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CYANOALKYL COMPLEXES OF PLATINUM(II)

II*. UNCHARGED AND CATIONIC *o*-CYANOBENZYL COMPLEXES

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Summary

The oxidative addition of *o*-$XCH_2C_6H_4CN$ to PtL_4 yields *trans*-$PtX(CH_2C_6H_4CN)L_2$ (L = PPh_3, $AsPh_3$; X = Cl, Br). The *trans* complex is the thermodynamically stable isomer, but *cis—trans* isomerization occurs readily in dichloromethane and is catalyzed by free L. Displacement of L by bidentate phosphorus ligands and insertion of CO in the σ Pt—C bond occurs readily. Abstraction of X gives a *cis* cationic complex in which the CN group is coordinated and is prone to nucleophilic attack by alcohols to give stable *cis* imino ether complexes.

Introduction

In the first paper of this series [1] we reported the preparation and spectroscopic properties of various cyanoalkyl complexes of Pt^{II}. A description of some cyanomethyl complexes of Pt^{II} has also appeared recently [2]. The cyanoalkyl moiety is a potential bidentate ligand if the alkyl chain is long enough to allow the right orientation of CN with respect to the metal center. The nitrile group can be *N*-bonded or π-bonded via its p_π—p_π system to the metal atom. Clark et al. [3] have found both modes of bonding in a series of methyl—platinum(II)—dinitrile complexes and observed that they were prone to nucleophilic attack. This paper deals with the *o*-cyanobenzyl complexes $PtX(CH_2C_6H_4CN)L_2$ and $[Pt(CH_2C_6H_4CN)L_2]BF_4$ which among the cyanoalkyls examined show the widest range of reactions, i.e. displacement and insertion reactions, *cis—trans* isomerization, coordination of CN and nucleophilic attack by alcohols on the nitrile group of the cationic complexes.

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TABLE 1

^{1}H AND ^{31}P NMR SPECTRAL DATA FOR *o*-CYANOBENZYL COMPLEXES OF Pt^{II}

	Complex	$\delta(CH_2)^a$ (ppm)	$^2J(PtCH)$ (Hz)	$^3J(PPtCH)$ (Hz)	$\delta(P)^b$ (ppm)	$^1J(PtP)$ (Hz)	$^2J(PP)$ (Hz)
Ia	*trans*-$PtCl(CH_2C_6H_4CN)(PPh_3)_2$	2.32t	91	8	25.8s	3040	
Ib	*trans*-$PtBr(CH_2C_6H_4CN)(PPh_3)_2$	2.48t	90	8	25.8s	3020	
Ic	*trans*-$PtCl(CH_2C_6H_4CN)(AsPh_3)_2$	2.55s	96				
Id	*trans*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$	2.35t	88	7.5	25.7s	3010	
IIa	*cis*-$PtCl(CH_2C_6H_4CN)(PPh_3)_2$	2.75q	76	5(*cis*)	22.0d	1750^c	16.0
				9(*trans*)	21.2d	4360	
IIb	*cis*-$PtBr(CH_2C_6H_4CN)(PPh_3)_2$	3.00q	76	6(*cis*)	19.5d	1765^c	16.0
				9(*trans*)	20.4d	4355	
IIc	$PtCl(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)$	3.13q	78	4.5(*cis*)			
				11(*trans*)			
IIIa	*cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]BF_4$	2.52m	86		19.1d	1780^c	19.8
		3.37m			12.9d	4450	
IIIb	*cis*-$[Pt(CH_2C_6H_4CN)(AsPh_3)_2]BF_4$	3.05d	80				
IIIc	$[Pt(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)]BF_4$	3.12q	77	4(*cis*)			
				10(*trans*)			
IV	$[Pt(CH_2C_6H_4CN)(PPh_3)_3]BF_4$	2.83dt	65	9(*cis*)	18.3t	1865^c	21.0
				5(*trans*)	21.9d	2850	
Va	*cis*-$[Pt\{CH_2C_6H_4C(OCH_3)NH\}(PPh_3)_2]BF_4$	$2.93q^d$	63	6(*cis*)	27.3d	1900^c	15.2
				8(*trans*)	16.0d	4000	
Vb	$[Pt\{CH_2C_6H_4C(OCH_3)NH\}(C_2H_2P_2Ph_4)]BF_4$	2.94q	62	5(*cis*)			
				9(*trans*)			
VIa	*trans*-$PtCl(COCH_2C_6H_4CN)(PPh_3)_2$	3.43s	< 6		19.7s	3375	
VIb	*trans*-$PtBr(COCH_2C_6H_4CN)(PPh_3)_2$	3.17s	< 6		18.7s	3360	

[a] In $CDCl_3$; TMS as internal standard. [b] In CD_2Cl_2 at 21°, positive sign for a resonance at lower field than 85% H_3PO_4 (external reference); $\delta(PPh_3)$ −5.8 ppm. [c] P *trans* to CH_2. [d] (OCH_3) 3.10(s,3H) for Va, 3.93 for Vb.

Results and discussion

Preparation

The oxidative addition of *o*-$XCH_2C_6H_4CN$ to $Pt(PPh_3)_4$ in benzene gives *trans*-$PtX(CH_2C_6H_4CN)(PPh_3)_2$ (Ia, X = Cl, Ib, X = Br) in good yields, the side products being *cis*-$PtX_2(PPh_3)_2$ and the phosphonium salt $[PPh_3CH_2C_6H_4CN]X$. The oxidative addition to $Pt(AsPh_3)_4$, which seems not to have been carried out with simple haloalkanes, takes place in this case, albeit to give only a low yield of *trans*-$PtCl(CH_2C_6H_4CN)(AsPh_3)_2$ (Ic). (These latter complexes are stable white solids, soluble in $CHCl_3$, CH_2Cl_2 and THF, less so in acetone and insoluble in ether and methanol.) The metathesis reactions of Ia with LiBr or NaN_3 give the corresponding bromide Ib and azide Id. The neutral ligands of Ia and Ic are displaced by the chelating diphosphine, *cis*-1,2-bis(diphenylphosphino)ethylene in benzene to form $PtCl(CH_2C_6H_4CN)(PPh_2CH{=}CHPPh_2)$ (IIc). The complexes were characterized by ^1H and ^{31}P NMR (Table 1), IR and Raman spectra and elemental analysis (Table 2).

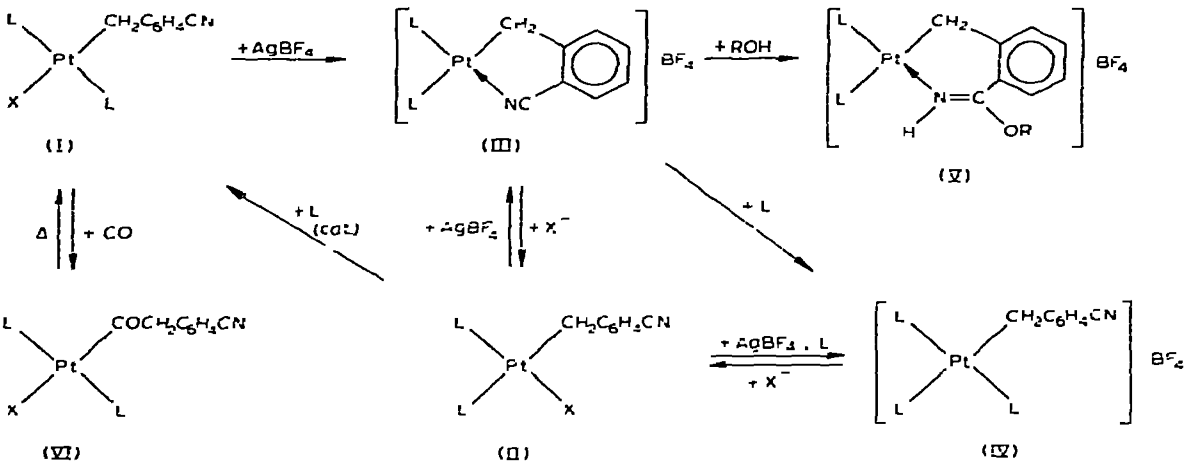
The compounds Ia,b,d have a methylene resonance split into a triplet (1/2/1) by two equivalent phosphorus atoms with satellites due to coupling with platinum and a ^{31}P resonance split into a triplet (1/4/1) by ^{195}Pt. They thus have a *trans* configuration of phosphines. The decrease of $^2J(PtCH)$ follows the order of increasing *trans*-influence $Cl(Ia) < Br(Ib) < N_3(Id) < PPh_3(IIa)$. The corresponding *cis* isomers IIa and IIb have a methylene resonance split into four lines of equal intensity by the non-equivalent phosphorus atoms. It is not possible to deduce here whether a particular $^3J(PPtCH)$ coupling refers to the phosphorus *trans* or *cis* to the alkyl group, and so we have followed the assignment of Benett et al. [4] for methylplatinum complexes. The proton decoupled ^{31}P spectra present two doublets of equal intensity. The expression for $^1J(PtP)$ given by Pidcock et al. [5] shows that smaller coupling constants are associated with platinum—phosphorus bonds of lower *s*-character. Thus in IIa, IIb, IIIa, IV and Va, the smaller coupling constant corresponds to the phosphorus *trans* to alkyl. The assignment of the *cis—trans* stereochemistry of bis(triphenylphosphine)-platinum complexes proposed by Mastin [6] and based on the relative intensity of an IR and Raman band at ca. 550 cm^{-1} has been found valid without exception in this new series of complexes (Table 2).

Cationic complexes

The addition of a stoichiometric amount of $AgBF_4$ to a suspension of the *trans* complexes Ia,b and Ic or of IIc gives the cationic *cis*-$[Pt(CH_2C_6H_4CN)L_2]$-BF_4 (IIIa, IIIb and IIIc respectively) (Scheme 1).

The ^{31}P spectrum of IIIa presents an AX pattern indicating that the two phosphines are *cis* to each other. Conductance measurements show that IIIa is a 1/1 salt in nitromethane (see Experimental section). The IR spectra of IIIa,b,c have a band at ca. 2260 cm^{-1} assigned to $\nu(CN)$ which can be compared to 2220 cm^{-1} for IIa. The stretching frequency of a *N*-bonded CN generally increases by 70—110 cm^{-1} whereas it decreases by 150—200 cm^{-1} for side-on coordination [3]. Thus, the *o*-cyanobenzyl group acts as a chelating ligand and the CN is σ-bonded, even though Dreiding molecular models show that considerably more strain is involved in the σ- than in the π-arrangement. Chelation seems to be the driving force of the unusual *trans—cis* isomerization Ia → IIIa.

SCHEME 1



Each of these complexes exhibits conformational interconversion in solution. The two methylene protons of IIIa are magnetically non-equivalent, since two multiplets of equal intensity (separated by 50 Hz in $CDCl_3$) are observed at low temperature [J(PCH) and J(HCH) are indistinguishable]. Upon heating a reversible coalescence process occurs in the kinetic window of ^{1}HNMR. This is best shown for the parent compound IIIb in which phosphorus is replaced by arsenic to avoid additional coupling (Fig. 1).

At low temperature in CD_2Cl_2 the methylene resonance presents two doublets of equal intensity with $J(H_AH_B)$ 10 Hz and $\Delta\nu^o_{AB}$ 18 ± 1 Hz (in absence of exchange). The calculated *AB* pattern gave correct line intensities. The signals coalesce at 27 ± 1°C. The residence time and the free enthalpy of activation are

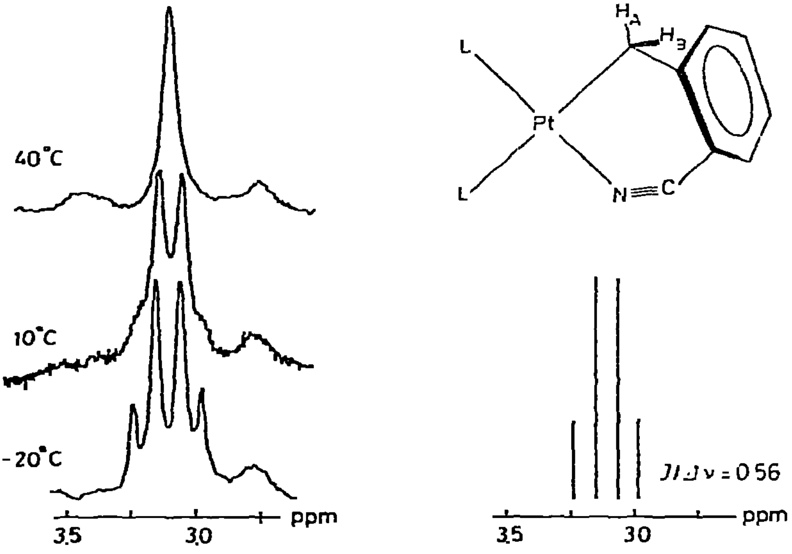


Fig. 1. Methylene resonance of *cis*-[$Pt(CH_2C_6H_4CN)(AsPh_3)_2$]$BF_4$ in CD_2Cl_2.

given by $1/\tau = k = 2.2\,\Delta\nu^{\circ}_{AB}$ [7] and $\Delta G^{\ddagger} = RT\ln(k_BT/hk)$ respectively. Therefore, $k_{300} = 40 \pm 2\ s^{-1}$ and $\Delta G^{\ddagger}_{300} = 15.3 \pm 0.2$ kcal/mol. The coalescence temperature does not depend on the concentration of IIIb and IR and ^{31}P spectra remain unchanged up to the boiling point of the solvent. The unique explanation we see for the temperature dependence of the *AB* pattern is a flipping of the strained chelated cyanoalkyl moiety above and below the PPtP plane. This movement creates two equivalent conformations, with each of the methylene protons occupying intermittently the magnetic site of the other. In the case of IIIa, which involves Pt—P bonds, which are shorter than Pt—As, the resulting steric crowding is greater than in IIIb, and the coalescence of the methylene signals is not complete even at 75° in $CDCl_3$. In IIIc, where one phenyl group is missing from each phosphorus, the coalescence occurs at ca. −35° probably because the rigid PCH=CHP chain holds the bulky groups further away from the methylene protons.

Cis—trans isomerization reactions

The thermodynamically unstable *cis*-$PtX(CH_2C_6H_4CN)(PPh_3)_2$ (IIa, X = Cl), (IIb, X = Br) are obtained by adding Ph_4AsCl and LiBr respectively to a dichloromethane solution of IIIa. These in turn isomerize slowly to the corresponding *trans* isomers Ia and Ib (the equilibrium position is at > 99.5% *trans*). The isomerization is catalyzed by free PPh_3, as is often the case for Pt—phosphine complexes [8]. The observed rate law is first order in both IIa and PPh_3. Addition of PPh_3 to IIIa yields $[Pt(CH_2C_6H_4CN)(PPh_3)_3]BF_4$ (IV). The decoupled ^{31}P spectrum shows an AX_2 pattern with a triplet (1/2/1) for the phosphorus *trans* to alkyl, with the smaller ^3J(PPtCH) for the phosphorus *trans* to CH_2 than for the *cis* ones. This tris complex is stable in solution as long as no halide is present. Upon adding a stoichiometric amount of Ph_4AsCl to a dichloromethane solution of IV, the *cis* isomer $PtCl(CH_2C_6H_4CN)(PPh_3)_2$ forms very rapidly (^1H and ^{31}P spectra are identical to those of IIIa) with liberation of PPh_3. This indicates that the *trans*-effect of triphenylphosphine is greater than that of a cyanoalkyl. The PPh_3 catalyzed isomerization to Ia proceeds then to completion. The possibility that $[Pt(CH_2C_6H_4CN)(PPh_3)_3]^+Cl^-$ is an intermediate in the thermal isomerization is under study.

Reactivity

Insertion of CO into the σ Pt—C bond of Ia or Ib takes place to give good yields of *trans*-$PtX(COCH_2C_6H_4CN)(PPh_3)_2$ (VIa, X = Cl) and (VIb, X = Br). There is no insertion into $PtCl(CH_2CN)(PPh_3)_2$ [1,2]. Complete evolution of CO occurs upon heating crystals of Va and Vb, and the corresponding starting material is reformed.

The nitrile group of $[Pt(CH_2C_6H_4CN)L_2]BF_4$ IIIa, IIIc is very prone to nucleophilic attack, and at least three factors contribute to this: the positive charge on the complex, the σ coordination of CN to form a strained cycle, and the stabilisation of the induced positive charge on carbon by the phenyl group. Heating IIIa or IIIb in methanol at 50° gives *cis*-$[Pt\{CH_2C_6H_4C(OCH_3)NH\}(PPh_3)_2]BF_4$ (Va) and $[Pt\{CH_2C_6H_4C(OCH_3)NH\}(Ph_2PCH{=}CHPPh_2)]BF_4$ (Vd) respectively in quantitative yields. The formation of an imino group is revealed by the decrease of ν(CN) by ca. 600 cm^{-1} down to the region normally assigned to C=N stretching frequencies and by the appearance of a ν(NH) around 3300 cm^{-1}. The formation of imino ether complexes has been observed by Wilkinson et al. [9] for Re—NCCH$_3$ complexes and by Clark et al. [3] for Pt^{II}—pentafluorobenzonitrile and —dinitriles. The coordination of the imino ether group through nitrogen favours again the *cis*-arrangement of the phosphines in Va (Table 1). Indeed the methylene resonance is a quartet (1/1/1/1) and the ^{31}P spectrum shows two doublets of equal intensity with the larger ^1J(PtP) issuing from the phosphorus *trans* to the imino group. This coupling constant is greater than that for IIIa, which indicates that the *trans*-influence of the imino ether group is greater than that of a nitrile group. Attack by other nucleophiles, e.g. H_2O, R_2NH, RSH is under investigation.

Experimental

^{1}H and ^{31}P NMR spectra were recorded with Bruker WP-60 (60 MHz) and Bruker HX-90 (36.43 MHz) spectrometers, respectively, IR spectra (in Nujol and in CH_2Cl_2) with a Perkin—Elmer 577 spectrometer, and Raman spectra (of powdered complexes) with a Spex Compact 1403 spectrometer equipped with an Argon(II) laser source. The kinetics of *cis—trans* isomerization of IIa were followed by integrating the methylene resonance of both isomers up to 70% reaction. Dornis und Kolbe (Mulheim) and E. Thommen (Institut für Organisches Chemie, Basel) made the microanalyses.

Conductance measurements were carried out with a Metrohm E 365 conductometer equipped with a Jones cell using Feltham and Hayter's method [10]. Conductance of IIIa in nitromethane at 23.5°: cell constant 0.745 cm^{-1}; Λ_0 78 ohm^{-1} cm^2 mole^{-1}; (Λ_e, $\sqrt{c}$): (75.66, 0.0226) (76.08, 0.0358) (72.17, 0.0566) (68.91, 0.0894) (64.07, 0.1414). $\Lambda_0 - \Lambda_e = B\sqrt{c}$ is a straight line with a slope B of 101 ohm^{-1} cm^{2}mol^{-1}. This value is closer to 288 for $[Ru_2Cl_3(PEt_2Ph)_2]ClO_4$ [10] than to 510 for $[Pd(Ph_2PC_2H_4PPh_2)_2](ClO_4)_2$ [10]. Conductance of Va in nitromethane at 23.5°: Λ_0 84 ohm^{-1} cm^2 mol^{-1}; (Λ_e, $\sqrt{c}$): (78.7, 0.0566) (75.43, 0.0894) (70.78, 0.1414). B = 94 ohm^{-1} cm^2 mol^{-1}. Thus, Va is also a 1/1 electrolyte.

Preparation of complexes

All solvents were purified and dried by standard methods.

trans-PtCl(CH$_2$C$_6$H$_4$CN)(PPh$_3$)$_2$ (Ia). *o*-ClCH$_2$C$_6$H$_4$CN (prepared according to ref. 11) (7.4 g) was added to a solution of Pt(PPh$_3$)$_4$ (20 g) in benzene (120 ml) and heated at 60° under nitrogen for 30 h. Precipitation was completed by adding ether (300 ml), and Ia was obtained as white crystals by recrystallization from THF/MeOH. Yield 80%.

trans-PtBr(CH$_2$C$_6$H$_4$CN)(PPh$_3$)$_2$ (Ib). The method used for Ia was employed, but with *o*-BrCH$_2$C$_6$H$_4$CN (Aldrich) and at 25° for 3 h. The side products were [PPh$_3$CH$_2$C$_6$H$_4$CN]Br (m.p. 232—234°; δ(CH$_2$) 5.63 ppm (d, 2H), J(PH) 15 Hz, δ(H$_{arom}$) 7.6 ppm (m, 19H), ν(CN) 2227 cm^{-1} (the phosphonium salt prepared directly by treating PPh$_3$ with *o*-BrCH$_2$C$_6$H$_4$CN in benzene has the same physical and spectroscopic characteristics), and *cis*-PtBr$_2$(PPh$_3$)$_2$. The

TABLE 2

ANALYTICAL, IR AND RAMAN SPECTRAL DATA

Complex	M.p. (dec.) (°C)	Analysis found (calcd.)(%)				ν(CN) (cm^{-1})	Band at 550 ± 5 cm^{-1} [b]	Others (cm^{-1})
		C	H	N	X			
Ia	211–213	60.73 (60.66)	4.30 (4.16)	1.70 (1.61)	3.99 Cl[a] (4.07)	IR 2226 R 2222	552 vw 547 m	283 ν(Pt—Cl) 280
Ib	218–220	57.42 (57.71)	4.20 (3.96)	1.43 (1.53)		IR 2222 R 2216	547 vw 546	184 ν(Pt—Br)
Ic	206–208	55.16 (55.10)	3.76 (3.78)	1.48 (1.46)	3.86 Cl (3.70)	IR 2220 R 2214		282 ν(Pt—Cl) 285
Id	163–164	60.14 (60.20)	4.14 (4.13)	6.44 (6.38)		IR 2225	549 vw	2051 $\nu(N_3)_{as}$ IR 1274 $\nu(N_3)_s$
IIa	213–215	60.60 (60.66)	4.20 (4.16)	1.58 (1.61)		IR 2220	540 s	292 ν(Pt—Cl) 292
IIc	240–241				26.3 Pt (26.25)	IR 2218 R 2215		320 ν(Pt—Cl) 316
IIIa	237–239	57.30 (57.28)	3.90 (3.93)	1.48 (1.52)	8.29 F (8.24)	IR 2265 R 2258	548 s 549 w	1055[c] $\nu(BF_4)$
IIIb	234–237	52.40 (52.29)	3.65 (3.59)	1.41 (1.40)		IR 2262		1060[c] $\nu(BF_4)$
IIIc	270–275	51.35 (51.40)	3.59 (3.55)	1.75 (1.77)	9.30 F (9.56)	IR 2258		1050[c] $\nu(BF_4)$
IV	215–218	62.80 (62.85)	4.39 (4.34)	1.19 (1.18)	7.85 F (7.84)	IR 2220		1055[c] $\nu(BF_4)$
Va	235–237	56.50 (56.62)	4.28 (4.22)	1.43 (1.47)	7.93 F (7.96)	IR 1621	550 s	3338 ν(N—H) IR 1232 $\nu(=COMe)_{as}$
Vb	212–217	50.90 (50.86)	3.88 (3.90)	1.73 (1.70)	9.08 F (9.19)	IR 1606		3305 ν(N—H) IR 1233 $\nu(=COMe)_{as}$
VIa	145–165 (CO↑) 211–214	60.01 (60.10)	3.98 (4.03)	1.60 (1.57)	4.01 Cl (3.94)	IR 2227 R 2224	553 vw 549 m	272 ν(Pt—Cl) IR 1647 ν(CO)
VIb	150–165 (CO↑) 216–218				20.8 Pt (20.67)	IR 2225 R 2218	540 vw 550 m	1655 ν(CO) 184 ν(Pt—Br)

[a] % P 7.06 (7.11). [b] Mastin's identification method [6] 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* [c] Broad

amount of the latter formed is very sensitive to the purity of *o*-$BrCH_2C_6H_4CN$.

trans-$PtCl(CH_2C_6H_4CN)(AsPh_3)_2$ *(Ic).* *o*-$ClCH_2C_6H_4CN$ (3.5 g) was added to a suspension of $Pt(AsPh_3)_4$ (8 g) in benzene (80 ml) and heated at 75° under nitrogen for 24 h. The reaction mixture was reduced to a small volume and ether added. Dissolution of the crude product in CH_2Cl_2 and precipitation with MeOH gave a product contaminated by *cis*-$PtCl_2(AsPh_3)_2$ (50%). The mother liquor kept at −25° for 5 days gave white crystals of IIc. Yield 15%.

trans-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$ *(Id).* Ia (0.5 g) was stirred with NaN_3 (0.5 g) in MeOH (40 ml) for one hour at 60°. Crystallisation took place overnight at room temperature and was completed by adding 10 ml H_2O. Yield 80%.

cis-$PtCl(CH_2C_6H_4CN)(PPh_3)_2$ *(IIa).* HCl 25% (0.12 ml) was added to a suspension of IIIa (0.7 g) in acetone (10 ml) and CH_2Cl_2 (4 ml) and the mixture was agitated for 2 min until complete dissolution. IIa (white microcrystals) was precipitated with ether/hexane without delay to avoid isomerization, and washed with ether. Yield 80%.

cis-$PtBr(CH_2C_6H_4CN)(PPh_3)_2$ *(IIb).* Same method as for IIa with HBr. As the isomerization is more rapid, only a *cis—trans* mixture (20/80) was obtained. The reported spectra are those of a solution of IIIa + PPh_4Br (1/1).

$PtCl(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)$ *(IIc).* A suspension of Ia (2.6 g) and *cis*-$Ph_2PCH{=}CHPPh_2$ (Aldrich) (1.3 g) in benzene (150 ml) was stirred for 10 h at room temperature. The volume was reduced to 50 ml and the white precipitate recrystallized from MeOH and washed with ether/hexane. Yield 77%.

cis-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]BF_4$ *(IIIa).* $AgBF_4$ (0.78 g) was added to a solution of Ia (3.49 g) in CH_2Cl_2 (50 ml). AgCl was filtered and the filtrate reduced to a small volume. Addition of ether gave a white precipitate which was recrystallized from CH_2Cl_2/benzene. Yield 90%. Use of acetone instead of CH_2Cl_2 gave a hemiacetone solvate.

cis-$[Pt(CH_2C_6H_4CN)(AsPh_3)_2]BF_4$ *(IIIb),* $[Pt(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)]BF_4$ *(IIIc).* Same method as for IIIa, starting with Ic and IIc respectively. Yields. ca. 95%.

$[Pt(CH_2C_6H_4CN)(PPh_3)_3]BF_4$ *(IV).* PPh_3 (0.22 g) was added to a solution of IIIa (0.69 g) in CH_2Cl_2 (15 ml). White microcrystals formed which were recrystallized from CH_2Cl_2/benzene. Yield 90%.

cis-$[Pt\{CH_2C_6H_4C(OCH_3)NH\}(PPh_3)_2]BF_4$ *(Va) and* $[Pt\{CH_2C_6H_4C(OCH_3)NH\}(C_2H_2P_2Ph_4)]BF_4$ *(Vb).* A suspension of IIIa (0.5 g) or IIIc in MeOH (40 ml) was stirred for 5 h at 50°. A yellow precipitate formed on addition of ether/hexane, and was recrystallized from MeOH/ether to give pale yellow needles. Yield 80%.

trans-$PtCl(COCH_2C_6H_4CN)(PPh_3)_2$ *(VIa) and trans-*$PtBr(COCH_2C_6H_4CN)(PPh_3)_2$ *(VIb).* A solution of Ia (3.0 g) or Ib in CH_2Cl_2 (30 ml) was kept under CO (90 atm) for 3 days at room temperature. A white precipitate formed on addition of hexane, and was recrystallized from CH_2Cl_2/benzene. Yields ca. 95%.

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