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Synthesis of *cis*- and *trans*-dichloro(dimethylphenylphosphine) × -(1-methyl-1,4,5,6-tetrahydropyrimidine)platinum(II) and their spectral and structural characterization

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Abstract

Interaction of $[\{Pt(\mu\text{-}Cl)Cl(PMe_2Ph)\}_2]$ with 1-methyl-1,4,5,6-tetrahydropyrimidine, L (R = Me), in boiling toluene produced a mixture of *cis*- and *trans*- isomers of $[PtCl_2(PMe_2Ph)\{\overline{N=CH(Me)CH_2CH_2CH_2}\}]$; *trans*-complex **2** isomerizes to give thermodynamically more stable corresponding *cis*-complex **1** in boiling ethanol. Spectroscopic and X-ray diffraction data permit generalizations about *cis*- and *trans*- isomeric pairs to be made. In addition, the *trans* influence of the ligand L is reliably assessed.

Keywords: Tetrahydropyrimidine complexes; Platinum(II); *Trans*-influences; *Cis-trans*-isomerizations

1. Introduction

Nitrogen containing aromatic heterocycles coordinated to the platinum metals continue to play an important role both in catalysis [1,2] and in search for effective antitumor drugs [3–5]. In this context, a number of mononuclear metal systems have been structurally characterized [6–9]. Recently, we have been interested in synthesis and reactivity of the late transition-metal complexes containing partially reduced rings such as L or L′ as ligands.

Some of the resulting complexes behave as catalysts for the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran [10] or for the cyclopropanation of ethyl diazoacetate and styrene [11]. They also exhibit selective antimicrobial activity [12]. As a continuation of this work we describe in this paper (i) the preparation; (ii) NMR spectroscopic characterization of *cis*- and *trans*- isomers of $[PtCl_2(PMe_2Ph)\{\overline{N=CH(Me)CH_2CH_2CH_2}\}]$ and (iii) the single-crystal X-ray structures **1** and **2**.

2. Results and discussion

Di-μ-chlorobis[chloro(trialkylphosphine)platinum(II)] has been used in the synthesis of mononuclear platinum compounds via cleavage of the bridging Pt–Cl bonds [11]. In a related way, we have used 1-methyl-1,4,5,6-tetrahydropyrimidine, L (R = Me), as a nucleophile.

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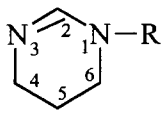
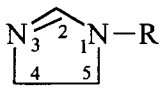
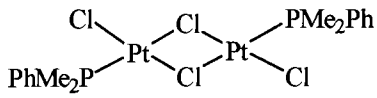


L



L'

R = Me, Et, CH_2Ph, Ph



+ 2 L ⟶ $[PtCl_2(PMe_2Ph)\{N{=}CHN(Me)CH_2CH_2CH_2\}]$ (1

1 *cis*
2 *trans*

Thus, reaction of the dimer with 2 mol equivalent of L in boiling toluene leads to the rapid formation of a mixture of **1** and **2** in essentially quantitative yield: the ratio of the isomers formed is **1**:**2** = 40:60, based on yields of the recovered material. This is somewhat surprising because under identical conditions reaction of related ligand L′ (R = Et, or CH_2Ph) with [{Pt(μ-Cl)Cl(PEt_3)}$_2$] has given only *trans*- isomer [11].

While the complex **1** is white, **2** is yellow and both products are stable towards oxygen and moisture. When *trans*- complex **2** was heated (4 h) in ethanol under reflux, the yellow colour was discharged to give white cubic crystals of **1**. In contrast, the *cis*-complex did not isomerize in refluxing ethanol after 4h. It is noteworthy that whereas *cis* → *trans* isomerizations are well known in platinum chemistry (thermally [13], photochemically [14] or in the presence of catalytic amount of bases [6,15]) the reverse process is relatively novel [15–18]. The isomeric pair have been characterized by elemental analysis (C, H, N), IR and NMR spectroscopy and X-ray diffraction techniques. The IR spectra of the products show a band at ca. 1645 cm^{-1} attributable to ν(C=N).

C^2 and C^2–H of the heterocycle L and dimethylphenylphosphine are effective probes for NMR spectroscopic studies (Tables 1 and 2). Thus, non-decoupled ^{13}C-NMR spectra of **1** and **2** exhibit C^2 carbon as doublets which exclude tautomerization within the ligand. The ^{1}H-NMR spectra indicate a significant difference between the isomers: All resonances assigned to the protons on the ligand L of the *trans*- isomer have shifted into low field in comparison with the *cis*- isomer. The spectra of **1** and **2** show doublets at δ 1.80 and 1.81 assigned to P–CH_3. The presence of ^{195}Pt satellites [33.7% natural abundance, ^3J(Pt–H) = 37.1 and 25.2 Hz] demostrates that **1** and **2** are *cis*- and *trans*- isomers, respectively [19]. Consistent with these, the ^{13}C-NMR spectra of complexes **1** and **2** give C^2 signals with coupling constants ^3J(Pt–C) = 54.3 and 32.6 Hz, respectively.

The ^{31}P{H}-NMR spectra of **1** and **2** show singlets at −23.8 and −18.2 ppm [relative to H_3PO_4] with ^{195}Pt satellites ^1J(Pt–P) = 3880 and 3251 Hz, respectively. In the related *trans*-[$PtCl_2$(N=CHN(R)CH_2CH_2)(PEt_3)] complexes, 1-alkyl-2-imidazoline (L′) nitrogen atom showed coupling constants ^1J (^{31}P–^{195}Pt) = 3345 and 3314 Hz for R = Et and CH_2Ph, respectively [11]. Variations in ^1J(Pt–P) in platinum(II) complexes can be used as a measure of the *trans*- influence of the ligand *trans* to P. In this procedure a high ^1J(Pt–P) implies a low *trans*- influence for the appropriate ligand [20]. Accordingly, we should have the *trans*- influence order: PR_3 > L > L′ > Cl^-.

Table 1
^{1}H-NMR spectral data of the compounds L[a], **1** and **2** in $CDCl_3$[b]

Compound	C^2H	C^4H_2	C^5H_2	C^6H_2	N–CH_3	P–CH_3	C_6H_5
L	6.90 (s)	3.20 (m)	1.80 (q)	3.2 (m)	2.80 (s)	—	—
1	6.84 (t)	3.07 (t)	1.51 (q)	2.83 (t)	2.68 (s)	1.80 (d)	7.43 (m)
	J_{PtH} = 45.5	J_{HH} = 5.6	J_{HH} = 5.8	J_{HH} = 5.9		J_{PH} = 11.6	7.60 (m)
						J_{PtH} = 37.1	
2	7.44[c]	3.60 (t)	1.93 (q)	3.15 (t)	2.97 (s)	1.81 (d)	7.44 (m)
		J_{HH} = 5.3	J_{HH} = 5.8	J_{HH} = 6.0		J_{PH} = 11.4	7.86 (m)
						J_{PH} = 25.2	

[a] Included for the sake of comparison.
[b] Chemical shifts, δ, are with reference to $SiMe_4$ in $CDCl_3$ solutions. Coupling constants, J, are in Hz.
[c] Obscured by the multiplets of the phenyl protons.

Table 2
^{13}C-NMR and ^{31}P spectral data of the isomeric compounds in $CDCl_3$[a]

Compound	C^2H	C^4H_2	C^5H_2	C^6H_2	$N-CH_3$	$P-CH_3$	C_6H_5		δ[b] (PMe_2Ph)
L	162.8	32.6	51.4	54.7	35.4	—		—	—
1	155.6 $J_{CH} = 194.1$ $J_{PtC} = 54.3$	21.6	47.9	44.9	41.2	12.7 (d) $J_{PC} = 43.8$	129.1 131.0, 132.0	129.2, 131.2,	−189.2 $J_{PtP} = 38.5$
2	154.5 $J_{CH} = 194.6$ $J_{PtC} = 32.6$	20.9	45.6	43.6	40.8	12.6 (d) $J_{PC} = 43.9$	128.4, 131.2,	130.4, 132.2	−23.9 $J_{PtP} = 3283$

[a] Chemical shifts, δ, are with reference to $SiMe_4$.
[b] With reference to H_3PO_4; coupling constants, J, are in Hz.

In order to confirm the above conclusion, we have studied the structures of **1** and **2**. It is worth noting that although structural data on divalent platinum complexes are becoming more available, such data on the isomeric pairs are still rare [17,18]. The molecular structures of the isomers are illustrated in Figs. 1 and 2. For a summary of crystal data, data collection and refinement details, see Section 4. *Cis*- and *trans*- complexes crystallize in triclinic and orthorhombic systems, respectively, composed of discrete molecules, $C_{12}H_{21}Cl_2N_2PPt$. For a full listing of final coordinates and temperature factors and the selected bond lengths and angles, see Section 4. In both isomers the Pt^{2+} ion has a slightly distorted square-planar coordination (Figs. 1 and 2) involving two Cl atoms, the P atom of the dimethylphenylphosphine ligand and an N atom of the 1-methyltetrahydropyrimidine ligand. The *trans*-complex has a more planar coordination plane than the *cis*-isomer. The distance of the Pt^{2+} ion to the best plane going through the coordination atoms Cl1, Cl2, N1 and P is 0.0272(4) Å for *trans*-and 0.0467(1) Å for *cis*-complex.The range of the bond angles in *cis*-and *trans*-isomers are 87.32(3)–94.94(8)° and 88.7(2)–92.7(0)° respectively.The *trans*-isomer has equal Pt–Cl distances[2.299(3) Å] while the Pt–Cl1 [2.385(1) Å] and Pt–Cl2 [2.3115(9) Å] bond lengths in *cis*-isomer differ slightly from each other and they are longer than the Pt–Cl bond lengths observed in the *trans*-isomer.The Pt–N distances [2.015(3) Å] for *cis* and [2.102(8) Å] for *trans* have values further apart than the Pt–P distances [2.2193(8)] and [2.237(3)] Å, respectively. The phenyl ring is planar with expected bond length and bond angle values.The pyrimidine ring is not planar.The distances of the C3 atoms from the least squares plane through the ring atoms N1, C1, N2, C2 for *cis*- and *trans*-complexes are 0.612(5) and 0.60(1) Å, respectively. The methyl C5 atoms are also out of the plane mentioned above, namely 0.278(5) Å for *cis*- and 0.06(1) Å for *trans*-isomerDeviation from planarity for C3 and C5 occur in opposite directions. For the *cis*- and *trans*-complexes the interplanar-angles between the coordination plane and the phenyl rings are 70.1(1) and 78.9(3)°, respectively.

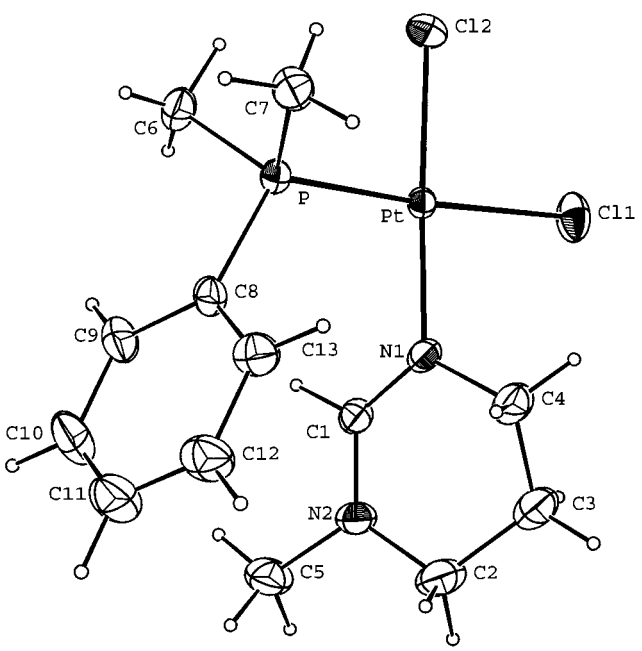


Fig. 1. ORTEPII drawing of the structure of the *cis*-complex **1**, showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.

In conclusion, the main differences between *cis*- and *trans*- complexes, **1** and **2**, are as follows: (i) *cis*- is white, *trans*- is yellow; (ii) solubility in non-polar solvents (*trans* > *cis*); (iii) ^1J(Pt–P), ^2J(Pt–C^2) and ^3J(Pt–H) (*cis* > *trans*); (iv) ν(C=N) (*cis* > *trans*); (v) l(Pt–P) (*trans* > *cis*); (vi) l(Pt–N^3) (*trans* > *cis*); (vii) l(C^2–N^3) (*trans* < *cis*). Many of these features are attributed to the greater ionic character of the *cis* compared with the *trans* complex, which in turn relates to the *trans* influence order.

3. Experimental

All experiments were carried out under an atmosphere of dry, purified argon. Glassware was dried and

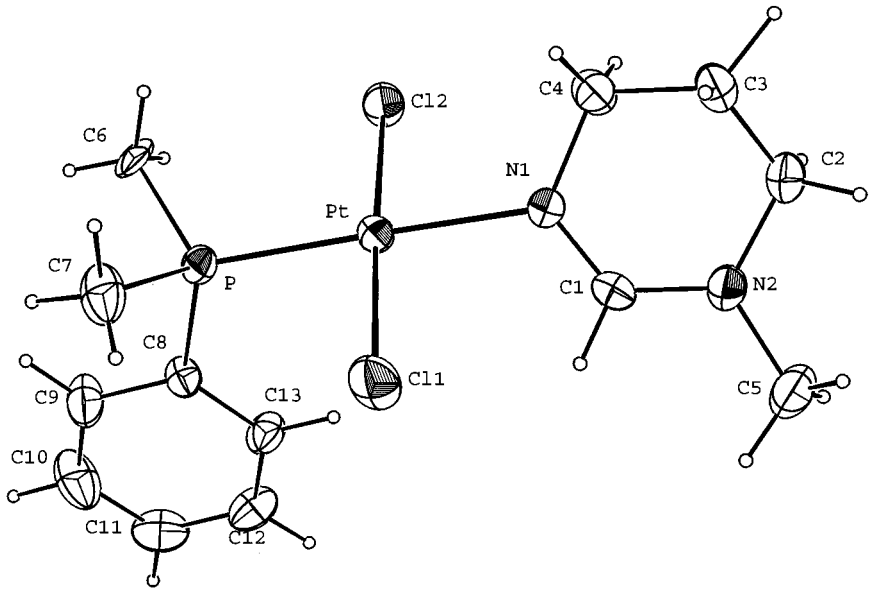


Fig. 2. ORTEPII drawing of the structure of the *trans*-complex **2**, showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.

filled with argon, and solvents were distilled and kept under argon. Instruments: NMR, Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H), 121.50 MHz (^{31}P) and 75.47 MHz (^{13}C), $SiMe_4$ as internal standart; IR, spectra were recorded in the 4000–400 cm^{-1} region on a Pye Unicam spectrometer. Starting materials were either commercially available or were prepared following literature procedures: $\overline{N{=}CH(Me)CH_2CH_2CH_2}$ [21], $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$ [19,22].

3.1. Synthesis of complexes *1* and *2*

A solution of the tetrahydropyrimidine (0.18 g, 1.84 mmol) in toluene (10 ml) and $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$ (0.61 g, 0.75 mmol) were heated for 2 h under reflux. *n*-Hexane (15 ml) was added to the solution in order to obtain pale-yellow product. Recrystallization from CH_2Cl_2 (5 ml)/Et_2O (10 ml) at -25°C, gave white and yellow crystals of **1** and **2** which were manually separated. The ratio of *cis*/*trans*-isomers was ca. 40/60 and total yield 0.66 g (89%).

1: M.p. 203–204°C. ν(C=N, KBr, cm^{-1}) = 1649. Anal.Found: C, 30.99; H, 4.32; N, 5.55. $C_{12}H_{21}N_2Cl_2PPt$ (490.271). Calc.: C, 31.13; H, 4.22; N, 5.59. **2**: m.p. 152–153°C. ν(C=N, KBr, cm^{-1}) = 1643. Anal.Found: C, 30.95; H, 4.30; N, 5.50.

3.2. Isomerization of *2* into *1*

The *trans*-complex (0.06 g) was heated in refluxing ethanol for 4 h. Upon cooling white crystals of *cis*-isomer deposited. The crystals were filtered off, washed with ether and dried in vacuo (0.05 g). They were identified by ^{1}H-NMR spectroscopy.

The *cis*-complex did not change in refluxing ethanol after 4 h.

3.3. X-ray crystallography

Suitable single crystals for X-ray diffraction were grown by cooling the CH_2Cl_2/Et_2O solution and the isomers were separated manually. The weighting scheme used was $w = 1/\sigma^2(F)$ and $w = 1/[\sigma^2(F) + (0.02)^2 + 1.0]$ except $w = 0$ if $F^2 < 6\sigma^2F$ for *cis*- and *trans* complexes, respectively. All non-H atoms were refined with anisotropic displacement parameters. H atoms of the phenyl ring were placed geometrically 0.950 Å from their parent atoms. Other H atoms were refined for a few cycles.For all H atoms a riding model was used with $B_{eq}(H) = 1.3B_{eq}(C)$. For data collection CAD4-Express, [23] for data reduction, structure solution and refinement MoIEN [24], for molecular graphics ORTEPII [25] programs were used.

4. Supplementary material available

Crystal data, data collection and refinement details, final coordinates, temperature factors, and selected bond lengths and angles are available on request from the author.

References

[1] (a) S.-B. Park, N. Sakata, H. Nishiyama, Chem. Eur. J. 2 (1996) 303. (b) M.P. Doyle, C.S. Peterson, Qi-L. Zhou and H. Nishiyama, J. Chem. Soc. Chem. Commun. (1997) 211.

[2] H. Brunner, B. Nuber, M. Prommesberger, J. Organomet. Chem. 523 (1996) 179.

[3] M.J. Bloemink, H. Engelking, S. Karentzopoulos, B. Krebs, J. Reedijk, Inorg. Chem. 35 (1996) 619.

[4] M.V. Beusichem, N. Farrell, Inorg. Chem. 31 (1992) 634.

[5] (a) A. Gund, B.K. Keppler, Angew. Chem. Int. Ed. Engl. 33 (1994)186. (b) B.K. Keppler, D. Wehe, H. Endres, W. Rupp, Inorg. Chem. 26 (1987) 844. (c) B.K. Keppler, W. Rupp, U.M. Juhl, H. Endres, R. Niebl, W. Balzer, Inorg. Chem. 26 (1987) 4366.

[6] F.O. Rochon, P.C. Kong, R. Melanson, Can. J. Chem. 59 (1981) 195.

[7] A.W. Roszak, O. Clement, E. Buncel, Acta. Cryst. C52 (1996) 1362; idem C52 (1996) 1645.

[8] (a) M.R. Silva, J.A. Paixao, A.M. Beja, L.A. Veiga, J.M. Gil, F.J.M. Gil, Acta. Cryst. C52 (1996) 2450. (b) J. Macycek, G. Gencheva, M. Mitewa, Acta. Cryst. C52 (1996) 2429.

[9] S. Karentzopulos, H. Engelking, B. Bremer, N. Paschke, B. Krebsao, Acta Cryst. C52 (1997) 172.

[10] B. Çetinkaya, I. Özdemir, B. Alici, C. Bruneau, P.H. Dixneuf, J. Organomet. Chem. in press.

[11] B. Çetinkaya, E. Çetinkaya, P.B. Hitchcock, M.F. Lappert, I. Özdemir, J.Chem.Soc. Dalton Trans. (1997) 1359.

[12] B. Çetinkaya, E. Çetinkaya, H. Küçükbay, R. Durmaz, Arzneim.-Forsch/Drug Res. 46 (1996) 821.

[13] G.B. Kauffman, L.A. Teter, Inorg. Synth. 7 (1963) 245.

[14] S.H. Mastin, P. Haake, Chem. Commun. (1970) 202.

[15] J. Chatt, J.M. Davidson, J. Chem. Soc. (1964) 2433.

[16] R. Ellis, T.A. Weil, M. Orchin, J. Am. Chem. Soc. 92 (1970) 1078.

[17] B. Çetinkaya, E. Çetinkaya, M.F. Lappert, J.Chem.Soc. Dalton Trans. (1973) 906.

[18] Lj. Manojlovic-Muir, K.W. Muir, J. Chem. Soc. Dalton Trans. (1974) 2427 and references cited therein.

[19] J.M. Jenkins, B.L. Shaw, J. Chem. Soc. A (1966) 770.

[20] (a) A. Pidcock, R.E. Richards, L.M. Venanzi, J. Chem. Soc. A (1966) 1707. (b) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 35.

[21] B. Alici, E. Çetinkaya, B. Çetinkaya, Heterocycles 45 (1997) 29.

[22] R.J. Goodfellow, L.M. Venanzi, J. Chem. Soc. (1965) 7533.

[23] Enraf-Nonius,CAD-4 EXPRESS Software, version 1.1 Enraf-Nonius, Delft, The Netherlands, 1993.

[24] C.K. Fair, MoIEN: An Interactive Intelligent System for Crystal Structure Analysis Enraf-Nonius, The Netherlands, 1990.

[25] C.K. Johnson, ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA, 1976.