(DAH)PdBr$_2$, 87191-60-4; *cis*-(DAO)PdBr$_2$, 87191-52-4; *trans*-(DAO)PdBr$_2$, 87191-64-8; (DAD)PdBr$_2$, 87191-62-6; (DADOD)-PdBr$_2$, 87191-45-5; (DAHD)PdBr$_2$, 87191-46-6; (DAH)PdI$_2$, 87191-66-0; (DAO)PdI$_2$, 87191-68-2; (DAD)PdI$_2$, 87191-70-6; (DADOD)PdI$_2$, 87191-47-7; (DAHD)PdI$_2$, 87191-48-8; (DAH)Pd-(CNS)$_2$, 87191-72-8; (DAO)Pd(CNS)$_2$, 87191-74-0; (DAD)Pd-(CNS)$_2$, 87191-76-2; (DADOD)Pd(CNS)$_2$, 87191-49-9; (DAHD)-Pd(CNS)$_2$, 87191-50-2; Ph$_3$As, 603-32-7; Ph$_2$AsCl, 712-48-1; Br(CH$_2$)$_6$Br, 629-03-8; Br(CH$_2$)$_7$Br, 4549-31-9; Br(CH$_2$)$_8$Br, 4549-32-0; Br(CH$_2$)$_9$Br, 4549-33-1; Br(CH$_2$)$_{10}$Br, 4101-68-2; Br(CH$_2$)$_{11}$Br, 16696-65-4; Br(CH$_2$)$_{12}$Br, 3344-70-5; Br(CH$_2$)$_{16}$Br, 45223-18-5; DAH, 82195-43-5; DAHP, 82195-44-6; DAO, 82195-45-7; DAN, 82195-46-8; DAD, 82195-47-9; DAY, 82195-48-0; DADOD, 82195-49-1; DAHD, 82195-50-4.

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Head-to-Head and Head-to-Tail Isomers of Binuclear Complexes of Platinum(I) and Palladium(I) Involving 2-(Diphenylphosphino)pyridine as a Bridging Ligand

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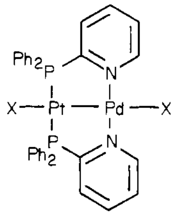
Reaction of Pt(Ph$_2$Ppy)$_2$Cl$_2$ (Ph$_2$Ppy is 2-(diphenylphosphino)pyridine) with Pd$_2$(dba)$_3$·CHCl$_3$ (dba is dibenzylideneacetone) or Pt(dba)$_2$ yields PtPd(μ-Ph$_2$Ppy)$_2$Cl$_2$ or Pt$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$, respectively. Extensive ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR studies show these exist as the head-to-tail (*HT*) isomers where the phosphorus atoms are bound to different metal atoms. Metathesis of Pt$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$ with sodium iodide yields the *HT* isomer of Pt$_2$(μ-Ph$_2$Ppy)$_2$I$_2$. Treatment of Pt(Ph$_2$Ppy)$_2$I$_2$ with Pd$_2$(dba)$_3$·CHCl$_3$ or Pt(dba)$_2$ yields PtPd(μ-Ph$_2$Ppy)$_2$I$_2$ or Pt$_2$(μ-Ph$_2$Ppy)$_2$I$_2$, respectively. These exist as the head-to-head (*HH*) isomers with both phosphines bound to the same platinum atom through phosphorus. The *HH* → *HT* isomerization of PtPd(μ-Ph$_2$Ppy)$_2$I$_2$ occurs on heating the *HH* complex in chloroform solution. In order to account for the selective preparation of *HT* isomers from Pt(Ph$_2$Ppy)$_2$Cl$_2$ and the formation of *HH* isomers from Pt(Ph$_2$Ppy)$_2$I$_2$, the solution composition of these two Pt(II) complexes has been examined. In solution, Pt(Ph$_2$Ppy)$_2$I$_2$ exists as a mixture of cis and trans isomers along with the salt [Pt(Ph$_2$Ppy)$_2$I]I while Pt(Ph$_2$Ppy)$_2$Cl$_2$ exists as the cis isomer and the salt [Pt(Ph$_2$Ppy)$_2$Cl]Cl. These salts contain one chelating and one monodentate phosphorus-bound Ph$_2$Ppy. An explanation for the selective formation of *HT* or *HH* isomers is offered.

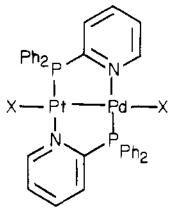
Introduction

Binuclear, metal–metal-bonded compounds of Pt(I) and Pd(I) are readily prepared by a conproportionation reaction involving appropriate compounds of M(II) and M(0) (M = Pt or Pd).[1] For example, the unbridged dimer Pd$_2$(CNCH$_3$)$_6$$^{2+}$ is formed by the reaction between methyl isocyanide, Pd^{II}(CNCH$_3$)$_4$$^{2+}$ and Pd$^0_2$(μ-dba)$_3$ (dba is dibenzylideneacetone, which coordinates as an olefin).[2] Likewise, the highly reactive dimer Pd$_2$(μ-dpm)$_2$Cl$_2$ (dpm is bis(diphenylphosphino)methane) is reproducibly formed in good yield by the reaction between (PhCN)$_2$Pd^{II}Cl$_2$, Pd$_2$(μ-dba)$_3$, and dpm.[3] Heterobinuclear dimers are also produced in this way. For example, mixing of Pt(dba)$_2$ with Pd(CNCH$_3$)$_4$$^{2+}$ in the presence of methyl isocyanide yields PtPd(CNCH$_3$)$_6$$^{2+}$ in high yield and in excellent purity.[2] This unbridged dimer retains its integrity under a variety of reaction conditions and establishes the robust character of the Pt–Pd bond.[2,4] Similarly, PtPd(μ-dpm)$_2$Cl$_2$ has been formed from the reaction between Pd^0(PPh$_3$)$_4$, (*t*-BuCN)$_2$PtCl$_2$, and dpm.[5]

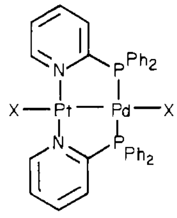
In recent years we have been interested in constructing binuclear complexes using 2-(diphenylphosphino)pyridine (Ph$_2$Ppy) as a bridging ligand.[6,10] We have reported that Pd(Ph$_2$Ppy)$_2$Cl$_2$ reacts with Pd$^0_2$(μ-dba)$_3$·CHCl$_3$ to form Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$ and with Pt^0(dba)$_2$ to form a mixture of Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$ and PtPd(μ-Ph$_2$Ppy)$_2$Cl$_2$.[11] With an unsymmetrical bridging ligand such as Ph$_2$Ppy, it is possible to obtain stereoisomers that differ in the relative orientations of the bridging ligands. For a heterobinuclear species such as PtPd(μ-Ph$_2$Ppy)$_2$X$_2$, three isomers (the two head-to-head (*HH*) isomers **1** and **2** and the head-to-tail (*HT*) isomer **3**)



1, *HH*(PPt)



3, *HT*



2, *HH*(PPd)

can exist while, for a homobinuclear species such as Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$, only two isomers (one *HH* and the other *HT*) are possible. Preliminary evidence suggests that the PtPd(μ-Ph$_2$Ppy)$_2$Cl$_2$ formed by reaction 1 consisted exclusively of the

$$\mathrm{Pd^{II}(Ph_2Ppy)_2Cl_2 + Pt^0(dba)_2 \rightarrow PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2\ \{+Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2\}} \quad (1)$$

HT isomer.[11] These conproportionation reactions can be run

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in two ways that differ in whether the Ph_2Ppy is initially bound to palladium(II) as in reaction 1 or to platinum(II) as in reaction 2. Because platinum(II) is substitutionally more inert

$$Pt^{II}(Ph_2Ppy)_2X_2 + {}^1/_2Pd^0{}_2(\mu\text{-dba})_3 \rightarrow PtPd(\mu\text{-}Ph_2Ppy)_2X_2 \qquad (2)$$

than palldium(II), utilization of reaction 2 appears to offer two advantages over reaction 1. Less ligand exchange, which is required to form the homonuclear $Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2$, should occur, and consequently, a higher yield of, hopefully pure, $PtPd(\mu\text{-}Ph_2Ppy)_2X_2$ should result. Additionally, it might be possible to obtain examples of both *HT* and *HH*(PPt) isomers by this route.

Experimental Section

Preparation of Compounds. Ph_2Ppy,[8] $Pt(1,5\text{-COD})I_2$,[12] $Pt(dba)_2$,[13] $Pd_2(dba)_3CHCl_3$,[14] and $Pt(Ph_2Ppy)_2Cl_2$[9] were prepared by published procedures.

$Pt(Ph_2Ppy)_2I_2$. A solution of 0.152 g (0.27 mmol) of $Pt(1,5\text{-COD})I_2$ in 15 mL of dichloromethane is added dropwise to a solution of 0.153 g (0.58 mmol) of Ph_2Ppy in 10 mL of dichloromethane. The scent of 1,5-COD is present immediately upon reaction of the two solutions. Ethyl ether is added dropwise to precipitate a yellow solid, which is collected by filtration and dried under vacuum; yield 0.265 g, 99%. Anal. Calcd for $C_{34}H_{28}I_2N_2P_2Pt$: C, 41.87; H, 2.89; N, 2.87. Found: C, 41.22; H, 2.87; N, 2.73.

$[Pt(Ph_2Ppy)_2I][PF_6]$. A saturated solution of ammonium hexafluorophosphate in methanol was added to a solution of 0.11 g (0.11 mmol) of $Pt(Ph_2Ppy)_2I_2$ in 20 mL of methanol. An ivory precipitate formed upon the addition. The precipitate was collected by filtration, washed with methanol, and vacuum dried; yield 0.075 g, 72%. Anal. Calcd for $C_{34}H_{28}F_6IN_2P_3Pt$: C, 41.12; H, 2.84; N, 2.82. Found: C, 41.10; H, 2.80; N, 2.81.

$Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*). A filtered solution of 0.442 g (0.66 mmol) of $Pt(dba)_2$ in 60 mL of dichloromethane was added to a solution of 0.50 g (0.63 mmol) of $Pt(Ph_2Ppy)_2Cl_2$ in 40 mL of dichloromethane. After the mixture was heated under reflux under nitrogen for 24 h, the black solution was filtered to remove a black insoluble solid (presumably platinum metal) and the volume of the filtrate was reduced to 15 mL. Ethyl ether was added dropwise to precipitate 200 mg of a dark brown solid. After ca. 20 mL of ethyl ether was added, the solution was filtered. A ^{31}P NMR spectrum of the brown solid in chloroform-*d* indicates that the predominant phosphorus-containing species present are $Pt(Ph_2Ppy)_2Cl_2$ and $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*). Even employing excess $Pt(dba)_2$, it is difficult to achieve complete utilization of $Pt(Ph_2Ppy)_2Cl_2$, apparently because of the facile formation of platinum metal from $Pt(dba)_2$. Ethyl ether was added dropwise to the orange-brown filtrate to precipitate the title compound as an orange solid. After ca. 15–20 mL of ethyl ether was added, the solution was filtered and the orange solid vacuum dried; yield 0.15 g, 24%. Addition of 40 mL of ethyl ether to the remaining filtrate precipitates a tan solid (0.14 g), which is predominantly $Pt(Ph_2Ppy)_2Cl_2$, and a small quantity of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) (verified by ^{31}P NMR). The remaining yellow filtrate was evaporated down to yield a yellow solid identified as the ligand dba (mp (found) 103–107 °C, mp (Eastman) 110–113 °C). Anal. Calcd for $C_{34}H_{28}Cl_2N_2P_2Pt_2$: C, 41.35; H, 2.86; N, 2.84. Found: C, 41.57; H, 2.90; N, 2.71.

$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)). A solution containing 0.23 g (0.23 mmol) of $Pt(Ph_2Ppy)_2I_2$ and 0.154 g (0.23 mmol) of $Pt(dba)_2$ in 50 mL of dichloromethane was heated under reflux in a nitrogen atmosphere for 24 h. The volume of the solution was reduced to 10 mL by the use of a rotary evaporator. A 5-mL portion of ethyl ether was added to the filtered solution dropwise to precipitate a black solid, which was collected by filtration. Ethyl ether was added to the filtrate in 1-mL portions followed by filtration until an orange precipitate of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)) started to form (ca. 5 mL of ethyl ether had been added). A 15-mL portion of ethyl ether was then added dropwise, and the orange solid was collected by filtration; yield 0.110 g, 33%. Anal. Calcd for $C_{34}H_{28}I_2N_2P_2Pt_2$: C, 34.89; H, 2.41; N, 2.39; I, 21.68. Found: C, 34.79; H, 2.38; N, 2.39; I, 21.26.

$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*). A solution of 0.05 g (0.05 mmol) of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) in 3 mL of dichloromethane was added dropwise to a solution of NaI in 5 mL of acetone. After a few minutes, red crystals of the title compound began to precipitate out. The crystals were collected and vacuum dried. Additional crystals were obtained from the solution by allowing it to stand at room temperature for 24 h. Total yield: 0.03 g, 51%. Anal. Calcd for $C_{34}H_{28}I_2N_2P_2Pt_2$: C, 34.89; H, 2.41; N, 2.39. Found: C, 33.87; H, 2.32; N, 2.25.

$PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*). A solution containing 0.149 g (0.15 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ and 0.237 g (0.30 mmol) of $Pt(Ph_2Ppy)_2Cl_2$ in 50 mL of dichloromethane was heated under reflux for 2 h under an atmosphere of nitrogen. The solution was then cooled to room temperature, and ethyl ether was added slowly to precipitate a greenish brown solid. The precipitate was collected by filtration and vacuum dried; yield 0.085 g, 73%. Anal. Calcd for $C_{34}H_{28}Cl_2N_2P_2PdPt$: C, 45.43; H, 3.14; N, 3.12. Found: C, 44.93; H, 3.15; N, 3.68.

$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)). A filtered solution of 0.063 g (0.12 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ in 25 mL of dichloromethane was added dropwise to a solution of 0.119 g (0.12 mmol) of $Pt(Ph_2Ppy)_2I_2$ in 25 mL of dichloromethane. Ethyl ether was added dropwise to the mixture to precipitate a dark brown crystalline solid that was collected by vacuum filtration. The volume of the filtrate was reduced to 10 mL by rotary evaporation, and the ethyl ether was added to precipitate additional compound; yield 0.091 g, 69%. Anal. Calcd for $C_{34}H_{28}I_2N_2P_2PdPt$: C, 37.75; H, 2.61; N, 2.59. Found: C, 37.34; H, 2.63; N, 2.54.

$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*). A solution of 0.158 g (0.16 mmol) of $Pt(Ph_2Ppy)_2I_2$ and 0.84 g (0.09 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$ in 50 mL of dichloromethane was refluxed under nitrogen for 2 h. After cooling to room temperature, the solution was filtered, and ethyl ether was added dropwise to precipitate a brown solid, which was collected by filtration and vacuum dried; yield 0.121 g, 69%. Anal. Calcd for $C_{34}H_{28}I_2N_2P_2PdPt$: C, 37.75; H, 2.61; N, 2.59. Found: C, 37.47; H, 2.61; N, 2.58.

Physical Measurements. $^{31}P\{^1H\}$ and ^{195}Pt NMR were recorded on a Nicolet NT-200 Fourier transform spectrometer at 81 and 42 MHz, respectively. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra, and an external 0.1 M H_2PtCl_6 solution in H_2O was used as the reference for the ^{195}Pt NMR spectra. The high-frequency-positive convention, recommended by IUPAC, has been used in reporting all chemical shifts.

Simulations of the ^{31}P and ^{195}Pt NMR spectra were performed with use of the iterative simulation routine of the Nicolet software on a 1180 Nicolet data system. This simulation routine is a modified version of the LAOCN3 program. The fit of the simulation was based on matching the individual peak positions of the observed and the calculated spectra.

Conductivity measurements were performed on an Industrial Instruments conductivity bridge with 1 mM solutions.

Results

Synthesis of Binuclear Compounds. The preparations of the new binuclear complexes are outlined in Scheme I. The reaction between $Pt(Ph_2Ppy)_2Cl_2$ and $Pd_2(dba)_3{\cdot}CHCl_3$ or $Pt(dba)_2$ in dichloromethane solution yields the *HT* isomers of $PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ and $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$, respectively. Metathesis of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) with sodium iodide in acetone solution produces $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*). When $Pt(Ph_2Ppy)_2I_2$ is used in the conproportionation reaction, however, *HH*(PPt) isomers are the predominant species formed. Thus, treatment of $Pt(Ph_2Ppy)_2I_2$ with $Pd_2(dba)_3{\cdot}CHCl_3$ yields $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)), while a similar reaction with $Pt(dba)_2$ forms $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*) along with a minor amount (13% by $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixture) of the *HT* isomer. The binuclear complexes have been isolated as colored solids (brown, red, or orange) that have good solubility in dichloromethane, chloroform, or acetone but negligible solubility in alcohol, ether, or alkanes. They are nonelectrolytes in acetone solution as shown by the conductivity data given in Table I. Structural characterization of these compounds has relied heavily on the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopic data presented in the next section.

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Scheme I

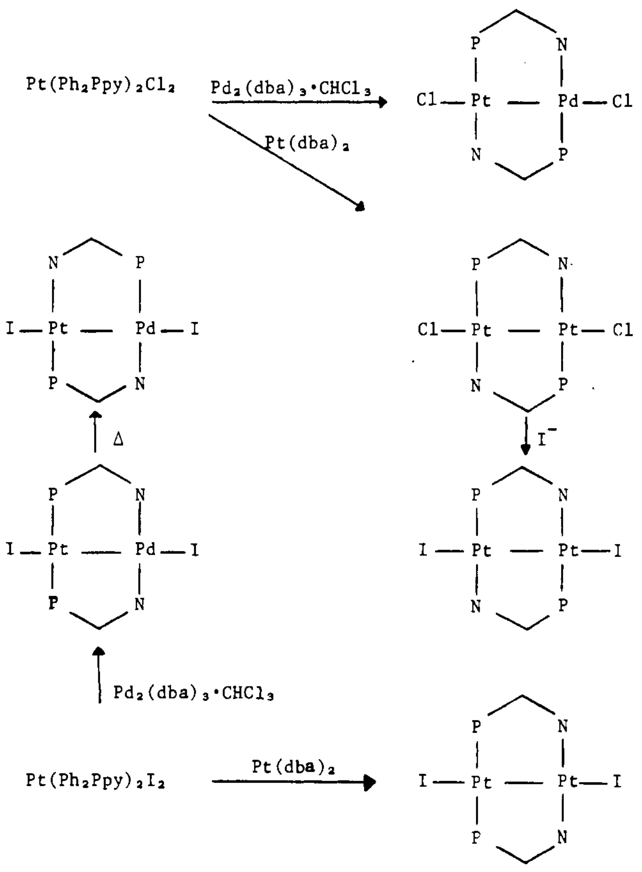


Table I. Conductivity of 2-(Diphenylphosphino)pyridine Complexes

compd[a]	Λ_m[b]	compd[a]	Λ_m[b]
$[(C_4H_9)_4N]I$	137	$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*)	11
$Pt(Ph_2Ppy)_2Cl_2$	5	$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*)	2
$Pt(Ph_2Ppy)_2I_2$	49	$PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*)	3
$[Pt(Ph_2Ppy)_2I][PF_6]$	150	$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt))	1
$Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*)	8	$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*)	6

[a] In acetone solution. [b] In cm² mol⁻¹ Ω⁻¹.

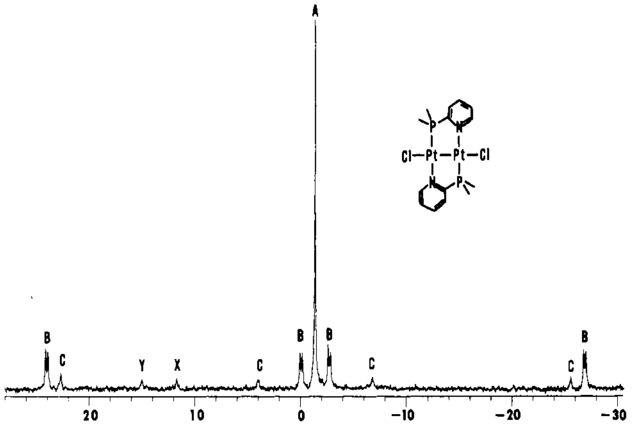
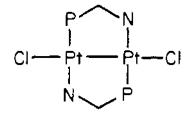
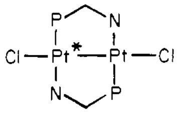


Figure 1. The 81-MHz $^{31}P\{^1H\}$ NMR spectrum of a chloroform solution of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*). Peaks labeled X and Y are impurities; other labels are identified in the text.

NMR Spectroscopy of Binuclear Complexes. The parameters derived from the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of the new complexes are summarized in Table II. Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$. The spectral pattern can be understood by considering the three isotopomers **4A**–**4C** with the natural abundances indicated arising from the presence of ^{195}Pt (Pt*) with 33.8% natural abundance and nuclear spin of $^1/_2$. The large central peak A in Figure 1 arises from the unlabeled isotopomer **4A**. The doublet of doublets labeled B arises from the singly labeled isotopomer **4B**. The chemical shifts of the two phosphorus atoms in this isotopomer are expected to be essentially identical and the same as found in isotopomer **4A**. This part of the spectrum has been successfully analyzed as a special case of the ABX spin system where $\delta A = \delta B$ and $J(A,X) - J(B,X) \gg J(A,B)$. Under these conditions, the spectrum appears as a pseudo-first-order spectrum. In fact, the overall appearance of this spectral pattern is that of a first-order spectrum with the outermost set of doublets due to the phosphorus bonded to the spin-labeled platinum center and the innermost pair of doublets due to the phosphorus bonded to the non-spin-labeled platinum. The separation between the outermost set of doublets is 4124 Hz, which is in the range normally found for one-bond platinum–phosphorus coupling constants.[15] The


4A
43.8%


4B
44.8%

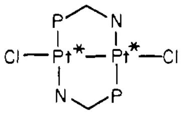

4C
11.4%

Table II. $^{31}P\{^1H\}$[a] and $^{195}Pt\{^1H\}$[b] NMR Data for 2-(Diphenylphosphino)pyridine Complexes

	δ			|J|, Hz				
compd	Pt-P	Pd-P	Pt-P	^1J(Pt,P)	^1J(Pt,Pt')	^2J(Pt,P)	^2J(P,P)	^3J(P,P)
cis-$Pt(Ph_2Ppy)_2Cl_2$	11.6			3676				
cis-$Pt(Ph_3P)_2Cl_2$	14.7			3669				
cis-$Pt(Ph_2Ppy)_2I_2$	6.7			3514				
cis-$Pt(Ph_3P)_2I_2$	11.9			3453				
trans-$Pt(Ph_3P)_2Cl_2$	20.6			2634.5				
trans-$Pt(Ph_2Ppy)_2I_2$	9.8			2503				
trans-$Pt(Ph_3P)_2I_2$	12.6			2490				
$[Pt(Ph_2Ppy)_2Cl][Rh(CO)_2Cl_2]$	15.2 −50.3			3704 3339			*c*	
$[Pt(Ph_2Ppy)_2I][PF_6]$	19.3 −61.2			3637 3241			*c*	
$Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*)	−1.5		−4346	4124	10260	215		17.8
$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*)	−5.7			3905		198		17.8
$Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*)	9.6		−5034	3263		153		
$PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*)	−6.7	7.4		4048		106		14.3
$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (HH(PPt))	−0.06		−4833	3213				
$PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*)	−10.5	3.9	−4260	3891		65		16.0

[a] In chloroform-*d*. [b] In dichloromethane. [c] Less than the natural line width.

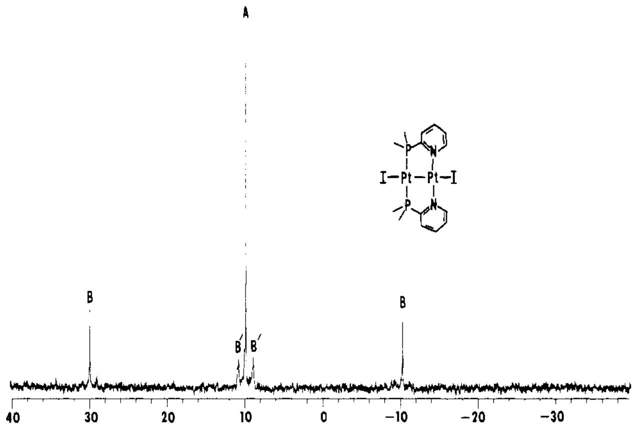
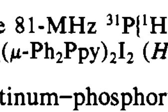


Figure 2. The 81-MHz $^{31}P\{^1H\}$ NMR spectrum of a chloroform solution of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*).

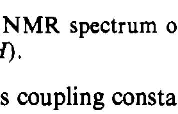
two-bond platinum–phosphorus coupling constant is expected to be much smaller,[16,17] and a value of 215 Hz is found for the separation between the inner pair of doublets. The phosphorus atoms are inequivalent in this isotopomer, and as a result, each large doublet is split further by a phosphorus–phosphorus coupling of 17.8 Hz, which compares favorably with the $^3J(P,P)$ found in other binuclear complexes with bridging Ph_2Ppy ligands.[6–9] The remaining four lines in the spectrum, those labeled C, arise from isotopomer **4C**, which belongs to the AA′XX′ spin system. Analysis of this spectrum, using the previously obtained spectral parameters, allows one additional parameter, $^1J(Pt,Pt')$, to be evaluated. The large value of $^1J(Pt,Pt')$ (10 269 Hz) is consistent with other values observed for species containing direct Pt–Pt bonds.[18]

The $^{31}P\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*) is similar to that of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*), and the parameters are given in Table II.

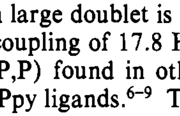
In contrast, the $^{31}P\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)), which is shown in Figure 2, displays significant differences from the spectra of the *HT* isomers. There are four isotopomers, **5A**, **5B**, **5B′**, and **5C**, that need to be considered. The strong central line A in Figure 2 is due to the unlabeled isotopomer, **5A**. The outer pair of satellites, labeled B, arise from the singly labeled isotopomer, **5B**. The splitting between these two lines gives a value of $^1J(P,Pt)$ (3263 Hz), which is consistent with the presence of phosphorus–platinum bonds.[15] These outer satellites lack the splitting shown by the corresponding satellites of the *HT* isomer. The inner satellites, labeled B′, are assigned to isotopomer **5B′**. Notice that they are considerably broader but *not* less intense than the outer



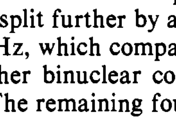
5A
43.8%



5B
22.4%



5B′
22.4%



5C
11.4%

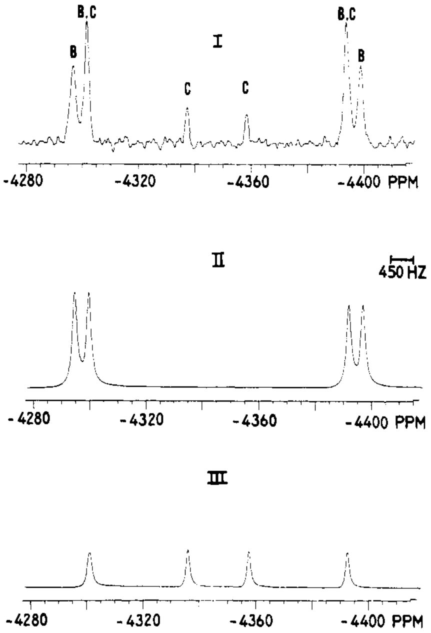


Figure 3. The 42-MHz $^{195}Pt\{^1H\}$ NMR spectrum of a dichloromethane solution of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*). The top trace (I) is the experimental spectrum. Trace II is the spectrum calculated for the isotopomer containing one ^{195}Pt atom. Trace III is the spectrum calculated for the isotopomer containing two ^{195}Pt atoms.

satellites. The broadening is ascribed to an increased rate of relaxation transmitted from the quadrupolar nitrogen atoms through the labeled platinum atom, which is spin coupled to the phosphorus atoms. Additional evidence for an enhancement in the relaxation rate of the ^{195}Pt bonded to pyridine relative to the ^{195}Pt bound to phosphorus is available from the $^{195}Pt\{^1H\}$ NMR spectra (vide infra). The magnitude of the phosphorus–platinum coupling (153 Hz in isotopomer **5B′**) is in the range anticipated for a two-bond coupling. The signal-to-noise ratio in the spectrum in Figure 2 is not sufficiently good to allow identification of the peaks of isotopomer **5C**.

The $^{195}Pt\{^1H\}$ NMR spectra of these diplatinum molecules reinforce the structural assignments made on the basis of the $^{31}P\{^1H\}$ NMR spectra. The $^{195}Pt\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) is shown in the top trace of Figure 3. This spectrum is a composite of the spectra of the two isotopomers **4B** and **4C**, which contain spin-labeled ^{195}Pt. The peaks labeled B and C in Figure 3 correspond to the isotopomers **4B** and **4C**, respectively. As in the case of the AB portion of this spectrum, the X portion of this ABX spin system, under the conditions $\delta A \cong \delta B$ and $J(A,X) - J(B,X) \gg J(A,B)$, is expected to appear as a first-order spectrum. A doublet of doublets is therefore expected with the larger separation corresponding to the $^1J(Pt,P)$ and the smaller separation corresponding to $^2J(Pt,P)$. This is what is observed. The large separation in the outer doublets is found to be 4165 Hz, which compares with 4124 Hz found in the $^{31}P\{^1H\}$ NMR spectrum. The smaller separation is 222 Hz, which compares with 215 Hz found in the $^{31}P\{^1H\}$ NMR spectrum. The center of the spectrum gives the Pt chemical shift, which is –4346 ppm. The line intensities are, however, not what is expected for a first-order spectrum. This anomaly can be understood by considering the $^{195}Pt\{^1H\}$ NMR spectrum of the isotopomer **4C**. By virtue of its high symmetry, the splitting patterns of the A and X portions of this AA′XX′ spin system are expected to be identical. In the lower two traces of Figure 3, the simulated spectra expected for **4B** and **4C** are given. These simulations are based on the coupling constants derived from the $^{31}P\{^1H\}$ NMR spectra. The only new parameter introduced is the ^{195}Pt chemical shift. It is apparent from the simulations

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(15) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979.

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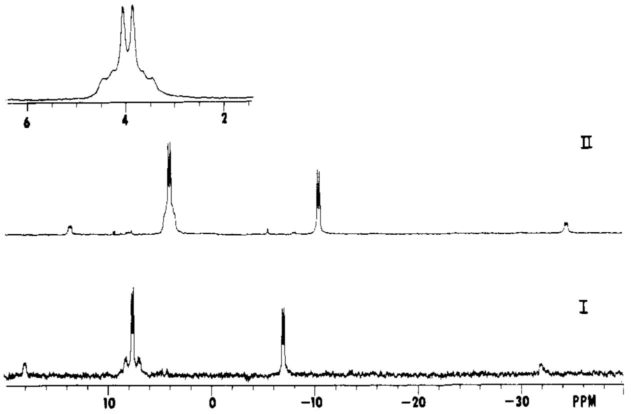


Figure 4. The 81-MHz $^{31}P\{^1H\}$ NMR spectra of chloroform solutions of (I) $PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) and (II) $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*). The insert at the top is an expansion of the region from 2 to 6 ppm in trace II.

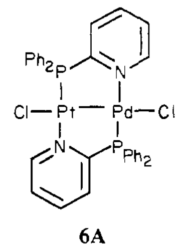
that the skewing of the intensities of the outer four lines results from the overlap of the outer lines of the AA′XX′ spin system of **4C** with the inner lines of the ABX spin system of **4B**.

Due to poor solubility, the $^{195}Pt\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*) has not been obtained.

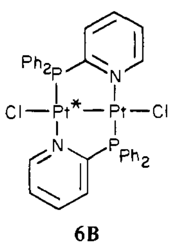
The $^{195}Pt\{^1H\}$ NMR spectrum of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*) consists of a triplet centered at −5034 ppm with a splitting of 3270 Hz. This compares well with the value of ^1J(Pt,P) found in the $^{31}P\{^1H\}$ NMR spectrum of 3263 Hz, and therefore the triplet is due to the isotopomer where the two equivalent phosphorus atoms are bonded to the spin-labeled platinum center. The natural line width of the lines is 13 Hz, which is narrower than the 48 Hz found for the lines in the $^{195}Pt\{^1H\}$ NMR spectrum of **4**. This difference is most likely due to the presence of the quadrupolar ^{14}N nuclei trans to the phosphorus atoms in the *HT* isomer. This results in a broadening of these lines. In **5B**, the phosphorus nuclei are trans to each other, and the lines are narrower.

The resonances of isotopomer **5B′**, which should also appear as a triplet with a smaller coupling of ^2J(Pt,P) of 153 Hz, are conspicuously absent from the spectrum. The spectrum has been scanned over the range 43.00–42.76 MHz, where ^{195}Pt nuclei are normally observed. The absence of signals due to this isotopomer may be explained as a result of the presence of both ^{14}N nuclei on the ^{195}Pt center, which causes broadening of this signal into the base line. The effect of the ^{14}N nuclei on the line widths of the adjacent phosphorus nuclei has already been noted in the $^{31}P\{^1H\}$ NMR spectrum of this isotopomer. Also absent in this spectrum are the lines expected for the isotopomer **5C**. This is most likely due to its low abundance and the relatively large number of resonances (12) over which the low intensity must be spread.

The $^{31}P\{^1H\}$ NMR spectrum of the structurally similar platinum–palladium complexes are intrinsically simpler than the platinum–platinum complexes since spin coupling to palladium is not observed. The $^{31}P\{^1H\}$ NMR spectrum of $PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (*HT*) is given in Figure 4, trace I. Following a similar analysis as used for the platinum–platinum complexes, the $^{31}P\{^1H\}$ NMR spectrum is a composite spectrum of the two isotopomers **6A**, which contains no spin-labeled platinum, and **6B**, which contains spin-labeled Pt. The two large doublets at −6.7 and 7.4 ppm are due to the isotopomer **6A**. They show a phosphorus–phosphorus coupling of 14.3 Hz, which is comparable to the value found in the $^{31}P\{^1H\}$ NMR spectrum of **4**. The doublets centered around each large doublet are from the AMX spin system of isotopomer **6B** and allow the peaks centered at −6.7 ppm, which exhibit the large Pt–P coupling of 4048 Hz, to be assigned to the phosphorus bonded to the platinum atom. The peaks centered at 7.4 ppm, which exhibit a much smaller Pt–P coupling of 106 Hz, are accordingly assigned to the phosphorus atom bonded to the palladium center. Thus, the $^{31}P\{^1H\}$ NMR spectrum indicates that the two bridging Ph_2Ppy ligands are in the head-to-tail orientation.



6A



6B

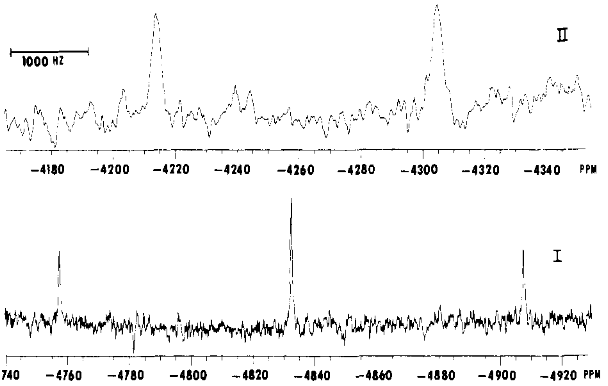


Figure 5. The 42-MHz $^{195}Pt\{^1H\}$ NMR spectra of dichloromethane solutions of (I) $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)) and (II) $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*).

The $^{31}P\{^1H\}$ NMR spectrum of $PtPd(\mu\text{-}Ph_2Ppy)I_2$ (*HT*) is given in Figure 4, trace II. The overall spectral pattern closely resembles that obtained for the chloride analogue. Comparison of the chemical shifts and coupling constants in Table I indicates that these complexes must be isostructural.

The $^{31}P\{^1H\}$ NMR spectrum of $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)) consists of a single line at 0.06 ppm flanked by ^{195}Pt satellites with ^1J(P,Pt) of 3213 Hz. The pattern is consistent with the *HH*(PPt) structure where both phosphorus atoms are bound to platinum. It is significant that both *HH*(PPt) isomers (for $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ and $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$) show smaller values for ^1J(Pt,P) than the corresponding *HT* isomers. This occurs because ^1J(Pt,P) is always larger for phosphorus trans to nitrogen as found in the *HT* isomers than for phosphorus trans to phosphorus as occurs in the *HH* isomer.

The $^{195}Pt\{^1H\}$ NMR spectrum of $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HT*) is given in Figure 5, trace II. Following a first-order analysis, a doublet of doublets is expected from the one-bond and two-bond platinum–phosphorus couplings in the isotopomer containing ^{195}Pt. However, only a broad doublet centered at −4260 ppm with a separation of 3887 Hz is observed. This corresponds well with the ^1J(Pt,P) (3891 Hz) found in the $^{31}P\{^1H\}$ NMR spectrum. The ^2J(Pt,P) coupling is not observed here since the expected value of this coupling constant (ca. 65 Hz) is less than the natural line width of the lines (80 Hz) in Figure 5.

The $^{195}Pt\{^1H\}$ NMR spectrum of the corresponding *HH* complex $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ is given in Figure 5, trace I. Here, a triplet is expected from the coupling of the two equivalent phosphorus atoms with the ^{195}Pt center. In fact, a triplet is observed (centered at −4833 ppm) with a coupling of 3212 Hz, which compares well with the ^1J(Pt,P) (3213 Hz) found in the $^{31}P\{^1H\}$ NMR spectrum. The lines in the spectrum are expected to be narrower than the lines observed for the *HT* complex since the phosphorus atoms are trans to phosphorus atoms rather than quadrupolar nitrogen atoms. In fact, the natural line width of the *HH* isomer is only 20 Hz, while it is 80 Hz for the *HT* isomer.

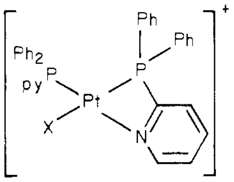
***HH*/*HT* Isomerizations.** The conversion of $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)) to the *HT* isomer has been effected. Heating a dichloromethane solution of the *HH* isomer under reflux for 2 h results in the complete conversion of the *HH*(PPt) isomer into the *HT* isomer. The reaction has been monitored by $^{31}P\{^1H\}$ NMR spectroscopy. It is a clean conversion with neither of the homobinuclear species, $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ or $Pd_2(\mu\text{-}Ph_2Ppy)_2I_2$, forming. This conversion can be catalyzed by free Ph_2Ppy. Adding 0.1 equiv of Ph_2Ppy to $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ in dichloromethane solution results in complete isomerization within 20 min at room temperature. These experiments establish the *HT* isomer as the thermodynamically stable isomer and indicate that the *HH* isomer is formed under kinetic control. Catalysis of the *HH* to *HT* isomerization by Ph_2Ppy suggests that isomerization can occur through an associative mechanism that is related to ligand substitution pathways in coordinatively unsaturated species.

The interconversion of the *HH*(PPt) and *HT* isomers of $Pt_2(\mu\text{-}PhPpy)_2I_2$ has not been observed. Heating a benzene solution of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (*HH*(PPt)) under reflux for 48 h results in no detectable isomerization as determined by measurement of $^{31}P\{^1H\}$ NMR spectra.

Solution Behavior of $Pt(Ph_2Ppy)_2X_2$ (X = I, Cl). The nature of the halide appears to exert a significant and surprising role in determining whether *HH* or *HT* isomers result from the synthesis of the binuclear complexes described in the previous sections. This effect can be traced, in part, to the solution structure of $Pt(Ph_2Ppy)_2X_2$.

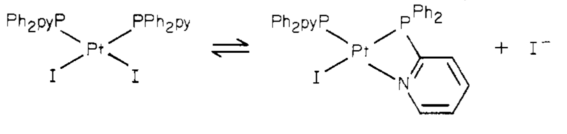
The $^{31}P\{^1H\}$ NMR spectra of a dichloromethane solution of $Pt(Ph_2Ppy)_2I_2$ at various temperatures are shown in Figure 6. At −55 °C, three species are present. The resonances labeled A are assigned, on the basis of $^1J(Pt,P)$, as resulting from *trans*-$Pt(Ph_2Ppy)_2I_2$. Those labeled B are ascribed to the cis isomer. These structures have been assigned so that $^1J(Pt,P)$ is larger for the cis isomer than for the trans isomer, as is usual. The magnitudes of $^1J(Pt,P)$ are in accord with other values reported for complexes containing *cis*- of *trans*-PtI_2P_2 cores.[15] For example, corresponding data for *cis*- and *trans*-$Pt(Ph_3P)_2I_2$ are given in Table II. Notice the similarity in the parameters for related isomers.

The six peaks in Figure 6 labeled C and C′ are assigned to the chelated and monodentate phosphines, respectively, in the cation **7A**. This cation has been isolated as the hexafluorophosphate salt. The related cation, **7B**, has been characterized by an X-ray crystal structure of the $[Rh(CO)_2Cl_2]^-$ salt.[9] The magnitude of $^1J(Pt,P)$, as well as the fact that $^2J(P,P)$ is too small to be resolved, is indicative of a structure in which the two phosphorus atoms are cis to one another.



7A, X = I
B, X = Cl

Upon warming, the resonances labeled B, C, and C′ in Figure 6 broaden until at 20 °C they merge into the base line. This broadening is ascribed to rapid exchange between the cis and the chelated isomers (eq 3). Throughout this temperature range, the resonances of the trans isomer remain narrow. Consequently, the trans isomer is uninvolved in the process and isomerization between the cis and trans isomers is a slower process than that expressed in eq 3. In addition to the broadening, it is also apparent that the populations of the various isomers are changing as the temperature changes. At −55 °C the proportion trans:cis:chelate **7** is 1.6:1.0:1.6, while at −40 °C the ratio is 0.9:1.0:0.9. Thus, low temperature favors ionic dissociation of the iodide ligand.



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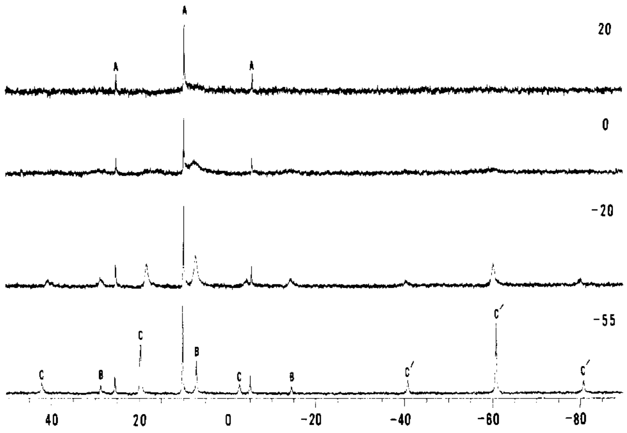

Figure 6. The 81-MHz $^{31}P\{^1H\}$ NMR spectra of a chloroform solution of $Pt(Ph_2Ppy)_2I_2$ at various temperatures. Peaks labeled A are due to the trans isomer, those labeled B are due to the cis isomer, and C and C′ are the chelated form **7**.

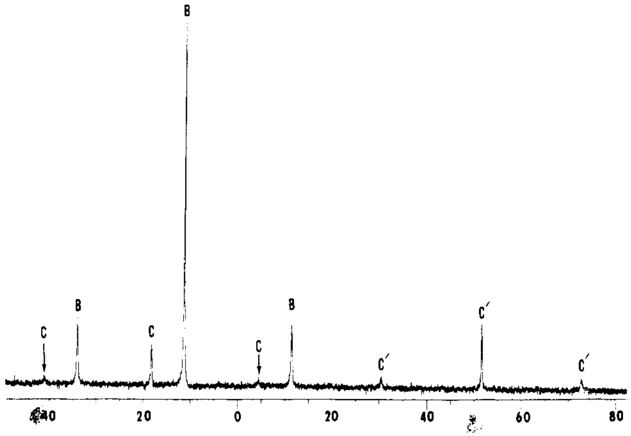

Figure 7. The 81-MHz $^{31}P\{^1H\}$ NMR spectrum of a chloroform solution of $Pt(Ph_2Ppy)_2Cl_2$ at −55 °C.

The $^{31}P\{^1H\}$ NMR spectrum of $Pt(Ph_2Ppy)_2Cl_2$ in dichloromethane solution at −55 °C is shown in Figure 7. Peaks labeled B in Figure 7 are assigned to the cis isomer, and peaks labeled C and C′ are ascribed to the chelated form **7B**. The $^{31}P\{^1H\}$ NMR spectrum of **7B** alone has been described previously. Noticeably absent from Figure 7 are any peaks due to the trans isomer. All attempts to detect *trans*-$Pt(Ph_2Ppy)_2Cl_2$ have failed. Photolysis of *cis*-Pt(tertiary phosphine)$_2$Cl$_2$ is a common method used to form the corresponding trans isomers.[19] However, photolysis has no effect on *cis*-$Pt(Ph_2Ppy)_2Cl_2$. We presume that this occurs because the equilibrium between *cis*- and *trans*-$Pt(Ph_2Ppy)_2Cl_2$ lies strongly in favor of the cis isomer (i.e., the cis isomer is much more stable for the case of $Pt(Ph_2Ppy)_2Cl_2$ than for $Pt(Ph_2Ppy)_2I_2$) and that equilibration between the cis and trans isomers is achieved more rapidly than is customary for planar complees of platinum(II). The presence of uncoördinated nitrogen atoms in $Pt(Ph_2Ppy)_2Cl_2$ offers a route to a five-coordinate intermediate that could easily facilitate cis/trans isomerization in

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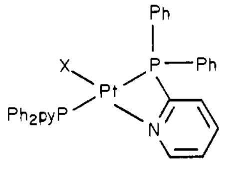
this system. In a separate related experiment, we have noted that pyridine catalyzes the trans/cis isomerization for Pt($Ph_3P)_2Cl_2$.

The absence of the trans chelated cation **8** in the solutions of Pt($Ph_2Ppy)_2X_2$ can be attributed to the operation of the trans effect, which selectively labilizes halo ligands trans to phosphine.



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The electrical conductivities of solutions of Pt($Ph_2Ppy)_2Cl_2$ and Pt($Ph_2Ppy)_2I_2$ in acetone (Table I) show that there is appreciable ionic dissociation occurring in this solvent at room temperature.

Discussion

The preceding sections have shown that *HH*(PPt) and *HT* isomers of $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ and PtPd(μ-$Ph_2Ppy)_2I_2$ are isolable species, with the *HT* isomers being more stable thermodynamically. *HH* to *HT* isomerization occurs readily for the PtPd compound. What remains to be explained is why the *HT* isomer is formed in analogous reactions involving Pt($Ph_2Ppy)_2I_2$. We believe the following explanation is tenable. *trans*-Pt($Ph_2Ppy)_2X_2$ reacts more rapidly than *cis*-Pt($Ph_2Ppy)_2X_2$ with sources of platinum(0) or palladium(0) and, because of the orientation of the phosphine ligands, yields the *HH*(PPt) isomer under kinetic control. Thus, Pt($Ph_2Ppy)_2I_2$, with a detectable amount of trans isomer present, preferentially reacts through this isomer to yield the *HH*(PPt) isomer. Pt($Ph_2Ppy)_2Cl_2$, which in solution contains a negligible amount of trans isomer, is forced to use a different pathway to form the binuclear products. This is a slower process and results in the formation of the more stable *HT* isomer. We have observed that the synthesis of the binuclear complexes is more rapid when Pt($Ph_2Ppy)_2I_2$ is used than when Pt($Ph_2Ppy)_2Cl_2$ is the starting material (i.e., the *HH*(PPt) products are formed more rapidly than the *HT* products).

HH and *HT* isomers have been found for other Ph_2Ppy-bridged complexes. [RhPd(μ-$Ph_2Ppy)_2(CNCH_3)_2Cl_2]^+$ has been isolated in both isomeric forms, and the *HH* isomer rearranges to two *HT* isomers upon warming in solution.[10] With RuPd(μ-$Ph_2Ppy)_2(CO)Cl_3$, the *HT* isomer is isolated but a *HH* isomer has been identified as a transient precursor. Although in all these cases the *HT* isomers are the favored forms, it should not be assumed that this will always be the case. Indeed as we will show elsewhere, the reaction of Pt($Ph_2Ppy)_2Cl_2$, with (norbornadiene)$MoCl_4$ forms PtMo(μ-$Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl$, which exists in a thermodynamically favored *HH*(PPt) form.[20]

HH and *HT* isomers can also exist for other unsymmetrical bridging ligands. Particularly relevant to the present work are the existence and structural characterization of *HH* and *HT* isomers of $[(NH_3)_2Pt(\mu\text{-}C_6H_7H_2O_2)]_2^{2+}$ (where the bridging ligand is the anion of 1-methylthymine).[21,22] Nothing is reported about the interconversion of these isomers.[23]

Acknowledgment. We thank the National Science Foundation (Grant CHE 7924575) for support and N. Rutherford for experimental assistance. J.P.F. and F.E.W. were Earl C. Anthony and University of California Regents Fellows.

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