Synthesis and X-ray Structural Characterization of Two Unbridged Diplatinum(III) Compounds: *cis-* and *trans*-Bis[bis(1-imino-1-methoxyethane)trichloroplatinum(III)]. Transient Species in the Oxidation of Platinum(II) to Platinum(IV)

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Abstract: Unbridged Pt[III] dimers, *cis-* and *trans*-[PtCl$_3$L$_2$]$_2$ (L = (*E*)-HN═C(OMe)Me, *cis*-**2** and *trans*-**2**), are formed, as transient species, in the oxidation with excess chlorine of the Pt[II] compounds *cis-* and *trans*-[PtCl$_2$L$_2$] (*cis*-**1** and *trans*-**1**) to the corresponding Pt[IV] species, *cis-* and *trans*-[PtCl$_4$L$_2$] (*cis*-**3** and *trans*-**3**). Complexes *cis*-**2** and *trans*-**2** are rather stable at low temperature (<0 and −20 °C for *cis*-**2** and *trans*-**2**, respectively), while at higher temperature (20 °C) they readily oxidize to Pt[IV] ($\tau_{1/2}$ = 80 and 5 min for *cis*-**2** and *trans*-**2**, respectively). The structures of the Pt[III] species have been solved by single-crystal X-ray diffraction. The compounds are neutral dimers composed of two square-planar PtCl$_2$L$_2$ units perpendicularly connected by a Pt−Pt bond and capped by axially coordinated chloride ligands. Bond distances and angles within the equatorial PtCl$_2$L$_2$ units are normal. The axial Pt−Cl bond lengths are *ca.* 0.14 Å longer than the equatorial ones, indicating a strong trans influence of the intermetallic bond. The intermetallic bond distances are typical of either unbridged or pyrophosphite four-bridged Pt[III] dimers, while they are much longer than those found in other Pt[III] complexes with either two (>0.10 Å) or four bridging ligands (>0.20 Å). In *cis*-**2**, the iminoether ligands are in equivalent pairs, and a 90° rotation of one platinum subunit with respect to the other about the Pt−Pt vector interchanges the ligand positions and converts the complex into its enantiomeric form. Both enantiomers are found in the crystal and in solution, where a ΔG^* of 16.9 ± 0.2 kcal mol^{-1} was calculated for the interconversion process (^{1}H NMR). The formation of intermediate Pt[III] dimers appears to be a relatively common, although overlooked, feature of platinum chemistry. The oxidation of Pt[II] to Pt[IV] requires the removal of two electrons by the oxidant (an acid), assisted by a ligand (a base) entering the coordination sphere from the opposite side. A second Pt[II] unit can act as a base contributing two d$_{z^2}$ electrons and binding face-to-face from the axial direction. The resulting dimer completes the coordination sphere of the adjoined platinum unit by binding an extra ligand.

Introduction

Interest in Pt[III] chemistry[1] arises from the occurrence of mixed-valence, one-dimensional materials[2] and from the participation of Pt[III] in Pt[II]/Pt[IV] redox processes[3] and in the photocatalytic activation of C−H and C−X bonds.[4]

Monomeric Pt[III] has an unpaired electron and only a few complexes of this type have been reported.[5] Well-documented

examples are [PtR$_4$]$^-$ (R = C$_6$Cl$_5$ and C$_6$F$_5$),[5a,b] [Pt(diphenyl-gliossimato)$_2$]$^+$,[5c] [Pt(1,8-diamino-3,6,10,13,16,19-hexaazabicyclo-[6,6,6]icosane)]$^{3+}$,[5d] and [Pt(1,4,7-trithiacyclononane)$_2$]$^{3+}$.[5e] In all cases, the ability of the ligands (often macrocycles) to shield the metal center appeared to be crucial for stabilizing such otherwise unstable compounds.

In contrast, several binuclear Pt[III] compounds containing a metal−metal bond, supported by two or four bridging ligands, have been characterized.[1,6] The Pt[II] precursors already were dimers with two face-to-face platinum units with only one axial position per platinum atom open to attack by the oxidant.

Only recently have Pt[III] dimers, unsupported by covalent bridging ligands, been discovered.[7,8] In these cases, there was neither shielding of the Pt[II] metal center nor close association of two Pt[II] units in a dimer.

(1) Umakoshi, K.; Sasaki, Y. *Adv. Inorg. Chem.* **1994,** *40,* 187. Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989,** *22,* 55. Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms;* Wiley: New York, 1982. Zipp, A. P. *Coord. Chem. Rev.* **1988,** *84,* 47. Woollins, J. D.; Kelly, P. F. *Coord. Chem. Rev.* **1985,** *65,* 115. O'Halloran, T. V.; Lippard, S. J. *Isr. J. Chem.* **1985,** *25,* 130.

(2) Renn, O.; Albinati, A.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 84. Kurmoo, M.; Clark, R. J. H. *Inorg. Chem.* **1985,** *24,* 4420.

(3) Glennon, C. S.; Hand, T. D.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1980,** 19. Gupta, K. K. S.; Sen, P. K.; Gupta, S. S. *Inorg. Chem.* **1977,** *16,* 1396. Halpern, J.; Pribanic, M. *J. Am. Chem. Soc.* **1968,** *90,* 5942.

(4) Chan, C. V.; Cheng, L. K.; Che, C. M. *Coord. Chem. Rev.* **1994,** *114,* 87.

(5) (a) Forniés, J.; Menjon, B.; Sanz-Carrillo R. M.; Tomas, M.; Connelly, N. G.; Crossley, J. G.; Orpen, A. G. *J. Am. Chem. Soc.* **1995,** *117,* 4295. (b) Uson, R.; Forniés, J.; Tomas, M.; Menjon, B.; Sunkel, K.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1984,** 751. (c) Endres, H.; Keller H. J.; van de Sand, H.; Dong, V. Z. *Naturforsch. B* **1978,** *33,* 843. (d) Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983,** *105,* 4652. (e) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Lavery, A. J.; Odulate, M. O.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1987,** 118.
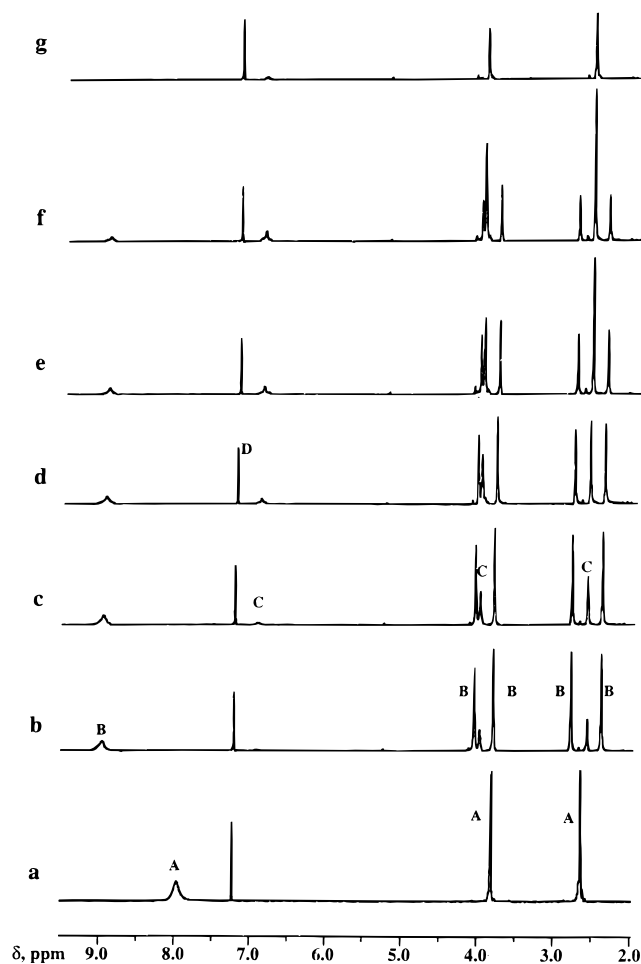
In this paper, we describe two new binuclear complexes featuring an unsupported $Pt^{III}-Pt^{III}$ bond. Both complexes have been characterized by single-crystal X-ray diffraction and solution measurements.

The Pt^{II} precursors were platinum complexes with iminoether ligands, $[PtCl_2\{HN=C(OMe)R\}_2]$. These complexes are prepared by reaction of the corresponding nitrile complexes, $[PtCl_2(N\equiv CR)_2]$, with methanol under basic conditions. The iminoether ligands can have either E or Z configuration, depending upon the relative position of the methoxy and platinum residues with respect to the C=N double bond (Z and E configurations for cis and trans positions, respectively).[9,10] The Z isomer is kinetically preferred and corresponds to the trans addition of the alcohol to the C≡N triple bond. Subsequently, Z-to-E isomerization can take place. The thermodynamic stability of the Z isomer decreases, as a function of the nitrile R group, in the order Bu^t > Ph > Et > Me. Therefore, the Z isomer remains stable only for R = Bu^t, while for R = Ph an equilibrium is reached with the two isomers present in comparable concentrations; finally, for R = Et or Me the transformation into the E isomer is complete. The X-ray structures of *cis*- and *trans*-$[PtCl_2\{(E)-HN=C(OMe)Me\}_2]$ showed a "quasiplanarity" of the iminoether moiety with electron charge delocalization over the N···C···O moiety. As a consequence, all the groups attached to the N···C···O skeleton, comprising the O-bonded Me group, share the same plane and can cause considerable intramolecular steric strain. Thus, the methoxy group will prefer the position trans to platinum (E isomer) except in the case of competition with the very bulky Bu^t group.[11]

These platinum iminoether compounds were found to have interesting biological properties that prompted us to extend the investigation to the corresponding oxidized Pt^{IV} species: *cis*- and *trans*-$[PtCl_4\{(E)-HN=C(OMe)Me\}_2]$.[12,13]

Results

The Oxidation Reaction. The oxidation of the Pt^{II} species, *cis*- and *trans*-$[PtCl_2\{(E)-HN=C(OMe)Me\}_2]$ (*cis*- and *trans*-

(6) Matsumoto, K.; Harashima, K. *Inorg. Chem.* **1991**, *30*, 3032. Peterson, E. S.; Bancroft, D. P.; Min, D.; Cotton, F. A.; Abbott, E. H. *Inorg. Chem.* **1990**, *29*, 229. Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 1633. Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763. Lippert, B.; Schöllhorn, H.; Thewalt, U. *Inorg. Chem.* **1986**, *25*, 407. Goodgame, D. M. L.; Rollins, R. W.; Skapski, A. C. *Inorg. Chim. Acta* **1984**, *83*, L11. Hollis, L. S.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 3637. Conder, H. L.; Cotton, F. A.; Falvello R. L.; Han, S.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1887. Bellitto, C.; Flamini, A.; Gastaldi, L.; Scaramuzza, L. *Inorg. Chem.* **1983**, *22*, 444. Che, C. M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253. Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709. Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897.

(7) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Am. Chem. Soc.* **1991**, *113*, 7805.

(8) (a) Baxter, L. A. M.; Heath, G. A.; Raptis, R. G.; Willis, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6944. (b) Prenzler, P. D.; Heath, G. A.; Lee, S. B.; Raptis, R. G. *J. Chem. Soc., Chem. Commun.* **1996**, 2271.
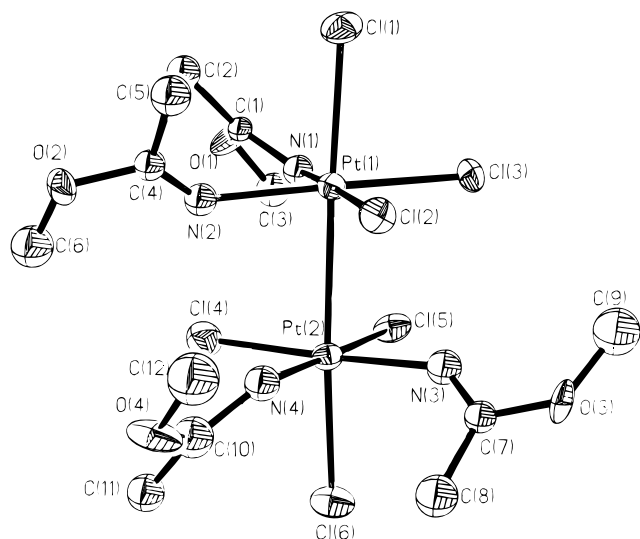
(9) Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947.

(10) Lopez, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Martì, J. M.; Hermoso, J. A.; Vegas, A.; Martinez-Ripoli, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.
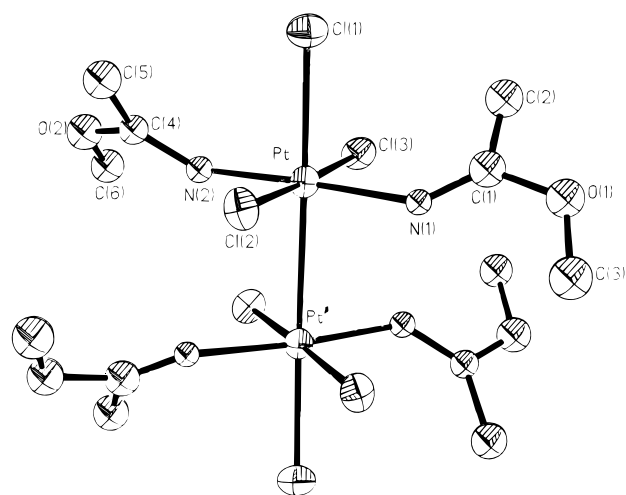
(11) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130.

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

(13) Substitution of iminoether for ammines has the effect of reversing the activity of *cis*- and *trans*-platinum complexes. Thus, the iminoether complex *trans*-$[PtCl_2\{(E)-HN=C(OMe)Me\}_2]$ shows the greatest *in vitro* cytotoxicity and *in vivo* antitumor activity, equivalent to or even greater than that of *cis*-$[PtCl_2(NH_3)_2]$.

Figure 1. ^{1}H NMR spectra as a function of time for *cis*-$[PtCl_2\{(E)$-HN=C(OMe)Me$\}_2]$ (*cis*-**1**) dissolved in deuteriochloroform (5 mg in 0.5 mL of solvent) and treated with excess Cl_2 (0.2 mL of a solution 1 M in CCl_4), temperature 25 °C. (a) Spectrum of starting *cis*-**1**; (b−g) spectra at 4, 16, 48, 80, 124, and 500 min after the addition of Cl_2, respectively. **A**, **B**, **C**, and **D** mark the resonance peaks of the Pt^{II} (*cis*-**1**), Pt^{III} (*cis*-**2**), Pt^{IV} (*cis*-**3**), and $CHCl_3$ species, respectively. Partial precipitation of *cis*-**3** is responsible for the lower intensity of the resonance peaks in spectrum g.

1), to the corresponding Pt^{IV} species, *cis*- and *trans*-$[PtCl_4\{(E)$-HN=C(OMe)Me$\}_2]$ (*cis*-**3** and *trans*-**3**), proved to be a non-single-step process. Thus, the initially yellow solution (CH_2Cl_2) of the Pt^{II} species, after addition of excess Cl_2 (CCl_4 solution), turns first red and then yellow again (Figure 1). The intermediate Pt^{III} species can be trapped by performing the reaction at low temperature (0 and −20 °C for *cis*-**2** and *trans*-**2**, respectively) in the dark (the yield is nearly quantitative in the case of *cis*-**2** and *ca.* 50% in the case of *trans*-**2**, where some Pt^{IV} species is also formed). They were crystallized from CH_2Cl_2 solution layered under benzene (at 0 °C for *cis*-**2** and at −20 °C for *trans*-**2**, in the dark) to give orange-red (*cis*-**2**) and red crystals (*trans*-**2**).

Compounds **2** readily disproportionate into **1** and **3** (at room temperature, the disproportionation reaction is complete in the time of dissolution, even for the more stable *cis*-**2**). The Pt^{III} species gain stability in the presence of excess oxidant ($\tau_{1/2}$, for the oxidation to the Pt^{IV} species in the presence of 50 mM Cl_2, of 80 and 5 min for *cis*-**2** and *trans*-**2**, respectively); however, exposure to the light must be avoided, otherwise immediate oxidation to the corresponding Pt^{IV} species takes place (photochemical activation is a standard method for enhancing the reactivity of molecular chlorine).[14,15]

Figure 2. ORTEP view of *cis*-[PtCl₃{(*E*)-HN=C(OMe)Me}₂]₂ (*cis*-**2**) showing the atom labeling scheme. The thermal ellipsoids are drawn at 40% probability. The benzene molecule of solvation has been omitted for clarity.

Figure 3. ORTEP view of *trans*-[PtCl₃{(*E*)-HN=C(OMe)Me}₂]₂ (*trans*-**2**) showing the atom labeling scheme. The thermal ellipsoids are drawn at 40% probability. The benzene molecule of solvation has been omitted for clarity.

X-ray Structures. The molecular structures of *cis*-**2** and *trans*-**2** from crystal structure analyses are shown in Figures 2 and 3, respectively; selected bond distances and angles are given in Table 2. The compounds are neutral dimers composed of two planar PtCl₂L₂ units perpendicularly connected by a Pt—Pt bond and capped by axially coordinated chloride ligands. The two PtCl₂L₂ units are crystallographically independent in *cis*-**2** and related by a twofold symmetry axis that bisects the Pt—Pt′ bond in *trans*-**2**.

The iminoether ligands have the expected *E* configuration and geometrical parameters similar to those found in the corresponding Pt^{II} species, with extensive electron charge delocalization over the N···C···O moiety and "quasi planarity" of all non-hydrogen atoms (within 0.02 and 0.04 Å for *cis*-**2** and *trans*-**2**, respectively).[11] The Pt atom lies in the plane of the ligand. The C—Me groups extend toward the apical chloride

Table 1. ¹H NMR Data (δ, Downfield from SiMe₄; CDCl₃ Solvent) for the Pt^{II}, Pt^{III}, and Pt^{IV} Iminoether [L, (*E*)-HN=C(OMe)Me] Complexes

compound	NH	OMe	CMe
cis-[PtCl₂L₂] (*cis*-**1**)	7.97	3.82	2.65
cis-[PtCl₃L₂]₂ (*cis*-**2**)	8.96[a]	4.06, 3.82	2.82, 2.42
cis-[PtCl₄L₂] (*cis*-**3**)	6.89	3.96	2.59
trans-[PtCl₂L₂] (*trans*-**1**)	7.40	3.77	2.64
trans-[PtCl₃L₂]₂ (*trans*-**2**)	8.76	3.91	2.67
trans-[PtCl₄L₂] (*trans*-**3**)	6.96	3.99	2.70

[a] Broad signal which at lower temperature splits into two peaks separated by 0.05 ppm.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-**2**·C₆H₆ and *trans*-**2**·C₆H₆

		cis-**2**·C₆H₆	
Pt(1)—Pt(2)	2.765(2)	Pt(2)—Pt(1)—Cl(1)	178.0(2)
Pt(1)—Cl(1)	2.474(7)	Pt(2)—Pt(1)—Cl(2)	90.8(2)
Pt(1)—Cl(2)	2.328(7)	Pt(2)—Pt(1)—Cl(3)	91.7(2)
Pt(1)—Cl(3)	2.330(7)	Pt(2)—Pt(1)—N(1)	86.8(6)
Pt(1)—N(1)	1.98(2)	Pt(2)—Pt(1)—N(2)	86.8(6)
Pt(1)—N(2)	2.09(2)	Pt(1)—Pt(2)—Cl(4)	91.5(2)
Pt(2)—Cl(4)	2.331(8)	Pt(1)—Pt(2)—Cl(5)	91.8(2)
Pt(2)—Cl(5)	2.323(7)	Pt(1)—Pt(2)—Cl(6)	176.4(2)
Pt(2)—Cl(6)	2.465(7)	Pt(1)—Pt(2)—N(3)	86.2(6)
Pt(2)—N(3)	2.03(2)	Pt(1)—Pt(2)—N(4)	87.1(6)
Pt(2)—N(4)	2.04(2)	Cl(2)—Pt(1)—Cl(3)	91.0(2)
		N(1)—Pt(1)—N(2)	89.8(8)
		Cl(4)—Pt(2)—Cl(5)	89.1(3)
		N(3)—Pt(2)—N(4)	91.8(9)
		trans-**2**·C₆H₆	
Pt—Pt′ [a]	2.758(3)	Pt′—Pt—Cl(1)	178.6(2)
Pt—Cl(1)	2.450(6)	Pt′—Pt—Cl(2)	91.3(2)
Pt—Cl(2)	2.307(6)	Pt′—Pt—Cl(3)	91.2(2)
Pt—Cl(3)	2.322(6)	Pt′—Pt—N(1)	88.1(4)
Pt—N(1)	2.02(2)	Pt′—Pt—N(2)	88.3(4)
Pt—N(2)	2.04(2)	Cl(2)—Pt—Cl(3)	177.5(2)
		N(1)—Pt—N(2)	175.8(6)

[a] At −*x*, *y*, ½ − *z*.

and may interact with it. In contrast, the O—Me groups are directed toward the twin subunit and may contribute to the steric repulsion between twin subunits.

Each equatorial PtCl₂N₂ moiety is approximately planar (within 0.02 and 0.06 Å for *cis*-**2** and *trans*-**2**, respectively), with angles between cis ligands deviating from 90° by less than 2° (*cis*-**2**) and 5° (*trans*-**2**). The Pt—N distances [within 1.98-(2) and 2.09(2) Å] are in the range of those reported for square-planar Pt^{II} and octahedral Pt^{IV} complexes.[11,16] Also, the Pt—Cl_{eq} distances [within 2.31(1) and 2.33(1) Å] are comparable to those found in K₂[PtCl₄] and K₂[PtCl₆] [2.316(2)[17] and 2.323-(1) Å,[18] respectively].

The axial Pt—Cl bond lengths [2.474(7) and 2.465(7) Å for *cis*-**2**, 2.450(6) Å for *trans*-**2**] are similar to the value of 2.458-(3) Å found in [Pt^{III}Cl₃{(*Z*)-HN=C(OH)Bu^t}₂]₂ (**4**)[7] but longer than those reported for [Pt^{III}Cl{C(=NOH)C(=NO)(CH₂)₅CH₂}₂]₂ (**5**) [2.386(2) and 2.409(2) Å],[8a] indicating that, in **2** and **4**, there are unfavorable steric interactions between the axial chlorides and the ligand arms (C—Me and C—OH, respectively) protruding toward them. The much longer Pt—Cl_{ax} distances, as compared to Pt—Cl_{eq}, are indicative of a strong trans influence exerted by the Pt^{III}—Pt^{III} bond.

(14) Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Eméleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, 1973; Vol. 2, Chapter 26, pp 1141−1172.

(15) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; Chapter 14.
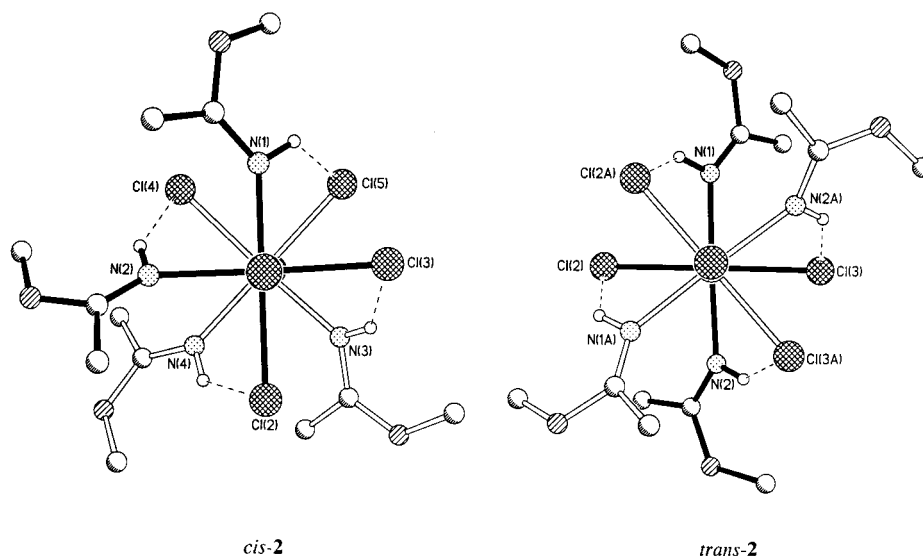
(16) Mais, R. H. B.; Owston, P. G.; Wood, A. M. *Acta Crystallogr.* **1972**, *B28*, 393.

(17) Williams, R. J.; Dillon, D. R.; Milligan, W. O. *Acta Crystallogr.* **1973**, *B29*, 1369.

(18) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers: London, 1973. Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press Inc.: London, 1974.

cis-2　　　　　　　　　　　　　　　　*trans-2*

Figure 4. Crystal structures of *cis*-[PtCl₃{(*E*)-HN=C(OMe)Me}₂]₂ (*cis*-**2**) and *trans*-[PtCl₃{(*E*)-HN=C(OMe)Me}₂]₂ (*trans*-**2**) viewed along the Pt−Pt bond axis. H atoms involved in the N−H···Cl bridges were set in calculated positions, and their ellipsoids have an arbitrary scale.

The Pt^III−Pt^III bond lengths [2.765(2) and 2.758(3) Å for *cis*-**2** and *trans*-**2**, respectively] are greater than the values reported for other metal−metal bonds unsupported by covalent bridges, i.e., 2.694(1) and 2.6964(5) Å for **4**[7] and **5**,[8a] respectively. The difference is significant and rather surprising, particularly in comparison with the strictly related amide complex **4**. The lengthening is unlikely to have an electronic origin and is most probably caused by steric repulsion. In **2**, the O−Me groups are held in fixed positions because of the N···C···O electron delocalization; in contrast, in **4**, the Bu^t groups are free to rotate about the C−Bu^t bond so as to reduce steric interactions between twin subunits.

Four interfacial hydrogen bonds are formed between iminoether ligands and equatorial chlorides of twin subunits. Moreover, in this staggered conformation (Cl−Pt−Pt−N torsion angles close to 45°), the planes of the iminoether ligands are tilted by 41−51°, with respect to the equatorial platinum coordination plane, in such a way as to direct the N-hydrogen toward the closest chloride of the twin subunit (Figure 4). As a result, the H···Cl distances are in the range 2.30−2.50 Å, and the N−H···Cl angles in the range 130−150°.

Although the interfacial H-bonds can contribute to the stability of the Pt^III dimer, they are not expected to influence the intermetallic distance. In fact, the H-bonds between the twin subunits tend to place the dimer in an eclipsed conformation,[19] with the plane of the iminoether ligands perpendicular to the platinum coordination plane and with a greater intermetallic distance, as observed in a Pt^II dimer.[11] Therefore, only the Pt−Pt covalent bond can bring the two subunits close together while allowing a staggered conformation with small interfacial steric interactions.

The different arrangement of the equatorial ligands in *cis*-**2** and *trans*-**2** causes *trans*-**2** to have (i) a larger deviation from planarity of the iminoether ligands, (ii) a more tetrahedral distortion of the PtCl₂N₂ units, (iii) a greater difference in the values of the equatorial N−Pt−Cl angles, and (iv) a more linear Cl_ax−Pt−Pt axis.

¹H NMR. The ¹H NMR spectra contain a peculiar feature: the chemical shift of the iminic protons by *ca.* 1 ppm downfield on going from Pt^II to Pt^III and *ca.* 1 ppm upfield on going from Pt^II to Pt^IV (Table 1). The change in chemical shifts between

the Pt^II and Pt^IV species could be attributed to the anisotropy of the d⁸ metal ion in a square-planar geometry, causing a deshielding of the NH nuclei lying above the coordination plane.[20,21] On the other hand, the chemical shifts of the N−H protons in the Pt^III species were *ca.* 1 and 2 ppm downfield with respect to the corresponding signals in the Pt^II and Pt^IV species, respectively. It is conceivable that such a downfield shift is analogous to the well-known effect of hydrogen bonding on shifts since there are N−H···Cl interactions between twin subunits.

Compound *cis*-**2** admits four conformations (**A**−**D** in Chart 1) and a total of four ¹H NMR signals for each type of equivalent protons [in each conformer, the four iminoether ligands are equivalent in pairs, and the four conformers constitute two couples of enantiomers (**A**−**B** and **C**−**D** in Chart 1)]. However, the NMR spectra showed only two resonances, of equal intensity, for each type of protons (two O−Me and two C−Me resonance signals). This is in accord with the presence of only one couple of enantiomers, most probably **A**−**B**, found in the solid state, for which only two iminoether ligands (one per each platinum subunit) are forced to be close to one another.

A 90° rotation of one platinum subunit with respect to the other about the Pt−Pt vector interchanges the ligand positions and converts one conformer into its enantiomeric form. NMR spectra at higher temperatures showed a broadening of the two O−Me and the two C−Me resonance signals, in accord with an increasingly faster interchange between enantiomers; however, coalescence could not be reached because of compound decomposition. The activation energy for rotation was estimated to be 16.9 ± 0.2 kcal mol⁻¹.

Discussion

Starting from monomeric Pt^II compounds, the dimerization reaction, leading to binuclear Pt^III species, has to take place during the oxidation process. In a simple model, the oxidation of Pt^II to Pt^IV requires the removal of two electrons by the oxidant (an acid), assisted by a ligand (a base) entering the coordination sphere from the opposite side. A second Pt^II unit could act as a base, contributing two d_{z²} electrons and binding

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

(20) Buckingham, A. D.; Stephens, J. P. *J. Chem. Soc.* **1964**, 4583.
(21) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511.

Chart 1

A   B

D   C
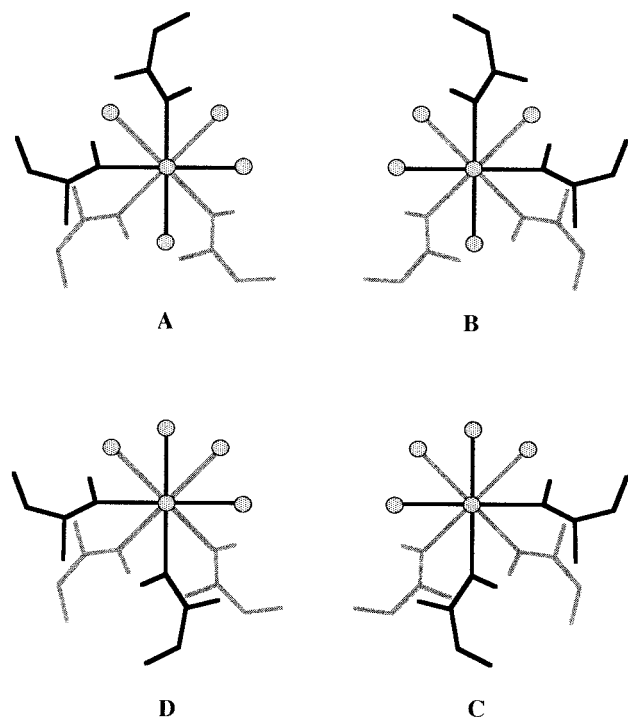
^{a} Conformations **A**, **B**, **C**, and **D** are obtained, in the given order, by 90° clockwise rotation of the upper twin subunit (dark line). Two enantiomeric couples of staggared conformations (**A**–**B** and **C**–**D**) are permitted.

along the axial direction in a face-to-face fashion (Chart 2).[22] The resulting dimer would be a formally Pt^{III} species; this formal oxidation state still requires another ligand to complete the coordination sphere of the adjoined platinum unit. Support for this hypothesis came from the observation that oxidation of *cis*-**1** by Cl$_2$ performed in the presence of a 5-fold excess of Cl$^-$ ion leads directly to formation of the Pt^{IV} species with a negligible amount of the Pt^{III} dimer.

Once formed, the coordinately-saturated dimeric Pt^{III} species is rather inert to further oxidation by excess Cl$_2$ if kept in the dark (in the presence of light, photoreactions with homolytic cleavage of Pt–X, Pt–Pt, and X–X bonds can take place).[14,15,23] Moreover, the presence of excess Cl$_2$ inhibits the disproportionation of the Pt^{III} dimer into monomeric Pt^{II} and Pt^{IV} species. It is conceivable that the disproportionation reaction takes place by reductive elimination of Cl$_2$ with formation of Pt^{II} monomers rather than by heterolytic intramolecular Pt^{III}–Pt^{III} bond cleavage. This elimination mechanism would account for both the stabilizing effect of the excess Cl$_2$ (inhibition of the reductive elimination step) and the formation of the Pt^{IV} species (oxidation of the Pt^{II} monomer from the released Cl$_2$). This hypothesis was tested by performing the reaction between *cis*-**2** and a 4-fold excess (based on platinum atoms) of a Pt^{II} complex containing a different iminoether (*cis*-[PtCl$_2$L$'_2$], L$'$ = (*E*)-HN=C(OEt)-Me). Heterolytic cleavage of the Pt^{III}–Pt^{III} bond would be expected to lead mainly to formation of the Pt^{IV} species *cis*-**3**, while reductive elimination followed by oxidation of a Pt^{II} species by Cl$_2$ would be expected to lead to the formation of a large amount of [PtCl$_4$L$'_2$], since *cis*-[PtCl$_2$L$'_2$] was present in

excess with respect to *cis*-**1**. Indeed, [PtCl$_4$L$'_2$] was the major reaction product, fully supporting the hypothesis. Also, the reduced stability of *cis*-**2** in the presence of excess Cl$_2$ if Cl$^-$ ion was added to the solution is in accord with the Pt^{III} dimer being in equilibrium with Cl$_2$ and Pt^{II} monomers. The Cl$^-$ ion favors the direct oxidation of Pt^{II} to Pt^{IV}. The very long Pt–Cl$_{ax}$ distances, as compared to Pt–Cl$_{eq}$, in the Pt^{III} dimer are also consistent with a facile reductive elimination step.

Interfacial hydrogen bonds can play a role in the early stage of the dimerization process (a type of molecular recognition)[24,25] and in the stabilization of conformers **A** and **B** with respect to **C** and **D** in *cis*-**2** (Chart 1). In fact, **C** and **D** allow only two N–H···Cl H-bonds; moreover, interconversions between **A** and **D** and **B** and **C** require disruption of all four H-bonds. In contrast, H-bonds appear to influence neither the intermetallic distance (they would tend to place the dimer in an eclipsed conformation with longer intermetallic distance) nor the rate of ratcheting back and forth of one platinum unit with respect to the other [interconversion between conformers **A** and **B** (Chart 1) does not require disruption of any of the four interfacial H-bonds present in these two conformations].

In the Pt^{III} species, because of the face-to-face association of the two monomeric units in the dimer, steric factors become important and appear to be responsible for both the lengthening of the Pt–Pt bond and the greater barrier to rotation about this bond of the twin subunits (as measured by ΔG^* for the interconversion of **A**–**B** conformers) observed in *cis*-**2** as compared to **4**.

Conclusions

The two compounds reported here increase to four the number of diplatinum(III) complexes unsupported by covalent bridges which have been structurally characterized. Evidence has also been obtained that the formation of dimeric Pt^{III} species may be a relatively common, although overlooked, feature of platinum chemistry.[26]

The Pt^{III} dimer is formed by attack of a second Pt^{II} unit on the sixth coordination position of a Pt^{II} species undergoing two-electron removal by an oxidant acting on the opposite side of the platinum coordination plane. This reaction could easily apply also to other d^8-ML$_4$ species, as suggested by a recent theoretical investigation.[22]

The Pt^{III} dimer disproportionates to monomeric Pt^{II} and Pt^{IV} species *via* reductive elimination of chlorine, generating Pt^{II} monomers subsequently oxidized to Pt^{IV} by the released chlorine. The facile reductive elimination of chlorine from the Pt^{III} dimer is in accord with the very long Pt^{III}–Cl$_{ax}$ distance (as compared to Pt^{III}–Cl$_{eq}$).

The presence on the Pt^{II} precursor of two ligands capable of donating H-bonds and the other two ligands capable of accepting H-bonds appears to be particularly suitable for promoting the association of two monomers in a dimer. These features could also be useful for the synthesis of monodimensional materials.

(22) In this respect, particularly instructive is a recent theoretical investigation showing that removal of electrons from a dimer made of d^8-ML$_4$ units (M being either Pt^{II} or Rh^I metal centers) steeply increases the intermetallic bond strength (Novoa, J. J.; Aullon, G.; Alemany, P.; Alvarez, S. *J. Am. Chem. Soc.* **1995**, *117*, 7169).

(23) Che, C. M.; Lee, W. M.; Cho, K. C. *J. Am. Chem. Soc.* **1988**, *110*, 5407.

(24) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.

(25) Association, in the solid, of two Pt^{II} units in a dimer has been observed in quite a few cases, in which two platinum ligands were capable of donating a H-bond and the other two ligands were capable of accepting a H-bond. H-donor ligands include ammine (Milburn, G. H. W.; Truter, M. R. *J. Chem. Soc. A* **1966**, 1609), amines (Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chem.* **1988**, *27*, 2422), amides,[19] and iminoethers (Casas, J. M.; Chisholm, M. H.; Sicilia, M. V.; Streib, W. E. *Polyhedron* **1991**, *10*, 1573).

(26) Transient red colors in the Pt^{II}/Cl$_2$ oxidative-addition reaction were noted since the early 1950s, e.g.: Basolo, F.; Bailar, J. C., Jr.; Tarr, B. R. *J. Am. Chem. Soc.* **1950**, *72*, 2433. Kauffman, G. B. *Inorg. Synth.* **1963**, *7*, 236.

Chart 2
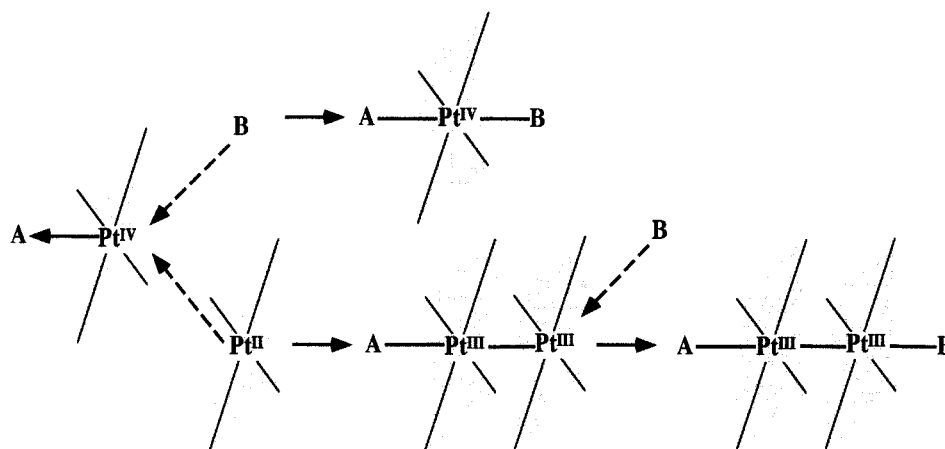
a Competition between a base (**B**) and an extra molecule of Pt^{II} complex for providing a lone pair of electrons to the transient Pt^{IV} species formed by interaction of the Pt^{II} substrate with the oxidant (**A**) leads to formation of either a Pt^{IV} monomer (upper line) or a Pt^{III} dimer (lower line).

Finally, the photolytic cleavage of the intermetallic bond in a Pt^{III} species not supported by covalent bridges, like those reported in this paper, can lead to formation of highly reactive 17-electron metal center radicals which could be useful for the activation of C−H and C−X bonds.

Experimental Section

Starting Materials. Commercial reagent grade chemicals were used without further purification. The complexes *cis-* and *trans-*[PtCl$_2$-(N≡CMe)$_2$] were prepared by the reported procedures.[27]

Preparation of Complexes. *cis-*[PtCl$_2${(*E*)-HN=C(OMe)Me}$_2$] (*cis-*1) and *cis-*[PtCl$_2${(*E*)-HN=C(OEt)Me}$_2$]. The complexes were prepared by the procedure reported in ref 10: yield 55%. Anal. Calcd for C$_6$H$_{14}$Cl$_2$N$_2$O$_2$Pt: C, 17.5; H, 3.4; N, 6.8. Found (*cis-*1): C, 17.6; H, 3.4; N, 6.7. Calcd for C$_8$H$_{18}$Cl$_2$N$_2$O$_2$Pt: C, 21.8; H, 4.1; N, 6.4. Found: C, 21.9; H, 4.1; N, 6.4.

***trans-*[PtCl$_2${(*E*)-HN=C(OMe)Me}$_2$] (*trans-*1).** The complex was prepared by a slightly different procedure than that reported in ref 11. *trans-*[PtCl$_2$(N≡CMe)$_2$] (0.5 g, 1.44 mmol) was suspended in methanol (10 mL) and treated with KOH (0.1 g, 1.8 mmol). After the solution was stirred for 2 h at 20 °C, the yellow solid was collected by filtration of the mother liquor and washed with methanol. The solid was composed mostly of isomer *ZZ* plus a small amount of isomer *EZ*, while the more soluble *EE* isomer of *trans-*1 was left in the mother liquor. The mother liquor was neutralized with 3 M HCl and taken to dryness by evaporation of the solvent; the solid residue was extracted with dichloromethane and the extract taken to dryness by evaporation of the solvent. The solid was composed of the *EE* isomer containing a trace amount of the *EZ* isomer. The final purification was performed on an open column of silica gel using dichloromethane/acetone (8:2 v/v) as eluant. Isomer *EE* of *trans-*1 was eluted in the first fraction. The initially obtained solid fraction (composed mostly of the *ZZ* isomer) could be converted to the *EE* isomer by suspension in methanol (450 mL), acidification of the medium with HCl (0.10 mL of concentrated HCl), and stirring of the slurry for 24 h at 55 °C. The formed yellow solution (containing essentially the soluble *EE* isomer) was filtered, concentrated to small volume, and chromatographed on an open column of silica gel under conditions similar to those described above. The overall yield was 70%. Anal. Found: C, 17.5; H, 3.5; N, 6.8.

***cis-*[Pt$_2$Cl$_6${(*E*)-HN=C(OMe)Me}$_4$] (*cis-*2).** The complex *cis-*[PtCl$_2${(*E*)-HN=C(OMe)Me}$_2$] (*cis-*1, 0.05 g, 0.12 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL), and the solution treated with an excess of Cl$_2$ in CCl$_4$ solution (2 mL of a 0.5 M solution) at 0 °C in the dark. Immediately the solution turned red. An equal volume of benzene was layered on the top of the solution, and the mixture was kept at 0 °C in the dark for a few days; meanwhile, nicely shaped red crystals of *cis-*2 and yellow crystals of *cis-*[PtCl$_4${(*E*)-HN=C(OMe)Me}$_2$] (*cis-*3) sepa-

rated out. The mother liquor was filtered, and crystals of *cis-*2 and *cis-*3 separated mechanically. Anal. Calcd for C$_{12}$H$_{28}$Cl$_6$N$_4$O$_4$Pt$_2$: C, 16.1; H, 3.1; N, 6.3. Found: C, 16.2; H, 3.2; N, 6.2.

***trans-*[Pt$_2$Cl$_6${(*E*)-HN=C(OMe)Me}$_4$] (*trans-*2).** The complex *trans-*[PtCl$_2${(*E*)-HN=C(OMe)Me}$_2$] (*trans-*1, 0.05 g, 0.12 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL), and the solution was cooled to −20 °C. An equal volume of benzene containing an equimolar amount of C$_6$H$_5$-ICl$_2$ was layered on the top of the solution, and the mixture was kept at −20 °C in the dark for a few days; meanwhile, nicely shaped red crystals of *trans-*2 and yellow crystals of *trans-*[PtCl$_4${(*E*)-HN=C-(OMe)Me}$_2$] (*trans-*3) separated out. The mother liquor was filtered, and crystals of *trans-*2 and *trans-*3 were separated mechanically. Anal. Found: C, 16.0; H, 3.2; N, 6.2.

***cis-* and *trans-*[PtCl$_4${(*E*)-HN=C(OMe)Me}$_2$] (*cis-*3 and *trans-*3).** The Pt^{II} complex (either *cis-* or *trans-*1, 0.05 g, 0.12 mmol), was dissolved in CH$_2$Cl$_2$ (5 mL), and the solution was treated with an excess of Cl$_2$ in CCl$_4$ solution (2 mL of a 0.5 M solution). An equal volume of pentane was layered on the top of the solution, and the mixture was kept at 0 °C for a few days; meanwhile, yellow crystals of the Pt^{IV} complex (*cis-*3 and *trans-*3, respectively) separated out: yield 80%. Anal. Calcd for C$_6$H$_{14}$Cl$_4$N$_2$O$_2$Pt: C, 14.9; H, 2.9; N, 5.8. Found (*cis-*3): C, 15.2; H, 3.0; N, 5.8. Found (*trans-*3): C, 15.1; H, 2.9; N, 5.7.

Mechanistic Investigations. Oxidation of Pt^{II} (*cis-*1) by Cl$_2$ in the Presence of Cl$^-$ Ion. A solution of *cis-*1 (2 mg, 4.8 mmol) and (Ph$_4$As)Cl·H$_2$O (10 mg, 23 mmol) in CDCl$_3$ (0.5 mL), placed in a NMR tube, was treated with an excess of Cl$_2$ (100 μL of a 0.5 M solution in CCl$_4$), and the spectrum was monitored immediately after mixing. The Pt^{IV} species *cis-*3 was the major reaction product, while only a trace amount of the Pt^{III} species *cis-*2 could be detected. Under similar conditions, but in the absence of added Cl$^-$ ion, the Pt^{III} species *cis-*2 is formed in over 80% yield.

Effect of Cl$^-$ Ion on the Stability of the Pt^{III} Species (*cis-*2). A solution of *cis-*2 (2 mg, 2.2 mmol) in CDCl$_3$ (0.5 mL), stabilized by the addition of Cl$_2$ (100 μL of a 0.5 M solution in CCl$_4$), was placed in the NMR tube, and the spectrum was monitored. Under these conditions, *cis-*2 is oxidized to Pt^{IV} (*cis-*3) with a $\tau_{1/2}$ of *ca.* 80 min. (Ph$_4$As)Cl·H$_2$0 (10 mg, 23 mmol) was added to the NMR tube, and the spectrum was monitored again. A steep increase of the oxidation rate was observed ($\tau_{1/2}$ of *ca.* 5 min).

Decomposition of Pt^{III} Species (*cis-*2) in the Presence of Another Pt^{II} Complex (*cis-*[PtCl$_2${(*E*)-HN=C(OEt)Me}$_2$]). A solution of *cis-*[PtCl$_2${(*E*)-HN=C(OEt)Me}$_2$] (8 mg, 18 mmol) in CDCl$_3$ (0.5 mL), placed in a NMR tube, was treated with *cis-*2, and the spectrum was monitored. In the absence of excess Cl$_2$, the disproportionation reaction is complete in the mixing time. The most abundant Pt^{IV} species was *cis-*[PtCl$_4${(*E*)-HN=C(OEt)Me}$_2$] and not *cis-*3 (molar ratio *ca.* 4:1).

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 spectrophotometers. ^{1}H NMR spectra were obtained with Varian XL

(27) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1019.

Table 3. Crystallographic Data for the Structure Determinations of *cis*-**2**·C_6H_6 and *trans*-**2**·C_6H_6

	cis-**2**·C_6H_6	*trans*-**2**·C_6H_6
empirical formula	$C_{12}H_{28}Cl_6N_4O_4Pt_2$·$C_6H_6$	
formula weight	973.4	
a/Å	13.372(7)	11.218(9)
b/Å	12.838(8)	11.649(11)
c/Å	18.645(12)	23.00(2)
β/deg	110.98(4)	95.94(7)
V/Å^3	2989(2)	2989(3)
Z	4	
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
D_{calc}, g/cm^3	2.163	
μ, cm^{-1}	99.2	
λ (Mo Kα), Å	0.710 73	
T, K	293	
no. of observed reflns	1454	1260
R^a	0.054	0.066
$wR2^b$	0.124	0.158
GOF^c	0.81	1.12

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma(w(|F_o|^2 - |F_c|^2)^2)/\Sigma(w|F_o^2|^2)]^{1/2}$. ^{c} GOF $= [\Sigma[w(|F_o|^2 - |F_c|^2)^2]/(n\text{-}p)]^{1/2}$.

200 and Bruker AM 300 spectrometers. Variable temperature ^{1}H NMR spectra were recorded on a Bruker AM 300 instrument. The temperature of the probe was measured (± 2 °C) by a thermocouple inserted in a NMR tube filled with toluene to the same depth as the solution in the sample tube. The spectral simulation was performed using the SIM2 and SIM3 programs.[28] The C−Me and O−Me protons of the iminoether ligands were used to analyze the rotation of the two platinum subunits about the Pt−Pt bond in *cis*-**2**. Satisfactory fit between simulated and observed spectra was judged by visual comparison. Values of ΔG^* were calculated using the Eyring equation.

X-ray Crystallography. The experimental X-ray data for *cis*-**2**·C_6H_6 and *trans*-**2**·C_6H_6 are summarized in Table 3. Further details

(28) Lunazzi, L. SIM2 and SIM3 programs, University of Bologna, Italy.

are provided in the Supporting Information. After considerable difficulty, suitable crystals were obtained by cutting larger specimens, which were inserted into quartz capillaries previously filled with petroleum jelly to preserve the crystals during the X-ray exposure. Nevertheless, the crystals, particularly those of *trans*-**2**·C_6H_6, in the time undergo decomposition, and, consequently, a high speed for data collection was used. Data were corrected for Lorentz, polarization, and decay effects, and no absorption correction was applied. The structures were solved by Patterson techniques and refined by full-matrix least-squares using the SHELXS-86 and SHELXL-93 program packages.[29,30] Refinement proceeded routinely, and no anomalies in temperature factors or excursions of electron density in the final Fourier maps were observed. The benzene ring of *cis*-**2**·C_6H_6 was treated as a rigid body, and, in the packing of *trans*-**2**·C_6H_6, the centroids of the benzene rings were located at (0,0,0) and ($^1/_2$,$^1/_2$,$^1/_2$).

Supporting Information Available: Tables of crystal data and experimental conditions (Table S1), atomic positional parameters (Table S2), bond lengths (Table S3), bond angles (Table S4), and anisotropic temperature factors (Table S5) for both complexes, along with crystal packing diagrams [Figures 5 (*cis*-**2**·C_6H_6) and 6 (*trans*-**2**·C_6H_6)] (7 pages). See any current masthead page for ordering and Internet access instructions.

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(29) Sheldrick, G. M. SHELXS-86. A Program for Crystal Structure Solution. University of Göttingen, Germany, 1990.

(30) Sheldrick, G. M. SHELXL-93. Crystal Structure Refinement. University of Göttingen, Germany, 1993.