Chiral Recognition in Platinum Complexes of 1,2-Diphenyl-*N,N'*-bis[(2,4,6-trimethylphenyl)methyl]-1,2-diaminoethane. Stereoselective Coordination of Olefins and Molecular Structure of a Trigonal Bipyramidal Adduct

Maria Elena Cucciolito, Mohamud A. Jama, Federico Giordano, and Aldo Vitagliano*

Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy

Vincenzo De Felice

Facoltà di Agraria, Università del Molise, via Tiberio 21/A, 86100 Campobasso, Italy

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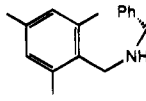
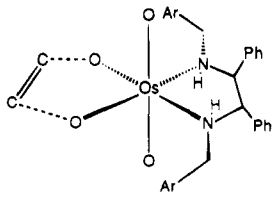
Trigonal bipyramidal olefin–platinum complexes of the title chiral diamine (mestien) have been synthetized and their stereochemistry has been investigated by ^1H and ^{13}C NMR spectroscopy. The molecular structure of the complex PtClMe ((E)-ClCH=CHCl) (mestien) has been determined by X-ray diffraction analysis. The coordinated nitrogen atoms display a single configuration, and a high enantioface selectivity is observed in the coordination of prochiral olefins having a moderate lateral bulk. The selectivity can be correlated to the conformation adopted by the diamine ligand, which shows a remarkable similarity to those calculated for a proposed intermediate in the enantioselective dihydroxylation of olefins by osmium tetraoxide.

Introduction

The title diamine (henceforth referred as mestien) has been recently used as a very effective controller ligand for the enantioselective[1] and diastereoselective[2] dihydroxylation of olefins by osmium tetraoxide. Although molecular mechanics models have been developed[1,3] to explain the observed selectivities, no metal complexes of mestien have been described so far. One of the proposed intermediates has a C_2 symmetric structure (**i**), with the double bond lying in the same plane



mestien



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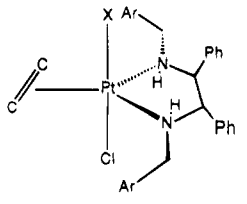

ii

containing the two nitrogen atoms and the metal. From a geometrical point of view, species **i** closely resembles a bipyramidal complex (**ii**), whose structure can be thought as derivable from **i** by removing the two oxygen atoms and approaching the olefin to the metal by 1–1.5 Å. Species **ii** could be anticipated to reveal strong chiral induction effects in the coordination of olefins. In addition, if species **i** correctly represents the active dihydroxylation intermediate (which is still under debate[4]), species **ii** could offer a useful stereochemical model for such an intermediate. Following the above considerations and our general interest in five-coordinate olefin complexes of Pt(II),[5] we were prompted to synthetize complexes of the type **ii** and to investigate their stereochemical properties, also in view of possible uses in other stereoselective processes.

Results and Discussion

Synthesis of the Complexes. Bipyramidal Pt(II) complexes of mestien were prepared by described procedures,[5] according to Scheme 1. Path A was used with olefins bearing electron-releasing substituents, while path B was used with olefins bearing electron-withdrawing substituents. The reason for this choice resides in the effect of the substituents on the stability of platinum–olefin complexes, which follows opposite trends in four- and five-coordinate complexes.[5b,6] Accordingly, ethene is easily displaced from the starting dimer **1** by electron-rich olefins, while electron-withdrawing sub-

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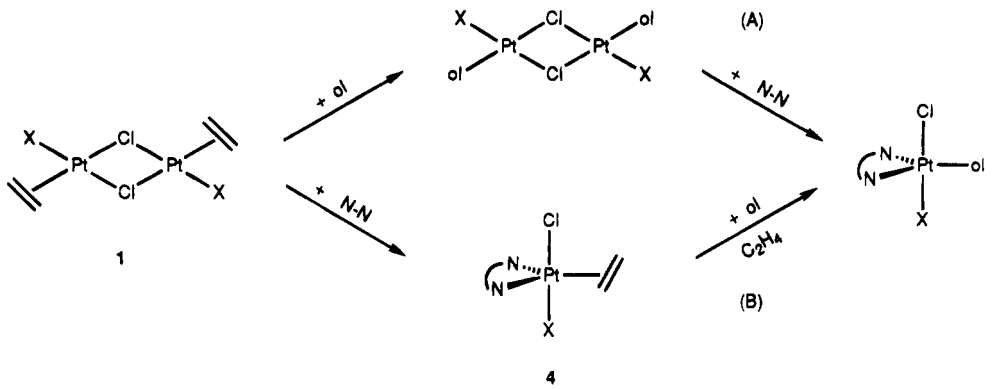
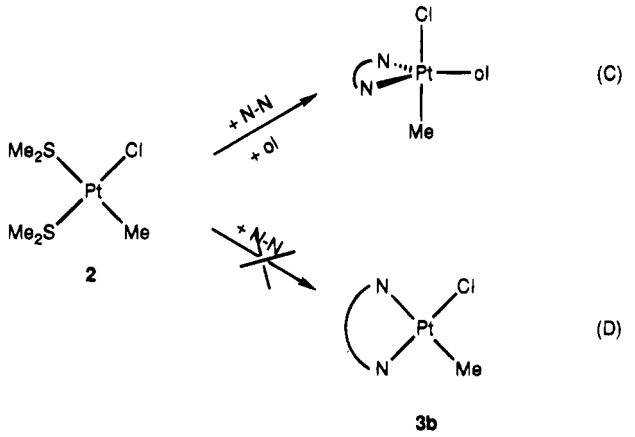
Scheme 1



a	X = Cl	**7**	ol = 1-butene
b	X = Me	**8**	ol = styrene
4	ol = ethene	**9**	ol = *E*-dichloroethene
5	ol = *E*-2-butene	**10**	ol = fumaronitrile
6	ol = propene	**11**	ol = 1-buten-3-ol

stituents are generally required to displace ethene from the bipyramidal complexes **4**.

The complexes containing a σ-bonded methyl group (type **b**) could be prepared by an alternative procedure starting from the dimethyl sulfide complex **2** (path C).[5b]



However, the latter method worked nicely only in the case of ethene and olefins bearing electron-withdrawing substituents. The reaction was sluggish with propene and did not take place at all with (E)-2-butene, most likely as a consequence of the above cited trend controlling the stability of five-coordinate complexes. Some attempts to prepare the four-coordinate complex **3b** by directly displacing dimethyl sulfide from complex **2** (path D) failed. Either no reaction was observed or decomposition took place when drastic conditions (e.g., refluxing toluene) were used.

A number of (mestien)(olefin)$PtCl_2$ complexes (**4a**–**8a**) and (mestien)(olefin)PtClMe complexes (**4b**, **5b**, **8b**–**11b**) were synthetized and characterized by ^1H and ^{13}C NMR spectroscopy. Elemental analyses were performed only when crystalline products were obtained. Racemic mestien was used in all cases, except that of **11b**, which was made with pure (S,S)-(+)-mestien. The bipyramidal structure was confirmed in all cases by the multiplicity of the NMR signals and by the high field at which the olefinic ^1H and ^{13}C resonances were observed.[5,6]

The original purpose for preparing the methyl-substituted complexes **b** was to enable the observation of olefin association–dissociation equilibria, which were previously shown to be facilitated by the presence of σ-bonded carbon ligands.[5a,b] Actually, olefin loss was observed upon warming (at 60 °C) a chloroform solution of the (E)-2-butene complexes **5a** and **5b**. The dichloro complex **5a** gave the expected four-coordinate complex **3a**, while **5b** gave a mixture of products which we did not further characterize. In both cases, the olefin loss was not reversible. We have no evidence allowing us to state whether the lack of reversibility was due to kinetic or thermodynamic reasons. However, since in the present work we are mainly concerned with the stereochemical features of the complexes, we did not try to investigate further the thermodynamical aspects of the olefin coordinations in these species.

Stereochemistry of the Complexes. General Considerations. The diamine mestien contains, besides the two chiral carbon centers, two chiral nitrogen atoms, which of course very quickly epimerize in the free ligand as a consequence of fast nitrogen inversion. The nitrogen chirality is "frozen" upon coordination, so that in principle different diastereomers can be formed, depending on the configuration adopted by the coordinated nitrogen centers. The number of possible diastereomers can further increase, according to the overall symmetry of the PtClX(olefin) fragment. In the simplest case of a metal–olefin fragment having C_{2v} symmetry, as for complex **4a**, three diastereomers could be formed. When a chiral (racemic) olefin is used and the diamine–metal fragment lacks the C_2 axis (complex **11b**), up to 32 different diastereomers are possible! At first glance, the diastereomeric population of a given complex could be straightforwardly determined by inspection of the NMR spectra. However, the number of isomers that would actually be observed by NMR depends not only on their relative abundances (matching their relative stabilities, in the case an equilibrium is attained) but also on their interconversion rates. Three different dynamic processes can take place in solution, each one interconverting a subset of all the possible isomers: (a) nitrogen inversion; (b) olefin rotation; (c) olefin exchange. A general discussion of the actual occurrence of these three processes for complexes **4**–**11** seems worthwhile.

Table 1. Diastereomeric Distribution of [PtClX(olefin)(mestien)] Complexes

complex	possible isomers[a]	obsd isomers (within 95% of total)	% of major Isomer[b]	suggested configuration of the olefinic carbon(s)[c]
4a	3	1	100	
5a	6	2	92	*S, S*
6a	6	2	84	*S*
7a	6	2	91	*S*
8a	6	2	55	
4b	4	1	100	
5b	8	2	85	*S, S*
8b	16	4	41	
9b	8	2	88	*R, R*[d]
10b	8	2	57	
11b	32	2	86[e]	

[a] Only isomers retaining the usual tbp structure, with equatorial N–N and olefinic ligands, are considered. [b] Approximate equilibrium population. [c] Referred to the major diastereomer in the complex containing (*R,R*)-mestien. [d] Unequivocally assigned *via* X-ray structure. [e] Isomeric population in the actually isolated complex.

(a) Nitrogen Inversion. This was shown to be fast at room temperature for some (diamine)(C_2H_4)$PtCl_2$ complexes,[7] with the nitrogen atoms displaying the same configuration (trans arrangement of the substituents) in the largely predominating isomer.[7,8] In our case, this process could be directly revealed by variable-temperature NMR only if appreciable amounts of different diastereomers were present at equilibrium. As a matter of fact, only one isomer was detected in a wide temperature range for complexes **4a** and **4b**. In the case of other complexes, minor species were detected (see Table 1), which could be ascribed to the coordination of different olefinic enantiofaces (see later). Therefore, we can reasonably infer that the nitrogen atoms selectively adopt one configuration, (trans configuration according to the retention of the C_2 axis in complexes **4a** and **5a**), but we lack direct evidence about the *rate* of nitrogen inversion. However, we can consider that this could occur either via proton dissociation or via nitrogen dissociation, and in both cases proton exchange should occur at a comparable rate. With the possible exception of the (E)-2-butene complex **5a**, at room temperature proton exchange is slow on the NMR ν time scale, since coupling to the vicinal CH protons was invariably observed. In most cases it is also slow on the laboratory time scale, since deuterium exchange ($CDCl_3$ saturated with D_2O) occurred with half-lives ranging between 1 min (**4a**) and 1 day (**9b**). The above observations give indirect evidence that nitrogen inversion in most if not all complexes is slow at room temperature on the NMR ν time scale.

(b) Olefin Rotation. When both the olefin and the metal fragment lack a C_2 axis, this process interconverts two different rotamers. We found that at room temperature olefin rotation is slow on the NMR ν time scale and sometimes also slow on the T_1 time scale. Thus, in the case of the propene complex **6a**, at 300 K two separate couples of sharp singlets are observed for the mesityl methyl groups belonging to opposite sides of the diamine ("slow" rotation), which at 330 K are coalesced into a single couple of sharp singlets ("fast" rotation). In the case of the dichloroethene complex **9b**, rotation is much slower, as evidenced by the nonequivalence of the two olefinic protons (δ = 4.68 ppm and δ = 3.62 ppm, respectively) at 330 K, and by the absence of saturation transfer between the two protons even at this temperature.

(c) Olefin Exchange (Dissociation–Association). This process can interconvert all the isomers that differ by the spatial orientation of the olefin (rotamers and re–si isomers) or by the enantiomeric olefin being coordinated (in the case of racemic chiral alkenes). We found that at room temperature and in the presence of free olefin in all cases the exchange occurs with half-lives larger than 1 min, since no saturation transfer was ever observed between the signals of free and coordinated olefin. The exchange was actually monitored in a few cases, and half-lifes of the order of 10–30 min were observed for olefins bearing electron-releasing substituents. The exchange is accelerated by traces of acid (CF_3COOH), in agreement with a mechanism involving the dissociation of one nitrogen atom, as suggested by van Koten et al.[9] The exchange is much slower for electron-withdrawing olefins (several days in the case of the fumaronitrile complex **10b**), but ultimately an equilibrium is reached between the possible diastereomers.

The above observations point to the conclusion that at room temperature for all the complexes investigated the NMR signals of the possible isomers are not averaged by exchange phenomena. Therefore the actual populations of the various isomers can be directly inferred by the multiplicity and intensity of the signals observed in the NMR spectra. The number of isomers that were observed and the abundance of the major one are listed in Table 1, in comparison with the total number of the possible diastereomers. Inspection of Table 1 shows that in most cases a remarkable stereoselectivity controls the formation of the five-coordinate adducts. Before discussing in detail some stereochemical features of the complexes, as inferred by the NMR data, we shall present the results of the X-ray structural analysis of complex **9b**.

Molecular Structure of PtClMe[(E)-(1-R,2-R)-CHCl=CHCl][(R-C,R-C′,4S-N,S-N′)mestien] (9b). The crude complex **9b** consisted of a mixture of diastereomers containing a major component in nearly 90% abundance. Crystallization from methylene chloride–ethanol gave single crystals of the major isomer which were suitable for X-ray diffraction. Crystals (space group $P2_1/c$) contained enantiomorphic molecules, (racemic mestien was used in the preparation) displaying the trigonal bipyramidal (tbp) structure that is usual for five-coordinated olefin complexes of platinum(II).[6] An ORTEP drawing of the molecule, showing the atom numbering scheme, is shown in Figure 1. Relevant geometric parameters are given in Tables 2 and 3. The Pt–C(2) and Pt–C(3) distances (2.04(1) and 1.98(1) Å, respectively) are the shortest observed for similar complexes.[6] The short Pt–C distances are accompanied by a considerable lengthening of the C(2)–C(3) double bond (1.50(2) Å) and by a large bending-back of the two chlorine atoms (torsion angle Cl(2)–C(2)–C(3)–Cl(3) = −123(1)°). All together, the above data indicate a strong metal–olefin bond, with a contribution of π-back-dona-

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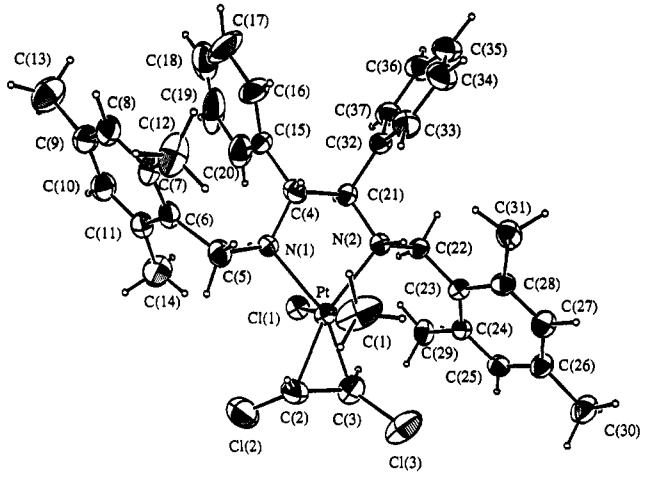

Figure 1. ORTEP view of PtClMe[(*E*)-ClCH=CHCl)](mestien) (**9b**) showing the atom labeling scheme. Thermal ellipsoids are drawn at the 25% probability level.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of the Non-Hydrogen Atoms[a]

	x	*y*	*z*	B_{eq}[b]
Pt	0.45657(4)	0.24069(3)	0.60620(4)	4.65(1)
Cl(1)	0.3611(3)	0.2453(2)	0.4292(2)	6.0(1)
Cl(2)	0.5049(5)	0.0948(3)	0.5145(4)	11.5(2)
Cl(3)	0.7311(3)	0.2410(3)	0.6832(4)	11.3(2)
N(1)	0.2876(7)	0.2210(5)	0.5973(7)	5.1(3)
N(2)	0.4018(7)	0.3475(5)	0.6220(6)	4.3(2)
C(1)	0.531(1)	0.2460(9)	0.760(1)	11.1(5)
C(2)	0.548(1)	0.1551(8)	0.607(1)	7.8(4)
C(3)	0.601(1)	0.2221(8)	0.598(1)	7.0(4)
C(4)	0.238(1)	0.2825(6)	0.626(1)	5.8(3)
C(5)	0.275(1)	0.1544(7)	0.647(1)	6.2(4)
C(6)	0.156(1)	0.1294(6)	0.613(1)	5.5(3)
C(7)	0.100(1)	0.1292(7)	0.671(1)	5.8(3)
C(8)	−0.010(1)	0.1156(8)	0.635(1)	7.4(4)
C(9)	−0.069(1)	0.0980(8)	0.542(1)	7.3(4)
C(10)	−0.010(1)	0.0922(8)	0.483(1)	7.6(4)
C(11)	0.102(1)	0.1056(7)	0.515(1)	6.9(4)
C(12)	0.154(1)	0.1457(9)	0.780(1)	9.5(5)
C(13)	−0.195(1)	0.0905(9)	0.499(1)	10.4(6)
C(14)	0.163(1)	0.0995(9)	0.449(1)	10.2(5)
C(15)	0.110(1)	0.2858(7)	0.580(1)	7.1(4)
C(16)	0.049(1)	0.2977(9)	0.636(1)	12.8(5)
C(17)	−0.066(1)	0.3013(9)	0.597(2)	21(1)
C(18)	−0.117(2)	0.2903(9)	0.499(2)	16(1)
C(19)	−0.058(2)	0.2786(9)	0.442(3)	24(2)
C(20)	0.055(1)	0.2757(9)	0.481(2)	11.4(8)
C(21)	0.279(1)	0.3487(6)	0.594(1)	4.8(3)
C(22)	0.432(1)	0.4066(6)	0.569(1)	4.7(3)
C(23)	0.552(1)	0.4186(6)	0.602(1)	4.5(3)
C(24)	0.609(1)	0.4111(6)	0.541(1)	5.0(3)
C(25)	0.718(1)	0.4247(7)	0.571(1)	5.4(3)
C(26)	0.780(1)	0.4502(8)	0.664(1)	5.8(3)
C(27)	0.723(1)	0.4606(8)	0.724(1)	6.1(4)
C(28)	0.612(1)	0.4466(7)	0.698(1)	5.4(3)
C(29)	0.548(1)	0.3890(8)	0.435(1)	6.3(4)
C(30)	0.902(1)	0.4627(9)	0.698(1)	8.2(5)
C(31)	0.556(1)	0.4628(8)	0.766(1)	7.1(4)
C(32)	0.245(1)	0.4126(6)	0.636(1)	5.5(3)
C(33)	0.281(1)	0.4246(8)	0.734(1)	6.7(4)
C(34)	0.253(1)	0.4840(9)	0.769(1)	8.5(5)
C(35)	0.185(1)	0.5323(9)	0.702(1)	8.9(5)
C(36)	0.146(1)	0.5210(8)	0.608(1)	8.4(5)
C(37)	0.176(1)	0.4609(8)	0.573(1)	7.0(4)

[a] ESDs in parentheses. [b] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_ia_j$.

tion which seems to be relevant even within the class of five-coordinate complexes.[6] The Pt−N(1) and Pt−N(2) bond distances (2.210(9) and 2.223(9) Å, respectively) are also slightly shorter than those observed for other five-coordinate olefin complexes with diamine ligands.[6] This could be a secondary consequence of the larger π-back-donation, which in turn should promote a better σ-donation by the nitrogen ligand on the opposite side.

Table 3. Selected Bond Lengths (Å) and Relevant Valence Angles (deg)[a]

Bond Lengths					
Pt−Cl(1)	2.450(2)	N(2)−C(21)	1.50(1)	Cl(3)−C(3)	1.73(1)
Pt−N(1)	2.210(9)	C(2)−C(3)	1.50(2)	N(1)−C(5)	1.52(1)
Pt−C(2)	2.04(1)	Pt−C(1)	2.12(1)	N(2)−C(22)	1.52(1)
Cl(2)−C(2)	1.72(1)	Pt−N(2)	2.223(9)	C(4)−C(21)	1.53(2)
N(1)−C(4)	1.49(1)	Pt−C(3)	1.98(1)		
Bond Angles					
N(1)−Pt−N(2)	78.8(5)	C(2)−Pt−C(3)	43.7(9)		
N(1)−Pt−C(2)	116.1(8)	N(2)−Pt−C(3)	122.1(8)		
Cl(1)−Pt−N(1)	81.6(4)	Cl(1)−Pt−N(2)	91.6(4)		
Cl(1)−Pt−C(2)	95.2(7)	Cl(1)−Pt−C(3)	92.7(7)		
C(1)−Pt−C(2)	90.4(9)	C(1)−Pt−C(3)	91.0(9)		
N(1)−Pt−C(1)	96.4(8)	N(2)−Pt−C(1)	82.9(8)		
Pt−C(2)−C(3)	66(1)	Pt−C(3)−C(2)	70(1)		
Pt−C(2)−Cl(2)	122(1)	Pt−C(3)−Cl(3)	128(1)		
Cl(2)−C(2)−C(3)	122(2)	Cl(3)−C(3)−C(2)	119(2)		
Pt−N(1)−C(4)	113(1)	Pt−N(1)−C(5)	114(1)		
Pt−N(2)−C(21)	110(1)	Pt−N(2)−C(22)	119(1)		
C(4)−N(1)−C(5)	113(1)	C(21)−N(2)−C(22)	108(1)		
N(1)−C(5)−C(6)	113(2)	N(2)−C(22)−C(23)	114(1)		
N(1)−C(4)−C(15)	115(2)	N(1)−C(4)−C(21)	109(1)		
C(15)−C(4)−C(21)	107(2)	N(2)−C(21)−C(4)	112(1)		
N(2)−C(21)−C(32)	111(1)	C(4)−C(21)−C(32)	110(1)		
Cl(1)−Pt−C(1)	174.4(7)				

[a] ESDs in parentheses.

Concerning the stereochemistry of the diamine ligand, the two nitrogen atoms display the same configuration, which is the opposite of that of the two chiral carbon centers. The torsion angles Pt−N(1)−C(5)−C(6) and Pt−N(2)−C(22)−C(23) (−161(1)° and −63(1)°, respectively) are such that one of the two mesityl groups is extended toward the olefin ligand, while the other one is withdrawn and stacked in front of one of the phenyl rings in the back of the molecule. In a recent MM2 modeling of a postulated dihydroxylation intermediate,[3] the same configuration was found for the two chiral nitrogen atoms, and two conformations very similar to the above were calculated to be the only acceptable. The two conformations were close in energy, differing by ~2 kJ/mol for each mesityl group. The conformational similarity found between two chemically different species (**i** and **ii**) suggests that the steric constraints arising in the diamine frame after chelation are strong enough to overwhelm the effects of the packing forces and those resulting from the difference in the remaining molecular fragment. The chiral environment created around the platinum center by the outstretched diamine "arm" is most likely responsible for the high selectivity observed in the olefin coordination. As pointed out in the previously cited MM2 work,[3] no selectivity would be expected in the case where both "arms" of the diamine were withdrawn toward the back of the molecule.

Stereochemistry of the Complexes. Specific Aspects. Having in mind the molecular structure of **9b**, we shall now discuss the stereochemical features of a number of selected complexes, as inferred by the NMR data.

4a. The presence of only one species can be detected from the ^{1}H NMR spectrum of this compound in the range 190−300 K. As mentioned before, the chemical equivalence of the two halves of the diamine indicates that the C_2 axis is retained in the complex molecule,

which means that the two nitrogen atoms adopt the same configuration (most likely the opposite to that of the chiral carbon atoms, according to the structure of **9b**). A remarkable molecular rigidity is revealed by variable-temperature ^{1}H NMR spectroscopy. In the room-temperature spectrum (270 MHz), the protons of the phenyl groups give rise to a single broad band centered at δ = 7.2 ppm. At 253 K, this is split into five different broad signals which at 233 K become two sharp doublets and three sharp triplets (2 H each). This indicates restricted rotation around the C–phenyl bonds, causing nonequivalence of the two ortho (and meta) protons within each phenyl group, but retaining the chemical equivalence between the two halves of the coordinated diamine. On lowering the temperature to 203 K, the ortho methyls of the mesityl groups, which at room temperature give rise to a singlet (12 H) at δ 2.31, also split into two broad singlets (6 H each) at δ = 2.13 ppm and 2.48 ppm, respectively. This indicates restricted rotation around the C–mesityl bond. It is worth noting that the observed rigidity is a consequence of the coordination, since no splitting whatsoever is observed for the resonances of the free ligand, down to 180 K. The rigidity of the coordinated diamine indicates that a limited conformational space is available to the complex. This is consistent with the previously cited MM2 analysis and with the high selectivity observed upon coordination of prochiral olefins (see later).

5a. The ^{1}H and ^{13}C NMR spectra (298 K) show the presence of one dominant isomer (92 ± 2% abundance). Similarly to the ethene complex **4a**, a C_2 axis is present in the molecule, indicating that the two nitrogen atoms adopt the same configuration, which is most likely the opposite of that of the chiral carbon atoms, as shown by the crystal structure of complex **9b**. A minor species (~8% abundance) is also detectable through the signal of the olefinic methyl groups (doublet at δ = 1.12 ppm, $^3J_{H-Pt}$ = 40 Hz). Other signals from the minor species are not positively assignable in the proton spectrum due to overlapping by the resonances of the major isomer. Further evidence of the minor isomer is provided by the carbon spectrum (see Experimental Section). Since the C_2 symmetry is retained by the minor species, the latter is most likely due to the coordination of the other olefinic enantioface. This assignment was confirmed by preparing the complex *in situ*, mixing equivalent amounts of the starting dimer **1** and mestien directly in the NMR tube. The first spectrum, recorded ~2 min after mixing, showed comparable amounts (ratio 55:45) of the two isomers. The mixture then evolved to the final equilibrium composition with an half-life of ~8 min, a figure that gives the estimate of the (E)-2-butene exchange rate.

The ^{1}H NMR spectrum (270 MHz) of **5a** shows a temperature dependence which resembles that of the ethene complex **4a**, with the addition of some more complicated features. The behavior of the phenyl proton signals and that of the mesityl CH_3 and aromatic protons is similar to that of the ethene complex **4a**. Most interesting is the temperature behavior of the olefin methyl resonances. In the temperature range explored (190–320 K), the methyl groups give rise to a single resonance signal, which at 320 K appears as a doublet, with the expected ^{195}Pt satellite peaks ($J_{Pt} \cong$ 40 Hz). At 293 K the signal is broad, such that the Me–CH coupling is not longer detectable and the ^{195}Pt satellites appear as shoulders of the main peak. At 250 K the signal is sharp again, the Me–CH coupling and satellite peaks are easily measurable. Further cooling results in broadening, such that at 210 K no coupling is detectable. The chemical shift of the butene methyl protons (and, to a lesser extent, that of the olefinic protons) is strongly affected by the temperature, moving from δ = +0.25 ppm at 320 K to δ = −0.42 ppm at 190 K. (The =CH protons move from δ = 3.5 ppm to δ = 3.0 ppm in the same temperature range.) The successive sharpening–broadening–sharpening of the butene methyl signal that occurs upon warming from 190 to 320 K is consistent with the occurrence of two or more exchange processes in two different temperature ranges. In the temperature range where either dynamic process is frozen, splitting of the butene resonances should occur. Since no splitting is actually observed, most likely both exchange processes involve minor species, whose signals are not easily detected. We tentatively suggest that the high-temperature process (range 290–320 K) involves inversion of configuration at nitrogen. Indeed, complex **5a** is the only one for which fast NH proton exchange can be observed at 320 K (loss of coupling to CH and CH_2 protons), consistent with the possibility of fast nitrogen inversion as discussed above. The low-temperature process might result from a progressive freezing of the conformational mobility of the diamine "arms", allowing the existence at low temperature of different atropoisomers of the complex. The temperature dependence of the chemical shifts of the butene methyl protons deserves some further discussion. At 320 K, the methyl groups display their resonance at an unusually high field (δ = 0.25 ppm), while in a more usual range is the corresponding chemical shift of the minor diastereomer (δ = 1.15 ppm). This strongly points to a dynamically averaged conformation similar to that observed in the solid state for the sterically analogous complex **9b**, where one of the chlorine atoms is just facing the middle of a mesityl benzene ring, thus experiencing its paramagnetic shielding. The shielding increases upon cooling, and at 190 K the methyl signal moves to δ = −0.4 ppm. This suggests the dominance at low temperature of the more stable conformation[3] in which both the diamine mesityl groups are extended toward the olefin and facing its methyl substituents. In such conformation, a higher enantioface selectivity should be expected. Accordingly, the observed population of the minor diastereomer was lower at 240 K (6 ± 2%) than at 320 K (11 ± 2%). The above data, in connection to the molecular structure of **9b**, suggest that the butene methyl groups in **5a** experience the same sterical environment as the chlorine atoms in **9b**. It seems very likely, therefore, that in the molecules containing (R,R)-mestien, the (E)-2-butene adopts the S,S configuration[10] in the major diastereomer. A NOE experiment was performed at 298 K to get independent configurational evidence. The result was a partial success, in that the only nontrivial NOE was detected between the butene methyl protons and the mesityl CH protons. Although this observation is consistent with all the above considerations, it does not give any conclusive evidence about the butene configuration.

(10) The formal inversion with respect to complex **9b** is due to a change in the priority sequence of the substituents when methyl is substituted for chlorine.

6a. The ^1H and ^{13}C NMR spectra show the presence of one dominant isomer in 84 ± 2% abundance at 298 K. Also, in this case the population of the major isomer increases upon cooling (89 ± 2% at 253 K). In the range 213−300 K, the diamine signals show a temperature dependence similar to that of the ethene and (E)-2-butene complexes **4a** and **5a**, indicating comparable skeletal rigidity. In the low-temperature range, the signal of the propene methyl group behaves similarly to the (E)-2-butene complex **5a**, although a lesser variation of the chemical shift is observed (δ = +0.18 ppm at 313 K, δ = −0.11 ppm at 213 K). As in the case of **5a**, this can be explained by conformational changes of the diamine side chains, and the high field at which the methyl signal is observed is consistent with it facing the mesityl benzene ring and experiencing its paramagnetic shielding. As for **5a**, the only nontrivial NOE was observed between the propene methyl protons and the mesityl CH protons. In analogy to **5a**, we suggest the S configuration for the coordinated propene carbon (when (R,R)-mestien is bound). At room temperature and below, the two halves of the diamine ligand are not equivalent, due to restricted rotation around the Pt−double bond axis. Rotation of the olefin becomes apparent after warming at 320 K. At this temperature, the mesityl CH and Me signals, which at 298 K (400 MHz) appear as three couples of singlets (δ 6.76, 6.79, 2 + 2 H; δ 2.29, 2.34, 6 + 6 H; δ 2.20, 2.22, 3 + 3 H), coalesce into three sharp singlets. The NH protons, which have a larger difference of chemical shift ($\Delta\delta \cong$ 1 ppm) still give separate resonances.

11b. This compound was obtained by displacing ethene from complex **4b** (pure (S,S)-(+)-mestien was used in this case) with an excess of the racemic allylic alcohol 1-buten-3-ol. Several attempts to crystallize the product failed, and the complex was only obtained as a crude vitreous solid after evaporation of the solvent. The ^1H and ^{13}C NMR spectra indicated the presence of two isomers **11b′** and **11b″** in ~6:1 ratio. A third species, in ~4% abundance, was detected through its Pt−Me proton signal at δ = 0.10 ppm. Even excluding configurational isomerism of the coordinated nitrogen atoms, the two major species **11b′** and **11b″** could in principle differ according to three kinds of isomerism: coordination of different enantiomers of the olefin, coordination of different faces of the same enantiomeric olefin, and rotational isomerism around the Pt−double bond axis. In order to clarify the stereochemical relation between the two major species, we added to a sample of the complex 4 equiv of racemic free olefin. The ^1H NMR spectrum of the mixture showed the increase of the population of the minor isomer **11b″** to ~19%. Moreover, we also prepared the complex by olefin exchange on the starting dimer **1** and successive addition of the optically pure diamine (S,S)-(+)-mestien (path A in Scheme 1). The ^1H NMR spectrum of the product showed the presence of the two isomers **11b′** and **11b″** in about equimolar amounts. Thus, **11b′** and **11b″** differ by the coordination of enantiomeric olefins, and the equilibrium constant for the exchange between the two enantiomeric olefins can be estimated to be ~4.

When we observed the fair chiral discrimination reported above, we argued that the same would probably be observed in the case of complexes having a different metal but similar symmetry. While this work was in progress, we exploited the idea by investigating Cu(I) olefin complexes of mestien. Apart from the absence of axial ligands, these are expected to display the same trigonal arrangement of ligands around the metal center[11] as the five-coordinate platinum species **ii**. By using (S,S)-(+)-mestien, crystalline Cu(I) complexes were obtained with many olefins.[12] In the case of racemic secondary allylic alcohols, selective coordination of one enantiomer (better than 90% ee) was indeed observed, disclosing a very effective method for the resolution of allylic alcohols.[12] It is worth noting that the coordination of the same enantiomer ((R)-(−)-1-buten-3-ol) is preferred both in Cu(I) and in Pt(II) complexes of (S,S)-(+)-mestien. This was shown by comparing the allylic alcohol, isolated after treatment of **11b′** with NaCN, with an authentic sample obtained through the resolution procedure using the Cu(I) complex. From the above comparison, **11b′** turned out to be the complex with (R)-(−)-1-buten-3-ol. The enantiomeric alcohol (S)-(+)-1-buten-3-ol is therefore contained in **11b″**.

Conclusions

The results we have reported, including the remarkable steric similarity between **9b** and the MM2 model of the postulated osmium intermediate **i**, indicate that a limited number of conformations are available to the diamine skeleton after coordination. The whole structure is scarcely flexible, and the mesityl groups either point toward the olefin on the opposite side (resulting in good chiral induction) or are withdrawn toward the phenyl groups in the back of the molecule (resulting in poor chiral induction). Inspection of Table 1 shows that in most cases a very high selectivity was observed in the coordination of prochiral olefins. The two olefins that gave poor selectivity were fumaronitrile and styrene. Both have in common a rigid substituent on the double bond, a "stick" in the former case and a ring in the latter. A reasonable explanation for the poor selectivity comes from the inspection of the molecular structure of **9b** (Figure 1). The Cl(3) substituent is close to a fair van der Waals contact with one mesityl benzene ring (distance from the mean plane of the ring, 3.81 Å). A methyl group (complexes **5a** and **6a**) or a flexible alkyl chain (complex **7a**) should be easily accommodated in about the same position. By contrast, a rigid substituent in the same position would hit the mesityl ring, thus forcing the diamine "arm" to turn back in the alternative conformation, with consequent loss of selectivity. In conclusion, mestien appears to be very efficient in creating a "chiral pocket" around the metal. The size and shape of the pocket are suitable for the enantioselective "in-plane" coordination of olefins in a trigonal environment. The scope of the chiral induction is limited to moderately sized olefins. Rigid substituents creating a large lateral bulk result in the opening of the "pocket" with consequent loss of selectivity.

Experimental Section

^1H NMR and ^{13}C spectra were recorded on a Bruker WH-400 or a Bruker AC-270 spectrometer, respectively. ^1H NMR

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chemical shifts are reported in δ (ppm) relative to the solvent ($CHCl_3$, 7.26; $CDHCl_2$, 5.33). ^{13}C NMR chemical shifts are given in δ values relative to the solvent ($CDCl_3$, 77.0 ppm). Unless otherwise stated, the reported data refer to spectra recorded at 25 °C. The following abbreviations are used in descriptions of NMR multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; app, apparent, br, broadened; J_{Pt} = coupling constant to ^{195}Pt (when satellite peaks are unambigously detected). Protons are identified as shown in footnote.[13] When necessary, the NMR assignments were done using decoupling techniques. Solvents and reagents were of AnalaR grade and were used without further purification. Unless otherwise stated, platinum complexes were prepared and stored in air.

Materials. The diamine mestien was prepared[1] and resolved as previously described.[14] $[PtClMe(\eta^2\text{-ethene})]_2$[15] and $[PtClMe(SMe_2)_2]$[16] were prepared as previously described.

Synthesis of [$PtCl_2$(mestien)(η^2-olefin)]. General Procedure.[5c] A 0.285 g (0.5 mmol) sample of $[PtCl_2(\eta^2\text{-ethene})]_2$ was dissolved in 4 mL of methylene chloride at 0 °C, and a large excess of the appropriate olefin was added. The solution was evaporated in vacuo, the residue was dissolved again in methylene chloride, and the above sequence was repeated once. The residue was dissolved in 10 mL of methanol at 0 °C, and 1.1 mmol of mestien was added under stirring at 0 °C. A yellow precipitate formed, which after 30 min of stirring was collected on a filter and dried, giving the required $[PtCl_2(\text{mestien})(\eta^2\text{-olefin})]$ in 85−90% yield.

Synthesis of [PtClMe(mestien)(η^2-olefin)]. General Procedure A.[5b] The procedure was the same as above except that the starting compound was $[PtClMe(\eta^2\text{-ethene})]_2$[15] and diethyl ether was used as solvent in place of methanol in the second step.

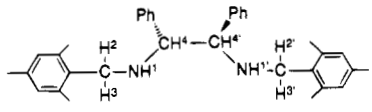
General Procedure B. A 0.5 mmol sample of the ethene or (E)-2-butene complexes (obtained through procedure A) was dissolved in 10 mL of methylene chloride, and a large excess of appropriate olefin was added. The solution was evaporated in vacuo, the residue was dissolved again in methylene chloride, and the above sequence was repeated once giving the required complex, which was recrystallized from methylene chloride−diethyl ether.

General Procedure C. Some complexes could be prepared from $[PtClMe(SMe_2)_2]$[16] according to a previously reported procedure.[5b]

[$PtCl_2$(mestien)(η^2-ethene)] (4a): ^1H NMR (270 MHz, $CDCl_3$) δ 2.20 (s, 6 H, Ar-*Me*), 2.31 (s, 12 H, Ar-*Me*), 2.30 (2 H, =CH*H*),[17] 2.42 (m, 2 H, $J_{Pt} \cong 70$ Hz, =C*H*H),[18] 3.56 (dd, 2 H, $J_{Pt} \cong 35$ Hz, H^2, $H^{2'}$), 4.15 (m, 4 H, H^3, $H^{3'}$, H^4, $H^{4'}$), 4.30 (m, 2 H, H^1, $H^{1'}$), 6.73 (s, 4 H, Ar-*H*), 7.17 (br, 10 H, *Ph*). Anal. Calcd for $PtC_{36}H_{44}Cl_2N_2$: C, 56.10; H, 5.75; N, 3.63. Found: C, 55.83; H, 5.72; N, 3.45.

[$PtCl_2$(mestien)(η^2-E-2-butene)] (5a): ^1H NMR (400 MHz, $CDCl_3$) δ 0.11 (br s, 6 H, *Me*CH=), 2.18 (s, 6 H, Ar-*Me*), 2.34 (s, 12 H, Ar-*Me*), 3.39 (br s, 2 H, C*H*=), 3.59 (br d, 2 H, H^2, $H^{2'}$), 4.17 (br s, 2 H, H^4, $H^{4'}$), 4.3 (m, 4 H, H^1, $H^{1'}$, H^3, $H^{3'}$), 6.76 (s, 4 H, Ar-*H*), 7.12 (m, 10 H, *Ph*); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 17.3 (J_{Pt} = 35 Hz, *Me*CH=), 20.6 (Ar-*Me*), 20.7 (Ar-*Me*), 47.8 (NCH_2, $N'C'H_2$), 54.2 (br, J_{Pt} = 290 Hz, *C*H=), 69.2 (*C'*HPh, *C*HPh), 127.9, 128.3, 129.3, 131.1, 136.9, 137.4, 138.1. Signals from the minor isomer (~8%) are detectable. ^{13}C NMR δ 17.9 (*Me*CH=), 49.5 (NCH_2, $N'C'H_2$), 70.0 (*C*HPh, *C'*HPh),

(13)



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(17) Overlapped by Ar-*Me* signals.

(18) A part of AA'BB' multiplet.

Anal. Calcd for $PtC_{38}H_{48}Cl_2N_2$: C, 57.14; H, 6.06; N, 3.51. Found: C, 56.68; H, 5.81; N, 3.32.

[$PtCl_2$(mestien)(η^2-propene)] (6a): ^1H NMR (400 MHz, CD_2Cl_2) δ 0.05 (d, 3 H, $J_{Pt} \cong 40$ Hz, =CH*Me*), 2.20 (1 H, =C*H*H),[17] 2.20 (s, 3 H, Ar-*Me*), 2.22 (s, 3 H, Ar-*Me*), 2.29 (s, 6 H, Ar-*Me*), 2.34 (s, 6 H, Ar-*Me*), 2.41 (d, 1 H, =CH*H*), 3.24 (d app quintet, 1 H, $J_{Pt} \cong 75$ Hz, =C*H*Me), 3.50 (app d, 2 H, H^2, $H^{2'}$), 4.00 (br app t, 1 H, $H^{1'}$), 4.2 (m, 4 H, H^3, $H^{3'}$, H^4, $H^{4'}$), 4.40 (br app t, 1 H, H^1), 6.76 (s, 2 H, Ar-*H*), 6.79 (s, 2 H, Ar-*H*), 7.0−7.4 (br, 10 H, *Ph*). Minor isomer (~15%) ^1H NMR δ 0.62 (d, 3 H, =CH*Me*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9 (*Me*CH=), 20.7 (Ar-*Me*), 37.1 (J_{Pt} = 290 Hz, CH_2=), 47.2 (NCH_2), 48.1 ($N'C'H_2$), 51.4 (J_{Pt} = 310 Hz, *C*H=), 68.6 (PhCH), 70.2 (PhC'H), 128.1, 128.3, 128.6, 129.0, 129.1, 129.4, 131.0, 131.9, 136.7, 136.8, 137.0, 137.1, 137.4, 137.6, 138.0. Signals from the minor isomer are detectable. ^{13}C NMR δ 17.6 (*Me*CH=), 37.8 (CH_2=) 47.5 (NCH_2), 49.7 ($N'C'H_2$ or *C*H=), 69.8 (PhCH), 70.6 (PhC'H). Anal. Calcd for $PtC_{37}H_{46}Cl_2N_2$: C, 56.63; H, 5.91; N, 3.57. Found: C, 56.40; H, 5.80; N, 3.36.

[$PtCl_2$(mestien)(η^2-1-butene)] (7a): ^1H NMR (270 MHz, $CDCl_3$) δ 0.01 (m, 1 H, =CHCH*H*), 0.68 (t, 3 H, CH_2*Me*), 0.95 (m, 1 H, =CHC*H*H), 2.18 (s, 3 H, Ar-*Me*), 2.21 (s, 3 H, Ar-*Me*), 2.3 (1 H, =CH*H*),[17] 2.30 (s, 6 H, Ar-*Me*), 2.32 (s, 6 H, Ar-*Me*), 2.47 (d, 1 H, =C*H*H), 3.17 (d app q, 1 H, J_{Pt} = 75 Hz, =C*H*), 3.1−3.3 (m, 4 H, H^3, $H^{3'}$, H^4, $H^{4'}$), 3.53 (app d, 1 H, H^2), 3.60 (app d, 1 H, $H^{2'}$), 4.05 (app t, 1 H, $H^{1'}$), 4.40 (app t, 1 H, H^1), 6.75 (s, 4 H, Ar-*H*), 7.1−7.2 (br, 10 H, *Ph*). Minor isomer (~8%) ^1H NMR δ 0.87 (t, 3 H, CH_2*Me*). Anal. Calcd for $PtC_{38}H_{48}Cl_2N_2$: C, 57.14; H, 6.06; N, 3.51. Found: C, 56.81; H, 5.90; N, 3.26.

[$PtCl_2$(mestien)(η^2-styrene)] (8a). Complex **5a** (80 mg, 0.1 mmol) was dissolved in 2 mL of methylene chloride, and 0.1 mL of styrene was added. The solution was evaporated to dryness, and the procedure was repeated once. The crude residue was washed with pentane and dried, giving a yellow powder (70 mg, 82% yield). The complex decomposes in solution in a few hours, giving **3a** and free styrene. ^1H NMR (270 MHz, $CDCl_3$), only the methyl singlets are assignable (approximate relative intensities in parentheses) at δ 1.98 (3), 1.99 (6), 2.02 (6), 2.06 (2.5), 2.12 (5), 2.28 (2.5), 2.42 (3), 2.45 (5). Complex overlapping multiplets appear in the δ range 3.4−5.3 and 6.4−7.5. The observed pattern of methyl singlets is consistent with the presence of two isomers in ~6:5 ratio, both displaying hindered rotation of the olefin around the Pt−double bond axis.

[$PtCl_2$(mestien)] (3a). The complex was obtained as crystalline precipitate by decomposition of **8a** in methanol solution, recrystallized from methylene chloride−diethyl ether: ^1H NMR (270 MHz, $CDCl_3$) δ 1.99 (s, 6 H, Ar-*Me*), 2.10 (s, 12 H, Ar-*Me*), 3.97 (dd, 2 H, H^4, $H^{4'}$), 4.64 (dd, 2 H, H^2, $H^{2'}$), 5.30 (dd, 2 H, H^3, $H^{3'}$), 5.48 (m, 2 H, H^1, $H^{1'}$), 6.39 (s, 4 H, Ar-*H*), 6.9 (m, 10 H, *Ph*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5 (Ar-*Me*), 20.7 (Ar-*Me*), 54.4 (NCH_2, $N'C'H_2$), 77.4 (*C*HPh, *C'*HPh), 126.3, 128.0, 129.0, 129.4, 129.9, 136.4, 137.0, 137.5. Anal. Calcd for $PtC_{34}H_{40}Cl_2N_2$: C, 54.99; H, 5.43; N, 3.77. Found: C, 54.65; H, 5.30; N, 3.57.

[PtClMe(mestien)(η^2-ethene)] (4b). Procedures A and C: ^1H NMR (400 MHz, $CDCl_3$−CD_3OD 10:1)[19] δ −0.16 (s, 3 H, J_{Pt} = 70 Hz, Pt-*Me*), 0.81 (app t, 1 H, J_{Pt} = 65 Hz, =C*H*), 0.89 (app t, 1 H, J_{Pt} = 65 Hz, =C*H*), 1.81 (app t, 1 H, J_{Pt} = 85 Hz, =C*H*), 2.00 (app t, 1 H, J_{Pt} = 85 Hz, =C*H*), 2.10 (s, 3 H, Ar-*Me*), 2.13 (s, 3 H, Ar-*Me*), 2.16 (s, 6 H, Ar-*Me*), 2.25 (s, 6 H, Ar-*Me*), 3.48 (d, 1 H, H^3), 3.55 (d, 1 H, $H^{3'}$), 3.72 (d, 1 H, $H^{4'}$), 3.78 (d, 1 H, $H^{2'}$), 4.18 (d, 1 H, H^2), 4.54 (d, 1 H, H^4), 6.62 (s, 2 H, Ar-*H*), 6.67 (s, 2 H, Ar-*H*), 6.9−7.3 (m, 10 H, *Ph*); ^{13}C NMR (100 MHz, $CDCl_3$−CD_3OD 10:1) δ −12.6 (J_{Pt} = 730 Hz, Pt-*Me*), 20.1 (Ar-*Me*), 20.3 (Ar-*Me*), 20.5 (Ar-*Me*), 20.6 (Ar-*Me*), 28.1 (J_{Pt} = 355 Hz, =CH_2), 29.5 (J_{Pt} = 375 Hz, =CH_2), 47.6 (NCH_2, $N'C'H_2$), 69.5 (PhCH), 70.5 (PhC'H), 127.8, 128.2,

(19) In pure $CDCl_3$ the NH protons signals appear as double triplets at δ 3.09 (J_{Pt} = 30 Hz) and 4.35 (J_{Pt} = 45 Hz).

128.4, 128.5, 128.8, 128.9, 131.5, 131.7, 136.2, 136.6, 136.7, 137.6, 137.9. Anal. Calcd for $PtC_{37}H_{47}ClN_2$: C, 59.23; H, 6.31; N, 3.73. Found: C, 58.85; H, 6.38; N, 3.58.

[PtClMe(mestien)(η^2-(E)-2-butene)] (5b). Procedure A: ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.03 (d, 3 H, J_{Pt} = 65 Hz, =CH*Me*), 0.10 (s, 3 H, J_{Pt} = 75 Hz, Pt-*Me*), 0.45 (d, 3 H, J_{Pt} = 60 Hz, *Me*HC=), 1.8 (m, 1 H, =C*H*Me), 2.22 (s, 12 H, Ar-*Me*), 2.35 (s, 6 H, Ar-*Me*), 2.86 (m, 1 H, Me*H*C=), 3.04 (m, 1 H, H^1), 3.62 (m, 1 H, H^3), 3.78 (app t, 1 H, $H^{4'}$), 3.98 (app t, 1 H, $H^{2'}$), 4.50 (app t, 1 H, H^2), 4.62 (app t, 1 H, H^4), 4.75 (m, 1 H, $H^{1'}$), 6.70 (s, 2 H, Ar-*H*), 6.76 (s, 2 H, Ar-*H*), 7.0−7.3 (m, 10 H, *Ph*). Minor isomer (~15%) ^{1}H NMR δ 0.48 (s, 3 H, J_{Pt} = 75 Hz, Pt-*Me*).

[PtClMe(mestien)(η^2-styrene)] (8b). Procedure A: ^{1}H NMR (270 MHz, $CDCl_3$). The only clearly assignable signals are four Pt−Me singlets at δ −0.10 (J_{Pt} = 70 Hz), −0.04 (J_{Pt} = 75 Hz), 0.47 (J_{Pt} = 75 Hz), 0.68 (J_{Pt} = 66 Hz) (relative abundances 7:4:3:3). The Ar−Me groups give several signals (at least nine) in the range 2.0−2.5 ppm, and the rest of the spectrum is made of complex overlapping multiplets as in the case of **8a**. The composition of **8b** was indirectly confirmed by bubbling ethylene through a solution of the compound in methylene chloride, which quantitatively yielded **4b** and free styrene.

[PtClMe(mestien)(η^2-(E)-dichloroethene)] (9b). Procedures B and C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 3 H, J_{Pt} = 70 Hz, Pt-*Me*), 2.01 (s, 3 H, Ar-*Me*), 2.05 (s, 3 H, Ar-*Me*), 2.16 (s, 6 H, Ar-*Me*), 2.24 (s, 6 H, Ar-*Me*), 3.27 (d app t, 1 H, H^1), 3.43 (d, 1 H, J_{Pt} = 42 Hz, =C*H*), 3.75 (m, 3 H, H^2, $H^{2'}$, $H^{4'}$), 4.13 (dd, 1 H, $H^{3'}$), 4.48 (d, 1 H, J_{Pt} = 83 Hz, =C*H*), 4.49 (app t, 1 H, H^4), 4.54 (app t, 1 H, H^3), 4.92 (m, 1 H, $H^{1'}$), 6.53 (s, 2 H, Ar-*H*), 6.62 (s, 2 H, Ar-*H*), 6.6−7.6 (br, 8 H),[20] 6.96 (app t, 1 H, *Ph*), 7.03 (app t, 1 H, *Ph*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6 (J_{Pt} = 725 Hz, Pt-*Me*), 20.2 (Ar-*Me*), 20.4 (Ar-*Me*), 42.6 (J_{Pt} = 475 Hz, =*C*H), 42.9 (J_{Pt} = 425 Hz, =*C*H), 49.2, 49.4 (N*C*H_2, N′*C*′H_2), 70.9, 71.3 (Ph*C*H, Ph*C*′H), 128.5, 128.7, 128.8, 129.3, 129.6, 129.7, 130.0, 136.0, 136.3, 136.5, 136.6, 137.1, 137.2. Anal. Calcd for $PtC_{37}H_{45}Cl_3N_2$: C, 54.25; H, 5.54; N, 3.42. Found: C, 53.67; H, 5.40; N, 3.24.

[PtClMe(mestien)(η^2-fumaronitrile)] (10b). Procedures B and C: ^{1}H NMR (270 MHz, $CDCl_3$) isomer A (43% abundance) δ 0.51 (s, 3 H, J_{Pt} = 67 Hz, Pt-*Me*), 1.64 (d, 1 H, J_{Pt} = 61 Hz, =C*H*), 2.21 (s, 3 H, Ar-*Me*), 2.22 (s, 3 H, Ar-*Me*), 2.27 (s, 6 H, Ar-*Me*), 2.34 (s, 6 H, Ar-*Me*), 2.95 (d, 1 H, J_{Pt} = 86 Hz, =C*H*), 3.6−4.6 (6 H),[21] 4.82 (app t, 1 H, H^2), 5.52 (m, 1 H, H^1), 6.81 (s, 2 H, Ar-*H*), 6.84 (s, 2 H, Ar-*H*), 6.6−7.6 (br, 10 H, *Ph*); isomer B (57% abundance) ^{1}H NMR δ 0.93 (s, 3 H, J_{Pt} = 65 Hz, Pt-*Me*), 2.09 (s, 3 H, Ar-*Me*), 2.14 (s, 3 H, Ar-*Me*), 2.27 (s, 6 H, Ar-*Me*), 2.29 (d, 1 H, J_{Pt} = 61 Hz, =C*H*), 2.34 (s, 6 H, Ar-*Me*), 3.35 (d, 1 H, J_{Pt} = 81 Hz, =C*H*), 3.6−4.6 (7 H),[21] 5.60 (m, 1 H, H^1), 6.56 (s, 2 H, Ar-*H*), 6.64 (s, 2 H, Ar-*H*), 6.6−7.6 (br, 10 H, *Ph*). Anal. Calcd for $PtC_{39}H_{45}ClN_4$: C, 58.53; H, 5.67; N, 7.00. Found: C, 57.98; H, 5.51; N, 6.88.

[PtClMe{(S,S)-(+)-mestien}(η^2-1-buten-3-ol)] (11b′). Procedure B: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3 H, J_{Pt} = 70 Hz, Pt-*Me*), 0.74 (dd, 1 H, J_{Pt} = 81 Hz, =C*H*H), 0.84 (d, 3 H, CH*Me*), 1.86 (dd, 1 H, =C*H*), 2.18 (app s, 12 H, Ar-*Me*), 2.31 (app s, 6 H, Ar-*Me*), 2.38 (dd, 1 H, =CH*H*), 2.51 (app q, 1 H, C*H*OH), 2.91 (d app t, 1 H, H^1), 3.52 (dd, 1 H, H^3), 3.59 (dd, 1 H, $H^{3'}$), 3.76 (app t, 1 H, $H^{4'}$), 3.85 (app t, 1 H, $H^{2'}$), 4.28 (app t, 1 H, H^2), 4.64 (app t, 1 H, H^4), 4.77 (d app t, 1 H, $H^{1'}$), 6.72 (s, 4 H, Ar-*H*), 6.8−7.4 (br, 10 H, *Ph*); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ −10.0 (J_{Pt} = 730 Hz, Pt-*Me*), 20.2 (Ar-*Me*), 20.5 (Ar-*Me*), 20.6 (Ar-*Me*), 23.5 (CH*Me*), 24.6 (J_{Pt} = 350 Hz, =*C*H_2), 47.2 (N*C*H_2), 47.3 (N′*C*′H_2), 53.5 (J_{Pt} = 380 Hz, =*C*H), 66.6 (J_{Pt} = 35 Hz, *C*HOH), 68.1 (Ph*C*H), 70.3 (Ph*C*′H), 127−138 (*Ar, Ph*).[22]

(20) At 25 °C the signals are coalesced in a single flat band.
(21) Overlapped multiplets from both A and B isomers.
(22) The aromatic carbon resonances overlap in that range.

Table 4. Summary of Crystallographic Data

crystal size/mm	0.10 × 0.12 × 0.30
formula	$PtCl_3N_2C_{37}H_{45}$
fw	819.2
crystal system	monoclinic
space group	$P2_1/c$
a/Å	13.163(2)
b/Å	19.274(4)
c/Å	14.906(2)
β	112.56(2)
V/Å^3	3492(2)
Z	4
$F(000)$	1640
D_c/g cm^{-3}	1.56
D_m/g cm^{-3}	1.53
λ(Cu Kα)/Å	1.5418
θ_{max}/deg	72
μ/cm^{-1}	99.6
no. of indep. refls.	6859
no. of refls. above 3$\sigma(I)$	3918
no. of refined parameters	388
goodness of fit	1.075
R	0.059
R_w	0.069

11b″. This diastereomer, which contains the opposite enantiomer of the butenol, was obtained in equimolar mixture with **11b′** by using procedure A for the preparation: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 3 H, J_{Pt} = 70 Hz, Pt-*Me*), 1.30 (d, 3 H, CH*Me*), 2.10 (app s, 6 H, Ar-*Me*), 2.25 (app s, 12 H, Ar-*Me*), 3.12 (app t, 1 H, H^1), 4.52 (app t, 1 H, H^2 or H^4). Other signals are not assignable due to overlapping with the signals of the other diastereomer. ^{13}C NMR (67.9 MHz, $CDCl_3$) δ −9.3 (Pt-*Me*), 19.0 (Ar-*Me*), 20.5 (Ar-*Me*), 22.8 (CH*Me*), 31.1 (=*C*H_2), 45.6 (N*C*H_2), 47.6 (N′*C*′H_2), 53.6 (=*C*H), 63.0 (*C*HOH), 69.7 (Ph*C*H), 71.1 (Ph*C*′H), 127−138 (*Ar, Ph*).[20]

Structure Determination and Refinement of [PtClMe(mestien)((E)-dichloroethene)] (9b). Crystals suitable for X-ray analysis were obtained as follows. The complex (0.06 mmol) was dissolved in 30 mL of CH_2Cl_2−ethanol (25:75 v/v) at T = 40 °C. The resulting solution was kept at room temperature, producing colorless crystals, which were isolated. Many of the details of the structure analysis are listed in Table 4. X-ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Cu Kα graphite-monochromated radiation operated in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the θ range 23 ≤ θ ≤ 29°. Three monitoring reflections, measured every 500, showed intensity fluctuations within 5%. The structure was solved by routinary application of the Patterson and Fourier techniques. The full-matrix least-squares refinement minimized the quantity $\sum w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 1]$ where σ is derived from counting statistics. All non-hydrogen atoms were refined anisotropically. The H atoms were added at calculated positions with isotropic thermal parameters 1.2 times larger than the B of the carrier atoms and held fixed during the refinement. A correction for absorption effects was applied according to Walker and Stuart,[23] by using the computer program DIFABS (maximum and minimum values of the absorption correction were 1.4 and 0.7). The final Fourier difference map was within 1.3 e Å^{-3}. Neutral atomic scattering factors were taken from the literature.[24] All calculations, carried out on a Vax 750 at the Centro Interdipartimentale di Metodologie Chimico-fisiche of the Università di Napoli, were performed with the Enraf-Nonius (SDP) set of programs.[25] Complete lists of bond distances and angles, hydrogen atom parameters, and anisotropic thermal param-

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(24) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.
(25) B. A. Frenz & Associates Inc. Structure Determination Package (SDP), College Station, TX, and Enraf-Nonius, Delft, The Netherlands, 1982.

eters of the non-hydrogen atoms have been deposited as supplementary material.

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Supplementary Material Available: Tables of positional and thermal parameters of the H atoms (Table 5s), anisotropic thermal parameters of the non-hydrogen atoms (Table 6s), and complete bond distances and angles (Table 7s) (4 pages). Ordering information is given on any current masthead page.

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