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Trans-Chelation in Transition Metal Complexes: Synthesis and Characterization of Platinum(II) Complexes of Bis(diphenylarsino)alkanes

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Cis *and* trans *complexes of the type* $Pt(ligand)Cl_2$ *(ligand =* $Ph_2As(CH_2)_nAsPh_2$*, n = 6–12, 16) have been synthesized, together with the bromo, iodo and thiocyanato derivatives for n = 10 and 12. The* cis *complexes are essentially dimeric. The complexes have been characterized by elemental analyses, infrared and proton NMR spectroscopy, solid state reflectance and visible/UV spectroscopy and vapor phase osmometry. Formation of the* cis *or* trans *isomer for the complexes* $Pt(ligand)Cl_2$ *is critically dependent on the choice of complex precursor: potassium tetrachloroplatinate(II) yields the* cis *isomer, whilst Zeise's salt gives the* trans *isomer. The bromo, iodo and thiocyanato derivatives prepared* via *an exchange reaction give* cis *complexes. Evidence is presented for the existence of Pt–NCS and Pt–SCN linkages both in the solid state and in solution for the thiocyanato derivatives. Product distribution and stereochemistry in all of the complexes are discussed in terms of the factors governing* trans *chelation.*

Introduction

Recent studies [1–6] have shown that bidentate phosphines with suitably long chelate backbones can chelate *trans* to square-planar rhodium(I), iridium(I), palladium(II) and platinum(II). Although the presence of bulky substituents, especially t-butyl groups, appears to aid the isolation of *trans* chelates [1, 2], studies by ourselves [6] and others [5] have shown that ligands with phenyl substituents can form this type of complex, providing the chelate backbone is of suitable length. *Trans* chelated complexes with donor atoms other than phosphorus are not as common, but such complexes with both arsenic [7–9] and sulphur [10] donor atoms have been reported with sterically undemanding phenyl and methyl substituents. It appears, therefore, that the presence of bulky terminal substituents on the donor atoms is not a prerequisite for *trans* chelation and other factors must play important roles in determining the stereochemistry of the complexes. As part of our investigations of the factors that promote *trans* chelation we report here the synthesis of platinum(II) complexes with bis(diphenylarsino)alkanes. The choice of complex precursor is critical for the synthesis of the *cis* or *trans* isomer with these ligands and the effect of other factors such as (a) the donor atoms present in the ligands, (b) the electronic effects of the groups attached to the donor atoms, (c) the nature of the central metal atom and (d) the nature of the coordinated anion are discussed in terms of their influence on the stereochemistry of the products.

Results and Discussion

The synthesis [11] and characterization [11, 12] of the ditertiary arsine ligands $Ph_2As(CH_2)_nAsPh_2$ (n = 6–12, 16)** are reported elsewhere. Platinum(II) complexes of the type *cis*-$Pt(ligand)Cl_2$

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**The diarsine ligands used in the study are abbreviated thus: $Ph_2As(CH_2)_nAsPh_2$, n = 6(DAH), n = 7(DAHP), n = 8(DAO), n = 9(DAN), n = 10(DAD), n = 11(DAU), n = 12(DADOD), n = 16(DAHD).

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TABLE I. Analytical Data for the Platinum(II)–Diarsine Complexes.

Complex	Colour	%C	%H	%Cl	%X[b]	Mol wt.[c]
cis-$Pt(DAH)Cl_2$	White	44.6(44.0)[a]	4.0(4.3)	8.8(9.1)		1571(808)
trans-$Pt(DAH)Cl_2$	Yellow	44.6(43.8)	4.0(4.3)	8.8(8.5)		782(808)
cis-$Pt(DAHP)Cl_2$	White	45.3(46.8)	4.1(4.5)	8.6(9.0)		1597(822)
trans-$Pt(DAHP)Cl_2$	Yellow	45.3(45.4)	4.1(3.8)	8.6(9.1)		801(822)
cis-$Pt(DAO)Cl_2$	White	45.9(45.3)	4.3(4.5)	8.5(8.8)		
trans-$Pt(DAO)Cl_2$	Yellow	45.9(45.6)	4.3(4.3)	8.5(8.9)		
cis-$Pt(DAN)Cl_2$	White	46.6(46.3)	4.5(5.1)	8.4(8.3)		1599(850)
trans-$Pt(DAN)Cl_2$	Yellow	46.6(46.5)	4.5(4.4)	8.4(8.2)		809(850)
cis-$Pt(DAD)Cl_2$	White	47.2(48.2)	4.6(4.8)	8.2(7.8)		
trans-$Pt(DAD)Cl_2$	Yellow	47.2(47.6)	4.6(5.3)	8.2(8.0)		
cis-$Pt(DAU)Cl_2$	White	47.8(48.2)	4.8(4.2)	8.1(8.4)		1620(878)
trans-$Pt(DAU)Cl_2$	Yellow	47.8(48.2)	4.8(3.7)	8.1(8.5)		852(878)
cis-$Pt(DADOD)Cl_2$	White	48.4(47.9)	4.9(5.1)	8.0(7.8)		
trans-$Pt(DADOD)Cl_2$	Yellow	48.4(47.8)	4.9(5.0)	8.0(8.2)		
cis-$Pt(DAHD)Cl_2$	White	50.6(51.1)	5.5(5.3)	7.5(7.6)		
trans-$Pt(DAHD)Cl_2$	Yellow	50.6(50.8)	5.5(4.8)	7.5(7.2)		
$Pt(DAD)Br_2 \cdot CHCl_3$	Yellow/brown	39.1(40.0)	3.8(3.9)	9.9(9.4)	14.9(15.0)	
$Pt(DAD)I_2 \cdot \frac{1}{2}CHCl_3$	Brown	37.4(37.5)	3.7(4.0)	4.8(5.0)	22.9(23.0)	
$Pt(DAD)(CNS)_2 \cdot CHCl_3$	Orange/red	43.2(43.4)	4.0(4.3)	10.4(10.7)	2.7(2.5)	
$Pt(DADOD)Br_2 \cdot CHCl_3$	Yellow/brown	40.7(40.1)	4.1(4.8)	9.8(9.2)	14.7(15.2)	
$Pt(DADOD)I_2 \cdot \frac{1}{2}CHCl_3$	Brown	38.6(38.5)	3.9(4.3)	4.7(5.0)	22.4(21.6)	
$Pt(DADOD)(CNS)_2 \cdot CHCl_3$	Orange/red	44.3(44.3)	4.3(4.8)	10.1(9.8)	3.6(3.1)	

[a] Expected (found). [b] X = Br, I or N. [c] In $CHCl_3$ Fd. (Calc. for monomer).

(ligand = diarsine) were prepared by reacting the ligand with potassium tetrachloroplatinate(II) in a 1:1 mol ratio in refluxing absolute ethanol for a period of 24 hours. The bromo, iodo and thiocyanato derivatives (n = 10 and 12) were prepared by the exchange reaction previously reported [13]. The analytical data for the complexes appear in Table I.

$$K_2PtCl_4 + L \xrightarrow[\text{reflux}]{\text{ethanol}} \textit{cis-}[Pt(ligand)Cl_2]$$

Platinum(II) complexes of the type *trans*-Pt(ligand)Cl_2 were prepared by reacting the ligand with Zeise's salt in a 1:1 mol ratio in an acetone/toluene solution at room temperature. The ligand, dissolved in toluene, was added dropwise to the Zeise's salt to avoid *cis*/*trans* isomerization observed in the presence of excess ligand [14].

$$K[PtCl_3(C_2H_4)] + L \xrightarrow[\text{toluene}]{\text{acetone}} \textit{trans-}[Pt(ligand)Cl_2]$$

The chloro-complexes prepared from potassium tetrachloroplatinate(II) exhibited two bands in the far infra-red spectrum characteristic of *cis* chlorine atoms [15–17]. On the other hand, the chloro-complexes prepared from Zeise's salt exhibited only one band in the far infra-red spectrum at 340 cm^{-1} characteristic of *trans* chlorine atoms [15–18] (see Table II). The infra-red spectra of the bromo complexes (see Table III) prepared via the halide exchange reaction, show two bands at 220 and 198 cm^{-1} indicative of *cis* bromine atoms [15, 16]. Platinum-iodine stretching vibrations occur below 180 cm^{-1} and were not observed.

In coordination compounds the thiocyanate ion can be bound to the central metal atom in three ways: through the nitrogen atom (M–NCS), through the sulphur atom (M–SCN) or by means of a bridging structure (M–NCS–M) [19–22]. It appears that both electronic and stereochemical factors are important in determining the mode of bonding of the thiocyanate group and attempts to explain the known facts in terms of only steric [21, 23] or only electronic [24, 25] factors are unlikely to be successful [26].

Examination of the infra-red spectra of the thiocyanato derivatives shows the presence of both N- and S-bonded thiocyanate groups as evidenced by ν(CN): the N-bonded stretch appears at 2090 cm^{-1}

TABLE II. The Far Infrared Spectra of the Chloro-Platinum(II) Complexes of the Diarsine Ligands.

Complex	ν(M–X)	
	I[a]	II[b]
Pt(DAH)Cl$_2$	291, 318 cm^{-1}	341 cm^{-1}
Pt(DAHP)Cl$_2$	288, 320 cm^{-1}	340 cm^{-1}
Pt(DAO)Cl$_2$	293, 315 cm^{-1}	341 cm^{-1}
Pt(DAN)Cl$_2$	288, 318 cm^{-1}	338 cm^{-1}
Pt(DAD)Cl$_2$	285, 315 cm^{-1}	341 cm^{-1}
Pt(DAU)Cl$_2$	284, 310 cm^{-1}	337 cm^{-1}
Pt(DADOD)Cl$_2$	285, 312 cm^{-1}	340 cm^{-1}
Pt(DAHD)Cl$_2$	288, 318 cm^{-1}	345 cm^{-1}

[a] Potassium tetrachloroplatinate(II) used as complex precursor. [b] Zeise's salt used as complex precursor.

TABLE III. The Infra-red Spectra of the Bromo- and Thiocyanato-Platinum(II) Complexes of the Diarsine Ligands ($n = 10, 12$).

Complex	ν(C–N)	ν(M–X)
Pt(DAD)Br$_2$		223, 200 cm^{-1}
Pt(DADOD)Br$_2$		220, 198 cm^{-1}
Pt(DAD)(SCN)$_2$	2090 cm^{-1} (m)	
	2119 cm^{-1} (m)	
	2160 cm^{-1} (w)	
Pt(DADOD)(SCN)$_2$	2090 cm^{-1} (m)	
	2120 cm^{-1} (m)	

TABLE IV. The Proton NMR Spectra of the Chloro-Platinum(II) Complexes of the Diarsine Ligands.

Complex	δ_{H^1} [a]	
	I[b]	II[c]
Pt(DAH)Cl$_2$	7.10	6.98(3), 7.79(2)
Pt(DAHP)Cl$_2$	7.08	7.01(3), 7.80(2)
Pt(DAO)Cl$_2$	7.10	7.00(3), 7.80(2)
Pt(DAN)Cl$_2$	7.10	6.98(3), 7.78(2)
Pt(DAD)Cl$_2$	7.03	7.03(3), 7.81(2)
Pt(DAU)Cl$_2$	7.18	7.07(3), 7.82(2)
Pt(DADOD)Cl$_2$	7.10	7.03(3), 7.81(2)
Pt(DAHD)Cl$_2$	7.09	6.99(3), 7.79(2)

[a] Peaks measured relative to TMS internal standard, relative intensities in parentheses. [b] Potassium tetrachloroplatinate(II) used as complex precursor, all peaks were broad. [c] Zeise's salt used as complex precursor.

TABLE V. The Proton NMR Spectra of the Bromo, Iodo and Thiocyanato Platinum(II) Complexes of the Diarsine Ligands ($n = 10, 12$).

Complex	δH^1 [a]
Pt(DAD)Br$_2$	7.10
Pt(DAD)I$_2$	7.08
Pt(DAD)(SCN)$_2$	7.10
Pt(DADOD)Br$_2$	7.11
Pt(DADOD)I$_2$	7.10
Pt(DADOD)(SCN)$_2$	7.09

[a] Peaks measured relative to TMS internal standard, relative intensities in parentheses, all peaks were broad.

and the S-bonded counterpart at 2120 cm^{-1} in agreement with the literature [27, 28]. The C–S stretch and NCS deformation modes are obscured by ligand bands. A third component in the ν(CN) region is observed at 2160 cm^{-1} for $n = 10$, characteristic of a bridging –NCS– group, indicating the presence of a polymeric species in the solid state. This band is absent in the solution spectrum.

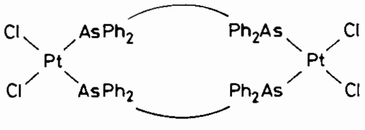
Moore and Robinson [29] found that for triphenylphosphine, -arsine or -stibine complexes of a wide range of platinum metals studied in deuterobenzene, a clear distinction could be made between *cis* and *trans* pairs of EPh$_3$ ligands (E = P, As or Sb) by examination of the aromatic region of the proton nmr spectra. The phenyl region for a given ligand could be clearly resolved into two complex resonances – relative intensity 2:3 – attributable to the *ortho* and *meta/para* protons, respectively. The magnitude of the separation between the centres of these two resonances is dependent upon the coordination geometry of the complex. For a *trans* pair of EPh$_3$ ligands, the separation is >0.5 ppm, whereas for a *cis* pair the separation is <0.5 ppm. The size of the separation appears to be irresponsive to changes in the identity of the central metal atom, its oxidation state and the nature of auxiliary ligands and holds for square-planar, square pyramidal and octahedral coordination arrangements. This phenomenon only holds true for complexes examined in deuterobenzene and the use of other deuterated solvents, *e.g.* CD$_2$Cl$_2$, gives ambiguous results.

The proton NMR spectra of the complexes studied here are listed in Tables IV and V. The chloro-complexes obtained from potassium tetrachloroplatinate(II) give spectra in the aromatic region consistent with a *cis* geometry for the diarsine ligands. In contrast, the chloro-complexes obtained using Zeise's

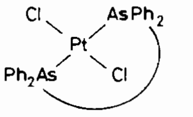
TABLE VI. The Electronic Spectra of the Platinum(II)–Diarsine Complexes.

Complex	Electronic Spectra	
	Dichloromethan solution[a]	Solid Reflectance[b]
cis-$Pt(DAH)Cl_2$	29.9(3,200)	26.2
trans-$Pt(DAH)Cl_2$	29.9(3,150)	26.2
cis-$Pt(DAHP)Cl_2$	29.8(3,200)	26.2
trans-$Pt(DAHP)Cl_2$	30.0(4,000)	26.3
cis-$Pt(DAO)Cl_2$	29.9(3,800)	26.2
trans-$Pt(DAO)Cl_2$	29.8(3,200)	26.2
cis-$Pt(DAN)Cl_2$	29.8(2,900)	26.2
trans-$Pt(DAN)Cl_2$	29.9(2,500)	26.3
cis-$Pt(DAD)Cl_2$	29.9(2,800)	26.3
trans-$Pt(DAD)Cl_2$	30.0(3,100)	26.3
cis-$Pt(DAU)Cl_2$	29.9(3,000)	26.2
trans-$Pt(DAU)Cl_2$	29.9(3,200)	26.2
cis-$Pt(DADOD)Cl_2$	30.0(3,150)	26.3
trans-$Pt(DADOD)Cl_2$	28.8(3,150)	26.1
cis-$Pt(DAHD)Cl_2$	29.8(3,400)	26.2
trans-$Pt(DAHD)Cl_2$	30.0(3,100)	26.3
$Pt(DAD)Br_2$	25.8(3,100)	24.7
$Pt(DAD)I_2$	21.4(4,200)	23.1
$Pt(DAD)(SCN)_2$	27.0(2,000)	25.4
$Pt(DADOD)Br_2$	25.9(3,150)	24.6
$Pt(DADOD)I_2$	21.5(4,200)	23.0
$Pt(DADOD)(SCN)_2$	26.9(2,100)	25.4

[a] λ_{max} in $cm^{-1} \times 10^{-3}$ absorbance measured in 1 cm^{-1} mol^{-1} in parentheses. [b] λ_{max} in $cm^{-1} \times 10^{-3}$ all peaks were broad.



(a) Cis Dimers



(b) Trans Monomers

Fig. 1. Structure of the Platinum(II)–diarsine complexes.

salt as the complex precursor give a chemical shift separation $\Delta\tau$ between the *ortho* and *meta/para* protons consistent with a *trans* geometry for the diarsine ligands. These results confirm the stereochemical assignments made on the basis of the far infra-red spectra of the complexes.

The bromo, iodo and thiocyanato derivatives prepared *via* the halide exchange reaction show spectra indicative of a *cis* orientation for the diarsine ligands. The bromo derivatives exhibited two bands in the far infra-red spectrum (*vide supra*) at 220 and 198 cm^{-1} and so these results are also consistent with the infra-red data.

The electronic spectra were recorded in the solid state and in solution and appear in Table VI. The bands observed, including the presence of a second band above 31 kK, are in keeping with a square planar geometry for the complexes both in the solid state and in solution [30, 31] and the band positions move to lower energy in the order Cl > CNS > Br > I. This unusual order is in keeping with the fact that both N and S bonded thiocyanato groups are present in these complexes [31, 32].

Molecular weight data show that the *cis* chelated complexes are essentially dimeric in solution, whilst the corresponding *trans* bonded analogues are monomeric, Table I. This mirrors the corresponding bis(diphenylphosphino)alkane dichloroplatinum(II) complexes which exhibit similar behaviour [54]. The structures of the complexes are shown in Fig. 1.

It has long been known that *cis* isomers of square planar platinum(II)–phosphine complexes are thermodynamically more stable than their *trans* analogues [33, 34] and that *cis/trans* isomerization is promoted by high temperatures and polar solvents [35]. The employment of relatively high temperatures and the use of a polar solvent would therefore favour the formation of the *cis* isomer: these are the reaction conditions that are used in the synthesis of the *cis*-$Pt(ligand)Cl_2$ complexes starting from potassium tetrachloroplatinate. Complexes of this type can be considered to be products of thermodynamic control: a stronger platinum–arsenic bond being formed when the coordinated arsenic is *trans* to chlorine which has a weak *trans* influence. X-ray crystallographic studies [36–41] indicate that the arsine group can exert a strong *trans* influence. The arsine group can also exhibit a *trans* effect similar to that observed for an alkyl carbon group [42]. There therefore exists a fine balance between two opposing forces: the thermodynamic driving force to form the stable *cis* isomer and the kinetic driving force manifested in the large *trans* effect of the arsenic donor atom which will direct the second donor atom in a bidentate chelate to a position *trans* to itself in complex formation, thus forming the *trans* isomer. In palladium(II) complexes of monophosphines [43–45], diphosphines [6] and diarsines [11] the product observed in almost all cases is the *trans* isomer. The preparation of the elusive *cis* derivatives has proved to be difficult and has been achieved by photochemical means [46–48] or by the employment of unusual complex precursors

[49]. The formation of the *trans* complexes, with palladium(II), even though the *cis* complexes are thermodynamically more stable [50], indicates that the products are those of kinetic control; this is due to the fact that palladium(II) complexes are far more labile than the corresponding platinum(II) derivatives [51].

For platinum(II) complexes the basicity of the donor atoms appears to play an important role in determining the formation of *cis* and *trans* isomers. The presence of phenyl groups on phosphorus favors the *cis* isomer over the *trans* counterpart [52, 53] and the synthesis of *trans* chelated platinum(II) complexes of bis(diphenylarsino)alkanes is therefore critically dependent on the choice of the platinum(II) salt used as starting material and the reaction conditions employed: potassium tetrachloroplatinate and the ligand in refluxing ethanol will yield the *cis*- isomer whilst Zeise's salt and the ligand will give the *trans* isomer in the absence of heat or a polar solvent.

The formation of the *cis* chelated complexes in the exchange reaction [13] indicates that the presence of a *trans* labelizing group in the complex precursor is necessary to produce the *trans* isomer. In the absence of such a group, even when the reaction conditions are less severe, and polar solvents and high temperatures are not employed, the products are those which are favoured from a thermodynamic standpoint.

Conclusions

The important factors governing *trans* chelation in platinum(II) complexes are therefore (a) the nature of the complex precursor and (b) the electronic effects of the groups attached to the donor atoms in the ligands.' The nature of the donor atoms present in the ligand are unimportant, except that they must possesss a *trans* effect greater than that of chlorine. The nature of the coordinated anion (*viz.* the exchange reaction) does not play a role in determining the product stereochemistry. Moreover, the presence of bulky terminal substituents attached to the donor atoms is not a prerequisite for *trans* chelation, which can be explained by simple classical arguments. The nature of thiocyanate bonding does not depend on chelate ring size in complexes of the type reported here. Finally, a new experimental technique (proton NMR), previously valid only for $AsPh_3$ and PPh_3 complexes has been extended to bidentate phosphine and arsine groups to confirm *cis* or *trans* chelation in these complexes.

Experimental

The proton NMR spectra of the complexes were recorded on a Varian CFT-20 FT spectrometer at 80 MHz in deuterobenzene using tetramethylsilane as internal standard. The solid state infra-red spectra of the complexes were recorded on a Perkin-Elmer 580 spectrometer using potassium bromide plates and Nujol and HCBD mulls. The far intra-red spectra were recorded in a Nujol mull between polyethylene plates. The solution spectra were recorded in chloroform using 1 mm pathlength polyethylene or potassium bromide cells. The solution electronic spectra of the complexes in methylene chloride were recorded on a Cary 17 spectrometer using 1 cm pathlength cuvets. The solid state reflectance spectra were recorded on the same Cary 17 spectrometer fitted with the reflectance attachment and using magnesium carbonate as the base line standard. Molecular weights were determined by vapor phase osmometry in chloroform solution. Elemental analyses were performed by the U.M.I.S.T. microanalytical service and by Galbraith Laboratories, Knoxville, Tennessee.

Solvents were dried by the recommended literature routes [55, 57].

The Preparation of the Cis *Platinum(II) Chloro Complexes of the Diarsine Ligands (n = 6–12 and 16)*

Potassium tetrachloroplatinate(II) (0.207 g, 0.0005 mol) and the ligand (0.0005 mol) were placed in a 125 ml round bottom flask fitted with a reflux condenser; 50 cm^3 of dry ethanol and 10 cm^3 of DMP were added and the mixture refluxed for 24 hours. The red crystalline K_2PtCl_4 gradually disappears to yield a white solid which is insoluble in boiling ethanol. The mixture was filtered and washed thoroughly with three 10 ml portions of water to remove the unwanted potassium chloride. The solid residue was then washed with two 10 cm^3 portions of ethanol and two 10 cm^3 portions of ether and then dried under vacuum.

(Yields: n = 6, 52%; n = 7, 34%; n = 8, 46%; n = 9, 35%; n = 10, 51%; n = 11, 39%; n = 12, 51%; n = 16, 40%).

The Preparation of Trans-*Platinum(II) Dichloro Complexes of the Diarsine Ligands (n = 6–12, 16)*

Zeise's salt (0.185 g, 0.0005 mol) was dissolved in 50 ml of dry acetone and placed in a 125 cm^3 flat bottomed flask. The ligand (0.0005 mol) dissolved in 15 cm^3 of toluene was then added dropwise to the stirred salt solution over a period of 30 minutes. The mixture was filtered and the precipitate washed with 3 × 10 cm^3 portions of toluene. The acetone/toluene filtrate was then evaporated to dryness and the solid redissolved in toluene and filtered again to remove any traces of potassium chloride. The solution was evaporated to dryness to yield the appropriate complex which was dried under vacuum.

(Yields: n = 6, 42%; n = 7, 33%; n = 8, 48%; n = 9, 37%; n = 10, 53%; n = 11, 38%; n = 12, 43%; n = 16, 37%).

The *Cis*- Platinum(II) Bromo, Iodo and Thiocyanato Complexes of the Diarsine Ligands (n = 10 and 12) were prepared by the literature route [13].

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