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Chelate Complexes of Phosphorus–Nitrogen Ligands. 1. Deprotonation, Cis–Trans Isomerism, and Anion-Catalyzed Isomerization in Platinum(II) Complexes of (*o*-Aminophenyl)diphenylphosphine

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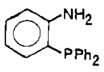
The new hybrid ligand (*o*-aminophenyl)diphenylphosphine (PNH_2) has been synthesized and bis-ligand chelate complexes of platinum(II) have been prepared. Facile deprotonation of the coordinated amino group has allowed the preparation of both cis and trans isomers of $[Pt(PNH_2)_2]X_2$, $[Pt(PNH^-)(PNH_2)]X$, and $[Pt(PNH^-)_2]$ (X^- is a noncoordinating anion and PNH^- is the conjugate base of PNH_2). The stereochemistries have been assigned using ^{31}P NMR spectroscopy. The first observation of anion-catalyzed isomerization in square-planar complexes is reported.

Introduction

We are interested in arylphosphines containing a nitrogen donor group in the ortho position. One such ligand (*o*-dimethylaminophenyl)diphenylphosphine ($PNMe_2$) has long been known.[1,2] The corresponding primary amine, which is potentially more interesting from the point of view of reactivity of the coordinated ligand has not been reported. We have now synthesized this ligand (*o*-aminophenyl)diphenylphosphine (PNH_2, I) and some of its platinum(II) complexes including a series of bis-chelate geometrical isomers. Such isomerism is rare in complexes of platinum(II); the only examples in the literature involve the amino acid ligands glycine,[3] valine,[4] and alanine.[5]



I, PNH_2

Experimental Section

Melting points were obtained on a hot stage microscope and are uncorrected. ^{31}P NMR spectra were obtained in chloroform-*d*, acetonitrile-d_3, or Me_2SO-d_6 with a Bruker HFX 90 spectrometer operating at 36.43 MHz in the Fourier transform mode. The external reference was triphenyl phosphite but chemical shifts are reported relative to P_4O_6 using a chemical shift difference of −15.5 ppm.[6] IR spectra were obtained in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 457 spectrometer and visible spectra in chloroform solution on a Beckman Acta V instrument. Conductivities were obtained at 20 °C using a Philips conductivity bridge. Microanalyses were performed by Alfred Bernhardt Laboratories, Germany, or CSIRO Microanalytical Service, Melbourne. Most of the complexes absorbed moisture rapidly on exposure to air and so, where stable, were dried under vacuum at 120 °C immediately before analysis.

(*o*-Aminophenyl)diphenylphosphine oxide was prepared essentially by the method of Cadogan[7] as outlined below. Ethyl diphenylphosphinite[8] and *o*-dinitrobenzene reacted in dimethylformamide to give (*o*-nitrophenyl)diphenylphosphine oxide. The use of crude reactants had little effect on the yield. A second crop of product was obtained by removal of the dimethylformamide on a rotary evaporator (90 °C), followed by addition of diethyl ether and storage at −20 °C. This crop was washed twice with acetone to remove any unreacted *o*-dinitrobenzene which also crystallizes under these conditions. The combined products were recrystallized from ethanol. Reduction of the nitro group by iron powder on a scale of 120 g resulted in an 89% yield of (*o*-aminophenyl)diphenylphosphine oxide.

(*o*-Aminophenyl)diphenylphosphine (PNH_2). A mixture of the dry phosphine oxide (89 g, 0.30 mol), methylpolysiloxane (92 g, 1.53 mol), and diphenyl ether (600 mL) was stirred and heated to reflux for 4 h in a fume hood (the reaction is conveniently monitored by hydrogen evolution). The cooled reaction mixture was diluted with twice its volume of methanol and allowed to stand for 2 h. The upper layer was carefully decanted and the lower layer washed with methanol. A concentrated solution of $Ni(NO_3)_2{\cdot}6H_2O$ (50% excess) in methanol was added gradually to the combined methanol extracts. The yellow solution was allowed to stand for 30 min and the yellow-orange crystalline nickel complex was then isolated by filtration. The ligand was recovered by boiling the complex in a 50% benzene–water mixture until dissolution was complete. The benzene phase was passed through a short column of florisil to remove the yellow impurity and then evaporated to dryness. The residue was recrystallized from ethanol to give 60 g (70%) of fluffy white needles mp 82.5–83.0 °C. The yield in different runs varied from 60 to 80% even though quantitative evolution of hydrogen occurred. This method of separation allows virtually quantitative recovery of the ligand from a methanolic solution provided that the solution is not basic and that no coordinating anions (e.g., chloride) are present.

cis-**$[Pt(PNH_2)_2][PtCl_4]$.** Potassium tetrachloroplatinate (3.0 g, 7.2 mmol) was dissolved in water (20 mL) and acetonitrile (100 mL) added. The mixture was heated to 60 °C and a solution of PNH_2 (2.0 g, 7.2 mmol) in acetonitrile (10 mL) was added dropwise with stirring. After 30 min the product was filtered off, washed with water, ethanol, and petroleum spirit (bp 40–60 °C), and dried in a stream of air (yield 3.7 g, 95%). The same compound precipitated immediately on addition of an ethanolic solution of Na_2PtCl_4 to an ethanolic solution of *cis*-$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$.

cis-**$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$.** The above reaction was repeated using 4.1 g (14.8 mmol) of PNH_2. After 30 min, water (100 mL) was added. The product which precipitated was recrystallized from ethanol and dried under vacuum (yield 5.6 g, 93%).

cis-**$[Pt(PNH_2)_2](PF_6)_2$.** A mixture of *cis*-$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$ (200 mg) and NH_4PF_6 (200 mg) was stirred in 1,2-dichloroethane (20 mL) overnight. The solution was heated to boiling and filtered hot. The filtrate was evaporated to dryness and the residue crystallized from acetonitrile by addition of ether (205 mg, 81%).

cis-**$[Pt(PNH^-)(PNH_3^+)Cl]Cl$.** A suspension of *cis*-$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$ (200 mg) in chlorobenzene (20 mL) was heated to reflux for 4 h. The bright yellow product was washed with chloroform and dried under vacuum. The conversion is quantitative. The same product was obtained in powdered form by simply heating *cis*-$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$ to 120 °C overnight.

cis-**$[Pt(PNH^-)_2]$.** This crystallized in high yield on the addition of excess triethylamine, hydrazine hydrate, or ethanolic potassium hydroxide to a solution of *cis*-$[Pt(PNH_2)_2]Cl_2{\cdot}H_2O$ in hot ethanol or acetonitrile. The product was washed with ethanol and dried at 120 °C under vacuum. The comound is somewhat air and light sensitive and is best stored under nitrogen in the dark.

cis- **and** *trans*-**$[Pt(PNH^-)_2]$.** PNH_2 (4.0 g, 14.4 mmol) in acetonitrile (20 mL) was added gradually to a gently refluxing solution of potassium tetrachloroplatinate (3.0 g, 7.2 mmol) in water (20 mL), acetonitrile (80 mL), and triethylamine (5 mL). After 50 min, the reaction mixture was diluted slowly with water (100 mL) and cooled to room temperature. Filtration gave a mixture of orange and yellow crystals which were washed with ethanol and dried in air. The mixture was suspended in 1,2-dichloroethane (100 mL) and with vigorous stirring was treated dropwise with a saturated solution of hydrogen chloride in ethanol until no color remained. The fine white precipitate was filtered off (with difficulty), washed with 1,2-dichloroethane, and suspended in 1,2-dichloroethane (50 mL). Treatment of the vigorously stirred suspension with triethylamine (2 mL) gave an almost clear orange solution which was filtered, diluted with ethanol (150 mL), and stored overnight at −20 °C. Pure *trans*-$[Pt(PNH^-)_2]$ (2.2 g, 41%)

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Table I. Melting Point Microanalytical and Phosphorus NMR Data

		%C		%H		%P		%Pt		^1J(PtP), kHz	
	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		δ,[f] ppm
PNH_2	82.5–83.0	77.96	78.08	5.82	5.78	11.17	11.0				132.1
cis-$[Pt(PNH_2)_2][PtCl_4]$[a]	280 dec	39.79	39.65	2.97	3.07	5.70	5.74	35.91	35.83	3.28[g]	87.4[g]
cis-$[Pt(PNH_2)_2]Cl_2 \cdot H_2O$[b]	297–299 dec	51.66	51.44	4.09	4.12			23.26	23.42	3.32	85.9
cis-$[Pt(PPh_3)_2Cl_2]$	310 dec[d]									3.67[h]	97.4
cis-$[Pt(PNH_2)_2](PF_6)_2$	306–310 dec	41.59	41.98	3.10	3.19	11.92	12.0			3.37[i]	88.6[i]
cis-$[Pt(PNH^-)(PNH_3^+)Cl]$[a,c]	315 dec	52.69	52.84	3.93	4.12					[j]	
cis-$[Pt(PNH^-)_2]$[a]	339–342 dec	57.83	57.77	4.04	3.99	8.28	8.20	26.09	26.02	3.03	85.0
trans-$[Pt(PNH^-)_2]$[a]	240	57.83	57.79	4.04	4.06					2.84	79.0
cis-$[Pt(PNH_2)_2](CF_3COO)_2$[a]	307 dec	49.24	49.20	3.31	3.37	6.35	6.42			3.31	87.6
trans-$[Pt(PNH_2)_2](CF_3COO)_2$[a]	260	49.24	49.44	3.31	3.39	6.35	6.40			2.50	75.3
cis-$[Pt(PNH^-)(PNH_2)]CF_3COO \cdot H_2O$	*e*	51.88	51.79	3.78	3.60	7.04	6.74			2.72	76.8
trans-$[Pt(PNH^-)(PNH_2)]CF_3COO \cdot 2H_2O$	*e*	50.84	50.84	3.93	3.55	6.90	7.13			3.16	84.8

[a] Dried at 120 °C immediately before analysis. [b] % Cl: calcd, 8.45; found, 8.31. [c] % Cl: calcd, 8.64; found, 8.51. [d] Lit.[9] 310–312 °C dec. [e] See text. [f] Relative to P_4O_6, positive values are to high field of reference. [g] Me_2SO-d_6. [h] Previously measured only in liquid HCl and found to be 3.87 kHz.[27] [i] CH_3CN-d_3. [j] Too insoluble for phosphorus NMR spectrum to be obtained.

was obtained after drying at 120 °C as bright orange crystals. The complex should be protected from light. The original 1,2-dichloroethane filtrate was reduced in volume to 25 mL, treated with triethylamine (5 mL), and diluted with ethanol (150 mL) to give bright yellow crystals of *cis*-$[Pt(PNH^-)_2]$ (2.4 g, 44%).

***cis*-$[Pt(PNH_2)_2](CF_3COO)_2$.** *cis*-$Pt[(PNH^-)_2]$ (400 mg) was dissolved in chloroform (10 mL) and trifluoroacetic acid added dropwise until the solution was just colorless. The solvent was evaporated on a rotary evaporator (50 °C), and the white solid was recrystallized from boiling ethanol and dried to constant weight at 120 °C under vacuum (yield 417 mg, 80%).

***trans*-$[Pt(PNH_2)_2](CF_3COO)_2$.** *trans*-$[Pt(PNH^-)_2]$ (1 g) was dissolved in dichloromethane (10 mL) and trifluoroacetic acid added dropwise until the solution was just colorless and then ethanol (50 mL) added immediately. The solvent was removed on a rotary evaporator (25 °C) and the residue recrystallized twice from ethanol by addition of water. The white product was dried at 40°C in vacuo (yield 900 mg, 69%). Solutions of the complex are yellow due to partial deprotonation. The color disappears on addition of trifluoroacetic acid.

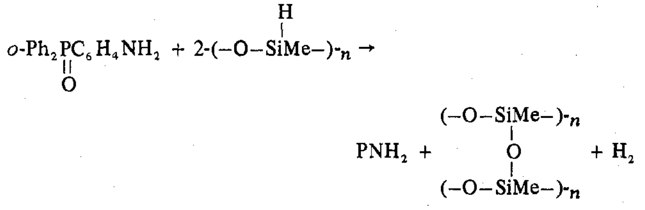
***cis*-$[Pt(PNH^-)(PNH_2)]CF_3COO \cdot H_2O$.** *cis*-$[Pt(PNH^-)_2]$ (540 mg, 0.72 mmol) was suspended in 1,2-dichloroethane (10 mL) and a solution of trifluoroacetic acid (82 mg, 0.72 mmol) in 1,2-dichloroethane (5 mL) added with shaking. The filtered solution was stored at −20 °C for 2 days, and the yellow crystals were filtered off, washed with 1,2-dichloroethane, and dried in a stream of air (yield 507 mg, 80%).

***trans*-$[Pt(PNH^-)(PNH_2)]CF_3COO \cdot 2H_2O$.** *trans*-$[Pt(PNH^-)_2]$ (500 mg) was suspended in chloroform (5 mL). Trifluoroacetic acid was added dropwise until the color had just changed from orange to yellow. Diluting with diethyl ether (5 mL) and cooling gave the yellow microcrystalline product which was washed with diethyl ether and dried in a stream of air (yield 300 mg, 50%).

cis-**$Pt(PPh_3)_2Cl_2$** was prepared by the method of Jensen, as reported in ref 9.

Results and Discussion

PNH_2 was prepared as an air-stable solid by reduction of the corresponding phosphine oxide with methylpolysiloxane,[10,11] according to the following equation:

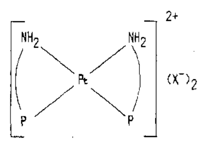


$$o\text{-}\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{C_6H_4NH_2} + 2\text{-}(\text{—O—}\overset{\overset{\mathrm{H}}{|}}{\mathrm{Si}}\mathrm{Me}\text{—})\text{-}_n \rightarrow \mathrm{PNH_2} + \begin{array}{c}(\text{—O—SiMe—})\text{-}_n\\ |\\ \mathrm{O}\\ |\\ (\text{—O—SiMe—})\text{-}_n\end{array} + \mathrm{H_2}$$

The use of trichlorosilane, the more common reagent for reduction of phosphine oxides[12,13] or hexachlorodisilane[14] gave only low yields of the phosphine, possibly because of reaction between the amino group and the silicon–chlorine bond. The ligand was isolated from the reaction via its nickel nitrate complex, which can be dissociated by boiling with water. This method of separation is also useful in recovering excess ligand from a reaction mixture or testing whether free ligand is present in solution. Full details of the preparation of PNH_2 and its complexes are given in the Experimental Section. Melting point, analytical data, and phosphorus NMR data are listed in Table I.

The ^{31}P NMR spectra of all the complexes recorded consisted of only a single peak with ^{195}Pt sidebands, indicating that both ligands are equivalent (on the NMR time scale). The ^{195}Pt–^{31}P coupling constant, ^1J(PtP), is a sensitive indicator of the donor group trans to phosphorus in platinum–phosphine complexes.[6,15,16] It is large for phosphorus trans to ligands of low trans influence such as halides and becomes lower as the trans influence of the trans ligand increases.[16] This has proved invaluable in assigning the structure and stereochemistry of complexes of PNH_2, an area in which the measurement of other physical properties such as conductivity and ^1H NMR has been of little use.

Reaction of K_2PtCl_4 with an equimolar quantity of PNH_2 yields an off-white compound which analyzes correctly for the expected product $[Pt(PNH_2)Cl_2]$. Conductivity and IR and ^{31}P NMR spectral data, however, show that the complex should be formulated as the bis-ligand Magnus type salt *cis*-$[Pt(PNH_2)_2][PtCl_4]$ (II, X = $^1/_2PtCl_4$). The IR spectrum in the Pt–Cl stretching region contains only a single peak at 322 cm^{-1}, which is in the same position as found for simple salts of the $PtCl_4^{2-}$ ion.[17] Complexes of the type $[Pt(L\text{-}L')Cl_2]$ show two distinct absorptions in this region.[1,2] The complex is appreciably soluble in dimethyl sulfoxide but virtually insoluble in other common solvents. The conductivity of a 1 mM solution is 37 Ω^{-1} cm^2 mol^{-1}, which is in the range expected for a 1:1 electrolyte.[18] In the ^{31}P NMR spectrum, the value of ^1J(PtP) is 3.28 kHz which is 390 Hz lower than that of *cis*-$[Pt(PPh_3)_2Cl_2]$ (Table I) confirming that the phosphorus is not trans to chloride and that the complex must therefore contain the $[Pt(PNH_2)_2]^{2+}$ cation. It is also much higher than normally found for trans phosphines and thus a cis arrangement of the ligands is implied. A value of around 3.30 kHz is also found for other complexes containing the *cis*-$[Pt(PNH_2)_2]^{2+}$ cation (Table I). *cis*-$[Pt(PNH_2)_2][PtCl_4]$ also precipitates immediately when a solution of K_2PtCl_4 is added to a solution containing the *cis*-$[Pt(PNH_2)_2]^{2+}$ cation and this lends further support to the proposed structure.

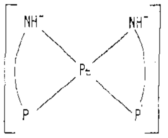


II

When the reaction is performed with an excess of PNH_2, white *cis*-$[Pt(PNH_2)_2]Cl_2$ (II, X = Cl) is obtained as the monohydrate. The complex is quite soluble in chloroform and to a lesser extent in methanol, ethanol, and acetonitrile. The solubility in water is very low (ca. 10^{-4} M). The IR spectrum (mull) contains broad bands at 3430 cm^{-1} due to $\nu(OH)$ and at 3000 cm^{-1} due to $\nu(NH)$ of the coordinated amino groups and there are no strong absorptions in the $\nu(PtCl)$ region. The low value of $\nu(NH)$ is caused by hydrogen bonding with the chloride ions.[19] In the ^1H NMR spectrum of the complex, the resonance of the OH and NH_2 protons (which are exchanging rapidly) occurs under the aromatic proton resonances (as shown by D_2O exchange). In the ^{31}P NMR spectrum the value of $^1J(PtP)$ (Table I) is close to that of the $PtCl_4^{2-}$ salt implying that the bis-chelate structure persists in chloroform solution. The conductivity of the complex is concentration dependent but approaches the value of a 2:1 electrolyte in nitromethane at infinite dilution.[19]

The ready formation of bis-ligand platinum(II) complexes of PNH_2 is in marked contrast to the behavior of its tertiary amine analogue $PNMe_2$, which *under the same conditons* gives only $[Pt(PNMe_2)Cl_2]$.[1] The failure of $PNMe_2$ to yield such complexes was ascribed, on the basis of molecular models, to the steric properties of the phenyl groups.[1] Since both ligands contain the diphenylphosphino group, it appears that substitution on the nitrogen is the dominant factor.

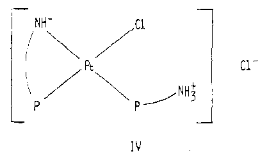
Substituted aniline complexes of platinum(II) have been found to be acidic[20] and both *cis*-$[Pt(PNH_2)_2]Cl_2$ and *cis*-$[Pt(PNH_2)_2][PtCl_4]$ react with bases to form the very stable, bright yellow complex *cis*-$[Pt(PNH^-)_2]$ (III) in which the ligands have been deprotonated. The compound is nonconducting in acetonitrile and can be sublimed at 300 °C under vacuum. The color is due to a single absorption in the visible region, λ_{max} 422 nm, ϵ 5.67×10^3. Only two peaks of relative intensity above 10% are observed in the mass spectrum (200 °C, 70 eV): the molecular ion, *m/e* 747 (100%), and the doubly charged molecular ion, *m/e* 373.5 (12%). The N–H stretching vibration at 3395 cm^{-1} is an unusually sharp peak and we have found such a peak diagnostic of a deprotonated aniline in these complexes. The trans influence[6,16,21] of the nitrogen increases on deprotonation as shown by the decrease in $^1J(PtP)$ (Table I).



III

As stated above, *cis*-$[Pt(PNH_2)_2]Cl_2$ was obtained as the monohydrate. When this complex was heated to 120 °C in an effort to remove the water, a bright yellow powder was obtained. The same product was obtained in crystalline form when the complex was heated in boiling chlorobenzene. The color indicated deprotonation of one or both of the ligands, possibly by loss of HCl. The elemental analysis, however, was correct for the expected anhydrous complex, suggesting that some form of isomerization had occurred.

The IR spectrum contains a sharp peak at 3360 cm^{-1}, assignable to a deprotonated amino (amido) group and a series of peaks between 2500 and 3000 cm^{-1} characteristic of a quaternary ammonium group.[22] The appearance of a peak at 305 cm^{-1} indicates that at least one chloride has coordinated to the platinum. We tentatively propose the structure *cis*-$[Pt(PNH_3^+)(PNH^-)Cl]Cl$ (IV), which is curious in that it contains both a cationic and an anionic phosphorus ligand. This species is apparently the thermodynamically stable form of the complex at high temperatures. The complex is only very slightly soluble in ethanol and $CHCl_3$ and insoluble in other common solvents. The solubility was too low in $CHCl_3$ for a phosphorus NMR spectrum to be obtained.



IV

During one preparation of *cis*-$[Pt(PNH^-)_2]$ in which triethylamine was added to *cis*-$[(Pt(PNH_2)_2]Cl_2$ prepared in situ, the solution developed an orange tinge and the product was contaminated with a very small quantity of an *orange* crystalline compound which was obtained pure by mechanical separation of the crystals.[23] The IR spectrum was similar to that of *cis*-$[Pt(PNH^-)_2]$ to which it was converted by heating. This suggested that the compound might be the trans isomer. We reasoned that a deprotonated nitrogen might have a trans effect approaching that of a phosphine, and, since closure of chelate rings is known to be rapid,[24] deprotonation of the coordinated nitrogen before entry of the second ligand might result in a mixture of isomers being formed. Thus the small amount of orange compound could have been the result of addition of the triethylamine before the initial reaction was complete. That this was the case, was shown by the isolation of a mixture containing approximately 50% of the *orange* compound when the reaction between the ligand and the tetrachloroplatinate was performed in the presence of excess triethylamine. The compound was subsequently proved to be *trans*-$[Pt(PNH^-)_2]$ by its elemental analysis and phosphorus NMR spectrum (Table I).

The isomers are similar in physical properties and could not be easily separated by chromatography or fractional crystallization. However, treatment of a 1,2-dichloroethane solution of the mixture with hydrogen chloride in ethanol gives a white precipitate of the protonated trans isomer which is converted back to *trans*-$[Pt(PNH^-)_2]$ by base. The filtrate contains the other isomer as *cis*-$[PtPNH_2)_2]Cl_2$ and the separation is quantitative. *trans*-$[Pt(PNH^-)_2]$ has a single absorption in the visible spectrum, λ_{max} 500 nm, ϵ 4.77×10^3. Irreversible isomerization to the cis isomer occurs above 240 °C in the solid state. In solution, conversion occurs at a lower temperature, being rapid at 150 °C in mesitylene. It is also photoinduced by daylight at room temperature.

Addition of excess trifluoroacetic acid to a solution of *trans*-$[Pt(PNH^-)_2]$ protonates both nitrogens to give the colorless complex *trans*-$[Pt(PNH_2)_2](CF_3COO)_2$. Retention of the trans configuration follows from the low value of $^1J(PtP)$ (Table I) and the fact that *trans*-$[Pt(PNH^-)_2]$ is regenerated by base. *cis*-$[Pt(PNH^-)_2]$ is also reversibly protonated by the acid to give the corresponding cis isomer with $^1J(PtP)$ close to the values discussed earlier for the chloride and the tetrachloroplatinate salts. The trans isomer changes rapidly and irreversibly to the cis form at 130 °C in the solid state but is stable at room temperature. The most convenient method of monitoring this isomerization is to deprotonate the sample with triethylamine in chloroform and determine the isomer ratio from the absorbance at 422 and 500 nm.

It seemed likely that the pK_a's for the two protons would be different for both the cis and the trans isomers since the first proton is being added to a neutral species and the second to a positively charged species. The addition of successive small quantities of trifluoroacetic acid to a solution of *trans*-$[Pt(PNH^-)_2]$ in chloroform causes the orange color to turn to yellow then colorless. The spectral changes during the addition are shown in Figure 1.

The peak at 500 nm is due to the starting material and the peak at 438 nm, which grows and then disappears, is due to

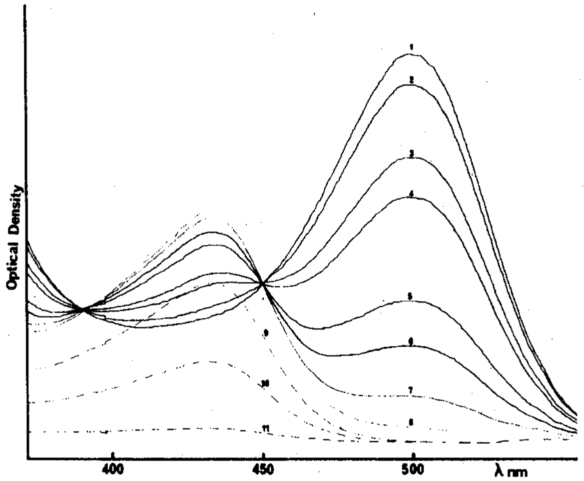


Figure 1. Curves 2–11 represent the spectral changes of a $CHCl_3$ solution of *trans*-$[Pt(PNH^-)_2]$ (curve 1) on the addition of successive small quantities of CF_3COOH. Curve 8 is the spectrum of the monoprotonated cation *trans*-$[Pt(PNH^-)(PNH_2)]^+$.

the yellow monoprotonated cation *trans*-$[Pt(PNH^-)(PNH_2)]^+$. In spectrum 8 the starting material has virtually all reacted but the curve still passes through the isosbestic points indicating that virtually none of the *diprotonated* species has formed up to this point, i.e., the first protonation step is complete before the second step begins to take place. The actual values of pK_1 and pK_2 for this complex could not be determined due to the lack of solubility in suitable solvents. Protonation of *cis*-$[Pt(PNH^-)_2]$ also occurs stepwise as shown by the fact that a suspension of this complex in ethanol dissolves completely to give a yellow solution on addition of only 1 molar equiv of trifluoroacetic acid.

Under the conditions specified in the Experimental Section it was possible to isolate the yellow crystalline salt, *trans*-$[Pt(PNH^-)(PNH_2)]CF_3COO$ (λ_{max} 438 nm), in hydrated form. The corresponding yellow cis isomer (λ_{max} 428 nm) was also isolated as a hydrate. The trans complex reverts to the orange fully deprotonated form at 130 °C, whereas the cis isomer is stable (24 h) at this temperature but slowly decomposes at 165 °C.

Although in both the cis and the trans isomers the two phosphorus atoms are in different environments only a single resonance with ^{195}Pt satellites is observed in the ^{31}P NMR spectra of each. This is consistent with the rapid exchange of a proton between the two nitrogens which would make the two phosphorus atoms equivalent on the NMR time scale. In agreement with this explanation, the coupling constant of each compound is intermediate to the values of the corresponding conjugate acid and base.

The four protonated complex cations have been fully characterized as the trifluoroacetate salts. We have also prepared the analogous complexes containing the noncoordinating anions, perchlorate, tetrafluoroborate, and *p*-toluenesulfonate, by using the appropriate acid. Since the acetate ion is more basic, acetic acid yields only monoprotonated complexes.

The relationship between the bis-ligand platinum complexes derived from PNH_2 is summarized in Figure 2.

The most interesting aspect of this work is the anion-catalyzed isomerization of *trans*-$[Pt(PNH_2)_2]^{2+}$ in solution (Figure 2, *). Although the trifluoroacetate salt is stable for at least 2 weeks in ethanol or water solution, isomerization in chloroform is complete (>99%) within 7 h. We observed that in each of the above solvents the addition of more strongly coordinating anions greatly increased the rate of isomerization. A preliminary kinetic study using a 100-fold excess of the anion in 10^{-4} M solutions of the complex was made. The reaction was monitored by observing the change in absorbance at 270 nm or by the sampling and deprotonation method described above. The reaction is irreversible and first order with respect to the platinum complex. The anion dependence of the rate in ethanol is $I^- \approx NCS^- > Br^- > Cl^- \gg CF_3COO^-$ and there is a marked dependence on the polarity of the solvent, with the rate increasing from water to ethanol to chloroform. The role of the anion is in fact catalytic since the isomerization goes to completion in the presence of only 0.1 molar equiv of the added anion.

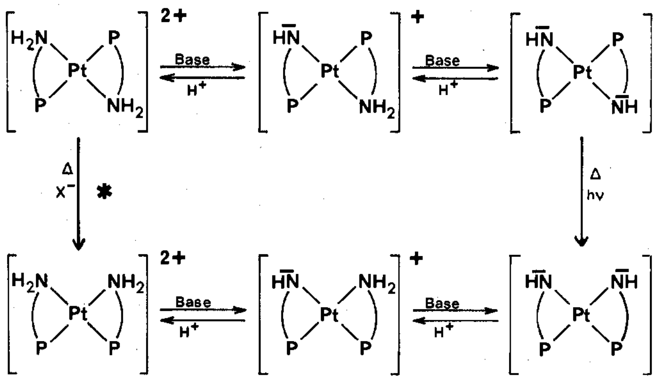


Figure 2. Summary of the relationship between the platinum bis-ligand chelate complexes derived from PNH_2.

These results are in accordance with a mechanism involving equilibrium association of the anion, followed by rearrangement of the five-coordinate intermediate as shown below.

$$trans\text{-}[Pt(PNH_2)_2]^{2+} + X^- \overset{K}{\rightleftharpoons} [Pt(PNH_2)_2X]^+ \xrightarrow{\text{several steps}} cis\text{-}[Pt(PNH_2)_2]^{2+} + X^-$$

The rate of isomerization will depend on the magnitude of the equilibrium constant K which will become larger as the polarity of the solvent decreases and as the coordinating ability of the anions toward platinum increases.

Although catalysis of isomerization in square-planar complexes by neutral (usually phosphine) ligands has been well documented,[25,26] this is the first reported example in which an anion behaves as the catalyst. We are investigating this system in more detail to see whether the mechanism of rearrangement[25] can be unambiguously determined.[28]

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Registry No. (*o*-Aminophenyl)diphenylphosphine oxide, 23081-74-5; PNH_2, 65423-44-1; *cis*-$[Pt(PNH_2)_2][PtCl_4]$, 65441-67-0; *cis*-$[Pt(PNH_2)_2]Cl_2$, 65441-68-1; *cis*-$[Pt(PNH_2)_2](PF_6)_2$, 65441-69-2; *cis*-$[Pt(PNH^-)(PNH_3^+)Cl]Cl$, 65441-70-5; *cis*-$[Pt(PNH^-)_2]$, 65441-71-6; *trans*-$[Pt(PNH^-)_2]$, 65494-16-8; *cis*-$[Pt(PNH_2)_2](CF_3COO)_2$, 65441-73-8; *trans*-$[Pt(PNH_2)_2](CF_3COO)_2$, 65494-18-0; *cis*-$[Pt(PNH^-)(PNH_2)]CF_3COO$, 65441-75-0; *trans*-$[Pt(PNH^-)(PNH_2)]CF_3COO$, 65494-20-4; *cis*-$Pt(PPh_3)_2Cl_2$, 15604-36-1.

References and Notes

(1) H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi, *J. Chem. Soc.*, 5210 (1965).
(2) T. B. Rauchfuss, F. T. Patino, and D. M. Roundhill, *Inorg. Chem.*, **14**, 652 (1975).
(3) F. W. Pinkard, E. Sharratt, and W. Wardlaw, *J. Chem. Soc.*, 1012 (1934); V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1234 (1965); L. M. Volshtein, G. G. Motyagina, and M. F. Mogilevkina, *Zh. Neorg. Khim.*, **6**, 1105 (1961); *Russ. J. Inorg. Chem.*, 564 (1961).
(4) L. M. Volshtein and G. D. Zegzhda, *Zh. Neorg. Khim.*, **7**, 2315 (1962); *Russ. J. Inorg. Chem.*, 1199 (1962).
(5) L. M. Volshtein and I. O. Volodina, *Zh. Neorg. Chem.*, **7**, 2685 (1962); *Russ. J. Inorg. Chem.*, 1399 (1962).
(6) F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc. A*, 2087 (1970).
(7) J. I. G. Cadogan, D. J. Sears, and D. M. Smith, *J. Chem. Soc. C*, 1314 (1969).

(8) R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4623 (1961).

(9) J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

(10) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964).

(11) Diphenylsilane also reduced the phosphine oxide at 160 °C in the absence of solvent.

(12) Y. Segall, I. Granoth, and A. Kalir, *J. Chem. Soc., Chem. Commun.*, 501 (1974).

(13) L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).

(14) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).

(15) F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 2700 (1968).

(16) B. T. Heaton and A. Pidcock, *J. Organomet. Chem.*, **14**, 235 (1968).

(17) A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, **3**, 1775 (1964).

(18) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(19) IR and conductivity studies still in progress show that substantial ion pairing occurs in this complex and in other complexes of PNH_2 which contain anions capable of hydrogen bonding to the primary amino groups. As might be expected, the PF_6^- anion in *cis*-$[Pt(PNH_2)_2](PF_6)_2$ does not hydrogen bond as shown by the fact that the complex is a 2:1 electrolyte in nitromethane (1 mM solution). Consequently the N–H stretching vibrations of the coordinated amino group are sharp and occur about 300 cm^{-1} higher in energy than in the chloride complex. $^1J(PtP)$ is about the same for both species (Table I) since both contain phosphorus trans to an amino group.

(20) T. O. Blyumental', T. Ya. Paperno, V. V. Razumovskii, and L. V. Konovalov, *Zh. Obschch. Khim.*, **45**, 2296 (1975); *J. Gen. Chem. USSR*, **45**, 2254 (1975).

(21) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

(22) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd ed, Chapman and Hall, London, 1975, p 272.

(23) L. Pasteur, *C. R. Hebd. Seances Acad. Sci.*, **26**, 535 (1848); *Ann. Chim. (Paris)*, **24**, 442 (1848).

(24) L. Cattalini in "Reaction Mechanisms in Inorganic Chemistry", M. L. Tobe, Ed., University Park Press, Baltimore, Md., 1972, p 293.

(25) D. A. Redfield and J. H. Nelson, *J. Am. Chem. Soc.*, **96**, 6219 (1974), and references therein.

(26) R. Roulet and C. Barkey, *Helv. Chim. Acta*, **56**, 2179 (1973).

(27) K. B. Dillon, T. C. Waddington, and D. Younger, *J. Chem. Soc., Dalton Trans.*, 790 (1975).

(28) Since receipt of this paper, W. J. Louw, *Inorg. Chem.*, **16**, 2147 (1977), has reported iodide catalyzed isomerization of $[Pt(PEt_3)_2I_2]$.

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Solution Photosubstitution Chemistry of Amine Pentacarbonyl Derivatives of the Group 6B Metals in the Presence of ^{13}CO. An Example of Stereospecific Incorporation of ^{13}CO

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The ligand photosubstitution chemistry of $M(CO)_5$(amine) derivatives (M = Cr, Mo, W; amine = piperidine, pyridine) in the presence of ^{13}C-labeled carbon monoxide has been demonstrated to involve both CO and amine loss at 366 and 313 nm. The relative quantum yields for CO vs. unique ligand (amine) dissociation were found to be highly dependent on the metal center, with the chromium complexes exhibiting a greater propensity for CO dissociation as opposed to amine loss. On the other hand, molybdenum and tungsten were shown (consistent with and as an extension of previous studies) to undergo amine dissociation with a greater quantum efficiency than CO loss. More importantly, it has been clearly established that for the process involving CO photosubstitution with ^{13}CO the products are stereospecifically labeled metal pentacarbonyl derivatives, *cis*-$M(CO)_4(^{13}CO)$(amine). These experiments demonstrate that there is either exclusively equatorial carbonyl photosubstitution occurring (affording a C_s intermediate) or a facile rearrangement of the C_{4v} form of the intermediate, $[M(CO)_4(\text{amine})]$, to the C_s structure prior to recombination with an incoming ^{13}CO ligand.

Introduction

The ligand photosubstitution chemistry of $M(CO)_5L$ complexes, where M = Mo or W and L = amine, has been demonstrated to involve both CO and L substitution via a dissociative mechanism with M–L cleavage (eq 1) and not M–CO cleavage (eq 2) being dominant.[1-3] Wavelength-dependent quantum yield studies indicate that CO substitution becomes more important at shorter excitation wavelengths.[2,4,5]

$$M(CO)_5L + CO \xrightarrow{h\nu} M(CO)_6 + L \tag{1}$$

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO \tag{2}$$

We have previously reported stereoselective incorporation of ^{13}CO into $M(CO)_5L$ derivatives (M = Mo, W; L = NHC_5H_{10}) upon broad-wavelength irradiation of the substrates in the presence of labeled carbon monoxide in tetrahydrofuran.[6,7] In this paper we present results on the quantum efficiency for reactions 1 and 2 carried out in the presence of ^{13}CO where both M–L and M–CO cleavage could be observed simultaneously, i.e., as noted by the appearance of $M(CO)_5(^{13}CO)$ and $M(CO)_4(^{13}CO)L$. These studies were performed at excitation wavelengths of 313 and 366 nm where CO loss is expected to be enhanced. In contrast to the earlier reports for molybdenum and tungsten derivatives,[1-3] we found in the chromium analogues that M–CO bond rupture proceeds with a quantum efficiency equal to or greater than that of M–N bond dissociation at 313 and 366 nm for amine = NHC_5H_{10} or NC_5H_5. Furthermore, it is shown that reactions involving CO photosubstitution yield the stereospecifically labeled metal pentacarbonyl derivatives *cis*-$M(CO)_4(^{13}CO)$(amine).

Experimental Section

Materials. Reagent grade hexane was distilled under nitrogen from calcium sulfate (no special precautions were used to remove trace olefins). Molybdenum and tungsten hexacarbonyls were generous gifts from Climax Molybdenum Corp., whereas chromium hexacarbonyl was purchased from Strem Chemicals. Piperidine and pyridine were reagent grade chemicals obtained from Aldrich and Baker Chemical Co., respectively. ^{13}CO gas enriched to >90% was acquired from Prochem, B.O.C. Ltd., London.

Compound Preparations. The metal pentacarbonyl amine complexes were prepared photochemically in an Ace Glass circular photochemical reaction vessel from the metal hexacarbonyls with excess amine in THF.[8] After removal of solvent, excess $M(CO)_6$ was recovered by vacuum sublimation at 35–50 °C. The bright yellow products were purified by recrystallization from hexane at −79 °C.

Instrumentation. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Sodium chloride solution cells (1.0-mm path length) were used with hexane solvent in the reference cell. Ultraviolet–visible spectra were recorded on a Cary 14 recording spectrophotometer using 1-cm quartz cells.

Sample Preparation. All samples were handled under red, photographic safe light during mixing and throughout analysis. Typically, a 25-mL solution of reactants was prepared and mixed thoroughly.

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