

Five-Coordinate Ethylene Complexes of Platinum(II) Containing Different Types of N-Donor Bidentate Ligands

L. MARESCA, G. NATILE and L. CATTALINI

Istituto di Chimica Generale ed Inorganica, Università di Venezia, Italy

Received January 3, 1975

Diimines, aliphatic and aromatic diamines react with Zeise's salt to give stable five-coordinate complexes of general formula $[Pt(C_2H_4)Cl_2(N-N)]$, which have trigonal bipyramidal structure with the chlorine atoms in the apical positions and the bidentate ligand in the equatorial plane. The five-coordinate species decompose releasing ethylene and giving square-planar complexes of formula $[PtCl_2(N-N)]$.

Introduction

Recently we published that biacetylbisN-methylN-phenyl-hydrazone reacts with the Zeise's salt giving a stable five-coordinate complex $[Pt(C_2H_4)Cl_2(N-N)]$.¹ Other osazones with various substituents on the nitrogen and carbon atoms gave analogous results.² We now report studies which show that this reaction is common to different types of bidentate N-donor ligands such as diimines (N,N'-bis(cyclopropyl)biacetyldiimine (L₁); N,N'-bis(p-tolyl)biacetyldiimine (L₂); N,N'-bis(p-tolyl)acenaphthenequinonediimine (L₃); 2,2'-bipyridyl (L₄); 1,10-phenanthroline (L₅); N,N,N',N'-tetramethylethylenediamine (L₆)). Although some of these ligands have been used for long time in reactions with Zeise's salt, evidence for the formation of a five-coordinate intermediate, even in kinetic studies, has never been found.^{3,4}

Experimental

Starting Materials

2,2'-bipyridyl, 1,10-phenanthroline and N,N,N',N'-tetramethylethylenediamine were commercially available, the other ligands were prepared as follows:

N,N'-bis(cyclopropyl)biacetyldiimine was prepared according to the method of Bock *et al.*⁵ Biacetyl (2.1 g, 24.4 mmol) and the stoichiometric amount of cyclopropylamine (2.8 g, 49.1 mmol) were refluxed in benzene for five hours under nitrogen atmosphere, the solvent was distilled and by sublimation of the oily residue (0.05 mmHg, 60°C) the pure ligand was obtained as large colourless crystals.

N,N'-bis(p-tolyl)biacetyldiimine was prepared treating 4.3 g of biacetyl with 10.7 g of p-toluidine (molar ratio 1:2), the mixture was heated at 50°C and kept under stirring for about an hour. The reaction mixture was then cooled to room temperature and the oily raw product treated with 40 ml of MeOH; a yellow crystalline solid separated out which was filtered, washed with methanol and diethyl ether and dried.

N,N'-bis(p-tolyl)acenaphthenequinonediimine. Following the method of Matei *et al.*⁶ to a solution of acenaphthenequinone (4.8 g) in warm acetic acid (300 ml) was added p-toluidine (7.5 g, small excess over the stoichiometric amount) followed by ZnCl₂ (9.5 g). The mixture was refluxed for 30 min, cooled, filtered and repeatedly washed with warm acetic acid to give the yellow-orange N,N'-bis(p-tolyl)acenaphthenequinonediimine-ZnCl₂. The zinc complex was refluxed with a 50% solution of potassium carbonate in water, the solution filtered and the residue washed repeatedly with water; recrystallization of the raw product from hot heptane afforded orange yellow needles of the free ligand.

Zeise's salt was prepared according to the method of Cramer *et al.*⁷ from potassium platinitate and ethylene gas.

Preparation of Complexes

The complexes were prepared adding to a stirred solution of $K[Pt(C_2H_4)Cl_3] \cdot 11H_2O$ in methanol (0.5 g in 5 ml of solvent) cooled at 0°C the stoichiometric amount of the ligand dissolved in the same solvent. Ligands L₂ and L₃ which are sparingly soluble in methanol were added directly as solids. The reaction was complete in a few minutes, in all cases the complexes separated out as crystalline solids. They were filtered, washed with methanol and diethyl ether and dried. Complex with L₆ was the most unstable and filtering and washing had to be done keeping the temperature rigorously at 0°C.

Apparatus

The i.r. spectra in the range 4000–300 cm⁻¹ were recorded as KBr pellets with a Perkin-Elmer 456

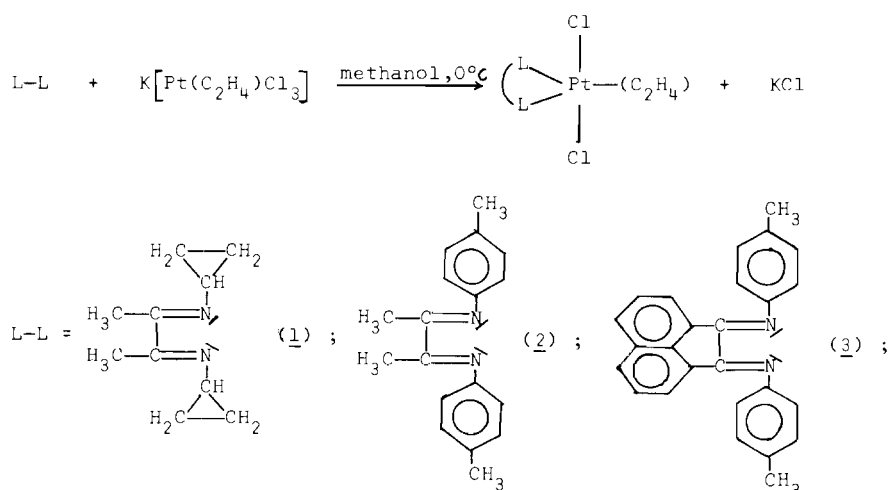
spectrophotometer, the spectra in the range 500–100 cm^{-1} were recorded as nujol mulls or polythene pellets with a Beckman IR 11. The ^1H n.m.r. spectra were obtained with a Varian NV 14 spectrometer with CDCl_3 or DMF-d_7 as solvents and tetramethylsilane as internal standard. Conductivities of $10^{-3}M$ solutions of complexes in nitromethane at 0°C were measured with an LKB Conductolyzer.

Results

The complexes were prepared by simple mixing of the appropriate ligand with Zeise's salt at 0°C in methanol. At the used concentration the five-coordinate adduct precipitated out as crystalline compound,

the colour being red (ligand L_3) orange (ligand L_2) or yellow (ligands L_1 , L_4 , L_5 and L_6). Except the complex with L_6 which was isolated and stored in the cold (0°C), all other compounds were stable in the solid state from some to several days at room temperature and could be stored almost indefinitely at -20°C ; in the decomposition process they released ethylene giving the corresponding square-planar complexes $[\text{PtCl}_2(\text{N}-\text{N})]$. The same decomposition occurred more readily in solution in the common organic solvents but could be repressed by keeping the solution at -10 , -20°C . All complexes gave satisfactory elemental analyses (the data are collected in Table I), were non-conducting in nitromethane solution at 0°C and their i.r. and n.m.r. spectra were in accord with the given formulation. The n.m.r. data are listed in Table II.

Reaction scheme



2,2'Bipyridyl (4); 1,10Phenanthroline (5); N,N,N',N' -Tetramethylethylenediamine (6).

TABLE I. Analytical Data.

Compound	C		H		Cl		N	
	calc.	found	calc.	found	calc.	found	calc.	found
L_1	73.1	73.0	9.8	9.8	—	—	17.1	17.1
L_2	81.8	81.6	7.6	7.4	—	—	10.6	10.4
L_3	86.6	86.5	5.6	5.5	—	—	7.8	7.5
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_1)]$	31.5	31.4	4.4	4.5	15.5	15.4	6.1	5.9
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_2)]$	43.0	42.7	4.3	4.1	12.7	12.5	5.0	4.8
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_3)]$	51.4	51.7	3.7	3.6	10.8	10.8	4.3	4.0
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_4)]$	32.0	31.7	2.7	2.7	15.7	15.4	6.2	5.9
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_5)]$	35.4	34.9	2.5	2.4	14.9	15.3	5.9	5.9
$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_6)]$	23.4	22.9	4.9	5.1	17.3	17.5	6.8	7.0

TABLE II. ¹H N.m.r. Spectral Data downfield from Me₄Si, Values for Chemical Shift are on the δ Scale.

Complex	Solvent	Temp., °C	Ligand Protons	Ethylene Protons
[Pt(C ₂ H ₄)Cl ₂ (L ₁)]	CDCl ₃	R.T.	2.53(6H, J _{Pt, H} 4.5Hz), 2.25–1.83(10H)	3.25(4H, J _{Pt, H} 67Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₂)]	CDCl ₃	-50	7.37(8H), 2.57(6H), 2.48(6H)	3.27(4H, J _{Pt, H} 69.5Hz)
		-10	7.33(8H), 2.48(6H), 2.43(6H)	3.27(4H, J _{Pt, H} 69.5Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₃)]	CDCl ₃	R.T.	7.33(8H), 2.47(6H), 2.43(6H)	3.27(4H, J _{Pt, H} 69.5Hz)
		-30	8.33–7.25(14H), 2.55(6H)	3.54(4H, J _{Pt, H} 71Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₄)]	CDCl ₃	R.T.	8.33–7.25(14H), 2.55(6H)	3.56(4H, J _{Pt, H} 71Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₅)]	DMFd ⁷	-20	9.66–7.25(8H)	3.67(4H, J _{Pt, H} 70Hz)
		-30	10.00–8.00(8H)	3.52(4H, J _{Pt, H} 70Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₆)]	CDCl ₃	-13	10.00–8.00(8H)	3.54(4H, J _{Pt, H} 70Hz)
		0	10.00–8.00(8H)	3.55(4H, J _{Pt, H} 70Hz)
[Pt(C ₂ H ₄)Cl ₂ (L ₆)]	CDCl ₃	-40	2.71(12H, J _{Pt, H} 15Hz), 2.57(4H, J _{Pt, H} 12Hz)	3.28(4H, J _{Pt, H} 69Hz)
		-10	2.69(12H, J _{Pt, H} 15Hz), 2.54(4H, J _{Pt, H} 12Hz)	3.28(4H, J _{Pt, H} 69Hz)

TABLE III. I.r. Spectra (cm⁻¹).^a

Compound	Pt–Cl Stretching	Other Bands
L ₁	–	1610s, 1443ms, 1418ms, 1373s, 1352s, 1200w, 1180s, 1105s, 1040s, 1013s, 980s, 910s, 856w, 810s, 668ms, 540ms, 385ms, 345w.
[Pt(C ₂ H ₄)Cl ₂ (L ₁)]	330s	1630s, 1560s, 1450w, 1470w, 1408s, 1383s, 1303s, 1225m, 1215s, 1180s, 1158ms, 1085mw, 1050sh, 1043s, 1030s, 1005s, 965ms, 915s, 875mw, 823s, 787m, 672s, 570mw, 520ms, 490ms, 445mw, 375ms.
L ₂	–	1615s, 1568w, 1500ms, 1360ms, 1305w, 1215w, 1205m, 1165w, 1120s, 1107s, 1045mw, 1020w, 963w, 945w, 937mw, 843s, 827s, 815s, 750ms, 715ms, 650mw, 633w, 540ms, 495s, 455w, 415mw, 375mw, 350mw.
[Pt(C ₂ H ₄)Cl ₂ (L ₂)]	340s	1575s, 1503s, 1413mw, 1310w, 1292m, 1242s, 1220w, 1210w, 1182w, 1162m, 1137mw, 1113mw, 1013mw, 1005m, 995w, 987w, 973w, 950w, 868ms, 855w, 840s, 817w, 803w, 788w, 775m, 605w, 568w, 557w, 525s, 495ms, 487ms, 375m, 348ms.
L ₃	–	1625s, 1585s, 1498s, 1485mw, 1415m, 1365mw, 1267m, 1237m, 1213mw, 1180mw, 1107m, 1085m, 1045m, 1015m, 945w, 930s, 835sh, 828s, 817s, 688s, 737m, 715m, 590mw, 547ms, 535ms, 505s, 490m, 440ms, 400m.
[Pt(C ₂ H ₄)Cl ₂ (L ₃)]	335s	1665m, 1615s, 1575s, 1490s, 1415ms, 1355w, 1285m, 1250m, 1225m, 1215w, 1120m, 1105w, 1050m, 1020m, 860m, 830s, 820s, 780s, 750mw, 710w, 600m, 555w, 530m, 520m, 485mwbr, 420m.
L ₄	–	1580s, 1560ms, 1445vs, 1410vs, 1250ms, 1212mw, 1140mw, 1088ms, 1064m, 1040ms, 992ms, 893mw, 758vs, 740mw, 650m, 618ms, 400s.
[Pt(C ₂ H ₄)Cl ₂ (L ₄)]	330s	1600m, 1593s, 1570mw, 1485ms, 1445s, 1410ms, 1310s, 1250mw, 1225mw, 1180mw, 1172w, 1162m, 1138m, 1105w, 1080w, 1054w, 1040w, 1022s, 1000s, 978w, 952m, 812m, 770vs, 758w, 730ms, 712w, 650ms, 627ms, 490w, 467w, 420mw, 360w.
L ₅	–	1640m, 1615mw, 1585m, 1560m, 1495s, 1420s, 1337mw, 1220mw, 1140mw, 1095m, 990mw, 885w, 858s, 780mw, 740s, 728w, 695mbr, 627ms, 413w.
[Pt(C ₂ H ₄)Cl ₂ (L ₅)]	330s	1620m, 1600w, 1583w, 1575ms, 1510s, 1490m, 1427s, 1408m, 1340m, 1222ms, 1180w, 1152w, 1140ms, 1100m, 905w, 868mw, 850vs, 827w, 805mw, 780ms, 728s, 722s, 718s, 640ms, 500w, 582mw, 438w, 422m.

^a The i.r. spectrum of [Pt(C₂H₄)Cl₂(L₆)] has not been recorded since the compound decomposes at temperature above 0° C.

The presence of a single sharp signal for the methyl protons of the biacetyl (L_1 , L_2), the methyl groups of the *p*-tolyl (L_2 , L_3), the four methyl and two methylene groups of the tetramethylethylenediamine (L_6) clearly indicate that the ligands are bidentate and occupy two equatorial positions of the trigonal bipyramid. A rapid head-to-tail rearrangement of a monodentate ligand would give rise to similar spectra but the low temperature n.m.r. data rule out this hypothesis. On the other hand, for ligands L_3 and L_5 the inflexibility of the molecule and the closeness of the donor nitrogens would seem to preclude the coordination through a single nitrogen atom. The ethylene protons always appear as a triplet of relative intensity 1:4:1 due to coupling with ^{195}Pt ($I = 1/2$, 34% abundance). Qualitative observations show that for structurally analogous ligands, such as osazones, the more stable complexes are those with highest δ value for the ethylene protons;² this does not hold true for the complexes we report here, for instance complex $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_1)]$ which is the most stable has the same δ value as complex $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(L_6)]$ which is by far the most labile.

The i.r. absorption frequencies for all compounds are reported in Table III. The overlap of the ligand absorptions with those of ethylene does not permit to distinguish between them. In the region below 600 cm^{-1} there are expected to occur the platinum-ethylene, the platinum-nitrogen and the platinum-chlorine stretchings; however, a reliable assignment has been possible only for the metal-halogen stretching since the platinum-nitrogen vibrations are expected to couple with the platinum-ethylene ones. All compounds showed only one band for the platinum-chlorine stretching indicating that they are mutually *trans* and therefore occupy the apical positions of the trigonal bipyramid. Compound with L_4 by releasing the ethylene molecule gives initially the red form of the *cis*-dichloro-diamine complex which in turn transforms into the yellow form.

Conclusions

Although five-coordination has been always postulated in the substitution reactions in square planar substrates and several studies concerning the arrangement of the substituents in the transition state have appeared,⁸ rather few direct pieces of evidence, such as isolation of the intermediates, have been reported so far.

The complexes we now describe show that five-coordinate $\text{Pt}^{\text{II}}-\pi$ -olefin compounds can be obtained not only with particular olefins (with highly electronegative substituents or particular types of ligands⁹) but also with mere ethylene and all different types of N-donor ligands.

Moreover this study seems to indicate that, as reported by Hubert *et al.* in the case of the reaction with bipyridyl of Bukhovet's salt $\text{K}[\text{Pt}(\text{ac})\text{Cl}_3]$ (ac = 2,5-dimethyl-3-hexine-2,5-diol),¹⁰ also in the reaction of Zeise's salt with bidentate nitrogen donors a five-coordinate intermediate could be present in the course of the substitution reaction.

Acknowledgements

We thank the Italian Council of Research (C.N.R., Rome) for financial support.

References

- 1 L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, *J.C.S., Chem. Comm.*, 369 (1973).
- 2 L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, to be published.
- 3 P. Uguagliati, U. Belluco, U. Croatto and R. Pietropaolo, *J. Am. Chem. Soc.*, **89**, 1336 (1967).
- 4 F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, **8**, 524 (1969).
- 5 H. Bock and H. Tom Dieck, *Chem. Ber.*, **100**, 228 (1967).
- 6 I. Matei, T. Lixandru, *Bul. Inst. Politeh. Iasi*, **13** (1, 2), 245 (1967); *Chem. Abst.*, **70**, 3623m (1969).
- 7 R. D. Cramer, E. L. Jenner, R. V. Lindsey and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).
- 8 F. Basolo, 'Mechanisms of Inorganic Reactions', ed. R. F. Gould, *Advances in Chemistry Series, A. C. S.*, 1965, n. 49.
C. H. Langford and H. B. Gray, 'Ligand Substitution Reactions', Benjamin, New York, 1965.
L. Cattalini, 'Reaction Mechanisms in Inorganic Chemistry', *Inorganic Chemistry Series One*, **9**, Butterworths, London, 1972.
M. L. Tobe, 'Inorganic Reaction Mechanisms', T. Nelson and Sons, London, 1972.
J. C. Chottard, D. Mansuy and J. F. Bartoli, *J. Organometal. Chem.*, **65**, C19 (1974).
- 9 H. C. Clark and L. E. Manzer, *J. Am. Chem. Soc.*, **95**, 3812 (1973) and references therein.
- 10 J. Hubert and T. Theophanides, *Inorg. Chim. Acta*, **3**, 391 (1969).