Nucleophilic Attack at Co-ordinated Isocyanides promoted by the 2-Pyridyl Ligand†

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The co-ordinated isocyanide in the 2-pyridyl intermediate $[Pt(CNR)(C_5H_4N\text{-}C^2)(dppe)]^+$ [R = C_6H_4-OMe-4, dppe = 1,2-bis(diphenylphosphino)ethane] is readily attacked by protic nucleophiles, such as water, alcohols and primary amines. It is hydrolysed to CO and RNH_2 by trace amounts of water in commercial benzene or acetone, and also reacts with the small amount of ethanol, present as a stabilizer in commercial chloroform, to yield the (ethoxy)aminocarbene complex $[Pt\{C(OEt)NHR\}(C_5H_4N\text{-}C^2)(dppe)]^+$. The reaction with *p*-anisidine (RNH_2) is remarkably fast and gives the diaminocarbene complex $[Pt\{C(NHR)_2\}(C_5H_4N\text{-}C^2)(dppe)]^+$. Similar but slower reactions with H_2O and RNH_2 occur for the 2-pyrazyl derivative $[Pt(CNR)(C_4H_3N_2\text{-}C^2)(dppe)]^+$. The cationic complex $[Pt(CNR)(C_5H_4NMe\text{-}C^2)(dppe)]^{2+}$ ($C_5H_4NMe\text{-}C^2$ = 1-methyl-2-pyridylium) also reacts with RNH_2 to form $[Pt\{C(NHR)_2\}(C_5H_4NMe\text{-}C^2)(dppe)]^{2+}$, but at significantly lower rates. The enhanced reactivity of the isocyanide ligand in $[Pt(CNR)(C_5H_4N\text{-}C^2)(dppe)]^+$ is ascribed to the highly basic 2-pyridyl group in *cis* position, which assists the nucleophilic attack at the isocyanide carbon by hydrogen bonding with the incoming protic nucleophile. The complex cations $[Pt\{C(NHR)_2\}(C_5H_4N\text{-}C^2)(dppe)]^+$ and $[Pt\{C(OEt)(NHR)\}(C_5H_4N\text{-}C^2)(dppe)]^+$ are better characterized through their $ZnCl_2$ adducts, upon deprotonation of the carbene ligand with NEt_3. The crystal and molecular structure of the binuclear complex $[(dppe)Pt\{C(NHR){=}NR\}(C_5H_4N\text{-}C^2)ZnCl_2]$ has been determined by an X-ray analysis. This compound crystallizes in the orthorhombic system: space group $Pna2_1$, with a = 24.206(3), b = 14.269(3), c = 12.875(3) Å and Z = 4. A total of 3265 reflections have been used in the refinement, resulting in a final R value of 0.029 and R' of 0.027. The structure is characterized by a six-membered ring of boat conformation, formed by the platinum and zinc metal centres and the bridging carbon and nitrogen atoms of the 2-pyridyl and amidino ligands. A distorted square geometry is present around the platinum centre, with bond distances in the normal ranges: Pt–P 2.305(3) and 2.297(3) Å, Pt–C(2-pyridyl) 2.044(10) and Pt–C(amidino) 2.035(8) Å. Some distortion from tetrahedral geometry is present also around the zinc centre. The Zn $\cdots$ Pt distance of 3.238(1) Å appears too long for any metal–metal bonding interaction.

Isocyanides co-ordinated to metal centres in higher oxidation states may undergo nucleophilic attack at the terminal carbon atom by a variety of reagents.[1] In particular, with protic nucleophiles, such as primary and secondary amines or alcohols, the reaction yields metal–carbene complexes [equation (1); Y = NHR^1, NR^1R^2 or OR^3 (R^1, R^2, R^3 = alkyl or aryl)].

$$L_nM{-}CNR + HY \longrightarrow L_nM{-}C\begin{matrix}\cdot\!\!\cdot\ NHR \\ \cdot\!\!\cdot\ Y\end{matrix} \qquad (1)$$

The reactions of palladium(II)–isocyanide substrates with aromatic amines occur through a stepwise mechanism involving a prior nucleophilic attack to form an intermediate which rearranges to the final product by proton transfer between the nitrogen atoms.[2a] The latter step is catalysed by the entering amine itself or by other amines carrying a nitrogen-bonded proton. The corresponding reactions with analogous platinum(II)–isocyanide complexes take place at considerably reduced rates[2b] so as to prevent any kinetic investigation by conventional spectrophotometric techniques.

In the course of our studies on the chemistry of 2-pyridyl d^8 metal complexes[3] we noted that in the cationic intermediate $[Pt(CNR)(C_5H_4N\text{-}C^2)(dppe)]^+$ [R = C_6H_4OMe-4, dppe = 1,2-bis(diphenylphosphino)ethane] the isonitrile group appears particularly prone to attack by protic nucleophiles. As reported below, such enhanced reactivity has been related to the presence of the highly basic 2-pyridyl ligand[4] in *cis* position.

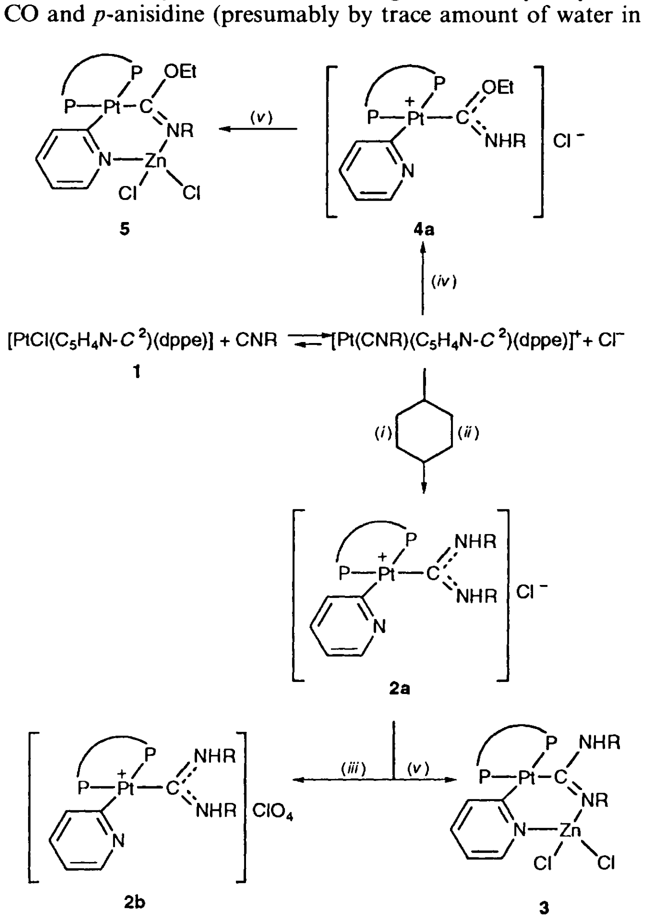
Results and Discussion

Reactions of the Co-ordinated Isocyanide.—The complex $[PtCl(C_5H_4N\text{-}C^2)(dppe)]$ **1** reacts initially with 4-methoxyphenyl isocyanide (Scheme 1) yielding the cationic intermediate $[Pt(CNR)(C_5H_4N\text{-}C^2)(dppe)]^+$, characterized in chloroform or in acetone by a ν(C≡N) band at 2195 cm^{-1} and by a molar conductivity of 101.9 S cm^2 mol^{-1} at 25 °C for a 10^{-3} mol dm^{-3} acetone solution (prepared from the appropriate amount of **1** and a two-fold excess of the isocyanide).

When the reaction is carried out in benzene with a **1**:CNR molar ratio of 1:2, a yellowish oily precipitate, presumably $[Pt(CNR)(C_5H_4N\text{-}C^2)(dppe)]Cl$, is immediately obtained, which slowly changes into an off-white powder $[Pt\{C(NHR)_2\}(C_5H_4N\text{-}C^2)(dppe)]Cl$ **2a** if the mixture is stirred for *ca*. 24 h at ambient temperature. During this time, carbon monoxide is also evolved, as revealed by the IR spectrum of the vapour phase. The product **2a** contains a chloride anion (which can be replaced by ClO_4^- to give **2b**) and a diaminocarbene

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

group, as can be inferred from the results of an X-ray structural analysis of the related binuclear complex [(dppe)Pt{C(NHR)=NR}(C_5H_4N-C^2)$ZnCl_2$] **3** (see below). In the latter compound, the 2-pyridyl ligand (originally present in **1**) and the amidino group, resulting from deprotonation of the diaminocarbene ligand of **2a** by NEt_3 [step (*iv*) of Scheme 1], are *N*-co-ordinated to the same zinc centre. The formation of the carbene moiety in **2a** implies that a nucleophilic attack by *p*-anisidine at the terminal isocyanide carbon of [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ has occurred in step (*i*). In fact, when the cationic intermediate, generated in chloroform solution from the 1 : 1 reaction of **1** with CNR, is subsequently treated with a two-fold excess of *p*-anisidine [step (*ii*)], the same product **2a** is formed in a surprisingly fast reaction (*ca.* 1 h for completion). For comparison, *p*-toluidine was reported to react with *trans*-[PtCl(CNR')$(PEt_3)_2$]$^+$ (R' = Ph or $C_6H_4NO_2$-4) under forcing conditions to yield the diaminocarbene derivative *trans*-[PtCl{C(NHR')NHC_6H_4Me-4}$(PEt_3)_2$]$^+$ (3 d in refluxing chloroform, in the presence of an excess of *p*-toluidine). From these results it appears that in the course of the reaction in benzene an isocyanide molecule undergoes a slow hydrolysis to CO and *p*-anisidine (presumably by trace amount of water in



Scheme 1 R = C_6H_4OMe-*p*, PP = dppe. (*i*) +H_2O, +CNR, −CO in C_6H_6; (*ii*) RNH_2 in $CHCl_3$; (*iii*) $NaClO_4$; (*iv*) EtOH in $CHCl_3$; (*v*) NEt_3, $ZnCl_2$

the commercial solvent), while the second molecule is attacked, upon co-ordination, by the amine to give the diaminocarbene ligand of **2a**. A much slower hydrolysis of the isocyanide to CO and RNH_2 (R = C_6H_4OMe-4) is found to occur also in acetone, when the binuclear complex [{Pt(μ-C_5H_4N-C^2,*N*)(dppe)}$_2$][ClO_4]$_2$ with bridging 2-pyridyl ligands is allowed to react with CNR (Pt : CNR 1 : 2, Scheme 2).

In this case, the cationic intermediate [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ is initially formed *via* a bridge-splitting reaction, as shown by the appearance of the typical ν(C≡N) band at 2195 cm^{-1} for the co-ordinated isocyanide. With time, this band and that of the free ligand at 2125 cm^{-1} slowly disappear due to the second step of Scheme 2, which yields the diaminocarbene product **2b** (*ca.* 5 d for completion).

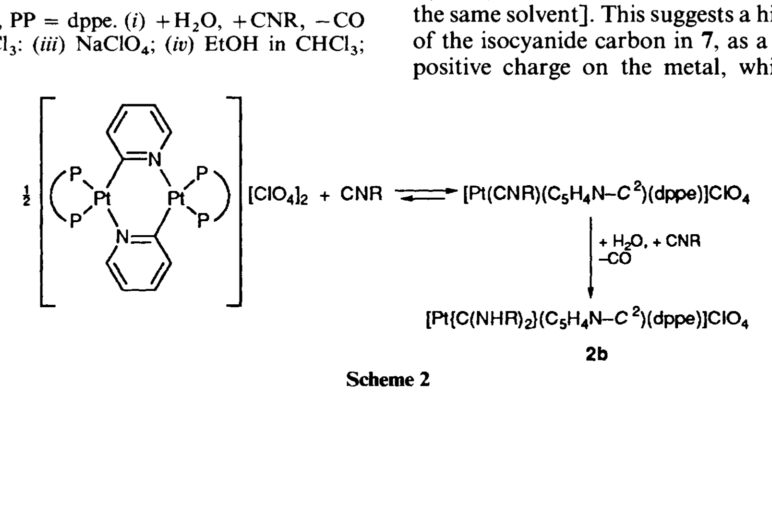
By considering the enhanced basic properties of the 2-pyridyl group[4] and the reactivity of co-ordinated isocyanide[1] and carbamoyl[5] ligands, we propose the mechanism of Scheme 3 for the hydrolysis of CNR and formation of the diaminocarbene group.

The complex [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ undergoes a slow nucleophilic attack by water to produce a reactive intermediate containing a 2-pyridylium and a carbamoyl ligand, which rearranges to a carbonyl derivative with concomitant formation of the amine RNH_2, according to a well documented reaction of carbamoyl groups with protic acids.[5] Displacement of CO by the second molecule of isocyanide in the system regenerates the starting compound, which is readily attacked by RNH_2 to yield the final carbene product.

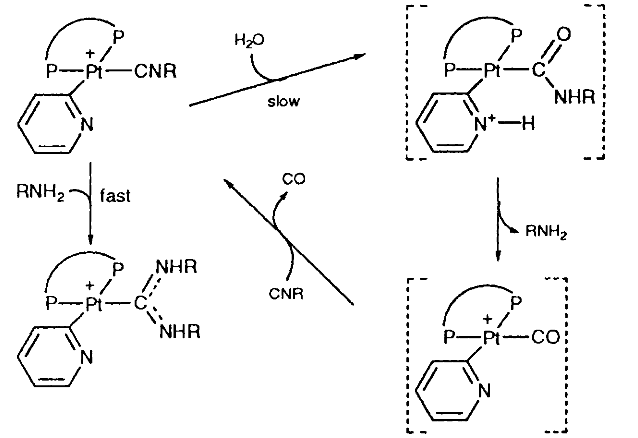
Consistently, the cationic complex [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ reacts also with oxygen nucleophiles, *e.g.* with ethanol present in small amount (0.75%) as a stabilizer in chloroform [step (*v*) of Scheme 1]. This reaction takes *ca.* 1 d for completion at ambient temperature, and yields an (ethoxy)amino carbene compound [Pt{C(OEt)NHR}(C_5H_4N-C^2)(dppe)]Cl **4a**, which is better characterized through its $ZnCl_2$ adduct [Pt(dppe){C(OEt)=NR}(C_5H_4N-C^2)$ZnCl_2$] **5**, upon deprotonation with NEt_3. The latter complex exhibits IR and NMR spectral features which parallel those of **3** (see Table 2 in the Experimental section). In particular, in the ^1H NMR spectrum (CD_2Cl_2) the methyl proton resonances appear as a singlet at δ 3.71 (for the methoxy group) and as a triplet at δ 0.95 (for the ethoxy group, *J* 7.0 Hz), while the OEt diastereotopic methylene protons give rise to two complex multiplets centred at δ 4.73 and 3.84, respectively (ABX_3 spin system).

The enhanced reactivity of the co-ordinated isocyanide in [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ towards protic nucleophiles may arise from either the positive charge on the complex, or the presence of the basic 2-pyridyl ligand in *cis* position, or a combination of both factors. In order to check the influence of positive charges, we have prepared the dicationic complex [Pt(CNR)(C_5H_4NMe-C^2)(dppe)][ClO_4]$_2$ **7** through the sequence of reactions of Scheme 4.

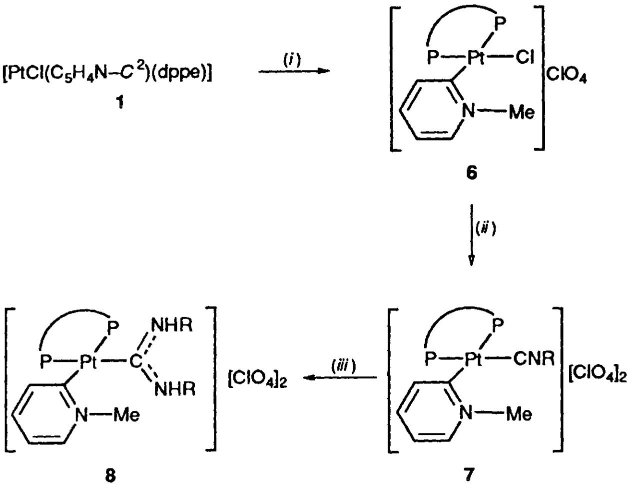
The IR spectrum of **7** in $CHCl_3$ solution exhibits a ν(C≡N) band at 2215 cm^{-1}, at higher frequency (20 cm^{-1}) relative to the corresponding band of [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ [*cf.* the ν(C≡N) value of 2120 cm^{-1} for the unco-ordinated isocyanide in the same solvent]. This suggests a higher electrophilic character of the isocyanide carbon in **7**, as a consequence of the greater positive charge on the metal, which depresses the Pt–CNR



Scheme 2



Scheme 3 Proposed mechanism for hydrolysis of the co-ordinated isocyanide; R = C_6H_4OMe-4



Scheme 4 R = C_6H_4OMe-4; PP = dppe. (*i*) Me_2SO_4, $NaClO_4$; (*ii*) CNR, $NaClO_4$; (*iii*) RNH_2 in $CHCl_3$

d ⟶ π* back donation.[6] However, the reaction of **7** with *p*-anisidine, yielding the carbene derivative [Pt{C(NHR)$_2$}(C_5H_4NMe-C^2)(dppe)][ClO_4]$_2$ **8**, is much slower and takes *ca.* 7 h for completion, under comparable experimental conditions (**7**:RNH_2 = 1:2, in $CHCl_3$ at ambient temperature). Although the increased electrophilic character may be counterbalanced to some extent by the greater steric requirements of the *cis* 1-methyl-2-pyridylium ligand of **7**, the observed decrease in reactivity suggests that the positive charge on the complex plays only a minor role in the activation mechanism. On the other hand, we have also examined some reactions of [PtCl($C_4H_3N_2$-C^2)(dppe)] **9**, analogous to **1** but containing the less basic 2-pyrazyl group (Scheme 5).*

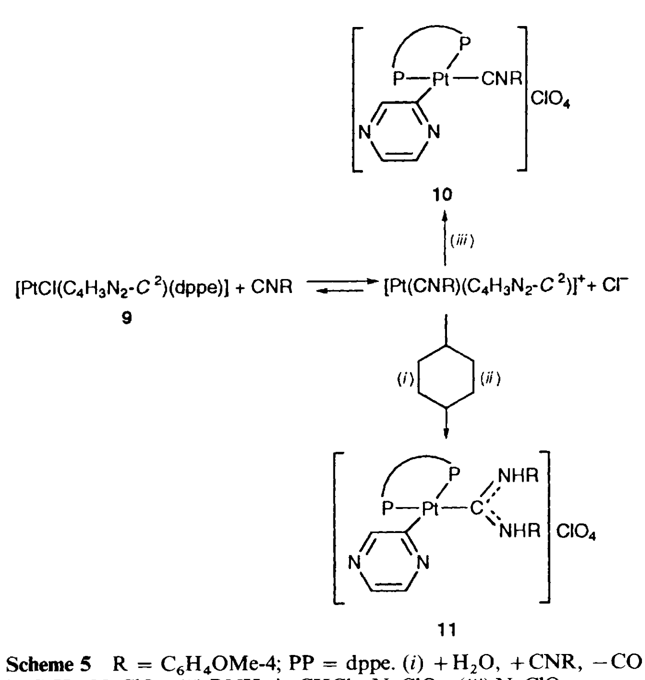
In the reaction of **9** with an equimolar amount of 4-methoxyphenyl isocyanide in chloroform, the cationic intermediate [PtCl($C_4H_3N_2$-C^2)(dppe)]$^+$ [ν(C≡N) 2195 cm^{-1} in $CHCl_3$] is formed which undergoes nucleophilic attack by *p*-anisidine (Pt:RNH_2 1:2) to yield the final carbene derivative [Pt{C(NHR)$_2$}($C_4H_3N_2$-C^2)(dppe)]ClO_4 **11** (*ca.* 4 h for completion at ambient temperature). The latter product is also formed at lower rates (*ca.* 5 d for completion) in the reaction of **9** with 2 equivalents of isocyanide in benzene. The concomitant evolution of carbon monoxide indicates that also in this case a CNR molecule has undergone hydrolysis to CO and RNH_2. It thus appears that complex **9** reacts similarly to [PtCl(C_5H_4N-C^2)(dppe)], but at significantly lower rates. In this context, it is noteworthy that the intermediate [Pt(CNR)($C_4H_3N_2$-C^2)(dppe)]$^+$ can be isolated and characterized as the perchlorate salt **10** (see Experimental section), whereas this can hardly be achieved for the more reactive [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ analogue.

From the observed reactivity trend [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ > [Pt(CNR)($C_4H_3N_2$-C^2)(dppe)]$^+$ > [Pt(CNR)(C_5H_4NMe-C^2)(dppe)]$^{2+}$ it can be argued that the *cis* heterocyclic ligand is of relevant importance in promoting the attack by protic nucleophiles, and the activating role increases with increasing basic properties.

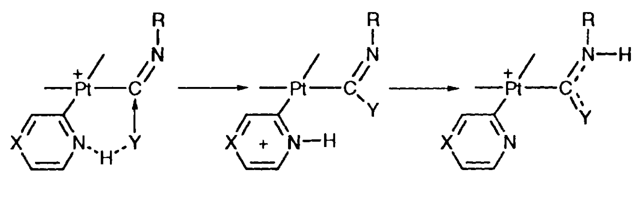
By taking into account the mechanism proposed for the reaction of primary and secondary anilines with palladium(II)–isocyanide complexes,[1] the role of C_5H_4N-C^2 and $C_4H_3N_2$-C^2 ligands and the rate sequence C_5H_4N-C^2 > $C_4H_3N_2$-C^2 may be explained by hydrogen bonding with the incoming nucleophile H–Y, which lowers the activation energy to the labile intermediate **I** in the first step of the process, and possibly takes part in the subsequent proton transfer to the carbene derivative **II** (Scheme 6, X = CH or N).

X-Ray Crystal Structure Analysis of [Pt(dppe){C(NHR)=NR}(C_5H_4N-C^2)$ZnCl_2$] **3**.—An ORTEP view of complex **3** is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The complex **3** is binuclear, the two metal atoms Pt and Zn being connected *via* two N–C bridges {from 2-pyridyl [N(2), C(2)] and from the amidino ligand [C(1), N(1)]} with formation of a six-membered ring of boat conformation. The two metals lie out of the plane formed by the bridging

* Titration with $HClO_4$ of *trans*-[PtCl(C_5H_4N-C^2)(PPh_3)$_2$][3] and *trans*-[PtCl($C_4H_3N_2$-C^2)(PPh_3)$_2$] [5 × 10^{-4} mol dm^{-3} solutions in water–1,4-dioxane (1:3 v/v)] involves protonation of the nitrogen atom at position 1 on the heterocyclic ligand[7] and gives pK_a values of 7.80 and 4.34, respectively. The pK_a measurement for **9** is prevented by the low solubility of this compound in the above mixture of solvents.



Scheme 5 R = C_6H_4OMe-4; PP = dppe. (*i*) +H_2O, +CNR, −CO in C_6H_6, $NaClO_4$; (*ii*) RNH_2 in $CHCl_3$, $NaClO_4$; (*iii*) $NaClO_4$



I II

Scheme 6

Table 1 Selected bond distances (Å) and angles (°) for complex **3**

Pt–P(1)	2.305(3)	Pt–P(2)	2.297(3)
Pt–C(1)	2.035(8)	Pt–C(2)	2.044(10)
Zn–Cl(1)	2.241(3)	Zn–Cl(2)	2.258(3)
Zn–N(1)	2.021(8)	Zn–N(2)	2.057(8)
P(1)–C(7)	1.83(1)	P(1)–C(8)	1.82(1)
P(1)–C(14)	1.83(1)	P(2)–C(20)	1.86(1)
P(2)–C(21)	1.81(1)	P(2)–C(27)	1.81(1)
N(1)–C(1)	1.32(1)	N(1)–C(40)	1.44(1)
N(2)–C(2)	1.38(1)	N(2)–C(6)	1.34(2)
C(1)–N(3)	1.37(1)	C(2)–C(3)	1.38(2)
C(3)–C(4)	1.36(2)	C(4)–C(5)	1.38(2)
C(5)–C(6)	1.40(2)	C(7)–C(20)	1.51(2)
N(3)–C(33)	1.43(1)	N(3)–H	0.82(8)
C(36)–O(1)	1.40(1)	O(1)–C(39)	1.42(2)
C(43)–O(2)	1.40(2)	O(2)–C(46)	1.33(2)
C(1)–Pt–C(2)	89.6(4)	P(2)–Pt–C(2)	91.2(3)
P(2)–Pt–C(1)	173.1(2)	P(1)–Pt–C(2)	168.5(3)
P(1)–Pt–C(1)	95.2(3)	P(1)–Pt–P(2)	82.8(1)
N(1)–Zn–N(2)	98.2(3)	Cl(2)–Zn–N(2)	106.2(3)
Cl(2)–Zn–N(1)	109.7(2)	Cl(1)–Zn–N(2)	112.5(2)
Cl(1)–Zn–N(1)	118.3(3)	Cl(1)–Zn–Cl(2)	110.8(1)
Pt–P(1)–C(14)	117.9(3)	Pt–P(1)–C(8)	120.0(3)
Pt–P(1)–C(7)	101.6(3)	C(8)–P(1)–C(14)	104.7(4)
C(7)–P(1)–C(14)	107.0(5)	C(7)–P(1)–C(8)	104.2(5)
Pt–P(2)–C(27)	116.1(4)	Pt–P(2)–C(21)	116.0(4)
Pt–P(2)–C(20)	107.8(4)	C(21)–P(2)–C(27)	105.2(5)
C(20)–P(2)–C(27)	107.3(5)	C(20)–P(2)–C(21)	103.4(5)
Zn–N(1)–C(40)	122.9(6)	Zn–N(1)–C(1)	116.3(6)
C(1)–N(1)–C(40)	120.3(7)	Zn–N(2)–C(6)	120.4(9)
Zn–N(2)–C(2)	118.3(7)	C(2)–N(2)–C(6)	120.8(9)
Pt–C(1)–N(1)	119.5(6)	N(1)–C(1)–N(3)	117.5(8)
Pt–C(1)–N(3)	122.9(6)	Pt–C(2)–N(2)	114.2(7)
N(2)–C(2)–C(3)	117.6(9)	Pt–C(2)–C(3)	128.0(8)
C(2)–C(3)–C(4)	122(1)	C(3)–C(4)–C(5)	120(1)
C(4)–C(5)–C(6)	118(1)	N(2)–C(6)–C(5)	122(1)
P(1)–C(7)–C(20)	109.8(7)	P(2)–C(20)–C(7)	111.7(8)
C(1)–N(3)–C(33)	126(1)	C(36)–O(1)–C(39)	117(1)
C(43)–O(2)–C(46)	120(1)		

nitrogen and carbon atoms by −1.1924(4) Å for Pt and −0.815(1) Å for Zn.

The two p-MeOC$_6$H$_4$ moieties are rotated with respect to the planar C(40)–N(1)–C(1)–N(3) amidino fragment by 42.2(7) and 95.7(7)° respectively. The highest rotation corresponds to the p-MeOC$_6$H$_4$ group closer to the Zn co-ordination sphere in order to minimize intramolecular contacts.

The two carbon atoms of the bridging groups are *cis*-bound to platinum while the other co-ordination positions are occupied by the phosphorus atoms of the dppe ligand with a rather distorted square geometry around the Pt metal centre. The angles subtended to the Pt atom deviate from the ideal value of 90° due to the bite angle of 82.8(1)° of the chelating diphosphine ligand. The Pt–P distances 2.305(3) Å for P(1) and 2.297(3) Å for P(2) are equivalent within experimental error indicating a comparable *trans* influence of the opposite ligand atoms. Their values are as expected for similar bonds as in [(dppe)IPt{μ-C(S)SC(SMe)$_2$}Pt(dppe)]I.[8] The conformation of the dppe ethylene chain is between *syn* and skew according to the P(1)–C(7)–C(20)–P(2) torsion angle of 39.4(10)°. The Pt–C values of 2.035(8) [C(1)] and 2.044(10) Å [C(2)] are usual for Pt–C(sp^2) bonds[9] and in particular agree with the value of 2.046(18) Å reported for the previously mentioned compound.[8]

Two sites of the zinc co-ordination sphere are occupied by the nitrogen atoms N(1) and N(2) associated with the bridging groups, with two chlorines completing the tetrahedral geometry around the metal. Some distortion from tetrahedron is related to the restricted position of the two nitrogens which form an angle of 98.2(3)° with the central Zn, while Cl(1)–Zn–Cl(2) has the usual tetrahedral value of 110.8(1)°. The Zn–Cl bond distances 2.241(3) and 2.258(3) Å and the Zn–N 2.021(8) and 2.057(8) Å have values comparable to those reported for [bis(benzothiazol-2-yl)phenylmethanol]dichlorozinc(II),[10] where a flattened boat conformation of the central six-membered ring is present. The transannular Zn ··· Pt distance of **3** is rather short [3.238(1) Å] when compared to the Zn ··· Pt transannular distance of 4.39 Å reported for the hetero-binuclear complex [(Ph$_2$MeP)$_2$Pt{OSP(OR)$_2$}$_2$ZnCl$_2$][11]

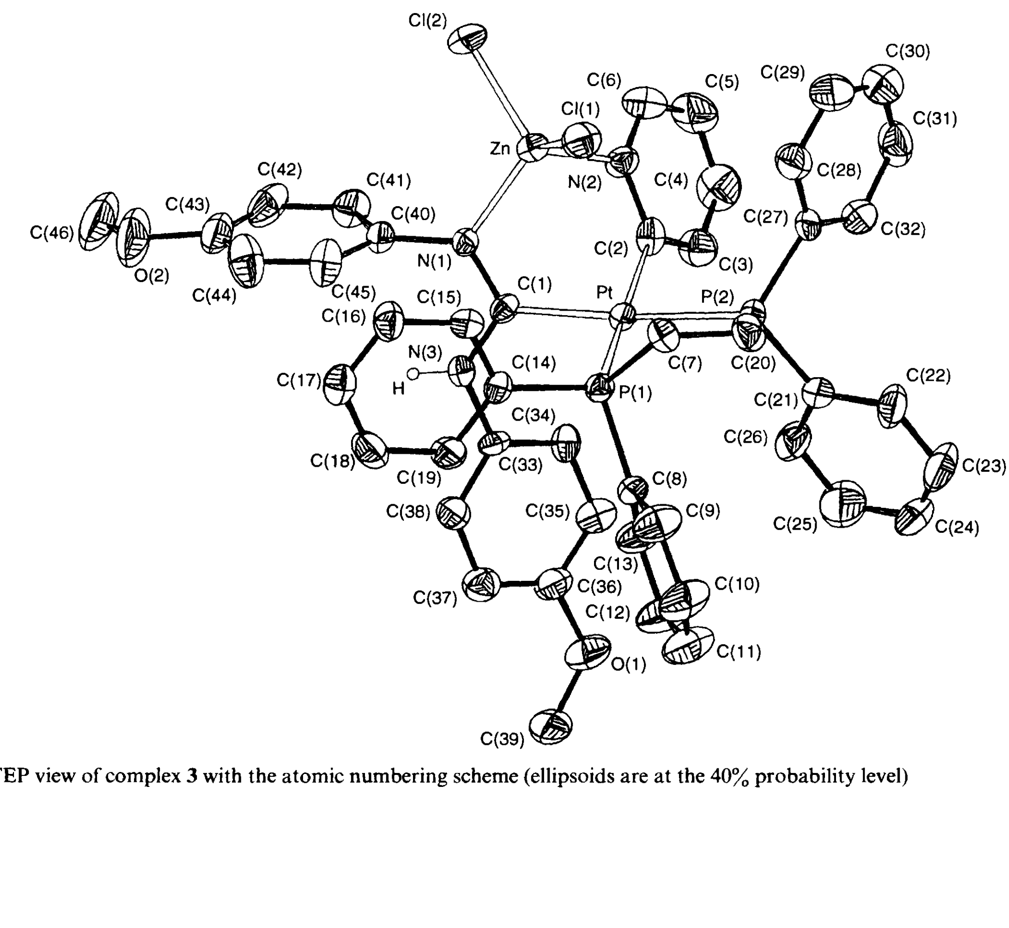


Fig. 1 An ORTEP view of complex **3** with the atomic numbering scheme (ellipsoids are at the 40% probability level)

containing a bridging thiophosphate ligand. However, it is too large for a metal-bond interaction which was found to occur in *cis*-[$(H_3N)_2$Pt(mura)$_2$Zn$(H_2O)_3$]SO_4·$2H_2O$[12] (Hmura = methyluracil) where a Pt–Zn bond distance of 2.760(1) Å was detected.

Experimental

The complexes [PtCl(C_5H_4N-C^2)(dppe)] **1**[3] and [{Pt(μ-C_5H_4N-C^2,*N*)(dppe)}$_2$][ClO_4]$_2$,[3] and the 4-methoxyphenyl isocyanide (CNR)[13] were prepared by published methods. *p*-Anisidine was purified by sublimation at reduced pressure. All other chemicals and solvents were reagent grade, and were used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparations.—[PtCl(C_5H_4NMe-C^2)(dppe)]ClO_4 **6**. Dimethyl sulfate (1.26 g, 10 mmol) was added to a stirred solution of [PtCl(C_5H_4N-C^2)(dppe)] **1** (0.71 g, 1 mmol) in benzene (100 cm^3). After standing overnight at room temperature, the mixture was concentrated to small volume and diluted with diethyl ether to precipitate a white compound, which was filtered off, redissolved in CH_2Cl_2 and treated with a solution of $NaClO_4$·H_2O (0.28 g, 2 mmol) in MeOH (10 cm^3). After stirring for 10 min, the solvents were evaporated to dryness and the solid residue was extracted with CH_2Cl_2 (*ca.* 80 cm^3) and charcoal. After filtration and addition of MeOH (*ca.* 30 cm^3) to the clear solution, the more volatile dichloromethane was slowly evaporated to precipitate the product **6**, which was further purified by reprecipitation from the same mixture of solvents (0.70 g, 85.2% yield, based on the theoretical amount).

[Pt(CNR)(C_5H_4NMe-C^2)(dppe)][ClO_4]$_2$ **7**. A stirred solution of **6** (0.41 g, 0.5 mmol) in CH_2Cl_2 (50 cm^3) was first treated with 4-methoxyphenyl isocyanide (0.067 g, 0.5 mmol) and, after 10 min, with $NaClO_4$·H_2O (0.14 g, 1 mmol) dissolved in MeOH (5 cm^3). The resulting mixture was worked up as above for the preparation of **6**, to give the white product **7** (0.33 g, 64.8%).

trans-[PtCl($C_4H_3N_2$-C^2)$(PPh_3)_2$]. A suspension of [Pt$(PPh_3)_4$] (4.38 g, 3.52 mmol) in toluene (250 cm^3) containing chloropyrazine (0.61 g, 5.32 mmol) was heated at 95 °C for 6 h under N_2. After standing overnight at room temperature, the mixture was concentrated to small volume and diluted with Et_2O to yield the crude product (2.82 g), contaminated by a small amount of *cis*-[$PtCl_2(PPh_3)_2$]. The solid was extracted with benzene (*ca.* 2000 cm^3) in the presence of charcoal. After filtration, the solution was evaporated to small volume and diluted with Et_2O to precipitate the white 2-pyrazyl complex (2.62 g, 89.2%) (Found: C, 57.7; H, 4.0; N, 3.3. $C_{40}H_{33}ClN_2P_2Pt$ requires C, 57.60; H, 4.00; N, 3.35%); IR (Nujol, cm^{-1}), ν(Pt–Cl) 288m; ^{31}P NMR ($CDCl_3$), δ 23.1 [s, ^1J(Pt–P) 3082 Hz].

[PtCl($C_4H_3N_2$-C^2)(dppe)] **9**. The ligand dppe (0.20 g, 0.5 mmol) was added to a stirred suspension of *trans*-[PtCl($C_4H_3N_2$-C^2)$(PPh_3)_2$] (0.42 g, 0.5 mmol) in benzene (*ca.* 150 cm^3). After 15 min, a clear solution was obtained, which was stored overnight at ambient temperature. Concentration to small volume and dilution with Et_2O caused the precipitation of the white product **9** (0.31 g, 87.6%).

[Pt(CNR)($C_4H_3N_2$-C^2)(dppe)]ClO_4 **10**. A stirred solution of **9** (0.354 g, 0.5 mmol) in $CHCl_3$ (50 cm^3) was first treated with 4-methoxyphenyl isocyanide (0.067 g, 0.5 mmol) and, after 10 min, with $NaClO_4$·H_2O (0.28 g, 2 mmol) dissolved in acetone (10 cm^3). The solvents were evaporated to dryness and the solid residue was extracted with 1,2-dichloroethane (*ca.* 30 cm^3) in the presence of charcoal. After filtration, the solution was concentrated to small volume and diluted with Et_2O to precipitate the off-white product **10** (0.31 g, 68.5%).

Reactions of Isocyanide Complexes.—(*a*) *With water in benzene.* Addition of *p*-methoxyphenyl isocyanide (0.532 g, 4 mmol) to a stirred suspension of the 2-pyridyl complex **1** (1.42 g, 2 mmol) in benzene (200 cm^3) caused the immediate precipitation of a yellowish oily product. The mixture was stirred at ambient temperature for 2 d and the progress of the reaction was monitored by IR spectroscopy, following the decrease in intensity of the ν(C≡N) band of the unco-ordinated isocyanide at 2120 cm^{-1} in the solution. Partial evaporation of the solvent and dilution with Et_2O completed the precipitation of **2a** as an off-white powder {1.70 g; Λ_M 78.9 S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} methanol solution at 25 °C; IR (Nujol, cm^{-1}): 3190(br) m [ν(N–H)] and 1545ms [ν(C═N)]}. In a separate experiment, the isocyanide (1 mmol) and **1** (0.5 mmol) were mixed in benzene (50 cm^3) in a 100 cm^3 round-bottom flask. When the reaction was complete (*ca.* 1 d) the vapour phase was transferred into an evacuated IR cell (10 cm pathlength). The IR spectrum showed the typical vibrorotational pattern of the C–O stretching of carbon monoxide, centred at 2143 cm^{-1}.

The complex **2a** (0.78 g) was redissolved in CH_2Cl_2 (*ca.* 50 cm^3) and treated with a solution of $NaClO_4$·H_2O (0.28 g, 2 mmol) in MeOH (10 cm^3). The mixture was worked up as described for the preparation of **6** to yield **2b** (0.60 g).

Dropwise addition of NEt_3 (0.3 cm^3) to a stirred suspension of **2a** (0.96 g, 1 mmol) and anhydrous $ZnCl_2$ (0.20 g) in MeOH (10 cm^3) caused initial dissolution of the solid, followed by slow crystallization of the binuclear compound **3**. The mixture was set aside for 3 h. The white microcrystals were filtered off and washed with cold MeOH (0.96 g, 90.3%).

The reaction of the 2-pyrazyl complex **9** (0.71 g, 1 mmol) with *p*-methoxyphenyl isocyanide (0.266 g, 2 mmol) in benzene (100 cm^3) was carried out in the same way as described for the 2-pyridyl analogue **1**. In this case, however, a longer time is required for completion (*ca.* 5 d). After stirring for 6 d, the reaction mixture was worked up as above for **2a** and **2b**, to yield the final product **11** (0.75 g, 72.9%) upon addition of $NaClO_4$·H_2O (0.28 g, 2 mmol).

(*b*) *With water in acetone.* Upon addition of *p*-methoxyphenyl isocyanide (0.133 g, 1 mmol) to [{Pt(μ-C_5H_4N-C^2,*N*)(dppe)}$_2$][ClO_4]$_2$ (0.386 g, 0.25 mmol) in acetone (50 cm^3), a slow bridge-splitting reaction took place to give [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ as revealed by the IR spectra of the solution, recorded at different times. After 3 h, both the ν(C≡N) bands of co-ordinated (2195 cm^{-1}) and free (2120 cm^{-1}) isocyanide began to decrease in intensity, and eventually disappeared in *ca.* 5 d. After standing for a further day, the solution was concentrated to small volume and the product **2b** (0.46 g, 89.5%) was precipitated upon dilution with Et_2O.

(*c*) *With* 4-MeO$C_6H_4NH_2$ (*in* $CHCl_3$). The amine (0.123 g, 1 mmol) was added to a solution containing the 2-pyridyl complex **1** (0.35 g, 0.5 mmol) and 4-MeOC_6H_4NC (0.066 g, 0.5 mmol) in $CHCl_3$ (50 cm^3). The subsequent reaction, involving nucleophilic attack by the amine at the isocyanide carbon of the reversibly formed intermediate [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$, was monitored by IR spectroscopy, following the decay of the ν(C≡N) band at 2195 cm^{-1} (*ca.* 1 h for completion at ambient temperature). After 3 h from the mixing of the reactants, the solution was concentrated to small volume and diluted with Et_2O to precipitate the product **2a** (0.34 g), from which either **2b** or **3** could be prepared.

A similar reaction occurred when the amine (0.123 g, 1 mmol) was added to a solution containing the 2-pyrazyl complex **9** (0.35 g, 0.5 mmol) and the isocyanide 4-MeOC_6H_4NC (0.066 g, 0.5 mmol) in $CHCl_3$ (50 cm^3). After completion (*ca.* 4 h), a solution of $NaClO_4$·H_2O in MeOH (5 cm^3) was added and the mixture was stirred for 10 min. The solvents were evaporated to dryness and the solid residue was worked up as described above for the preparation of **6**, to give the complex **11** (0.38 g, 73.9%).

Nucleophilic attack at the co-ordinated isocyanide also occurred when the amine (0.123 g, 1 mmol) was added to a solution of **7** (0.51 g, 0.5 mmol) in $CHCl_3$ (50 cm^3). After completion (*ca.* 7 h), the solution was kept aside overnight.

Table 2 Selected analytical, conductivity, IR and ^{31}P-{^{1}H} NMR data

Compound	Analysis[a] (%) C	H	N	Λ_M/S cm^2 mol^{-1}	IR bands[b]/cm^{-1} ν(N–H)	ν(CN)	ν(M–Cl)	^{31}P NMR[c]
2b	53.4 (53.80)	4.3 (4.30)	4.1 (4.10)	103.7[d]	3270m, 3220 (sh)	1545ms		40.0(d) (^2J 4.5, ^1J 1736), 39.4(d) (^1J 2339)
3	51.5 (51.95)	4.0 (4.10)	3.9 (3.95)		3340m	1512s	290(br)s[e]	37.9(s) (^1J 1838), 35.9(s) (^1J 2092)
5	49.7 (49.95)	4.0 (4.10)	2.9 (2.85)			1520s	298ms[e] 282ms[e]	38.6(d) (^2J 1.3, ^1J 2111), 36.9(d) (^1J 1809)
6	46.9 (46.80)	3.7 (3.80)	1.7 (1.70)	95.2[d] 126.6[f]			306m[g]	39.8(d) (^2J 6.5, ^1J 2067), 38.4(d) (^1J 3583)
7	47.3 (47.15)	3.9 (3.75)	2.6 (2.75)	206.0[f]		2220s		43.3(d) (^2J 6.5, ^1J 1881), 42.0(d) (^1J 2850)
8	49.2 (49.45)	4.1 (4.15)	3.6 (3.70)	170.0[d]	3360(br) (sh), 3300mw, 3250mw	1540ms		39.7(d)[h,i] (^2J 6.4, ^1J 2079), 38.5(d)[h,i] (^1J 2065)
9	51.0 (50.90)	3.9 (3.85)	3.9 (3.95)				302ms[g]	37.6(d) (^2J 3.9, ^1J 1690), 36.7(d) (^1J 4097)
10	50.4 (50.40)	3.8 (3.80)	4.5 (4.65)	91.3[d]		2190s		44.0(d)[j] (^2J 8.0, ^1J 1586), 42.4(d)[j] (^1J 3185)
11	52.7 (52.55)	4.3 (4.20)	5.4 (5.45)	89.3[d]	3280ms	1545s		40.4(d)[i] (^2J 4.8, ^1J 1710), 38.3(d)[i] (^1J 2345)

[a] Calculated values in parentheses. [b] As Nujol mulls. [c] In CD_2Cl_2 solution, unless otherwise stated; chemical shifts (δ) in ppm from 85% H_3PO_4 as external standard, downfield shifts being taken as positive; s = singlet, d = doublet; ^1J = ^1J(^{195}Pt–P), ^2J = ^2J(P–P) in Hz. [d] For 10^{-3} mol dm^{-3} methanol solution at 25 °C. [e] ν(Zn–Cl). [f] For 10^{-3} mol dm^{-3} acetone solution at 25 °C. [g] ν(Pt–Cl). [h] In $(CD_3)_2SO$ solution. [i] Major isomer, see text. [j] In $CDCl_3$ solution.

Table 3 Crystal data, experimental conditions and refinement for complex **3**

Formula	$C_{46}H_{43}Cl_2N_3O_2P_2PtZn$
M	1063.19
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	24.206(3)
b/Å	14.269(3)
c/Å	12.875(3)
U/Å^3	4447(2)
Z	4
D_c/g cm^{-3}	1.59
F(000)	2112
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	39.59
Relative transmission coefficients	0.78, 1.00
Reflections measured	4879
Scan method	θ–2θ
Reflections [$I \geqslant 3\sigma(I)$]	3265
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.029
$R' = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.027
Weighting scheme w	$[\sigma^2(F_o) + 0.000\ 220(F_o^2)]^{-1}$
Goodness of fit, S	1.21

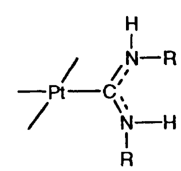
Concentration to small volume and dilution with Et_2O gave the off-white product **8**, which was purified by reprecipitation from a CH_2Cl_2–MeOH solution, upon evaporation of CH_2Cl_2 (0.41 g, 71.8%).

(*d*) *With* EtOH (*in* $CHCl_3$). When a solution of *p*-methoxyphenyl isocyanide (0.133 g, 1 mmol) and the complex **1** (0.71 g, 1 mmol) in $CHCl_3$ (100 cm^3) was kept at ambient temperature for a prolonged time, the co-ordinated isocyanide of the reversibly formed intermediate [Pt(CNR)(C_5H_4N-C^2)(dppe)]$^+$ was slowly attacked by the ethanol of the commercial chloroform, as indicated by the slow decrease with time of the ν(C≡N) band at 2195 cm^{-1} in the IR spectra. This band disappeared almost completely in *ca.* 1 d. After standing for another day, the solution was concentrated to small volume and diluted with Et_2O to precipitate the product **4a** as an off-white powder {0.58 g, Λ_M 73.3 S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} methanol solution at 25 °C; IR (Nujol, cm^{-1}): 3200(br) w [ν(N–H)] and 1560ms [ν(C≡N)]}.

Dropwise addition of NEt_3 (0.3 cm^3) to a stirred suspension of **4a** (0.30 g, 0.34 mmol) and anhydrous $ZnCl_2$ (0.10 g) in MeOH (5 cm^3) caused the initial dissolution of the solid, followed by slow crystallization of the binuclear compound **5** (0.21 g, 62.9%).

Characterization of the Products.—The new compounds were characterized by elemental analyses, conductivity measurements, IR spectroscopy in the solid, ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy (Table 2).

The molar conductivity values are in good agreement with those reported for 1:1 and 1:2 electrolytes in methanol or acetone.[14] The ^{1}H NMR spectral data are not reported in Table 2 as they are of little relevance. In most cases, the 2-pyridyl and 2-pyrazyl protons are masked by the intense phenyl protons signals of the phosphine ligands in the range δ 7–8. According to the ^{1}H NMR spectrum of **2b** (CD_2Cl_2), the carbene moiety is essentially in a *Z,E* configuration.



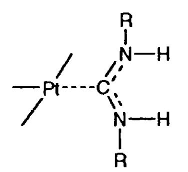
Two (OMe) singlets of 1:1 intensity ratio are in fact detected at δ 3.87 and 3.76, suggesting the presence of two non-equivalent C_6H_4OMe-4 substituents. Such a configuration is retained in the amidino group of **3**, as shown by its crystal structure. Accordingly, in the ^{1}H NMR spectrum of **3** (CD_2Cl_2), the C_6H_4OMe-4 methyl protons resonate as two well separated 1:1 singlets at δ 3.92 and 3.70, respectively.

The ^{1}H and ^{31}P NMR spectra of **8** and **11** indicate the presence of two isomers with different diaminocarbene configuration. The major isomer has a *Z,E* configuration characterized by two 1:1 OMe and N–H proton resonances, the latter being flanked by ^{195}Pt satellites with different ^3J(Pt–H) coupling constants: as an example, for **11** in CD_2Cl_2 the OMe signals occur at δ 3.85 and 3.75, while the N–H signals are detected at δ 9.80, with a ^3J(Pt–H) of 81.2 Hz (N–H *trans* to Pt),[15] and at

Table 4 Fractional atomic coordinates for complex **3**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt	0.12 991(1)	0.34 970(2)	0.250 0	C(22)	0.197 5(5)	0.037 8(8)	0.203 0(11)
Zn	0.17 645(5)	0.556 59(8)	0.195 0(1)	C(23)	0.175 9(7)	−0.050 7(9)	0.193 3(14)
Cl(1)	0.253 4(1)	0.515 1(2)	0.280 0(2)	C(24)	0.121 0(7)	−0.061 6(9)	0.188 0(13)
Cl(2)	0.185 8(1)	0.700 4(2)	0.123 8(3)	C(25)	0.085 7(6)	0.013 2(11)	0.182 2(15)
P(1)	0.148 8(1)	0.315 1(2)	0.421 2(2)	C(26)	0.107 7(5)	0.103 8(9)	0.191 2(11)
P(2)	0.192 5(1)	0.231 8(2)	0.219 8(2)	C(27)	0.238 5(4)	0.248 8(8)	0.110 5(9)
N(1)	0.103 6(3)	0.548 3(5)	0.271 0(7)	C(28)	0.283 1(6)	0.308 5(9)	0.121 1(12)
N(2)	0.158 3(4)	0.467 1(6)	0.074 4(7)	C(29)	0.315 3(7)	0.327 0(11)	0.034 5(17)
C(1)	0.082 4(3)	0.463 8(6)	0.281 8(7)	C(30)	0.305 4(8)	0.288 9(11)	−0.057 8(15)
C(2)	0.129 8(4)	0.385 9(7)	0.096 4(8)	C(31)	0.261 9(6)	0.232 7(10)	−0.068 2(10)
C(3)	0.108 0(5)	0.336 2(9)	0.013 6(9)	C(32)	0.227 2(5)	0.210 3(8)	0.015 7(9)
C(4)	0.116 0(6)	0.363 2(11)	−0.086 3(12)	N(3)	0.030 1(3)	0.457 2(6)	0.321 8(7)
C(5)	0.147 4(6)	0.441 4(11)	−0.107 9(11)	C(33)	−0.002 9(4)	0.374 3(6)	0.326 1(8)
C(6)	0.167 7(6)	0.493 0(12)	−0.023 8(12)	C(34)	−0.002 3(4)	0.310 4(6)	0.242 3(12)
C(7)	0.223 3(4)	0.294 3(8)	0.416 8(8)	C(35)	−0.035 1(4)	0.230 0(7)	0.248 2(13)
C(8)	0.120 8(4)	0.208 9(6)	0.479 6(8)	C(36)	−0.069 4(5)	0.218 1(8)	0.332 2(10)
C(9)	0.149 5(5)	0.160 8(9)	0.558 1(11)	C(37)	−0.073 2(4)	0.281 9(8)	0.410 5(10)
C(10)	0.128 0(6)	0.078 9(9)	0.597 2(12)	C(38)	−0.038 0(4)	0.359 7(7)	0.407 3(8)
C(11)	0.078 1(6)	0.043 5(10)	0.559 4(13)	O(1)	−0.101 5(3)	0.136 5(5)	0.328 1(7)
C(12)	0.049 4(5)	0.090 6(9)	0.485 9(13)	C(39)	−0.134 5(5)	0.115 9(9)	0.416 2(12)
C(13)	0.071 4(4)	0.172 1(7)	0.443 5(10)	C(40)	0.072 1(4)	0.629 7(6)	0.300 8(8)
C(14)	0.136 8(4)	0.406 4(7)	0.518 0(7)	C(41)	0.041 8(5)	0.679 1(7)	0.231 5(9)
C(15)	0.171 2(6)	0.481 7(9)	0.526 0(10)	C(42)	0.009 9(4)	0.757 6(7)	0.262 0(15)
C(16)	0.160 2(5)	0.553 9(8)	0.593 7(9)	C(43)	0.010 4(5)	0.782 0(8)	0.365 6(14)
C(17)	0.113 1(5)	0.551 6(8)	0.652 6(9)	C(44)	0.041 1(5)	0.733 0(10)	0.433 0(12)
C(18)	0.077 4(5)	0.476 7(9)	0.642 5(10)	C(45)	0.071 3(5)	0.659 1(8)	0.402 1(10)
C(19)	0.089 9(5)	0.403 5(9)	0.579 4(10)	O(2)	−0.020 2(4)	0.854 6(7)	0.409 9(11)
C(20)	0.236 2(4)	0.219 7(9)	0.337 8(10)	C(46)	−0.057 2(7)	0.900 3(10)	0.352 3(17)
C(21)	0.163 8(5)	0.115 4(7)	0.202 5(10)	H	0.015(3)	0.499(6)	0.353(6)

δ 9.15, with a ^{3}J(Pt–H) of *ca.* 30 Hz (N–H *cis* to Pt).[15] The minor isomer has presumably a *Z,Z* configuration which eliminates any steric strain between the N–R substituents.



Physical Measurements and Instrumentation.—The conductivity measurements were carried out with a CDM83 conductivity meter. The ^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded on a Varian FT80A spectrometer, operating at 79.542 and 32.203 MHz respectively. The IR spectra were recorded on a Perkin Elmer 983G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}, and CaF_2 cells of 0.5 mm width for solution samples in the range 2500–1500 cm^{-1}.

X-Ray Measurements and Structure Determination.—The crystal and refinement data for complex **3** are summarized in Table 3. A prismatic white crystal, grown from CH_2Cl_2–Et_2O, of dimensions 0.16 × 0.18 × 0.30 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 diffractometer with graphite-monochromated Mo-Kα radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and φ over a range of 120°, with $8 \leqslant \theta \leqslant 9°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leqslant \theta \leqslant 14°$ were considered. Integrated intensities for *hkl* reflections in the interval h = 0–29, k = 0–17, l = 0–15 were measured, and two standard reflections were measured every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption, by following the method of North *et al.*;[16] no correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with full matrix least squares; anisotropic thermal parameters were assigned to all the non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d_{C-H} = 0.98 Å and U = 0.06 Å^2), except for the amidino N–H hydrogen which was located in the final difference map and refined isotropically. The function minimized was $\Sigma w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. Final residuals were R = 0.0289 and R' = 0.0267. The largest peak in the final difference map (0.7 e Å^{-3}) was located near the platinum atom positions. Data processing and computation were carried out by using the SHELX 76 program package[17] with the atomic scattering factors taken from ref. 18 and for drawings ORTEP.[19] The atomic coordinates are reported in Table 4.

The refinement of a model with inverted coordinates gave R^* = 0.0373, R'^* = 0.0355. The application of Hamilton's R factor ratio test[20] gives R'^*/R' = 1.330. A comparison with the theoretical value for acceptance of the second configuration at the 99.5% probability level ($R_{1,2941,0.005}$ = 1.0013) indicates that the configuration here reported is correct.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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