacts with $SnCl_2$ giving $[\{PtCl_2(CO)\}_2SnCl_2]^{2-}$.[36]

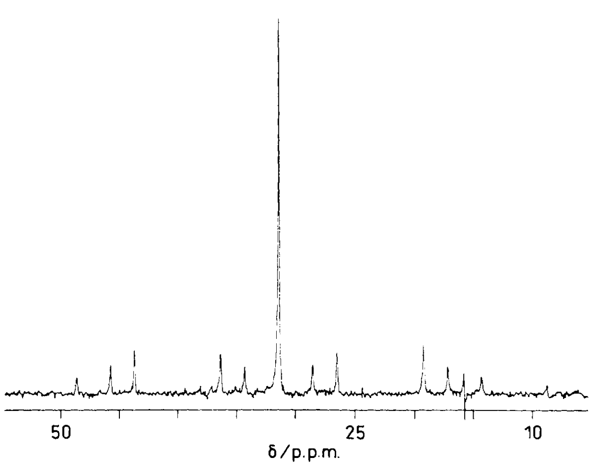

Figure 2. ^{31}P-{H} N.m.r. spectrum of complex (**1**) in $CDCl_3$ (reference 85% H_3PO_4)

$$[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2] + 2CNC_6H_4Me\text{-}p \longrightarrow [Pt_2(C_6F_5)_2(CNC_6H_4Me\text{-}p)_2(PPh_3)_2] + 2CO \quad (2)$$

No oxidative-addition reactions have been observed by treating complex (**1**) with an excess of MeI in CH_2Cl_2; however it reacts with I_2. When complexes (**1**), (**2**), (**5**), and (**6**) are treated with I_2 (molar ratio 1:1) in CH_2Cl_2 the corresponding mononuclear platinum(II) derivatives [equation (3); X = F, L = CO (**7**) or CNC_6H_4Me-*p* (**8**), X = Cl, L = CO (**9**) or CNC_6H_4Me-*p* (**10**)] are obtained.

$$[Pt_2(C_6X_5)_2L_2(PPh_3)_2] + I_2 \longrightarrow 2[Pt(C_6X_5)IL(PPh_3)] \quad (3)$$

Analytical results, molecular weights, and some i.r. information for complexes (**7**)—(**10**) are collected in Table 1. The pentafluorophenyl complexes (**7**) and (**8**) show an absorption due to the C_6F_5 group (near 960 cm^{-1}) at higher wavenumber than for the corresponding starting materials, in accordance with the increase of the formal oxidation state of the platinum.[22] Similar shifts are observed for the absorptions due to ν(CO) or ν(CN). It is not possible from our spectroscopic data to assign unequivocally the structure of complexes (**7**)—(**10**); fact three isomers are possible. The ^{31}P n.m.r. spectra of complexes (**7**) and (**8**) in $CDCl_3$ show a very narrow singlet at 7.8 or 7.9 p.p.m. respectively with platinum satellites ^1J(Pt–P) = 3 236.2 or 3 524.6 Hz, respectively]. However, no couplings between ^{31}P and ^{19}F nuclei are observed so that the isomer which contains C_6F_5 and PPh_3 in *trans* position can be ruled out.

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates or in CH_2Cl_2 solution. Molecular weights were determined in $CHCl_3$ solution on a Knauer apparatus. Phosphorus-31 n.m.r. spectra were recorded at room temperature on a Varian XL-200 instrument (200 MHz for ^1H).

The complexes $[Pt(C_2H_4)(PPh_3)_2]$,[37] *cis*-$[Pt(C_6X_5)_2(CO)_2]$ (X = F or Cl),[38] and *cis*-$[Pt(C_6F_5)_2(CNR)_2]$ (R = C_6H_4Me-*p*, C_6H_{11}, or Bu^t)[39] were prepared as described elsewhere. The complex *cis*-$[Pt(C_6Cl_5)_2(CNC_6H_4Me$-*p*$)_2]$ was prepared in a similar way to *cis*-$[Pt(C_6F_5)_2(CNR)_2]$ using *cis*-$[Pt(C_6Cl_5)_2(thf)_2]$[38] as starting material.

$[Pt_2(C_6X_5)_2L_2(PPh_3)_2]$ (X = F *or* Cl; L = CO *or* CNR).—$[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ (**1**). To a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.511 g, 0.683 mmol) in dry tetrahydrofuran (15 cm^3) at 0 °C, was added *cis*-$[Pt(C_6F_5)_2(CO)_2]$ (0.400 g, 0.683 mmol) in thf (15 cm^3) under N_2. The resulting solution was stirred at room temperature for 2 h, refluxed for 1 h, and then evaporated to dryness. The residue was dissolved in benzene (25 cm^3) and the solution obtained was concentrated to *ca.* 2 cm^3. By addition of diethyl ether (*ca.* 4 cm^3) a white crystalline solid (**1**) precipitated. Complex (**1**) was washed with 2 × 2 cm^3 of cyclohexane–diethyl ether (1:1); yield 0.570 g, 64%.

Complexes (**2**) (yellow, 65%), (**3**) (white, 43%), (**4**) (white, 30%), (**5**) (white, 45%), and (**6**) (yellow, 50% yield) were prepared as for (**1**).

Reaction of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ *with p*-MeC_6H_4NC.—To a solution of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ (0.094 g, 0.072 mmol) in CH_2Cl_2 (15 cm^3), *p*-MeC_6H_4NC (18.2 μl, 0.144 mmol) was added and the mixture was stirred at room temperature for 2 h. The solution was evaporated to *ca.* 2 cm^3 and Et_2O (*ca.* 10 cm^3) was added. The complex $[Pt_2(C_6F_5)_2(p\text{-}MeC_6H_4NC)_2(PPh_3)_2]$ was obtained (0.064 g, 60% yield).

Reactions of $[Pt_2(C_6X_5)_2L_2(PPh_3)_2]$ *with* I_2.—$[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$. To a solution of $[Pt_2(C_6F_5)_2(CO)_2(PPh_3)_2]$ (0.094 g, 0.072 mmol) in CH_2Cl_2 (10 cm^3) was added I_2 (0.018 g, 0.072 mmol) in CH_2Cl_2 (10 cm^3). After stirring at room temperature for 10 min, the colourless solution was evaporated to 2 cm^3; addition of n-hexane caused precipitation of a white solid, (**7**) (0.104 g, 92% yield).

Complexes (**8**)—(**10**) were prepared in a similar way. The precipitation was accomplished by adding diethyl ether [(**8**), white, 70%; (**9**), white, 80%)] or acetone [(**10**), pale yellow, 86% yield].

Molecular Structure Determination.—Crystal data. $C_{50}H_{30}F_{10}O_2P_2Pt_2\cdot0.4CHCl_3$, $M = 1\,352.64$, monoclinic, $a = 18.272(4)$, $b = 16.006(3)$, $c = 17.787(5)$ Å, $\beta = 101.046(19)°$, $U = 5\,105.9(20)$ Å^3 (from 25 centred reflections, $13 < \theta < 15°$), space group $C2/c$, $Z = 4$, $D_c = 1.744$ g cm^{-3}, $F(000) = 2\,580$, $\mu(Mo\text{-}K_\alpha) = 57.16$ cm^{-1}.

Data collection and processing. CAD4 diffractometer fitted with an ULT1 apparatus operating at 185 °K. Mo-K_α radiation ($\bar{\lambda} = 0.7106\,9$ Å). ω—2θ scans in 96 steps, with ω scan width $0.8 + 0.35 \tan\theta$. $\theta_{max.} = 25°$. 4 654 Reflections measured ($\pm h$, $+k$, $+l$), 4 493 unique, merging $R = 0.0162$. Empirical absorption correction applied.[40] 3 449 Data with $F \geqslant 6\sigma(F)$ were used. No perceptible crystal decay or movement over 70 *X*-ray hours.

Structure solution and refinement. Solved by Patterson synthesis (Pt) with further non-H atoms located by subsequent Fourier difference maps. Full-matrix least-squares refinement with all non-hydrogen atoms allowed anisotropic thermal motion. Phenyl rings of PPh_3 ligands were treated as rigid bodies and included in the refinement with idealised hexagonal symmetry (C–C 1.395 Å). All hydrogen atoms were included in calculated positions (C–H 1.08 Å) and $U = 0.076(9)$ Å^2. Near the end of the structure development a difference map showed a disordered molecule of $CHCl_3$; the three highest peaks were assigned to Cl atoms. The multiplicities and displacement parameters of the Cl atoms were refined alternately, yielding a model with a multiplicity of 0.2 and a group U for the Cl atoms of 0.162(6) Å^2. A difference map following convergence had maxima *ca.* 1.5 e Å^{-3} located either in the area of the disordered $CHCl_3$ molecule or the central metal atom. Weighting scheme: $w^{-1} = \sigma^2(F) + 0.002\,373F^2$. R and R' 0.0378 and 0.0439 respectively for 276 variables. Computer programs CADABS,[41] DIFABS,[40] and SHELX 76.[42]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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