

X-ray Structures of the First Platinum Complexes with Z Configuration Iminoether Ligands: *trans*-Dichlorobis(1-imino-1-methoxy-2,2'-dimethylpropane)platinum(II) and *trans*-Tetrachlorobis(1-imino-1-methoxy-2,2'-dimethylpropane)platinum(IV)

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Platinum complexes with Z configuration iminoether ligands (*trans*-[PtCl₂{HN=C(OMe)Bu^t}₂], **1**, and *trans*-[PtCl₄{HN=C(OMe)Bu^t}₂], **2**) have been structurally characterized for the first time. The nearly planar Pt–N–C–O–C chain, all atoms being in gauche conformation, brings the terminal Pt and C atoms very close to one another. The steric clash is released by considerably increasing the Pt–N–C, N–C–O, and C–O–C bond angles (133, 124, and 121° for **1**, respectively; 147, 129, and 127° for **2**, respectively), which are well above the expected values (120° for Pt–N–C and N–C–O; less than 120° for C–O–C owing to the repulsive effect exerted by the lone pair of electrons on the oxygen atom). In the platinum(II) case the smaller increase of bond angles is accompanied by a greater value of the Pt–N–C–O torsion angle (27.3 and 15.6° for **1** and **2**, respectively). The stabilization of the Z configuration, notwithstanding the steric clashes described above, has been achieved by a careful choice of the R substituent in the iminoether moiety (a bulky *tert*-butyl group). The reactions of the platinum(IV) species (**2**) in basic and acidic conditions and with triphenylphosphine have been investigated. Bases and acids both interact with the coordinated ligand in such a way to weaken the coordinative bond and promote the release of the iminoether ligands. The phosphine promotes a ready and complete reduction of the platinum(IV) complex to the corresponding platinum(II) species (**1**). Compound **1** reacts with a stoichiometric amount of phosphine (1:1 molar ratio) to form *cis*-[PtCl₂(PPh₃)₂]{Z-HN=C(OMe)Bu^t} and with excess phosphine to form [PtCl₂(PPh₃)₂] and free iminoether. The latter two reactions leading to formation of a mixed phosphine/iminoether platinum species and to free iminoether, which can be used as a synthon for further organic transformations, can be of synthetic utility.

Introduction

It has recently been reported that some analogues of clinically ineffective *trans*-diamminedichloroplatinum(II) (transplatin) exhibit antitumor activity.^{1–3} One of these new classes of platinum compounds contains iminoethers as carrier ligands.^{4–9} The active iminoether complexes are

similar to transplatin in having two chloride and two nitrogen-donor ligands; moreover, the nitrogen atoms carry a proton suitable for hydrogen-bond formation.

Iminoether complexes are generally prepared from related platinum nitrile complexes by reaction with alcohol under basic conditions. They can have either *E* or *Z* configuration

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- (1) Natile, G.; Coluccia, M. In *Metallopharmaceuticals I*; Clarke, M. J., Sadler, P. J., Eds.; Springer-Verlag: Berlin, 1999; p 74.
- (2) Kelland, L. R.; Barnard, C. F. J.; Evans, I. G.; Murrer, B. A.; Theobald, B. R. C.; Wyer, S. B.; Goddard, P. M.; Jones, M.; Valenti, M.; Bryant, A.; Rogers, P. M.; Harrap, K. R. *J. Med. Chem.* **1995**, 38, 3016.
- (3) Farrell, N. In *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1996; Vol 32, p 603.

- (4) Coluccia, M.; Nassi, A.; Loseto, F.; Boccarelli, A.; Mariggiò, M. A.; Giordano, D.; Intini, F. P.; Caputo, P.; Natile, G. *J. Med. Chem.* **1993**, 36, 510.

- (5) Coluccia, M.; Boccarelli, A.; Mariggiò, M. A.; Cardellicchio, N.; Caputo, P.; Intini, F. P.; Natile, G. *Chem. Biol. Interact.* **1995**, 98, 251.

- (6) Brabec, V.; Vrana, O.; Novakova, O.; Kleinwachter, V.; Intini, F. P.; Coluccia, M.; Natile, G. *Nucleic Acid Res.* **1996**, 24, 336.

- (7) Zaludova, R.; Zakovska, A.; Kasparkova, J.; Balkarova, Z.; Vrana, O.; Coluccia, M.; Natile, G.; Brabec, V. *Mol. Pharmacol.* **1997**, 52, 354.

depending upon the positions of the substituents with respect to the C=N double bond (*E* and *Z* stand for the platinum and the alkoxy groups trans and cis with respect to the double bond, respectively).^{10,11,12} The X-ray structure of the first platinum iminoether complex, [PtCl₂{HN=C(OPrⁱ)Me}₂], was reported 10 years ago.¹² The *E* configuration found in the solid state was assumed to be the preferred one and to stem from cis addition of the alcohol to the nitrile triple bond.

The crystal structures of other two platinum iminoether complexes, *cis*- and *trans*-[PtCl₂{HN=C(OMe)Me}₂], reported somewhat later, had again *E* configuration of the iminoether ligands.¹³ However it was demonstrated that the *E* isomer was not the first isomer to be formed. Monitoring of the reaction course by NMR indicated that, in basic (KOH) alcoholic solution (MeOH), the platinum nitrile undergoes trans addition of the alcohol to the C≡N triple bond and formation of the *Z* isomer. However, under the basic conditions required for the addition of the alcohol to the nitrile, fast isomerization of the *Z* into the *E* isomer takes place, and this latter is generally obtained as final product.

In a previous paper we searched the conditions for the preparation of the *Z* isomer and found that it can be conveniently prepared under conditions in which it precipitates from solution as soon as it is formed. Therefore, high concentration of the reactants, low temperature (0 °C), and removal of the precipitate from the mother liquor soon after formation ensure good yield of the *Z* isomer. In most cases purification by column chromatography was also required as a final step.¹³ However, different attempts to characterize the *Z* isomer by X-ray crystallography were unsuccessful either because undesired *Z* → *E* ligand isomerization took place during the crystallization process or because the crystals, obtained under fast crystallization conditions, were not suitable for X-ray investigation.

Despite the experimental difficulties, a full characterization of the *Z* isomer of platinum iminoether complexes was highly desirable for at least two reasons: (i) The X-ray structure of the *E* isomer revealed a “quasi planarity” of the iminoether moiety with a lone pair of electrons of the oxygen atom participating in the imine π system and consequent electron charge delocalization over the N–C–O moiety. In the *E* isomer, the Pt atom and the R group, within the Pt–N–C–R moiety (the R group comes from the former nitrile ligand), are forced to be very close to one another with consequent steric repulsion between the two. Such an

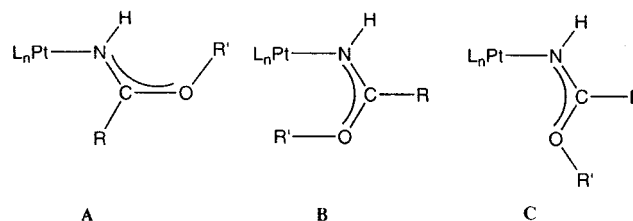


Figure 1. Possible configurations for a coordinated iminoether ligand. A, B, and C represent the *E*, *Z*-syn, and *Z*-anti configurations, respectively.

interaction is expected to be even greater in the *Z* isomer since the longer Pt–N–C–O–R' skeleton will bring the terminal R' group (the R' radical comes from the added alcohol) even closer to the platinum center. (ii) In principle, the *Z* iminoether ligand could avoid the steric clash between the terminal R' group and the Pt atom by switching from a syn to an anti conformation (see Figure 1). Such a configuration (which has never been observed so far for iminoether complexes) would release the Pt–R' steric interaction but place the terminal R and R' groups, within the planar R–C–O–R' moiety, in a gauche conformation.

New interest in the *Z* configuration of the iminoether ligands arose from the discovery that the configuration of the iminoether ligands can modulate the antitumor potential of the platinum complexes and species with the *Z* configuration can be more active than those with the *E* configuration.^{14–16}

In this paper we sought the conditions for the stabilization of the *Z* configuration of the iminoether ligands and succeeded in performing the X-ray structural characterization of two of such complexes, one having a 4-coordinate square-planar arrangement and the second a 6-coordinate octahedral structure. The steric clash between the alkoxy group and the platinum center, cis to one another with respect to the C=N double bond, is particularly high, especially in the 6-coordinate Pt^{IV} species. How the steric strain could influence the reactivity of these species has also been investigated.

Results and Discussion

The reactivity of coordinated nitriles depends very much upon the oxidation state of the platinum center, and weak nucleophiles react only with platinum(IV) species but do not react with the platinum(II) counterparts.^{17,18} However, even in the case of platinum(II), the addition of a catalytic amount of base (KOH) is sufficient for promoting the rapid and complete addition of a weak nucleophile such as an alcohol (R'OH) to the coordinated nitrile (RC≡N). There is no impediment to the latter reaction stemming from either steric

- (8) Zaludova, R.; Natile, G.; Brabec, V. *Anti-Cancer Drug Des.* **1997**, *12*, 295.
- (9) Coluccia, M.; Mariggiò, M. A.; Boccarelli, A.; Loseto, F.; Cardellicchio, N.; Caputo, P. A.; Intini, F. P.; Pacifico, C.; Natile, G. In *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*; Pinedo, H. M., Schornagel, J. H., Eds.; Plenum Press: New York, 1996; Vol 2, p 27.
- (10) Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947.
- (11) Lopez, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Martì, J. M.; Hermoso, J. A.; Vegas, A.; Martinez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.
- (12) Casas, J. M.; Chisholm, M. H.; Sicilia, M. V.; Streib, W. E. *Polyhedron* **1991**, *10*, 1573.
- (13) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130.

- (14) Boccarelli, A.; Coluccia, M.; Intini, F. P.; Natile, G.; Locker, D.; Leng, M. *Anti-Cancer Drug Des.* **1999**, *14*, 253.
- (15) Coluccia, M.; Nassi, A.; Boccarelli, A.; Giordano, D.; Cardellicchio, N.; Locker, D.; Leng, M.; Sivo, M.; Intini, F. P.; Natile, G. *J. Inorg. Biochem.* **1999**, *77*, 31.
- (16) Leng, M.; Locker, D.; Giraud-Panis, M. J.; Schwartz, A.; Intini, F. P.; Natile, G.; Pisano, C.; Boccarelli, A.; Giordano, D.; Coluccia, M. *Mol. Pharmacol.* **2000**, *58*, 1525.
- (17) Kukushkin, V. Yu.; Packhomova, T. B.; Kukushkin, Yu. N.; Herrmann, R.; Wagner, G.; Pombeiro, A. J. L. *Inorg. Chem.* **1998**, *37*, 6511.
- (18) Kukushkin, V. Yu.; Packhomova, T. B.; Bokach, N. A.; Wagner, G.; Kuznetsov, M.; Galanski, M. L.; Pombeiro, A. J. L.; *Inorg. Chem.* **2000**, *39*, 216.

or electronic properties of the coordinated nitrile and of the incoming alcohol. The new ligand resulting from the addition reaction has been named "iminoether" since the pioneer work of Chisholm et al.¹² Imidoester was initially used by ourselves;¹⁰ however, the former name has been widely accepted and will be adopted also in this paper.

Coordinated iminoethers can have either *E* or *Z* configuration depending upon the relative position of the substituents about the C=N double bond (the platinum and the alkoxy groups cis or trans to one another for the *Z* and *E* isomers, respectively). A cis addition of the alcohol to the nitrile triple bond would lead to direct formation of a *E* isomer, while a trans addition would lead to formation of a *Z* isomer. In a previous paper it was demonstrated that always the first formed isomer has a *Z* configuration indicating that the addition of the alcohol is of trans type; i.e., the alkoxy group and the proton add to the triple bond from opposite sides.¹³

The *Z* configuration is generally unstable under basic conditions (the same conditions used for promoting the addition of the alcohol to the coordinated nitrile) and readily undergoes isomerization to the *E* form, which appears to be thermodynamically favored. The greater stability of the *E* isomer appears to be of steric origin. The involvement of the oxygen atom in electron conjugation with the adjacent C=N π -system renders the whole iminoether skeleton nearly planar. Already in the *E* isomer the terminal groups in the sequence Pt—N—C—R come close to one another, and some steric clash between the Pt and R groups was evident from the X-ray structures. Such a steric clash would be even greater in the *Z* isomer for which the Pt—N—C—O—R' chain (all members being coplanar and in gauche positions) is one unit longer (Figure 1). These considerations suggested the way how to increase the thermodynamic stability of the *Z* isomer with respect to the *E* isomer.

Stability of the *Z* Isomer for *trans*-[PtCl₂{HN=C(OMe)Bu'}₂], 1. Being that the steric interaction between the platinum center and either the R' (*Z* isomer) or the R substituent (*E* isomer) is the dominant factor in determining the relative stabilities of the *Z* and *E* isomers, an increase of the bulk of the R group with respect to R' should destabilize the *E* isomer with respect to the *Z* isomer. Hence the platinum complex with *tert*-butyl nitrile *trans*-[PtCl₂(NCBu')₂] was reacted with methanol in the presence of a catalytic amount of base. The formed iminoether complex kept the initial configuration (expected to be *Z*) and did not undergo isomerization after prolonged standing in basic solution. The *Z* configuration of the iminoether was deduced not only from the reaction stereochemistry, which contemplates trans addition of the alcohol to the nitrile triple bond, but also from the chemical shift values of the ligand protons, particularly those of the alkoxy group, which in a *Z* configuration (the methoxy group close to an axial site of the platinum center) experience a strong deshielding effect exerted by the platinum center (the resonance of the methoxy group falls at ca. 5 ppm in the present isomer while it is expected to be close to 3.8 ppm in a *E* isomer).¹³

It was possible to demonstrate that the lack of isomerization was due to a thermodynamic preference for the *Z* isomer

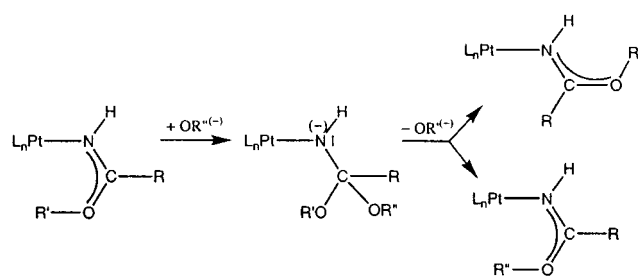


Figure 2. Common reaction intermediate in the base-catalyzed alkoxy exchange and configuration change for a coordinated iminoether ligand.

and not to a kinetic impediment. Substitution of CD₃O for CH₃O in the coordinated iminoether ligand 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 the isomerization reaction, was readily accessible (Figure 2).¹⁰

The platinum(II) compound with HN=C(OMe)Bu' iminoether ligands is the only one, among the several species investigated (R = Me, Et, Prⁱ, Bu'; R' = Me, Et, Prⁱ), for which the *Z* configuration is the only one observed in solution as well as in the solid state. This is because the size of the R group (Bu') is such that no release of steric strains can be attained by placing the Bu' group, instead of the OMe group, in a position cis to platinum with respect to the C=N double bond.

Platinum(IV) Iminoether Complex [PtCl₄{*Z*-HN=C(OMe)Bu'}₂], 2. Given the stability of the *Z* isomer for the iminoether with a bulky C—Bu' substituent, we wanted to investigate if the shielding of the metal center by the O—Me group could have any effect on the oxidation of platinum(II) to platinum(IV) by chlorine and on the stability of the 6-coordinate platinum species obtained therefrom.

The oxidation reaction by chlorine took place readily in chlorinated solvents and led to the quantitative formation of the related platinum(IV) species. This latter could be crystallized from chloroform/hexane to give yellow crystals suitable for X-ray diffraction analysis.

The chemical shift value of the O—Me protons was 0.5 ppm at higher field with respect to the chemical shift of the corresponding platinum(II) species but still ca. 0.7–0.8 ppm at lower field with respect to the chemical shift value observed for O—Me in a platinum(II) iminoether complex with *E* configuration. To demonstrate that a reduced downfield shift of the iminoether alkyl substituent gauche to platinum (O—R' and C—R for *Z* and *E* isomers, respectively) is a common feature of 6-coordinate platinum(IV) species with respect to the 4-coordinate platinum(II) counterparts, platinum(II) iminoether complexes with established *E* or *Z* configuration of the iminoether ligands were oxidized to the corresponding platinum(IV) species by chlorine and analyzed by NMR. It was observed that the chemical shifts of the OMe groups for the *Z* and *E* ligands, respectively, which fall at 4.96 and 3.77 ppm in *trans*-[PtCl₂{*Z*-HN=C(OMe)Me}{*E*-HN=C(OMe)Me}], fall at 4.07 and 3.92 ppm in *trans*-[PtCl₄{*Z*-HN=C(OMe)Me}{*E*-HN=C(OMe)Me}]. Similarly, the chemical shift of the C—Me groups for the *Z* and *E* ligands, respectively, which fall at 2.20 and 2.60 ppm in

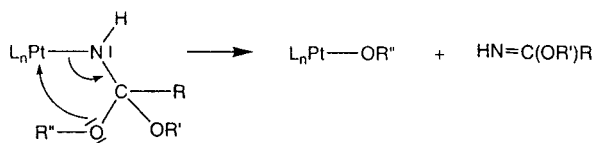


Figure 3. Base-catalyzed release of an iminoether ligand from a platinum(IV) substrate.

trans-[PtCl₂{Z-HN=C(OMe)Me}{E-HN=C(OMe)Me}], fall at 2.52 and 2.69 ppm in *trans*-[PtCl₄{Z-HN=C(OMe)Me}{E-HN=C(OMe)Me}]. It can be seen how in the Pt^{IV} species the chemical shifts of a given substituent does not change much upon its position *cis* or *trans* to platinum with respect to the C=N double bond; therefore, the chemical shifts of the O-R' and C-R alkyl groups, which were very diagnostic for the iminoether configuration in the case of 4-coordinate platinum(II) species, are no longer so in the case of 6-coordinate platinum(IV). In the present case, however, that the iminoether ligands keep the original *Z* configuration upon oxidation of Pt^{II} to Pt^{IV} was clearly demonstrated by the X-ray structures of both compounds.

Reaction of the Pt^{IV} Complex with Acids and Bases.

The platinum(IV) species is stable in chloroform solution and only after several days at 25 °C gives a small amount of decomposition products (free ligand and some Pt^{II} species).

The Pt^{IV} species reacts readily with acids (HCl) and bases (KOH). Both reagents lead to displacement of the iminoether ligands which are released in the free (KOH solution) or protonated forms (HCl solution). The metallic species could be recovered as hexachloroplatinate anion in both cases (in the reaction with base it was sufficient to neutralize with HCl before recovering the complex anion).

The fast displacement of the iminoether ligand from the platinum(IV) species was rather unexpected owing to the well-known inertness of 6-coordinate Pt^{IV} substrates. Moreover it was possible to demonstrate that the platinum(IV) complex remains stable in the presence of excess chloride under neutral conditions, indicating that are the acidic or basic conditions responsible for the weakening of the platinum–iminoether bond. We propose that the mechanism by which the metal–iminoether bond is weakened is similar to that by which the acidic and basic conditions catalyze the iminoether isomerization (*E* ↔ *Z*) in the platinum(II) species. The catalysis under basic conditions has been already described (Figure 2). It 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, afterward, reeliminates the alkoxide restoring the iminoether ligand.¹³ It is conceivable that an alkoxide anion from the amido ketal intermediate could be transferred to the platinum center while the reconstituted iminoether ligand is released (Figure 3).

Under acidic conditions an electrophilic attack of the proton on the C=N π system was proposed to lead to a N-bisprotonated species, which could undergo *Z* → *E* isomerization before releasing of the added proton.¹⁰ It is conceivable that N-protonation also weakens the Pt–N bond favoring the dissociation of the iminoether ligand in its protonated form (Figure 4).

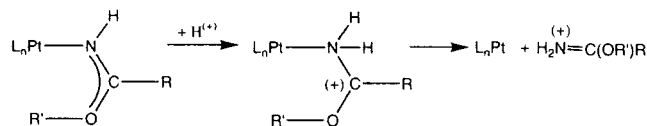


Figure 4. Acid-catalyzed release of an iminoether ligand from a platinum(IV) substrate.

Reaction of the Pt^{IV} Complex with PPh₃. Addition of a stoichiometric amount of a weak reducing agent such as PPh₃ to a chloroform solution of the platinum(IV) species (**2**) leads to the quantitative formation of the platinum(II) complex (**1**). It is known that platinum(IV) species can be readily reduced to platinum(II) complexes by several reducing agents such as N₂H₄·H₂SO₄, NH₂OH·HCl, oxalate, and ascorbate (in water solution) and SO₂, formaldehyde, and olefins (in nonaqueous media). More recently carbonyl-stabilized phosphorus ylides (Ph₃P=CHCO₂R) have been proposed as versatile reagents for the reduction of different classes of Pt^{IV} compounds to the corresponding Pt^{II} species in nonaqueous media.¹⁹ Triphenylphosphine can be used as well although, if used in excess, it can also lead to ligand substitution in the newly formed platinum(II) complex (see following discussion).

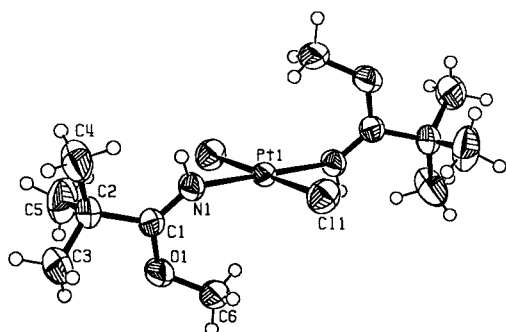
Reaction of the Pt(II) Complex with PPh₃. It was already anticipated that the platinum(II) complex formed by reaction of the platinum(IV) counterpart with PPh₃ reacts with PPh₃ present in excess to give ligand substitution. The reaction of the platinum(II) species with a stoichiometric amount of PPh₃ was investigated in detail in chloroform solution. The first step of the reaction is substitution of one chloro ligand by the phosphine and formation of *trans*-[PtCl(PPh₃){Z-HN=C(OMe)Bu'}₂]⁺. The formation of this reaction product is in accord with the greater *trans* effect of chloro ligands (as compared with N-donor iminoether ligands) in the starting substrate and accounts for the chloride being the leaving group in the reaction of the same substrate with biologically relevant molecules (glutathione, nucleotides, etc.). However, on standing of the species in methanol solution, displacement of one iminoether ligand from the previously released chloride and formation of *cis*-[PtCl₂(PPh₃){Z-HN=C(OMe)Bu'}] and free iminoether is observed. The latter reaction is probably favored by the low dielectric constant of the solvent (4.8 for chloroform as compared to 78.5 for water) which could favor the formation of an ionic couple between the cationic *trans*-[PtCl(PPh₃){Z-HN=C(OMe)Bu'}₂]⁺ species and the chloride anion. The latter reaction can represent an alternative route to the synthesis of *cis*-platinum complexes with mixed ligands (in the present case phosphine and iminoether).

In the presence of excess PPh₃ both iminoether ligands are displaced from platinum leading to formation of [PtCl₂(PPh₃)₂] and free iminoether. This latter reaction can have a practical application in case the iminoether molecules are used as synthons for further organic transformations.

(19) Wagner, G.; Packhomova, T. B.; Bokach, N. A.; Frausto da Silva, J. J. R.; Vicente, J.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2001**, *40*, 1683.

Table 1. Selected Crystal Data and Structure Refinement for *trans*-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], **1**, and *trans*-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu'}₂], **2**

param	1	2
empirical formula	C ₁₂ H ₂₆ Cl ₂ N ₂ O ₂ Pt	C ₁₂ H ₂₆ Cl ₄ N ₂ O ₂ Pt
fw	496.34	567.24
temp/K	293(2)	293(2)
wavelength/Å	0.710 73	0.710 73
cryst system, space group	monoclinic, C2/m	monoclinic, P2 ₁ /c
unit cell dimens		
<i>a</i> /Å	15.796(1)	8.647
<i>b</i> /Å	11.420(1)	11.116(1)
<i>c</i> /Å	5.075(1)	10.880(1)
β/deg	102.14(1)	109.52(2)
<i>V</i> /Å ³	895.0(2)	985.7(1)
Z, calcd density/Mg m ⁻³	2, 1.842	2, 1.911
abs coeff/mm ⁻¹	8.137	7.664
cryst size/mm	0.10 × 0.15 × 0.20	0.20 × 0.15 × 0.10
θ range for data collcn/deg	2.22–30.00	2.50–25.00
reflens collcd/unique	1636/1369 [R(int) = 0.0130]	2334/1733 [R(int) = 0.0345]
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
data/restraints/params	1369/0/115	1733/0/98
final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0160, wR2 = 0.0400	R1 = 0.0274, wR2 = 0.0714
final R indices (all data)	R1 = 0.0160, wR2 = 0.0400	R1 = 0.0351, wR2 = 0.0772

**Figure 5.** Drawing of the complex molecule for *trans*-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], **1**. Ellipsoids enclose 30% probability.**Table 2.** Selected Bond Lengths (Å) for *trans*-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], **1**, and *trans*-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu'}₂], **2**^a

vector	1	2	3	4	5	6
Pt(1)–N(1)	2.020(4)	2.044(4)	2.016(4)	2.017(4)	1.999(7)	2.010(8)
Pt(1)–Cl(1)	2.309(1)	2.316(1)	2.313(1)		2.300(2)	2.303(2)
Pt(1)–Cl(2)		2.320(1)				
O(1)–C(1)	1.323(7)	1.290(7)	1.334(7)	1.325(7)	1.31(1)	1.33(1)
O(1)–C(6)	1.438(8)	1.420(8)	1.475(8)	1.444(8)	1.43(1)	1.45(1)
N(1)–C(1)	1.280(7)	1.269(6)	1.276(7)	1.280(7)	1.30(1)	1.27(1)
C(1)–C(2)	1.525(7)	1.536(7)	1.487(7)	1.500(7)	1.51(1)	1.52(1)
C(2)–C(3)	1.510(16)	1.519(8)				
C(2)–C(4)	1.483(15)	1.522(8)				
C(2)–C(5)	1.570(18)	1.529(8)				
C(2)–C(3A)	1.54(2)					
C(2)–C(4A)	1.51(3)					
C(2)–C(5A)	1.46(2)					

^a Previously reported bond distances for Pt(II) iminoether complexes are also listed for comparison: *cis*-[Pt^{II}Cl₂{*E*-HN=C(OPrⁱ)Me}₂], **3** (ref 12), [Pt^{II}{*E*-HN=C(OEt)Et}₂]²⁺, **4** (Prenzler, P. D.; Hockless, D. C. R.; Heath, G. A. *Inorg. Chem.* **1997**, 36, 5845), *trans*-[Pt^{II}Cl₂{*E*-HN=C(OMe)Me}₂], **5** (ref 13), and *cis*-[Pt^{II}Cl₂{*E*-HN=C(OMe)Me}₂], **6** (ref 13).

X-ray Crystallography of *trans*-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], **1.** The Pt atom of **1** has the usual square planar coordination arrangement (Figure 5 and Tables 2 and 3). The chlorine atoms occupy positions trans to each other and are located on the mirror plane (perpendicular to the *b* axis). The metal atom is also located on the mirror plane and sits on the 2-fold axis. The two iminoether ligands (trans to each other), as well as the chlorine ligands, are related by the

Table 3. Selected Bond Angles (deg) for *trans*-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], **1**, and *trans*-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu'}₂], **2**^a

vectors	1	2
Cl(1)–Pt(1)–Cl(2)		88.38(6)
Cl(1)–Pt(1)–Cl(2)#1		91.62(6)
N(1)–Pt(1)–Cl(1)	94.61(12)	95.66(13)
N(1)–Pt(1)–Cl(2)		83.50(13)
Cl(1)–Pt(1)–Cl(1)#1	180.0	180.0
N(1)–Pt(1)–Cl(1)#1	85.39(12)	84.34(13)
N(1)–Pt(1)–Cl(2)#1		96.50(13)
N(1)–Pt(1)–N(1)#1	180.0	180.0
C(1)–N(1)–Pt(1)	133.3(4)	147.3(4)
C(1)–O(1)–C(6)	120.7(5)	127.1(5)
N(1)–C(1)–O(1)	124.1(5)	129.0(5)
O(1)–C(1)–C(2)	111.4(5)	110.2(4)
N(1)–C(1)–C(2)	124.5(5)	120.8(5)
C(3)–C(2)–C(1)	112.3(7)	109.3(4)
C(4)–C(2)–C(1)	113.7(9)	112.5(4)
C(5)–C(2)–C(1)	103.8(8)	106.3(5)
C(4)–C(2)–C(3)	113.9(14)	109.1(5)
C(3)–C(2)–C(5)	105.4(13)	110.3(5)
C(4)–C(2)–C(5)	109.0(15)	109.4(5)
C(3A)–C(2)–C(1)	106.8(10)	
C(4A)–C(2)–C(1)	108.9(10)	
C(5A)–C(2)–C(1)	113.8(10)	
C(3A)–C(2)–C(4A)	106(2)	
C(3A)–C(2)–C(5A)	105(2)	
C(4A)–C(2)–C(5A)	116(2)	

^a Symmetry transformations used to generate equivalent atoms: for **1**, #1 = $-x + 1, -y, -z + 1$; for **2**, #1 = $-x + 1, -y, -z$.

binary axis. Since the iminoether ligand is located in general position, two distinct orientations of the coordination square around the *x* axis are present in the cells at 50% probability each (see Experimental Section for the occupancies of the atoms).

The bond distances relevant to the Pt–Cl (2.309(1) Å) and Pt–N (2.020(4) Å) linkages and all bond lengths within the iminoether ligands are in excellent agreement with those previously found for *trans*- and *cis*-[PtCl₂{*E*-HN=C(OMe)Me}₂].¹³

The configuration of the iminoether ligand can be described as *Z*, the methoxy group and the platinum atom being cis to one another with respect to the C=N double bond. As a consequence, the C–OMe branch of the ligand molecule

Table 4. Contact Distances between the Pt Atom and the Closest H(C) Atoms for the Selected Structures of Pt(II) Iminoether Complexes^a

compd	C...Pt/Å, $\sigma = 0.006$ [H...Pt/Å, $\sigma = 0.08$]	C...norm/Å, $\sigma = 0.005$ [H...norm/Å, $\sigma = 0.07$]
<i>trans</i> -[PtCl ₂ {Z-HN=C(OMe)Bu ^t } ₂]	3.164 [2.672]	1.558 [0.964]
<i>trans</i> -[PtCl ₂ {E-HN=C(OMe)Me} ₂] ^b	3.290 (C2) [2.655]	2.284 [1.343]
	3.357 (C5) [2.741]	2.434 [1.550]
<i>cis</i> -[PtCl ₂ {E-HN=C(OMe)Me} ₂] ^b	3.322 [2.715]	2.278 [1.223]

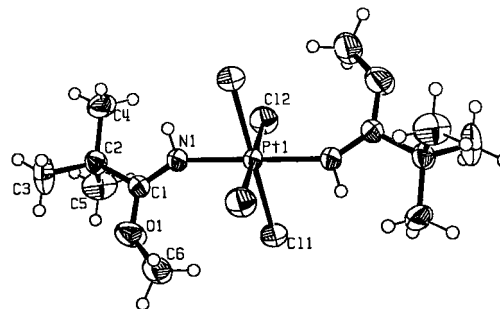
^a The distances between the Pt atom and the closest H(C) atom, as well as those between the normal to the plane which passes through the metal center (norm) and the closest H(C) atoms have also been reported. ^b From ref 13.

protrudes over the coordination plane. It has to be recalled that both the *trans*- and *cis*-[PtCl₂{E-HN=C(OMe)Me}₂] complexes described in ref 13 had the methoxy group *trans* to the platinum atom with respect to the C=N double bond (*E* configuration of the ligand) while was the C-Me group to be *cis* to platinum and protruding toward the metal center. The steric bulk of the *tert*-butyl group renders the *E* configuration highly unfavorable for the present case.

The N(1), C(1), C(2), and O(1) ligand atoms are coplanar within $\pm 0.003(3)$ Å (plane 1) as expected owing to the sp² hybridization of the N(1) and C(1) atoms linked by a double bond. Moreover, as already pointed out in a previous paper, whenever an oxygen atom is bound to a carbon atom engaged in a double bond, a lone pair of the oxygen atom gets involved in the π -system.¹³ The π -bond delocalization over the N-C-O moiety extends the planarity of the iminoether ligand also to the O-Me carbon atom (C(6)). The C(6) and Pt atoms deviate significantly from plane 1 (0.288(7) and -0.660(1) Å, respectively). Such a deviation suggests the presence of a steric interaction between the O-Me group and the platinum center which can be relieved by displacement of the Pt and C(6) atoms from the ligand plane (Pt-N(1)-C(1)-O(1) and N(1)-C(1)-O(1)-C(6) torsion angles of 27.3(5) and 12.9(5)°, respectively). In the corresponding platinum(II) species with *E* configuration of the iminoether ligands the maximum deviations from the ligand plane (plane 1) were 0.019(3) and -0.195(1) Å for the carbon atom of the methoxy group and the Pt atom, respectively.

The presence of a relevant steric interaction between the O-Me and the platinum center is also evident from the analysis of bond angles. The Pt-N(1)-C(1), N(1)-C(1)-O(1), and C(1)-O(1)-C(6) bond angles (133.3(4), 124.1(5), and 120.7(5)°, respectively) are all above the expected values (120° for Pt-N(1)-C(1) and N(1)-C(1)-O(1) and less than 120° for C(1)-O(1)-C(6) owing to the repulsive effect exerted by the lone pair of electrons on the oxygen atom) and larger than corresponding values for the iminoether complexes with *E* configuration (average values 126.2, 123.0, and 118.5°, respectively).¹³ The difference is particularly relevant for the Pt-N(1)-C(1) bond angle.

Notwithstanding the torsions along the Pt-N(1)-C(1)-O(1)-C(6) chain and the enlargements of the Pt-N(1)-C(1), N(1)-C(1)-O(1), and C(1)-O(1)-C(6) bond angles, the O-Me is much closer to Pt in **1** (C(6)···Pt contact distance of 3.162(6) Å) than was the C-Me in *trans*- and *cis*-[PtCl₂{E-HN=C(OMe)Me}₂] (average C...Pt contact distance of 3.32 Å;¹³ see Table 4). It is to be noted that the sum of the van der Waals radii for C and Pt atoms is 3.3 Å.²⁰ All these facts suggest that a severe clash between the

**Figure 6.** Drawing of the complex molecule for *trans*-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu^t}₂], **2**. Ellipsoids enclose 30% probability.

methoxy methyl and the platinum coordination center is present in **1**.

As expected, the two iminoether molecules are nearly perpendicular to the coordination plane (dihedral angle between the plane defined by the coordination square atoms (plane 2) and the plane of the iminoether ligands (plane 1) of 95.3(5)°).

Weak intermolecular interactions could be found between N(1) and Cl(1) ($-x + 1, -y, -z$) (contact distance 3.469(6) Å), between O(1) and C(3) ($-x + 1, -y - 1, -z + 1$) (contact distance 3.505(7) Å), and between Cl(1) and several methyl groups from the *tert*-butyl group (contact distances in the range 3.75(1)–4.00(1) Å).

X-ray Crystallography of *trans*-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu^t}₂], **2.** The complex molecule is represented in Figure 6, and selected geometrical parameters are listed in Tables 2 and 3. The coordination sphere arrangement can be described as pseudooctahedral with the two nitrogen atoms from the iminoether ligands occupying the axial positions and the four chloride ligands occupying the equatorial sites.

The Pt-Cl (average, 2.316(1) Å) and Pt-N (2.044(4) Å) bond lengths are not significantly longer than those found for **1** and for other Pt(II) iminoether complexes.

Some bond angles, within the coordination sphere, deviate significantly from the idealized value of 90°. Two angles are particularly large (95.7(1) and 96.5(1)° for N(1)-Pt-Cl(1) and N(1)-Pt-Cl(2) ($-x + 1, -y, -z$), respectively), and two are particularly small (83.5(1) and 84.3(1)° for N(1)-Pt-Cl(2) and N(1)-Pt-Cl(1) ($-x + 1, -y, -z$), respectively). The largest angles involve the nitrogen atom and the two chloride ligands which are *syn* with respect to the O-Me group. This indicates a relevant steric interaction between the methoxy group and the chloride ligands close to it (intramolecular C(6)···Cl contact distances of 3.335(6) and 3.376(6) Å for Cl(1) and Cl(2), respectively).

(20) Bondi, A. J. *Phys. Chem.* **1964**, 68, 441.

The N(1), C(1), C(2), and O(1) atoms of the iminoether ligands are coplanar within $\pm 0.008(3)$ Å (plane 1), and as already observed for the platinum(II) complex, the Pt and C(6) atoms deviate significantly (although less than in complex **1**) from the least-squares iminoether plane (displacements of Pt and C(6) from plane 1 of $-0.337(1)$ and $0.243(3)$ Å, respectively). The dramatic increase of interligand steric interaction on passing from 4-coordinate platinum(II) to 6-coordinate platinum(IV) is revealed by the Pt–N(1)–C(1) ($147.3(4)^\circ$), N(1)–C(1)–O(1) ($129.0(5)^\circ$), and C(1)–O(1)–C(6) ($127.1(5)^\circ$) bond angles which are greater by 14, 5, and 6° , respectively, than corresponding values for complex **1** (see Table 3).

The iminoether plane (plane 1) is almost staggered with respect to the Pt–Cl bonds (Cl(1)–Pt–N(1)–C(1) torsion angle of $28.0(5)^\circ$) so that the interligand steric repulsions are minimized.

Weak intermolecular interactions involve the Cl(1) atom and the methyl groups C(5) ($-x + 1, y + 0.5, -z + 0.5$) and C(6) ($x, -y - 0.5, z + 0.5$) (contact distances 3.771(7) and 3.891(7) Å, respectively) and the O(1) atom and the methyl group C(6) ($-x + 1, -y + 1, -z$) (contact distance 3.831(7) Å).

Conclusions

The conditions for the stabilization of the *Z* configuration in complexed iminoether ligands have been found. Since in the planar Pt(H)N=C(OR')R moiety more sterically demanding substituents will tend to go *trans* to one another with respect to the C=N double bond, a R radical (Bu') larger than R' (Me) will go preferentially *trans* to platinum as found in the *Z* configuration. In the iminoether ligands the oxygen atoms gets involved in electron delocalization with the C=N π system; as a consequence, not only the oxygen atom but also the R' radical is forced to be coplanar with the azomethene moiety. In principle the R' group could be either *syn* or *anti* to R; however only the latter conformation has been found both in 4-coordinate platinum(II) and 6-coordinate platinum(IV) complexes.

The X-ray structures (the first for an iminoether complex with *Z* configuration) has shown that the terminal atoms in the sequence Pt–N–C–O–C (all five atoms being nearly coplanar and *gauche* to one-another) come very close to one another. The steric clash is released by an increase of the Pt–N–C, N–C–O, and C–O–C angles (respectively 133, 124, and 121° in the case of platinum(II) and 147, 129, and 127° in the case of platinum(IV)) which are well above the expected values (120° for Pt–N–C and N–C–O and less than 120° for C–O–C). In the case of the C–O–C bond angle a value smaller than 120° is expected and, indeed, has been observed in iminoether complexes with *E* configuration, because of the repulsion exerted by the lone pair of electrons on the oxygen atom. In the case of platinum(II) the smaller increase of bond angles (as compared to the platinum(IV) case) is compensated by greater values of Pt–N–C (27°) and N–C–O–C (13°) torsion angles.

The reactivity of the Pt(IV) complex (**2**) toward a base (KOH), an acid (HCl), and a phosphine ligand (PPh₃) has

been investigated. Both the acid and the base favor the displacement of the strained iminoether ligand. Such a displacement is most probably promoted by an interaction of either the base or the acid with the ligand moiety, resulting in a weakening of the coordinative bond with platinum. The reaction with phosphine leads to fast reduction of the platinum(IV) species (**2**) to the corresponding platinum(II) complex (**1**). The reaction of the platinum(II) species with excess phosphine leads to the displacement of the iminoether ligands. This latter reaction can be of synthetic utility in case the iminoethers are used as synthons for further organic transformations. It is interesting to note that the reaction with a stoichiometric amount of PPh₃ can lead to the formation of mixed phosphine–iminoether platinum(II) species; this latter reaction can also be of synthetic utility.

Experimental Section

Starting Materials. Commercial reagent grade chemicals were used without further purification. The complex *trans*-[PtCl₂-(NCBu')₂] was prepared by the reported procedure.²¹

Preparations. *trans*-[PtCl₂{Z-HN=C(OMe)Bu'}₂], **1**. The procedure was similar to that described for the preparation of similar compounds in ref 13. *trans*-[PtCl₂(NCBu')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; meanwhile a yellow solid separated out. This was collected by filtration of the mother liquor, washed with methanol, and dried. Yield: 65%. Anal. Calcd for C₁₂H₂₆Cl₂N₂O₂Pt (**1**): C, 29.0; H, 5.3; N, 5.6. Found: C, 29.3; H, 5.3; N, 5.5. ¹H NMR in CDCl₃ (δ): 1.17 (s, 9H, CBU'), 5.08 (s, 3H, OMe), 6.70 (s, br, 1H, NH).

trans-[PtCl₂{Z-HN=C(OMe)Bu'}₂], **2**. *trans*-[PtCl₂{Z-HN=C(OMe)Bu'}₂] (0.063 g, 0.127 mmol) dissolved in 2 mL of CHCl₃ was treated with a saturated solution of chlorine in carbon tetrachloride (3 mL). A layer of hexane was placed on the reaction solution and the reaction vessel left standing at room temperature overnight. Yellow crystals of the desired product were formed. Evaporation of the mother liquor under reduced pressure allowed the recovery of a further crop of the desired product. Yield: 90%. Anal. Calcd for C₁₂H₂₆Cl₄N₂O₂Pt (**2**): C, 25.4; H, 4.6; N, 4.9. Found: C, 25.5; H, 4.7; N, 4.9. ¹H NMR in CDCl₃ (δ): 1.30 (s, 9H, CBU'), 4.54 (s, 3H, OMe), 7.64 (s, br, 1H, NH).

trans-[PtCl{Z-HN=C(OMe)Bu'}₂(PPh₃)]Cl. A chloroform solution (30 mL) of **1** (0.52 g, 1.01 mmol) was treated with PPh₃ (0.32 g, 1.2 mmol) and stirred at room temperature for 15 min. The colorless solution was then covered with a supernatant layer of hexane (300 mL) and left on standing 4 h at 4 °C. The formed white precipitate was recovered by filtration of the mother liquor. Yield: 80%. Anal. Calcd for C₆₁H₈₃N₄O₄P₂Cl₇Pt₂ ([PtCl{Z-HN=C(OMe)Bu'}₂(PPh₃)]Cl·1/2CHCl₃): C, 44.7; H, 5.1; N, 3.4. Found: C, 44.3; H, 5.0; N, 3.3. ¹H NMR in CDCl₃ (δ): 0.87 (s, 18H, CBU'), 4.86 (s, 6H, OMe), 7.98 (s, br, 2H, NH), 7.50 (m, 9H, *meta* + *para* PPh), 7.86 (d, 6H, *ortho* PPh).

cis-[PtCl₂{Z-HN=C(OMe)Bu'}₂(PPh₃)], *trans*-[PtCl{Z-HN=C(OMe)Bu'}₂(PPh₃)]Cl (0.35 g, 0.46 mmol) was dissolved in CHCl₃ (50 mL) and the solution kept for 4 h at 55 °C. After cooling, the solution was covered with a supernatant layer of hexane (500 mL) and left on standing at 4 °C overnight. The resulting white

(21) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Am. Chem. Soc.* **1993**, *115*, 5123.

crystalline solid was collected by filtration of the mother liquor, washed with hexane, and dried in a stream of dry air. Yield: 80%. Anal. Calcd for $C_{24}H_{28}NOCl_2Pt$: C, 44.8; H, 4.4; N, 2.2. Found: C, 45.1; H, 4.4; N, 2.0. 1H NMR in $CDCl_3$ (δ): 0.80 (s, 9H, *CBu'*), 4.85 (s, 3H, *OMe*), 6.09 (s, br, 1H, *NH*), 7.44 (m, 9H, *meta* + *para* PPh), 7.76 (m, 6H, *ortho* PPh).

cis-[PtCl₂(PPh₃)₂], trans-[PtCl₂{Z-HN=C(OMe)Bu'}₂] (0.06 g, 0.12 mmol) and an excess of PPh₃ (0.15 g, 0.6 mmol) were dissolved in $CHCl_3$ (20 mL), and the solution was kept under stirring for 20 h at room temperature. After evaporation of the solvent under reduced pressure, the white residue was transferred on a filter, washed carefully with diethyl ether (which removes excess PPh₃), and dried in a stream of dry air. Yield: 80%. Anal. Calcd for $C_{36}H_{30}Cl_2P_2Pt$: C, 54.7; H, 3.8. Found: C, 54.7; H, 3.9. 1H NMR in CD_2Cl_2 (δ): 7.48 (m, 2H, *ortho* PPh), 7.21 (m, 2H, *meta* PPh) 7.37 (m, 1H, *para* PPh). The *cis* configuration of the compound was deduced on the basis of spectral features already reported for this compound^{22,23}.

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 a Perkin-Elmer FT 1600 spectrophotometer. 1H NMR spectra were obtained with a Bruker Avance DPX 300WB spectrometer.

X-ray Structure Determinations. **trans-[Pt^{II}Cl₂{Z-HN=C(OMe)Bu'}₂], 1. (a) Data Collection.** A pale yellow prism of **1** (dimensions 0.10 × 0.15 × 0.20 mm) was selected at the polarizing microscope and mounted on a glass fiber. The diffraction data were collected through a four-circle automatic Siemens P4 diffractometer, by using graphite-monochromatized Mo K α radiation (λ , 0.710 73 Å). The cell constants (see Table 1) were determined via full-matrix least-squares refinement of the values of 26 carefully centered randomly selected reflections in the range $11^\circ \leq 2\theta \leq 42^\circ$. The data were collected at 293 ± 2 K and then corrected for Lorentz–polarization and absorption effects (ψ -scan technique). The independent observed reflections ($I > 2\sigma(I)$) were 1369 out of a total of 1636 collected reflections ($[R(int) = 0.0130]$). The space group ($C2/m$, No. 12) is in agreement with the systematic extinctions and with the structure solution and refinement (see below). Three standard reflections were monitored periodically (97 reflections) during the data collection; no appreciable decay was observed.

(b) Structure Solution and Refinement. The structure was solved through the Patterson and Fourier techniques. The Pt atom is located on a mirror plane and on a 2-fold crystallographic axis, whereas the chlorine atom is located on the mirror plane. All the other atoms are located in general position. As a consequence, the structure is disordered as regard to the iminoether ligands. The occupancy of atoms N(1), C(1), C(2), O(1), and C(6) was fixed to 0.5. Two sets of three peaks each was generated by the Fourier-difference synthesis around C(2). This was interpreted as a further statistical disorder of the *tert*-butyl group. The two sets of peaks were assigned as carbon atoms (namely, C(3), C(4), and C(5) and C(3A), C(4A), and C(5A)) at the occupancy of 0.25 each. All the non-hydrogen atoms were treated as anisotropic during the subsequent 12 cycles of least-squares refinement. The Fourier-difference synthesis performed at this stage showed a low intensity new peak, close to the N(1) atom. This peak was assigned to a hydrogen atom linked to N(1), and its position was refined freely in the subsequent

least-squares cycles. The hydrogen atoms for the methyl groups were located in computed positions and allowed to ride on the carbon atoms to which they are linked. All the hydrogen atoms were refined isotropically, and their thermal parameters were restrained to 1.2 times those ($U(eq)$) of the atoms to which they are bound. The agreement factors converged to $R_1 = 0.0160$ and $wR_2 = 0.0400$ over the independent observed reflections with $I > 2\sigma(I)$.

All the calculations were carried out using XSCANS,²⁴ XEMP,²⁵ SHELXS 97,²⁶ SHELXL 97,²⁷ PARST 97,²⁸ PLATON 98,²⁹ XPM-A-ZORTEP,³⁰ and ORTEP 3³¹ computer programs implemented on Pentium machines.

trans-[Pt^{IV}Cl₄{Z-HN=C(OMe)Bu'}₂], 2. (a) Data Collection. A yellow prism of **2** (dimensions 0.10 × 0.15 × 0.20 mm) was used for the X-ray analysis through the techniques and the devices already reported above for **1**. The cell constants (see Table 1) were determined from the values of 42 carefully centered randomly selected reflections in the range $11^\circ \leq 2\theta \leq 44^\circ$. The data were collected at 293 ± 2 K and then corrected for Lorentz–polarization and absorption effects (ψ -scan technique). The independent observed reflections ($I > 2\sigma(I)$) were 1445 out of a total of 2334 collected reflections ($R(int) = 0.0345$). The space group ($P2_1/c$, No. 14) is in agreement with the systematic extinctions and with the structure solution and refinement (see below). Three standard reflections were monitored periodically (97 reflections) during the data collection; no appreciable decay was observed.

(b) Structure Solution and Refinement. The structure was solved through the Patterson and Fourier techniques. The Pt atom is located on an inversion center. Two chloride ligands and a Z-HN=C(OMe)Bu' ligand, which complete the asymmetric unit, are in general positions. As a consequence the structure of the complex molecule is pseudooctahedral. All the non-hydrogen atoms were treated as anisotropic during the subsequent 12 cycles of least-squares refinement. All the hydrogen atoms for the Z-HN=C(OMe)-Bu' group were located in computed positions, allowed to ride on the atoms to which they are linked, and refined isotropically. The agreement factors converged to $R_1 = 0.0274$ and $wR_2 = 0.0714$ over the independent observed reflections with $I > 2\sigma(I)$.

All the calculations were carried out using the packages and machines described above for **1**.

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(22) Gillard, R. D.; Pilbrow, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2320.

(23) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Helv. Chim. Acta* **1980**, 63, 2519.

(24) *XSCANS Users Manual*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(25) *Xemp Empirical Absorption Correction Program*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(26) Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(27) Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(28) Nardelli, M. *PARST 97, A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analyses*; University of Parma: Parma, Italy, 1997.

(29) Spek, A. L. *PLATON 98*; Utrecht University: Utrecht, The Netherlands, 1998. Windows Implementation by L. J. Farrugia, University of Glasgow, 1998.

(30) Zsolnai, L. *XPM-A-ZORTEP 98*; University of Heidelberg: Heidelberg, Germany, 1998.

(31) Johnson, C. K.; Burnett, M. N. *ORTEP-3 for Windows*; Oak Ridge National Laboratory: Oak Ridge, TN, 1998. 32-bit Implementation by L. J. Farrugia, University of Glasgow.

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Supporting Information Available: X-ray crystallographic files, in CIF format and listings of positional and thermal parameters

and some metrical parameters which do not appear in the text. This material is available free of charge via Internet at <http://pubs.acs.org>.

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