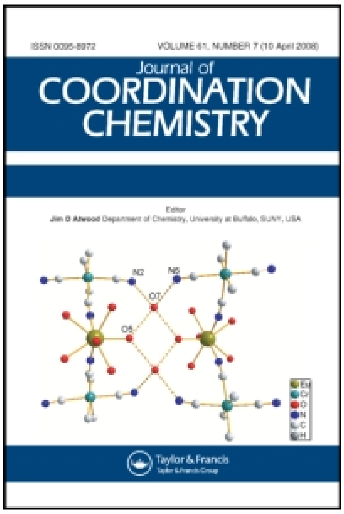

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SOME NEW CATIONIC COMPLEXES OF PLATINUM: METAL-CHLORINE INFRARED STRETCHING FREQUENCIES AND THE *CIS*-INFLUENCE

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The preparation of the new cationic platinum complexes *cis*-[PtXL(dppe)]$^+$ClO$_4^-$ (X = Cl, Br; L = Me$_3$CNC, P(OPh)$_3$, P(OMe)$_3$, PEt$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and *cis*-[PtXL(dmpe)]$^+$ClO$_4^-$ (X = Cl, Br; L = Me$_3$CNC, P(OPh)$_3$, PEt$_3$; dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) is described. Metal-chlorine infrared stretching frequencies have been measured and are discussed in terms of the evidence they provide as to the relative *cis*- and *trans*-influences of the ligands L.

INTRODUCTION

Molecular orbital calculations by Zumdahl and Drago[1] on complexes of the type PtCl$_2$L(NH$_3$), where L represents a variety of σ-bonding ligands, have suggested that the ligands L should exert a *cis*-influence comparable in magnitude to their *trans*-influence. However, subsequent experimental studies making use of such different physical techniques as ^{35}Cl n.q.r. spectroscopy,[2] ^{31}P n.m.r.,[3,4] and X-ray photoelectron spectroscopy[5] seem to show that the *cis*-influence of a ligand is, in general, less in magnitude than its *trans*-influence, and suggest that the theoretical calculations may be inaccurate as far as this particular conclusion is concerned.

In their paper, Zumdahl and Drago point out that the main body of infrared data on square-planar Pt(II) complexes obtained prior to their work is not in conflict with their conclusions.[1] A recent detailed infrared study of an extensive series of such complexes, however, emphasizes the fact that information about the relative magnitudes of *cis*- and *trans*-influences, which can be obtained from the sole use of this technique, is limited. Infrared results on the series of complexes MX$_3$L$^-$ (M = Pd, Pt; X = I, Cl, Br; L = PMe$_3$, AsMe$_3$, PEt$_3$, AsEt$_3$)[6] did nevertheless suggest that the M—X bond *trans* to L is weaker than the M—X bonds *cis* to L in accordance with other experimental data.

We have previously reported a *trans*-influence series for a wide range of neutral ligands L based on metal–chlorine stretching frequencies in the complexes *trans*-[PtClL(PEt$_3$)$_2$]$^+$ClO$_4^-$.[7] In order to compare the *cis*-influence of L on νM—Cl in a related series of cationic Pt(II) complexes, we have now synthesized the new complexes *cis*-[PtXL(dppe)]$^+$ClO$_4^-$ (X = Cl, Br; L = Me$_3$CNC, P(OPh)$_3$, P(OMe)$_3$, PEt$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and *cis*-[PtXL(dmpe)]$^+$ClO$_4^-$ (X = Cl, Br; L = Me$_3$CNC, P(OPh)$_3$, PEt$_3$; dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) and have studied their far-infrared spectra to determine the values of νM—Cl.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin–Elmer 257 grating spectrometer. Far-infrared spectra were recorded in nujol mulls between caesium bromide plates on a Perkin-Elmer 521 grating spectrometer purged with dry air.

All phosphorus ligands were commercial samples used without further purification except for 1,2-bisdiphenylphosphinoethane, prepared by the method of Chatt,[8] and 1,2-bis-dimethylphosphinoethane which was obtained using a modification of the method of Wymore.[9] *t*-Butyl isocyanide was prepared by the method of Ugi and Meyr.[10]

cis-PtCl$_2$(dppe) was prepared by the action of dppe on K$_2$PtCl$_4$, followed by refluxing with ethanol/conc. HCl,[11] and *cis*-PtBr$_2$(dppe) by an

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analogous procedure using K_2PtBr_4 and HBr. All reactions were carried out under nitrogen.

cis-*Dichloro-(1,2-bisdimethylphosphinoethane) platinum(II)* cis-*$PtCl_2$(dmpe)*

To dichlorobisbenzonitrileplatinum(II) (1 g., 2.12 mmoles)[12] dissolved in deaerated chloroform (20 ml) was added 1,2-bisdimethylphosphinoethane (0.32 g. 2.14 mmoles). The mixture was shaken overnight and the white precipitate which had formed was filtered off and washed with petroleum-ether (b.p. 30–40°). It was then dissolved in dimethylformamide (30 ml.) and refluxed for 2 days at 220° after which the solution was concentrated under vacuum to *c.* 10 ml. and diethylether added dropwise until the complex precipitated (as white plates). These were filtered off and recrystallized by dissolution in boiling dimethylformamide followed by addition of ether to the solution when cool to give white needles of $PtCl_2$[dmpe]; m.p. $> 300°$ lit., [13]*c.* 340°); (Found: C, 17.2; H, 3.3; Calc. for $C_6H_{16}Cl_2P_2Pt$: C, 17.3 H, 3.9%).

cis-*Dibromo-bis-(1,2-dimethylphosphinoethane) platinum(II)*; cis-*$PtBr_2$ (dmpe)*

Prepared as for $PtCl_2$ (dmpe) from dibromobisbenzonitrileplatinum(II) (5 g., 8.9 mmoles) and 1,2-bisdimethylphosphinoethane giving $PtBr_2$ (dmpe); m.p. $> 350°$; (Found: C, 14.8; H, 3.4; Calc. for $C_6H_{16}Br_2P_2Pt$: C, 14.3; H, 3.2%).

cis-*Chloro(t-butylisocyanide)bis-1,2-dimethylphosphinoethane platinum(II)*; cis *$[PtCl(Bu^tNC)dmpe]^+ ClO_4^-$*

t-Butylisocyanide (21.9 mg. 0.026 mmoles) in acetone (20 ml.) was added dropwise over a period of 1 hour to a vigorously stirred suspension of *cis*-$PtCl_2$(dmpe) (110 mg. 0.026 mmoles) in acetone (40 ml.) containing $NaClO_4.H_2O$ (36 mg., 0.026 mmoles). After the addition of the isocyanide had been completed, the reaction mixture was stirred for a further ½ hr and then centrifuged. This removed the NaCl which had precipitated out during the reaction as the complex itself dissolved. The solution was then evaporated on a rotary evaporator to a volume of *c.* 10 ml. and diethyl ether added dropwise until the complex crystallized. It was recrystallized to give white needles by extraction with CH_2Cl_2 and addition of ether. Yield 104 mg. (70%).

All other bis-dimethylphosphinoethane complexes were prepared analogously from *cis*-PtCl(dmpe) or *cis*-$PtBr_2$(dmpe) and the bis-diphenylphosphinoethane complexes were similarly prepared from *cis*-$PtCl_2$(dppe) or *cis*-$PtBr_2$(dppe).

RESULTS AND DISCUSSION

A complete list of the new cationic complexes we have prepared is presented in Table I together with analytical data. The complexes are all air-stable white crystalline compounds which are soluble in polar solvents such as acetone and dichloromethane and are virtually insoluble in non-polar solvents such as benzene or petroleum ether.

TABLE I

Analytical data on the new cationic Pt(II) complexes

L	Found		Calculated %	
	(*a*) *cis*-$[PtCl(L)(dppe)]^+ClO_4^-$			
$CNCMe_3$	46.0	4.3	45.9	4.1
$P(OPh)_3$	51.5	4.1	50.9	3.8
$P(OMe)_3$	41.2	3.9	40.8	3.9
PEt_3	45.3	4.5	45.4	4.6
	(*b*) *cis*-$[PtBr(L)(dppe)]^+ClO_4^-$			
$CNCMe_3$	43.2	4.1	43.5	3.9
$P(OPh)_3$	49.0	3.9	48.8	3.6
$P(OMe)_3$	39.4	3.9	38.8	3.7
PEt_3	43.1	4.6	43.1	4.4
	(*c*) *cis*-$[PtCl(L)(dmpe)]^+ClO_4^-$			
Me_3CNC	23.6	4.7	23.4	4.5
$P(OPh)_3$	36.7	4.0	36.4	4.0
PEt_3	24.0	4.5	24.1	5.2
	(*d*) *cis*-$[PtBr(L)(dmpe)]^+ClO_4^-$			
Me_3CNC	21.3	4.0	21.7	4.1
$P(OPh)_3$	34.4	4.0	34.5	3.7
PEt_3	22.3	4.9	22.4	4.8

The *trans*-influence of a series of ligands L, which we have previously deduced from a study of νM—Cl in the complexes *trans*-$[PtCl(L)(PEt_3)_2]^+$ ClO_4^- and *trans*-$[PtCl(L)(AsEt_3)_2]^+ - ClO_4^-$, increases in the order: CO $<$ RNC $<$ ArNC $<$ $P(OPh)_3 \simeq P(OMe)_3 < AsEt_3 \simeq PEt_3$.[7,14] It was our intention to synthesize a more or less complete series of analogous *cis*-complexes of the type *cis*-$[PtX(L)(dppe)]^+ClO_4$ for comparative purposes (X = Cl, Br), but we were unable to obtain the complexes *cis*-$[PtX(CO)dppe]^+ClO_4^-$ by treating *cis*-PtX_2(dppe) with CO in acetone solution in the presence of sodium perchlorate. It was noted that the precipate of NaCl which formed in every other reaction tried, did not appear in this particular case. To investigate the effect on νM–Cl of changing the chelating phosphine ligand, we also prepared a series of complexes of the type *cis*-$[PtX(L)(dmpe)]^+ClO_4^-$ (X = Cl, Br) but again we were not able to prepare the complexes *cis*-$[PtX(CO)(dmpe)]^+ClO_4^-$. This failure to prepare the CO complexes presumably arises from the presence of a *trans* phosphorus donor ligand which destabilizes the Pt—CO bond. We did not attempt to prepare any *cis*-complexes with L = $AsEt_3$.

The metal-chlorine stretching frequencies in the infrared spectra of the two series of *cis*-complexes were identified by comparing the far-infrared spectra of the chloride complexes with those of the bromide complexes, and are presented in Table II.

TABLE II

Metal-chlorine i.r. stretching frequencies[a]

cis-$[PtCl(L)(dppe)]^+ClO_4^-$				
L	$P(OPh)_3$	$P(OMe)_3$	$CNCMe_3$	PEt_3
νM—Cl	322	320	315	306
cis-$[PtCl(L)(dmpe)]^+ClO_4^-$				
L	$P(OPh)_3$		$CNCMe_3$	PEt_3
νM—Cl	315		306	301

[a] In cm^{-1}; Frequencies are $\pm 2\ cm^{-1}$.

The observed νM–Cl values cover a range of only $16\ cm^{-1}$ compared with $46\ cm^{-1}$ when the same ligands L are *trans* to the M—Cl bond. Although the metal-chlorine stretching frequencies undoubtedly couple to some extent with other symmetrically similar molecular vibrations, the fact that the range of *relative* frequencies within each series is smaller by a factor of 3 in the *cis* complexes is almost certainly significant in terms of the *cis* influence of the ligands L being less in magnitude than their *trans*-influence. Evidence that the coupling of molecular vibrations does not significantly affect the relative order of νM—Cl is provided by the fact that on changing the chelating phosphine ligand from dppe to dmpe, all the observed frequency values shift downwards to approximately the same extent. Molecular orbital calculations[1] suggest that the ligand order in any *cis*- and *trans*-influence series for σ-bonding ligands should be the same. Although νM—Cl is lowest for L = PEt_3 in both *cis* and *trans* complexes, the positions of $CNCMe_3$ and $P(OR)_3$ in the *cis* and *trans* influence series, which may be derived from the infrared data, are interposed. In view of the small frequency differences involved, any comment on this change of order is probably not justified. It is noteworthy, however, that on the basis of ^1JPt–P n.m.r. data Allen and Sze conclude that there does not seem to be any simple relationships between the *cis*-influence and the *trans*-influence of a given ligand.[4]

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