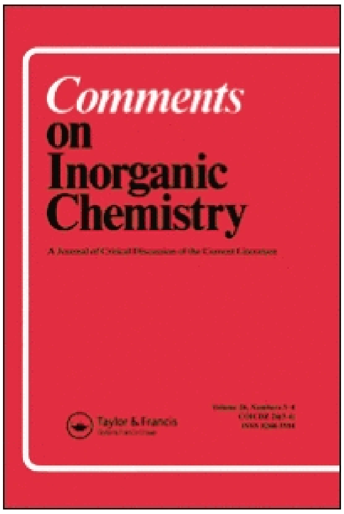

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Five-Coordination in Platinum(II) and Palladium(II) Chemistry

Luciana Maresca[a]; Giovanni Natile[a]
[a] Dipartimento Farmaco-Chimico, Bari, Italy

To cite this Article Maresca, Luciana and Natile, Giovanni(1993) 'Five-Coordination in Platinum(II) and Palladium(II) Chemistry', Comments on Inorganic Chemistry, 14: 6, 349 — 366

To link to this Article: DOI: 10.1080/02603599308048668

URL: http://dx.doi.org/10.1080/02603599308048668

Five-Coordination in Platinum(II) and Palladium(II) Chemistry

LUCIANA MARESCA and GIOVANNI NATILE
Dipartimento Farmaco-Chimico,
via G. Amendola 173,
70126 Bari, Italy

Received March 20, 1992

In recent years a number of chelating ligands, when combined with a π-acid such as an alkene, have been found to stabilize five-coordination in palladium(II) and platinum(II) chemistry. The complexes have invariably a trigonal bipyramidal geometry with the bidentate ligand and the alkene in the equatorial plane. The π-acceptor capacity of the alkene and a small bite of the chelate ligand (between 70 and 85°) are both required for accommodating them in the equatorial plane where the d_{z^2} electron concentrations (which in the square planar d^8 complexes are located above and below the coordination plane) are also confined. Two monodentate ligands, in place of one chelate, do not stabilize the five-coordination since for entropic reasons the dissociation of one of them is strongly favored. A great bulk of the chelate ligand is also found to stabilize five-coordination since interligand steric interactions are smaller in the trigonal plane of a five-coordinate complex than in the square-plane of a four-coordinate species. Moreover the same steric factors that destabilize four- versus five-coordination can also destabilize four- versus three-coordination, and T-shaped ML_3 species appear to provide a low energy path for the interconversion between four- and five-coordinate complexes. The alkene is strongly bound to the metal, the metal–carbon bond distances are shorter, and the bending back of the alkene substituents is greater than those found in four-coordinate compounds. The activation energy for alkene rotation is also greater in five-coordinate species, and in a number of cases atropisomers are generated. The chelate dinitrogen ligand also lying in the equatorial plane is, on the other hand, loosely bound to the metal, and dissociation of one end of this ligand

Comments Inorg. Chem.
1993, Vol. 14, No. 6, pp. 349–366
Reprints available directly from the publisher
Photocopying permitted by license only

appears to be the preliminary step in all substitution processes involving the alkene, the axial ligands, and the bidentate ligand itself. These processes should therefore occur through a mechanism analogous to that operating in four-coordinate complexes. The dissociation of one end of the bidentate ligand also provides a low energy path to proton exchange and inversion of configuration at coordinated nitrogens. Other aspects related to the conformation of the alkene and of the chelate ligand as well as to the preparation and reactivity of this class of compounds are discussed.

Key Words: *five-coordination, alkene complexes, π-acid ligands, Pt(II), Pd(II)*

INTRODUCTION

Five-coordinate intermediates have been postulated in a number of important processes involving platinum(II) and palladium(II) compounds. The reactions of ligand substitution, cis-trans isomerization and alkene insertion into metal–carbon σ bonds are all believed to occur through intermediates involving trigonal-bipyramidal geometries.[1]

Over the last two decades five-coordinate platinum(II) compounds containing a good π-acceptor ligand (generally alkenes but also alkynes), together with a bidentate or a tridentate σ-donating nitrogen ligand, have been extensively studied.[2-5] More recently some analogous five-coordinate complexes of palladium(II) have been reported.[6,7]

We wish to offer some comments on this class of coordinatively saturated platinum(II) and palladium(II) complexes since future developments of important processes involving d^8 metal ions must rely on our understanding of the structure, bonding and reactivity of five-coordinate species.

REQUIREMENTS FOR A STABLE FIVE-COORDINATE SPECIES

It is widely known that d^8 metal ions can give two different types of compounds: four-coordinate square-planar and five-coordinate trigonal bipyramidal or square pyramidal complexes. The former are coordinatively unsaturated and nevertheless more common.

They were synthesized first and have given a relevant contribution to the development of coordination chemistry. The latter, in spite of the fact that they are coordinatively saturated and have been postulated as intermediates in several substitution, isomerization and insertion reactions, have been synthesized much more recently and until the seventies only a few of them were known.[8]

In 1973 two platinum(II) five-coordinate complexes were reported, almost simultaneously (Fig. 1).[9] Both had an alkene and a chelate ligand in the equatorial plane. Moreover, in one of the two compounds the chelating ligand had a third donor atom linked to the metal in an axial site. However, as shown in later work, the crucial features for stabilizing the five-coordinate trigonal bipyramidal geometry are an alkene and a bidentate ligand both lying in the equatorial plane; the bridging of equatorial with axial ligands does not add to the stability of these compounds.

The 1973 species showed from the beginning the peculiar features of this type of complexes which can be summarized as follows:

(i) The Pt-axial ligand distances are very close to those found in four-coordinate complexes.

(ii) The equatorial platinum–alkene bond distances are shorter than those found in square-planar species and are accompanied by a greater bending back of the carbon substituents (about twice as much as the values found in four-coordinate species). The alkene protons are more shielded and their resonance frequencies shifted ca. 2 ppm to higher field with respect to those of four-coordinate complexes. Also the activation energy for rotation about the platinum–alkene bond is usually greater for five-coordinate complexes[6] than it is for square-planar species.[10] All these features point to a stronger platinum–alkene bonding interaction in five-coordinate complexes than in four-coordinate species.

(iii) On the other hand, the equatorial Pt–N bonds of five-

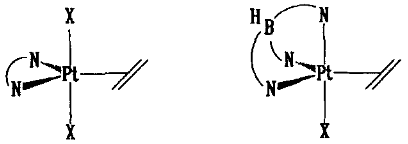

FIGURE 1 Schematic drawings of the two five-coordinate platinum(II) complexes reported in 1973 (Ref. 9).

coordinate complexes are about 0.2 Å longer than those of square–planar species. The nitrogen protons, if present, are more shielded and less acidic, but the rate of substitution of D for H and the rate of inversion of configuration at nitrogen are greater than those of square–planar species.[3d] These features are in accord with the presence, in five-coordinate species, of weaker platinum nitrogen bonds. Moreover, the processes of proton exchange and inversion of configuration at nitrogen should not occur (like in four-coordinate complexes) through the initial dissociation of a proton, while the nitrogen remains bound to the metal atom, but through dissociation of one end of the bidentate ligand while the proton is still bound to the nitrogen.

In the mid-seventies a theoretical study by Hoffmann and coworkers concerned with five-coordinate complexes of d^8 metal ions was published.[11] The authors concluded that in a trigonal bipyramidal geometry a greater electron charge is concentrated in the equatorial plane than in the axial direction. Therefore σ donor ligands give stronger bonding interactions in axial than in equatorial positions, whereas π acceptor ligands can form stronger bonds in equatorial than in axial sites. Furthermore, single faced ligands such as the alkenes should prefer the in-plane orientation. These conclusions are in accord with the experimental results. For instance, in the above-quoted examples, among σ donor ligands, the halogens in axial positions are more strongly bound to the metal than the equatorial nitrogens. Moreover, the alkene is strongly coordinated to the metal and lies in the equatorial plane.

Five-coordinate complexes bearing one bidentate and three monodentate ligands were the object, in the same period, of another theoretical study.[12] In this case the authors concluded that in the two possible geometries, square pyramid and trigonal bipyramid, the bidentate ligand can occupy two basal sites in the former case and bridge one axial and one equatorial position or two equatorial positions in the latter case. The change from a situation to the next one in the given order should be favored by an increase of the ligand bite. Experimental findings are in disagreement with the above conclusions, since in our compounds the bite angle does not exceed 80° and the bidentate ligand occupies two equatorial sites, a situation which would have required the largest possible bite. Moreover, when a comparison was made among bidentate ligands of increasing bite such as 1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane, it was found that the most stable five-coordinate species was obtained with the ligand having the smallest bite.[3c]

THE ROLE OF THE EQUATORIAL LIGANDS

Why does an alkene and a bidentate ligand of small bite in the equatorial plane of a trigonal bipyramid stabilize five- versus four-coordination in platinum(II) chemistry?

A series of platinum(II) complexes was prepared having the formula, $[Pt(Me_2phen)(L)X_2]$, where L is either an alkene or a ligand with a C, N or P donor atom (L = C_2H_4, CO, PPh_3, ONPh), Me_2phen is 2,9-dimethyl-1,10-phenanthroline, and X is Cl, Br, or I.[13] In all cases ^1H NMR spectra down to −90°C were in accord with a symmetric phenanthroline molecule in the NMR time response. However, the X-ray structures showed that this was not the case in the solid state. Instead, depending upon the nature of L, the phenanthroline shifted from a symmetric doubly bonded to a non-symmetric singly bonded situation (Fig. 2). Ab initio molecular orbital calculations showed that all L ligands were good σ donors (as expected from the 2+ oxidation state of the metal), but, in contrast, the π-accepting capability varied dramatically along the series $C_2H_4 > CO > PH_3 > ONCH_3$ (Table I).[13] Therefore, in the complexes containing L ligands different from an alkene, the second end of the phenanthroline is not allowed to enter the coordination sphere of platinum because of the repulsion caused by the d_z^2 electron concentrations located above and below the square-planar coordination plane. On the contrary, when a strong π-acceptor ligand like an alkene is present, these electron concentrations are reduced to allow the second nitrogen of the diamine to donate its lone pair to the metal. The residual repulsion between the nitrogen lone pairs and the d_z^2 electron clouds causes the two platinum nitrogen bonds to be longer than those found in square-planar compounds. This establishes the role of the alkene in stabilizing five-coordination.

Why must the other equatorial ligand be bidentate and have a small bite?

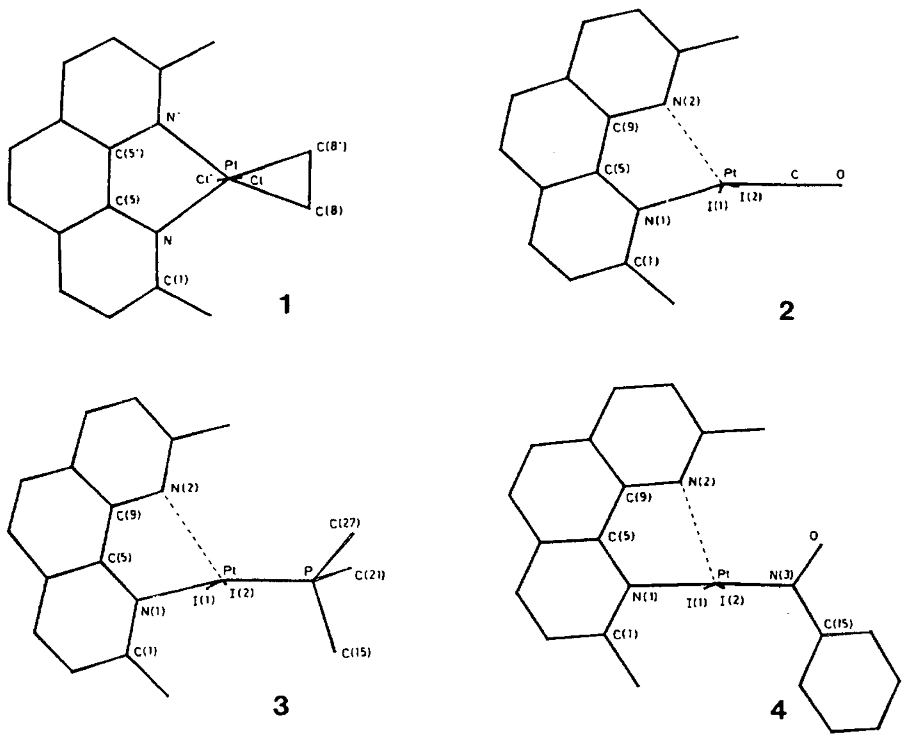

FIGURE 2 Schematic projections of complexes **1–4** ([Pt(2,9-dimethyl-1,10-phenanthroline)(L)X_2]: X = Cl, L = C_2H_4 **1**; X = I, L = CO **2**, PPh_3 **3**, ONPh **4**) on the plane defined by the N(1), N(2) and Pt atoms. In complex **3** only the P-attached carbon atoms of the phenyl groups have been represented for clarity.

TABLE I

Results of the CSOV analysis of change in interaction energy (ΔE_{int}, kJ mol^{-1}) and dipole moment ($\Delta\mu$, au) in [Pt(bipy)F_2(L)] complexes (L = C_2H_4, CO, PH_3, $ONCH_3$) (Ref. 13).

L	r_e(Pt–L)/Å	σ-Donation		π-Back Donation	
		ΔE_{int}/kJ mol^{-1}	$\Delta\mu$/au	ΔE_{int}/kJ mol^{-1}	$\Delta\mu$/au
C_2H_4	2.10	180	+0.49	179	−0,94
CO	2.13	104	+0.33	83	−0.41
PH_3	2.53	200	+1.22	37	−0.18
ONMe	2.08[a]	99	+0.29	59	−0.18

[a] Distance not optimized.

The latter question will be addressed first since it is somewhat related to the point discussed above. Theoretical calculations on the rate of exchange of the ammine ligand trans to L in *trans*-[Pt(L)Cl_2(NH_3)] have been recently performed by Hall and coworkers.[14] The entering and leaving ammine, the L ligand and the two electron concentrations, which in the square-planar precursor are located above and below the coordination plane, are confined in the equatorial plane of the trigonal bipyramidal activated complex. The optimum angle between the two metal ammine links has been found to range between 70 and 85°, which is coincident with the values found in structurally characterized five-coordinate species of this type.[3b] Therefore, now we have an answer to the question, "Why does a small ligand bite favor the formation of trigonal bipyramidal five-coordinate species?" These species are similar to the activated complex discussed above which is favored when the bite angle between the equatorial nitrogens is small.

We are now left with the final question, "Why do we need a bidentate ligand?" In the above-quoted paper of Hall *et al.*[14] the energy profile along the reaction coordinate was also calculated. It was found that even in the most favorable case, that is when there is an alkene trans to the exchanging ammine, the trigonal bipyramidal activated complex is higher in energy than the reagents (the square-planar complex and the free ammine). To reverse the relative stability of these two situations, along the reaction coordinate, we need to circumvent the favorable entropic contribution of the two separate reagents which become bound together in the transition state. A reduction of this entropic stabilization can best be achieved by linking together the two reagents and this is what has been really, although unintentionally, done by employing a bidentate ligand.

SYNTHETIC PROCEDURES

From a Four-Coordinate Precursor

The five-coordinate complexes are easily prepared by substitution of a bidentate ligand (usually with two N-donor atoms) for a monodentate ligand in a four-coordinate complex already containing the alkene (type 1). There are, however, other possible ways to go from four- to five-coordinate species: addition of the alkene to a four-coordinate compound containing a bidentate ligand and two monodentate ligands (type 2), or addition of a monodentate ligand to a complex having a bidentate ligand, a monodentate ligand and the alkene in the metal coordination sphere (type 3). The last two procedures, however, do not work except in very special cases which deserve further discussion. Why?

If we draw a scheme for the reaction pathways, according to the classical associative mechanism operating in square-planar complexes (Fig. 3),[1a] we can see how, starting from complexes of type 2 and 3, the stable five-coordinate configuration can be reached only by passing through intermediate five-coordinate species. These species contain the alkene in an apical position, and for the reason previously discussed the formation of these species is not favored. On the contrary, by starting from a compound of type 1, the stable five-coordinate structure can be directly attained without passing through reaction intermediates having the alkene in apical positions.

There are, however, a few cases in which it has been possible to convert a complex of type 2 into a stable five-coordinate species by direct addition of an alkene. One of these exceptions was reported by Albano *et al.*[4g] In their complex, [PtClMe(6-MePy-2-CH=N-CHMePh)], one of the two Pt–N bonds is 0.22 Å longer than the other and therefore it can be easily broken. The reasons for the weakness of this bond have to be found in the labilizing

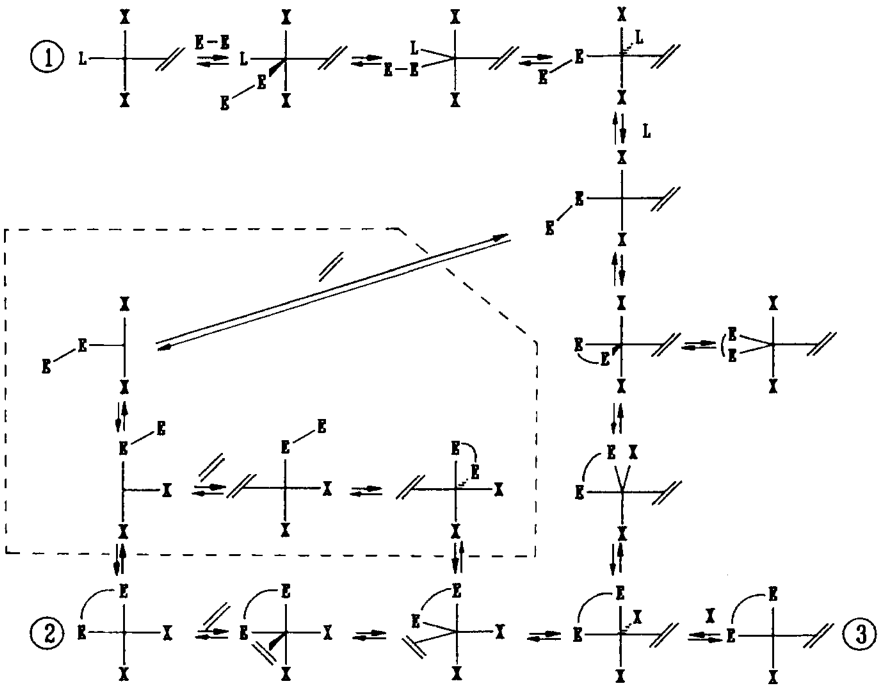

FIGURE 3 Schematic drawing of the reaction pathways leading from four-coordinate complexes of type 1, 2 and 3 to the stable five-coordinate species. The scheme has been drawn according to the classical associative mechanism except for the part included in a dashed frame for which a dissociative mechanism has been proposed.

influence of the trans alkyl ligand and in the steric interaction between the adjacent methyl substituent of the pyridine ring and the cis chloride ligand.

Another exception is given by the complexes of platinum and palladium with 2,9-dimethyl-1,10-phenanthroline.[6] In this case the steric interaction between the methyl groups in the ortho position with respect to the nitrogens and the cis chlorides causes a narrowing of the Cl–Pt–Cl angle (85°), a folding (like butterfly wings) of the two external rings of phenanthroline (16°), and a remarkable rotation of the phenanthroline average plane with respect to the platinum coordination plane (28°) (Fig. 4). In this complex, as in the previous one, the dissociation of one end of the bidentate ligand could be a likely first step allowing a dissociative low energy pathway for the addition of the alkene and formation of the stable five-coordinate species. This is shown in Fig. 3 in a dashed frame.

It is to be noted that the initially formed T-shaped intermediate has to isomerize before adding the alkene. Otherwise, it leads to the formation of an intermediate species of the normal reaction pathway which we have seen to be strongly disfavored.

The formation of five-coordinate complexes with tripodal ligands (hydrotrispyrazolylborate) by uptake of the alkene from a sub-

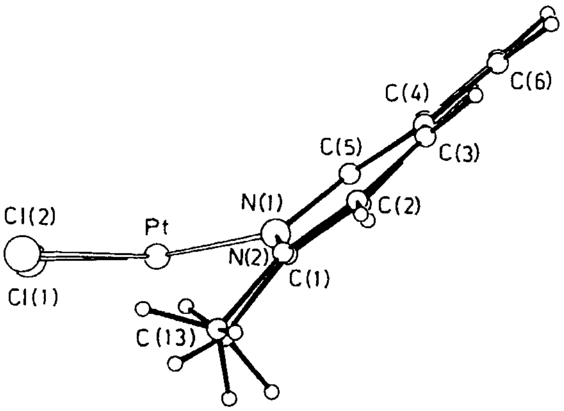

FIGURE 4 Projection of the structure of [PtCl$_2$(2,9-dimethyl-1,10-phenanthroline)] along the N–N vector showing the bending of the phenanthroline ligand and its rotation with respect to the platinum coordination plane.

strate of formula [Pt(tripodal ligand)X]$_n$($n \geq 1$),[2,9b] can be related to the above-quoted dissociative mechanism since the tripodal ligand can only act as a bidentate ligand toward the same metal ion in a square-planar geometry.[15]

From a Three-Coordinate Precursor

A completely different synthetic route to five-coordinate complexes of platinum(II) and palladium(II) involves the oxidative addition of electrophilic reagents to three-coordinate [M(η^2-alkene)(N–N)] complexes of Pt^0 and Pd^0 containing N–N ligands with suitable steric demand.[16] This procedure is particularly useful for the synthesis of five-coordinate complexes in which one axial ligand is an alkyl group. The complementary reaction, that is reductive elimination from a five-coordinate complex of Pt^{II} to give a three-coordinate Pt^0, can also take place.[17] Both reactions are rather interesting and are somewhat related to the much better known and widely exploited oxidative addition reductive elimination processes involving Pt^{II} and Pt^{IV} species.

From Another Five-Coordinate Complex

The reaction of ligand exchange does not bring any variation into the stereochemistry of five-coordinate complexes. This reaction can involve the alkene,[4a] the axial ligands[2c] and the bidentate ligand itself[5c] and can be a useful tool for the preparation of new five-coordinate species. The most likely mechanism for the exchange reactions implies the dissociation of one end of the weakly bound chelate ligand and formation of a four-coordinate species which undergoes substitution reaction by the usual associative mechanism. This step is followed by ring closing of the bidentate ligand in the substituted species and restoring of the trigonal bipyramidal geometry.

DECOMPOSITION PATTERNS

The reactivity of five-coordinate species is mainly related to loss of the alkene, loss of an axial ligand and insertion of the unsaturated ligand into a metal–carbon or metal–halide σ bond.

Loss of the Alkene

The thermodynamic stability of the five-coordinate species can range from cases in which the alkene can be lost only at high temperature (close to the decomposition temperature of the whole molecule) to cases where the alkene is lost easily at rather low temperature and in the solid state. The steric requirements of the chelate ligand, and in particular the in-plane bulk of the nitrogen substituents, appear to be the most important factors in determining such a stabilization. The increase of the interligand contacts which takes place when the bidentate ligand is removed from a trigonal plane and placed into a square-planar arrangement results in an increased thermodynamic stability of the five- versus four-coordinate species.

There are very few cases in which the loss of the alkene is a reversible process and these are restricted to the few exceptions in which it is possible to treat a species of type 2 directly with an alkene to form the five-coordinate complex.[4g,6] As already shown only a dissociative mechanism like that depicted in Fig. 3 can provide a low energy path for such a reaction. Some data showing the dependence of the equilibrium constants upon the alkene, the axial ligands and the metal are given in Table II.[6]

TABLE II

K_f (mol^{-1} dm^3) for the reaction: [MX_2(2,9-Me_2-phen)] + alkene $\rightleftharpoons$ [MX_2(η^2-alkene)(2,9-Me_2-phen)], calculated from ^{1}H NMR data in $CDCl_3$ at 25°C [M = Pt, X = Cl (**1**), Br (**2**), I (**3**); M = Pd, X = Cl (**4**), Br (**5**)] (Ref. 6).

Complex	Alkene	K_f (mol^{-1} dm^3)[a]
1	ethylene	8.3×10^2
1	propene	3.3×10^2
1	1-butene	1.1×10^2
1	*Z*-2-butene	1.1×10
1	styrene	5.5
1	*E*-2-butene	1.7
2	*E*-2-butene	1.5×10
3	*E*-2-butene	4.6×10^2
4	ethylene	4.5×10
4	propene	9.1×10^{-1}
5	propene	4.2

[a] Estimated error within ±5%.

Loss of an Axial Ligand

Another decomposition pattern for five-coordinate trigonal bipyramidal species is the loss of an apical ligand and formation of a square-planar complex still containing the alkene and bearing a positive charge. The role of the solvent appears to be critical in determining which ligand will be lost (the alkene, as in the previous case, or an axial ligand). Polar solvents, such as methanol, appear to favor the formation of ionic compounds of type 3 (see Fig. 3) while solvents such as chloroform or dichloromethane appear to favor the formation of neutral compounds of type 2.[18] By this procedure a stable and very reactive compound has been prepared $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)]^+$.[19] This reacts with any sort of nucleophile to give the corresponding addition products.[20]

Insertion of the Alkene in a Metal–Axial σ Bond

Five-coordinate complexes can evolve to a square-planar geometry also via insertion of the unsaturated ligand into an axial metal–carbon σ bond. This reaction pattern is favored when the alkene carries electron withdrawing substituents and the axial ligand is a phenyl.[21] Insertion of the unsaturated ligand into an axial platinum–iodide bond has also been reported.[22] This investigation is at the very beginning and is likely to give some substantial contribution to the knowledge of factors influencing this type of reactivity.

CONFORMATIONS OF THE EQUATORIAL LIGANDS

The Alkene

Alkenes can have different symmetry (e.g., ethene, D_{2h}; Z-2-butene, C_{2v}; E-2-butene, C_{2h}; propene, C_s) and in a five-coordinate environment they can give different stereoisomers. The coordination of a prochiral alkene (C_{2h}, C_s symmetry) affords two enantiomeric species.[23] Five-coordinate complexes with various enantiomeric excesses have been prepared by substitution of a bidentate ligand (N–N) for a monodentate one in a resolved square-planar species. The absolute configuration of these compounds appears to be related to the sign of a CD band.[24]

If another chiral center besides that formed by the prochiral alkene is present in the complex (this can be the metal itself in the case in which both the axial ligands and the two ends of the chelate ligand are chemically different) two pairs of enantiomers are formed in different yields. In some cases, the diastereomeric mixture has been partially resolved by fractional crystallization.[25]

Atropisomers can be generated by hindered rotation of the alkene in the case in which both the alkene has C_{2v} or C_s symmetry and the axial ligands and/or the equatorial ends of the chelate ligand are chemically different. The two atropisomers are in an enantiomeric relationship if the alkene has C_{2v} symmetry and the C_2 axis projects over two chemically equivalent platinum bonded groups.

Depending upon the steric requirements of the alkene and of the ancillary ligands, complexes in which the equilibrium ratio between atropisomers ranges from 1:1 to the almost exclusive presence of only one isomer have been prepared.[4h,7]

The Bidentate Ligand

A further type of isomerism can arise when the bidentate ligand is a prochiral diamine. In the case of a symmetrically substituted ethylenediamine, two geometric isomers are formed; these are generally indicated as cis and trans isomers depending upon the mutual orientation of the nitrogen substituents with respect to the plane of the chelate ring. The cis isomer has both substituents on the same side of the trigonal plane; the absolute configurations of the two nitrogens are different and one N-substituent is in a quasi-axial and the other in a quasi-equatorial position. The trans isomer has the two substituents on opposite sides of the trigonal plane; the absolute configurations of the two nitrogens are equal and both N-substituents are in a quasi-equatorial position.[3d]

Unlike four-coordinate complexes, the five-coordinate species have, at room temperature, fluxional configuration at the nitrogen atoms that "freezes out" as the temperature is lowered. The trans conformation appears to be preferred since it minimizes steric

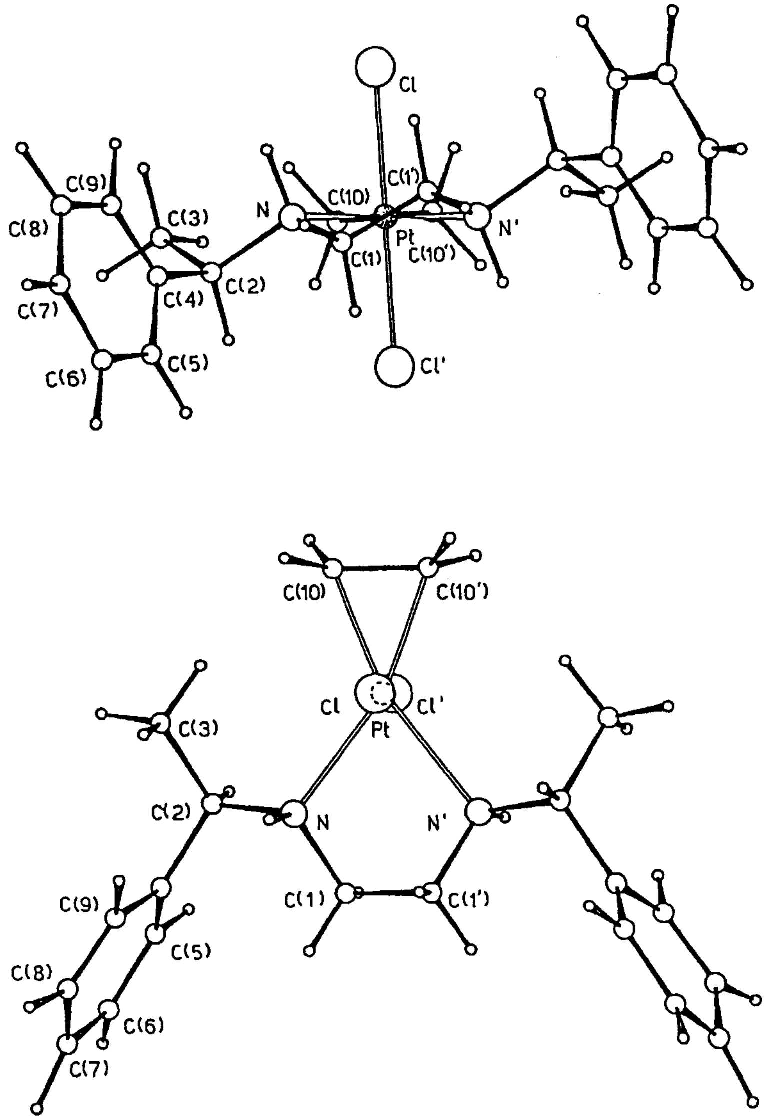

FIGURE 5 Molecular structure of the complex [Pt(η^2-C_2H_4)Cl_2{N,N'-bis(α-methylbenzyl)ethylenediamine}] in which the adjacent N and C atoms have equal configuration (*R*). A different configuration on these two atoms would have exchanged the relative position of the Ph and Me groups.

interactions between the quasi-equatorial N-substituents and the apical ligands.

The influence of a chiral N-substituent on the configuration of the coordinating nitrogen has also been investigated for symmetrically substituted ethylenediamines such as N,N′$(CHMePh)_2$-1,2-diaminoethane. Since the bidentate ligand is forced to assume a trans conformation for the reason given above, the effect of asymmetry induction is restricted to the preference for one of two possible diostereomeric trans isomers differing in the absolute configuration of the nitrogen atoms. Experimental results have led to the conclusion that the preferred configuration for the nitrogens is the one which allows the chiral alkyl substituents to direct the least bulky group toward the apical ligand and the next bigger group toward the equatorial alkene ligand. When the priority of the groups for assignment of the absolute configuration parallels their bulk, this corresponds to equal configuration on adjacent C and N atoms (Fig. 5).[3d]

CONCLUSIONS

This Comment have dealt with only one class of five-coordinate complexes of platinum(II) and palladium(II). Nevertheless, some general features concerned with the electron distribution and bonding, the structural and conformational preferences, the reaction mechanisms and reactivity have been elucidated. We hope that this treatment will contribute to a better understanding of the versatile chemistry of these metal species.

References

1. (a) F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (Wiley, New York, 1967). (b) U. Belluco, *Organometallic and Coordination Chemistry of Platinum* (Academic Press Inc., London, 1974), pp. 35–40. (c) G. Wilkinson, G. A. Stone and E. W. Abel, *Comprehensive Organometallic Chemistry* (Pergamon Press Ltd., Oxford, 1982), Vol. 6. (d) J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms* (Brooks/Cole Publishing Co., Monterey, CA, 1985). (e) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, CA, 1987). (f) D. L. Thorn and R. Hoffmann, J.

Am. Chem. Soc. **100**, 2079 (1978). (g) D. Eisenstein and R. Hoffmann, J. Am. Chem. Soc. **103**, 4308 (1981).

2. (a) H. C. Clark and L. E. Manzer, Inorg. Chem. **13**, 1996 (1974). (b) L. E. Manzer, Inorg. Chem. **15**, 2354 (1976). (c) H. C. Clark and M. A. Mesubi, J. Organomet. Chem. **215**, 131 (1981).
3. (a) L. Maresca, G. Natile and L. Cattalini, Inorg. Chim. Acta **14**, 79 (1975). (b) L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, J. Chem. Soc., Dalton Trans. 2386 (1976). (c) L. Maresca, G. Natile and L. Cattalini, J. Chem. Soc., Dalton Trans. 1140 (1979). (d) F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. M. Manotti-Lanfredi and A. Tiripicchio, Inorg. Chem. **27**, 2422 (1988).
4. (a) A. De Renzi, A. Panunzi, A. Saporito and A. Vitagliano, Gazz. Chim. Ital. **107**, 549 (1977). (b). A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone and A. Vitagliano, Inorg. Chem. **19**, 960 (1980). (c) V. G. Albano, F. Demartin, A. De Renzi, G. Morelli and A. Saporito, Inorg. Chem. **24**, 2032 (1985). (d) V. G. Albano, F. Demartin, B. Di Blasio, G. Morelli and A. Panunzi, Gazz. Chim. Ital. **115**, 361 (1985). (e) P. Ammendola, M. R. Ciajolo, A. Panunzi and A. Tuzi, J. Organomet. Chem. **254**, 386 (1983). (f) A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, Gazz. Chim. Ital. **117**, 445 (1987). (g) V. G. Albano, D. Braga, V. De Felice, A. Panunzi and A. Vitagliano, Organometallics **6**, 517 (1987). (h) M. E. Cucciolito, V. De Felice, A. Panunzi and A. Vitagliano, Organometallics **8**, 1180 (1989).
5. (a) H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C. H. Stam, J. Organomet. Chem. **175**, C21 (1979). (b) H. van der Poel and G. van Koten, J. Organomet. Chem. **187**, C17 (1980). (c) H. van der Poel and G. van Koten, Inorg. Chem. **20**, 2950 (1981). (d) H. van der Poel, G. van Koten and G. C. van Stein, J. Chem. Soc. Dalton Trans. 2164 (1981).
6. F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, M. Lanfranchi and A. Tiripicchio, J. Chem. Soc. Dalton Trans. 1007 (1991).
7. V. G. Albano, C. Castellari, M. E. Cucciolito, A. Panunzi and A. Vitagliano, Organometallics **9**, 1269 (1990).
8. F. R. Hartley, *The Chemistry of Platinum and Palladium* (Applied Science Publishers, London, 1973), pp. 143–149.
9. (a) L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, J. Chem. Soc. Chem. Commun. 369 (1973). (b) H. C. Clark and L. E. Manzer, J. Am. Chem. Soc. **95**, 3812 (1973).
10. C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, J. Chem. Soc. (A) 53 (1969); *ibid.* 1653 (1970). J. Ashley-Smith, Z. Douek, B. F. G. Johnson and J. Lewis, J. Chem. Soc. Dalton Trans. 128 (1974).
11. A. R. Rossi and R. Hoffmann, Inorg. Chem. **14**, 365 (1975).
12. J. C. Dewan and D. L. Kepert, J. Chem. Soc. Dalton Trans. 959 (1975).
13. F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, J. Chem. Soc. Chem. Commun. 333 (1992).
14. Z. Lin and M. B. Hall, Inorg. Chem. **30**, 646 (1991).
15. P. E. Rush and J. D. Oliver, J. Chem. Soc. Chem. Commun. 996 (1974).
16. V. De Felice, M. Funicello, A. Panunzi and F. Ruffo, J. Organomet. Chem. **403**, 243 (1991).
17. B. Akermark, V. De Felice, A. Panunzi and F. Ruffo, Acta Chemica Scandinavica. **46**, 499 (1992).
18. G. Natile, L. Maresca, L. Cattalini, U. Belluco, P. Uguagliati and U. Croatto, Inorg. Chim. Acta **20**, 49 (1976).

19. G. Gervasio, S. A. Mason, L. Maresca and G. Natile, Inorg. Chem. **25**, 2207 (1986).
20. (a) L. Maresca, G. Natile, A. M. Manotti-Lanfredi and A. Tiripicchio, J. Am. Chem. Soc. **104**, 7661 (1982). (b) L. Maresca and G. Natile, J. Chem. Soc. Chem. Commun. 40 (1983). (c) F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile and F. Gasparrini, J. Chem. Soc. Dalton Trans. 1019 (1990). (d) F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, J. Chem. Soc. Dalton Trans. 309 (1992). (e) L. Maresca, G. Natile and F. P. Fanizzi, J. Chem. Soc. Dalton Trans. 1867 (1992).
21. A. De Renzi, personal communication.
22. N. Chaudhury and R. J. Puddephatt, Canad. J. Chem. **57**, 2549 (1979).
23. G. Mestroni, E. Alessio, G. Zassinovich and L. G. Marzilli, Comments Inorg. Chem. **12**, 67 (1991).
24. A. De Renzi, M. Funicello, G. Morelli, A. Panunzi and C. Pellecchia, J. Chem. Soc. Perkin Trans. II 427 (1987).
25. A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, Gazzetta Chim. Ital. **115**, 247 (1985).