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^{31}P and ^{195}Pt NMR Characteristics of New Binuclear Complexes of $[Pt_2X_4(PR_3)_2]$ *cis/trans* Isomers and of Mononuclear Analogs

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Abstract

The ^{31}P and ^{195}Pt chemical shifts are reported for the first time for complexes of binuclear platinum(II) of the type $[Pt_2(\mu\text{-}X)_2(X)_2(PR_3)_2]$. These were identified as intermediate from the reaction of the $[PtX_2COD)]$ complex with different tertiary phosphines (where X may be Cl or I and PR_3 may be PBz_3, PCy_3, $PCyPh_2$, PCy_2Ph or $PPh_2C_6F_5$). In addition, *cis* and *trans*-$[PtX_2(PR_3)_2]$ were produced in the final step, and their ^{31}P and ^{195}Pt are also described (X = Cl or I; $PR_3 = PBz_3$, PCy_3, $PPhCy_2$, PPh_2Cy, $PPh_2{}^iPr$, $PPh_2C_6F_5$, PPh_3, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, PBu_3, $PPhMe_2$, PPh_2Me, (bis-1,2-Ph_2P)-C_6H_4, $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$).

The platinum-195 chemical shift is shown to be relatively sensitive to the nature of complex geometry. The unsymmetrical (unsym.) *cis* isomer absorbs at a lower frequency (upfield) than the symmetrical (sym.) *trans* isomer and in a somewhat higher platinum chemical shift than in the equivalent terminal complexes $[PtX_2(PR_3)_2]$. The $^1J(Pt-P)$ couplings are consistent and related to the cone-angle data of the ligand and the ^1J value of sym. *trans* form is 1.26 times that for the unsym. *cis* form and shows some solvent dependency. Interestingly, two isomers of the unsym. *cis* dimer were identified, and then one of the isomers isomerized to the sym. *trans* dimer.

The nature of the reaction intermediate and products was found to be very dependent on both the reactants and conditions.

Introduction

Transition-metal complexes of weak donor ligands, and in particular platinum and palladium complexes of the type $[MX_2L_2]$ (M = Pd or Pt, X = anionic ligand, L = weak donor ligand), are useful starting materials in organometallic synthesis [1]. Their usefulness lies in the ease with which the donor ligands are simply replaced by incoming nucleophiles.

Recently, Anderson *et al.* [2, 3] described reactions of monodentate tertiary phosphine and bidentate phosphorus ligands with platinum diolefin complexes [PtXY(COD)] (X, Y = halide, alkyl or aryl, COD = 1,5-cyclooctadiene), where in most but not all cases, simple displacement of the diolefin was found to occur. In this paper we report the results of thorough spectroscopic studies on the reactions of $[PtX_2(COD)]$ (X = Cl or I) with a series of monodentate tertiary phosphine $[PR_2R']$ (R = R′ = ^{n}Bu, Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, Bz, Cy; R = Ph, R′ = Me, ^{i}Pr, Bz, Cy, C_6F_5; R = Me, Cy, R′ = Ph) and with a series of bidentate phosphorus ligands $[Ph_2P(CH_2)_nPPh_2]$ (*n* = 1(dppm), *n* = 2(dppe)) and bis-(1,2-Ph_2P)C_6H_4.

$^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy has been employed to identify the species formed in solution and in particular the intermediate species which have been identified by careful addition of ligand to the starting material $[PtX_2(COD)]$. However ^{31}P and ^{195}Pt NMR spectroscopy were used to differentiate between possible molecularities of oligomeric products and geometrical arrangements of unsymmetrical species. Comparisons were made between the results reported here and other results reported for the same complexes, whenever these existed in the literature.

Results and Discussion

The effects of addition of monodentate and bidentate phosphorus ligands to $[PtCl_2(COD)]$ or $[PtI_2(COD)]$ have been examined in detail by ^{31}P and ^{195}Pt NMR spectroscopy. The nature of the reaction intermediate and products was found to be very dependent on both the reactants and conditions.

Reactions with Bulky Monodentate Phosphines

Reaction of [$PtCl_2$(COD)] (I) and [PtI_2(COD)] (II) with Phosphines

Reactions of I with tribenzylphosphine (PBz_3)

The simplest reaction was the addition of 0.5 mol equivalent of PBz_3 to a chloroform-d suspension of **I** (0.107 M) in the NMR tube at ambient temper-

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ature (colorless solution), which yielded four phosphine-containing species, assigned on the basis of their $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra as the symmetrical (50%) and unsymmetrical (40%) isomers of the dimer $[Pt_2(\mu\text{-}Cl)_2(Cl_2)(PBz_3)_2]$ and traces of the monomers *cis* and *trans*-$[PtCl_2(PBz_3)_2]$ (10%) in the presence of unreacted complex **I**. Addition of a further 0.5 mol equivalent of phosphine resulted in a partial conversion of dimers into *cis* and *trans* monomers (Tables I and II) and **I**. Evaporation of the solution *in vacuo* gave a mixture of yellow and white solid, which was redissolved in a small quantity of $CDCl_3$, whose $^{31}P\{^1H\}$ NMR spectrum indicates the presence of the *trans* monomer and both dimers (*cis* monomer is less soluble in $CDCl_3$ and can be separated). Addition of a further equivalent of phosphine resulted in total conversion of the dimers to the mononuclear *cis* and *trans* products and the rest of complex I reacted completely with the phosphine. The net result of this reaction is the displacement of cyclooctadiene from **I** by PBz_3 yielding *cis*-$[PtCl_2(PBz_3)_2]$ (60%) and *trans*-$[PtCl_2(PBz_3)_2]$ (40%) isomers, in the ratio *trans/cis*, 0.66. When the above reaction was carried out in benzene-d_6, only *trans*-$[PtCl_2(PBz_3)_2]$ (100%) was obtained.

Reactions of II with PBz_3

Treatment of **II** with PBz_3 in $CDCl_3$ in the same manner as in case of complex **I**, afforded three phosphine-containing species assigned as the symmetrical dimer $[Pt_2(\mu\text{-}I)_2(I_2)(PBz_3)_2]$ (red solid) and *cis–trans* monomers $[PtI_2(PBz_3)_2]$ (Table II). Addition of 2.0 mol equivalents of phosphine resulted in total conversion of the dimer to the *trans* monomer. The net result of this reaction is the formation of *trans/cis* isomers, in the ratio 2.6. Treatment of **II** with PBz_3 in C_6D_6 in the same manner as in $CDCl_3$, yielded immediately both *trans/cis* monomers in the ratio 1.9. For the above reactions, *cis* and *trans* products were characterized by comparing their ^{31}P NMR spectra with those of the authentic samples, which were prepared by the reported methods [4, 5]. The chloride and iodide symmetric bridges were characterized in a straightforward manner. They are readily cleaved upon addition of excess phosphine to yield the expected product [1, 6] *trans*-$[PtX_2(PBz_3)_2]$. Also, the dimers were identified by their characteristic ^{31}P and ^{195}Pt NMR spectra (Table I). The ^{31}P NMR spectra are straightforward and similar to analogous reported dimers [3]. For each dimer, the ^{195}Pt NMR spectrum consists of doublet, $^1J(^{195}Pt-^{31}P)$ 3798 for sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBz_3)_2]$ and doublet, $^1J(^{195}Pt-^{31}P)$ 3636 for sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PBz_3)_2]$ (Table I), as expected for dimer complexes [7]. The unsymmetric isomer of the dimer unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBz_3)_2]$ assigned on the basis of both ^{31}P and ^{195}Pt NMR spectra (Table I) and compared with reported dimer $[(Pt_2(\mu\text{-}Cl)_2(Ph_2)(P(o\text{-tolyl})_3)_2]$ [8]. The $^1J(Pt-P)$ couplings found here are in the range and are typical for halogen-bridged binuclear species and are considerably lower than the corresponding coupling constants of their analogous dimers containing tertiary organophosphines (*ca.* 3900–5500 Hz) [8]. Of interest is that the reaction of **I** and **II** with PBz_3 provides further evidence that a dimeric species is initially formed. The symmetrical isomer,

TABLE I. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR Spectral Data of $[Pt_2(\mu\text{-}X_2)_2(X)_2(PR_3)_2]$ Complexes[a] at 25 °C

Complexes	Solvent	$^{31}P\{^1H\}$ NMR[b] δ (ppm)	$^{195}Pt\{^1H\}$ NMR[c] δ (ppm)	$^1J(Pt-P)$ (Hz)	% At 1 equivalent
Sym. *trans*-$[Pt_2Cl_4(PBz_3)_2]$	$CDCl_3$	−6.7 (t)	−3481 (d)	3798	40
Sym. *trans*-$[Pt_2I_4(PBz_3)_2]$	$CDCl_3$	−2.4 (t)		3636	18
Sym. *trans*-$[Pt_2Cl_4(PCy_3)_2]$	$CDCl_3$	+11.1 (t)	−3467 (d)	3760	35
Sym. *trans*-$[Pt_2I_4(PCy_3)_2]$	$CDCl_3$	+22.9 (t)		3612	100
Sym. *trans*-$[Pt_2Cl_4(PPh_2Cy)_2]$	$CDCl_3$	+15.1 (t)		3569	60
Sym. *trans*-$[Pt_2Cl_4(PPhCy_2)_2]$	$CDCl_3$	+13.3 (t)	−3518 (d)	3867	50
Sym. *trans*-$[Pt_2Cl_4(PPhCy_2)_2]$	C_6D_6	+13.9 (t)		3892	30
Sym. *trans*-$[Pt_2I_4(PPhCy_2)_2]$	$CDCl_3$	+23.7 (t)		3608	100
Sym. *trans*-$[Pt_2I_4(PPhCy_2)_2]$	C_6D_6	+24.3 (t)		3657	10
Sym. *trans*-$[Pt_2Cl_4(PPh_2C_6F_5)_2]$	$CDCl_3$	+4.1 (t)		3740	20
Unsym. *cis*-$[Pt_2Cl_4(PBz_3)_2]$	$CDCl_3$	+18.5 (t)	−3870 (d)	3060	30
Unsym. *cis*-$[Pt_2Cl_4(PCy_3)_2]$*	$CDCl_3$	+31.8 (t)	−3892 (d)	2905	55
*	$CDCl_3$	+13.4 (t)	−3837 (d)	3108	35
Unsym. *cis*-$[Pt_2Cl_4(PPhCy_2)_2]$*	$CDCl_3$	+25.2 (t)	−3897(d)	2956	35
*	$CDCl_3$	+15.4 (t)	3883 (d)	3202	5
Unsym. *cis*-$[Pt_2Cl_4(PPh_2C_6F_5)_2]$	$CDCl_3$	+11.6 (t)	−3992 (d)	2793	80

An asterisk indicates two unsymmetric isomers present. [a]Abbreviations: d, 1:1 doublet; t, 1:2:1 triplet. [b]δ-Values relative to 85% H_3PO_4 (external), positive shifts representing deshielding, [c]δ Pt relative to Na_2PtCl_6 for ^{195}Pt NMR.

TABLE II. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR Spectral Data of *cis/trans*-$[PtX_2(PR_3)_2]$ Complexes[a] at 25 °C

Complexes	Solvent	$^{31}P\{^1H\}$ NMR[b] δ (ppm)	$^{195}Pt\{^1H\}$ NMR[c] δ (ppm)	^1J(Pt–P) (Hz)	% At 1 equivalent
trans-$[PtCl_2(PBz_3)_2]$	$CDCl_3$	+5.8 (t)	−3926 (t)	2460	10
trans-$[PtCl_2(PBz_3)_2]$	C_6D_6	+6.7 (t)		2471	100
trans-$[PtI_2(PBz_3)_2]$	$CDCl_3$	−9.9 (t)		2339	72
	C_6D_6	−9.0 (t)		2344	65
trans-$[PtCl_2(PPh_2Bz)_2]$	C_6D_6	+16.0 (t)		2593	100
trans-$[PtI_2(PPh_2Bz)_2]$	$CDCl_3$	−2.9 (t)		2432	20
	C_6D_6	+4.7 (t)		2433	100
trans-$[PtCl_2(PCy_3)_2]$	$CDCl_3$	+16.5 (t)	−3850 (t)	2395	–
	C_6D_6	+14.7 (t)	−3870 (t)	2416	100
trans-$[PtI_2(PCy_3)_2]$	$CDCl_3$	+10.3 (t)		2295	40
trans-$[PtI_2(PPh_2Cy)_2]$	$CDCl_3$	+11.1 (t)		2373	40
	C_6D_6	+12.5 (t)		2373	100
trans-$[PtCl_2(PPhCy_2)_2]$	$CDCl_3$	+22.5 (t)	−3952 (t)	2514	10
trans-$[PtI_2(PPhCy_2)_2]$	$CDCl_3$	+13.1 (t)		2386	–
	C_6D_6	+14.0 (t)		2388	90
trans-$[PtCl_2(PPh_2C_6F_5)_2]$	C_6D_6	+11.3 (t)		2802	100
trans-$[PtI_2(PPh_2C_6F_5)_2]$	$CDCl_3$	+2.9 (t)		2640	100
	C_6D_6	+3.5 (t)		2336	100
trans-$[PtI_2(PBu_3)_2]$	$CDCl_3$	−8.2 (t)		2256	50
trans-$[PtI_2(P(m\text{-tolyl})_3)_2]$	$CDCl_3$	+12.1 (t)		2485	45
trans-$[PtI_2(P(p\text{-tolyl})_3)_2]$	$CDCl_3$	+9.9 (t)		2463	35
cis-$[PtCl_2(PBz_3)_2]$	$CDCl_3$	+5.5 (t)		3657	20
cis-$[PtI_2(PBz_3)_2]$	$CDCl_3$	+3.0 (t)		3486	10
	C_6D_6	+5.0 (t)		3468	35
cis-$[PtCl_2(PPh_2Bz)_2]$	$CDCl_3$	+9.7 (t)	−3721 (t)	3740	100
cis-$[PtI_2(PPh_2Bz)_2]$	$CDCl_3$	+5.8 (t)		3532	80
cis-$[PtCl_2(PPh_2Cy)_2]$	$CDCl_3$	+13.3 (t)		3696	100
cis-$[PtCl_2(PPh_2{}^i Pr)_2]$	$CDCl_3$	+16.3 (t)	−4344 (t)	3696	100
cis-$[PtCl_2(PPh_3)_2]$	$CDCl_3$	+14.2 (t)		3674	100
cis-$[PtCl_2(P(m\text{-tolyl})_3)_2]$	$CDCl_3$	+14.2 (t)		3687	100
cis-$[PtCl_2(P(p\text{-tolyl})_3)_2]$	$CDCl_3$	+12.4 (t)		3687	100
cis-$[PtI_2(P(m\text{-tolyl})_3)_2]$	$CDCl_3$	+11.5 (t)		3465	55
cis-$[PtI_2(P(p\text{-tolyl})_3)_2]$	$CDCl_3$	+9.9 (t)		3474	65
cis-$[PtCl_2(PBu_3)_2]$	$CDCl_3$	+0.9 (t)		3517	100
cis-$[PtCl_2(PPh_2Me)_2]$	$CDCl_3$	−1.0 (t)		3623	100
cis-$[PtCl_2(PPhMe_2)_2$	$CDCl_3$	−15.3 (t)		3547	100

[a]Abbreviations: d, 1:1 doublet; t, 1:2:1 triplet. [b]δ-Values relative to 85% H_3PO_4 (external), positive shifts representing deshielding. [c]δ Pt relative to Na_2PtCl_6 for ^{195}Pt NMR.

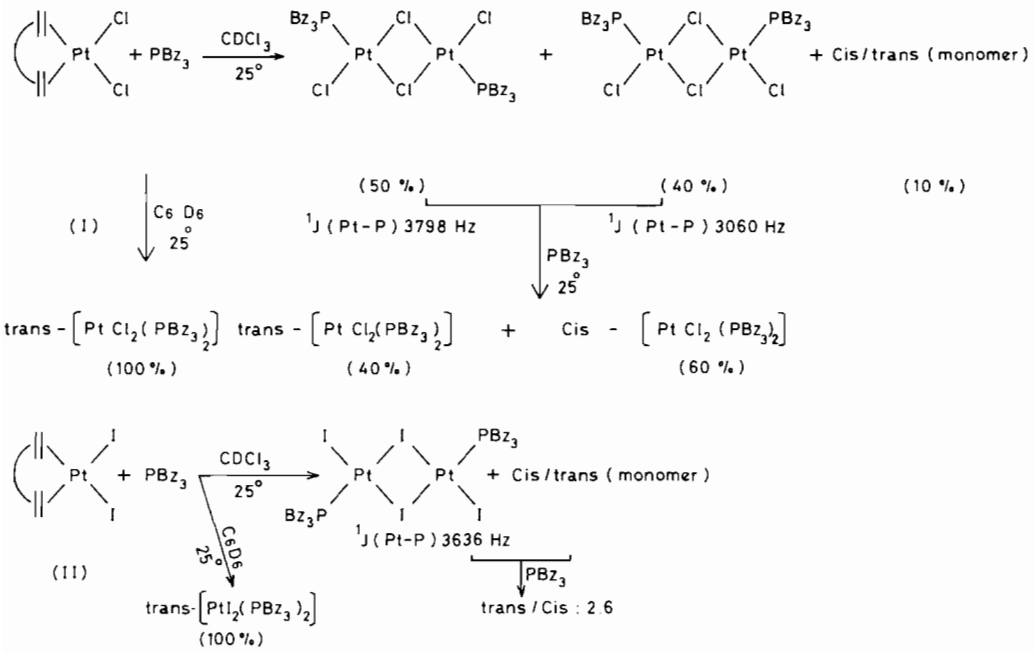
sym. *trans*-$[Pt_2(\mu\text{-}X)_2(X)_2(PBz_3)_2]$ cleavaged by PBz_3 and yielded *trans*-$[PtX_2(PBz_3)_2]$. The case was different in the unsymmetrical isomer, unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBz_3)_2]$ cleavaged by PBz_3, yielded *cis*-$[PtCl_2(PBz_3)_2]$ (Scheme 1).

In the majority of applications of the bridge-cleavage reaction, however, little attention has been paid to the isomeric nature of the products. $[Pt_2(\mu\text{-}Cl)_2(Ph)_2(PMePh_2)_2]$ exists in solution both as *cis* and *trans* isomers [6], yet bridge cleavage by CO in $CDCl_3$ at −60 °C produces almost exclusively the product with CO *trans* to $PMePh_2$. Here, both *cis* and *trans* dimers exist in solution, and bridge cleavage by PBz_3 in $CDCl_3$ at ambient temperature produces *cis* and *trans* monomers, respectively. Interconversion between the two dimeric isomers occurs readily in solution for most, and possibly for all, of these bridged complexes [8, 9]. Thus, the ratios of *trans* to *cis* isomers adjust rapidly in different solvents, and usually only one isomer (*trans*) predominates in the less polar solvent (Table II).

Reaction of I with tricyclohexylphosphine (PCy_3)

The most complicated reactions were the addition of PCy_3 to **I**. In four experiments 0.5, 1.0, 2 and 3 mol equivalents of PCy_3 were added to $CDCl_3$ solution of **I** (0.24 M) at ambient temperature, and the ^{31}P and ^{195}Pt NMR spectra of the mixtures were recorded each time.

When less than 1 mol equivalent of PCy_3 was added to **I**, a colorless solution resulted and two phosphine-containing species were formed and



Scheme 1.

assigned, on the basis of their ^{31}P and ^{195}Pt NMR spectra, as two unsymmetrical [(55%) $^1J(^{195}Pt-^{31}P)$ 2905 Hz and (35%) $^1J(^{195}Pt-^{31}P)$ 3108 Hz], isomers of the dimer $[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_3)_2]$ and unreacted **I** (see Table I) along with two unidentified minor products (These had ^{31}P NMR signals grouped in two triplets, ^1J(Pt–P) 1528 and 1533 Hz and ^{195}Pt NMR spectra consist of two doublets of ^1J values similar to the ^1J(Pt–P) values.) These probably assigned to a species having the phosphine *trans* to the olefin group similar to the analogous complex when phosphine is *trans* to the methyl or phenyl group (^1J 1680–860 Hz) [10, 11]. (Investigations are in progress to isolate these species.) When the solution was left for 1 h and the ^{31}P NMR spectrum was remeasured, a new peak was observed with $^1J(^{195}Pt-^{31}P)$ 3760 Hz (55%), with the disappearance of the signal having ^1J 3108 Hz and the existence of the other signal of ^1J 2905 Hz (54%). The color of the solution became yellow, which indicated the formation of the symmetric isomer of the dimer $[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_3)_2]$. ^{195}Pt NMR, spectra of the above solution consist of two doublets for both isomers (see Table I).

When 1 to 2 mol equivalents of PCy_3 were added to the above solution, three phosphorus-containing species, were formed, *trans*-$[PtCl_2(PCy_3)_2]$, symmetric isomer of the dimer, ^1J 3760 Hz and the signals of unidentified products of ^1J 1528 and 1533 Hz and complex **I** completely soluble. Addition of excess (3 mol equivalents) of PCy_3, leads to the formation of a yellow precipitate *trans*-$[PtCl_2(PCy_3)_2]$, $^1J(^{195}Pt-^{31}P)$ 2395 Hz and slight-yellow solution, containing traces of the *trans* isomer of the monomer and unidentified species of ^1J 1528 and 1533 Hz.

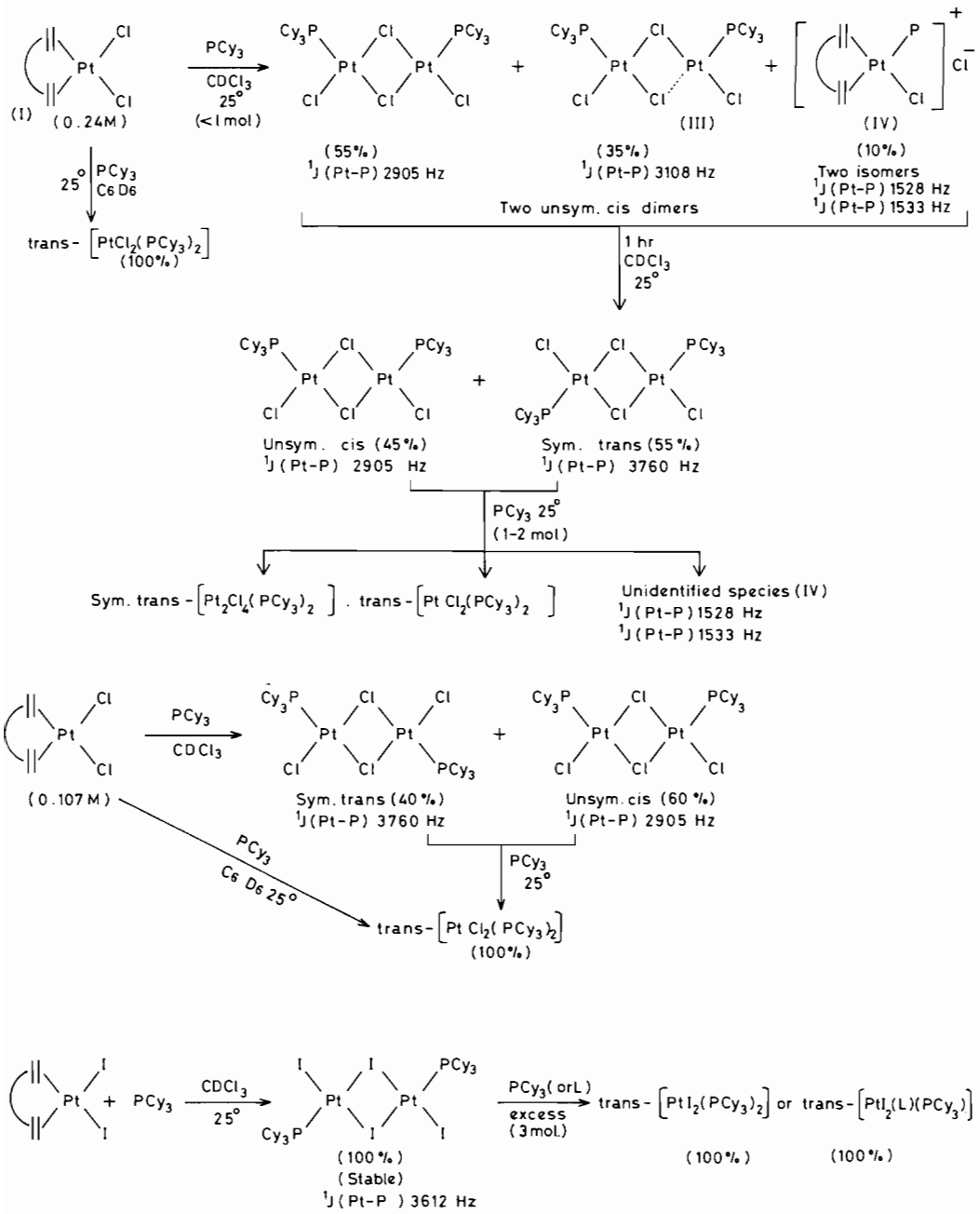
When the above experiment was repeated in dilute solution (0.107 M), in the first step (1 mol equivalent added) only the two isomers of the dimer existed (sym. and unsym. dimers), ^1J 3760 Hz, 40%, ^1J 2905 Hz, 60%, respectively.

Analysis of the above data indicates the straightforward formation of unsymmetric bridges (in intermediate step) as a colorless solution (*cis* dimer), followed by rearrangement of one of these *cis* dimers (less stable one, **III**) into the symmetric, *trans* dimer (yellow solution). Addition of 2 mol equivalents leads to the formation of *trans*-$[PtCl_2(PCy_3)_2]$ monomer, as a result of bridge-cleavage reactions.

When the above reaction was carried out in benzene-d_6, it yielded only *trans*-$[PtCl_2(PCy_3)_2]$, 100% (Scheme 2).

Reaction of (II) with PCy_3

Treatment of **II** with PCy_3 in $CDCl_3$ in the same manner as in the case of complex **I**, afforded a red precipitate (at 1 mol equivalent) of sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PCy_3)_2]$ dimer, slightly soluble in $CDCl_3$, $^1J(^{195}Pt-^{31}P)$, 3612 Hz. Addition of 2 mol equivalent produced *trans*-$[PtI_2(PCy_3)_2]$ (40%) and 60% of the symm. dimer. When 3 mol equivalent were added, it resulted in the formation of *trans*-$[Pt(I)_2(PCy_3)_2]$ (100%). The dimer was isolated



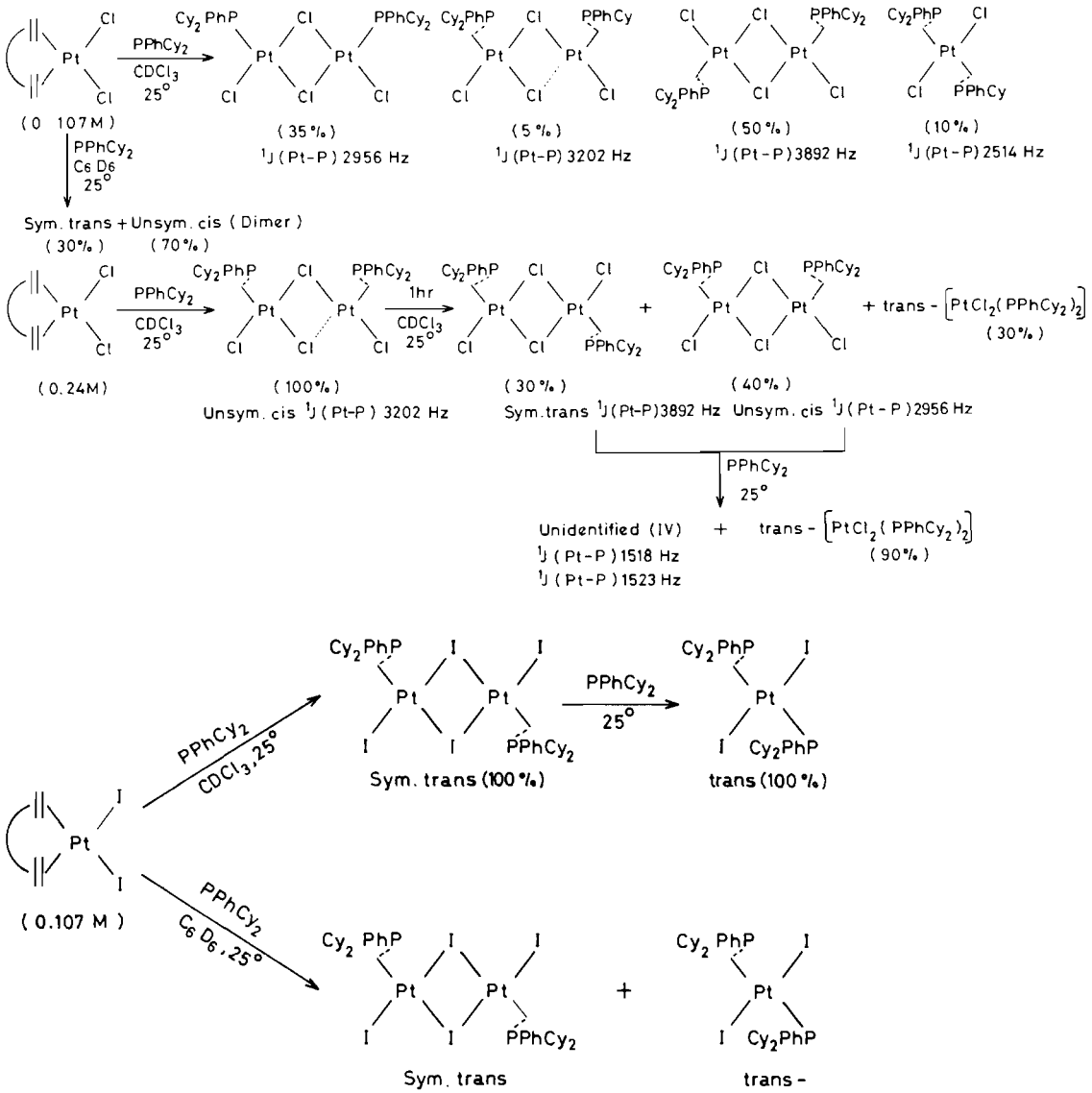
Scheme 2.

and analyzed and reacted with a different ligand, *i.e.* $NHEt_2$, to give *trans*-$[PtI_2(PCy_3)(NHEt_2)]$, $^1J(^{195}Pt-^{31}P)$ 3260 Hz, (see Table II), Scheme 2.

Reaction of I with dicyclohexylphenylphosphine (PCy_2Ph)

Treatment of **I** (0.107 M) in $CDCl_3$ with 1 mol equivalent of PCy_2Ph, afforded four phosphine-containing species assigned as sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_2Ph)_2]$ (50%) ^1J 3892 Hz, two isomers of unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_2Ph)_2]$ of the dimer (35%) ^1J 2956 Hz, (5%) ^1J 3202 Hz and *trans*-$[PtCl_2(PCy_2Ph)_2]$, (10%) ^1J 2514 Hz, monomer.

Repeating the above experiment using 0.214 M of **I**, resulted in the formation of only one phosphine-containing species, and assigned as unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_2Ph)_2]$, (100%) $^1J(^{195}Pt-^{31}P)$ 3202 Hz. After 1 h the ^{31}P and ^{195}Pt NMR spectra show the presence of three species, assigned as sym. *trans* dimer (30%), ^1J 3892 Hz, unsym. *cis* dimer (40%), ^1J 2956 Hz and *trans* monomer (30%), ^1J 2514 Hz.



Scheme 3.

This result indicates the disappearance of the unsym. *cis* dimer formed in the first step which transformed into three new species. Addition of 2 or 3 mol equivalents of PCy_2Ph to the above solution, leading to the formation of the *trans* monomer (90%) and an unidentified species (**IV**) of ^1J 1518 and 1523 Hz, as in the case of PCy_3.

Treatment of **I** with PCy_2Ph in benzene-d_6, resulted in the formation of two isomers of sym. (30%) and unsym. (70%) dimer (see Table I).

Reaction of II with PCy_2Ph

Addition of 1 mol equivalent of PCy_2Ph to **II** in $CDCl_3$, leads to the formation of sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PCy_2Ph)_2]$ (100%). When 2 or 3 mol equivalents were added to the above solution, it resulted in the formation of *trans*-$PtI_2(PCy_2Ph)_2]$ monomer.

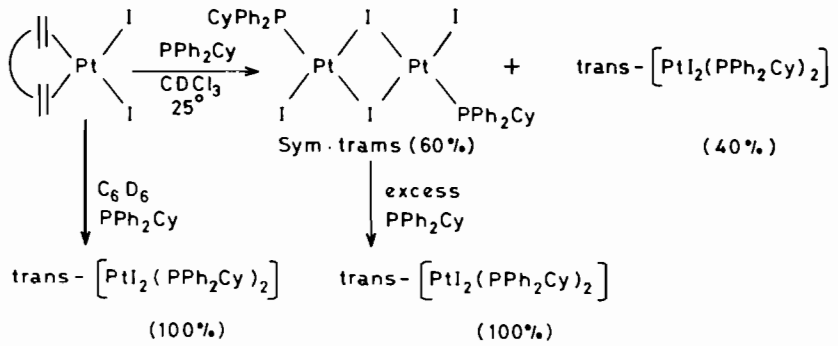
Treatment of **II** with PCy_2Ph in benzene-d_6, leads to the formation of *trans*-$[PtI_2(PCy_2Ph)_2]$, and sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PCy_2Ph)_2]$ dimer (see Table I) (Scheme 3).

Reaction of I with cyclohexyldiphenylphosphine ($PCyPh_2$)

Treatment of **I** with $PCyPh_2$ in $CDCl_3$, leads to the formation of only the *cis*-$[PtCl_2(PCyPh_2)_2]$ monomer.

Reaction of II with $PCyPh_2$

Treatment of **II** with $PCyPh_2$ 1 mol equivalent in $CDCl_3$, results in the formation of the sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PCyPh_2)]$ (60%) dimer and *trans*-$[PtI_2(PCyPh_2)_2]$ (40%) monomer. Excess of $PCyPh_2$,



Scheme 4.

produces the *trans* monomer (see Table II). In benzene-d_6 the only phosphine-containing product was *trans*-$[PrI_2(PCyPh_2)_2]$ (Scheme 4).

Reaction of I with triphenylphosphine (PPh_3)

Addition of PPh_3 to a solution of I in $CDCl_3$ produced *cis*-$[PtCl_2(PPh_3)_2]$ as the only phosphorus-containing product (see Table II).

Reaction of I and II with P(o-tolyl)$_3$, P(m-tolyl)$_3$ and P(p-tolyl)$_3$

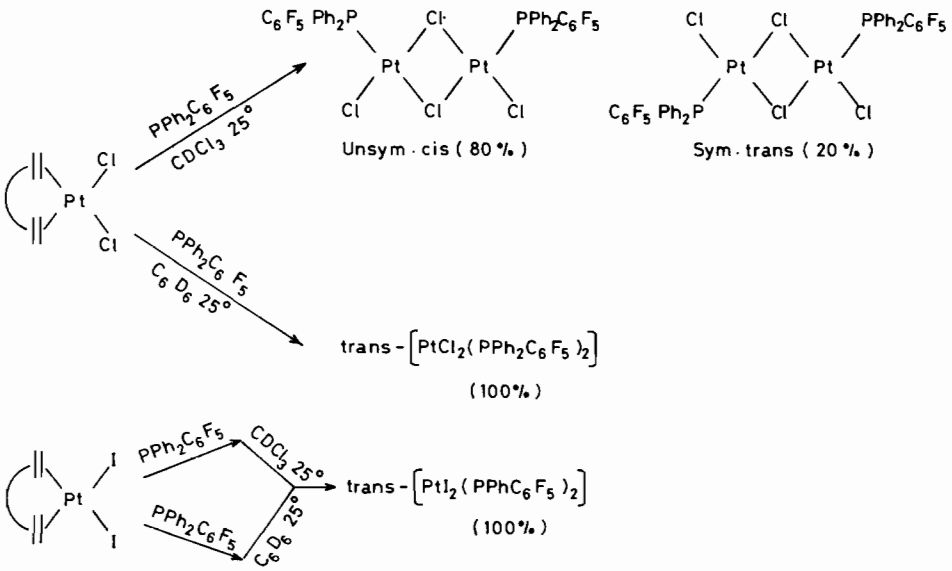
Solid P(*o*-tolyl)$_3$ (1 equivalent) was added to a chloroform-d solution of **I** or **II** and stirred for 10 h. Examination by $^{31}P\{^1H\}$ NMR showed no reaction in either case. The same experiment was reported in benzene, and no reaction occurred [3]. But treatment of **I** in chloroform-d by P(*m*-tolyl)$_3$ and P(*p*-tolyl)$_3$ (1–2 equivalent) afforded one phosphine-containing species, and assigned as *cis*-$\{PtCl_2[P(m\text{-tolyl})_3]_2\}$ and *cis*-$\{PtCl_2[P(p\text{-tolyl})_3]_2\}$ respectively, Table II. Treatment of **II** with P(*m*-tolyl)$_3$ and P(*p*-tolyl)$_3$ (1–2 equivalent), resulted in the formation of *cis* and *trans* monomers of $\{PtI_2[P(m\text{-tolyl})_3]_2\}$ and $\{PtI_2[P(p\text{-tolyl})_3]_2\}$ respectively, Table II.

Reaction of I with ^{iso}propyldiphenylphosphine ($PPh_2{}^iPr$)

Addition of $PPh_2{}^iPr$ to a solution of I in $CDCl_3$ in the same manner, produced *cis*-$[PtCl_2(PPh_2{}^iPr)_2]$ as the only phosphorus-containing product (see Table II).

Reaction of I with pentafluorophenyldiphenylphosphine [$PPh_2C_6F_5$]

Treatment of **I** with $PPh_2C_6F_5$ in $CDCl_3$ solution produced 80% of the unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PPh_2C_6F_5)_2]$ (colorless solution) and 20% of the sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PPh_2C_6F_5)_2]$ isomer of the dimer. The ^{31}P and ^{195}Pt NMR spectra of both isomers of the dimer are straightforward and similar to the above reported complexes (see Table II). When the above reactions were carried out in benzene-d_6, *trans*-$[PtCl_2(PPh_2C_6F_5)_2]$ was the only product (Scheme 5).



Scheme 5.

Reaction of II with $PPh_2C_6F_5$

Addition of $PPh_2C_6F_5$ to **II** in either $CDCl_3$ or benzene-d_6 produced only the *trans*-$[PtI_2(PPh_2C_6F_5)_2]$ monomer (Scheme 5).

Reaction of I with benzyldiphenylphosphine ($PBzPh_2$)

Addition of $PBzPh_2$ to **I** in $CDCl_3$ solution produced only the *cis*-$[PtCl_2(PBzPh_2)_2]$ monomer. When the reaction was carried out in benzene-d_6 it produced the *trans*-$[PtCl_2(PBzPh_2)_2]$ monomer and a white precipitate was formed (*cis* monomer).

Reaction of II with $PBzPh_2$

Treatment of **II** with $PBzPh_2$ in $CDCl_3$, yielded *cis*-$[PtI_2(PBzPh_2)_2]$ (80%) and *trans*-$[PtI_2(PBzPh_2)_2]$ (20%) monomers. But in benzene-d_6 only *trans*-$[PtI_2(PBzPh_2)_2]$ was formed (see Table II).

Reaction of I with tributylphosphine (PBu_3)

Treatment of **I** with PBu_3 in $CDCl_3$ solution produced only the *cis*-$[PtCl_2(PBu_3)_2]$ monomer.

Reaction of II with PBu_3

Treatment of **II** with 1 mol equivalent of PBu_3 in $CDCl_3$ gives a red solution which became yellow within a few seconds and its ^{31}P NMR spectrum showed two phosphorus-containing species and assigned as *trans*-$[PtI_2(PBu_3)_2]$ (50%) $^1J(^{195}Pt-^{31}P)$ 2256 Hz as yellow solution and an unidentified product (50%) of ^1J(Pt–P) 3366 Hz. This may be one form of the sym. *trans*-isomer $[Pt_2(\mu\text{-}I)_2(I)_2(Bu_3P)_2]$. Addition of 2 mol equivalents of PBu_3 to the $CDCl_3$ solution of **II** gave *trans*-$[PtI_2(PBu_3)_2]$, showing clearly that a straightforward bridge-cleavage reaction operates.

Reaction with Bidentate Phosphorus Ligand

Reaction of I with bis-diphenylphosphine benzene [bis(1,2-Ph_2P)C_6H_4].

Treatment of **I** with 1 mol equivalent of bis-1,2-$Ph_2P)C_6H_4$ in $CDCl_3$ produced only the *cis*-$[PtCl_2(P–P)]$ monomer as expected (see Table II).

Reaction of I with diphenylphosphinemethane (dppm)

Treatment of **I** in $CDCl_3$ solution with 1 mol equivalent of dppm produced a colorless solution, and the ^{31}P NMR showed only one phosphorus-containing product, *cis*-$[PtCl_2(P–P)]$; after few minutes a white solid was precipitated. This result is in agreement with the reported result of the same compound, $\delta\,^{31}P$ −64.24(t), $^1J(^{195}Pt-^{31}P)$ 3076 Hz [2].

Reaction of II with dppm

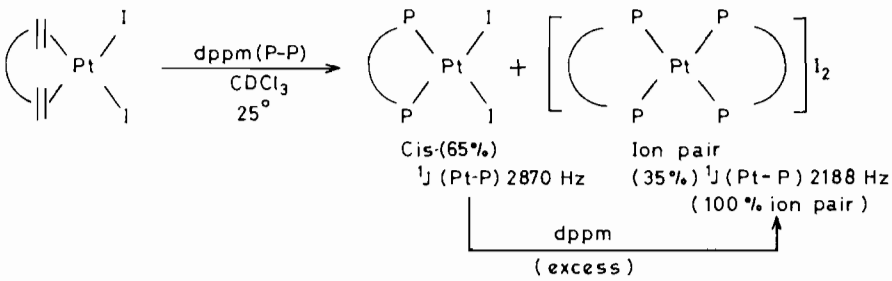
Treatment of **II** with 1 mol equivalent of dppm in $CDCl_3$ solution produced two phosphorus-containing species. The two complexes present in solution were identified as *cis*-$[PtI_2(dppm)]$ (65%) and ion-pair complex $[Pt(dppm)_2]I_2$ (35%) (see Table III). The ^{31}P NMR parameters for the complex $[Pt(dppm)_2]I_2$ are almost identical to the complex obtained from treatment of chloroform solution of $[Pt(dppm)_2]Cl_2$ with excess $Bu_4^+I^-$, which produced $[Pt(dppm)_2]I_2$ [2] ($\delta\,^{31}P$ −58.6, $^1J(^{195}Pt-^{31}P)$ 2188 Hz). In the *cis*-$[PtI_2(dppm)]$ complex $^1J(^{195}Pt-^{31}P)$ 2870 Hz is lower than that of the chloride *cis* complex $^1J(^{195}Pt-^{31}P)$ 3076 Hz, as expected.

Addition of excess dppm to the $CDCl_3$ solution, leads to the formation of only one product, the ion-pair complex of $[Pt(dppm)_2]I_2$.

This result indicates that first *cis*-$[PtI_2(dppm)]$ is formed, which then converts to bis-(bidentate ligand) platinum(II) dication in the presence of 2 mol equivalents of dppm (Scheme 6).

Reaction of I with diphenylphosphineethane (dppe)

Careful addition of 1 mol equivalent of dppe to 0.107 M solution of $CDCl_3$ of **I**, afforded three phosphine-containing species, two of them assigned on the basis of reported results as $[PtCl_2(dppe)]$ (85%), and $[Pt(dppe)_2]Cl_2$ (5%) [2] see Table III, and a new complex observed for the first time. The ^{31}P NMR spectra of the new complex appear downfield at $\delta\,^{31}P$ −109.2, as a triplet, $^1J(^{195}Pt-^{31}P)$ 4357 Hz. Addition of 2 mol equivalents of dppe



Scheme 6.

TABLE III. $^{31}P\{^1H\}$ NMR Spectral Data of $[PtX_2(P-P)]$ and some Other Complexes[a] at 25 °C

Complexes	Solvent	$^{31}P\{^1H\}$ NMR[b] δ (ppm)	^1J(Pt–P) (Hz)	%[c] At 1 equivalent
$[PtCl_2(P-P)]$ P–P = bis(1,2-Ph_2P)C_6H_4	$CDCl_3$	+6.7 (t)	3610	100
$[PtCl_2(Ph_2PCH_2PPh_2)]$	$CDCl_3$	−64.2 (t)	3076	100
$[PtI_2(Ph_2PCH_2PPh_2)]$	$CDCl_3$	−70.7 (t)	2870	65
$[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$	$CDCl_3$	+41.0 (t)	3617	85
$[PtI_2(Ph_2PCH_2CH_2PPh_2)]$	$CDCl_3$	+45.8 (t)	3366	100
trans-$[PtI_2(Et_2NH)(PCy_3)]$	$CDCl_3$	+13.9 (t)	3260	–
$[Pt(Ph_2PCH_2PPh_2)_2]I_2$	$CDCl_3$	+57.0 (t)	2167	35
$[Pt(Ph_2PCH_2CH_2PPh_2)_2]Cl_2$	$CDCl_3$	+47.2 (t)	2260	5
$[Pt(Ph_2PCH_2CH_2PPh_2)_2]I_2$	$CDCl_3$	+47.4 (t)	2307	–
$[PtCl(PPhMe_2)_3]Cl$	$CDCl_3$	−4.8 (d-t)	2324	–
	$CDCl_3$	−17.2 (t)	3570	–
$[PtCl_2(COD)] + PCy_3$	$CDCl_3$	+18.5 (t)	1528	δPt-3710(d)
(Unidentified product)	$CDCl_3$	+19.8 (t)	1533	δPt-3795(d)
$[PtCl_2(COD) + PCy_2Ph$	$CDCl_3$	+24.7 (t)	1518	δPt-3795(d)
(Unidentified product)	$CDCl_3$	+25.5 (t)	1523	δPt−3802(d)
$[PtCl_2(COD)] + PBu_3$ (Unidentified)	$CDCl_3$	+45.8 (t)	3366	50
$[PtCl_2(COD)] + Ph_2PCH_2CH_2PPh_2$ (Unidentified product)	$CDCl_3$	−109.2 (t)	4357	10

[a]Abbreviations: d, 1:1 doublet; t, 1:2:1 triplet; d-t, doublets of triplet. [b]δ-Values relative to 85% H_3PO_4 (external), positive shifts representing deshielding. [c]δ-Pt of some of these complexes are given below.

to the $CDCl_3$ solution of the above reaction resulted in the formation of a white precipitate (*cis* isomer). The NMR spectrum of the resulted $CDCl_3$ solution showed only two phosphorus-containing species $[PtCl_2(dppe)]$ (small signal), and $[Pt(dppe)_2]Cl_2$.

Reaction of II with dppe

Treatment of **II** with more than 1 equivalent of dppe in $CDCl_3$ produced two phosphorus-containing species, identified as $[PtI_2(dppe)]$ and $[Pt(dppe)_2]I_2$ (see Table III). After a few minutes, a yellow precipitate formed, $[Pt(dppe)_2]I_2$ and the remaining solution spectrum showed only the ^{31}P signal for $[PtI_2(dppe)]$.

NMR Chemical Shifts and Coupling Constants

Steric effects are extremely important to structures, spectroscopic properties, and chemical behavior of phosphorus ligands and their complexes [12]. In this study, a wide range of ligand types were used in order to reach conclusions about the relative importance of steric and electronic effects.

The cone-angle data of Tolman [12] allows some comparisons of relative ligand steric effects to be made and demonstrates that phosphine ligands such as PBz_3 (165°), PCy_3 (170°), PCy_2Ph (*ca.* 162°), $PPh_2C_6F_5$ (158°), PPh_2Cy (*ca.* 154°), $PBzPh_2$ (*ca.* 153°) [*ca.*, cone-angle calculated mathematically as follows: *i.e.* θ for PCy_2Ph is two-thirds of the way between PPh_3 (145°) and PCy_3 (170°) or 162°] are far more sterically demanding than other phosphine ligands presented in Table IV and V. The more steric phosphine ligands (except, P(*o*-tolyl)$_3$, θ, 194°, and P(mesityl)$_3$, θ, 212°) [3], are very useful ligands for the preparation of dimeric products when these react with **I** and **II**, compared with a less steric ligand, *i.e.*, PPh_3, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, PMe_2Ph, PBu_3 and $PMePh_2$, which react with **I** and **II** and favor the formation of *cis* and *trans* mononuclear isomers.

This observation suggests that dimeric species are formed as an intermediate, then bridge cleavage occurs to give a mononuclear product; the latter step being more rapid for less steric ligands than that for more steric ligands. Furthermore, there now appears to be considerable evidence that complexes of the type $[Pt_2(\mu\text{-}X_2)(X)_2(PR_3)_2]$ exist in solution as mixtures of *cis* and *trans* isomers. In general the ratio of the concentrations of the two major isomers (*cis*/*trans*) is dependent on the solvent. The major isomer is favored by the more polar solvent and assigned *trans* configuration (X = Cl, solvent $CDCl_3$). The most surprizing of the products are obtained from the reaction of PCy_3 with **I** in $CDCl_3$ solution. Initially, the unsym. *cis*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_3)_2]$ is formed, which rapidly isomerizes to the *trans* configuration. The concentration ratio of *cis*/*trans* isomers ⩾1. The same behavior was observed when $PPh_2C_6F_5$ reacted with **I**, the *cis*/*trans* ratio is 4 (Schemes 2 and 3). The proportion of *cis*/*trans* isomers produced from the reactions of **II** and PR_3 in benzene-d_6 on the other hand, were markedly reduced in favor of the *trans* isomer as expected (*i.e.* $PR_3 = PCy_3$, X = I, 100% sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PCy_3)_2]$. The *trans*/*cis* ratio is generally favored by bulkier PR_3 and by iodide over chloride

TABLE IV. $^{195}Pt-^{31}P$ Spin–Spin Coupling Constants (Hz) in $[Pt_2(\mu\text{-}X)_2(X)_2(PR_3)_2]$ in $CDCl_3$ Solution at Ambient Temperature

Complexes	*trans* isomer	*cis* isomer	$^1J_{trans}/^1J_{cis}$	θ (°)[a]
$[Pt_2Cl_4(PBz_3)_2]$	3798	3060	1.24	165
$[Pt_2I_4(PBz_3)_2]$	3636	–		
$[Pt_2Cl_4(PCy_3)_2]$	3760	3108	1.21	170
		2905	1.29	
$[Pt_2I_4(PCy_3)_2]$	3612	–		
$[Pt_2Cl_4(PCy_2Ph)_2]$	3867	3202	1.21	*ca.* 162
		2956	1.30	
	(3892)*	(3169)*	1.23	
$[Pt_2I_4(PCy_2Ph)_2]$	(3608)*	--		
$[Pt_2I_4(PCyPh_2)_2]$	3569	–		
$[PtCl_4(PPh_2C_6F_5)_2]$	3740	2793	1.34	158

An asterisk indicates in C_6D_6 solution at ambient temperature. [a]Values of the ligand cone-angle θ, from ref. 12.

TABLE V. The Effect of Ligand and Geometric Isomerization on $\delta^{195}Pt$

Complexes	$\delta^{195}Pt$ (ppm)	Reference	θ (°)[a]
trans-$[PtCl_2(PMe_3)_2]$	−3950	7	118
trans-$[PtCl_2(PBu_3)_2]$	−3929	7	131
trans-$[PtCl_2(PBz_3)_2]$	−3926		165
trans-$[PtCl_2(PCy_3)_2]$	−3850		170
trans-$[PtCl_2(PPhCy_2)_2]$	−3952		
Sym. *trans*-$[Pt_2Cl_4(PMe_3)_2]$	−3410	7	118
Sym. *trans*-$[Pt_2Cl_4(PBu_3)_2]$	−3404	15	131
Sym. *trans*-$[Pt_2Cl_4(PBz_3)_2]$	−3481		165
Sym. *trans*-$[Pt_2Cl_4(PCy_3)_2]$	−3467		170
Sym. *trans*-$[Pt_2Cl_4(PPhCy_2)_2]$	−3518		*ca.* 162
cis-$[PtCl_2(PMe_3)_2]$	−4408	7	118
cis-$[PtCl_2(PBu_3)_2]$	−4448	7	131
Unsym. *cis*-$[Pt_2Cl_4(PBz_3)_2]$	−3870		165
Unsym. *cis*-$[Pt_2Cl_4(PCy_3)_2]$	−3837	two isomers	170
	−3892		
Unsym. *cis*-$[Pt_2Cl_4(PPhCy_2)_2]$	−3897	two isomers	*ca.* 162
	−3883		
Unsym. *cis*-$[Pt_2Cl_4(PPh_2C_6F_5)_2]$	−3992		158
Sym. *trans*-$[Pt_2Br_4(PMe_3)_2]$	−3985	7	118
Sym. *trans*-$[Pt_2I_4(PMe_3)_2]$	−5297	7	118
Sym. *trans*-$[Pt_2Cl_4(AsMe_3)_2]$	−3034	7	–
Sym. *trans*-$[Pt_2Br_4(AsMe_3)_2]$	−3701	7	
Sym. *trans*-$[Pt_2I_4(AsMe_3)_2]$	−5212	7	–

[a]Values of the ligand cone-angle θ, from ref. 12.

[12]. However, in complexes of mononuclear product of the type $[PtX_2(PR_3)_2]$, the *trans/cis* ratio is generally favored by bulkier PR_3 and by iodide over chloride, and in less polar solvents and by benzene over chloroform. The most remarkable features of the spectra are the $^1J(^{195}Pt-^{31}P)$ coupling constants in both *cis* and *trans* dimer isomers. The $^1J(^{195}Pt-^{31}P)$ couplings found here for dimeric complexes are in the range typical of halogen-binuclear species containing tertiary phosphines, *i.e.* sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PBu_3)_2]$, ^1J 3820 Hz [13–15], sym. *trans*-$[Pt_2(\mu\text{-}I)_2(I)_2(PBu_3)_2]$, ^1J 3528 Hz [9], and for sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PMe_2Ph)_2]$ ^1J 3931 Hz (16). Unfortunately the $^1J(^{195}Pt-^{31}P)$ value obtained for sym. *trans*-$[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PCy_3)_2]$, 3760 Hz is different from the reported value, 3875 Hz [3]. The values reported from this work are consistent and related to the cone-angle data and Pt chemical shift. ^1J for PCy_3 complex, 3760 Hz (θ, 170°); PBz_3 complex, 3798 Hz (θ, 165°); PCy_2Ph complex, 3867 Hz (θ, *ca.* 162°); and $PPhMe_2$ complex, 3931 Hz (θ, 122°).

Increasing the size of the substituents on phosphorus will tend to reduce the s character in the phosphorus lone pair, thus decreasing $^1J(M-P)$ [12].

Another interesting point which was investigated is the $^1J_{trans}/^1J_{cis}$ of the dimer. As can be seen from Table IV, the coupling constant for the *trans* isomer is *ca.* 1.26 times that for the *cis* isomer. The values show some solvent dependence, but in the same solvent the *trans* isomer displays a coupling 650–740 Hz greater than the *cis* form. The values reflect dependence on the halogen bridges. However, tetrahalides have considerably lower couplings than the corresponding coupling constants for their dichlorobis(organo)-counterparts. Thus, $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ shows coupling ^1J *cis* 5420 Hz and ^1J *trans* 5310 Hz [8]. It has been suggested that the high *trans*-influence of terminal organic groups could cause bridge weakening and thus affect the value of ^1J(Pt–P) [17]. Alternatively, these variations may reflect the differing *cis*-influence of terminal organo and chloro ligands. This view is consistent with the near equality of the ^1J(Pt–P) values for *cis* and *trans* isomers of the organo-phosphorus dimer [8] and a great difference in the absence of these organic groups, as in the case in tetrahalide bridges.

It is worth noting that the coupling constant (^1J) for the *trans* isomer is greater than that of the *cis* form. This was expected, in term of *trans* influence of phosphine ligand to one halogen atom of the bridge (in the *cis* form), which may be transmitted to the other phosphine ligand *trans* to this halogen and contribute to some extent in the weakening the Pt–P bond. This is similar to ^1J of the *trans* mononuclear compound with less effect.

Further evidence supporting the assignment of *cis*/*trans* dimetallic isomers, comes from the ^{195}Pt NMR data. The ^{195}Pt chemical shifts shown in Table I range between 3992 to 3837 ppm in the *cis* isomer and between 3518 to 3467 ppm in the *trans* form upfield (lower frequency) for Na_2PtCl_6.

In general, there is a dependence of δ^{195}Pt on complex geometry. For $[PtX_2L_2]$ types, where X is a relatively hard ligand such as Cl^-, and L = PR_3, the *cis* complex is upfield of the *trans* analog by 400–500 ppm [18, 19]. The bridging chloride ion in $[Pt_2Cl_4(PR_3)_2]$ does seem to result in a somewhat higher platinum chemical shift (downfield) than in the equivalent terminal complexes $[PtCl_2(PR_3)_2]$. A similar observation was reported in dimeric complexes of the type $[Pt_2X_4(PMe_3)_2]$ and $[Pt_2X_4(AsMe_3)_2]$, X = Cl, Br or I [19], see Table V. These results indicate that the effect of a bridging halide on δ Pt is less than for a terminal halide. Thus the unsym. *cis* complex is upfield of the sym. *trans* analog by 365–390 ppm (Table V).

Experimental

General

^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded at 40.27 and 21.37 MHz, respectively, on a JEOL JNM FX-100 Fourier transform [FT] instrument with a 10 mm tunable probe, 16 K data points and internal lock on solvent deuterium. All the spectra were recorded at ambient temperature 25 °C.

The compounds were studied for 0.107 and 0.24 M solutions in $CDCl_3$ and C_6D_6. Chemical shift data for ^{31}P and ^{195}Pt NMR spectra were determined relative to 85% H_3PO_4 (external), more positive values representing deshielding for phosphorus-31 and relative to Na_2PtCl_6 (aq) for platinum-195.

Starting Materials

$PtCl_2$(COD) was prepared by the method of Drew and Doyl [20].

PtI_2(COD) was prepared by adding a very slight excess of iodine to the colorless acetone solution (10 ml) of $PtCl_2$(COD) complex. The intense color of the iodine immediately disappeared and a yellow solution was obtained. The solvent was removed under vacuum to give a yellow solid. Excess iodine was removed by washing the product with a small volume of CCl_4. Phosphine ligands were obtained from Strem Chemicals and Winlab Comp.

Reactions of [PtX_2(COD)] (X = Cl or I) were performed as follows

To a solution of $[PtX_2(COD)]$ (0.08 or 0.16 g) in $CDCl_3$ (or C_6D_6) (2 ml) in a 10 mm NMR tube was added the proper ligand, PR_3, in 0.5, 1, 2 and 3 mol equivalents. It was well shaked (1 min) and then the NMR spectra were recorded immediately for each addition.

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