

# SYNTHESIS, REACTIVITY AND REDISTRIBUTION REACTIONS OF HOMO- AND HETERO-BINUCLEAR PALLADIUM(II) AND PLATINUM(II) COMPLEXES

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Homo- and hetero-binuclear complexes of the type  $[MM'(\mu-x)(\mu-y)Z_2L_2]$  ( $M = M' = \text{Pt or Pd}$ ;  $M = \text{Pt}, M' = \text{Pd}$ ;  $X = Y = \text{Cl}, SR$ ;  $X = \text{Cl}, X = SR'$ ;  $Z = \text{Cl}, \text{SnCl}_3$ ,  $R, L = \text{tertiary phosphine}$ ) have been synthesized and characterized. The complex  $[\text{Pt}_2\text{Me}_2(\mu-\text{Cl})_2(\text{PMe}_2\text{Ph})_2]$ , reported earlier as *cis* isomer, has been shown to be a mixture of *cis* and *trans* isomers. The bridge cleavage reactions employing various donor ligands have been studied. These reactions give various products depending on the nature of  $X, Y, Z$  and  $L$ . The heterobinuclear complexes tend to symmetrize to give homo-binuclear complexes. These reactions proceed via a tetranuclear reaction intermediate of the type  $[M_2(\mu-x)_2Z_2L_2M'(\mu-y)_2Z_2L_2]$ . When  $X = Y = \text{Cl}$  redistribution is fast at NMR time scale. The catalytic activity of some of these complexes in presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as co-catalyst in homogeneous hydrogenation and hydroformylation has been described. The complexes  $[\text{Pt}_2(\mu-SR')(\mu-\text{Cl})\text{Cl}_2(\text{PR}_2)_2]$  show fairly high catalytic activity.

**Key Word :** Homo-binuclear Complexes; Hetero-binuclear Complexes; Homogeneous Catalysis; Heterogeneous Catalysis; Binuclear Palladium(II) and Platinum(II) Complexes

## INTRODUCTION

THE last 15 years have seen the arrival of a new wave of inorganic and organometallic compounds, which contain two or more, alike or different, metal centres. The interest in such molecules is primarily two-fold :-

- (i) To study the chemistry, spectroscopic properties, reactivity patterns of these molecules and their structural features.
- (ii) Homogeneous catalysis by such molecules is of interest. The surface reactions in heterogeneous catalysis are believed to involve bi- and poly-nuclear intermediates. Hence, the bi- and poly-nuclear metal complexes can serve as models for the proposed intermediates in heterogeneous catalysis and can possibly be used for the preparation of supported poly-metallic heterogeneous catalysts. Heterobinuclear complexes are expected to show unique reactivity features as a result of combining the different reactivity properties of the constituent metals.

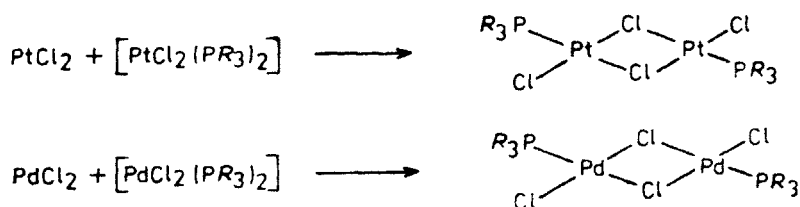
These molecules have either of the following features :—

- (a) They may have metal-to-metal bond which may be supported with bridging ligand or unsupported. The metal-to-metal bond may be integral (1, 2, 3 or 4) or fractional ( $1/2$ ,  $3/2$ ,  $5/2$  or  $7/2$ ), localized or delocalized as in poly-nuclear metal carbonyls.
- (b) Complexes having no metal-to-metal bond but stabilized through bridging ligands, like Cl, Br, I, SCN, N<sub>3</sub>, H, CH<sub>2</sub>, SR, S, PR<sub>2</sub>, ligands having small bite (dppm, bis(diphenyl-phosphino)methane).

The chemistry of category (a) compounds of platinum group metals is underway in our laboratory. The author here has concentrated on the complexes of category (b) of palladium(II) and platinum(II).

### RESULTS AND DISCUSSION

The chloro-bridged compounds of platinum and palladium are very well known<sup>1-3</sup> and have been proved to be excellent starting materials for a large number of preparations. They can simply be prepared by the following reactions.



These molecules usually have symmetrical *trans* structure, from x-ray structural analyses.<sup>4,5</sup> However, in some cases existence of both *cis* and *trans* isomers in solution has been demonstrated.<sup>6</sup>

One would expect heterobimetallic complex if one of the reactants in the above reactions is interchanged. Thus treatment of  $[\text{PtCl}_2(\text{PR}_3)_2]$  with  $\text{PdCl}_2$  or  $[\text{PdCl}_2(\text{PR}_3)_2]$  with  $\text{PtCl}_2$  in refluxing xylene gives an orange crystalline solid readily soluble in dichloromethane, chloroform, benzene, toluene or xylene. The infrared spectra of these complexes displayed vibrations assignable to both terminal Pt-Cl, Pd-Cl and bridging Pt-Cl and Pd-Cl modes.<sup>7</sup>

The <sup>31</sup>P NMR spectra display four phosphorus resonances two of them showing platinum-195 couplings assigned to platinum bound phosphorus and the other two to palladium bound phosphorus (Fig. 1). Similarly, the platinum-195 NMR spectra display two doublets (Fig. 2) suggesting the presence of two platinum species in solution. From these data one can conclude that, as has been reported for  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PPh}_3)_2]$ ,<sup>6</sup> two isomers *cis* and *trans* exist in solution.

The structure of one compound has been established by X-ray diffraction data.<sup>7</sup> The structure of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$  consists of discrete molecules of the binuclear complex. The molecule lies at the inversion centre that demand



FIG 1  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{PBu}_3\text{ClPd}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$  in  $\text{CDCl}_3$

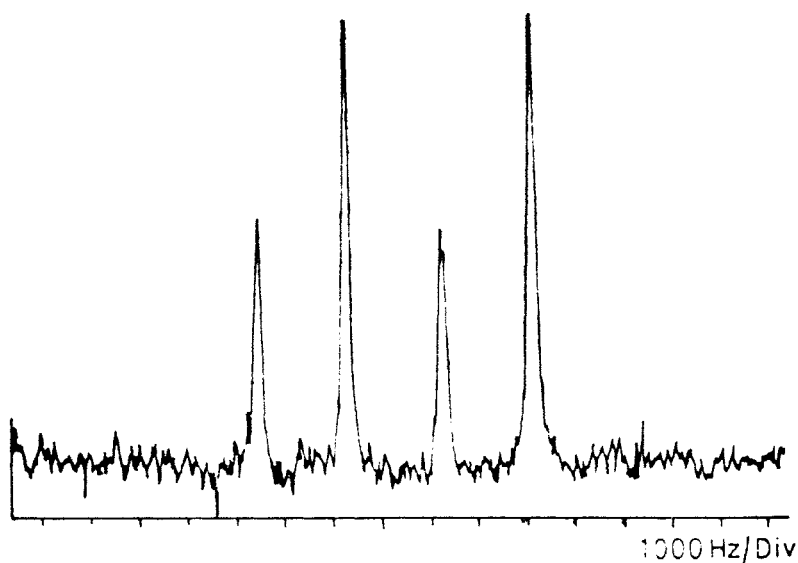


FIG 2  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectrum of  $[(\text{PBu}_3)\text{ClPd}(\mu\text{-Cl})_2\text{PtCl}(\text{PBu}_3)]$

equal disorder of the Pd and Pt atoms. The geometry around the metal atom is slightly distorted square planar (Fig. 3). Because of the disorder of the Pd and Pt atoms we cannot distinguish between Pd-Cl and Pt-Cl dimensions nor between Pd-P and Pt-P distances.

We were puzzled when we noticed that the ratio of our *cis* and *trans* isomers does not change with temperature ( $-70$  to  $+80$  °C) nor with the nature of tertiary phosphine ligands. On careful examination of the  $^{31}\text{P}$  NMR spectra and on comparing these spectra with those of the homo-binuclear ( $\text{Pd}_2$  and  $\text{Pt}_2$ ) complexes we found that two of the observed peaks (one with platinum satellites and one without) are attributable to the homo-binuclear complexes, leaving expected two resonances for hetero-binuclear complexes. This suggests that the heterometallic complexes disproportionate readily in solution to establish the equilibrium :

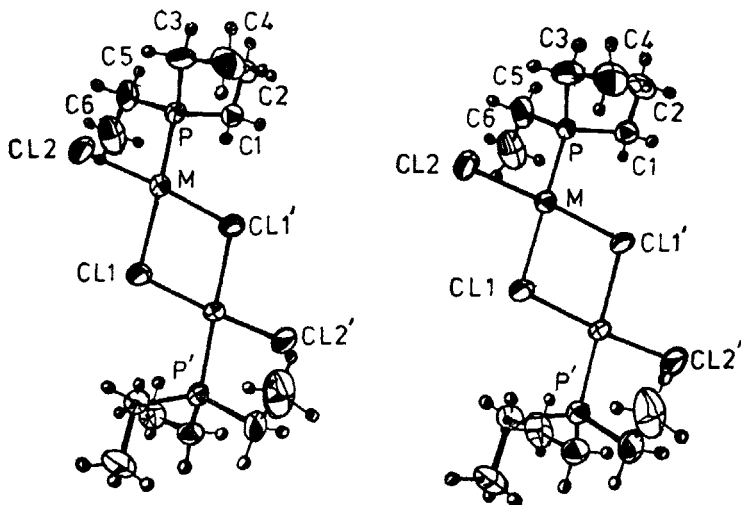


FIG 3 X-ray structure of  $[(PEt_3)_2ClPd(\mu-Cl)_2PtCl(PEt_3)]$



This was confirmed by mixing chloroform solutions containing equimolar amounts of  $[Pd_2Cl_4(PR_3)_2]$  and  $[Pt_2Cl_4(PR_3)_2]$ , to generate a  $^{31}P$  NMR spectrum identical with that observed with a solution of the hetero-bimetallic complex. In both cases, therefore, the three species described by the above equilibrium appear to be present in 2.2 : 1 : 1 ratio.

The mass spectra of  $[Pd_2Cl_4(PEt_3)_2]$ ,  $[Pt_2Cl_4(PEt_3)_2]$ ,  $[PdPtCl_2(\mu-Cl)_2 (PEt_3)_2]$  and a mixture of  $[Pd_2Cl_4(PEt_3)_2]$  and  $[Pt_2Cl_4(PEt_3)_2]$  were recorded at 225 °C. At this temperature palladium dimer did not show any reasonably defined isotopic pattern while the platinum dimer displayed an intense peak at  $m/e$  768 with an isotopic pattern corresponding to the calculated. The heterobimetallic dimer displayed two peaks in the region  $m/e$  660-780 with the isotopic patterns corresponding to heterobimetallic dimer and diplatinum complex. In fact, the total spectrum thus obtained for this complex was identical with that obtained from equimolar mixture of  $Pt_2$  and  $Pd_2$  complexes. Since all of these dimers melt with decomposition in the range 217-230 °C, it appears that such decomposition occurs in the mass spectrometer (225 °C) prior to electron impact. Accordingly, the mass spectra of these dimers were recorded at 70 °C by the field desorption method in chloroform (Fig. 4). The intensities for homobinuclear complexes differ considerably from each other, which could be due to different ionization efficiencies of two dimers. The mass spectral data do confirm the existence of heterobimetallic complex but they do not provide evidence as to whether the original solid consists of pure complex that then disproportionates or alternatively consists of heterobimetallic complex together with equimolar amounts of  $Pd_2$  and  $Pt_2$  complexes. Solid state  $^{195}Pt$  NMR data might show such differentiation,

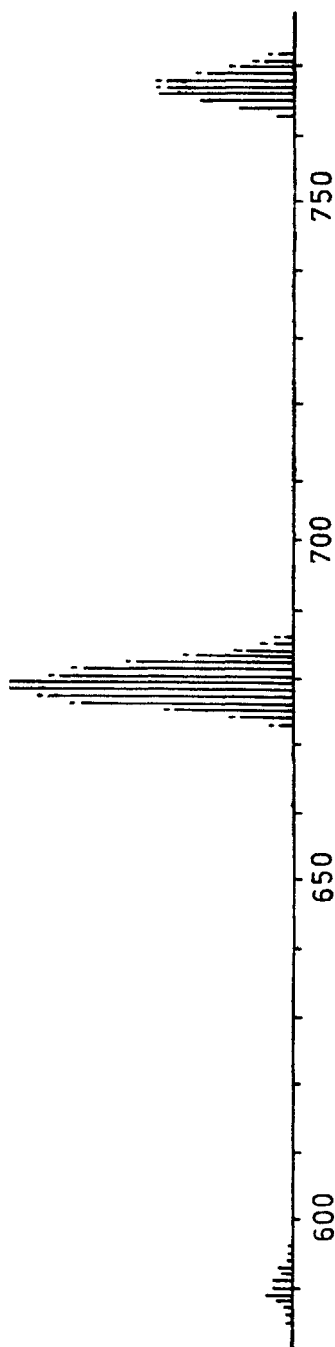
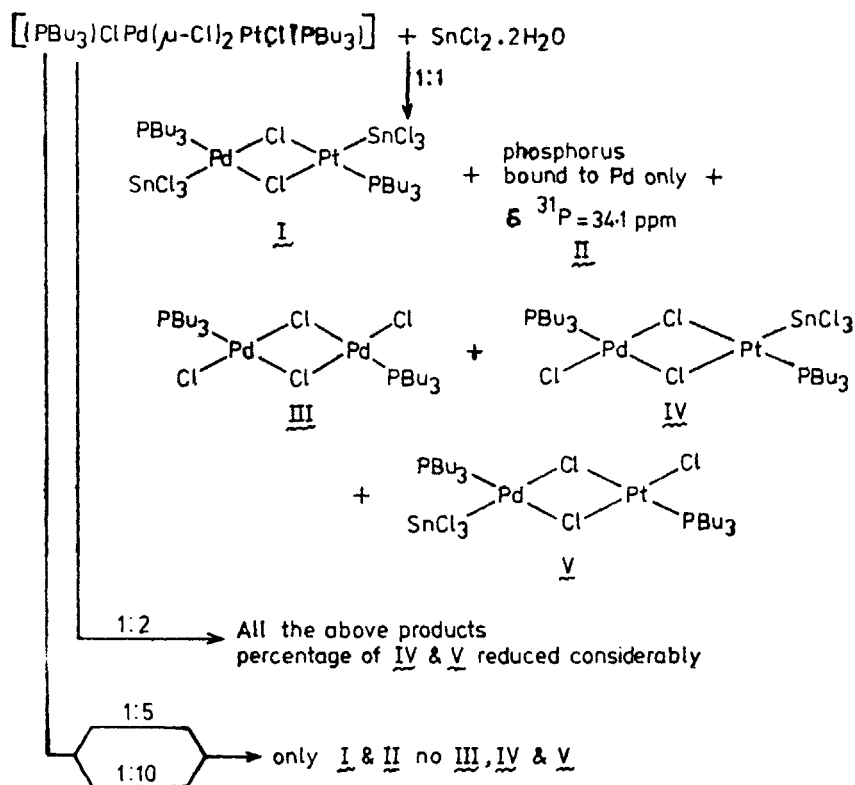


FIG 4 FD Mass spectrum of  $[(PEt_3) ClPd(\mu-Cl)_2 PtCl(PEt_3)]$  at  $70^\circ C$

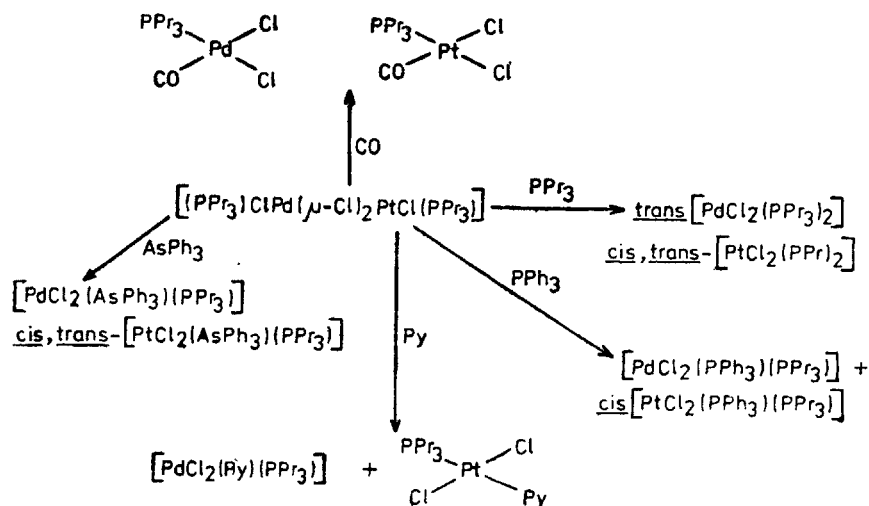
however, we found that line widths are too great to distinguish between PdPt and Pt<sub>2</sub> species.

In order to understand the nature of these species we carried out a large number of reactions and in most cases <sup>31</sup>P NMR spectroscopy was employed to follow the course of reactions as well as to determine the geometry of the products. The reaction of [PdPtCl<sub>2</sub>(μ-Cl)<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] with SnCl<sub>2</sub>·2H<sub>2</sub>O in various stoichiometries in dichloromethane has been carried out and products have been identified where possible by comparison of the observed chemical shifts and coupling constants with those previously reported for complexes. Reactions with 1 : 1 and 1 : 2 stoichiometry (Scheme 1) appear to be complex and give at least 5 phosphorus containing species. Reactions in 1 : 5 or 1 : 10 (PdPt/Sn) stoichiometry appear to be completed, as they give identical spectra showing the presence of I and II only.



SCHEME 1

Reaction with carbon monoxide results in 100 per cent conversion to mononuclear products in which each metal atom contains one phosphine ligand (Scheme 2). Similar reaction with pyridine yields palladium and platinum mononuclear complexes. Treatment with tertiary phosphines or arsines gives mononuclear complexes; the platinum complex having *cis* or *trans* geometry.

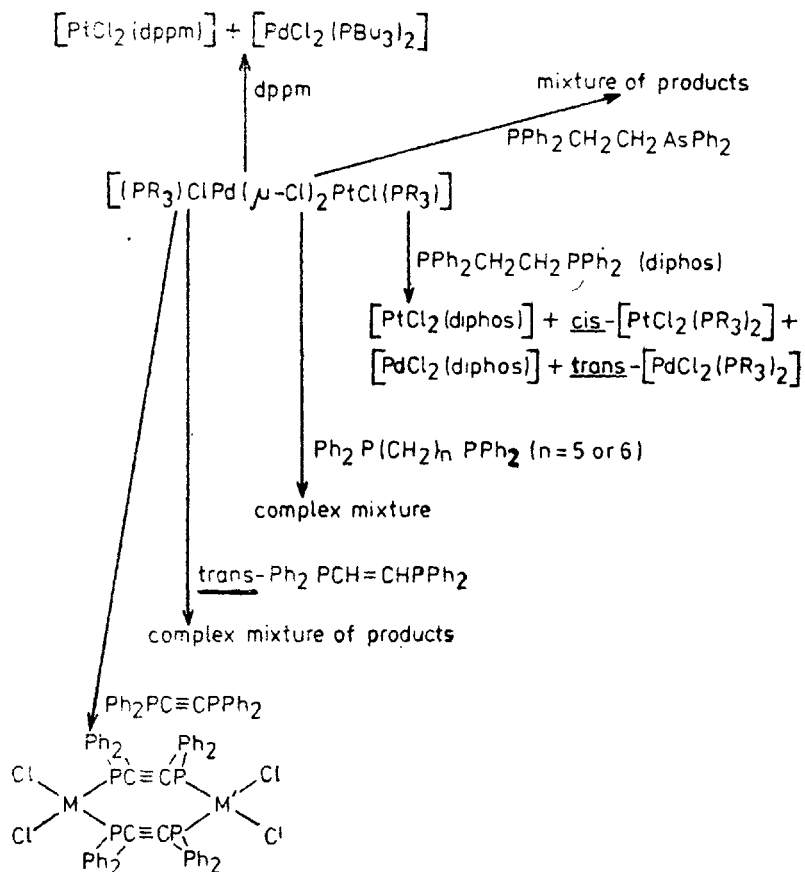


SCHEME 2

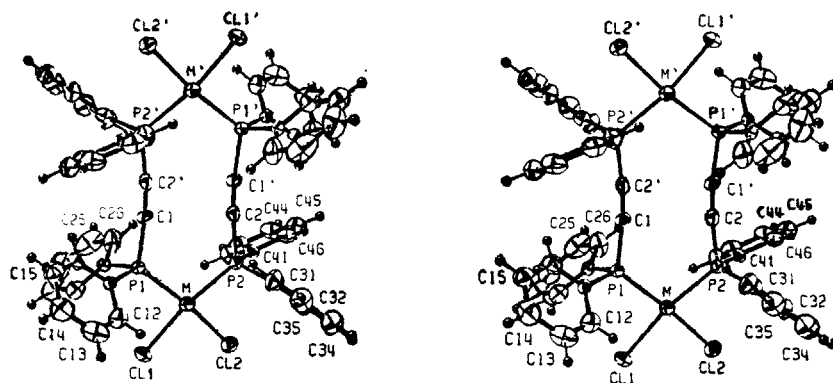
Reaction of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  with ditertiary phosphines were complex and variety of products were formed (Scheme 3). Treatment with diphos [bis(diphenylphosphino)ethane] results in the formation of mono-nuclear complexes. *Trans*-1,2-bis(diphenylphosphino)ethylene and 1,2-bis(diphenylphosphino)acetylene, in which the rigidity of the unsaturated carbon back bone forces two phosphorus atoms to remain too far apart and coordinate to single metal atom, were allowed to react with  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  to prepare heterobimetallic complexes by bridge cleavage reactions. With *trans*-1,2-bis(diphenylphosphino)ethylene a complex mixture of products including a heterobimetallic complex formed; attempted separation was unsuccessful. However, with bis(diphenylphosphino)acetylene, a yellow crystalline product was isolated whose crystal structure was determined (Fig. 5). The product crystallizes as the bis-(chloroform) solvate two molecules in the unit cell.<sup>8</sup> Molecules lie about inversion centres that demand equal disorder of both Pd and Pt atoms in the centrosymmetric dimer. The results of the crystal structure can be analysed as :-

- (i) The heterobimetallic complex has formed with equal disorder of Pd and Pt.
- (ii) No heterobimetallic molecules are formed and crystal contains *equal* amounts of disordered Pd-Pd and Pt-Pt dimers.
- (iii) Some heterobimetallic molecules are formed and both Pd-Pd and Pt-Pt dimers are present in *equal* amounts but disordered to scramble Pd and Pt equally in the solid state.

Spectral data,  $^{31}\text{P}\{^1\text{H}\}$  (Fig. 6) and  $^{195}\text{Pt}\{^1\text{H}\}$  (Fig. 7) NMR, lead us to believe that case (iii) is the more likely situation in solution, but in the solid state, no unambiguous distinction could be drawn among *i-iii*.



SCHEME 3

FIG 5 Stereoview of  $[\text{Cl}_2\text{Pd}(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)_2\text{PtCl}_2]$



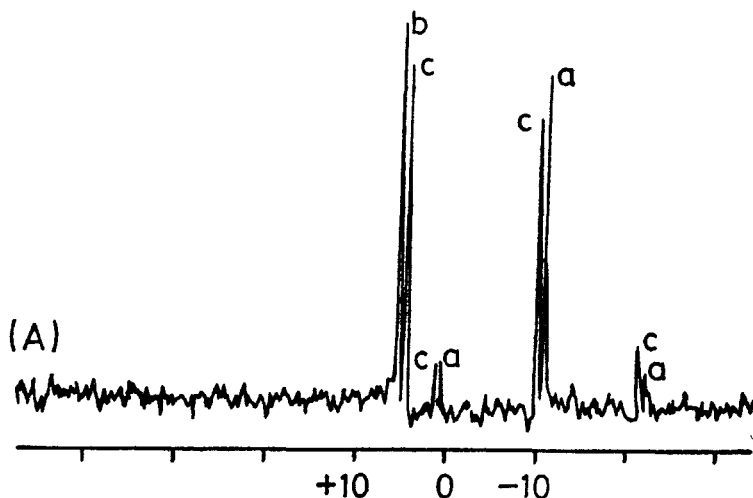


FIG 6  $^{31}\text{P}$  NMR spectrum of  $[\text{Cl}_2\text{Pd}(\text{Ph}_2\text{PC}\equiv\text{CPh})_2 \text{PtCl}_2]$

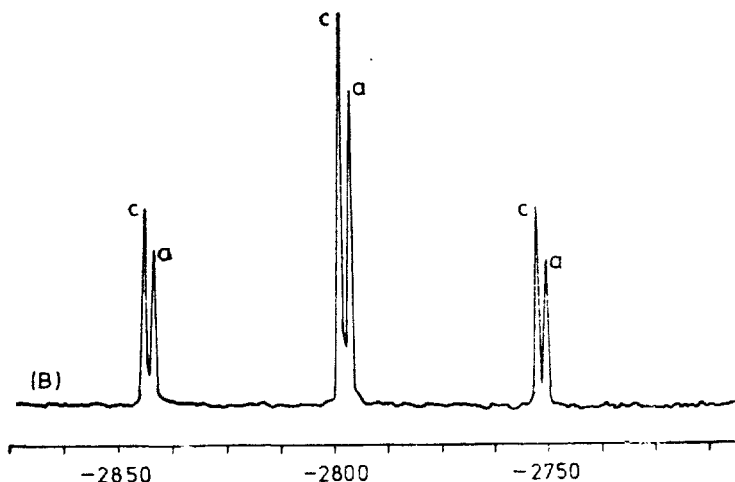
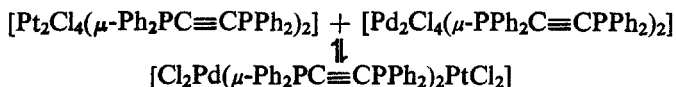



FIG 7  $^{195}\text{Pt}$  NMR spectrum of  $[\text{Cl}_2\text{Pd}(\text{Ph}_2\text{PC}\equiv\text{CPh})_2 \text{PtCl}_2]$

Identical spectra were obtained when equimolar amounts of  $[\text{Pt}_2\text{Cl}_4(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh})_2]$  and  $[\text{Pd}_2\text{Cl}_4(\mu\text{-PPh}_2\text{C}\equiv\text{CPh})_2]$  were mixed in chloroform solution suggesting disproportionation in solution.



Reactions of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  with neutral bidentate nitrogen ligands (capable of bridge cleavage) have also been studied.<sup>9</sup> Thus reaction of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  ( $\text{PR}_3 = \text{PBu}_3$ ) with 4-cyanopyridine in 1 : 1 stoichiometry in dichloromethane solution gave quantitative yields of hexane insoluble

$[\text{Pd}_2\text{Cl}_4(\text{PBU}_3)_2]$  and hexane soluble *trans*- $[\text{PtCl}_2(\text{PBU}_3)(4\text{-CNpy})]$ . This suggests that reaction occurs preferentially at the Pt  Pt bridge and consumption of this species causes further disproportionation of the heterobimetallic complex.

Contrary to the reactions discussed so far, only products containing Pd and Pt in a 1 : 1 ratio were obtained in the reactions of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  with bis(1-pyrazolyl)methane or with N,N'-dialkyl-1,2-diiminoethanes (Scheme 4). Treatment of  $[\text{PdPtCl}_2(\mu\text{-Cl})_2(\text{PMe}_2\text{Ph})_2]$  with bis(1-pyrazolyl)methane in dichloromethane affords a yellow crystalline product of composition  $[(\text{PMe}_2\text{Ph})\text{Cl}_2\text{Pd}(\text{pz}_2\text{CH}_2)\text{PtCl}_2(\text{PMe}_2\text{Ph})]$  in which pyrazolyl rings provide the bridge between the two metal centres. The  $^{31}\text{P}$  NMR spectrum of this complex shows three resonances, two of which display  $^{195}\text{Pt}$  satellites.<sup>9</sup> This might indicate that two forms of the product exist containing either a *cis* or a *trans* geometry at platinum but the same geometry at Pd in both forms.

Cleavage by N, N'-dialkyl-1,2-diiminoethanes ( $R'\text{N}=\text{CHCH}=\text{NR}'$ ;  $R$  = cyclohexyl or tert-butyl) ( $\text{dim}R'$ ) gives products of composition  $[(\text{PR}_3)_2\text{Cl}_2\text{Pd}(\text{dim}R')\text{PtCl}_2(\text{PR}_3)]$  as stable yellow crystalline solids.<sup>9</sup> The  $^{31}\text{P}$  NMR spectra displayed two resonances of equal intensity, only one of which showed couplings with platinum. The infrared spectra displayed two bands attributable to  $\nu_{\text{C}=\text{N}}$ , only one such band is observed for free ligand.

NMR data do establish that these products preserve 1 : 1 Pt-Pd ratio, while the products might be pure heterobimetallic complexes, each might also be a 1 : 1 mixture of the  $\text{Pt}_2$  and  $\text{Pd}_2$  dimers or mixtures of all three.

The single crystal structure determination of  $[(\text{PBU}_3)_2\text{Cl}_2\text{Pd}(\text{dimBu}^t)\text{PtCl}_2(\text{PBU}_3)]$  (Fig. 8) is consistent with products maintaining the 1 : 1 Pd : Pt ratio.<sup>9</sup> The molecule lies about an inversion centre which demands equal disorder of Pd and Pt atoms, geometry around the metal atom is distorted square planar. Because of disorder of the Pd and Pt atoms, we cannot distinguish between Pd- $X$  and Pt- $X$  dimensions ( $X = \text{Cl}, \text{P}$  or  $\text{N}$ ).

It is not clear as to which ligand cleavage of heterobimetallic species will be asymmetrical. More interestingly the mechanism by which the halobridged heterobimetallic species is converted to a new heterobimetallic complex with different bridging ligand so as to preserve 1 : 1 PtPd ratio is by no means obvious.

Formation of tricoordinate reaction intermediates in *cis*  $\rightleftharpoons$  *trans* isomerization of halogen bridged palladium and platinum complexes has been suggested. Formation of such intermediates is not expected from mercapto bridged complexes as they are stable. Thus when *cis*- $[(\text{PR}_3)_2\text{Pd}_2\text{Cl}_2(\text{SEt})_2]$  and *cis*- $[(\text{PR}_3)_2\text{Pt}_2\text{Cl}_2(\text{SEt})_2]$ <sup>10</sup> were mixed in 1 : 1 stoichiometry in  $\text{CDCl}_3$  at room temperature, no heterobimetallic complex of the type  $[(\text{PR}_3)_2\text{PdPtCl}_2(\text{SEt})_2]$  appeared to be formed as the  $^{31}\text{P}$  NMR spectrum was unchanged over a period of days. However, when an equimolar mixture of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SR})_2(\text{PR}_3)_2]$  and  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  was heated under reflux in benzene chloro-mercapto bridged complexes were isolated.<sup>11</sup>

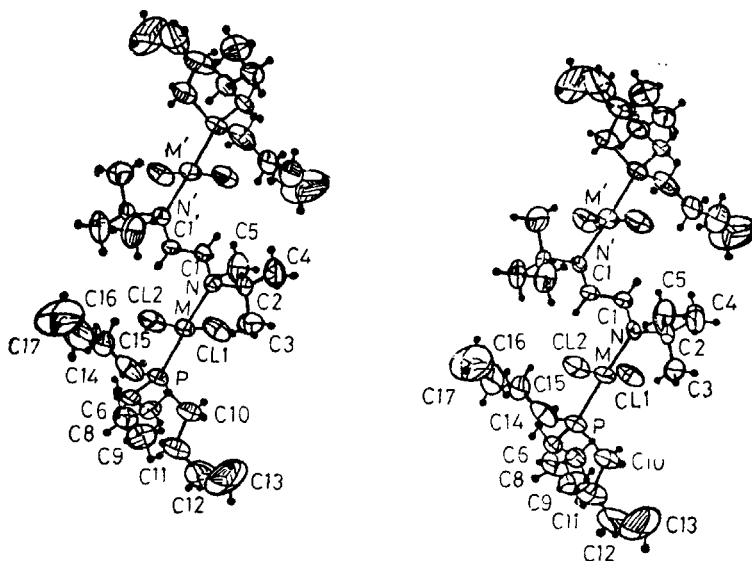


Fig 8 Structure of  $[(PBu_3)_2Cl_2Pd(Bu' N = CHCH = NBu') PtCl_2(PBu_3)_2]$

The reaction was slow in benzene and took 3–5 days for completion, however, in chloroform they were completed within a few hours (4–8). Thus the progress of the reaction of  $[Pt_2Cl_2(\mu-Cl)_2(PPR_3)_2]$  with *trans*- $[Pt_2Cl_2(SPr^t)_2(PPR_3)_2]$  in benzene- $d_6$  was monitored at room temperature by  $^{31}P$  NMR spectroscopy. The spectrum obtained immediately after mixing displayed resonances attributable to two molecular species, none of them belonging to the starting dimers of the two species, the one present in small amounts can be identified as the redistribution product  $[Pt_2Cl_2(\mu-Cl)(\mu-SPr^t)(PPR_3)_2]$  and the other one was a reaction intermediate with complex  $^{31}P$  NMR pattern (Fig. 9). The latter resonances gradually reduced in their intensities and finally disappeared after 72 hrs leaving only  $[Pt_2Cl_2(\mu-Cl)(\mu-SPr^t)(PPR_3)_2]$  as the final product.<sup>11</sup>

The observed pattern for the intermediate can be interpreted as originating from a tetranuclear species (Fig. 10) formed by interaction of dichloro- and dimercapto-bridged dinuclear platinum complexes. The spectrum showed following interesting features.

- (i) Shielding of the  $^{31}P$  NMR chemical shifts for the two interacting dimers of the tetranuclear species has been observed compared to the free dimers.
- (ii) Small couplings ( $^4J(P-P) = \sim 5\text{Hz}$ ) between phosphorus nuclei of two dimers have been observed.
- (iii) The  $^1J(Pt-P)$ ,  $^3J(Pt-P)$  and  $^4J(P-P)$  have been reduced for mercapto bridged dimer while for chloro-bridged dimer the magnitude of these couplings has increased.

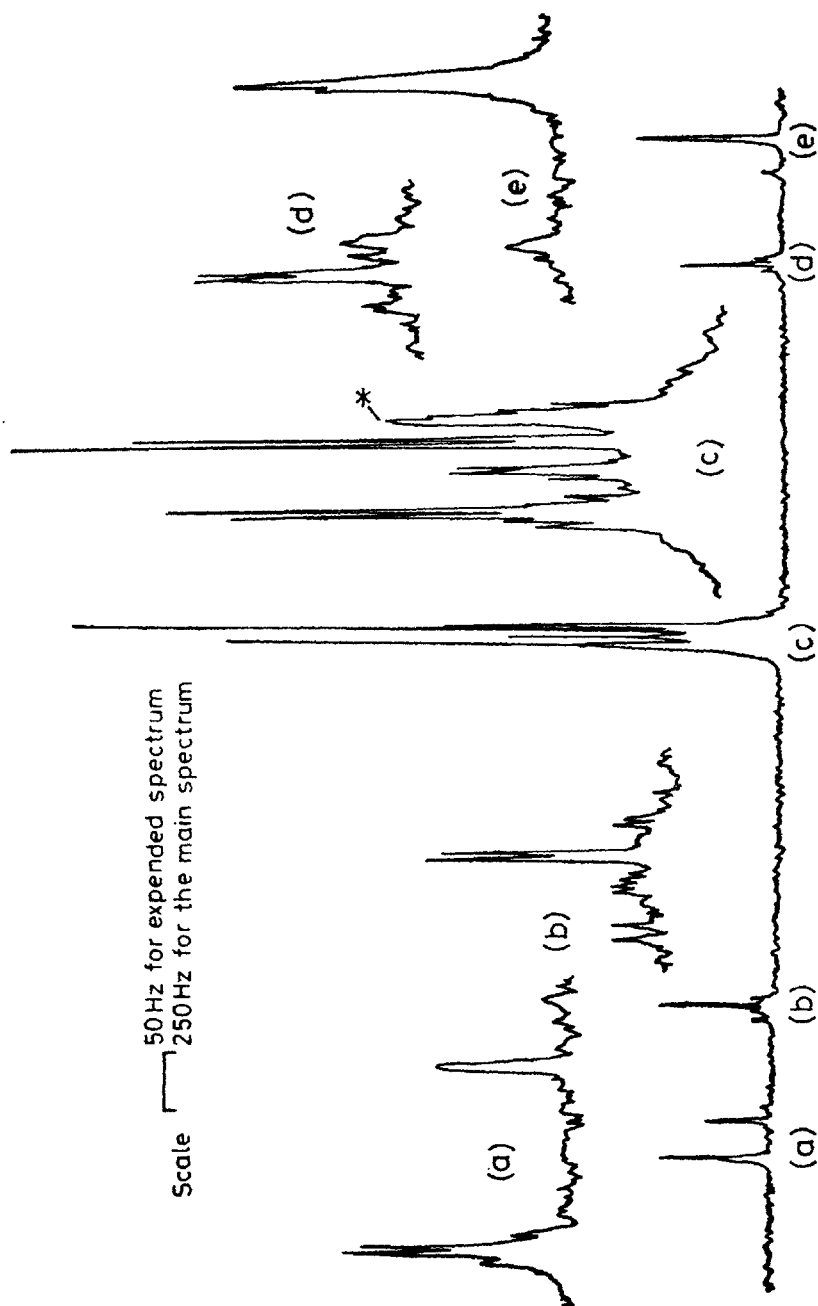


Fig 9  $^{51}\text{P}$  NMR spectrum of  $[\text{Pt}_3\text{Cl}_3(\mu\text{-Cl})_3(\text{PPR}_3)_3]$  and  $[\text{Pt}_2\text{Cl}(\mu\text{-SPR}')_2(\text{PPR}_3)_2]$  in  $\text{C}_6\text{D}_6$ , obtained immediately after mixing

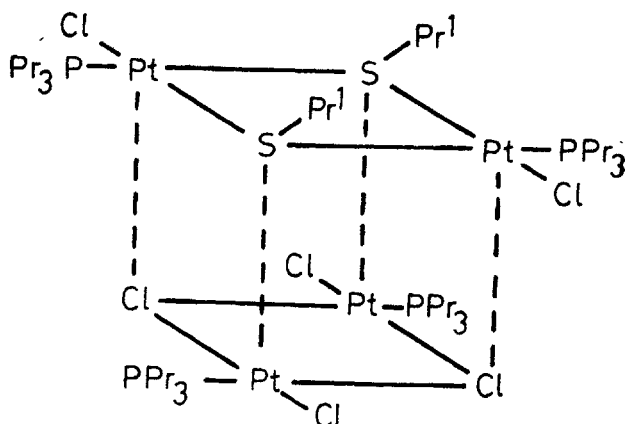


FIG 10 Tetranuclear reaction intermediate

The changes in coupling constants reflect the changes in bonding. Accordingly the bridging Pt-Cl bond *trans* to phosphine in the chloro bridged dimer and Pt-S bond *trans* to chloride in mercapto bridged dimer of the tetranuclear intermediate weaken and finally after their cleavage afford stable dinuclear platinum complexes containing both chloro and mercapto bridges. We believe that such intermediates are involved in *cis*  $\rightleftharpoons$  *trans* isomerization of dinuclear platinum(II) complexes.

The spectroscopic data are consistent with the *cis*-phosphine geometry. The crystal structure of two compounds,<sup>12,13</sup> viz.,  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SEt})(\text{PMe}_2\text{Ph})_2]$  (triclinic, space group P1; a, 9.219; b, 13.644; c, 10.907 Å;  $\alpha$ , 91.90;  $\beta$ , 118.74;  $\gamma$ , 87.20° with  $Z = 2$ ) and  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SEt})(\text{PMe}_3\text{Ph})_2]$  (triclinic,  $\text{P}\bar{1}$ ) are in progress.

The chloro-mercapto bridged dinuclear platinum complexes adopt a *trans* geometry when terminal X ligand have sufficiently strong *trans* influence like trichloro stannate. The  $^{31}\text{P}$  NMR spectra of  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-Cl})(\mu\text{-SR})(\text{PR}_3)_2]$ <sup>11</sup> displayed two phosphorus resonances attributable to phosphine ligand *trans* to bridging chloride and bridging mercapto group. The spectra showed following remarkable features :

- (i) The  $^3\text{J}(\text{Pt-P})$  for the ligand *trans* to chloride is smaller (11.5Hz) than that of the ligand *trans* to  $\text{SR}'$  ( $\sim 33\text{Hz}$ ).
- (ii) The  $^4\text{J}(\text{P-P})$  for the ligand *trans* to chloride is slightly higher than that of the *trans*  $\text{SR}'$  ligand. This indicates that  $^3\text{J}(\text{Pt-P})$  and  $^4\text{J}(\text{P-P})$  couplings take place *via* two independent routes (one *via* Cl and other *via*  $\text{SR}'$ ) and their magnitudes reflect the bond strength, the Pt-Cl-Pt being slightly longer than the one observed in  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ .

The redistribution reaction which gives chloromercapto bridged dinuclear platinum complexes can be employed for the synthesis of dipalladium and hetero-bimetallic complexes.

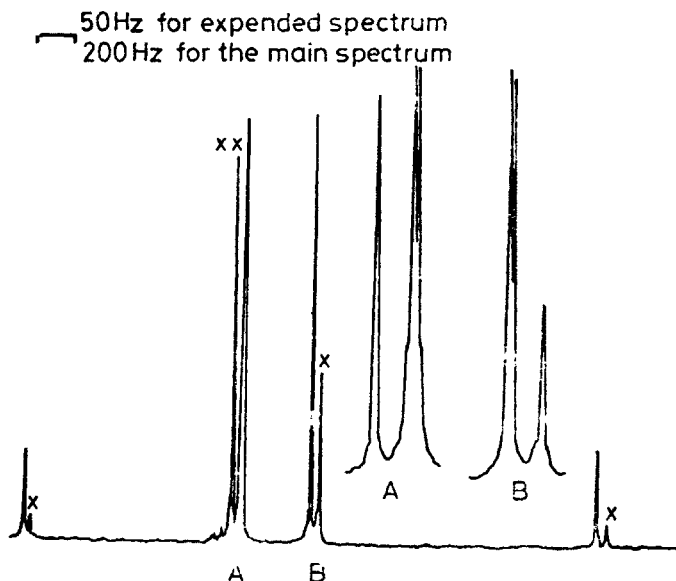


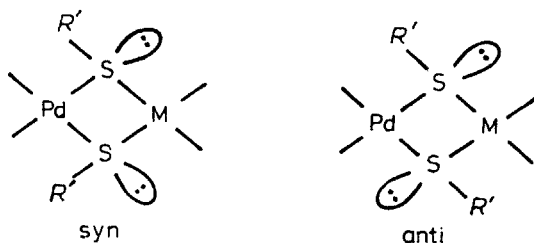
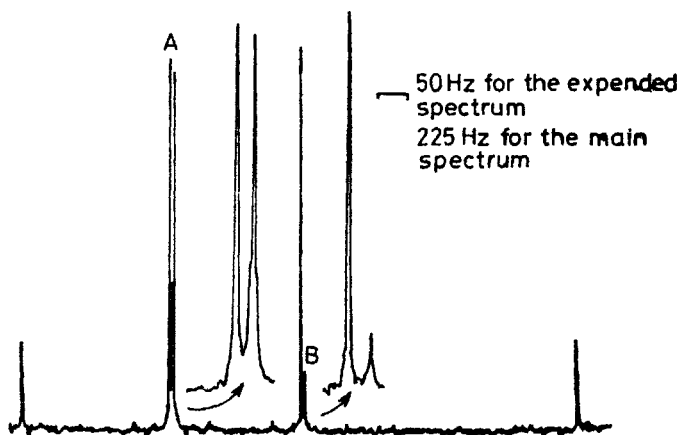
Fig 11  $^{31}\text{P}$  NMR spectrum of  $[\text{PdPtCl}_2(\mu\text{-SEt})_2(\text{PPr}_3)_2]$

The reaction of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SR}')_2(\text{PR}_3)_2]$  with  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$  was extremely slow and could not complete over a period of few weeks at room temperature. However, when dimercapto palladium compound was used as  $\text{SR}'$  group carrier, redistribution was complete in two-three hours at room temperature giving all three ( $\text{Pd}_2$ ,  $\text{PtPd}$ ,  $\text{Pt}_2$ ) dimers. Unlike chloro-bridged compounds their relative abundance can be altered by recrystallizations but in no case the products were free from symmetrical species.<sup>14</sup>

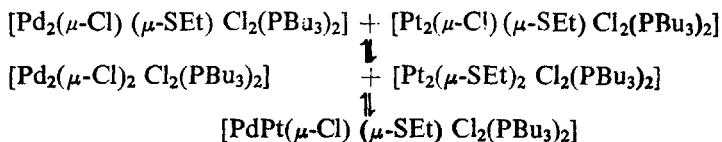
Treatment of these complexes with  $\text{R}'\text{SH}$  in acetone gives stable heterobimetallic dimercapto bridged complexes whose spectra remain unchanged over a period of few days. Because of non-equivalence, resonances for  $\text{Pd-P}$  and  $\text{Pt-P}$  in  $\text{PdPt}$  complexes appeared as a doublet ( $^4\text{J}(\text{P-P}) = 6\text{Hz}$ ) (Fig. 11) and the palladium-bound resonance showed  $^3\text{J}(\text{Pt-P})$  of the order of 12–19Hz suggesting *cis* geometry for these complexes.

The dimercapto bridged complexes may exist in *syn* and *anti* configurations (Fig. 12) depending on the rearrangement of  $\text{R}'$  groups with respect to each other. Isomerization of *syn* and *anti* forms is usually fast and involves inversion at sulphur atom. Possibly due to such a fast inversion process we could not detect *syn* and *anti* forms by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy and also no CD bands for heterobimetallic complex could be observed in the CD spectra, inspite of chiral sulphur centres.<sup>10,14</sup>

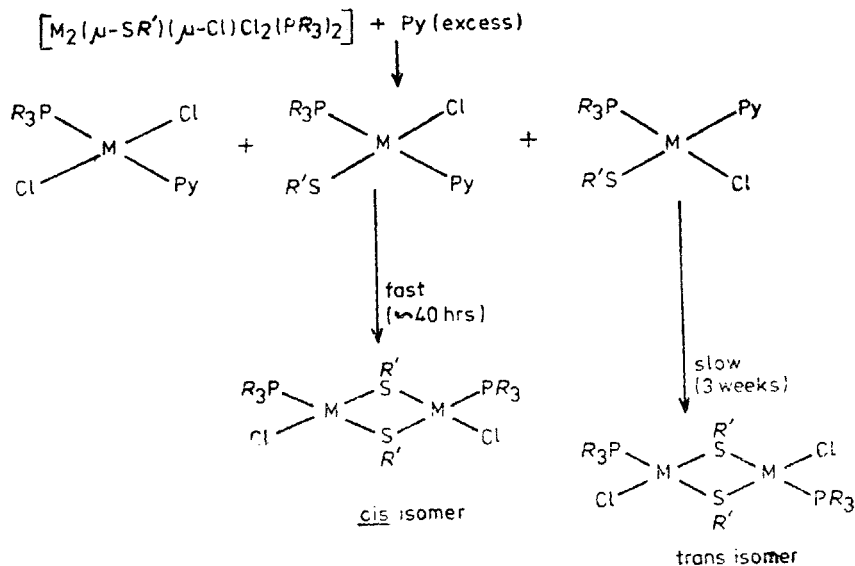
The  $^{31}\text{P}$  NMR spectra of chloro-mercaptopto bridged heterobimetallic complexes displayed resonances for all the three species (Fig. 13). The  $^4\text{J}(\text{P-P})$  appears to be vanishingly small, in some cases  $^3\text{J}(\text{Pt-P})$  ( $\sim 7\text{Hz}$ ) could be resolved.

FIG 12 *syn* and *anti* isomersFIG 13  $^{31}\text{P}$  NMR spectrum of  $[\text{PdPt}(\mu\text{-SPr}')(\mu\text{-Cl})\text{Cl}_2(\text{PPr}_3)_2]$  in  $\text{CDCl}_3$ 

The reaction between  $[\text{Pd}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PBu}_3)_2]$  and  $[\text{Pt}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PBu}_3)_2]$  in chloroform was investigated with the hope that redistribution of these dimers would yield chloro-mercapto bridged heterobimetallic complex quantitatively. A  $^{31}\text{P}$  NMR spectrum obtained just after mixing  $\text{CDCl}_3$  solutions of these dimers in 1 : 1 stoichiometry, showed two additional resonances assignable to  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PBu}_3)_2]$  and  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SEt})_2(\text{PBu}_3)_2]$  in small concentrations. Concentration of the latter two dimers increased with time and after a week all four dimers were present in 1 : 1 : 1 : 1 ratio. Subsequently, another species began to form whose resonances were attributable to heterobimetallic complex. On keeping the solution for another week the concentration of heterobimetallic chloro-mercapto bridged species increased. No further noticeable change could be seen on keeping the solution for next few days. It can, therefore, be concluded that following equilibrium has been attained.

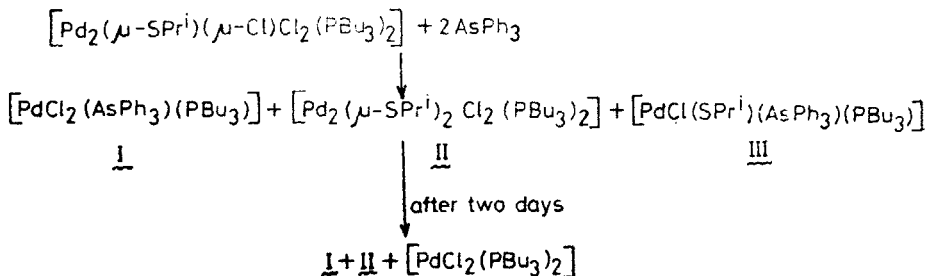


A few bridge cleavage reactions of dipalladium and diplatinum mercapto bridged complexes were carried out. Reactions of dipalladium complexes with neutral donor ligands were facile while reactions with platinum compounds were slow. Reaction with excess pyridine yields  $[MCl_2(py)(PR_3)]$  and  $[M_2Cl_2(\mu-RS)_2(PR_3)_2]$  which is formed *via* an intermediate  $[MCl(SR)(py)(PR_3)]$ . This rearranges to more stable dinuclear complex probably due to lack of symmetry (Scheme 4).



SCHEME 4

Reaction of  $[M_2(\mu-Cl)(\mu-SR)Cl_2(PR_3)_2]$  with triphenylarsine in 1 : 2 stoichiometry proceeds similarly. Initially three species were formed but after two days the last species disappeared completely (Scheme 5). Treatment with triphenylphosphine gives a complex mixture of mononuclear complexes.



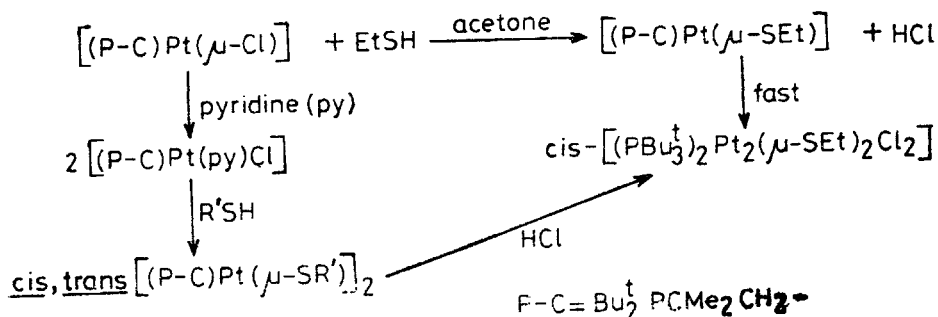
SCHEME 5



The dimercapto bridged complexes of platinum do not undergo bridge cleavage reactions including with tertiary phosphines. However, the dipalladium compounds slowly react with triphenylphosphine to give a complex mixture of mononuclear complexes.

Our general observations regarding the geometry of  $[M_2X_2(\mu-Y)(\mu-Z)(PR_3)_2]$  complexes are as follows :—

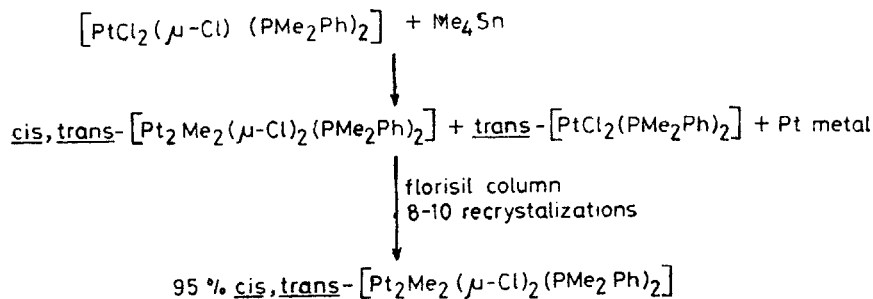
- (i) The tendency of mercapto bridged complexes to adopt a *cis* geometry, when  $R'$  group is alkyl, is so high that even with bulky phosphine ligand (Scheme 6) this is the predominated isomer.



SCHEME 6

However, when ( $Y = Z = SR'$ ) mercapto group contain an aryl group *trans* geometry is preferred. When terminal  $X$  group has a high *trans* influence mixture of *cis* and *trans* isomers are usually formed.

- (ii) When  $Y = Z = Cl$  and  $X =$  strong *trans* influencing group, mixture of *cis* and *trans* isomers usually forms. Only exception to this was  $[Pt_2Me_2(\mu-Cl)_2(PMe_2Ph)_2]$ , reported by Puddephatt and Thomson,<sup>15</sup> for which *cis* geometry was proposed. In fact, this complex exists as a mixture of *cis* and *trans* isomers<sup>16</sup> (Scheme 7) (Fig 14, 15).



SCHEME 7

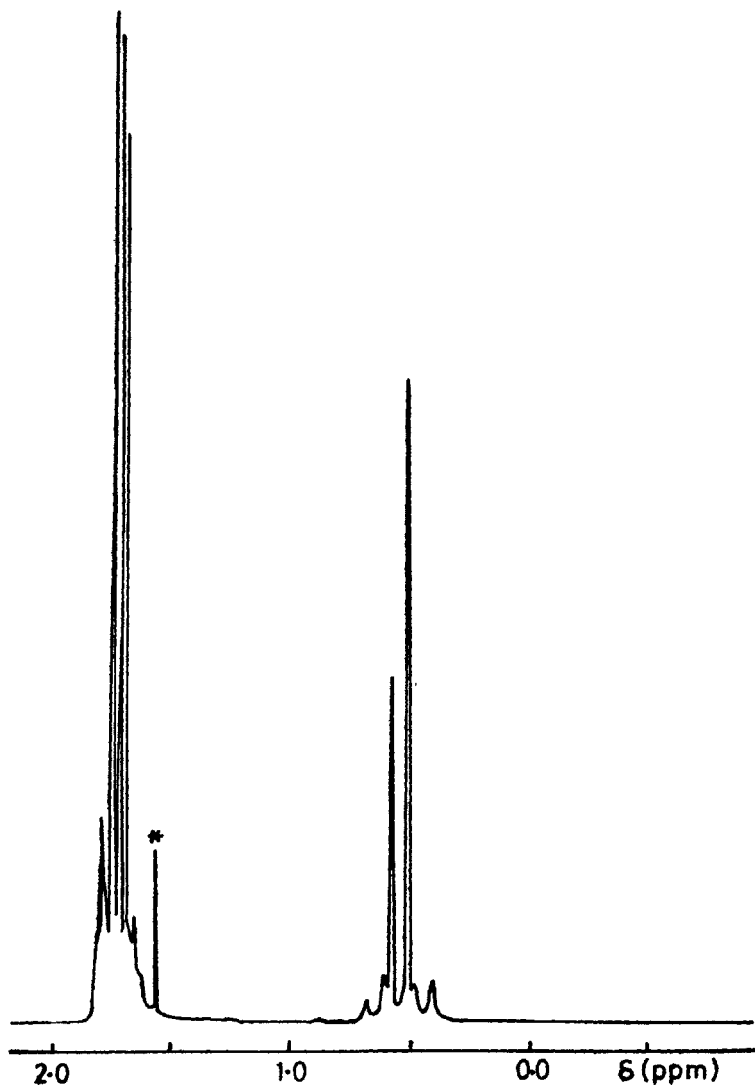


FIG 14  $^1\text{H}$  NMR spectrum of  $[\text{Pt}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PMe}_2\text{Ph})_2]$

- (iii) When  $Y = \text{Cl}$ ,  $Z = \text{SR}$ , and  $X = \text{Cl}$ , a *cis* geometry is predominated however when  $X$  is a strong *trans* influencing ligand, *trans* is the predominated geometry.

As I said in the beginning the binuclear complexes are of interest in homogeneous catalysis. In order to assess the catalytic activity of our compounds as homogeneous catalyst we have carried out hydrogenation<sup>10,11</sup> of styrene employing these complexes. The chloro mercapto bridged complexes showed higher activity. The effect of phosphine and  $\text{SR}'$  ligands are evident from Table I.

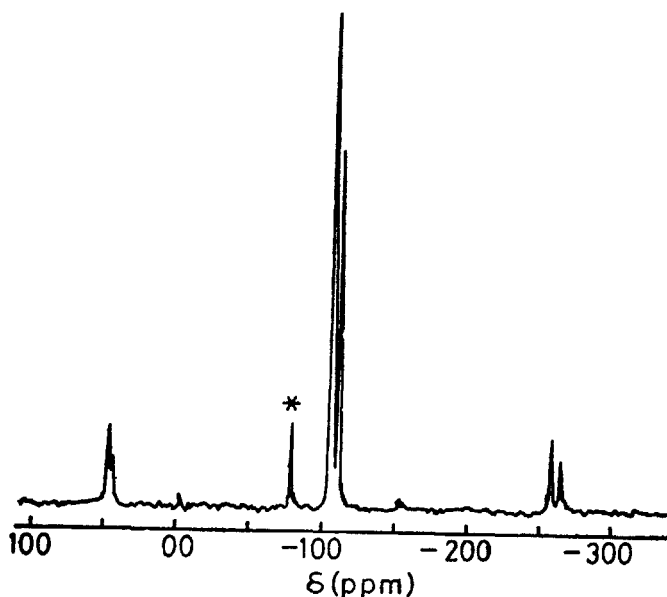
FIG 15  $^{31}\text{P}$  NMR spectrum of  $[\text{Pt}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PMe}_2\text{Ph})_2]$ 

TABLE I

*Hydrogenation of styrene to ethylbenzene using  $[\text{Pt}_2\text{Cl}_2(\mu\text{-SR}')(\mu\text{-X})(\text{PR}_3)_2]/\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  as homogeneous catalyst at 60–70 °C*

Complex	$n\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{H}_2$ pressure (PSi)	Turnover number
$[\text{Pt}_2\text{Cl}_2(\text{SEt})_2(\text{PEt}_3)_2]$	0	800	0
	1	650	6
	1	1050	28
	2	1050	51
	5	1050	94
	10	1150	84
	1	1600	41
$[\text{Pt}_2(\text{SPi}')(\text{Cl})\text{Cl}_2(\text{PR}_3)_2]$	0	800	18
	1	800	27
	2	800	32
	5	800	348
	10	800	1221
$[\text{Pt}_2(\text{SPr}')(\text{Cl})(\text{SnCl}_4)_2(\text{PPR}_3)_2]$	0	800	49
$[\text{Pt}_2(\text{SEt})(\text{Cl})\text{Cl}_2(\text{PPR}_3)_2]$	11	800	748
$\text{Pt}_2(\text{SPr}')(\text{Cl})\text{Cl}_2(\text{PEt}_3)_2]$	11	800	724
$[\text{Pt}_2(\text{SPr}')(\text{Cl})\text{Cl}_2(\text{PBu}_3)_2]$	11	800	1322
$[\text{Pt}_2(\text{SPr}')(\text{Cl})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$	10	800	271

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