

Acknowledgment. The pulse Fourier transform nmr spectrometer and associated computer utilized in this research were acquired by the Department of Chem-

istry via a grant from the National Science Foundation. This work was supported in part by the Office of Naval Research.

Synthesis and Reactions of Nucleophilic Complexes of Rhodium(I) Containing *o*-(Diphenylphosphino)-*N,N*-dimethylaniline¹

Thomas B. Rauchfuss and D. Max Roundhill*

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. Received December 1, 1973

Abstract: The complexes $[\text{Rh}(\text{PN})_2]\text{X}$ ($\text{X} = \text{Cl}, \text{PF}_6, \text{SbF}_6, \text{BPh}_4, \text{ClO}_4$) where PN is *o*-(diphenylphosphino)-*N,N*-dimethylaniline are described. The trans addition of Cl_2 and CH_3I gives $[\text{RhCl}_2(\text{PN})_2]\text{X}$ and $[\text{RhCH}_3\text{I}(\text{PN})_2]\text{X}$. Oxygen and cyanogen add to give $[\text{RhO}_2(\text{PN})_2]\text{X}$ and $[\text{Rh}(\text{CN})_2(\text{PN})_2]\text{X}$ where the adduct groups occupy cis positions. $[\text{Rh}(\text{PN})_2]\text{X}$ adds carbon monoxide to form $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{X}$ where the dimethylamino arms of the chelate are displaced. Heating the dicarbonyl in boiling toluene favors the reverse reaction. $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$ reacts with CH_3I to give $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$ because of the likely presence of iodide in the reaction medium. The low conductivity of $\text{RhCl}(\text{PN})_2$ is due to ion pairing. The complexes $\text{RhClCO}(\text{PN})$, $\text{RhCl}(\text{PF}_6)(\text{PN})$, and $\text{Rh}(\text{C}_5\text{H}_5\text{O}_2)(\text{PN})$ have been isolated. $\text{RhClCO}(\text{PN})$ is converted into $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$ by reaction with PN and NH_4PF_6 under a CO atmosphere. $\text{RhClCO}(\text{PN})$ adds allyl chloride to form $\text{RhCl}_2(\sigma\text{-C}_3\text{H}_5)\text{CO}(\text{PN})$. $\text{RhClCO}(\text{PN})$ reacts with CH_3I in the presence of NaI to give $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$. Two separate isomers of the acetyl complex have been isolated. The number of nonequivalent *N*-methyl resonances for the coordinated dimethylamino group is used to identify the stereochemistry of many of the above complexes. $\text{Ir}_2\text{Cl}_2(\text{cyclooctene})_4$ reacts with PN and NH_4PF_6 to give $[\text{IrHCl}(\text{PN})_2]\text{PF}_6$.

Platinum metal complexes of substituted phosphines have become of considerable importance recently because of their use as homogeneous catalysts. The features which appear to be desirable are a low oxidation state, a high basicity or nucleophilicity, and an ability to undergo facile ligand dissociation to generate coordinately unsaturated intermediates. One of the most significant complexes of the group VIII metals which have been used in this work is chlorotris(triphenylphosphine)rhodium(I). The catalytic hydrogenation of olefins using this complex has been studied in considerable detail,² and it has been found that dissociation of a triphenylphosphine ligand is a necessary and fundamental step in the hydrogenation mechanism. This requirement of a low-valent complex to dissociate one or more ligands in order to be catalytically active has been found to be critically important in a number of cases. At the onset of work on the catalytic activity of these compounds there was no way to predict in advance that these coordinated π -acceptor ligands would show the necessary lability. Since this is an important aspect of the direct synthesis of compounds of likely catalytic activity, it appeared to us that it would be valuable to prepare nucleophilic complexes which would predictably displace ligands in the presence of incoming electrophiles or π acceptors. We believe that the results of this work represent one of the first successful attempts to synthesize compounds having such desirable features.

Our approach to this problem has been to prepare low-valent complexes of substituted amines. Since, however, an amino group will not stabilize a low-valent transition metal complex because of the failure of such a ligand to be involved in $d-\pi$ back-bonding, it is necessary for π -acid ligands to be also present in order for the compounds to be isolable. The compound *o*-(diphenylphosphino)-*N,N*-dimethylaniline (Figure 1) can be conveniently used as a ligand for complexes of this type since the presence of the diphenylphosphino group will effectively stabilize low-valent transition metal complexes. The dimethylamino arm can then coordinate through the nitrogen to form a chelate complex, which can be verified in a convenient manner from the chemical shift of the dimethylamino group in the ¹H nmr spectrum. A further advantage of the use of an amine as ligand for a low-valent complex is that the coordination of a basic σ -donor ligand will confer a high nucleophilicity to the complex. This combination of features, lability to generate coordinately unsaturated complexes and nucleophilicity of the central metal atom, is the main requirement for an active homogeneous catalyst.^{3,4} This paper reports the synthesis and chemistry of some rhodium complexes which have been specifically designed to be nucleophilic and to contain ligands which can be replaced by incoming π -acceptor ligands.

o-(Diphenylphosphino)-*N,N*-dimethylaniline, abbreviated PN, has been used as a chelating ligand in a number of group VIII complexes. These compounds

(1) See T. Rauchfuss and D. M. Roundhill, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, Abstract No. 153.

(2) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(3) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(4) G. N. Schrauzer, Ed., "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971.

have contained the metal in its "common" oxidation state; for example, complexes have been isolated for Ni(II), Co(II), Pd(II), and Pt(II). These complexes have both the diphenylphosphino and dimethylamino arms of the chelate coordinated and are of the general formula $MX_2(PN)_2$.^{5,6} In this work we have prepared a number of nucleophilic rhodium(I) complexes containing this PN ligand and have made an extensive study of the chemistry of these compounds as shown in Scheme I. The aim of this project has been to try and

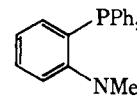
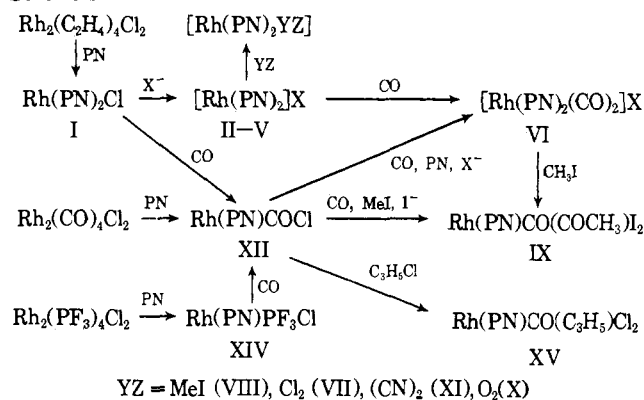


Figure 1. Structure of the ligand PN.

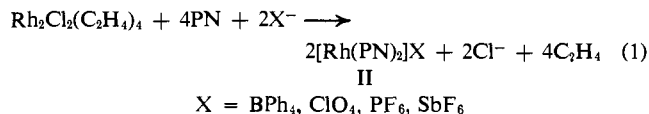
Scheme I



use the ligand PN to prepare nucleophilic complexes having a substitution labile donor ligand.

Results and Discussion

Bis(chelate) Complexes. When di- μ -chloro-tetrakis(ethylene)dirhodium(I) is treated with 4 equiv of PN in the presence of a noncoordinating anion such as PF₆⁻, the orange microcrystalline complex [Rh(PN)₂]₂PF₆ (II) precipitates and can be isolated in good yield (eq 1). Complex II is very air sensitive in solution but



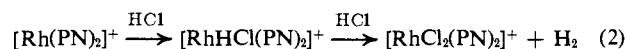
the dry solid can be stored in air without deterioration. The conductivity of the hexafluorophosphate salt in nitrobenzene is 20.3 ohm⁻¹ cm² equiv⁻¹. The ¹H nmr spectrum of II consists of a phenyl multiplet and an *N*-methyl singlet which is 3.30 ppm downfield of TMS. This resonance frequency is 0.66 ppm downfield of the methyl resonance of the free ligand. This downfield shift is due to coordination of the dimethylamino group to the rhodium atom which causes the *N*-methyl group to be deshielded.

The stereochemistry of complex II has not been determined by any definitive method. The multiplicity of the Rh-N and Rh-P stretching modes in the far-infrared spectrum appeared to present a convenient approach to elucidate the stereochemistry of the complex. The method was unsuccessful, however, since these separate stretching frequencies could not be unambiguously identified because the critical region of the spectrum in each case was complicated by the presence of bands due to other ligand vibrations. It is probable, however, that the diphenylphosphino groups

are mutually trans for the following reasons: (i) models show that steric repulsion is minimized when the diphenylphosphino groups are trans and (ii) all known bis-substituted phosphine complexes of rhodium(I) and iridium(I) have a trans stereochemical arrangement of the phosphine ligands

A solution of the hexafluoroantimonate salt III reacts with Cl₂ to give the orange compound [RhCl₂(PN)₂]₂SbF₆ (VII). The ¹H nmr spectrum of this compound shows only a single *N*-methyl resonance consistent with mutually trans chlorides.

When II is allowed to react with HCl either in solution or in the solid state, the dichloride VII is obtained in good yield and only a trace of a hydro complex could be isolated (eq 2). This behavior is character-



istic of a hydrido complex of a transition metal which has considerable hydridic character.⁷ A similar sequence has been reported for Rh[P(OMe)₃]₄⁺. This cation reacts with HBr to give RhHBr[P(OMe)₃]₄⁺ which converts to RhBr₂[P(OMe)₃]₄⁺ when refluxed with excess HBr.⁸ With [Rh(Ph₂PCH=CHPPh₂)₂]⁺ the dibromo compound is obtained at room temperature from HBr.⁹ Although we have been unable to purify the hydrido complex for a complete characterization, a small amount of a cream-colored complex has been obtained. This compound can be spectroscopically characterized as [RhHCl(PN)₂]⁺. The infrared spectrum shows a band at 2220 cm⁻¹ for the Rh-H stretch, and a high-field resonance in the ¹H nmr spectrum centered 15.3 ppm upfield of TMS. The high-field resonance consists of two overlapping triplets due to coupling of the hydrogen with the two *cis* phosphorus ($J_{\text{P-H}} = \text{Hz}$) and the rhodium ($J_{\text{Rh-H}} = 10 \text{ Hz}$)¹⁰ nuclei to give the expected pattern.

The complex II oxidatively adds CH₃I to give [Rh(CH₃(PN)₂)]PF₆ (VIII). The ¹H nmr spectrum of this complex shows two resonances due to the *N*-methyl groups at τ 6.28 and 6.90, along with a resonance due to the methyl group on rhodium at τ 8.75. The observation of two separate resonances for the dimethylamino groups shows that the methyl iodide has added to give the stereochemistry with the CH₃ and I ligands in a mutually trans arrangement (see Appendix). It is noteworthy that whereas the trans adduct VII from Cl₂ shows only one *N*-methyl resonance, the trans adduct VIII shows two resonances for this group. This occurs because in complex VIII the nonidentical trans CH₃ and I ligands cause the *N*-methyl groups above and below the plane of the PN ligands to be in a nonequivalent environment. With the dichloro complex VII the ligands above and below the plane of the PN ligands are identical and only a single resonance is found for

(7) P.-C. Kong and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 187 (1974).

(8) L. M. Haines, *Inorg. Chem.*, **10**, 1693 (1971).

(9) J. T. Mague, *Inorg. Chem.*, **11**, 2558 (1972).

(10) P.-C. Kong and D. M. Roundhill, *Inorg. Chem.*, **11**, 1437 (1972).

(5) H. P. Fritz and K. E. Schwarzahns, *J. Organometal. Chem.*, **5**, 103 (1966).

(6) H. P. Fritz, I. R. Gordon, K. E. Schwarzahns, and L. M. Venanzi, *J. Chem. Soc. A*, 5210 (1965).

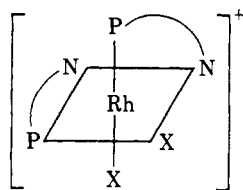
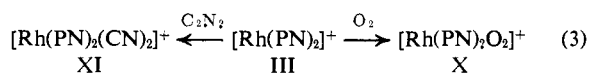


Figure 2. Stereochemistry of the oxygen and cyanogen adducts of $[\text{Rh}(\text{PN})_2]\text{SbF}_6$.

the NMe group. The nonequivalence of methyl substituents on the ligand because of environmental effects has been shown previously for the compounds dichloro[2-phenylphosphinobis(*N,N*-dimethylaniline)]-platinum⁶ and $h^5\text{-CpMoX}(\text{CO})_2(\text{PMe}_2\text{Ph})$.¹¹ These results show that the chemical shift of the methyl resonance is dependent on the stereochemical arrangement of the methyl resonance.

The complex III irreversibly adds oxygen when solutions are exposed to the air. The complex $[\text{Rh}(\text{PN})_2\text{O}_2]\text{SbF}_6$ (X) is obtained as brown crystals and displays a band of medium intensity in the infrared spectrum at 872 cm^{-1} which is characteristic for dioxygen complexes. The hexafluoroantimonate complex was prepared in preference to the hexafluorophosphate one since the oxygen adduct of the former is free from interfering bands in the $800\text{--}900\text{-cm}^{-1}$ region of the infrared spectrum. In the case of the latter complex, broad strong bands for $\nu_{\text{P-F}}$ obliterate this region. The ^1H nmr spectrum consists of four resonances due to the dimethylamino group. This nonequivalence of all four methyl groups can only occur with the structure and stereochemistry shown in Figure 2 (see Appendix). The complex III also adds cyanogen to form the dicyano complex XI (eq 3). The infrared spectrum



shows two bands at 2138 and 2140 cm^{-1} for the CN stretch, and the ^1H nmr spectrum is analogous to the spectrum of $[\text{RhO}_2(\text{PN})_2]^+$ showing resonances due to four nonequivalent methyl groups. The stereochemistry is therefore analogous to that of the O_2 complex but different from that of the dichloro complex. The addition of cyanogen is irreversible. Previous workers^{12,13} have studied the oxidative addition of cyanogen to $\text{RhCl}(\text{PPh}_3)_3$; however, this reaction is reversible and cyanogen can be removed from the solid at room temperature. *This irreversibility of the cyanogen addition as compared to the reversibility of the analogous reaction with $\text{RhCl}(\text{PPh}_3)_3$ shows that this bis(*o*-diphenylphosphino)-*N,N*-dimethylaniline]rhodium(I) cation has considerable nucleophilic character.* The difference in stereochemistry of the adduct of the pseudohalogen cyanogen from that of the addition of chlorine was a rather unexpected result. The steric interactions in the cis adduct make it unlikely that this isomer is the favored one solely on thermodynamic considerations; however, it may be significant that the isomer obtained from the addition of cyanogen is the same as the one formed with

(11) R. J. Mawby and G. Wright, *J. Organometal. Chem.*, **21**, 169 (1970).

(12) M. Bressan, G. Favero, B. Corain, and A. Torco, *Inorg. Nucl. Chem. Lett.*, **7**, 203 (1971).

(13) A. J. Argento, P. Fitton, J. E. McKeon, and E. A. Rick, *Chem. Commun.*, 1427 (1969).

oxygen. This similarity may arise from the fact that the coordination of cyanogen resembles the bonding of π acceptors such as oxygen where the bond between the two coordinated atoms is stretched rather than completely broken. Such a coordination of the carbon atoms of cyanogen to a transition metal would lead to a considerable bending of the molecule into a cisoid geometry which would be consistent with the observation of two bands for $\nu_{\text{C=N}}$ in the infrared spectrum. This explanation adequately satisfies the observation that cyanogen adds to low-valent transition metal complexes to give cis adducts, as well as explaining the reversibility of the addition in a number of cases. Nevertheless, it will be necessary to carry out a single-crystal structure determination for the carbon-carbon bond distance in the coordinated cyanogen before a distinction between the two types of bonding can be made. The ^1H nmr spectrum of $[\text{RhO}_2(\text{PN})_2]^+$ and $[\text{Rh}(\text{CN})_2(\text{PN})_2]^+$ shows that two of the phenyl hydrogens are shifted upfield by 60 Hz. A similar upfield shift has been observed previously¹⁴ for the complexes $[\text{IrO}_2(\text{dppe})_2]^+$ and $[\text{IrSe}_2(\text{dppe})_2]^+$. The results of this work have confirmed that the anomalous shift is due to steric interaction of the coordinated ligand with the ortho hydrogens on the coordinated dppe. The observation of such a shift in the ^1H nmr spectrum of $[\text{RhO}_2(\text{PN})_2]^+$ shows that the axial position of the coordinately unsaturated complex $[\text{Rh}(\text{PN})_2]^+$ is sterically restricted as to the type of adduct which will be isolable.

Carbon monoxide reacts with II to give the yellow dicarbonyl complex $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$ (VI). The ^1H nmr spectrum of VI shows a single resonance for the dimethylamino group at τ 7.35. This position is upfield by 0.66 ppm from the resonance in II and is identical with that of the free ligand PN. This shows that the dimethylamino arms of the chelate have been displaced by CO and that the complex is four coordinate and square planar.¹⁵ This result was predicted at the outset of this work since the dimethylamino group is solely a σ donor and therefore a relatively poor ligand for univalent rhodium. In the presence of a good π acceptor such as CO this arm of the chelate is readily replaced since the resulting rhodium(I) complex formed is much more effectively stabilized in the low oxidation state because of the presence of the coordinated carbonyls. The infrared spectrum of the dicarbonyl complex VI shows a single strong band in the carbonyl region at 1971 cm^{-1} which is consistent with a *trans*-dicarbonyl (D_{2h}) stereochemistry. This reaction is of direct importance to the development of complexes which are potential homogeneous catalysts. *The significant feature of the reaction is that we can add π -acceptor ligands to a low-valent transition metal complex without decreasing the degree of coordinate unsaturation about the central metal atom.* The carbonylation reaction is readily reversible since, if the compound VI is heated in boiling toluene, the CO is eliminated and compound II re-formed. The conductivity of $[\text{Rh}(\text{PN})_2]\text{PF}_6$ ($\Lambda = 20.3\text{ ohm}^{-1}\text{ cm}^2\text{ equiv}^{-1}$ in nitrobenzene) is not changed on carbonylation.

No detailed study has been made of the mechanism of this reaction. Two conceivable mechanisms are the

(14) A. P. Ginsberg and W. E. Lindell, *Inorg. Chem.*, **12**, 1983 (1973).

(15) T. Rauchfuss and D. M. Roundhill, *J. Organometal. Chem.*, **59**, C 30 (1973).

dissociation of a dimethylamino arm of the chelate followed by addition of CO or the addition of CO into the fifth coordination position with concomitant displacement of the dimethylamino arm of the chelate. The ^1H nmr spectrum of II has been obtained at -27° and is identical with the spectrum obtained at 35° , which shows that if the dimethylamino arms of the chelate are undergoing reversible dissociation in solution, the exchange rate must be fast.

Complex VI reacts with CH_3I under CO to give the complex $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$ (IX), which shows a band in the infrared spectrum at 1693 cm^{-1} assignable to a rhodium acetyl complex. If the reaction is carried out under N_2 , the ^1H nmr spectrum of the compound formed shows four methyl resonances. The resonance at τ 7.82 is unambiguously due to a methyl iodide in the coordination sphere since when the reaction is carried out under an atmosphere of CO this resonance is absent, and the acetyl complex IX formed shows a new band in the infrared spectrum due to a coordinated carbonyl at 2055 cm^{-1} . A similar compound with CH_3I in the coordination sphere of rhodium has been reported previously.¹⁶ The other methyl resonances are due to two nonequivalent dimethylamino groups and an acetyl resonance. The stereochemistry of the carbonyl complex is shown in Figure 3. This structure has been designated isomer A; however, when the acetylcarbonyl complex is obtained from hexane a different isomer, designated B, is obtained. This acetyl complex has been obtained by a more convenient method starting from $\text{RhClCO}(\text{PN})$.

This reaction is rather novel in that it involves the isolation of an uncharged rhodium complex in good yield from the reaction of a cationic rhodium complex with an alkyl halide. The reaction occurs with the elimination of one PN. This displacement shows the steric instability of the bis(chelate) complexes, although the removal of one PN would be facilitated because the ligand is monodentate in the dicarbonyl complex VI. The CH_3I was carefully purified prior to use and the reaction has been carried out for $\text{X} = \text{PF}_6, \text{SbF}_6, \text{or ClO}_4$. In each case, the neutral diiodorhodium(III) complex was obtained. The dimethylamino arm of the chelate is coordinated in the acetyl complex IX, although in the dicarbonyl complex VI from which it was prepared the nitrogens are free. This is to be anticipated, however, since the rhodium in a $3+$ oxidation state is expected to be much less nucleophilic, and the dimethylamino group will coordinate more strongly. The origin of the second iodide is unknown, although it appears likely that it arises from the alkylation of the free PN by methyl iodide.

In an attempt to displace the dimethylamino groups of II with other good acceptor ligands, we have reacted the complex with trifluorophosphine and hexafluorobutene-2. The reaction with PF_3 gave a gold-colored solution which differed from $[\text{Rh}(\text{PN})_2]\text{X}$ in being stable toward oxygen. We have been unable to purify this new complex sufficiently for it to be unambiguously characterized; however, since the dimethylamino arms of the chelate remain coordinated, it appears that PF_3 coordinates to the fifth coordination position of the cationic rhodium(I) complex and thereby prevents reaction with oxygen. The failure to displace the di-

(16) I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).

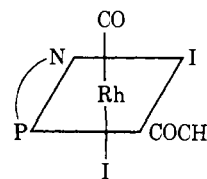
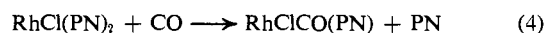


Figure 3. Proposed structure of one of the isomers of $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$ (IX).

methylamino arms of the chelate is almost certainly due to steric rather than electronic effects since the π -acceptor abilities of CO and PF_3 are very similar.

Neutral Complexes. When $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ was allowed to react with PN in ethanol in the absence of a noncoordinating anion, the orange complex $\text{RhCl}(\text{PN})_2$ (I) was obtained. This complex is more soluble in ethanol than II and a better yield is obtained when the reaction is carried out in ether. Compound I can be readily converted into the cationic complexes $[\text{Rh}(\text{PN})_2]\text{X}$ ($\text{X} = \text{PF}_6, \text{SbF}_6, \text{BPh}_4, \text{ClO}_4$) by metathesis in ethanol as solvent; this synthetic method is the favored one for the preparation of $[\text{Rh}(\text{PN})_2]\text{ClO}_4$. The conductivity of complex I in nitrobenzene is $11.6\text{ ohm}^{-1}\text{ cm}^2\text{ equiv}^{-1}$, approximately one-half of the value found for the hexafluorophosphate complex II. This low value for the conductivity could be due either to ion pairing or to an equilibrium between the five-coordinate uncharged rhodium(I) compound and the cationic rhodium(I) chloride compound. The infrared spectrum in the region of 300 cm^{-1} shows no bands which can be assigned to the Rh-Cl stretch. This datum, taken along with the observation that the compound is a conductor of electricity, supports the proposal that the compound exists as an intimate ion pair in nitrobenzene solution. $\text{RhCl}(\text{PN})_2$ differs from $[\text{Rh}(\text{PN})_2]\text{PF}_6$ in its reaction toward CO. Compound I is converted into $\text{RhClCO}(\text{PN})$ in the presence of CO with the concomitant loss of one molecule of PN (eq 4). A result which is consistent

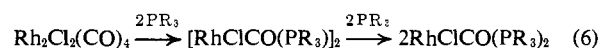


with a reaction of this type is that the conductivity of $\text{RhCl}(\text{PN})_2$ changes from 11.6 to $4.9\text{ ohm}^{-1}\text{ cm}^2\text{ equiv}^{-1}$ when CO is passed through the solution. A similar reaction occurs with PF_3 to give $\text{RhCl}(\text{PF}_3)(\text{PN})$. The elimination of one PN from the complex in these reactions again shows the instability of these bis complexes of PN toward loss of one of the chelate ligands (eq 5).



These rhodium complexes indeed appear to be the first compounds isolated where two molecules of PN are chelated about a single metal, and models show that there is considerable steric strain within the system.

The reaction of di- μ -dichloro-tetrakis(carbonyl)dirhodium(I) with substituted phosphines is currently attracting considerable interest.^{17,18} The final product of the reaction is usually a compound of general formula $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ and it is believed to be formed by the reaction sequence shown in eq 6. When the compound



(17) D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 2161 (1972).

(18) P. Uguagliati, A. Palazzi, G. Deganello, and V. Belluco, *Inorg. Chem.*, **9**, 724 (1970).

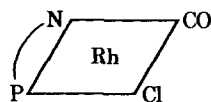


Figure 4. Stereochemistry of RhClCO(PN) (XII).

PN is allowed to react with $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, effervescence occurs and the yellow crystalline complex RhClCO(PN) (XII) is formed. XII is only moderately air stable both in the solid state and in solution. This instability was also found with RhClCO(diphos) where the chelating ligand causes the Cl and CO to be in a mutually cis stereochemical arrangement.¹⁹ The stereochemistry is shown in Figure 4 where the carbonyl is trans to the phosphorus. The carbonyl stretch in XII, when measured in solution, is at 2005 cm^{-1} , which is characteristic of a carbonyl trans to a substituted phosphine in an uncharged rhodium(I) complex. In support of this, values of 2010 and 2005 cm^{-1} have been reported for the carbonyl stretching frequencies of RhClCO(diphos) and chlorocarbonyl[1,1,1-tris(diphenylphosphinomethyl)ethane]rhodium.²⁰ The Rh-Cl stretching frequency for RhClCO(PN) is at 295 cm^{-1} .

RhClCO(PN) does not react with excess PN under mild conditions. If, however, CO and a noncoordinating anion such as hexafluorophosphate are added, reaction occurs to give $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$ (eq 7), the RhClCO(PN) + PN + CO + $\text{NH}_4\text{PF}_6 \rightarrow [\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6 + \text{NH}_4\text{Cl}$ (7)

nature of the product being confirmed by ir, nmr, and microanalysis. When a solution of XII in acetone is treated with methyl iodide, the color becomes deep orange. The ^1H nmr spectrum of the reaction product in the methyl region is complex because of the presence of a considerable number of inequivalent dimethylamino groups. A single resonance at τ 7.82, characteristic of methyl iodide, is present. This methyl iodide molecule is labile and when the complex is recrystallized from CH_2Cl_2 , the CH_3I is partially replaced by the solvent. The compound is therefore a mixture of rhodium(III) acetyls containing a molecule of solvent in one of the coordination positions. Thick-layer chromatography allowed the partial separation of two different acetyl complexes each having two resonances in the ^1H nmr spectrum due to the dimethylamino group and one due to the acetyl. Similar results were obtained when this reaction was carried out in the presence of an atmosphere of CO except that now the complexes formed showed a band in the infrared spectrum characteristic of a terminal carbonyl coordinated to Rh(III), and there was no solvent coordinated to the rhodium. In this case, the complexes were separable because of their different solubilities in ether. Similar results have been reported by Wilkinson, *et al.*, who found that the reaction of RhClCO(PPh_3)₂ with CH_3I gave an acetyl-rhodium(III) complex which contained a labile methyl iodide.¹⁶

The scheme shown in Figure 5 adequately accounts for these observations. Initial oxidative addition of methyl iodide to RhClCO(PN) can occur to give a cis or a trans complex when the reaction is carried out

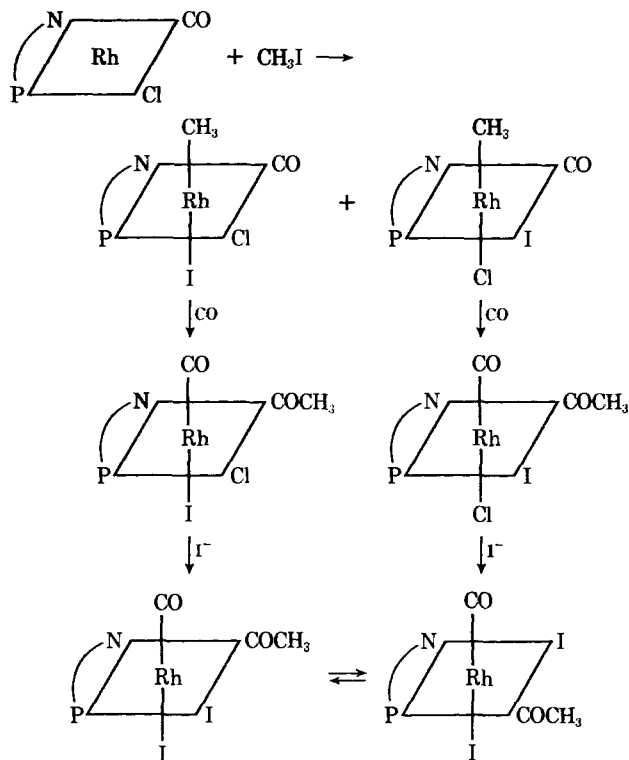


Figure 5. Suggested formation of isomers of $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$ (IX); isomerization is assumed to occur between anionic ligands.

in polar solvents such as acetone. This reaction is rapidly followed by migratory insertion to form the acyl. The stereochemistries of the complexes shown have been deduced on the assumption of alkyl migration to the coordinated carbonyl. However, since these complexes have six different ligands coordinated to the central metal atom, a considerable number of isomers are possible and we cannot unambiguously determine the stereochemistry by spectroscopic methods.

Complexes which could be more completely characterized have been obtained by carrying out the reaction of methyl iodide with RhClCO(PN) in the presence of excess sodium iodide and carbon monoxide to give a good yield of the diiodo complex $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$. The compound was obtained as large crystals which had a metallic luster similar to that of copper. The ^1H nmr spectrum shows three resonances in the methyl region of equal intensity which can be assigned to the coordinated dimethylamino group (two lines) and the acetyl. The infrared spectrum shows strong bands at 2055 and 1693 cm^{-1} which can be assigned to the stretch modes of a terminal carbonyl and of an acetyl, respectively. The observation of two dimethylamino resonances eliminates the possibility of the isomer with mutually trans iodides. This complex is identical with the second isomer (B) which was obtained from the reaction of $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$ with CH_3I . The interconversion is carried out by dissolving isomer B in ether and slowly evaporating the resultant solution when a quantitative conversion to A occurs. The identity of the isomers obtained by the two methods has been shown by comparison of their infrared and nuclear magnetic resonance spectra, as well as by their behavior on thin-layer chromatography. The observation of a facile migratory insertion reaction is probably associated

(19) W. Hieber and R. Kunner, *Chem. Ber.*, **100**, 148 (1967).

(20) W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971).

with the high nucleophilicity of the rhodium carbonyl complex, which causes the coordinated methyl group to have carbanionic character.

Complex XII reacts readily with allyl chloride to form the yellow crystalline air-stable σ -allylrhodium(III) complex (eq 8). The ^1H nmr spectrum of the complex $\text{RhClCO(PN)} + \text{CH}_2=\text{CHCH}_2\text{Cl} \rightarrow$



shows a complex multiplet in the region of 4–7 ppm downfield of TMS which is analogous to the observed spectra of other σ -allyls of rhodium(III). The dimethylamino groups are nonequivalent which excludes the isomer where the chlorines are mutually trans to each other. If the carbonyl group remains trans to the diphenylphosphino group, the stereochemistry is the one shown in Figure 6. The complex does not undergo migratory insertion to form an acyl presumably because of the electrophilic nature of the methylene group. Although the σ -allyl complex can be readily isolated, there is a slow isomerization in solution to the π -allyl. More than one product is formed, and the mechanism of this isomerization is currently under investigation.

The trifluorophosphine complex $\text{RhCl(PF}_3\text{)(PN)}$ (XIV) has been prepared by the reaction of di- μ -chlorotetrakis(trifluorophosphine)dirhodium(I) with excess PN in ether. The ^1H spectrum of XIV shows a single band for the dimethylamino resonance in the position characteristic of a coordinated nitrogen. The infrared spectrum of XIV shows strong bands at 855 and 880 cm^{-1} characteristic of P–F. When XIV is allowed to react with CO, the PF_3 is displaced and RhClCO(PN) is formed.

A further rhodium(I) complex containing a coordinated PN has been formed from the reaction of 2,4-pentanedionotobis(ethylene)rhodium(I) with PN in ether. The compound obtained has the formula $\text{Rh}(\text{C}_5\text{H}_8\text{O}_2)(\text{PN})$. This new complex is extremely air sensitive in solution but in the solid state is sufficiently robust for complete characterization. Although neither RhCl(PN)_2 nor RhClCO(PN) were active catalysts for the hydrogenation of olefins, preliminary experiments show that $\text{Rh}(\text{C}_5\text{H}_8\text{O}_2)(\text{PN})$ will catalyze the low-pressure hydrogenation of 1-hexene. Catalytic studies with a number of these complexes are currently in progress and it is anticipated that the results will be reported at a later date.

Iridium Complexes. Since the corresponding iridium(I) complexes of the PN ligand would be anticipated to be more nucleophilic than their rhodium(I) analogs, we have carried out the reaction of $\text{Ir}_2\text{Cl}_2(\text{C}_6\text{H}_4)_4$ with PN in the presence of NH_4PF_6 . The product, however, was not the anticipated Ir(I) compound but the hydrido-chloroiridium(III) complex XVI where the hydrogen has come from the ammonium ion.⁹ It appears that even if iridium(I) complexes containing PN are formed during the reaction, they are sufficiently basic that protonation occurs with the ammonium ion. The same complex is obtained from the reaction of $\text{Ir}_2\text{Cl}_2(\text{C}_6\text{H}_4)_4$ and PN with NH_4Cl or with NH_4Cl and NaPF_6 ; however, the hydrido complex is not formed when PN and NaPF_6 only are used. Dry acetonitrile was used for these reactions.

Conclusions

1. Rhodium(I) complexes of *o*-(diphenylphosphino)-

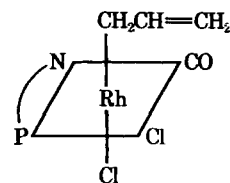


Figure 6. Stereochemistry of $\text{RhCl}_2(\sigma\text{-allyl})\text{CO(PN)}$ (XV).

N,N-dimethylaniline, having the dimethylamino group coordinated, have been shown to be readily isolable.

2. The bis-ligand complexes are highly nucleophilic and, in addition to undergoing facile oxidative addition with methyl iodide, will coordinate cyanogen irreversibly. The sensitivity of the *N*-methyl resonance to environment provides a convenient method for determining the stereochemistry of many of the complexes. This nmr method verified that cyanogen had added to $[\text{Rh(PN)}_2]\text{X}$ to give a cis adduct, whereas with chlorine and methyl iodide the product was the trans isomer.

3. We have conclusively shown that the dimethylamino arm of the chelate will predictably and reversibly dissociate in the presence of an incoming π acceptor such as carbon monoxide.

4. The carbonyl complexes will readily undergo migratory insertion reactions with methyl iodide to form acetylrhodium(III) compounds.

5. The iridium complexes of *o*-(diphenylphosphino)-*N,N*-dimethylaniline are sufficiently basic to be protonated by ammonium ion.

Experimental Section

Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz., or by using a Perkin-Elmer Model 240 elemental analyzer. Halogen analyses were carried out by Galbraith Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained on a Varian T60 spectrometer. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 467 spectrometer. All reactions were carried out under a nitrogen atmosphere. NH_4PF_6 (City Chemical) was washed with small portions of water, ethanol, and ether and then dried prior to use. The compound was then stored in a polyethylene bottle. *n*-Butyllithium was used as a 1.6 *M* solution in hexane (Foote). Chlorodiphenylphosphine (Aldrich) was purified by vacuum distillation under nitrogen and used immediately. *o*-Bromo-*N,N*-dimethylaniline, bp 108–109.5° (12 mm) was prepared from *o*-bromoaniline (Baker) by methylation with alkaline Me_2SO , according to the procedure of Gilman.²¹ *o*-(Diphenylphosphino)-*N,N*-dimethylaniline (PN) was prepared by the metalation of *o*-bromo-*N,N*-dimethylaniline with butyllithium followed by treatment with chlorodiphenylphosphine. The compound was recrystallized from ethanol: mp 117–118° (lit. 113–114°). $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$, $\text{Rh}(\text{C}_5\text{H}_8\text{O}_2)(\text{C}_2\text{H}_4)_2$, $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$,^{22,23} and $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ were prepared by literature methods.

Bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Chloride [RhCl(PN)_2], I. Solid PN (858 mg) was added to a suspension of $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ (280 mg) in degassed ether (18 ml). The reaction was stirred for 20 min and the product was filtered and washed with water, ether (5 ml), and hexane (5 ml). The complex was dried *in vacuo* at 40°: yield 1.0 g (91%); τ 6.88 (s, NMe_2). *Anal.* Calcd for $\text{C}_{40}\text{H}_{40}\text{ClN}_2\text{P}_2\text{Rh}$: C, 64.1; H, 5.34; Cl, 4.74; N, 3.74. Found: C, 63.2; H, 5.30; Cl, 4.82; N, 3.61.

Bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluorophosphate [$[\text{Rh(PN)}_2]\text{PF}_6$], II. Ethanol (80 ml) was degassed by refluxing and cooling under nitrogen. PN (1.63 g) and NH_4PF_6 (0.95 g) were slurried with the ethanol for 10 min and $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ (0.51 g) was added. The mixture was stirred vigorously for 20 min

(21) H. Gilman and I. Banner, *J. Amer. Chem. Soc.*, **62**, 344 (1940).

(22) M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, **10**, 2387 (1971).

(23) J. F. Nixon and J. R. Swain, *J. Chem. Soc., Dalton Trans.*, 1044 (1972).

during which time ethylene was evolved and bright yellow-orange precipitate formed. This compound was filtered, washed with water (2 × 15 ml), ethanol (30 ml), and ether (20 ml), and dried *in vacuo*: yield 2.08 g (85%); mp 245° (in sealed tube); Λ_m (nitrobenzene) = 20.3 ohm⁻¹cm²equiv⁻¹; τ 6.70 (s, NMe₂).

Anal. Calcd for C₄₀H₄₀F₆N₂P₃Rh: C, 55.9; H, 4.66; N, 3.26; P, 10.18. Found: C, 55.1; H, 4.64; N, 3.02; P, 10.4.

Bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluoroantimonate [[Rh(PN)₂]SbF₆, III]. The complex was prepared in an analogous manner to the PF₆ salt: $\nu_{\text{Sb-F}}$ 656 cm⁻¹ (vs).

Bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Tetraphenylboron [[Rh(PN)₂]BPh₄, IV]. The complex was prepared in an analogous manner to the PF₆ salt.

Bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Perchlorate [[Rh(PN)₂]ClO₄, V]. RhCl(PN)₂ (200 mg) was added to a solution containing LiClO₄ (200 mg) in oxygen-free ethanol (10 ml). Ether (2 ml) was slowly added, followed by hexane (6 ml) to give the complex: ν_{ClO_4} 1090 cm⁻¹ (vs).

trans-Dicarbonyl[bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluorophosphate [[Rh(PN)₂(CO)₂]PF₆, VI]. CO was bubbled through stirred acetone (5 ml) for 15 min in a two-necked flask. [Rh(PN)₂]PF₆ (150 mg) was added and the solution heated to ca. 50°. A rapid stream of carbon monoxide was passed over the solution until the volume was reduced to 2 ml; oxygen-free ethanol (10 mg) was added, followed by the dropwise addition of ether until the solution just became cloudy. The yellow precipitate was stirred for 20 min, filtered, and dried *in vacuo*: yield 120 mg (75%); mp 258°; $\nu_{\text{C-O}}$ 1971 cm⁻¹ (vs); τ 7.30 (s, NMe₂). *Anal.* Calcd for C₄₂H₄₀F₆N₂O₂P₃Rh: C, 55.1; H, 4.37; N, 3.06. Found: C, 55.1; H, 4.54; N, 2.91.

trans-Dichloro[bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluoroantimonate [[RhCl₂(PN)₂]SbF₆, VII]. A saturated solution (3 ml) of Cl₂ in CH₂Cl₂ was added to a solution of [Rh(PN)₂]SbF₆ (150 mg) in CH₂Cl₂ (10 ml). The solution was stirred for 15 min and the solution evaporated to dryness. The crude product was dissolved in boiling ethanol (30 ml), filtered hot, and evaporated to 5-ml volume. The addition of ether gave a solid compound which was recrystallized from CH₂Cl₂ and MeOH to give the complex as orange crystals: yield 160 mg (quantitative); mp 261–263°; $\nu_{\text{Rh-Cl}}$ 280 (s), 289 (s); τ 6.78 (s, NMe₂). *Anal.* Calcd for C₄₀H₄₀Cl₂F₆N₂P₂RhSb: C, 47.1; H, 3.92; Cl, 6.95; N, 2.74. Found: C, 46.6; H, 3.86; Cl, 7.93; N, 2.60.

Iodomethyl[bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluorophosphate [[RhI(CH₃)(PN)₂]PF₆, VIII]. Methyl iodide was degassed and distilled on a vacuum line and then distilled on the [Rh(PN)₂]PF₆ (100 mg) at -78°. The solution was warmed to 35° and stirred for a further 20 min. The yellow solution was concentrated to ca. 2 ml and cooled to -78°. Oxygen-free ether (7 ml) was distilled into the reaction flask and the solution stirred until it warmed to room temperature. The precipitate was filtered and recrystallized from CH₂Cl₂ by the slow addition of ether: mp 158–160°; τ 6.28, 6.90 (NMe₂), 8.75 (Me). *Anal.* Calcd for C₄₁H₄₃F₆N₂I₂P₃Rh: C, 49.2; H, 4.30; N, 2.80; I, 12.7. Found: C, 49.4; H, 4.12; N, 2.62; I, 12.8.

Diiodoacetylcarbonyl[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [RhI₂(COCH₃)CO(PN), IX]. Acetone (10 ml) was saturated with CO. To this solution was added [Rh(PN)₂]PF₆ (200 mg) and the mixture stirred until the reaction was homogeneous. When the carbonylation of the rhodium(I) complex was complete, as evidenced by a color change from orange to yellow, methyl iodide (1.5 ml) was added. The reaction was stirred for 1 hr under CO and then the solution evaporated to dryness. The product was extracted with ether (6 × 50 ml). Removal of the solvent gave the complex: yield 100 mg (60%); ν_{CO} 2055 (vs), 1693 cm⁻¹ (vs); τ 6.30, 6.92, 7.02 (Me). This compound was designated isomer A.

When the above reaction product was obtained by the slow addition of hexane to an acetone solution, a second complex, designated isomer B, was obtained: mp 171–173°; ν_{CO} 2055 cm⁻¹ (vs); ν_{COCH_3} 1693 cm⁻¹ (vs); τ 6.53, 6.74, 7.26 (Me). This compound was designated isomer B.

Dioxygen[bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluoroantimonate [[Rh(O₂)(PN)₂]SbF₆, X]. Oxygen or air was bubbled through a solution of [Rh(PN)₂]SbF₆ in CH₂Cl₂ for 5 min. The solvent was reduced to 2 ml and ether added slowly to give brown crystals: mp 164°; τ 6.61, 6.70, 7.24, 7.91 (NMe₂). *Anal.* Calcd for C₄₀H₄₀F₆N₂O₂P₃RhSb: C, 48.9; H, 4.07; N, 2.85. Found: C, 48.6; H, 4.02; N, 2.70.

Dicyano[bis[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium Hexafluoroantimonate [[Rh(CN)₂(PN)₂]SbF₆, XI]. Cyanogen

was prepared by treating CuSO₄·H₂O (3 g) with a freshly prepared aqueous solution (9 ml) of KCN (5 g). The C₂N₂ was scrubbed with a solution of AgNO₃ and swept with N₂ into a solution of [Rh(PN)₂]SbF₆ (250 mg) in oxygen-free CH₂Cl₂ (5 ml). The pale gold-colored solution was filtered through cellulose pulp. This solution was combined with the washings from the filter material and the CH₂Cl₂ removed. The oil which formed was dissolved in a minimum of CH₂Cl₂, diluted with methanol (40 ml), and allowed to stand for 36 hr at 0°. The complex was obtained as colorless crystals which were washed with methanol (1 ml) and ether (10 ml) and dried *in vacuo* at 75°: yield 100 mg (38%); mp 234–235°; ν_{CN} 2138, 2140 cm⁻¹ (w); τ 6.58, 7.19, 7.33, 7.56 (NMe₂). *Anal.* Calcd for C₄₂H₄₀F₆N₄P₃RhSb: C, 50.4; H, 4.0; N, 5.6; P, 6.19. Found: C, 49.4; H, 3.68; N, 5.38; P, 6.18.

Chlorocarbonyl[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [RhClCO(PN), XII]. Rh₂Cl₂(CO)₄ (30 mg) was dissolved in ethanol (3 ml) and PN (95 mg) was added. The reaction was stirred for 10 min and cooled to 0° and the yellow crystals were filtered, washed with ether, and dried *in vacuo*: yield 65 mg (86%); mp 256–260° dec (in sealed tube); $\nu_{\text{C=O}}$ 2005 cm⁻¹ (vs) (as a solution in CH₂Cl₂); τ 6.79 (s, NMe₂). *Anal.* Calcd for C₂₁H₂₀ClNO₂P₂Rh: C, 53.5; H, 4.24; N, 2.97; P, 6.57; mol wt, 471. Found: C, 52.9; H, 4.09; N, 2.86; P, 6.44; mol wt, 497 (benzene).

Reaction with PN, NH₄PF₆, and CO. Formation of [Rh(PN)₂](CO)₂]PF₆ (VI). Into a 25-ml flask was placed RhClCO(PN) (39 mg), NH₄PF₆ (25 mg), PN (25 ml), and ethanol (10 ml). CO was bubbled through the suspension for 6 hr. The yellow complex was filtered and dried *in vacuo*. *Anal.* Calcd for C₄₂H₄₀F₆N₂O₂P₃Rh: C, 55.1; H, 4.37; N, 3.06. Found: C, 55.2; H, 4.41; N, 2.84.

2,4-Pentanedionato[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [Rh(C₅H₈O₂)(PN), XIII]. Rh(C₅H₈O₂)(C₂H₅)₂ (129 mg) was dissolved in ether (10 ml). PN (152 mg) was added and the solution stirred for 20 min. The orange crystals were filtered, washed with ether, and dried *in vacuo*: yield 195 mg (97%); mp 126°; $\nu_{\text{C=O}}$ 1580 cm⁻¹ (s). *Anal.* Calcd for C₂₅H₂₇NO₂P₂Rh: C, 59.2; H, 5.32; N, 2.76. Found: C, 59.7; H, 5.57; N, 2.40.

Chloro(trifluorophosphine)[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [RhCl(PF₃)(PN), XIV]. Rh₂Cl₂(PF₃)₄ (95 mg) was dissolved in dry ether (5 ml) in a flask fitted with a side arm. PN (95 mg) in ether was added dropwise over a period of 2–3 min. The reaction was stirred for 20 min and the yellow compound allowed to settle. The supernatant liquid was decanted and ether (7 ml) added to the slurry. The supernatant liquid was again decanted. This procedure was repeated two more times. The solid was dried under a stream of nitrogen and finally *in vacuo*: yield 120 mg (80%); mp 200° dec (in sealed tube); $\nu_{\text{P-F}}$ 850 (vs), 878 (vs); τ 6.80 (s, NMe₂). *Anal.* Calcd for C₂₀H₂₀ClF₃N₂P₂Rh: C, 45.1; H, 3.77; N, 2.64. Found: C, 45.1; H, 3.79; N, 2.56.

Dichloro- σ -allylcarbonyl[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [RhCl₂(σ -C₃H₅)CO(PN), XV]. RhClCO(PN) (250 mg) was dissolved in freshly distilled allyl chloride (ca. 10 ml) and the solution stirred for 35 min. The infrared spectrum of this solution showed only a single band in the carbonyl region. The solvent was removed and the product washed with methanol (0.5 ml) and pentane (10 ml). The yield of crude product was 250 mg. This material was dissolved in the minimum of CH₂Cl₂. The solution was filtered and the filtrate diluted with a solution (5 ml) containing equal amounts of ether and methanol. Cooling the solution to -10° for several hours gave gold-colored crystals, which were filtered and dried *in vacuo* at 78°: yield 110 mg (39%); mp 131°; $\nu_{\text{C=O}}$ 2057 cm⁻¹ (s); $\nu_{\text{Rh-Cl}}$ 315 (m), 284 cm⁻¹ (s); τ 6.92 (t), 6.83 (t), 3.0–5.85 (mult). *Anal.* Calcd for C₂₄H₂₃Cl₂NO₂P₂Rh: C, 52.1; H, 4.52; N, 2.53. Found: C, 52.4; H, 4.52; N, 2.53.

Diiodoacetylcarbonyl[*o*-(diphenylphosphino)-*N,N*-dimethylaniline]rhodium [RhI₂(COCH₃)CO(PN), IX]. RhClCO(PN) (150 mg), sodium iodide (450 mg), methyl iodide (0.5 ml), and acetone (20 ml) were stirred under an atmosphere of CO for 1 hr. The red solution was evaporated to dryness and extracted with CH₂Cl₂, and the sodium halides were filtered. The filtrate was evaporated to dryness and the oil remaining triturated with ethanol (3 ml). Hexane (10 ml) was added and the slurry filtered. The acetone-soluble portion of this material was dissolved in the minimum volume of CH₂Cl₂ and diluted with ethanol (the volume of ethanol used was approximately twice the volume of CH₂Cl₂). Cooling this solution to 0° and allowing it to stand for 12 hr gave bronze needles which were filtered, washed with hexane, and dried *in vacuo*: mp 171–173°; ν_{CO} 2055 (vs), 1693 cm⁻¹ (vs); τ 6.53 (Me), 6.74 (Me), 7.26 (Me). *Anal.* Calcd for C₂₂H₂₃I₂NO₂P₂Rh: C, 37.6; H, 3.13;

I, 34.7; N, 1.91; P, 4.07. Found: C, 37.4; H, 3.20; I, 33.0; N, 1.84; P, 4.22. Tlc on silica gel using toluene as eluent showed this complex to be identical with isomer B prepared from $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$.

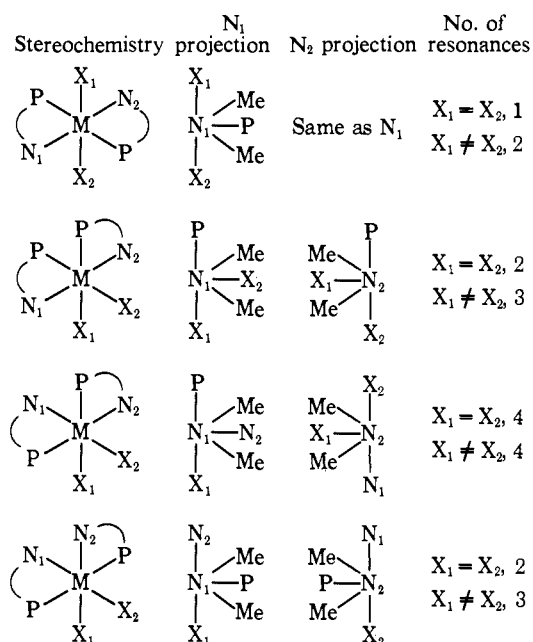
Hydridochloro[bis(*o*-(diphenylphosphino)-*N,N*-dimethylaniline)]-iridium Hexafluorophosphate $[\text{IrHCl}(\text{PN})_2]\text{PF}_6$, XVI. PN (310 mg) and ammonium hexafluorophosphate (100 mg) were suspended in acetonitrile (10 ml) under nitrogen. $\text{Ir}_2\text{Cl}_2(\text{C}_6\text{H}_4)_4$ (250 mg) was added and the slurry stirred for 40 min. The reaction mixture was pale yellow. The solvent was evaporated *in vacuo* and the gelatinous residue triturated with ether. The solid was filtered and washed with ether (10 ml). The off-white residue was dissolved in CH_2Cl_2 . The solution was filtered and the ethanol (10 ml) added to the filtrate. The volume of the solution was reduced to 7 ml on a rotary evaporator, and on cooling the solution to 0° colorless crystals were obtained: yield 480 mg (90%); mp 148° ; $\nu_{\text{Ir-H}}$ 2240 cm^{-1} ; $\nu_{\text{Ir-D}}$ 1604 cm^{-1} ; τ 6.45, 6.51 (NMe₂), 32.0 ($J_{\text{P-H}} = 8$ Hz, Ir-H). Anal. Calcd for $\text{C}_{40}\text{H}_{41}\text{ClF}_6\text{IrN}_2\text{P}_3$: C, 48.8; N, 4.16; Cl, 3.53; Ir, 2.84; P, 8.87. Found: C, 48.9; H, 3.97; Cl, 3.61; N, 2.98; P, 9.45.

Acknowledgment. We wish to thank the National Science Foundation for support of this work under Grant No. GP 38775. This work was also supported in part by the Graduate School Research Fund.

Appendix

One of the attractive features of *o*-(diphenylphosphino)-*N,N*-dimethylaniline complexes is the ease with which their stereochemistries can be deduced. The multiplicity of the *N*-methyl resonances in the ^1H nmr spectrum can frequently be used to confirm the structure of an individual complex. The chelate ring obtained when both the phosphorus and nitrogen are

coordinated is a planar one. The anticipated number of methyl resonances for a given stereochemistry is obtained by viewing down a projection along the N-metal bond. In a number of complexes having two of the chelating ligands, the nitrogens are not identical and a projection is drawn down each N-metal bond.



Electronic Absorption and Emission Spectral Studies of Square-Planar Rh(I) and Ir(I) Complexes. Evidence for a Charge-Transfer Emitting State

Gregory L. Geoffroy, Mark S. Wrighton, George S. Hammond, and Harry B. Gray*

Contribution No. 4767 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, the Division of Natural Sciences, University of California, Santa Cruz, California 95060, and the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 3, 1973

Abstract: Absorption and emission spectra for the square-planar complexes $[\text{Rh}(\text{2-phos})_2]\text{Cl}$, $[\text{Rh}(\text{2=phos})_2]\text{Cl}$, $[\text{Ir}(\text{2-phos})_2]\text{Cl}$, and $[\text{Ir}(\text{2=phos})_2]\text{Cl}$ [2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene] have been measured in the solid state and in frozen EPA [ethyl ether-isopentane-ethyl alcohol (5:5:2)] solution at 77°K . Of the four complexes, only $[\text{Rh}(\text{2-phos})_2]\text{Cl}$ fails to luminesce in the solid state at room temperature. At 77°K in EPA the emission maxima fall in the range 16.8–18.4 kcm^{-1} , and the emission lifetimes are between 8.2 and 20.8 μsec ; $[\text{Ir}(\text{2=phos})_2]\text{Cl}$ exhibits an unusually sharp, strongly overlapping emission-absorption system, with an emission quantum yield of 0.93 ± 0.07 . It is suggested that in the Ir(I) cases emission occurs from a square-planar $d^7 a_{2u}$ charge-transfer state of $E_u(^3A_{2u})$ symmetry. The fact that the emission maxima of the two Rh(I) complexes are both red-shifted by about 4000 cm^{-1} from the lowest absorption peak is discussed in terms of an admixture of d-d character in the primarily $d^7 a_{20}$ emitting state, which could give rise to a distortion of the RhP_4 core toward tetrahedral geometry.

There has been very little previous effort devoted to the elucidation of the electronic structures and

spectroscopic properties of low-spin d^8 square-planar complexes of Rh(I) and Ir(I). Only ambient tempera-