Aromatic Substitution Reactions of an Arylplatinum(IV) Complex

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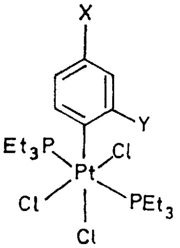
The synthesis of *abd*-trichloro-*f*-phenyl-*ce*-bis(triethylphosphine)platinum (1a) and novel reactions involving the aryl ligand of this complex are described. Lewis acid-catalysed chlorination of complex (1a) formed exclusively the *p*-chlorophenyl analogue leaving the aryl–metal bond intact. Taft substituent parameters for the $(PEt_3)_2PtCl_3$ group, viewed as an aryl substituent, were determined from ^{19}F n.m.r. studies on the *p*- and *m*-fluorophenyl analogues of (1a). In a novel rearrangement the complex gave phenyltriethylphosphonium trichloro(triethylphosphine)platinate (2) when heated in polar solvents. The possible mechanisms of this rearrangement are discussed.



a, X = Y = H
b, X = Cl, Y = H
c, X = F, Y = H
d, X = H, Y = F

(1)

THE first arylplatinum(IV) complexes were reported in 1959[1,2] but little work on their chemistry has been reported. Probably their apparent[2] chemical inertness has deterred further investigation. We have been investigating a typical arylplatinum(IV) complex (1a) and have encountered novel reactions which dispute the notion of inertness.

RESULTS AND DISCUSSION

Complexes (1a), (1c), and (1d) were prepared by treating the corresponding Pt^{II} complexes[2,3] (either *cis* or *trans*) with an equivalent of chlorine. The *trans*-orientation of the phosphine ligands in the resulting Pt^{IV} complexes was confirmed by the ^1H n.m.r. spectra which

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[1] For a description of the nomenclature used see 'Nomenclature of Inorganic Chemistry,' 2nd edn., IUPAC, Butterworths, London, 1970, p. 57.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

[3] G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 704.

revealed a characteristic virtual[4] coupling involving the methylene protons and phosphorus. Further confirmation came from the hydrogen-decoupled ^{31}P n.m.r. spectrum of (1a) which showed a single resonance accompanied by satellites arising from the coupling to ^{195}Pt (34% abundance). The value observed for $^{1}J_{Pt-P}$ (1610 Hz) was considered reasonable based on the expectation[5] of finding this coupling constant diminished by a factor of *ca.* 0·6 when compared with that of *trans*-$(PEt_3)_2Pt(Ph)Cl$ ($^{1}J_{Pt-P}$ 2800 Hz).[6]

Although complex (1a) was inert to chlorine in nitromethane at room temperature, addition of 0·25 equiv. of $AlCl_3$ effected an immediate reaction. Characterization of the product indicated the formation of complex (1b). The structure assignment followed directly from the ^{1}H n.m.r. spectrum.

Since this chlorination represents a unique example of an aromatic electrophilic substitution on a substrate possessing a transition metal σ-bonded to the ring, it was of interest further to investigate this system. Competitive chlorinations of mixtures of complex (1a) and benzene or toluene revealed a relative reactivity order of toluene > (1a) > benzene. Thus the $(PEt_3)_2$-$PtCl_3$ group, viewed as a substituent, appears to activate the aromatic ring. None (limit of detection <*ca.* 5%) of the *ortho*-isomer of (1b) could be detected by n.m.r. analysis of the crude reaction mixture. This high selectivity is probably a reflection of the steric congestion in the vicinity of the *ortho*-positions caused by the Pt^{IV} substituent. In support of this hypothesis, further chlorination of (1b) did not occur under the previously described conditions.

A quantitative assessment of the substituent effects of the $(PEt_3)_2PtCl_3$ group was obtained from an investigation of the ^{19}F chemical shifts (relative to fluorobenzene), $\delta_F{}^p$ and $\delta_F{}^m$, of (1c) and (1d), respectively. These chemical shifts and those reported for the substituents $(PEt_3)_2PtCl$ and Me are summarized in the Table. In general, the upfield chemical shifts of the Pt^{IV} complexes are smaller than those of the corresponding Pt^{II} complexes. This, of course, is reasonable in view of the increased charge density at platinum in the Pt^{IV} complexes. Following the Taft treatment[7,8] of substituent effects, we calculated values for the substituent constants, σ_I and $\sigma_R{}^{\circ}$, from the corresponding δ_F values according to the relationships (1) and (2) (see

$$\delta_F{}^p = -29{\cdot}5\sigma_R{}^{\circ} + \delta_F{}^m \qquad (1)$$

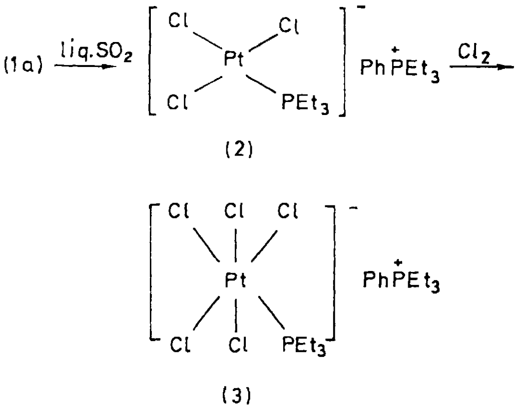
$$\delta_F{}^m = -7{\cdot}1\sigma_I + 0{\cdot}60 \qquad (2)$$

Table). Judged from the values of the constants obtained, activation of the aryl ring towards electrophilic attack would be expected[9] in the case of the platinum substituents. This has now been observed with the Pt^{IV} complexes. Unlike most activating substituents,[7] however, this activation phenomenon appears to involve positive contributions from *both* inductive and resonance effects ($d\pi \longrightarrow p\pi$). Of the more common substituents, the σ constants reported for the methyl group (see Table) most closely approximate those found for the platinum(IV) substituent. However, a quantitative comparison of the reactivities of toluene and complex (1a) based on substituent constants, is probably unwise in view of the large ponderal effects[10] expected between molecules possessing such large mass differences.

^{19}F N.m.r. chemical shifts and σ constants[a]

Compound	$\delta_F{}^m$	$\delta_F{}^p$	σ_I	$\sigma_R{}^{\circ}$	Ref.
(1) trans-$(PEt_3)_2Pt(Ph)Cl$	2·11	10·1	−0·21	−0·27	3,8
(2) $(PEt_3)_2Pt(Ph)Cl_3$ (1a)	0·64	6·06	−0·01	−0·18	—
(3) PhMe	1·18	5·40	−0·08	−0·14	7

[a] $\delta_E{}^m$ and $\delta_E{}^p$ represent the ^{19}F chemical shift/p.p.m. of the *meta*- and *para*-fluorophenyl analogues of the given compounds, respectively, relative to fluorobenzene. A positive value indicates the chemical shift is to high field. The compounds are all compared in acetone solution (5—10% w/w).



SCHEME 1

The attempted reaction of (1a) with sulphur dioxide resulted instead in a novel rearrangement (Scheme 1). The structure of the product obtained (2) was suggested by a hydrogen-decoupled ^{31}P n.m.r. spectrum showing the presence of two distinct phosphorus environments of which only one gave evidence of spin coupling to ^{195}Pt. Final confirmation of the structure came from a hydrogen-decoupled ^{13}C n.m.r. spectrum which verified the location of the aryl group. Both the ^{31}P–^{13}C spin coupling constants and the chemical shifts of each aryl carbon compare well with those reported[11] for methyltriphenylphosphonium iodide. Finally, complex (2) was found to add chlorine giving (3). As expected both the

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[4] (*a*) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279; (*b*) R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[5] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[6] B. T. Heaton and A. Pidcock, *J. Organometallic Chem.*, 1968, **14**, 235.

[7] P. R. Wells, S. Emerson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 286, 302

[8] R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, 1970, **92**, 2170.

[9] (*a*) R. W. Taft, jun., and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; (*b*) *ibid.*, 1958, **80**, 2436.

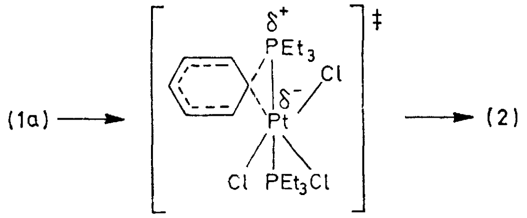
[10] P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold, J. D. H. Makie, *J. Chem. Soc.*, 1955, 3200.

[11] F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, 1973, **12**, 313.

^{31}P and ^{13}C n.m.r. spectra of complex (3) were qualitatively similar to those found for (2).

Since this rearrangement involves a separation of charges, its rate should be accelerated by increases in solvent polarity. Indeed, it was found that the reaction proceeded much more rapidly in sulphur dioxide or nitromethane than in benzene.

A priori, several distinct mechanisms are possible for this rearrangement. The possibility that the reaction involves a prior fragmentation of complex (1a) to chlorobenzene and either *cis*- or *trans*-$(PEt_3)_2PtCl_2$ was ruled out by the failure to observe any reaction between these compounds under the conditions of the rearrangement. The more likely possibility of a mechanism involving a prior dissociation of a triethylphosphine ligand is also considered unlikely in view of the failure to observe, by n.m.r. spectroscopy, the formation of the phenyltrimethylphosphonium cation while conducting the rearrangement in the presence of an equivalent of free trimethylphosphine. Thus, the evidence suggests that the actual mechanism requires an intramolecular S_N2-type displacement of the aryl group by an adjacent triethylphosphine ligand (Scheme 2). A Referee's suggestion that the actual mechanism may involve attack of solvent at platinum followed by internal migration of the phenyl group to co-ordinated triethylphosphine is considered unlikely since this would imply the formation of a very sterically congested seven-co-ordinate Pt^{II} complex. Solvent participation would be more likely to occur if Pt^{II} catalysis [12] were involved. In this case an intermediate four-co-ordinate Pt^{II} complex could easily interact with solvent. However, Pt^{II} catalysis is also not considered likely since one would then have expected phosphine exchange to have occurred before reaction.



Scheme 2

EXPERIMENTAL

Physical Measurements.—The ^{1}H n.m.r. spectra were recorded on a Varian HR220 or a Varian A60 spectrometer. The ^{19}F n.m.r. spectra were determined at 94·1 MHz on a Varian HA-100 spectrometer with proton noise decoupling and are referenced to internal fluorobenzene. The proton-decoupled ^{31}P n.m.r. spectra were determined at 36·43 MHz or 40·5 MHz with a Bruker HFX-90 spectrometer equipped with a Fourier Transform unit or a Varian HA-100 spectrometer, respectively. The proton-decoupled ^{13}C n.m.r. spectrum of complex (2) was also obtained with the Bruker HFX-90 spectrometer.

Preparation of abd-*Trichloro*-f-*phenyl*-ce-*bis*(*triethylphosphine*)*platinum*(IV) (1a).—To a solution of *cis*-chlorophenylbis(triethylphosphine)platinum [3] (5·44 g; 10 mmol) in dry carbon tetrachloride (50 ml) was added a solution of chlorine in carbon tetrachloride (0·67M, 16·4 ml). After *ca.* 15 min the solution was freed from volatile materials by rotary evaporation. The residue was recrystallized from hot hexane (*ca.* 250 ml) giving yellow crystals, m.p. 102·0—102·5 °C (4·39 g). The mother-liquor yielded a residue which on recrystallization gave yellow crystals, m.p. 101·8—102·3 °C (0·90 g, 87% yield) (Found: C, 34·9; H, 5·6; P, 10·1; Pt, 31·2. Calc. for $C_{18}H_{35}Cl_3P_2Pt$: C, 35·2; H, 5·75; P, 10·2; Pt, 31·8%). ^{1}H N.m.r. (220 MHz) ($CDCl_3$): δ/p.p.m. 1·10 (CH_3, quintuplet, $|^{3}J_{PH} + {}^{5}J_{PH}| + {}^{3}J_{HH}$ 16 Hz, $^{3}J_{Et}$ 8 Hz), 2·13 (CH_2, nontuplet, $|^{2}J_{PH} + {}^{4}J_{PH}| + {}^{3}J_{HH}$) 8 Hz, $^{3}J_{Et}$ 8 Hz), 7·10 (*meta*- and *para*-phenyl hydrogens, mult.), 7·92 (*ortho*-phenyl hydrogens, broad doublet, $^{3}J_{HH}$ 15 Hz, $^{3}J_{Pt-H}$ 38·5 Hz). ^{31}P N.m.r. [CH_2Cl_2, reference $P(OEt)_3$, hydrogen decoupled]: δ 10·59 p.p.m. to high field, singlet with ^{195}Pt satellites, $^{1}J_{Pt-P}$ 1610 Hz.

Rearrangement of abd-*Trichloro*-f-*phenyl*-ce-*bis*(*triethylphosphine*)*platinum* (1a).—Complex (1a) (0·923 g; 1·5 mmol) and sulphur dioxide (5 g) was placed in a 10 cm^{3} Hastelloy C-lined autoclave and heated at 100 °C for 3 h. The product was washed out with benzene, freed from volatile substances, and recrystallized from ethyl acetate–benzene (2 : 1) (*ca.* 15 ml). Yellow needles (0·61 g) of complex (2) separated, m.p. 123·9—124·9 °C. The mother-liquor gave a yellow solid (0·22 g). Similar results were obtained by running the reaction in sealed heavy-walled glass ampoules [Found: C, 35·3; H, 5·8; Cl, 16·4; *M* (0·28% in $CHCl_3$ at 37 °C), 625. Calc. for $C_{18}H_{34}Cl_3P_2Pt$: C, 35·2; H, 5·75; Cl, 17·3%; *M*, 614·86]. ^{1}H N.m.r. (220 MHz, $CDCl_3$): δ 1·06—1·44 p.p.m. (m, 18H), 1·73—2·05 (m, 6H), 2·73—3·02 (m, 6H), 7·73 (s, 3H), 7·98—8·18 (broad s, 2H). ^{31}P N.m.r. (36·43 MHz, $CHCl_3$, relative to triethylphosphine): δ/p.p.m. 23·7 to low field (singlet with ^{195}Pt satellites, $^{1}J_{Pt-P}$ 3710 Hz); 54·6 to low field (singlet). ^{13}C N.m.r. (90 MHz, $CDCl_3$): δ 6·37 p.p.m. ($^{2}J_{PC}$ 4·7), 7·71 ($^{2}J_{PC}$ 2·4, $^{3}J_{PtC}$ 20·5), 13·47 ($^{1}J_{PC}$ 47), 14·40 ($^{1}J_{PC}$ 38·6, $^{2}J_{PtC}$ 18·5), 117·0 ($^{1}J_{PC}$ 80), 130·4 ($^{2}J_{PC}$ 12), 132·9 ($^{3}J_{PC}$ 9·2), 134·3 ($^{4}J_{PC}$ 8 Hz).

Preparation of Phenyltriethylphosphonium Pentachloro(*triethylphosphine*)*platinate*(IV) (3).—Complex (2) (0·616 g; 1·0 mmol) in chloroform (4 ml) was treated with gaseous chlorine (27 ml). The resulting solution was freed from volatile substances on the rotary evaporator and the residue recrystallized from boiling ethanol (14 ml). Yellow-orange crystals of (3) (0·50 g), m.p. 135·1—135·3 °C, were filtered off and washed with a minimum of ethanol (Found: C, 31·8; H, 5·2; P, 8·95; Pt, 28·4. Calc. for $C_{18}H_{35}Cl_5P_2Pt$: C, 31·55; H, 5·15; P, 8·90; Pt, 28·4%). ^{31}P N.m.r. (36·43 MHz, $CHCl_3$, relative to triethylphosphine): δ/p.p.m. 38·9 to low field (singlet with ^{195}Pt satellites, $^{1}J_{Pt-P}$ 2098 Hz); 54·6 to low field (singlet). ^{1}H N.m.r. (220 MHz, $CDCl_3$, relative to internal tetramethylsilane): δ/p.p.m. 1·06—1·51 (mult., 18H), 2·29—2·65 (mult., 6H), 2·65—2·99 (mult., 6H), 7·69 (sing., 3H), 8·04 (broad sing., 2H).

Preparation of abd-*Trichloro*-f-(p-*chlorophenyl*)-ce-*bis* (*triethylphosphine*)*platinum*(IV) (1b).—A solution of aluminum chloride (0·067 g; 0·50 mmol) in dry nitromethane (10 ml) was prepared under nitrogen. *abd*-Trichloro-*f*-phenyl-*ce*-bis(triethylphosphine)platinum (1a) (1·23 g; 2·0 mmol) was dissolved in the previously prepared solution

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[12] F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, 1960, **29**, 1.

(4 ml) along with dry nitromethane (3 ml). A measured amount of chlorine gas (53 ml; 2·20 mmol) was slowly admitted during 8 min. After stirring for an additional 10 min, water (*ca.* 0·2 ml) was added and the resulting solution evaporated to dryness on the rotary evaporator. The residue was recrystallized from hot hexane (*ca.* 30 ml) giving yellow crystals (0·61 g), m.p. 123—137 °C. Recrystallization from hexane gave (1b), m.p. 137—138 °C (0·43 g) (Found: C, 32·3; H, 5·2; Cl, 21·4; Pt, 30·6. Calc. for $C_{18}H_{34}Cl_4P_2Pt$: C, 33·3; H. 5·30; Cl, 21.8; Pt, 30·1%). ^1H N.m.r. ($CDCl_3$, 60 MHz): δ 1·10 p.p.m. (CH_3, pentuplet, $|{}^3J_{PH} + {}^5J_{PH}| + {}^3J_{HH}$ 16 Hz, $^3J_{Et}$ 8 Hz), 2·10 (CH_2, nontuplet, $|{}^2J_{PH} + {}^4J_{PH}| + {}^3J_{HH}$ 8 Hz, $^3J_{Et}$ 8 Hz), 6·53 (*meta*-phenyl hydrogens, AB pattern, J_{AB} 8·5 Hz, $^3J_{PtH}$ 38·5 Hz).

Competitive Chlorinations of abd-*Trichloro*-f-*phenyl*-ce-*bis*(*triethylphosphine*)*platinum*(IV) (1a) *and Aromatic Hydrocarbons.*—A mixture of (1a) (0·304 g; 0·50 mmol) and benzene (11·2 µl; 0·50 mmol) was chlorinated as described for the preparation of (1b). The volatile portion was collected on a vacuum line and analysed for chlorobenzene by g.l.c. None was found (limit of detection = 1% of amount corresponding to complete reaction). The residue remaining was analysed by n.m.r. and found to consist of >90% pure (1a). When a control experiment was run without (1a) being present, no chlorobenzene was formed. Hence, the reactivity of (1a) with chlorine is at least 90 times that of benzene under these conditions.

A similar competition experiment in the presence of toluene (5 mmol) in place of the benzene gave only chlorination of the toluene. No chlorination of (1a) was detectable (limit of detection, *ca.* 5% reaction). This result appears to indicate a greater reactivity of toluene in this case. It should also be noted that the reactivity ratio of toluene compared with benzene in this system was of the order of 1000.

Preparation of abd-*Trichloro*-f-(p-*fluorophenyl*)-ce-*bis*-(*triethylphosphine*)*platinum*(IV) (1c).—To a solution of *trans*-chlorobis(triethylphosphine)(*p*-fluorophenyl)platinum[3] (1·00 g; 1·78 mmol) in dry carbon tetrachloride (10 ml) was added chlorine gas (48·8 ml; 2·0 mmol) during 4 min with stirring. The solution was stirred for 10 min before rotary evaporation. The residue was recrystallized from hot hexane (35 ml) giving yellow crystals (0·881 g) (m.p. 112·1—112·5 °C) of (1c). The mother-liquor yielded a residue which on recrystallization gave additional product (0·154 g) (m.p. 112·0—112·5 °C), thus giving a yield of 92% (Found: C, 34·1; H, 5·6; Cl, 17·2; Pt, 31·45. Calc. for $C_{18}H_{34}Cl_3FP_2Pt$: C, 34·2; H, 5·40; Cl, 16·80; Pt, 30·8%). ^1H N.m.r. ($CDCl_3$, 60 MHz): δ 1·08 p.p.m. (quintuplet, $|{}^3J_{PH} + {}^5J_{PH}| + {}^3J_{HH}$ 16 Hz, $^3J_{Et}$ 8 Hz, 18H), 2·08 (nontuplet, $|{}^2J_{PH} + {}^4J_{PH}| + {}^3J_{HH}$ 8 Hz, $^3J_{Et}$ 8 Hz, 12H), 6·81 (t, J_{PH} 9 Hz = J_{H-H} 2H), 7·92 (q, J_{FH} 6 Hz, J_{HH} 9 Hz, 2H). ^{19}F N.m.r. (94·1 MHz, acetone, C_6H_5F reference): δ 6·06 p.p.m. to high field (singlet, with ^{195}Pt satellites, $^5J_{Pt-F}$ *ca.* 10 Hz).

Preparation of abd-*Trichloro*-f-(m-*fluorophenyl*)-ce-*bis*-(*triethylphosphine*)*platinum*(IV) (1d).—Following the procedure described for the preparation of trichlorobis(triethylphosphine)(*p*-fluorophenyl)platinum, we prepared a sample (0·786 g, 69% yield) of (1d), m.p. 124·1—124·8 °C (Found: C, 34·0; H, 5·4. Calc. for $C_{18}H_{34}Cl_3FP_2Pt$: C, 34·2; H, 5·40%). ^1H N.m.r. (CCl_4): δ 0·72—1·45 p.p.m. (p, 18·2 H), 1·70—2·50 (m, 12·1 H), 6·65—8·30 (m, 3·62 H). ^{19}F N.m.r. (94·1 MHz, acetone, C_6H_5F reference): δ, p.p.m., 0·64 to low field (singlet with ^{195}Pt satellites, $^4J_{Pt-F}$ 25·4 Hz).

Rearrangement of abd-*Trichloro*-f-*phenyl*-ce-*bis*(*triethylphosphine*)*platinum* (1a) *in Presence of Trimethylphosphine.*—An ampoule containing (1a) (0·304 g; 0·50 mmol) and trimethylphosphine and (50 ml; 0·50 mmol) in liquid sulphur dioxide (1 ml) was heated at 100 °C for 3 h. The resulting dark red-brown solution was freed from volatile substances at *ca.* 10 mmHg pressure, leaving a residue. A solution of this residue in $CDCl_3$ was examined by n.m.r. spectroscopy (60 MHz) showing that all of the aromatic resonances could be accounted for as being due to the presence of PhP^+Et_3 cations. This was easily ascertained since the aromatic and methylene resonances of the cation were clearly separated from the rest of the spectrum and were identical in character and position to the resonances of the corresponding groups in complex (2). In a separate experiment, complex (2) and 2 equiv. of trimethylphosphine similarly treated as above gave an n.m.r. spectrum similar to that obtained above.

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