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AN INVESTIGATION OF THE CHELATE EFFECT: THE BINDING OF BIDENTATE PHOSPHINE AND ARSINE CHELATES IN SQUARE-PLANAR TRANSITION METAL COMPLEXES

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CONTENTS

ABBREVIATIONS

dpm	$n = 1$	$Ph_2P(CH_2)_nPPh_2$
dpe	$= 2$	
dpp	$= 3$	
dpb	$= 4$	
dam	$n = 1$	$Ph_2As(CH_2)_nAsPPh_2$
dae	$= 2$	
vpp		$Ph_2PCHCHPPh_2$
vaa		$Ph_2AsCHCHAsPPh_2$
dpae		$Ph_2PCH_2CH_2AsPPh_2$

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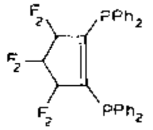
vpa	$Ph_2PCHCHAsPh_2$
pp	$o\text{-}C_6H_4(PPh_2)_2$
aa	$o\text{-}C_6H_4(AsPh_2)_2$
das	$o\text{-}C_6H_4(AsMe_2)_2$
ap	$o\text{-}C_6H_4(AsPh_2)(PPh_2)$
dmpe	$Me_2PCH_2CH_2PMe_2$
edas	$Me_2AsCH_2CH_2AsMe_2$
	f_6fos

A. INTRODUCTION

The chelate effect is one of the oldest concepts in coordination chemistry and has been successfully explained largely in terms of the entropy change involved in the chelation process. The stability of *cis* chelate complexes varies with the chelate ring size and reaches a maximum for five membered rings such as those formed by bidentate ligands with bimethylene or *o*-phenylene bridges between the two donor atoms; thus the vast majority of chelate complexes have been synthesized from bidentate ligands possessing relatively short backbones. Recently, however, there has been renewed interest in the synthesis of bidentate ligands with longer backbones in order to examine the precise role that the length and nature of the backbone plays in determining the stereochemistry of their complexes with transition metal ions. This investigation has been pioneered by Venanzi and co-workers and Shaw and co-workers, who have isolated novel chelate complexes employing ditertiary phosphine ligands.

In this article we wish to do two things: (a) review the formation of square planar complexes with bidentate ligands containing tertiary phosphine or arsine donors and examine the modes of binding of these ligands in their complexes with rhodium(I), iridium(I), palladium(II), platinum(II), gold(III) and, in certain cases, nickel(II), and (b) to attempt to draw conclusions about the nature of these chelates and factors involved in producing them.

Figure 1 illustrates the major ways in which a bidentate ligand can bind to a metal in a square planar configuration: (a) as a monodentate, (b) as a bridging bidentate forming a binuclear complex but without chelate ring formation, (c) as a *cis* bonded bidentate forming a binuclear complex and a large macrocyclic ring system, (d) as a *cis* bonded monomeric chelate, (e) as a *trans* bonded monomeric chelate and (f) as a *trans* bonded bidentate

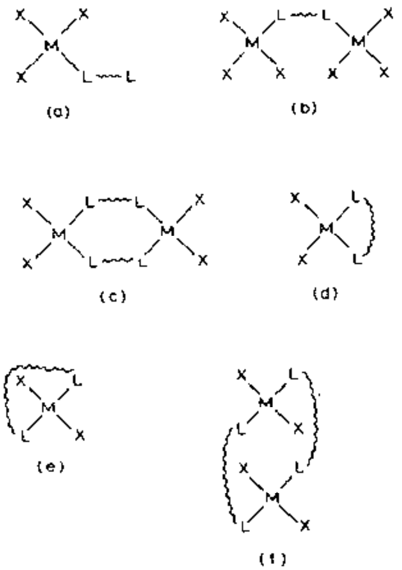


Fig. 1. Bidentate ligand bonding modes in a square planar complex.

forming a binuclear complex and a large macrocyclic ring system. All of these possible modes of binding have been observed, but the factors that determine the stereochemistry of a particular complex or group of complexes are still not clearly defined nor well understood. In general terms, those factors that appear to be important include: the nature of the central metal atom, the nature of the ligand donor atoms, the chelate chain length, the rigidity of the chelate backbone, the steric effects of the atoms or groups attached to the donor atoms and the nature of the coordinated anions. Solvent polarity and reaction temperature may also play crucial roles in determining the geometry of the resulting complexes. All of these factors will be examined in the light of experimental results and it may be possible to delineate those that dictate the geometry of the different classes of square planar transition metal complexes.

Reviews of both ditertiary phosphine [1] and ditertiary arsine [2] ligands have shown that previously it was extremely difficult to predict a priori the behavior of bidentate chelates due to the small amount of information available. This situation has changed somewhat in recent years [3] and it is now possible to make some firm predictions as to the mode of binding of bidentate phosphine and arsine chelates in d^8 metal systems. This review concentrates on recent developments in this area which allows these predictions to be made.

B. NICKEL(II) COMPLEXES

The first *trans* bonded bidentate chelate complex was isolated by Issleib [4] in 1961 as part of some work on the behavior of ligands of the type $(Cy)_2P(CH_2)_nP(Cy)_2$ (n = 3–5). The complex $[NiBr_2\{(Cy)_2P(CH_2)_5P(Cy)_2\}]$ was thought to possess a *trans* geometry due to its unusually low dipole moment, measured as 2.37 D, which is markedly lower than the corresponding *cis* isomers isolated in the study, whose dipole moments were of the order of 10 D. This observation was interesting as all other chelating bidentate ligands prior to this discovery were thought to bind in a *cis* orientation in square planar complexes. Later discussion of this complex [5] indicated that the structure may not be rigorously square planar, as molecular models and consideration of bond lengths and bond angles suggested that the P–Ni–P bond angle would be appreciably distorted from the expected 180° planarity.

Contrary to an earlier report [6] chelate complexes of nickel(II) with dpm can be obtained and are stable [7,8]. The complexes $[Ni(dpm)X_2]$ (X = Cl, Br and I) are formed by reaction of anhydrous NiX_2 with a deficit of dpm in a variety of solvents. The products are diamagnetic, with electronic spectra consistent with planar nickel(II). The iodo complex is converted into $[Ni_2(dpm)_2I_4]$ on recrystallization from dichloromethane and is a slightly soluble diamagnetic iodo-bridged dimer. The reaction of $Ni(NCS)_2$ with dpm yields the *trans* $[Ni(dpm)_2(NCS)_2]$ containing monodentate dpm which can be converted into $[Ni_2(dpm)_2(NCS)_4]$ by allowing its concentrated solution to stand. Nickel(II) cyanide forms yellow $[Ni(dpm)_2CN]CN$ which is planar and contains both chelating and monodentate dpm. The $[Ni(dpe)X_2]$ (X = Cl, Br) complexes appear to be square planar and diamagnetic and the report [9] of a paramagnetic $[Ni(dpe)I_2]$ seems to be in error since other workers [6,10] have obtained only the diamagnetic complex. Planar $[Ni(L \sim L)Cl_2]$ ($L \sim L = Me_2P(CH_2)_2PPh_2$ [11] and $(Me_3CCH_2)_2P(CH_2)_2P(CH_2CMe_3)_2$ [12]) have been briefly reported. The ligand 1,2-bis(diethylphosphino)ethane (dee) forms planar $[Ni(dee)X_2]$ (X = Cl, Br, I, NCS, CN) and $[Ni(dee)_2](BPh_4)_2$ complexes [13]. The trimethylene bridged ligand $Me_2P(CH_2)_3PMe_2$ contains powerful donor groups and forms only 1:1 planar $[Ni(L \sim L)X_2]$ (X = Cl, Br, I, NCS, CN) complexes [14] in contrast to the corresponding complexes of dpp, which exhibit planar $\rightleftharpoons$ tetrahedral equilibria [6].

Planar, diamagnetic $[Ni(L \sim L)X_2]$ (X = Cl, Br, I, NCS) species have been prepared with a range of other ligands: ape [15], *cis*-vpa [16], pp [17], o-$C_6H_4(PPh_2)AsPh_2$ [18], 9, 10 bis(diphenylphosphino)phenanthrene [16], 1,2-bis(diphenylphosphino)tetrafluorobenzene [19], o-carborane$(PPh_2)_2$ [20], o-carborane$(PMe_2)_2$ and ferrocene-1,1′-$(PMe_2)_2$ [21]. Comparison of the electronic spectra of the appropriate complexes allows the assignment of a spectrochemical series of these bidentate ligands; in all cases, the series are as expected (i.e. donor order PP > AsP > AsAs [17]; backbone *cis*-CHCH > CH_2CH_2 > *o*-C_6H_4 [15] and CH_2CH_2 > $CH_2CH_2CH_2$ [14] and substituents Me, Et > Ph [13]).

The phenyl-substituted diarsines vaa, dae and aa have less tendency to coordinate to nickel(II) than do their phosphorus analogs and only [Ni(L ~ L)X_2] (X = Cl, Br) can be isolated in the solid state [17]. Bis(diphenylarsino)methane forms Ni(dam)I_2 in the absence of hydroxylic solvents: this complex is monomeric, a non-electrolyte, with a magnetic moment of 1.6 B.M. and is of unknown structure. Bennetin et al. [22] have succeeded in isolating 1 : 1 planar complexes of 1,8-bis(dimethylarsino)naphthalene by using an excess of NiX_2 (X = Cl, Br, I, NCS). The 2 : 1 complexes have also been reported [23].

A comparison of nickel(II) complexes of PhMeAs$(CH_2)_n$AsMePh (n = 2,3) demonstrates the marked difference between di- and tri-methylene bridged ligands. When $n = 2$, planar [Ni(L ~ L)X_2] (X = Cl, Br, I and NCS) species are formed, while for $n = 3$, green paramagnetic $[Ni(L \sim L)X_2]_n$ (X = Cl, Br; $\mu = 3.2$ B.M.) complexes are formed which are pseudooctahedral in the solid state. A brown, pseudotetrahedral [Ni(L ~ L)I_2] (μ_{eff} = 2.98 B.M.) complex can also be isolated when $n = 3$. All of these complexes decompose rapidly in solution. The [Ni(L ~ L) $NCS)_2$] ($n = 3$) complex is planar and also decomposes rapidly in solution into [$Ni_2(L \sim L)_3(NCS)_4$] and $Ni(NCS)_2$ [24].

Little is known about nickel(II) nitrate complexes although $Me_2P(CH_2)_2PMe_2$ and dpe do form planar $[Ni(L \sim L)_2](NO_3)_2$ complexes [25]. Interestingly, the very bulky $Cy_2P(CH_2)_2PCy_2$ ligand forms a red-brown diamagnetic complex Ni(L ~ L) $(H_2O)(NO_3)_2$ which is a nonelectrolyte in methylene chloride but is a 1 : 1 electrolyte in nitromethane: the IR spectrum as a mull shows only evidence for coordinated nitrate ions [25]. Nickel(II) perchlorate compounds of the type $[Ni(L \sim L)_2](ClO_4)_2$ are formed with diphosphines, arsine-phosphines and alkyl substituted diarsines [13–17,19, 26,27]. The ligand *cis*-$Me_2As(CH{=}CH)AsPh_2$ appears to be a borderline case as the complex formed with it is planar in the solid state but is a 1 : 1 electrolyte in 1,2-dichloroethane and a 1 : 2 electrolyte in nitromethane [28]; the *cis*-edas complexes [Ni(*cis*-edas)$_2$]Y_2 (Y = BF_4 or PF_6) are planar [29]. The rigid ligand bis(diphenylphosphinomethyl)benzo[c]phenanthrene (see Fig. 2) forms *trans* planar complexes of the type [Ni(L ~ L)X_2](X = Cl, Br, I and NCS) [30,31]. The *trans* vinyl ligand, *trans*-edas, is incapable of chelation and forms tetrahedral [Ni(*trans*-edas)$_2X_2$] (X = Br or NCS) and [Ni(*trans*-edas)Cl_2] · 2 EtOH complexes [29] which readily oxidize in solution to give the arsine oxide ligand. These complexes are paramagnetic, possibly pseudooctahedral polymers.

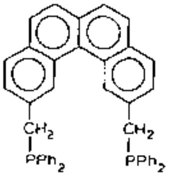


Fig. 2. The structure of Venanzi's ligand, 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene.

Nickel(II) complexes with longer chelate backbones have received less attention in the literature. Complexes of the type $[Ni(L \sim L)X_2]$ where $L = Ph_2P(CH_2)_nPPh_2$ ($n = 4, 5$; X = Cl, Br) are high spin, with a distorted tetrahedral geometry in contrast to their shorter chain analogs (vide supra) which are low spin, square planar complexes [33,34]. The introduction of an oxygen atom in place of the central methylene group in the $n = 5$ ligand gives the ligand $Ph_2P(CH_2)_2O(CH_2)_2PPh_2$(POP) whose nickel(II) complex $[Ni(L \sim L)Cl_2]$ is also high spin and possesses a distorted tetrahedral geometry [35]. Reaction of 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$(POOP) with NiI_2 gives a monomeric, diamagnetic complex whose X-ray structure shows a very distorted *trans* square planar configuration [36,37]; $[Ni(POOP)X_2]$ complexes (X = Cl, Br, NCS) have also been isolated [38]. The chloro and bromo derivatives possess pseudotetrahedral geometry in the solid state and all are square planar in methylene chloride solution. An X-ray structure of the thiocyanate complex shows a monomeric planar species with the presence of a *trans* coordinated bidentate diphosphine ligand (Fig. 3). The pseudooctahedral $Ni(POOP)Cl_2 \cdot$

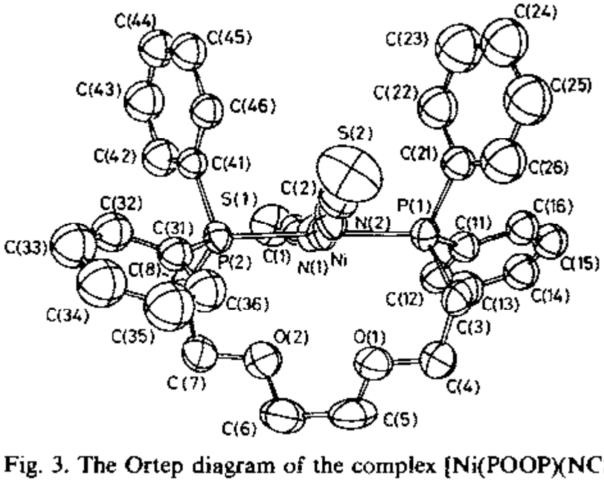


Fig. 3. The Ortep diagram of the complex $[Ni(POOP)(NCS)_2]$.

H_2O and the planar Ni(POOP)$(BF_4)_2(H_2O)_2$ complexes have also been isolated. The subtle effects governing the coordination properties of the POOP ligand are illustrated by the isolation of the blue, planar Ni(POOP)$Br_2 \cdot$ toluene complex [38]. The corresponding long chain diphosphine, 1,8-bis(diphenylphosphino)octane, dpo, forms pseudotetrahedral [Ni(dpo)X_2] (X = Cl, Br and I) complexes; molecular weight data indicate that [Ni(dpo)I_2] is dimeric in chloroform and thus contains bridging bidentate diphosphine ligands. The thiocyanato complex is diamagnetic and square planar [39].

Tetramethyldiphosphine forms [Ni(Me_4P_2)(NCS)$_2$], [Ni(Me_4P_2)$_2X_2$] and [$Ni_2(Me_4P_2)_3X_4$] (X = Cl, Br, I) complexes [40], whereas tetraethyldiphosphine yields [Ni(Et_4P_2)X_2] (X = Cl, Br, I) and [Ni(Et_4P_2)$_2Br_2$] complexes [41]. Assignment of structures to those complexes is difficult, but the R_4P_2 ligands are more likely to be present as monodentate or bridging bidentate ligands than as chelates.

Ligand scrambling occurs on reaction of $(Cp)_2Ni$ with [Ni(dpe)X_2] in organic solvents to yield [CpNi(dpe)][NiX_4] (X = Cl, Br), [{CpNiX}$_2$dpe] (X = CN, I) and [CpNi(dpe)]Y (Y = I, PF_6) [42]. The [CpNi(dpm)CN] complex can function as a bidentate ligand: for example, it forms [CpNi(μ-CN)(μ-dpm)Mo(CO)$_4$] [43].

C. PALLADIUM(II), PLATINUM(II) AND RELATED SPECIES

Palladium(I) and platinum(I) are very rare oxidation states and until recently very few compounds had been characterized. The compound [Pd(dpe)Br]$_2$ was first reported [44] in 1971 and X-ray studies show that the compound contains a direct Pd–Pd bond [45,46]. The complexes [Pd(dam)X]$_2$ (X = Cl, Br) obtained from Pd(CO)X and dam in methylene chloride must also contain a Pd–Pd bond [47]. Carbon monoxide can insert into the metal–metal bond to produce complexes of the type [Pd_2Cl_2(CO)(dam)$_2$] [46,48,49]. Balch and co-workers [50–52] have also shown that carbon monoxide, isocyanides and sulphur dioxide insert reversibly into the Pd–Pd bonds of the complexes [Pd_2X_2(dpm)$_2$] (X = Cl, Br) and X-ray structural determinations show the absence of direct Pd–Pd bonds in these products. Insertion of aryldiazonium ions in [Pd_2Cl_2(dpm)$_2$] has been reported [53]. The complex [Pd_2(dpm)$_2$XY] (X = Cl; Y = $SnCl_3$) has also been prepared [54]. In all the above cases, the bidentate ligands are bridging. Addition of the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$–4) or *cis*-$Ph_2PCH{=}CHPPh_2$ to [$Pd_2(CNCH_3)_6$][PF_6]$_2$ yields complexes of the general formula [Pd_2(diphosphine)$_2$ $(CNCH_3)_2$] [PF_6]$_2$ [55]. Spectroscopic data indicate that the diphosphines each chelate a single palladium atom, and the complexes do not possess a bridged structure.

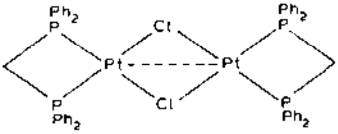


Fig. 4. Proposed structure for $Pt_2Cl_2(dpm)_2$.

The platinum(I) complex $[Pt_2(dpm)_2Cl_2]$ is formed by refluxing $Hg(SiMe_3)_2$ and $[Pt_2(dpm)_2Cl_4]$ in benzene [56,57]; the ^1H NMR, IR and mass spectral data together with the magnetic moment measurements are all consistent with the structure shown in Fig. 4. In contrast Brown et al. have synthesized a number of binuclear compounds in which the ligand adopts a bridging role [58–64] and these compounds undergo insertion reactions similar to those observed for the palladium(I) analogs [65]. The related ligand dam gives an analogous carbonyl complex namely $[Pt_2Cl_2CO(dam)_2]$ although the complex $[Pt_2Cl_2(dam)_2]$ is unknown [62]. Some palladium(0) and platinum(0) complexes of dpe have been prepared by electrochemical reduction of the metal(II) complexes [66]; here the ligand is chelated.

Numerous complexes of the type *cis*-$[M(L \sim L)X_2]$ have been prepared with dpm [67–72], dpe [67,68,72–74], dpp [67,68,70,72], dae [71,73–75], das [76], $Me_2P(CH_2)_2PPh_2$ [11], $Et_2P(CH_2)_2PEt_2$ [13], $Me_2P(CH_2)_2PMe_2$ [77], pp [78] and aa [79], to name but a few examples. The diprimary phosphine $H_2P(CH_2)_3PH_2$ reacts with Na_2PdCl_4 to form a phosphido complex $[Pd_2\{HP(CH_2)_3PPH\}\{H_2P(CH_2)_3PH_2\}_2]$ for which the structure shown in Fig. 5 has been proposed [80].

Direct reaction of MX_4^{2-} with $L \sim L$ often leads to the formation of insoluble Magnus-type salts $[M(L \sim L)_2]MX_4$. The stability of the latter with respect to rearrangement into $[M(L \sim L)X_2]$ appears to depend markedly upon the nature of the ligand. The $[M(L \sim L)X_2]$ (X = Cl, Br, I, NCS) complexes are planar, diamagnetic and generally soluble in organic solvents in which they are monomeric non-electrolytes. It is possible to avoid Magnus salt formation by employing MX_2 instead of MX_4^{2-} although the poor solubility of MX_2 in suitable solvents makes the reaction slow. Displacement of a neutral ligand from a preformed complex, often $[M(PhCN)_2X_2]$, can also be used as a method to obtain *cis*-$[M(L \sim L)X_2]$ complexes.

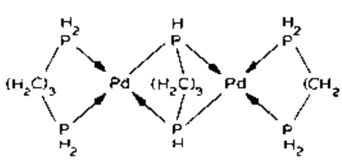


Fig. 5. Proposed structure for the palladium(II) phosphido complex (ref. 80).

All of the above ligands are chelates that possess a short backbone between the two donor atoms and the length of the chelate backbone precludes the formation of the *trans* isomer on steric grounds: the distance between the two donor atoms is insufficient to span the *trans* positions.

Venanzi and co-workers [81] synthesized the ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene which forms *trans* bonded planar $[M(L \sim L)X_2]$ (M = Pd, Pt; X = Cl, Br, I) complexes. This ligand, because of the distance between the phosphorus atoms and the rigidity of the structure is ideal for *trans* bonding in d^8 metal complexes. A crystal structure of $[Pd(L \sim L)Cl_2]$ [81] shows that the metal atom is four coordinate with a slightly distorted square planar configuration. The complex structure is characterized by a strong out-of-plane deformation of the benzophenanthrene system as a consequence of severe overcrowding.

Trans chelation has also been achieved with flexible ligands of the correct backbone length under appropriate conditions [5,82,83]. Shaw and co-workers [83] prepared ligands of the type $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$ ($n = 8$–10, 12) which were used to synthesize *trans* bonded complexes of the type $[M(L \sim L)Cl_2]_n$ (M = Pd, Pt and $n = 1$–3) by reacting *trans*-bis(benzonitrile)dichloroplatinum(II) or *trans*-bis(benzonitrile)dichloropalladium(II) with the ligand in a suitable solvent [83]. Analogous ligands with shorter chain lengths ($n = 5$–8) give complexes of the type $[Pd(L \sim L)Cl_2]_x$ (where $x = 2$ for $n = 5$, 7, 8 [32] but x is unknown for $n = 6$); these complexes are all *trans* bonded [84]. A cyclometallated complex $[PdCl\{(t\text{-Bu})_2PCH_2CH_2CHCH_2CH_2P(t\text{-}Bu)_2\}]$ is also obtained when $n = 5$. Treatment of $[Pt(PhCN)_2Cl_2]$ or $[Pt(t\text{-}BuCN)_2Cl_2]$ with $(t\text{-Bu})_2P(CH_2)P(CH_2)_5P(t\text{-Bu})_2$ gives the *trans* bonded complex $[Pt(L \sim L)Cl_2]_n$ where n is unknown, and again a cyclometallated complex $[PtCl\{(t\text{-Bu})_2PCH_2CH_2CHCH_2P(t\text{-Bu})_2\}]$ can be isolated. The compound $(t\text{-Bu})_2P(CH_2)_6P(t\text{-Bu})_2$ with $[Pt(PhCN)_2Cl_2]$ gives the analogous *trans* bonded $[Pt(L \sim L)Cl_2]_n$ where n is again unknown and the cyclometallated complex $[PtCl\{(t\text{-Bu})_2PCH_2CH_2CHCH_2CH_2P(t\text{-Bu})_2\}]$. The complexes *trans*-$[Pd_2(Ph_2P(CH_2)_5PPh_2)_2Cl_4]$ and *cis*-$[Pt_2(Ph_2P(CH_2)_5PPh_2)_2Cl_4]$ were also isolated [84].

Hill et al. [85] prepared ligands of the general type $Ph_2P(CH_2)_nPPh_2$ ($n = 6$, 8, 10, 12) and successfully isolated the palladium(II) complexes of general formula $[Pd(L \sim L)X_2]$ (X = Cl, Br, I and SCN). The complexes all possess a *trans* geometry and molecular weight measurements showed that when $n = 6$, the complexes were polymeric, when $n = 8$ or 10 the complexes were dimeric and when $n = 12$ the complexes were monomeric. Synthesis and characterization of the diarsine ligands $Ph_2As(CH_2)_nAsPh_2$ ($n = 6$–12, 16) and their complexes with palladium(II), $[Pd(L \sim L)X_2]$ (X = Cl, Br, I, CNS; $n = 6$, 8, 10, 12, 16) and $[Pd(L \sim L)Cl_2]$ ($n = 7$, 9, 11) indicates that the *trans* isomer is the only product when $n > 9$ and is the predominant one for $n < 9$.

Fig. 6. The conversion of the tetradentate diarsinedithioether ligand to the *trans*-bonding diarsine ligand (ref. 87).

The molecular weights of the complexes are a function of chelate chain length: polymeric species being favored for short ligands, while for the longer chain analogs ($n = 12$, 16), monomeric units are preferred [86].

The potentially tetradentate ligand 1,3-bis(3-dimethylarsinopropylthio)propane, $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$, forms palladium(II) and platinum(II) complexes which when dissolved in halocarbon solvents adopt *trans* geometry with an As_2X_2 donor set (see Fig. 6) [87,88]. The complications that potentially arise due to the presence of donor atoms in the ligand backbone can be overcome by synthesizing an arsenic donor ligand such as bis(dimethylarsino)dodecane, $Me_2As(CH_2)_{12}AsMe_2$. Reaction of this ligand with the tetrachloropalladate ion yields the *trans* bonded monomeric complex [89].

The platinum(II) dichloro complexes of a series of bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ ($n = 6–12$, 16) have been synthesized; *cis*-complexes are formed when the complex precursor is potassium tetrachloroplatinate(II) or bis(benzonitrile)dichloroplatinum(II), while the *trans* isomers are preferred when the starting material is Zeise's salt [90]. The *trans* isomers revert to their *cis* analogs in the presence of heat or excess diphosphine. The *cis* dimers are the most stable isomers for the majority of the *cis* complexes and the preferred ring size for *cis* chelated monomeric complexes is 12 and 19 membered chelate rings. Ring contributions Δ_R (Δ_R is the difference between coordination chemical shift of *trans*-[Pt(n-BuPPh$_2$)$_2$Cl$_2$] and the coordination chemical shifts of the corresponding diphosphine complex) for the *trans* monomers decrease with increasing ring size and reach zero at a chelate ring size of fifteen members. Thus, ring contributions in *trans* monomeric complexes can be used as a measure of ring strain. Large flexible rings (19 membered or above) appear to be unstable as monomeric structures in the *trans* configuration.

The corresponding diarsine ligands of general formula $Ph_2As(CH_2)_nAsPh_2$ ($n = 6–12$, 16) form analogous *cis* and *trans* dichloroplatinum(II) complexes [91] by employing the same complex precursors as in the case of the bis(diphenylphosphino)alkanes described above. The bromo, iodo and thiocyanato derivatives formed by an exchange reaction [92] give *cis* bonded complexes with the $Ph_2As(CH_2)_nAsPh_2$ ($n = 10$, 12) ligands.

Bis ligand complexes $[M(L \sim L)_2Cl_2]$ or $[M(L \sim L)Cl_2]$ and $L \sim L$ react with sodium perchlorate or dilute $HClO_4$ in a suitable solvent to give $[M(L \sim L)_2](ClO_4)_2$. The perchlorate ion in these complexes can also be exchanged for BF_4^-, PF_6^-, and BPh_4^-. Examples of these types of complexes are formed with pp, ap, aa [78,93] and ferrocene-1,1′-$(AsMe_2)_2$, and in all cases the ligands behave as bidentate chelates. The $[M(L \sim L)_2X_2]$ complexes ($X = Cl$, Br, I; $L \sim L =$ pp, ap and aa) decompose on heating in the solid state to give $[M(L \sim L)X_2]$ and $L \sim L$ [78,79]. The ^{31}P NMR of $[M\{(Ph_2PCH_2C(CF_3)CHPPh_2\}X_2]$ ($M = Pd$, Pt; $X = Cl$, CNS) has been reported [95] and shows evidence for NCS and SCN linkages.

D. GOLD(III) AND RELATED COMPLEXES

Gold(III) usually reacts with tertiary phosphines to give gold(I) complexes and oxidized ligand; with bidentate ligands there is no evidence of 1:1 complexes with the half oxidized ligands, i.e. reaction (1) occurs in preference to reaction (2)

$$2L \sim L + 2[AuX_4]^- \rightarrow XAu(L \sim L)AuX + X_2L \sim LX_2 \qquad (1)$$

$$2L \sim L + 2[AuX_4]^- \rightarrow 2[AuX(L \sim LX_2)] \qquad (2)$$

Bidentate ligands coordinate to two separate gold atoms in most cases [96–101], but with some ligands 1:1 complexes are obtained even in the presence of excess gold. In view of the geometry of the ligands involved, these complexes are almost certainly chelated since all have rigid *cis*-vinylic or *o*-phenylene backbones which would be condusive to chelation [102]. The reaction of $Ph_2As(CH_2)_nAsPh_2$ ($n = 2,4$) with $HAuCl_4$(+NaX or LiX) yields $[Au(L \sim L)X]$ ($X = Cl$, I; $n = 4$), $[Au(L \sim L)_2]Br$ with both ligands and $[(AuX)_2(dae)_3]$ [103]. McAuliffe et al. [102] have prepared a series of $[(AuCl)_2(L \sim L)]$ ($L \sim L =$ dpe, vpa, dpm and dam) complexes which, on the basis of the IR spectra are monomeric two-coordinate gold species. *Trans*-vpp gives an insoluble $[Au(L \sim L)Cl]_n$ complex which may be polymeric with bridging $L \sim L$ and ionic chloride ions [102]. In $[Au_2(dpe)X_2]$ complexes ($X = SCN$, NCO and SeCN) the anions are bonded through S, N and Se, respectively. Oxidation with bromine converts these to Au(III) species: $[Au_2(dpe)Br_4X_2]$ ($X = SCN$, NCS), but $[Au_2(dpe)(SeCN)_2]$ yields only $[Au_2(dpe)Br_6]$ [104]. Venanzi and co-workers have reported the synthesis [31] and X-ray crystal structure [105] of $[Au(L \sim L)Cl]$ where $L \sim L$ is 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene (see Fig. 7) as well as the synthesis of the complexes $[Au(L \sim L)]X$ ($X = I$, NO_3, BF_4). The metal center is 3-coordinate and monomeric when $X = Cl$ with a chelated

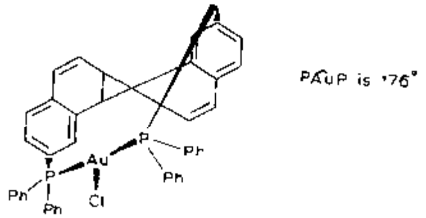


Fig. 7. Structure of chloro[2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene]gold(I).

ligand. The nitrate and perchlorate complexes are 1 : 1 electrolytes in nitromethane indicating a two coordinate $[Au(L \sim L)]^+$ structure in solution.

E. RHODIUM(I) AND IRIDIUM(I) COMPLEXES

The diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 3, 4$) form *trans*-carbonyl complexes of rhodium(I) in which the diphosphines bridge two metal atoms to form dimeric species [106, 107], while the corresponding complex with dpe is mononuclear and *cis* chelated [1,108,109]. Other complexes include $[Rh(CO)Cl(dpm)]_2$ [108,109], $[Rh(dpe)_2Cl]$ [108–110], $[Rh(CO)Cl($*cis*-vpp$)]_n$ [109], $[Rh($*cis*-vpp$)_2][Rh(CO)_2Cl_2]$ [109] and $[Rh(CO)(dmpe)_2Cl]$ [111]. The X-ray crystal structure determination of $[Rh(CO)Cl(dpm)_2]$ shows it to be isomorphous with its diphosphine analog [112], and reaction of dpae with $[Rh_2(COD)_2Cl_2]$ and carbon monoxide gives the *trans* bonded dimeric complex [107]. A similar bridged dimer is formed by the ligand $(t\text{-}Bu)_2P(CH_2)_{10}P(t\text{-}Bu)_2$ [82] and Shaw and co-workers have also reported the synthesis and structures of *trans*-$[RhCl(CO)\{(t\text{-}Bu)_2P(CH_2)_4CH{=}CH(CH_2)_4P(t\text{-}Bu)_2\}]$ and $[RhCl(t\text{-}Bu)_2P(CH_2)CH{=}CH(CH_2)_2P(t\text{-}Bu)_2]$ [113]. The complex of empirical formula $[Rh(f_6fos)(CO)Cl]$ has a $[Rh(f_6fos)_2][Rh(CO)_2Cl_2]$ structure with a *cis* planar anion and a planar cation [114].

The importance of reaction conditions in determining product distribution is illustrated by the reaction of $[Rh_2(COD)_2Cl_2]$ with diphosphines in the presence or absence of carbon monoxide [107]. In the presence of carbon monoxide only complexes containing one carbonyl per rhodium atom and no coordinated COD are obtained. In the absence of carbon monoxide the chlorine bridged precursor was cleaved, but the product retained coordinated COD. Reaction of *cis*-vpp with $[Rh_2(COD)_2Cl_2]$ and carbon monoxide yields the solvated $[Rh($*cis*-vpp$)_2]$ $[Rh(CO)_2Cl_2]$ [108]. An excess of diphosphine gives complexes of the type $[Rh(L \sim L)_2]Cl$ or $[Rh(CO)(L \sim L)_2Cl]$ [107].

Reaction of $[Ir(COD)_2Cl_2]$ with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n =$

1–4) results in the formation of novel *trans* bonded complexes of stoichiometry $[Ir(CO)ClL]_n$ in which the diphosphines ($n = 1, 3, 4$) bridge the metal atom. Contrary to a previous postulate, the corresponding complex with dpe has the structure $[Ir(CO)(L \sim L)_2][Ir(CO)_2Cl_2]$ [72].

The iridium(I) complexes $[Ir(CO)(L \sim L)_2]Y$ ($Y = Cl, BPh_4$, etc.) are best obtained by treatment of $[Ir(CO)(PPh_3)Cl]$ in benzene with $L \sim L$ and have been isolated for dpm, dpe [115], dpp [115,116], vpp [80,117] and vpa [116]. Aryldiarsines do not displace triphenylphosphine from Vaska's compound but *trans*-$[Ir(CO)(AsPh_3)_2Cl]$ reacts with vaa or dae to form $[Ir(L \sim L)_2CO]Y$. In high boiling hydrocarbons, the CO is lost to form planar complexes $[Ir(L \sim L)_2]Y$ [80,115–118]. The $[M(dpe)_2]ClO_4$ ($M = Rh, Ir$) can be electrochemically reduced in acetonitrile in the presence of carbon monoxide to give anionic carbonyl complexes [119]. The dicarbonyl iridium complex $[Ir(CO)_2(dae)Cl]$ is rapidly converted to $[Ir(CO)_2(dae)]BPh_4$ [120,121]. The long chain $(t\text{-}Bu)_2P(CH_2)_{10}P(t\text{-}Bu)_2$ reacts with "carbonylated" chloroiridic acid to form $[Ir(L \sim L)(CO)Cl]$ [5] which, unlike the dimeric rhodium(I) analog, is a monomer with the diphosphine again functioning as a *trans* chelate [82,122]. Diacetylene diphosphines of the type $(t\text{-}Bu)_2P{-}C{\equiv}C{-}(CH_2)_n{-}C{\equiv}C{-}P(t\text{-}Bu)_2$ ($n = 4, 5$) give, with sodium chloroiridate and carbon monoxide in boiling ethanol, large ring mono or binuclear *trans* bonded species: the X-ray structure of *trans*-$[Ir(CO)Cl(t\text{-}Bu)_2PC{\equiv}C(CH_2)_5C{\equiv}CP(t\text{-}Bu)_2]$ has been reported [123]. These diphosphines, which contain rigid acetylene linkages in the ligand backbone, illustrate the importance of the effect of the conformation of the ligand backbone on the stereochemistry of the resulting complexes.

Alcock et al. have investigated the effect of the presence of oxygen donor atoms in the chelate backbone [124–126] using the ligands 1,5-bis(diphenylphosphino)-3-oxapentane (POP), 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (POOP) and 1,11-bis(diphenylphosphino)-3,6,9-trioxaundecane (POOOP). The Rh(I) complexes of these ligands show interesting geometrical features. As shown by X-ray crystallography, the oxygen atom in the POP ligand coordinates upon complexation, as does one of the two oxygen atoms in the POOP ligand. The case of the potentially pentadentate POOOP ligand is quite remarkable: a molecule of water is bound both to the central rhodium atom and via hydrogen bonds, to the outermost two oxygen atoms of the ligand. A complex of POOP was isolated with a molecule of ethanol coordinated to the central rhodium atom. A *trans* dimeric structure with POP was also reported, indicating that the eight membered ring formed in monomeric *trans* coordination is strained and that the preferred conformation is the dimeric *trans* coordinated 16 membered macrocycle.

The $[M(L \sim L)_2]X$ complexes can be obtained by heating the carbonyl precursors $[M(L \sim L)_2CO]X$ in vacuo or in a high boiling hydrocarbon solvent (M = Rh, Ir; L ~ L = vpp, dpe, vpa) [127,128]. Other methods include dehydrohalogenation of [Ir(L ~ L)$_2$HCl]Cl with alkali (L ~ L = vpp) [128] and treatment of [Rh(COD)Cl]$_2$ with L ~ L in acetonitrile (L ~ L = vaa, das, $Me_2P(CH_2)_2PMe_2$) [129]. The corresponding complexes of general formula [Ir(L ~ L)$_2$]Y (Y = Br, I, PF_6, ClO_4 and BPh_4) are easily obtained by metathesis [128,130]. The cyano derivatives are most easily prepared by anion exchange of the chloro complexes via a cyanide anion exchange resin [131,132] and are five-coordinate in non-polar solvents; [Rh$_2$(dppe)$_3$(CN)$_2$] is formed on stirring [Rh(dpe)$_2$CN] in benzene and is believed to be the diphosphine bridged dimer [131].

The electronic spectra of [M(L ~ L)$_2$]$^+$ ions have all been examined in the solid state and in solution (M = Rh, Ir; L L = dpm, dpe, vpp, dpp) and all except the [Rh(dpe)$_2$]$^+$ ion exhibit photoluminescence [133,134].

F. DISCUSSION

(i) Nickel(II)

The square planar ⇌ tetrahedral equilibria that exists for four coordinate nickel(II) complexes with a P_2X_2 donor set has been well established [135] and studies with monodentate phosphines have shown that the influence of the substituents attached to the phosphorus donor atoms is almost entirely electronic rather than steric in origin [136]. This is demonstrated by the complexes [NiL$_2$X$_2$] (L = PPh_2Bu, PCy_3) where the phosphines ligands are of approximately the same size: in dichloromethane solution when L = PPh_2Bu the complexes are tetrahedral, while when L = PCy_3 the corresponding complexes are square planar. For the compound [Ni{($C_6H_5CH_2$)Ph_2P}$_2$ Br$_2$] both tetrahedral and square planar species can be isolated together in the same crystal in the solid state [135].

For species of the type [Ni{$R_2P(CH_2)_nPR_2$}X$_2$] (R = alkyl or aryl, $n = 1$ or 2) the structures are invariably square planar and contain chelated or monodentate diphosphines. In these cases, the short chelate chain length appears to preclude the formation of tetrahedral species, even with those ligands that are weak donors. When the chain length is increased to three methylene units, the ligand $Me_2P(CH_2)_3PMe_2$ forms square planar complexes as expected, but the corresponding ligand $Ph_2P(CH_2)_3PPh_2$ which does not possess powerful σ-donor groups forms complexes which exhibit square planar tetrahedral equilibria [6,14]. This behavior is mirrored by the diarsine ligands of similar structure, such as $PhMeAs(CH_2)_nAsMePh$ ($n = 2$, 3), but which are less stable in solution than their diphosphine analogs [24].

Those diphosphine or diarsine ligands with short, rigid backbones, with the donor atoms orientated in a *cis* configuration (such as *cis*-vpa) form planar complexes, with the diarsine complexes again showing less tendency to coordinate to nickel(II) than the corresponding diphosphines. The rigid ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene, designed to possess a chelate "bite" sufficient to span the *trans* position, does indeed yield complexes of *trans* square planar structure. Interestingly, the ligand *trans*-vpp, which is incapable of chelation, forms tetrahedral $[Ni(L\sim L)X_2]$ complexes ($X = Cl$, Br or I) but planar $[Ni(L\sim L)X_2]$ complexes when $X = NCS$ or CN, containing dimeric or polymeric units [16]. Clearly, the donor power of the halide or pseudohalide is important in determining the complex geometry in cases such as this, where small chelate rings do not exist.

Nickel(II) complexes of ligands with long, flexible chelate backbones such as $[Ni(L\sim L)X_2]$ (where $L\sim L = Ph_2P(CH_2)_nPPh_2$; $n = 4, 5, 8$; $X = Cl$, Br) are tetrahedral, as is the iodo derivative for $n = 8$ [33,34]. However the thiocyanato complex for $n = 8$ is square planar; this is reminiscent of the role that the counter-ion plays in determining the geometry of the *trans*-vpp complexes (vide supra).

Long chain diphosphine ligands which possess other donor atoms in the ligand backbone show more complicated behavior. The complex $[Ni(POP)Cl_2]$ is tetrahedral as expected [35], but although the complexes $[Ni(POOP)X_2]$ ($X = Cl$ or Br) are tetrahedral in the solid state, they are square planar in solution. $[Ni(POOP)X_2]$ ($X = I$ or NCS) are square planar both in the solid state and in solution, and pseudo-octahedral solvated and hydrated species have also been reported (e.g. $Ni(POOP)(BF_4)_2(H_2O)_2$ and $Ni(POOP)Br_2$ toluene) [36–38]. This area clearly requires further careful investigation before any firm conclusions can be drawn.

(ii) Palladium(II), platinum(II) and related compounds

For palladium(II) complexes with dpm and dam [44,45], the ligand backbone is so short that the bidentate ligands adopt a bridging configuration whereas those with longer backbones are capable of chelating to a single palladium atom. The situation is not so clear-cut for the corresponding platinum(II) derivatives which can possess a bridging or chelated dpm ligand.

Ligands with short chelate backbones such as dpe, dpp, dpb, das, etc., form *cis* chelated complexes with both palladium(II) and platinum(II) of general formula $[M(L\sim L)_2]MX_4$ or $[M(L\sim L)X_2]$ [67–80]. In these cases, the length of the chelate backbone prevents the formation of the *trans* chelate since it is not sufficient to span the *trans* positions in a square planar complex.

Ligands specifically designed to overcome this difficulty result in the formation of the desired *trans* chelated species. For example the ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene used by Venanzi to form *trans* bonded square planar nickel(II) complexes can be used in the same fashion to synthesize the analogous palladium(II) and platinum(II) derivatives [81]. The rigid phenanthrene backbone positions the donor phosphorus atoms ideally for *trans* chelation.

The synthesis by Shaw and co-workers [82–84], of long chain flexible diphosphine ligands containing bulky tertiary butyl substituents on the donor atoms and the subsequent reaction of these ligands with palladium(II) and platinum(II) to produce *trans* bonded mono and dinuclear complexes, indicates that the presence of a rigid chelate backbone is not the only factor that may promote *trans* chelation. The presence of bulky t-butyl groups (or any other sterically demanding substituent) on the donor atoms precludes the formation of *cis* chelated complexes on steric grounds and the length of the chelate backbone (and hence the chelate "bite"), would favor *trans* chelation if the methylene chain linking the two donor atoms is of a suitable length. Shaw and co-workers proposed that "internal entropy" effects and chain length are related factors: a short chain length would result in a strained complex configuration in the *trans* case, hence species with chain lengths of five methylene units or less would not be able to coordinate in a *trans* geometry. Arguments based on the probability of a *trans* donor atom "finding" the *trans* bonding site in a molecule indicate that for chain lengths of greater than twelve methylene units, the probability of dimer and trimer formation is high. Shaw and co-workers were also unable to synthesize the Pd(II) and Pt(II) complexes with the ligands $Ph_2P(CH_2)_{10}PPh_2$ and $Me_2As(CH_2)_{12}AsMe_2$ and proposed that the presence of bulky substituents on the ligand donor atom is a prerequisite for *trans* chelation. Indeed a detailed discussion of steric effects led Shaw and co-workers to propose [84] that *trans* chelation is mainly a function of bond lengths, bond angles, torsion angles and atomic sizes and is an inorganic equivalent of the well known Thorpe–Ingold or "gem-dimethyl effect" in organic chemistry.

However, McAuliffe and co-workers noticed [87,88] during work with the ligand 1,3-bis(3-dimethylarsinopropylthio)propane, $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$, that the Pd(II) and Pt(II) complexes of this ligand, when dissolved in halocarbon solvents, adopted a *trans* geometry with a As_2X_2 donor set (Fig. 6). The reasons cited for this unusual structural rearrangement were the inherent instability of platinum(II) and palladium(II) five-coordinate complexes in relation to square planar four coordinate geometry for 4*d* and 5*d* d^8 transition metals and the instability of the 1 : 1 electrolytes in low polarity halocarbon solvents. Moreover, the fact that the arsenic donor atoms possess sterically undemanding methyl substituents and yet form *trans* chelated species in solution, is clearly of great interest. Further investigations

[89] with the ligand 1,12-bis(dimethylarsino)dodecane, a ligand which again possesses non bulky methyl substituents but whose coordination chemistry is not complicated by the presence of other donor atoms (i.e. sulfur) in the backbone, resulted in the isolation of a *trans* bonded monomeric complex of Pd(II) with an As_2Cl_2 donor set using tetrachloropalladate(II) as the starting material. This provides further evidence that *trans* chelation is not restricted to phosphine donor ligands, or to ligands with donor atoms possessing bulky substituents.

The ligands of the general type $Ph_2P(CH_2)_nPPh_2$ ($n = 6,8,10,12$) and their palladium(II) complexes of formula $[Pd(L \sim L)X_2]$ (X = Cl, Br, I, CNS) were prepared [85]. The complexes all possess *trans* geometries and the length of the ligand backbone seems to be of paramount importance in determining the mode of binding of the ligands to palladium(II). For $n = 6$, polymeric *trans* bonded species are produced upon coordination. Backbones containing 8 and 10 methylene units produce large ring *trans* bonded dimeric palladium(II) complexes, while the 12 methylene bridged diphosphine acts as a *trans* chelating ligand. Parallel work [86] with the corresponding diarsine ligands $Ph_2As(CH_2)_nAsPh_2$ ($n = 6$–12, 16) indicates that the *trans* isomer is the only product when $n > 9$ and is the predominant one for $n < 9$. Once again, the degree of oligomerization is a function of chelate chain length, with polymeric species being favored for short chain ligands ($n = 6$) whilst for the longer chain analogs ($n = 12$) monomeric units are preferred.

Although many square planar platinum(II) complexes of the type $[PtL_2X_2]$ (X = halogen, L = tertiary phosphine) are known as both *cis* and *trans* isomers, the more labile palladium(II) complexes have usually been obtained as the *trans* form [137]. The occurrence of *cis-trans* isomerization in bis(phosphine)palladium(II) complexes is well established [138] and in some cases either form reverts rapidly to an equilibrium mixture [139,140]. However, in some cases only the *trans* form appears to exist in the solid state or in solution [141]. The preparation of the elusive *cis* derivatives has proved to be possible by photochemical means [142–144] or by the employment of unusual complex precursors [145]. The reaction of diphosphine or diarsine ligands with palladium(II) salts would therefore be expected to give the *trans* isomer, due to the lability of the groups coordinated to palladium(II) and the high *trans* effect of the first coordinated phosphorus or arsenic atom, which would labilize the position *trans* to itself in the square planar complex thus promoting *trans* coordination for the bidentate ligand. *Trans* chelation for these square planar palladium(II) complexes is therefore dependent upon the nature of the central metal atom and the high *trans* effect of the donor atoms present in the ligands and not due to the presence of bulky substituent groups on the donor atoms. The length of the chelate backbone appears to dictate whether open chain polynuclear species or large monomeric chelate rings are formed and this can be explained in terms of ring strain or entropy factors. In the case of palladium(II) the nature of the complex precursor, the electronic effects of the substituent groups attached to the donor atoms, and the nature of the coordinated anion do not appear to play any appreciable role in determining the stereochemistry of the resulting complexes. The formation of *trans* chelated complexes with palladium(II), even though *cis* complexes are thermodynamically more stable [146] indicates that the products are those of kinetic control.

Product distribution for the corresponding platinum(II) complexes cannot be explained in so straightforward a manner: in particular it should be noted that the choice of the complex precursor is usually crucial in determining the geometry of the complexes. The employment of potassium tetrachloroplatinate(II) or bis(benzonitrile)dichloroplatinum(II) as starting material in their reaction with bis(diphenyl)phosphinoalkanes yields *cis* dimeric species [90]. These results are in agreement with earlier reports [147,148] which indicated that the presence of phenyl groups on phosphorus favors the *cis* isomer over its *trans* counterpart. This cannot be a steric phenomenon, as Shaw and co-workers [83] have successfully isolated *trans* chelated diphosphine complexes with bulky t-butyl groups, and must therefore be electronic in origin. On the other hand, the use of Zeise's salt, a kinetically labile complex precursor, as starting material, results in the formation of the *trans* chelated complexes. The yields of the mononuclear *trans* chelated complexes are in agreement with the observations of Ogino and Fujita [149,150] on the yields of mononuclear cobalt(III) complexes with long chain diammines and the work of Sanger and Weiner-Fedorak [151] on the dithioether complexes of palladium(II). The reaction of diphenylarsino alkanes with platinum(II) salts [91] mirrors the reactivity of the diphenylphosphino alkanes discussed above. For platinum(II), the basicity of the donor atoms (manifested in the electronic effects of the groups attached to the donor atoms) and the nature of complex precursor (i.e. whether or not the precursor has a strong *trans* directing group present) are the two main factors that dictate the formation of *cis* or *trans* isomer for these bidentate chelates. The nature of the coordinated anion does not appear to be important and the presence of bulky terminal substituents on phosphorus is not a prerequisite for *trans* chelation.

Another factor to be considered is the reaction conditions employed in synthesis of the complexes. For example, in the synthesis of the *cis*-bis(diphenylphosphino)alkane platinum(II) or bis(diphenylarsino)alkane platinum(II) complexes [90,91], solid potassium tetrachloroplatinate(II) is refluxed with a solution of the ligand in boiling ethanol. The formation of *cis* isomers in platinum(II) complexes is favored by high temperatures and polar solvents; furthermore the complex is formed in the presence of excess ligand, such conditions being known to catalyze *cis-trans* isomerization. Indeed, the *cis* complexes can be prepared from their *trans* analogs by the addition of a trace of excess diphosphine. It is therefore not surprising that the choice of reaction conditions such as these leads to the formation of the *cis* isomers. The corresponding *trans* isomers are prepared at room temperature in a relatively non-polar solvent such as acetone/toluene with care taken to avoid the presence of excess ligand: such conditions are known to catalyze *cis-trans* isomerization.

It is therefore possible to tailor the reaction conditions to produce the desired *cis* or *trans* platinum(II) isomer by the judicious selection of complex precursor, ligand and the correct reaction conditions.

(iii) Gold(III) and related complexes

Gold(III) normally reacts with bidentate phosphine and arsine ligands in a redox manner: gold(III) is reduced to gold(I) with concomitant oxidation of the ligands. The information on gold(III) complexes that have been isolated is still too sparse to allow the observation of any trends in the coordination chemistry of bis chelates of this type.

(iv) Rhodium(I) and iridium(I) complexes

The vast majority of rhodium(I) and iridium(I) complexes isolated contain *trans* bonded diphosphine or diarsine ligands. This is illustrated by the formation of *trans* bonded polynuclear complexes with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 3, 4$). The ligand dpe appears to exhibit rather unusual behavior, forming a *cis* chelated complex with rhodium(I) and an ionic complex of structure $[Ir(CO)(L-L)_2][Ir(CO)_2Cl_2]$ with iridium(I). Longer chain diphosphines such as those synthesized by Shaw and co-workers [123] are all *trans* bonded. *Cis*-bonded complexes are rare and the ligands which form *cis* complexes are usually of an unusual nature which either preclude *trans* chelation (such as *cis*-vpp) or possess a short chelate backbone which favors *cis* chelation.

Most rhodium(I) and iridium(I) complexes exist mainly with carbon monoxide, tertiary phosphines or alkenes as ligands, all of which exhibit a high *trans* labilizing ability. Substitution in these complexes would be expected, therefore, to yield products that possess a *trans* square planar geometry and this is indeed what is observed experimentally. The degree of oligomerization in these *trans* chelates appears to be a function of chelate chain length in the ligands with flexible chelate backbones. The introduction of rigidity into the backbone, whether by the presence of acetylinic or olefinic linkages or by the presence of other potential donor atoms (e.g. an ether linkage) also promotes *trans* bonding in these complexes and also dictates the formation of oligomeric species, depending upon the resultant "chelate bite".

The propensity of rhodium(I) and iridium(I) to form five-coordinate complexes results in the formation of five-coordinate complexes with bidentate phosphine or arsine ligands, especially when carbon monoxide is the fifth ligand [80,115–117]. Loss of carbon monoxide from these complexes yields products with two bidentate ligands bound to a single metal atom center as *cis* chelates [80,115–117].

CONCLUSIONS

There has been much recent discussion of the chelate effect [84,152] and it is now becoming clear that the nature of the effect is not as well understood as was previously believed. In particular, the traditional concept that bidentate ligands occupy *cis* positions around a metal atom center [153] is one that has not been challenged until recent times. It is now evident that the factors that affect the stereochemistry of transition metal complexes with bidentate phosphorus or arsenic donor ligands are far more numerous and subtle than was generally realized.

Since the first report of a *trans* chelated bidentate chelate complex by Islieb and Hohlfield [4] in 1961, a wide range of *trans* chelated and *trans* bonded complexes has been isolated; indeed, specific routes are now available for the synthesis of complexes of this type for a wide range of d^8 transition metals. This goal can be achieved by the employment of a particular complex precursor, a particular type (or length) of chelate backbone and/or the judicious selection of reaction conditions. All of these factors are important in our understanding of the chelate effect and in predicting in what manner a bidentate chelate will bind to a transition metal ion.

Finally, we would like to emphasize that the work reviewed here merely provides a basis for further investigation; there are many important questions concerning the chelate effect that have not yet been answered in a satisfactory manner. However, we hope that we will stimulate discussion in this recently neglected area of coordination chemistry and that this will lead to a better understanding of the phenomenon known as "the chelate effect".

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