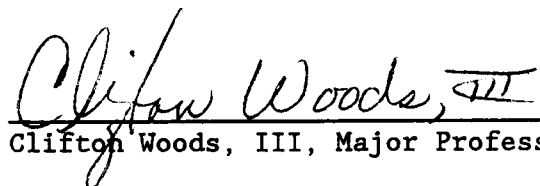
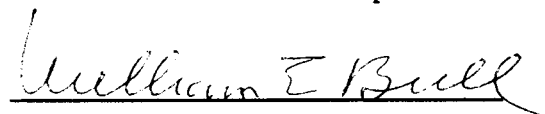


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SYNTHESIS AND CHARACTERIZATION OF DINUCLEAR COMPLEXES:

1. DIRHODIUM COMPLEXES;
2. PLATINUM-RHODIUM COMPLEXES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Jeffrey Craig Depriest

December 1988

DEDICATED TO MY MOM AND DAD

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ABSTRACT

PART I

Binuclear rhodium(I) complexes containing terminal carbon monoxide (or terminal tertiarybutylisocyanide), bridging (diphenylarsino)-(diphenylphosphino)methane ligands, and a pyrazolate (pyz) derivative in the bridgehead position have been investigated. Air-stable, paramagnetic products of some of the *t*-butylisocyanide containing species have been prepared via electrochemical oxidation.

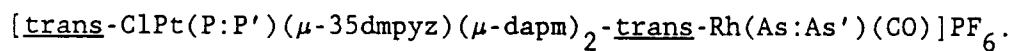
In solution these paramagnetic species exhibit a color change from green to red upon cooling to below room temperatures. Also, the ESR spectrum of $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-dapm})_2(\mu\text{-345Bpyz})][\text{PF}_6]_2$ in 4:1 methylene chloride/toluene solution at various temperatures (25°C to -150°C) revealed the existence of two isomers, an α isomer and a β isomer. The relative amounts of these isomers present varied with the temperature.

PART II

Novel heterobimetallic platinum(II)-rhodium(I) complexes employing either bis(diphenylphosphino)methane or (diphenylarsino)(diphenylphosphino)methane as the bridging transoid ligands and containing either a terminal carbon monoxide or a terminal *t*-butylisocyanide at the rhodium(I) atom, and containing either a cyano or a phenylacetylide ligand at the platinum(II) atom with a pyrazolate (pyz) derivative in the bridgehead position have been synthesized and characterized.

The novel heterobimetallic complex [*cis*-ClPt(P:P')(μ -35dmpyz)(μ -dapm) $_2$]-*trans*-Rh(As:As')(CO)]PF₆ has been synthesized and characterized. Refluxing a chloroform solution of this complex for several hours

revealed the formation of a new compound which was formulated as



Thus, isomerization of the cis-P-Pt-P unit to a trans-P-Pt-P unit in this complex has been demonstrated.

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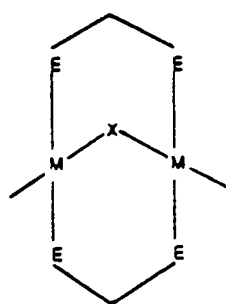
PART I:
DIRHODIUM COMPLEXES .

CHAPTER 1.1

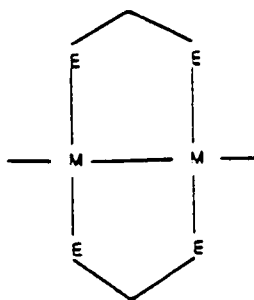
INTRODUCTION

A. Literature Review

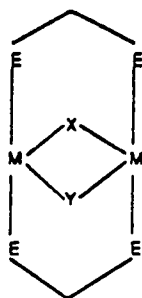
Homobimetallic complexes containing Pt, Pd, Rh or Ir metals and using both symmetrical and unsymmetrical bridging ligands have attracted much interest in recent years. The bridging ligands used have been ones that show a wide range of bite-sizes. The unsymmetrical ligand 2-diphenylphosphine pyridine, dppp, has a bite-size range of 2.1-2.8 Å and exhibits little flexibility in the P-C-N(py) angle.¹⁻³ The symmetrical bridging ligands bis(diphenylphosphino)methane, dppm, and bis(diphenylarsino)methane, dpam, are capable of supporting metal-metal distances between 2.1-4.4 Å; the wide range implies a large degree of flexibility compared to dppp. Another unsymmetrical ligand, (diphenylarsino)(diphenylphosphino)methane, dapm, has a bite-size range intermediate of dppm and dpam.⁴ Of the four bridging ligands mentioned, the one most commonly employed is dppm. Complexes formed from combinations of the above metals and bridging ligands are usually divided into the four classes shown below.⁵ The most commonly synthesized class is the one consisting of the A-frame. In the A-frame structure shown below, the "X" ligand is known as the apex ligand. A-frame complexes show an ability to coordinate small molecules such as carbon monoxide, sulfur dioxide, diazoalkanes, acetylenes (as vinyl groups) and halides. Coordination usually occurs at the site opposite the apex ligand which is referred to as the open-site.⁶



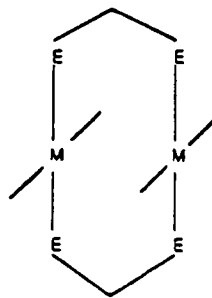
A-Frame



Side-to-side



Double-A-Frame



Face-to-face

The reactivity of the carboxylate A-frame complexes $[\text{Rh}_2(\mu\text{-O}_2\text{CR})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{R}=\text{CH}_3$, CH_2Cl , CH_2Cl_2 , CCl_3 , CF_3) with CO and H_2/CO mixtures demonstrates this coordination ability at the open site and the influence of the apex ligand.⁷ At ambient temperature and under one atmosphere of CO the acetate complex ($\text{R}=\text{CH}_3$) did not form a CO adduct. However, the halo carboxylate A-frame complexes do react under the same conditions to give labile adducts of the type $[\text{Rh}_2(\mu\text{-O}_2\text{CR})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$. None of the carboxylate complexes investigated reacted with dihydrogen alone. Only the halocarboxylates with H_2/CO mixtures slowly react to generate the complex $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2][\text{ClO}_4]$.

Synthesis of certain A-frame complexes may be accomplished via the insertion of small molecules into the metal-metal bond of the dppm-bridged system $M_2X_2(dppm)_2$ ($M=Pd(I), Pt(I)$ and $X=Cl, Br$) as previously reported.⁸⁻¹⁰ This general synthesis method is illustrated in Figure 1. The scheme in Figure 1 is based solely upon experimental results.⁸ Some examples of these A-frames produced via insertion reactions follow.

One of the first A-frame complexes was reported by Balch¹¹ et al. in 1977. The red crystalline Pd(I) dimer, $PdCl_2(\mu-CO)(\mu-dppm)_2$, easily loses the bridging CO when heated to 56°C under vacuum to give the metal-metal bonded (side-to-side) complex $Pd_2Cl_2(\mu-dppm)_2$. Addition of one equivalent of an isocyanide to the side-to-side dimer yields a bridging isocyanide complex. The complex $Pd_2Cl_2(\mu-CO)(\mu-dppm)_2$ is regenerated by addition of carbon monoxide to $Pd_2Cl_2(\mu-dppm)_2$. However, the bridging isocyanide complex did not display similar reversible behavior.

Addition of gaseous hydrogen sulfide, H_2S , to the metal-metal bonded Pd(I) dimer, $Pd_2Cl_2(\mu-dppm)_2$ results in the quantitative reduction of H_2S to S^{-2} and H_2 gas.¹² This reaction is illustrated in Figure 2.

In 1982 Eisenberg⁸ et. al. reported the Rh analogue of the Pd(I) dimer (Figure 3A, p 6) featuring Rh(0) in the complex $[Rh_2(CO)_2(\mu-dppm)]$. This complex was prepared by addition of sodium borohydride to $[Rh_2Cl_2(CO)_2(\mu-dppm)_2]$ under anhydrous and oxygen-free conditions. Formally this is a reduction of the Rh atom from Rh(I) to Rh(0). As shown in Figure 3 this Rh(0) dimer will add CO and H^+ to give the

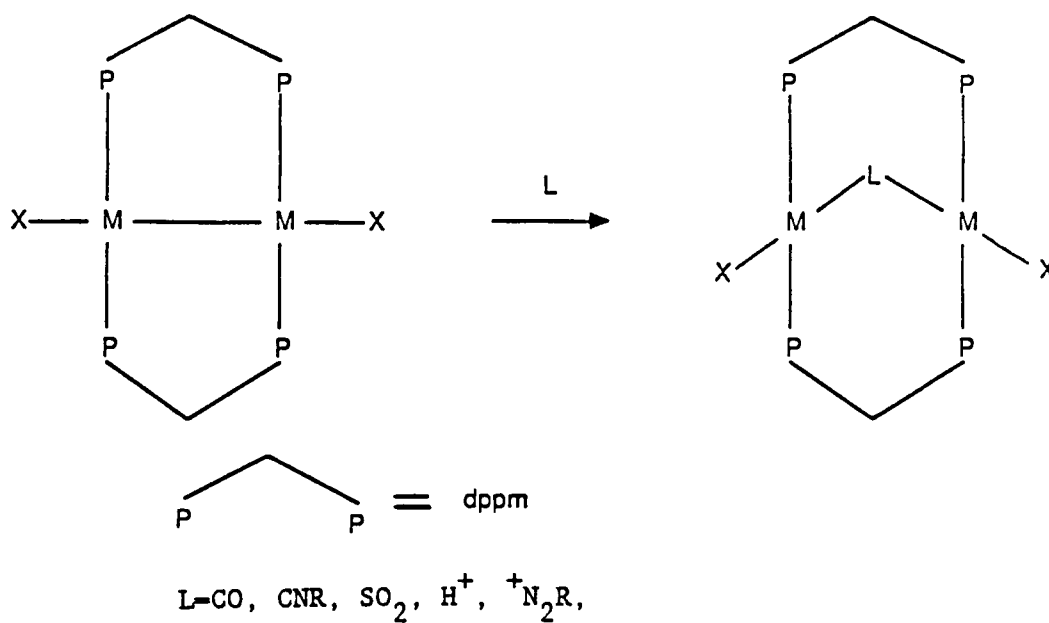


FIGURE 1. A scheme for the insertion of small molecules into $\text{M}_2\text{X}_2(\text{dppm})_2$

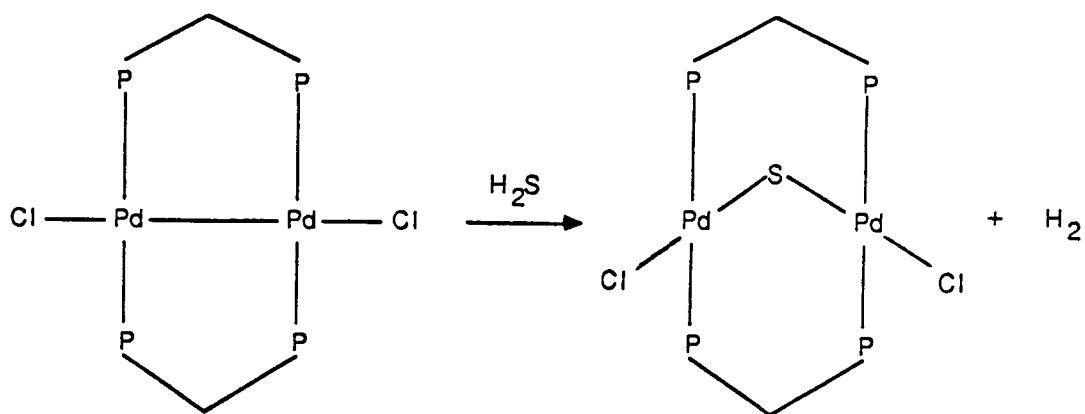


FIGURE 2. A scheme for the synthesis of $\text{Pd}_2\text{Cl}_2(\mu\text{-S})(\text{dppm})_2$

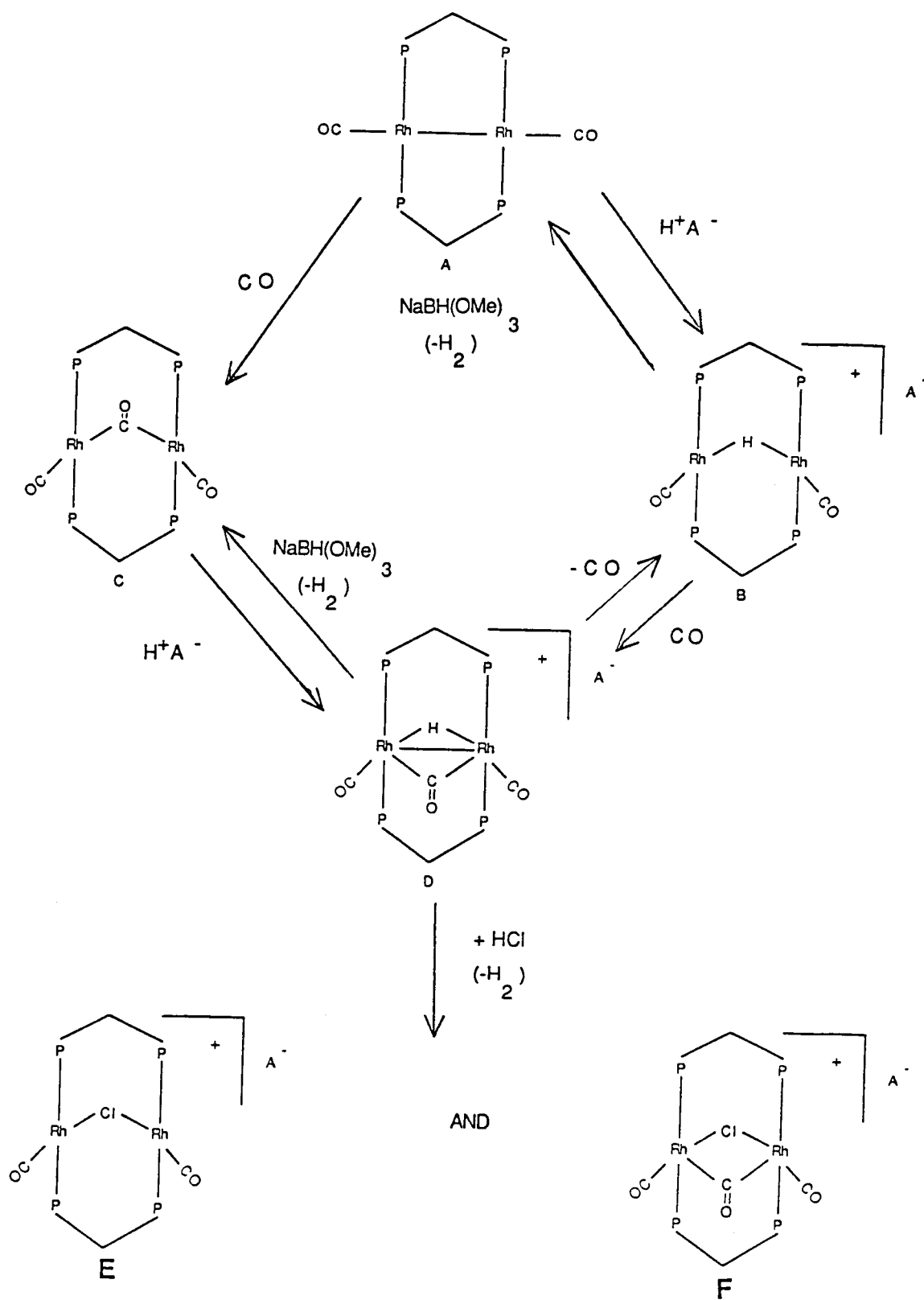


FIGURE 3. Reactions involving $\text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2$

bridging carbonyl complex $\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2$ and the bridging hydride $[\text{Rh}_2(\mu\text{-H})(\text{CO})_2(\text{dppm})_2]\text{PF}_6$, respectively.⁸ The IR spectrum for the bridging carbonyl complex shows its bridging carbonyl stretch at 1835 cm^{-1} and two terminal carbonyl stretches at 1940 (s, sh) and $1920\text{ (vs)}\text{ cm}^{-1}$. The ^{31}P NMR spectrum reveals a symmetrical pattern indicative of chemically equivalent phosphorus donor atoms of a $\text{AA}'\text{A}''\text{A}''' \text{XX}'$ spin system. This type of pattern is characteristic for Rh_2P_4 A-frame structures reported previously by Balch and others.

An X-ray structural study undertaken by Woodcock and Eisenberg¹³ in 1985 revealed that the complex $\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2$ was not of the A-frame type. Instead the structure revealed that the complex consists of two Rh atoms linked by a single Rh-Rh bond of length $2.739\text{ \AA}$ and also by two bridging dppm ligands. The first Rh atom has a coordination number of four (C.N.=4) with a terminal CO trans to the Rh-Rh bond and two trans P donor atoms from the dppm ligands. The second Rh atom has a coordination number of five with an approximately trigonal bipyramidal geometry. The two P donor atoms and a carbonyl occupy the equatorial positions with the axial positions occupied by the first Rh atom and a second carbonyl. The symmetrical pattern obtained from the ^{31}P NMR spectrum was due to the fluxionality of the complex in solution. The fluxional behavior was made apparent only by the lack of two distinct resonances for the methylene protons of dppm (^1H NMR spectrum) normally occurring in A-frame complexes.⁸

Both the bridging hydride and the bridging carbonyl complexes under different conditions yield the complex $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{A}^-$ ($\text{A}^- = \text{PF}_6^-$ or $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$) as illustrated in Figure 3. This

complex is similar to $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-dppm})_2]\text{PF}_6$ in structure.⁸ An X-ray structural analysis reveals a Rh-Rh separation of 2.732 Å. This, along with other structural parameters is indicative of a Rh-Rh single bond.

The insertion of CO_2 into the Rh-H-Rh bond of $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2]\text{A}$ yields the formate complex, $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO}_2\text{CH})(\mu\text{-dppm})_2]\text{A}$ and carbon monoxide. This is accomplished by bubbling CO_2 through a d_6 -benzene solution of the Rh-H-Rh containing species. This process is reversed upon addition of excess carbon monoxide.

Addition of an excess of 37% (by weight) aqueous HCl to the complex $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})]\text{A}$ produces hydrogen gas and two previously characterized¹⁴ ionic Rh(I) dimers, $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2]\text{PF}_6$ and $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{PF}_6$. (Theses are shown in Figure 3, E and F.)

The first Rh(I) dimer having an A-frame structure was characterized by Kubiak and Eisenberg¹⁵ in 1977. The addition of Na_2S to a yellow suspension of the face-to-face complex trans- $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{dppm})_2$ in acetone yields a red crystalline complex of formula $\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2$. The bridging sulfide is easily displaced by adding methyl iodide, MeI, to the dimer under an atmosphere of CO to give the ionic double A-frame complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-I})(\mu\text{-CO})(\text{dppm})_2]\text{I}$.¹⁶ Treatment of this complex with excess Na_2S regenerates the starting material.¹⁵ The sulfide-bridged complex reacts with electrophilic reagents such as OEt_3PF_6 , HPF_6 and PhCH_2PF_6 to yield bridging alkylated sulfur complexes of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-SX})-(\text{dppm})_2]\text{PF}_6$ (X = Et, H, PhCH_2).¹⁵

The ionic double A-frame Rh(I) dimer $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{dppm})_2]\text{PF}_6$ was structurally characterized (in 1978) by Cowie, Sanger and Mague¹⁷ following the preceeding work. Treatment of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ in ethanol with equimolar amounts of dppm in chloroform and NaBPh_4 in ethanol under a CO atmosphere yields the complex that contains the bridging chloride and the bridging carbonyl. An IR spectrum of this yellow complex shows two absorption bands at 1992(s) and 1977(vs) cm^{-1} due to the terminal carbonyls and an additional band at 1863(s) cm^{-1} due to the bridging carbonyl. The $^{31}\text{P}\{^1\text{H}\}$ NMR reveals an AA'A"XX' spin system with $\delta(\text{Rh-P}) = 25.5$ ppm (from 85% H_3PO_4). The four P atoms are chemically, but not magnetically, equivalent.¹⁷

Flushing a CH_2Cl_2 (or acetone) solution of $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$ with N_2 (or Argon) results in the displacement of the bridging CO to give the A-frame complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$ which shows terminal carbonyl stretches at 1997(s) and 1978(vs) cm^{-1} . The double A-frame complex may be regenerated quantitatively by passing CO through a CH_2Cl_2 solution of the bridging chloride complex. Thus, the bridging chloride complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$ is the ionic analogue of $\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2$ and the double A-frame complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$ is also an ionic analogue of the bridging sulfide with a carbon monoxide molecule occupying the active site.¹⁷

The electronic spectra of face-to-face complexes like $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-lig})_2$ and $\text{Rh}_2(\text{CNR})_4(\mu\text{-lig})_2$ (lig = dppm, dpam) show a metal-centered low energy absorption band resulting from the electronic transition $\sigma^*(4\text{dz}^2) \rightarrow \sigma$ (5pz). The term "proximity-shifted" charge

transfer was coined by Balch and Tulyathan¹⁸ to refer to these transitions. Electronic spectra of Rh(I) dimers using bridging ligands that allow more distance between the Rh(I) metal centers (i.e. distances greater than 4.1 Å, e.g. $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 3,4$) do not show the proximity shifted bands, but instead show absorption bands about 100 nm lower in wavelength. These bands have been assigned to electronic transitions from the highest occupied metal d orbital (d_{z^2}) to empty ligand-localized, π orbitals. In complexes showing the proximity shifted bands, the energy gap between the highest filled metal orbitals and the lowest empty π orbitals is diminished due to the overlap of the two filled metal d_{z^2} orbitals and of the two empty ligand π orbitals. The closing of the energy gap produces the shift of the metal-to-ligand charge transfer absorption bands to higher wavelength.¹⁸ Figure 4 illustrates the proximity-shifted scheme involving the ML_4 metal centers.

The yellow A-frame complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$ also shows a proximity-shifted band at 445 nm in the electronic spectrum. In A-frame complexes the ligands are arranged about the Rh(I) atom (d^8 configuration) in approximately square planar fashion. The same orientation of ligands to metal is found in face-to-face complexes without a metal-metal bond. Thus it is reasonable to assume that the molecular orbital scheme for both of these structure classes will be very similar. This assumption was put forth by Eisenberg¹⁵ and Balch,¹⁸ and has been demonstrated in subsequent studies.⁶

The formation of a metal-metal bond results in the disappearance of the proximity-shifted transition. For example, for the complex

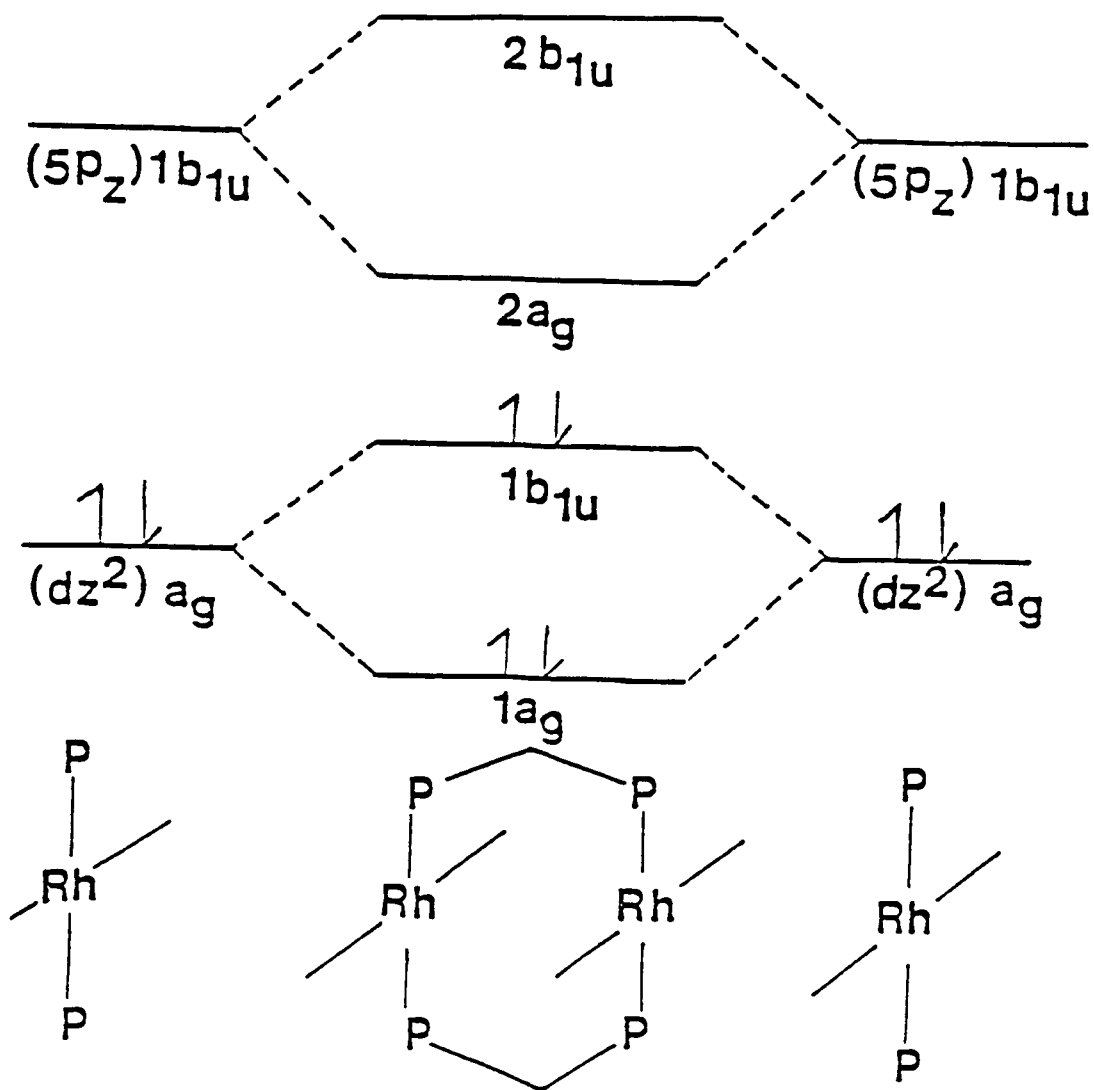


FIGURE 4. Simplified molecular orbital diagram showing the resulting orbital interactions of the approach of two square-planar Rh(I) units

$[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{dppm})_2]\text{BPh}_4$, discussed above, the electronic spectrum shows a blue shifted absorption band at 373 nm.¹⁸

The dpam ligand is the arsenic analogue of dppm; the arsenic atom is slightly larger than the phosphorus atom and has slightly different donor properties. The dpam ligand has a larger bite-size than dppm, and this leads to a comparatively larger separation between the metal atoms in bimetallic complexes employing dpam as the bridging ligand. Metal-metal separations have been shown to affect the stabilities of some complexes. For example, complexes containing ketonic carbonyl ligands with Pd(II) or Pt(II) and bridged by dpam are more stable than their dppm analogues.¹⁹ However, when Rh(I) is employed, the dppm complex is the more stable of the two.²⁰ It is accepted that the stabilities of complexes containing ketonic carbonyl ligands are dependent on the preferred metal-metal separations and thus on the transoid ligands employed (dppm or dpam).

In 1969 Mague and Mitchner reported the synthesis of the face-to-face Rh(I) dimer $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dpam})_2$.²¹ The Rh-Rh separation in this complex is 3.396Å and for the complex solvated with CH_2Cl_2 the Rh-Rh distance is 3.236Å. The difference between the Rh-Rh separation values of 0.160Å was explained by Cowie based on the steric requirements for the solvated and unsolvated complexes. The bromine analogue $\text{Rh}_2\text{Br}_2(\text{CO})_2(\text{dpam})_2$ was also prepared by Mitchner.²¹

Addition of iodine, I_2 or bromine, Br_2 to a CH_2Cl_2 solution of $\text{Rh}_2\text{Br}_2(\text{CO})_2(\text{dpam})_2$ results in the oxidative addition by the halogen and the formation of a Rh(II)-Rh(II) single bond. A series of IR spectra tracking the addition of one equivalent of I_2 (or Br_2) in small

portions shows a decrease of the absorption band at $1968(s) \text{ cm}^{-1}$ due to the starting material and the growth of a new band at $2025(s) \text{ cm}^{-1}$. After one equivalent of halogen is added, only the carbonyl band at 2025 cm^{-1} is observed. This increase of 60 cm^{-1} is indicative of a Rh(I) to Rh(II) oxidation. The resulting complexes are formulated as $\text{Rh}_2\text{Br}_2\text{X}_2(\text{dppm})_2$ ($\text{X} = \text{Br}, \text{I}$).²²

Successive addition of four molar equivalents of *n*-butylisocyanide and five molar equivalents of sodium tetraphenylborate, NaBPh_4 , to $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dpam})_2$ yields the ionic complex $[\text{Rh}_2(\text{n-BuNC})_4(\text{dpam})_2][\text{BPh}_4]_2$. The infrared spectrum of this compound indicates that only terminal isocyanide ligands are present. Formation of similar complexes using different isocyanides (RNC , $\text{R} = \text{CH}_3$, C_6H_{11} , $\text{t-C}_4\text{H}_9$) was also achieved. The isocyanide stretching frequencies are characteristic for Rh(I) compounds, occurring in the range $2200\text{--}2130 \text{ cm}^{-1}$.²³

Titration of any of the above mentioned isocyanide complexes with an acetone solution of I_2 produces Rh(II)-Rh(II) compounds of the type $[\text{Rh}_2(\text{RNC})_4\text{I}_2(\text{dpam})_2][\text{BPh}_4]_2$ which contain metal-metal single bonds. All these Rh(II) complexes show terminal isocyanide stretching frequencies in their IR spectra about 40 cm^{-1} higher than in the parent complexes.²³

Binuclear Rh(I) complexes employing the unsymmetrical transoid ligand (diphenylarsino)(diphenylphosphino) methane, dapm , were first reported in 1983 by Enlow and Woods.²⁴ Some of the complexes characterized were; (1) the face-to-face dimer $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$, (2) the ionic A-frame complex $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\text{dapm})_2]\text{PF}_6$, and (3) the ionic

double A-frame complex $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2(\text{dapm})_2]\text{PF}_6$. The dppm analogues for these complexes have been discussed above.

The dapm complexes exist as two possible isomers. The head-to-head arrangement (HH) is such that both phosphorus donor atoms are bound to one Rh(I) atom and the head-to-tail arrangement (HT) is such that one phosphorus donor atom and one arsenic donor atom are trans to each other about a Rh(I) atom. (Figure 5.)

The neutral complex $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$ was initially prepared by refluxing a mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in aqueous ethanol under a CO atmosphere until the reflux solution adopted a lemon-yellow color at which time the solution was cooled and the necessary amount of the dapm ligand in acetone was added. Rapid stirring of the orange solution yielded the product as orange crystals from ethanol. By this method both the HH and HT isomers were obtained. The formation of both HT and HH isomers in a 7:1 ratio was reported by Balch and Guimerans for $[\text{Rh}_2(\text{dapm})_2(\mu\text{-Cl})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ and the face-to-face dimer $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$.²⁵ Repeated recrystallizations from CH_2Cl_2 /diethyl ether (or hot ethanol) were performed on the mixture of isomers of $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$ which effectively removed the HH isomer. Thus only the HT isomer of $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$ was used by Enlow and Woods as the starting material for the complexes discussed below.

The complex $[\text{Rh}_2(\mu\text{-CO})(\mu\text{-Cl})(\text{CO})_2(\text{dapm})_2]\text{PF}_6$ exhibits much of the same behavior as its dppm analogue. An IR spectrum obtained immediately after isolation reveals the presence of a bridging carbonyl, $\nu(\text{CO}) = 1981$ and 1967 cm^{-1} . This yellow solid complex loses CO during a 10 hour period to give the bridging chloride,

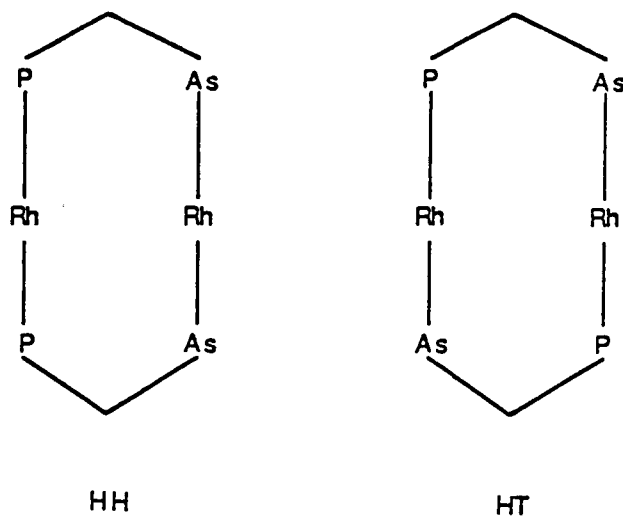


FIGURE 5. The framework of the $\text{Rh}_2(\text{dapm})_2$ ring showing both HH and HT isomers

$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{dapm})_2]\text{PF}_6$. The same behavior is demonstrated by the dppm complex, $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\text{dppm})_2]\text{PF}_6$, but not by the analogous dpam complex which defies isolation as a solid due to its apparent instability.²⁴

Addition of one equivalent of t-BuNC to $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{dapm})_2]\text{PF}_6$ yielded a face-to-face dimer with the bridging chloride becoming terminally bound. Addition of a second equivalent of t-BuNC resulted in the replacement of the carbonyl trans to the initially bonded t-BuNC as shown in Figure 6.

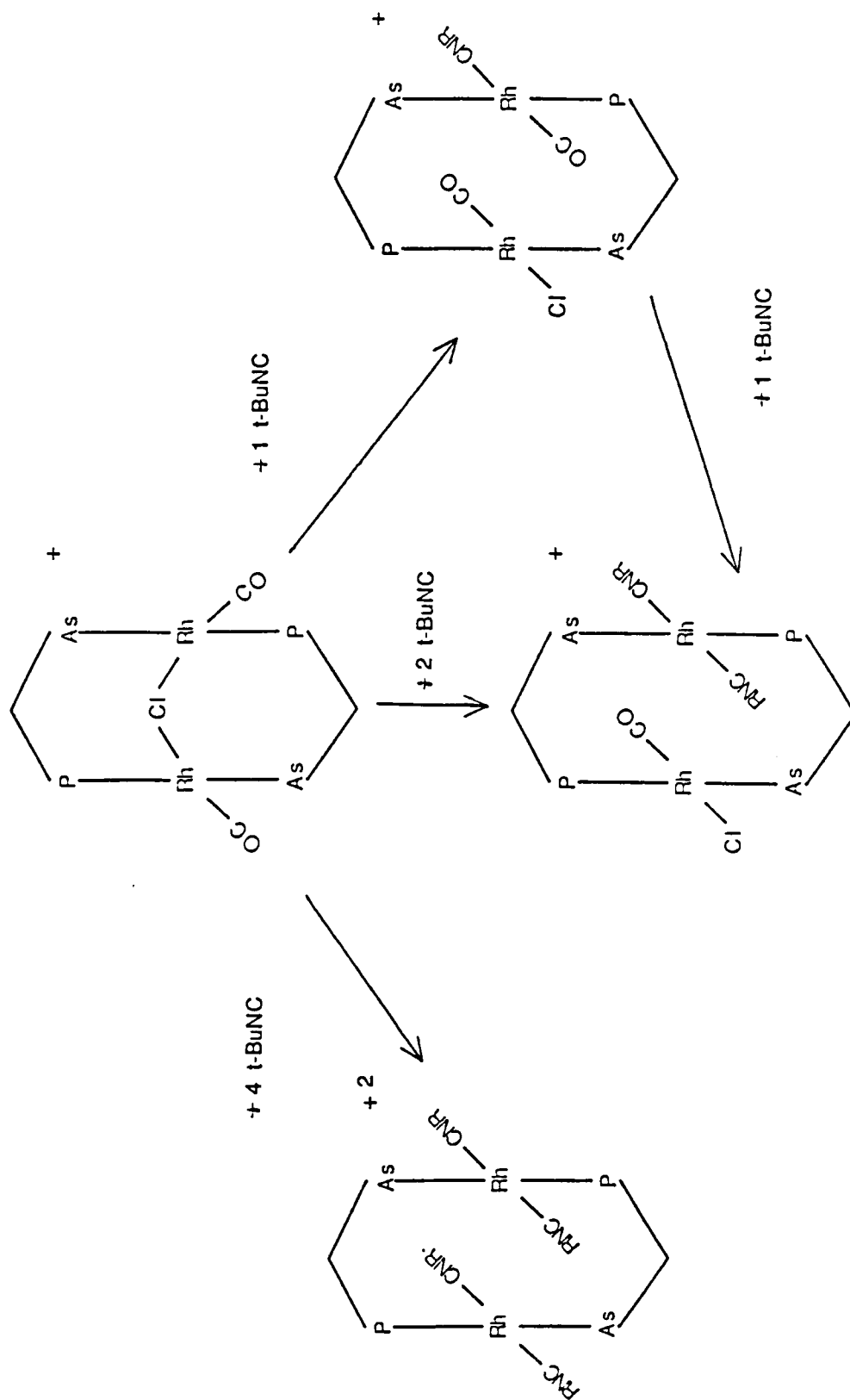


FIGURE 6. Reaction of $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-dapm})_2]\text{PF}_6$ with various equivalent amounts of $t\text{-BuNC}$

Treatment of the face-to-face dimer $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dapm})_2$ with four equivalents of RNC and two equivalents of BF_4^- , BPh_4^- or PF_6^- salts resulted in complexes of the type $[\text{Rh}_2(\text{RNC})_4(\text{dapm})_2]\text{X}_2$, where $\text{R} = i\text{-C}_3\text{H}_7$, C_6H_{11} or $t\text{-C}_4\text{H}_9$. The electronic spectra of these tetrakis-isocyanide complexes revealed their similarity to the dppm and dpam analogues.²⁴ The range of the proximity-shifted metal-to-ligand charge transfer for the dppm, dapm and dpam complexes is 588 nm for $[\text{Rh}_2(\text{CH}_3\text{NC})_4(\text{dpam})_2][\text{BPh}_4]_2$ (in acetonitrile)²³ to 517 nm for $[\text{Rh}_2(t\text{-BuNC})_4(\text{dapm})_2][\text{PF}_6]_2$ (in CH_2Cl_2).²⁴

In 1983 a side-to-side Pt(I) dimer using dapm as the bridging ligand was reported by Guimerans and Balch.²⁵ This complex was formulated as $\text{Pt}_2\text{Cl}_2(\text{dapm})_2$ and its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed the existence of both HH and HT isomers. Also reported was the preparation of the complex $\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dapm})_2$ the dapm analogue of the first Rh(I) A-frame $\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2$. The HT:HH ratio is 4:1 for $\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{dapm})_2$.²⁵

Rh(I) complexes of the A-frame type with a pyrazolate derivative at the bridgehead position were initially reported in 1985 by Oro and co-workers.²⁷ The addition of a pyrazolate salt to an acetone suspension of trans- $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{dppm})_2$ yielded complexes of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-Xpyz})(\text{dppm})_2]\text{Cl}$ (Xpyz = pyrazolate (pyz), 3-methylpyrazolate (3mpyz), 3,5-dimethyl pyrazolate (35dmpyz), 4-bromo-3,5-dimethylpyrazolate (4B35dmpyz)). In each complex the chloride counterion was replaced by bulkier anions such as BPh_4^- or ClO_4^- by addition of NaBPh_4 and AgClO_4 , respectively. In all cases, the $^{31}\text{P}\{^1\text{H}\}$ NMR revealed a symmetric multiplet indicative of an $\text{AA}'\text{A}'''\text{XX}'$ spin

system. The values of $\delta(\text{Rh-P})$ are in the range 22.9-25.3 ppm and $[\text{J}(\text{Rh-P}) + {}^1\text{J}(\text{Rh-P})]$ values are in the range 128.9-137.5 Hz. Infrared spectra of these complexes reveal two absorption bands (range: 2000-1975 cm^{-1}) indicative of the presence of two terminal carbon monoxide ligands.

An X-ray crystal structure of $[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\mu\text{-dppm})_2]\text{ClO}_4$ confirmed the assigned A-frame structure (See Figure 7A). It was suggested by Oro that the Rh-Rh separation of 3.060 Å allowed for weak metal-metal interaction which in turn caused a deviation of each Rh center from a square planar coordination towards the other Rh center.²⁷ The deviation for one Rh atom was 0.058 Å and 0.055 Å for the other Rh atom. The electronic spectra for these compounds showed proximity-shifted bands (ca. 495 nm) with molar absorption coefficients in the range 9,000-19,000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Addition of I_2 to complexes of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-xpyz})(\mu\text{-dppm})_2]\text{ClO}_4$ yielded compounds of the type $[\text{Rh}_2\text{I}_2(\text{CO})_2(\mu\text{-xpyz})(\mu\text{-dppm})_2]\text{ClO}_4$ as shown in Figure 7B. The X-ray crystal structure of 5B reveals a Rh-Rh separation of 2.725 Å which is typical of a Rh-Rh single bond. The infrared spectrum of the diiodide product displays an increase of 65 cm^{-1} for the terminal carbonyl absorption band relative to the starting compound. This is indicative of an increase in the formal oxidation state from Rh(I) to Rh(II).

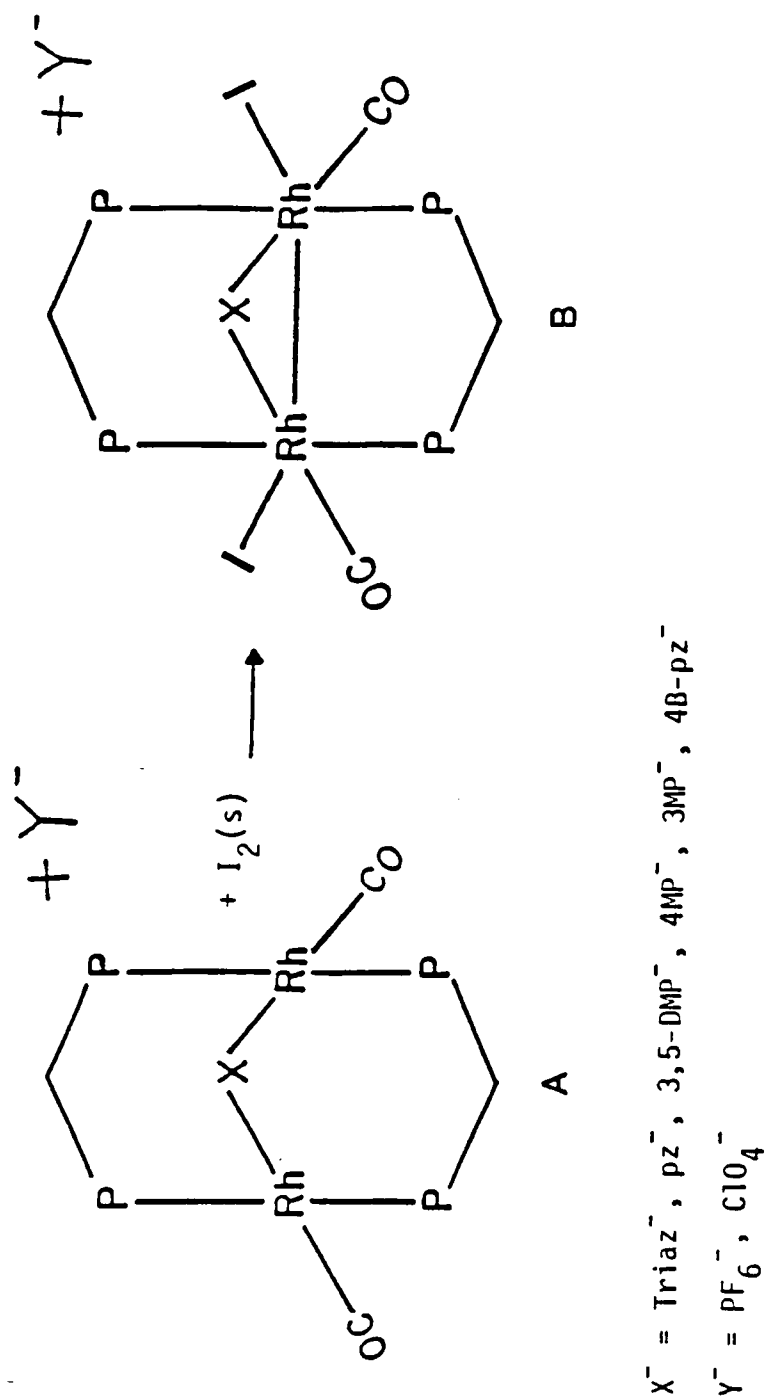


FIGURE 7. The oxidative addition of I_2 to $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-dppm})_2]\text{PF}_6$

During Oro's investigation of pyrazolate-containing A-frames, similar work was being conducted by Woods et al.^{5,6,28} The preparation of the A-frame complexes, as originally outlined by Janke,⁵ required addition of n -BuLi to the appropriate pyrazole derivative in tetrahydrofuran (THF). This pyrazolate solution was then added to a THF solution of $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-LL})_2]\text{PF}_6$ (LL = dppm, dapm, dpam), which, after stirring and the addition of diethyl ether, yielded the desired product, $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-LL}')]\text{PF}_6$ (X = 4-methylpyrazolate (4mpyz), triazolate (trz), 35dmpyz, pyz).

Addition of I_2 to compounds of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-dppm})_2]\text{PF}_6$ (X = pyz, 4mpyz, 35dmpyz) gave Rh(II)-Rh(II) metal-metal single bonded complexes with structures analogous to that of $[\text{Rh}_2\text{I}_2(\text{CO})_2(\mu\text{-35dmpyz})(\mu\text{-dppm})_2]\text{ClO}_4$ as reported by Oro, et al.²⁷ In the cases where the halogen used was Br_2 or Cl_2 , the pyz and 35dmpyz derivatives added three halogen atoms per molecule; thus one halogen atom was added at each Rh(I) site and one halogen in the 4-position of the aromatic pyrazolate derivative. The complex containing the 4mpyz did not add a halogen atom at the 4-position because the position was blocked to halogenation.²⁸ The addition of a bromine atom in the 4-position was supported by the results from the electrochemical reductive-elimination reaction of $[\text{Rh}_2\text{Br}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2]\text{PF}_6$. Controlled potential electrolysis at -0.65V gave the Rh(I) complex $[\text{Rh}_2\text{Br}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2]\text{PF}_6$.

Complexes of the type $[\text{Rh}_2(\text{CO})(t\text{-BuNC})(\mu\text{-X})(\mu\text{-dppm})_2]\text{PF}_6$ result when one equivalent of $t\text{-BuNC}$ is added to the dicarbonyl complex(es) $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-dppm})]\text{PF}_6$ (X = pyz, 35dmpyz, 4mpyz, trz). Similarly,

the addition of two equivalents of t -BuNC to the dicarbonyl complexes gives diisocyanide derivatives, $[\text{Rh}_2(t\text{-BuNC})_2(\mu\text{-Xpyz})(\mu\text{-dppm})]\text{PF}_6$.

Attempts to prepare the mono- and diisocyanide derivatives of $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-LL}')]\text{PF}_6$ (LL' = dapm, dpam) were met with limited success.²⁹

The lowest energy electronic transition for the complexes $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-dppm})_2]\text{PF}_6$ moves to lower energy upon replacement of one CO by t -BuNC and moves to still lower energy upon replacement of both CO groups by t -BuNC. This trend is viewed as a decrease in the separation of the HOMO and LUMO as the more electron rich t -BuNC substitutes for the CO ligand. The lowest-energy electronic transition for complexes of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-X})(\mu\text{-LL})_2]\text{PF}_6$ moves to higher energy as the bidentate transoid ligands are changed from a smaller to a larger bite-size in going from dppm to dapm to dpam. (Bite-size: $\text{dpam} > \text{dapm} > \text{dppm}$.) Such a change in the transoid ligands employed increases the Rh-Rh separation and thereby decreases the overlap of the metal d_z^2 and pz orbitals which in turn decreases the energy of the HOMO. Overall, the addition of a larger bite-size transoid ligand causes an increase in the separation between the HOMO and LUMO.²⁸

B. Statement of Purpose

This work investigates the spectroscopic and electrochemical properties of binuclear Rh(I) A-frame complexes in which a pyrazolate derivative occupies the bridgehead position and two dapm ligands serve as the transoid ligands. Since the dppm and dpam analogues of these complexes have been recently characterized^{5,6,28,29} and since the bite-

size of dapm is intermediate of dppm and dpam, it was of interest to study the properties of these complexes.

Compounds of the type $[\text{Rh}_2(\text{L})_2(\mu\text{-EE})_2(\mu\text{-xpyz})][\text{PF}_6]_2$ (xpyz = substituted pyrazolate; EE = dppm, dpam; L = CO or t-BuNC) are air-stable, paramagnetic and result from the one-electron electrochemical oxidation of the diamagnetic parent complexes, $[\text{Rh}_2(\text{L})_2(\mu\text{-EE})_2(\mu\text{-xpyz})]\text{PF}_6$. These paramagnetic complexes display thermochromism (green $\rightarrow$ red) upon cooling to lower-than-room temperatures using either dry ice or liquid nitrogen. It was therefore of interest to generate the paramagnetic dapm analogues for comparison of the effects of the transoid ligand bite-size upon the spectroscopic properties of this class of compounds.

CHAPTER 1.2

EXPERIMENTAL

A. Chemicals

1. Solvents

a. Methylene Chloride, CH₂Cl₂, Mallinckrodt, ACS grade CH₂Cl₂ was used as purchased for synthesis work. For UV-Vis and electrochemical experiments, CH₂Cl₂ was dried over CaCl₂ and distilled from P₂O₅ before use.

b. Acetone, Mallinckrodt. ACS grade acetone was used without further purification.

c. Absolute Ethanol, Ethanol, U.S. Industrial Chemicals. Ethanol was used as purchased.

d. Methanol, Mallinckrodt. Methanol was used as purchased for most synthesis work. For isolation of products the methanol was distilled before use.

e. Distilled Water, Water, H₂O, Departmental distilled water was used without further purification.

f. Anhydrous Diethyl Ether, Ether, Mallinckrodt. ACS grade anhydrous ether was used as purchased.

g. Hexanes, Mallinckrodt. ACS grade hexanes were used as purchased.

2. Gases

- a. Argon, Ar, MG Industries. Prepurified Ar was used without further purification.
- b. Nitrogen, N₂, MG Industries. Prepurified N₂ was used without further purification.
- c. Carbon Monoxide, CO, MG Industries. Prepurified CO was used as purchased.

3. Reagents

- a. Diphenylchloroarsine, Ph₂ClAs, Pfaltz and Bauer. High purity Ph₂ClAs sealed in an ampoule was used without further purification.
- b. Methyldiphenylphosphine, CH₃Ph₂P or MePh₂P, Strem. MePh₂P was used as purchased.
- c. Normal Butyllithium, n-BuLi, Aldrich n-BuLi (1.6M in hexanes) was used as purchased.
- d. Tetramethylethylenediamine, TMEDA, Aldrich. TMEDA was used as purchased.
- e. Rhodium (III) chloride trihydrate, RhCl₃·3H₂O, Johnson-Matthey. Reagent grade RhCl₃·3H₂O was used without further purification.
- f. Rhodium (I) dichlorotetracarbonyl, Rh₂Cl₂(CO)₄. Rh₂Cl₂(CO)₄ is prepared by bubbling ethanol saturated with CO through purple RhCl₃·3H₂O (powdered) on an enclosed glass frit. A brick red solid is claimed and sublimed for about ten hours at 70°C. The resulting red solid is stored under vacuum.
- g. Pyrazole, pyzH, Aldrich. Reagent grade pre-dried pyzH was used as purchased.

h. 4-Methylpyrazole, 4mpyzH, Aldrich. Reagent grade 4mpyzH was used as purchased.

i. 3,5-Dimethylpyrazole, 35dmpzH, Aldrich. Reagent grade 35dmpzH was used as purchased.

j. 4-Bromo-3,5-dimethylpyrazole, 4B35dmpyzH, Pfaltz and Bauer. Reagent grade 4B35dmpyzH was used as purchased.

k. 3,4,5-Tribromopyrazole, 345BpyzH. 345BpyzH was synthesized by the method used by the Upjohn Company.³¹

l. (Diphenylarsino)(Diphenylphosphino)methane, dapm. The dapm ligand was synthesized by the method of P. D. Enlow and C. Woods.²⁴

m. Tertiarybutylisocyanide, t-BuNC, Aldrich. Reagent grade t-BuNC was used without further purification.

n. Potassium hexafluorophosphate, KPF₆, Aldrich. Reagent grade KPF₆ was used as purchased.

o. Tetra-n-butylammonium iodide, TBAI, Aldrich. Reagent grade TBAI was used as purchased.

p. Ammonium hexafluorophosphate, NH₄PF₆, Aldrich. Reagent grade NH₄PF₆ was dried under vacuum for at least ten hours at 70°C before use.

q. Tetra-n-butylammonium hexafluorophosphate, TBAH. TBAH was prepared by the metathesis of TBAI and KPF₆ (1:1) in water. TBAH was purified by at least three recrystallizations from acetone/water followed by vacuum drying for about ten hours at 70°C.

4. Miscellaneous

a. Potassium hydroxide, KOH, Mallincrodt. Reagent grade KOH was used as purchased.

- b. Sodium metal, Na, Fisher Scientific. Reagent grade Na was used as purchased.
- c. Bromine, Br₂, Aldrich. Reagent grade Br₂ was used without further purification.
- d. Nujol, Plough, Inc. Nujol was used after drying over Na.
- e. Phosphorus pentoxide, P₂O₅, Mallinckrodt. ACS grade P₂O₅ was used as purchased.
- f. Calcium chloride, CaCl₂, Mallinckrodt. Anhydrous CaCl₂ was used as purchased.

B. Spectroscopy

1. Nuclear Magnetic Resonance (NMR)

³¹P(¹H) NMR spectra were recorded on a JEOL FX90Q Fourier Transform NMR spectrometer at 36.21 MHz using 85% phosphoric acid as the external reference. The instrument was locked on the deuterium signal of acetone-d₆, (CD₃)₂CO, contained in a flame-sealed 5 mm tube put into a 10 mm sample tube. The solvents used were degassed with Ar before use.

2. Infrared Spectroscopy (IR)

Infrared spectra were recorded on a Digilab FTS-20C/V Fourier Transform Infrared Spectrometer or a Perkin-Elmer 1330 Infrared Spectrophotometer. Solid samples (usually 8-12 mg) were ground into Nujol mulls and sealed between two thin sheets of polyethylene.

3. Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-visible spectra were obtained using a Cary 219 Spectrophotometer. Quartz cells (Fisher Scientific) of 1.0 cm pathlength were used with freshly distilled and argon degassed CH_2Cl_2 as the solvent. All spectra were recorded at room-temperature using the solvent in the reference beam.

4. Electron Spin Resonance (ESR)

The ESR spectra were obtained in 4:1 CH_2Cl_2 /toluene solutions employing a JEOL JES-PE-IX ESR spectrometer. Spectra obtained at temperatures below room temperature required the use of variable temperature accessories using liquid N_2 as the coolant.

C. Electrochemistry

1. Instrumentation

Bulk electrolysis, coulometry, and cyclic voltammetry experiments were accomplished using a BAS 100 Electrochemical Analyzer (Bioanalytical Systems, Inc.) with a DMP-40 series digital plotter (Houston Instrument).

2. Electrodes

For Bulk electrolysis and coulometry experiments a three electrode system was employed. The working electrode was a 25 cm^2 platinum grid and the reference electrode was a standard saturated calomel electrode (SCE) separated from the bulk solution by a fine fritted glass jacket. The counter electrode was a carbon rod mounted through a rubber septum;

this electrode was placed in a compartment separate from the working and reference electrodes.

For cyclic voltammetry experiments the working electrode was a 0.24 cm^2 platinum button electrode (Beckman) and the counter electrode was a 2.76 cm^2 platinum grid. A SCE served as the reference electrode.

3. Cells

An H-shaped, three-compartment cell was employed for bulk electrolysis and coulometry experiments. The three compartments were separated by two fine glass frits and the working compartment was fitted with a glass frit bottom to allow for constant purging of the solution with Ar. This purging stirred the solution and ensured exclusion of air from the electrolyte solution.

A one-compartment cell was used for cyclic voltammetry. The one-compartment cell was also fitted with a glass frit bottom and side arm to degass the solution with Ar.

4. Comments

a. The scan rate for cyclic voltammograms was 0.100 V/sec unless otherwise stated.

b. Coulometry experiments were performed with a minimum of two trials using different sample sizes to verify reproducibility.

D. Preparation of Dirhodium Complexes

1. Dicarbonyldichlorobis[μ -((diphenylarsino)(diphenylphosphino)-methane)-As:P]-dirhodium(I), $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dapm})_2]$, 1.

In separate flasks $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$ (550 mg, 1.41 mmol) and (diphenylarsino)(diphenylphosphino)methane, dapm, (1.21 g, 2.82 mmol) were dissolved using about 40-50 mL of toluene for each. The dapm solution was quantitatively added dropwise to the rapidly stirred $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$ solution at 20°C. After stirring for one hour, a finely divided orange-red precipitate formed which was filtered from the solution and recrystallized from dichloromethane-diethyl ether. Yield: 95.1%.

IR spectrum: (Nujol) $\nu(\text{CO}) = 1975 \text{ cm}^{-1}(\text{s})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: $\delta(\text{Rh-P}) = 27.34 \text{ ppm}$ (85% H_3PO_4), $^1\text{J}(\text{Rh-P}) = 148.9 \text{ Hz}$ (HT) and $\delta(\text{Rh-P}) = 22.54 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 124.5 \text{ Hz}$ (HH).

2. Dicarbonyl- μ -4-methylpyrazolato-N:N'bis[μ -((diphenylarsino)-(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2(\mu\text{-4mpyz})(\mu\text{-dapm})_2]\text{PF}_6$, 2.

The compound $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dapm})_2]$ (355 mg, 0.300 mmol) was dissolved in 50 mL of reagent grade acetone. To this solution was added predried NH_4PF_6 (48.9 mg, 0.300 mmol) and the resulting yellow suspension stirred for one hour. Meanwhile, in a separate flask 4-methylpyrazole, 4mpyzH, (30.5 mg, 0.450 mmol) and the appropriate amount of a KOH/methanol solution (7.14 mL, 0.300 mmol KOH) were combined resulting in the deprotonation of the 4-methylpyrazole to form the 4-methylpyrazolate anion. The 4-methylpyrazolate solution was added dropwise to the yellow suspension and allowed to stir for an additional hour during which time the solution color changed from yellow to deep red. The solvent was removed via a rotary evaporator using a 40°C water bath. The crude product was dissolved in

dichloromethane and filtered to remove water-soluble salts such as KCl and/or NH_4Cl . To the dichloromethane filtrate was added anhydrous diethyl ether until precipitation was complete. The red product was collected by filtration and stored under vacuum. Yield: 85%.

IR spectrum: (Nujol) $\nu(\text{CO}) = 1970 \text{ cm}^{-1}(\text{br})$. The spectrum also shows PF_6^- peaks at $839(\text{s})$ and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 [$\lambda_{\text{max}} (\epsilon)$]: $487 \text{ nm} (13,640)$ and $302 \text{ nm} (13,110)$ (shoulder). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 28.24 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 151.4 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 25.22 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 126.9 \text{ Hz}$.

3. Dicarbonyl- μ -pyrazolato-N:N'-bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate, -
 $[\text{Rh}_2(\text{CO})_2(\mu\text{-pyz})(\mu\text{-dapm})_2]\text{PF}_6$, 3.

Compound **3** was prepared by the same procedure used to make **2** by using $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dapm})_2]$ (360 mg, 0.303 mmol), NH_4PF_6 (49.5 mg, 0.303 mmol), pyrazole (37.4 mg, 0.455 mmol) and KOH/methanol (7.3 mL, 0.303 mmol). The product was obtained as a red powder. Yield: 87%.

IR spectrum: (Nujol) $\nu(\text{CO}) = 1970 \text{ cm}^{-1}(\text{s})$ and $1930 \text{ cm}^{-1}(\text{sh})$. The spectrum also showed PF_6^- peaks at $839 \text{ cm}^{-1}(\text{s})$ and 557 cm^{-1} . UV-Vis spectrum in CH_2Cl_2 [$\lambda_{\text{max}} (\epsilon)$]: $483 \text{ nm} (15,000)$ and $316 \text{ nm} (7730)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 28.34 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 151.4 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 25.48 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 127.0 \text{ Hz}$.

4. Dicarbonyl- μ -3,5-dimethylpyrazolato-N:N'-bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$, 4.

Compound 4 was prepared by the same method as used for 2 by using $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dapm})_2]$ (263 mg, 0.221 mmol), NH_4PF_6 (36.1 mg, 0.221 mmol), 3,5-dimethylpyrazole (31.9 mg, 0.332 mmol) and KOH/methanol (5.3 mL, 0.221 mmol). The product was obtained as a fine orange-red powder. Yield: 81%.

IR spectrum: (Nujol) $\nu(\text{CO}) = 1970 \text{ cm}^{-1}(\text{s})$ and $1945 \text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF_6^- peaks at $839 \text{ cm}^{-1}(\text{s})$ and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 484 nm (11,600) and 302 nm (12,600). $^{31}\text{P}(^1\text{H})$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 27.94 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 153.8 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 23.87 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 127.0 \text{ Hz}$.

5. Dicarbonyl- μ -4-bromo-3,5-dimethylpyrazolato-N:N'-bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)-hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$, 5.

Compound 5 was prepared by the same procedure as used for 2 by using 1 (305 mg, 0.256 mmol), NH_4PF_6 (41.8 mg, 0.256 mmol), 4-bromo-3,5-dimethylpyrazole (67.3 mg, 0.384 mmol) and KOH/methanol (6.13 mL, 0.256 mmol KOH). The product was a finely divided orange powder. Yield: 90%.

IR spectrum: (Nujol) mull) $\nu(\text{CO}) = 1970 \text{ cm}^{-1}(\text{s})$ and $1945 \text{ cm}^{-1}(\text{w})$. The spectrum also shows PF_6^- peaks at $839 \text{ cm}^{-1}(\text{s})$ and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 484 nm (13,100) and 302 nm (15,100). $^{31}\text{P}(^1\text{H})$ NMR spectrum. (HT) $\delta(\text{Rh-P}) = 27.51 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 151.4 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 23.22 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 124.5$.

6. Dicarbonyl- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate, [Rh₂(CO)₂(μ -345Bpyz)(μ -dapm)₂]PF₆, 6.

Compound 6 was made using the procedure for 2 by using 1 (331 mg, 0.279 mmol), NH₄PF₆ (45.4 mg, 0.279 mmol), 3,4,5-tribromopyrazole (127 mg, 0.412 mmol) and KOH/methanol (6.65 mL, 0.279 mmol KOH). The product was obtained as a finely divided orange-yellow powder. Yield: 90%.

IR spectrum: (Nujol mull) ν (CO) = 1972 cm⁻¹(s) and 1940 cm⁻¹(sh). The spectrum also indicated the presence of PF₆⁻ peaks at 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis spectrum in CH₂Cl₂ [λ_{max} (ϵ): 481 nm (8,200) and 306 nm (16,800)]. ³¹P{¹H} NMR spectrum: (HT) δ (Rh-P) = 26.52 ppm, ¹J(Rh-P) = 146.5 Hz and (HH) δ (Rh-P) = 21.48 ppm, ¹J(Rh-P) = 124.5 Hz.

7. Bis(t-butylisocyanide)- μ -4-methylpyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate, [Rh₂(t-BuNC)₂(μ -4mpyz)(μ -dapm)₂]PF₆, 7.

Compound 2 (118 mg, 0.088 mmol) was dissolved in 50 mL of freshly distilled CH₂Cl₂ to which was added 50 mL of freshly distilled methanol. The red solution was cooled to 0°C and t-BuNC, (16.8 mg, 22.3 μ L, 0.202 mmol) was added via microsyringe at a rate of one drop per one minute. Upon addition of the t-BuNC the solution became deep red in color. After stirring for 15 minutes, the solution was evaporated via a rotary evaporator using a 60°C water bath until just dry. The minimum amount of CH₂Cl₂ required to completely dissolve the crude product was used. Addition of a 50:50 mixture of anhydrous diethyl ether:hexanes yielded the desired product from solution as a

deep red powder. The product was collected by filtration and stored under vacuum. Yield: 60%.

IR spectrum: (Nujol mull) $\nu(\text{NC}) = 2120 \text{ cm}^{-1}(\text{s})$ and $2050 \text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF_6^- peaks at 839 (s) and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 508 nm (7370) , 308 nm (8740) . $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 27.20 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 168.5 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 23.50 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 136.7 \text{ Hz}$.

8. Bis(t-butylisocyanide)- μ -pyrazolato-N:N'bis[μ -((diphenylarsino)-(diphenylphosphino)methane)-As:P]dirhodium(I)hexafluorophosphate. $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-pyz})(\mu\text{-dapm})_2]\text{PF}_6$, **8**.

Compound **8** was produced by the same method as **7** using **3** (151 mg, 0.113 mmol) and *t*-BuNC (21.6 mg, $28.7 \mu\text{l}$, 0.261 mmol). Yield: 65%.

IR spectrum: (Nujol) $\nu(\text{NC}) = 2110 \text{ cm}^{-1}(\text{br})$ and $2060 \text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF_6^- peaks at 839 (s) and $557 \text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 27.00 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 168.5 \text{ Hz}$ and (HH) $\delta(\text{Rh-P}) = 23.73 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 136.7 \text{ Hz}$.

9. Bis(t-butylisocyanide)- μ -3,5-dimethylpyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)-hexafluorophosphate. $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$, **9**.

Compound **9** was produced by the same method as for **7** by using **4** (70 mg, 0.0515 mmol) and *t*-BuNC (9.42 mg, $12.5 \mu\text{L}$, 0.113 mmol). Yield: 65%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2105(\text{s})$ and $2060 \text{ cm}^{-1}(\text{sh})$. PF_6^- peaks also shown at 839 (s) and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , [λ_{max} (ϵ)]: 504 nm (6290) and 309 nm (8240) . $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum: (HT) $\delta(\text{Rh-P}) = 27.50$ ppm, $^1\text{J}(\text{Rh-P}) = 170.9$ Hz and (HH) $\delta(\text{Rh-P}) = 21.82$ ppm, $^1\text{J}(\text{Rh-P}) = 139.2$ Hz.

10. Bis(t-butylisocyanide)- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)-hexafluorophosphate, $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$, 10.

Compound 10 was prepared by the same method as for 7 using 5 (256 mg, 0.178 mmol) and t-BuNC (33.9 mg, 45.1 μL , 0.410 mmol). Yield: 62%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2100$ (br.) and 2060 cm^{-1} (sh). The spectrum also shows PF_6^- peaks at 839 (s) and 557 cm^{-1} . UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]$: 504 nm (4770) and 308 nm (8200).

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 27.10$ ppm, $^1\text{J}(\text{Rh-P}) = 168.5$ Hz and (HH) $\delta(\text{Rh-P}) = 21.18$ ppm, $^1\text{J}(\text{Rh-P}) = 136.7$ Hz.

11. Bis(t-butylisocyanide)- μ -3,4,5 tribromopyrazolato-N:N'bis(μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(I)-hexafluorophosphate, $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2]\text{PF}_6$, 11.

Compound 11 was prepared by the same method as used for 7 using 6 (225 mg, 0.143 mmol) and t-BuNC (11.9 mg, 36.4 μL , 0.330 mmol). Yield: 61%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2120(\text{s})\text{ cm}^{-1}$. The spectrum also shows PF_6^- peaks at 839(s) and 557(m) cm^{-1} . UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]$: 496 (5,600) and 308 (7,400). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (HT) $\delta(\text{Rh-P}) = 25.9$ ppm, $^1\text{J}(\text{Rh-P}) = 166.0$ Hz and (HH) $\delta(\text{Rh-P}) = 20.6$ ppm, $^1\text{J}(\text{Rh-P}) = 124.5$ Hz.

12. Bis(t-butylisocyanide- μ -3,5-dimethylpyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(1.5)-[Rh₂(t-BuNC)₂(μ -35dmpyz)(μ -dapm)₂][PF₆]₂, 12.

Fifty mL of a CH₂Cl₂ solution of 9 (88.8 mg, 0.06 mmol) with 0.1 M TBAH was oxidized at +0.30 V using controlled potential electrolysis. The resulting green oxidized solution was evaporated to dryness using a rotary evaporator. The dried green residue was dissolved in a minimal amount of freshly distilled methanol and stirred for about 30 minutes, after which a green precipitate formed. The precipitate was collected by filtration and recrystallized from CH₂Cl₂-diethyl ether/hexanes. Yield: 80%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2163 \text{ cm}^{-1}(\text{s})$ and $2130 \text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF₆⁻ peaks at 839 (s) and 557 cm⁻¹(m). UV-Vis spectrum in CH₂Cl₂, [λ_{max} (ϵ)]: 435 nm (8860) and 625 nm (670).

13. Bis(t-butylisocyanide)- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]dirhodium(1.5)-hexafluorophosphate.[Rh₂(t-BuNC)₂(μ -4B35dmpyz)(μ -dapm)₂][PF₆]₂, 13.

The method employed to prepare compound 12 was also used for 13. A fifty mL CH₂Cl₂ solution of 10 (107 mg, 0.07 mmol) was oxidized at +0.4 V via controlled potential electrolysis. Yield: 80%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2170 \text{ (s)}$ and $2110 \text{ cm}^{-1} \text{ (sh)}$. The spectrum also shows PF₆ peaks at 839 (s) and 557 cm⁻¹ (m). UV-Vis spectrum in CH₂Cl₂, [λ_{max} (ϵ)]: 433 nm (9860) and 620 nm (800).

14. Bis(t-butylisocyanide)- μ -3,4,5-tribromopyrazolato-N:N'bis-
 $[\mu((\text{diphenylarsino})(\text{diphenylphosphino})\text{methane})\text{-As:P}]\text{dirhodium}(1.5)$
hexafluorophosphate, $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$, 14.

The method for making compound 12 was also employed for 14. A fifty mL CH_2Cl_2 solution of 11 (146 mg, 0.087 mmol) was oxidized at +0.5 V using controlled potential electrolysis. Yield: 85%.

IR spectrum in Nujol: $\nu(\text{NC}) = 2186 \text{ cm}^{-1}(\text{s})$. The spectrum also gives PF_6^- peaks at $839(\text{s})$ and $557 \text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}} (\epsilon)]: 426 \text{ nm} (13,600)$ and $650 \text{ nm} (870)$.

RESULTS AND DISCUSSION

Table I lists all compounds appearing in the Results and Discussion by number. All abbreviations are explained at the end of Table I.

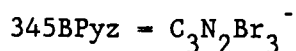
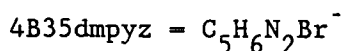
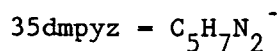
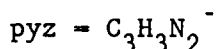
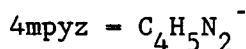
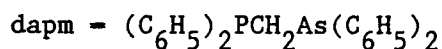
Binuclear Rh(I) A-frame complexes (2-6) employing the unsymmetrical ligand dapm as the transoid bridging ligands with a pyrazolate derivative situated in the bridgehead position were prepared by adding the potassium salt of the appropriate pyrazolate to an acetone suspension of 1:1 molar NH_4PF_6 and $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dapm})_2$, (1).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes 1-6 display two sets of doublets in a ratio of ca. 7:1. As previously shown,^{24,25} the dapm ligand generates head-to-head (HH) and head-to-tail (HT) isomers; the more intense resonance is due to the HT isomer. The simple doublet pattern for both HH and HT isomers implies that second-order effects and three-bond Rh-P coupling (long-range) are small. The chemical shifts for complexes 2-6 are in the range 28.4-26.5 ppm and $^1\text{J}(\text{Rh-P})$ are in the range 146.5-153.8 Hz for the HT isomers. The HH isomers for a given pyrazolate show a chemical shift upfield of the HT values and in a range of 25.5-21.5 ppm. The HH isomers also show smaller coupling constants, $^1\text{J}(\text{Rh-P})$, in the range of 124.5-127.0 Hz. Figure 8 shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 5, which is typical of the ^{31}P NMR spectra of complexes 1-11.

TABLE I
COMPOUND IDENTIFICATION

Compound Number	Compound
1	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dapm})_2$
2	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4mpyz})(\mu\text{-dapm})_2]\text{PF}_6$
3	$[\text{Rh}_2(\text{CO})_2(\mu\text{-pyz})(\mu\text{-dapm})_2]\text{PF}_6$
4	$[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$
5	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$
6	$[\text{Rh}_2(\text{CO})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2]\text{PF}_6$
7	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4mpyz})(\mu\text{-dapm})_2]\text{PF}_6$
8	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-pyz})(\mu\text{-dapm})_2]\text{PF}_6$
9	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$
10	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2]\text{PF}_6$
11	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2]\text{PF}_6$
12	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$
13	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$
14	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$

NOTES:



CO = carbonyl ligand

$\underline{\text{t}}\text{-BuNC}$ = tertiary butyl isocyanide, $(\text{CH}_3)_3\text{CNC}$

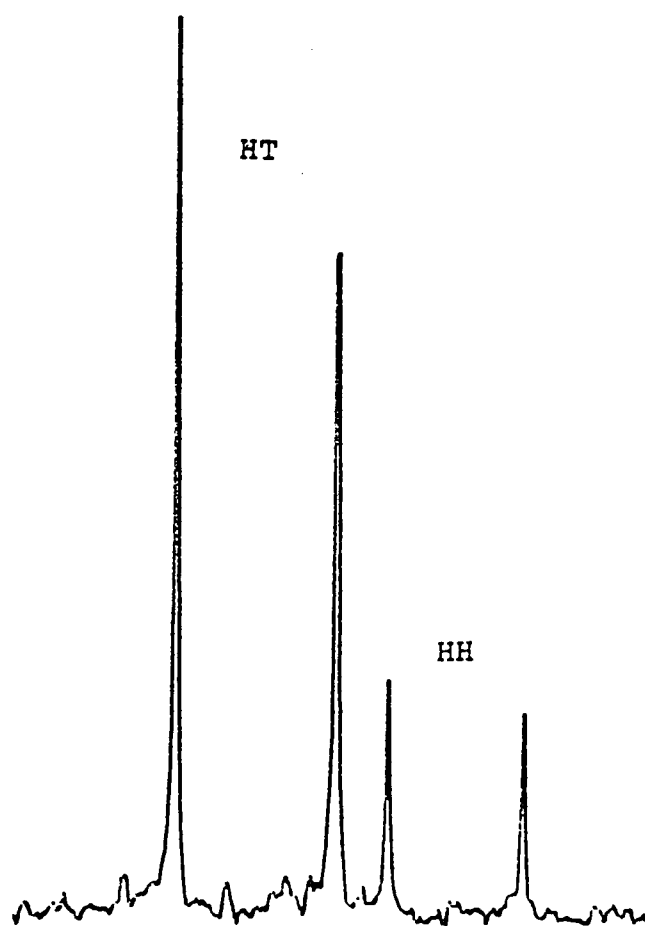


FIGURE 8. $^{31}\text{P}(^1\text{H})$ NMR spectrum of $[\text{Rh}_2(\text{CO})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2]\text{PF}_6$,
6, in CH_2Cl_2

The magnitude of one-bond metal-phosphorus coupling constants generally increases with a decrease in the oxidation state of the metal.³⁰ In a HT isomer the Rh(I) metal centers have more electron density from the coordinated P and As donor atoms than does the Rh(I) atom in a HH isomer with two P donor atoms. Hence, the HT isomers exhibit overall larger one-bond Rh-P coupling constants than do the HH isomers. Also, the smaller amount of electron density on Rh(I) in the HH isomers is consistent with their slightly upfield chemical shift.³⁰

The infrared spectra of complexes 2-6 typically show an intense absorption band (range: 1970-1972 cm^{-1}) accompanied by a shoulder (range: 1930-1940 cm^{-1}) due to the terminal CO ligands. The IR spectra also show PF_6^- peaks at 839(s) and 557(m) cm^{-1} .

Addition of two equivalents of t-BuNC to a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution of one of the dicarbonyl complexes (2-6) at 0°C yields the diisocyanide complexes (7-11), respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for complexes 7-11 are similar in appearance to those of the dicarbonyl species. As expected, the one-bond Rh-P coupling constants for both HT and HH isomers show an increase relative to their dicarbonyl counterparts. This is due to the larger amount of electron density provided the Rh(I) atoms by the relatively electron rich tertiarybutylisocyanide ligand. Also, the t-BuNC ligands do not accept π back-bonding as well as the terminal CO ligands. By either view, more electron density is contributed to the Rh(I) atom in the isocyanide complexes. The chemical shifts of the HT isomers occur in the range of 168-170 Hz and those of the HH isomers occur in the range of 124-139 Hz. With regard to chemical shift values of the HT and HH isomers, the same trend as

noted above for the dicarbonyl complexes 2-6 is noticed for the diisocyanide complexes, 7-11. Table II shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data for complexes 2-11.

The IR spectra of complexes 7-11 show strong absorption bands in the range of $2100\text{-}2120\text{ cm}^{-1}$. This indicates the presence of terminally bound t-BuNC ligands on Rh(I) . These same spectra also show PF_6^- peaks at $839(\text{s})$ and $557(\text{m})\text{ cm}^{-1}$ (Table III).

The electronic spectra of the dicarbonyl complexes, 2-6, have λ_{max} values in the range $487\text{-}481\text{ nm}$ with molar absorption coefficients in the range of $15,000\text{-}8,200\text{ L mol}^{-1}\text{ cm}^{-1}$ (Table IV). Similarly, the electronic spectra of the diisocyanide complexes, 7-11, exhibit λ_{max} values in the range $508\text{-}496\text{ nm}$ with a range of $7,400\text{-}4,800\text{ L mol}^{-1}\text{ cm}^{-1}$ (Table IV) for the molar absorption coefficients. In each case these metal-centered low energy proximity shifted bands result from the electronic transition $1b_{1u} (4d_z^2) \rightarrow 2a_g (5p_z)$. (The origin of the proximity shifted term was discussed earlier^{5,6,22} and also presented in Part A of Chapter 1.1.)

As expected, the UV-Vis data do not differ greatly with a change in the pyrazolate derivative. However, the lowest energy proximity-shifted band shifts to lower energy upon replacement of the CO ligands of complexes 2-6 with t-BuNC to give compounds 7-11. Therefore, the addition of the t-BuNC causes a decrease in the separation of the HOMO and LUMO.²⁸ The UV-Vis spectral data of diisocyanide complexes of the type $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-X})(\mu\text{-LL})_2]\text{PF}_6$ ($\text{X} = 4\text{ mpyz}, \text{pyz}, 35\text{dmpyz}, 4\text{B}35\text{dmpyz}, 345\text{Bpyz}$ LL = dppm or dpam) show similar trends compared to their parent dicarbonyl complexes.^{6,26}

TABLE II
 $^3\text{I}_\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR COMPOUNDS 2-11^{a, b}

Number	Compound	HH Isomer		HT Isomer	
		δ , ppm	$^1\text{J}(\text{Rh-P})$ Hz	δ , ppm	$^1\text{J}(\text{Rh-P})$ Hz
2	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	25.22	126.9	28.24	151.4
3	$[\text{Rh}_2(\text{CO})_2(\mu\text{-pyz})(\text{dapm})_2]\text{PF}_6$	25.48	127.0	28.38	151.4
4	$[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	23.87	127.0	27.94	153.8
5	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	23.22	124.5	27.51	151.4
6	$[\text{Rh}_2(\text{CO})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	21.49	124.5	26.52	146.5
7	$[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	23.50	136.7	27.20	168.5
8	$[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-pyz})(\text{dapm})_2]\text{PF}_6$	23.73	136.7	27.00	168.5
9	$[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	21.82	139.2	27.50	170.9
10	$[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	21.18	136.7	27.01	168.5
11	$[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	20.60	124.5	25.89	166.0

^aAll Chemical shifts relative to 85% H_3PO_4 .

^b $\delta(\text{Rh-P}) + 0.1$ ppm, $^1\text{J}(\text{Rh-P}) + 0.6$ Hz.

TABLE III
IR SPECTRAL DATA FOR COMPOUNDS 2-11

Number	Compound	$\nu(\text{RNC})$ or $\nu(\text{CO}), \text{ cm}^{-1}$
2	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	1970(s)
3	$[\text{Rh}_2(\text{CO})_2(\mu\text{-pyz})(\text{dapm})_2]\text{PF}_6$	1970(s), 1930(sh)
4	$[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	1970(vs), 1945(sh)
5	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	1970(vs), 1945(sh)
6	$[\text{Rh}_2(\text{CO})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	1972(vs), 1940(sh)
7	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	2120(vs), 2050(sh)
8	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-pyz})(\text{dapm})_2]\text{PF}_6$	2110(vs), 2060(sh)
9	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	2105(vs), 2060(sh)
10	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	2100(s), 2060(sh)
11	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	2120(vs)

$\text{RNC} = (\text{CH}_3)_3\text{NC}$

TABLE IV

UV-VIS SPECTRAL DATA FOR COMPOUNDS 2-11

Number	Compound	$\lambda_{\text{max, nm}} (\epsilon)$
2	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	487 (13,600) 302 (13,100)
3	$[\text{Rh}_2(\text{CO})_2(\mu\text{-pyz})(\text{dapm})_2]\text{PF}_6$	483 (15,000) 316 (7,700)
4	$[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	484 (11,600) 302 (12,600)
5	$[\text{Rh}_2(\text{CO})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	484 (13,100) 302 (15,100)
6	$[\text{Rh}_2(\text{CO})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	481 (8,200) 306 (16,800)
7	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4mpyz})(\text{dapm})_2]\text{PF}_6$	508 (7,400) 308 (8,700)
9	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2]\text{PF}_6$	504 (6,300) 309 (8,200)
10	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2]\text{PF}_6$	504 (4,800) 308 (8,200)
11	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\text{dapm})_2]\text{PF}_6$	496 (5,600) 308 (7,400)

Further comparison of the dppm, dapm and dpam analogues of the dicarbonyl and diisocyanide species reveals a trend where the lowest energy electronic transition moves to higher energy on going from dppm to dapm to dpam.^{6,28} This trend can be rationalized by noting the increase in Rh-Rh separation on going from dppm to dapm to dpam which decreases the orbital interaction between the Rh(I) centers and thereby increases the separation between the HOMO and LUMO.²⁸

Figure 9 illustrates a typical cyclic voltammogram observed for the dicarbonyl complexes 2-6 in freshly distilled CH_2Cl_2 and 0.1M TBAH. With regard to Figure 9, peaks A and D are the first oxidation-reduction couple and peaks B and C are the second oxidation-reduction process. These oxidation-reduction couples will be referred to as the first and second redox couples. Initially, the complexes 2-11 have a Rh_2^{2+} core, i.e. Rh(I)-Rh(I). Peak A is the oxidation process converting the Rh_2^{2+} core to Rh_2^{3+} , a species of mixed-valency (Rh(I)-Rh(II)) and therefore paramagnetic. Peak B is indicative of the further oxidation of the Rh_2^{3+} core to Rh_2^{4+} , Rh(II)-Rh(II). Peak C corresponds to the reduction of the product formed during the oxidation at peak B. Peak D is the reduction of Rh_2^{3+} to the original starting material having a Rh_2^{2+} core. Typically the oxidation potentials for both the first and second couples (Peaks A and B) are more positive for a given dicarbonyl complex than for the corresponding diisocyanide.

The diisocyanide complexes have higher-energy HOMO's than do their dicarbonyl counterparts as verified by the UV-Vis spectral data reported herein and elsewhere.^{6,28} Hence, the diisocyanides should be

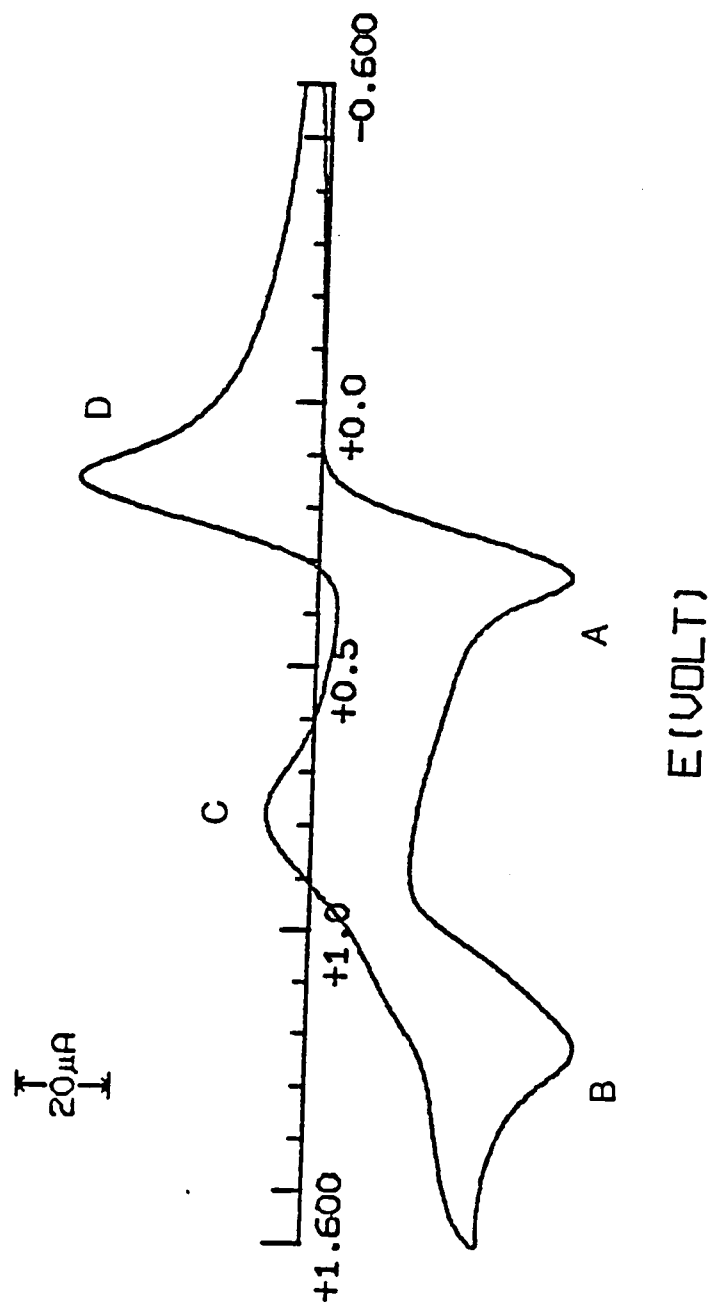


FIGURE 9. A cyclic voltammogram of $[\text{Rh}_2(\mu\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\mu\text{-dapm})_2\text{PF}_6]_{10}$, in CH_2CH_2 and 0.1 M TBAH

easier to oxidize since oxidation at either of the two couples removes an electron from the metal-centered HOMO.

Although complexes 2-11 exhibit both HH and HT isomers, as verified by $^{31}\text{P}\{^1\text{H}\}$ NMR of the samples, separate redox couples for these isomers are not indicated in the cyclic voltammograms.

Table V shows electrochemical data for the first redox couple (Peaks A and D). Inspection of the voltammetric data indicates the following: (1) the midpoint potentials, $E_{1/2}$ were invariant with the sweep rate and (2) the potential difference between E_{pa} and E_{pc} , ΔE , increases with an increase in sweep rate. The behavior exhibited indicates a quasi-reversible electron transfer process. Further, experiments employing controlled-potential coulometry indicate that each oxidation (i.e. peaks A and B) is a one-electron transfer.

Complexes 12, 13 and 14 are prepared from their diisocyanide precursors, complexes 9, 10 and 11, respectively by controlled-potential electrolysis in CH_2Cl_2 and 0.1M TBAH. An oxidation was performed at a potential between the two oxidation waves (peaks A and B, Figure 6) and the oxidation was indicated by a gradual color change of the solution from red starting material to a green product. The green product was isolated from the electrolyte by evaporation of the CH_2Cl_2 solvent via a rotary evaporator, followed by the addition of the minimum volume of warm methanol necessary to dissolve the contents. After stirring for about 30 minutes, the green product was precipitated from the TBAH/methanol solution and collected by filtration.

Attempts to isolate the one-electron oxidized products of the dicarbonyl complexes, 2-6, were unsuccessful. Addition of methanol to

TABLE V
CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES $2-11^a$

Complex	V^b	E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	$E_{1/2}$ (mV)
<u>2</u> , $[Rh_2(CO)_2(\mu-4mpyz)(\mu-dapm)_2]PF_6$	50	828	735	93	781
	100	828	729	99	779
	200	836	720	116	778
	300	844	713	131	779
	400	848	708	140	778
	500	853	703	150	778
<u>3</u> , $[Rh_2(CO)_2(\mu-pyz)(\mu-dapm)_2]PF_6$	50	852	752	100	802
	100	857	744	113	801
	200	869	735	134	802
	300	876	727	149	801
	400	883	720	163	801
	500	889	714	175	801
<u>4</u> , $[Rh_2(CO)_2(\mu-3,5dmpyz)(\mu-dapm)_2]PF_6$	50	867	755	112	811
	100	875	750	125	812
	200	888	743	145	815
	300	898	737	161	817
	400	906	731	175	817
	500	912	727	185	820
<u>5</u> , $[Rh_2(CO)_2(\mu-4B35dmpyz)(\mu-dapm)_2]PF_6$	50	927	843	84	885
	100	930	841	89	885
	200	934	833	101	884
	300	939	824	115	882
	400	943	818	125	881
	500	946	812	134	879

Complex	V^b	E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	$E_{1/2}$ (mV)
<u>6</u> , $[\text{Rh}_2(\text{CO})_2(\mu-345\text{Br}_3\text{pyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	1040	914	125	977
	100	1049	910	139	979
	200	1063	900	163	981
	300	1074	892	182	982
	400	1079	885	194	982
	500	1085	880	205	982
<u>7</u> , $[\text{Rh}_2(\text{t-BuNC})_2(\mu-4\text{mpyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	167	97	70	132
	100	168	100	68	134
	200	171	98	73	134
	300	177	97	80	137
	400	178	97	81	138
	500	179	95	84	137
<u>8</u> , $[\text{Rh}_2(\text{t-BuNC})_2(\mu-\text{pyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	183	98	85	141
	100	189	98	91	143
	200	198	92	106	145
	300	206	88	118	147
	400	212	86	126	149
	500	216	84	132	150
<u>9</u> , $[\text{Rh}_2(\text{t-BuNC})_2(\mu-3,5\text{dmpyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	200	97	103	148
	100	203	89	114	146
	200	209	74	135	141
	300	214	64	150	139
	400	220	55	165	138
	500	221	48	173	135

Complex	V^b	E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	$E_{1/2}$ (mV)
<u>10</u> , $[\text{Rh}_2(\text{t-BuNC})_2(\mu-4\text{B}35\text{dmpyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	214	140	74	177
	100	222	146	76	184
	200	222	140	82	181
	300	229	137	92	183
	400	231	136	95	184
	500	235	137	98	186
<u>11</u> , $[\text{Rh}_2(\text{t-BuNC})_2(\mu-345\text{Bpyz})(\mu-\text{dapm})_2]\text{PF}_6$	50	348	258	90	303
	100	356	258	98	307
	200	364	252	112	308
	300	371	248	123	309
	400	376	243	133	310
	500	383	240	143	312

^aData obtained at 25°C in CH_2Cl_2 containing 0.10 M TBAH and are the average of at least three measurements with a range of + 4 mV.

^b V = Sweep Rate in mV/sec.

this crude product immediately resulted in a color change of the crude product solution from green to red. Isolation of the red product and characterization by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed that the red product was starting material. Similarly, attempts to isolate the one-electron oxidized products of the diisocyanide complexes 7 and 8 proved futile. The use of different solvents in attempts to isolate the above products gave no better results. Apparently, the one-electron oxidized products of complexes 2-8 defy isolation due to their instability.

Attempts by Burn²⁹ to prepare the Rh_2^{3+} species of the dpam analogues to complexes 2-8 gave similar results. However, as shown by Tortorelli,⁶ the dpmm analogues to complexes 7-11 can be electrochemically oxidized and the green oxidation products isolated under the stated conditions.

Complexes 12-14 show only the phosphorus resonance due to PF_6^- in the $^{31}\text{P}\{^1\text{H}\}$ NMR. This is expected for these paramagnetic species where the singly occupied HOMO is primarily metal-based. The IR spectral data for 12-14 show absorption bands due to terminal isocyanide ligands about 60 cm^{-1} higher than their corresponding parent compounds. This increase in stretching frequency indicates an increase in the oxidation state of the two Rh atoms.²² Since the infrared spectra of these complexes show only one type of terminal isocyanide ligand, the oxidation state of the two Rh nuclei are the same, i.e. $\text{Rh}(1.5)$. The analogous dpmm complexes, studied recently by Tortorelli,⁶ show the same trend in magnitude for the shift of these absorption bands. The IR spectra of 12-14 also show the expected PF_6^- peaks at 839(s) and

557(m) cm^{-1} . The IR spectral data for complexes 12-14 is located in Table VI.

The UV-Vis spectral data for complexes 12-14 are presented in Table VII. Complexes 12-14 exhibit two bands in the UV-Vis spectrum, an intense band and a much weaker band. For each complex, these data show that the more intense transition occurs at a wavelength higher than that of the lowest-energy transition of the corresponding parent compound. This intense band is in the range of 426-435 nm for 12-14. As mentioned above, the IR data show only one type of terminal isocyanide ligand indicating that in the Rh_2^{3+} complexes each Rh atom has the same oxidation state. Formally the Rh_2^{3+} species has a bond-order of one-half which implies that the Rh-Rh separation has decreased and this thereby decreases the HOMO-LUMO separation. Although this argument implies that the more intense transition is the lowest-energy proximity-shifted transition (compare to the parent complexes), it should be noted that other transitions are made possible by the singly-occupied HOMO becoming an acceptor orbital for transitions from filled lower-levels.

Complexes 12-14 also show two transitions in the near-IR spectral region, one in the range 865-878 nm and one in the range 1020-1039 nm. The parent Rh_2^{2+} core species show no such absorptions in the near-IR. It is suggested that these near-IR absorptions are due to transitions to the singly occupied HOMO from nearby filled orbitals. The UV-Vis spectra of these complexes also show a very weak and broad absorption band in the region 620-650. (See Table VIII)

TABLE VI
IR SPECTRA DATA FOR COMPLEXES 12-14

Number	Compound	$\nu(\text{RNC})$, cm^{-1}
12	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	2163(s), 2130(sh)
13	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	2170(s), 2110(s)
14	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\text{dapm})_2][\text{PF}_6]_2$	2186(s)

TABLE VII
UV-VIS SPECTRAL DATA FOR COMPOUNDS 12-14

Number	Compound	$\lambda_{\text{max, nm}} (\epsilon)$
12	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	435 (8900) 625 (670)
13	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	433 (9900) 620 (800)
14	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\text{dapm})_2][\text{PF}_6]_2$	426 (13,600) 650 (900)

TABLE VIII
NEAR IR SPECTRAL DATA FOR COMPOUNDS 12-14

Number	Compound	$\lambda_{\text{max, nm}} (\epsilon)$
12	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	1039(440), 878(780)
13	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35dmpyz})(\text{dapm})_2][\text{PF}_6]_2$	1035(470), 873(830)
14	$[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$	1020(490), 865(820)

Cooling a CH_2Cl_2 room-temperature solution of any one of complexes 12-14 in liquid N_2 results in a color change from green at room temperature to red. ESR spectra were obtained for complex 14 at various temperatures using 4:1 CH_2Cl_2 /toluene as the solvent system. These ESR spectra are presented in Figure 10. The ESR spectrum at 20°C of a green solution of 14 is shown in Figure 8A; this signal is isotropic and shows no hyperfine splitting.

Figure 10B shows the ESR spectrum of 14 at -120°C . The purple-colored solution displays an ESR spectrum that results from the overlap of the ESR spectra of two isomers. The first isomer, designated as the α isomer, has an ESR spectrum comprised of three resonances. The resonance at $g = 2.03$ appears to be an unresolved triplet resulting from the hyperfine coupling between the unpaired electron and the two equivalent ^{103}Rh atoms (100% abundance, $I = 1/2$). The resonance at $g = 2.18$ also exhibits an unresolved triplet resulting from the hyperfine coupling between the odd electron and the two equivalent ^{31}P atoms (100% abundance, $I = 1/2$) of the bridging dapm ligands. The resonance at $g = 2.21$ is attributed to the α isomer also and overlaps the resonance at $g = 2.18$. The hyperfine coupling constant between the odd electron and the two ^{31}P nuclei is $20.82 \times 10^{-4} \text{ cm}^{-1}$.

The second isomer, the β isomer, of 14 shows two resonances. The resonance at $g = 2.00$ is attributed to the overlap of two of the three anticipated resonances for this anisotropic system and hence is more intense than the second resonance at $g = 2.06$.

The ESR spectrum of the α isomer bears close resemblance to the ESR spectrum of the dppm analogue to complex 14, specifically, $[\text{Rh}_2(\text{t-}$

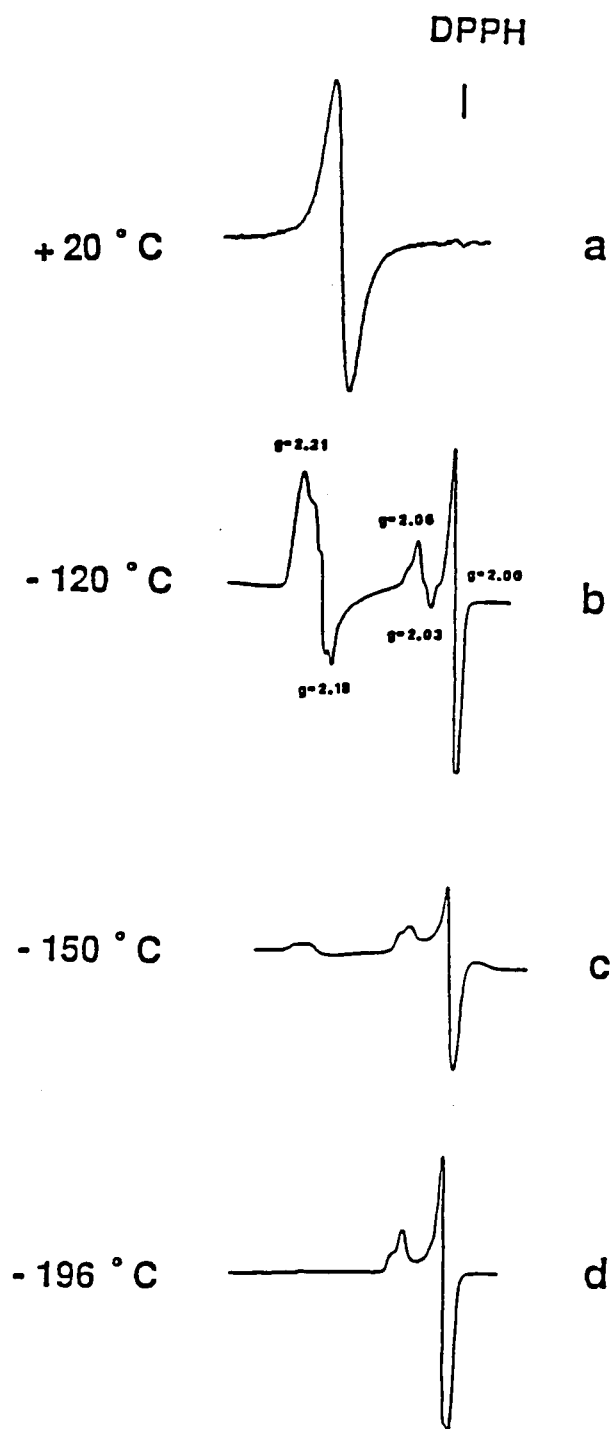
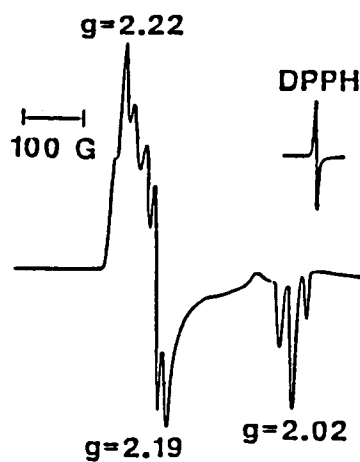


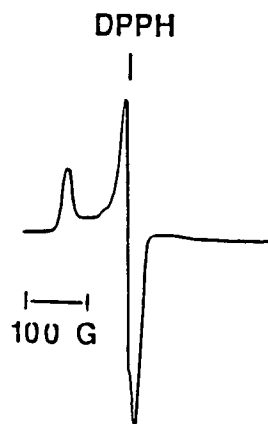
FIGURE 10. Variable temperature ESR spectra of $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$, 14, in 4:1 CH_2Cl_2 /toluene

$\text{BuNC})_2(\mu\text{-dppm})_2(\mu\text{-345Bpyz})][\text{PF}_6]_2$ (See Figure 11A) as observed by Tortorelli.⁶ The resonance at $g = 2.02$ is clearly split into a triplet resulting from the hyperfine coupling between the equivalent ^{103}Rh atoms and the odd electron ($A = 20.05 \times 10^{-4} \text{ cm}^{-1}$). The resonance at $g = 2.19$ is split into a five-line pattern resulting from hyperfine coupling between the odd electron and the four equivalent P nuclei. Since this spectrum is that of an orthorhombic system, the sixth line of the multiplet near $g = 2.22$ is expected and overlaps the resonance at $g = 2.19$. The 4:1 CH_2Cl_2 /toluene solution of $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-dppm})_2(\mu\text{-345Bpyz})][\text{PF}_6]_2$ remained green upon cooling to -196°C . However, complexes of the type $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-dppm})_2(\mu\text{-xpyz})][\text{PF}_6]_2$ ($\text{Xpyz} = 4\text{mpyz}, 35\text{dmpyz}, \text{pyz}, 4\text{B35dmpyz}$) demonstrate thermochromism upon immersion into liquid N_2 . At room temperature CH_2Cl_2 solutions of these complexes are green and upon cooling the solutions undertake a red color. These paramagnetic complexes exhibit ESR spectra similar to that attributed to the β isomer of complex 14. The ESR spectrum of $[\text{Rh}_2(\text{t-BuNC})_2(\mu\text{-dppm})_2(\mu\text{-4B35dmpyz})][\text{PF}_6]_2$ is shown in Figure 11B and is typical in appearance to the spectra of the other Xpyz complexes. These ESR spectra are due to anisotropic systems and show two resonances, the more intense resonance is due to the overlap of the mid-field and high-field absorptions. The less intense resonance is the low field absorption. The g values for these absorptions cannot be assigned accurately due to the overlap mentioned.

At -150°C , the ESR spectrum of 14 indicates that mostly the β isomer remains (Figure 10C). At this temperature, the solution is



a



b

FIGURE 11. The ESR spectra of (a) $[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-dppm})_2(\mu\text{-345Bpyz})][\text{PF}_6]_2$ and (b) $[\text{Rh}_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-dppm})_2(\mu\text{-4B35dmpyz})][\text{PF}_6]_2$ at room temperature in 4:1 CH_2Cl_2 /toluene

reddish-purple color. At -196°C , the ESR spectrum of 14 shows no trace of the α isomer and the solution is red (Figure 10D).

As discussed previously, the parent complex of 14 (complex 11) exhibits both HH and HT isomers as verified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy with the HT isomer the more prevalent of the two. The ESR spectra of complex 14 at various temperatures (Figures 10A-D) show no resonances that can be attributed to a paramagnetic HH isomer.

CHAPTER 1.4

CONCLUSIONS

This investigation has employed various spectroscopic techniques to characterize some new dirhodium(I) A-frame complexes with a pyrazolate derivative at the bridgehead position, two terminal carbon monoxide ligands and two bridging transoid (diphenylarsino)(diphenylphosphino)methane ligands. It has been shown that addition of 2.2 mole equivalents of tertiary butylisocyanide to any of the carbon monoxide complexes yields the analogous di-tertiary butylisocyanide substituted species.

The one-electron oxidized species of complexes of the type $[\text{Rh}_2(\underline{\text{t-BuNC}})_2(\mu\text{-Xpyz})(\mu\text{-dapm})_2]\text{PF}_6$ (X = 35dmpyz, 4B35dmpyz, 345Bpyz) were generated electrochemically in CH_2Cl_2 and 0.1 M TBAH. A CH_2Cl_2 solution of any of these paramagnetic, oxidized species is green at room temperature and changes to red upon cooling by immersion of the solution into a liquid N_2 bath. This same thermochromic effect is observed in the analogous dppm and dpam complexes.^{6,29}

An ESR spectrum of $[\text{Rh}_2(\underline{\text{t-BuNC}})_2(\mu\text{-345Bpyz})(\mu\text{-dapm})_2][\text{PF}_6]_2$, 14, is isotropic at room temperature. Upon cooling to -120°C the solution changes color from green to purple and the ESR spectrum at this temperature reveals the existence of two isomers, assigned as the α isomer and the β isomer.

Further cooling of the sample on which the ESR spectrum is obtained demonstrates a significant change in the relative amounts of the α and β isomers with the β isomer becoming overwhelmingly dominant as the temperature is decreased.

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REFERENCES FOR PART I

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PART II:

PLATINUM-RHODIUM COMPLEXES

CHAPTER 2.1

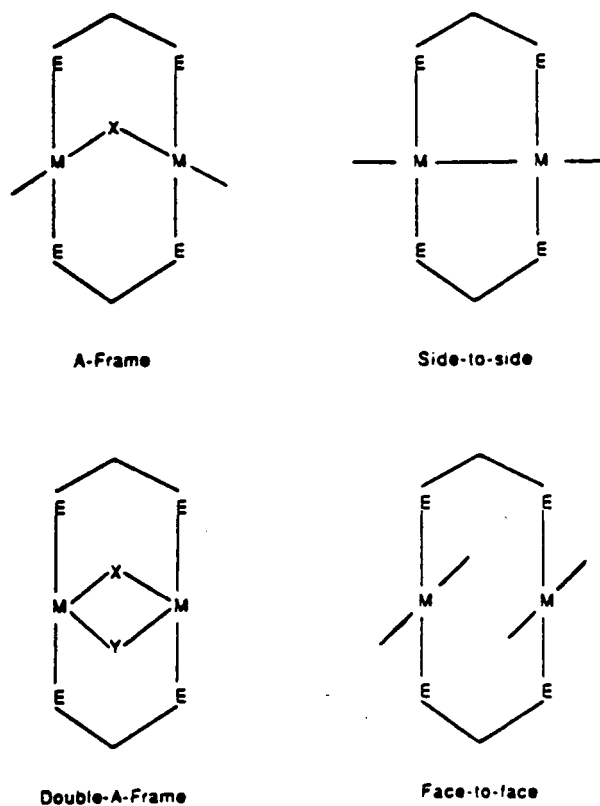
INTRODUCTION

A. Literature Review

The interest in heterobimetallic transition-metal complexes in which both metal atoms are held in close proximity stems from their potential to act as metal catalysts. In such complexes the two metal centers may act in concert or independently in the binding and activation of small organic molecules, thus the resulting reactivity of the heterobinuclear complex is intensified over that of the corresponding monomers. Bidentate transoid ligands can vary the reactivity of each metal center depending upon their electron donating ability through N, P or As atoms and their bite-sizes. Ligands which provide these criteria are bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm), bis(diphenylarsino)methane (dpam), and 2-(diphenylphosphino)pyridine (dppp).

Homobimetallic and heterobimetallic complexes containing these ligands have shown four types of geometrical arrangements.¹ These are shown on the next page.

The most common geometries demonstrated for heterobimetallic complexes are the face-to-face and the A-frame. In both heterobimetallic and homobimetallic complexes the arrangement of ligands about the metal centers is square planar. Metal atoms with d^8 configurations have great propensity to exist in such an environment.



The first heterobimetallic complexes using the dppm ligand employed Pt(II) as one metal center and Rh(I), Ir(I) or W(O) as the other metal center. One of these complexes, an A-frame complex with Pt(II) and Rh(I), was prepared by Shaw and co-workers² by treatment of trans-(MeC≡C)₂Pt(dppm-P)₂ with Rh₂Cl₂(CO)₄ in benzene (50°C) to produce trans-[(MeC≡C)Pt(μ-MeC≡C)(μ-dppm)₂Rh(CO)]Cl. This structure is shown in Figure 1. The IR spectrum of this compound shows a terminal methyl acetylide (MeC₂⁻) stretch at 2118 cm⁻¹ and a weakly π-bridged (to the Rh atom) MeC₂ absorption band at 2040 cm⁻¹. The terminal carbonyl (CO)

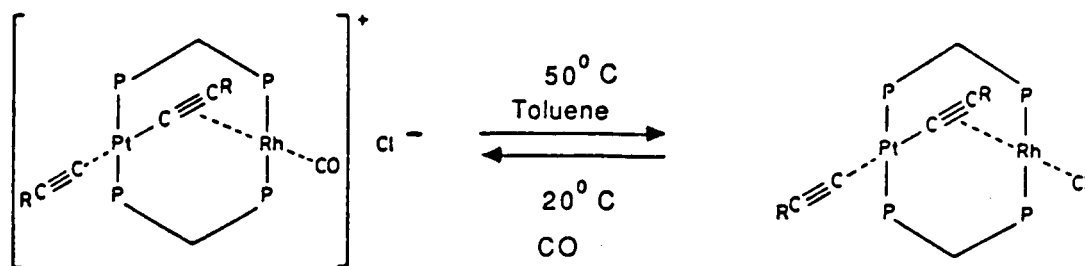


FIGURE 1. Thermal conversion of a Pt-Rh diacetylide complex

(R = p-tolyl, phenyl)

stretch occurs at 1980 cm^{-1} . Analogous complexes were prepared where the methyl group was substituted by para-toluene or a phenyl group. These complexes are assigned ionic structures based on electrical conductivity experiments and the easy replacement of the Cl^- with a PF_6^- counterion by treatment with a five-fold excess of NH_4PF_6 .

Refluxing trans- $[(\text{RC}_2)\text{Pt}(\mu\text{-RC}_2)(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{Cl}$ (R = p-toluene, phenyl) for 3 hours in toluene under argon resulted in the production of trans- $(\text{RC}_2)\text{Pt}(\mu\text{-RC}_2)(\mu\text{-dppm})_2\text{RhCl}$ and a loss of CO. These latter complexes were non-conducting in an acetone solution. The IR spectrum

of the phenylacetylide revealed an absorption band at 2110 cm^{-1} due to a terminal acetylide stretch and a strongly-bridged acetylide stretch at 1900 cm^{-1} . No evidence of a terminal or bridging CO was present. These complexes readily add CO to yield the original chloride salt (See Figure 1).

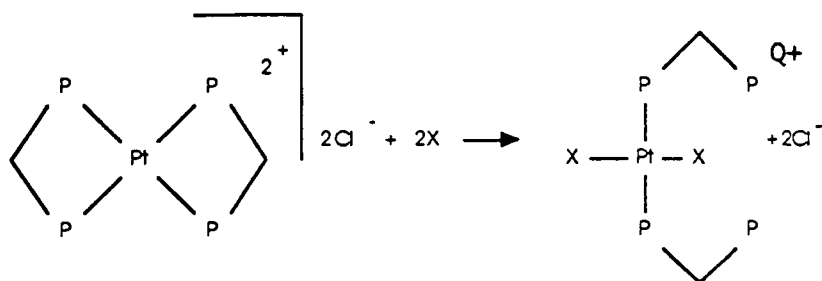
The ionic p-tolylacetylide complex was heated in toluene at 110°C for 3 hours forming species which gave a complicated ^{31}P NMR spectrum and not the expected AA'XX' pattern. Refluxing for 14 hours gave the neutral complex (i.e. Rh bound to Cl, Figure 1A) in nearly quantitative yield.³ On this basis, it was decided that the reaction mechanism was more complicated than a simple nucleophilic displacement of CO by Cl. However, the mechanism was not further investigated.

Heterobimetallic complexes containing Pt(II) and Rh(I) may be prepared via transmetallation. This involves displacement of a d^{10} metal atom from a previously made compound. For example, treatment of $(\text{PhC}_2)_2\text{Pt}(\mu\text{-dppm})_2\text{MCl}$ ($\text{M} = \text{Ag(I)}, \text{Cu(I)} \text{ or } \text{Au(I)}$) with one-half an equivalent of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in CH_2Cl_2 at 20°C gives high yield of the complex $[(\text{PhC}_2)\text{Pt}(\mu\text{-PhC}_2)(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{Cl}$. The successful synthesis of the above complexes via transmetallation prompted other attempts to prepare analogous compounds in which the ligands about Pt would be varied, but the ligands about Rh would remain unchanged.²

In 1983, Shaw and coworkers reported the synthesis of the complex $(\text{PhC}_2)\text{ClPt}(\mu\text{-dppm})_2\text{AgCl}$ in high yield by treatment of $[\text{Pt}(\text{dppm})_2\text{-P,P'}]\text{Cl}_2$ with one equivalent of silver acetate, and excess phenylacetylene.² An acetone suspension of this Pt-Ag complex was treated with one-half an equivalent of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ to yield the Pt-Rh

complex $[\text{ClPt}(\mu\text{-PhC}_2)(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{AgCl}_2$. The AgCl_2^- anion was replaced by addition of NH_4PF_6 to yield the much more soluble complex $[\text{ClPt}(\mu\text{-PhC}_2)(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ and AgCl . The IR spectral data of the Pt-Rh complex with the PF_6^- counterion show absorption bands corresponding to a bridging acetylide ($\mu\text{-PhC}_2$) at 2072 cm^{-1} and a terminal CO at 1988 cm^{-1} . The Pt-Rh separation in this compound was determined by X-ray structure analysis to be $3.10\text{\AA}$. The accepted length for a Pt-Rh single bond ranges from $2.6\text{-}2.8\text{\AA}$. Thus no Pt-Rh metal-metal bond was proposed.

The scheme shown below outlines the method initiated by Shaw for preparing a general precursor to heterobimetallic complexes using the symmetrical dppm ligand and Pt(II) or Pd(II).



The "X" ligands employed must be isoelectronic with the acetylide ion. This type of ligand prefers to bind mutually trans (if another is available) or trans to a good sigma donor such as a halide. The $\text{PtX}_2(\text{dppm-P})_2^{Q+}$ complex formed has two P atoms which may then coordinate

with other metal fragments. If the "X" ligand is negatively charged, then the chelating Pt complex, $\text{PtX}_2(\text{dppm-P})_2$, and the heterobimetallic complexes formed are neutral species ($Q=0$). When the "X" ligand is neutral, the complexes formed are ionic ($Q=2$). Examples employing both neutral and anionic "X" ligands are discussed below.

Attempts to produce the organic isonitrile, RNC, analogues to the biacetylide complexes discussed previously met with partial success. Face-to-face cationic complexes of the type $[(\text{RNC})_2\text{M}(\mu\text{-dppm})_2\text{M}'\text{Ln}]^{Q+}$ ($\text{M} = \text{Pt}, \text{Pd}$; $\text{M}' = \text{Ag}, \text{Hg}, \text{Rh}$; $\text{Ln} = \text{Cl}, \text{CO}$) were synthesized but proved inseparable from side-product contaminants such as $\text{M}(\text{dppm-P};\text{P}')\text{Cl}_2$ or $[\text{M}(\text{dppm-P};\text{P}')_2]\text{Cl}_2$. Consequently, none of these products could be fully characterized.⁴

Platinum-silver containing complexes of the type $[(\text{RNC})\text{ClPt}(\mu\text{-dppm})_2\text{AgCl}]\text{X}$ ($\text{R} = \text{Me}, (\text{CH}_3)_3\text{C}-, \text{P-CH}_3\text{C}_6\text{H}_4$; $\text{X} = \text{Cl}^-$ or BPh_4^-) were prepared by treatment of $[\text{Pt}(\text{dppm-P};\text{P}')_2]\text{Cl}_2$ in CH_2Cl_2 with two equivalents of the organic isonitrile followed by the immediate addition of one-fourth an equivalent of $[\text{AgCl}(\text{PPh}_3)]_4$. After five minutes of stirring, addition of diethyl ether gave the product in 95% yield. The Pt-Rh analogue of this Pt-Ag complex was prepared in 64% yield via transmetallation using $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. These latter Pt-Rh complexes were formulated as $[(\text{RNC})\text{ClPt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}]\text{X}$, where X^- is either $[\text{RhCl}_2(\text{CO})_2]^-$ or BPh_4^- . The ^{31}P NMR data reported for these Pt-Rh organic isonitrile complexes were not much different from those reported for the mono-acetylide complexes in either chemical shift or one-bond coupling constants.⁴ The IR spectrum for the cationic complex with a BPh_4^- counterion shows $\nu(\text{RNC}) = 2225 \text{ cm}^{-1}$ and $\nu(\text{CO}) = 1995 \text{ cm}^{-1}$.

The cationic complex with the $[\text{RhCl}_2(\text{CO})_2]^+$ counterion shows an additional carbonyl stretching band at 2070 cm^{-1} .

The neutral species $\text{Pt}(\text{CN})_2(\text{dppm-P})_2$ was prepared in 94% yield by treatment of the ionic complex $[\text{Pt}(\text{dppm-P:P}')_2]\text{Cl}_2$ with 2.25 equivalents of NaCN in methanol.⁵ A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 20°C showed two broad resonances at -23.5 ppm and at $+7.4\text{ ppm}$ but no coupling to Pt-195 was observed (no Pt satellites) presumably because of the broadness of the resonances. This broadness was attributed to a rapid "end-over-end" exchange of the monohapto dppm ligands (See Figure 2). At -25°C the $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data correspond to the static structure of Figure 2A. The resonance at -26.5 ppm was assigned to the uncoordinated P atom and the resonance at $+7.1\text{ ppm}$ was assigned to the Pt-bound phosphorus atom. The suggested structure is supported by the value for $^1J(\text{Pt-P})$ of 2329 Hz which is typical for two trans P atoms.

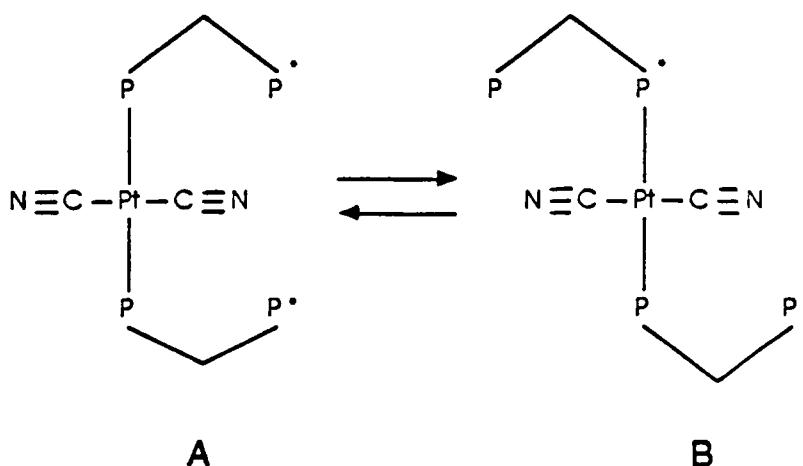
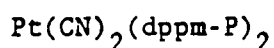


FIGURE 2. The "end-over-end" exchange of dppm P nuclei in

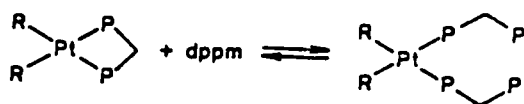


Pt(II). A CH_2Cl_2 solution of the complex is non-conducting. The complex exhibits an absorption band at 2125 cm^{-1} in the infrared region due to the terminal cyanide ligands.⁵

The neutral platinum precursor, $\text{Pt}(\text{CN})_2(\text{dppm-P})_2$, was treated with one-half an equivalent of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ to give the neutral face-to-face complex $(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$. The IR spectrum of this Pt-Rh complex showed absorption bands at 2125 and 1978 cm^{-1} which were assigned to the terminal cyanide and carbonyl ligands, respectively. The complex was non-conducting in a nitrobenzene solution. As expected, the ^{31}P NMR spectrum revealed an AA'XX' pattern with the values of $^1\text{J}(\text{Pt-P}) = 2531\text{ Hz}$ and $^1\text{J}(\text{Rh-P}) = 149\text{ Hz}$. The chemical shift values were unremarkable with $\delta(\text{Pt-P}) = 1.4\text{ ppm}$ and $\delta(\text{Rh-P}) = 20.9\text{ ppm}$.⁵

Heterobimetallic complexes using dppm have been prepared employing alkyl or aryl ligands in place of the acetylide. These type complexes show a cis orientation for the dppm P atoms about the Pt center and consequently a greater separation between the metal centers.⁶ Treatment of cis- $\text{PtR}_2(\text{dppm-P:P}')$ ($\text{R} = \text{CH}_3$ - or 1-naphthyl) with one equivalent of dppm results in the equilibrium situation shown below in Figure 3. High concentration and low temperatures (-30°C) would tend to favor the right-hand side of the equation shown.⁶

A Pt-Rh complex formulated as cis-($\sigma\text{-C}_{10}\text{H}_7$)₂ $\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$ was obtained upon addition of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ to an equilibrium mixture of dppm and cis-($\sigma\text{-C}_{10}\text{H}_7$)₂ $\text{Pt}(\text{dppm-P:P}')$ at -30°C in CH_2Cl_2 ($\text{C}_{10}\text{H}_7 = 1\text{-naphthyl}$). This Pt-Rh complex was obtained in 67% yield as both syn and anti isomers (See Figure 4).



R = Me
R = Naphthyl ($C_{10}H_7$)

FIGURE 3. The equilibrium between $PtR_2(dppm-P)$, dppm and $PtR_2(dppm-P)_2$ (R = CH_3 or 1-naphthyl)

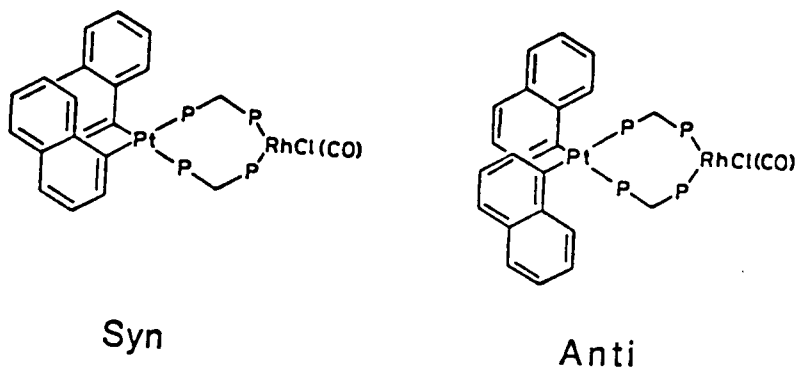


FIGURE 4. Structures proposed for the syn and anti isomers of cis-(σ - $C_{10}H_7$) $_2Pt(\mu-dppm)_2Rh(CO)Cl$

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex shown in Figure 4 gives broad resonances for Pt-bound and Rh-bound phosphorus atoms that exhibit the expected Rh-103 ($I = 1/2$) one-bond coupling and the Pt-195 satellites (25°C). At -80°C, the spectrum was extremely complicated. This was accounted for by the adoption of a static structure by the eight-membered $\text{Pt}(\mu\text{-dppm})_2\text{Rh}$ ring. Presumably, the ring at low temperatures has a twisted-saddle conformation which results in the P nuclei becoming nonequivalent. At +50°C, the resonances did not sharpen and this was explained by the presence of the syn and anti isomers. The absorption band at 1972 cm^{-1} is unremarkable for a CO terminally bound to Rh(I). The complex was non-conducting in a nitrobenzene solution proving it to be a neutral species.

In 1987 Jacobsen and Shaw introduced a Pt-Hg complex employing dpam as the transoid bridging ligands. This complex was prepared by adding equimolar amounts of the monomer trans- $\text{PtCl}_2(\text{dpam-As})_2$ in benzene and HgCl_2 in THF. The product trans- $\text{Cl}_2\text{Pt}(\mu\text{-dpam})_2\text{HgCl}_2$ is obtained in 72% yield by precipitation. This product was characterized by elemental analysis, ^1H NMR and infrared spectroscopies. The suggested structure for the Pt-Hg dpam complex is shown in Figure 5.⁷ No Pt-Rh complexes using dpam have been reported.

The ligand 2-(diphenylphosphino)pyridine, dppp, shows an interesting ability to serve as the transoid ligand in both homobimetallic and heterobimetallic complexes. Some of the homobimetallic complexes using dppp include $\text{Rh}_2(\mu\text{-CO})(\mu\text{-dppp})_2\text{Cl}_2$ ⁸ and $\text{Pd}_2(\mu\text{-dppp})_2\text{Cl}_2$.⁹ The homobimetallic complexes exhibit two structural isomers, (1) a head-to-head isomer (HH), and (2) a head-to tail isomer (HT).

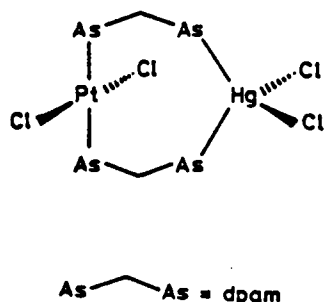


FIGURE 5. The suggested structure for trans-Cl₂Pt(μ-dpam)₂HgCl₂

The synthesis scheme illustrated below in Figure 6 was suggested by Balch and coworkers.¹⁰ This synthetic method for both hetero- and homobimetallic species was based upon the fact that with transition metals (M) the dppp ligand preferentially coordinates through the P atom to produce monomer complexes of the type trans- M(dppp-P)₂X (X = Cl⁻, Br⁻, CO, NC-) (Figure 6A). These monomers have an uncoordinated pyridine nitrogen which could bond to another metal fragment (M') in solution.

In 1980 Balch¹⁰ reported the synthesis of the Pd-Rh complex Cl₂(CO)Rh(μ-dppp)₂PdCl via the general method outlined in Figure 6. Figure 7 shows the overall reaction using RhCl(CO)(dppp-P)₂ and PdCl₂(COD) (COD = 1,5 cyclooctadiene).

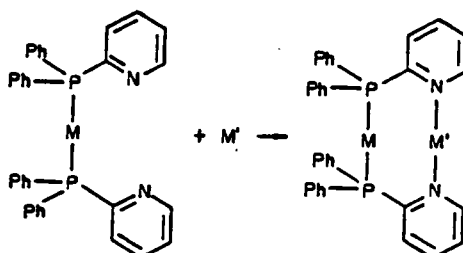


FIGURE 6. Idealized capture of a metal fragment, M' , by $M(dppp-P)_2$

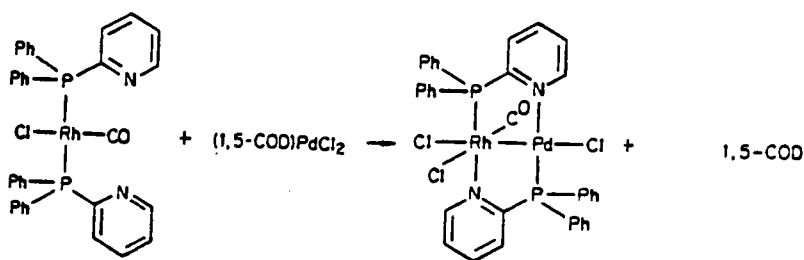


FIGURE 7. Formation of $Cl_2(CO)Rh(\mu-dppp)_2PdCl$

Inspection of the Pd-Rh product shows two unexpected features. First, the Pd metal fragment was complexed by the free pyridine nitrogens, however this was accompanied by the oxidative-addition of a Pd-Cl bond to the Rh monomer. The formal oxidation states of the metal centers are Pd(I) and Rh(II). Second, for heterobimetallic complexes using the dppp ligand three structural isomers are possible. These isomers are: (A) a head-to-head arrangement with both P atoms about Rh (H-H-Rh); (B) a head-to-head arrangement with both P nuclei around Pd (H-H-Pd); (C) a head-to-tail arrangement (HT). These isomers, A-C, are shown in Figure 8.

The HH-Rh isomer was expected because both P atoms were initially bound to the Rh atom. Unexpectedly, the HT isomer was the sole product. The same end-product was obtained using $\text{Pd}(\text{dppp-P})_2\text{Cl}_2$ and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ as the starting materials. Both synthetic methods give a 72% product yield.

A Pt-Rh analogue to the Pd-Rh complex with dppp was synthesized in 1983 by Balch and coworkers.¹¹ Originally the same general method outlined in Figure 6 was employed using $\text{PtCl}_2(\text{COD})$ and $\text{trans-RhCl}(\text{CO})(\text{dppp-P})_2$. This approach did not yield the desired product but instead gave $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2$ and cis- $\text{Pt}(\text{dppp-P})_2\text{Cl}_2$.

Dichloromethane solutions of cis- $\text{Pt}(\text{dppp-P})_2\text{Cl}_2$ and $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in a 1:1 stoichiometry gave a salt of the formula $[\text{Pt}(\text{dppp-P})_2\text{Cl}][\text{Rh}(\text{CO})_2\text{Cl}_2]$. The cationic complex $[\text{Pt}(\text{dppp-P})_2\text{Cl}]^+$ exhibits two resonances in the ^{31}P NMR spectrum. One resonance occurs at -50.3 ppm and is assigned to a chelated phosphine with $^1\text{J}(\text{Pt-P}) = 3339$ Hz. The second resonance is at +15.24 ppm with $^1\text{J}(\text{Pt-P}) = 3704$ Hz and is due to

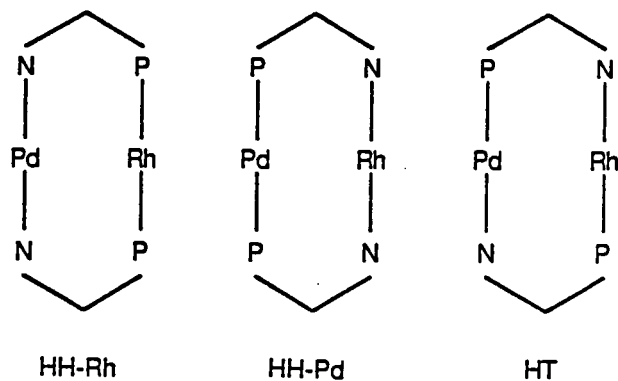


FIGURE 8. Possible isomers of $\text{Cl}_2(\text{CO})\text{Rh}(\mu\text{-dppp})_2\text{PdCl}$ displaying only the ring nuclei

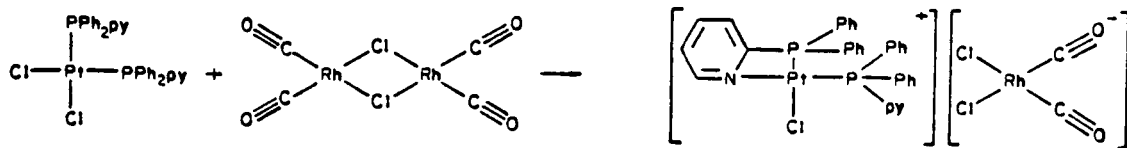


FIGURE 9. Formation of the salt $[\text{Pt}(\text{dppp-P})(\text{dppp-N:P})\text{Cl}][\text{RhCl}_2(\text{CO})_2]$

the monohapto dppp ligand coordinated through its P atom. The first resonance at -50.3 ppm was assigned by comparison to the resonance for the chelated complex $\text{Ru}(\text{dppp-P:N})(\text{CO})_2\text{Cl}_2$. The IR spectrum of the salt reveals strong absorption bands at 2068 and 1989 cm^{-1} due to the CO ligands of the $\text{Rh}_2(\text{CO})_2\text{Cl}_2^-$ ion. An X-ray crystal structure analysis of this salt revealed that the Pt is indeed chelated by one dppp and coordinated to the P atom of the other dppp ligand. The synthesis as well as the structure of this salt is illustrated in Figure 9.

Refluxing a benzene solution of the salt under a N_2 atmosphere for five hours and cooling to room temperature yielded the neutral complex $\text{ClPt}(\mu\text{-dppp})_2\text{Rh}(\text{CO})\text{Cl}_2$ in 69% yield exclusively as the HT isomer. This new orange-red compound is a nonelectrolyte in an acetone solution and it exhibits a strong absorption band at 2055 cm^{-1} which implies the presence of a terminal CO ligand bound to a Rh(II) metal center. The formation of this Pt-Rh complex also exhibits a formal oxidation of Rh(I) to Rh(II) accompanied by a reduction of Pt(II) to Pt(I) resulting in the formation of a Pt-Rh single bond. The Pt-Rh complex is comparable to the previously described Pd-Rh complex. The $^1\text{J}(\text{Rh-P})$ value of 114 Hz is close to the same for the Pd-Rh complex with $^1\text{J}(\text{Rh-P}) = 112.7\text{ Hz}$. The chemical shifts of these complexes are also comparable with $\delta(\text{Rh-P}) = 24.6\text{ ppm}$ for the Pt-Rh complex and $\delta(\text{Rh-P}) = 21.9\text{ ppm}$ for the Pd-Rh complex.^{10,11}

Addition of chlorine gas to a CH_2Cl_2 solution of $\text{ClPt}(\mu\text{-dppp})_2\text{RhCl}_2(\text{CO})$ results in the oxidative addition of chlorine to the Pt center to give the neutral complex $\text{Cl}_3\text{Pt}(\mu\text{-dppp})_2\text{RhCl}_2(\text{CO})$ in 99% yield. In this latter compound the terminal carbonyl absorption band

(CO bound to Rh(II)) shows an increase of 27 cm^{-1} in comparison to the starting material. Usually, oxidation increases this parameter by 60 cm^{-1} ; thus the overall decrease in electron density at the Rh(II) atom is small.¹² For the chlorinated Pt-Rh complex the ^{31}P NMR parameters show little change for the Rh-bound P nuclei whereas the same parameters of the Pt-bound P nuclei change dramatically. As such, the chlorinated Pt-Rh complex exhibits a decrease in chemical shift, $\delta(\text{Pt-P})$, by 18.9 ppm to $\delta(\text{Pt-P}) = -17.9$ ppm and the value of $^1J(\text{Pt-P})$ decreases by 1200 Hz to $^1J(\text{Pt-P}) = 2793$ Hz as compared to the starting Pt-Rh complex. Such changes are fully consistent with an oxidative addition solely at the Pt atom.¹¹ Figure 10, below, shows a scheme for the Cl_2 addition to $\text{ClPt}(\mu\text{-dppp})_2\text{RhCl}_2(\text{CO})$ to yield $\text{Cl}_3\text{Pt}(\mu\text{-dppp})_2\text{RhCl}_2(\text{CO})$.

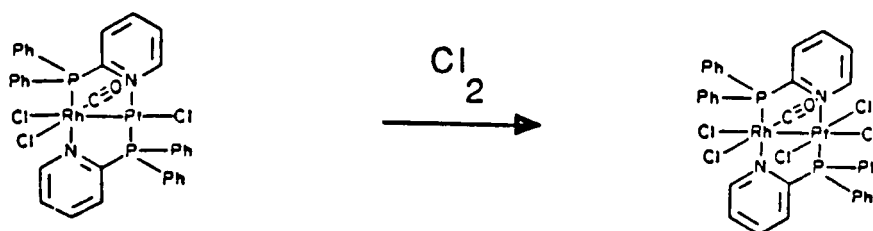


FIGURE 10. Oxidative addition of Cl_2 to $\text{ClPt}(\mu\text{-dppp})_2\text{Rh}(\text{CO})\text{Cl}_2$

Synthesis of heterobimetallic complexes using the dppp ligand resulted in the oxidative-addition of a metal-halogen bond to the second metal center as discussed above. Recently Balch and coworkers¹³ have suggested that the dppp ligand forces the formation of a metal-metal bond due to its relatively small bite-size (range: 2.2-2.8Å) compared to the more flexible dppm ligand (range: 2.1-4.1Å). The required non-bonded metal-metal separation is suited by the symmetrical ligands dppm and dpam and by the unsymmetrical ligand (diphenylarsino)(diphenylphosphino)methane, dapm. The bite-size of dapm lies between that of the symmetrical ligands dppm and dpam.¹⁴

The dapm ligand preferentially binds via its P atoms as does the dppp ligand. The addition of equal molar amounts of dapm and $\text{PtCl}_2\text{-(COD)}$ produces the neutral monomer $\text{PtCl}_2(\text{dapm-As:P})$ in 60% yield. Treatment of this monomer with an additional molar amount of dapm results in the production of the neutral complex $\text{cis-PtCl}_2(\text{dapm-P:P'})_2$ in 71% yield. This second Pt monomer has two unbound As atoms; the $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data suggest that the P atoms are in a cis configuration, where $\delta(\text{Pt-P}) = 6.1$ ppm and $^1\text{J}(\text{Pt-P}) = 3675$ Hz.¹⁴

Addition of one-half an equivalent of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with one-equivalent of cis- $\text{PtCl}_2(\text{dapm-As:P})_2$ in CH_2Cl_2 at -10°C produces the orange neutral complex cis- $\text{Cl}_2\text{Pt(P:P')}(μ\text{-dapm})_2\text{-trans Rh(As:As')}(CO)Cl$ (hereafter known as cis-Pt-trans-Rh) in 70% yield (See Figure 11A).

The IR spectrum of the cis-Pt-trans-Rh complex exhibits a band at 1986 cm^{-1} due to a terminal CO bound to Rh(I). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals $\delta(\text{Pt-P}) = 15.0$ ppm and $^1\text{J}(\text{Pt-P}) = 3826$ Hz with no resonances due to P nuclei bond to Rh(I), implying the existence of

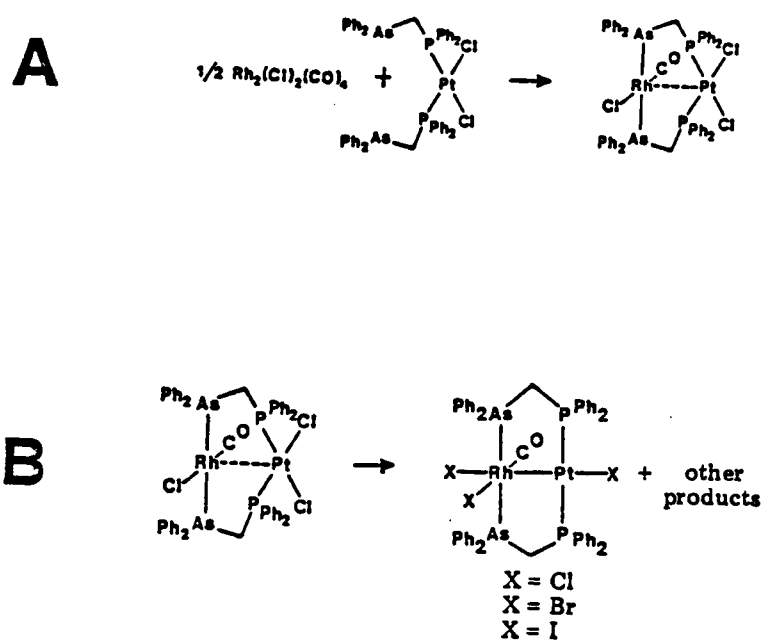


FIGURE 11. (A) Production of cis-Pt-trans-Rh and (B) Production of trans-Pt-trans-Rh

only the HH-Pt isomer. The $^1\text{J}(\text{Pt-P})$ value of 3826 Hz strongly suggests that the cis-orientation of the Pt monomer is retained. An X-ray crystal structure confirms the cis-orientation and reveals a Pt-Rh separation of 3.043 Å which is longer than the typical value of 2.6 Å anticipated for a Pt-Rh single bond.¹⁴ Usually the dapm ligand coordinates such that there is a trans arrangement of P (and As) about the metal centers. Examples of this trans-arrangement include the species; $\text{PtCl}_2(\mu\text{-dapm})_2$ ¹⁵, $\text{PtCl}_2(\mu\text{-CO})(\mu\text{-dapm})_2$,¹⁶ and $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dapm})_2$.¹⁷

The X-ray crystal structure of cis-Pt-trans-Rh shows that each metal-donor atom unit is distorted from the ideal bond angles of 180° about the trans-As-Rh-As unit and 90° about the cis-P-Pt-P unit. The As-Rh-As bond angle is closed to 169.0° and the P-Pt-P bond angle is opened slightly to 104.0°. The P-C-As bond angle is 117.6° for one dapm ligand and 117.9° for the other; this is considered normal for dapm.¹⁴ The Rh(I)-bound CO ligand is situated over the PtCl_2 fragment but the infrared data does not suggest any weak π interactions between Pt(II) and the terminal CO ligand.

The neutral complex trans-ClPt(P:P')(μ -dapm)₂-trans-Rh(As:As')(CO)Cl₂ was prepared in 19% yield by refluxing a chloroform solution of the cis-Pt-trans-Rh complex for two hours (See Figure 11B). (Hereafter the complex trans-ClPt(P:P')(μ -dapm)₂-trans-Rh(As:As')(CO)Cl₂ will be known as trans-Pt-trans-Rh.) Initially a mixture of several complexes was obtained including the trans-Pt-trans-Rh complex, the cis-Pt-trans-Rh complex, the Pt monomer cis-PtCl₂(dapm-As:P) and both the HH and HT isomers of $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dapm})_2$.

Separation required multiple recrystallizations from CH_2Cl_2 /diethyl ether.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data of the trans-Pt-trans-Rh complex reveals $\delta(\text{Pt-P}) = 16.4$ ppm. The $^1\text{J}(\text{Pt-P})$ value of 2880 Hz is typical for a trans P-Pt-P unit.

Formally, the production of the trans-Pt-trans-Rh complex was accompanied by the oxidative-addition of a Pt-Cl bond to the Rh center of the starting material. Usually an oxidation of Rh(I) to Rh(II) increases the terminally bound CO stretching frequency by about 60 cm^{-1} . The CO in the trans-Pt-trans-Rh complex exhibits an absorption band at 2006 cm^{-1} , which is about $20\text{-}40\text{ cm}^{-1}$ lower than expected.

An X-ray crystal structure analysis of the trans-Pt-trans-Rh complex reveals that the Pt-Rh single bond length is $2.692\text{ \AA}$. The CO is closer to the Pt atom in the trans-Pt-trans-Rh complex than it is in the cis-Pt-trans-Rh complex. Thus in the trans-Pt-trans-Rh complex the carbonyl acts as a very weak π -donor to the Pt(I) atom and this interaction lowers the carbonyl stretching frequency by $20\text{-}40\text{ cm}^{-1}$. Similar trends in the infrared spectral data are observed for the bromine and iodine analogues of the trans-Pt-trans-Rh complex.¹⁶

B. Statement of Purpose

This work involves the synthesis and characterization of new A-frame platinum-rhodium complexes, in which a pyrazolate (Xpyz) derivative is incorporated into the bridgehead position and either bis(diphenylphosphino)methane or (diphenylarsino)(diphenylphosphino)methane ligands are employed as the bridging transoid ligands. Constituent

variations of these PtRh complexes include a phenylethynyl, a chloride or a cyano ligand at the Pt(II) atom, and either a terminal carbon monoxide or a tertiary butylisocyanide ligand at the Rh(I) atom.

Eisenberg prepared the first dirhodium A-frame formulated as $\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\mu\text{-dppm})_2$. The first pyrazolate bridged A-frame type complexes were reported by Oro, et al.¹⁸ in 1985. These were dirhodium complexes of the type $[\text{Rh}_2(\text{CO})_2(\mu\text{-Xpyz})(\mu\text{-dppm})_2]\text{X}$ (Xpyz = pyrazolate derivatives; X = ClO_4^- , PF_6^-). The first platinum-rhodium complexes were prepared by Shaw² and coworkers in 1982. Both the dirhodium A-frames and the platinum-rhodium A-frames exhibit the ring structure $\text{MM}'(\mu\text{-dppm})_2$ (M = M' = Rh for Rh_2 complexes; M = Pt, M' = Rh for PtRh complexes). Also, in each type complex the metal center has a d^8 configuration (e.g. Rh(I) and Pt(II)). Since the Rh_2 and PtRh complexes exhibit such structural similarities, it was of interest to prepare the pyrazolate derivatives of some selected PtRh compounds.

The synthesis of these novel pyrazolate bridged PtRh complexes presents an opportunity to acquire data concerning the effect of Pt(II) and Rh(I) in close proximity. Also, the structural similarity of the $\text{RhP}_2(\text{CO})$ unit in both Rh_2 and PtRh complexes permits comparison of ^{31}P NMR spectral data for Rh(I) bound P nuclei.

CHAPTER 2.2

EXPERIMENTAL

A. Chemicals

1. Solvents

- a. Methylene Chloride, CH_2Cl_2 , Mallinckrodt. ACS grade CH_2Cl_2 was used as purchased for synthesis work. For UV-Vis and electrochemical experiments, CH_2Cl_2 was dried over CaCl_2 and distilled from P_2O_5 before use.
- b. Acetone, Mallinckrodt. ACS grade acetone was used without further purification.
- c. Absolute ethanol, ethanol, U.S. Industrial Chemicals. Ethanol was used as purchased.
- d. Methanol, Mallinckrodt. Methanol was used as purchased.
- e. Normal propanol, n-propanol, Fisher Scientific. Reagent grade n-propanol was used as purchased.
- f. Distilled water, water, H_2O . Departmental distilled water was used without further purification.
- g. Chloroform, CHCl_3 , Mallinckrodt. ACS grade chloroform was used as purchased.
- h. Anhydrous Diethyl Ether, ether, Mallinckrodt. ACS anhydrous ether was used as purchased.
- i. Hexanes, Mallinckrodt. ACS hexanes were used as purchased.

2. Gases

- a. Argon, Ar, MG Industries. Prepurified Ar was used without further purification.
- b. Nitrogen, N₂, MG Industries. Prepurified N₂ was used without further purification.
- c. Carbon Monoxide, CO, MG Industries. Prepurified CO was used as purchased.

3. Reagents

- a. Cycloocta-1,5-diene, 1,5(COD), Aldrich. Reagent grade 1,5(COD) was used without further purification.
- b. Tin(II) Chloride, Sn(II)Cl₂, Aldrich. Anhydrous Sn(II)Cl₂ was used without further drying.
- c. Platinous Potassium Chloride, K₂PtCl₄, Fisher Scientific. K₂PtCl₄ was used without further purification.
- d. Bis(diphenylphosphino)methane, dppm, Strem. Reagent grade dppm was used without further purification.
- e. Diphenylchloroarsine, Ph₂ClAs, Pfaltz and Bauer. High purity, ampoule-sealed Ph₂ClAs was used without further purification.
- f. Methyldiphenylphosphine, CH₃Ph₂P, Strem. CH₃Ph₂P was used as purchased.
- g. Normal Butyllithium, n-BuLi, Aldrich. n-BuLi (1.6M in hexanes) was used as purchased.
- h. Tetramethylethylenediamine, TMEDA, Aldrich. TMEDA was used without further purification.
- i. Phenylacetylene, PhC₂H, Aldrich. Phenylacetylene was used without further purification.

j. Rhodium(III) chloride trihydrate, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Johnson Matthey. Reagent grade $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was used without further purification.

k. Rhodium(I)dichlorotetracarbonyl, $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ is prepared by bubbling ethanol saturated with CO through purple (powdered) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ on an enclosed glass frit at 90°C for four hours. A brick red solid is claimed and sublimed about ten hours at 70°C . The resulting red solid is stored under vacuum.

l. 4-Methylpyrazole, 4mpyzH, Aldrich. Reagent grade 4mpyzH was used as purchased.

m. Pyrazole, pyzH, Aldrich. Reagent grade pyzH was used as purchased.

n. 3,5-Dimethylpyrazole, 35dmpyzH, Aldrich. Reagent grade 35dmpyzH was used as purchased.

o. 4-Bromo-3,5-dimethylpyrazole, 4B35dmpyzH, Pfaltz and Bauer. Reagent grade 4B35dmpyzH was used as received.

p. Bromine, Br_2 , Aldrich. Reagent grade Br_2 was used without further purification.

q. Tertiarybutylisocyanide, t-BuNC, Aldrich. Reagent grade t-BuNC was used without further purification.

r. Ammonium hexafluorophosphate, NH_4PF_6 , Aldrich. Reagent grade NH_4PF_6 was dried under vacuum at 70°C for at least ten hours before use.

4. Miscellaneous

a. Silver Acetate, $\text{AgC}_2\text{H}_3\text{O}_2$, Aldrich. $\text{AgC}_2\text{H}_3\text{O}_2$ was used as purchased.

- b. Potassium hydroxide, KOH, Mallinckrodt. Reagent grade KOH was used as purchased.
- c. Sodium cyanide, NaCN, Fisher Scientific. NaCN was used as purchased.
- d. Sodium metal, Na, Fisher Scientific. Reagent grade Na was used as purchased.
- e. Nujol, Plough, Inc. Nujol was used after drying over Na metal.
- f. Phosphorus pentoxide, P₂O₅, Mallinckrodt. ACS grade P₂O₅ was used as purchased.
- g. Calcium Chloride, CaCl₂, Mallinckrodt. Anhydrous CaCl₂ was used as purchased.

B. Spectroscopy

1. Nuclear Magnetic Resonance (NMR)

³¹P{¹H} NMR spectra were recorded on a JEOL FX90Q Fourier Transform NMR spectrometer at 36.21 MHz using 85% phosphoric acid as the external reference. The instrument was locked on the deuterium signal of acetone-d₆, (CD₃)₂CO, contained in a flame-sealed 5 mm tube put into a 10 mm sample tube. The solvents used were degassed with Ar before use.

2. Infrared Spectroscopy (IR)

Infrared spectra were recorded on a Digilab FTS-20C/V Fourier Transform Infrared Spectrometer or a Perkin-Elmer 1330 Infrared Spectrophotometer. Solid samples (usually 8-12 mg) were ground into Nujol mulls and sealed between two thin sheets of polyethylene.

3. Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-visible spectra were obtained using a Cary 219 Spectrophotometer. Quartz cells (Fisher Scientific) of 1.0 cm pathlength were used. Freshly distilled and argon degassed CH_2Cl_2 was used as the solvent. All spectra were recorded at room-temperature using the solvent in the reference beam.

C. Elemental Analysis

Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

D. Preparation of Ligands

1. 3,4,5-Tribromopyrazole, 345BpyzH

3,4,5-Tribromopyrazole was prepared by the method used by the Upjohn Company.²¹

2. (Diphenylarsino)(diphenylphosphino)methane, dapm

The dapm ligand was synthesized by the method P. D. Enlow and C. Woods.¹⁷

E. Preparation of Platinum Monomer Precursors

1. Dichloro(cycloocta-1,5-diene)platinum (II), $\text{Pt}(\text{COD})\text{Cl}_2$

This complex was prepared by the method of H. C. Clark and L. E. Manzer.²²

2. Bis-[methylenebis(diphenylphosphine)-P:P']platinum(II)chloride, $[\text{Pt}(\text{dppm}-\text{P:P}')_2]\text{Cl}_2$

Method One: This compound was initially prepared by the method of M. P. Brown and R. J. Puddephatt²³ in 65% yield using $\text{PtCl}_2(\text{COD})$ (552 mg, 1.76 mmol) and dppm (1.511 g, 3.93 mol).

Method Two: The ligand dppm (2.5371 g, 6.60 mmol) was dissolved in 10 mL of CH_2Cl_2 to give a clear solution. The compound K_2PtCl_4 (1.1694 g, 2.81 mmol) was dissolved in distilled water to give a red solution. The two immiscible solutions were then refluxed together for about three hours during which time the water layer (top layer) changed from red to colorless and the CH_2Cl_2 layer (bottom layer) changed from colorless to light green. The CH_2Cl_2 layer contained the desired product and was easily separated from the water layer using a separatory funnel. Addition of diethyl ether precipitated the product as a fine white powder in quantitative yield (2.915 g or 2.81 mmol). The product obtained by this method gave the same $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data as the product of method one.

3. Trans-Dicyano Bis-[methylenebis(diphenylphosphine)]-P:P'platinum(II), $\text{Pt}(\text{CN})_2(\text{dppm-P})_2$

This compound was prepared by the method of P. G. Pringle and B. L. Shaw.⁵

4. Cis-dichlorobis-[[(diphenylarsino)(diphenylphosphino)methane]-P:P'platinum(II), $\text{PtCl}_2(\text{dapm})_2$

This compound was prepared by the method of A. L. Balch, R. R. Guimerans, J. Linehan and F. E. Wood.¹⁴

F. Preparation of Platinum-Rhodium Complexes

1. Bis[μ -bis(diphenylphosphino)methane-P:P']-2-carbonyl-1-chloro- μ -[phenylethynyl-C¹(Pt)-C¹⁻²(Rh)]-platinumrhodium hexafluorophosphate, [ClPt(σ , η -C $\equiv$ CPh)(μ -dppm)₂Rh(CO)]PF₆, **1**.

A modification of the procedure of Pringle³ et al. was used to prepare **1**. To a solution of Pt(dppm)-P:P')₂Cl₂ (1.7569g, 1.70 mmole) in acetone was added AgC₂H₃O₂ (0.2834g, 1.70 mmole) as a dry solid and a five fold excess of phenylacetylene, C₈H₆, (0.1529g, 8.50 mmole). The resulting yellow suspension was stirred in darkness for two hours. An acetone solution of Rh₂(CO)₄(μ -Cl)₂ (0.3300g, 1.71 mmole) was slowly added dropwise to the above solution. Stirring for half an hour resulted in a color change from dark yellow to orange. Next, NH₄PF₆ in ten fold excess (2.7674g, 17.70 mmol) was added as a dry solid and the resulting suspension stirred for about ten hours.

The product was isolated by filtering to remove excess NH₄PF₆ and AgCl from the acetone solution. The red acetone solution was then evaporated until dry and the product recrystallized twice from CH₂Cl₂/diethyl ether and dried in vacuo. The yield was 80%. Note: No spectroscopic data were given for compound **1** in reference 3.

IR spectrum: ν (CO) in Nujol = 1983 cm⁻¹(s). The spectrum also shows PF₆⁻ peaks at 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis spectrum in CH₂Cl₂, [$\lambda_{\max}$ (ϵ)]: 425 nm (3200). ³¹P{¹H} NMR spectrum: (shifts from 85% H₃PO₄) δ (Pt-P) = 0.58 ppm, ¹J(Pt-P) = 2358.4 Hz, δ (Rh-P) = 19.02 ppm, ¹J(Rh-P) = 112.3 Hz, N = 31.7 Hz N = ²J(P_{Pt}-P_{Rh}) + ⁴J(P_{Pt}-P_{Rh}).

2. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-carbonyl- μ -3,5-dimethylpyrazolato-N:N'-1-phenylethynylplatinumrhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 2.

a. Method 1. To an acetone solution of 1 (0.300g, 0.217 mmol) was added 3,5-dimethyl pyrazole (0.1049g, 1.085 mmol) as a dry solid. The solution changed color from an orange to a reddish orange after stirring for one hour. After stirring, the solution was evaporated to dryness and the product was recrystallized from CH_2Cl_2 /diethyl ether and collected by filtration. The yellowish-orange solid was dried in vacuo. The yield was 87%.

b. Method 2. Compound 1 (0.3000g, 0.2170 mmol) was dissolved in 40 mL of acetone. In a separate flask, 3,5-dimethylpyrazole (0.0210g, 0.2170 mmol) was deprotonated by the addition of 2.72 mL KOH of a 0.08 M KOH/methanol solution (0.2170 mmol KOH). The slow dropwise addition of the ligand solution to the solution of 1 resulted in a color change from orange to reddish-orange. The reddish-orange solution was stirred for 20 minutes, after which it was evaporated to dryness. The crude reddish-orange solid was recrystallized from CH_2Cl_2 /diethyl ether and collected by filtration. The yellowish-orange product was dried in vacuo. The yield was 83%.

IR spectrum (Nujol): $\nu(\text{CO}) = 1983 \text{ cm}^{-1}$ (s) and $\nu(\text{Ph-C}\equiv\text{C}) = 2129 \text{ cm}^{-1}$ (w). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]: 435 \text{ nm}$ (14680), 350 nm (6000). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 4.08 \text{ ppm}$, 2646.5 , $\delta(\text{Rh-P}) = 20.40 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 129.3 \text{ Hz}$, -44.0 Hz .

3. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-carbonyl- μ -4-methylpyrazolato-N:N'-1-phenylethynylplatinumrhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-4mpyz})(\mu\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 3.

Compound 3 was prepared by the same procedures used to make 2. Employing method 1, using 4-methylpyrazole (30 mg, 0.36 mmol) and 1 (100 mg, 0.072 mmol), a yellow-orange solid was obtained. Yield: 90%. By method 2, using 4-methylpyrazole (7.42 mg, 0.090 mmol), KOH (5.04 mg, 0.090 mmol) and 1 (124 mg, 0.090 mmol), a yellow-orange solid was claimed. Yield: 82%.

IR spectrum (Nujol): $\nu(\text{CO}) = 1983 \text{ cm}^{-1}$ (s) and $\nu(\text{PhC}\equiv\text{C}) = 2126 \text{ cm}^{-1}$ (w). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}} (\epsilon)]$: 438 nm (14600), 352 nm (5400). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 6.44 \text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2667.0 \text{ Hz}$, $\delta(\text{Rh-P}) = 21.31 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 129.4 \text{ Hz}$, $N = 46.4 \text{ Hz}$.

Anal. Calcd. for $\text{C}_{63}\text{H}_{54}\text{F}_6\text{N}_2\text{O}_5\text{PtRh}$: C, 53.21; H, 3.84. Found: C, 53.29; H, 3.84.

4. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-carbonyl- μ -pyrazolato-N:N'-1-phenylethynylplatinumrhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-pyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 4.

Compound 4 was produced by the same procedures used to make 2. Employing method 1, using pyrazole (37 mg, 0.545 mmol) and 1 (150 mg, 0.109 mmol) a 90% yield was obtained. By method 2, using pyrazole (7.6 mg, 0.109 mmol), KOH (6.11 mg, 0.109 mmol) and 1 (150 mg, 0.109 mmol) a yellow-orange solid was obtained. The yield was 81%.

IR spectrum (Nujol): $\nu(\text{CO}) = 1983 \text{ cm}^{-1}$ (s) and $\nu(\text{PhC}\equiv\text{C}) = 2122 \text{ cm}^{-1}$ (w). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis spectrum in CH_2Cl_2 [$\lambda_{\text{max}}(\epsilon)$]: 437 nm (15200), 350 nm (6300). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 6.77$ ppm, $^1\text{J}(\text{Pt-P}) = 2658.7$ Hz, $\delta(\text{Rh-P}) = 21.51$ ppm, $^1\text{J}(\text{Rh-P}) = 127.0$ Hz, N = 46.4 Hz. Anal. Calcd. for $\text{C}_{62}\text{H}_{52}\text{F}_6\text{N}_2\text{P}_5\text{PtRh}$: C, 52.89; H, 3.73. Found: C, 53.00, H, 3.79.

5. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-carbonyl- μ -4bromo-3,5dimethylpyrazolato-N:N'-1-phenylethynylplatinumrhodium hexaflourophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 5.

Compound 5 was prepared only by method 2 of the procedure for making 2, using 4-Bromo-3,5-dimethylpyrazole (18.3 mg, 0.105 mmol), KOH (6.11 mg, 0.105 mmol) and 1 (144.1 mg, 0.105 mmol) a yellow-orange solid was obtained. The yield was 90%.

IR spectrum (Nujol): $\nu(\text{CO}) = 1983 \text{ cm}^{-1}$ (s) and $\nu(\text{PhC}\equiv\text{C}) = 2122 \text{ cm}^{-1}$ (w). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis spectrum in CH_2Cl_2 , [$\lambda_{\text{max}}(\epsilon)$]: 435 nm (13,400), 350 nm (5,000). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 3.60$ ppm, $^1\text{J}(\text{Pt-P}) = 2634.3$ Hz, $\delta(\text{Rh-P}) = 19.69$ ppm, $^1\text{J}(\text{Rh-P}) = 127.0$ Hz, N = 44.0 Hz.

6. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-carbonyl- μ -3,4,5tribromopyrazolato-N:N'-1-phenylethynylplatinumrhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-345Bpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 6.

Compound **6** was produced only by method 2 of the procedure for making **2**, using 3,4,5-tribromopyrazole (46.1 mg, 0.151 mmol), KOH (8.47 mg, 0.151 mmol) and **1** (209 mg, 0.151 mmol) an orange solid was obtained. The yield was 75%.

IR spectrum: $\nu(\text{CO}) = 1987 \text{ cm}^{-1}$ (s) and $\nu(\text{PhC}\equiv\text{C}) = 2133 \text{ cm}^{-1}$ (w). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}} (\epsilon)]: 435 \text{ nm} (13,400), 350 \text{ nm} (5000)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 2.80 \text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2607.4 \text{ Hz}$, $\delta(\text{Rh-P}) = 17.74 \text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 127.0 \text{ Hz}$, $N = 39.1 \text{ Hz}$.

Anal. Calcd. for $\text{C}_{62}\text{H}_{49}\text{Br}_3\text{F}_6\text{N}_2\text{OP}_5\text{PtRh}$: C, 45.28; H, 3.01. Found: C, 45.00; H, 3.01.

7. Bis[μ -bis((diphenylphosphino)methane)-P:P']]-2-(*t*-butylisocyanide)- μ -3,5dimethylpyrazolato-N:N'-1-phenylethynylplatinum-rhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$, **7**.

Compound **2** (125 mg, 0.091 mmol) was dissolved in 40 mL of acetone and cooled to 0°C. *Tert*-butylisocyanide (11.1 μL , 0.100 mmol) was added dropwise via microsyringe. The solution was stirred for 20 minutes, which resulted in a color change from orange to red. The total volume of the solution was reduced to 8 mL using a rotary evaporator and a 40°C water bath. A light orange solid was obtained upon addition of diethyl ether and collected by filtration. The solid was recrystallized from acetone/diethyl ether and dried in vacuo. The yield was 90%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2122\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]$: 453 nm (14,000), 371 nm (4,200). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from H_3PO_4) $\delta(\text{Pt-P}) = 1.39\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2707.5\text{ Hz}$, $\delta(\text{Rh-P}) = 18.01\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 136.7\text{ Hz}$, $N = 44.0\text{ Hz}$.

Anal. Calcd. for $\text{C}_{68}\text{H}_{67}\text{F}_6\text{N}_3\text{P}_5\text{PtRh}$: C, 54.77; H, 4.39. Found: C, 54.99; H, 4.45.

8. Bis[μ -bis((diphenylphosphino)methane)-P:P']-2-(*t*-butylisocyanide)- μ -4bromo-3,5-dimethylpyrazolato-N:N'-1-phenylethynyl-platinumrhodium hexafluorophosphate, $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$, 8.

Compound 8 was obtained by the same procedure as 7. Using 5 (109 mg, 0.0750 mmol) and *tert*-butylisocyanide (9.1 μL , 0.0824 mmol). An orange solid was obtained. The yield was 90%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2106\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]$: 454 nm (14,000), 370 nm (4300). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from H_3PO_4) $\delta(\text{Pt-P}) = 0.92\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2695.3\text{ Hz}$, $\delta(\text{Rh-P}) = 18.01\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 136.7\text{ Hz}$, $N = 44.0\text{ Hz}$.

9. Bis[μ -bis((diphenylphosphino)methane)-P:P']-2-carbonyl-2-chloro-1-dicycanoplatinumrhodium, $(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$, 9.

Compound 9 was prepared using the methods outlined by Pringle and Shaw.⁵ Using $\text{Pt}(\text{CN})_2(\text{dppm-P})_2$ (1.962g, 1.93 mmol) and $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (375 mg, 0.966 mmol) a light yellow solid was obtained. The yield after two recrystallizations from CH_2Cl_2 /diethyl ether was 65%.

IR spectrum: $\nu(\text{CO})$ in Nujol = $1975\text{ cm}^{-1}(\text{s})$; $\nu(\text{CN})$ in Nujol = $2129\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)]$: $426\text{ nm}(7400)$.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from $85\% \text{H}_3\text{PO}_4$) $\delta(\text{Pt-P}) = -0.90\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2529.3\text{ Hz}$, $\delta(\text{Rh-P}) = 18.62\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 127.0\text{ Hz}$, $\text{N} = 44.0\text{ Hz}$.

10. Bis[μ -bis((diphenylphosphino)methane)-P:P']]- μ -3,5-dimethyl-pyrazolato-N:N'-2-carbonyl-1-cyanoplatinumrhodium hexafluorophosphate, $[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 10.

Compound **9** (159 mg, 0.134 mmol) was dissolved in 5 mL of CH_2Cl_2 and 100 mL of acetone. NH_4PF_6 (44 mg, 0.27 mmol) was added as a dry solid and the resulting yellow suspension was stirred for one hour. In a separate flask, 3,5-dimethylpyrazole (26 mg, 0.27 mmol) was deprotonated by the addition of a methanol solution of KOH (7.6 mg, 0.134 mmol). The 3,5-dimethylpyrazolate solution was slowly added dropwise by transfer needle to the yellow suspension. After stirring for two hours, the yellow solution was stripped to dryness and the dry contents redissolved in CH_2Cl_2 . The orange CH_2Cl_2 solution was filtered to remove excess NH_4PF_6 , KCN and KCl. A light yellow solid precipitated upon addition of diethyl ether and was collected by filtration. The product was usually recrystallized a minimum of four times from CH_2Cl_2 /diethyl ether to remove impurities. Yield: 50%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2120\text{ cm}^{-1}(\text{s})$; $\nu(\text{CO}) = 1992\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)] = 427\text{ nm}(9100)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (All shifts from $85\% \text{H}_3\text{PO}_4$) $\delta(\text{Pt-P}) = 0.59\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2404.8\text{ Hz}$, $\delta(\text{Rh-P}) = 19.46\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 129.4\text{ Hz}$, $\text{N} = 34.2\text{ Hz}$.

Anal. calcd. for $C_{57}H_{51}F_6N_3OP_5PtRh$: C, 50.31; H, 3.80. Found: C, 48.90; H, 4.15.

11. Bis[μ -bis((diphenylphosphino)methane)-P;P']]- μ -4-bromo-3,5-dimethylpyrazolato-N:N'-2-carbonyl-1-cyanoplatinumrhodium hexafluorophosphate, [(CN)Pt(μ -4B35dmpyz)(μ -dppm) $_2$ Rh(CO)]PF $_6$, 11.

Compound 11 was produced by the same procedure used to make 10. Using 4-bromo-3,5-dimethyl pyrazole (47 mg, 0.27 mmol), NH $_4$ PF $_6$ (44 mg, 0.27 mmol), KOH (7.6 mg, 0.135 mmol) and 9 (160 mg, 0.135 mmol) a light yellow solid was obtained. Yield: 40%.

IR spectrum: ν (CN) in Nujol = 2123 cm $^{-1}$ (m); ν (CO) = 1991 cm $^{-1}$ (s). The spectrum also shows PF $_6^-$ peaks at 839 cm $^{-1}$ (s) and 557 cm $^{-1}$ (m). UV-Vis spectrum in CH $_2$ Cl $_2$, [λ_{max} (ϵ)] = 426 nm (8600). $^{31}P\{^1H\}$ NMR spectrum: (All shifts from 85% H $_3$ PO $_4$) δ (Pt-P) = 0.72 ppm, ^1J (Pt-P) = 2397 Hz, δ (Rh-P) = 19.29 ppm, ^1J (Rh-P) = 127.0 Hz, N = 34.2 Hz.

12. Bis[μ -bis((diphenylphosphino)methane)-P;P']]- μ -3,4,5-tribromopyrazolato-N:N'-2-carbonyl-1-cyanoplatinumrhodium hexafluorophosphate, [(CN)Pt(μ -345Bpyz)(μ -dppm) $_2$ Rh(CO)]PF $_6$, 12.

Compound 12 was produced by the same procedure as 10. Using 3,4,5-tribromopyrazole (59 mg, 0.380 mmol), NH $_4$ PF $_6$ (62 mg, 0.380 mmol), KOH (11 mg, 0.190 mmol) and 9 (225 mg, 0.190 mmol) a light yellow solid was obtained. Yield: 50%.

IR spectrum: ν (CN) in Nujol = 2124 cm $^{-1}$ (m); ν (CO) = 1989 cm $^{-1}$ (s). The spectrum also shows PF $_6^-$ peaks at 839 cm $^{-1}$ (s) and 557 cm $^{-1}$ (m). UV-Vis spectrum in CH $_2$ Cl $_2$, [λ_{max} , (ϵ)] = 428 nm (8700). $^{31}P\{^1H\}$ NMR

spectrum: (All shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = 0.78$ ppm, $^1\text{J}(\text{Pt-P}) = 2369.4$ Hz, $\delta(\text{Rh-P}) = 19.43$ ppm, $^1\text{J}(\text{Rh-P}) = 127.0$ Hz, $N = 36.6$ Hz.

13. Bis[(μ -bis((diphenylphosphino)methane)-P:P')]- μ -3,5-dimethyl-pyrazolato-N:N'-2-(*t*-butylisocyanide)-1-cyanoplatinumrhodium hexafluorophosphate, [(CN)Pt(μ -3,5dmpyz)(μ -dppm) $_2$ Rh(*t*-BuNC)]PF $_6$, 13.

Compound 10 (201 mg, 0.150 mmol) was dissolved in 40 mL of freshly distilled CH_2Cl_2 and 40 mL of freshly distilled methanol and cooled to 0°C . After purging with prepurified argon gas, *t*-BuNC (13.5 mg, 0.165 mmol) was added dropwise via microsyringe. The solution changed color from orange to dark red after stirring for fifteen minutes. The red solution was evaporated to dryness and the dry red solid was recrystallized from acetone/diethyl ether to yield an orange solid. Yield: 75%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2141\text{ cm}^{-1}(\text{s})$ and $2120\text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)] = 450(6100)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (Shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = -0.43$ ppm, $^1\text{J}(\text{Pt-P}) = 2500.0$ Hz, $\delta(\text{Rh-P}) = 16.57$ ppm, $^1\text{J}(\text{Rh-P}) = 148.5$ Hz, $N = 53.9$ Hz.

Anal. Calcd. for $\text{C}_{60}\text{H}_{60}\text{F}_6\text{N}_4\text{P}_5\text{PtRh}$: C, 51.74; H, 4.27. Found: C, 52.80, H, 4.42.

14. Bis[(μ -bis((diphenylphosphino)methane)-P:P')]- μ -4-bromo-3,5-dimethyl-pyrazolato-N:N'-2-(*t*-butylisocyanide)-1-cyanoplatinum-rhodium hexafluorophosphate, [(CN)Pt(μ -4B35dmpyz)(μ -dppm) $_2$ Rh(*t*-BuNC)]PF $_6$, 14.

Compound 14 was prepared by the same procedure as 13. Using 11 (73.4 mg, 0.05/mmol) and t-BuNC (4.7 mg, 0.056 mmol). Yield: 75%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2140\text{ cm}^{-1}(\text{s})$ and $2120\text{ cm}^{-1}(\text{sh})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{sh})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)] = 450(6300)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from 85% H_3PO_4) $\delta(\text{Pt-P}) = -0.43\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2500.0\text{ Hz}$, $\delta(\text{Rh-P}) = 16.60\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 146.5\text{ Hz}$, $N = 51.3\text{ Hz}$.

15. Trans-dicyanobis[μ -((diphenylarsino)(diphenylphosphino)methane)-P]Platinum(II), $\text{Pt}(\text{CN})_2(\text{dapm-P})_2$, 15.

$\text{PtCl}_2(\text{dapm-P})_2$ (260 mg, 0.231 mmol) was dissolved in 10 mL CH_2Cl_2 , after which 50 mL of absolute ethanol was added. NaCN (22.5 mg, 0.463 mmol) was dissolved in 100 mL of ethanol and added quantitatively to the first solution. The solution was stirred for fifteen minutes and then evaporated (via rotary evaporator) to one-third the initial volume and diethyl ether added until precipitation of the white product was complete. The product was recrystallized from CH_2Cl_2 /diethyl ether and collected by filtration. Yield: 87%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2135\text{ cm}^{-1}(\text{s})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (from 85% H_3PO_4) $\delta(\text{Pt-P}) = 7.92\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2324.3\text{ Hz}$.

Anal. Calcd. for $\text{C}_{52}\text{H}_{44}\text{As}_2\text{N}_2\text{P}_2\text{Pt}$: C, 56.58; H, 4.02. Found: C, 56.43; H, 4.19.

16. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]-2-carbonyl-2-chloro-1-dicyanoplatinumrhodium, $(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$, 16.

Compound 15 (219 mg, 0.198 mmol) was dissolved in 10 mL CH_2Cl_2 and in a separate flask $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (38.6 mg, 0.099 mmol) was dissolved in 10 mL CH_2Cl_2 and cooled to 0°C . The clear solution of 15 was slowly added dropwise to the yellow $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ solution. After stirring for 30 minutes, the solution was evaporated to dryness by use of a rotary evaporator at room temperature. The resulting orange solid was recrystallized from CH_2Cl_2 /diethyl ether and collected by filtration. The yellow product was dried in vacuo. Yield: 78%.

IR spectrum: $\nu(\text{CO})$ in Nujol = $1973\text{ cm}^{-1}(\text{s})$ and $\nu(\text{CN}) = 2129\text{ cm}^{-1}(\text{s})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)] = 417(8100)$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from 85% H_3PO_4) head-to-head isomer: (both P atoms on Pt) $\delta(\text{Pt-P}) = 3.47\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 2509.9\text{ Hz}$. head-to-tail isomer (one P on Pt, one P on Rh). $\delta(\text{Pt-P}) = 1.12\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 3037.1\text{ Hz}$, $\delta(\text{Rh-P}) = 25.92\text{ ppm}$, $^1\text{J}(\text{Rh-P}) = 148.9\text{ Hz}$.

Anal. Calcd. for $\text{C}_{53}\text{H}_{44}\text{As}_2\text{ClN}_2\text{OP}_2\text{PtRh}$: C, 50.12; H, 3.49. Found: C, 50.18; H, 3.55.

17. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P]- μ -3,5-dimethylpyrazolato-N:N'-2-carbonyl-1-cyanoplatinumrhodium hexafluorophosphate, $[(\text{CN})\text{Pt}(\mu\text{-3,5dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 17.

Compound 17 was produced by the same procedure as 10. Using 16 (104 mg, 0.082 mmol), NH_4PF_6 (26.6 mg, 0.164 mmol), KOH (4.61 mg, 0.082 mmol) and 3,5-dimethylpyrazole (15.8 mg, 0.082 mmol). A yellow solid was obtained and dried in vacuo. Yield: 78%.

IR spectrum: $\nu(\text{CO})$ in Nujol = $1991\text{ cm}^{-1}(\text{s})$ and $\nu(\text{CN}) = 2120\text{ cm}^{-1}(\text{m})$. The spectrum also shows PF_6^- peaks at 839 cm^{-1} and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , $[\lambda_{\text{max}}(\epsilon)] = 417(8100)$. $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum: (shifts from 85% H_3PO_4) head to head isomer: (Both P atoms on Pt) $\delta(\text{Pt-P}) = 2.47$ ppm, $^1\text{J}(\text{Pt-P}) = 2392.6$ Hz. head to tail isomer: (one P atom and one As atom on Pt) $\delta(\text{Pt-P}) = 0.98$ ppm, $^1\text{J}(\text{Pt-P}) = 2902.8$ Hz, $\delta(\text{Rh-P}) = 23.43$ ppm, $^1\text{J}(\text{Rh-P}) = 149.0$ Hz.

Anal. Calcd. for $\text{C}_{57}\text{H}_{51}\text{As}_2\text{F}_6\text{N}_3\text{OP}_3\text{PtRh}$: C, 47.25; H, 3.55. Found: C, 46.85; H, 3.67.

18. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P)]- μ -3,5-dimethylpyrazolato-N:N'-2-(*t*-butylisocyanide)-1-cyano-platinumrhodium hexafluorophosphate, [(CN)Pt(μ -3,5dmpyz)(μ -dapm) $_2$ Rh(*t*-BuNC)]PF $_6$, 18.

Compound 18 was made by the same procedure as used for 13, using 17 (119 mg, 0.081 mmol) and *t*-BuNC (7.44 mg, 0.09 mmol). Yield: 85%.

IR spectrum: $\nu(\text{CN})$ in Nujol = $2140\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF $_6^-$ peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis spectrum in CH_2Cl_2 , [λ_{max} (ϵ)] = 452 (7200). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (shifts from 85% H_3PO_4) head-to-head isomer: $\delta(\text{Pt-P}) = 3.20$ ppm, $^1\text{J}(\text{Pt-P}) = 2483.0$ Hz. head-to-tail isomer: $\delta(\text{Pt-P}) = 2.20$ ppm, $^1\text{J}(\text{Pt-P}) = 3063.0$ Hz, $\delta(\text{Rh-P}) = 21.75$ ppm, $^1\text{J}(\text{Rh-P}) = 168.9$ Hz.

Anal. Calcd. for $\text{C}_{60}\text{H}_{60}\text{As}_2\text{F}_6\text{N}_4\text{P}_3\text{PtRh}$: C, 48.72; H, 4.02. Found: C, 47.76; H, 4.20.

19. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:P)]-2-carbonyl-2-chloro-cis-1-dichloroplatinumrhodium, cis-Cl $_2$ Pt(P:P')(μ -dapm) $_2$ -trans-Rh(As:As')(CO)Cl, 19.

Compound 19 was prepared by the method of A. L. Balch, R. R. Guimerans, J. Linehan and F. E. Wood,¹⁴ using PtCl $_2$ (dapm-P) $_2$ (329 mg, 0.29 mmol) and Rh $_2$ Cl $_2$ (CO) $_4$ (57.8 mg, 0.15 mmol).

IR spectrum: $\nu(\text{CO})$ in Nujol = $1987\text{ cm}^{-1}(\text{s})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (from 85% H_3PO_4) $\delta(\text{Pt-P}) = 14.31\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 3825.7\text{ Hz}$. Spectroscopic data from the reference is as follows; IR spectrum: $\nu(\text{CO})$ in Nujol = $1987\text{ cm}^{-1}(\text{s})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: (from 85% H_3PO_4) $\delta(\text{Pt}) = 15.0\text{ ppm}$, $^1\text{J}(\text{Pt-P}) = 3826.0\text{ Hz}$.

20. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:As'(Rh)-cis-P:P'(Pt)]- μ -3,5dimethylpyrazolato-N:N'-2-carbonyl-1-chloro-platinum-rhodium hexafluorophosphate, [cis-ClPt(P:P')(μ -dapm) $_2$ (μ -35dmpyz)-trans-Rh(As:As')(CO)]PF $_6$, 20.

Compound 19 (117 mg, 0.091 mmol) was dissolved in 10 mL of CH_2Cl_2 and 40 mL of acetone. NH_4PF_6 (15 mg, 0.091 mmol) was added as a dry solid and the resulting yellow suspension was cooled to 0°C and stirred for 1 hour. In another flask, 3,5-dimethylpyrazole (13 mg, 0.14 mmol) and KOH/methanol (1.1 mL, 5.10 mg, 0.09 mmol) were combined and allowed to stand for five minutes. The 3,5-dimethylpyrazolate solution was quantitatively added dropwise to the yellow suspension. The mixture stirred at 0°C for 20 minutes after the addition was complete and for 10 minutes while warming to room temperature. The yellow solution was evaporated by dryness by use of a rotary evaporator at room temperature. The resulting light yellow solid was dissolved in freshly distilled CH_2Cl_2 and filtered. To the yellow filtrate was added anhydrous diethyl ether/hexanes (50/50) until precipitation was complete. A light yellow solid was collected by filtration and dried in vacuo. Yield: 70%.

IR spectrum: $\nu(\text{CO})$ in Nujol = $1979\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum: (from 85% H_3PO_4) $\delta(\text{Pt-P}_A) = 7.04$ ppm, $^1\text{J}(\text{Pt-P}_A) = 4050.2$ Hz, $\delta(\text{Pt-P}_B) = -0.02$ ppm, $^1\text{J}(\text{Pt-P}_B) = 3003.0$ Hz, $^2\text{J}(\text{P}_A\text{-P}_B) = 19.53$ Hz.

Where P_A and P_B designate the two P atoms in cis positions about the Pt atom.

Anal. Calcd. for $\text{C}_{56}\text{H}_{51}\text{As}_2\text{ClF}_6\text{N}_2\text{OP}_3\text{PtRh}$: C, 46.13; H, 3.53.

Found: C, 46.14; H, 3.76.

21. Bis[μ -((diphenylarsino)(diphenylphosphino)methane)-As:As'(Rh)-trans-P:P'(Pt)]- μ -3,5-dimethylpyrazolato-N:N'-2-carbonyl-1-chloroplatinumrhodium hexafluorophosphate, [trans-ClPt(P:P')(μ -dapm) $_2$ (μ -35dmpyz)-trans-Rh(As:As')(CO)]PF $_6$, 21.

Compound 20 (70 mg, 0.048 mmol) was dissolved in 30 mL of chloroform and refluxed for a two hour period. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture revealed the presence of both compounds 20 and 21. Subsequent refluxing of the mixture for periods of time up to twelve hours did not appreciably alter the relative amounts of complexes 20 and 21. Attempts to separate the two isomers using CH_2Cl_2 /diethyl ether recrystallizations proved unsuccessful.

IR spectrum: $\nu(\text{CO}) = 1980\text{ cm}^{-1}(\text{s})$. The spectrum also shows PF_6^- peaks at $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: $\delta(\text{Pt-P}) = 6.37$ ppm and $^1\text{J}(\text{Pt-P}) = 2597.7$ Hz. Since 21 could not be separated from 20 the data for 21 are taken from the IR and ^{31}P NMR spectra of the mixture since 20 can be obtained independently of 21.

Note: The nomenclature for complexes 1-21 is derived primarily from reference 3 and 6.

CHAPTER 2.3

ADDITION OF PYRAZOLATE DERIVATIVES TO SELECTED Pt-Rh

A-FRAME COMPLEXES

The synthesis of the Pt-Rh complexes presented in the following discussion was based upon the replacement of an anion (Cl^- and/or CN^-) with a pyrazolate derivative. Thus an ionic complex of the general formula, $[(\text{X})\text{Pt}(\mu\text{-Ypyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ ($\text{X} = \text{PhC}_2^-$, CN^- ; Ypyz = pyrazolate derivative) resulted. A similar experimental method was used to synthesize the binuclear Rh(I) complexes of the general formula $[\text{Rh}_2(\text{CO})_2(\mu\text{-LL})(\mu\text{-Ypyz})]\text{A}$ ($\text{LL} = \text{dppm}$, dapm , dpam ; $\text{A} = \text{PF}_6^-$, Cl^- , ClO_4^-) as previously reported.^{18,19}

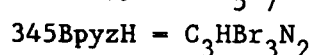
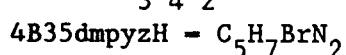
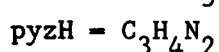
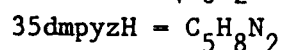
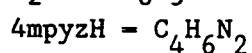
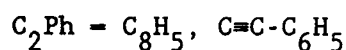
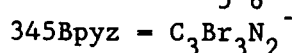
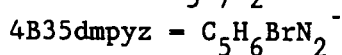
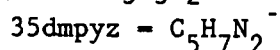
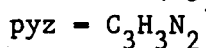
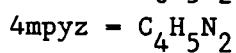
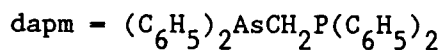
Structurally, the binuclear Rh(I) substituted pyrazolate A-frames and these novel Pt-Rh complexes bear a strong resemblance to each other, differing by the substitution of a Pt(II) metal center for a Rh(I) metal center. This comparison is illustrated in Figure 12. The known proven structure of the Rh(I) complexes is shown as Figure 12A and the suggested general structure for the Pt-Rh complexes is given as Figure 12B.

The same ligands are arranged about the Rh(I) centers in both the Rh_2 and PtRh complexes. Addition of alkylisocyanides to the Rh_2 complexes (12A) resulted in the substitution of the terminal CO ligands by isocyanides.¹⁹ The terminal CO on the Rh(I) center in the Pt-Rh complexes was also susceptible to isocyanide substitution. Hence, the isocyanide substitution reaction was performed using selected Pt-Rh complexes. These complexes appear in Table I.

TABLE I
COMPOUND IDENTIFICATION

Number	Compound
1	$[\text{ClPt}(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
2	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
3	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-4mpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
4	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-pyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
5	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
6	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-345Bpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
7	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$
8	$[(\sigma\text{-C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$
9	$(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$
10	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
11	$[(\text{CN})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
12	$[(\text{CN})\text{Pt}(\mu\text{-345Brpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$
13	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$
14	$[(\text{CN})\text{Pt}(\mu\text{-4B35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$
15	$\text{Pt}(\text{CN})_2(\text{dapm-P})_2$
16	$(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$
17	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$
18	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$
19	$\text{cis-Cl}_2\text{Pt}(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})\text{Cl}$
20	$[\text{cis-ClPt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})]\text{PF}_6$
21	$[\text{trans-ClPt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})]\text{PF}_6$

NOTES:



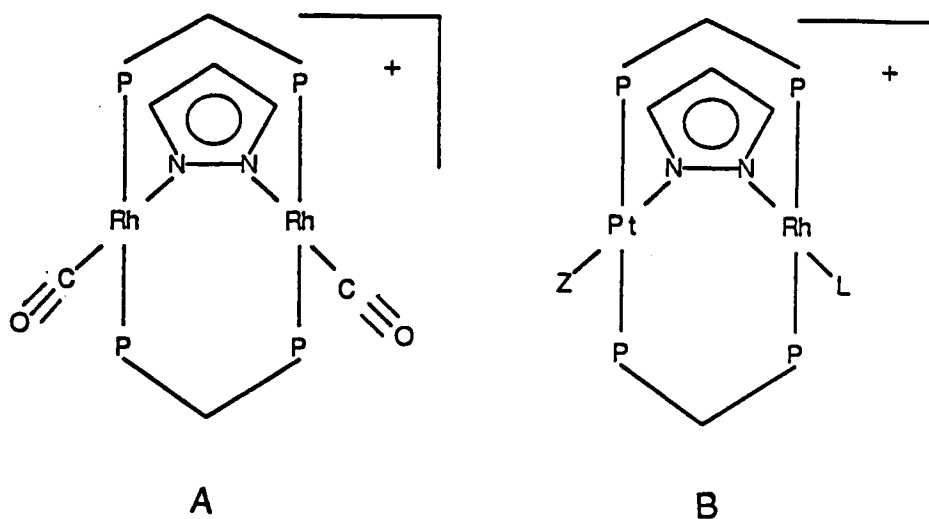


FIGURE 12. General structural formulas for dirhodium and platinum-rhodium cationic complexes

A. Platinum-Rhodium Complexes With A Terminal
Phenylethynyl Ligand At The Pt Atom

Platinum-Rhodium A-frame complexes (2-6) with a pyrazolate derivative at the bridgehead position were synthesized by the addition of the appropriate potassium salt to an acetone-methanol solution of $[\text{ClPt}(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 1. When the pyrazoles 35dmpyzH, 4mpyzH or pyzH were individually added to an acetone-methanol solution of 1, the complexes 2, 3 and 4 were obtained, respectively. This was verified by obtaining $^{31}\text{P}(^1\text{H})$ NMR, infrared and electronic spectral

data identical to that for complexes obtained by using the appropriate potassium salt. The pyrazoles 4B35dmpyzH or 345BpyzH and 1 were combined in acetone-methanol and gave only starting materials; the bromine-substituted pyrazolate derivatives were produced only by use of their potassium salts.

In complex 1, initially characterized by McEwan et al.,² the bridging phenylethynyl (phenylacetylde) was shown to be σ -bound to the Pt(II) atom and weakly π -bonded to the Rh(I) atom. When a pyrazolate derivative coordinates to the Pt(II) and Rh(I) metal centers of complex 1 the Pt(II) atom loses its chloride anion (Cl^-) and the π -bonding of the phenylethynyl to Rh(I) must be lost to make the necessary coordination sites available.

The substituted pyrazolate anions vary in their ability to donate electron density to the metal atoms depending upon the nature and position of the ring substituents. The pyrazolates with weakly donating methyl substituents (e.g. 4mpyz and 35dmpyz) or with no substituent (e.g. pyz) can donate more electron density than those containing a weakly withdrawing bromo group (e.g. 4B35dmpyz and 345Brpyz). From the experimental evidence, pyrazole and the methyl substituted pyrazoles are better able to compete with the π -bonded phenylacetylde for the Rh(I) site than the bromine substituted pyrazoles. Also, the coordinating ability of the pyrazolates is much superior to that of the pyrazole since all the various pyrazolate anions give the desired products.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 2, shown in Figure 13, is typical of the ^{31}P NMR spectra of compounds 1-6. Essentially, these

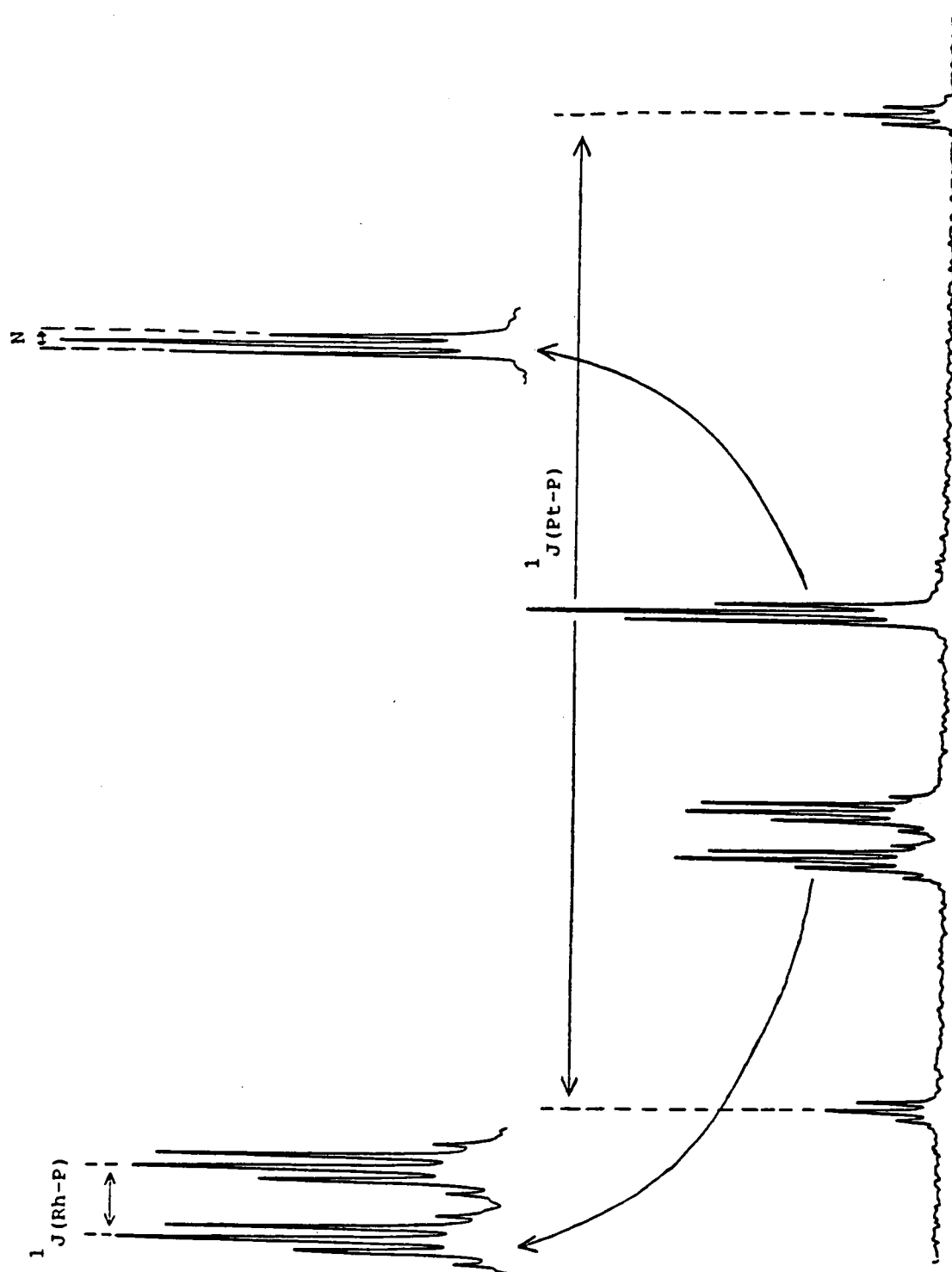


FIGURE 13. $^{31}\text{P}(^1\text{H})$ NMR spectrum of $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6 \cdot 2$

spectra show three types of P nuclei present in complexes 1-6. First, the resonance due to the presence of a PF_6^- counterion always appears far downfield from the other resonances. The other two types of P nuclei are: (1) P bound to Rh(I) and (2) P bound to Pt(II). The P nuclei bound to ^{103}Rh (100% abundance, $I = 1/2$) exhibit a chemical shift, $\delta(\text{Rh-P})$, in the range 21.5-17.4 ppm and a one-bond metal to phosphorus coupling constant, $^1J(\text{Rh-P})$, range from 127-112 Hz.

The phosphorus atoms bound to Pt(II) display an intense resonance and a set of symmetrically placed satellite resonances of much weaker intensity. The more intense resonance is due to P nuclei bound to Pt (66.6% abundance, $I = 0$) and the satellites are due to P nuclei bound to ^{195}Pt (33.4% abundance, $I = 1/2$). Complexes 1-6 display a $\delta(\text{Pt-P})$ range of 6.8-0.58 ppm (from 85% H_3PO_4) and a $^1J(\text{Pt-P})$ range of 2666-2358 Hz.

Both types of phosphorus (P bound to Rh(I) and P bound to Pt(II)) resonances show further coupling due to these chemically and magnetically nonequivalent P atoms (See Figure 13). Figure 14 shows a framework for the Pt-Rh complexes containing two transoid dppm ligands.

Hence, P_A may couple to P_B and also to P_C . The term for two-bond phosphorus-phosphorus coupling is designated as $^2J(P_A-P_B)$ or simply as $^2J(\text{P-P})$ and the term for four-bond phosphorus-phosphorus coupling is designated as $^4J(P_A-P_C)$ or as $^4J(\text{P-P})$. Each virtual triplet arises from the overlap of peaks from the two-bond and four-bond phosphorus-phosphorus coupling. Following Shaw³ and coworkers the virtual triplet values shall be designated as N, where $N = ^2J(\text{P-P}) + ^4J(\text{P-P})$. These N

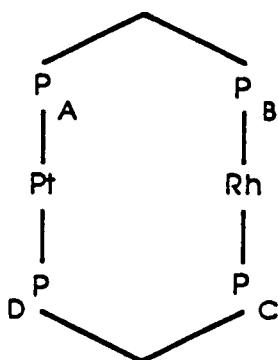


FIGURE 14. The structural framework for a $\text{Pt}(\text{dppm})_2\text{Rh}$ ring

constants are determined by the frequency difference between the outer-two peaks of each virtual triplet and for complexes 1-6 range from 46.4 to 31.7 Hz.

Figure 13 also shows the magnified resonance of P bound to Rh(I) (left) and the more intense resonance of P bound to Pt(II) (right) where $^1\text{J}(\text{Rh-P})$ and N are designated.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of binuclear Rh(I) complexes, e.g. $[\text{Rh}_2(\text{CO})_2(\mu\text{-35dmpyz})(\mu\text{-dppm})_2]\text{PF}_6$, show a symmetric multiplet featuring an AA'A''A'''XX' pattern. Such a pattern implies that all four phosphorus atoms are chemically but not magnetically equivalent. These spectra are of a second-order nature. The strongest coupling occurring

in the Pt-Rh complexes (1-21) is definitely of a first-order nature, but the spectrum shown in Figure 13 exhibits the presence of comparatively smaller peaks. It is suggested that these smaller peaks are due to second-order coupling. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data for complexes 1-8 are presented in Table II.

The IR spectrum of 1, the parent compound for complexes 2-6, shows a terminal carbonyl band at 1985 cm^{-1} (s) and a bridging phenylacetylide stretch at 2040 cm^{-1} (w) with PF_6^- peaks at the expected values of 839 cm^{-1} (s) and 557 cm^{-1} (m).

Each IR spectrum for compounds 2-6 shows an absorption band typical of a terminal acetylide ligand, here phenylacetylide, in the range $2133\text{-}2121\text{ cm}^{-1}$. Also, complexes 2-6 show terminal carbonyl bands ranging from 1987 to 1982 cm^{-1} with the bands indicative of the PF_6^- counterion also present. Table III lists the IR spectral data for complexes 1-8.

Addition of one equivalent of t-BuNC to complex 2 (or 5) results in the substitution of the terminal CO by t-BuNC at the Rh(I) center to yield complex 7 (or 8). Attempts to prepare the t-BuNC substituted products of CO complexes 3, 4, and 6 resulted in the production of various species which proved inseparable from the desired complexes.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes 7 and 8 resemble those of complexes 1-6 in appearance. The $\delta(\text{Rh-P})$ value is 18.01 ppm , $^1\text{J}(\text{Rh-P})$ is 136.72 Hz and the N value is 43.95 Hz for both complexes 7 and 8. However, the $\delta(\text{Pt-P})$ values of 7 and 8 differ by 0.47 ppm and the $^1\text{J}(\text{Pt-P})$ values differ by 12.2 Hz . These values are expectedly close

TABLE II

 $^{31}\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR COMPOUNDS 1-8^{a, b}

Number	Compound	$\delta(\text{Pt-P}), \text{ppm}$	$^1\text{J}(\text{Pt-P}), \text{Hz}$	$\delta(\text{Rh-P}), \text{ppm}$	$^1\text{J}(\text{Rh-P}), \text{Hz}$	N, Hz ^c
1	$[\text{ClPt}(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	0.58	2358.4	19.02	112.3	31.7
2	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	4.08	2646.5	20.40	129.3	44.0
3	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4mpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	6.44	2666.0	21.31	129.4	46.4
4	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-pyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	6.77	2658.7	21.51	127.0	46.4
5	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	3.60	2634.3	19.69	127.0	44.0
6	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-345Bpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2.80	2607.4	17.74	127.0	39.1
7	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$	1.39	2707.5	18.01	136.7	44.0
8	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$	0.92	2695.3	18.01	136.7	44.0

^a All chemical shifts relative to 85% H_3PO_4 .^b $\delta(\text{Pt-P})$ and $\delta(\text{Rh-P}) + 0.1 \text{ ppm}$; $^1\text{J}(\text{Ph-P})$ and $^1\text{J}(\text{Rh-P}) + 0.6 \text{ Hz}$.^c $N = ^2\text{J}(\text{P}_{\text{Pt}}\text{-P}_{\text{Rh}}) + ^4\text{J}(\text{P}_{\text{Pt}}\text{-P}_{\text{Rh}})$.

TABLE III

IR SPECTRAL DATA FOR SELECTED COMPOUNDS 1-8^a

Number	Compound	$\nu(\text{C}\equiv\text{C})$, $\nu(\text{CO})$ or $\nu(\text{RNC})^b$, cm^{-1}
1	$[\text{ClPt}(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2040(w) ^d , 1983(s)
2	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2129(w), 1983(s)
3	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4mpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2126(w), 1983(s)
4	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-pyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2122(w), 1983(s)
5	$[(\text{C Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2122(w), 1983(s)
6	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-345Brpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	2133(w), 1987(s)
7	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-3,5dmpyz})(\text{dppm})_2\text{Rh}(\text{RNC})]\text{PF}_6^c$	2122(s)
8	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4B3,5dmpyz})(\text{dppm})_2\text{Rh}(\text{RNC})]\text{PF}_6^c$	2106(s)

^aComplexes 1-8 all show PF_6^- peaks at 839(s) and 557(m) cm^{-1} .^b $\text{RNC} = (\text{CH}_3)_3\text{NC}$.^cIn complexes 7 and 8 only the RNC peak may be accurately assigned.^d $\nu(\text{C}\equiv\text{C})$ not determined in reference 3.

because 7 and 8 differ structurally only by the presence of a bromide atom at the 4-position of the pyrazolate ring in complex 8.

The infrared spectra of complexes 7 and 8 exhibit absorption bands at 2122(s) and 2106(s) cm^{-1} , respectively. These spectra do not show absorption bands due to terminal CO ligands but do show anticipated PF_6^- peaks. The position of these broad peaks is typical of a t-BuNC ligand terminally bound to a Rh(I) atom. Table III contains the infrared spectral data for 7 and 8.

Table IV presents the electronic spectral data for complexes 1-8. With the exception of 1, these complexes exhibit an intense absorption band ranging from 453 to 435 nm and a weaker band between 370 and 350 nm. Inspection of Table IV reveals that the t-BuNC substituted complexes show a decrease in the energy for both the intense and weaker transitions when compared to their parent carbonyl complexes. The molar absorption coefficients lie in the range 15,200-12,000 $\text{L mol}^{-1} \text{cm}^{-1}$ for the more intense transition, and 6,300-4,200 $\text{L mol}^{-1} \text{cm}^{-1}$ for the less intense transition.

The results of elemental analysis of complexes 3, 4, 6 and 7 for %C and %H agreed with calculated values which were based on the proposed structure illustrated in Figure 15. (See Table V for elemental analysis data.) This proposed structure is supported by the elemental analysis data as well as the previously discussed $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectral data.

TABLE IV
UV-VIS SPECTRAL DATA FOR COMPOUNDS 1-8

Number	Compound	$\lambda_{\text{max, nm}} (\epsilon)$
1	$[\text{ClPt}(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	425 (3200)
2	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	435 (14,680) 350 (6,000)
3	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4mpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	438 (14,600) 352 (5,400)
4	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-pyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	437 (15,200) 350 (6,300)
5	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	435 (13,400) 350 (5,000)
6	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-345Bpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	431 (12,000) 350 (5,300)
7	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$	453 (14,000) 371 (4,200)
8	$[(\text{C}_2\text{Ph})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$	454 (14,000) 370 (4,300)

TABLE V
ELEMENTAL ANALYSIS DATA FOR SELECTED COMPOUNDS ^a

Number	Compound	% C	% H
3	$[(C_2Ph)Pt(\mu-4mpyz)(dppm)_2Rh(CO)]PF_6$	53.29 (53.21)	3.84 (3.84)
4	$[(C_2Ph)Pt(\mu-pyz)(dppm)_2Rh(CO)]PF_6$	53.00 (52.89)	3.79 (3.73)
6	$[(C_2Ph)Pt(\mu-345Bpyz)(dppm)_2Rh(CO)]PF_6$	45.00 (45.28)	3.01 (3.01)
7	$[(C_2Ph)Pt(\mu-35dmpyz)(dppm)_2Rh(\underline{t}-BuNC)]PF_6$	54.99 (54.77)	4.45 (4.39)
10	$[(CN)Pt(\mu-35dmpyz)(dppm)_2Rh(CO)]PF_6$	48.90 (50.31)	4.15 (3.80)
13	$[(CN)Pt(\mu-35dmpyz)(dppm)_2Rh(\underline{t}-BuNC)]PF_6$	52.80 (51.74)	4.42 (4.27)
15	$Pt(CN)_2(dapm-P)_2$	56.43 (56.58)	4.19 (4.02)
16	$(CN)_2Pt(\mu-dapm)_2Rh(CO)Cl$	50.18 (50.12)	3.55 (3.49)
17	$[(CN)Pt(\mu-35dmpyz)(dapm)_2Rh(CO)]PF_6$	46.85 (47.25)	3.67 (3.55)
18	$[(CN)Pt(\mu-35dmpyz)(dapm)_2Rh(\underline{t}-BuNC)]PF_6$	47.76 (48.72)	4.20 (4.02)
20	$[ClPt(\mu-3,5dmpyz)(dapm)_2Rh(CO)]PF_6$	46.14 (46.13)	3.76 (3.53)

^aThe calculated values for % C and % H content for each listed compound are in parenthesis.

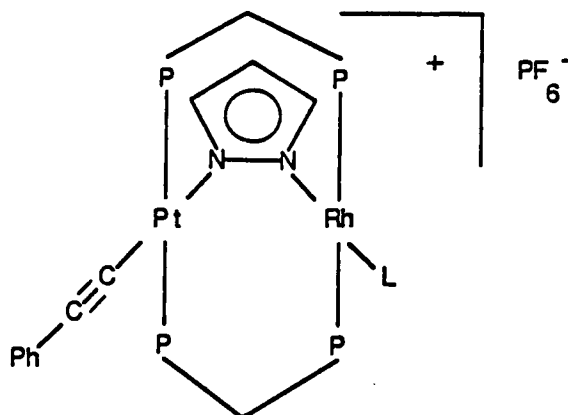


FIGURE 15. Proposed structure for complexes of the type $[(\sigma\text{-PhC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-Xpyz})\text{Rh}(\text{L})]\text{PF}_6$, 2-8 (xpyz = pyrazolate derivatives; L = CO or $\underline{t}$ -BuNC)

B. Platinum-Rhodium Complexes With A Terminal Cyanide Ligand at The Pt Atom

Complexes 10-12 were prepared by addition of the appropriate potassium salt to a yellow suspension of NH_4PF_6 and $(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$, 2, in acetone. After stirring for two hours, the yellow suspension was dissolved in CH_2Cl_2 and filtered to remove excess NH_4PF_6 and the unwanted salts such as KCl or KCN. Usually, this reaction yields at least two phosphorus containing products of which the characterized product is overwhelmingly predominant. However, several recrystallizations from CH_2Cl_2 /diethyl ether are required to give the desired product in pure form.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data for complexes 9-14 are presented in Table VI. The chemical shifts and coupling constants for both sets of P nuclei are similar for the parent complex, 9, and its daughter complexes 10, 11, and 12. For complexes 10-12, $\delta(\text{Rh-P})$ ranges from 19.29 to 19.46 ppm; $^1\text{J}(\text{Rh-P})$ ranges from 127.0 to 129.4 Hz and the N values range from 34.2 to 36.6 Hz.

Comparison of the carbonyl complexes 10 and 11 with their respective $\underline{\text{t}}\text{-BuNC}$ derivatives 13 and 14 reveals an increase in $^1\text{J}(\text{Rh-P})$ and $^1\text{J}(\text{Pt-P})$ values. An increase in one-bond metal-phosphorus coupling constants is indicative of an increase of electron density on the metal atom.¹¹ Also, $\underline{\text{t}}\text{-BuNC}$ is a better σ -donor and poorer π -acceptor of electron density than is the terminal CO. Consequently, the electron density at a Rh(I) center bound to $\underline{\text{t}}\text{-BuNC}$ should be greater than the same Rh(I) center bound to a terminal CO. Complexes 13 and 14 exhibit $^1\text{J}(\text{Rh-P})$ values of 148.5 and 146.5 Hz, respectively; this shows an average increase of about 20 Hz compared to the $^1\text{J}(\text{Rh-P})$ values of their parent complexes. Also, a similar comparison of $^1\text{J}(\text{Pt-P})$ values reveals an increase of about 100 Hz. It is suggested that the increase in $^1\text{J}(\text{M-P})$ values ($\text{M} = \text{Pt}, \text{Rh}$) implies that the gain of electron density at the Rh(I) atom due to $\underline{\text{t}}\text{-BuNC}$ substitution is shared by the Pt(II) metal center. The appearance of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes 9-14 resembles the spectra of complexes 1-8 shown and discussed earlier (See Figure 13).

Table VII presents the infrared spectral data for complexes 9-14. Compound 9 exhibits a terminal carbonyl stretch at 1975 cm^{-1} and a terminal cyanide stretch at 2129 cm^{-1} . The cyanide ligand bound to

TABLE VI

 $^{31}\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR COMPLEXES 9-14^{a,b}

Number	Compound	$\delta(\text{Pt-P}), \text{ppm}$	$^1\text{J}(\text{Pt-P}), \text{Hz}$	$\delta(\text{Rh-P}), \text{ppm}$	$^1\text{J}(\text{Rh-P}), \text{Hz}$	N, Hz^c
9	$(\text{CN})_2\text{Pt}(\text{dppm})_2\text{Rh}(\text{CO})\text{Cl}$	-0.90	2529.3	18.62	127.0	44.0
10	$[(\text{CN})\text{Pt}(\mu-35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	0.59	2404.8	19.46	129.4	34.2
11	$[(\text{CN})\text{Pt}(\mu-4835\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	0.72	2397.5	19.29	127.0	34.2
12	$[(\text{CN})\text{Pt}(\mu-345\text{Brpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	0.78	2369.4	19.43	127.0	36.6
13	$[(\text{CN})\text{Pt}(\mu-35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$	-0.43	2500.0	16.57	148.5	54.0
14	$[(\text{CN})\text{Pt}(\mu-4835\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$	-0.43	2500.0	16.60	146.5	51.0

^aAll chemical shifts relative to 85% H_3PO_4 .^b $\delta(\text{Pt-P})$ and $\delta(\text{Rh-P}) \pm 0.1 \text{ ppm}$; $^1\text{J}(\text{Pt-P})$ and $^1\text{J}(\text{Rh-P}) \pm 0.6 \text{ Hz}$.^c $N = 2J(\text{P}_{\text{Pt}}-\text{P}_{\text{Rh}}) + {}^4J(\text{P}_{\text{Pt}}-\text{P}_{\text{Rh}})$.

TABLE VII

IR SPECTRAL DATA FOR COMPLEXES 9-14^a

Number	Compound	$\nu(\text{CO})$, $\nu(\text{CN})$ or $\nu(\text{RNC})^b$, cm^{-1}
9	$(\text{CN})_2\text{Pt}(\text{dppm})_2\text{Rh}(\text{CO})\text{Cl}$	1975(s), 2129(m)
10	$[(\text{CN})\text{Pt}(\mu-35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	1992(s), 2120(m)
11	$[(\text{CN})\text{Pt}(\mu-4\text{B}35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	1991(s), 2123(m)
12	$[(\text{CN})\text{Pt}(\mu-345\text{Brpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	1989(s), 2124(m)
13	$[(\text{CN})\text{Pt}(\mu-35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{RNC})]\text{PF}_6^c$	2141(s)
14	$[(\text{CN})\text{Pt}(\mu-4\text{B}35\text{dmpyz})(\text{dppm})_2\text{Rh}(\text{RNC})]\text{PF}_6^c$	2140(s)

^aComplexes 10-14 exhibit PF_6^- peaks at 839(s) and 557(m) cm^{-1} .^b $\text{RNC} = (\text{CH}_3)_3\text{NC}$.^cIn complexes 13 and 14 only the RNC peak may be accurately assigned.

Pt(II) is less IR active than a carbonyl ligand bound to Rh(I); the CN^- absorption bands are less intense in the IR spectrum. The IR spectra of complexes 10-12 exhibit terminal carbonyl absorption bands in the range 1989-1992 cm^{-1} and terminal cyanide ligand bands between 2124 and 2120 cm^{-1} ; the PF_6^- counterion is also present, leading to peaks at 839 and 557 cm^{-1} . In complexes 10-12 the carbonyl stretching frequency increases relative to that for complex 2. Also, by similar comparison, the cyanide stretching frequency decreases.

An increase in the absorption frequency for the neutral carbonyl ligand implies a loss of electron density from its antibonding molecular orbitals. This is caused by competition for the electron density on the Rh(I) atom with the substituted pyrazolate anion. Thus, the substituted aromatic pyrazolate anion is a weaker π -donor than is the chloride ligand.

A decrease in the absorption frequency for the cyanide ligand implies a gain of electron density in its antibonding molecular orbitals. By a reasoning similar to that employed for the carbonyl ligand case, the cyanide ligand is a better π -acceptor of electron density than the pyrazolate derivatives. Hence, the descending order of π -donor ability among these ligands is $\text{Cl}^- > \text{Xpyz}^- > \text{CN}^-$.

The IR spectrum of complex 13 displays a strong absorption band due to a terminal $\underline{t}$ -BuNC on Rh(I) at 2140 cm^{-1} accompanied by a shoulder at 2120 cm^{-1} . The PF_6^- bands are also present and no terminal carbonyl bands are observed. The $\underline{t}$ -BuNC absorption band is more intense than the CN^- band in the IR spectrum and these bands overlap enough such that the isocyanide band covers the cyanide band. The

shoulder at 2120 cm^{-1} may be the cyanide ligand absorption band since this is the same value for the CN^- stretch in the parent carbonyl complex. However, the CN^- band may be shifted considerably for the complexes containing $t\text{-BuNC}$ and thus the accurate assignment of the cyanide absorption band is quite difficult. Complex 14 exhibits IR data similar in both spectrum appearance and band shifts.

The electronic spectral data for complexes 9-14 is presented in Table VIII. These complexes all show a single absorption band in the range 250-900 nm. For the carbonyl complexes, 9-12, this band 426 and 428 nm with molar absorption coefficients 7400 and $9100\text{ L mol}^{-1}\text{ cm}^{-1}$. The $t\text{-BuNC}$ complexes 13 and 14 show a single transition at 450 nm with molar absorption coefficients of $6100\text{ L mol}^{-1}\text{ cm}^{-1}$ for 13 and $6300\text{ L mol}^{-1}\text{ cm}^{-1}$ for 14.

Complexes 10 and 13 were subjected to elemental analysis for % C and % H. The results are shown in Table V on page 119. Based on the $^{31}\text{P}\{^1\text{H}\}$ NMR and infrared spectral data and the elemental analysis the general structure illustrated in Figure 16 is proposed for complexes 10-14.

TABLE VIII
UV-VIS SPECTRAL DATA FOR COMPLEXES 9-14

Number	Compound	$\lambda_{\text{max. nm}} (\epsilon)^a$
9	$(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$	426(7400)
10	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	427(9100)
11	$[(\text{CN})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	426(8600)
12	$[(\text{CN})\text{Pt}(\mu\text{-345Bpyz})(\text{dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$	428(8700)
13	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\text{dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$	450(6100)
14	$[(\text{CN})\text{Pt}(\mu\text{-4B35dmpyz})(\text{dppm})_2\text{Rh}(\underline{\text{t}}\text{-BuNC})]\text{PF}_6$	450(6300)

^aThe molar absorption coefficient, ϵ , is expressed in
 $\text{L mol}^{-1} \text{ cm}^{-1}$.

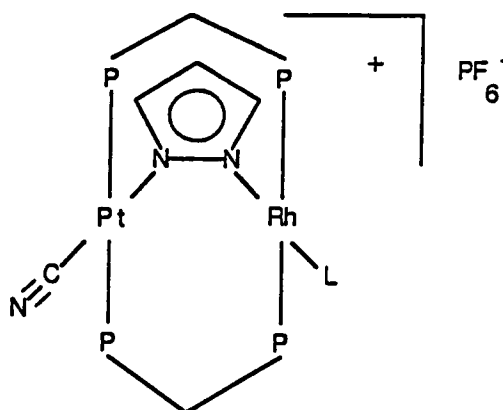


FIGURE 16. Proposed structure for complexes of the type $[(\text{CN})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-Xpyz})\text{Rh}(\text{L})]\text{PF}_6$, 10-14 (Xpyz = pyrazolate derivatives; L = CO or $\underline{t}$ -BuNC)

C. Platinum-Rhodium Complexes With A Terminal Cyanide
Ligand At The Pt Atom and Two Transoid Dapm Ligands

Compound 15, $\text{Pt}(\text{CN})_2(\text{dapm-P})_2$, was prepared by the addition of an ethanol solution of NaCN (2.25 equivalents) to a CH_2Cl_2 /ethanol solution of $\text{cis-PtCl}_2(\text{dapm-P})_2$. After the initial isolation and subsequent recrystallization the yield was 87%.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 15 reveals $\delta(\text{Pt-P})$ at 7.92 ppm and a $^1\text{J}(\text{Pt-P})$ of 2324.2 Hz. The $^1\text{J}(\text{Pt-P})$ value is typical of a trans P-Pt-P arrangement.¹⁶ The infrared spectrum of complex 15 shows a sharp absorption band at 2135 cm^{-1} due to two terminal cyanide ligands. The

electronic spectrum of 15 gave only an undiscernable shoulder at the limit of the CH_2Cl_2 solvent employed. The elemental analysis for % C and % H agree with calculated values. Figure 17A shows the structure of 15.

Complex 15 is the dapm analogue to trans- $\text{Pt}(\text{CN})_2(\text{dppm-P})_2$ initially prepared by Shaw and co-workers.⁵ At 25°C, the dppm Pt monomer exhibits fluxional behavior between the bound and unbound P nuclei as verified by variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy experiments. The Pt monomer cis- $\text{PtCl}_2(\text{dapm-P})_2$ shows no fluxional behavior between the Pt bound P nuclei and the unbound As atoms at various temperatures as proven by $^{31}\text{P}\{^1\text{H}\}$ NMR experiments.¹⁴ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 15 at 25°C is sharp and well defined which suggests either that the static structure shown in Figure 17A is correct or the existence of a rapid equilibrium between bound and unbound P and As nuclei.

Compound 16 is prepared by mixing 15 and one-half an equivalent of $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ in CH_2Cl_2 followed by the addition of diethyl ether until the precipitation of the product is complete. The proposed structure for compound 16 is depicted in Figure 17B.

For complex 16 two structural isomers are possible; these are designated as the head-to-head (HH) isomer where both P nuclei are bound to Pt and the head-to-tail isomer (HT) where one P atom is Pt bound and the other P nucleus is Rh bound. Figure 17B depicts the HH isomer.

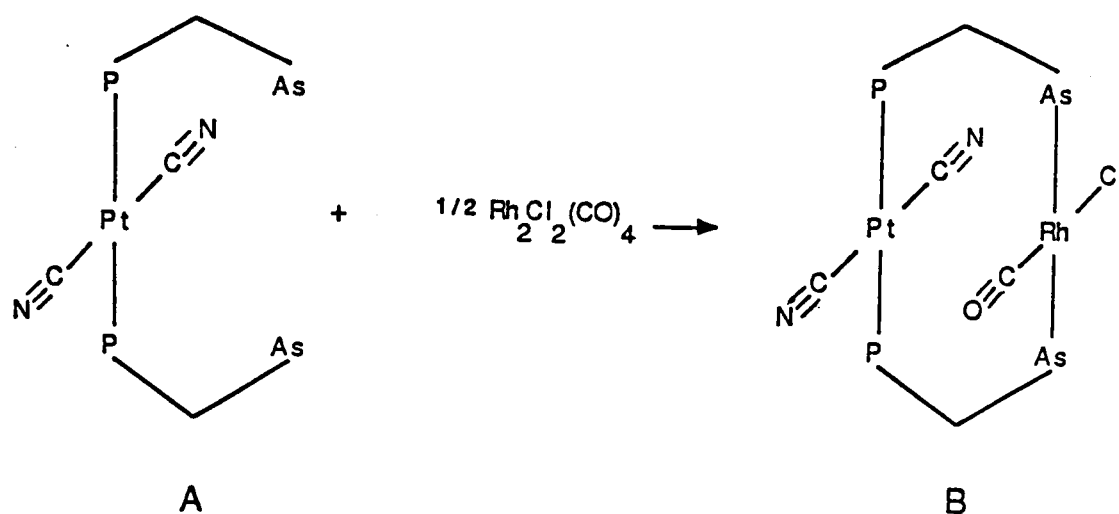


FIGURE 17. Synthesis scheme for production of $(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$, 16

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 16 indicates the presence of both HH and HT isomers and is shown in Figure 18. The HH isomer displays $\delta(\text{Pt-P}) = 3.47$ ppm and $^1J(\text{Pt-P}) = 2509.8$ Hz and the HT isomer has $\delta(\text{Pt-P}) = 1.12$ ppm and $^1J(\text{Pt-P}) = 3037.2$ Hz. The magnitude of both $\delta(\text{Rh-P})$ (25.92 ppm) and $^1J(\text{Rh-P})$ (148.9 Hz) for the HT isomer is similar to that for other complexes containing the trans-RhPAsCl(CO) core (See Table IX).

Complex 16 exhibits absorption bands due to a terminal carbonyl (1973 cm^{-1}) and two equivalent terminal cyanide ligands (2129 cm^{-1}) in its IR spectrum. These values are close to those for the dppm analogue of 16, namely $(\text{CN})_2\text{Pt}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}$, 9.

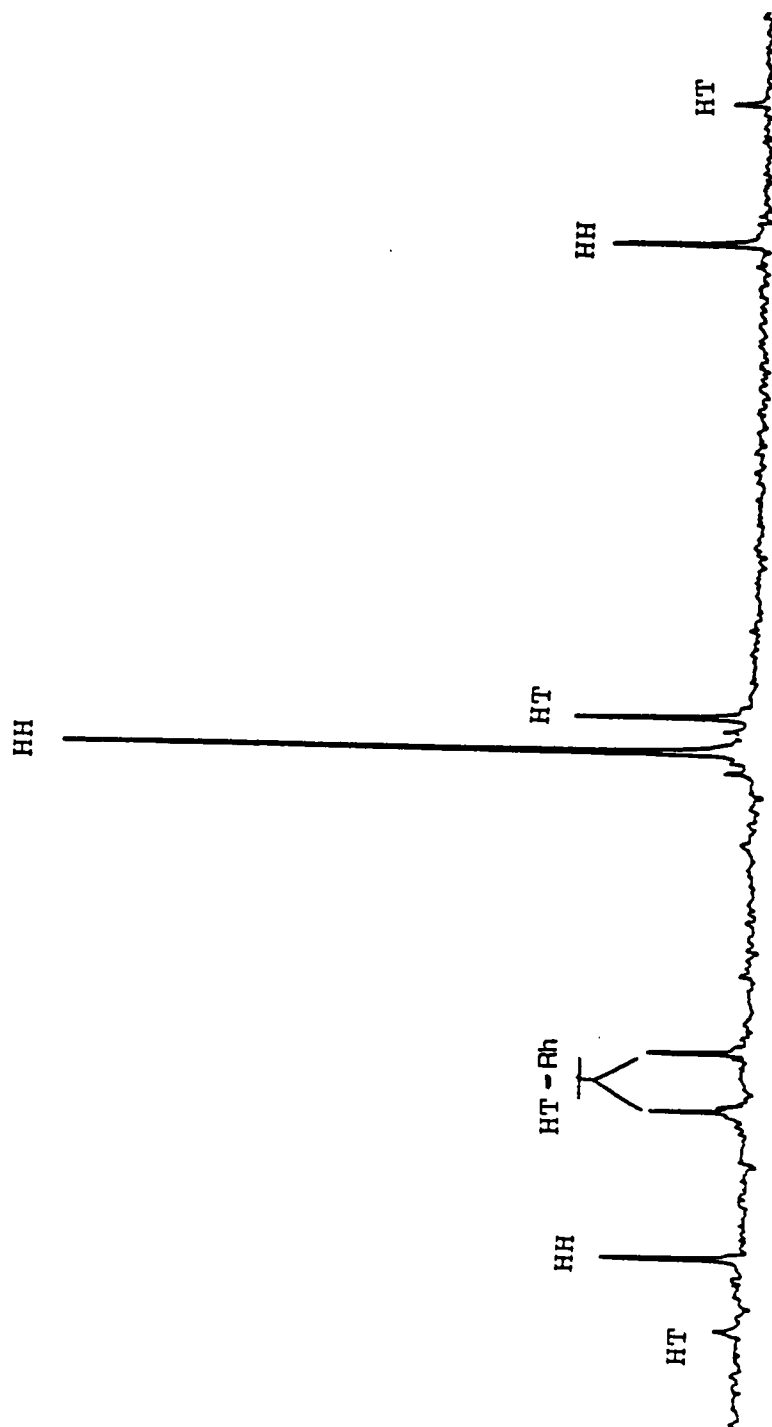


FIGURE 18. $^{31}\text{P}(^1\text{H})$ NMR spectrum of $(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$, 16

TABLE IX

 $^3\text{I}_\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR COMPLEXES 15-18^{a, b}

Number	Compound	$\delta(\text{Pt-P}), \text{ppm}$	$^1\text{J}(\text{Pt-P}), \text{Hz}$	$\delta(\text{Rh-P}), \text{ppm}$	$^1\text{J}(\text{Rh-P}), \text{Hz}$
15	$\text{Pt}(\text{CN})_2(\text{dapm-P})_2$	7.92	2324.2		
16	$(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}(\text{HH})^c$	3.47	2509.8		
16	$(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}(\text{HT})^c$	1.12	3037.1	25.92	148.9
17	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6(\text{HH})^c$	2.46	2392.6		
17	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6(\text{HT})^c$	0.98	2902.8	23.43	149.0
18	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6(\text{HH})^c$	3.20	2483.0		
18	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6(\text{HT})^c$	2.20	3063.0	21.75	168.9

^aAll chemical shifts relative to 85% H_3PO_4 .^b $\delta(\text{Pt-P})$ and $\delta(\text{Rh-P}) + 0.1 \text{ ppm}$; $^1\text{J}(\text{Pt-P})$ and $^1\text{J}(\text{Rh-P}) + 0.6 \text{ Hz}$.^cHH = head-to-head isomer; HT = head-to-tail isomer.

Complex 17 was prepared via the addition of the potassium salt of 3,5-dimethylpyrazole to a yellow suspension of NH_4PF_6 and compound 16 in acetone. The product was isolated from the acetone solution and recrystallized at least four times from CH_2Cl_2 /diethyl ether to remove impurities. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 17 reveals the presence of both HH and HT isomers and is similar in appearance to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 16. Values for $\delta(\text{Pt-P})$, $\delta(\text{Rh-P})$, $^1\text{J}(\text{Pt-P})$ and $^1\text{J}(\text{Rh-P})$ were as anticipated and these values are given in Table IX.

It is worth comparing the IR spectral data for compound 17 with that of the dppm analogue, 10. For complex 17 the terminal carbonyl ligand exhibits an absorption band at 1991 cm^{-1} and the terminal cyanide stretch occurs at 2120 cm^{-1} . In relation to its parent complex, 16, the carbonyl band is shifted to higher energy and the cyanide band is shifted to lower energy for complex 17. The dppm analogues of 16 and 17 (namely 9 and 10, respectively) show the same trend in the terminal ligand shifts. The IR spectrum of 17 also shows the presence of PF_6^- . The IR spectral data are presented in Table X.

Complex 18 is synthesized by the addition of one equivalent of *t*-BuNC to 17. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 18 resembles that of 16 and exhibits the presence of HH and HT isomers. It should be noted that the $^1\text{J}(\text{Rh-P})$ and $^1\text{J}(\text{Pt-P})$ values for 18 are larger than those of the parent carbonyl complex, 17. This same trend was noticed in comparing the dppm analogues of 17 and 18, namely the carbonyl complexes 10 and 11 with their respective *t*-BuNC complexes 13 and 14.

TABLE X
IR SPECTRAL DATA FOR COMPLEXES 15-18

Number	Compound	$\nu(\text{CO})$, $\nu(\text{CN})$ or $\nu(\text{RNC})^b$, cm^{-1}
15	$\text{Pt}(\text{CN})_2(\text{dapm-P})_2$	2135(s)
16	$(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$	1973(s), 2129(m)
17	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6^a$	1991(s), 2120(m)
18	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{RNC})]\text{PF}_6^{a,c}$	2140(s)

^aComplexes 17 and 18 exhibit PF_6^- peaks at 839(s) and 557(m) cm^{-1} .

^b $\text{RNC} = (\text{CH}_3)_3\text{NC}$.

^cIn complex 18 only the RNC peak may be accurately assigned.

The IR spectrum of complex 18 reveals a terminal t-BuNC absorption band at 2140 cm^{-1} which apparently completely masks the terminal cyanide absorption band. Also, PF_6^- peaks are indicated.

Unlike their dppm analogues, complexes 16-18 exhibit no phosphorus-phosphorus coupling in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. This lack of coupling implies that second-order effects are small in the HT isomer. In the case of the HT isomer long-range four-bound phosphorus-phosphorus coupling must be negligible.

The UV-Vis data for compounds 16-18 are given in Table XI. These complexes exhibit a single absorption band in the range 300-900 nm. The transition bands for 16 and 17 respectively occur at 416 nm and 417 nm. Expectedly, the absorption band for 18 occurs at a lower energy than from 16 or 17, 451 nm. the molar absorption coefficients for these complexes range from $7200\text{-}8100\text{ L mol}^{-1}\text{ cm}^{-1}$. Similar trends were noticed in the UV-Vis data for the dppm analogues of complexes 16-18. The absorption bands for the t-BuNC containing species of both the dapm and dppm complexes are of lower energy than the bands of their parent carbonyl complexes. Also, the molar absorption coefficients are in nearly the same range for both the carbonyl and the t-BuNC complexes using either dapm or dppm as the transoid ligands.

Figure 19 illustrates the HT isomer of the proposed general structure for complexes 17 and 18. This structure is based upon the spectral data and upon the correlation between the calculated versus found values of % C and % H for compounds 17 and 18.

TABLE XI

UV-VIS SPECTRAL DATA FOR COMPLEXES 16-18

Number	Compound	$\lambda_{\text{max, nm}} (\epsilon)$
16	$(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$	416(7500)
17	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\text{dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$	417(8100)
18	$[(\text{CN})\text{Pt}(\mu\text{-35dmpyz})(\text{dapm})_2\text{Rh}(\text{t-BuNC})]\text{PF}_6$	452(7200)

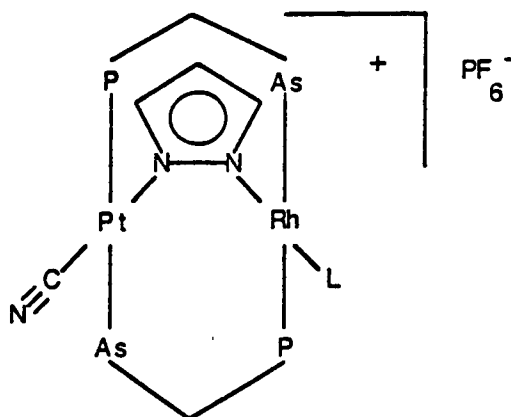


FIGURE 19. Proposed structure of the HT isomer of $[(\text{CN})\text{Pt}(\mu\text{-dapm})_2(\mu\text{-35dmpyz})\text{Rh}(\text{L})]\text{PF}_6$ ($\text{L} = \text{CO}$, 17; $\text{L} = t\text{-BuNC}$, 18)

D. Synthesis And Reactivity of $[\text{cis-ClPt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$

Complex 19, $\text{cis-PtCl}_2(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})\text{Cl}$, was initially characterized by Balch and coworkers¹³ in 1984. Mixing $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with $\text{cis-PtCl}_2(\text{dapm})_2$ in methylene chloride solution at -5°C produces 19 as orange crystals upon addition of methanol. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 19 exhibits $^1\text{J}(\text{Pt-P}) = 3826$ Hz, which is typical for a cis-P-Pt-P unit, and $\delta(\text{Pt-P}) = 14.3$ ppm. The infrared spectrum of 19 shows an absorption band at 1987 cm^{-1} , which is typical for a CO ligand terminally bound to a Rh(I) atom.

An X-ray crystal structure analysis of 19 revealed the Pt-Rh separation to be $3.043\text{ \AA}$ which is longer than the value of $2.6\text{ \AA}$ expected for a Pt-Rh single bond.¹⁴ The complex contains two planar d^8 metal centers; one is a $\text{trans-Rh}(\text{CO})\text{ClAs}_2$ unit and the other is a cis-

PtCl_2P_2 unit. The two metal centers are connected by two transoid dapm ligands. A perspective drawing of compound 19 is shown in Figure 20.

Refluxing a chloroform solution of 19 for two hours produces several products; (1) an isomer of 19, trans- $\text{ClPt}(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})\text{Cl}$, (2) both HH and HT isomers of $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dapm})_2$; (3) the Pt monomer $\text{PtCl}_2(\text{dapm-P:As})$ and (4) the starting material, compound 19. The trans isomer of 19 was separated from the mixture by multiple recrystallizations from methylene chloride/diethyl ether to produce the pure product in 19% yield.¹⁶ A drawing of trans- $\text{ClPt}(\mu\text{-dapm})_2\text{-trans-Rh}(\text{CO})\text{Cl}$ is shown in Figure 21.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the trans isomer of 19 (hereafter known as trans-Pt-trans-Rh) exhibits $\delta(\text{Pt-P}) = 16.4$ ppm. The value for $^1\text{J}(\text{Pt-P}) = 2280$ Hz is in the range for a trans-P-Pt-P unit.¹⁶ The infrared spectrum shows a terminal carbonyl peak at $2006(\text{w})\text{ cm}^{-1}$. Generally terminal carbonyl groups bound to Rh(I) have stretching frequencies in the range $1950\text{-}2000\text{ cm}^{-1}$.¹² Oxidation of the Rh(I) atom to Rh(II) usually raises the carbonyl stretch values above 2020 cm^{-1} .^{10,11} Thus Balch originally suggested that the trans isomer of 19 retained the Rh(I) and Pt(II) oxidation states.¹³

However, an X-ray crystal structure analysis of trans-Pt-trans-Rh reveals a Pt-Rh separation of $2.692\text{ \AA}$. This separation is in the range for Pt-Rh single bond lengths (Figure 21 shows a Pt-Rh bond). Thus, the thermal isomerization of 19 results in the transfer of one chloride ligand from Pt(II) to Rh(I) and a decrease in the Pt-Rh separation by $0.35\text{ \AA}$ forming the Pt-Rh single bond. As a result of the chloride transfer, the two P nuclei of the dapm ligands on Pt assume a trans

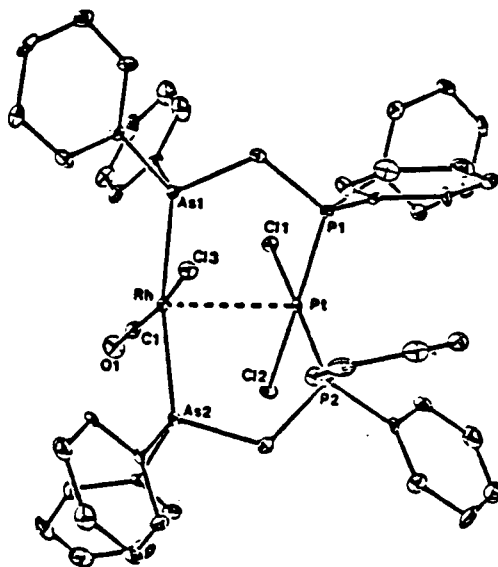


FIGURE 20. A perspective drawing of cis- $\text{Cl}_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$, 19

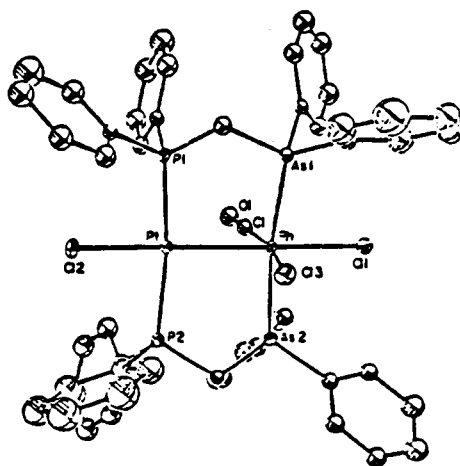


FIGURE 21. A perspective drawing of trans- $\text{PtCl}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}_2$,
the trans isomer of 19

orientation. Formally, the thermal isomer of 19 contains a Pt(I) and a Rh(II) center. However, the carbonyl stretching frequency for trans-Pt-trans-Rh is unexpectedly low for a terminal carbonyl on a Rh(II) center.

The X-ray crystal structure reveals that the Rh(II) bound carbonyl is tilted toward the trans-PtClP₂ unit enough to allow for weak π -donation of electron density to the Pt(II) atom by the carbonyl ligand. This perturbation is significant enough to lower the carbonyl stretch by 20-40 cm⁻¹.

The interest in preparing a pyrazolate derivative of 19 was twofold. First, to determine if the PtP₂Cl unit retains its cis geometry upon addition of the pyrazolate ligand. Second, if the cis-geometry was retained, then attempt to prepare the trans isomer. It was hoped that a bridging pyrazolate ligand might facilitate a cis-to-trans isomerization.

Compound 20 was prepared by mixing a 1:1 mole ratio of NH₄PF₆ and 19 in acetone at 0°C followed by the addition of one mole of the potassium salt of 3,5-dimethylpyrazole. After stirring the mixture for 20 minutes at 0°C, the acetone solvent was removed at room temperature using a rotary evaporator. The light yellow product was purified by recrystallization from CH₂Cl₂ by addition of 50:50 diethyl ether:hexanes until precipitation of the product was complete. The yield was 70%.

The infrared spectrum of compound 20 shows an absorption band at 1979 cm⁻¹, typical of a terminally bound CO ligand on Rh(I). Also, the PF₆⁻ counterion was indicated by peaks at 839(s) and 557(m) cm⁻¹. The

elemental analysis shows that the %C and %H correspond well with the calculated values based on the formula $[\text{ClPt}(\mu\text{-}3,5\text{dmpyz})(\mu\text{-dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$ (Table V, p 119).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 20 is shown in Figure 22. It is evident from this spectrum that two types of phosphorus nuclei exist in this compound and that these P nuclei are bound to Pt(II) in a cis orientation. The two P resonances exhibited are typical of P bound to Pt in that they each show a major resonance and two symmetrically placed satellite resonances. The intense resonances and their corresponding satellite resonances are labelled as either A or B. No evidence exists, particularly from the $^{31}\text{P}\{^1\text{H}\}$ NMR, for the presence of a Rh bound P atom. Thus only the HH-Pt isomer exists.

At each resonance, A and B, two-bond phosphorus-phosphorus coupling is exhibited and $^2\text{J}(\text{P}_\text{A}\text{-P}_\text{B}) = 19.5$ Hz. Resonance A has $\delta(\text{Pt-P}) = 7.04$ ppm and $^1\text{J}(\text{Pt-P}) = 4050$ Hz; this $^1\text{J}(\text{Pt-P})$ value is typical of related complexes with a cis-P-Pt-P arrangement with a chloride ligand trans to the P atoms²⁰ (e.g. complex 19 (3826 Hz) and cis- $\text{PtCl}_2(\text{dapm-P})_2$ (3875 Hz)). Hence, P_A and P_B are in a cis orientation about the Pt atom. Resonance B shows $\delta(\text{Pt-P}) = -0.03$ ppm. The value of $^1\text{J}(\text{Pt-P}) = 3003$ Hz does not fall within the range of observed values for chloride containing cis-P-Pt-P units. However, the nature of the coordinating ligand trans to the P atom can have a pronounced effect on $^1\text{J}(\text{Pt-P})$.²⁰ Notice that the value of $^1\text{J}(\text{Pt-P})$ for resonance A is 1047 Hz larger than the corresponding value for resonance B. Hence, resonance A is most likely due to the P atom trans to the chloride ligand and resonance B is assigned to the P atom trans to the aromatic N atom of

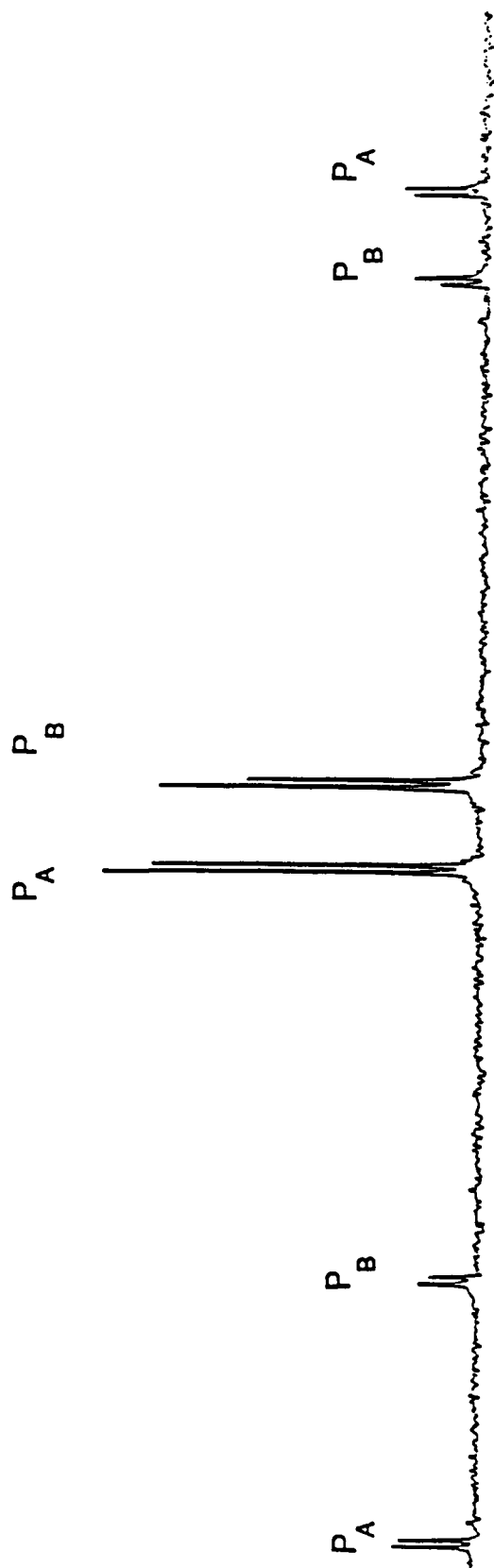


FIGURE 22. $^{31}\text{P}(\text{}^1\text{H})$ NMR spectrum of $[\text{cis-ClPt}(\mu\text{-35dmpyz})_2\text{Rh(CO)}]\text{PF}_6 \cdot 20\text{H}_2\text{O}$

the 3,5-dimethylpyrazolate ligand. Figure 23 illustrates the proposed structure of compound 20 as deduced from the data presented. Also, Figure 23 shows the assigned resonances of the P nuclei.

Refluxing the light yellow chloroform solution of 20 for two hours produced no color change. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the refluxed solution revealed the formation of the trans isomer of 20 by the appearance of a new peak between the resonances A and B of compound 20. (See Figure 24.) For this new resonance $\delta(\text{Pt-P})$ (6.37 ppm) and the value of $^1\text{J}(\text{Pt-P})$ (2598 Hz) suggests a trans P-Pt-P orientation. Also no evidence was present in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for a Rh bound P atom. Thus the new complex exists solely as the HH-Pt isomer. Based on the $^1\text{J}(\text{Pt-P})$ value for the new peak, the new complex is most likely

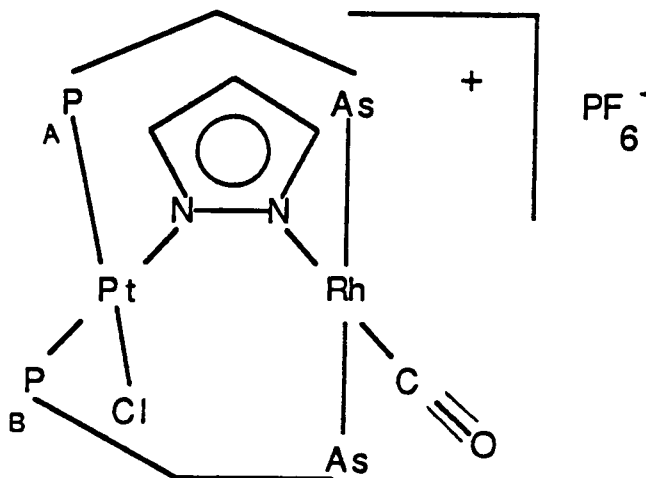


FIGURE 23. Proposed structure of [cis-ClPt(μ -35dmpyz)(μ -dapm)₂Rh(CO)]PF₆, 20

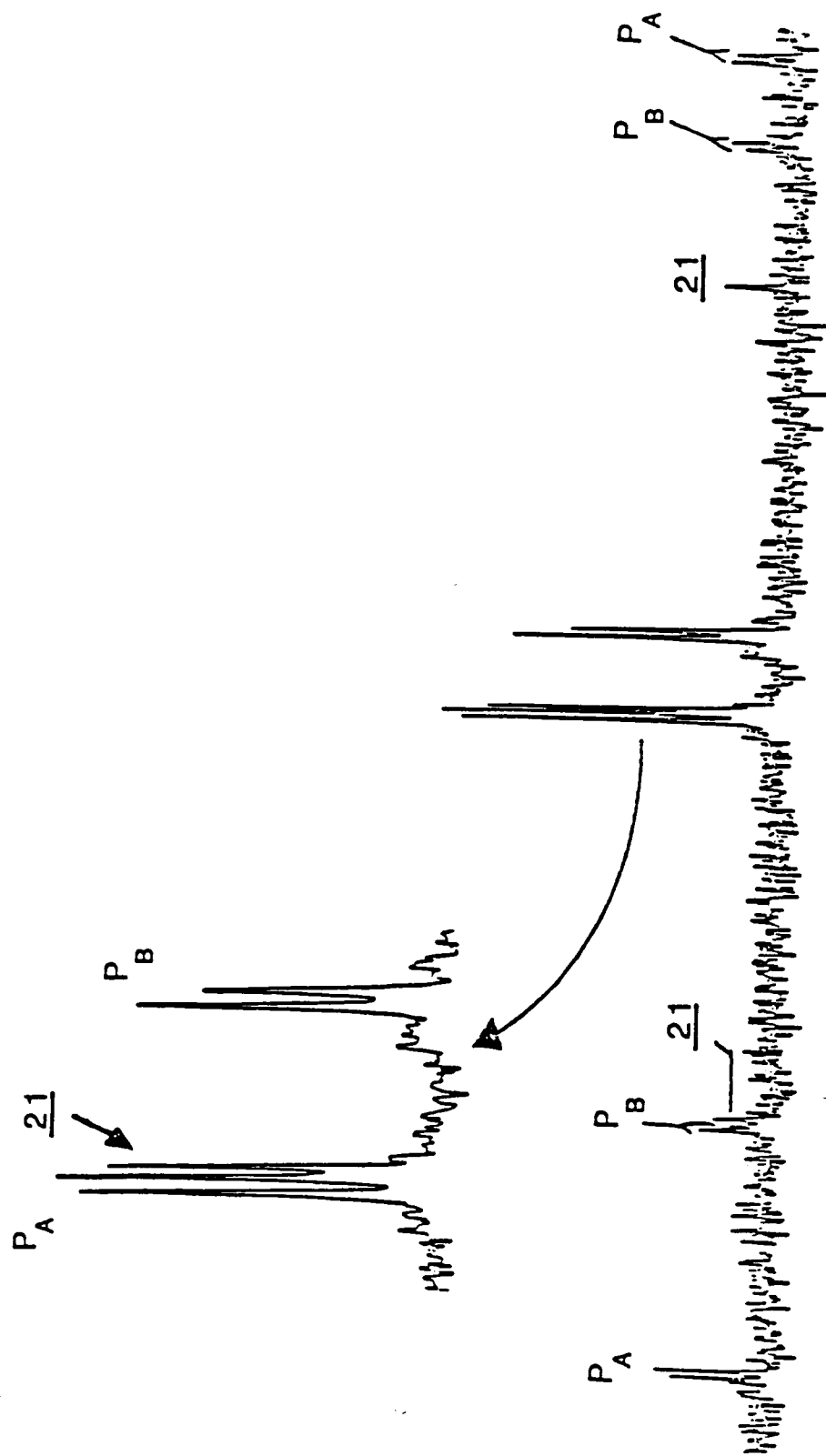


FIGURE 24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reflux solution of $[\text{cis-ClPt}(\mu\text{-35dmpyz})(\mu\text{-dapm})_2\text{Rh(CO)}]\text{PF}_6$

the trans-P-Pt-P isomer of 20, formulated as [trans-ClPt(μ -35dmpyz)(μ -dapm)₂-trans-Rh(CO)]PF₆ complex 21. The ³¹P NMR spectral data for complexes 19-21 are presented in Table XII.

Subsequent refluxing of the ³¹P(¹H) NMR sample for periods of time up to twelve hours did not significantly alter the relative amounts of 20 and 21 present. Also, from the ³¹P(¹H) NMR spectrum of this refluxed solution it appears that the conversion of 20 to 21 is relatively clean in comparison to the conversion of 19 to its trans isomer as performed by Balch.¹⁶ Figure 24 shows the resonances from the ³¹P(¹H) NMR spectrum of the refluxed solution containing compounds 20 and 21.

The infrared spectrum of the refluxed solution reveals a broad absorption band centered at 1980 cm⁻¹. This value is consistent with a terminal CO on a Rh(I) center. The carbonyl absorption bands for 20 and 21 are very similar in shift such that the two could not be distinguished in the infrared. The carbonyl stretch of 20 was obtained before refluxing. The infrared spectral data for complexes 19-21 are presented in Table XIII.

The infrared data exhibited no evidence for either the formation of a Pt-Rh single bond or any significant oxidation of the Rh(I) center in complex 21. This result is unlike that obtained for the trans isomer of 19 mentioned previously. Due to the small amount of material available isolation attempts of 21 from 20 proved futile. The proposed structure for compound 21 is illustrated below in Figure 25.

TABLE XII

 $^{31}\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR COMPLEXES 19-21^a

Number	Complex	$\delta(\text{Pt-P})\text{ppm}$	$^1\text{J}(\text{Pt-P})\text{Hz}$
19	cis-Cl ₂ Pt(μ -dapm) ₂ Rh(CO)Cl	14.31	3825.7
	trans-ClPt(μ -dapm) ₂ Rh(CO)Cl ₂	16.40 ^d	2880 ^d
20	[cis-ClPt(μ -35dmpyz)(dapm) ₂ Rh(CO)]PF ₆ ^b		
	P trans to Cl ⁻ , P _A	7.04	4050.2
	P trans to Npyz, P _B ^c	-0.02	3003.0
21	[trans-ClPt(μ -35dmpyz)(dapm) ₂ Rh(CO)]PF ₆	6.37	2597.7

^aAll chemical shifts relative to 85% H₃PO₄.^bFor complex 20, $^2\text{J}(\text{P}_\text{A}-\text{P}_\text{B}) = 19.5$ Hz.^cNpyz = N atom of the bridging 3,5dimethylpyrazolate anion.^dValues for $\delta(\text{Pt-P})$ and $^1\text{J}(\text{Pt-P})$ are from reference 16.

TABLE XIII
IR SPECTRAL DATA FOR COMPLEXES 19-21

Number	Complex	$\nu(\text{CO}), \text{cm}^{-1}$
19	$\text{cis-Cl}_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$	1987
	$\text{trans-ClPt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}_2$	2006 ^a
20	$[\text{cis-ClPt}(\mu\text{-35dmpyz})(\text{dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$	1979 ^b
21	$[\text{trans-ClPt}(\mu\text{-35dmpyz})(\text{dapm})_2\text{Rh}(\text{CO})]\text{PF}_6$	1980 ^b

^aTaken from reference 16.

^bComplexes 20 and 21 show PF_6^- peaks at 839(s) and 557(m) cm^{-1} .

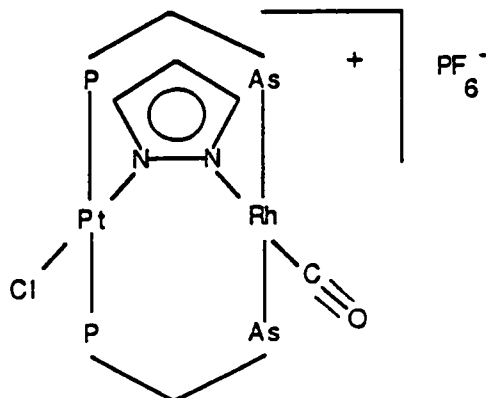


FIGURE 25. The proposed structure of [trans-ClPt($\mu\text{-35dmpyz}$)($\mu\text{-dapm}$)₂Rh(CO)]PF₆, 21

CHAPTER 2.4

CONCLUSIONS

In this work novel platinum-rhodium A-frame complexes employing the symmetrical ligand bis(diphenylphosphino)methane, dppm, as the bridging transoid ligands with either an acetylide or a cyano group terminally bound to the Pt(II) atom, and either a carbon monoxide or a tertiary butylisocyanide ligand terminally bound to the Rh(I) atom, and with a pyrazolate derivative in the bridgehead position have been prepared and successfully characterized via various spectroscopic techniques.

In a structurally similar PtRh A-frame compound two (diphenylarsino)(diphenylphosphino)methane ligands were employed as the transoid ligands with two terminal cyano groups at the Pt(II) atom and a carbon monoxide and a chloride terminally bound at the Rh(I) atom. This complex was formulated as $(\text{CN})_2\text{Pt}(\mu\text{-dapm})_2\text{Rh}(\text{CO})\text{Cl}$, 16 and served as the parent compound in the synthesis of complexes of the type $[(\text{CN})\text{Pt}(\mu\text{-dapm})_2(\mu\text{-35dmpyz})\text{Rh}(\text{L})]\text{PF}_6$ ($\text{L} = \text{CO}$, 17; $\text{L} = t\text{-BuNC}$, 18).

Finally, a PtRh complex formulated as $[\text{cis-ClPt}(\mu\text{-dapm})_2(\mu\text{-35dmpyz})\text{Rh}(\text{CO})]\text{PF}_6$, 20, was synthesized using cis-Cl₂Pt($\mu\text{-dapm}$)₂Rh(CO)Cl, 19, and the potassium salt of 35dmpyzH. Refluxing a chloroform solution of 20 for several hours resulted in the formation of [trans-ClPt($\mu\text{-dapm}$)₂($\mu\text{-35dmpyz}$)Rh(CO)]PF₆, 21, the trans isomer of 20. The thermally induced cis-to-trans isomerization of a P-Pt-P unit is not unprecedented. In 1985 Balch demonstrated the cis-to-trans isomerization of complex 19. However, the thermally induced

isomerization of 19 resulted in several side products and gave the desired product in only 19% yield. Although complex 21 could not be isolated from 20 due to the small amounts of 20 available, it is apparent from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reflux solution of 20 and 21 that no other phosphorus containing side-products were generated.

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VITA

Jeffrey Craig DePriest, the first of five children, was born in Hyattsville, Maryland on October 29, 1962. In Stanley, Virginia he attended Stanley Elementary School and graduated from Page County High School in May 1980. He received a B.S. in Chemistry in May 1984 from Bridgewater College. In September 1984 he accepted a Graduate Research/Teaching Assistantship from The University of Tennessee, Knoxville. In June 1986 he began the research project presented in this thesis. He was awarded the M.S. degree in Chemistry from The University of Tennessee, Knoxville in December 1988.