

an enolate intermediate to which a proton is added. It would be presumed that this protonation would result in racemization in the absence of any steric hindrance.

An inspection of Figure 5 shows that there is no steric hindrance to the approach of a proton to C(10), although experimental results indicate a proton adds preferentially from the top of this figure, inverting the configuration. It might be thought that either O(3) of the decarboxylation product (CO₂) is slow to leave (compared to the time for protonation) or that another molecule, perhaps water, is hydrogen bonded to N(3) at this site, partially blocking rapid protonation. Figure 5 shows that pathway of a proton to give inversion of configuration is less obstructed.

E. Summary. In conclusion we have found (1) that three-point attachment provides a sufficient condition for chiral recognition of "equivalent" groups in a symmetrical, prochiral molecule, (2) that the product distribution upon addition of α,α -aminomethylmalonate (or any α -amino acid) to a Co(III) tetramine can be explained by invoking a trans intermediate, and (3) that resolution of CD spectra into component Cotton

effects can provide useful information as to the chirality of asymmetric centers induced on complexation. The fact that complexing to an agent with two open binding sites may derive stereospecific recognition *via* the presence of a third, hydrogen bonding, site opens new avenues for the creative design of template molecules.

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Supplementary Material Available. A listing of structure factor amplitudes for the α,α -aminomethylmalonate complex will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5741.

Stereochemical Rigidity in ML₅ Complexes. II. Preparations and Intermolecular Exchange of Cationic ML₅ Complexes of Cobalt(I), Rhodium(I), Iridium(I), Nickel(II), Palladium(II), and Platinum(II)

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Abstract: A series of complexes of the form ML₅ⁿ⁺(X⁻)_n have been synthesized (M = Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II); L = phosphite). The Pd(II) and Pt(II) species are novel in that they represent the first ML₅ compounds for these metals; complexes in this class have been described previously for the other four metals. We report new preparative techniques for Co(I) and Ir(I) and extend the scope of known complexes for several of the metals. The steric range within which ML₅ species may be prepared is defined in connection with the equilibrium ML₅ ⇌ ML₄ + L and the steric size of L. Intermolecular exchange effects associated with the above equilibrium are analyzed. Preparative problems associated with transesterification are discussed.

The question of stereochemistry and fluxional behavior in five-coordinate transition metal complexes has been a problem of considerable interest since the early nmr experiments of Cotton, *et al.*¹ Recently we have reported the first nmr evidence for stereochemical rigidity and trigonal bipyramidal equilibrium stereochemistry for complexes of the form RhL₅⁺X⁻ (L = phosphite)^{2,3} together with a detailed line shape analysis indicating that the permutational nature of the exchange process² is consistent with the Berry mechanism.⁴ As a continuing part of this investigation a substantial

number of ML₅ complexes of Co(I), Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II) have been prepared; some preliminary results with regard to stereochemistry and stereochemical rigidity in these complexes have been communicated.⁵ The present paper describes the preparation of the ML₅ⁿ⁺(X⁻)_n complexes together with an analysis of intermolecular exchange in Rh[P(OCH₃)₃]₅⁺B(C₆H₅)₄⁻.

Prior to this work, the only well-established five-coordinate species of the type ML₅ for platinum was Pt(SnCl₃)₅³⁻;⁶ there appeared to be no well-characterized ML₅ species for Pd. The PtL₅²⁺ and PdL₅²⁺ phosphite complexes described here are therefore signif-

(1) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

(2) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).

(3) P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 7272 (1973).

(4) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(5) J. P. Jesson and P. Meakin, *Inorg. Nucl. Chem. Lett.*, **9**, 1221 (1973).

(6) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stoberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965).

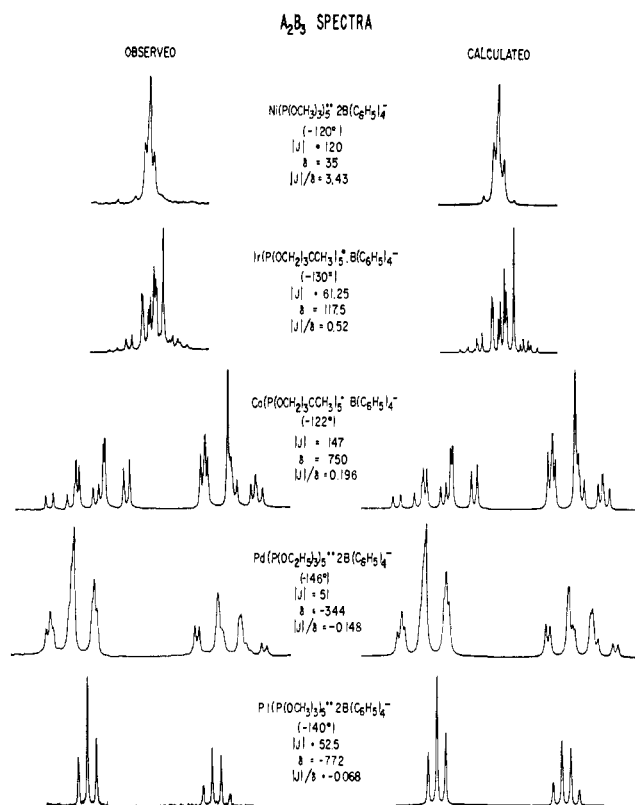
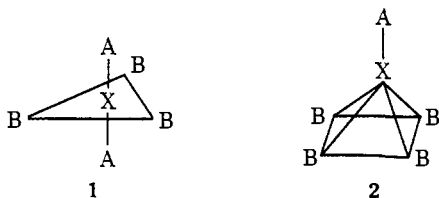


Figure 1. The $^{31}\text{P}\{^1\text{H}\}$ spectra for a variety of ML_5 complexes together with simulations using an A_2B_3 model. The spin-spin coupling constants are in hertz and the chemical shift differences are in hertz at 36.43 MHz.

icant extensions of the known scope of five-coordination. Transesterification reactions occur rather easily with most of the compounds and can cause preparative problems since the effects are not always apparent from chemical analysis. ^{31}P nmr provides a clear indication of when such side reactions have occurred.

Results

Stereochemistries of ML_5 Complexes. The slowing down of the intramolecular exchange allows one to determine unambiguously for the first time the stereochemistry of a class of ML_5 species in solution. Two idealized geometries (the trigonal bipyramid **1** and the square pyramid **2**) have been established for ML_5 species



in the solid state using X-ray techniques. Configuration **1** would give rise in the slow exchange limit to A_2B_3 $^{31}\text{P}\{^1\text{H}\}$ patterns for $\text{X} = \text{Co}$, Ir , Ni , and Pd , to $\text{A}_2\text{B}_3\text{X}$ patterns for $\text{X} = \text{Rh}$ (^{103}Rh is 100% abundant with $I = 1/2$), and to a superposition of A_2B_3 (67% of the intensity) and $\text{A}_2\text{B}_3\text{X}$ (33% of the intensity) for $\text{X} = \text{Pt}$ (^{195}Pt is 33% abundant). Configuration **2** would give AB_4 patterns for $\text{X} = \text{Co}$, Ir , Ni , and Pd , to AB_4X patterns for $\text{X} = \text{Rh}$ and to a combination of AB_4 and AB_4X patterns for $\text{X} = \text{Pt}$. For both cases, the limiting fast exchange spectra would be A_5 or A_5X patterns.

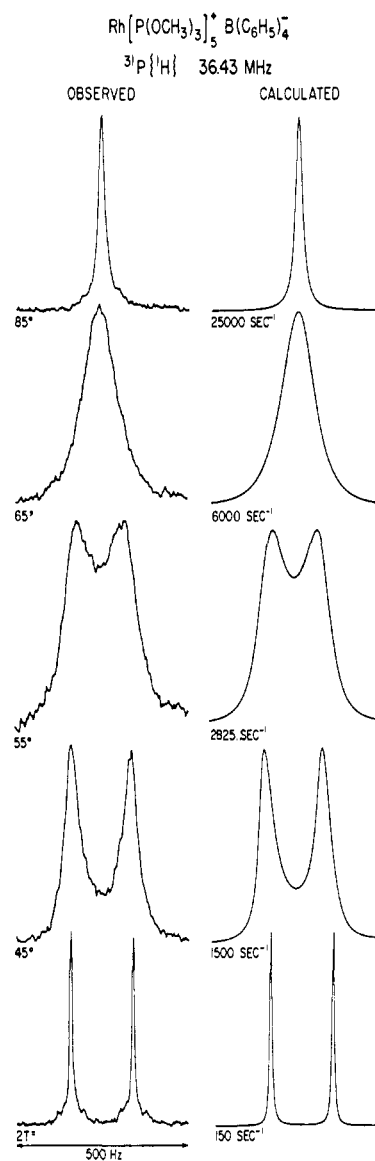


Figure 2. Observed and calculated $^{31}\text{P}\{^1\text{H}\}$ nmr spectra for a solution of $\text{Rh}[\text{P}(\text{OCH}_2\text{CH}_3)_3]^+\text{B}(\text{C}_6\text{H}_5)_4^-$ (0.125 M) in acetonitrile over the temperature range for which intermolecular exchange effects can be observed.

For all the molecules studied in the present paper slow exchange limit spectra have been observed and they all correspond to the trigonal bipyramidal structure **1**. A series of low temperature limit spectra encompassing a wide range of J/δ are shown in Figure 1 together with simulations using an A_2B_3 model. It seems likely that the trigonal bipyramidal geometry will prevail for most d^8 ML_5 complexes in solution and that deviations from this stereochemistry in the solid state can often be ascribed to crystal packing effects. It should be remembered that the energy difference between configurations **1** and **2** is commonly less than 4 kcal mol⁻¹ (assuming that intramolecular exchange takes place *via* the Berry process⁴ in which case **1** is the ground state and **2** the transition state).

Rapid intramolecular exchange occurs for all the ML_5 complexes at higher temperatures, and the expected A_5 or A_5X fast exchange limit spectra are observed. At still higher temperatures ligand dissociation (eq 1) causes a collapse of the A_5X doublets into a single

Table I. Chemical Shifts and Coupling Constants for ML_5 Complexes at the Temperatures Noted

Complex	δA^a	δB^a	$ J_{AB} $	J_{AX}	J_{BX}	Temp, °C
Co⁺						
$P(OCH_3)_3$	-11.5	-5.0	148			-138
$P(OC_2H_5)_3$	-4.3	-10.4	148			-138
$P(OCH_2)_3CCH_3$	-8.6	11.9	147			-122
Rh⁺						
$P(OCH_3)_3$	11.0	-3.7	68	±143	±206	-136
$P(OC_2H_5)_3$	18.1	-0.6	68	±143	±205	-131
$P(OC_4H_9)_3$	30.8	18.9	70	±142	±205	-113
$P(OCH_2)_3CCH_3$	14.8	25.4	69.5	±140	±208	-127
$P(OCH_2)_3CC_2H_5$	13.6	24.3	69.5	±140	±208	-137
$P(OCHCH_2)_3$	-5.0	-0.9	69.5	±141	±207.5	-92
Ir⁺						
$P(OCH_3)_3$	55.8	26.9	59			-152
$P(OC_2H_5)_3$	64.4	34.1	60			-130
$P(OC_4H_9)_3$	61.4	43.6	59.5			-77
$P(OCH_2)_3CCH_3$	54.0	57.2	59			-109
Ni²⁺						
$P(OCH_3)_3$	28.5	29.4	120.0			-120
$P(OCH_2)_3CCH_3$	21.4	36.8	121.0			-123
$P(OCH_2)_3CC_2H_5$	23.1	38.7	119.5			-125
$P(OCHCH_2)_3$	9.7	17.1	117.0			-109
Pd²⁺						
$P(OCH_3)_3$	40.2	30.4	48.5			-157
$P(OC_2H_5)_3$	47.7	38.2	51.0			-146
$P(OCH_2)_3CCH_3$	40.6	47.2	~50.0			-160
Pt²⁺						
$P(OCH_3)_3$	79.8	58.6	52.5	±2840	±4100	-140
$P(OC_2H_5)_3$	81.9	63.4	47.0	±2845	±4060	-130
$P(OCH_2)_3CCH_3$	75.4	72.0	52.0	±2744	±4123	-135

^a Parts per million upfield from $P(OCH_3)_3$ in $CHClF_2$.

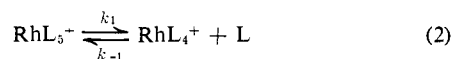


line due to loss of coupling in the bond breaking process or a broadening of the A_5 spectra in the presence of added ligand due to an averaging of free and bound ligand resonances.

The chemical shifts and coupling constants for the $^{31}P\{^1H\}$ spectra of the ML_5 species are given in Table I. It should be noted that in some cases the chemical shifts and chemical shift separations are markedly temperature dependent³ so that comparisons of the parameters can only be made at the temperatures noted. The coupling constants are insensitive to temperature variation.

Intermolecular Exchange in the $Rh[P(OCH_3)_3]_5^+ - Rh[P(OCH_3)_3]_4^+ - P(OCH_3)_3$ System. The $^{31}P\{^1H\}$ nmr spectrum for solutions of $Rh[P(OCH_3)_3]_5^+ B(C_6H_5)_4^-$ in acetonitrile near room temperature consists of a sharp doublet ($J(^{31}P-^{103}Rh) = 182$ Hz). As the temperature is raised, the doublet begins to broaden and eventually collapses into a sharp single line (Figure 2). The loss of the $^{103}Rh-^{31}P$ coupling in the high temperature limit is characteristic of an intermolecular process involving breaking of the phosphorus-rhodium bonds.

Figure 3 shows the temperature-dependent $^{31}P\{^1H\}$ nmr spectra for a 0.125 M solution of $Rh[P(OCH_3)_3]_5^+ B(C_6H_5)_4^-$ in CH_3CN to which 0.5 mol l^{-1} of $P(OCH_3)_3$ has been added. Since addition of free ligand does not markedly accelerate the rate of exchange, the process must be dissociative (eq 2) with the equilibrium far to the left.



The calculated spectra shown in the right-hand column of Figure 2 were obtained assuming that the concentrations of RhL_4^+ and L are negligible in the RhL_5^+

solution. Since only one out of five possible ligands dissociates in a single dissociation step, and since 50% of these will return to a RhL_4^+ cation with the same component of ^{103}Rh spin angular momentum as that from which it dissociated, the nmr line shapes can be obtained using the two-site (one spin) model shown in Figure 4. (At each site four-fifths of the ligands do not dissociate in a single event thus retaining their coupling to the ^{103}Rh spin and one-tenth of the ligands return to a ^{103}Rh spin with the original orientation for a total of $4/5 + 1/10 = 9/10$; only one-tenth of the total appears at the site with opposite orientation of the ^{103}Rh spin.)

Similarly, the nmr line shapes for the $RhL_5^+ - L$ system shown in Figure 3 can be calculated using a three-site model based on eq 2. This three-site (one spin) model is shown in Figure 5 and the simulated spectra obtained are shown on the right-hand side of Figure 3. (At each of the two possible Rh sites four-fifths of the ligands do not dissociate in a single event thus retaining their coupling to the ^{103}Rh spin and one-fifth of the ligands join the pool of free ligand in solution.)

For both Figures 2 and 3 the observed and calculated spectra are in very good agreement and the calculated values of the rate constant k_1 are quite close at any particular temperature. Similar calculations were also carried out for a solution with 0.25 mol l^{-1} of added $P(OCH_3)_3$. From the nmr line shape analysis of the RhL_5^+ solutions with 0, 0.25 and 0.5 mol l^{-1} of $P(OCH_3)_3$, we obtain the Arrhenius rate expression

$$k_1(T) = 10^{14.6} e^{-16,500/RT}$$

or in terms of the Eyring equation $\Delta G^\ddagger_{300} = 14.0$ kcal mol^{-1} , $\Delta H^\ddagger_{300} = 15.9$ kcal mol^{-1} , and $\Delta S^\ddagger_{300} = 6.2$ cal $mol^{-1} deg^{-1}$. The small positive entropy of activation is consistent with a dissociative process.

Figure 6 shows the observed $^{31}P\{^1H\}$ nmr spectra for

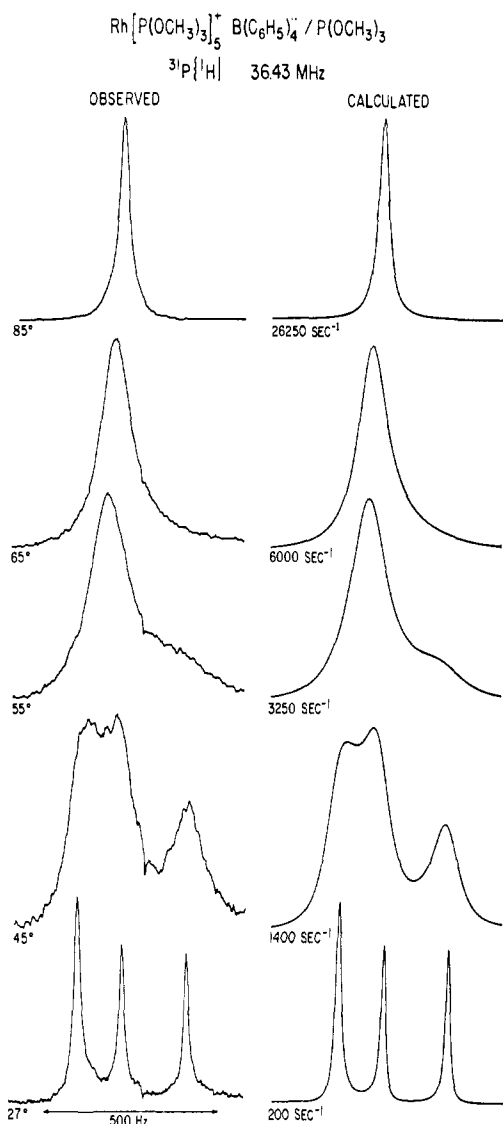


Figure 3. Observed and calculated $^3\text{P}\{^1\text{H}\}$ nmr spectra for a solution containing $\text{Rh}[\text{P}(\text{OCH}_3)_3]_5^+ \text{B}(\text{C}_6\text{H}_5)_4^-$ (0.125 M) and $\text{P}(\text{OCH}_3)_3$ (0.5 M) in acetonitrile over the temperature range for which intermolecular exchange effects can be observed.

two $\text{RhL}_5^+ - \text{RhL}_4^+$ solutions as a function of temperature. Again, the total rhodium concentration is 0.125 mol l^{-1} with CH_3CN as the solvent. These spectra have been analyzed in terms of the exchange process given in eq 2 using the four-site (one spin) model shown in Figure 7. It is assumed that the free ligand concentration is negligibly small. (At either of the two RhL_5^+ sites a single dissociation process will put the remaining undissociated four-fifths fraction of ligands into one of the two RhL_4^+ sites corresponding to an unchanged z component for the ^{103}Rh spin; the one-fifth fraction of dissociated ligand has an equal probability of returning to either of the RhL_5^+ sites {one-tenth to each}.) Calculations were carried out for the two different $[\text{RhL}_5^+]:[\text{RhL}_4^+]$ ratios ($\sim 2:1$ and $\sim 1:2$). Reasonable agreement between the calculated and observed spectra was obtained although not as good as that shown in Figures 2 and 3. The values for the rate constant k_1 were similar to those from the analyses of the RhL_5^+ and $\text{RhL}_5^+ - \text{L}$ spectra.

The good agreement between the rates obtained for

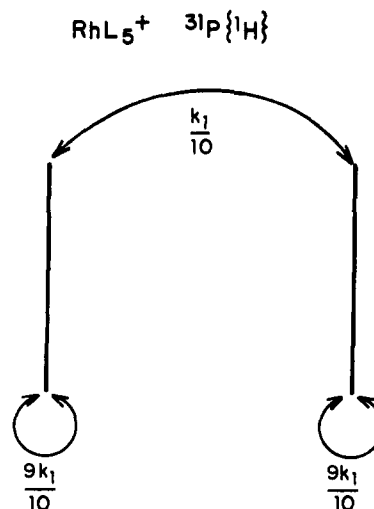


Figure 4. Exchange diagram for two-site (one spin) model used to calculate intermolecular exchange spectra for RhL_5^+ solutions (see Figure 2).

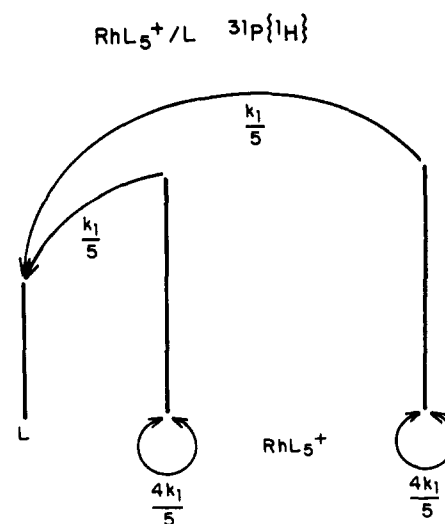


Figure 5. Exchange diagram for three-site (one spin) model used to calculate intermolecular exchange spectra for $\text{RhL}_5^+ - \text{L}$ solutions (see Figure 3). Only the forward reaction path is shown in the diagram. The reverse path must, of course, be included in setting up the exchange matrix from the exchange diagram.

the $\text{RhL}_4^+ - \text{RhL}_5^+$, the RhL_5^+ and the $\text{RhL}_5^+ - \text{L}$ systems at all temperatures in the range 27–85° is taken to support the validity of the model used (eq 2) and the assumption that the degree of dissociation of RhL_5^+ is small in acetonitrile over this temperature range. Since the ML_5^+ complex is undergoing very rapid intramolecular rearrangement in the temperature range 0–85°, it is not possible to tell if it is an axial or an equatorial ligand which dissociates.

It should be noted that *the broadening of the RhL_5^+ resonances on adding free ligand in the slow-medium exchange region (compare particularly the 27° spectra in Figures 2 and 3) is not a result of a change in the preexchange lifetime ($1/k_1$) of the RhL_5^+ cation.* If the RhL_5^+ cation is present in solution without significant RhL_4^+ and L concentrations the *effective* preexchange lifetime for a line in the RhL_5^+ spectrum is $10/k_1$ (*vide supra* and Figure 4). If free ligand is added to the

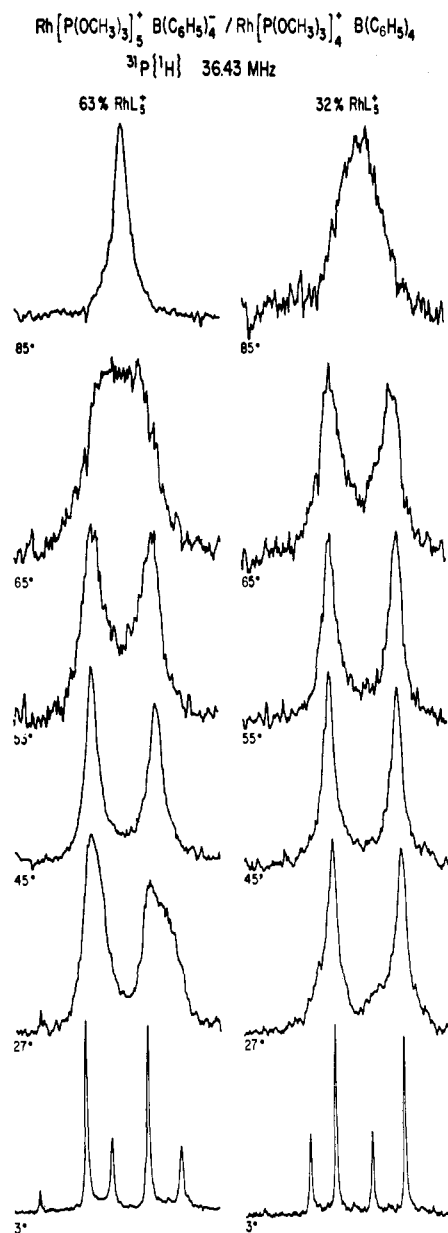


Figure 6. Observed $^{31}\text{P}\{\text{H}\}$ nmr spectra for two solutions of $\text{RhL}_5^+ - \text{RhL}_4^+$ mixtures in acetonitrile over the temperature range where intermolecular exchange effects can be observed. The left-hand column is for a solution with 63% RhL_5^+ and the right-hand column is for a solution with 32% RhL_5^+ .

solution, one-fifth of the ligands in a RhL_5^+ ion exchange with the free ligand pool in a single dissociation and the *effective* preexchange lifetime for a line in a RhL_5^+ spectrum is $5/k_1$, provided the concentration of added ligand is sufficiently large. Consequently, the addition of appreciable concentrations of free ligand should effectively double the width of the RhL_5^+ resonances even though there is no change in the true preexchange lifetime ($1/k_1$). This result has been confirmed by repeating the line shape calculations shown in Figure 2 using the model shown in Figure 5 with a very low free ligand concentration.

The left-hand side of Figure 8 shows a simulation of the $\text{RhL}_5^+ - \text{L}$ system as a function of added ligand concentration using the model shown in Figure 5, keeping k_1 fixed at 500 sec^{-1} and varying $[\text{L}]$. These calculations

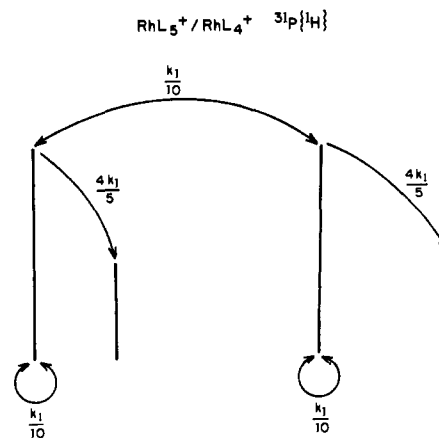


Figure 7. Exchange diagram for four-site (one spin) model used to calculate intermolecular exchange spectra for $\text{RhL}_5^+ - \text{RhL}_4^+$ solutions. Again only the effects of the forward part of the reaction are shown. The RhL_4^+ doublet is to the right side of the RhL_5^+ doublet.

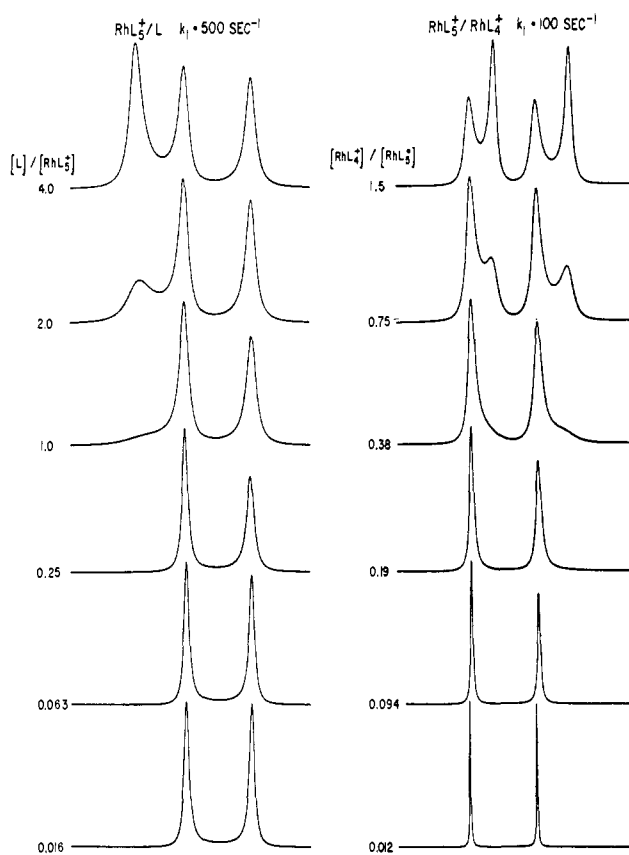


Figure 8. The left-hand side shows a simulation for the $\text{RhL}_5^+ - \text{L}$ system as a function of $[\text{L}]/[\text{RhL}_5^+]$ keeping k_1 fixed at 500 sec^{-1} . The calculations on the right-hand side are for $\text{RhL}_5^+ - \text{RhL}_4^+$ mixtures with k_1 fixed at 100 sec^{-1} . A large transverse relaxation time was used in these calculations; consequently, only the exchange contributions to the line widths are shown. The models shown in Figures 5 and 8 were used for the left and right columns, respectively.

tions show that as the free ligand concentration is lowered the widths of the two lines assigned mainly to the RhL_5^+ cation decrease until, at a sufficiently small free ligand concentration, a limiting value of half of that calculated in the presence of large $[\text{L}]$ is obtained. The 2:1 ratio of the line widths in the limit of high and

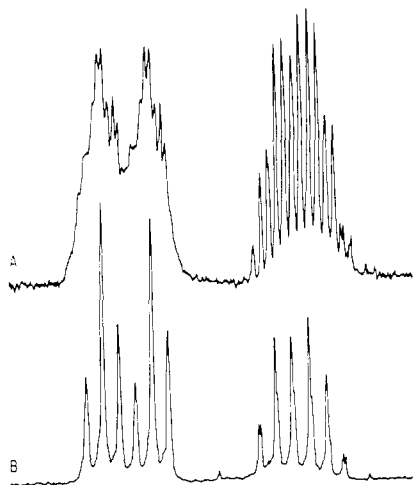


Figure 9. Two attempts to prepare $\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_3^+\text{B}(\text{C}_6\text{H}_5)_4^-$: (A) in methanolic solution, the product has undergone partial transesterification; (B) in ethanolic solution, the correct product is obtained.

low $[\text{L}]$ can be established quantitatively from the spectral vector.^{7,8}

The effect can be seen even more dramatically by comparing the 27° spectra in Figures 2 and 6. In the presence of RhL_4^+ each dissociation step puts four-fifths of the ^{31}P nuclei in a RhL_5^+ cation into the RhL_4^+ pool and transfers one-tenth of the RhL_5^+ ^{31}P nuclei to a site at which the ^{103}Rh spin has changed orientation (*via* a free ligand site present in vanishingly small concentration). Consequently, the *effective* preexchange lifetime for a line in the RhL_5^+ spectrum is $(k_1/10 + 4k_1/5)^{-1} = 10/9k_1$ (Figure 7) and addition of RhL_4^+ to the RhL_5^+ solution will increase the RhL_5^+ line width by a factor of 9 (again there is no change in the true preexchange lifetime $1/k_1$ of the ML_5^+ cation).

The above considerations show that a superficial analysis of the spectra shown in Figures 2, 3, and 6 (*e.g.*, comparing line widths at a given temperature) could lead to the *erroneous conclusions* that addition of either free ligand or RhL_4^+ to a solution of RhL_5^+ shortens the lifetime of a RhL_5^+ cation, that the dissociation is not first order, and that the mechanism implied by eq 1 is not consistent with all the data presented. The right-hand side of Figure 8 shows a simulation for the $\text{RhL}_5^+-\text{RhL}_4^+$ system as a function of $[\text{RhL}_4^+]$ using the model shown in Figure 7. In this calculation, k_1 was kept fixed at 100 sec^{-1} and $[\text{RhL}_4^+]$ was varied. An examination of the spectral vectors⁷ in the limits of high and low RhL_4^+ concentration confirms the 9:1 ratio of line widths.

Preparation Methods for ML_5 Complexes. At the time when this work was completed, ML_5 cations had been described in the literature for $\text{Rh}(\text{I})$,⁹ $\text{Ni}(\text{II})$,¹⁰⁻¹³

(7) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

(8) We have observed that on addition of increasing amounts of free ligand to a solution of $\text{Rh}[\text{P}(\text{OCH}_3)_3]_3^+\text{B}(\text{C}_6\text{H}_5)_4^-$ in CH_3CN at 27° , the RhL_5^+ line width at first increases and then levels off at twice the line width observed in the absence of added ligand; this is exactly the behavior predicted by the calculations assuming a dissociative mechanism.

(9) L. M. Haines, *Inorg. Chem.*, **10**, 1685 (1971).

(10) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **2**, 944 (1963).

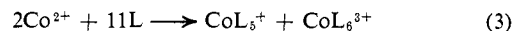
(11) T. J. Huttemann, B. Foxman, C. Sperati, and J. G. Verkade, *Inorg. Chem.*, **4**, 950 (1965).

(12) K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Advan. Chem. Ser.*, No. **62**, 590 (1966).

(13) J. G. Verkade and K. J. Coskran in "Organic Phosphorus Compounds," Vol. 2, G. M. Kosolapoff and L. Maier Ed., Wiley, New York, N. Y., 1972, Chapter 3B.

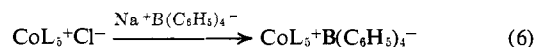
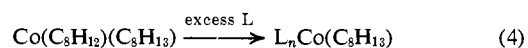
and $\text{Co}(\text{I})$.¹⁰⁻¹⁴ While this paper was in preparation complexes of $\text{Ir}(\text{I})$ were reported¹⁵ using a different synthetic route.

Cobalt(I). The earliest preparative method involved a disproportionation reaction of Co^{2+} in the presence of phosphite ligand¹⁰⁻¹³ (eq 3). More recently a route



involving photolysis of $\text{Co}(\text{CO})[\text{P}(\text{OCH}_3)_3]_4^+$ (obtained from $\text{Co}_2(\text{CO})_8 + \text{excess P}(\text{OCH}_3)_3$) in the presence of $\text{P}(\text{OCH}_3)_3$ has been described.¹⁴

We have developed a method starting from $\text{Co}(\text{C}_8\text{H}_{12})$ - $(\text{C}_8\text{H}_{13})$ which is simple and quite general. $\text{Co}(\text{C}_8\text{H}_{12})$ - $(\text{C}_8\text{H}_{13})$ itself is, however, quite difficult to prepare;¹⁶ starting from this compound near quantitative yields are obtained by the following reaction sequence carried out in alcoholic solution.



The initial addition of excess ligand displaces the cyclooctadiene, subsequent addition of 1 equiv of acetyl chloride generates 1 equiv of HCl by reaction with the solvent alcohol, and the HCl cleaves the $\text{Co}-\text{C}$ bond in $\text{L}_n\text{Co}(\text{C}_8\text{H}_{13})$. These phases of the reaction sequence are carried out without isolation of any of the products and result in a clear alcoholic solution from which $\text{CoL}_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$ can be precipitated quantitatively by addition of sodium tetraphenylborate.

In situ preparations in nmr tubes could be carried out for all six metals, in the absence of alcohol (to avoid transesterification), using CH_2Cl_2 , CH_3CN , or CHClF_2 as solvents and, for Co , CF_3COOH to cleave the $\text{Co}-\text{C}$ bond.

Rhodium(I). RhL_5^+ phosphite species were first synthesized from $[(\text{C}_8\text{H}_{12})\text{RhCl}]_2$ by addition of excess ligand to an alcoholic solution and precipitation with $\text{B}(\text{C}_6\text{H}_5)_4^-$ or PF_6^- .⁹ Our procedure is similar starting from $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$; it was found that if the preparation was carried out in an alcohol which did not correspond to the phosphite ligand being used (*e.g.*, if methanol were used as the solvent for the preparation of $\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_3^+$) the clean $\text{A}_2\text{B}_2\text{X}$ $^{31}\text{P}\{^1\text{H}\}$ spectra described in the first paper in this series were not always observed. A comparison of the spectrum for the solids obtained from an attempted preparation of $\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_3^+$ in methanol (Figure 9A) and the spectrum for the same preparation in ethanol (Figure 9B) is shown in Figure 9. It is clear that appreciable transesterification has occurred in the former case and that a clean product is obtained in the latter case. In addition, it was found that, while preparations of tetraphenylborate salts were uniformly successful if the correct alcohol was used, attempts to precipitate hexafluorophosphate salts often led to solids which did not give the correct $^{31}\text{P}\{^1\text{H}\}$ spectra. It is possible that problems of the type discussed above could pass undetected if normal chemical analysis were used for characterization.

(14) S. Attali and R. Poilblanc, *Inorg. Chim. Acta*, **6**, 475 (1972).

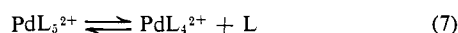
(15) L. M. Haines and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1891 (1972).

(16) The preparative details were worked out by Dr. L. W. Gosser and Mr. M. A. Cushing (to be submitted for publication).

Iridium(I). Although RhL_5^+ species can be prepared by reaction of excess ligand with $[(\text{C}_8\text{H}_{12})\text{RhCl}]_2$ at room temperature,⁹ the corresponding reaction for Ir(I) does not go to completion under these conditions. Several runs were made using $[(\text{C}_8\text{H}_{12})\text{IrCl}]_2$ and in all cases, using $^{31}\text{P}\{^1\text{H}\}$ nmr as the analytical tool, no appreciable amounts of IrL_5^+ were detected. Rather than running at higher temperatures, which can apparently give satisfactory results,¹⁴ we looked for a starting complex in which the ligands were more easily displaced than cyclooctadiene. On the assumption that the chelation effect contributes significantly to the stability of $[(\text{C}_8\text{H}_{12})\text{IrCl}]_2$, a complex with nonchelating olefin ligands, $[(\text{C}_8\text{H}_{14})_2\text{IrCl}]_2$, was synthesized; the cyclooctene groups are easily displaced by phosphites at room temperature. The procedures were similar to those used for Rh(I) and are described in the Experimental Section.

Nickel(II). The starting material of choice was $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$; experiments with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, for instance, usually proved unsuccessful due possibly to the ability of the nitrate ion to coordinate to the central metal. $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in alcohol in the presence of excess ligand; $\text{NiL}_5^{2+}(\text{BF}_4^-)_2$ salts are normally more soluble in alcohol than are the salts of heavier anions such as SbCl_6^- or $\text{B}(\text{C}_6\text{H}_5)_4^-$ so that compounds containing the heavier ions can readily be obtained by precipitation. Tetrafluoroborate salts can be obtained by concentrating and chilling the alcoholic solutions.

Palladium(II). Although PdL_5^{2+} species have not previously been prepared, the synthetic approach used in this paper is quite straightforward. An alcoholic suspension of PdCl_2 is stirred in the presence of excess phosphite ligand until the major portion of the solids dissolve. The solution is filtered and a precipitating agent such as $\text{Na}^+\text{B}(\text{C}_6\text{H}_5)_4^-$ is added. The only precaution which must be observed is to avoid loss of the fifth ligand in PdL_5^{2+} during the recrystallization and washing processes since ligand dissociation (eq 7) occurs



at an appreciable rate at room temperature. The simplest technique for suppressing this decomposition reaction is to wash with solvent containing appreciable amounts of phosphite and to recrystallize slowly from chilled solutions containing some excess phosphite.

Platinum(II). The preparative procedures are precisely analogous to those described in the previous section for Pd^{2+} . Single crystals of the salts $\text{Pt}[\text{P}(\text{OCH}_3)_3]_5^{2+}(\text{PF}_6^-)_2$ and $\text{Pt}[\text{P}(\text{OCH}_3)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$ were grown by slow evaporation, and a preliminary X-ray examination was undertaken. The hexafluorophosphate salt gives monoclinic crystals with the space group $P2_1/C$; the unit cell has the parameters $a = 10.07 \text{ \AA}$, $b = 11.89 \text{ \AA}$, $c = 37.34 \text{ \AA}$, and $\beta = 105.7^\circ$.

Transesterification of Phosphites. Transesterification of free phosphites with alcohols can in some cases occur rapidly;^{17,18} evidence has been presented to suggest that coordinated phosphites transesterify much less easily.¹⁸

(17) F. W. Hoffmann, R. J. Ess, and R. P. Usinger, Jr., *J. Amer. Chem. Soc.*, **78**, 5817 (1956), detected transesterification in $\text{P}(\text{OR})_3 + \text{R}'\text{OH}$ solutions by heating the mixture to remove ROH reaction product.

(18) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 4545 (1972).

In cases where the alcohol corresponding to the phosphite of choice is a good solvent, this preparative problem can be avoided by using the appropriate alcohol as solvent. In other cases where the alcohol is not a suitable solvent, the preparations can sometimes be carried out successfully in other solvents such as THF. In still other cases the transesterification reaction is sufficiently slow that good preparations can be carried out using an alcohol solvent that does not correspond to the phosphite; here it is important to work close to room temperature. In reactions of this type which were carried out under reflux transesterification were always extensive and often complete. A room temperature preparation of $\text{Ir}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$ in methanolic solution gave the correct product both by elemental analysis and $^{31}\text{P}\{^1\text{H}\}$ nmr. On the other hand, an attempted preparation of $\text{Pt}[\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$ in ethanal under refluxing conditions gave $\text{Pt}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$ quantitatively.

Chemical Shifts and Coupling Constants. The absolute values of the ^{31}P shift separations for constant ligand increase on going down a vertical triad and are uniformly higher for the doubly charged metal relative to the corresponding singly charged metal, an effect which has previously been observed in other iso-electronic isostructural series.¹⁹ The complex $\text{Ni}[\text{P}(\text{OCHCH}_2)_3]_5^{2+}(\text{ClO}_4^-)_2$ is the only ML_5 species of the type we are considering for which an X-ray crystal structure determination has been made.²⁰ The cation is an accurate trigonal bipyramid with the axial bond lengths measurably shorter than the equatorial bond lengths. It may be noted from Table I that for this cation the phosphorus resonances associated with the equatorial ligands are to high field of those associated with the axial ligands and also for a given metal the sign of the axial-equatorial ^{31}P shift difference can be different for different ligands; it would be of interest on the basis of suitably chosen cases to compare shift differences with ratios of axial to equatorial bond lengths for other complexes.

The phosphorus-phosphorus coupling constants are remarkably constant for a given metal and are much bigger for the first-row metals than for the remainder ($\sim 150 \text{ Hz}$ for Co^+ , $\sim 120 \text{ Hz}$ for Ni^{2+}). The values for the four second- and third-row metals lie in a narrow range ($\sim 50\text{--}70 \text{ Hz}$).

Similar constancy is found for the $M_{\text{ax}}\text{-P}$ and $M_{\text{eq}}\text{-P}$ couplings for Rh^+ and Pt^{2+} . For both metals $J_{\text{eq}} > J_{\text{ax}}$ and the ratio $J_{\text{ax}}/J_{\text{eq}} = 0.7$ despite the large change in absolute magnitudes; if the mechanism for transmission of spin correlation is primarily Fermi contact, the ratio would roughly reflect the ratio of the s characters for the two types of bond with the equatorial bonds having appreciably greater s character.

Experimental Section

$^{31}\text{P}\{^1\text{H}\}$ Fourier mode nmr spectra were recorded as described in the first publication in this series.³ Methods of preparation of the compounds are described in the appropriate sections below.

I. Cobalt Complexes. A. $\text{Co}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{13})$ Precursor. The preparation of π -cyclooctenyl- π -cycloocta-1,5-dienecobalt has been

(19) K. J. Coskran, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, **89**, 4535 (1967).

(20) E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, **413**, 407 (1970).

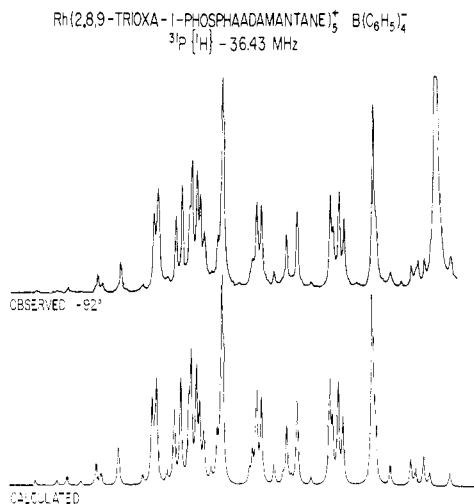


Figure 10. The $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of $\text{Rh}[\text{P}(\text{OCH}_2\text{CH}_2)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$ in the presence of excess ligand together with a spectrum simulated using an $\text{A}_2\text{B}_3\text{X}$ model.

discussed briefly in the literature.^{21,22} The method used here is based on the approach of Otsuka and Rossi²² and will be described in detail in a future publication.¹⁶

B. CoL_3^+ Salts. (i) $\text{Co}[\text{P}(\text{OCH}_2)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. A 125-ml erlenmeyer flask was charged with 50 ml of methanol and π -cyclo-octenyl- π -cycloocta-1,5-dienecobalt (1.00 g, 0.0036 mol). After stirring 10 min, trimethyl phosphite (6.0 g, 0.048 mol) was added dropwise over a 5-min period; the solution was then stirred for an additional hour and acetyl chloride (0.40 g, 0.0044 mol) in 20 ml of methanol was added. Sodium tetraphenylborate (2.50 g, 0.007 mol) was dissolved in approximately 20 ml of methanol and added, dropwise, to the stirred solution to precipitate pale yellow crystals. The resulting yellow crystals were separated on a medium-fritted disk funnel and dried *in vacuo* for 2 hr.

(ii) $\text{Co}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^+\text{Cl}^-$. This complex was prepared by Dr. L. W. Gosser using a different preparative approach from the one described above.

(iii) $\text{Co}[\text{P}(\text{OCH}_2)_2\text{CCH}_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. The procedure was similar to that described under (i) using THF as the solvent.

II. Rhodium Complexes. A. $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ Precursor. The method follows closely that described by Cramer.²³

B. RhL_3^+ Salts. (i) $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. A 125-ml erlenmeyer flask was charged with 50 ml of dry methanol and $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ (1.16 g, 0.003 mol). After stirring at room temperature for 5 min trimethyl phosphite (5.00 g, 0.040 mol) was added dropwise over a period of 5 min; stirring was continued for 30 min until all the solids were in solution.

Sodium tetraphenylborate (2.50 g, 0.007 mol) was dissolved in 20 ml of methanol and added dropwise to the green-yellow solution to precipitate off-white solids. The solids were collected on a medium-fritted disk funnel and dried *in vacuo* for 1 hr. The crude product was then dissolved in a minimum amount of dry methylene chloride and filtered through a medium-fritted disk funnel. Methanol was added slowly to the stirred solution to precipitate white crystals. The final product was collected on a medium-fritted disk funnel and dried *in vacuo* for 3 hr at room temperature and at a pressure of 0.01 mm.

(ii) $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{PF}_6^-$. (a) Attempts to prepare this salt using a procedure similar to (i) but substituting NH_4PF_6 in water for $\text{NaB}(\text{C}_6\text{H}_5)_4$ in methanol invariably led to ligand deficient products both by C, H, and P analysis and by $^{31}\text{P}\{^1\text{H}\}$ nmr. The latter technique did show $\text{A}_2\text{B}_3\text{X}$ signals at low temperatures due to $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{PF}_6^-$; however, there was also a strong doublet (>50% of the intensity) assigned to $\text{Rh}[\text{P}(\text{OCH}_2)_3]_4^+\text{PF}_6^-$.

(b) Successful *in situ* preparations were carried out in nmr tubes; to 0.5 ml of CH_2Cl_2 in a 10-mm nmr tube at room temperature were added 97.3 mg of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$, 290 μl of $\text{P}(\text{OCH}_2)_3$, and 81.5 mg

of NH_4PF_6 . After ethylene evolution was complete, the tube was cooled in Dry Ice and the total volume was raised to 4 ml by addition of CHClF_2 (bp -40°). The tube was cooled to -70° and shaken to ensure complete mixing. The $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum was examined at low temperature revealing the characteristic $\text{A}_2\text{B}_3\text{X}$ pattern assigned to $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{PF}_6^-$ together with a signal assigned to the excess $\text{P}(\text{OCH}_2)_3$. Compounds iii-vi were prepared in a similar manner.

(iii) $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{AsF}_6^-$.

(iv) $\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\text{SbF}_6^-$.

(v) $\{\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\}_2\text{SiF}_6^{2-}$.

(vi) $\{\text{Rh}[\text{P}(\text{OCH}_2)_3]_5^+\}_2\text{GeF}_6^{2-}$.

(vii) $\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. The compound was prepared successfully in a manner similar to (i) using methanol as solvent. Preparations in methanol gave partial transesterification. $^{31}\text{P}\{^1\text{H}\}$ spectra are compared in Figure 9.

(viii) $\text{Rh}[\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. Procedures analogous to (i) with *n*-butyl alcohol as solvent and analogous to (ii) (b) with CH_2Cl_2 - CHClF_2 as solvent were successful. Attempts using methanol as solvent gave products with some transesterification (determined by $^{31}\text{P}\{^1\text{H}\}$ nmr).

(ix) $\text{Rh}[\text{P}(\text{OCH}_2)_2\text{CCH}_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. A method similar to (i)⁴ was employed using methanol as solvent at room temperature.

(x) $\text{Rh}[\text{P}(\text{OCH}_2)_2\text{CC}_2\text{H}_5]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. This complex was prepared *in situ* in a manner similar to that described under (ii) (b).

(xi) $\text{Rh}[\text{P}(\text{OCH}_2\text{CH}_2)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. The 2,8,9-trioxa-1-phosphadamantane complex was also prepared *in situ* from a small quantity of ligand kindly supplied by Professor J. G. Verkade. The $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum is shown in Figure 10 together with a simulation using an $\text{A}_2\text{B}_3\text{X}$ model.

(xii) $\text{Rh}[\text{P}(\text{OCH}_2)_3]_4^+\text{B}(\text{C}_6\text{H}_5)_4^-$. A 500-ml erlenmeyer flask was charged with 200 ml of nitrogen-saturated methanol. $[(\text{C}_2\text{H}_4)_2\text{-RhCl}]_2$ (1.94 g, 0.005 mol) was added followed by $\text{P}(\text{OCH}_2)_3$ (4.97 g, 0.040 mol); the mixture was stirred until ethylene evolution ceased and all the solids were dissolved. A solution of $\text{NaB}(\text{C}_6\text{H}_5)_4$ (3.44 g, 0.01 mol) in 30 ml of methanol was introduced slowly. The mixture was partially stripped, filtered, and dried. $^{31}\text{P}\{^1\text{H}\}$ studies showed the presence of only a trace of RhL_3^+ with the desired RhL_4^+ . This compound was used for the intermolecular exchange studies involving RhL_4^+ .

III. Iridium(I). A. $[(\text{C}_5\text{H}_{14})_2\text{IrCl}]_2$ Precursor. The procedure follows closely that described by van der Ent and Onderdelinden.²⁴

B. IrL_3^+ Salts. (i) $\text{Ir}[\text{P}(\text{OCH}_2)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. A 125-ml erlenmeyer flask was charged with 25 ml of methanol and $[(\text{C}_5\text{H}_{14})_2\text{IrCl}]_2$ (0.90 g, 0.001 mol). $\text{P}(\text{OCH}_2)_3$ (1.66 g, 0.013 mol) was added to the slurry over a period of 2 min and stirring was continued until all went into solution. Sodium tetraphenylborate (0.83 g, 0.0024 mol) was dissolved in approximately 5 ml of methanol and added slowly, dropwise, to the solution to precipitate off-white crystals. The crystals were collected on a medium-fritted disk funnel and dried *in vacuo* for 20 min. The complex was also prepared by *in situ* procedures similar to those described under (iv) below.

(ii) $\text{Ir}[\text{P}(\text{OCH}_2)_3]_5^+\text{PF}_6^-$. Attempts to prepare this complex by a procedure similar to that described for the corresponding rhodium complex in section II B (ii) led to similar results, *i.e.*, products which were >50% contaminated with IrL_4^+ as shown by $^{31}\text{P}\{^1\text{H}\}$ nmr measurements.

(iii) $\text{Ir}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. The compound was prepared and isolated in a manner similar to III B (i) and was prepared *in situ* by procedures similar to those described under (iv) below.

(iv) $\text{Ir}[\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. The complex was prepared *in situ* in a 10-mm nmr tube by adding 224 mg of $[(\text{C}_5\text{H}_{14})_2\text{IrCl}]_2$, 625 mg of $\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_3$, and 171 mg of $\text{NaB}(\text{C}_6\text{H}_5)_4$ to 1 ml of CH_2Cl_2 . After a short period the tube was cooled in Dry Ice and the total volume was raised to 4 ml by addition of CHClF_2 . The tube was cooled to -80° and shaken to ensure complete mixing.

(v) $\text{Ir}[\text{P}(\text{OCH}_2)_2\text{CCH}_3]_5^+\text{B}(\text{C}_6\text{H}_5)_4^-$. $[(\text{C}_5\text{H}_{14})_2\text{IrCl}]_2$ (1.5 g, 0.0016 mol), $\text{P}(\text{OCH}_2)_2\text{CCH}_3$ (3.0 g, 0.02 mol), and $\text{NaB}(\text{C}_6\text{H}_5)_4$ (1.4 g, 0.004 mol) were added to 75 ml of THF in a 125-ml erlenmeyer flask equipped with a Teflon-coated magnetic stirrer. The mixture was refluxed for 5 min and stirred overnight, and the solids were collected on a medium frit and dried *in vacuo*.

IV. Nickel Complexes. The precursor for all NiL_3^{2+} preparations was commercial $\text{Ni}[\text{BF}_4]_2 \cdot 6\text{H}_2\text{O}$.

(21) H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organometal. Chem.*, **30**, 407 (1971).

(22) S. Otsuka and M. Rossi, *J. Chem. Soc. A*, 2630 (1968).

(23) (a) R. D. Cramer, *Inorg. Chem.*, **1**, 722 (1962); (b) *Inorg. Syn.*, in press.

(24) A. van der Ent and A. L. Onderdelinden, *Inorg. Syn.*, **14**, 92 (1973).

(i) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}(\text{BF}_4^-)_2$. A 250-ml erlenmeyer flask was charged with 200 ml of methanol and nickel tetrafluoroborate (3.00 g, 0.0088 mol). After stirring 10 min, all went into solution, and trimethyl phosphite (15.00 g, 0.12 mol) was added dropwise to the green solution, which, upon addition of ligand, changed to orange-red.

A 50-ml portion of the solution was partially stripped and chilled (-40°) under nitrogen overnight. White needle-like crystals were formed and collected on a medium-fritted disk funnel. The product was dried *in vacuo* for 2 hr. The remaining 200 ml of solution from the first part of this reaction was used in 50 ml portions for the preparation of compounds ii-v. In each case, the appropriate anion was added to precipitate the product, followed by filtration.

(ii) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$.

(iii) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}(\text{PF}_6^-)_2$.

(iv) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}(\text{AsF}_6^-)_2$.

(v) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}(\text{SbF}_6^-)_2$.

(vi) $\text{Ni}[\text{P}(\text{OCH}_2)_3]_5^{2+}\text{SiF}_6^{2-}$. NiSiF_6 (0.9 g, 0.0045 mol) was added to 25 ml of methanol in a 125-ml erlenmeyer flask followed by 4.5 g (0.036 mol) of $\text{P}(\text{OCH}_2)_3$. The solids went into solution after stirring for 20 min; the solution was stripped to an orange oil and used in this form for the nmr studies.

(vii) $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_5^{2+}(\text{BF}_4^-)_2$. A procedure analogous to (i) was employed for this compound and for compound viii using ethanol as the solvent.

(viii) $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]_5^{2+}(\text{BF}_4^-)_2$.

(ix) $\text{Ni}[\text{P}(\text{OCHCH}_2)_3]_5^{2+}(\text{BF}_4^-)_2$. The 2,8,9-trioxa-1-phosphadamantane complex was prepared *in situ*. To 0.25 ml of CH_3CN in a 10-mm nmr tube was added 50 mg of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 166 mg of $\text{P}(\text{OCHCH}_2)_3$. The volume was raised to 4 ml by adding CHClF_2 at Dry Ice temperature and the solution was shaken to ensure complete mixing.

V. Palladium Complexes. The precursor for all PdL_3^{2+} preparations was commercial grade PdCl_2 .

(i) $\text{Pd}[\text{P}(\text{OCH}_2)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. A 125-ml erlenmeyer flask was charged with 50 ml of methanol and palladium chloride (0.88 g, 0.0049 mol) under nitrogen. Trimethyl phosphite (6.80 g, 0.054 mol) was added and stirring was continued until all solids went into solution. Sodium tetraphenylborate (6.84 g, 0.02 mol) was dissolved in a minimum amount of methanol and added slowly to the solution to precipitate white solids. After the addition was com-

plete, stirring was continued for an additional 10 min. The product was then collected on a medium-fritted disk funnel and dried *in vacuo* for 2 hr.

(ii) $\text{Pd}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. The procedure was analogous to (i) using ethanol as solvent and refluxing prior to precipitation.

(iii) $\text{Pd}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. The preparation was analogous to (ii) using THF as solvent and recrystallizing from nitromethane-ether.

VI. Platinum Complexes. The precursor for all PtL_3^{2+} preparations was commercial grade PtCl_2 .

(i) $\text{Pt}[\text{P}(\text{OCH}_2)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. A 125-ml erlenmeyer flask was charged with 50 ml of methanol and platinum chloride (1.32 g, 0.0049 mol). Trimethyl phosphite (6.80 g, 0.054 mol) was added, and the mixture was stirred until all went into solution. Sodium tetraphenylborate (6.84 g, 0.02 mol), dissolved in a minimum amount of methanol, was added dropwise to the solution giving a white precipitate. After the addition was complete, stirring was continued for 10 min. The product was then isolated on a medium-fritted disk funnel and dried *in vacuo* at room temperature for 2 hr.

The crystals used for the X-ray measurements described in the text were obtained by slow evaporation from methylene chloride in the presence of a slight excess of ligand. A similar procedure was adopted to obtain crystals of $\text{Pt}[\text{P}(\text{OCH}_2)_3]_5^{2+}(\text{PF}_6^-)_2$.

(ii) $\text{Pt}[\text{P}(\text{OC}_2\text{H}_5)_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. The preparation was similar to (i); the reaction was carried out in refluxing methanol, the initial precipitate was dissolved in CH_2Cl_2 , and crystals were obtained on addition of ethanol.

(iii) $\text{Pt}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_5^{2+}[\text{B}(\text{C}_6\text{H}_5)_4^-]_2$. The procedure precisely parallels (ii) with the substitution of THF for ethanol as solvent.

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