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CYANOALKYL COMPLEXES OF PLATINUM(II)

III*. ALCOHOLYSIS AND HYDROLYSIS OF THE CN GROUP

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Summary

Nucleophilic additions of alcohols, thiols and water to the σ-coordinated CN group of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ give quantitative yields of stable N-bonded iminoether, iminothioether and amide complexes. The proposed mechanism involves a fast replacement of the σ-coordinated CN by the nucleophile HY followed by the intramolecular attack of HY on the ligand in the *cis* position. π-Coordination of CN to Pt^{II} has not been observed. The addition of methanol to other cyanoalkyls did not lead to stable iminoether complexes. The amide complex *cis*-$[Pt(CH_2C_6H_4CONH_2)(PPh_3)_2]_2(BF_4)_2$ is converted into the nonionic imide *cis*-$[Pt(CH_2C_6H_4CONH)(PPh_3)_2]_2$ in methanolic KOH but it catalyzes for a few cycles the conversion of benzonitrile to benzamide by water under neutral conditions. The imino and isonitrile have a higher *trans* effect than alkyl groups whereas their *trans* influence as indicated by $^1J(PtP)$ coupling constants is smaller.

Introduction

We previously reported [1] the preparation and spectroscopic properties of various cyanoalkyl complexes of the type $PtX(RCN)L_2$ and $[Pt(RCN)L_2]_2(BF_4)_2$ ($R = (CH_2)_n$, n = 1-3, o-$CH_2C_6H_4$; L = PPh_3, PPh_2Me, $AsPh_3$; X = Cl, Br). In the cationic complexes the cyanoalkyl functions as a bidentate ligand and its

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[*] For part I see ref. 1a and for part II see ref. 1b.

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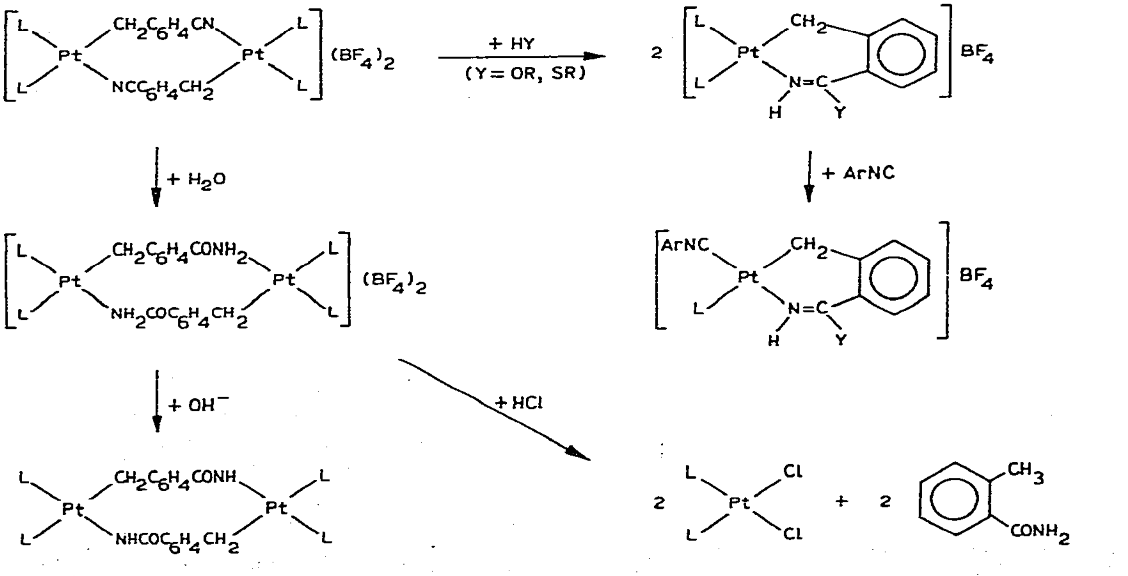
CN group should thus be prone to nucleophilic attack. Clark et al. [2] have obtained iminoether complexes by addition of alcohol to pentafluorobenzonitrile— and 2,3,5,6-tetrafluoroterephtalonitrile—Pt^{II} complexes and have proposed that initial π-CN—Pt bond formation is essential for nucleophilic attack. Conversion of the C≡N function to carboxamides has been obtained in the case of Co^{III} and Ru^{III} complexes of aminoacetonitrile [3], benzonitrile, acetonitrile [4] and 3- and 4-cyanophenol [5]; ions such as Ni^{2+}, Co^{2+} and Cu^{2+} catalyze the hydrolysis of CN in 2-cyanopyridine [6,7], 2-cyano-1,10-phenanthroline [8] and 2-cyano-8-hydroxyquinoline [9]. Bennett et al. [10] have reported an elegant preparation of dialkyls of Pt^{II} from hydroxo complexes, and have found [11] that $Pt(C_6H_9)(OH)(diphos)$ (C_6H_9 : σ-cyclohexenyl) and other nonionic tertiary phosphine hydroxy complexes catalyze the hydration of simple aliphatic nitriles under neutral conditions. This paper deals with the addition of alcohols, thiols and water to the CN group of *o*-cyanobenzyl platinum(II) complexes to give stable iminoether, iminothioether and amide complexes, and with the use of the amide complex in catalytic hydration of benzonitrile to benzamide.

Results and discussion

The cyanoalkyl *trans*-$PtX(CH_2C_6H_4CN)(PPh_3)_2$ (X = Cl, Br), prepared by the oxidative addition of *o*-$XCH_2C_6H_4CN$ to $Pt(PPh_3)_4$, can be readily transformed by abstraction of halide with $AgBF_4$ into the cationic dimer *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$. The CN group of this *o*-cyanobenzyl complex is σ-coordinated [1], and remarkably prone to nucleophilic attack by alcohols, thiols and water. Stable iminoether, iminothioether, amide and imide complexes are obtained on heating the cyanoalkyl in ROH, RSH/Me_2CO or H_2O/Me_2CO, respectively (Scheme 1, L = PPh_3).

SCHEME 1



The complexes were characterized by ^1H and ^{31}P NMR (Table 1), IR and

Raman spectra and elemental analysis (Table 2). The iminoether complexes I-V are yellow crystalline solids stable in air, and behave as 1/1 electrolytes in nitromethane (see Experimental). They have a *cis* geometry: the $^{31}P\{^1H\}$ -FT NMR spectra present an *AX* pattern indicating two non-equivalent triphenylphosphines with different $^1J(PtP)$ coupling constants. As shown by Pidcock et al. [12], the smaller coupling constant is associated with a platinum—phosphorus bond of lower *s*-character and corresponds thus to the phosphorus *trans* to alkyl. The methylene resonance is split into four lines of equal intensity by two non-equivalent phosphorus nuclei with satellites due to coupling with ^{195}Pt. The iminoether is strongly coordinated to platinum: it could not be displaced from I by PPh_3 in excess. The addition of a stoichiometric amount of ArNC (2,6-dimethylphenylisocyanide) did not displace the iminoether but instead the phosphine *trans* to the latter giving $[Pt\{CH_2C_6H_4C(=NH)OCH_3\}(CNAr)(PPh_3)]BF_4$ (V). Comparison of its coupling constant $^1J(PtP)$ with that of I indicates that the triphenylphosphine is *trans* to alkyl. The imino group $HN{=}C\lessdot$ has thus a higher *trans* effect than alkyl whereas its *trans* influence (as indicated by the values of $^1J(PtP)$ for the phosphorus *trans* to each group) is smaller. The benzyloxy group of IV is not replaced by MeO by refluxing in methanol, nor is I transformed into an amidine complex of the type $[Pt\{CH_2C_6H_4C(=NH)NMe_2\}(PPh_3)_2]BF_4$ [15] by adding an excess of dimethylamine. The imino hydrogen is exchanged on dissolving II in deuterated ethanol (ν(ND) 2470 cm^{-1}).

The rate of the nucleophilic addition of alcohols to *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ was measured by UV spectrophotometry (see Experimental); the identity of the products in solution was easily confirmed in the infrared by the disappearance of the $\nu(C{\equiv}N)$ around 2200 cm^{-1} and the appearance of $\nu(NH)$ and $\nu(C{=}N)$ around 3300 and 1600 cm^{-1}, respectively. Under similar conditions, the rate of the addition reaction decreases in the sequence $MeOH \sim EtOH >$ $i\text{-}PrOH \gg BzOH \ggg t\text{-}BuOH \sim PhOH$ (no reaction) which is that of increasing steric hindrance by the alkoxy group. The starting material *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ is a dimer in the solid state and probably also in weakly coordinating solvents, and was incorrectly formulated [1] as a monomer: a X-ray crystal structure determination has shown that the parent compound *cis*-$[Pt(CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ is dimeric [13]. Moreover the IR and Raman spectra are identical in Nujol mull and in CH_2Cl_2 solution, and the non-ionic manganese complex of the same ligand $[Mn(CH_2C_6H_4CN)(CO)_4]_2$ was found by osmometry to be dimeric in 1,2-dichloroethane [14].

Several arguments favour a two step mechanism of addition:

$$cis\text{-}[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2^{++} + 2HY \rightleftharpoons 2cis\text{-}[Pt(CH_2C_6H_4CN)(HY)(PPh_3)_2]^+ \quad (1)$$

$$cis\text{-}[Pt(CH_2C_6H_4CN)(HY)(PPh_3)_2]^+ \rightarrow cis\text{-}[Pt\{CH_2C_6H_4C(=NH)Y\}(PPh_3)_2]^+ \quad (2)$$

(a) the bridge splitting equilibrium of the dimer takes place in nitromethane and in coordinating solvents: two bands are present at 2265 and 2220 cm^{-1}, corresponding respectively to the frequency of σ-coordinated and free CN; *(b)* the rate of addition increases with the sequence $MeOH < MeSH < NHMe_2$, which

(continued on p. 276)

TABLE 1

^{1}H AND ^{31}P NMR SPECTRAL DATA FOR PRODUCTS OF NUCLEOPHILIC ATTACK ON *o*-CYANOBENZYL—Pt(II) COMPLEXES

Complex	δ(CH$_2$) [b] (ppm)	^2J(PtCH) (Hz)	^3J(PPtCH) (Hz)	δ(others) (ppm)	δ(P) [d] (ppm)	^1J(PtP) (Hz) [e]	^2J(PP) (Hz)
I *cis*-[Pt{$CH_2C_6H_4C(=NH)OCH_3$}$(PPh_3)_2$]BF_4	2.93q	63	6 (*cis*) 8 (*trans*)	3.10s (OCH_3)	27.3d 16.0d	1900 4000	15
II *cis*-[Pt{$CH_2C_6H_4C(=NH)OC_2H_5$}$(PPh_3)_2$]BF_4	2.93q	63	6 (*cis*) 9 (*trans*)	3.2q (OCH_2) 1.3t (CH_3)	27.2d 16.2d	1910 4045	15
III *cis*-[Pt{$CH_2C_6H_4C(=NH)O$-i-Pr}$(PPh_3)_2$]BF_4	2.92q	66	6 (*cis*) 9 (*trans*)	3.30q (OCH) 1.08d (CH_3)	26.9d 16.2d	1904 4060	15
IV *cis*-[Pt{$CH_2C_6H_4C(=NH)OBz$}$(PPh_3)_2$]BF_4	2.96q	66	6 (*cis*) 9 (*trans*)	4.15s (OCH_2)	27.3d 16.3d	1928 4080	16
V [Pt{$CH_2C_6H_4C(=NH)OCH_3$}(CNAr)(PPh_3)]BF_4 [a]	3.57d	65	10	3.38s (OCH_3) 1.98s (CH_3) [a]	22.7	1623	
VI *cis*-[Pt{$CH_2C_6H_4C(=NH)SCH_3$}$(PPh_3)_2$]BF_4	2.80q	63	6 (*cis*) 8 (*trans*)	2.70s (SCH_3)	26.2d 15.5d	1956 4055	15
VII *cis*-[Pt{$CH_2C_6H_4C(=NH)SC_2H_5$}$(PPh_3)_2$]BF_4	2.78q	65	6 (*cis*) 8 (*trans*)	1.99q (SCH_2) 1.13t (CH_3)	26.0d 15.5d	1945 4060	14
VIII *cis*-[Pt{$CH_2C_6H_4C(=NH)SBz$}$(PPh_3)_2$]BF_4	2.77q	63	6 (*cis*) 9 (*trans*)	3.24s (SCH_2)	26.2d 15.6d	1972 4060	15
IX *cis*-[$Pt(CH_2C_6H_4CONH_2)(PPh_3)_2$]$_2(BF_4)_2$	2.75q	50	4 (*cis*) 9 (*trans*)		31.1d 12.7d	2032 4840	14
X *trans*-[$Pt(CH_2C_6H_4CONH_2)(CNAr)_2(PPh_3)$]$BF_4$ [a]	3.69d	78	10	4.13 (NH_2) (broad) 1.92 (CH_3Ar)			
XI *cis*-[$Pt(CH_2C_6H_4CONH)(PPh_3)_2$]$_2$	2.78t	72	8 [c]		25.5d 19.3d	1805 3579	12
XII *cis*-[Pt(*o*-$NCC_6H_4CH_2CH_2C_6H_4CN)(PPh_3)_2$]$(BF_4)_2$	2.98s				2.4s	3713	

[a] ArNC = 2,6-dimethylphenylisocyanid. [b] In $CDCl_3$; TMS as internal standard. [c] The two ^3J are equal within 0.5 Hz. [d] In $CDCl_3$; positive sign for a resonance at lower field than 85% H_3PO_4 (external reference); δ(PPh_3) −5.8 ppm. [e] Smaller ^1J for P *trans* to CH_2.

TABLE 2

ANALYTICAL, IR AND RAMAN SPECTRAL DATA

Complex	M.p. (dec.) (°C)	Analysis found (calcd.) (%)				ν(NH) region (cm^{-1})[c]	ν(C=N) region (cm^{-1})[f]	Band at 550 ± 5 cm^{-1}[g]	Others (cm^{-1})
		C	H	N	F				
II	252-255	57.10 (57.03)	4.40 (4.37)	1.50 (1.45)	7.91[a] (7.85)	3355w[i]	1620 s	IR 549s R 545w	1232s $\nu(COC)_{as}$ IR 1052[h] $\nu(BF_4)$
III	240-242	56.76 (57.43)	4.26 (4.51)	1.62 (1.42)	6.95 (7.73)	3358w	1613s	IR 549s R 545w	1239s $\nu(COC)_{as}$ IR 1050[h] $\nu(BF_4)$
IV	236-237	59.20 (59.42)	4.10 (4.30)	1.63 (1.36)	6.80 (7.37)	3325w	1615s	IR 550s	1235s $\nu(COC)_{as}$ IR 1055[h] $\nu(BF_4)$
V	192-194	52.33 (52.50)	4.48 (4.16)	3.60 (3.40)		3310w	1615s		1248s $\nu(COC)_{as}$ IR 2185s $\nu(N{\equiv}C)$
VI	215-225	55.01 (55.67)	4.10 (4.15)	1.44 (1.44)	7.68[b] (7.83)	3332w	1575s, 1550s	IR 550s R 545vw	1055[h] $\nu(BF_4)$
VII	214-220	56.25 (56.09)	4.05 (4.29)	1.46 (1.42)		3338w	1572s, 1545s	IR 549s R	1055[h] $\nu(BF_4)$
VIII	203-205	57.63 (58.51)	4.26 (4.24)	1.76 (1.34)		3320w	1571s, 1545s	IR 545s	1060[h] $\nu(BF_4)$
IX	226-228	55.83 (56.18)	4.28 (4.07)	1.62 (1.49)	8.05 (8.08)	3410vw[d] 3338w, 3250vw	1650s, 1530s	IR 553s R 550 vw	1055[h] $\nu(BF_4)$
X	148-149	55.79 (56.18)	4.18 (4.39)	4.01 (4.47)		3515w, 3400w[e]	1675s, 1585m		2200s $\nu(N{\equiv}C)$ IR 1060[h] $\nu(BF_4)$
XI	241-247	59.50 (61.97)	4.28 (4.37)	1.93 (1.64)		3345w	1585s, 1555s	IR 548s R	
XII	230-241	53.80 (55.47)	3.76 (3.79)	2.63 (2.49)				IR 556s	2280m $\nu(C{\equiv}N)$ IR 1057vs[h] $\nu(BF_4)$

[a] % OEt, 4.79 (4.65). [b] % S, 3.21 (3.30). [c] IR in Nujol mull. [d] On partial deuteration: ν(ND) 2565vw, 2480w, 2390w. [e] In CH_2Cl_2. [f] Sharp bands of medium intensity at 1600 ± 5 (IR) and 1580 ± 5 cm^{-1} (IR and R) are present in all spectra and are tentatively assigned to ν(C=C) of phenyl groups. [g] Mastin's identification method [16] of isomers of $Pt(PPh_3)_2XY$; the band should be strong in IR and weak in Raman for *cis* and the reverse for *trans.* [h] vs, broad. [i] ν(ND) 2470 cm^{-1}.

is also the order of increasing equilibrium constant for eqn. 1 [15]. In the case of NH_3, the substituted complex *cis*-$[Pt(CH_2C_6H_4CN)(NH_3)(PPh_3)_2]BF_4$ has been isolated; *(c)* precoordination of nucleophile and subsequent addition are distinct in one case [15]: in this case adding N_3^- to the dimer gives *cis*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$ stable at room temperature and cyclisation occurs by heating in CH_2Cl_2 giving the tetrazolate complex *cis*-$Pt(CH_2C_6H_4CN_4)(PPh_3)_2$; *(d)* the direct attack on the σ-coordinated CN group of the dimer (which should be π-bonded before reacting as proposed by Clark et al. [2] for a similar reaction) should give a dimeric product and not the observed monomer, as the iminoether cannot be displaced by any of the species in solution.

We were not able to isolate stable Pt^{II}—iminoether complexes with other cationic cyanoalkyls $Pt—\{(CH_2)_nCN\}L_2^+$ ($n = 1$-3). The dinitrile chelate *cis*-$[Pt(o\text{-}NCC_6H_4CH_2CH_2C_6H_4CN)(PPh_3)_2](BF_4)_2$ (XII) did not react with methanol (both CN groups are σ-bonded to platinum: ν(CN) 2280 cm^{-1} compared to 2225 for the free dinitrile). The activation of CN by a formal positive charge on the complex and the stabilisation of the induced positive charge on carbon by a phenyl group are not sufficient to promote the formation of an iminoether complex.

The characterisation of the iminothioether complexes VI-VIII was similar to that of I (Table 1 and 2). Hydrogen sulfide does not add to the CN group of *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ in acetone; it liberates instead the cyanoalkane, and an insoluble complex tentatively formulated as *cis*-$[Pt(PPh_3)_2(SH)]_2(BF_4)_2$ precipitates (see Experimental).

The hydration of the CN group of *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ in H_2O/Me_2CO with or without added HBF_4, gives quantitatively a stable dimeric amide complex $[Pt(CH_2C_6H_4CONH_2)(PPh_3)_2]_2(BF_4)_2$ (IX) of *cis* geometry (Table 1). The synthesis in D_2O/H_2O gives a partially deuterated complex having in the IR the expected $\nu(ND)/\nu(NH)$ ratio of 0.74 ± 0.01. It behaves as a 2/1 electrolyte in nitromethane (see Experimental). The N-coordinated amide is easily displaced by 2,6-dimethylphenylisocyanide (ArNC), and an excess of isocyanide substitutes further the triphenylphosphine *trans* to ArNC giving *trans*-$[Pt(CH_2C_6H_4CONH_2)(PPh_3)(ArNC)_2]BF_4$ (X). Its ^1H NMR spectrum has a doublet at 3.69 ppm for the methylene coupling with one phosphorus and a broad resonance at 4.13 ppm due to NH_2. ArNC has thus a higher *trans* effect than alkyl whereas its *trans* influence based on $^1J(PtP)$ is smaller (Table 1). On addition of dilute hydrochloric acid to IX in acetone, *cis*-$PtCl_2(PPh_3)_2$ precipitated out quantitatively and *o*-toluamide was liberated. A strong base such as KOH in methanol added to IX abstracts a proton of each amide group; this yields quantitatively the nonionic imide complex *cis*-$[Pt(CH_2C_6H_4CONH)(PPh_3)_2]_2$ (X) (Scheme 1). This compound was shown to be dimeric in dichloromethane by vapour pressure osmometry. Its methylene resonance is a 1/2/1 triplet (Table 1); this is due to an accidental degeneracy of the *cis* and *trans* coupling constants $^3J(PPtCH)$, for the ^{31}P NMR spectrum shows the expected AX pattern of a *cis* geometry.

Since complex IX has an easily displacable amide ligand, it was thought that a small quantity of an hydroxo complex of the type $Pt(OH)(CH_2C_6H_4CONH_2)(PPh_3)_2$ could form in water and act as catalyst for the hydration of nitriles. Such an homogeneously catalyzed hydration of nitriles to carboxamides has been observed by Bennett et al. [11]. In fact, heating of a mixture of benzonitrile and water in presence of IX gives only a small amount of catalytic conversion (about 5 moles benzamide per mole catalyst); at the end of the process, the complex is recovered as XI, in which the imide group blocks the fourth position of coordination and apparently destroys the catalytic activity.

The reaction between other cyanoalkyls and alcoholic NaOH giving hydrido complexes of the type *trans*-$PtH(CH_2CN)(PPh_3)_2$ is under investigation.

Experimental

The spectroscopic techniques were described earlier [1]. Dornis and Kolbe (Mulheim) carried out the microanalyses.

Conductance measurements were carried out with a Metrohm E 365 conductometer equipped with a Jones cell using Feltham and Hayter's method [17]. Conductance of II in nitromethane at 22 ± 1°C: cell constant 0.745 cm^{-1}; Λ_0 85 Ω^{-1} cm^2 mol^{-1}; ($\sqrt{c}$, Λ_e): (0.0224 *M*, 90.4 Ω^{-1} m^2 mol^{-1}) (0.0319, 81.8) (0.0548, 78.7) (0.0896, 74.3) (0.1414, 70.8). $\Lambda_0 - \Lambda_e = B\sqrt{c}$ is a straight line with a slope *B* of 150 Ω^{-1} cm^2 mol^{-1}. Conductance of IX: Λ_0 86; ($\sqrt{c}$, Λ_e): (0.0106, 83.3) (0.0167, 78.1) (0.0264, 76.5) (0.0418, 71.3); *B* 350. References for 1/1 electrolytes: $[Pt(CH_2C_6H_4CN)(PPh_3)_3]BF_4$, Λ_0 83, (0.0114, 94.1) (0.0144, 84.2) (0.0227, 79.8) (0.0359, 76.6) (0.0658, 74.3), *B* 180 and $[n\text{-}Bu_4N]Br$, *B* 183 [17]; for 2/1 electrolytes: $[Pd_2(PEt_3)_2(o\text{-phen})](BPh_4)_2$, *B* 392 [17]. Thus II is a 1/1 and IX a 2/1 electrolyte.

Osmometry: molecular weight of XI in dichloromethane: found 1710 ± 30 (calculated for a dimer 1706).

UV spectrophotometry: the addition of alcohol to *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ was followed at 343 mm for 60-80% of reaction (ϵ of starting material and of I: 1.19×10^{-4} and 0.13×10^{-4} M^{-1} cm^{-1}, respectively). A typical run is shown in Fig. 1: [Pt] 1.4×10^{-4} *M*; ROH 50% in CH_2Cl_2; 21.0 ± 0.5°C. Half-lives: MeOH ~ EtOH 140, i-PrOH 570, BzOH 1500 min. The reaction was not of first order in [BzOH] over the entire range of concentrations examined.

Preparation of complexes

All solvents were purified and dried by standard methods.

cis-$[Pt\{CH_2C_6H_4C(=NH)OR\}(PPh_3)_2]BF_4$ *(I: R = Me, II: R = Et. III: R = i-Pr, IV: R = Bz)*

A suspension of *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ (A) [1] (0.5 g) in the appropriate alcohol (40 ml) was stirred for 5 h at 50°C (I), 5 h at 65°C (II, III), 8 h at 65°C (IV), respectively. For I-III: a yellow precipitate formed on addition of ether/hexane, and was recrystallized from MeOH/ether to give pale yellow needles. Yield 80%. For IV: ether was added (80 ml) and the mixture cooled at —25°C. The yellow powder was stirred for 6 h in ether and filtered. Yield 90%. Complex A did not react with phenol or t-BuOH.

$[Pt\{CH_2C_6H_4C(=NH)OMe\}(PPh_3)(ArNC)]BF_4$ *(V)*

2,6-dimethylphenylisocyanide (0.06 g) was added to a solution of A (0.4 g) in CH_2Cl_2 (15 ml). After 3 h, the solution was evaporated to 3 ml and ether/hexane (1/1) added. The yellow product was washed with ether. Yield 65%.

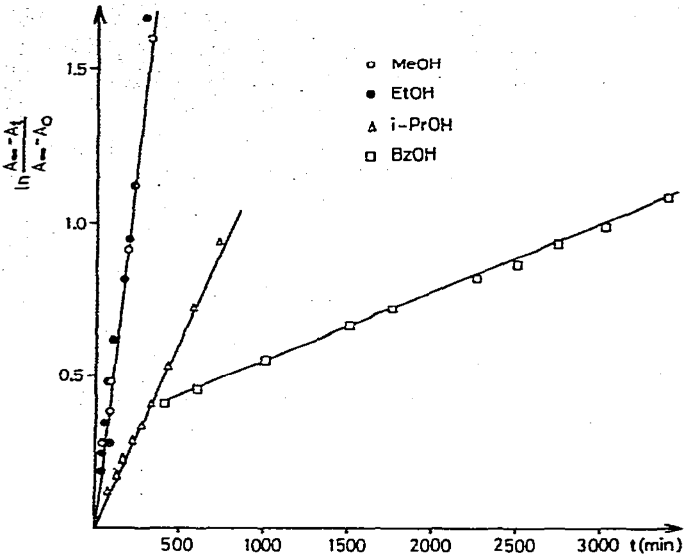


Fig. 1. Reaction *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2^{++}$ + ROH in CH_2Cl_2.

cis-$[Pt\{CH_2C_6H_4C(=NH)SR\}(PPh_3)_2]BF_4$ *(VI: R = Me, VII: R = Et, VIII: R = Bz)*

MeSH, EtSH and BzSH, respectively, was added in excess to a suspension of A in acetone and the mixture stirred for 2 h (VI) or 10 h (VII, VIII). A precipitate formed on addition of ether/hexane and was recrystallized from CH_2Cl_2/benzene (yellow microcrystals). Yields 70-95%. Complex A did not react with thiophenol. Reaction with hydrogen sulfide: H_2S was bubbled through a solution of A in CH_2Cl_2. *o*-$CH_3C_6H_4CN$ was liberated and a yellow insoluble material precipitated out, probably *cis*-$[Pt(PPh_3)_2(SH)]_2(BF_4)_2$ (analysis found: C, 52.60; H, 4.08; P, 7.74; S, 3.99. Calcd.: C, 51.57; H, 3.82; P, 7.38; S, 3.82%.) Two very weak bands are present in the ν(SH) region, $\nu(BF_4)$ 1075 cm^{-1} (broad), the IR band at 545 cm^{-1} is intense (indicating a *cis* geometry).

cis-$[Pt(CH_2C_6H_4CONH_2)(PPh_3)_2]_2(BF_4)_2$ *(IX)*

A (1.5 g) and HBF_4 40% (0.3 g) were added to a mixture of acetone (50 ml) and water (10 ml) and heated at 60°C for 10 h. The acetone was evaporated and water (30 ml) added. The white precipitate was washed with water, then ether, and recrystallized from CH_2Cl_2/ether. Yield 85%. Reaction with HCl: dilute HCl was added to IX (0.2 g) in acetone (10 ml). *cis*-$PtCl_2(PPh_3)_2$ precipitated quantitatively; the liberated organic product was recrystallized from acetone/water and identified as *o*-toluamide by its IR and NMR spectra. Catalytic hydration of benzonitrile: in a typical experiment, a blank consisting of benzonitrile (5 ml) and water (5 ml), and the same mixture with 10 mg IX added, were heated at 50°C for 8 h. The resulting solutions were analyzed by gas chromatography and the second contained 5 moles benzamide per mole Pt.

trans-$[Pt(CH_2C_6H_4CONH_2)(PPh_3)(ArNC)_2]BF_4$ (X)

2,6-Dimethylphenylisocyanide (2 moles per mole Pt) was added to a solution of IX in CH_2Cl_2 and the mixture stirred for 2 h. A white precipitate formed on addition of ether, and was recrystallized from CH_2Cl_2/ether. Yield 80%.

cis-$[Pt(CH_2C_6H_4CONH)(PPh_3)_2]_2$ (XI)

A stoichiometric amount of KOH was added to a suspension of IX in methanol and stirred for one hour. The white solid was washed with water, then MeOH, and was recrystallized from CH_2Cl_2/ether. Yield 90%.

cis-$[Pt(o\text{-}NCC_6H_4CH_2CH_2C_6H_4CN)(PPh_3)_2](BF_4)_2$ (XII)

$AgBF_4$ (2 equivalents) was added to a suspension of *cis*-$PtCl_2(PPh_3)_2$ in acetone/CH_2Cl_2 (1/3). AgCl was filtered and a white precipitate formed on addition of one equivalent of dinitrile to the filtrate. Precipitation was completed by adding ether. Yield 90%.

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