Mechanistic and Stereochemical Investigation of Imino Ethers Formed by Alcoholysis of Coordinated Nitriles: X-ray Crystal Structures of *cis*- and *trans*-Bis(1-imino-1-methoxyethane)dichloroplatinum(II)

Renzo Cini,[†] Paola A. Caputo,[‡] Francesco P. Intini,[‡] and Giovanni Natile*,[‡]

Dipartimento di Chimica, Università di Siena, Pian dei Mantellini 44, 53100 Siena, Italy, and Dipartimento Farmaco-Chimico, Università di Bari, via E. Orabona 4, 70125 Bari, Italy

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Addition of alcohols (HOR′) to the coordinated nitriles (NCR) in the platinum complexes $[PtCl_3(NCR)]^-$ and *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = Me, Et, Ph, Bu^t) takes place readily under basic conditions. The *Z* isomer, corresponding to a trans addition of the alcohol to the C≡N triple bond, is the first reaction product, subsequently undergoing isomerization to the *E* form. An increase of the steric bulk of the R group stabilizes the *Z* isomer with respect to the *E* isomer; in contrast, an increase of the steric bulk of the R′ group stabilizes the *E* over the *Z* isomer. The structures of *trans*- and *cis*-$[PtCl_2\{E\text{-}HN{=}C(OMe)Me\}_2]$ (**5*EE*** and **9*EE***, respectively) have been solved by single-crystal X-ray diffraction. **5*EE*** crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 8.491(6)$ Å, $b = 8.603(2)$ Å, $c = 8.973(2)$ Å, $\alpha = 75.56(1)°$, $\beta = 67.52(2)°$, $\gamma = 85.62(2)°$, $V = 586.4(2)$ Å^3, and $Z = 2$. **9*EE*** crystallizes in the space group *C*2/*c* (No. 15) with $a = 15.854(3)$ Å, $b = 8.123(2)$ Å, $c = 9.471(2)$ Å, $\beta = 93.72(3)°$, $V = 1217.1(4)$ Å^3, and $Z = 4$. In each complex, the Pt atom is linked to two Cl^- anions and two imino ether N atoms, the coordination geometry is strictly planar, and the Pt−Cl and Pt−N bond distances have normal values. An unexpected feature resulting from the crystallographic data was the "quasi-planarity" of the imino ether moiety and electron charge delocalization over the $N\overset{\cdots}{-}C\overset{\cdots}{-}O$ moiety. As a consequence, all the groups attached to the $N\overset{\cdots}{-}C\overset{\cdots}{-}O$ skeleton share the same plane, causing considerable steric strain, as indicated by deviations (5° or even more) of some bond angles from canonical values.

Introduction

Over the past 20 years considerable attention has been focused on the reactions of nucleophilic attack upon coordinated nitriles in metal complexes.[1] These include reactions with alcohols, amines, and carbanions to form imino ethers,[2–7] amidines,[8–13] and imines;[14,15] and base-catalyzed hydrolysis to amidates[13,16–19] and amides.[20]

Platinum nitriles (*cis*- and *trans*-$[PtCl_2(NCR)_2]$, R = Me, Ph) were reported to react with methanol, under basic conditions, to give imino ether derivatives, $[PtCl_2\{HN{=}C(OMe)R\}_2]$, with different configurations at the imino ether ligands (*E* and *Z* for the platinum and alkoxide groups trans and cis with respect to the C=N double bond, respectively).[21,22] The structures were assigned on the basis of NMR data, but conclusions about the kinetic and thermodynamic preference for either isomer were not given (*E* and *Z* configurations correspond to cis- and trans-addition of the alcohol to the C≡N triple bond, respectively).

[†] Università di Siena.

[‡] Università di Bari.

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The X-ray structure of a platinum–imino ether complex, [PtCl$_2${HN=C(OPr^i)Me}$_2$], was also reported.[23] The *E* configuration found in the solid state was assumed to be the preferred one and to stem from the cis-addition of the alcohol to the triple bond. An interesting feature of the crystal structure was the face-to-face association of two molecular units in a dimer with four intramolecular NH$\cdots$Cl hydrogen bonds and a relatively short Pt–Pt distance [3.327(1) Å]. Such an association of platinum units in a dimer has been found in a few other cases in which two platinum ligands are capable of donating a H-bond and the other two ligands are able to accept a H-bond (H-donor ligands include ammine,[24] amines,[25] amides,[20b] and imino ethers[23]). Whether the solid state dimeric structure of these compounds has any effect on their solution chemistry (e.g. the possibility of giving Pt^{III}–Pt^{III} dinuclear compounds) is a subject of debate.[20a,23]

New interest in the chemistry of platinum–imino ether compounds arises from the discovery that some of these compounds have antitumor activity.[21b] Moreover, substitution of imino ethers for ammines has the effect of reversing the biological activity of cis and trans isomers. The complex with trans geometry shows the greatest *in vitro* cytotoxicity against P388 leukemia cells, equivalent to or even greater than that of *cis*-DDP itself, and displays a relevant antitumor activity in P388- and P388/DDP-bearing mice. In this article we report a thorough investigation of the synthesis, characterization, and stereochemistry of the imino ether complexes.

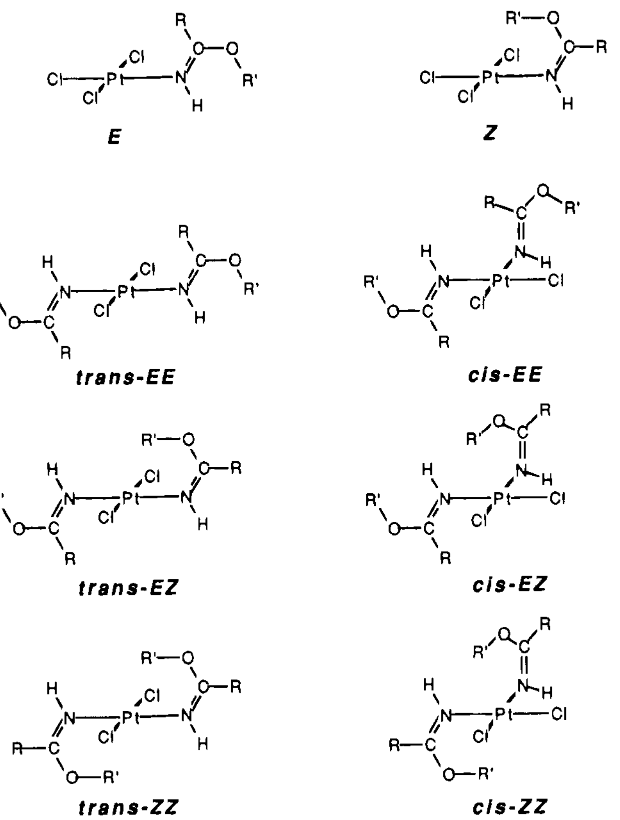
Results and Discussion

General Description of the Reactions and Products. The addition of methanol to nitriles coordinated to platinum takes place readily in the presence of a base. The imino ether ligand formed can have either *E* or *Z* configuration at the C=N double bond; complexes with one imino ether ligand can have two isomeric forms (*E* and *Z*), and complexes with two imino ether ligands, three isomeric forms (*EE*, *EZ*, and *ZZ*) (Chart 1). The coordination about the metal center (cis or trans) is preserved during the addition of the alcohol to the nitrile. The most compelling evidence against isomerization stems from the absence of common reaction products from either the cis or the trans isomer of [PtCl$_2$(NCR)$_2$]. The configuration of the imino ether ligand can be assigned on the basis of the NMR data. A downfield shift is expected for the protons which come close to platinum:[26] the alkoxide protons (R′) in the *Z* configuration and the nitrile protons (R) in the *E* configuration. A complete list of isolated compounds and ^{1}H NMR data are given in Table 1.

The configuration of the imino ether ligand is stable under normal conditions, and the complex isomers can be separated by fractional crystallization and chromatography. However isomerization takes place through nucleophilic attack of an alkoxide anion (alcohol + base) upon the carbon atom of the imino residue, leading to the formation of an amido ketal which afterwards re-eliminates the alkoxide, restoring the imino ether ligand (Scheme 1).[21]

The reaction pathway for the formation of the imino ether complexes was monitored. Experiments were performed in which a base (KOH) was added to a solution of the nitrile complexes in CD$_3$OD and the appearance of the resonance patterns of the imino ether species monitored from time to time (Figure 1). Compounds **1**–**4** were used for this purpose since they are more soluble in this solvent than neutral species **5**–**12**. In all cases examined, the first species formed had the *Z* configuration. Subsequently *Z* → *E* isomerization took place. The transformation was complete for R = Me and Et; but for R = Ph an equilibrium was reached with the two isomers present in comparable concentrations. For R = Bu^t the *Z* isomer was stable and did not isomerize.

Chart 1


E *Z*
trans-EE *cis-EE*
trans-EZ *cis-EZ*
trans-ZZ *cis-ZZ*

These experiments demonstrated the following: (i) The addition of alcohol (HOR′) to the coordinated nitrile (NCR) leads to the formation of the *Z* isomer corresponding to a trans-addition of the alcohol (the alkoxide and the hydrogen add to the triple bond from opposite sides). (ii) For a given alkoxide (OMe) the stability of the *E* isomer as a function of the nitrile R group decreases in the order Me > Et > Ph > Bu^t, indicating that an increase of the steric bulk of the R group destabilizes the *E* isomer (in which the R group is cis to the platinum) more than the *Z* isomer (in which the R group is trans to platinum). This result adds confidence to our stereochemical assignments based on chemical shifts. Related NMR experiments demonstrated that the lack of isomerization in the case of Bu^t (compound **4**) was due to a thermodynamic preference for the *Z* isomer and not to a kinetic impediment. Substitution of CD$_3$O for CH$_3$O took place readily in deuteriomethanol under basic conditions, indicating that the reaction intermediate (or transition state), which is common to the methoxide exchange and to isomerization, was readily accessible. (iii) Interestingly, in deuteriomethanol, compound **1** exchanges the protons of the R group with deuterium at a rate which is comparable with those of isomerization (*Z* → *E*) and methoxide exchange. Such an exchange has also been observed for H8 of guanine and adenine platinated at N7 and appears to be a common feature for C–H protons which come close to platinum.[27]

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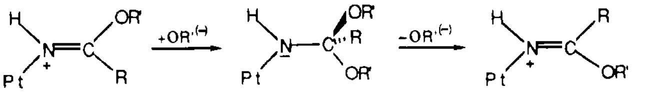
Table 1. Proton Chemical Shifts [δ, Downfield from SiMe$_4$ or TSP] of the Complexes

compd	formula	solvent	NH	OCH$_3$	CH$_3$	C*H*$_2$CH$_3$	CH$_2$C*H*$_3$	C(CH$_3$)$_3$	C$_6$H$_5$
1*E*	K[PtCl$_3${*E*-HN=C(OMe)Me}]	*c*		3.76	2.61				
1*Z*	K[PtCl$_3${*Z*-HN=C(OMe)Me}]	*c*		4.77	2.20				
2*E*	K[PtCl$_3${*E*-HN=C(OMe)Et}]	*c*		3.77		3.15	1.29		
2*Z*	K[PtCl$_3${*Z*-HN=C(OMe)Et}]	*c*		5.06		2.42	1.08		
3*Z*	K[PtCl$_3${*Z*-HN=C(OMe)Ph}]	*c*		5.35					7.70 (o), 7.44 (m), 7.51 (p)
4*Z*	K[PtCl$_3${*Z*-HN=C(OMe)Bu^t}]	*c*	7.40	5.24				1.16	
5*EE*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Me}$_2$]	*a*		3.82	2.61				
		b	7.40	3.77	2.64				
5*EZ*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Me}{*Z*-HN=C(OMe)Me}]	*a*		4.18	2.57				
				3.81	2.36				
		b	8.11	4.93	2.58				
			7.35	3.76	2.21				
5*ZZ*	*trans*-[PtCl$_2${*Z*-HN=C(OMe)Me}$_2$]^d								
6*EE*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Et}$_2$]	*b*	7.73	3.78		3.13	1.35		
6*EZ*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Et}{*Z*-HN=C(OMe)Et}]	*b*	8.35	5.05		3.08	1.31		
			7.73	3.78		2.43	1.11		
6*ZZ*	*trans*-[PtCl$_2${*Z*-HN=C(OMe)Et}$_2$]	*b*	7.67	4.92		2.43	1.12		
7*EE*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Ph}$_2$]	*b*	8.36	4.06					8.56 (o), 7.35−7.65 (m, p)
7*EZ*	*trans*-[PtCl$_2${*E*-HN=C(OMe)Ph}{*Z*-HN=C(OMe)Ph}]	*b*	9.11	5.00					8.44 (o), 7.30−7.65 (m, p)
			8.54	4.06					7.84 (o)
7*ZZ*	*trans*-[PtCl$_2${*Z*-HN=C(OMe)Ph}$_2$]	*b*	8.10	5.30					7.75 (o), 7.40−7.60 (m, p)
8*ZZ*	*trans*-[PtCl$_2${*Z*-HN=C(OMe)Bu^t}$_2$]	*b*	6.66	5.08				1.17	
9*EE*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Me}$_2$]	*a*		3.82	2.57				
		b	7.97	3.82	2.65				
9*EZ*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Me}{*Z*-HN=C(OMe)Me}]	*a*		4.04	2.55				
				3.80	2.34				
		b	8.90	4.38	2.66				
			7.81	3.80	2.27				
9*ZZ*	*cis*-[PtCl$_2${*Z*-HN=C(OMe)Me}$_2$]	*a*		4.10	2.32				
10*EE*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Et}$_2$]	*b*	7.94	3.83		3.19	1.23		
10*EZ*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Et}{*Z*-HN=C(OMe)Et}]	*b*	8.73	4.66		3.20	1.23		
			7.83	3.83		2.48	1.13		
10*ZZ*	*cis*-[PtCl$_2${*Z*-HN=C(OMe)Et}$_2$]	*b*	8.50	4.63		2.47	1.15		
11*EE*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Ph}$_2$]	*b*	7.95	3.78					8.34 (o), 7.30−7.50 (m, p)
11*EZ*	*cis*-[PtCl$_2${*E*-HN=C(OMe)Ph}{*Z*-HN=C(OMe)Ph}]	*b*	8.94	4.34					8.45 (o), 7.20−7.65 (m, p)
			8.72	4.16					7.58 (o)
11*ZZ*	*cis*-[PtCl$_2${*Z*-HN=C(OMe)Ph}$_2$]^e	*b*		4.78					
12*ZZ*	*cis*-[PtCl$_2${*Z*-HN=C(OMe)Bu^t}$_2$]	*b*	7.86	5.06				1.16	

[a] D$_2$O. [b] CDCl$_3$. [c] CD$_3$OD. [d] Insoluble. [e] This isomer was not isolated; the spectrum of a solution in which it was in equilibrium (*ca.* 5%) with **11***EE* and **11***EZ* allowed the accurate determination of only the most intense methyl resonance.

Scheme 1



The information gained on the time course of the alcoholysis reaction leading to the *Z* isomer and subsequent isomerization to the *E* isomer was used for the preparation of the pure isomeric species. In general, the kinetically favored *Z* isomer could be conveniently prepared with conditions and procedures in which this isomer precipitates and is collected soon after formation: a high concentration of the reactants, a low temperature (0 °C), and product collection after a short time. In contrast, lower concentrations, a higher temperature (20 °C), and product collection after a longer time allowed preparation of the thermodynamically more preferred *E* isomer.

In the case of ionic compounds **1**−**4**, the preparation of the pure isomers was complicated by their instability under chromatographic conditions. In the case of **1** and **3**, the pure *Z* isomers precipitate as yellow solids from concentrated solutions of the reactants. The subsequent transformation of the *Z* into the *E* isomer was complete for **1** but not for **3**, so preventing in the latter case the isolation of the pure *E* form. In the case of **2** and **4**, the *Z* isomers were soluble in methanol, but while **2***Z* undergoes fast isomerization to **2***E* and was not isolated in a pure form, **4***Z* proved to be a stable isomer.

In the case of neutral compounds **5**−**12**, the preparation of the pure isomers was facilitated by chromatography on silica gel. In the case of trans complexes, the three isomers (*ZZ*, *EZ*, and *EE*) were isolated for **5**, **6**, and **7** while for **8** there was no isomerization to the *E* form. In the case of cis complexes, the three isomers *ZZ*, *EZ*, and *EE* were isolated only for **9** and **10**. For **11**, the fast isomerization prevented the isolation of the first formed *ZZ* isomer, while for **12** no isomerization to the *E* form took place.

Spectroscopy. N−H stretching bands in the range 3220−3340 cm^{-1} and strong bands due to C=N stretching in the range 1630−1660 cm^{-1} are clearly indicative of the presence of the NH=C(OR′)R moiety. The N−H stretching frequencies are slightly higher for the mono derivatives (**1**−**4**) than for the bis(imino ether) derivatives (**5**−**12**).

^{1}H NMR spectral data for these complexes are collected in Table 1. All samples exhibit N−H signals as broad singlets in the range 7.4−9.0 ppm, methoxide group signals in the range 3.7−5.1 ppm, and signals corresponding to the nitrile R group in the expected region. The *EE* and *ZZ* isomers, having equal ligand configurations, show only one set of resonances, the *EZ* isomer, with different ligand configurations, two sets of resonances. A downfield shift is experienced by the protons which come close to platinum: the alkoxide protons (R′) in the *Z* configuration and the nitrile protons (R) in the *E* configuration.

It is possible to appreciate the differences between the *E* and *Z* configurations within the same molecule in the case of *EZ* complexes.

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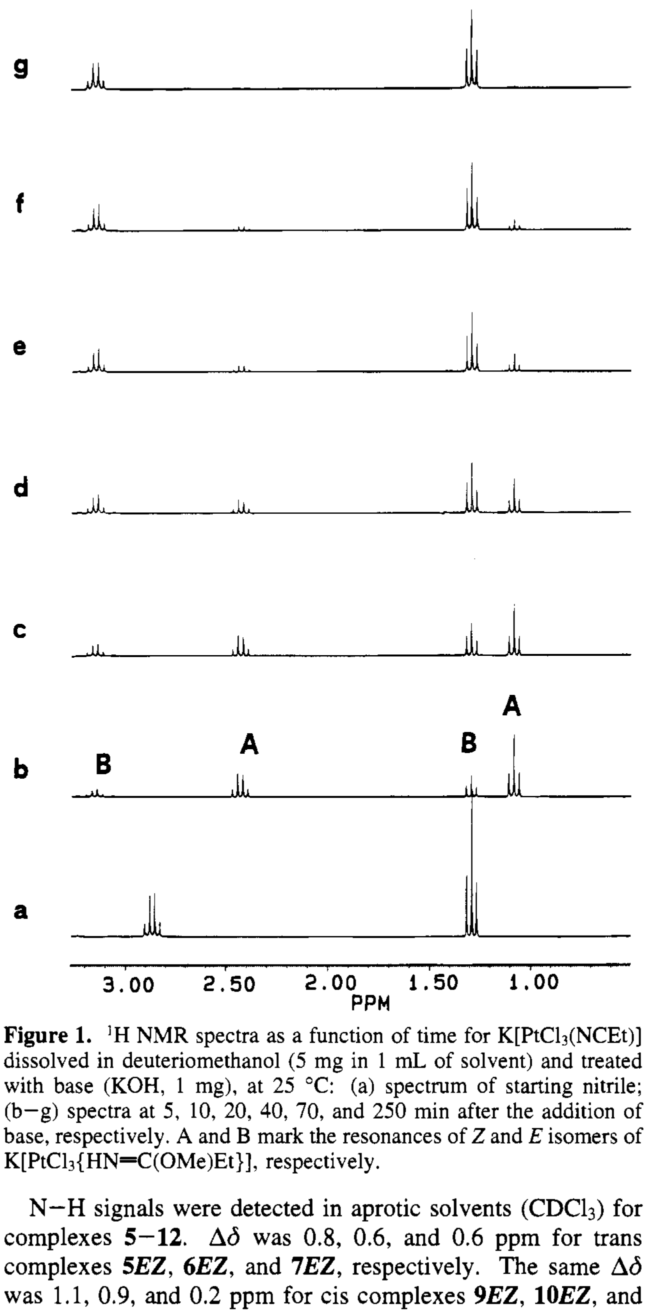

Figure 1. ^{1}H NMR spectra as a function of time for K[PtCl$_3$(NCEt)] dissolved in deuteriomethanol (5 mg in 1 mL of solvent) and treated with base (KOH, 1 mg), at 25 °C: (a) spectrum of starting nitrile; (b–g) spectra at 5, 10, 20, 40, 70, and 250 min after the addition of base, respectively. A and B mark the resonances of *Z* and *E* isomers of K[PtCl$_3${HN=C(OMe)Et}], respectively.

N–H signals were detected in aprotic solvents (CDCl$_3$) for complexes **5**–**12**. $\Delta\delta$ was 0.8, 0.6, and 0.6 ppm for trans complexes **5*EZ***, **6*EZ***, and **7*EZ***, respectively. The same $\Delta\delta$ was 1.1, 0.9, and 0.2 ppm for cis complexes **9*EZ***, **10*EZ***, and **11*EZ***, respectively. The chemical shift separation of only 0.2 ppm observed for **11*EZ*** is probably the result of an anisotropic effect of the Ph groups of mutually cis ligands which masks the effect of different configurations of the ligands. In all cases examined, the chemical shift value at higher field belongs to the NH of the ligand assigned to the *E* configuration (NH cis to the methoxide group).

Also the chemical shifts of the methoxide groups fall in a wide range of values. The chemical shift separations between *E* and *Z* configurations ($\Delta\delta$) are 1.0, 1.3, and 1.4 ppm for mono(imino ether) derivatives (**1**, **2**, and **3**, respectively; CD$_3$OD solvent); 1.2, 1.3, and 1.0 ppm for trans imino ether derivatives (**5*EZ***, **6*EZ***, and **7*EZ***, respectively; CDCl$_3$ solvent); and 0.6, 0.8, and 0.2 ppm for cis imino ether complexes (**9*EZ***, **10*EZ***, and **11*EZ***, respectively; CDCl$_3$ solvent). The signal to lower field belongs always to the *Z* ligand (methoxide group cis to platinum).

Finally the ^{1}H NMR signals of R also have shifts strongly dependent upon the configuration of the ligand. For methyl, ethyl CH$_2$, and phenyl ortho protons, the $\Delta\delta$ values are 0.4, 0.7, and 1.2 ppm for compounds **1**, **2**, and **3**, respectively; 0.4, 0.65, and 0.6 ppm for compounds **5*EZ***, **6*EZ***, and **7*EZ***, respectively; and, finally, 0.4, 0.7, and 0.9 ppm for compounds **9*EZ***, **10*EZ***, and **11*EZ***, respectively. The signal at lower field belongs to the *E* ligand in which the R group approaches cis to platinum.

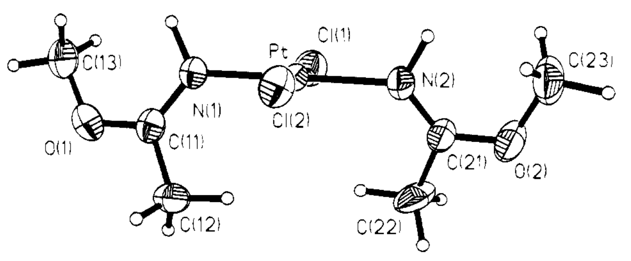

Figure 2. ORTEP drawing of *trans*-[PtCl$_2${*E*-HN=C(OMe)Me}$_2$] (**5*EE***) showing also the labeling scheme. Ellipsoids enclose 30% probability. H atoms were set in calculated positions, and their thermal ellipsoids have an arbitrary scale.

X-ray Crystallography of 5*EE*. The Pt atom of **5*EE*** is linked to two trans Cl$^-$ anions and to two imino ether N atoms (Figure 2 and Table 2). The coordination square is strictly planar (deviations from the plane defined by the donor atoms: Cl(1), −0.002(3); Cl(2), −0.002(3); N(1), 0.016(8); N(2), 0.020(9); Pt, 0.0080(5) Å). The Pt–Cl (average 2.300(2) Å) and Pt–N (average 1.999(7) Å) bond distances as well as the Cl–Pt–Cl (179.4(1)°), N–Pt–N (179.1(2)°), and N–Pt–Cl (87.6(2)–92.8(2)°) angles have normal values.[28]

The two imino ether molecules have the *E* configuration and similar geometrical parameters. The N–C bond distances (average 1.300(11) Å) are in agreement with a double-bond character and an sp^2 hybridization of the N atom.[23,29] The C(sp^2)–O and C(sp^3)–O bond distances average 1.310(11) and 1.433(14) Å, respectively. The difference (more than 0.1 Å) is far too large to be explained only on the basis of a different hybridization of the C atoms involved and points to a partial double-bond character of C(1)–O. It is to be noted that, in the case of strictly related carbon–carbon bonds, the sp^2 hybridization of one carbon atom does not shorten the C–C single-bond distance by more than 0.03 Å [average values: C(sp^3)–C(sp^3), 1.530 Å; C(sp^2)–C(sp^3), 1.507 Å];[30] in contrast, the change of length between single and double bonds is of the order of 0.20 Å [average C(sp^2)=C(sp^2), 1.316 Å].[30] The latter value (0.20 Å) is similar to the change of length between single and double bonds in the case of carbon–oxygen interactions [typical values: C(sp^3)–OR, 1.43; C(sp^2)=O, 1.22 Å].[30] The distance of 1.310(11) Å found for C(1)–O falls halfway between those of single and double carbon–oxygen bonds and is similar to the values found in most C(sp^2)–OR moieties. This could indicate that whenever an oxygen atom is bound to a carbon atom engaged in a double bond, a lone pair of the oxygen participates in the π system.

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Table 2. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for ***5EE*** and ***9EE***

5EE				***9EE***	
		Bond Distances			
Cl(1)−Pt	2.298(2)	Cl(2)−Pt	2.301(2)	Cl(1)−Pt	2.303(3)
N(1)−Pt	1.989(7)	N(2)−Pt	2.009(8)	N−Pt	2.010(8)
C(11)−O(1)	1.315(11)	C(21)−O(2)	1.306(11)	C(1)−O	1.327(12)
C(13)−O(1)	1.411(14)	C(23)−O(2)	1.455(14)	C(3)−O	1.446(11)
C(11)−N(1)	1.307(11)	C(21)−N(2)	1.294(12)	C(1)−N	1.273(12)
C(12)−C(11)	1.502(12)	C(22)−C(21)	1.519(14)	C(2)−C(1)	1.522(12)
		Bond Angles			
Cl(2)−Pt−Cl(1)	179.4(1)			Cl(1)−Pt−Cl(1)	91.9(2)
N(1)−Pt−Cl(1)	87.8(2)	N(2)−Pt−Cl(1)	92.8(2)	N−Pt−Cl(1)	89.4(3)
N(1)−Pt−Cl(2)	91.7(2)	N(2)−Pt−Cl(2)	87.6(2)		
N(2)−Pt−N(1)	179.1(2)			N−Pt−N	89.4(5)
C(13)−O(1)−C(11)	119.4(8)	C(23)−O(2)−C(21)	117.9(8)	C(3)−O−C(1)	118.5(7)
HN(1)−N(1)−Pt	117.1(2)	HN(2)−N(2)−Pt	116.8(2)	HN−N−Pt	117.4(2)
C(11)−N(1)−Pt	125.6(6)	C(21)−N(2)−Pt	126.7(7)	C(1)−N−Pt	126.4(7)
C(11)−N(1)−HN(1)	117.3(5)	C(21)−N(2)−HN(2)	116.5(5)	C(1)−N−HN(1)	116.2(6)
N(1)−C(11)−O(1)	124.4(8)	N(2)−C(21)−O(2)	125.1(9)	N−C(1)−O	125.2(8)
C(12)−C(11)−O(1)	113.4(8)	C(22)−C(21)−O(2)	111.1(8)	C(2)−C(1)−O	111.3(8)
C(12)−C(11)−N(1)	122.2(8)	C(22)−C(21)−N(2)	123.7(8)	C(2)−C(1)−N	123.3(9)

Further evidence in favor of a partial double-bond character of C(1)−O comes from the value of the C−O−C angle of 118.6(8)°, which is greater than the canonical value of 109.5° expected for sp^3 but close to the value of 120° expected for sp^2. Therefore the structural data are in accord with a π bond delocalized over the N−C−O moiety.

Delocalization explains the "quasi-planar" arrangement of the imino ether ligand with C−O−C−C and C−O−C−N torsion angles of 178(1) and −2(1)°, respectively. It is to be noted that such a planar arrangement is attained notwithstanding the relevant steric interaction between the O−Me and the imino nitrogen as shown by the very close CH••HN contacts of 2.11(10) Å and the increase of the N−C−O angle to 124.7(8)° (a value which is significantly greater than the 120° expected for a trigonal carbon).

The Pt−N−C [average value 126.1(6)°] and N−C−C angles [average value 123.0(8)°] are significantly greater than the 120° value expected for sp^2-hybridized N and C atoms. Both values indicate another steric interaction which takes place between the R group and the platinum moiety which are cis to one another with respect to the C=N double bond.

The increase of the N−C−C and N−C−O angles and consequent compression of the C−C−O angle [112.2(8)°] lower the intra-ligand strains (Pt••R and N••R′).

Delocalization in the ligand π system results in the ionic resonance form

$$\mathrm{H{-}\underset{\cdot\cdot}{N}^{-}{-}C(Me){=}\underset{\cdot\cdot}{O}^{-}{-}Me}$$

which could be stabilized by coordination to platinum. However there is crystallographic evidence indicating that π delocalization and consequent planarity of the imino ether moiety apply also to the free ligand.[31]

X-ray Crystallography of *9EE*. The square planar coordination geometry around the Pt atom consists of two cis Cl atoms and two N atoms from the imino ether molecules (Figure 3, Table 2). The metal atom sits on a 2-fold crystallographic axis which bisects the Cl−Pt−Cl and N−Pt−N bond angles; as a consequence, the five atoms of the coordination sphere are strictly coplanar. The Pt−Cl [2.303(3) Å] and Pt−N [2.010(8) Å] bond distances and the Cl−Pt−Cl [91.9(2)°], Cl−Pt−N [89.4(3)°], and N−Pt−N [89.4(5)°] angles have normal values for a Pt^{II} complex.[28]

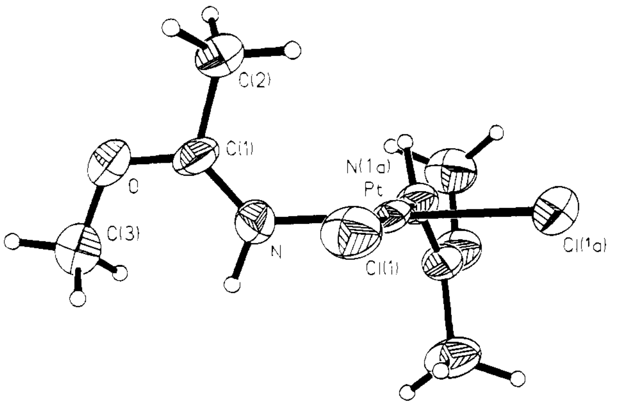

Figure 3. ORTEP drawing of *cis*-[PtCl$_2${*E*-HN=C(OMe)Me}$_2$] (***9EE***) showing also the labeling scheme. Ellipsoids enclose 30% probability. H atoms were set in calculated positions, and their thermal ellipsoids have an arbitrary scale.

The C(1)−N [1.273(12) Å] bond length is in agreement with a double-bond character and an sp^2 hybridization of N and C(1). On the other hand, the C(1)−O [1.327(12) Å] bond length is shorter than expected, indicating a partial double-bond character. In accord with a double-bond delocalization over the N, C(1), and O atoms is the quasi-planar arrangement of the imino ether ligand with C(2)−C(1)−O−C(3) and N−C(1)−O−C(3) torsion angles of −179(1) and 5(1)°, respectively. The C(1)−C(2) [1.522(12) Å] and C(3)−O [1.446(11) Å] distances are those expected for a single bond.

The increase of Pt−N−C(1) [126.4(7)°] and N−C(1)−C(2) angles [123.3(9)°] above 120° is indicative of a steric interaction between the C−Me and the platinum moieties. Also the increased value of the N−C(1)−O angle [125.2(8)°] is indicative of a steric interaction between the O−Me and N−H moieties. The compression of the C(2)−C(1)−O angle [111.3(8)°] lowers the intra-ligand strains.

The strict analogy between the stereochemistry of the imino ether ligands in compounds ***5EE*** and ***9EE*** indicates that intra-ligand interactions play a major role while inter-ligand and inter-molecular interactions do not have significant influence.

The relative orientations of the imino ether ligands are head to head (HH) in compound ***5EE*** and head to tail (HT) in compound ***9EE***. The HT arrangement of the two imino ether

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ligands in compound **9*EE*** can have either Λ or Δ conformation.[32] In the solid state, both conformations are found in a 1:1 ratio.

Crystal Packing. As far as the association of molecular units *via* hydrogen bonds is concerned, the results obtained for **5*EE*** and **9*EE*** are rather different from those reported for [$PtCl_2${HN=C(OPr^i)Me}$_2$].[23] In **5*EE*** and **9*EE***, the complexes are formed in stacks with parallel coordination planes and an eclipsed conformation. In **5*EE***, each molecular unit is linked by hydrogen bonds to two other molecules of neighboring stacks, thus forming polymeric chains intersecting the stacks (Figure 4, supplementary material). The N−H··Cl hydrogen bonds involve symmetry-related (inversion) molecules [Cl(1)··H−N(1)($-x$, $-y$, $-z + 1$), d(Cl··N) = 3.472(8) Å, $\hat{a}$ = 164.0(7)°; C(12)··H−N2($-x + 1$, $-y$, $-z + 1$), d(Cl··N) = 3.427(8) Å, $\hat{a}$ = 160.2(8)°]. The shortest Pt··Pt distance is among atoms of the same stack, and the average value is 5.377(1) Å. In compound **9*EE***, each molecular unit forms two hydrogen bonds with the molecule standing above and two hydrogen bonds with the molecule standing below within the same stack (Figure 5, supplementary material) [N−H··Cl($-x$, $-y$, $-z$), d(N··Cl) = 3.397(10) Å, $\hat{a}$ = 153.4(8)°]; the result is polymeric chains of complexes coincident with stacks having Pt··Pt distances of 4.756(1) Å (significantly shorter than that observed in **5*EE***). The polymers are held together in the crystal only by hydrophobic interactions. Finally, in the already reported complex [$PtCl_2${HN=C(OPr^i)Me}$_2$],[23] couples of molecules interact face to face, forming an eclipsed dimer with the two NH groups of one molecule interacting with the chloride ligands of the second molecule and vice versa.

Conclusions

The addition of alcohols (HOR′) to coordinated nitriles (NCR) takes place readily under basic conditions initially forming the *Z* isomer, corresponding to a trans-addition of the alcohol to the C≡N triple bond. Subsequently, under the same experimental conditions, the *Z* isomer isomerizes to the *E* form. The large steric bulk of the R group stabilizes the *Z* isomer with respect to the *E* isomer, and for compounds **4**, **8**, and **12**, for which R = Bu^t, only the *Z* form (R trans to platinum with respect to the C=N double bond) was isolated. Conversely, a large steric bulk of the R′ group should stabilize the *E* over the *Z* isomer and alcohols with bulky R′ groups could give cis-addition to nitriles forming the *E* isomer directly. Addition of 2-propanol to coordinated acetonitrile showed that the *Z* isomer is always formed first. Subsequently, the *Z* isomer isomerizes to the *E* isomer.[33]

An unexpected feature of the crystallographic data was the "quasi-planarity" of the imino ether moiety arising from electron delocalization over the N⌐C⌐O moiety. As a consequence, all the groups bound to the N⌐C⌐O atoms share the same plane causing considerable steric strain. In both **5*EE*** and **9*EE***, R and R′ were small Me groups; nevertheless, severe intra-ligand strains were indicated by some bond angle increases of 5° or more above their canonical values. It is also worth noting that, because of the planar arrangement of the imino ether ligand, the NH is made sterically inaccessible by the alkoxide group in the *E* isomer.

In spite of the different crystallographic arrangements of **5*EE***, **9*EE***, and [$PtCl_2${HN=C(OPr^i)Me}$_2$] (the last compound being the only one to have couples of platinum units placed face to face and forming four interfacial hydrogen bonds), the three compounds react with chlorine to give dimeric platinum(III) species.[33] Therefore it appears that a dimeric structure of the type observed in [$PtCl_2${HN=C(OPr^i)Me}$_2$] and in analogous amide species[20b] is not a prerequisite for the oxidation of a platinum(II) compound to platinum(III) dimers.

Work in progress indicates that the planarity of the imino ether ligand and the steric effect of the alkoxide group on the NH proton in the *E* isomer and on the metal center in the *Z* isomer are crucial to the DNA sequence specificity and biological activity of the complexes described here.[21b]

Experimental Section

Starting Materials. Commercial reagent grade chemicals were used without further purification. The complexes K[$PtCl_3$(NCR)] (R: Me, **1**; Ph, **3**; Bu^t, **4**),[20b] *trans*- and *cis*-[$PtCl_2$(NCMe)$_2$] (**5** and **9**, respectively),[34] *trans*- and *cis*-[$PtCl_2$(NCPh)$_2$] (**7** and **11**, respectively),[21a] and *trans*- and *cis*-[$PtCl_2$(NCBu^t)$_2$] (**8** and **12**, respectively)[20b] were prepared by the reported procedures.

K[$PtCl_3$(NCEt)], 2. Potassium tetrachloroplatinate(II) (0.40 g, 1 mmol) dissolved in water (10 mL) and the nitrile (2 mmol) were stirred at 70 °C for 10−20 min until appearance of a yellow precipitate of the neutral disubstituted product. The reaction mixture was extracted with CH_2Cl_2 to remove the neutral species, the water solvent was evaporated under reduced pressure, and the solid residue was extracted with methanol. The methanol solution, by evaporation of the solvent, afforded a yellow solid of K[$PtCl_3$(NCEt)] (yield 55%). Anal. Calcd for $C_3H_5Cl_3KNPt$ (**2**): C, 9.1; H, 1.3; N, 3.5. Found: C, 9.0; H, 1.3; N, 3.3.

***trans*-[$PtCl_2$(NCEt)$_2$], 6.** Potassium tetrachloroplatinate(II) (0.5 g, 1.2 mmol) dissolved in water (10 mL) and propionitrile (0.69 g, 12.5 mmol) were stirred at 75 °C for 3 h. The aqueous phase turned from red to pale yellow, and the yellow precipitate which formed was extracted with dichloromethane. The organic solution, dried over anhydrous Na_2SO_4, after removal of the solvent afforded a yellow solid of *cis*- and *trans*-[$PtCl_2$(NCEt)$_2$]. The separation of the two isomers was accomplished by chromatography on an open column of silica gel using $CHCl_3$/acetone (9:1 v/v) as eluant. The first eluted fraction contained *trans*-[$PtCl_2$(NCEt)$_2$] (yield 68%). The second eluted fraction contained *cis*-[$PtCl_2$(NCEt)$_2$] (yield 8%). Anal. Calcd for $C_6H_{10}Cl_2N_2Pt$ (**6**): C, 19.2; H, 2.7; N, 7.4. Found: C, 19.3; H, 2.7; N, 7.4.

***cis*-[$PtCl_2$(NCEt)$_2$], 10.** This isomer could be prepared in a greater yield by the following procedure: Potassium tetrachloroplatinate(II) (0.5 g, 1.2 mmol) dissolved in water (4 mL) and propionitrile (0.3 g, 5.6 mmol) were stirred at room temperature for 24 h. The crystalline precipitate obtained from the solution was isolated by filtration of the mother liquor, washed with $CHCl_3$, and dried. Yield: 55%. Anal. Found: C, 19.4; H, 2.7; N, 7.4.

Preparation of Complexes. K[$PtCl_3${HN=C(OMe)Me}], isomers 1*E* and 1*Z*. K[$PtCl_3$(NCMe)] (0.46 g, 1.2 mmol) suspended in 2 mL of methanol and cooled to 0 °C was treated with KOH (0.1 g, 1.8 mmol) and kept under stirring at 0 °C for 1 h. The yellow solid was isolated by filtration of the mother liquor, washed with ethanol, and dried (yield 70%). The compound proved to be the *Z* isomer (**1*Z***). The *E* isomer (**1*E***) was prepared by a similar procedure but using more dilute conditions (0.3 mmol of **1** in 4 mL of methanol) and longer reaction time (16 h of stirring at 0 °C). The reaction solution was filtered to remove a trace amount of **1*Z***, and the filtrate was treated with 1 M HCl until neutral pH. The resulting solution was filtered to remove KCl, the solvent was evaporated under reduced pressure, and the oily residue was triturated with diethyl ether. The yellow solid was washed with ethanol and dried (yield 80%). Anal. Calcd for $C_3H_7Cl_3KNOPt$: C, 8.7; H, 1.7; N, 3.4. Found (**1*Z***): C, 8.2; H, 1.8; N, 3.2. Found (**1*E***): C, 8.5; H, 1.8; N, 3.3.

K[$PtCl_3${*E*-HN=C(OMe)Et}], 2*E*. The greater solubility of the *Z* isomer and the fast isomerization to the *E* form did not allow the isolation of **2*Z***. K[$PtCl_3$(NCEt)] (1.3 mmol) suspended in 2 mL of methanol and cooled to 0 °C was treated with KOH (0.1 g, 1.8 mmol) and kept under stirring at 0 °C for 1 h. The yellow precipitate was isolated by filtration of the mother liquor, washed with ethanol, and

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dried (yield 70%). The compound proved to have the *E* configuration at the azomethine double bond (**2*E***). Anal. Calcd for $C_4H_9Cl_3KNOPt$: C, 11.2; H, 2.1; N, 3.3. Found (**2*E***): C, 11.1; H, 2.2; N, 2.9.

K[PtCl$_3${*Z*-HN=C(OMe)Ph}], 3*Z*. K[PtCl$_3$(NCPh)] (1 mmol) suspended in 2 mL of methanol and cooled to 0 °C was treated with KOH (0.1 g, 1.8 mmol). Soon after the addition of the base, the nitrile complex dissolved completely, and from the clear solution, kept under stirring at room temperature for 5 min, a yellow solid precipitated. The mother liquor was filtered and the solid was washed with a small volume of methanol and dried (yield 50%). The compound proved to have the *Z* configuration at the azomethine double bond (**3*Z***). Anal. Calcd for $C_8H_9Cl_3KNOPt$: C, 20.2; H, 1.9; N, 2.9. Found (**3*Z***): C, 20.1; H, 1.8; N, 2.8.

K[PtCl$_3${*Z*-HN=C(OMe)Bu^t}], 4*Z*. K[PtCl$_3$(NCBu^t)] (0.55 g, 1.3 mmol) suspended in 2 mL of methanol and cooled to 0 °C was treated with KOH (0.1 g, 1.8 mmol) and kept under stirring at 0 °C for 1 h. In contrast to the previous cases, there was no formation of yellow precipitate but a clear solution formed. This was treated with 3 M HCl until neutral pH, the solvent was evaporated under reduced pressure, and the solid residue was extracted with MeOH. The alcoholic solution, after evaporation of the solvent, afforded a yellow solid of **4*Z*** (yield 80%). Anal. Calcd for $C_6H_{13}Cl_3KNOPt$: C, 15.8; H, 2.9; N, 3.1. Found (**4*Z***): C, 15.6; H, 2.7; N, 3.0.

trans*-[PtCl$_2${HN=C(OMe)Me}$_2$], Isomers 5*ZZ*, 5*EZ*, and 5*EE*.** The complex *trans*-[PtCl$_2$(NCMe)$_2$] (0.5 g, 1.44 mmol), suspended in methanol (10 mL), was treated with KOH (0.1 g, 1.8 mmol). The reaction mixture was stirred for 2 h at 20 °C, during which a yellow solid precipitated. This was collected by filtration of the mother liquor and washed with methanol. The yellow solid contained most of compounds **5*ZZ and **5*EZ*** (which is formed in small yield); the mother liquor, most of compound **5*EE***. The separation of **5*ZZ*** and **5*EZ*** was accomplished by extraction of the yellow solid with hot methanol in which **5*EZ*** is rather soluble. The solid remaining was pure **5*ZZ***, yield 60%. The methanol solution, concentrated to a small volume and cooled to 0 °C, afforded **5*EZ*** as a yellow solid which was isolated and dried in a stream of dry air; yield 3%. The mother liquor, containing compound **5*EE***, was neutralized with 3 M HCl and taken to dryness by evaporation of the solvent. The solid residue was extracted with dichloromethane; the extract was concentrated to a small volume and chromatographed on an open column of silica gel using dichloromethane/acetone (8:2 v/v) as eluant. Compound **5*EE*** was eluted in the first fraction; yield 13%. Anal. Calcd for $C_6H_{14}Cl_2N_2O_2Pt$: C, 17.5; H, 3.4; N, 6.8. Found (**5*ZZ***): C, 17.3; H, 3.3; N, 6.7. Found (**5*EZ***): C, 17.3; H, 3.3; N, 6.7. Found (**5*EE***): C, 17.5; H, 3.5; N, 6.8.

trans*-[PtCl$_2${HN=C(OMe)Et}$_2$], Isomers 6*ZZ*, 6*EZ*, and 6*EE*.** The procedure was similar to that described for compound **5**. *trans*-[PtCl$_2$(NCEt)$_2$] (0.5 g, 1.3 mmol) suspended in 4 mL of methanol was treated with KOH (0.002 g, 0.036 mmol), and the mixture was stirred at 20 °C for 5 min while a yellow solid precipitated. This was collected by filtration of the mother liquor and washed with methanol and dried. It proved to be compound **6*ZZ (yield 25%). Operating under more dilute conditions (0.5 g in 10 mL of methanol) but using a greater concentration of base (0.1 g of KOH) and longer reaction time (2 h), we obtained a clear solution. This was treated with 3 M HCl until neutral pH, the solvent was evaporated under reduced pressure, and the solid residue was extracted with CH_2Cl_2. The dichloromethane solution, after evaporation of the solvent, afforded a yellow solid of **6*EE*** and **6*EZ***, the latter present in small amount. The pure isomers were obtained by chromatography on a open column of silica gel using dichloromethane/acetone (8:2 v/v) as eluant (yield: **6*EE***, 90%; **6*EZ***, 5%). Anal. Calcd for $C_8H_{18}Cl_2N_2O_2Pt$: C, 21.8; H, 4.1; N, 6.4. Found (**6*ZZ***): C, 21.8; H, 4.1; N, 6.3. Found (**6*EZ***): C, 21.5; H, 4.0; N, 6.0. Found (**6*EE***): C, 21.9; H, 4.1; N, 6.4.

trans*-[PtCl$_2${HN=C(OMe)Ph}$_2$], Isomers 7*ZZ*, 7*EZ*, and 7*EE*.** These compounds were prepared as described in ref 21a. Anal. Calcd for $C_{16}H_{18}Cl_2N_2O_2Pt$: C, 35.8; H, 3.4; N, 5.2. Found (**7*ZZ): C, 36.3; H, 3.7; N, 5.0. Found (**7*EZ***): C, 35.5; H, 3.3; N, 5.0. Found (**7*EE***): C, 35.3; H, 3.2; N, 4.9.

trans*-[PtCl$_2${*Z*-HN=C(OMe)Bu^t}$_2$], Isomer 8*ZZ*.** The procedure was similar to that described for compound **6**. *trans*-[PtCl$_2$(NCBu^t)$_2$] (0.25 g, 0.58 mmol) dissolved in 10 mL of methanol was treated with KOH (0.1 g, 1.8 mmol) and kept under stirring at 20 °C for 10 min while a yellow solid precipitated. This was collected by filtration of the mother liquor, washed with methanol, and dried. It proved to be compound **8*ZZ (yield 65%). Anal. Calcd for $C_{12}H_{26}Cl_2N_2O_2Pt$: C, 29.0; H, 5.3; N, 5.6. Found (**8*ZZ***): C, 29.3; H, 5.3; N, 5.5.

Table 3. Crystallographic Data for **5*EE*** and **9*EE***

	5*EE*	**9*EE***
chemical formula	$C_6H_{14}N_2O_2Cl_2Pt$	$C_6H_{14}N_2O_2Cl_2Pt$
a, Å	8.491(6)	15.854(3)
b, Å	8.603(2)	8.123(2)
c, Å	8.973(2)	9.471(2)
α, deg	75.56(1)	
β, deg	67.52(2)	93.72(3)
γ, deg	85.62(2)	
V, Å^3	586.4(2)	1217.1(4)
Z	2	4
fw	412.2	412.2
space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)
T, °C	25	25
λ, Å	0.710 73	0.710 73
ϱ_{calcd}, g cm^{-3}	2.334	2.249
μ (Mo Kα), cm^{-1}	125.24	120.68
transm coeff	0.243−0.355	0.255−0.368
$R(F_o)^a$	0.0414	0.0393
$R_w(F_o)^b$	0.0444	0.0393

[a] $R(F_o) = \sum|F_o - |F_c||/\sum F_o$. [b] $R_w(F_o) = \sum w^{1/2}|F_o - |F_c||/\sum F_o w^{1/2}$.

cis*-[PtCl$_2${HN=C(OMe)Me}$_2$], Isomers 9*ZZ*, 9*EZ*, and 9*EE*.** The complex *cis*-[PtCl$_2$(NCMe)$_2$] (0.5 g, 1.44 mmol), suspended in methanol (10 mL), was treated with KOH (0.1 g, 1.8 mmol). The reaction mixture was stirred for 2 h at 20 °C while a yellow solid precipitated. This was collected by filtration of the mother liquor, washed with methanol, and then extracted with CH_2Cl_2 in which **9*EZ and **9*EE*** are soluble. The yellow solid which was left, containing pure **9*ZZ***, was dried in a stream of dry air; yield 35%. The dichloromethane solution, containing **9*EZ*** and **9*EE***, was concentrated to a small volume and chromatographed on a open column of silica gel using dichloromethane/acetone (8:2 v/v) as eluant. Compound **9*EE*** was eluted in the first fraction; yield 54%. Compound **9*EZ*** was eluted in the second fraction; yield 8%. Anal. Found (**9*ZZ***): C, 17.6; H, 3.5; N, 6.8. Found (**9*EZ***): C, 18.2; H, 3.4; N, 6.5. Found (**9*EE***): C, 17.6; H, 3.4; N, 6.7.

cis*-[PtCl$_2${HN=C(OMe)Et}$_2$], Isomers 10*ZZ*, 10*EZ*, and 10*EE*.** *cis*-[PtCl$_2$(NCEt)$_2$] (0.5 g, 1.3 mmol) suspended in 5 mL of methanol was treated with KOH (0.002 g, 0.036 mmol) and kept under stirring at 0 °C for 5 min. The yellow solid was isolated by filtration of the mother liquor, washed with a small volume of water, and dried. The solid residue was extracted with $CHCl_3$ to remove unreacted nitrile complex, which is sparingly soluble in this solvent; the chloroform solution, containing isomers **10*ZZ, **10*EZ***, and **10*EE*** (the last present in a small amount), was chromatographed on an open column of silica gel using dichloromethane/acetone (8:2 v/v) as eluant. The first eluted fraction contained compound **10*EE*** (yield 5%), the second fraction contained compound **10*EZ*** (yield 15%), and the third fraction contained compound **10*ZZ*** (yield 40%). When the reaction was performed under more dilute conditions (0.5 g of complex in 10 mL of methanol) but 0.1 g of KOH and a longer reaction time (2 h) were used, compound **10*EE*** was the major product (yield 95%). Anal. Found (**10*ZZ***): C, 21.9; H, 4.1; N, 6.2. Found (**10*EZ***): C, 21.7; H, 4.1; N, 6.4. Found (**10*EE***): C, 21.8; H, 4.2; N, 6.3.

cis*-[PtCl$_2${HN=C(OMe)Ph}$_2$], Isomers 11*EZ* and 11*EE*.** These compounds were prepared as described in ref 21a. Anal. Found (**11*EZ): C, 36.1; H, 3.4; N, 5.0. Found (**11*EE***): C, 36.0; H, 3.3; N, 5.1.

cis*-[PtCl$_2${*Z*-HN=C(OMe)Bu^t}$_2$], 12*ZZ*.** *cis*-[PtCl$_2$(NCBu^t)$_2$] (0.25 g, 0.58 mmol) dissolved in 10 mL of methanol was treated with KOH (0.1 g, 1.8 mmol) and kept under stirring at 20 °C for 10 min. The clear solution was treated with 3 M HCl until neutral pH, the solvent was evaporated under reduced pressure, and the solid residue was washed with methanol and diethyl ether and dried. Yield: 50%. Anal. Found (**12*ZZ): C, 29.0; H, 5.3; N, 5.5.

Physical Measurements. IR spectra in the range 4000−400 cm^{-1} were recorded as KBr pellets; spectra in the range 400−200 cm^{-1} were recorded as polythene pellets on Perkin-Elmer 283 and FT 1600

Table 4. Atomic Coordinates ($\times 10^4$) for ***5EE***

atom	*x/a*	*y/b*	*z/c*
Pt	2508(1)	1951(1)	4552(1)
Cl(1)	−243(3)	2027(3)	6404(3)
Cl(2)	5252(3)	1852(3)	2690(3)
O(1)	724(10)	3120(9)	660(9)
O(2)	4328(9)	3273(9)	7823(9)
N(1)	1551(9)	1914(9)	2855(9)
H(N1)	1021(9)	784(9)	2923(9)
N(2)	3503(9)	2013(10)	6240(10)
H(N2)	4073(9)	925(10)	6693(10)
C(11)	1503(10)	3137(11)	1671(11)
C(12)	2385(13)	4712(11)	1320(13)
H(12A)	2997(13)	4642(11)	2191(13)
H(12B)	1450(13)	5645(11)	1455(13)
H(12C)	3330(13)	4985(11)	70(13)
C(13)	−133(17)	1704(15)	832(16)
H(13A)	−699(17)	1904(15)	−90(16)
H(13B)	−1117(17)	1369(15)	2057(16)
H(13C)	776(17)	752(15)	651(16)
C(21)	3535(11)	3225(11)	6842(11)
C(22)	2708(14)	4816(13)	6424(15)
H(22A)	2058(14)	4732(13)	5620(15)
H(22B)	3663(14)	5768(13)	5804(15)
H(22C)	1798(14)	5073(13)	7558(15)
C(23)	5135(18)	1816(17)	8392(17)
H(23A)	5742(18)	2038(17)	9182(17)
H(23B)	6081(18)	1472(17)	7326(17)
H(23C)	4192(18)	862(17)	9078(17)

spectrophotometers. ^{1}H NMR spectra were obtained with Varian XL 200 and Bruker AM 300 spectrometers.

X-ray Crystallography for *5EE*. Single crystals of the title compound were grown from a DMF/water (1:1 v/v) solution. A well-formed, pale yellow prism (0.25 × 0.35 × 0.10 mm) was selected and mounted on a glass fiber for the X-ray data collection. Crystallographic data are reported in Table 3.

Unit cell parameters were obtained by least-squares refinement of the values of 25 carefully centered reflections at high 2θ angles (10−25°), chosen from different regions of the reflection sphere. The collected intensities were corrected for the Lorentz and polarization effects. An absorption correction was also performed via the ψ-scan technique by using three reflections: 502, $\underline{4}12$, 724.

The structure solution and refinement ($P\bar{1}$, No. 2 space group) were carried out by Patterson and Fourier methods, treating as anisotropic the Pt, Cl, O, N, and C atoms.

The full-matrix least-squares cycles converged to $R = 0.0414$ and $R_w = 0.0444$.[35] The isotropic thermal parameters for the imino protons were fixed at 0.08 Å^2, whereas the thermal parameters for the O−Me and the C−Me H atoms were refined to 0.0805 and 0.0929 Å^2, respectively. The atomic coordinates are listed in Table 4.

Table 5. Atomic Coordinates ($\times 10^4$) for ***9EE***

atom	*x/a*	*y/b*	*z/c*
Pt	0	271(1)	2500
Cl(1)	738(2)	2244(4)	1341(3)
O	1779(4)	−3131(9)	1133(7)
N	625(5)	−1487(11)	1501(8)
H(N)	290(5)	−2107(11)	625(8)
C(1)	1376(5)	−1976(12)	1818(8)
C(2)	1905(6)	−1381(16)	3118(10)
H(2A)	1570(6)	−436(16)	3657(10)
H(2B)	2494(6)	−889(16)	2789(10)
H(2C)	2033(6)	−2406(16)	3827(10)
C(3)	1370(7)	−3818(16)	−143(10)
H(3A)	1778(7)	−4743(16)	−552(10)
H(3B)	1264(7)	−2850(16)	−916(10)
H(3C)	773(7)	−4370(16)	77(10)

X-ray Crystallography for *9EE*. Pale yellow crystals of the title compound were obtained from methanol solution. A single crystal of approximately 0.20 × 0.20 × 0.30 mm was selected and mounted for data collection on a Siemens P4 four-circle diffractometer (some of the crystallographic details are listed in Table 3). The unit cell parameters were obtained by least-squares refinement of the values of 28 carefully centered high-intensity reflections measured at $15 < 2\theta < 25°$, chosen from different regions of the reflection sphere. The collected intensities were corrected for the Lorentz and polarization effects, as well as for the absorption of the X-ray radiation through the ψ-scan technique. Six reflections were used for the latter correction: $20\bar{5}$, $30\bar{6}$, $31\bar{8}$, $0\bar{1}4$, $\bar{1}26$, $\bar{1}08$.

Half the reflection sphere was collected. The structure was solved, via Patterson and Fourier techniques, in the $C2/c$ space group ($R_{\text{int}} = 0.029$). The model was refined by full-matrix least-squares techniques by applying anisotropic (Pt, Cl, O, N, and C) and isotropic (H) thermal parameters. The agreement indexes R and R_w converged to 0.0393.

The H atoms linked to N, C(2), and C(3) were included through the AFIX 43 and AFIX 33 options of SHELX-76.[35] The thermal factors for H(N), H(C2), and H(C3) were fixed at 0.06, 0.08, and 0.08 Å^2, respectively. The atomic coordinates are listed in Table 5.

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Supplementary Material Available: Listings of thermal parameters [Tables S1 (***5EE***) and S2 (***9EE***)], a full table of crystallographic data (Table S3), and crystal packing diagrams [Figures 4 (***5EE***) and 5 (***9EE***)] (6 pages). Ordering information is given on any current masthead page.

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