Oxidative Dimerisation of Arylamido Complexes of Platinum: *X*-Ray Structure of $[Pt_2(PEt_3)_4Cl_2(N_2C_{12}H_{10})]\,PF_6$†

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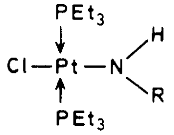
The phenyl groups of two molecules of the phenylamido complex $[Pt(PEt_3)_2Cl(NHPh)]$ are oxidatively coupled, in the *para* position, by $AgPF_6$ to give the dicationic complex $[Pt_2(PEt_3)_4Cl_2(N_2C_{12}H_{11})][PF_6]_2$ which can be deprotonated to the paramagnetic monocationic complex $[Pt_2(PEt_3)_4Cl_2(N_2C_{12}H_{10})]PF_6$. This has been examined by *X*-ray crystallography (orthorhombic, space group *Pnnm*, $R = 0.024$ for 2 854 diffractometer measured observed reflections). The structure shows a bridging benzidine group which is strictly planar with marked quinonoid character within the arene rings [C–C 1.355(5) and 1.427(6) Å]. The mononuclear *p*-tolyl complex undergoes a similar coupling in the *ortho* position, but the 1-naphthyl complex gives a neutral coupled complex because of the much reduced conjugation in the twisted 1,1′-binaphthyl system.

We report the reaction of phenyl-, *p*-tolyl-, and 1-naphthylamido derivatives of platinum (**1a**)—(**1c**) with silver ions. The reaction leads to an oxidative dimerisation of the arene group with C–C bond formation in all three cases. Some of these results were the subject of a preliminary communication.[1]



$$\mathrm{Cl{-}\underset{\overset{\uparrow}{PEt_3}}{\overset{\underset{\downarrow}{PEt_3}}{Pt}}{-}N\begin{smallmatrix}H\\R\end{smallmatrix}}$$

(**1a**) R = Ph
(**1b**) R = *p*-tolyl
(**1c**) R = 1-naphthyl

Results and Discussion

On treatment of a solution of the phenylamido complex (**1a**) in acetone with 1 molar equivalent of silver hexafluorophosphate in normal light the colour turns from yellow to deep red. A precipitate is formed and a silver analysis on this showed a silver content of 94% (75.3% in AgCl). A red salt (**2a**) (see Scheme) can be obtained from the red solution by the addition of diethyl ether. The observation that the silver ion is reduced to silver metal, rather than producing silver chloride by halide abstraction, indicates that an oxidation of (**1a**) has occurred, an unexpected result. The related phenyl complex *trans*-$[Pt(PEt_3)_2Cl(Ph)]$ undergoes the expected halide-abstraction reaction[2] on treatment with silver tetrafluoroborate in methanol, giving *trans*-$[Pt(PEt_3)_2(CH_3OH)Ph]^+$. We also attempted to abstract chloride from complex (**1a**) using thallium(I) nitrate in methanol but no reaction occurred. McKinney[3] has reported the oxidative coupling of cyclopentadienyl rings by Ag^+ involving complexes not containing halide. Connelly and co-workers[4] have summarised the reactions of Ag^+ with organometallic compounds and reported[5] the formation of silver–metal bonds in such reactions. It seems clear that the unusual reactivity of the halogeno complex (**1a**) is due to the phenylamido ligand.

Determination of the crystal structure of one of the products revealed that the oxidation of complex (**1a**) involved dimerisation of the aromatic amine ligand, and enabled us to understand the reactions involved. Similar oxidative dimerisations are involved in the use of aromatic amines as redox indicators.[6] The initial red product (**2a**) can be reversibly deprotonated to give a green complex, (**3**). Degradation studies on complexes (**1a**), (**2a**), and (**3**) showed that on reaction with potassium cyanide in methanol (**1a**) gave aniline, whereas (**2a**) and (**3**) gave an amine subsequently identified as benzidine (4,4′-diaminobiphenyl), but no aniline. We also found that the Pt–N bond in (**2a**) can be cleaved by concentrated hydrochloric acid in methanol to give *cis*-$[Pt(PEt_3)_2Cl_2]$ and (on basification) benzidine. Under the same conditions complex (**1a**) gave *cis*-$[Pt(PEt_3)_2Cl_2]$ and aniline. A similar cleaveage of a platinum–amide bond has been reported by Bellon *et al.*[7] More surprisingly, (**1a**) reacts with carbon monoxide in ethanol to give *trans*-$[Pt(PEt_3)_2H(Cl)]$ and aniline. In very concentrated solution the reaction with carbon monoxide precipitated a red solid. This is probably a polynuclear compound of the type reported by Chatt and Chini[8] though it has not been studied in detail.

The i.r. spectra of complexes (**2a**) and (**3**) show N–H absorptions and a broad band at *ca.* 830 cm^{-1} due to the hexafluorophosphate anion. The failure of attempts to measure the n.m.r. spectra of (**2a**) and (**3**) suggested that they might be paramagnetic. This was confirmed by Gouy-balance measurements which showed weak paramagnetism, while both compounds gave e.s.r. spectra. The large diamagnetic correction made a quantitative measurement of the paramagnetic moment unreliable, while the low symmetry of the complex and complexity of the e.s.r. spectrum (>1 000 lines expected) prevented its detailed interpretation; indeed even the e.s.r. spectrum of the much simpler tetramethylbenzidine cation has not been satisfactorily interpreted.[9] We expect, however, that the unpaired electron resides primarily in the π orbital of the organic part of the complex. The full characterisation of complex (**3**) was carried out by a single-crystal *X*-ray diffraction study. This established that it contains a dimeric 1+ cation (Figure) with a PF_6^- anion. In the cation, the benzene rings of two phenylamido ligands have coupled to form a benzidine derivative. Elemental analysis shows that the radical (**2a**) is a dication derived from (**3**) by protonation, though the site of

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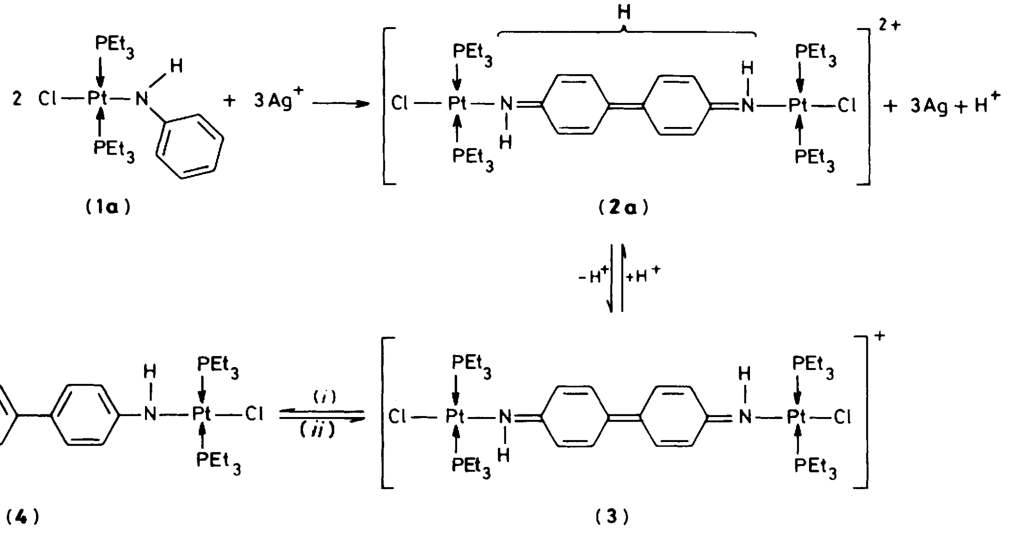
† *trans*-μ-[4-(4′-Iminocyclohexa-2′,5′-dien-1′-ylidene)cyclohexa-2,5-dien-1-ylideneamine-*NN*′]-bis[chlorobis(triethylphosphine)platinum] hexafluorophosphate.

Supplementary data available (No. SUP 56406, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



Scheme. (*i*) $Na_2S_2O_4$–OH^-; (*ii*) Ag^+

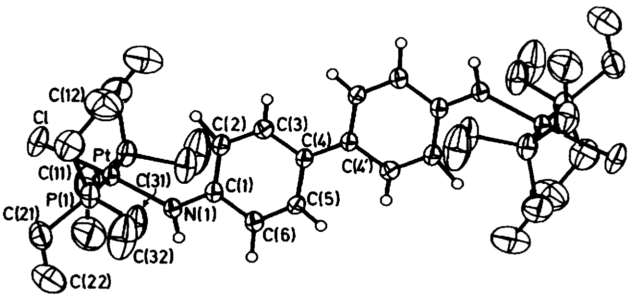
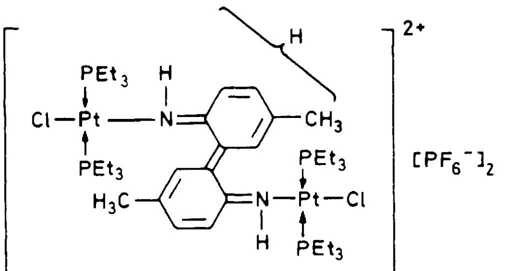


Figure. The cation of complex (**3**) showing the atomic numbering. Side-chain protons are omitted for clarity



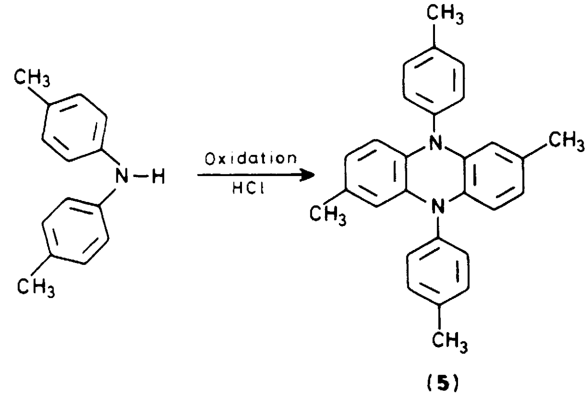
(**2b**)

protonation is not known. Reduction of either (**2a**) or (**3**) is also possible to give the neutral non-radical (**4**). A red solution of complex (**2a**) in methanol changes through green to yellow within seconds of adding an alkaline solution of sodium dithionite. A yellow solid was isolated from the mixture which we formulate as the neutral complex (**4**). This reduction is reversed with silver ion, a solution of (**4**) in acetone giving the red colour characteristic of (**2a**) on treatment with Ag^+. The conversions of (**1a**) → (**2a**) → (**3**) → (**4**) are summarised in the Scheme.

The conversion of complex (**1a**) into (**2a**) is shown as occurring with a 2:3 molar ratio of (**1a**) to silver ion. An alternative stoicheiometry, involving a 1:1 ratio, is also possible,[1] which has different implications for the coupling mechanism. We used a 1:1 ratio in our preparative work and did not investigate the variation of yield with varying molar ratios of silver ion.

The mechanism by which two aryl groups in aromatic amines are oxidatively coupled has been discussed by Bishop.[6] Although the picture is not totally clear, because much of the work was qualitative, it appears unlikely that substituted hydrazines are involved as intermediates. A more plausible mechanism involves the generation of free-radical aryl cations which then dimerize,[6,10] or attack a neutral molecule of the amine[9] at the *para* position. The substituted benzidines formed can then undergo further oxidation to give benzidine radical cations.

The oxidative coupling of aromatic amines leads to coupling in the *para* position if this bears hydrogen in the starting material. Thus *N*,*N*-dimethylaniline leads to *N*,*N*,*N'N'*-tetramethylbenzidine.[9,11] When the *para* position is blocked the reaction takes an alternative course: di-*p*-tolylamine produces the dihydrophenazine (**5**) on oxidation in hydrochloric acid solution[12] [equation (1)].



(1)

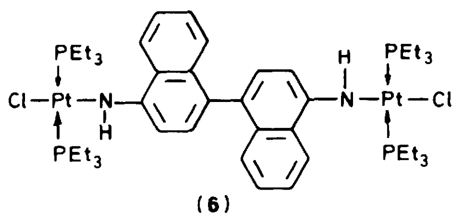
(**5**)

In order to investigate the effect of blocking the *para* position for platinum amides we prepared the new complex (**1b**) by the method of Beck and Bauder.[13] On reaction with silver hexafluorophosphate in methanol, (**1b**) undergoes a colour change from yellow to intense purple, and on concentration and cooling black crystals of (**2b**) were obtained.

The reaction of complex (**2b**) with concentrated hydrochloric acid in methanol gave *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] and, on basification, an amine which was identical with 6,6′-diamino-3,3′-dimethylbiphenyl prepared by the method of Lothrop.[14] The coupling has thus occurred in the positions *ortho* to the amido groups, rather than leading to a dihydrophenazine or promoting halide abstraction. *ortho*-Coupling is a minor pathway in the benzidine rearrangement of hydrazobenzenes.[15] The reaction of the 1-naphthylamido complex, (**1c**), has also been examined. This complex is a green solid which reacts with silver hexafluorophosphate in methanol to give a purple solution. We were not able to isolate a salt analogous to (**2a**) from this reaction and on basification obtained a green solid. The i.r. spectrum of this solid showed no hexafluorophosphate absorptions and the elemental analysis indicated formula (**6**). The coupled naphthylamide complex (**6**) was degraded by reaction with hydrochloric acid in methanol, yielding *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] and, on basification, 4,4′-diamino-1,1′-binaphthyl.

The isolation of the neutral product (**6**) under the same conditions used to generate the radical cation (**3**) indicates that the oxidation and dimerization of (**1c**) is more difficult than that of (**1a**). This probably results from the hydrogen–hydrogen repulsions which prevent planarity in 1,1′-binaphthyl systems.[16] In support of this, measurements of the half-wave reduction potentials of 1,1′-binaphthyl show that very little conjugation is possible along the twisted bond which joins the two naphthyl groups.[17]

The most striking feature of the structural results for complex (**3**) (Table 1) is that the benzidine system has considerable quinonoid character. Its bond distances are similar to those in the 1,4-bis(dimethylamino)benzene cation (Wurster's Blue cation),[18] to which the quinone and Kekulé canonical forms have been calculated[19] to contribute in the ratio *ca.* 60:40. Detailed comparison (Table 2) shows that the present compound is significantly more quinonoid than the above cation, particularly as judged by the external C–N bond. The comparison with biphenyl[20] reveals the substantial shortening of the C–C bond linking the rings associated with this quinonoid character. Unfortunately, accurate structures are not available for either benzidine itself or cations derived from it by oxidation, so it is not possible to be certain whether any of the quinonoid distortion arises from the presence of the Pt atom attached to N(1). The Pt–N(1)–C(1) angle is unexpectedly large [129.7(3)°], perhaps because of steric interaction between the benzene ring and the phosphine ligands. By forcing sp^2 hybridisation on N(1), this might increase the quinonoid character. Other distances and angles around Pt have standard values.[21]



(**6**)

Because of their facile oxidation–reduction interconversion, the possibility exists of using benzidine derivatives and their radical cations for photochemical splitting of water.[22] Tests were carried out on complexes (**1a**), (**3**), and (**4**) to explore this possible application. Compounds (**2a**) and (**3**) are intensely coloured with absorption coefficients in solution of *ca.* 40 000 l mol^{-1} cm^{-1}. Irradiation of (**1a**) or (**4**) appears to give (**2a**) from the colour change, but no electron transfer to methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dication) was observed.[23]

Experimental

Phenyl azide and 4-methylphenyl azide were prepared by the method of Lindsay and Allen.[24] 1-Naphthyl azide was prepared by the method of Boshev *et al.*[25]

The new arylamido complexes (**1b**) and (**1c**) were prepared from *trans*-chlorohydridobis(triethylphosphine)platinum(II)[26] in tetrahydrofuran and the corresponding azide by the method of Beck and Bauder[13] using a reaction time of *ca.* 28 h. *trans*-Chloro(4-methylphenylamido)bis(triethylphosphine)platinum(II), (**1b**), was obtained in 70% yield after recrystallisation from warm hexane as yellow crystals, m.p. 86—88 °C (Found: C, 40.0; H, 6.5; Cl, 6.75; N, 2.15. $C_{19}H_{38}ClNP_2Pt$ requires, C, 39.8; H, 6.7; Cl, 6.2; N, 2.45%). *trans*-Chloro(1-naphthylamido)bis(tri-

Table 1. Bond lengths (Å) and angles (°) for complex (**3**) with estimated standard deviations in parentheses

Pt–Cl	2.319(1)	Cl–Pt–P(1)	87.77(3)
Pt–P(1)	2.309(1)	Cl–Pt–N	176.6(1)
Pt–N	2.003(4)	P(1)–Pt–P(1′)	175.53(4)
P(1)–C(11)	1.815(6)	P(1)–Pt–N	92.22(3)
P(1)–C(21)	1.819(6)	Pt–P(1)–C(11)	112.7(2)
P(1)–C(31)	1.818(5)	Pt–P(1)–C(12)	111.3(2)
C(11)–C(12)	1.526(9)	Pt–P(1)–C(13)	115.0(2)
C(21)–C(22)	1.481(9)	P(1)–C(11)–C(12)	113.7(4)
C(31)–C(32)	1.538(8)	P(1)–C(21)–C(22)	114.0(4)
N(1)–C(1)	1.326(6)	P(1)–C(31)–C(32)	116.0(4)
C(1)–C(2)	1.419(7)	Pt–N(1)–C(1)	129.7(3)
C(1)–C(6)	1.434(7)	N(1)–C(1)–C(2)	122.8(4)
C(2)–C(3)	1.357(7)	N(1)–C(1)–C(6)	120.6(4)
C(3)–C(4)	1.427(6)	C(2)–C(1)–C(6)	116.6(4)
C(4)–C(5)	1.418(7)	C(1)–C(2)–C(3)	121.5(4)
C(4)–C(4″)	1.431(6)	C(2)–C(3)–C(4)	123.1(4)
C(5)–C(6)	1.352(7)	C(3)–C(4)–C(5)	114.2(4)
P(2)–F(1)	1.560(6)	C(3)–C(4)–C(4″)	122.9(4)
P(2)–F(2)	1.585(4)	C(4″)–C(4)–C(5)	123.0(4)
		C(4)–C(5)–C(6)	124.4(4)
		C(5)–C(6)–C(1)	120.2(4)

Singly primed atom at $x, y, -z$; doubly primed atoms at $1 - x, 1 - y, z$.

Table 2. Comparative bond distances (Å) (averaged)

		C–C			
Compound	Ref.	Ring end	Ring centre	External	External C–N
(**3**)	*	1.427(6)	1.355(5)	1.431(5)	1.326(6)
[C$_6$H$_4$(NMe$_2$)$_2$-1,4]ClO$_4$	18	1.415(3)	1.361(6)	—	1.355(5)
Biphenyl	20	1.379(2) 1.398(2)	1.387(2)	1.497(2)	—

* This work.

Table 3. Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	1 536.2(1)	1 958.0(1)	0.0	H(2)	2 302(88)	4 000(82)	0
Cl	−158.5(10)	1 652.8(13)	0.0	H(3)	3 347(50)	5 146(42)	0
P(1)	1 471.5(7)	1 942.9(8)	1 770.5(7)	H(5)	5 820(43)	3 625(41)	0
P(2)	5 000	0	0	H(6)	4 995(90)	2 256(84)	0
F(1)	4 201(4)	−782(4)	0	H(111)	−15(46)	2 446(42)	2 102(47)
F(2)	4 398(3)	553(2)	847(3)	H(112)	664(52)	2 768(50)	2 873(59)
N(1)	3 014(3)	2 143(3)	0	H(121)	1 276(44)	3 774(40)	2 326(47)
C(1)	3 539(3)	2 920(3)	0	H(122)	429(55)	3 693(49)	1 196(60)
C(2)	3 090(4)	3 808(4)	0	H(123)	178(73)	4 134(65)	2 164(76)
C(3)	3 646(3)	4 591(3)	0	H(211)	1 078(54)	887(53)	2 933(61)
C(4)	4 708(3)	4 586(3)	0	H(212)	503(51)	761(49)	1 988(56)
C(5)	5 136(3)	3 689(4)	0	H(221)	1 826(54)	−87(53)	1 199(61)
C(6)	4 606(4)	2 895(3)	0	H(222)	2 345(41)	178(38)	2 300(43)
C(11)	527(4)	2 714(4)	2 281(4)	H(223)	1 598(65)	−464(56)	2 123(69)
C(12)	623(6)	3 708(5)	1 903(6)	H(311)	3 067(36)	1 748(33)	2 166(40)
C(21)	1 114(4)	810(4)	2 250(4)	H(312)	2 771(42)	2 838(42)	2 209(47)
C(22)	1 781(6)	53(4)	1 915(7)	H(321)	2 158(33)	2 650(30)	3 631(36)
C(31)	2 631(3)	2 242(4)	2 408(4)	H(322)	2 617(43)	1 541(39)	3 658(47)
C(32)	2 616(5)	2 209(6)	3 587(5)	H(323)	3 318(69)	2 418(63)	4 028(71)
H(1)	3 481(54)	1 710(45)	0				

ethylphosphine)platinum(II), (**1c**), was obtained in 65% yield after recrystallisation from boiling diethyl ether as dark green crystals, m.p. 164—166 °C (Found: C, 43.6; H, 6.25; N, 2.15. $C_{22}H_{38}ClNP_2Pt$ requires C, 43.4; H, 6.3; N, 2.3%).

trans-μ-[4-(p-*Aminophenyl)phenylamido*-NN′]-*bis[chlorobis(triethylphosphine)platinum] Bis(hexafluorophosphate)*, (**2a**).—Complex (**1a**) (0.5 g, 0.89 mmol) in acetone (10 cm^3) was treated at room temperature in normal light with silver hexafluorophosphate (226 mg, 0.89 mmol) dissolved in acetone (5 cm^3). After 30 min the solution was filtered to remove silver metal, and diethyl ether was added to the concentrated filtrate to precipitate the product as a red solid (0.26 g, 42%), m.p. 179—183 °C (Found: C, 31.2; H, 5.3; Cl, 4.75; N, 2.0, P, 13.7; Pt, 29.0. $C_{36}H_{71}Cl_2F_{12}N_2P_6Pt_2$ requires C, 30.8; H, 5.1; Cl, 5.05; N, 2.0; P, 13.2; Pt, 27.7%).

trans-[2-(2′-*Amino-5′-methylphenyl)-4-tolylamido*-NN′]-*bis-[chlorobis(triethylphosphine)platinum] Bis(hexafluorophosphate)*, (**2b**).—Complex (**1b**) (1.47 g, 2.57 mmol) in nitrogen-saturated methanol (80 cm^3) was treated with silver hexafluorophosphate (0.65 g, 2.6 mmol) in methanol (10 cm^3) and the resulting mauve mixture was stirred at room temperature for 1 h. The precipitated silver metal was filtered off under nitrogen using Hyflo, and the filtrate concentrated to *ca.* 15 cm^3 by evaporation *in vacuo*. Cooling produced black crystals of the product which were filtered off, washed with methanol, and recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C). Yield 0.46 g (25%), m.p. 174—175 °C (Found: C, 31.9; H, 5.1; N, 1.95. $C_{38}H_{75}Cl_2F_{12}N_2P_6Pt_2$ requires C, 31.8; H; 5.3; N, 1.95%).

trans-μ-[4-(4′-*Iminocyclohexa-2′,5′-dien-1′-ylidene)cyclohexa-2,5-dien-1-ylideneamine*-NN′]-*bis[chlorobis(triethylphosphine)platinum] Hexafluorophosphate*, (**3**).—Complex (**2a**) (0.5 g) was dissolved in methanol (10 cm^3) containing potassium hydroxide (0.1 g). After stirring for 2 h at room temperature the mixture was poured into water (20 cm^3) and extracted with dichloromethane (20 cm^3). The product (0.33 g, 74%) was obtained from the organic layer as green crystals, m.p. 227—229 °C (Found: C, 34.6; H, 5.6; Cl, 5.25; N, 2.2. $C_{36}H_{70}Cl_2F_6N_2P_5Pt_2$ requires C, 34.3; H, 5.6; Cl, 5.6; N, 2.2%). The *X*-ray sample was recrystallised from dichloromethane to give green pleiochroic rods.

Complex (**4**).—Complex (**2a**) (0.5 g, 0.36 mmol) in methanol (50 cm^3) was treated with potassium hydroxide (0.3 g, 5 mmol) dissolved in the minimum volume of water. The colour of the solution changed from red to green. The mixture was stirred under nitrogen for 30 min and then treated with sodium dithionite (0.3 g, 2 mmol) and stirred for 40 min. Addition of water (50 cm^3) precipitated the *product* as a yellow powder which was filtered off and washed with methanol–water. Yield 0.35 g (88%), m.p. 185—188 °C. The compound is light sensitive, especially in solution (Found: C, 39.4; H, 6.2; N, 2.9. $C_{36}H_{70}Cl_2N_2P_4Pt_2$ requires C, 38.8; H, 6.3; N, 2.5%).

Complex (**6**).—Complex (**1c**) (0.47 g, 0.76 mmol) in methanol (30 cm^3) was treated with a solution of silver hexafluorophosphate (0.19 g, 0.75 mmol) in methanol (5 cm^3) and the resulting purple solution stirred for 2 h. The silver metal was filtered off and the filtrate concentrated to *ca.* 10 cm^3 by evaporation *in vacuo*. Sodium hydroxide (0.2 g, 5 mmol) was added and the mixture stirred for 1 h. The *product* formed as a green solid which was filtered off and washed with methanol and water; from its i.r. spectrum, it contained no PF_6^-. Recrystallisation from acetone–pentane gave dark green crystals (0.13 g, 45%), m.p. 193—197 °C (Found: C, 42.6; H, 6.0; N, 2.25. $C_{44}H_{74}Cl_2N_2P_4Pt_2$ requires C, 43.5; H, 6.1; N, 2.30%).

Reaction of Complex (**6**) *with Concentrated Hydrochloric Acid*.—Complex (**1c**) (0.76 g, 1.3 mmol) in warm methanol (50 cm^3) was treated with silver hexafluorophosphate (0.32 g, 1.3 mmol) in methanol (5 cm^3) and the solution stirred for 1 h. Silver metal was removed by filtration and the filtrate treated with concentrated hydrochloric acid (0.5 cm^3, 6 mmol) and refluxed for 12 h. The mixture was concentrated *in vacuo* and on addition of water a white precipitate of *cis*-$[Pt(PEt_3)_2Cl_2]$[26] was formed. The aqueous solution on basification yielded 4,4′-diamino-1,1′-binaphthyl which on recrystallisation from toluene gave cream crystals (0.1 g, 54%), m.p. 199—202 °C (lit.,[27] 200—202 °C) (Found: C, 84.3; H, 5.65; N, 10.2. Calc. for $C_{20}H_{16}N_2$: C, 84.5; H, 5.65; N, 9.9%).

Complex (**1b**) under similar conditions gave 6,6′-diamino-

3,3′-dimethylbiphenyl which was identified by comparison with an authentic sample.[14]

Crystallography for Complex (3).—*Crystal data.* $C_{36}H_{70}Cl_2F_6N_2P_5Pt_2$, M = 1 259.0, orthorhombic, space group *Pnnm*, a = 13.431(2), b = 14.470(3), c = 13.033(2) Å, U = 2 532.8(7) Å^3, D_m = 1.6 g cm^{-3}, Z = 2, D_c = 1.65 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 58.4 cm^{-1}, F(000) = 1 238.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 60°, with scan range ± 0.85(2θ) around the $K_{\alpha1} - K_{\alpha2}$ angles, scan speed 1—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. The density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 2 854 Observed reflections $[I/\sigma(I) \geqslant 3.0]$ were used in refinement (4 162 overall) and corrected for Lorentz, polarisation and absorption effects, the last with ABSCOR;[28] maximum and minimum transmission factors were 0.36 and 0.28. The crystal was bounded by {101}, 110 and 010, with dimensions 0.166 × 0.166 × 0.5 mm.

Systematic absences $0kl$, $k + l \neq 2n$; $h0l \neq 2n$ indicated space groups *Pnnm* or *Pnn*2. The Patterson function in *Pnnm* was interpreted in terms of one heavy atom (Pt), and refinement showed this to be the correct choice. Light atoms were added from successive Fourier syntheses (proceeding with caution, because the structure revealed was unexpected). The dimeric cation has $2/m$ symmetry as does the PF_6^- ion; the Pt and the aromatic rings lie in the mirror plane. Hydrogen atoms were refined with isotropic thermal parameters, and all other atoms were anisotropic. Final refinement was by least-squares methods in large blocks. An empirical weighting scheme was used, down-weighting reflections of low (sinθ)/λ or high F. This was shown to be satisfactory by weight analysis. The final R value was 0.024 (R' = 0.024). Computing was with the *X*-RAY 76 system[29] on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 30. Final atomic co-ordinates are given in Table 3, and bond lengths and angles in Table 1.

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