Nucleophilic Attack of Methanol on Bis(benzonitrile)dichloroplatinum: Formation of Mono- and Bis-imido Ester Derivatives

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The *trans* and *cis* isomers of $[PtCl_2(NCPh)_2]$ react stepwise with methanol, under basic conditions, to give the mono- and bis-imido ester derivatives $[PtCl_2(NCPh)\{HN{=}C(OMe)Ph\}]$ and $[PtCl_2\{HN{=}C(OMe)Ph\}_2]$. The isomerization about the C=N double bond is slow enough to allow separation of species with different conformations of the imido ester ligands (*E* or *Z*). Under basic conditions the isomerization becomes faster and takes place through reversible addition of an extra methoxide ion to the carbon atom of the azomethine residue. The composition of the isomeric mixture, in the case of the bis(imido ester) derivatives, indicates that the *E* conformation is slightly preferred over *Z*. This preference is more marked in the *cis* than in the *trans* complexes.

The synthetic and structural chemistry of co-ordinated nitriles which are susceptible to nucleophilic attack by water, alcohols, and amines to yield the corresponding amides, imidic esters, and amidines has been broadly established.[1] More recently it has been demonstrated that the platinum complex $[PtCl_2(NCPh)_2]$, which is widely used as a starting material for the preparation of organoplatinum(II) complexes,[2] also reacts readily with carbanions $[CH(PPh_2)X]^-$ (X = CO_2Et or CN)[3] and $CH(COMe)(COR)^-$ (R = Me or Ph)[4], primary amines (NH_2Bu^n),[5] and diamines (*N,N'*-di-t-butylethylenediamine)[6] to give the corresponding addition products.

In this paper we describe the hitherto unreported reaction of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ with alcohols.

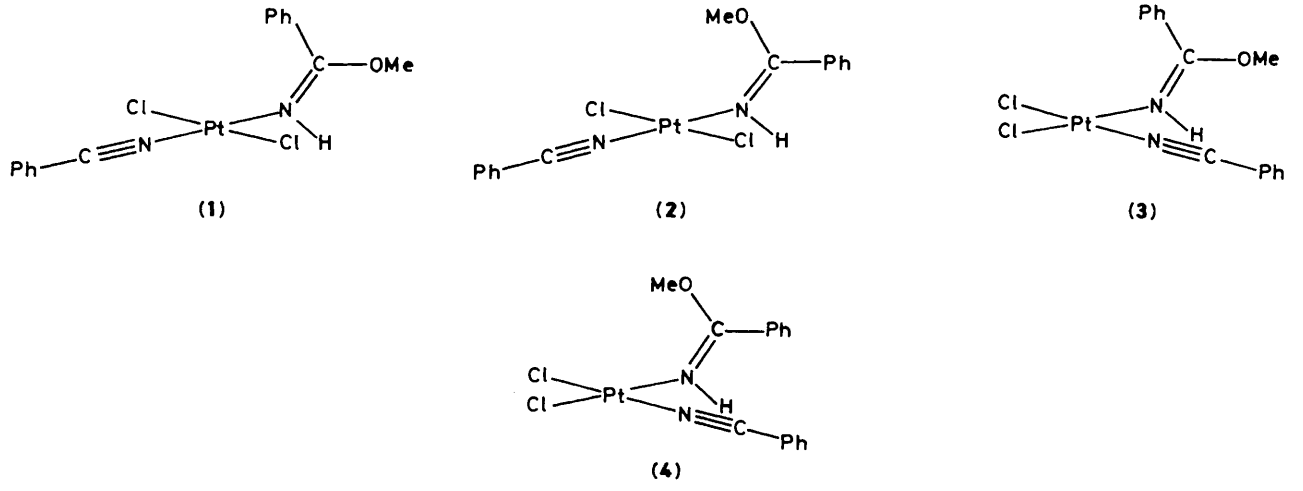
Results and Discussion

General Description of the Reaction and Products.—The addition of methanol to benzonitrile, in platinum complexes, takes place readily in the presence of a catalytic amount of base. If the quantity of methanol in the reaction solvent is small [dichloromethane–methanol (20:1, v/v)] and the reaction is stopped just before complete disappearance of the starting substrate, then the monoimido ester derivative is the prevailing product. On the other hand, using a solvent richer in methanol [dichloromethane–methanol (1:1, v/v)] and prolonging the reaction time until complete disappearance of the starting substrate, and of the intermediate monoimido ester species, it is possible to obtain the bis(imido ester) complex.

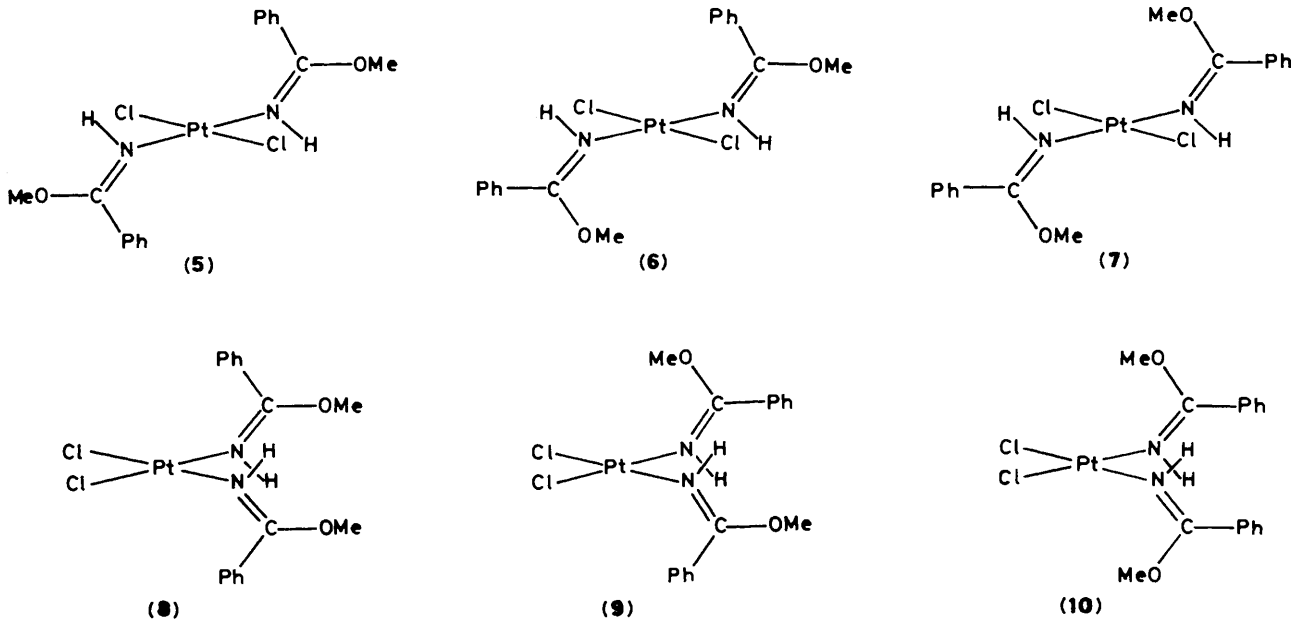
Starting with *trans*-$[PtCl_2(NCPh)_2]$, the monoimido ester complex is formed in two isomeric forms, with *E* and *Z* conformation of the ligand; compounds (**1**) and (**2**) of Scheme 1. Compound (**1**), being less soluble in dichloromethane, separates out as a yellow crystalline solid upon concentration of the dichloromethane–methanol solution. The second isomer, (**2**), can be recovered from the mother-liquor by chromatography on an open column of silica gel [eluant dichloromethane–acetone (50:1, v/v)].

Addition of methanol to the second molecule of benzonitrile leads to formation of the bis(imido ester) complex *trans*-$[PtCl_2\{HN{=}C(OMe)Ph\}_2]$, which can be obtained in three isomeric forms, with *EE*, *EZ*, and *ZZ* conformations at the imido ester ligands; compounds (**5**), (**6**), and (**7**) of Scheme 2.

In concentrated conditions {1 mmol of $[PtCl_2(NCPh)_2]$ and 0.03 mmol of KOH in 2 cm^3 of dichloromethane–methanol (1:1, v/v)} the solution formed soon after the mixing of the reagents, and left under stirring for 0.5 h, yields a yellow solid of pure (**6**). On leaving the mixture under further stirring for 1 d, complete transformation of (**6**) to (**7**) is observed. Under more dilute conditions (10 times as much solvent) the solution obtained after stirring for 1 h contains a mixture of the three



Scheme 1.



Scheme 2.

isomers which can be resolved by chromatography [open column of silica gel, eluant dichloromethane–acetone (20:1, v/v)]; isomer (**5**) is the last compound to be eluted.

Starting with *cis*-$[PtCl_2(NCPh)_2]$, the monoimido ester derivative *cis*-$[PtCl_2(NCPh)\{HN{=}C(OMe)Ph\}]$ is obtained in two isomeric forms, with *E* and *Z* conformation of the ligand; compounds (**3**) and (**4**) of Scheme 1. Separation of the two isomers was accomplished by fractional crystallization or chromatography [open column of silica gel, eluant dichloromethane–acetone (50:1, v/v)].

Addition of alcohol to the second benzonitrile leads to formation of the bis(imido ester) derivative *cis*-$[PtCl_2\{HN{=}C(OMe)Ph\}_2]$ which is present in three isomeric forms, with *EE*, *EZ*, and *ZZ* conformations of the ligands; compounds (**8**), (**9**), and (**10**) of Scheme 2.

Only compounds (**8**) and (**9**) were formed in significant quantities and could be isolated in the solid state. A mixture of these two compounds precipitates out directly from the solution obtained upon mixing of the reagents, after stirring for 0.5 h [1 mmol of substrate, 0.06 mmol of KOH, and 4 cm^3 of chloroform–methanol (1:1, v/v)]. If the precipitate is not driven off but the reaction mixture is left under further stirring for 1 d, complete conversion of the solid into pure compound (**8**) is observed.

I.r. and N.M.R. Spectra.—The main questions related to the structural characterization of the isolated compounds concern the co-ordination about the metal centre (*cis* or *trans*) and the conformation of the imido ester ligands (*E* or *Z*).

The most compelling evidence against isomerization of the complex during addition of methanol to benzonitrile stems from the absence of common reaction products starting from either the *cis* or the *trans* isomer of $[PtCl_2(NCPh)_2]$.

Further evidence in favour of retention of configuration comes from inspection of the i.r. spectra in the region of the Pt–Cl stretching bands, which are very sensitive to changes in the symmetry of the complex.[7] The mono- and bis-(imido ester) complexes derived from *trans*-$[PtCl_2(NCPh)_2]$ exhibit a single band assignable to Pt–Cl stretching. This occurs at slightly higher frequency for the mono- (340 cm^{-1}) than for the bis-(imido ester) species (320 cm^{-1}). On the other hand, the mono- and bis-(imido ester) complexes derived from *cis*-$[PtCl_2(NCPh)_2]$ exhibit two bands assignable to Pt–Cl stretching and in this case also the frequencies are slightly higher for the mono derivative (330 and 340 cm^{-1}) than for the bis-(imido ester) derivatives (*ca.* 320 and 330 cm^{-1}).

The conformation of the imido ester ligands (*E* or *Z*) could be assigned on the basis of the n.m.r. data. In Schemes 1 and 2 it is shown how the *ortho* protons of the phenyl, or, alternately, the methyl protons of the methoxy group, are arranged about the platinum atom depending upon the *E* or *Z* conformation of the imido ester ligand. As a consequence of this a downfield shift is expected for the *ortho* protons of the phenyl group, in the case of the *E* conformation, and for the methyl protons of the methoxy group, in the case of the *Z* conformation.[8] The data are summarized in the Table. It is to be noted that, with the exception of compound (**9**), which deserves further comment, the downfield shift experienced by the protons of the methoxy group, when it is *cis* to platinum, is more than 1 p.p.m.; on the other hand, the downfield shift of the *ortho* protons of phenyl, when it is *cis* to platinum, ranges from 0.6 to 1 p.p.m.

Compound (**9**) is rather peculiar since the two imido ester ligands have different conformations and consequently the MeO groups are in different positions with respect to platinum. However, the chemical shift separation between the methyl protons is only 0.2 p.p.m. instead of the expected value of 1 p.p.m. Probably, the two ligands *cis* to one another and containing a Ph group influence each other in such a way as to compensate partially for the magnetic effect of the metal.

Isomerization about the C=N *Double Bond.*—The configuration of the imido ester ligands is stable under normal conditions and the different isomeric complexes could be separated by fractional crystallization or chromatography. We searched for the conditions of fast isomerization and investigated whether there was a preference for one conformation over the other. It was found that the presence of a catalytic amount of base, which is required for the addition of methanol to the benzonitrile ligand, is also capable of inducing isomerization about the C=N double bond of the imido ester ligand. It is most likely that a methoxy group undergoes nucleophilic attack upon the carbon atom of the azomethine residue, leading to the

formation of an amidoketal which afterwards re-eliminates the methoxy group, reforming the imido ester ligand (see Scheme 3).

This reaction pathway was confirmed by an experiment in which the isomerization was carried out in basic deuteriomethanol. It could be demonstrated that isomerization and deuteriation of the imido ester ligand go hand in hand.

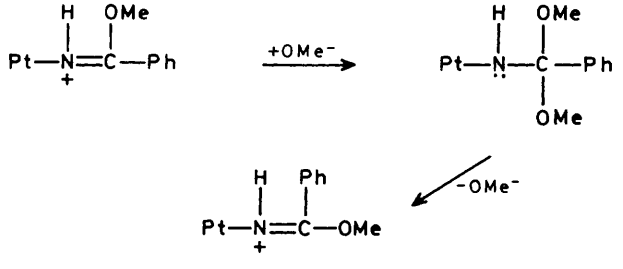
Since the conditions for isomerization and addition of methanol to benzonitrile are the same we could investigate the composition of the isomeric mixture, under conditions of fast isomerization, only in the case of the bis(imido ester) complexes. The experiment was performed by adding one drop of basic CH_3OD to a solution of the *EZ* isomer in deuteriochloroform and monitoring from time to time the appearance of the resonance patterns of the *EE* and *ZZ* isomers. The composition of the isomeric mixture was 3:8:1 for (**5**):(**6**):(**7**) (*trans* complexes) and 7:10:1 for (**8**):(**9**):(**10**) (*cis* complexes). This experiment showed that the *E* conformation is slightly favoured over the *Z* conformation. Moreover this preference is more marked in the case of the *cis* complexes in which a reciprocal influence between the two ligands is likely to occur.

The possible formation of *E* and *Z* isomers was already suggested in the case of *trans*-$[Ni(C_6Cl_5)(PMe_2Ph)_2\{HN{=}C(OMe)R\}]^+$ (R = Me, CH_2Ph, or Ph). However, such a mixture was not detected in all cases examined nor the conditions of isomerization investigated.[9] Isomerization about the C=N double bond was also observed in the amino amidine complex $[PtCl_2(PhCN)\{HN{=}CPh{-}NBu^tCH_2CH_2NHBu^t\}]$. The two different isomers could not be separated since the isomerization was fast under preparative conditions; perhaps we can now understand why?[6] The aminoamidine ligand contains a free aminic group which can give an internal cyclization reaction by nucleophilic attack upon the carbon atom of the azomethine residue. Reopening of the ring by dissociation of one end of the diamine would reproduce the original ligand and so provide a means for isomerization (Scheme 4).

Table. Proton chemical shifts (δ downfield from $SiMe_4$)[a] and ν(Pt–Cl) (cm^{-1}) of isolated compounds

	^1H N.m.r.				
			C_6H_5		I.r.
Complex	NH	OCH_3	*o*	*m*, *p*	ν(Pt–Cl)
(**1**)	*b*	4.08	8.72 7.82	7.20—7.75	340
(**2**)[c]	*b*	5.18	7.80 7.68	7.40—7.65	340
(**3**)	8.20	4.24	8.74 7.55	7.24—7.74	330, 340
(**4**)	8.90	5.34	8.00 7.84	7.38—7.74	330, 340
(**5**)	8.36	4.06	8.56 (4 H)	7.35—7.65	320
(**6**)	8.54 9.11	4.06 5.00	8.44 7.84	7.30—7.65	330
(**7**)	8.10	5.30	7.75 (4 H)	7.40—7.60	320
(**8**)	7.95	3.78	8.34 (4 H)	7.30—7.50	320, 330
(**9**)	8.72 8.94	4.16 4.34	8.45 7.58	7.20—7.65	315, 325
(**10**)[d]		4.78		7.15—7.70	

[a] Solvent $CDCl_3$. [b] Obscured by phenyl resonances. [c] Solvent CD_2Cl_2. [d] This isomer was not isolated, the spectrum of a solution in which it was in equilibrium (*ca.* 5%) with (**8**) and (**9**) allowed the accurate determination of only the most intense methyl resonance.



Scheme 3.

Conclusions

The reactivity of $[PtCl_2(NCPh)_2]$ towards anionic nucleophiles and amines has been extended to include alcohols. The reaction takes place in the presence of a catalytic amount of base and proceeds in two steps leading to the formation of mono- and bis-(imido ester) complexes. Formation of *E* and *Z* conformers, corresponding to *cis* and *trans* addition of the alcohol to the C≡N triple bond, has been observed. The rate of interconversion is slow under normal conditions allowing the separation of different isomers by fractional crystallization and chromatography. The isomerization process is catalyzed by the presence of a base and proceeds through addition of a further methoxy group to the imido ester ligand and formation of an intermediate amidoketal which re-eliminates the methoxide ion, reforming the imido ester species.

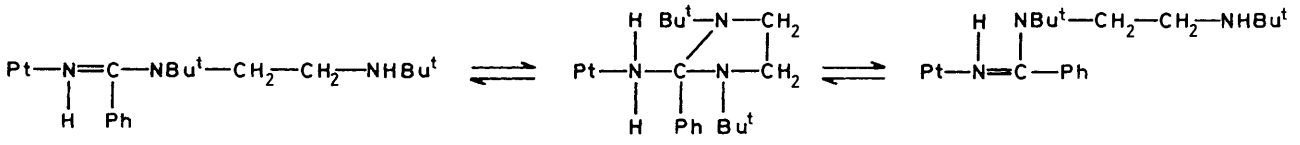
A similar process can be invoked to explain the fast isomerization about the C=N double bond observed in the aminoamidine complex $[PtCl_2(PhCN)\{HN{=}CPhNBu^tCH_2{-}CH_2NHBu^t\}]$ in which nucleophilic attack upon the azomethine carbon atom can be performed by the free aminic group present in the same ligand molecule.

The *cis* and *trans* isomers of $[PtCl_2(NCPh)_2]$ exhibit similar reactivity. However, the composition of the isomeric mixture (ratios *EE*:*EZ*:*ZZ*) was different in the two cases, suggesting a mutual influence between the two ligands. In no case was there evidence for a *cis*–*trans* isomerization of the complex and therefore the data of refs. 5 and 10 must be interpreted as the presence of a mixture of isomers in the starting substrate.

Experimental

Starting Materials.—Commercial reagent grade chemicals were used without further purification.

The complexes *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ were first separated and characterized by Uchiyama *et al.*[11] We have



Scheme 4.

prepared them by a slight modification of Hofmann's method.[12] Potassium tetrachloroplatinate(II) (dissolved in the minimum quantity of water) and benzonitrile (molar ratio 1:10) were stirred at 60 °C for 4 h. The aqueous phase turned from red to pale yellow and a yellow precipitate, imbued with benzonitrile, separated out. The mixture was extracted with dichloromethane and the organic extract, after removal of the solvent and trituration of the oily residue with light petroleum (b.p. 40—50 °C), afforded a yellow solid of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ (yield 90%). The mixture of the two isomers was extracted several times with small portions of chloroform. The *trans* isomer, being more soluble in this solvent, was removed, while the pure *cis* isomer was left as a solid residue (60% yield). The chloroform solution, containing the *trans* isomer and a small amount of the *cis* form, was taken to dryness *in vacuo* and crystallization from benzene of the solid residue yielded crystals of the *trans* complex (20% yield). The purity of the two compounds was checked by thin-layer chromatography (t.l.c.) on silica gel using dichloromethane as eluant.

Preparation of Complexes.—*trans*-$[PtCl_2(NCPh)\{(E)$-HN=C(OMe)Ph$\}]$ (**1**) *and trans*-$[PtCl_2(NCPh)\{(Z)$-HN=C(OMe)Ph$\}]$ (**2**) (E *and* Z *indicate that the* N-*hydrogen and the* C-*methoxy group are mutually* cis *and* trans *with respect to the* C=N *double bond*). The complex *trans*-$[PtCl_2(NCPh)_2]$ (0.7 g, 1.5 mmol), dissolved in dichloromethane (20 cm^3), was treated with a catalytic amount of KOH (0.07 mmol in 2 cm^3 of methanol). The base was added dropwise over a period of 1 h under vigorous stirring and the reaction stopped just before complete disappearance of the starting complex. Methanol (8 cm^3) was added to the solution which was concentrated to a small volume (5 cm^3) and a yellow precipitate separated. The solid was collected and chromatographed on an open column of silica gel [eluant dichloromethane–acetone (50:1, v/v)]. Compound (**2**) is eluted in the first fraction (65 mg, 10% yield) (Found: C, 35.3; H, 2.85; Cl, 14.3; N, 5.45. $C_{15}H_{14}Cl_2N_2OPt$ requires C, 35.7; H, 2.80; Cl, 14.1; N, 5.55%).

The methanol solution containing most of the other isomer was taken to dryness and the residue chromatographed on an open column of silica gel [eluant dichloromethane–acetone (200:1, v/v)]. The compounds eluted were, in order, (**2**), some by-products [mainly bis(imido ester) derivatives], and (**1**). After evaporation of the solvent and trituration of the oily residue with toluene a crystalline solid of (**1**) containing 0.33 molecules of solvent per molecule of complex was obtained (100 mg, 13% yield) (Found: C, 38.6; H, 3.10; Cl, 13.0; N, 5.25. (**1**) + $0.33(C_7H_8)$ requires C, 38.9; H, 3.15; Cl, 13.25; N, 5.20%).

cis-$[PtCl_2(NCPh)\{(E)$-HN=C(OMe)Ph$\}]$ (**3**) *and cis*-$[PtCl_2(NCPh)\{(Z)$-HN=C(OMe)Ph$\}]$ (**4**). The procedure was analogous to that described above. The complex *cis*-$[PtCl_2(NCPh)_2]$ (1.0 g, 2.1 mmol) dissolved in dichloromethane (50 cm^3) was treated with a catalytic amount of KOH (0.1 mmol in 3 cm^3 of methanol) added dropwise over a period of 1 h. Before the complete disappearance of the starting material, a further 50 cm^3 of methanol were added to the resulting yellow solution, and the solution was concentrated to half its initial volume under reduced pressure. A yellow crystalline precipitate of (**3**) separated out. This was collected by filtration of the mother-liquor and crystallized from methanol–chloroform (10:3, v/v), 25% yield (Found: C, 35.6; H, 2.80; Cl, 14.0; N, 5.45%).

The mother-liquor was evaporated to dryness and the yellow residue washed with benzene and chromatographed on an open column of silica gel [eluant dichloromethane–acetone (50:1, v/v)]. Compound (**4**) was eluted first and could be isolated as a yellow solid by evaporation of the solvent and trituration of the oily residue with benzene (yield 10%) (Found: C, 35.3; H, 2.70; Cl, 14.5; N, 5.15%).

trans-$[PtCl_2\{(E)$-HN=C(OMe)Ph$\}_2]$ (**5**), *trans*-$[PtCl_2\{(E)$-HN=C(OMe)Ph$\}\{(Z)$-HN=C(OMe)Ph$\}]$ (**6**), *and trans*-$[PtCl_2\{(Z)$-HN=C(OMe)Ph$\}_2]$ (**7**). For the preparation of the bis(imido ester) complexes the reaction was carried out in a solvent richer in methanol, and the reaction time prolonged until complete disappearance of the starting substrate and of the intermediate monoimido ester derivatives. The reaction of *trans*-$[PtCl_2(NCPh)_2]$ with a basic solution of methanol led to the formation of a mixture of the three isomers. However, under suitable experimental conditions, it was possible to obtain the preferential or exclusive precipitation of only one species. The reaction of *trans*-$[PtCl_2(NCPh)_2]$ (1 mmol), KOH (0.03 mmol), and dichloromethane–methanol (1:1, v/v; 2 cm^3) gave, soon after mixing, a yellow solution which, left under stirring for 0.5 h, yielded a yellow solid of pure (**6**). This was collected by filtration of the mother-liquor, washed with methanol, and dried (80% yield) (Found: C, 35.5; H, 3.30; Cl, 13.6; N, 5.05. $C_{16}H_{18}Cl_2N_2O_2Pt$ requires C, 35.8; H, 3.40; Cl, 13.2; N, 5.20%).

Performing the reaction under strictly analogous conditions but leaving the reaction mixture under stirring for 1 d, compound (**7**) was obtained as a yellow precipitate. This was separated out by filtration of the mother-liquor, washed with methanol and acetone, and dried (60% yield) (Found: C, 36.3; H, 3.70; Cl, 12.8; N, 5.00%).

Operating under more dilute conditions {*trans*-$[PtCl_2(NCPh)_2]$ (2 mmol), KOH (0.1 mmol), and dichloromethane–methanol (1:1, v/v; 40 cm^3)} a yellow solution of the three isomers was obtained after 1 h reaction time. Evaporation of the solvent and chromatography of the yellow residue [open column of silica gel, eluant dichloromethane–acetone (20:1, v/v)] afforded compounds (**7**), (**6**), and (**5**), in that order. The separation between (**7**) and (**6**) was, however, unsatisfactory and this procedure was used only for the preparation of (**5**) (20% yield) (Found: C, 35.3; H, 3.25; Cl, 13.5; N, 4.90%).

cis-$[PtCl_2\{(E)$-HN=C(OMe)Ph$\}_2]$ (**8**) *and cis*-$[PtCl_2\{(E)$-HN=C(OMe)Ph$\}\{(Z)$-HN=C(OMe)Ph$\}]$ (**9**). The third isomer, *cis*-$[PtCl_2\{(Z)$-HN=C(OMe)Ph$\}_2]$ (**10**), is formed in small amounts and was not isolated. In a typical experiment a solution of *cis*-$[PtCl_2(NCPh)_2]$ (1 mmol) in dichloromethane–methanol (1:1, v/v; 20 cm^3) containing a catalytic amount of base (KOH, 0.03 mmol) was allowed to react for 1 h under stirring. Evaporation of the solvent afforded a solid residue of (**8**) and (**9**) which was washed with methanol and dried.

Separation of the two components could be accomplished by chromatography on an open column of silica gel using dichloromethane–acetone as eluant. Using a solvent composition of 100:1 v/v, compound (**9**) was eluted and could be obtained as a yellow solid by evaporation of the solvent (20% yield) (Found: C, 36.1; H, 3.45; Cl, 12.8; N, 4.95%). Changing the solvent composition to dichloromethane–acetone (10:1, v/v), initially a mixture of (**9**) and (**8**) was eluted and then pure (**8**), which was recovered by evaporation of the solvent (30% yield) (Found: C, 36.0; H, 3.30; Cl, 13.1; N, 5.10%).

Performing the reaction under more concentrated conditions {*cis*-$[PtCl_2(NCPh)_2]$ (1 mmol), KOH (0.03 mmol), and chloroform–methanol (1:1, v/v; 2 cm^3)}, a clear solution was obtained soon after mixing the reagents. This solution, left under stirring for 1 h, separated out a yellow solid which was a mixture of (**8**) and (**9**). If the stirring was continued for 1 d the solid was converted completely into pure compound (**8**).

Acknowledgements

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