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## Substitution Reactions of Five-Coordinate Complexes. 2. Mechanism of Ligand Replacement in Trigonal-Bipyramidal Nickel(II) and Platinum(II) Complexes Containing the Tetradentate Ligand Tris(*o*-(diphenylarsino)phenyl)arsine

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Ligand replacement of the monodentate ligand in a series of trigonal-bipyramidal nickel(II) complexes containing the tetradentate ligand tris(*o*-(diphenylarsino)phenyl)arsine, QAS, is reported for methanol solutions. Entering ligands replacing Br<sup>-</sup> in order of decreasing rate were SC(NH<sub>2</sub>)<sub>2</sub> >> CN<sup>-</sup>, > N<sub>3</sub><sup>-</sup> > SCN<sup>-</sup> > I<sup>-</sup> > NO<sub>2</sub><sup>-</sup> >> PPh<sub>3</sub>. CN<sup>-</sup> replacement of leaving groups in order of decreasing rate were NCS<sup>-</sup> > N<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > I<sup>-</sup>. A second consecutive decomposition was observed to be several orders of magnitude slower than ligand replacement when CN<sup>-</sup> was the entering ligand. The kinetic data obtained at 0.050 M ionic strength and 25.0 °C are consistent with either an associative interchange, I<sub>a</sub>, mechanism or a mechanism involving formation of a four-coordinate intermediate via partial dissociation of the tetradentate ligand.

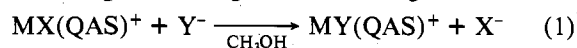
### Introduction

Tripod-like tetradentate ligands containing group 5A and 6A donor atoms<sup>1</sup> have been found to form a large number of transition-metal complexes. The majority of complexes containing geometrically constraining tripod ligands and d<sup>8</sup> transition-metal ions are five-coordinate trigonal bipyramids with the additional monodentate ligand in an axial position. The arrangement of donor atoms and phenyl groups for a complex of Ni(II) with tris(*o*-(diphenylarsino)phenyl)arsine, abbreviated as QAS, and a monodentate anion is illustrated in Figure 1. Since the early 1960s, research investigations of ligand field effects<sup>2,3</sup> in complexes containing tetradentate ligands have led to the synthesis of many five-coordinate complexes. Although the syntheses of the ligands are somewhat tedious, a large number of complexes containing these ligands have been characterized and are suitable for further chemical and physical investigations.

Detailed mechanistic information concerning ligand replacement in five-coordinate complexes in solution has not been as available as information for the same processes in four-coordinate and six-coordinate transition-metal complexes.<sup>4,5</sup> Sweigart and co-workers<sup>6</sup> results on ligand substitution reactions of five-coordinate complexes containing bidentate ligands have shown that the mechanisms may be associative, dissociative, or both for a given complex containing other than a d<sup>8</sup> metal ion. Only dissociative mechanisms were reported by them for low-spin d<sup>8</sup> metal complexes. Pearson, Muir, and Venanzi reported results of apparently the first investigation of ligand replacement in methanol for a series of five-coordinate trigonal-bipyramidal metal complexes containing a tetradentate ligand of the tripod type.<sup>7</sup> The study was conducted with platinum(II) and palladium(II) complexes containing the tetradentate ligand QAS. Results for a similar

kinetic study of platinum(II) and palladium(II) complexes in methanol containing the tripod-like tetradentate ligand tris(*o*-(dimethylarsino)phenyl)arsine, Qas, were reported by Morgan and Tobe.<sup>8</sup> Qas complexes are isostructural with the QAS complex of the former study.

As part of a program undertaken to elucidate the mechanisms of ligand replacement in five-coordinate complexes containing tetradentate ligands,<sup>9</sup> we have investigated reactions of QAS-containing nickel(II) complexes. The stoichiometric equation for ligand replacement in methanol is given by eq 1. The entering and leaving monodentate ligands that were



used were chosen to represent a wide range of nucleophilic character and size. Conclusions drawn from the results of this work in the light of previous studies form the basis of this article.

### Experimental Section

**Chemicals.** Starting material, *o*-bromoaniline, for synthesis of tris(*o*-(diphenylarsino)phenyl)arsine was obtained from Pfaltz and Bauer and from Eastman Organic Chemicals. Nickel(II) chloride tetrahydrate, nickel(II) bromide hexahydrate, nickel(II) perchlorate hexahydrate, nickel(II) nitrate hexahydrate, platinum(II) chloride, and sodium tetrachloroplatinum(II) tetrahydrate were obtained ultrapure from Alfa Inorganics, Inc. Dichloromethane and anhydrous methanol were obtained as "Baker Instra-Analyzed" from J. T. Baker Co. All other chemicals used were reagent grade from J. T. Baker Co.

**Synthesis and Analysis of QAS.** Tris(*o*-(diphenylarsino)phenyl)arsine, QAS, was prepared as previously reported<sup>10</sup> starting with *o*-bromoaniline. White crystalline material obtained after recrystallization from dichloromethane was found to melt at 241 °C. The reported melting point was 240 °C. Anal. Calcd for C<sub>54</sub>H<sub>42</sub>As<sub>4</sub>: C, 65.45; H, 4.28; As, 30.26. Found: C, 66.00; H, 4.20; As, 29.70.

**Synthesis and Analysis of Metal Complexes.** The complexes [NiCl(QAS)]ClO<sub>4</sub>, [NiBr(QAS)]Br, [NiI(QAS)]ClO<sub>4</sub>, [Ni(CN)(QAS)]ClO<sub>4</sub>, [Ni(NCS)(QAS)]ClO<sub>4</sub>, and [PtBr(QAS)]Br were prepared as reported previously in the literature.<sup>11,12</sup> The complexes were recrystallized twice from appropriate solvents, dried under vacuum, and analyzed. In all cases, they gave good agreement with literature values for absorption maxima and molar absorptivities of solutions of the complexes in dichloromethane and for decomposition points. This and elemental analysis data are given in Table I.

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Table I. Analytical Data<sup>a</sup> for Metal Complexes

		dec pt, °C	% C	% H	% metal	% I or B	% P or N	$\lambda_{\max}^b$ , nm	$10^3 \epsilon_{\max}$	ref
[NiCl(QAS)]ClO <sub>4</sub>	found	321-322	54.50	3.65	4.88	6.10 (Cl)	23.89 (As)	455, 615	0.30, 4.73	this work
	calcd	321-322	54.77	3.58	4.96	5.99	25.31	457, 617	0.33, 4.47	10
[NiBr(QAS)]Br	found	331-333	53.45	3.49	4.62	13.06	24.50 (As)	459, 633	0.44, 4.00	this work
	calcd	329-333	53.64	3.50	4.86	13.22	24.78	458, 633	0.45, 4.00	10
[NiI(QAS)]ClO <sub>4</sub>	found	338-339	52.15	3.44	4.60	10.09		475	1.15	this work
	calcd	338-339	50.84	3.32	4.60	9.95		476	1.16	10
[Ni(CN)(QAS)]ClO <sub>4</sub>	found	339-342	56.02	3.71	4.40		0.90	465	5.10	this work
	calcd	338-339	56.23	3.60	5.00		1.19	465	5.75	10
[Ni(NO <sub>2</sub> )(QAS)]ClO <sub>4</sub>	found	304-306	54.52	3.63	4.71		1.08	553, 590	5.29, 4.97	this work
	calcd		54.29	3.54	4.91		1.17			
[Ni(PPh <sub>3</sub> )(QAS)](ClO <sub>4</sub> ) <sub>2</sub>	found	296-298	56.97	4.14	3.47		1.82	384, 600	9.92, 4.03	this work
	calcd		57.25	3.80	3.89		2.05			
[Ni(N <sub>3</sub> )(QAS)]ClO <sub>4</sub>	found	300-302	54.15	3.64	4.63		3.61	467, 600	1.51, 3.79	this work
	calcd		54.47	3.56	4.93		3.52			
[Ni(NCS)(QAS)]ClO <sub>4</sub>	found	316-318	53.45	3.41	4.80	3.04 (Cl)	1.19	447, 593	1.59, 7.31	this work
	calcd	316-318	54.74	3.51	4.86	2.94	1.16	446, 585	1.90, 9.80	10
[PtBr(QAS)]Br	found	356-357	48.41	3.26	14.46	11.60	22.17 (As)	414, 448	9.80, 8.74	this work
	calcd	356-357	48.20	3.15	14.50	11.88	22.27	413, 448	10.00, 8.79	11

<sup>a</sup> Microanalyses performed by Galbraith Laboratories, Knoxville, TN. <sup>b</sup> These bands are only those occurring in the visible region and other bands may be observed at shorter wavelength. The solvent was CH<sub>2</sub>Cl<sub>2</sub> in all cases except the platinum complex where methanol was used.

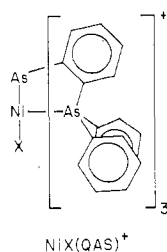


Figure 1. Structural arrangement of QAS in five-coordinate nickel(II) complexes.

[Ni(N<sub>3</sub>)(QAS)]ClO<sub>4</sub> was prepared by mixing 0.16 g of Ni(N<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 5 mL of ethanol with 0.05 g of NaN<sub>3</sub> in 5 mL of ethanol and then filtering the mixture into a warmed solution of 0.26 g of QAS in 10 mL of dichloromethane. The resultant mixture was allowed to reflux for 15 min and then filtered into a solution of 0.20 g of NaClO<sub>4</sub> in 10 mL of ethanol. Upon cooling of the mixture, dark blue crystals were obtained, recrystallized twice from ethanol, and dried under vacuum. Both [Ni(NO<sub>2</sub>)(QAS)]ClO<sub>4</sub> and [Ni(PPh<sub>3</sub>)(QAS)]ClO<sub>4</sub> were prepared by using a procedure analogous to that above. Data obtained for absorption maxima and molar absorptivities of complexes in dichloromethane, decomposition points, and elemental analysis are also given in Table I.

**Kinetic Measurements and Data Analysis.** Wavelengths of greatest difference in molar absorptivity between reactant and product complex ions in methanol were chosen to observe kinetic experiments and are given in Table II. Solutions of reactant and product complex ions, up to maximum concentrations used in kinetic experiments, indicated conformity to Beer's law. Visible spectra taken of reaction mixtures after completion indicated stoichiometric formation of product complex ions as given by eq 1.

Reactions were initiated by mixing the appropriate freshly prepared reactant solutions by using a Durrum stopped-flow spectrophotometer. Temperature was held constant at 25.0 ± 0.1 °C while ionic strength was maintained at 0.050 M with addition of LiClO<sub>4</sub>, except where noted. Concentrations of entering ligands were kept in large excess of concentrations of complex metal ions so that the experimentally measured reaction-rate data were pseudo first order. Straight-line plots using the standard integrated first-order rate expression

$$\ln(A_t - A_\infty) = -k_{\text{obsd}}t + \ln(A_0 - A_\infty) \quad (2)$$

where  $A$  is absorbance, were obtained for at least 2 half-lives. Absorbance values for each kinetic experiment were fitted to eq 2 by a nonlinear least-squares program<sup>13</sup> with use of a Univac 1108 computer. At least two replicate experiments were conducted for each set of reaction conditions. The reproducibility of  $k_{\text{obsd}}$  between identical

Table II. Kinetic and Reaction Data for Ligand Replacement in TBP Complexes in Methanol at 25.0 °C

reactants <sup>a</sup>	$n^\circ_{\text{Pt}}^b$	$\lambda,^c$ nm	$k,^d$ M <sup>-1</sup> s <sup>-1</sup>	$10^2 k_{\text{dec}},^e$ s <sup>-1</sup>
NiBr(QAS) <sup>+</sup> + NO <sub>2</sub> <sup>-</sup>	3.22	540	2.81 ± 0.08	
+ I <sup>-</sup>	5.42	610	23.1 ± 0.1	
+ SCN <sup>-</sup>	5.65	550	157 ± 1	
+ N <sub>3</sub> <sup>-</sup>	3.58	370	192 ± 2	
+ CN <sup>-</sup>	7.0	465	230 ± 30	8.0 ± 0.2
+ SC(NH <sub>2</sub> ) <sub>2</sub>	7.17	544	850 ± 30	
+ PPh <sub>3</sub>	8.79	<i>f</i>		
NiI(QAS) <sup>+</sup> + CN <sup>-</sup>	7.0	455	40 ± 1	6.3 ± 0.3
Ni(NO <sub>2</sub> )(QAS) <sup>+</sup> + CN <sup>-</sup>		460	144 ± 40	8.0 ± 0.1
NiCl(QAS) <sup>+</sup> + CN <sup>-</sup>		460	560 ± 20	7.0 ± 0.1
Ni(N <sub>3</sub> )(QAS) <sup>+</sup> + CN <sup>-</sup>		465	800 ± 10	7.8 ± 0.1
Ni(NCS)(QAS) <sup>+</sup> + CN <sup>-</sup>		575	1170 ± 30	4.3 ± 0.1
PtBr(QAS) <sup>+</sup> + SCN <sup>-</sup>		380	57 ± 4	

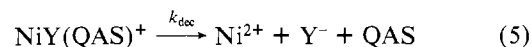
<sup>a</sup> Initial reactant complex concentrations varied in the range (2.97–8.85) × 10<sup>-5</sup> M, and entering ligand concentrations varied in the range 5.0 × 10<sup>-4</sup> to 1.5 × 10<sup>-2</sup> M at 0.050 M ionic strength maintained by LiClO<sub>4</sub>. Uncertainties represent plus and minus one standard deviation. <sup>b</sup>  $n^\circ_{\text{Pt}}$  values are nucleophilic reactivity factors based on the reaction of *trans*-Pt(py)<sub>2</sub>Cl<sub>2</sub> with these ligands in methanol at 30 °C as the standard.<sup>18</sup> <sup>c</sup> Wavelengths were chosen to give maximum difference between absorbances of reactant and product complexes. <sup>d</sup> Second-order rate constants were determined by using eq 3. <sup>e</sup> First-order decomposition rates are for the decomposition of cyano complexes produced in the ligand substitution reaction in the presence of ca. 0.0150 M cyanide. These were measured for ca. 15% of the decomposition reaction. <sup>f</sup> No reaction.

experiments was found to be within 1%. Second-order rate constants were determined from the relationship

$$k = k_{\text{obsd}} / [\text{ligand}]_0 \quad (3)$$

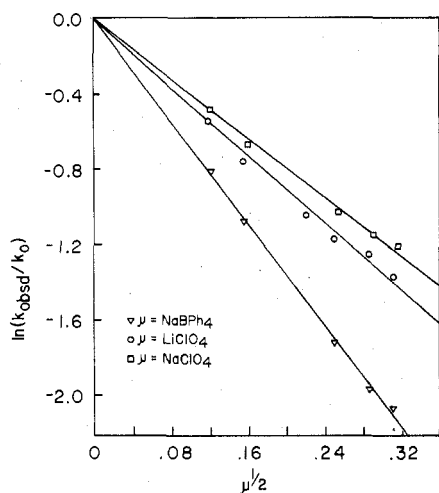
## Results and Discussion

The reaction stoichiometry for replacement of the monodentate ligand in an axial position was found to be that given by eq 4. We previously reported<sup>9</sup> that the complex ion



NiCl(QAS)<sup>+</sup> undergoes decomposition in methanol. This has now also been observed for ligand replacement reactions in which cyano complexes are formed. A white crystalline material, formed in reaction mixtures upon standing for a suitable period, was collected and identified as free ligand QAS by its

(13) The original program by Moore and Newton is described in publication LASL-2367 of the Los Alamos Laboratories.



**Figure 2.** Plots of  $\ln(k_{\text{obsd}}/k_0)$  vs.  $\mu^{1/2}$  for the replacement of  $\text{Br}^-$  in  $\text{NiBr}(\text{QAS})^+$  by  $\text{SCN}^-$  using different electrolytes to maintain constant ionic strength. Temperature was  $25.0^\circ\text{C}$ .

mass spectrum and melting point.

First-order rate data for the decomposition reactions given by eq 5 are listed in Table II. Reactions listed in Table II for which  $k_{\text{dec}}$  values are not present were not observed to undergo decomposition. Pseudo-first-order rate constants for the first step in this consecutive process were greater than 10 times the first-order rate constants for the subsequent decomposition reaction. This fact allowed the rate determination to be made by analyzing the two steps in the consecutive process separately. Rates of the decomposition step for reactions in which cyano complexes were formed were measured only at the maximum cyanide concentrations used in the study. Cyanide did not cause significant amounts of decomposition of reactant complexes in the ligand replacement reactions.

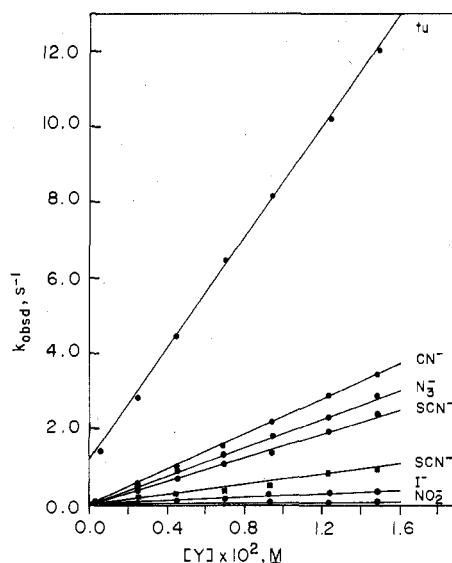
**Ionic Strength.** A study of ionic strength effects was undertaken because our work<sup>9</sup> showed that ionic strength significantly affected the rates of ligand replacement in five-coordinate nickel(II) complexes in methanol. Reactions in which ionic strength was not maintained constant resulted in plots of the pseudo-first-order rate constant,  $k_{\text{obsd}}$ , vs. entering ligand concentration exhibiting considerable curvature. However, when the ionic strength was maintained at a constant value of  $0.050\text{ M}$ , linear plots which passed through the origin were obtained. An insulating effect of increasing the ionic strength for reactions where reactants were of opposite charge was observed as the Brønsted-Bjerrum relationship predicts.<sup>14</sup> The greatest insulating effect was observed when the electrolyte used was  $\text{NaBPh}_4$  as shown in Figure 2.

Ionic strength was reported<sup>7</sup> not to affect kinetic results for ligand replacement in the complex  $\text{PtBr}(\text{QAS})^+$ . Because ionic strength has been shown to affect the value of rate constants and hence the mechanistic interpretation of kinetic data, ligand replacement of  $\text{Br}^-$  in  $\text{PtBr}(\text{QAS})^+$  by  $\text{SCN}^-$  was studied. A linear plot of  $k_{\text{obsd}}$  vs. entering ligand concentrations was obtained with a rate constant of  $57 \pm 4\text{ M}^{-1}\text{ s}^{-1}$  compared with ca.  $97\text{ M}^{-1}\text{ s}^{-1}$  of the earlier report.

The rate law found for reactions reported in this article is given by eq 6. This general rate law is consistent with the

$$\text{rate} = k[\text{MX}(\text{QAS})^+][\text{Y}^-] \quad (6)$$

mechanism of ligand replacement occurring as a single bimolecular rate-determining step. The observed rate law does not preclude the occurrence of a more complicated mechanism



**Figure 3.** Plots of  $k_{\text{obsd}}$  vs. entering ligand concentration in the replacement of  $\text{Br}^-$  in  $\text{NiBr}(\text{QAS})^+$  represented by solid circles and in  $\text{PtBr}(\text{QAS})^+$  represented by solid squares. Ionic strength was maintained at  $0.05\text{ M}$  by  $\text{LiClO}_4$  at a temperature of  $25.0^\circ\text{C}$ .

which could consist of a series of steps.

**Effect of Water.** The solvent in this kinetic study, methanol, is hygroscopic. Small amounts of water added to methanol are known to accelerate rates of formation of six-coordinate nickel(II) complexes.<sup>15,16</sup> In order to test the effect of water on ligand replacement in the present study, we conducted experiments between  $\text{NiBr}(\text{QAS})^+$  and  $\text{SCN}^-$  with varying amounts of water added to methanol. Lot analysis on the methanol gave  $0.03\%$  water in unopened bottles of methanol. This is equivalent to  $0.013\text{ M}$  water. In order to test the effect of water on rates, we added an amount of water equivalent to increasing the water concentration by  $0.078\text{ M}$ . Analysis of the total water concentration was determined by using the Karl Fischer method.<sup>17</sup> The theoretical concentration of  $0.091\text{ M}$  water was in good agreement with the experimentally analyzed water concentration of  $0.094\text{ M}$ . Kinetic experiments conducted under identical conditions by using these two methanol solutions gave  $k_{\text{obsd}}$  values of  $0.83 \pm 0.01$  and  $0.82 \pm 0.02\text{ s}^{-1}$ , with and without water added, respectively. Although the concentration of water is nearly equal the maximum concentration of nucleophiles used, the absence of a variation in rate with a sixfold increase in concentration indicates that the presence of water at this level has no effect on the reaction.

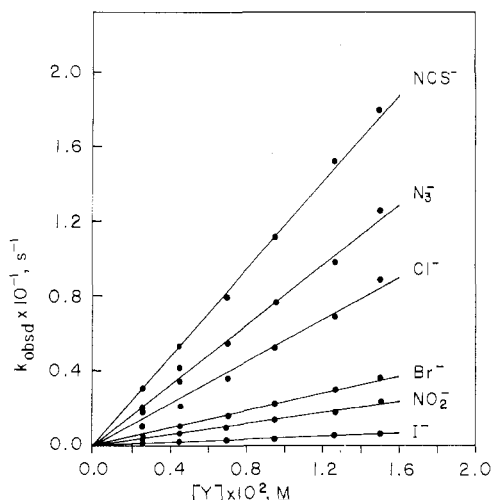
**Entering Groups.** The effect of entering groups of different nucleophilic character on the rates of ligand replacement was studied to determine the importance of an associative mechanism in the reaction. Plots of  $k_{\text{obsd}}$  values as a function of entering ligand concentrations in the replacement of bromide in  $\text{NiBr}(\text{QAS})^+$  are shown in Figure 3. Plots for cyanide, azide, thiocyanate, iodide, and nitrite entering ligands were linear with intercepts that were zero within experimental error, whereas the linear plot for thiourea appeared to have a significant nonzero intercept. The following order of decreasing rate with entering ligand was established:  $\text{SC}(\text{NH}_2)_2 \gg \text{CN}^- > \text{N}_3^- > \text{SCN}^- > \text{I}^- > \text{NO}_2^- \gg \text{PPh}_3$ . With the exception of  $\text{PPh}_3$ , the entering ligand order paralleled the ligand nu-

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**Figure 4.** Plots of  $k_{\text{obsd}}$  vs. leaving group concentration being replaced by cyanide at 0.05 M ionic strength maintained by  $\text{LiClO}_4$ . Temperature was 25.0 °C.

cleophilic reactivity constants,<sup>18</sup>  $n^\circ_{\text{Pt}}$ , of the entering ligand. No reaction was observed with  $\text{PPh}_3$  as the entering nucleophile.

The approximately 2 order of magnitude change in the second-order rate constants going from  $\text{NO}_2^-$  to thiourea as entering ligand is not as large as normally found for associative mechanisms. This is also reflected in a comparison of a nucleophilic discrimination factor,  $S$ , of 0.53 for these reactions with the value of 1.43 for substitution reactions of *trans*-Pt( $\text{PEt}_3$ )<sub>2</sub>Cl<sub>2</sub> in methanol.<sup>4</sup> The  $S$  value of 0.53 of this study compared with a value of 1.0 for the analogous study of  $[\text{PtBr}(\text{QAS})]\text{Br}$  is evidence of greater diminution of entering ligand nucleophilic character toward the nickel(II) complexes compared to the case for the platinum(II) complexes.

**Leaving Groups.** The effect that changes in leaving groups had on the rate of ligand replacement of  $\text{NiX}(\text{QAS})^+$  by  $\text{CN}^-$  is illustrated by the data given in Table II. The decreasing second-order rates of replacement of leaving groups with  $\text{CN}^-$  as shown in Figure 4 were in the order  $\text{NCS}^- > \text{N}_3^- > \text{Cl}^- > \text{Br}^- > \text{NO}_2^- > \text{I}^-$ . It appears that the larger the leaving group is the more slowly it is replaced. That this order is in contrast to nucleophilic strength suggests that the complexes are sterically constrained by the presence of QAS. A factor of a 30-fold change in rate for this series of leaving groups is much less than would be expected for a dissociative mechanism.

The general insensitivity of rates of ligand replacement to changes in the nucleophilic character of entering ligands used in this study indicated that another factor of greater importance must be predominant in controlling the rate-determining step. Steric hindrance by the bulky terminal phenyl groups about and below the equatorial plane of the complex, illustrated in Figure 1, must be significant. Morgan and Tobe<sup>8</sup> reported a remarkable enhancement in the rate of replacement of bromide in an analogous platinum(II) complex when six equatorial methyl groups were employed instead of six phenyl groups. The effect was particularly noticeable when bulky triphenylphosphine was the entering group. In the present investigation triphenylphosphine, which has the highest nucleophilic reactivity constant, gave no reaction with  $\text{NiBr}(\text{QAS})^+$ . This was in contrast to the substantial rate observed in the analogous platinum(II) complex substitution reaction.<sup>7</sup>

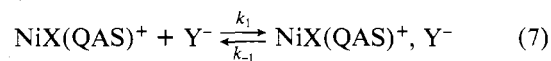
Steric hindrance about and below the equatorial plane can be seen to be greater for nickel(II) complexes due to the smaller size of the nickel(II) ion in comparison to platinum-

(II).<sup>2</sup> Platinum(II), having a large ionic radius than nickel(II), is displaced 0.46 Å below the trigonal plane created by the terminal arsenic donor atoms, whereas nickel(II) is displaced only 0.37 Å below the plane. In addition, the metal to equatorial arsenic donor atom distance for platinum(II)<sup>19</sup> is ca. 2.38 Å compared to a shorter value of ca. 2.29 Å for nickel(II).<sup>20</sup> The result of these factors is an increase in steric crowding in the region of the monodentate ligand due to the terminal phenyl groups of the tetradentate ligand which extend further below the equatorial plane in  $\text{NiBr}(\text{QAS})^+$  compared to the case of  $\text{PtBr}(\text{QAS})^+$  complexes.

A decrease in the second-order rate constant as the size of leaving groups increases is apparent for complexes in which the leaving groups are  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , respectively. The 12-fold decrease upon changing from  $\text{Cl}^-$  to  $\text{I}^-$  and the observation that the complex with the bulkiest leaving group,  $\text{NO}_2^-$ , is also only slowly replaced by cyanide further illustrate the controlling effect of the terminal phenyl groups on the rates substitution.

Although bond breaking by the leaving groups and bond making by entering groups are somewhat masked by the steric blocking caused by terminal phenyl groups of the geometrically constraining tetradentate ligand, they are a contributing factor to rates of substitution. The rate data appear to show a more noticeable trend of ligand nucleophilicity with entering groups than with leaving groups. Hence, any mechanism of substitution in  $\text{NiX}(\text{QAS})^+$  complexes must be consistent with this associative character.

A mechanism consistent with the rate data is given by eq 7–9, which is the associative interchange mechanism,  $I_a$ . The



second step in this mechanism is rate determining and yields the rate law given in eq 10 and 11, with the assumption of a

$$\frac{-d[\text{NiX}(\text{QAS})^+]}{dt} = \frac{d[\text{NiY}(\text{QAS})^+]}{dt} = \frac{k_1 k_2}{k_2 + k_{-1}} [\text{NiX}(\text{QAS})^+][\text{Y}^-] \quad (10)$$

$$k = \frac{k_1 k_2}{k_2 + k_{-1}} \quad (11)$$

“steady-state” concentration of the associative outer-sphere complex given by eq 7.

The associative interchange mechanism involves an incomplete expansion of the coordination sphere of nickel(II) due to the bulkiness of the tetradentate ligand. The simultaneous events of bond elongation of the leaving group and bond formation of the entering group would place severe steric stress on the complex.

An alternate mechanism proposed by Morgan and Tobe<sup>8</sup> for substitution in  $\text{PtBr}(\text{QAS})^+$  is also consistent with our rate data. The mechanism postulated for the structurally analogous complex  $\text{PtBr}(\text{Qas})^+$  involves the dissociation of a terminal arsenic group. This step occurs prior to a rate-determining bimolecular reaction between the more open four-coordinate intermediate and an entering nucleophile as shown in Figure 5.

(18) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(19) The value for the structure of  $[\text{PtCl}_2(\text{DAS})_2]$  is 2.375 Å: N. C. Stephenson, *Acta Crystallogr.*, **17**, 1517 (1964).

(20) The value for the structure of  $[\text{NiI}_2(\text{Das})_2]$  is 2.293 Å: N. C. Stephenson, *Acta Crystallogr.*, **17**, 592 (1964).

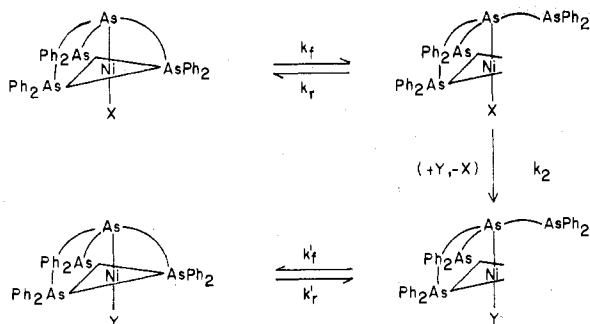


Figure 5. Mechanistic pathway for ligand replacement involving the partial tetradentate ligand dissociation in forming a four-coordinate intermediate.

By assuming occurrence of (i) a rapid preequilibrium that is the partial tetradentate ligand dissociation involving one terminal arsenic donor group, (ii) a steady-state concentration of the four-coordinate intermediate, and (iii) a rate-determining bimolecular step between the four-coordinate intermediate formed in the first step and the entering nucleophile, we obtain the rate law given by eq 12 and 13. For  $k_t \gg k_2$

$$-\frac{d[\text{NiX}(\text{QAS})^+]}{dt} = \frac{(k_f/k_r)k_2[\text{NiX}(\text{QAS})^+][\text{Y}^-]}{1 + (k_2/k_r)[\text{Y}^-]} \quad (12)$$

$$k = \frac{(k_f/k_r)k_2}{1 + (k_2/k_r)[\text{Y}^-]} \quad (13)$$

this rate law would yield linear plots of pseudo-first-order rate constants vs. the entering ligand concentrations that pass through the origin. This rate law theoretically differs from the previous one at higher concentrations of entering ligand.

Limited by solubilities, the maximum entering ligand concentration used did not allow a distinction between the two mechanisms to be made.

Although the evidence gathered in this investigation was not conclusive of a singular mechanism, it did suggest that an associative step is involved in the mechanism of ligand replacement. The observation of Morgan and Tobe<sup>8</sup> that Qas displaces QAS from  $\text{PtBr}(\text{QAS})^+$  is certainly consistent with our observations that  $\text{NiCl}(\text{QAS})^+$  undergoes decomposition in the absence of strongly nucleophilic ligands and that the strong nucleophile  $\text{CN}^-$  promotes decomposition of  $\text{Ni}(\text{CN})(\text{QAS})^+$ . The trialkylarsine  $(\text{C}_2\text{H}_5)_3\text{As}$  has an  $n^\circ_{\text{Pt}}$  equal to 7.54 compared to 6.75 for  $\text{Ph}_3\text{As}$  and 7.0 for  $\text{CN}^-$ . The  $n^\circ_{\text{Pt}}$  value for Qas is expected to be greater than that of QAS. Therefore, both Qas and  $\text{CN}^-$  would be predicted to displace QAS because of the greater nucleophilic character. The fact that complete tetradentate ligand dissociation occurs suggests, but is not conclusive of, a mechanism for monodentate ligand replacement via partial tetradentate ligand dissociation. The latter mechanism is particularly attractive because it is consistent with the prediction of Tolman that 18-electron systems favor dissociative processes.<sup>21</sup>

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**Registry No.**  $[\text{NiCl}(\text{QAS})]\text{ClO}_4$ , 41765-69-9;  $[\text{NiBr}(\text{QAS})]\text{Br}$ , 14239-42-0;  $[\text{NiI}(\text{QAS})]\text{ClO}_4$ , 14523-06-9;  $[\text{Ni}(\text{CN})(\text{QAS})]\text{ClO}_4$ , 14238-93-8;  $[\text{Ni}(\text{NO}_2)(\text{QAS})]\text{ClO}_4$ , 72138-06-8;  $[\text{Ni}(\text{PPh}_3)(\text{QAS})](\text{ClO}_4)_2$ , 72138-08-0;  $[\text{Ni}(\text{N}_3)(\text{QAS})]\text{ClO}_4$ , 72152-01-3;  $[\text{Ni}(\text{NCS})(\text{QAS})]\text{ClO}_4$ , 14238-94-9;  $[\text{PtBr}(\text{QAS})]\text{Br}$ , 72173-25-2;  $\text{NO}_2^-$ , 14797-65-0;  $\text{I}^-$ , 20461-54-5;  $\text{SCN}^-$ , 302-04-5;  $\text{N}_3^-$ , 14343-69-2;  $\text{CN}^-$ , 57-12-5;  $\text{SC}(\text{NH}_2)_2$ , 62-56-6.

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## Exchange Reactions in $(\text{CH}_3)_3\text{PPCF}_3$ , Phosphinidene Analogue of a Wittig Reagent

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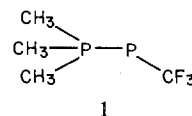
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The interaction of  $\text{Me}_3\text{P}$  with the homocyclic phosphines  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  has been investigated by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectroscopy. In excess  $\text{Me}_3\text{P}$  the predominant exchange pathway involves the bimolecular attack of  $\text{Me}_3\text{P}$  on the phosphine-phosphinidene complex  $\text{Me}_3\text{PPCF}_3$ . However, the kinetics are complicated by a side reaction which results in the production of the difluorophosphorane  $\text{Me}_3\text{PF}_2$ .

### Introduction

Main-group species with low coordination numbers play an important role in chemistry as models for reaction intermediates. They also raise interesting questions regarding structure and bonding as well as offering promise as synthetic reagents. In terms of group 5A chemistry much current emphasis has been placed on two-coordinate phosphorus and arsenic compounds. Several stable neutral molecules with this coordination number have been prepared in recent years; examples include phosphabenzene,<sup>1</sup> arsabenzene,<sup>2</sup> and compounds with  $\text{P}=\text{C}$ ,<sup>3</sup>

$\text{As}=\text{C}$ ,<sup>4</sup> and  $\text{P}=\text{N}$ <sup>5</sup> bonds. In this paper we are concerned with the rather unusual compound **1** which features both di-



and tetracoordinate phosphorus atoms.<sup>6</sup> Compound **1**, in fact, bears a striking resemblance to the classic Wittig reagents. Several years ago we noted in an NMR study<sup>7</sup> that the  $^{19}\text{F}$  resonance of **1** is temperature sensitive. Enthused by the possibility that **1** represents a potential source of phosphinidene

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