Reaction of Silver Ion with [ML_2X_2] (L = Amine or Phosphine; M = Pd or Pt; X = I, Cl, or SCN) leading to Orthometallation and Catalytic Activity. *X*-Ray Structure of *ab*-(2-Aminomethyl)phenyl-*c*-carbonyl-*d*-iodoplatinum(II) †

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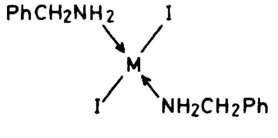
The reaction of *trans*-[$M(NH_2CH_2Ph)_2I_2$] (M = Pd or Pt) with two molar equivalents of $AgBF_4$ leads to *ortho*-metallation of one of the phenyl rings of the benzylamine ligands. The *X*-ray structure of [$\overline{Pt(C_6H_4CH_2N}H_2)(CO)I$] shows the Pt to be in a planar molecule σ-bonded to the phenyl ring. Crystals are orthorhombic, space group *Ibam*, with *a* = 18.376(8), *b* = 16.394(5), *c* = 6.970(1) Å, and *Z* = 8. *R* = 0.037 for 1 071 observed [$I/\sigma(I) \geqslant 3.0$] diffractometer data. Bond data include Pt–I 2.701(1), Pt–C(carbonyl) 1.842(16), Pt–C(aryl) 1.997(15), and Pt–N 2.053(13) Å. The reaction of *cis*-[$M(PMe_2Ph)_2I_2$] (M = Pd or Pt) with two molar equivalents of $AgBF_4$ gives cations which catalyse the addition of water to dimethyl acetylenedicarboxylate.

In the last century the reaction with silver ions of metal complexes containing halogen atoms was frequently used, and in 1938, King[1] reported that the reaction of [$Pt(NH_3)_2Cl_2$] with Ag^+ in aqueous solution gave [$Pt(NH_3)_2(OH_2)_2$]$^{2+}$. The reaction has been used with a range of amine complexes by Cleare[2] who observed that the reaction is best carried out using iodide complexes rather than the chlorides, because of the lower solubility of silver iodide compared with silver chloride. We have found that in some solvents benzylamine complexes undergo *ortho*-metallation when the halide complexes are reacted with silver ion.

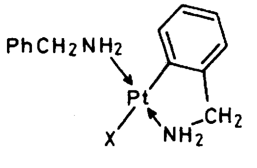
Results and Discussion

Amine Complexes.—The reaction of orange *trans*-bis(benzylamine)di-iodoplatinum(II) (1a) with two molar equivalents of silver tetrafluoroborate in acetone gives an immediate pale yellow precipitate of silver iodide which corresponds in weight to the loss of both iodide ions from the platinum complex. When the filtered solution is concentrated, taken up in aqueous methanol and subsequently treated with excess potassium iodide, a white precipitate is obtained. Analysis of this precipitate agrees with the formulation [$\overline{Pt(C_6H_4CH_2N}H_2)(NH_2CH_2Ph)I$] (2a), in which one of the phenyl rings has undergone internal metallation (see Scheme 1).

Analogous complexes can be prepared in which the iodide in (2a) is substituted by chloride or thiocyanate by adding potassium chloride or thiocyanate in place of potassium iodide. We have subsequently developed an improved procedure for the iodo-compound (see Experimental section). All three compounds were sparingly soluble in common organic solvents, but it was possible to measure the ^1H n.m.r. spectrum of (2a) in [$^2H_6$]dmso (dmso = dimethylsulphoxide) and compare it with the spectrum of the starting material (1a).



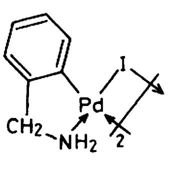
(1a), M = Pt
(1b), M = Pd



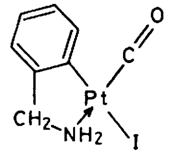
(2a), X = I
(2b), X = Cl
(2c), X = SCN

The spectrum of (2a) has two broad peaks at δ 7.0 and 7.4 in the ratio 4 : 5, whereas in (1a) the phenyl protons appear as an unresolved broad absorption at δ 7.5. The high-field region of the spectrum showed absorptions due to CH_2 and NH_2 but these could not be individually assigned with certainty. The i.r. spectrum of (2b) shows a strong absorption at 268 cm^{-1} characteristic[3a] of Pt–Cl *trans* to carbon. The i.r. spectrum of (2c) shows a single CN-stretching absorption at 2 075 cm^{-1}. This is a low frequency for an S-bonded thiocyanate, although earlier work would suggest that S coordination is more probable.[3b] The question as to whether (2c) is S or N bonded has not been resolved.

When *trans*-bis(benzylamine)di-iodopalladium(II) (1b) is reacted with two molar equivalents of silver tetrafluoroborate in acetone, a quantitative amount of silver iodide is produced. However, subsequent addition of potassium iodide resulted in the reformation of (1b), rather than the formation of an *ortho*-metallated compound as found with platinum. This difference between Pd and Pt was, at first, surprising, but we found that metallation of the phenyl ring by palladium could be effected by carrying out the reaction in ethyl acetate. There was a further difference with palladium in that the metallated compound was a gold coloured dimer (3), from which the unmetallated benzylamine ligand had been lost. The dimer (3) is sparingly soluble in common organic solvents.



(3)



(4)

The i.r. spectrum of (3) in the range 700—800 cm^{-1} is much simpler than either the starting material, (1b), or the *ortho*-metallated platinum compound, (2a). Compound (3) shows a single intense absorption at 729 cm^{-1} which can be assigned[4]

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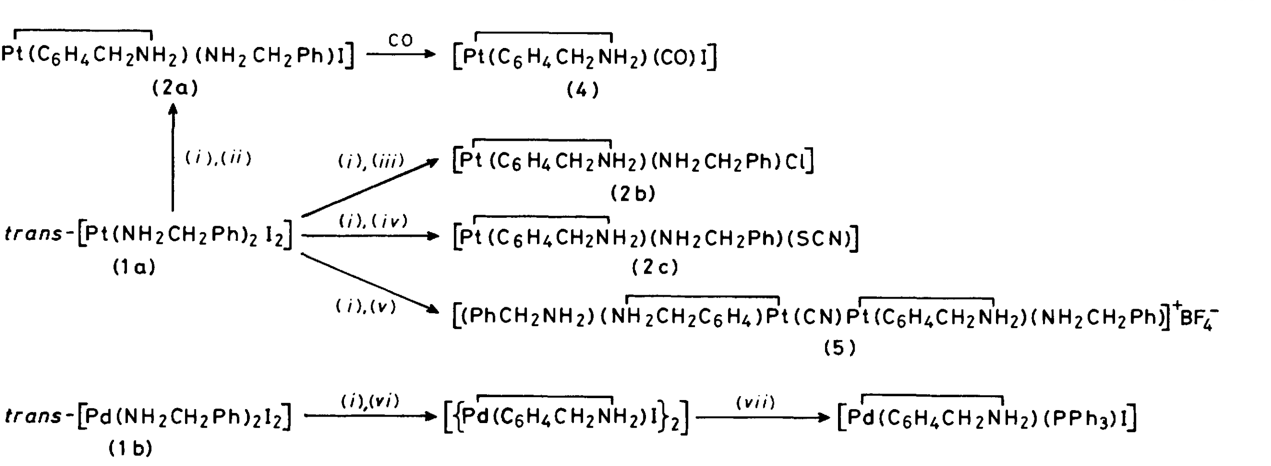
† *Supplementary data available* (No. SUP 23616, 13 pp.): anisotropic temperature factors, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. (*i*) $AgBF_4$; (*ii*) KI; (*iii*) KCl, (*iv*) KSCN; (*v*) KCN; (*vi*) NBu_4I; (*vii*) PPh_3 in acetone

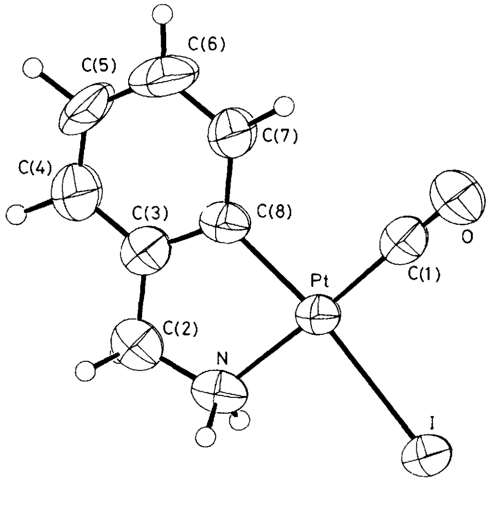


Figure. Molecular structure of (4), showing the atomic numbering

to the C–H out-of-plane deformation of a 1,2-disubstituted benzene ring. The complexes with pendant benzylamine ligands show at least two absorptions in this region.

The influence of solvent in determining the product in the palladium case prompted us to investigate the platinum reaction in methyl cyanide, which has been shown to stabilise dipositive platinum ions.[5] In this solvent the phenyl rings do not undergo metallation, and addition of potassium iodide gave back the starting material. We used this reaction for the preparation of *trans*-bis(benzylamine)dicyanoplatinum(II).[6]

Previous workers[7] in this area have shown that halide-bridged dimers analogous to (3) react with substituted phosphines to give tractable monomeric derivatives. When (3) was reacted with two mol equivalents of triphenylphosphine in acetone, a pale yellow crystalline product was obtained, which analysed for $[Pd(C_6H_4CH_2NH_2)(PPh_3)I]$. The ^1H n.m.r. spectrum of this adduct in $[^2H_6]$dmso showed several multiplets in the range δ 6.2—7.8 (19 H) assigned to the aromatic protons, together with peaks at δ 5.3 (2 H) and 4.2 (2 H) assigned to the NH_2 and CH_2 protons respectively.

The carbonylation of *cis*-bis[2-(*NN*-dimethylaminomethyl)-phenyl-C^1,*N*]platinum(II) has been reported by Chini and co-workers.[8] We have examined the reaction of (2a) with carbon monoxide (*ca.* 10^5 Pa) in methanol. The product of the reaction, which crystallised as fine pale yellow needles from methanol, showed an intense sharp band at 2 082 cm^{-1} in its i.r. spectrum which is indicative of a metal carbonyl.

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

Pt–I	2.701(1)	C(3)–C(4)	1.40(3)
Pt–C(1)	1.842(16)	C(3)–C(8)	1.39(2)
Pt–N	2.053(13)	C(4)–C(5)	1.33(3)
Pt–C(8)	1.997(15)	C(5)–C(6)	1.40(3)
C(1)–O	1.13(2)	C(6)–C(7)	1.36(3)
N–C(2)	1.48(2)	C(7)–C(8)	1.41(2)
C(2)–C(3)	1.48(2)		
I–Pt–C(1)	92.0(5)	C(4)–C(3)–C(8)	121.4(1.6)
I–Pt–N	90.6(3)	C(3)–C(4)–C(5)	118.9(1.7)
C(1)–Pt–C(8)	96.0(7)	C(4)–C(5)–C(6)	122.2(1.9)
N–Pt–C(8)	81.4(6)	C(5)–C(6)–C(7)	118.4(1.7)
Pt–C(1)–O	178.0(1.5)	C(6)–C(7)–C(8)	122.2(1.6)
Pt–N–C(2)	114.6(9)	C(7)–C(8)–C(3)	115.9(1.1)
N–C(2)–C(3)	110.3(1.3)	C(7)–C(8)–Pt	127.3(1.2)
C(2)–C(3)–C(4)	120.7(1.5)	C(3)–C(8)–Pt	116.9(1.4)
C(2)–C(3)–C(8)	117.9(1.4)		

The analytical data were consistent with the formulation $[Pt(C_6H_4CH_2NH_2)(CO)I]$ (4) in which the pendant benzylamine ligand has been displaced by carbon monoxide. In order to obtain full structural characterisation of an *ortho*-metallated benzylamine complex an *X*-ray structure determination of (4) was carried out. The molecular structure and atomic numbering are shown in the Figure. The bond lengths (Å) and angles (°) with standard deviations in parentheses are given in Table 1.

The packing shows no unusual intermolecular contacts, and a packing diagram is not included. All the atoms (except hydrogen) lie in a mirror plane, and the structure confirms the formation of a Pt–C bond at the *ortho* position of the phenyl ring. The carbonyl group is *trans* to nitrogen suggesting that in (2a) the nitrogen atoms are mutually *trans*. The Pt–I distance of 2.701(1) Å is slightly longer than the Pt–I distance of 2.597(1) Å reported in *trans*-di-iodobis(pyridine)platinum(II).[9] The Pt–N distances in (4) and *trans*-$[Pt(py)_2I_2]$ are indistinguishable [2.053(13) and 2.03(2) Å respectively]. The Pt–C(8) distance of 1.997(15) Å is slightly longer than in the dimeric *trans*-di-μ-chloro-bis(2-phenylazophenyl-C^1,*N'*)diplatinum [1.94(2) Å].[10] The dimensions of the Pt–C–O group are similar to those previously reported for Pt^{II} carbonyls.[11]

Attempts to produce the cyanide analogue of (2a) by reacting

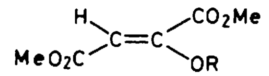
Table 2. Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Pt	87.7(3)	2 179.5(3)	0.0
I	974.2(5)	865.1(6)	0.0
N	−811(7)	1 436(7)	0
O	1 356(7)	3 303(8)	0
C(1)	866(9)	2 888(10)	0
C(2)	−1 515(9)	1 872(11)	0
C(3)	−1 394(9)	2 762(10)	0
C(4)	−1 985(10)	3 305(13)	0
C(5)	−1 853(10)	4 104(13)	0
C(6)	−1 146(14)	4 420(11)	0
C(7)	−580(9)	3 890(11)	0
C(8)	−682(9)	3 040(9)	0
H(1)	−801	1 096	−1 078
H(2)	−1 817	1 707	−1 113
H(4)	−2 508	3 087	0
H(5)	−2 297	4 475	0
H(6)	−1 144	4 993	0
H(7)	−120	4 140	0

the intermediate ion with potassium cyanide produced a complicated reaction. Rather than the expected monomeric product, a white powder was obtained which showed absorption due to both fluoroborate and cyanide in its i.r. spectrum. The fluoroborate absorption was the usual [12] broad band in the range 1 000—1 100 cm^{-1}, and the cyanide absorption occurs at 2 145 cm^{-1}. The analysis of this product suggests a formulation with both fluoroborate and cyanide, and with four benzylamine moieties for every two platinum atoms. The co-ordination requirements of the Pt atoms and the presence of both cyanide and fluoroborate in the compound are best accommodated by a structure with a bridging cyanide ligand, $[(PhCH_2NH_2)(\overline{NH_2CH_2C_6H_4)Pt}(CN)\overline{Pt(C_6H_4CH_2NH_2})(NH_2\text{-}CH_2Ph)]BF_4$ (5). The cyanide stretching frequency is above the range observed for terminal cyanide groups bonded to platinum, although slightly below the formal limit for bridging cyanides reported by Kharitonov *et al.*[13]

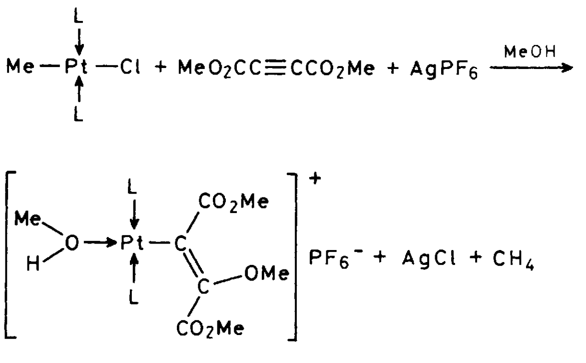
The metallation reactions described here are interesting as the conditions of the reaction strongly suggest that the reaction proceeds by electrophilic attack of the metal ion on the phenyl ring. In this case the electrophile is produced by generating a formal charge of +2 at the metal. However, in general *ortho*-metallation reactions are dependent on a number of factors. In their early work Cope and Friedrich [14] discovered that *NN*-dimethylbenzylamine undergoes *ortho*-metallation on reaction with $[PdCl_4]^{2-}$, but that benzylamine itself did not. Later Lewis and co-workers [15] showed that disubstitution at the benzylic carbon also promotes *ortho*-metallation. Shaw [16] has suggested that the reason for the different behaviour is that the disubstituted compounds lose less internal entropy on cyclisation compared with the parent compound. Our own results show that if the electronic factors are very favourable the cyclisation can occur with the unsubstituted ligands. The reactions of the new benzylamine complexes are being studied.

Phosphine Complexes.—Doubly charged cationic phosphine complexes of Pd and Pt have been reported by several groups.[5,17] Recently the use of this type of Pd complex as a hydrogenation catalyst was reported.[17] The reactions of complexes of the type $[M(diene)(MeCN)_2]^{2+}$ (M = Pd or Pt) have also been reported.[18] There have also been extensive studies, most notably by Maitlis,[19] of the reactions of acetylenes with palladium compounds. It appeared to us that the complexes $[M(PR_3)_2(solvent)_2]^{2+}$ might promote C–C bond formation, when reacted with acetylenes. An *ortho*-metallation reaction was also possible, but somewhat unlikely because four-membered rings, although known, are rare in *ortho*-metallated species.[20,21] We found that the reaction of dimethyl acetylenedicarboxylate (dmad) with $[M(PR_3)_2(solvent)_2]^{2+}$ in moist acetone leads to hydration of the acetylene. The complex *cis*-dichlorobis(dimethylphenylphosphine)-platinum(II) reacts with two molar equivalents of silver fluoroborate in acetone to produce a theoretically equivalent amount of silver chloride. The ^1H n.m.r. spectrum of the filtered solution measured using $[^2H_6]$acetone as the reaction solvent indicates that the configuration of the phosphorus atoms remains *cis* in the cationic species. Addition of potassium chloride to the solution regenerates the starting material and establishes that *ortho*-metallation does not occur in this system. If the platinum-containing cation, which we assume to be *cis*-$[Pt(PMe_2Ph)_2(Me_2CO)_2]^{2+}$, is refluxed with dmad the solution changes in colour through red to almost black over a period of *ca.* 18 h. Evaporation of the solvent and chromatography of the residue allows the recovery of the starting acetylene and small amounts of a crystalline solid. This solid was identified as oxalacetic acid dimethyl ester (6a), showing that the dmad had undergone hydration. Repeating this reaction in moist acetone with *cis*-$[Pd(PMe_2Ph)_2(Me_2CO)_2]^{2+}$ and dmad gave complete conversion to (6a) which is predominantly an enol at room temperature.



(6a), R = H
(6b), R = Me

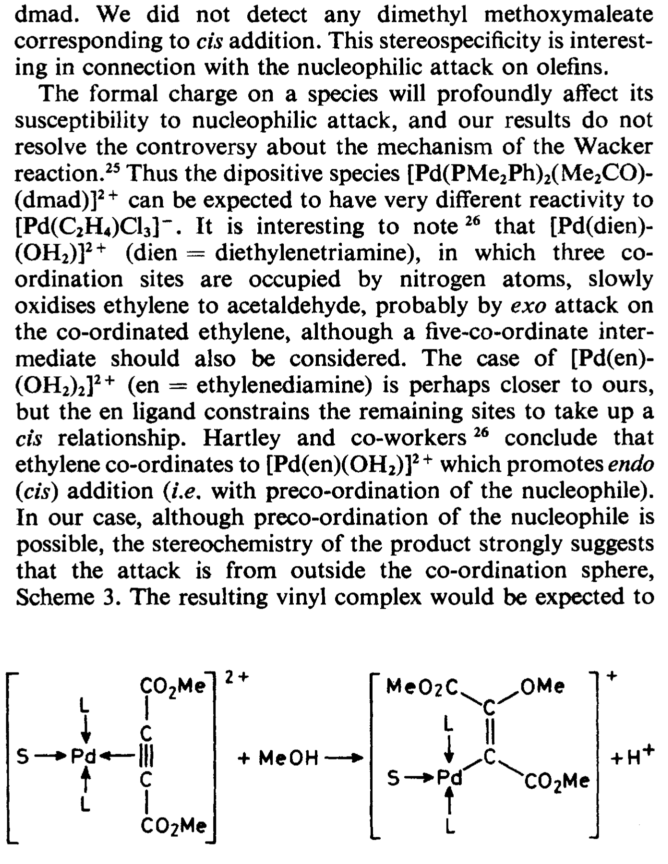
The addition of water to the triple bond of acetylenes is catalysed by a variety of acids and metal salts, especially mercury(II) salts. The formation of an enol from dmad and sulphuric acid was reported by Buchner in 1889.[22] More recently Halpern *et. al.*[23] reported that $RuCl_3$ catalyses the addition of water to acetylenes, and they have proposed a mechanism involving a vinyl alcohol group bonded to the metal atom. Related studies have been carried out by Chisholm and Clark,[24] see Scheme 2.



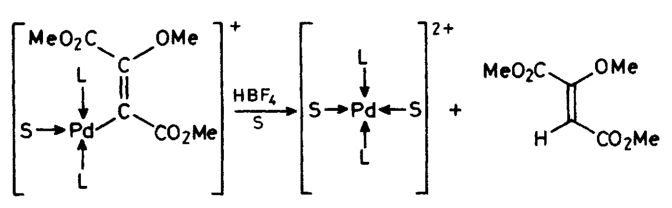
Scheme 2.

As the palladium complex gave a cleaner reaction than the platinum complex in the hydration reaction we investigated the reaction of $[Pd(PMe_2Ph)_2Cl_2]$ with two molar equivalents of silver tetrafluoroborate with dmad in methanol. This reaction gave a high-boiling organic product which was characterised as dimethyl methoxyfumarate (6b). This corresponds to *trans* addition of methanol to the triple bond of dmad. We did not detect any dimethyl methoxymaleate corresponding to *cis* addition. This stereospecificity is interesting in connection with the nucleophilic attack on olefins.

The formal charge on a species will profoundly affect its susceptibility to nucleophilic attack, and our results do not resolve the controversy about the mechanism of the Wacker reaction.[25] Thus the dipositive species $[Pd(PMe_2Ph)_2(Me_2CO)(dmad)]^{2+}$ can be expected to have very different reactivity to $[Pd(C_2H_4)Cl_3]^-$. It is interesting to note[26] that $[Pd(dien)(OH_2)]^{2+}$ (dien = diethylenetriamine), in which three co-ordination sites are occupied by nitrogen atoms, slowly oxidises ethylene to acetaldehyde, probably by *exo* attack on the co-ordinated ethylene, although a five-co-ordinate intermediate should also be considered. The case of $[Pd(en)(OH_2)_2]^{2+}$ (en = ethylenediamine) is perhaps closer to ours, but the en ligand constrains the remaining sites to take up a *cis* relationship. Hartley and co-workers[26] conclude that ethylene co-ordinates to $[Pd(en)(OH_2)]^{2+}$ which promotes *endo* (*cis*) addition (*i.e.* with preco-ordination of the nucleophile). In our case, although preco-ordination of the nucleophile is possible, the stereochemistry of the product strongly suggests that the attack is from outside the co-ordination sphere, Scheme 3. The resulting vinyl complex would be expected to be cleaved in the acidic reaction medium (Scheme 4). The lower reactivity of the Pt complex may be caused by the greater stability of the Pt–C bond at this stage. These results are in agreement with theoretical calculations on the nucleophilic attack on co-ordinated acetylenes, which suggest that the *trans* approach of a nucleophile and slippage towards a σ-bonded system is a favoured reaction path for both acetylenes[27] and olefins.[28]



Scheme 3. S = Solvent



Scheme 4. S = Solvent

Experimental

Reactions with metal salts were carried out in air with no special precautions. I.r. spectra were recorded as Nujol mulls using caesium iodide plates on a Perkin-Elmer model 325 spectrophotometer. *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ and *cis*-$[Pd(PMe_2Ph)_2Cl_2]$ were prepared by the method of Jenkins and Shaw[29] without modification. Melting point data are not given for the new amine complexes because they darken over a broad temperature range.

trans-*Bis*(*benzylamine*)*di-iodoplatinum*(II) (1a).—This complex was prepared by a method analogous to that described by Kauffman[30] for the preparation of *trans*-dichlorobis(pyridine)platinum(II).

Potassium tetrachloroplatinate(II) (1.0 g, 2.41 mmol) was treated with a large excess of benzylamine (5 cm^3) in water (100 cm^3). The resulting suspension was boiled until the initial precipitate of *cis*-$[Pt(NH_2CH_2Ph)_2Cl_2]$ dissolved to give a clear colourless solution. The solution was then filtered while hot and the excess amine neutralised by careful addition of concentrated hydriodic acid. A further amount (20 cm^3) of hydriodic acid was then added and the solution heated to near boiling temperature. The solution was then left to cool slowly to room temperature. The resulting yellow precipitate was filtered off, washed several times with water and dried *in vacuo*. Recrystallisation from hot acetone gave yellow needles (1.12 g) (Found: C, 25.7; H, 2.75; N, 4.15. $C_{14}H_{18}I_2N_2Pt$ requires C, 25.4; H, 2.75; N, 4.2%).

ab-(2-*Aminomethyl*)*phenyl*-c-*benzylamine*-d-*iodoplatinum*(II) (2a).—*Method A*. *trans*-Bis(benzylamine)di-iodoplatinum(II) (0.86 g, 1.30 mmol) in hot acetone (100 cm^3) was treated with silver tetrafluoroborate (0.5 g, 2.57 mmol) in acetone (10 cm^3). The resulting precipitate of silver iodide was filtered off and the filtrate evaporated to a minimum volume under reduced pressure. Water–methanol (150 cm^3, 2 : 1) was added to the residue and the resultant suspension warmed and left to stand for 30 min. The suspension was then filtered to give a clear colourless solution, which was treated with potassium iodide (0.5 g). The white precipitate which appeared immediately on the addition of potassium iodide was collected by filtration, washed several times with water and finally with a small portion of acetone. The solid (0.42 g) was dried under vacuum (Found: C, 31.4; H, 3.2; N, 5.25. $C_{14}H_{17}IN_2Pt$ requires C, 31.5; H, 3.0; N, 5.2%).

Method B. *trans*-Bis(benzylamine)di-iodoplatinum(II) (0.86 g, 1.30 mmol) in hot methanol (100 cm^3) was treated with silver tetrafluoroborate (0.5 g, 2.57 mmol) in methanol (10 cm^3). The resulting silver iodide precipitate was filtered off, and 100 cm^3 of water was added to the filtrate. This was then heated to 50 °C for 30 min, and an excess (0.5 g) of potassium iodide was then added. The resulting white precipitate was allowed to cool, then filtered off, washed with water and then a small quantity of acetone (yield 0.6 g).

ab-(2-*Aminomethyl*)*phenyl*-c-*benzylamine*-d-*chloroplatinum*(II) (2b).—The procedure described (Method A) for the preparation of *ab*-(2-aminomethyl)phenyl-*c*-benzylamine-*d*-iodoplatinum(II) was followed using potassium chloride (0.5 g) instead of KI. The product (0.36 g) was obtained as a white powder (Found: C, 36.6; H, 3.85; N, 6.25. $C_{14}H_{17}ClN_2Pt$ requires C, 37.9; H, 3.85; N, 6.3%).

ab-(2-*Aminomethyl*)*phenyl*-c-*benzylamine*-d-*thiocyanatoplatinum*(II) (2c).—The procedure described for the preparation of *ab*-(2-aminomethyl)phenyl-*c*-benzylamine-*d*-iodoplatinum(II) (Method A) was followed using potassium thiocyanate (0.5 g) instead of KI. The product (0.39 g) was obtained as a white powder (Found: C. 38.8; H, 3.65; N, 4.05. $C_{15}H_{17}N_3PtS$ requires C, 38.6; H, 3.7; N, 4.0%).

μ-Cyano-bis{[(2-*aminomethyl*)*phenyl*](*benzylamine*)-*platinum*(II)} *Fluoroborate* (5).—The procedure described for the preparation of *ab*-(2-aminomethyl)phenyl-*c*-benzylamine-*d*-iodoplatinum(II) (Method A) was followed using aqueous potassium cyanide (0.3 g, 10 cm^3) in place of KI. The aqueous KCN was added dropwise to the filtrate until precipitation of the white solid seemed complete. The white solid (0.38 g) was collected by filtration, washed several times with water and finally with a small quantity of cold acetone, then dried under vacuum (Found: C, 37.4; H, 3.65; N, 7.35. $C_{29}H_{34}BF_4N_5Pt_2$ requires C, 37.4; H, 3.7; N, 7.55%).

ab-(2-*Aminomethyl*)*phenyl*-c-*carbonyl*-d-*iodoplatinum*(II) (4).—Carbon monoxide was bubbled through a suspension of the complex *ab*-(2-aminomethyl)phenyl-*c*-benzylamine-*d*-iodoplatinum(II) (0.5 g, 0.93 mmol) in methanol (75 cm^3) at atmospheric pressure. After a period of about 24 h, the initial complex dissolved to give a light yellow-green solution. The solution was filtered and reduced to a small volume (20 cm^3) by boiling. On cooling, fine yellow-green crystals (0.26 g) were obtained which were collected by filtration, washed with a small quantity of diethyl ether and dried *in vacuo* (Found: C, 21.3; H, 1.7; N, 3.1. C_8H_8INOPt requires C, 21.1; H, 1.75; N, 3.1%).

trans-*Bis*(*benzylamine*)*di-iodopalladium*(II) (1b).—Palladium(II) chloride (2 g, 11.28 mmol) and sodium chloride (2 g) were heated in water (120 cm^3) to *ca.* 60 °C until dissolved. The filtered solution was treated at room temperature with aqueous benzylamine solution (30% v/v) until precipitation was complete. The crude dichloro-complex * was filtered off, washed with water and acetone, and then dissolved in a solution of lithium iodide monohydrate (3.5 g) in acetone (200 cm^3). The mixture was stirred on a water-bath at *ca.* 60 °C for 1 h, filtered and concentrated to a small volume *in vacuo*. The dark residue on recrystallisation from methanol gave the product as orange crystals (4.3 g, 66%) (Found: C, 29.4; H, 3.1; N, 4.85. $C_{14}H_{18}I_2N_2Pd$ requires C, 29.3; H, 3.15; N, 4.9%).

Di-μ-iodo-bis{[(2-*aminomethyl*)*phenyl*]*palladium*(II)} (3).—*trans*-Bis(benzylamine)di-iodopalladium(II) (1.75 g, 3.05 mmol) was taken up in ethyl acetate (50 cm^3) and treated with a solution of silver tetrafluoroborate (1.185 g, 6.1 mmol) in ethyl acetate (10 cm^3) and left to stand for 15 min. The resulting precipitate of silver iodide was then removed by filtration. The filtrate was made up to a larger volume (150 cm^3) with ethyl acetate and allowed to stand overnight at room temperature. A slight excess of tetrabutylammonium iodide (1.2 g, 3.8 mmol) was then added to the reaction mixture, and the resulting mixture stirred for 30 min. The mixture was then reduced to about 20 cm^3 on a rotary evaporator, and left to cool in an ice-salt bath. The resulting solid was collected by filtration, washed with water-acetone (1 : 1), followed by a small portion of neat acetone until the solid became light brown in colour. The product was recrystallised from acetone to give golden crystals (0.75 g, 73%) (Found: C, 24.8; H, 2.45; N, 4.1. $C_{14}H_{16}I_2N_2Pd_2$ requires C, 24.8; H, 2.4; N, 4.15%).

ab-(2-*Aminomethyl*)*phenyl*-d-*iodo*-c-*triphenylphosphine*-*palladium*(II).—Di-μ-iodo-bis{[(2-aminomethyl)phenyl]-palladium(II)} (3) (0.20 g, 0.29 mmol) was added to a solution of PPh_3 (0.15 g, 0.58 mmol) in acetone (30 cm^3). The mixture was warmed and stirred for about 5 min to dissolve all the solid. The resulting pale yellow solution was filtered, concentrated to a small volume and cooled to give the product as yellow crystals (0.25 g) (Found: C, 50.2; H, 3.85; N, 2.3. $C_{25}H_{23}INPPd$ requires C, 49.9; H, 3.85; N, 2.35%).

Reaction of cis-$[Pd(PMe_2Ph)_2(solvent)_2][BF_4]_2$ *with Dimethyl Acetylenedicarboxylate in Moist Acetone.*—*cis*-Dichlorobis(dimethylphenylphosphine)palladium(II) (0.46 g, 1.0 mmol) in acetone (40 cm^3) was treated with $AgBF_4$ (0.39 g, 2 mmol) in acetone (10 cm^3). The resulting silver chloride precipitate was then removed by filtration. Dimethyl acetylenedicarboxylate (3.0 g, 21.0 mmol) and water (0.5 cm^3) were added to the filtrate and the solution was refluxed overnight during which time it gradually darkened. The solution was then evaporated to a minimum volume under reduced pressure. The dark residue was taken up in benzene and transferred to a chromatography column (silica gel, 50 × 2.5 cm). A small amount of the unreacted dmad was first eluted with benzene. Further elution with benzene-ethyl acetate (97 : 3 v/v) gave oxalacetic acid dimethyl ester (6a). The sample was recrystallised from hexane (charcoal) to give colourless crystals (1.2 g), m.p. 75—77 °C, lit.[32] 76—78 °C (Found: C, 44.4; H, 4.9; O, 50.6; M^+, 160. Calc. for $C_6H_8O_5$: C, 45.0; H, 5.05; O, 50.0%; M^+, 160). ^1H N.m.r. ($CDCl_3$) showed absorptions at δ 5.8 (=CH); 3.7 and 3.62 p.p.m. (OMe). The ^1H n.m.r. spectrum is consistent with (6a) being in the enol form. Other workers[33] have found (6a) to be 80% enolic in chloroform and 50% enolic in methanol.

Reaction of cis-$[Pd(PMe_2Ph)_2(solvent)_2][BF_4]_2$ *with Dimethyl Acetylenedicarboxylate in Methanol.*—Silver tetrafluoroborate (0.39 g, 2.0 mmol) was accurately weighed out and taken up in methanol (10 cm^3). A stoicheiometric amount of *cis*-$[Pd(PMe_2Ph)_2Cl_2]$ (0.46 g, 1.0 mmol) was then weighed out, taken up in methanol and treated with the silver tetrafluoroborate solution. The resulting silver chloride precipitate was removed by filtration. Dimethyl acetylenedicarboxylate (5.0 g, 35 mmol) was added to the filtrate and the solution refluxed overnight. The excess methanol was then removed under reduced pressure leaving behind a dark oily residue. Dimethyl methoxyfumarate (6b) was isolated by distillation from the residue (3.5 g), b.p. 230 °C (Found: C, 48.6; H, 6.2. Calc. for $C_7H_{10}O_5$: C, 48.3; H, 5.8%). ^1H N.m.r. spectrum ($CDCl_3$) showed absorptions at δ 6.2 (=CH); 4.0, 3.9, and 3.8 p.p.m. (OMe) with appropriate intensity ratios 1 : 3 : 3 : 3. These values are in full agreement with literature values.[34]

Crystal Structure Determination of Complex (4).—Needle-shaped crystals were obtained from methanol. A crystal of dimensions 0.5 × 0.06 × 0.04 mm was used.

Crystal data. C_8H_8INOPt, $M = 456.1$, Orthorhombic, space group *Ibam*, $a = 18.376(8)$, $b = 16.394(5)$, $c = 6.970(1)$ Å, $U = 2\,100$ Å^3, $D_m = 2.64$ g cm^{-3}, $Z = 8$, $D_c = 2.88$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 77.8 cm^{-1}, $F(000) = 1\,616$.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range $\pm 0.9°$ (2θ)

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* Cope and Friedrich[14] have previously described a similar method for the preparation of bis(benzylamine)dichloropalladium(II); however, the configuration of the product was not specified. According to the *trans* effect, treating sodium tetrachloropalladate(II) with amines should result in the formation of the *cis* isomer. The i.r. spectrum of the crude sample showed two bands at *ca.* 305 and 318 cm^{-1} due to the symmetric and asymmetric Pd-Cl stretching vibrations. This is typical of two co-ordinating chloro-groups in mutually *cis* positions. According to Coe and Lyons[31] this method does not always afford the pure *cis* isomer. They observed that *cis*-bis(amine)dihalogenopalladium(II) complexes, especially the iodides, isomerise, even in the solid, to the corresponding *trans* isomers.

around the K_{α_1}–K_{α_2} angles, scan speed 1—29° min^{-1}, depending on the intensity of a 2-s prescan; backgrounds were measured at each end of the scan for 25% of the scan time. Three standard reflections were monitored every 100 reflections, and showed no changes during the data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fitting to 15 high-angle reflections. 1 071 Observed reflections [$I/\sigma(I) > 3.0$] were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR;[35] maximum and minimum transmission factors were 0.74 and 0.59.

Systematic absences hkl, $h + k + l = 2n$; $0kl$, $k = 2n$; and $h0l$, $h = 2n$ indicated space groups *Ibam* or *Iba*2. The former was selected and shown to be correct by the successful refinement. All the atoms (except H) lie in the mirror plane at $z = 0$ (special position 8*j*). The heavy atoms were located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors, $B = 5.0$ Å^2, and were not refined. Final refinement was by full-matrix least-squares methods.

A weighing scheme of the form $w = XY$ was used where $X = 1.0$, or $F/70$ for $F < 70.0$, or $100.0/F$ for $F > 100.0$; $Y = 1.0$, or $(0.35 \sin\theta)/\lambda$ for $(\sin\theta)/\lambda < 0.35$, or $0.4/[(\sin\theta)/\lambda]$ for $(\sin\theta)/\lambda > 0.4$. This was shown to be satisfactory by weight analysis. The final R value was 0.037. Computing was with the *X*-RAY 76 system,[36] on a Burroughs B6700 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 37. Bond lengths and angles are given in Table 1 and final atomic co-ordinates are in Table 2.

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