

Pt(IV) derivatives formed by oxidative addition of organic halides to $[\text{Pt}(\text{CH}_3)_2(\text{N},\text{N}\text{-chelate})]$ substrates: geometric isomers at equilibrium

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Dedicated to Professor Fausto Calderazzo on occasion of his 70th birthday.

Abstract

The geometrical isomerism at equilibrium of Pt(IV) derivatives of general formula $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{N}-\text{N})]$ ($\text{N}-\text{N}$ = 2,9-dimethyl-1,10-phenanthroline or 1,10-phenanthroline; R = σ C-bonded ligand; X = halide) has been investigated by variation of R , X , and $\text{N}-\text{N}$. The complexes have been obtained mainly through oxidative addition of RX to $[\text{Pt}(\text{CH}_3)_2(\text{N}-\text{N})]$. Some general trends can be traced in the relative stability of the geometrical isomers of the complexes, and attempts to discriminate steric and electronic factors have been presented. The first attainment of a compound of the general formula $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{N}-\text{N})]$ containing three different types of σ C-bonded groups is also reported. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Homogeneous oxidative addition reactions involving transition metals are pivotal steps of important stoichiometric and catalytic processes and have received intensive interest over the past four decades [1]. A good share of the studies concerning these reactions and possible further transformations of their products have dealt with Pt(II)/Pt(IV) systems. In these cases, in fact, it has been possible to gain, in addition to many synthetic achievements, plenty of results on thermodynamic, kinetic, mechanistic and stereochemical features, concerning both the oxidation process and ensuing reactions, such as reductive elimination or insertion [2]. Attention was mostly devoted to the attainment of polyalkyl mononuclear Pt(IV) complexes including a

N,N-chelate ($\text{N}-\text{N}$) which are also of practical interest, e.g. for the preparation of pendant organometallic polymers [3] and dendrimers [4], or the development of biological properties [5], and are the subject of a comprehensive recent review by Rendina and Puddephatt [6].

It is to note, however that an aspect of the stereochemistry of these compounds, i.e. the geometrical isomerism at equilibrium, has not been investigated systematically, while by far more interest was devoted to the kinetically controlled isomerism, which is relevant mechanistically. The geometry of a few equilibrium systems is known by previous studies (see below), but no comprehensive discussion of this aspect has been made. On the other hand, the polyalkyl complexes, which can easily display good stability and moderate lability, appear to be a rare example of octahedral system, whose isomeric equilibrium composition can be modulated by an ample variation of the stereoelectronic properties of the coordination sphere,

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with the sole constraint of N–N chelation. This work aimed to add information on the equilibrium stereochemistry with regard to Pt(IV) dimethyl derivatives, including a third σ C-bonded group R and a *N,N*-chelate with in plane sterical hindrance. They can be obtained as the product of the oxidative addition of organic halides RX to the good nucleophiles $[\text{Pt}(\text{CH}_3)_2(\text{N}-\text{N})]$. The equilibrium stereochemistry of the complexes $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{N}-\text{N})]$ (**I**) has been investigated by variation of R, X and N–N groups. In addition, this study has produced the attainment of a compound of general formula $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{N}-\text{N})]$ containing three different types of σ C-bonded groups. Also some cationic complexes of type $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{L}(\text{N}-\text{N})]\text{BF}_4$ (**II**) have been isolated. We observe that no attempt was made during this work to assess mechanistic features of the examined oxidative processes [5], but involvement of different mechanisms does not affect our results. Moreover, the attainment of type **I** complexes by processes other than oxidative additions is potentially useful for the aim of the work.

2. Experimental

^1H -NMR spectra were recorded on 250-MHz Bruker model AC-250 spectrometer. CDCl_3 and CD_3NO_2 were used as solvents, and CHCl_3 ($\delta = 7.26$) and CHD_2NO_2 ($\delta = 4.33$) as internal standards. The following abbreviations are used for describing NMR multiplicities: s, singlet; d, doublet; m, multiplet. Solvents were dried before use. All reactions have been carried out under a nitrogen atmosphere by using Schlenk techniques, and care has been taken in excluding oxygen and moisture, respectively for the synthesis of isopropyl and acyl derivatives. The ligands 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmphen) were available commercially (Aldrich). The syntheses of $[\text{Pt}(\text{CH}_3)_2(\text{N}-\text{N})]$ is reported elsewhere [7,8].

2.1. Oxidative addition reaction of RX to $[\text{Pt}(\text{CH}_3)_2(\text{N}-\text{N})]$

Addition of RX (0.1–1 mmol, depending on R) to a solution of $[\text{Pt}(\text{CH}_3)_2(\text{N}-\text{N})]$ (0.1 mmol, 0.424 g of dmphen or 0.396 g of phen) in diethylether caused precipitation of the type **I** product. In order to attain high yields, a high yield (80–90%) of precipitate times, ranging from ca. 1–24 h, according to the nature of RX, were required. The white–brown yellow precipitate was collected by filtration, washed with diethyl ether and dried in vacuum.

2.2. Halide exchange on **I** complexes

A 1 M solution of the required sodium halide in water (0.3 ml) was added to a solution of **I** (0.05 mol) in 2 ml of chloroform and the mixture was stirred 30 min at room temperature. The organic phase was separated, washed with 2×1 ml of water and dried with Na_2SO_4 . Addition of diethyl ether caused crystallization of the product.

2.3. Synthesis of $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{L}(\text{N}-\text{N})]\text{BF}_4$ complexes

To a solution of complex **I** (0.05 mmol) in 2 ml of chloroform, 0.5 ml of a 0.1 M solution of AgBF_4 in CH_3CN were added under stirring. After 1 h the silver halide was filtered off on a small Celite bed, the solution was concentrated under vacuum and diethyl ether was added to achieve crystallization of the product. Alternatively, the reaction was performed in CDCl_3 and the filtered solution was transferred to the ^1H -NMR tube for measurement of the spectrum.

The acetonitrile complex can be used as a starting material for the other cationic complexes here described. This is easily achieved by treatment with a stoichiometric amount of the neutral ligand L, at room temperature, of the compound dissolved in a minimum amount of methylene chloride–nitromethane (10:1). After 30 min stirring, the solvents and the released CH_3CN are removed in vacuo affording the nearly pure ionic complex **II**. Recrystallization could be made by methylene chloride–diethyl ether mixtures.

2.4. Reconversion of $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{L}(\text{N}-\text{N})]\text{BF}_4$ to **I**

A 2 M solution of the required sodium halide in water (0.3 ml) was added to a solution of **II** (0.05 mol) in 2 ml of chloroform containing a sufficient amount of nitromethane to ensure dissolution and the mixture was stirred for 30 min at room temperature. The organic phase was separated, washed with 2×1 ml of water and dried with Na_2SO_4 . Addition of diethyl ether caused crystallization of the product.

2.5. Synthesis of $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{dmphen})]$ complexes

To 5 ml of a 0.04 M solution of $[\text{Pt}(\text{CH}_3)_2(\text{R})-(\text{CH}_3\text{CN})(\text{dmphen})]\text{BF}_4$, 2 mmol of KR' were added. The solvent was tetrahydrofuran ($\text{R}' = \text{CH}-(\text{COOCH}_3)_2$) or nitromethane–methanol 4:1 ($\text{R}' = \text{CH}_2\text{NO}_2$). The suspension was stirred for 2 h at room temperature, filtered on a small Celite bed and the solvent was removed under vacuum. The residue was extracted with three portions of methylene chloride (1 ml each) and the extract was concentrated to ca. 1 ml. Addition of diethyl ether produced crystallization of the white product with ca. 85% yield. Selected ^1H -NMR

data (δ , in CDCl_3 , $J_{\text{Pt-H}}$ in Hz): $[\text{Pt}(\text{CH}_3)_2(\text{C}_2\text{H}_5)\{\text{CH}(\text{COOCH}_3)_2\}(\text{dmphen})]$, 3.75 (s, 60, PtCH), 3.25 (s, NCH_3), 2.96 (s, OCH_3), 1.25 (s, 81, PtCH₃), 0.72 (q, 65, PtCH₂), 0.20 (t, 54, CH_2CH_3); $[\text{Pt}(\text{CH}_3)_3\{\text{CH}(\text{COOCH}_3)_2\}(\text{dmphen})]$, 3.67 (s, 60, PtCH), 3.19 (s, NCH_3), 2.96 (s, OCH_3), 1.25 (s, 75, PtCH₃), –0.05 (s, 60, PtCH₃); $[\text{Pt}(\text{CH}_3)_3(\text{CH}_2\text{NO}_2)(\text{dmphen})]$, 4.65 (s, 50, PtCH₂), 3.14 (s, NCH_3), 1.24 (s, 73, PtCH₃), –0.08 (s, 53, PtCH₃).

3. Results and discussion

3.1. Reactions of organic halides with $[\text{Pt}(\text{CH}_3)_2(\text{dmphen})]$

All the type I compounds are identified by the R, X, and N–N groups, as listed in Tables 1–3, together with the ^1H -NMR data pertaining to each isomer. The oxidative addition reactions have been carried out in diethyl ether, obtaining precipitation of fairly pure compounds. Some runs were also carried out in acetone or benzene. In agreement with previous findings [9], which show that stability increases by increasing the rigidity of the bidentate ligand, the compounds are resistant to reductive elimination. Halide exchange reactions were performed in heterogeneous (chloroform–water) phase. In Table 2 the isomeric composition of the products is reported in case these were assessed (vide infra) to be at equilibrium. In the tables, as well as in the text, the notation equatorial designates ligands within the plane contain-

ing the chelate, while the other two positions are indicated as axial. This enables easy identification of the stereochemical features of the Pt(IV) derivatives.

3.2. Type I compounds, equilibrium assessment and description

The addition of the two fragments R and X deriving from the halide to the square precursor can produce in principle four different isomers. However, no trace of anyone of the two isomers bearing the halide in equatorial position was detected in any case by ^1H -NMR spectroscopy. Thus, only two isomers, with C_s and C_1 symmetry, respectively were observed, and we will refer to the former as *trans* and to the latter as *cis* (Fig. 1) for the sake of simple and immediate identification of the mutual position of R and X.

A preliminary requirement for further discussion is the discrimination between kinetic and equilibrium control of the observed *cis*–*trans* isomer ratio. In fact, we wished to discuss particularly the stereochemistry at equilibrium, in order to trace general trends and to attempt at least a coarse separation of the influence of electronic and steric factors on the thermodynamic control.

We recall that the preferred kinetically controlled stereochemistry for the oxidation reactions, considering previous results on similar processes [6] appears to be that affording *trans* derivatives. However, *cis* compounds can be preferentially or specifically formed by other mechanisms [10].

Table 1
 ^1H -NMR data for $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{dmphen})]$ complexes (R = unsubstituted hydrocarbyl group)^a

R	X	Pt–R	N–CH ₃	Pt–CH ₃ eq.	Pt–CH ₃ ax.
CH ₃	I		3.30(s)	1.72(s, 74)	0.22(s, 70)
CH ₃	Br		3.30(s)	1.60(s, 72)	0.12(s, 70)
CH ₃ CH ₂	I	0.96(q, 71, CH ₂), –0.43(t, 68, CH ₃)	3.29(s)	1.69(s, 74)	
CH ₃ CH ₂	I ^b	^c , 1.35(t, 54, CH ₃)	3.38(s), 3.28(s)	1.63 (s, 77)	0.18(s, 67)
CH ₃ CH ₂	Br	0.96(q, 82, CH ₂), –0.35(t, 68, CH ₃)	3.29(s)	1.59(s, 74)	
CH ₃ CH ₂	Br ^b	^c , 1.20(t, 50, CH ₃)	3.38(s), 3.28(s)	1.58(s, 77)	0.08(s, 67)
CH ₃ CH ₂ CH ₂	I	0.96(m, CH ₂), 0.33(t, CH ₃), 0.0(m, ^d , CH ₂ Pt)	3.29(s)	1.71(s, 74)	
CH ₂ =CHCH ₂	I	1.69(d, 94, CH ₂ Pt), 4.75(m, =CH), 4.00 and 3.73(2dd, =CH ₂)	3.27(s)	1.75(s, 74)	
CH ₂ =CHCH ₂	Br	1.69(d, 94.5, CH ₂ Pt), 4.8(m, =CH), 4.00 and 3.73(2dd, =CH ₂)	3.27(s)	1.65(s, 74)	
C ₆ H ₅ CH ₂	I	2.47(s, 95), 6.62(t, 1H); 6.31(t, 2H), 5.81(m, 2H)	3.18(s)	1.86(s, 74)	
C ₆ H ₅ CH ₂	Br	6.61(t, 1H), 6.37(t, 2H), 5.88(m, 2H), 2.45(s, 73, 2H),	3.25(s)	1.81(s, 73)	
(CH ₃) ₂ CH	I	2.33(m, ^d , CH), –0.40(d, 2CH ₃ , 60)	3.28(s)	1.73(s, 74)	
CH ₂ =CH	Br	5.76(dd, ^d , =CH), 5.14 and 3.90(2d, =CH ₂)	3.32(s)	1.78(s, 78)	
CH ₂ =CH	Br ^b	7.20(dd, ^d , =CH), 5.32 and 4.98(2d, =CH ₂)	3.35(s), 3.30(s)	1.60(s, 74)	0.20(s, 72)
CH ₂ =CH	I	5.85(dd, ^d , =CH), 5.06 and 3.85(2d, =CH ₂)	3.26(s)	1.90(s, 74)	
CH ₂ =CH	I ^b	7.40(dd, ^d , =CH), 5.40 and 5.02(2d, =CH ₂)	3.30(s), 3.22(s)	1.65(s, 74)	0.42(s, 74)

^a The reported figures refer to the *trans* isomer, unless otherwise stated. The spectra were recorded in CDCl_3 solution (reference δ 7.26, CHCl_3); the ^{195}Pt coupling constants (Hz) are reported in parentheses; abbreviations s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet). The chemical shifts of the heteroaromatic 2,9-dimethyl-1,10-phenanthroline protons are in the range: δ 8.5–8.3 (d, 2H), 7.9–7.75 (d, 2H), 7.8–7.7 (s, 2H).

^b *Cis* isomer.

^c CH₂ resonance obscured by other signals.

^d ^{195}Pt coupling constant not evaluable.

Table 2

¹H-NMR data for [Pt(CH₃)₂ (R)X(dmphen)] complexes (R = substituted hydrocarbyl group) ^a

R	X	Pt–R	N–CH ₃	Pt–CH ₃ eq.	Pt–CH ₃ ax.
C ₆ H ₅ CO	Cl ^b	8.40(d, 2H), 7.95(m, 3H)	3.32(s), 2.98(s)	1.56(s, 75)	0.48(s, 73)
C ₆ H ₅ CO	Br ^b	8.30(dd, 2H), 7.65(m, 3H)	3.34(s), 2.99(s)	1.61(s, 75)	0.54(s, 70)
C ₆ H ₅ CO	I ^b	8.30(dd, 2H), 7.65(m, 3H)	3.30(s), 2.95(s)	1.63(s, 76)	0.59(s, 70)
CH ₃ CO	Cl ^b	2.84(s, 8)	3.29(s), 3.00(s)	1.44(s, 75)	0.37(s, 73)
CH ₃ CO	Cl ^c	1.70(s, 12)	3.25(s)	1.80(s, 70)	
CH ₃ CO	Br ^b	2.94(s, 12)	3.31(s), 3.05(s)	1.50(s, 75)	0.46(s, 75)
CH ₃ CO	I ^b	2.95(s, 12)	3.22(s), 2.95(s)	1.50(s, 75)	0.49(s, 72)
CH ₃ CH ₂ CO	Cl ^b	3.87 and 3.78(2q, CH ₂), 1.09(t, CH ₃)	3.28(s), 2.94(s)	1.40(s, 73)	0.39(s, 75)
CH ₃ OCO	Cl ^b	3.81(s, 8)	3.29(s), 3.08(s)	1.90(s, 74)	0.60(s, 72)
CH ₃ OCO	Cl ^c	3.21(s, 8)	3.20(s)	1.69(s, 72)	
CH ₃ OCO	I ^b	3.80(s, 8)	3.28(s), 3.05(s)	1.80(s, 74)	0.78(s, 72)
CH ₃ OCO	I ^c	3.22(s, ^d)	3.20(s)	1.71(s, 72)	
NH ₂ COCH ₂	I ^b	4.18(d, 115), 3.08(d, 92); 6.3 and 5.2(2bm, NH ₂)	3.32(s), 3.34(s)	1.80(s, 72)	0.52(s, 68)
NH ₂ COCH ₂	I ^c	2.00(s, 132, CH ₂); 6.3 and 5.2(2bm, NH ₂)	3.28(s)	1.91(s, 71)	
CH ₃ OCOCH ₂	Br ^b	3.75(d, 113), 2.98(d, 100), 3.55(s, OCH ₃)	3.48(s), 3.31(s)	1.82(s, 72)	0.21(s, 68)
CH ₃ OCOCH ₂	Br ^c	1.77(s, 100, CH ₂), 2.85(s, OCH ₃)	3.25(s)	1.82(s, 72)	
CH ₃ OCOCH ₂	I ^b	3.98(d, 110), 3.10(d, 100), 3.52(s, OCH ₃)	3.50(s), 3.32(s)	1.83 (s, 72)	0.30(s, 66)
CH ₃ OCOCH ₂	I ^c	1.80(s, 95), 2.80(s, OCH ₃)	3.26(s)	1.82(s, 72)	
CH ₃ COOCH ₂	Br ^b	5.35(d, 60), 5.68(d, 70), 1.13(s, CH ₃)	3.40(s), 3.28(s)	1.85(s, 73)	0.10(s, 70)
CH ₃ COOCH ₂	Br ^c	3.95(s, 54), 1.13(s, CH ₃)	3.27(s)	1.68(s, 72)	
CH ₃ COOCH ₂	I ^b	5.40(d, 60), 5.75(d, 70), 1.13(s, CH ₃)	3.40(s), 3.28(s)	1.90(s, 73)	0.20(s, 70)
CH ₃ COOCH ₂	I ^c	3.90(s, 54), 1.13(s, CH ₃)	3.27(s)	1.65(s, 72)	
C ₆ H ₅ COCH ₂	Br ^b	4.95(d, 114), 3.88(d, 127), 7.0 and 7.25(2m, 5H)	3.38(s), 3.27(s)	1.50(s, 73)	0.42(s, 68)
C ₆ H ₅ COCH ₂	Br ^c	2.66(s, 107), 7.0 and 7.25(2m, 5H)	3.15(s)	1.82(s, 73)	
C ₆ H ₅ COCH ₂	I ^b	4.95(d, 114), 3.88(d, 127), 7.0 and 7.25(2m, 5H)	3.38(s), 3.27(s)	1.50(s, 73)	0.48(s, 68)
C ₆ H ₅ COCH ₂	I ^c	2.72(s, 102), 7.0 and 7.25(2m, 5H)	3.12(s)	1.98(s, 73)	
NCCH ₂	I ^b	3.72(d, ^d), 3.66(d, ^d)	3.37(s)	1.89(s, 72)	0.60(s, 64)
NCCH ₂	I ^c	1.26(s, 89)	3.29(s)	1.90(s, 69)	
NCCH ₂	Br ^b	3.50(d, ^d), 2.50(d, 80)	3.40(s), 3.32(s)	1.89(s, 72)	0.60(s, 64)
NCCH ₂	Br ^c	1.22(s, 89)	3.31(s)	1.78(s, 72)	
HOCH ₂ CH ₂	I ^b	3.90(m), 2.65(m, ^d), 2.40(m, ^d)	3.50(s), 3.30(s)	1.70(s, 75)	0.25(s, 70)
HOCH ₂ CH ₂	I ^c	3.90(m), 1.20(m, ^d)	3.32(s)	1.80(s, 75)	
HOCH ₂ CH ₂	Br ^b	3.80(m), 2.80(m, ^d), 2.45(m, ^d)	3.52(s), 3.29(s)	1.62(s, 72)	0.14(s, 70)
HOCH ₂ CH ₂	Br ^c	3.80(m), 1.50(m, ^d)	3.27(s)	1.68(s, 70)	
C ₆ H ₅ COCH ₂	Br ^c	2.66(s, 107), 7.0 and 7.25(2m, 5H)	3.15(s)	1.82(s, 73)	

^a The spectra were recorded in CDCl₃ solution (reference δ 7.26, CHCl₃); the ¹⁹⁵Pt coupling constants (Hz) are reported in parentheses; abbreviations s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet), bm (broad multiplet). The chemical shifts of the heteroaromatic 2,9-dimethyl-1,10-phenanthroline protons are in the range: δ 8.5–8.3 (d, 2H), 7.9–7.75 (d, 2H), 7.8–7.7 (s, 2H).

^b *Cis* isomer.

^c *Trans* isomer.

^d ¹⁹⁵Pt coupling constant not evaluable.

Spontaneous isomerization of kinetically controlled products of type **I** in order to attain equilibrium isomeric composition was previously observed, although metastable kinetically controlled systems are likely conceivable owing to possible inertness of complexes like **I**. According to ¹H-NMR spectroscopy we have obtained early products with *trans* or *cis* stereochemistry or *cis*–*trans* mixtures. In fact, the spectral patterns are generally sufficient to easily assess the isomeric composition of the products. The presence of only one signal for the two CH₃–Pt groups and a symmetric pattern for the chelate support a C_s symmetry (*trans* isomer), on consideration that a rapid intramolecular alkyl exchange is hardly conceivable. On the other hand two CH₃–Pt signals and the non-equivalence of the two halves of the chelate indicate a C₁ symmetry (*cis*).

After the examination of several oxidation reactions we could identify ca. 25 equilibrium systems. Their isomeric composition at 25°C in chloroform solution as determined by integration of the ¹H-NMR signals is reported in Table 4.

Of course, a question concerning the origin of the stereochemical control arises in case spontaneous isomerization of the early products could not be detected. We attempted to obtain isomerization in chloroform solution at room temperature. Lack of observed isomerization could be due to a very low isomerization rate or to the achievement of equilibrium before measurement of the isomer ratio. Moreover, the two conditions could in principle co-exist. It is also to note that the presence of a sole isomer in the product is not a favorable situation for easy and reliable affirmation of a putative equilibrium.

Table 3
Selected ^1H -NMR data for $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{phen})]$ complexes ^a

R	X	Pt–R	Pt–CH ₃ eq.	Pt–CH ₃ ax.
CH ₃ CH ₂	I ^b	^d	1.48(s, 72)	0.60(s, 74)
CH ₃ CH ₂	I ^c	1.49(q, 71, CH ₂), –0.90(t, 68, CH ₃)	1.64(s, 72)	
CH ₃ CO	Cl ^b	2.73(s, 12)	1.71(s, 72)	0.80(s, 74)
CH ₃ CO	Cl ^c	2.02(s, 15)	1.75(s, 61)	
CH ₃ CO	I ^b	2.80(s, 13)	1.96(s, 72)	0.80(s, 70)
CH ₃ CO	I ^c	1.98(s, 14)	1.95(s, 70)	
C ₆ H ₅ CO	Cl ^b	8.0(m, 3H), 7.4(d, 2H)	1.68(s, 75)	0.83(s, 74)
C ₆ H ₅ CO	Cl ^c	7.1(m, 3H), 6.80(d, 2H)	1.82(s, 75)	
C ₆ H ₅ CO	I ^b	8.0(m, 3H), 7.4(d, 2H)	1.82(s, 75)	0.93(s, 72)
C ₆ H ₅ CO	I ^c	8.0(m, 3H), 7.4(d, 2H)	2.02(s, 72)	
NH ₂ COCH ₂	I ^b	6.4 and 5.3(b, NH ₂), 3.38(s, 101, CH ₂)	1.82(s, 72)	0.90(s, 75)
NH ₂ COCH ₂	I ^c	4.8 and 4.3(b, NH ₂), 2.16(s, 93, CH ₂)	1.64(s, 72)	

^a Spectra recorded in CDCl₃ solution (reference δ 7.26, CHCl₃), the ^{195}Pt (Hz) coupling constants are reported in parentheses; abbreviations s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The chemical shifts of the heteroaromatic 1,10-phenanthroline protons are in the range: δ 9.8–9.2 (d, 2H), 8.6–8.4 (d, 2H), 8.0–7.9 (d, 2H), 8.1–7.9 (s, 2H).

^b *Cis* isomer.

^c *Trans* isomer.

^d CH₂CH₃ resonance obscured by other signals.

In order to clarify the actual situation, two types of procedures were applied to most of the isolated **I** compounds: (a) in case the products have been obtained as isomer mixtures, fractioning by crystallization or chromatography was attempted and the isomeric ratios of the starting mixture and of each fraction were compared. Some attempts to get variations of the initial ratio was made alternatively by performing the reaction in a different solvent and/or at a different temperature; (b) in case the above procedures were ineffective (e.g. owing to decomposition), the attainment of the compound by an alternative process was attempted. Thus, the transformation of the neutral product in the related cationic species $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{L}(\text{N}-\text{N})]\text{BF}_4$ (L = CH₃CN or other), the restoration of the initial halide complex, and the comparison of the ratios in the starting and regenerated product were performed. It is to note that the involvement of cationic species in the isomerization was claimed previously [9]. Other attempts to attain variation of the isomeric ratio were performed by halide exchange or by substitution of the halide with a fourth σ C-bonded group to give $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{N}-\text{N})]$, which could possibly be reacted in order to remove selectively a C-ligand and restore a type **I** compound (vide infra).

Some representative details concerning the results summarized in Table 4 are the following ones.

In case RX is CD₃I, CH₃COOCH₂Br, CH₃OOCH₂Br, or ICH₂CONH₂ the isomeric ratio of the products attains a constant equilibrium ratio in a time ranging from a few hours to about a week.

The reaction of all acyl halides afforded *cis* products specifically and the addition products were investigated with respect to equilibrium. In particular, lowering of the temperature to 0°C for a solution of the CH₃COCl

derivative drastically diminishes the *cis* content to 35%. As expected, aging of the solution of this mixture at

Table 4
Percentage of *cis* form in $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{N}-\text{N})]$ complexes at equilibrium in chloroform solution at 25°C

N–N	R	X	%
dmphen	CD ₃	I	50 ^a
dmphen	CH ₃ CH ₂	Cl	40 ^{b,c}
dmphen		Br	36 ^{b,c}
dmphen		I	28 ^{a,b}
dmphen	CH ₃ CH ₂ CH ₂	I	22 ^{a,d}
dmphen	CH ₂ =CH	Br	86 ^b
dmphen		I	94 ^b
dmphen	CH ₂ =CHCH ₂	I	5 ^e
dmphen	CH ₃ CO	Cl	100 ^a
dmphen		Br	100 ^c
dmphen		I	100 ^c
dmphen	C ₆ H ₅ COCH ₂	Br	15 ^{a,b}
dmphen		I	5 ^{b,c}
dmphen	COOCH ₃	Cl	68 ^{a,d}
dmphen		I	79 ^c
dmphen	NH ₂ COCH ₂	I	30 ^a
dmphen	CH ₃ OCOCH ₂	Br	38 ^a
dmphen		I	20 ^c
dmphen	CH ₃ COOCH ₂	Br	20 ^{a,b}
dmphen		I	30 ^c
phen	CH ₃ CH ₂	I	10 ^e
phen	CH ₃ CO	Cl	72 ^a
phen		I	84 ^c
phen	C ₆ H ₅ CO	Cl	77 ^a
phen		I	70 ^c
phen	NH ₂ COCH ₂	I	52 ^a

^a Isomerization spontaneous.

^b Isomerization after composition change via cationic complex formation.

^c Isomerization after composition change via halide substitution.

^d Isomerization via recrystallization or chromatography.

^e Composition unaffected by the procedures under ^b and ^c.

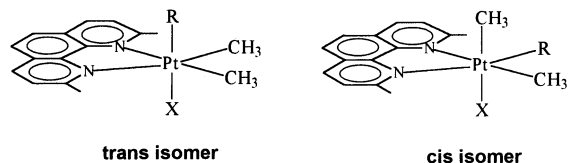


Fig. 1.

room temperature causes restoration of the pure *cis* compound, at equilibrium.

The addition product of $\text{C}_6\text{H}_5\text{COCH}_2\text{Br}$ in diethyl ether is 25% *cis* while the product from acetone is 100% *cis*. Both products isomerize to equilibrium (ca. 4 days) attaining a 15/85 *cis*–*trans* ratio.

By following a type (a) approach a ratio different from that occurring in the initial product could be obtained in the case of BrCH_2CN , ICH_2CN , $\text{BrCH}_2\text{CH}_2\text{OH}$ or $\text{ICH}_2\text{CH}_2\text{OH}$ derivatives. Although the work-up (recrystallization or chromatography) affords some decomposition it appeared that the new ratios were constant in solution for at least 48 h. Thus the earlier ratios are most probably kinetically controlled.

For instance, a type (b) approach was effectively adopted for $\text{RX}=\text{CH}_3\text{CH}_2\text{I}$, $\text{CH}_3\text{COOCH}_2\text{Br}$, and $\text{C}_6\text{H}_5\text{COCH}_2\text{Br}$. The products stemming from these electrophiles after conversion to cationic species can be recovered with isomeric ratio substantially different from that of the starting material. More precisely the *cis* percentages are formerly 28, 20, and 15, respectively, and turn to 22, 55 and 82. All the three latter mixtures change composition in a few hours till to restore the early isomer ratios, which therefore are equilibrium values. In case the electrophile is allyl iodide, the initial product is a mixture with very little *cis* isomer (less than 5%) while no *cis* form was detected for the benzyl derivative. Conversion to cationic species and restoration of the neutral products reproduces the starting composition in both cases. Thus, it appears that also in these two cases the former products are at equilibrium.

3.3. Sterical and electronic influences

The stereochemistry of all addition products at equilibrium can be discussed attempting a broad separation between steric and electronic influence. The latter ones should be debated taking first of all in account: (i) the repulse [11] of two alkyl groups of good donor ability and high *trans* influence to stay mutually *trans* (on this ground the lack of observation of two isomers, i.e. the two ones bearing X in equatorial position, is easily rationalized); (ii) the comparatively better balance for *trans* halide/alkyl or nitrogen/alkyl arrangements, for which however an a priori distinction seems difficult, on consideration of the compara-

ble *trans* influence of halides and aromatic nitrogen ligands.

As for steric effects it must be considered that due to the well known in-plane substantial hindrance of dmphen [12] an axial position should be preferred by the more sterically demanding alkyl group.

It appears reasonable that in case the R groups are unsubstituted hydrocarbonyl groups, whose high donor ability is, although different, fairly comparable, the sterical influence is the predominating factor in determining the equilibrium position. Thus, the observed preference for *trans* stereochemistry for R higher than methyl (Table 4) has a rationale.

The presence of substituents Z on R ($\text{R}=\text{CH}_2\text{Z}$) is expected to disfavor the *cis* form owing to higher sterical demand than for the unsubstituted methyl. Thus, also the observed comparatively high *trans* content for $\text{R}=-\text{CH}_2\text{COOCH}_3$, $-\text{CH}_2\text{OCOCH}_3$, $-\text{CH}_2\text{COC}_6\text{H}_5$ or $-\text{CH}_2\text{CONH}_2$ with respect to the methyl analogous, might find an explanation on sterical grounds. On the other hand, most of the Z substituents are electron withdrawing, and an electronic influence is expected. We note that a calculation based on the density functional theory (DFT) [13], shows nearly the same energy for the *cis* and *trans* geometry in the case $\text{N}-\text{N}=\text{dmphen}$, $\text{R}=\text{CF}_3$ and $\text{X}=\text{I}$, while in the case of $\text{N}-\text{N}$, the less hindering phen, the axial position of CF_3 appears to be slightly favored. This result indicates that the substitution in plane in $\text{N}-\text{N}$ and the ensuing hindrance are not always the predominating factors and electronic effects can play a substantial role. In fact, the equilibrium percent content in *cis* form of the dmphen–iodide derivatives with $\text{R}=\text{CH}_3\text{CH}_2$ or CH_2CONH_2 is, respectively, 28 and 30 and while the corresponding phen derivatives display 10 and 52 *cis* percent content. Moreover, the *cis* content at equilibrium in $[\text{Pt}(\text{phen})\text{I}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{COOCH}_3)]$ was 72% [14]. It is also to note that in case the rigidity of the chelate is to some degree relieved, i.e. in $[\text{Pt}(\text{CH}_3)(\text{CF}_3)_2\text{I}(2,2'\text{-bipyridine})]$ [11], both the more encumbering and electron withdrawing CF_3 groups are both found in *cis* position, most probably at equilibrium, while in $[\text{Pt}(\text{CH}_3)_2(\text{CH}_2\text{Cl})\text{Cl}(2,2'\text{-bipyridine})]$, the *cis* percentage at equilibrium is 20 [10].

As for the preference, noted above, of substituted R, it must be allowed that an homogeneous comparison should involve only R groups with equally hybridized carbons linked to the metal. Acyl halides afforded stereospecifically *cis* products, which at least in the three investigated cases proved to be at equilibrium. Table 4 shows that the *cis* geometry is specifically adopted also in the other two cases involving sp^2 carbon ligands, i.e. $\text{CH}=\text{CH}_2$ and COOCH_3 . This can be explained considering that the Csp^2 linked groups can present, in suitable conformation, a lower sterical

Table 5
Selected ^1H -NMR data for $[\text{Pt}(\text{CH}_3)_2(\text{R})(\text{dmphen})(\text{L})]\text{BF}_4$ complexes ^a and isomeric composition

R	L	Pt–R	L	N–CH ₃	Pt–CH ₃ eq.	Pt–CH ₃ ax.	%
CH ₃ ^b	CH ₃ CN		2.15(s)	3.15(s)	1.41(s, 70)	0.22(s, 75)	
CH ₃ ^b	C ₆ H ₅ CH ₂ CN		4.13(s, CH ₂)	3.04(s)	1.38(s, 71)	0.28(s, 75)	
CH ₃	C ₆ H ₅ NH ₂		5.88 and 4.60(2b, NH ₂)	3.03(s)	1.51(s, 69)	1.40(s, 75)	
CH ₃	CH ₂ CHCH ₂ NH ₂		5.60(m, =CH), 4.85(dd, =CH ₂) 2.90(bm, CH ₂)	3.12(s)	1.37(s, 70)	0.60(s, 75)	
CH ₃ ^b	(CH ₃) ₃ CCN		1.36(s, 9H)	3.15(s)	1.36(s, 70)	0.37(s, 74)	
CH ₃	(CH ₃) ₂ C ₆ H ₅ P		1.09(s, ³ J _{P–H} = 9.6 Hz)	3.05(s)	1.52(d ^c , 70)	1.38(d ^d , 57)	
CH ₃	(C ₆ H ₅) ₃ P		7.3(m), 6.70(t)	3.05(s)	1.60(d ^c , 70)	1.60(d ^e , 62)	
CH ₃	(CH ₃) ₂ S		2.06(s, 12)	3.15(s)	1.41(s, 70)	0.79(s, 68)	
CH ₃	(C ₆ H ₅) ₃ As		7.40(t), 7.25(t), 6.70(d)	3.05(s)	1.66(s, 71)	1.70(s, 68)	
CH ₃ CH ₂ ^b	CH ₃ CN ^f	^g , 0.25(bt, ^h)	2.40(s)	3.10(s)	1.32(s, 70)		50
CH ₃ CH ₂ ^b	CH ₃ CN ⁱ	^g , 1.20(t, ^h)	2.40(s)	3.18(s), 3.10(s)	1.32(s, 70)	0.18(s, 75)	50
CH ₃ CH ₂	C ₆ H ₅ NH ₂ ^f	2.32(q, 68), 0.55(t, 57)	5.85 and 4.48(2b, NH ₂)	3.09(s)	1.51(s, 70)		80
CH ₃ CH ₂	C ₆ H ₅ NH ₂ ⁱ	^g , 0.95(t, 60)	5.85 and 4.48(2b, NH ₂)	3.18(s), 3.02(s)	1.52(s, 67)	1.32(s, 74)	20
CH ₃ CH ₂ ^b	(CH ₃) ₂ S ^f	1.62(q, ^h), 0.12(t, 60)	1.93(s, 10)	3.13(s)	1.32(s, 70)		60
CH ₃ CH ₂ ^b	(CH ₃) ₂ S ⁱ	^g , 1.05(t, ^h)	2.04(s, 11)	3.22(s), 3.10(s)	1.32(s, 70)	0.51(s, 69)	40
CH ₂ =CHCH ₂	CH ₃ CN ^f	5.1(bm, 1H), 4.9(bm, 1H), 4.1 (bm, 1H), 3.8(bm, 1H), 1.7(bm, 1H)	2.35(s)	3.20(s)	1.45(s, 74)		100
CH ₂ =CHCH ₂	C ₆ H ₅ NH ₂ ^f	5.5(m, 1H), 4.74(d, 1H), 4.38 (d, 1H), 2.95(d, 90, 2H)		3.08(s)	1.58(s, 70)		100
CH ₂ =CH ^b	CH ₃ CN ⁱ	6.65(m, CH), 5.45(d, 130, =CH ₂) 4.58 (d, 81, =CH ₂)	2.25(s)	3.08(s), 3.00(s)	1.40(s, 71)	0.50 (s, 74)	75
CH ₂ =CH ^b	CH ₃ CN ^f	5.94(m, CH), 4.80(d, 135, =CH ₂), 4.18(d, 68, =CH ₂),	2.20(s)	3.05(s)	1.49(s, 70)		25
C ₆ H ₅ CH ₂	CH ₃ CN ^f	2.50(b, CH ₂)	2.29(s)	3.11(s)	1.62(s, 69)		100
C ₆ H ₅ CH ₂	C ₆ H ₅ NH ₂ ^f	3.32(s, 88, CH ₂)	5.88 (b, 1NH)	2.84(s)	1.68(s, 73)		100
(CH ₃) ₂ CH	CH ₃ CN ^f	2.25(bs, 1H), –0.32(d, 55, 6H)	2.25(s)	3.17(s)	1.48(s, 72)		100
(CH ₃) ₂ CH	C ₆ H ₅ NH ₂ ^f	2.5(bm, 1H), 0.35(d, 54, 3H)	4.75(b, 1NH)	3.05(s)	1.53(s, 71)		100
C ₆ H ₅ CO	CH ₃ CN	7.53(m, 5H)	2.53(s)	2.96(s)		1.20(b, ^h) ^j	
CH ₃ CO	CH ₃ CN	2.53(b, 3H)	2.53(b)	2.93(s)		1.43(s, 77) ^j	
CH ₃ COOCH ₂ ^b	CH ₃ CN ⁱ	6.20(d, 71), 5.08(d), 2.11(s)	2.04(s)	3.08(s), 3.04(s)	1.46(s, 70)	1.02(s, 77)	100
C ₆ H ₅ COCH ₂ ^b	CH ₃ CN ^f	2.70(s, 109, CH ₂)	2.37(s)	3.03 (s)	1.67(s, 72)		65
C ₆ H ₅ COCH ₂ ^b	CH ₃ CN ⁱ	4.18(d, 107, 1H), 3.35(d, 1H)	2.37(s)	3.08(s), 3.03(s)	1.48(s, 72)	0.52(s, 67)	35

^a Spectra recorded in CD₃NO₂ solution (reference δ 4.33, CHD₂NO₂), the ¹⁹⁵Pt coupling constants (Hz) are reported in parentheses; abbreviations s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet), b (broad). The chemical shifts of the heteroaromatic 2,9-dimethyl-1,10-phenanthroline protons are in the range: δ 8.5–8.3 (d, 2H), 7.9–7.75 (d, 2H), 7.8–7.7 (s, 2H).

^b CDCl₃ solution (reference δ 7.26, CHCl₃).

^c ³J_{P–H} = 9 Hz.

^d ³J_{P–H} = 5 Hz.

^e ³J_{P–H} = 8 Hz.

^f *Trans* isomer.

^g CH₂ resonance obscured by other signals.

^h ¹⁹⁵Pt coupling constant not evaluable.

ⁱ *Cis* isomer.

^j Fast exchange between axial and equatorial position.

demand than the Csp^3 bonded ligands. It is noted that the above cited DFT calculations [13], show a relevant energy difference (ca. 36 kJ mol⁻¹) in the case of $[\text{Pt}(\text{CH}_3)_2(\text{COCH}_3)\text{I}(\text{dmphen})]$ in favor of the *cis* form, while in the case of the analogous phen compound the difference drops to ca. 19 kJ mol⁻¹. We find that in $[\text{Pt}(\text{CH}_3)_2(\text{COCH}_3)\text{I}(\text{dmphen})]$ the only observed isomer is *cis*, while the *cis*–*trans* ratio in the analogous phen derivative is 84/16.

3.4. Cationic complexes

Cationic Pt(IV) complexes of the type $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{L}(\text{N}-\text{N})]^+$ are a fairly recent accomplishment of platinum chemistry. Previous results [9] disclosed their relationship with five-coordinate species, which are favored in the case of the anion and L lack of coordinating ability, and their relevance to isomerization and reductive elimination. The attainment of cations from the above general formula was attempted during this work aiming, firstly to obtain by successive halide treatment, changes of the isomer ratio of the starting neutral compound. The fair general stability displayed in solution by most of the cations, in keeping with the rigidity of the chelate, prompted us to attempt in some representative examples, the isolation of the cationic complexes themselves. We could isolate as crystalline solids the methyl cyanide derivatives with $\text{R}=\text{CH}_3$, CH_2CH_3 or COCH_3 . By ¹H-NMR spectroscopy (Table 5), it is inferred an equilibrium between coordinated and free CH_3CN for the complexes at 30°C in chloroform solution, as reported for similar cations [9]. Thus, the geometrical isomers of these cations are to be considered at equilibrium, and the *cis*–*trans* ratios are also reported in Table 5. The stereochemical behavior appears comparable with that of the neutral complexes.

3.5. $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{N}-\text{N})]$ derivatives

During this work *N,N*-chelate Pt(IV) mononuclear derivatives containing four σ C-bonded ligands were obtained. But for the previous report of tetramethyl ($\text{R}=\text{R}'=\text{Me}$) compounds [15], these $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{R}'(\text{N}-\text{N})]$ compounds are unprecedented. They could be prepared by the reaction of the above described cationic compounds with potassium salts of stabilized carbanions (KCH_2NO_2 or $\text{KCH}(\text{COOCH}_3)_2$). The synthesis of the novel compounds was suggested by the chance that they could be precursors of new trialkyl systems poorly attainable by another way, or of known trialkyls with unprecedented isomer composition. This seemed feasible by halogen treatment but since a quite preliminary result was not encouraging no further investigation on this point was attempted. No investigation was also made on

the stereochemical control of the isolated compounds but we note the necessary *trans* arrangement of two alkyls in these products should be more favored (i) in case one of the two alkyls bears electron withdrawing substituents and the other is a good donor. The observed specificity of *trans* stereochemistry in case $\text{R}=\text{CH}_3$, $\text{R}'=\text{CH}_2\text{NO}_2$ or $\text{CH}(\text{COOCH}_3)_2$ is in agreement with this observation. It is to note the same preference holds true in case $\text{R}=\text{C}_2\text{H}_5$ and $\text{R}'=\text{CH}(\text{COOCH}_3)_2$.

4. Conclusions

The geometrical isomerism of $[\text{Pt}(\text{CH}_3)_2(\text{R})\text{X}(\text{N}-\text{N})]$ complexes has been investigated on about 25 equilibrium systems. The influence of the sterical hindrance in plane of the chelate appears quite evident, although the steric pressure relief does not appear to be the prevailing effect in all cases. Also a clear electronic influence of the N–N substituents and a very moderate influence of the halide, whose nature induces a fine tuning of the relative stability of the isomers, can be inferred from the observed isomer ratios. A potentially useful procedure for the attainment of compounds $[\text{Pt}(\text{CH}_3)_2(\text{R})(\text{R}')(\text{N}-\text{N})]$ containing three different types of C-bonded groups has been a synthetic achievement of this work.

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